PHOTOCHEMICAL CONTROL OF MACROMOLECULAR CONFORMATIONS

Thesis submitted to the
University of Calicut for the partial fulfilment of the
requirements for the degree of

DOCTOR OF PHILOSOPHY IN CHEMISTRY

BY

SREEJITH P. MSc.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALICUT
2011

CERTIFICATE

This is to certify that the thesis entitled "**PHOTOCHEMICAL CONTROL OF MACROMOLECULAR CONFORMATIONS**" is an authentic record of the research work carried out by **Mr. SREEJITH. P** under my supervision and guidance during the period January 2001-January 2011 in partial fulfilment of the requirements for the degree of Doctor of Philosophy under the faculty of Science, University of Calicut . The work presented in this thesis has not been submitted for any degree or diploma earlier. It is also certified that **Mr. SREEJITH. P** has fulfilled the course requirements and passed the qualifying examination for the Ph.D., degree of this University.

University of Calicut
January 2011

Dr. E. PURUSHOTHAMAN
Supervising Teacher

DECLARATION

I hereby declare that the thesis entitled "**PHOTOCHEMICAL CONTROL OF MACROMOLECULAR CONFORMATIONS**" is an authentic record of the research work carried out by me under the supervision of **Dr. E. PURUSHOTHAMAN**, Professor, Department of Chemistry, University of Calicut. No part of this thesis has formed the basis for the award of any other degree or diploma of any University or Institution.

University of Calicut
January 2011

SREEJITH. P.

ACKNOWLEDGEMENTS

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Above all, I bow to the Almighty for always keeping my spirits up to carry out the work successfully.

SREEJITH. P.

Dedicated to

My Father

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AZO PVA 14-1a	-	Azo Polyester of PVA.MW.14000 (1:1)
AZO PVA 14-1b	-	Azo Polyester of PVA.M.W. 14000 (1:2)
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AZO DIOL	-	Azo Polyester of 1, 3 diol
AZO DEG	-	Azo Polyester of Diethylene glycol
AZO AP	-	Azo Polyester of 4,4´-Dihydroxyazobenzene
AZO OT	-	Azo Polyester of *Bis* (phenol-4-azo) -4,4´-(3,3´-dimethyl biphenyl)
DMSO	-	Dimethyl sulphoxide
DMF	-	N, N – Dimethyl formamide
DMA	-	N, N – Dimethyl acetamide
TG	-	Thermogravimetry
DTA	-	Differential thermal analysis
DSC	-	Differential scanning calorimetry
SEM	-	Scanning Electron microscope
η_{sp}	-	Specific viscosity
$[\eta]$	-	Intrinsic viscosity
Ti	-	Temperature of initiation
nm	-	Nanometre
A^0	-	Angstrom
Tm	-	Temperature of melting
Td	-	Temperature of dissociation
Tc	-	Crystallisation temperature
Tg	-	Glass transition temperature
λ	-	Wavelength
θ	-	Diffraction angle
cps	-	Cycles per second
β	-	Full wavelength half medium

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REFERENCES

1. I.Y. Galaev and B. Mattiasson, *Trends Biotechnol*, **1999**, *17*, 335-340.

2. S.J. Kim., S.J. Park., S.M. Lee., Y.M. Lee., H.C. Kim and S.I. Kim, *J. Appl. Polym. Sci.*, **2003**, *89*, 890-894.

3. J. Raula, J. Shan, M. Nuopponen, A. Niskanen, H. Jiang, E.I. Kauppinen and H. Tenhu, *Langmuir*, **2003**, *19*, 3499-3504.

4. M. Yamato, M. Utsumi, A. Kushida, C. Konno, A. Kikuchi and T. Okano, *Tissue Eng*., **2001**, *7*,473-480.

5. K. Ageishi., T. Endo and M. Okasawa, *J. Poly. Sci. Polym. Chem*. Edn. **1981**, *19*,1085.

6. A. Altomare, C. Carlini, F. Ciardelli, R. Solaro, J.L. Houben and N. Rosato, *Polymers*, **1983**, *24*,95.

7. J.E. Guillet, In *Polymers Photophysics and Photochemistry*, *An Introduction to the Study of Photoprocesses in Macromolecules*, Cambridge University, New York, **1985**.

8. D. Phillips (Ed.), *Polymer Photophysics, Luminescence, Energy Migration and Molecular Motion in Synthetic Polymers*, Chapman and Hall, New York, **1985**.

9. M. Irie. In *Photophysical and Photochemical Tools in Polymer Science*, M.A. Winnik (Ed.), Reidel, Dordrecht, **1986**, P.*269*.

10. W. Marckwald. Z. *Physik*. *Chem*., **1989**, *30,*140.

11. T. Seiki, In *Handbook of Photochemistry and Photobiology*, Harisingh Nalwa (Ed)., American Scientific., **2003**, P.*435*.

12. H. Rau. In “Photochemistry and Photophysics”, J.F. Rebeck (Ed.,), Vol. 2, CRC, F.L. Boca Raton, **1990**, P.*119.*

13. R.J. Gugliemetti, In *Photochromism Molecules and Systems,* H. Durr and H. Bour. Laurent (Ed.), Elsevier, Amsterdam, **1990**, P.*134*.

14. H. Rau, In *Photochromism Molecules and Systems*, H. Durr and H. Bour- Laurent (Ed.), Elsevier, Amsterdam, **1990**, P.*165*.

15. R.C. Bertelson, In *Organic and Thermochromic Compounds*, J.C Crano and R.J. Guglielmetti (Ed.), Plenum, New York, **1999**.

16. G.S. Kumar and D.C. Neckers, *Chem*. *Rev*. **1989**, *89*,1915.

17. M. Irie, *Adv*. *Polymer Sci.* **1990**, *94*,27.

18. H. Husy, E. Marian and G. Schetty, *Text*. *Res*. *J*, **1969**, *39*,94.

19. M. Irie and D. Kungwatchkun, *Macromolecules*, **1986**, *19*,2476.

20. Gigi Abraham and E. Purushothaman, *Indian J. Chem. Tech.* **2003**, *10*,175.

21. K.R. Girijan and E. Purushothaman, *Indian J. Chem. Tech,* **2008**, *15*,197-200.

22. H.S. Blair and C.B. McArdle, *Polymer*, **1984**, *25*, 1347.

23. M. Umeda and M. Hashimoto, *J. Appl. Phy.,* **1992**, *72,* 117.

24. P. Bull and C.H. Nicholls, *Dyes and Pigments,* **1982**, *3,* 5.

25. Y. Matsunga and N. Miyajima, *Bull. Chem. Soc.,* Japan, **1971**, *44*, 361.

26. J.E. Kudar, *Tetrahedron,* **1972**, *28,* 1973.

27. A.R. Monahan and J. B. Flannery, *Chem. Phy. Lett*, **1972**, *17,* 510.

28. K. J. Jiang, HZ. Chen., M. Wang, *Materials Science and Engineering*, **1999**, *B57 (2),* 87-91.

29. K.Y. Law, *Organic Photoconductive Materials, Recent Trends and Developments, Chemical Reviews,* **1993**, *93* (1), 449-86.

30. H. Rau and B. Bunsengers, *Physikalische Chemie,* **1968**, *72* (7), 637.

31. R.B. Champ and M.D. Shattuck, *U.S. Patent,* **1975**, *3*, 898, 084.

32. K. Tautsui *U.S. Patent*, **1985**, *4,* 540, 643.

33. M. Ohta, M. Sasaki and M. Shoshi, *U.S. Patent*, **1986**, *4*, 567, 124.

34. M. Hashimoto, *U.S. Patent*, **1986**, *4*, 618, 672.

35. K.Y. Law and I. W Tarnawskyj, *U.S. Patent*, **1989**, *4*, 797, 337.

36. T. Fukagai, M. Kimura, M. Ohta and M. Hashimoto, *U.S. Patent*, **1989**, *4*, 830, 942.

37. M. Hashimoto, M. Ohta, A. Kozima, K. Sakai and M. Sasaki, *U.S. Patent*, **1984**, *4*, 426, 327.

38. M. Hashimoto, *U.S. Patent*, **1990**, *4*, 916,039.

39. T. Murayama, S. Ostuka and H. Nagasaka, *Res. Dev. Rev. Mitsubishi Chem.,* **1987**, *1*, 57.

40. K.Y. Law and I.W. Tarnawskyj, *J. Photochem. Photobiol, A. Chem.,***1991**, *57*, 217.

41. K. Ishihara, S. Kato and I. Shinohara, *J. Appl. Polym. Sci.,* **1982**, *27*, 4273.

42. T.Kitamura, S. Imamura and M. Kawamato, *J. Imaging Technol.,* **1988**, *14*, 136.

43. T. Kitamura and N. Ueda, *Electrophotography,* **1988**, *28,* 269.

44. K.Y. Law and F.C. Bailey, *Dyes and Pigments*, **1988**, *9*, 85.

45. K. Seki., Y. Susuki and H. Yamanami, SPSE *Proceedings, VIIth International Congress on Advances in Non-impact Printing Technologies*, **1990**, *60.*

46. O. Murakami, T. Uenaka, S.Otsuka and T. Murayama, IS and T *Proceedings, VIIth International Congress on Advances in Non-impact Printing Technologies*, **1991**, 318.

47. Y. Chen, C.K. Liao, T.Z .Wu, *Polymer,* **2002**, *43 (17)* 4545-55.

48. Y.J. Kim., W.M. Frederik., L.S. Charlotte., T.H. Joseph. *Inorganica Chimica Acta*, **2001**, *318 (1)*, 53-60.

49. J. Xue, S. Wang, L. Zhang, X. Li., *Dyes and Pigments*, **2007**, *75*, 369-372.

50. A. Ahluwalia, R. Piolanti, D.D Rossi, *Langmuir,* **1997**, *13* 5909-5913

51. R. Lovrien, *Proc. Natl. Acad. Sci.,* USA, **1967**, *57*, 236-242.

52. L. Matejka, K. Dusek, *Makromol. Chem.* **1981**, *182*, 3223-3226.

53. M. L. Hallensleben, H. Menzel, *Br. Polym. J.* **1990**, *23*, 199-204.

54. M. Irie. Y. Hirano, S. Hashimoto, K. Hayashi, *Macromolecules* **1981**, *14*, 262-267.

55. G.S. Kumar, P. DePra, D.C. Neckers, *Macromolecules*, **1984**, *17*, 1912-1917.

56. G.S. Kumar, P. DePra, K. Zhang, D.C. Neckers, *Macromolecules* **1984**, *17*, 2463- 2467.

57. K. Kimura, *Coord. Chem. Rev*. **1996**, *148*, 41.

58. H. Tokuhisa, M. Yokoyama and K. Kimura. *Chem. Mater*., **1993**, *5*, 989.

59. H. Tokuhisa. M, Yokoyama and K. Kimura, *Macromolecules* **1994**, *27*, 1842.

60. H. Tokuhisa, M. Yokoyama and K. Kimura, *Bull. Soc. Chem.* Jpn, **1996**, *69*, 2123

61. M.V. Voinova, M. Jonson, *Biosensors and Bioelectronics* **2004**, *20*, 1106-1110.

62. R.H. Berg, S. Havilsted P.S, Ramanujam, *Nature*, **1996**, *383,* 505.

63. R.H. Berg, P.H. Rasmussen, S. Hvilsted, P.S. Ramanujam, *Proceeding of the IVth European Conference on Molecular Electronics*, **1997**, Cambridge, pp.3-6.

64. J. Bredenbeck, J. Helbing, A. Sieg, T. Scrader, W. Zinth,C. Renner R. Behrendt, L. Moroder, J. Wachtveitl, P. Hamm, *Proc. Natl. Acad. Sci.* USA, **2003**, *100* 6452-6457.

65. M. Doi. S.F. Edwards, *The Theory of Polymer Dyanamics*, *Cladendon Press*, Oxford, **1998**.

66. B.L. Feringa, *Molecular Electronics*. Wiley VCH, GmbH, Weinheim, **2001**.

67. H.R. Hafiz, F. Nakanishi. *Nanotechnology* **2003**, *14,* 649-654.

68. E. Katz, B. Willner, I. Willner. *Biosens. Bioelectron*, **1997**, *12,* 703-719.

69. T. Shimoboji, E. Larenas, T. Fowler, S. Kulkarni, A.S. Hoffman, P.S. Stayton, *Proc. Natl. Acad. Sci.* USA, **2002**, *99 (26),* 16592-16596.

70. I. Willner, E. Katz, *Angew. Chem. Int*. Ed. **2000**, *39,* 1180-1218.

71. I. Willner. N. Lapidot. A. Riklin, R. Kasher, E. Zahavy, E. Katz. *J. Am. Chem. Soc.*, **1994**, *116*, 1428-1441.

72. C.L. Forber, E.C. Kelusky, M.C. Zerner and N.J. Bunce., *J. Am. Chem. Soc.,***1985**, *107,* 5884.

73. T. Seki, T. Tanaka and K.Ichimura, *Adv. Mater*, **1997**, *9,* 563.

74. T. Seki, T. Tanaka and K. Ichimura, *Polymer,* **1998**, *30*, 646.

75. T. Seki, K. Fukuda and K. Ichimura, *Langmuir*, **1999**, *15*, 5098.

76. A.M. Hor, C.K. Hsiao and Di Paola- Baranyi, *J. Imaging Sci.,* **1990**, *34*,224.

77. H. Kamogawa, M. Kato and H. Sugiyama, *J. Polym. Sci.,* **1968**, *6***,** 2967.

78. M. Irie and H. Tanaka, *Macromolecules*, **1983**, *16,* 210.

79. J.L. Houben, O. Pieroni and A. Fissi, *Biopolymers,* **1978**, *17*, 799.

80. A. Ueno, K. Takahashi, J. Anzai and T. Osa, *J. Chem. Soc.*, **1981**, *103,* 6410.

81. J. Anzai, A. Ueno and T.Osa, *J. Chem. Soc., Perkin Trans*. II, **1987**, *67*.

82. H. Yamamato and A. Nishida, *J. Photochem. Photobiol.,* **1988**, *42*, 149.

83. A.Ueno, K. Adachi, J. Nakamura and T. Osa, *J. Polym. Sci. Poly. Chem.* Ed. **1990**, *28,* 1161.

84. A. Ueno, J. Anzai, T. Osa and Y. Kadoma, *Bull. Chem. Soc.* Japan, **1997**, *50*, 2995.

85. H.R. Maradiya, V. S. Patel, *Chemistry of Heterocyclic compounds* **2002**, *38* (11), 1324-30.

86. H.R. Maradiya, V.S. Patel, *Journal of the Serbian Chemical Society*, **2002**, *67* (1), 17-25.

87. H.R. Maradiya, *Turkish Journal of Chemistry*, **2001**, *25*, 441-50.

88. G. Hallas, A.D. Towns, *Dyes and Pigments* **1996**, *32 (3),* 135-49.

89. G. Hallas, A.D. Towns, *Dyes and Pigments*, **1997**, *35 (3)*, 219-37.

90. G. Hallas, A.D. Towns, *Dyes and Pigments*, **1997**, *33 (4),* 319-36.

91. G. Hallas, J-H Choi,. *Dyes and Pigments*, **1999**, *42*, 249-65.

92. H.S. Bhatti, S. Seshadri, *Dyes and Pigments*, **2004**, *62*, 83-92.

93. R.W. Sabnis, D.W. Rangnekar, *Dyes and Pigments*, **1989**, *10,* 295-302.

94. T.H. Afifi, A.Z. Sayed, *Journal of the Society of Dyers and Colourists,* **1997**, *113*, 256-8.

95. T.H. Afifi, *Advances in Colour Science and Technology,* **2003**, *6 (3)*, 63-72.

96. P.O. Astrand, P. Sommer- Larsen, S. Hvilsted. P.S. Ramanujam, K.L. Bak, S.P.A. Saver, *Chemical Physics Letters* **2000**, *325*, 115-9.

97. S.R. Selim, T.H. Afifi, *Advances in Colour Science and Technology*, **2001**, *4 (3)*, 82-8.

98. S. Alaa, A.E. Aziz, T.H. Afifi. *Dyes and Pigments*, **2006**, *70,* 8-17.

99. G. Hallas. J-H. Choi, *Dyes and Pigments*, **1999**, *40*, (2-3) 99-117.

100. G. Hallas. *Journal of the Society of Dyers and Colourists*, **1979**, *95*, 285-94.

101. K.L. Georgiadou, E.G. Tsatsaroni, *Dyes and Pigments*, **2002**, *53*, 73-8.

102. V.H. Patel, M.P.Patel, R.G. Patel, *Dyes and Pigments*, **2002**, *53*,191-8.

103. A. Higuchi, A. Hamamura, Y. Shindo, H. Kitamura, B.O. Yoon, T. Mori, T. Uyama and A. Umezawa, *Biomacromolecules,* **2004**, *5,* 1770.

104. J. Edahiro, K. Sumaru, Y. Tada, K. Ohi. T. Takagi, M. Kameda, T. Shinbo, T. Kanamori and Y. Yoshimi, *Biomacromolecules*, **2005**, *6*, 970.

105. G. Hayashi, M. Hagihara, C. Dohno and K. Nakatani, *J. Am. Chem. Soc.*, **2007**, *129*, 8678.

106. J. Auernheimer, C. Dahmen, U. Hersel, A. Bausch and H. Kessler, *J. Am. Chem. Soc.*, **2005**, *127*, 16107.

107. D. Person., A.J. Downard, A. Muscroft- Taylor and A.D. Abell. *J. Am. Chem. Soc.*, **2007**, *129*, 14862.

108. W. Stockenius., R.H. Lozier and R.A. Bogomolini, *Biochem Biophys. Acta.*, **1979**, *215*, 505.

109. V.D. Ermakova, V.D. Arsenov, M.I. Cherkashin and P.P. Kisilitsa, *Russ. Chem. Rev.*, **1977** *46*, 145.

110. M. Irie, A. Menju and K. Hayashi. *Macromolecules* **1979**, *12*, 1176.

111. D. Oesterhelt and B. Hess, *Eur. J. Biochem.*, **1973**, *37*, 316.

112. D.R. McCaslin and C. Tanford, *Biochem.*, **1981**, *20*, 5212.

113. H.B. Neori, P.A.G. Fortes and M. Montal, *Biochem.*, **1983**, *22*, 206.

114. U.A. Stewart, C.S. Johnson and D.A. Gabriel. *Macromolecules*, **1986**, *19*, 964.

115. Gigi Abraham and E. Purushothaman, *Indian J. of Chem. Tech.*, **1998**, *5*, 213.

116. C. H. Fan., K.W. Plaxco and A. J. Heeger, *Proc. Natl. Acad. Sci.* U.S.A., **2003**, *100*, 9134.

117. Y. D. Mao, C.X. Luo and Q. Ouyang, *Nucleic Acids Res*., **2003**, *31*,
e108.

118. F. Ricci, R.Y. Lai., A.J. Heeger, K.W. Plaxco and J.J. Sumner, *Langmuir*, **2007**, *23*, 6827.

119. C.E. Immoos, S. J. Lee and M.W. Grinstaff. *ChemBiochem.* **2004**, *5*, 1100.

120. U. Rant, K. Arinaga., S. Scherer., E. Pringsheim., S. Fujitha, N. Yokoyama., M. Tornow and G. Abstreiter, *Proc. Natl. Acad. Sci.* U.S.A., **2007**, *104*, 1110.

121. C.E. Immoos, S.J. Lee and M.W. Grinstaff, *J. Am. Chem. Soc.* **2004**, *126*, 10814.

122. Y. Xiao, A.A. Lubin, B.R. Baker, K.W. Plaxco and A.J. Heeger, *Proc. Natl. Acad. Sci.,* U.S.A, **2006**, *103*, 16677.

123. D.L. Huber., R.P. Manginell., M.A. Samara., B.I. Kim and B.C. Bunker, *Science*, **2003**, *301*, 352.

124. H. Yamanaka., K. Yoshizako., Y. Akiyama., H. Sota, Y. Hasegawa, Y. Shinohara, A. Kikuchi and T. Okano, *Anal Chem.* **2003**, *75*, 1658.

125. K. Yoshizako., Y. Akiyama., H. Yamanaka.,Y. Shinohara, Y. Hasegawa, E. Carredano, A. Kikuchi and T. Okano, *Anal. Chem.,***2002**, *74*, 4160.

126. K. Nagase, J. Kobayashi, A. Kikuchi, Y. Akiyama, H. Kanazawa and T. Okano, *Langmuir*, **2007**, *23*, 9409.

127. Y. Liu, L. Mu., B.H. Liu and J.L. Kong, *Chem. Eur. J.*, **2005**, *11*, 2622.

128. F. Zhou and W.T.S. Huck, *Phys. Chem. Chem. Phys.*, **2006**, *8*, 3815.

129. I.S. Choi and Y.S. Chi, *Angew*. *Chem*, *Intl*. Ed., **2006**, *45*, 4894.

130. P. Uhlmann, L. Ionov, N. Houbenov, M. Nitschke, K. Grundke, M. Motornov, S. Minko and M. Stamm, *Prog. Org. Coat.*, **2006**, *55*, 168.

131. C. Alexander and K. M. Shakesheff, *Adv. Mater.*, **2006**, *18*, 3321.

132. S.L. Gras, T. Mahmud, G. Rosengarten, A. Mitchell and K. Kalantar-Zadeh, *Chem Phy Chem.*, **2007**, *8*, 2036.

133. J.A. Howarter and J.R. Youngblood, *Adv. Mater.*, **2007**, *19*, 3838.

134. K. Ichimura, S.K. Oh and M. Nakagawa, *Science*, **2000**, *288*, 1624.

135. C.L. Feng., J. Jin. Y.J. Zhang., Y.L. Song., L.Y. Xie., G.R. Qu, Y. Xu and L. Jiang, *Surf. Interface Anal.*, **2001**, *32*, 121.

136. C.L. Feng., Y.J. Zhang. J. Jin, Y.L. Song, L.Y. Xie, G.R. Qu, L. Jiang and D. B. Zhu, *Langmuir*, **2001**, *17*, 4593.

137. C. Raduge, G. Papastavrou, D.G. Kurth and H. Motschmann, *Eur. Phys. J.E.*, **2003**, *10*, 103.

138. C.G.F. Cooper, J.C. MacDonald, E. Soto and W.G. McGimpsey. *J. Am. Chem. Soc.*, **2004**, *126*, 1032.

139. F. Hamelmamm., U. Heinzmann, U. Siemling, F. Bretthauer and J. V. derBruggen, *Appl. Surf. Sci.*, **2004**, *222*, 1.

140. R. Rosario, D. Gust, A. A. Garcia, M. Hayes, J. L. Taraci, T. Clement, J. W. Dailey and S.T. Picraux, *J. Phys. Chem. B.*, **2004**, *108*, 12640.

141. J. Berna, D.A. Leigh, M. Lubomska, S.M. Mendoza, E. M. Perez, P. Rudolf, G. Teobaldi and F. Zerbetto, *Nat. Mater*., **2005**, *4*, 704.

142. N. Delorme, J. F. Bardeau, A. Bulou and F. Poncin- Epaillard, *Langmuir*, **2005**, *21*, 12278.

143. W.H. Jiang, G.J. Wang, Y.N. He. X. G. Wang, Y.L. An, Y.L Song and L. Jiang, *Chem. Commun.,* **2005**, 3550.

144. N. Lake, J. Ralston and G. Reynolds, *Langmuir*, **2005**, *21*, 11922.

145. N.L. Abbott and G. M. Whitesides, *Langmuir*, **1994**, *10,* 1493.

146. J. A. M. Sondaghuethorst and L.G.J. Fokkink., *Langmuir*, **1994**, *10,* 4380.

147. X.M. Wang. A.B. Kharitonov, E. Katz and I. Willner, *Chem*. *Commun*., **2003**, 1542.

148. J. Lahann, S. Mitragotri, T.N. Tran, H. Kaido, J. Sundaram, I.S. Choi, S. Hoffer, G.A. Somorjai and R. Langer, *Science*, **2003**, *299,* 371.

149. E. Katz, O. Lioubashevsky and I. Willner, *J. Am. Chem. Soc.*, **2004**, *126*, 15520.

150. B. Zhao, W. J. Brittain, W.S. Zhou and S.Z.D. Cheng. *J. Am. Chem. Soc.,* **2000**, *122,* 2407.

151. D. Julthongpiput., Y.H. Lin., J. Teng. E.R. Zubarev., and V.V. Tsukruk, *J. Am. Chem. Soc.,* **2003**, *125,* 15912.

152. D. Julthongpiput, Y. H. Lin., J. Teng, E.R. Zubarev and V. V. Tsukruk, *Langmuir*, **2003**, *19*, 7832.

153. M. Motornov., S. Minko, K. J. Eichhorn, M. Nitschke, F. Simon and M. Stamm., *Langmuir*, **2003**, *19*, 8077.

154. Y.G. Takei, T. Aoki, K. Sanui, N. Ogata, Y. Sakurai and T. Okano, *Macromolecules*, **1994**, *27*, 6163.

155. G. B. Crevoisier, P. Fabre, J.M. Corpart and L. Leibler, *Science,* **1999**, *285*, 1246.

156. T.L. Sun, G.J. Wang, L. Feng, B.Q. Liu, Y.M. Ma, L. Jiang and D.B. Zhu., *Angew. Chem. Int*. Ed., **2004**, *43*, 357.

157. M.D. Wilson and G.M. Whitesides, *J. Am. Chem. Soc.*, **1988**, *110,* 8718.

158. H. Menzel and M.L. Hallensleben, *Polym. Bull*., **1991**, *27*, 89.

159. H. Menzel, *Macromolecules*, **1993**, *26*, 6226.

160. R. Lovrien, P. Pesheck and W. Tisel, *J. Am. Chem. Soc.*, **1974**, *96*, 244.

161. G. Vander Veen and W. Prins, *Photochem. Photobiol*., **1974**, *19*, 191.

162. G. Smets, *J. Polym. Sci. Polym. Chem.*(Ed.), **1975**, *13*, 2223.

163. E.S. Gil, S.M. Hudson., *Prog. Polym. Sci*. **2004**, *29*, 1173.

164. S. Fujishige, KKI. Ando., *J. Phy. Chem. A.,* **1989**, *93,* 3311.

165. J. C. Rodriguez- Cabello, J. Reguera, A. Girotti, M. Alonso, A.M. Testera, *Prog Polym. Sci.* **2005**, *30*,1119.

166. M. Alonso, V. Reboto, L. Guiscardo, A.S. Martin, J. C. Rodriguez- Cabello *Macromolecules* **2000**, *33*, 9480.

167. K. Kurata, A. Dobashi, *J. Macromole. Sci., Part A- Pure Appl. Chem*. **2004**, *41*, 143.

168. Y.B. Lim, S-A Han, H-U Kong, J-S Park, B. Jeong, S.W. Kim, *Biodegradable Polyesters, Pharm. Res*. **2000**, *17*, 811.

169. Y. Yu., M. Nakano and Y. Ikeda. *Nature.* **2003**, *425*, 145.

170. A. Lendlein, Y. Jiang, O. Juenger and R. Ianger. *Nature,* **2005**, *434*, 879-882.

171. Y. Zhao and J. He, *Soft Matter*, **2009**, *5*, 2686.

172. Q. Zeng, Z.A. Li, Z. Li, C. Ye, J.G. Qin and B.Z. Tang, *Macromolecules,* **2007**, *40*, 5634.

173. Z. Li, W. Wu, C. Ye, J. Qin and Z. Li. *Poly. Chem.,* **2010**, *1*, 78.

174. D.R. Wang, G. Ye, Y. Zhu and X.G. Wang, *Macromolecules*, **2009**, *42*, 2651.

175. W. H. Li, S. Nagano and T. Seki, *New. J. Chem.,* **2009**, *33*, 5019.

176. Y. Mutsunga and Niyajima, *Bull. Chem. Soc.* Jpn. **1971**, *44*, 361.

177. I. Y. Bershtein, O.F. Ginsburg, *Russ. Chem. Rev.,* **1972**, *41*, 97.

178. L.J. Guggenberger and G. Teuffer, *Acta Crystallogra.,* **1975**, *B31*, 785.

179. A. Whitaker, J. Soc. *Dyers Colourists,* **1978**, *94*, 431.

180. Von. D. Kobelt, E.F. Paulus and W. Kunstmann, *Acta Crystallogra,* **1972**, *B28*, 1319.

181. M. Hashimoto and M. Sasaki, *U.S. Patents,* **1990**, *4*, 916, 39, 4, 925, 758.

182. M. Hashimoto, M. Ohta, M. Kimura and T. Fukagai, *U.S. Patent,* **1989**, *4*, 830, 942.

183. S. Umehara and M. Matsumoto, T. Takiguchi and S. Ishikawa, *U.S. Patent,* **1989**, *4*, 830, 994.

184. D.H. Song, H.Y. Yoo, J.P. Kim., *Dyes and Pigments,* **2007**, *75*, 727-731.

185. G. Smets, *Advanced Polymer Science*, **1983**, *50*, 17.

186. R. Mani, C. Rangaswamy, K. Ramarajan and L. Ravikumar, *Macromol. Chem. Rapid Commun.* **1988**, *9*, 417.

187. C. Frenz, A. Fuchs, H.W. Schmidt, U. Theissen and D. Haarer, *Macromol. Chem. Phys.,* **2004**, *41*, 1246-1258.

188. T. Breiner, K. Kreger, R. Hagen, M. Hackel, L. Kador, A. H. E. Muller, E. J. Kramer and H.W. Schmidt, *Macromolecules*, **2007**, *40*, 2100-2108.

189. R. Sankar, W. Karo (Eds.), *Polymer Synthesis*, Vol. I. Academic, New York, **1974**.

190. E. L. Charsley and S. B. Warrington (Eds.) in *Thermal Analyses Techniques and Applications,* Cambridge, **1992**, P.*156.*

191. L. Contat- Rodrigo, A. Ribes- Greus and C.T. Imrie, *J. Appl. Polym. Sci.* **2002**, *86*, 174.

192. W.W. Wendlandt, *Thermal Methods of Analyses*, Wiley and Sons, New York, **1974**.

193. R.C. Mackenzie, *Thermochim. Acta.*, **1984**, *73*, 307.

194. W.Wm. Wendlandt, *Thermal Analysis,* III Edition, Wiley, New York, **1986**, *P.228*.

195. G.W.H. Hohne, H.K. Cammenga, W. Eysel, E. Gmelin and W. Hemminger, *Thermochim. Acta,* **1990**, *1*, 160.

196. K.R. Girijan*, Ph.D. Thesis*, Calicut University, Oct. **2006**.

197. H. P. Klug and L.E. Alexander, *X-ray Diffraction Procedures*, A Wiley Interscience Publication, **1974**, P.692-694.

198. J. S. Shelly, P. T. Mather and K.L. DeVaries, *Polymer*, **2001**, *43,* 5849.

199. A. Khan, C. Kaiser and Hecht, *Angew. Chem*., Int. Ed. **2006**, *45*, 1878.

200. C. J. Gabriel and J.R. Parquette, *J.Am. Chem. Soc.* **2006**, *128,* 13708.

201. M. Moniruzzaman, C. J. Sabey, and G.F. Fernando. *Macromolecules*, **2004**, *37*, 2572-2577.

202. H. Songawa, K. Terada, T. Masuda F. Sanda, *Polym. Bull,* **2009**, *63*. 803-813.

203. S. Sivaram (Ed.). *Polymer Science- Contemporary Themes*, Vol. 1. Tata McGraw Hill, New Delhi, India, **1991**, P.338.

204. M. Umeda, T. Nimi and M. Hashimoto, *Jpn, J. Appl. Phy.* **1990**, *29,* 2746.

SECTION I

INTRODUCTION AND OBJECTIVES

Polymer Science is said to have begun when Staudinger first hypothesized that polymers are giant molecules in which small molecules are connected in the form of long chains. Numerous experimental results proved this hypothesis, one of which is Carother's unambiguous synthesis by creating the first synthetic polymer, Nylon. The discovery of this synthesis opened the door to the rich industrial fields of technological developments and the science of polymer has been a great challenge to the human intellect. Research by scientists, including pioneers as Flory and Gennis, laid the foundations and established the physical principles of Polymer Science.

The tremendous potentials of polymers in our everyday life are being exploited and diversified day by day. The chemical, medical, agricultural, transport industries and many more in one way or other are heavily dependent on wide variety of polymers. Moreover, polymers are materials that nature chose as a vehicle for life processes that appeared on this earth. Inspite of dramatic advances in polymer science, biotechnology, and material science and engineering during the last several decades, our understanding and ability for disguising polymers are far from complete. Men are far behind nature, that so elegantly designed and created biopolymers and utilising them on the molecular machinery of life. The complete dependence of biotechnology on genetic information makes evident our ignorance of the principles underlying polymer design and our lack of understanding the mechanisms behind the marvelous biopolymer function that we see around. During the last decade, however, scientists have begun to understand the secrets behind biopolymers and have started to see the possibility of synthesising polymers that can mimic life processes. There appears to be an enormous amount of room to improve polymers in the direction of good performance, their strength, better efficiency and function.

The real challenge in polymer research today is creating materials that dynamically alter their structures and properties on demand, or in response to changes in their environment. Polymer surfaces represent an attractive area of focus, since they exert disproportionately large effects on properties such as wettability, adhesiveness, optical appearance and bioactivity, enabling pronounced changes in properties to be accomplished through subtle changes in interfacial structure. Recently, active and responsive polymer surfaces as a novel and multi-disciplinary subject in this field, have attracted great interest because of the contribution to research in smart materials and devices. As a novel field, the original research into active and responsive polymer surfaces comes from Polymer Chemistry. Physics and material science are mainly focussed on the theory, fabrication methods and material properties. However, having one or several activities or responsiveness to the external environment, these intelligent polymer surfaces have many potential application in biology, microelectronics, and bionics, such as artificial muscle, flexible display, protein separation and purification, cell tailoring and liquid self-transportation.

Many synthetic polymers that exhibit environmentally responsive behaviour are considered as biometric and their development is central to emerging ‘smart’ application in biology and medicine[1]. The synthetic or modified biological materials that can undergo conformational or phase changes in response to variations in temperature and/or pH, are being developed as diverse or bulk engineering and microscale application. Responsive polymers also play a major role in engineering nanoscale technologies.[2-4] For this reason, now is a crucial moment in science to advance our understanding of polymers in particular. The knowledge of the technical methods of characterising polymer systems is of inevitable importance to modern technologies spanning many different fields. It is essential to master the modern polymer techniques and technologies in all areas of experiment, theory, and computation to understand fully the up-to-date research as well as to open the doors to new research areas.

Organic photochemistry has also made considerable advances as a science during the last few decades. The Sun’s energy used during photosynthesis by chlorophyll to produce carbohydrate from atmospheric carbondioxide and liberation of oxygen back to atmosphere is clearly the Nature’s choice of photochemical energy conversion to chemical energy. The dye sensitized electrochemical solar cells for the conversion of visible light to electricity, the optoelectronic properties of oligosilanes, and polysilanes, photoinduced metal/metal oxide decomposition on semiconductors and redox reaction of transition metal complexes are all concerned with inorganic photochemistry. The industrial aspects of organic photochemistry opens new vistas of technological significance. Application of emission properties of excited molecules are utilized in optical brighteners and chemiluminescence. The excellent accepter ability of recently developed fullerene is a key feature of photoconductivity of fullerene-dopped polymer films. Understanding the photochemistry of drugs is essential for rationalizing the significant phototoxicity of many drugs and also in the field of photoimmunology, photodynamic therapy and photomedicine.

Chemically, chromophores are of prime importance in nature and play a fundamental role in many aspects of life, such as photosynthesis and the processes within the circulatory system. They also act as dyes and pigments in a wide variety of technological applications. In many of these, the organization of chromophores are crucial for the performance of the assembly as device. To arrange the chromophore into the fundamental architecture, scientists have developed a number of approaches for the precise positioning of chromophoric building blocks and these have been applied extensively in the last years, in particular in the field of material sciences. Often the very elegant and essential chromophoric arrays that can be found in nature are used as a source of inspiration and sometimes as a blue print for synthetic systems. Incorporating photochromic/chromophoric molecules into organic materials leads to photoresponsive systems, the properties of which can be manipulated by light. Photochromism is usually the reversible photoinduced transformation between two molecular states whose absorption spectra are significantly different. Besides this colour change, which is the most spectacular evidence of photochromism, many molecular and bulk properties also change along whith this transformation. For example at molecular level, switching of metal ion capture and energy or electron transfer can occur as a consequence of a photochromic reaction. As concerned with bulk properties, photostimulated viscosity changes or even phase separation is observed in polymeric solutions loaded with photochromes; more interesting, photostimulated conformational changes of polymeric chains in solids can induce macroscopic changes in the shape and size of polymers and solids.

The advances made in polymer systems incorporating photochromic moieties[5-10] give us ample information on the mobility of polymer matrix.[11] Several light sensitive chromophrores like azo groups, stilbene systems, spiro-benzopyran groups are known for their important photoresponsive properties[12-15], where the chromophoric groups become part of polymer in the backbone or as pendant groups, the photoresponsive character is induced to the macromolecules too. In the case of low molecular weight compounds their photochemical phenomena are related to structural modifications such as valence isomerisation, tautomerism, geometrical isomerisation and ring opening. By this molecular processes, physical properties such as pH, solubility, metal ion chelation, membrane permeability, surface wettability etc. in the polymer films and gels are changed.[16, 17] It is well known that photochemical reversible *cis*-*trans* isomerization is responsible for many changes in physical properties of the polymers having stilbene system and azo groups[18-21].

Blair[22] and Umeda[23] first reported azobenezene containing polymers in which azobenzene units introduced into the main chain undergo isomerisation from *trans*- *cis* form under UV-irradiation. This *cis* form can return thermally and photochemically to the *trans* form which is thermodynamically more stable. *Ortho*-substituted azo systems have attracted considerable attention owing to their outstanding photoconducting properties. Azo pigments formed from 2-naphthol groups exhibited moderate/high photoconductivity owing to the well documented *ortho*-hydroxyazo to ketohydrazone tautomerism both in solution and solid state.[24,25] Electron withdrawing functionality and the hydrogen bonding are the key driving forces that shift the equilibrium to the more thermodynamically favoured[26, 27] ketohydrazone form. The advance made in the field of organic photoconducting materials and the photochromic phenomena associated with azo systems prompted to design polymers having *ortho*-hydroxyazo group in the polymer backbone. Thus, the present investigation deals with the development of photoresponsive polymers and the property changes occuring in some hitherto unreported polyesters with *ortho*-hydroxyazo chromophores as pendant groups and in the polymer backbone. The main objectives of the investigation are:

(i) to synthesise photoresponsive polyesters having *ortho*-hydroxyazo groups as pendant groups and in the polymer backbone.

(ii) to characterise the synthesized polymers by different analytical and spectral methods.

(iii) to determine dilute solution photoinduced viscosity changes that occurring in the polymers.

(iv) to determine dilute solution conductivity changes of the synthesised polymers.

(v) to correlate the photoinduced viscosity and conductivity changes of the polymers with the conformation of the polymer chains in the dilute solution.

(vi) to assess the photoconductivity of polymers in the solid state.

The thesis is divided into 6 sections. An overview of the important properties of the photoresponsive azo pigments and polymers touching upon their applications are described in section 2. Section 3 describes the synthesis and characterisation of different *ortho*-hydroxy azobenzene containing polymers. The photoinduced property changes (viscosity and conductivity) of the synthesised azo polymers in dilute solutions are described in section 4. The solid state properties of *ortho*-hydroxyazo polymers prepared as pellets are described in section 5. The experimental methods used are described in section 6. Summary of the results and the conclusion that are arrived at, touching upon their future implications are also included. The references are given at the end of the thesis.

SECTION 2

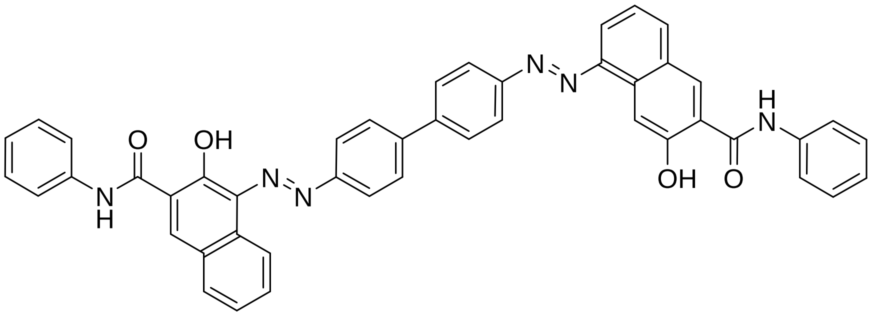
PROPERTIES OF PHOTORESPONSIVE AZO PIGMENTS AND POLYMERS

2.1. INTRODUCTION

Azodyes and pigments belong to a class of colourants which consists of azo chromophore (-N=N-) linking aromatic groups and are capable of undergoing both $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electronic transitions when irradiated with UV-visible light. The preparation of azo compounds by classical diazotisation or tetrazotisation method and coupling reaction is very simple, which enabled azo compounds to become the large group of synthetic colourants today. Likewise, when these azo chromophores attached to polymeric chains as backbone or as pendant groups, photoresponsive polymers are resulted. The photoinduced isomerisation of azobenzene, proceeds with good structural changes are reflected in the dipole moment and geometry and when the photochrome is a part of the long polymer chain, changes the configuration which affects the chain conformation. The conformational changes are eventually manifested in the physical properties. Analogous to the reversible solution viscosity changes, photocontrol of macromolecular conformation also significantly affects the solution conductivity. The well-illustrated *tran-cis* isomerisation is considered to be the key step in the photoinduced conductivity of polymers with azobenzene moieties. Therefore, it is thought worthwhile to review the important properties of azo chromophores containing pigments and polymers.

2.2. Photoconducting behaviour of azo compounds

Organic photoconductive materials have been rapidly developed because of their non-toxicity, low cost, magnitude and variability of development, mechanical and architectural flexibility[28]. Azo pigment was widely used as a charge generation material because of their technological advantages such as high sensitivity wide spectral range (450-800 nm) and excellent stability.[29] Rau[30] in 1968 reported the photoconductive properties of azo pigments based on the observation of photocurrent from thin layers of 1-phenylazonaphthol. Later, Champ and Shattuck[31] reported the photogenerating efficiency of biazo pigment, chlorodiane blue (**1**) for xerographic devices. This earlier work coupled with the ease of synthesis has led to intense research activities in photoreceptor industry. Later thousands of azo pigments[32-37] of new structures were synthesized and screened for photoreceptor applications.



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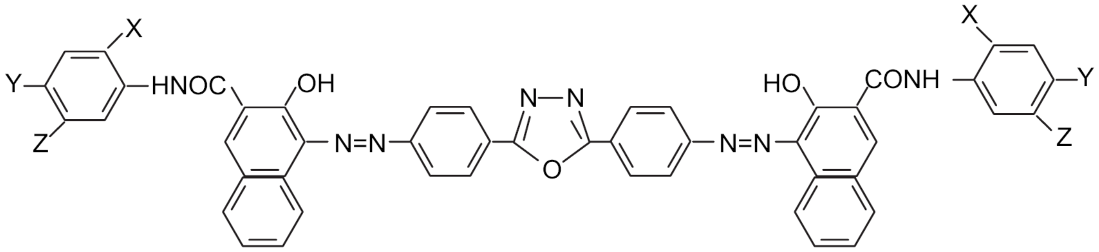
The azotisation and coupling reactions were carried out in an ice-bath (0-5°C). During base catalysed coupling reaction, a variety of bases including sodium hydroxide, and triethylamine etc, were used. Most of the synthesised pigments were purified prior to use as photoconductors. In general, purification were achieved by repetitive washings with water, very dilute solutions of DMF and DMSO.[38-40] The number of washings and the temperature of washings were found to be critical to photoconductive properties. The role of these washings on photoconductivity was not clear. It has been reported that the photoconductive azo pigments undergo morphological changes in ketonic solvents at elevated temperatures. The literature survey indicates that azo pigments from 1-naphthol couplers consistently exhibit moderate to high photoconductivity.

The photoconductive azo pigments were practically insoluble in common organic solvents and all having *ortho*-hydroxy substitutents. The optical absorptions were examined in the solid state (KBr pellet) since absorption chromophore has ketohydrazone unit. It was also known that substituents have no effect in the hydroxy to ketohydrazone tautomerism. Because of the same reason, the absorption wavelength was not expected to be sensitive to the structure of the aromatic azolinkages.[41] Most of the photoconductive azo pigments were sensitive in the visible region (450-650 nm) and generally found to be less crystalline according to XRD studies. One cannot, however, conclude that azo pigments are amorphous because broad and featureless patters can be obtained from materials having very small crystalline sizes. The observation of high photoconductivity of azo pigments is an indication that a certain degree of microscopic order must exist in these materials.

Both visible and IR sensitive azo pigments were known and from the numerous azo pigments so far prepared showed that the dark decay values were low compared to phthalocyanine and squaraines.[42-44] The high purity of these materials may be one of the reasons for the low dark decay value. The very high photosensitivity, excellent photoelectrical stability[45-46] and above all the low cost solution coating manufacturing techniques all contributes to the technological advantages of these azo pigments. The solid state photoconductivity of bisazo compound, 1,3,4-oxadiazole compound has outstanding capability of transporting electrons, especially its good thermal stability and antioxygenation given by its special structure[47 - 49] **2**.



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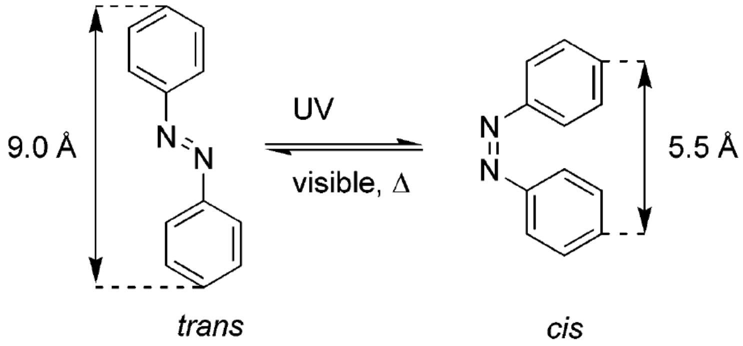
2.3. Properties of Photoresponsive azo polymers

2.3.1 Photoviscosity

Azobenzene and its derivatives undergo *trans to cis* isomerization when subjected to UV irradiation[50]. This isomerisation effectively reduces the distances between attachment points from 9.0 to 5.5 A° as illustrated in scheme 1.



Scheme 1

When the azobenzene molecule is attached chemically to a polymer chain, photoinduced isomerisation can result in conformational changes, which being induced in the polymer chains. This can cause significant changes in physical properties such as dipole moment, refractive index, and solution viscosity. Many of these changes can be reversed by heat or visible irradiation.

Viscosity changes in polymer solution associated with photoinduced conformational change of the narrow molecular framework was reported by Lovrien in 1966[51]. Lovrien reported that under the influence of UV light, the solution of a copolymer of methacrylic acid and N-(2,2′-dimethoxyazobenzene) acrylamide exhibited an increase in the intrinsic viscosity. The same author also investigated the photoviscosity effect of polymethacrylic acid and chrysophenine in water, reporting a decrease in intrinsic viscosity of 50% due to UV irradiation. Following from Lovrien's work many more studies have been conducted into the photoviscosity effect on azobenzene based polymers. The effects of azobenzene groups in the side chains of a polymer have been studied in a co-polymer of maleic anhydride with styrene[52], where irradiation was found to decrease the intrinsic viscosity of the solution between 24 and 30% in 1,4-dioxane and between 1 and 8% in THF. The magnitude of the effect was found to depend on the concentration of the azobenzene groups in the polymer and on the time of irradiation. The rate of conversion was shown to decrease with increasing solution concentration.

Hallensleben and Menzel[53] reported that due to irradiation ($\lambda > 470\,\mathrm{nm}$) the viscosity of a 1,4-dioxane solution (0.64 g/L) of poly [5-(4-phenylazobenzyl)-L-glutamate] decreased by 9% compared to that of the unirradiated sample. This change was accompanied by a 23% *cis* isomerization as inferred by UV-visible spectroscopy. Under UV-irradiation (360 nm) the viscosity dropped by a further 9% with a corresponding 86% *cis* isomerization.

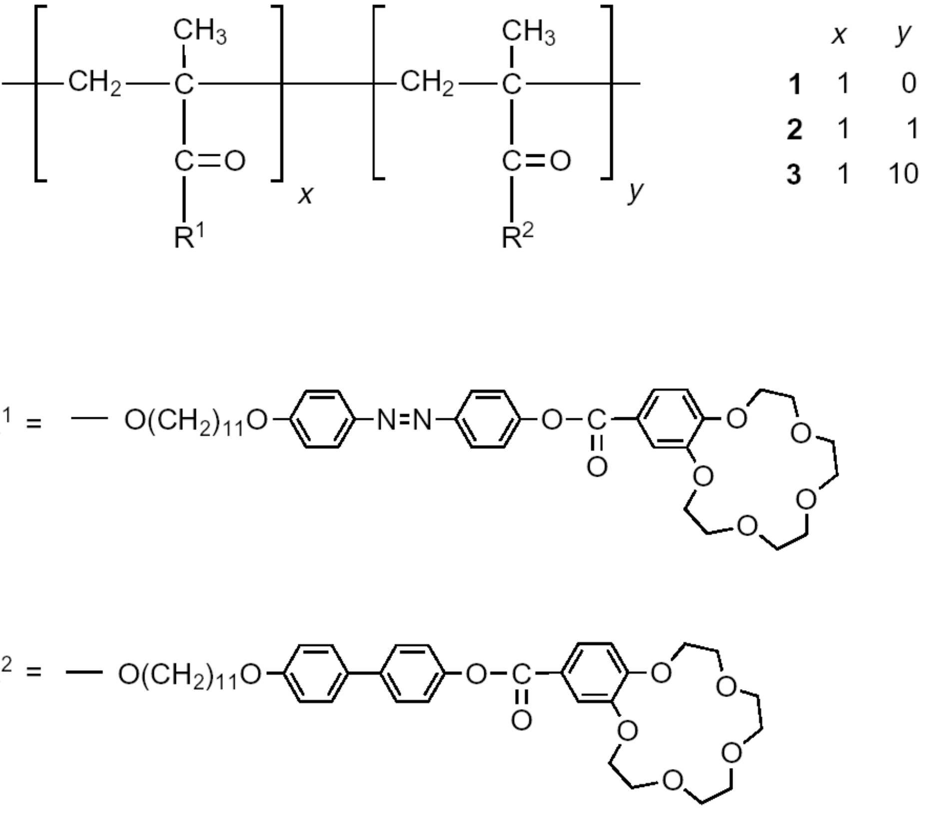
Irie and co-workers[54] synthesized a range of polyamides containing azobenzene groups in the backbone. All of the polyamides exhibited a remarkable decrease in the photoviscosity effect. They reported a 60% specific viscosity reduction due to irradiation (410 >λ > 350 nm) of a solution in N,N-dimethylacetamide. The initial viscosity was regained after 30 h of being stored in the dark at 20 °C. It was reported that the rate of recovery could be increased with the aid of visible irradiation (λ > 470 nm) with the recovery time being reduced from 30 h to 10 min. The authors investigated the influence of spacer groups in the polymer backbone and speculated that the magnitude of the photoinduced changes in the viscosity decrease with the addition of flexible units such as methylene groups.

Kumar and co-workers investigated a range of polyureas[55] with azobenzene groups in the polymer backbone in DMSO at 35°C. The intrinsic viscosity was found to be about 30% lower on irradiation (410 > λ > 350 nm) than in the dark. The photoviscosity change was attributed to a conformational change of the polymer chain rather than interchain interaction. The original viscosity was recovered in the dark after 8 h at 20 °C. A study of similar polyureas[56] was performed in DMSO at 30 °C., with the intrinsic viscosity reported to be about 40% lower during UV irradiation than in the dark.

A plausible interpretation of the results is that the intramolecular dipole-dipole interaction between neighbouring azobenzene chromophores play the most significant role in producing the photoviscosity effect. However, other effects such as temperature rise upon UV exposure, molecular weight distribution of the polymer, and water absorption by DMSO during the progress of the experiment may also have some influence. Under UV-irradiation, the azobenzene side chain undergo *trans*-to-*cis* isomerisation, including a dipole-across the N=N bond. Neighbouring dipoles are believed to orient and attract each other, contracting the polymer backbone and hence decreasing the viscosity.

2.3.2. Crowned azobenzene

Azobenzene derivatives incorporating a crown ether moiety[57], 'crowned azobenzene', can undergo photoinduced switching of ionic conductivity in composite films containing an alkali metal salt. This is based on the photoisomerization induced phase transition of azobenzene derivatives between their solid and liquid states and thereby the mobility changes of ion-conducting carrier[58]. Polymers carrying a crowned azobenzene moiety on the side chain such as in compound **3** are capable of forming highly ordered liquid crystal phases. On the other hand, the order-disorder cycle in the liquid crystal phase is induced by photoisomerisation of the azobenzene moiety between its *cis* and *trans* form. This brings about quite different behaviour in the photoinduced ionic conductivity changes from the corresponding low-molecular mass crowned azobenzene derivatives.[59, 60]



	x	*y*
1	1	0
2	1	1
3	1	10

3

UV-light induced isomerization of the azobenzene moiety causes some disorder in the crown ether moiety (an ion hopping site) in the liquid crystal state of the polymer, thus decreasing ionic conductivity and this is reversed by subsequent visible light irradiation. The highest magnitude in the photoinduced ionic conductivity changes was attained in polymer containing the highest crowned azobenzene content, owing to the more efficient photoinduced phase transition. Moreover, polymers with the highest content of crowned azobenzene moiety also showed the fastest response in photoinduced switching.

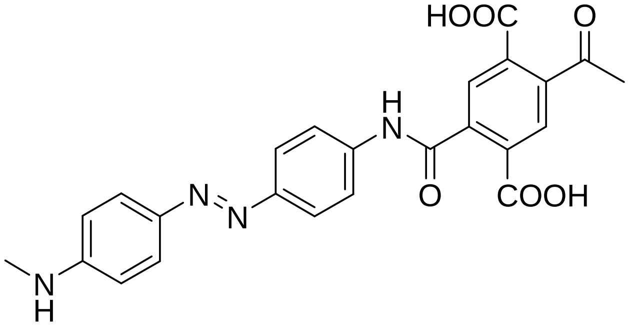
2.3.3. Enzyme biosensors

Recent advances in surface functionalisation of solid supports allow to engineer 'Smart' bioelectronic interfaces based on enzyme modified electrodes integrated with photoisomerisable polymer.[61] Polymer/peptides doped with azo units[62-67], exhibit light-stimulated structural transition (photoisomerisation) resulting in conformational changes of the polymer and allowing photostimulated control of enzyme activity.

Most enzyme biosensors are based on ion mediated electron transfer between the electrode and redox enzyme.[68] Electron transfer mediators are synthetic or biologically active charge carriers, which assist the electrical commmunication of redox enzymes with electrodes. Normally the contact of enzyme's action site (reaction site) with electrode surface is hindered by the enzyme's insulating shell. Azobenzene, a small photoactive benzene containing molecule when exposed to UV-irradiation undergoes a reversible *tran-cis-trans* conformational change (photoisomerisation) which produces a significant change in molecular geometry. This property has been used for fabrication of a single molecule of azobenzene enzyme photoswtich when the azo-dopped peptide (a photosensitizer) has been tailored precisely next to the active centre of a redox protein[69]. The unique property of azobenzene molecules suggested by Bredenbeck and co-workers is its picosecond *trans-cis-trans* conformational transition under illumination. Having only a few conformational degrees of freedom compared with a protein, the azo based photosensitizer behaves as an ultra-fast folding protein while protein conformational changes are usually slow ranging from microseconds to milliseconds relaxation times. This suggestion offers a mean for investigation of electron-conformational coupling both in meso and nano scale in azo-protein based molecule sensors, in particular, azobenzene is an excellent candidate for investigation of electron-conformational transition under irradiation. The use of azo-containing photoactive molecular assembly as a switching element is also a great challenge in optoelectronic applications[70,71] in memory devices, displays and for design of high speed molecular swtiches driven by light.

2.3.4. Spectral response

UV-visible spectroscopy has been extensively utilized to study photoisomerisations involved in polymers.[72-75] In 1990, Hor *et al*[76] observed similar type of spectral changes in photoresponsive polyamides having azobenzene group in the backbone of the polymer chain. The intense absorption at 390 nm was decreased when, N,N-dimethyl acetamide solution of the polyamide **4** was irradiated with UV light while the band at 510 nm was increased in intensity. The intense band at 390 nm was attributed to the *trans* form whereas the band at 510 nm due to *cis* form. The change in the intensity of the two bands is a clear evidence of the photoisomerisation of azobenzene resides in the chain backbone. It was also observed that the intensity of absorption at 390 nm increased gradually after cutting of the light and keeping the polymer solution at room temperature.



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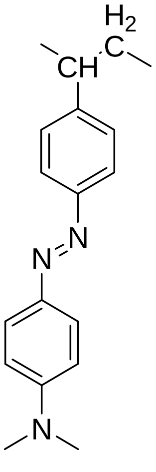
Kamogawa and co-workers[77] studied the spectral changes in 4-vinyl-4′-dimethylamino azobenzene polymer **5** with light irradiation from a 500 W tungston lamp spotlight. It was observed that upon irradiation, absorption peak of the polymer shift towards shorter wavelength and the absorbance at the original wavelength decreases simultaneously. The recovery of the original peak site was observed when the irradiated polymer was exposed to darkness. Following this, a detailed study was carried out on the spectral characteristics of a series of aminoazobenene polymer by the same research groups.



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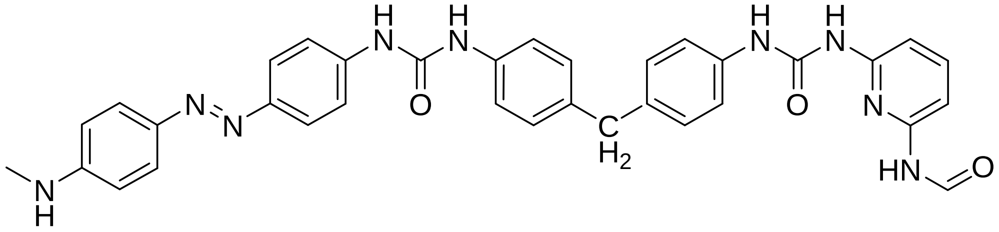
Absorption spectra of azo aromatic polyureas **6** in DMSO showing thermal recovery after irradiation with UV light (410 >λ >350 nm) have been studied by Sudheshkumar *et al*.[56]



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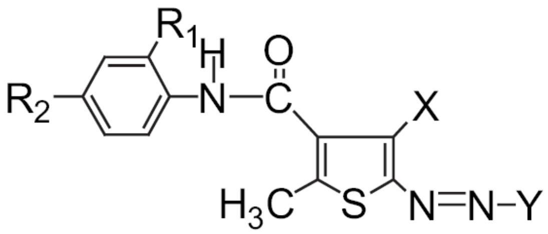
According to them, intensity of peak at 410 nm decreased after irradiation. The thermal isomerisation from the photogenerated *cis* form to the *trans* form was the explanation offered for the gradual increase in intensity at 410 nm of the polymer solution in the dark. Analogous spectral changes[78] were observed by Irie *et al* in polystyrene having azobenzene pendant groups. On irradiation of a cyclohexane solution of polymer with UV light (410 > λ > 350 nm), the intense absorption at 350 nm decreased while the absorption of 440 nm increased. The absorption band at 350 nm was due to π→π* transition of the *trans* form of the pendant azobenzene residue and the band at 440 nm, due to n→π* transition of the *cis* form. The intensity change of the 350 nm band and the 440 nm band was a clear evidence of the isomerisation of the pendant azobenzene residues.

The absorption spectra of several polypeptides with azobenzene moieties subjected to photoirradiation have been studied in detail.[79-83] The absorption spectra of co-polymers resemble that of azobenzene showing the absorption associated with π→ π* and n → π* transitions of the side chain azobenzene moieties around 320 nm and 450 nm respectively. The effect of photochromism and the absorption spectra of azobenzene modified crown ethers also have been reported.[84] Similar spectral changes before and after photoirradiation were also reported in azobenzene containing polyesters in the polymer backbone.

A number of researchers studied aminothiophene derivatives **7** as azo disperse dye in the dying of synthetic fibers[85-93]; blended polyesters/wool fibers[94,95] and more recently in optical data storage devices[96] and semi conducting properties.[97] The 2-aminothiophene based azo dyes have many advantages including a colour deepening effect and an excellent sublimation fastness as dyed films. Aminothiophene was diazotised and coupled with phenol or naphthol derivatives affording a variety of azo dyes based on thiophene moities. UV-visible studies[98] of these azo dyes in a number of polar solvents showed a considerable change in the λ_{max}. The introduction of various substituents of these azo dyes as well as the polarity of solvents resulted in absorption in the visible region ranging from 461 to 555 nm. Increasing the electron withdrawing strength of the substituents on the thiophene ring resulted in bathochromic shifts.



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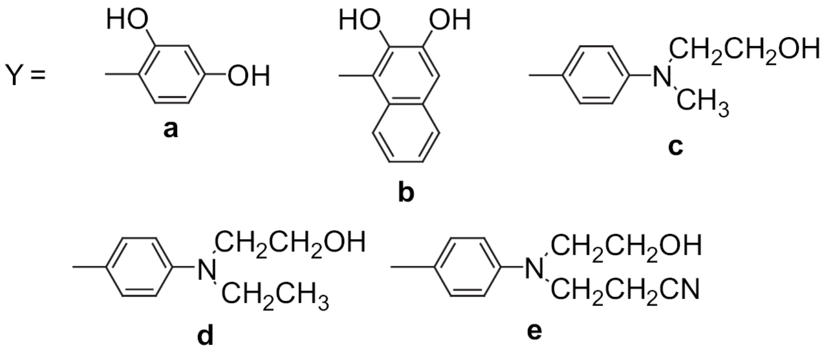


Absorption spectra of these azo dyes showed an absorption band in the region 469-540 nm in ethanol, 466-546 nm in acetone, 494-555 nm in DMF, 464-546 nm in DCM, and 461-546 nm in acetonitrile. These bands were due to electronic transitions involving the whole conjugate system, both of the phenyl and five membered sulphur heterocycle and the azo groups are assigned to a π-π* transition. The introduction of the cyano group, an electron withdrawing substituent onto the thiophene ring produces a bathochromic shift (29-31 nm) of the absorption band, while the replacement of the cyano group by an ethyl ester group gives a notable hypsochromic shift. This is attributed to more extensive electron delocalization and the smaller steric requirements of the rod like cyano group.[99]

Bathochromic shift of the visible absorption band were also observed on increasing solvent polarity. This is expected for a system in which the excited state is more polar than the ground state.[100,101] The change in the λ_{max} value depends on the nature of coupling site as well as the nature of the substituents at the terminal amino group. Bathochromic shifts (53-55 nm) were observed on replacing resorcinol at the coupling site with 2-(methyl phenyl amino) ethanol using the same solvent. However hypsochromic shift of 14-17 nm was noticed by replacing the methyl group at the terminal amino group of the coupling site by propiononitrile Inductive electron withdrawal by the propiononitrile group gives a reduction in the electron releasing tendency of the terminal nitrogen atom and a consequent hypsochromic shift of the visible absorption band. This is in agreement with that previously reported by Patel *et al.*[102] From this, it is clear that the absorption maxima of azo dyes have larger bathochromic shift in DMF than in other solvents. On changing substitutents in the phenyl ring of azo compounds there is no significant variation in λ_{max} value. However, the replacement of the cyano group on the thiophene ring by ethyl ester groups exerts hypsochromic shift of 29-31 nm.

2.3.5. Photoresponsive polymer films

Polymer films containing photoresponsive molecules such as spiropyran[103,104] represent attractive candidates for controlling protein and cell adhesion on surfaces. Spiropyran ring opening by illumination with UV light from the more hydrophobic spiro conformation to the polar hydrophilic zwitterionic mesocyanine conformation, while reverse isomerisation can be triggered by irradiation with visible light. This change from hydrophobic to hydrophilic state upon isomerisation has been applied to demonstrate UV light-induced detachment of fibrinogen, platelets and mesenchymal stem (KUSA-A1) cells from poly (spiropyran-*co*-methyl methacrylate)-coated glass plates. Hayashi *et al*[105] have shown that, when azobenzene moieties were incorporated into a peptide immobilised on a carboxy methylated dextran-coated gold surface, the structural changes in the azobenzene could lead to the photoregulation of peptide binding to its RNA aptamer. Also by taking advantage of the changes in azobenzene molecular dimension, which is decreased by approximately 3.4 A° upon isomerisation from the *trans* to *cis* conformation, Kessler *et al*[106], reported the control of cell adhesion properties on the peptide arginine-glycine-aspartic acid (RGD)- functionalised surfaces. The azobenzene derivative, 4-[(4-aminophenyl)azo]benzocarbonyl, was incorporated into the RGD peptide and tethered to a poly (methyl methacrylate) surface by UV irradiation. The photoswitchable RGD peptide coated surfaces exhibited enhanced cell adhesion in the *trans*- azobenzene configuration. On the other hand, the surfaces that had previously been UV irradiated at 366 nm showed a reduced cell plating efficiency as a result of shortening the distances of the RGD peptides to the surface by the *trans-cis* isomerization of the azobenzene derivative. The azobenzene molecule has also been incorporated into an enzyme inhibitor to provide a means of modulating the binding of α-chymotrypsin to a surface[107]. Photoregulation was also achieved by using a phenylalanine based trifluoromethyl ketone inhibitor containing a photoisomerisable azobenzene group, an oligoethylene glycol as a spacer, and a terminal alkyne for attachment to a surface bound azide using click chemistry. The azide modified surface was formed by covalently linking azido oligoethylene glycol amines to the carboxylic acid groups of a dextran polymer matrix coated gold surface. The surface-bound azobenzene inhibitor in the *trans* configuration exhibited a reduced binding of the functionalised surface, while with UV light (> 360 nm) induced isomerisation from the *trans* to the *cis* configuration was accompanied by a significant increase in enzyme binding to the surface.

2.3.6. pH and conductivity

Photostimulated changes in conformation of polymer give rise to changes not only to viscosity but to other solution properties like pH and conductivity. Light induced changes in pH is of particular importance in connection with the function of bacteriorhodopsin.[108] Photocontrol of conformation of poly (methacrylic acid) in solution at degrees of ionisation of 0.2 and pH 4.5-5.5 was possible with the use of cationic ligands based on *p*-(phenylazophenyl) trimethyl ammonium iodide.[109] The *cis*-*trans* photo isomerisation leads to a change in the degree of cooling of the polyelectrolyte molecules and thus the display of an induced photochemical jump in pKa value has been explained. Irie and co-workers[110] achieved photocontrol of conductivity and pH values on photoresponsive polyamides having terephthalic acid groups. Analogous to photoviscosity effect, the response of the conductivity correlates well with isomerisation of the azobenzene residues in the polymer backbone. Here, the conformational changes of the polymer chain influence the dissociation equilibrium of amide substituted terephthalic acid residues in the polymer backbone. Dissociation of the acid is stimulated in the compact conformation, while the extended conformation depresses the dissociation. A possible explanation for the increase in dissociation of the compact conformation is that the *cis* form of the azobenzene residues in the compact conformation has a polar structure compared with the *trans* form and hence the polar structure assists in dissociation of the acid. The changes in the equilibrium constant of dissociation of the acid in organic solvents by photoirradiation suggests the possibility of pH control in aqueous system. The photocontrol of pH using a synthetic polymer has special interest in view of its importance in constructing photoreceptor analogues.[111] The photo induced conductivity changes of polyvinyl esters having pendant azobenzene groups and polyesters with azobenzene groups in the polymer backbone were also reported.[20]

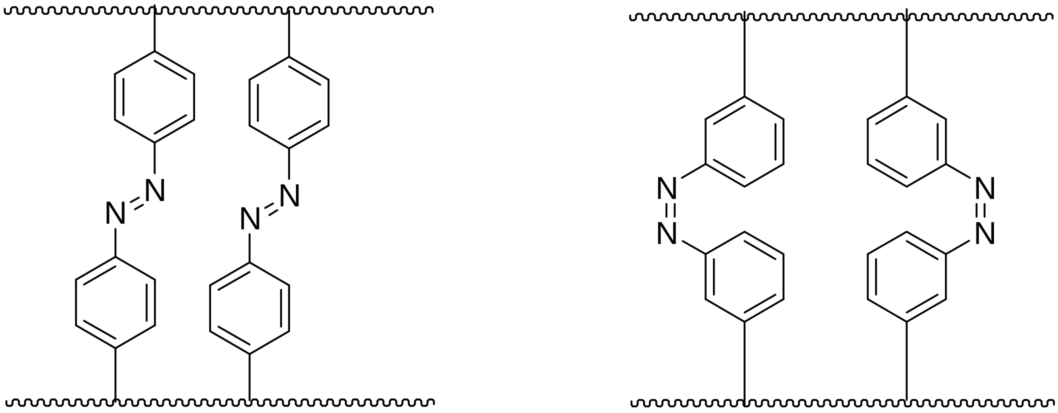
2.3.7. Solubility

When photoisomerisable chromophores are incorporated into the backbone of a polymer chain or as pendant groups, photoisomerisation of the chromophores will affect the physical properties of the polymers and polymer solutions, especially, if the isomerisation involves a change in polarity. Changes in the dipole moment of pendant groups upon photoirradiation resulting in expansion or contraction of polymer chain. The studies of polystyrene in cyclohexane in these direction are also the contribution of M. Irie.[54] The polystyrene with a small amount of azobenzene pendant groups become insoluble in cyclohexane upon irradiation with UV light ($410 > \lambda > 350$ nm) while low molecular weight azobenzene itself did not show any solubility change on photoirradiation. On visible irradiation ($\lambda > 470$ nm), the polymer again becomes soluble. In cyclohexane solution intermolecular interaction between polystyrene and the solvent is in balance with the intra-inter polymer interactions. As a result of isomerisation[72,] the dipole moment increases from 0.5 to 3.1 D. The dipole moment increase of the pendant groups by UV irradiations is considered to alter the balance of polymer-solvent and polymer-polymer interactions. The introduction of non-polar *trans* azobenzene into polystyrene as pendant groups scarcely affects the polymer-solvent interaction in cyclohexane while the polar *cis* form tends to decrease the polymer-solvent interaction. Therefore, on UV irradiation, the polymer-solvent interaction decreases considerably until the polymer precipitates. It was also reported that isomerisation of a few mol percent of azobenzene units in the polymer chains is large enough to cause a solubility change of the polymer, though the precipitation behaviour depends on the nature of the solvent.

On naturally occurring photoreceptor, several studies have been provided as evidence of changes in aggregation of protein matrices upon photoexcitation of the attached photochromic moiety.[112, 113] A photoinduced aggregation – disaggregation process has been reported in human immuno globulin labelled with azobenzene reagent.[114]

2.3.8. Swelling properties

A qualitative treatment on the mechanism of photostimulated gel dilation of azobenzene cross-linked polymer on the basis of photostimulation has been provided[115]. Here, polyvinyl esters having azobenzene cross links before irradiation are mainly in the *trans* configuration **8**. During photoirradiation, the *cis* content of the gel increases and as a result, the increase in the pore volume of the network polymer, is the best plausible explanation.



trans

cis

8

2.4. Applications

Photoresponsive polymers represent a new class of speciality polymers. In biological systems, light acts not only as an energy source for photochemical transformation but as an information source or trigger for the reversible control of the physical and chemical properties. Biological photoresponsive systems which contain photochromic moieties embedded in biopolymer matrices are mainly responsible for the photoisomerisation controlling the conformation and assembly of the biopolymers. The ability to modulate biomolecule activity on surfaces can be tremendously useful as a way to develop reagentless, sensitive and real-time biosensors.[116-122] Such smart surfaces have the potential to develop highly functional microfluidic, bioanalysis, and bioseperation systems.[123-126] Biosensors which transduce a biorecognition event into measurable electronic or optoelectronic signals, have a crucial role in a wide range of applications, including clinical diagnosis, environmental monitoring, forensic analysis and anti-terrorism. The demand for more reliable and efficient protein separation and purification methods are increasing with the rapid development of biotechnology and pharmaceutical potential of recombinant protein in the treatment of various diseases. Surfaces with stimuli responsive polymers have wide range of application in science and technology ranging from environmental clean up to data storage.[127-131] Smart surfaces with stimuli responsive changes in wettability, hydrophilic or hydrophobic are of interest for the development of, for instance, micro and nanofluidic devices self cleaning and anti-fog surfaces and sensor devices.[132, 133]. In addition to demonstrating photochemical[134-144], electrical[145-149], solvent[150-153], temparature[154-156], and pH[157] control over surface wettability, recent studies[134,141] have shown that stimulus driven molecular motion of surface bound molecules can be used to drive droplets of various liquids across these surfaces in a controlled fashion.

Another important area of research under investigation is the development of substitutes that dynamically regulate biological functions in response to applied stimuli, thereby mimicking the dynamic properties of biological systems. Surfaces that can modulate biomolecule activity, protein immobilisation, and cell adhesion and migration at the liquid-solid interface are also useful in diverse biological and medical applications.

The introduction of photochromic moieties into polymer chain can produce sudden changes in conformational properties as a result of photoirradiation. Several biological systems[158,159] and photochromic azo dyes[160-162] either covalently or non-covalently connected to macromolecules have been used to control polymer conformation and obtain photoregulation in membranes. The photoinduced reversible chirality inversion in polypeptides as a result of the photoisomerisation of azobenzene moieties, might permit photocontrol in chiral recognition or chiral catalytic reactions, when binding or catalytic functional groups are incorporated into the polypeptide sequences.

Besides the change of their UV-visible absorption spectra, photochromic molecules offer a large panel of linear and non-linear optical properties. The extra ordinary growth and development of non-linear optical materials during the past fifteen years have rendered photonic technologies as essential part of many components used in our day-to-day life, in computer networks and telecommunication system. The potential applications in reversible optical data storage, diffraction and holography have stimulated a great deal of experimental and theoretical work, which starts to extend to the use of different photochromic systems. Photobleaching of azo compounds by ultraviolet exposure of polymer gel film may be used for channel waveguide fabrication.

Living systems respond to external stimuli adapting themselves to changing conditions. Polymer scientists have been trying to mimic this behaviour for creating the so called smart polymers. These polymers undergo reversible, physical or chemical changes in response to very small external changes in the environmental conditions, such as temperature, pH, light, magnetic field or electric field, ionic factors, biological molecules etc. Smart polymers have promising application in the biological field[163, 164] such as delivery systems of therapeutic agents, tissue engineering scaffolds, cell culture supports, bioseparation devices, sensors or actuator systems. Polymers sensitive to temperature changes are the most studied class of environmentally sensitive polymers as they have potential application in the biomedicinal field. Rodriguez-Cabello's[165] group has extensively worked in the development of elastin-like polymer (ELPs) by genetic engineering owing to their extraordinary potential. They developed different materials by fermentation, which showed significant environmental advantages. The ELP's presented a modulated pH-and T-sensitivity covering the most interesting range of biomedical application and they have also been modified with photoresponsive molecules of azobenzene[165] and spiropyrans[166] to get photosensitive macromolecules. Kurata and Dobashi[167] studied the potential of intelligent drug carriers based on N-acryloyl-N ́-alkylamide derivatives of both L-glutamic acid and L-aspartic acid. New co-polymeric systems derived from N,N-dimethylamino ethylmethacrylate (DMAEM) and acrylic acid (AAc) or itaconic acid (IAc) have also be investigated. They responded to both pH and temperature as a polyampholyte according to the monomeric composition and combinations of temperature and pH conditions.[167] Photomechanical and photoviscosity effects and pH control systems are important by themselves and have possible commercial applications. Researchers have investigated more sophisticated pH sensitive polymer in order to take advantage of the pH changes that occur in nature. These materials are inspired by living organisms trying to mimic their response mechanisms. The most promising applications of pH-sensitive polymers are in non-viral gene carriers[168] and in the fabrication of insulin delivery for the treatment of diabetic patients.

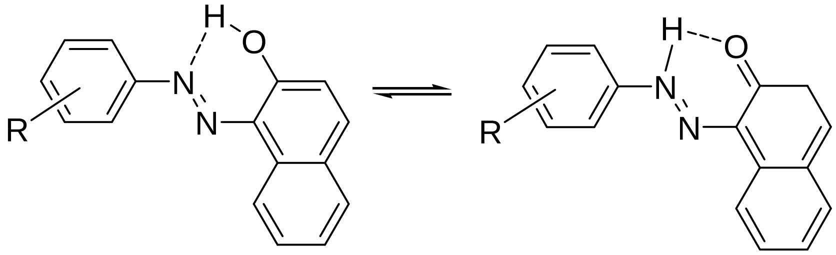
SECTION 3

SYNTHESIS AND CHARACTERISATION OF POLYMERS CONTAINING *ORTHO*-HYDROXYAZO CHROMOPHORES

3.1. **INTRODUCTION**

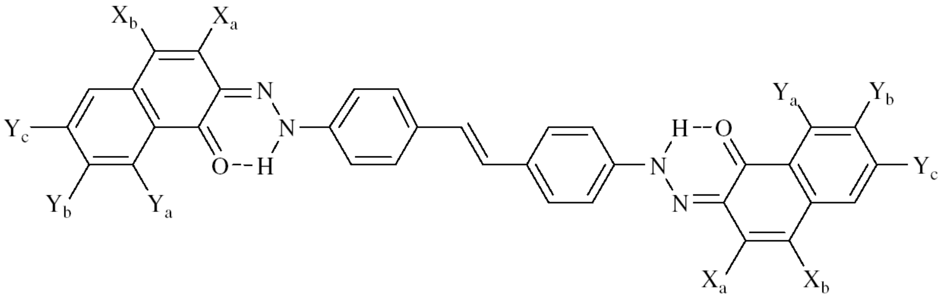
Significant advances have been made in stimuli sensitive materials in recent years. Substances can respond in a specific manner to certain external stimuli such as light, heat, pH, ionic strengths, electric field and nature of solvents. The major advantage of using light as a trigger is that it can be applied to the system without disturbing the surroundings. By incorporating a photoresponsive chromophore into a polymeric system, microscopic deformations of the chromophore efficiently transfer to the macroscopic dimensions of the polymer. Incorporating a photoresponsive chromophore into a polymer network, which can undergo photo-contraction under external stimuli is a well established strategy to convert light energy to mechanical energy[169]. Numerous photosensitive compounds like functionalized azobenzene derivatives, leuco derivatives of cinnamic acids, and spirobenzopyran compounds have been extensively studied.[170]

Azobenzene compounds were well known for their reversible *trans*-*cis*-*trans* isomerisation. The more stable *trans* form converts photochemically to the less stable *cis* isomer, and the latter may subsequently isomerise to the *trans* state either thermally or photochemically. These compounds are widely used as photoresponsive materials[171-175]. Many synthetic strategies have been used to incorporate azogroups in a polymer network. These includes co-polymerization with other monomers, incorporating it as a side chain or pendant groups, functionalized cross-linker molecule in liquid crystal networks etc. The hydroxyazo-ketohydrazone tautomerism of 1-(phenylazo)-2-naphthol and its derivatives were well documented, both in solution and in the solid state,[24, 176,177] as shown in scheme 3.1.



Scheme 3.1

Theoretical calculation show that the ketohydrazone form is thermodynamically favoured[26] and the electron withdrawing functionality[176,177] and hydrogen bonding (both inter and intra)[27, 178] are key driving forces that shift the equilibrium in favour of the ketohydrazone form. This conclusion is supported by X-ray analysis of several 1-(phenylazo)-2-naphthols bearing electron withdrawing groups.[179] X-ray structural analysis were also reported for 1-(2´, 5´-dichlorophenylazo)-2 hydroxy-3-naphtho-2´´, 5´´-dimethoxyanilide and the data indicate that it has a ketohydrazone structure in the solid state.[180] Law *et al.*[35] have studied the electronic structure of a number of photoconducting biazo pigments by C^{13} NMR spectroscopy. The data, which complemented by IR spectra indicate that photoconductive biazo pigments formed from 2-hydroxy-3-carboxy napthanilide derivatives have a ketohydrazone structure exclusively in the solid state.[34, 181] The studies were also extended to triazo and polyazo pigments and found that all photoconducting pigments exist as ketohydrazones in solids[182, 183]. Further it was found that 2-azo-1-naphthol derivatives of diazotised 4,4′-diamino stilbenes, the *ortho* position of hydroxyl group exist predominantly in the hydrazone form via intramolecular hydrogen bonding,[184] (Scheme 3.2) eventually result in the linear and coplanar configuration.



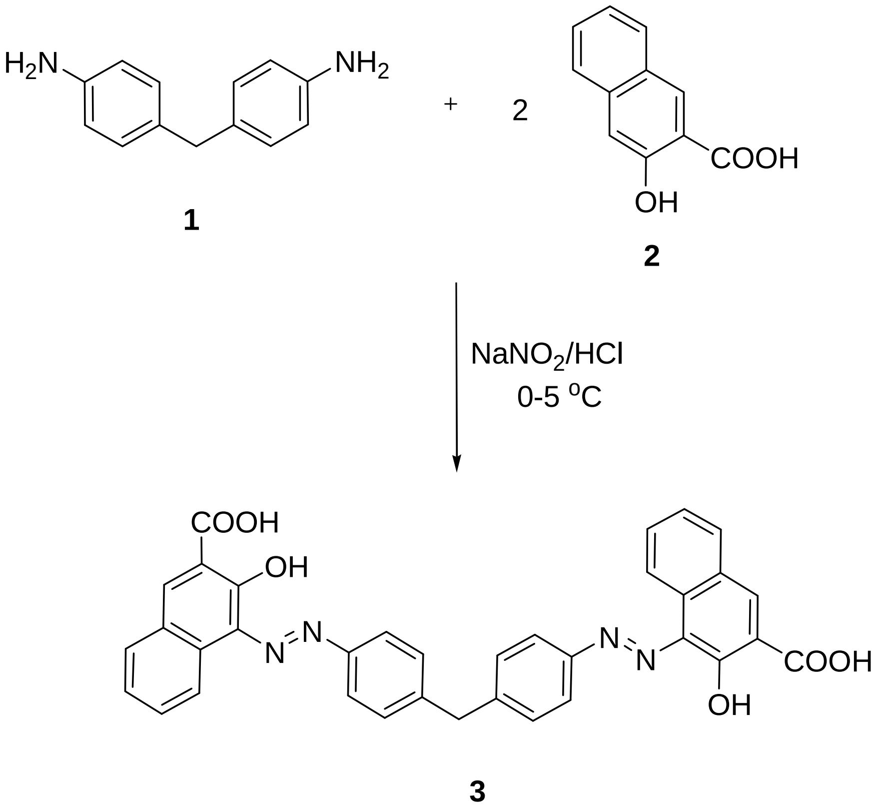
Scheme 3.2.

The photoconductivity associated with *ortho*-hydroxyazo compounds as a result of ketohydrazone tautomerism and the possible photoisomerisation of these photoresponsive systems which eventually lead to conformational changes in macromolecules prompted to synthesise polymers containing *ortho*-hydroxyazo aromatic systems and to systematically investigate their properties.

Thus, the present section deals with the synthesis and characterisation of the hitherto unreported photosensitive polyesters with azoarormatic residues in the backbone together with an *ortho*-hydroxyazo group that can undergo tautomerism, as shown in scheme 3.1.

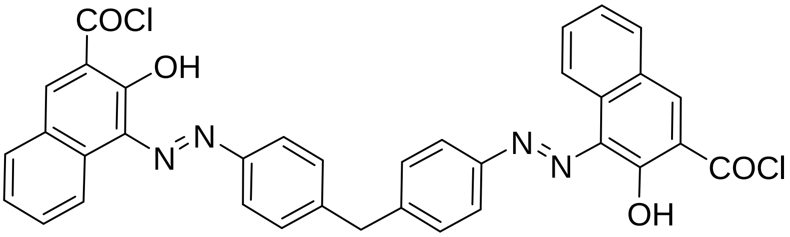
3.2. RESULTS AND DISCUSSION

3.2.1. Synthesis of polyesters with *ortho*-hydroxyazo aromatic groups



The first step towards the synthesis of polyesters was the tetrazotisation of 4,4´-diaminodiphenylmethane **(1)** with 2-hydroxy-3-carboxy naphthalene **(2)** to form 4,4´-azo*bis*phenylmethane di (-2-hydroxy-3-carboxy napthalene) **(3)**.

The dicarboxyclic acid was converted to the corresponding carbonyl chloride **(4)** by refluxing with excess of thionyl chloride in the presence of a few drops of N, N-dimethyl formamide catalyst.



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The excess of thionyl chloride was distilled off and the resultant solid was recrystallized from chloroform and was characterized by different analytical and spectral methods. The shift in characteristic IR stretching frequency from 1670 cm^{-1} (Fig. 3.1) to 1763 cm^{-1} (Fig 3.2) shows the replacement of carboxyl groups by carbonyl chloride. The stretching frequency at 1588 cm^{-1} is characteristic of–N=N-group, ^{1}H NMR spectrum of azo carboxyl acid **3** in $CDCl_3$ showed aromatic protons at δ 6.52-8.6, and carboxyl protons at δ 10.22 (Fig. 6.1). ^{1}H NMR spectrum of azo carbonyl chloride **5** gave aromatic protons at δ7.2-8.5 (Fig. 6.2) shown in section 6.

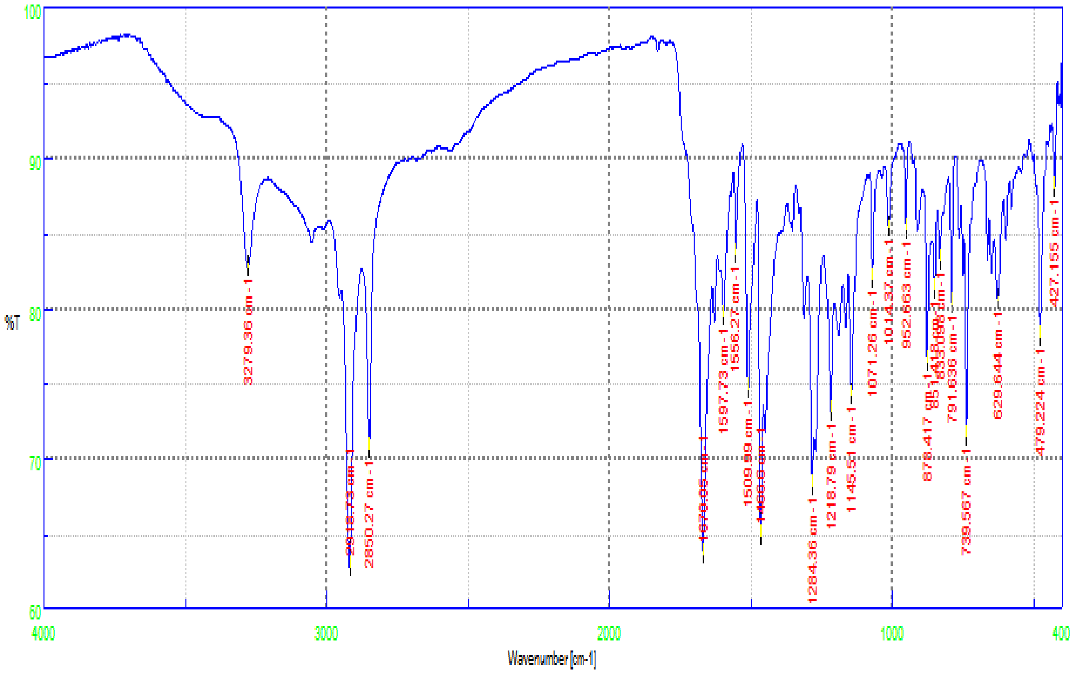


Fig. 3.1. IR (KBr) Spectrum of (3)

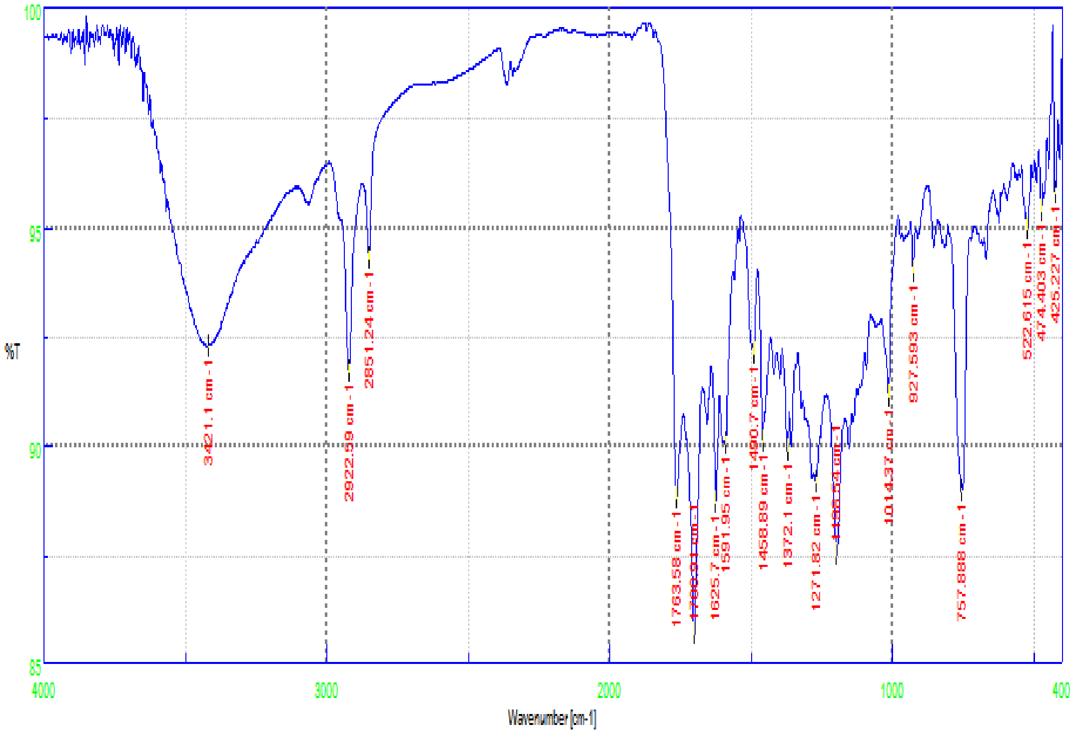
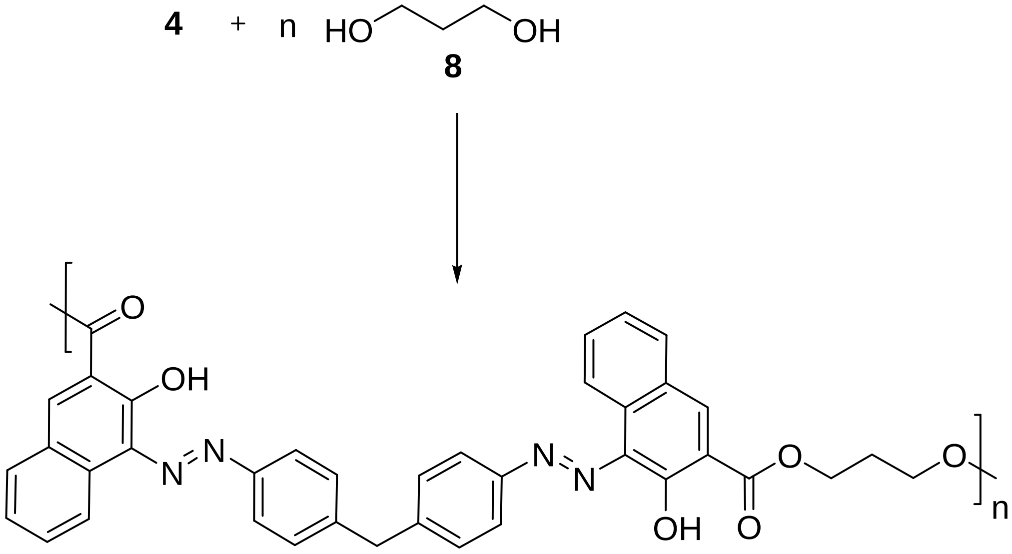


Fig. 3.2. IR (KBr) Spectrum of (4)

Interfacial polycondensation method[185, 186] was found to be effective to obtain the polymers in good yield. Polymer analogues esterification reaction between carbonyl chloride (or hydroxyl) groups and an azo compound with a hydroxyl (or carboxyl chloride) group appears to be one of the important methods in terms of the high functionalisation efficiencies[187,188]. Thus, 1,3 diol **(8)** was stirred with aqueous NaOH solution in presence of Na_2SO_4 under nitrogen atmosphere at room temperature and equimolar amount of the acid chloride (**4)** was added to minimum quantity of freshly distilled chloroform. The emulsified reaction mixture was stirred for 60 minutes and then poured into excess of acetone to coagulate the polymer. Filtration followed by purification by repeated washings with distilled water and dilute DMSO yielded a fibrous polymer, AZO DIOL **(9)**



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AZO DIOL

The structure of the polyester was confirmed by analytical and spectral methods. The polymer AZO DIOL thus obtained was found to be insoluble in most the solvents except in N, N-dimethyl acetamide, and DMF. The appearance of IR stretching frequency at 1210 cm^{-1} with a shoulder at 1146 cm^{-1} of C-O-C linkage confirmed the formation of polyester. The carbonyl stretching frequency (Fig. 3.3) of the polymer appeared at 1694 cm^{-1} which is characteristic of *ortho*-hydroxyazo esters which are hydrogen bonded.

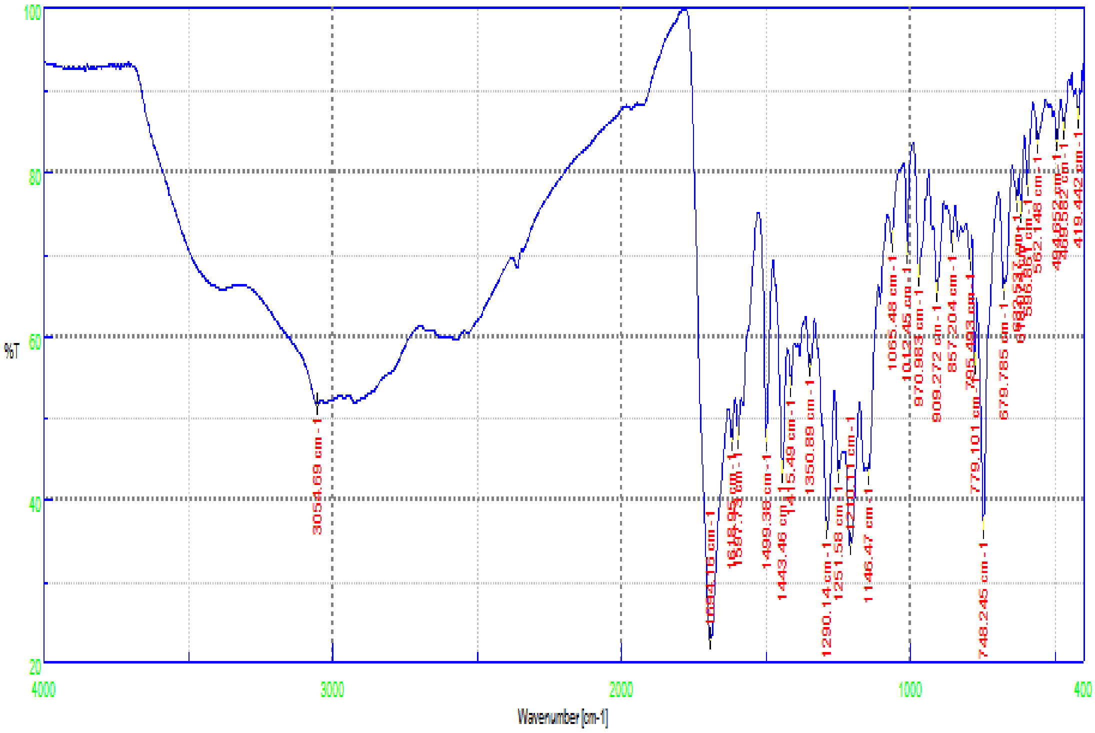


Fig. 3.3 IR (KBr) Spectrum of AZO DIOL (9)

The UV-visible spectrum (Fig 3.4) of the polymer **9** was recorded in N, N-dimethyl acetamide. An intense band at λ=270 nm and a weak band at 356 nm corresponds to π→π* transitions the very weak band appear at

462 nm is characteristic of n→π* transtions. The shift of the absorption band in the polymer when compared to unsubstituted azobenzene can be attributed to the substitutent effect [189].

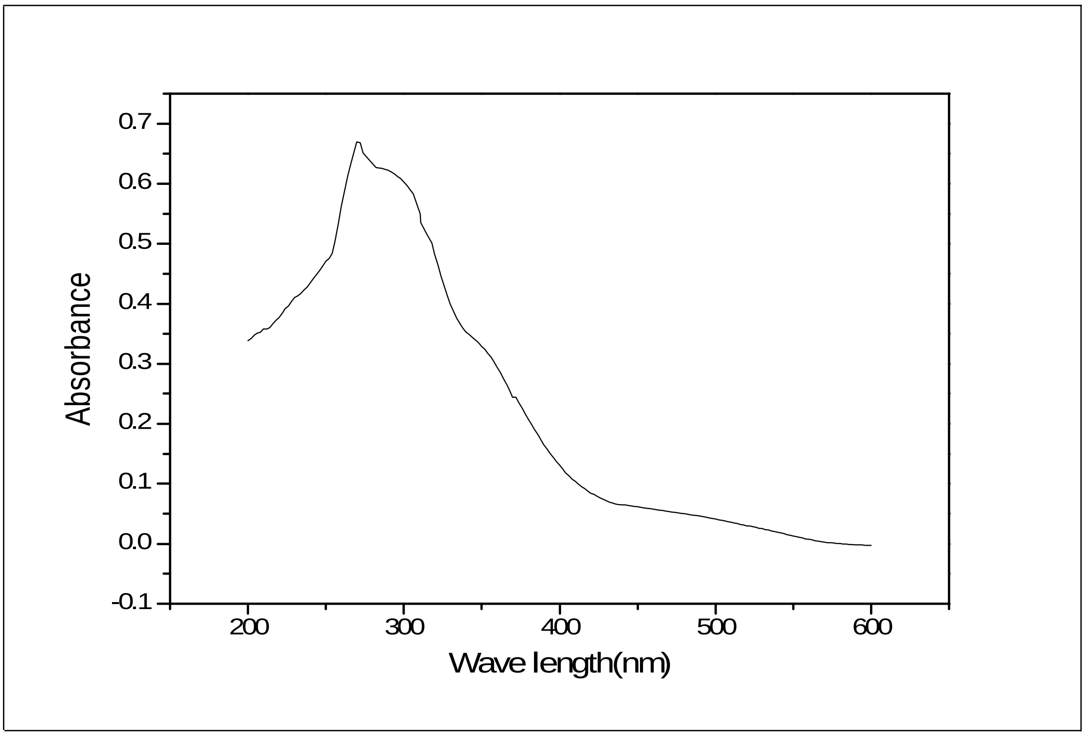


Fig. 3.4 UV-visible Spectrum (DMA) of AZO DIOL (9)

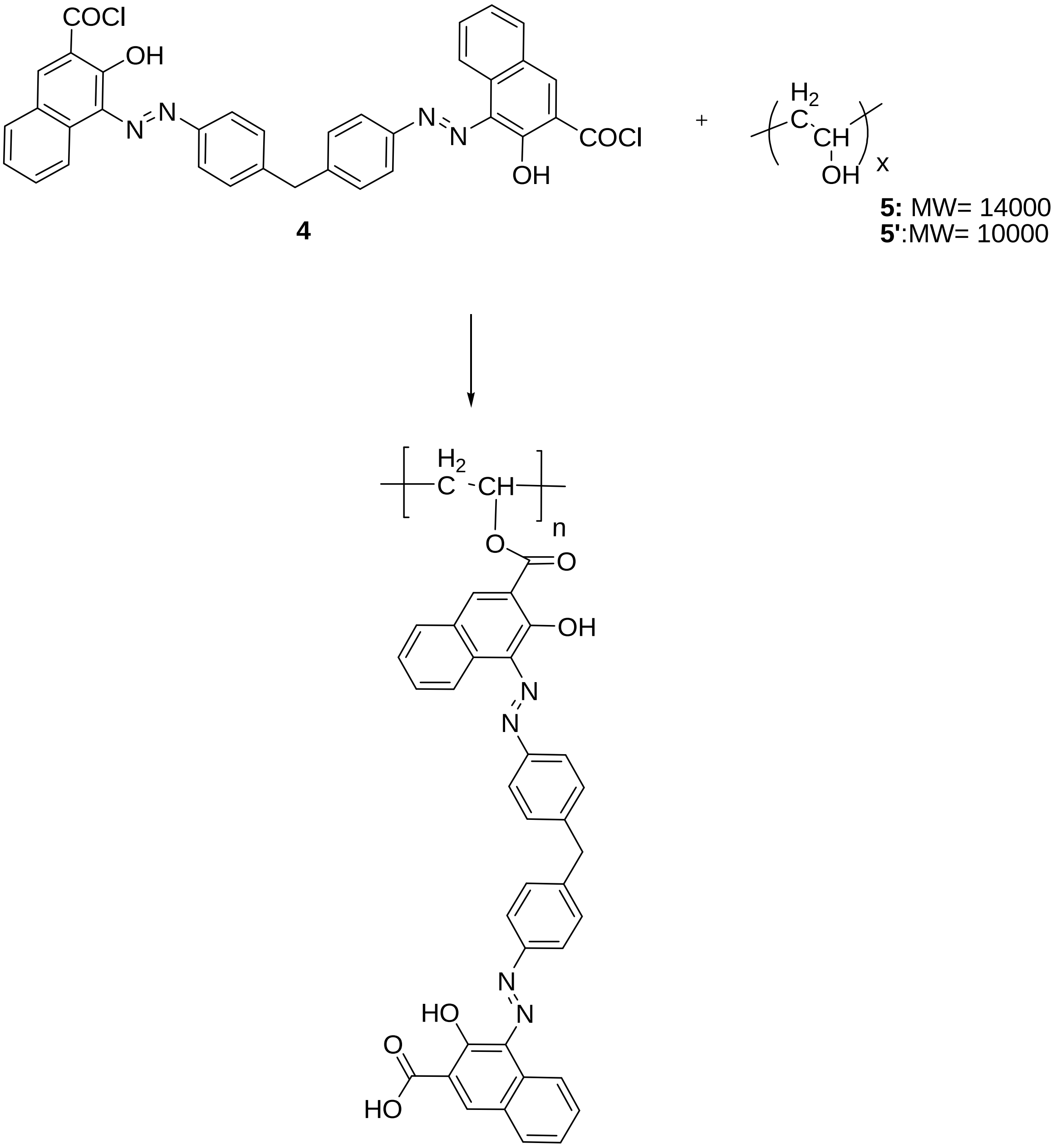
Similar interfacial polycondensation method was extended to the synthesis of other polyesters having azo linkages. These polyesters AZO PVA 14-1a (**6**), AZO PVA 10-1a (**6′**) are derived respectively from PVA, 14000 (**5**) and PVA, 10000 (**5′**) (alcohol and acid chloride in 1:1 molar ratio), whereas AZO PVA 14-1b (**7**) and AZO PVA 10-1b (**7′**) are respective interfacial polycondensation products of alcohol and acid chloride in 2:1 molar ratio. AZO DEG (**11**), AZO AP (**13**) and AZO OT (**15**) are derived respectively from diethylene glycol (**10**), 4, 4′-dihydroxyazobenzene (**12**) and *bis* (phenol-

4-azo) -4,4′-(3,3′-dimethyl biphenyl) (**14**). The analytical and spectral data of different polymers synthesised are given Table 3.1.

TABLE 3.1

Analytical and spectral data of polymers synthesized

Polymer	**Solvent**	**Melting point (^{O}C)**	**λ_{max} (nm)**	**IR (KBr) cm^{-1}**
AZOPVA 14-1a **(6)**	DMA	>300	296, 372, 468	3401, 1709, 1598 1208, 1160
AZOPVA14-1b **(7)**	DMA	>300	296, 372, 468	3352, 1703, 1598, 1207, 1148
AZOPVA10-1a **(6′)**	DMA	>300	272, 370, 486	3365, 1698, 1597, 1204, 1142
AZOPVA 10-1b **(7′)**	DMA	>300	270, 374, 482	3420, 1716, 1596, 1206, 1152
AZO DIOL **(9)**	DMA	278	270, 356, 462	3365, 1694, 1597, 1210, 1146
AZO DEG **(11)**	DMA	>300	270, 354, 452	3393, 1704, 1597, 1206, 1159
AZO AP **(13)**	DMA	285	270, 370, 422, 522	3220, 1703, 1597, 1208, 1163
AZO OT **(15)**	DMA	> 300	274, 380, 520	3370, 1698, 1597, 1209, 1141



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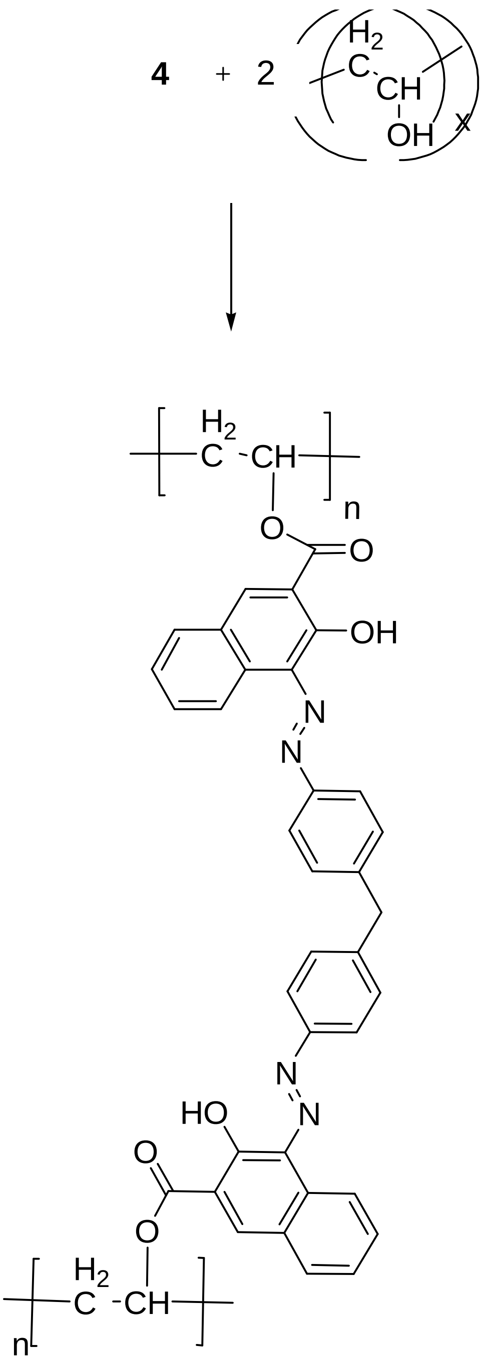
5: MW= 14000
5':MW= 10000

6: AZO PVA-14-1a

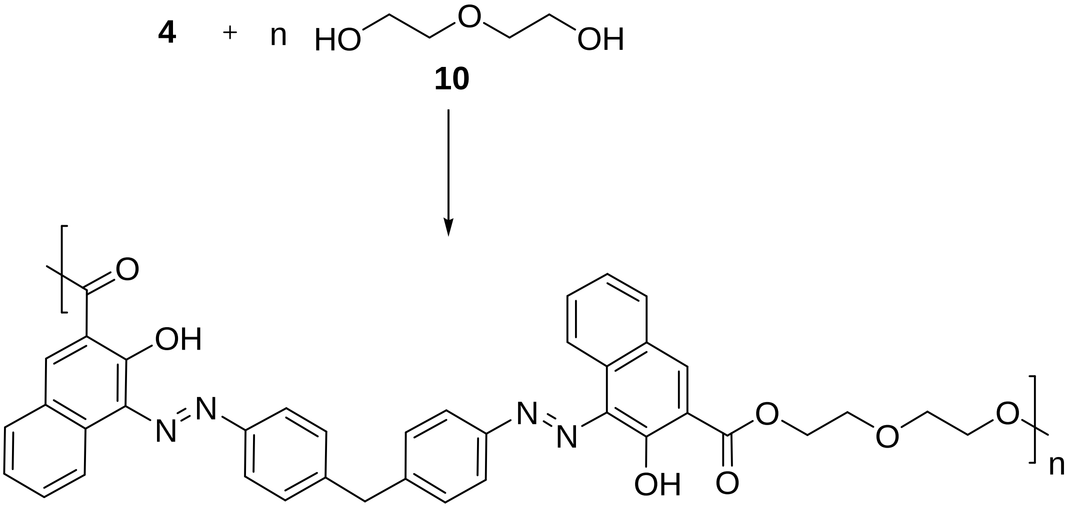
6': AZO PVA-10-1a



5:MW= 14000
5' MW= 10000

7: AZO PVA-14-1b

7': AZO PVA-10-1b



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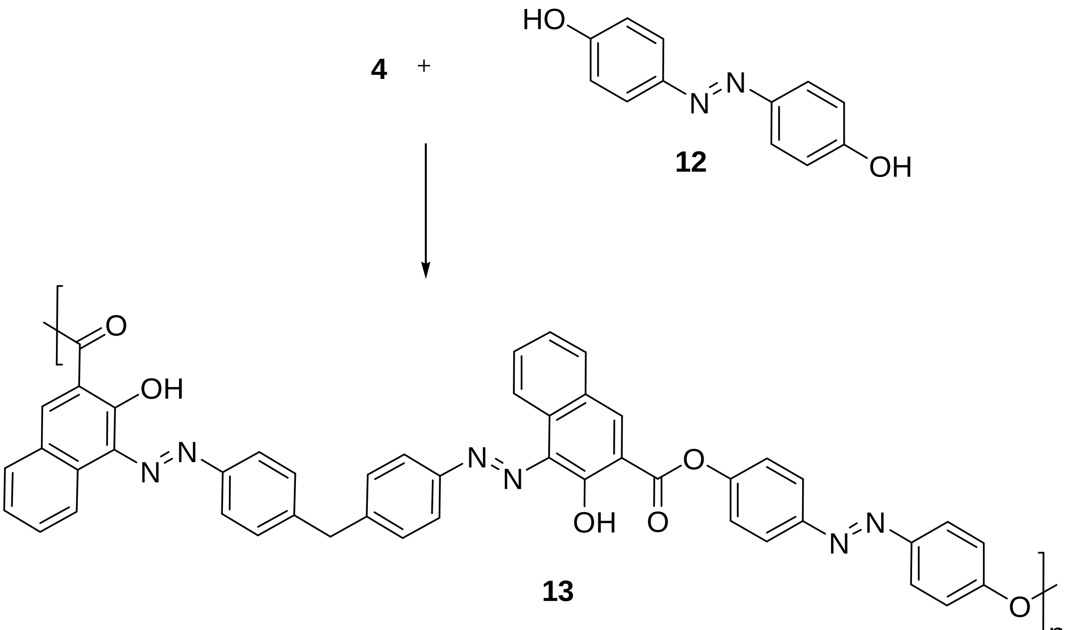
AZO DEG



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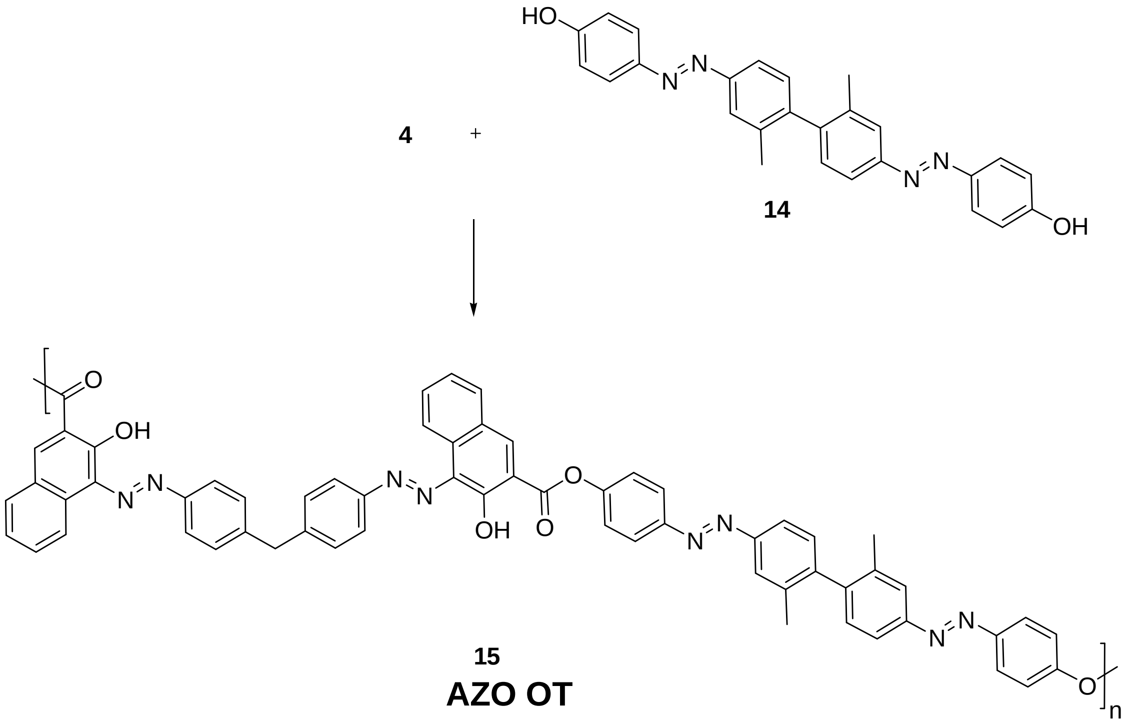
AZO AP



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AZO OT

3.2.2. Thermal studies of *ortho*-hydroxyazo polymers

Thermal analysis has become an important and useful tool in material characterisations. The increasing number of research papers[190, 191] on the structure-property relationship making use of various thermal analytical techniques show the significance of this study. Polymers have become major beneficiary of applications and several standard procedures for measurement of the degree of crystallinity involve these techniques. Since, polymers are mainly organic molecules, a lower temperature range,150-800 K is usually sufficient to carry out the decomposition study. Although, thermal analysis covers a diverse range of techniques, thermogravimetry (TG) has proved itself as a successful technique in determining the thermal stability of polymers. A thorough knowledge of the degradation and decomposition behaviour of macromolecules is needed when these materials are processed and fabricated.

Much attention has been focussed on the synthesis and photochromic properties of photoresponsive polymers, but only very little work has been done on their thermal stability, which indicates its ability to maintain the properties that are nearly unchanged as possible on heating[192, 193]. On heating the solid may undergo thermal decomposition in addition to their physical and chemical changes. In the present study, the techniques used for thermal analysis are non-isothermal thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC).

3.2.2. (i) Thermogravimetry

Differential thermal analysis is especially suitable for understanding the structural, changes within a solid at elevated temperature.[194,195] Thermal studies were carried out only to obtain qualitative results on the decomposition behaviour of polymers. The studies were conducted in an atmosphere of nitrogen at a flow rate of 50 mL/min, with a heating rate of 10° C/min using sample mass of 20-50 mg. On the graph, the percentage of mass loss of the sample was plotted against furnace temperature. The data obtained for DTA curves have been utilised for ascertaining the phenomenological aspects such as temperature of initiation (Ti), temperature of melting (Tm), completion of decomposition (Td) etc. These data give information regarding the region of stability, region of thermal decomposition etc. In DTA, the temperature of the sample is compared to that of an inert reference material while both are subjected to programmed change of temperature. If the sample undergoes any transition, it results in absorption or evolution of heat energy and a corresponding deviation will occur in its temperature from that of the reference. The difference in temperature between the sample and the reference in $T = T_{sample} - T_{reference}$ is recorded as a function of temperature in the DTA curve. When the temperature difference between the sample and the reference is zero, the sample does not undergo any physical or chemical change. Using thermal analysis technique, phase transition or chemical reactions can be followed by observing the heat evolved or absorbed. Physical changes usually result in endothermic curves whereas chemical reactions, particularly those of oxidative nature, are exothermic.

3.2.2 (ii) Differential scanning calorimetry

In differential scanning calorimetry (DSC), the difference in every inputs into a sample and the reference is measured as a function of temperature. A power compensated DSC was used for analysis and the rate of energy absorbed by the sample plotted against the temperature as the sample was heated at a constant rate. The deflection from the instrument baseline is a measure of the specific heat of the sample. If the sample undergoes a physical or chemical change, there will be a corresponding change in ethalpy. DSC is widely used to measure the glass transition temperature (Tg), crystallization kinetics and degree of crystallinity. The glass transition temperature (Tg) and crystallisation temperature (Tc) of all polymers studied are presented in Table 3.2.

TABLE 3.2.
DSC Data of azo polymers

No.	Polymer	Tg (^{o}C)	T_c (^{o}C)
1	AZO PVA 14 -1a	20	68
2	AZO PVA 14 -1b	15	68
3	AZO PVA 10-1a	30	69.44
4	AZO PVA 10-1b	18	73.8, 96, 119
5	AZO DIOL	30	77.9
6	AZO DEG	26	79.2
7	AZO AP	10	80.14
8	AZO OT	28	76.7

3.2.2. (iii) Thermal studies of AZO polymers

AZO PVA system

DSC curves of polymers of azo compound with different molecular masses and with different ratios are given in Fig. 3.5-3.8. Polymers show varied thermal profile indicating drastic morphological changes. So it is obvious that thermal properties depend upon the structure of polymers, in this case, on the microstructure of the polymer, the chromophore, and the extent of functionalisation

In DSC experiment, Tg of azo compound containing low concentration PVA (AZO PVA 14-1a and AZO PVA 10 -1a with azo compound and PVA in 1:1 molar ratio) noticed at 20 ^{0}C and 30 ^{0}C while at higher concentration of PVA (AZO PVA 14-1b and AZO PVA 10-1b with azo compound and PVA in 1:2 molar ratio) at 15 ^{0}C and 18 ^{0}C respectively. From this it is evident that Tg decreases with increase in concentration of PVA.

AZO PVA 10-1a containing azo compound and low molecular mass of PVA 10000 (azo compound and alcohol with 1:1 molar ratio) has a broad endothermic peak at 69.4 ^{0}C while AZO PVA 10-1b having azo compound at higher concentration of PVA 10000 with 1:2 molar ratio, a sharp endothermic peak at 73.8 ^{0}C. This is due to the enhanced interaction between carbonyl group of azo compound with hydroxyl group of PVA (1:2 molar ratio), which results in the increasing hydrogen bonding density. The aromatic structure and large dipolemoment of the side chain group due to higher concentration of PVA both 10000 and 14000 showed lower glass transition temperature (Tg), which is exhibiting good thermal stability. These results indicate that concentration of PVA has a major role on the mobility of chain.

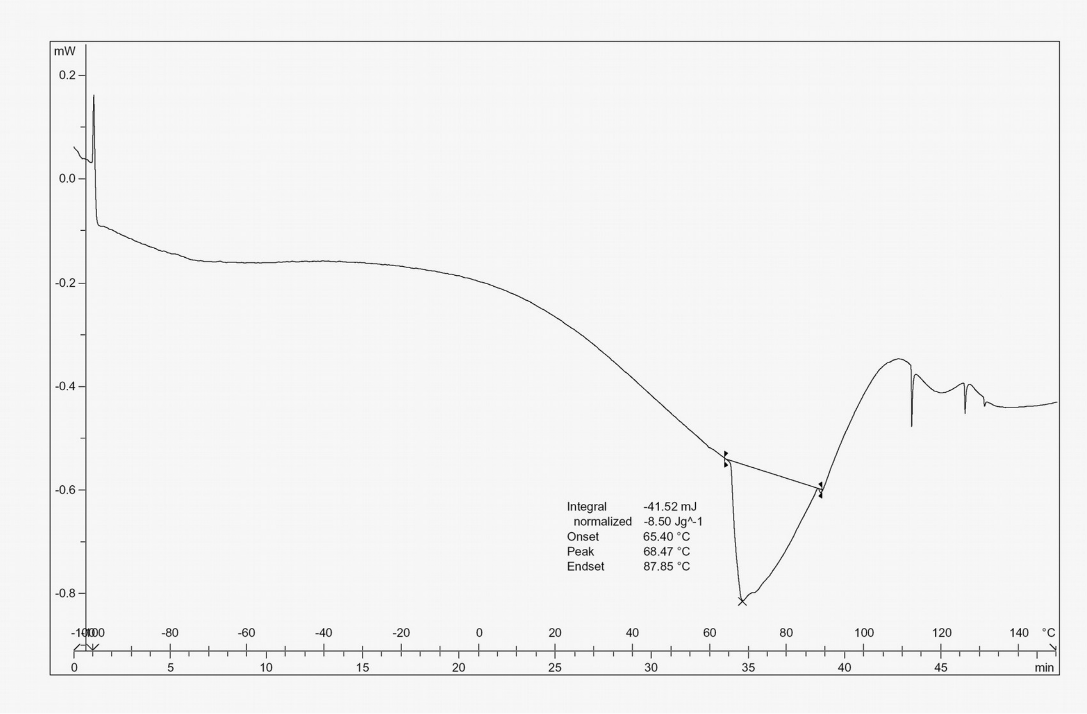


Fig. 3.5 DSC Curve of AZO PVA 14-1a (6)

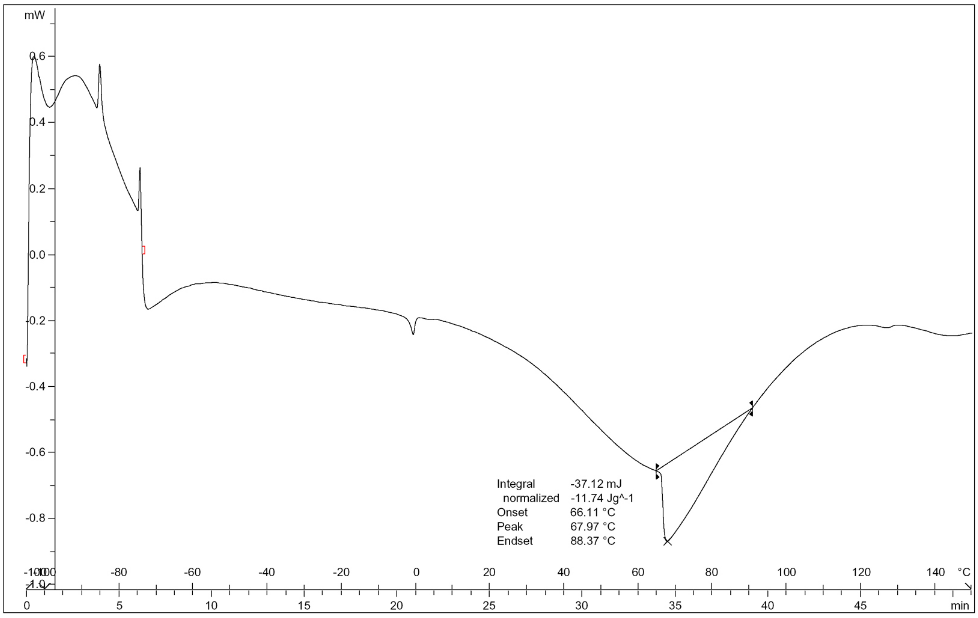


Fig. 3.6 DSC Curve of AZO PVA 14-1b (7)

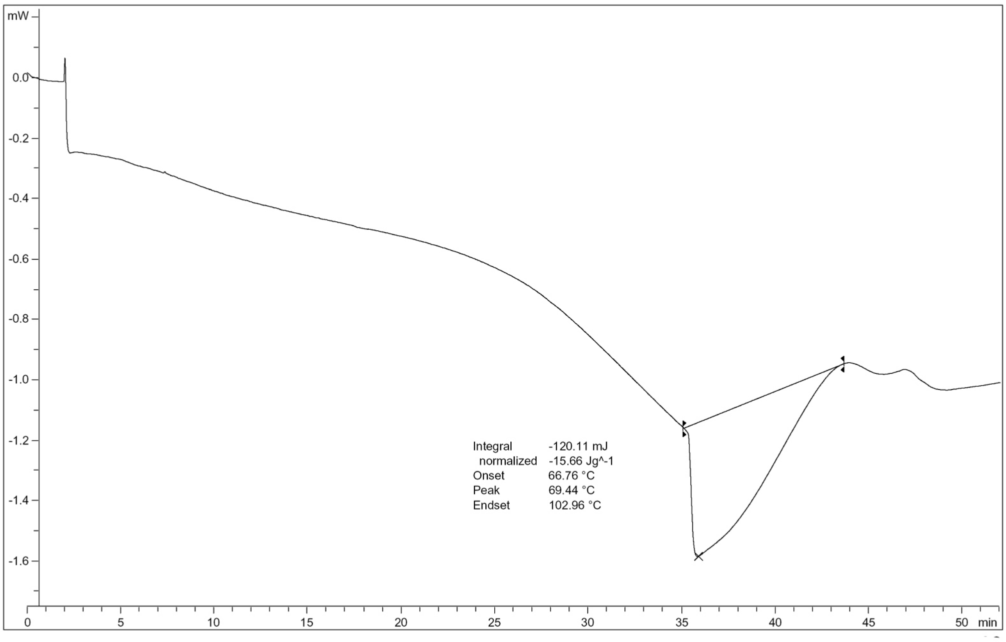


Fig. 3.7 DSC Curve of AZO PVA 10-1a (6′)

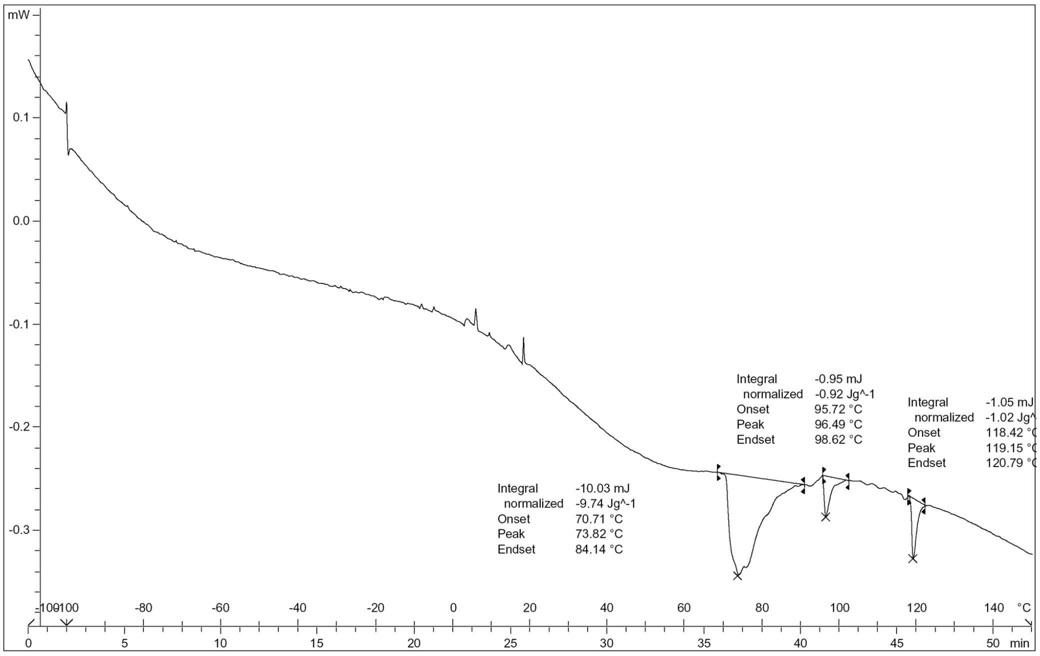


Fig. 3.8 DSC Curve of AZO PVA 10-1b (7′)

Fig. 3.9 – 3.12 show the TG curves of azo polymers with different ratios of PVA in varied molecular masses. The TG pattern of polymers containing azo compound and PVA , 14000 with 1:1 molar ratio (AZO PVA 14 -1a) shows three stage degradation, first at 200 ^{0}C, second at 400 ^{0}C and third at 900 ^{0}C while polymers having azo compound and PVA, 14000 with 1:2 molar ratio (AZO PVA 14-1b) shows a two stage degradation at 220 ^{0}C and finally at 920 ^{0}C. The excellent thermal resistance of these polymers is due to increased concentration of hydrogen bonding between azo carbonyl group with hydroxyl group of PVA. As the molecular mass increases from 10000 to 14000 thermal stability also increases. The improved thermal stability may be attributed to the increase in hydrogen bonding interaction of PVA and azo system in the polymer..

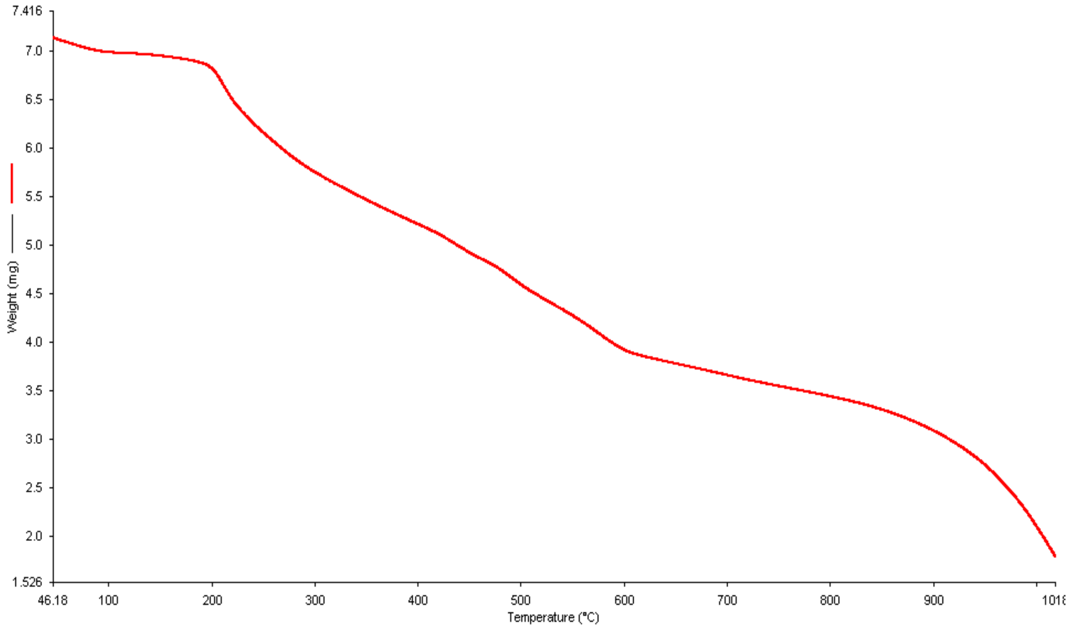


Fig. 3.9 TG Curve of AZO PVA 14-1a (6)

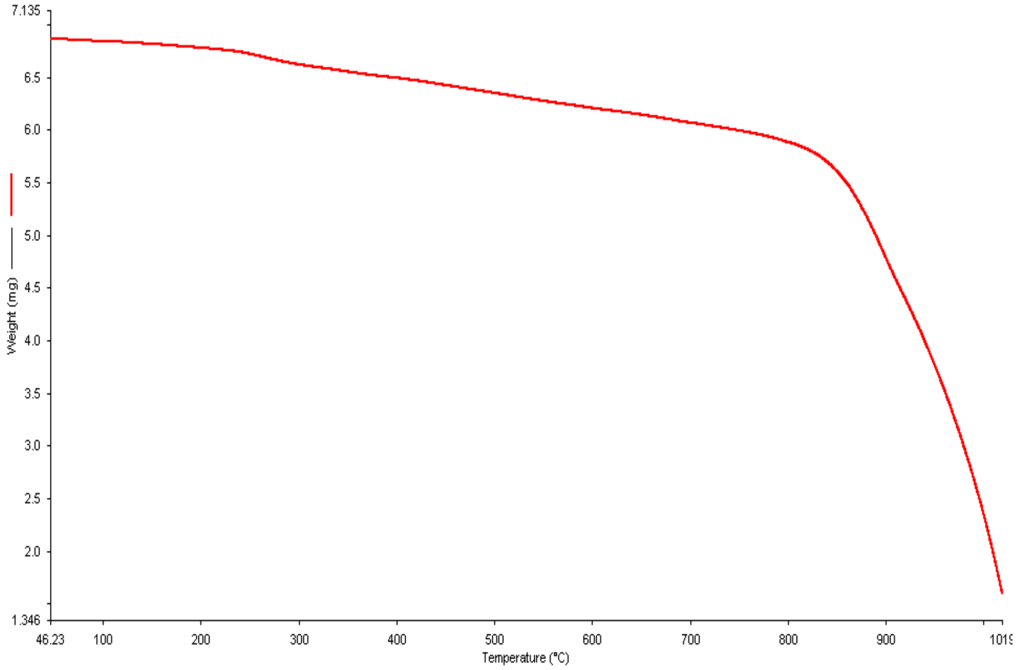


Fig. 3.10. TG Curve of AZO PVA 14-1b (7)

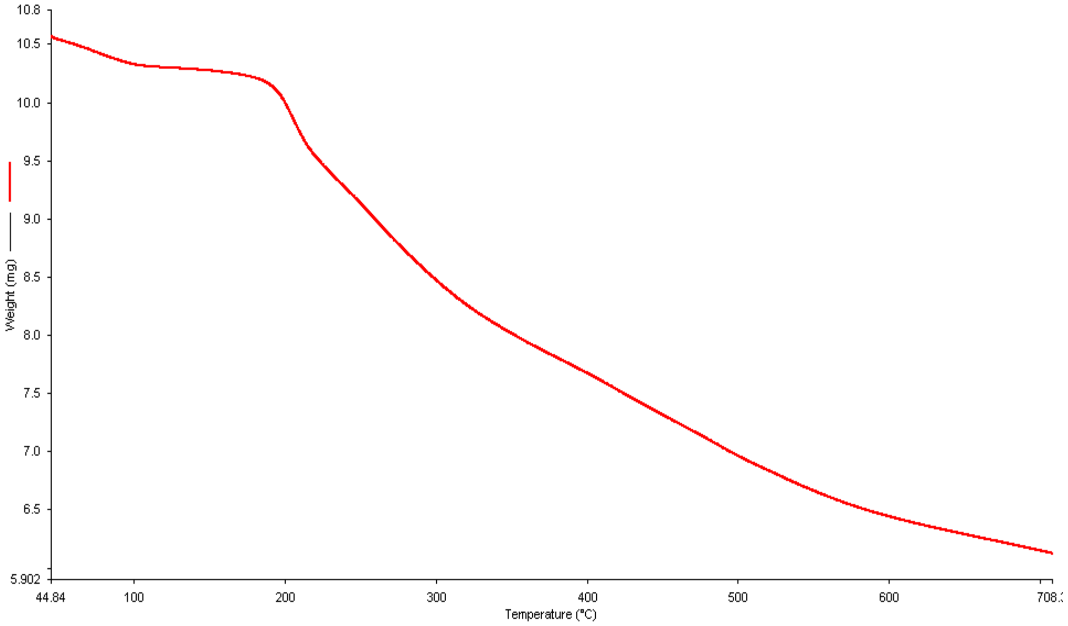


Fig. 3.11 TG Curve of AZO PVA 10-1a (6´)

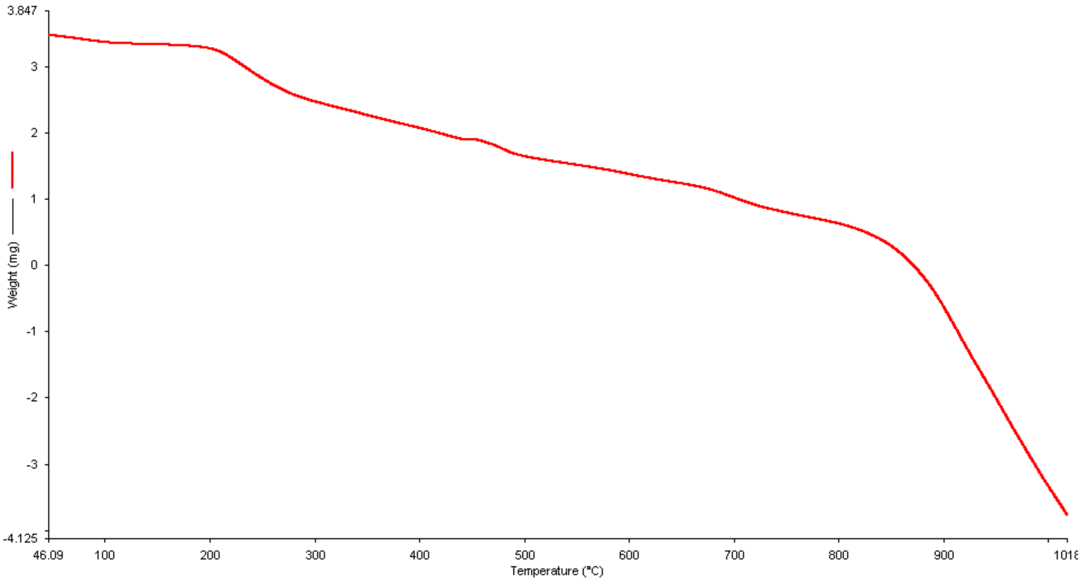


Fig. 3.12 TG Curve of AZO PVA 10-1b (7′)

Time taken for azo polymers with different ratios of PVA and various molecular masses are given in Table 3.3. Polymer of these AZO PVA systems are compared. It is clear that the time taken for 50% weight drop is more for polymer systems having azo compound with higher PVA concentration (1:2, AZO PVA 14-1b and AZO PVA 10-1b) than that of polymer systems having azo compound with lower PVA concentration (1:1 AZO PVA 14-1a and AZO PVA 10-1a). Therefore, it can be concluded that increasing concentration and molecular masses of PVA in azo system increases the thermal stability of these polymers. The increase in concentration of PVA not only enhances thermal stability but improves hydrogen bonding density.

TABLE 3.3.

Time taken for 50% weight drop

No.	Polymer	Time (min)
1	AZO PVA 14-1a	51
2	AZO PVA 14-1b	95
3	AZO PVA 10-1a	33
4	AZO PVA 10-1b	87

AZO DIOL and AZO DEG Systems

Fig. 3.13 and 3.14 shows the DSC curves of azo compound with diol and diethylene glycol respectively. The DSC analysis of the sample showed that Tg occures at 30 ^{0}C for AZO DIOL whereas, in the case of AZO DEG it appears at 26 ^{0}C. This proves that the interaction of azo carbonyl compound with diethylene glycol is more pronounced than that of AZO DIOL System. Similarly the endothermic peak of AZO DIOL and AZO DEG are 77.9^{0}C and 79.2^{0}C respectively. The melting endotherm is rather broad for AZO DIOL and becomes narrower for AZO DEG.

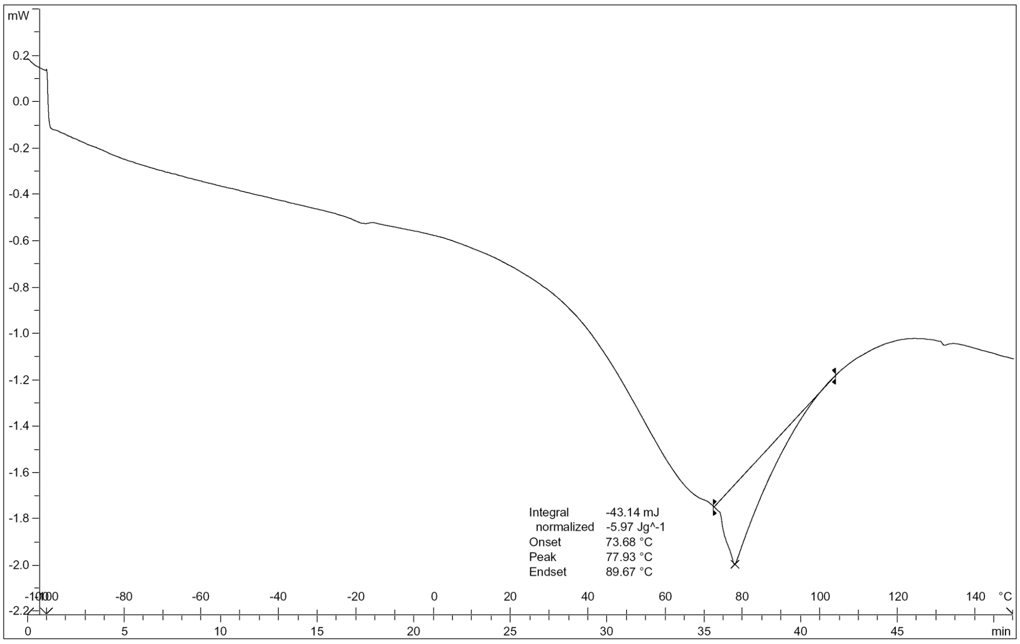


Fig. 3.13 DSC Curve of AZO DIOL (9)

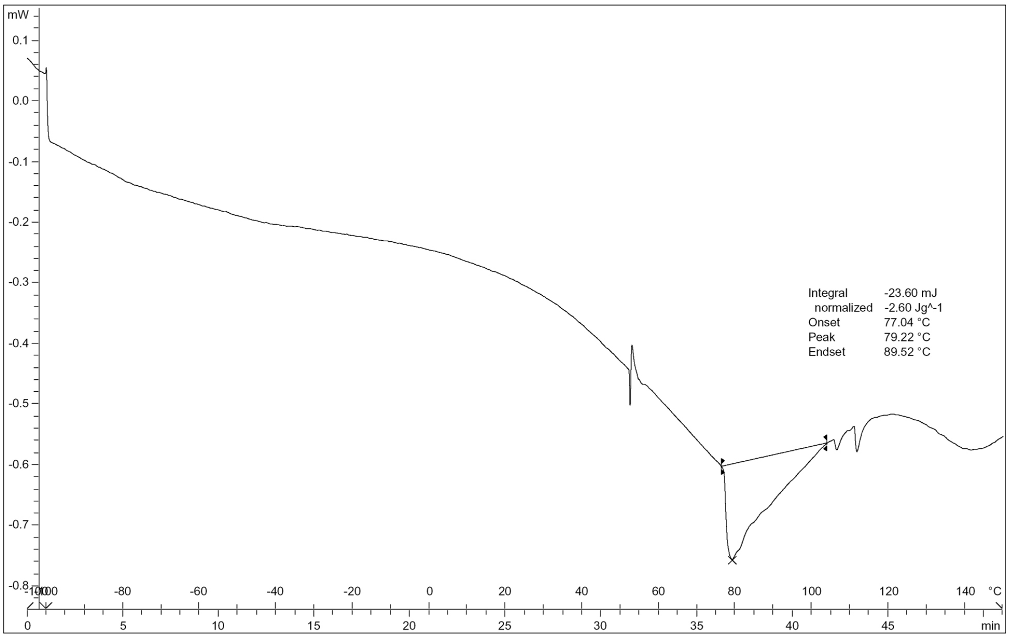


Fig. 3.14 DSC Curve of AZO DEG (11)

TG curves of AZO DIOL and AZO DEG are given as Fig. 3.15 and 3.16 respectively. In the case of TG curve of AZO DIOL, a three stage thermal degradation occures at 144 ^{0}C, 218 ^{0}C, 466 ^{0}C. But, in the case of AZO DEG system only a two stage degradation is observed (215 ^{0}C, 470 ^{0}C). This indicates that the interaction between azo carbonyl compound and 1, 3 diol is less than that of azo carbonyl compound with diethylene glycol.

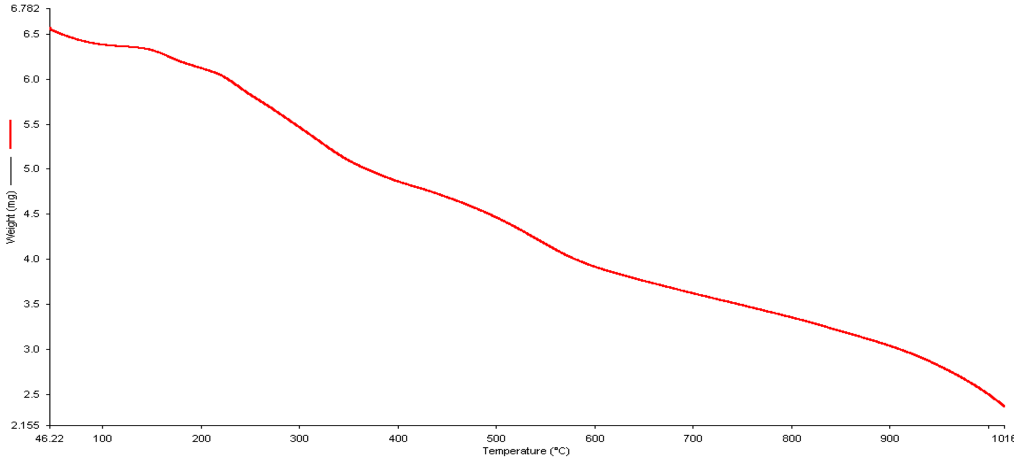


Fig. 3.15 TG Curve of AZO DIOL (9)

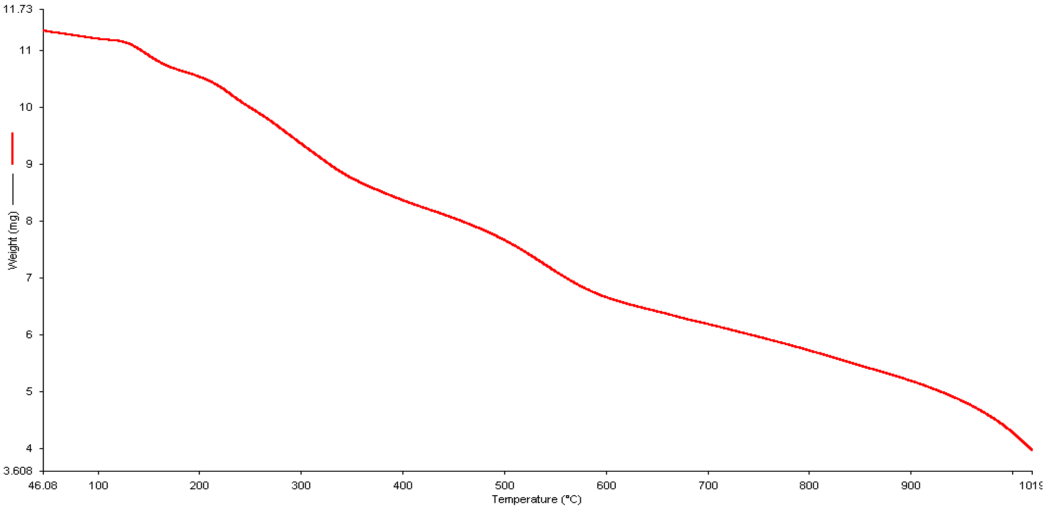
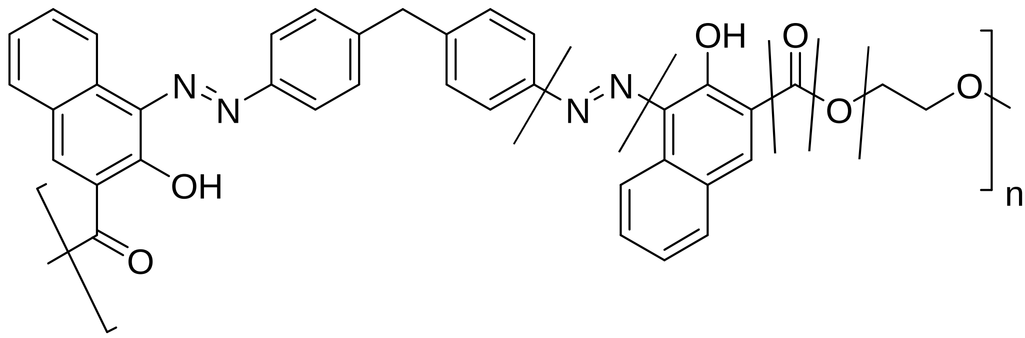


Fig. 3.16 TG Curve of AZO DEG (11)

In the TG curve of both polymers the peak observed around 470 ^{0}C corresponds to the expulsion of azo group as nitrogen. In the azo aromatic polyesters, facile cleavage of the O-C bond of the ester is the initial degradation step. The major primary process involves the loss of carbon dioxide. Considering these aspects, it is possible to explain all the degradation occurring in the synthesised polyesters of AZO DEG and AZO DIOL and corresponding thermogravimetric curves. Analogues to the degradation steps,[196] the mechanism of the scission of the polymer chain that occurs at high temperature can be shown as in scheme 3.3.



Scheme 3.3

AZO AP and AZO OT Systems

DSC and TG results of AZO AP and AZO OT are depicted in Fig 3.17 -3.20. Tg of AZO AP appears at 10 ^{0}C whereas that of AZO OT at 28 ^{0}C, indicating that the Tg values of the polymers decreased with an increase in the spacer length. Sharp crystalline melting point appears at 80 ^{0}C for AZO AP system while a weak peak at 77 ^{0}C for AZO OT System. This is attributed to the presence of bulky methyl group in AZO OT which prevents the hydrogen bonding interaction. The variation in Tg may be explained by plasticizing effect and degree of crosslinking. Thermogravimetric curve of AZO OT show two stages of decomposition at 223 ^{0}C and 460 ^{0}C whereas three stage decomposition at 154 ^{0}C, 488 ^{0}C and 906 ^{0}C for AZO AP system.

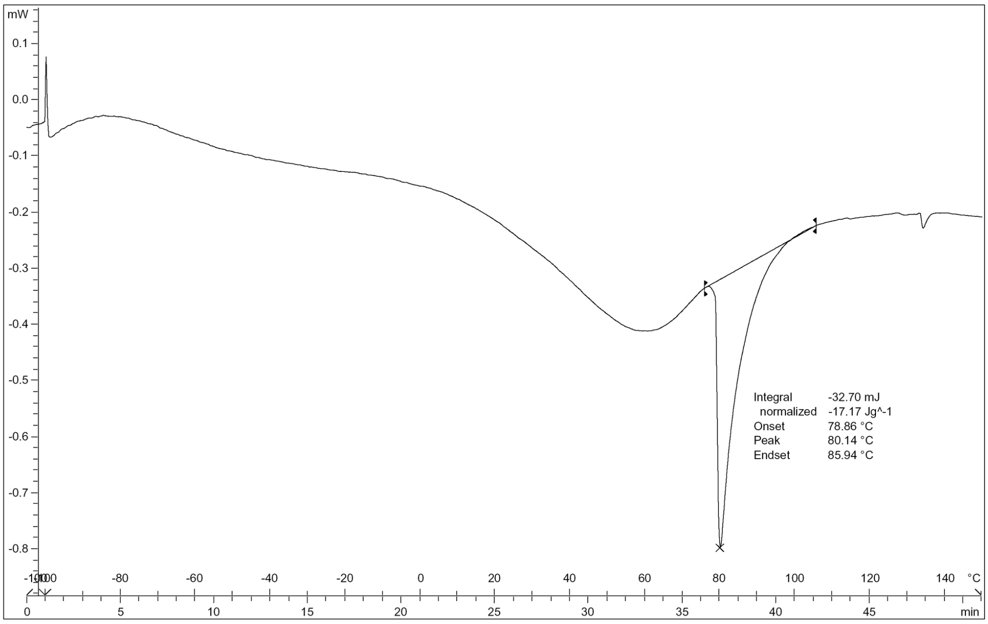


Fig. 3.17. DSC Curve of AZO AP (13)

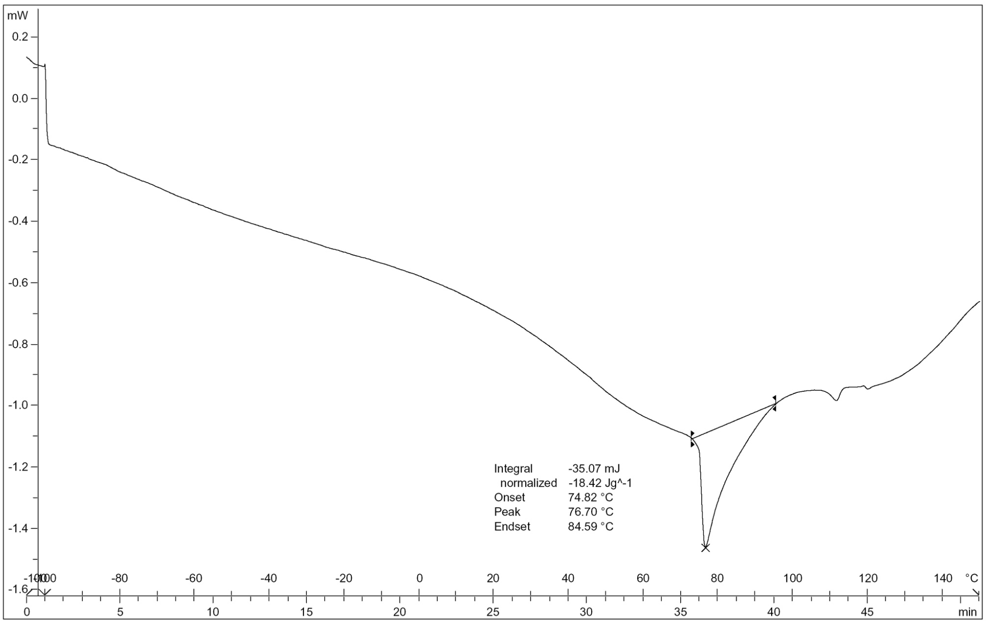


Fig. 3.18 DSC Curve of AZO OT (15)

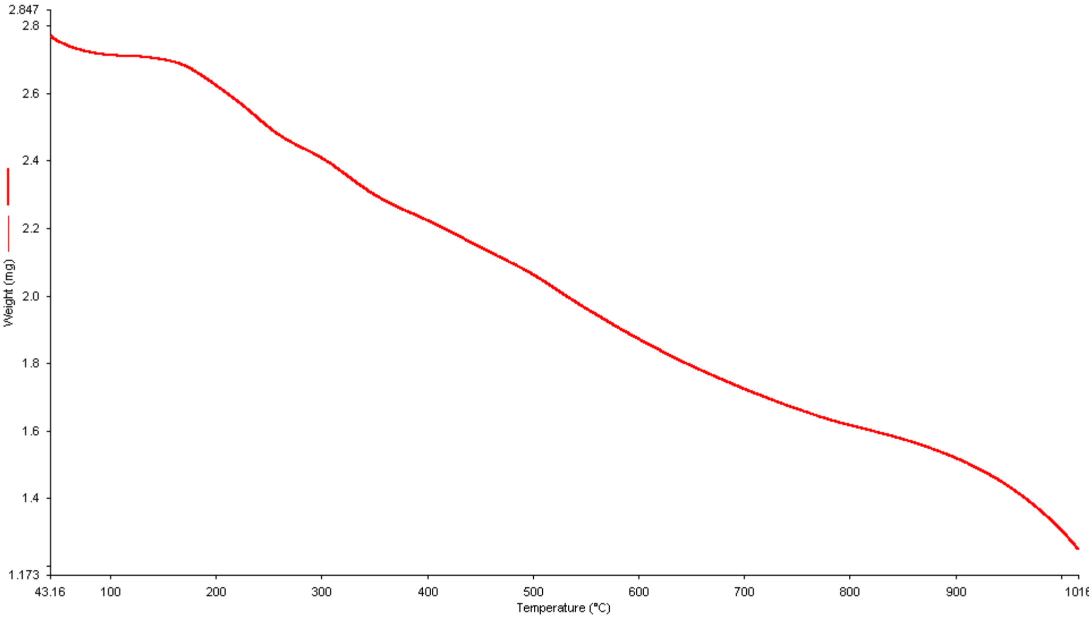


Fig. 3.19 TG Curve of AZO AP (13)

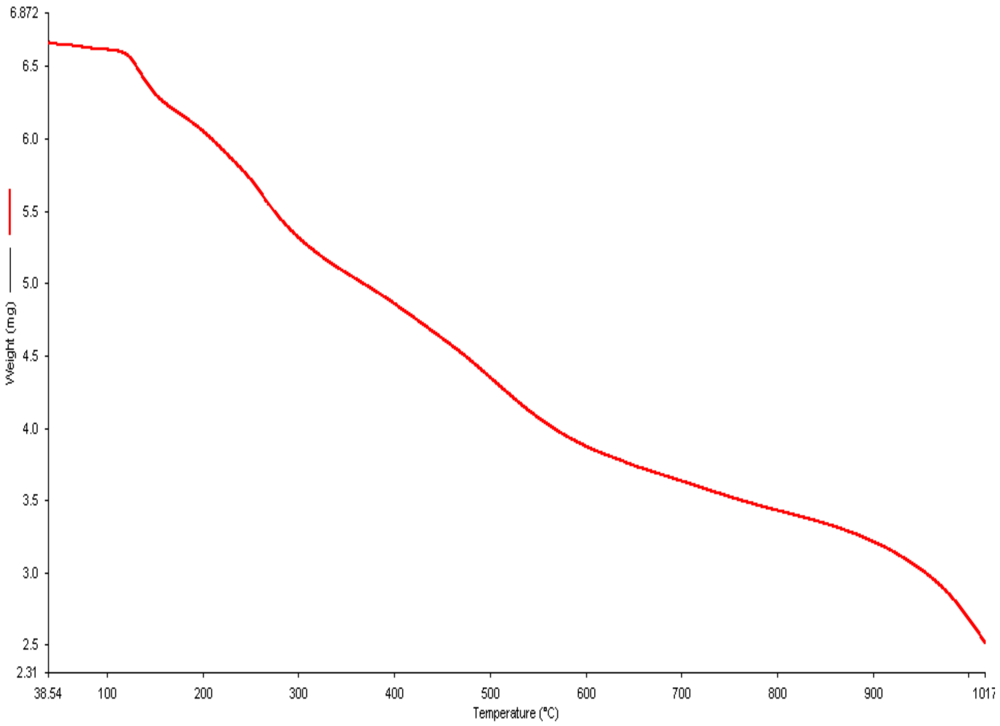


Fig. 3.20 TG Curve of AZO OT (15)

3.2.3. XRD Studies of *ortho*-hydroxyazo aromatic polymers

X-ray diffraction patterns are highly useful to characterise the polymers using wide angle X-ray scattering. The degree of crystallinity depends on the method of preparation and the technique of measurement of the sample.[197] Sharp patterns for the crystalline polymers and broad patterns for amorphous substances are obtained provided the samples are highly pure. XRD patterns of the all the synthesised polymers were recorded using X-ray wave length λ 1.5405A°. The particle size and the spacing between the planes are measured from XRD pattern. Particle size of the polymers is calculated using Scherrer equation.

Particle size = $0.9 \times \lambda/\beta \mathrm{Cos}\theta$

λ the Wavelength of the Cu K α line. θ the diffraction angle and B = FWHM in radian. (Full Wanlength Half Medium). The results of the X-ray analysis of different samples are given in Table 3.4.

TABLE 3.4

X-ray analysis data of azo polymers

Polymer	**2θ (rad)**	**β (rad)**	**Particle Size (A^0)**
AZO PVA 14-1a	44.72	$9.34 x 10^{-2}$	161.1
AZO PVA 14-1b	43.186	$4.83 x 10^{-3}$	308.9
AZO PVA 10-1a	15.218	$4.7 x 10^{-3}$	297.6
AZO PVA 10-1b	31.75	$1.05 x 10^{-2}$	137.4
AZO DIOL	24.312	$3.68 x 10^{-3}$	385.1
AZO DEG	12.564	$5.30 x 10^{-3}$	263.4
AZO AP	20.55	$6.49 x 10^{-3}$	217.0
AZO OT	25.791	$1.2 x 10^{-2}$	118.5

From the above data it is clear that molecular mass increases with particle size. The XRD pattern of these polymers suggest a decrease in the degree of crystallinity with increasing concentration of aromatic ring in the polymer matrix.

AZO PVA 14-1a and AZO PVA 14 -1b

A broad XRD peak is observed at 2θ value 22.3^0 for AZO PVA 14-1a (Fig. 3.21), whereas two peaks at 7.7^0 and 27.1^0 for AZO PVA 14-1b (Fig. 3.22). So AZO PVA 14-1a is more amorphous than AZO PVA-14 1b. As the PVA concentration increases polymer matrix becomes more crystalline.

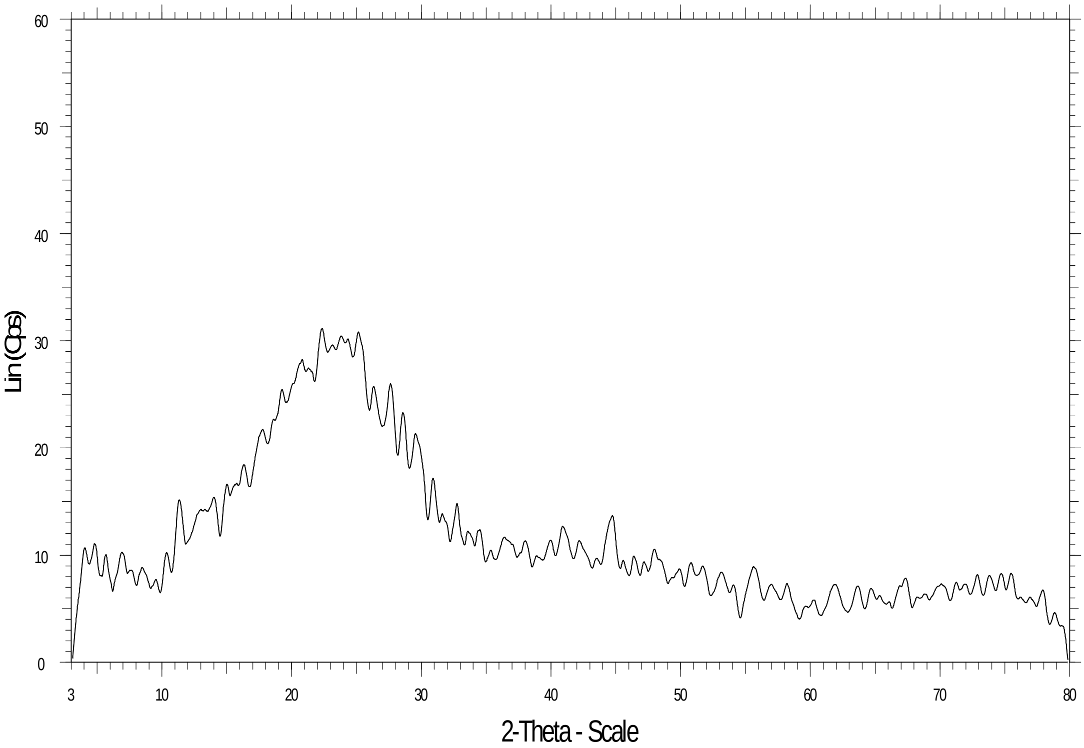


Fig. 3.21 XRD Spectrum of AZO PVA 14-1a (6)

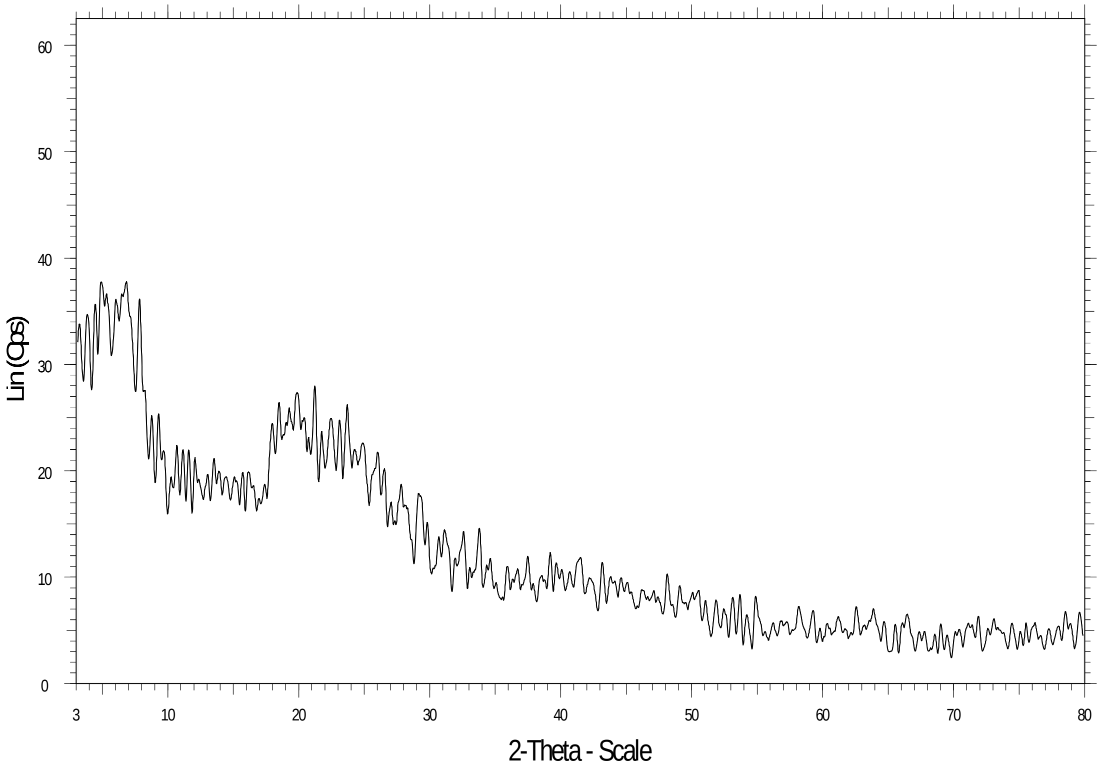


Fig. 3.22 XRD Spectrum of AZO PVA 14-1b (7)

AZO PVA 10-1a and AZO PVA 10-1b

A sharp narrow peak is observed at 2θ value 19.5^0 for AZO PVA 10-1a (Fig. 3.23). When the PVA concentration increases two sharp intense peak observed one at 31.7^0 and the other at 48.5^0 for AZO PVA 10-1b (Fig. 3.24), which shows that increase in concentration of PVA imparts crystallinity to the polymer. The XRD result also demonstrates the presence of a low amount of crystalline PVA aggregates in the AZO PVA 10-1a when compared to AZO PVA 10-1b.

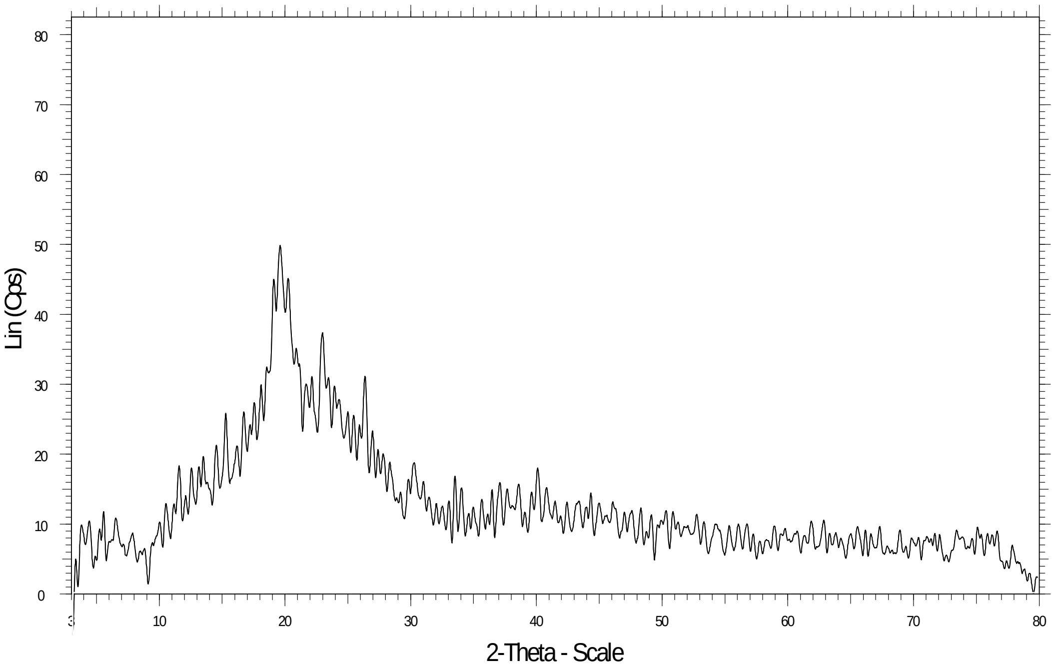


Fig. 3.23 XRD Spectrum of AZO PVA 10-1a (6′)

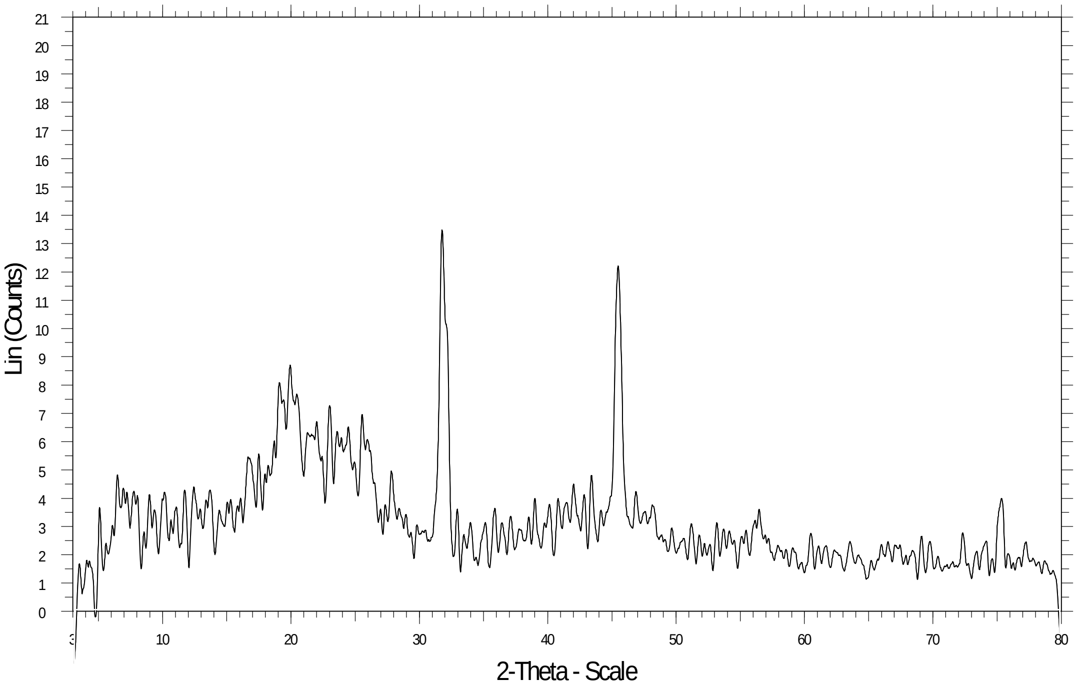


Fig. 3.24 XRD Spectrum of AZO PVA 10-1b (7′)

AZO DIOL and AZO DEG

In AZO DIOL a broad 2θ value is observed from 10 to 30^0 ((Fig. 3.25) whereas in AZO DEG the 2θ value broadening ranges from 8 to 18 ^{0} only (Fig. 3.26). Shifting of peak towards increase in 2θ value indicates that AZO DIOL is little more amorphous than AZO DEG. This can be explained in terms of less possible interaction between azo carbonyl compound and 1, 3 diol, compared with that of azo carbonyl compound and diethylene glycol. The above observation is in good agreement with the DSC data of AZO DIOL and AZO DEG.

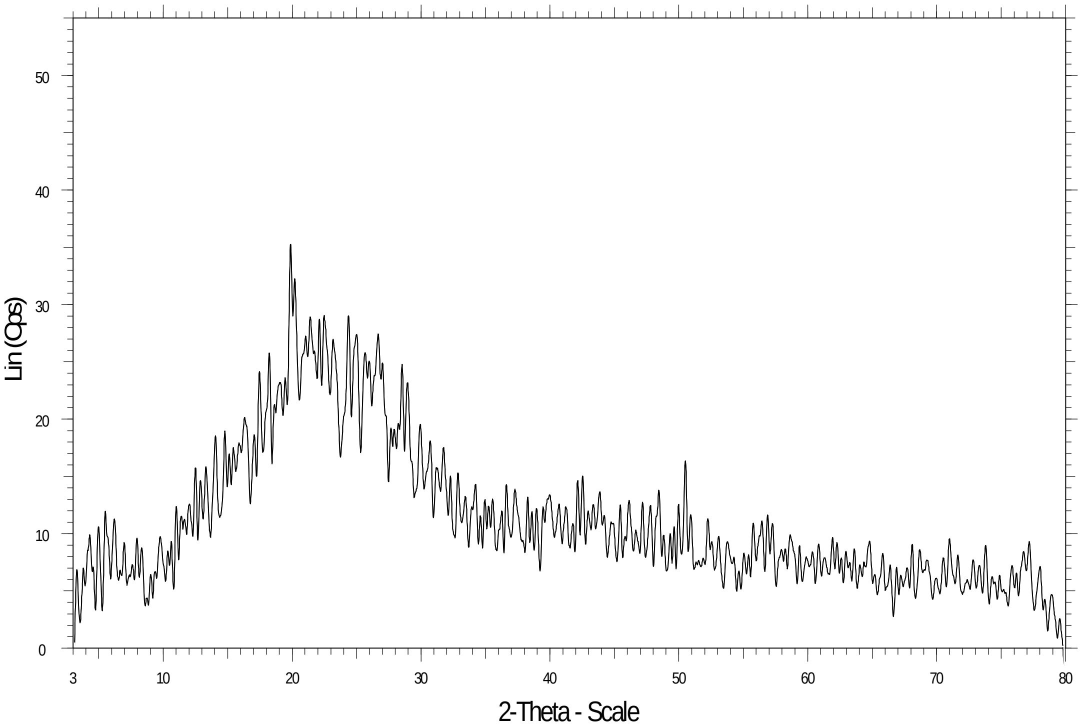


Fig. 3.25 XRD Spectrum of AZO DIOL (9)

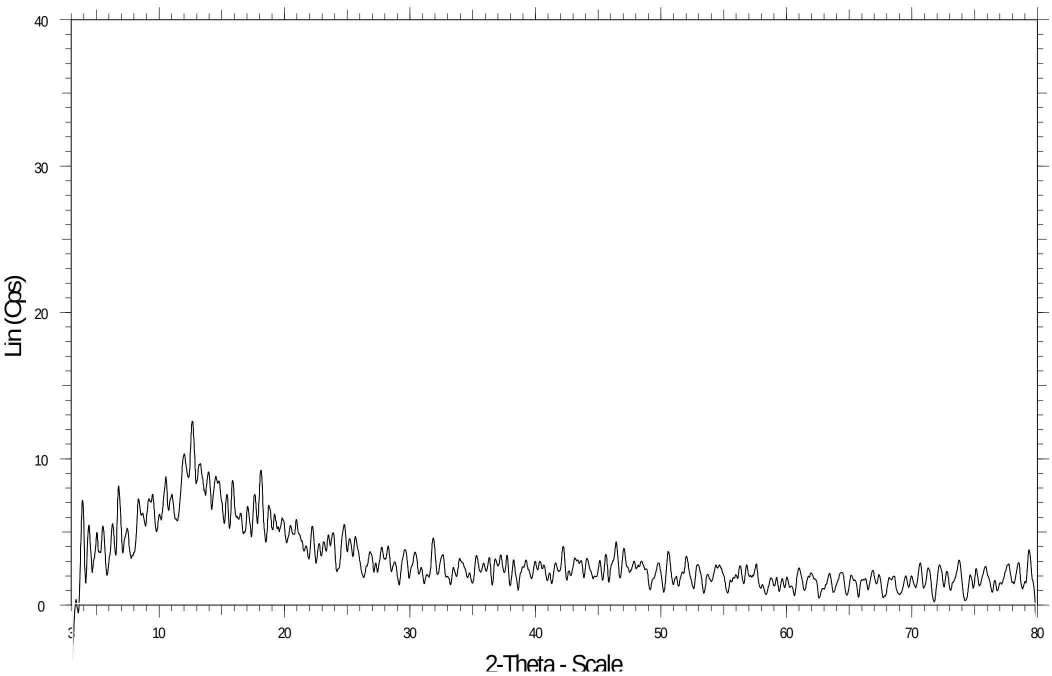


Fig. 3.26 XRD Spectrum of AZO DEG (11)

AZO AP and AZO OT

Almost similar broad peaks are obtained in both AZO AP and AZO OT system. The XRD spectrum of AZO AP and AZO OT are given as Fig 3.27 and 3.28 respectively.

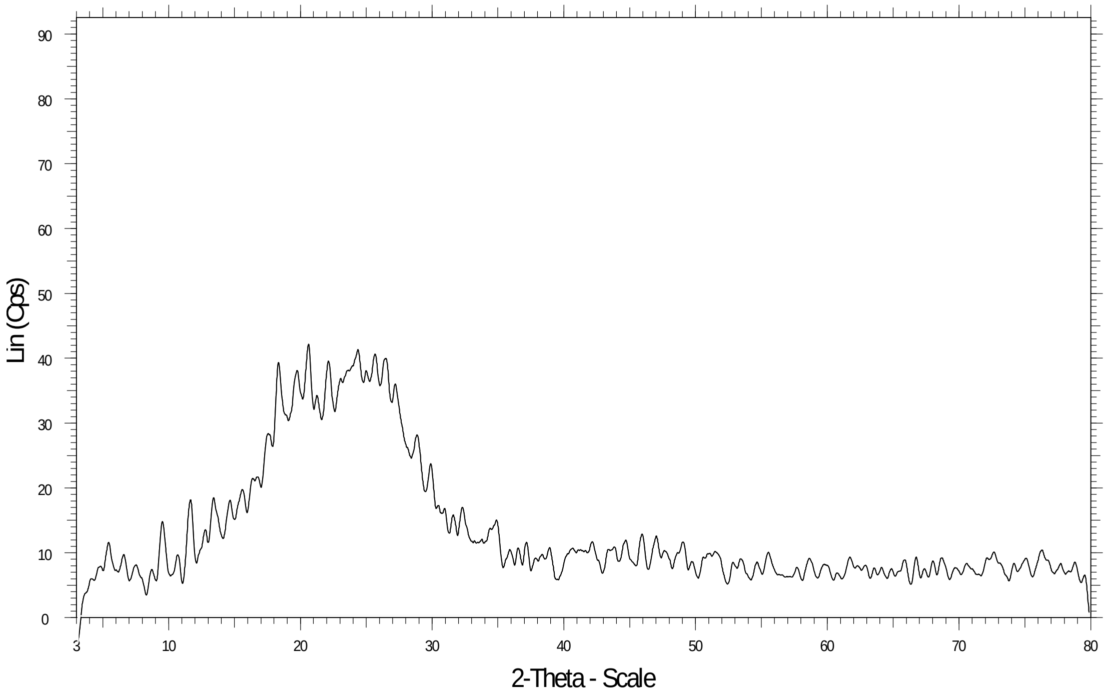


Fig. 3.27 XRD Spectrum of AZO AP (13)

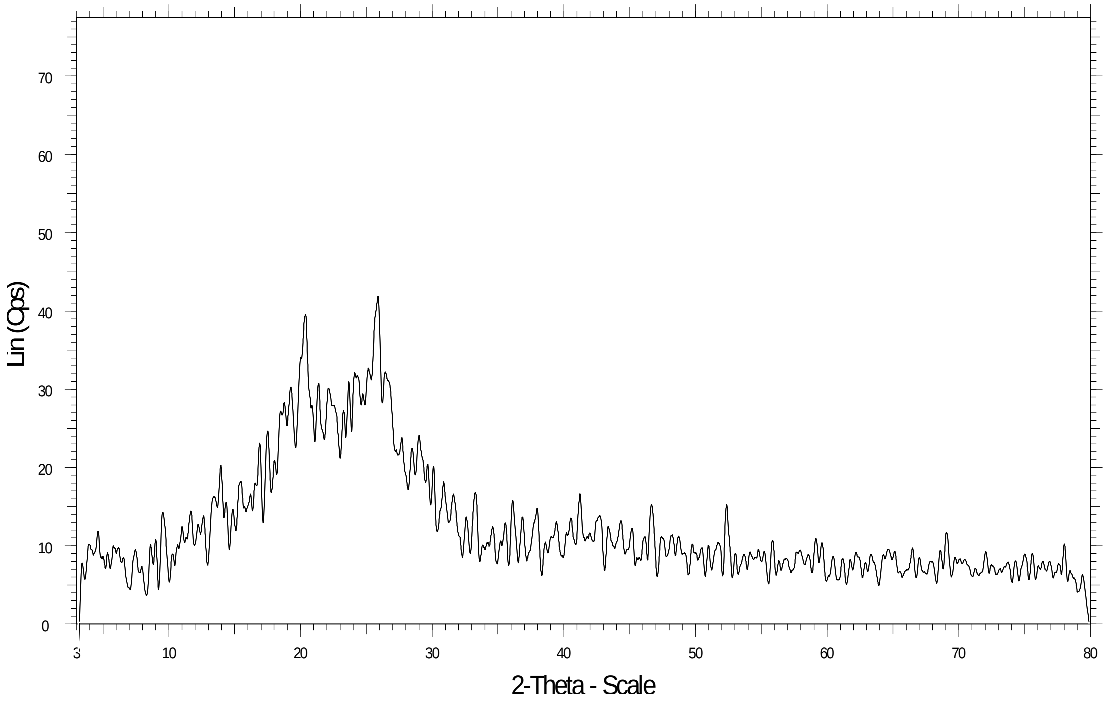


Fig. 3.28 XRD Spectrum of AZO OT (15)

3.2.4. SEM Studies of *ortho*-hydroxyazo polymers

The scanning electron microscope gives images of the sample surface by scanning it with a high energy electron beam. The electrons interact with the atoms that make up the sample, producing signals, that contain information about the sample’s surface topography, composition and other properties such as electrical conductivity. The type of signals produced by a SEM include secondary electrons, back scattered electrons, characteristic X-rays etc. (The signals results from the interactions of electron beam with atoms at or near the surface of the sample). In secondary electron imaging SEM can produce very high resolution images of a sample surface revealing details about 1nm-5 nm in size. Also SEM has a characteristic three dimensional appearance (The magnification power is about 250 times the magnification limit of the best light microscopes). There are signals due to back scattered in electrons (BSE), which are the beam of electrons that are reflected from the sample by elastic scattering. The intensity of the BSE signal is strongly related to the atomic number of the specimen and hence BSE signals can provide information about the distribution of different elements in the sample. Another type of signal produced by SEM is characteristic X-rays, emitted when the electron beams removes an inner shell electron from the sample, causing a high energy electron to fill the shell and release energy. These characteristics X- rays are used to identify the composition and measure the abundance of elements in the sample. SEM is an important tool used to study the surface morphology and microstructure of polymers and polymer based materials. The main aim of electron microscopy is to observe the relationship between adjacent particles and small group of particles. It is the fastest technique and allows one to reach interesting dimensions in polymers.

AZO PVA System

The surface morphology of AZO PVA polymers depends on the concentration of PVA as revealed by SEM. The pore size of the polymeric materials depends on those factors affecting micromorphology[198]. SEM of these AZO PVA exhibits some crystalline morphology (Fig. 3.29 to 3.32).

At low concentration of PVA (14000, 10000 with 1: 1 molar ratio), so many cavities are observed. In these polymers a layer by layer morphology is observed with some aggregation of particles. This is due to lower interaction of hydroxyl group of PVA with one end of carbonyl group of azo compound which makes more cavities. When the concentration of PVA increases as seen in 1:2 molar ratio (Fig. 3.30 and 3.32), an aggregation of particle is observed, which result the uniformity of adhesion of PVA with aromatic ring system. This is attributed to the stronger interaction between hydroxyl group of PVA with two ends of carbonyl group of azocompound which enhances the hydrogen bonding density. This also confirm the interaction of both sides of carbonyl group with PVA, which is further supported by TG, DSC and XRD data.

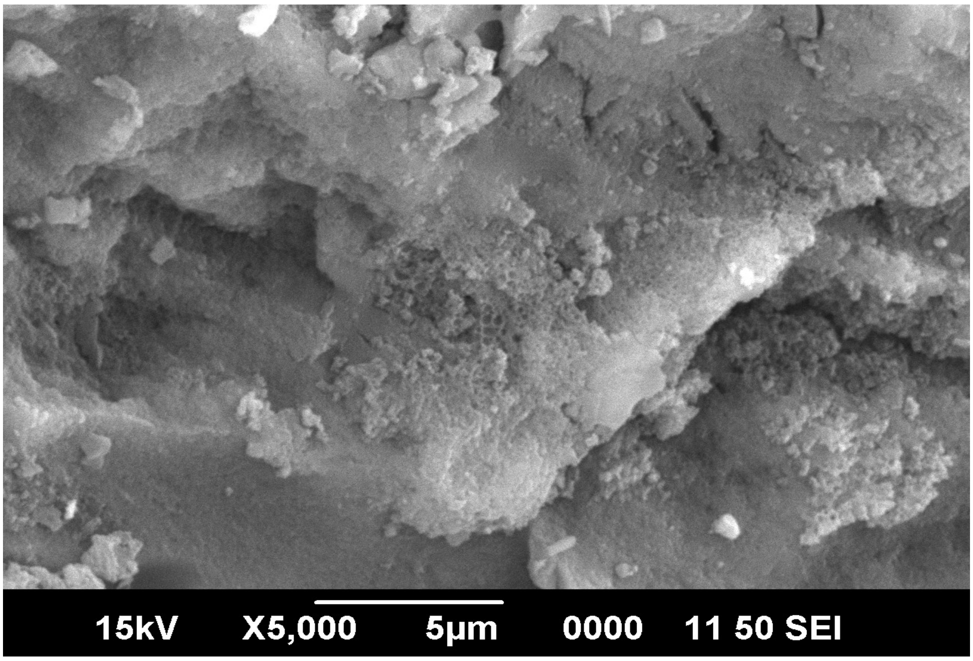


Fig. 3.29 SEM image of AZOPVA 14-1a (6)

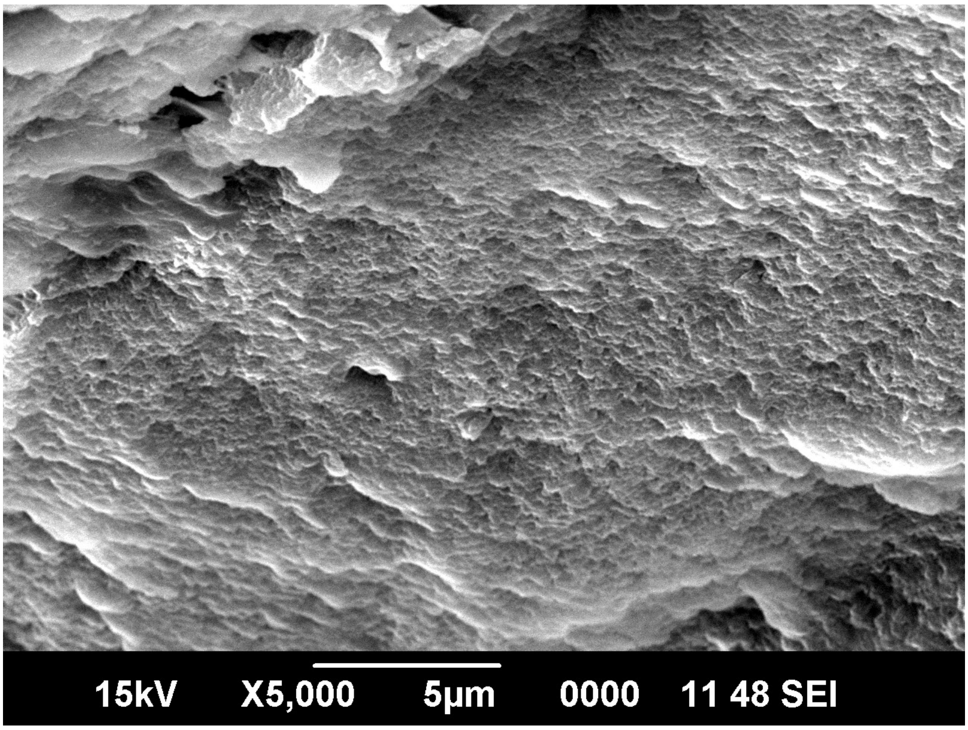


Fig. 3.30 SEM image of AZO PVA 14-1b (7)

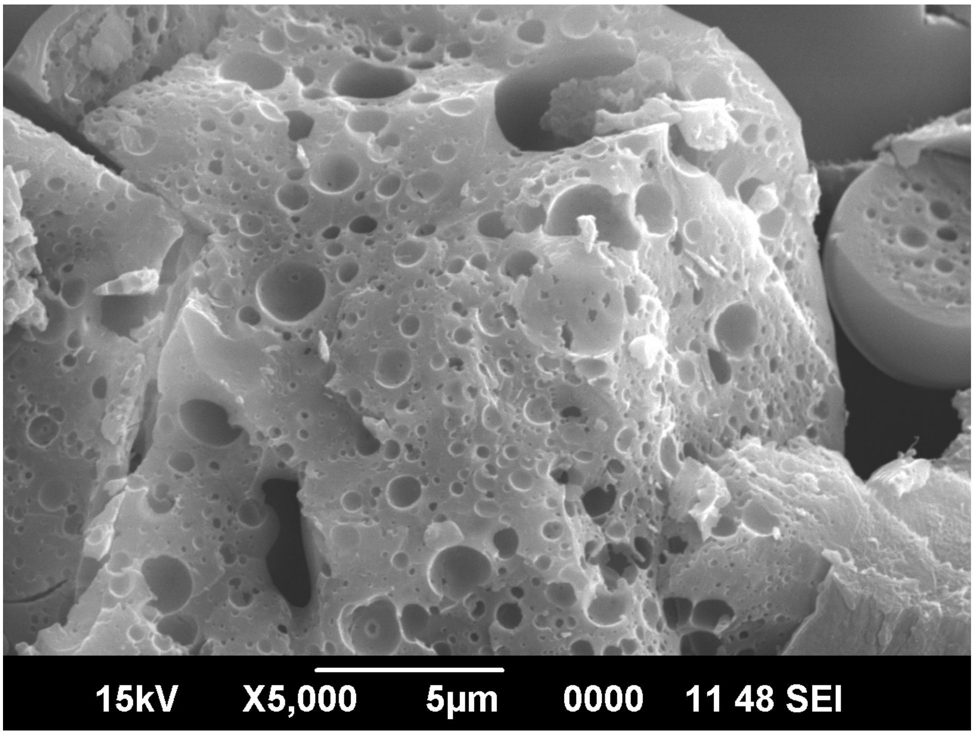


Fig. 3.31 SEM image of AZO PVA 10-1a (6′)

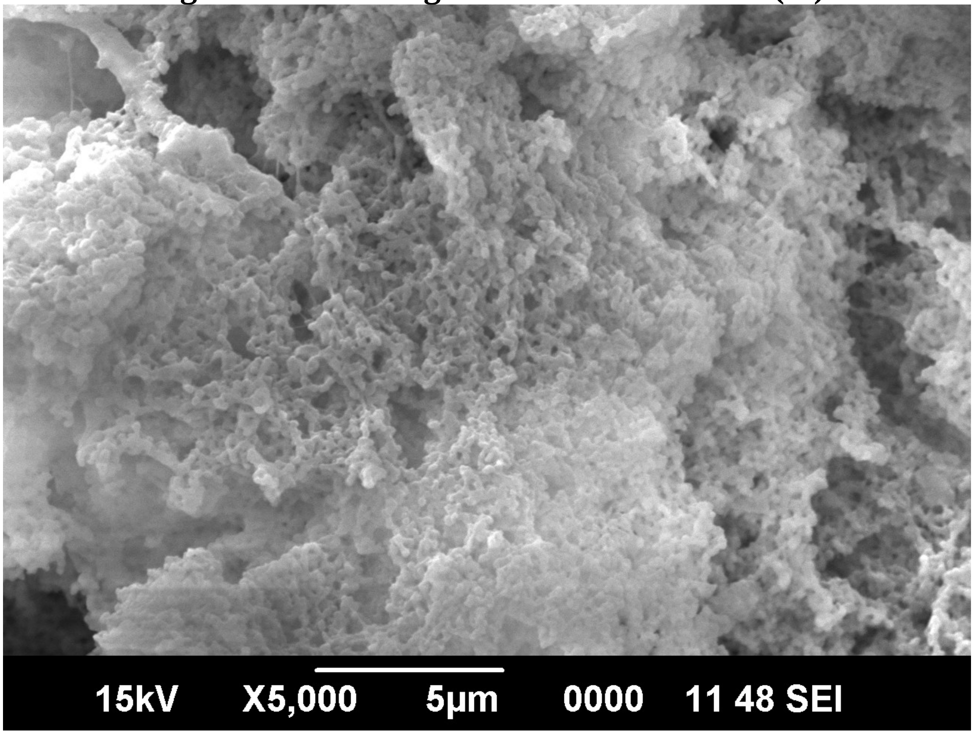


Fig. 3.32 SEM image of AZO PVA 10-1b (7′)

AZO DIOL and AZO DEG

In AZO DIOL, so many agglomeration of particles which results in irregular cavities are observed. But in AZO DEG , SEM images indicates the presence of ring-like and spheroidal objects of heterogeneous diameter. So there is regular order of cavities in all the system of AZO DEG. SEM images of AZO DIOL and AZO DEG given as Fig. 3.33 and 3.34 respectively.

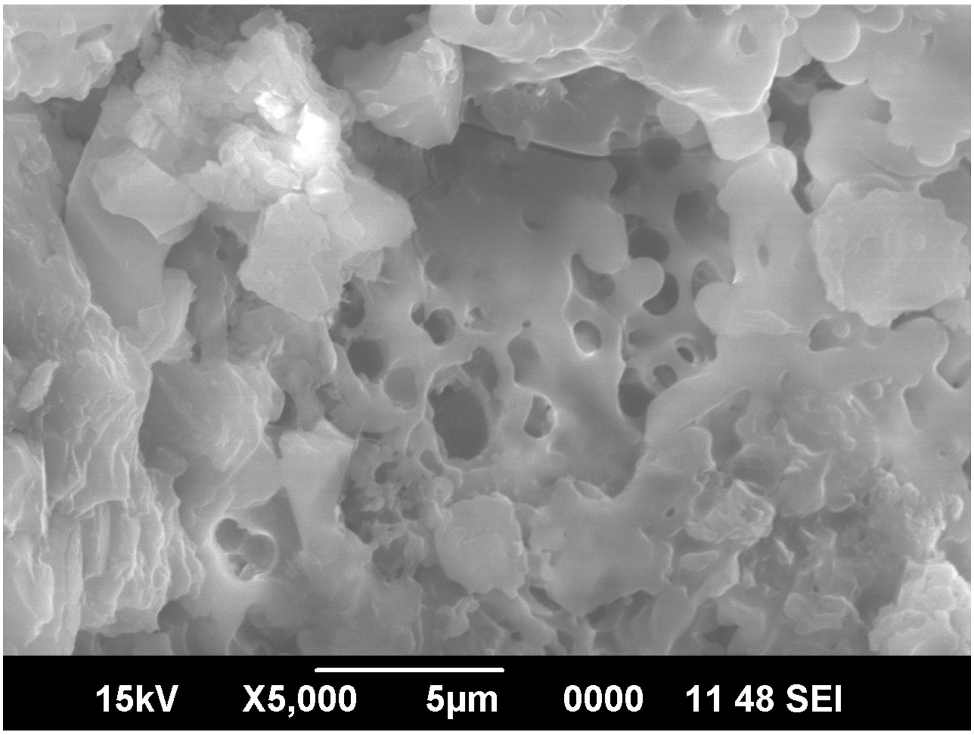


Fig. 3.33 SEM image of AZO DIOL (9)

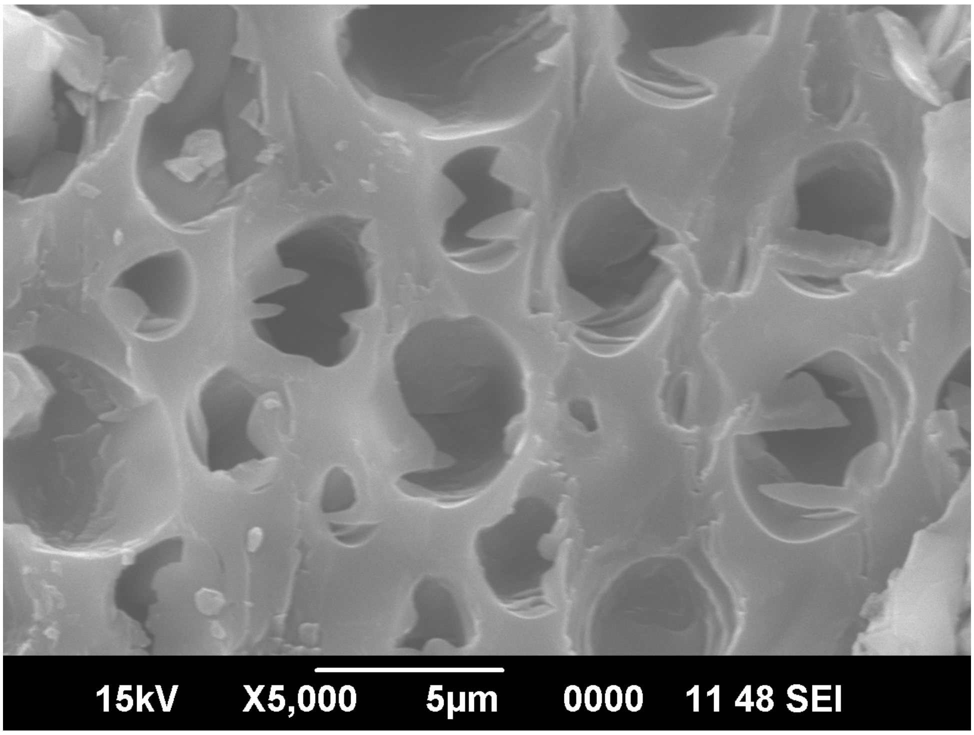


Fig. 3.34 SEM image of AZO DEG (11)

AZO AP and AZO OT

AZO AP is in hemispherical shape. Moreover the surface becomes irregular or coarse because of the wrapping of networks. SEM of AZO OT reveals the presence of globular particles. The particles formed by irregular aggregates. SEM images of AZO AP and AZO OT are given as Fig. 3.35 and 3.36 respectively.

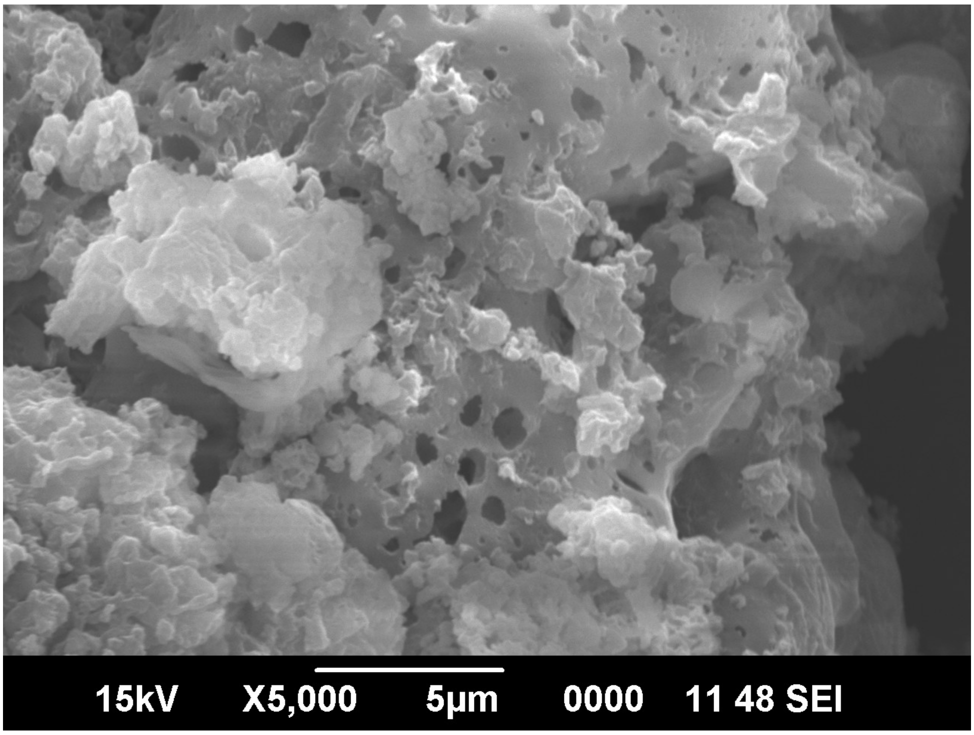


Fig. 3.35 SEM image of AZO AP (13)

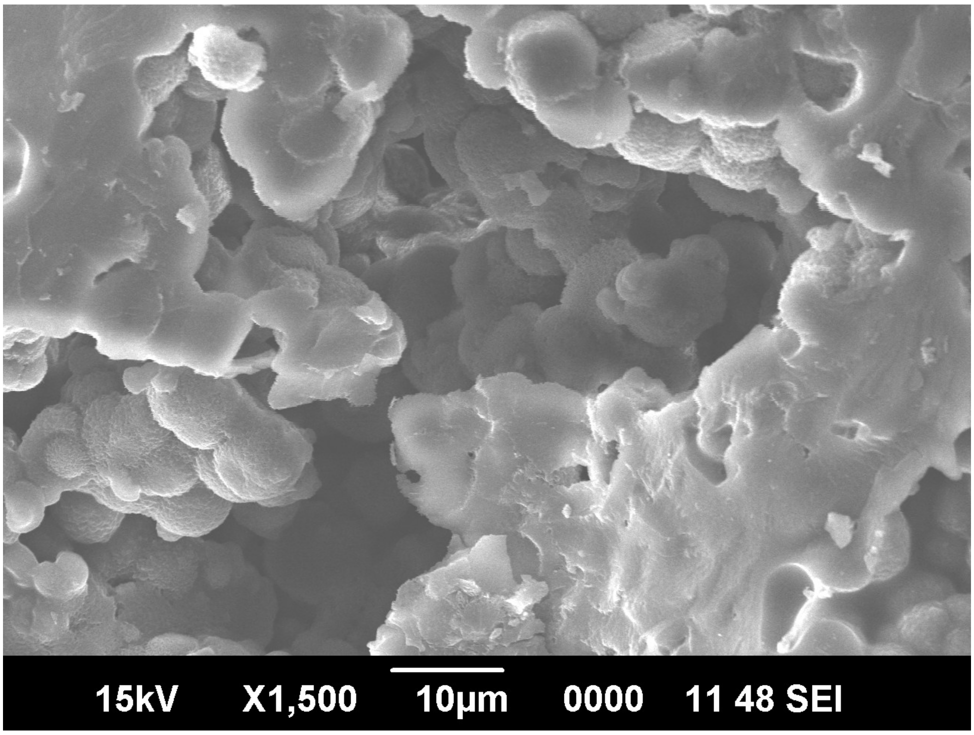


Fig. 3.36 SEM image of AZO OT (15)

SECTION 4

PHOTORESPONSIVE PROPERTY CHANGES OF *ORTHO*-HYDROXYAZO POLYMERS IN SOLUTIONS

4.1. INTRODUCTION

Photoresponsive macromolecules have attracted much interest and considerable progress has been achieved in this field during the last few decades. Incorporating photochromic moieties into organic compounds leads to photoresponsive systems, the properties of which can be manipulated by light. At molecular level, switching of metal ion capture or energy or electron transfer occurs as a consequence of a photochromic reaction but with regard to bulk properties, photostimulated viscosity changes or even phase separations are observed. Polymer film comprising photoresponsive molecules such as spiropyran represents attractive alternatives for controlling protein and cell adhesion on surfaces. The detailed investigations carried out on these systems revealed that molecular level *cis-trans* isomerisations[189,199] which ultimately lead to photochromic behaviour is the main justification attributed to the photoresponsiveness in azo group containing polymers. Changes in geometrical structures of the azobenzene residues incorporated in the polymers backbone or as pendant groups cause conformational changes[200,201] of the polymer chain affecting solution properties, since the isomerisation involves appreciable changes in polarity and geometrical structure. The dilute solution viscosity of a polymer system is a direct reflection of the conformation of a polymer chain. In solution, polymers with azo aromatic units in the backbone or as pendant groups are expected to behave like semi flexible rods. If such repeating unit of the polymer chain contains an azo aromatic group and if a major portion of them is in the *trans* configuration, then the polymer chain will be in the extended conformation. The extended shape of the semi flexible chain will form rather compact coils, when the configuration of the constituent azo aromatic units changes from *trans* to *cis* form. Photoirradiation can easily carry out this job without any fatigue to the polymer system.

The photodecrease in dilute solution viscosities of a number of polymers having azobenzene group in the polymer backbone were studied.[110] Similarly, dilute solution conductivity studies [20] were repeated with the same system of polymers. The photodecrease in conductivity was justified on the basis of the formation of more polar *cis* form during irradiation. Only very few reports are found in the literature making a correlation between the extent of photoismerisation and the solution viscosity and conductivity of polymers. So, apart from photoconductivity in the solid state of *ortho*-hydroxyazo aromatic polymers, it is thought interesting to investigate the dilute solution properties like viscosity and conductivity of the synthesised polymers as a consequence of irradiation. Thus the present section mainly focuses.

(i) to study of the spectral response (UV-visible) of the synthesised polymers.

(ii) to carry out the dilute solution viscosity changes of polymers having *ortho*-hydroxyazo aromatic groups.

(iii) to carry out the photoincrease in dilute solution conductivity of the synthesised polymers.

(iv) to correlate these photophysical property changes with the changes in configuration of azo aromatic groups and consequent conformational changes in the polymer.

4.2. RESULTS AND DISCUSSION

4.2.1. UV-visible absorption spectra of polymers having *ortho*-hydroxyazo aromatic groups.

UV-visible absorption spectra have been used to rationalize the photoisomerisation involved not only in low molecular weight compounds but in polymers to a large extent.[72-75] The nature of absorption spectra of azo group changes as the configuration alters from *trans* to *cis* form during irradiation. Azobenzene and nearly all its substituted derivatives are known[202] to change their absorption spectrum when the configuration changes from *trans* to *cis* form. Their principal absorption band $\pi \rightarrow \pi^*$ is in UV region and their colour is caused by a weak $n \rightarrow \pi^*$ absorption in the visible region. On conversion to the *cis* isomer by photoirradiation, a decrease in intensity $\pi \rightarrow \pi^*$ band with a shift to shorter wavelength region and an increase in the intensity of the $n \rightarrow \pi^*$ absorption is observed. Analogues spectral changes have been reported in photresponsive polyamides incorporated with azobenzene group in the polymer backbone. The changes in the intensity of two bands $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ have been considered as a token of evidence of photoisomerisation of azoaromatic residues in the polymer backbone. Thus, the absorption spectrum of AZO PVA 14-1a was recorded in N,N-dimethyl acetamide and is represented on Fig. 4.1.

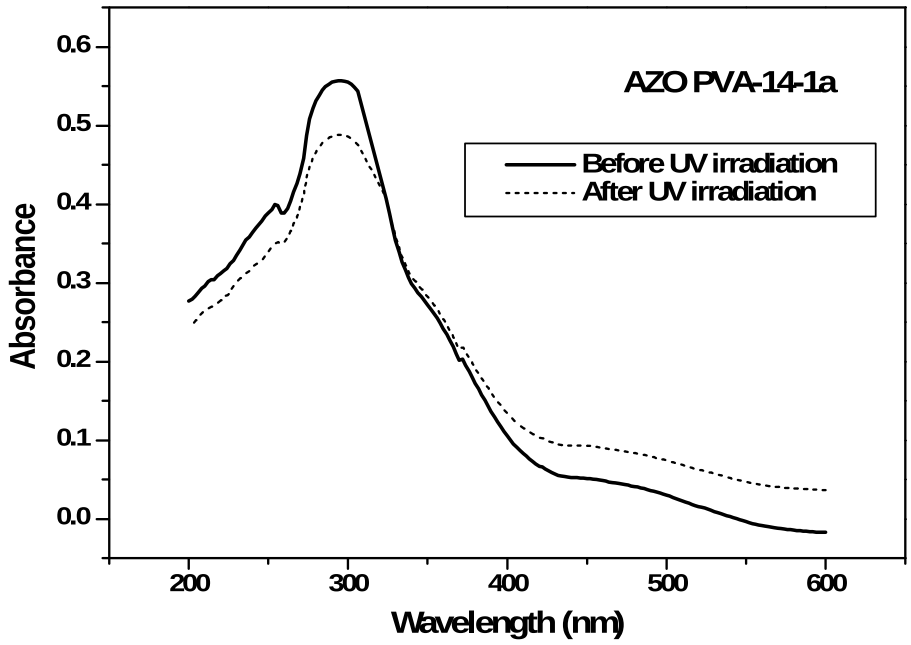


Fig. 4.1. UV-visible spectrum of AZO PVA 14 1-a in DMA

Two strong bands were obtained at 296 nm and 372 nm in the UV region, further, a weak band was obtained at 468 nm in visible region. On photoirradiation of the polymer in dimethyl acetamide solution, the intensity at 296 nm absorption band was decreased while the intensity of the band at 468 nm was slightly increased (Fig. 4.1). The spectral response curve of polymer AZO PVA 14-1b, AZO PVA 10-1a, AZO PVA 10-1b, AZO DIOL, AZO DEG, AZO AP, AZO OT in dimethyl acetamide solution are represented respectively (Fig. 4.2. – 4.8). In all the cases, a slight increase in intensity of n → π⋆ and a decrease in π → π⋆ band were observed after irradiation.

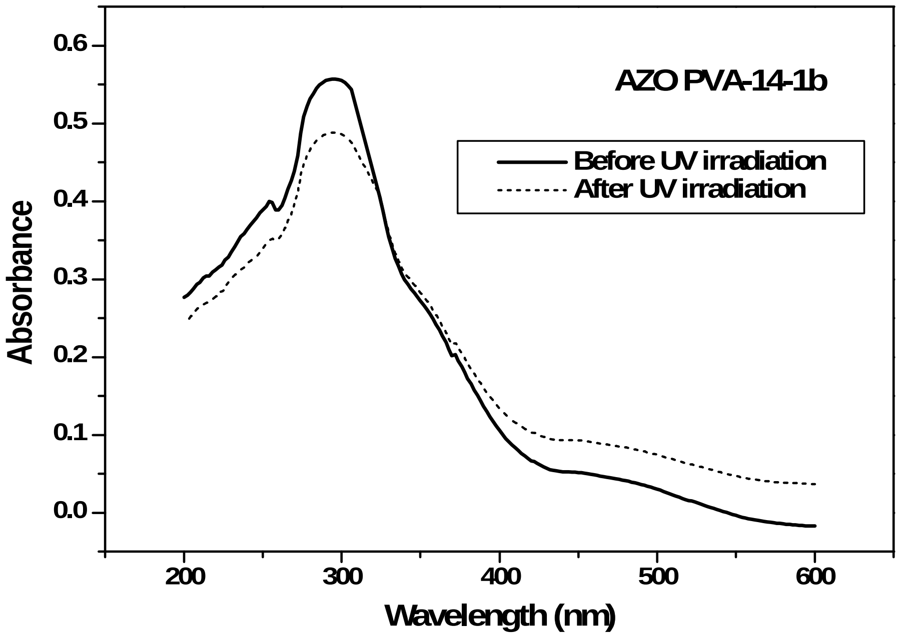


Fig. 4.2. UV-visible spectrum of AZO PVA 14 1-b in DMA

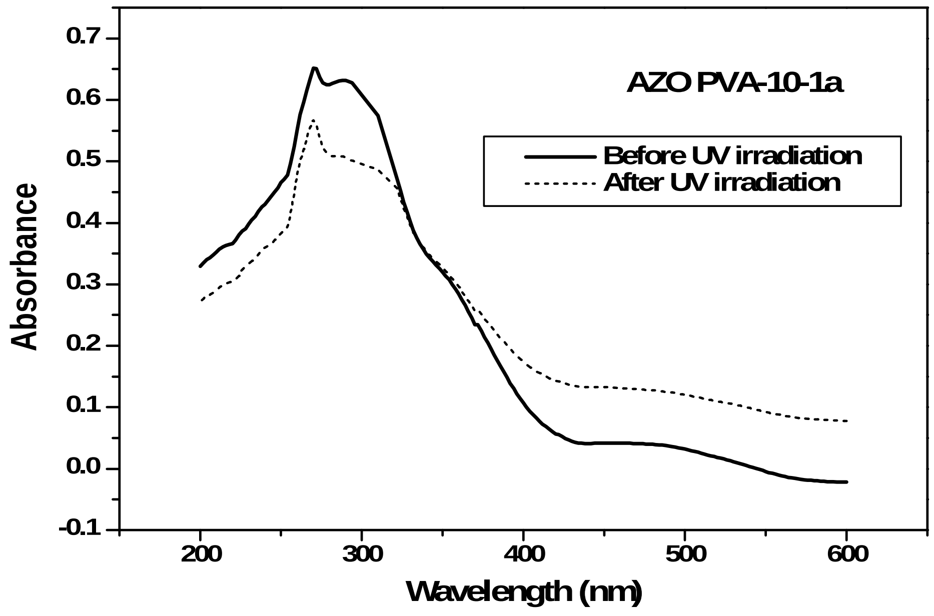


Fig. 4.3. UV-visible spectrum of AZO PVA 10-1 a in DMA

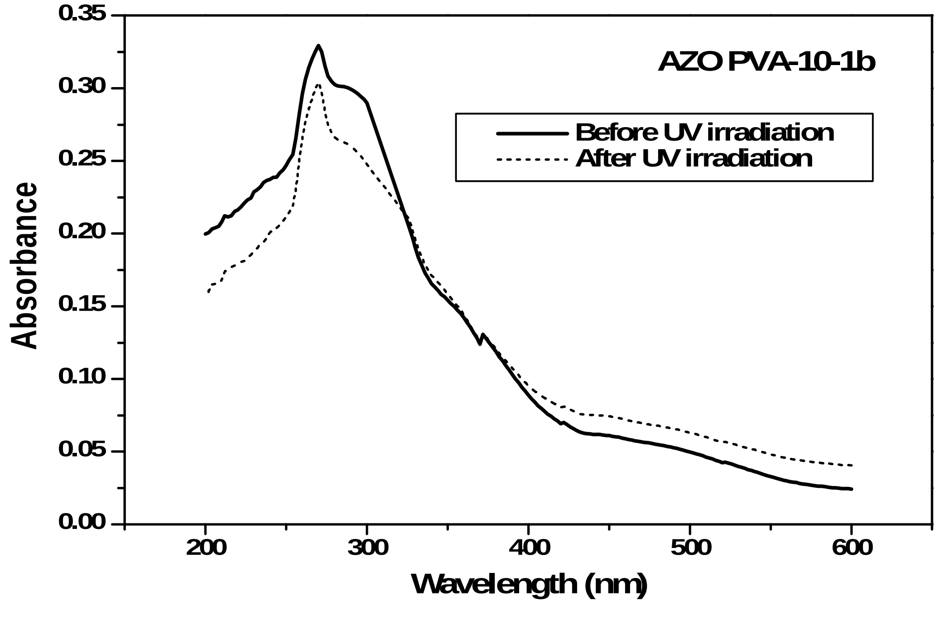


Fig. 4.4. UV-visible spectrum of AZO PVA 10-1b in DMA

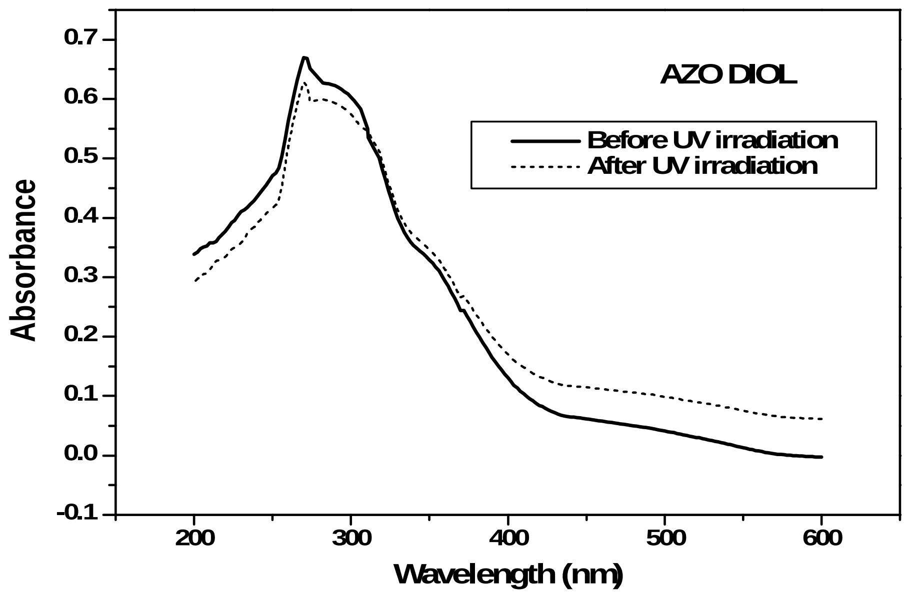


Fig. 4.5. UV-visible spectrum of AZO DIOL in DMA

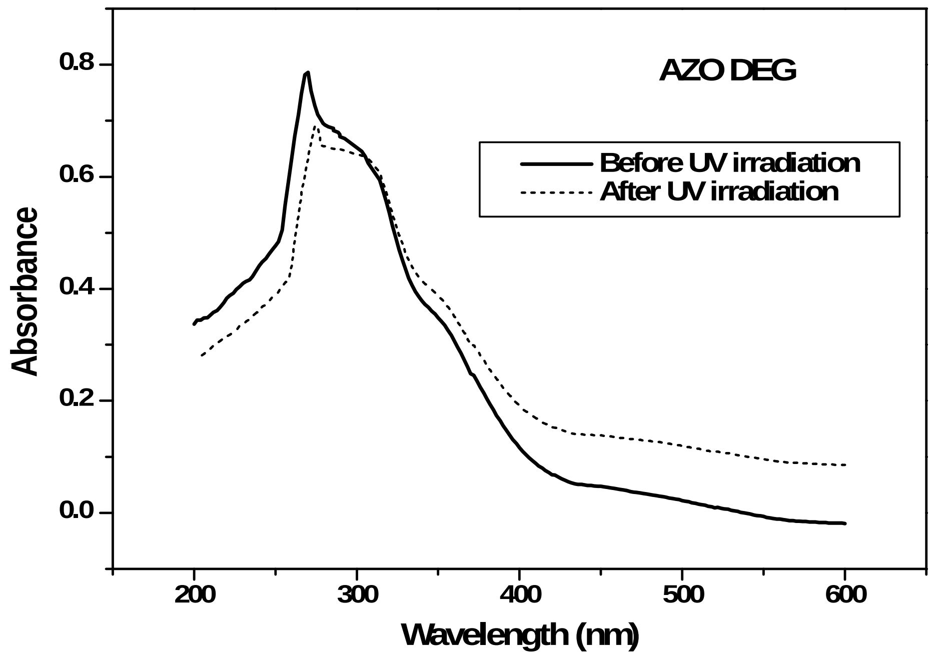


Fig. 4.6. UV-visible spectrum of AZO DEG in DMA

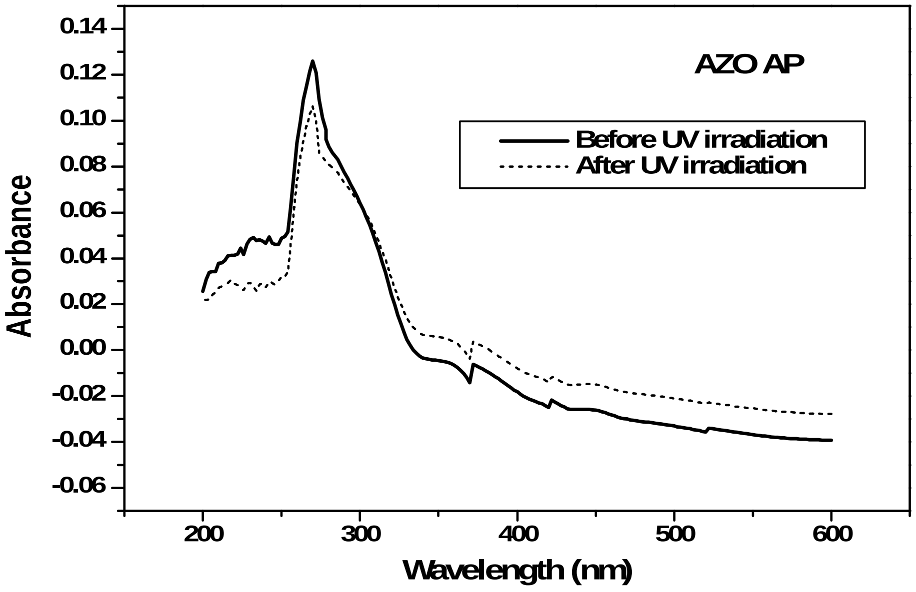


Fig. 4.7. UV-visible spectrum of AZO AP in DMA

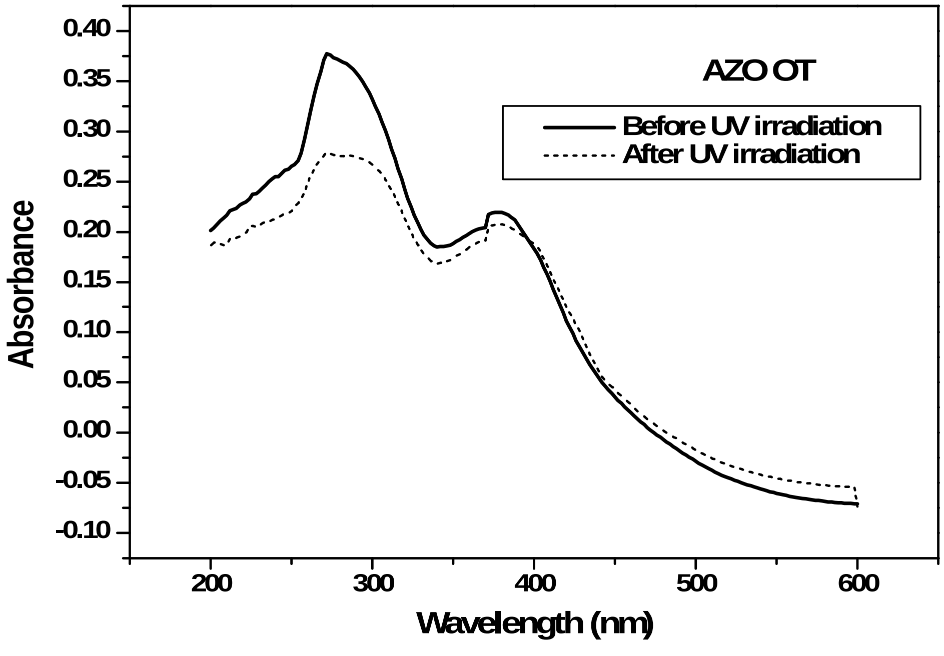


Fig. 4.8. UV-visible spectrum of AZO OT in DMA

4.2.2. Photoinduced dilute solution viscosity changes of polymers with *ortho*-hydroxyazo aromatic groups

The study of the spectral response curve of the synthesised polymers having *ortho*-hydroxy azo aromatic groups in the backbone and also as pendant groups reveals that during irradiation in UV-visible light, the isomerisation of *trans* to *cis* form is most probable molecular level interpretation. Though, there is no conclusive proof in the literature on the mechanism of photochemical isomerisation having N=N band, the "inversion mechanism" is suggested as the suitable pathway. This *trans* to *cis* photoisomerisation is expected to be manifested in the dilute solution viscosity of *ortho*-hydroxyazo aromatic polyesters which is characteristic in that they contain flexible methylene spacer and stiff biphelene residues in the main chain. Thus, when a dilute solution of the polymer AZO PVA 14-1a, in N,N-dimethyl acetamide (0.6g/dL) was irradiated with UV-visible light at 28 ^{0}C in a photochemical reactor and viscosities were measured at definite intervals of time, it was found that a steady decrease in viscosity was resulted after 8-10 h of irradiation. No further decrease in viscosity was observed eventhough, the solution was subjected to irradiation continuously for 12-14 h. The observed change was found to be reversible since the solution regained the original viscosity after keeping the solution under dark for 16 h at 28 ^{0}C. Irradiations followed by the viscosity measurements at definite time intervals were repeated with solution of different concentration (0.4g/dL and 0.2g/dL) and similar reversible photodecrease in viscosities were observed. Phtotodecrease in relative viscosities was graphically represented in fig. 4.9 (a) and intrinsic viscosity changes as Fig. 4.9 (b). The decrease in intrinsic viscosity as a result of photoirradiation was found to be 34%.

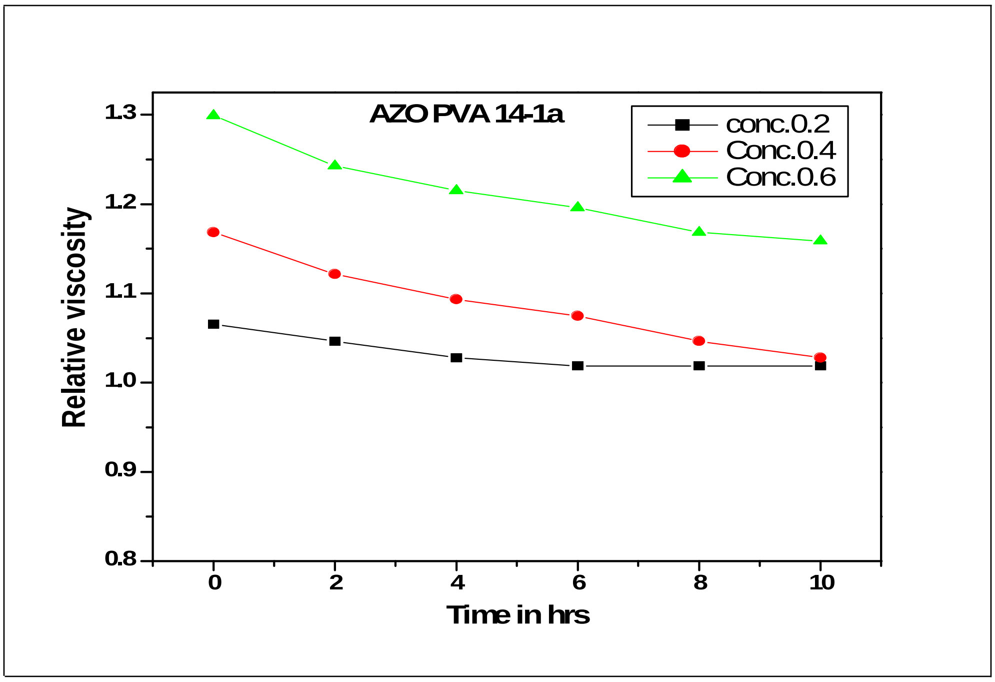
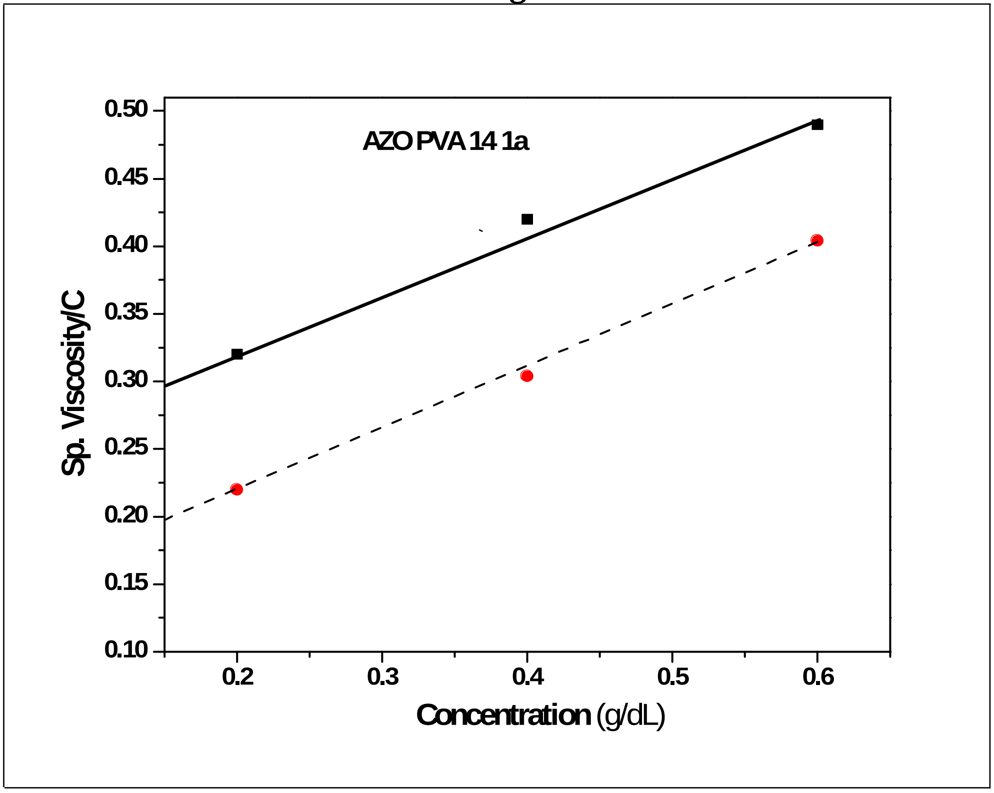


Fig. 4.9 (a) Relative dilute solution viscosity of polymer AZO PVA 14-1a in DMA during irradiation



— before irradiation, ----- after irradiation

Fig. 4.9 (b) Intrinsic viscosity of polymer AZO PVA 14-1a in DMA

The reversible photoinduced viscosity changes observed in AZO PVA-14-1a stimulated the interest in studying the behaviour of other polyesters having *ortho*-hydroxyazo aromatic residues. Thus, dilute polymer solutions of AZO PVA 14-1b, AZO PVA 10-1a, AZO PVA 10-1b, AZO DIOL, AZO DEG, AZO AP, AZO OT were irradiated and viscosities were measured before and after irradiation at different concentrations (0.6, 0.4 and 0.2 g/dL) In all these cases, the viscosities after 8-10 h of irradiation showed a decrease of 34-66%. The viscosity changes observed were reversible and the original viscosity was regained after keeping the solution in the dark for about 16 h. The relative viscosity changes during irradiation and intrinsic viscosity before and after irradiation of all the polymers are graphically represented in Fig. 4.10 (a, b) – 4.16 (a, b). The details of the photoviscosity effects carried out on different polymers are given in Table 4.1.

TABLE. 4.1

Photoviscosity effect of polymers

Sl. No	Polymers	Intrinsic viscosity (η) before irradiation	Intrinsic viscosity (η) after irradiation	Decrease in intrinsic viscosity (%)
1.	AZO PVA 14-1a	0.29	0.19	34
2.	AZO PVA 14-1b	0.26	0.17	34
3.	AZO PVA 10-1a	0.33	0.21	36
4.	AZO PVA 10-1b	0.27	0.17	37
5.	AZO DIOL	0.26	0.13	50
6.	AZO DEG	0.39	0.21	46
7.	AZO AP	0.57	0.20	65
8.	AZO OT	0.56	0.19	66

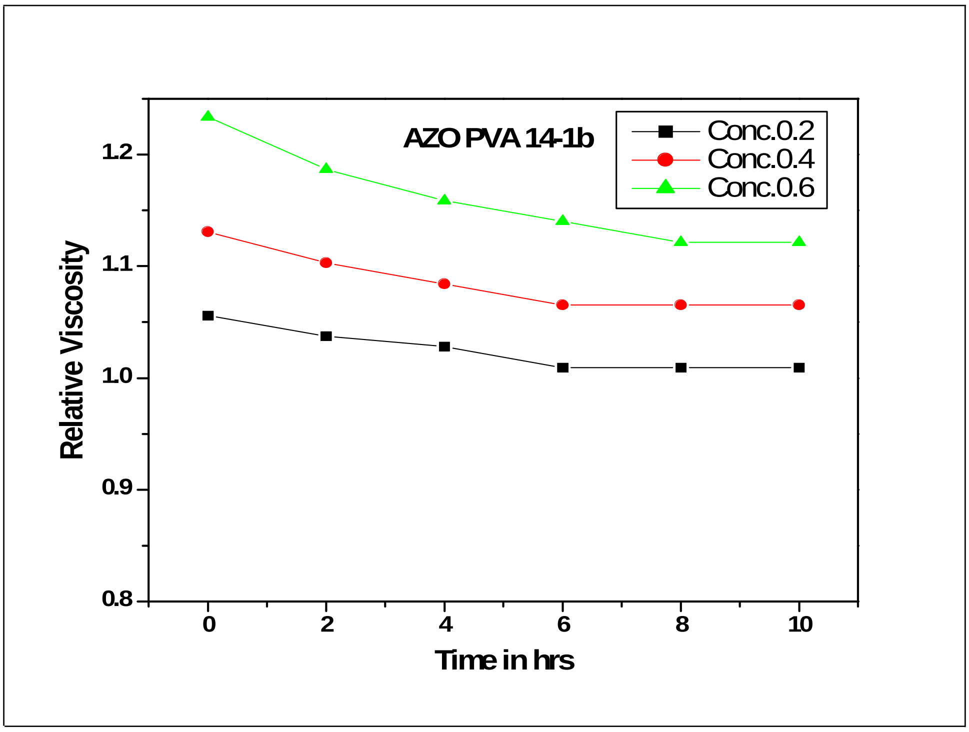
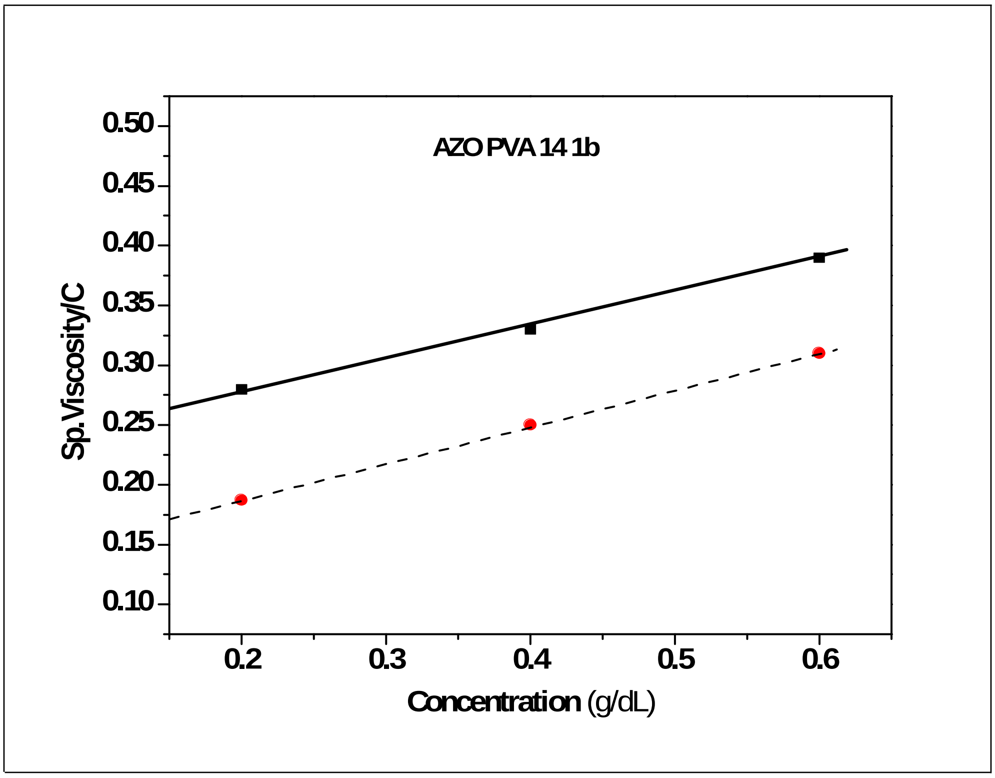


Fig. 4.10 (a) Relative dilute solution viscosity of polymer AZO PVA 14-1b in DMA during irradiation



— before irradiation, ----- after irradiation

Fig. 4.10 (b) Intrinsic viscosity of polymer AZO PVA 14-1b in DMA

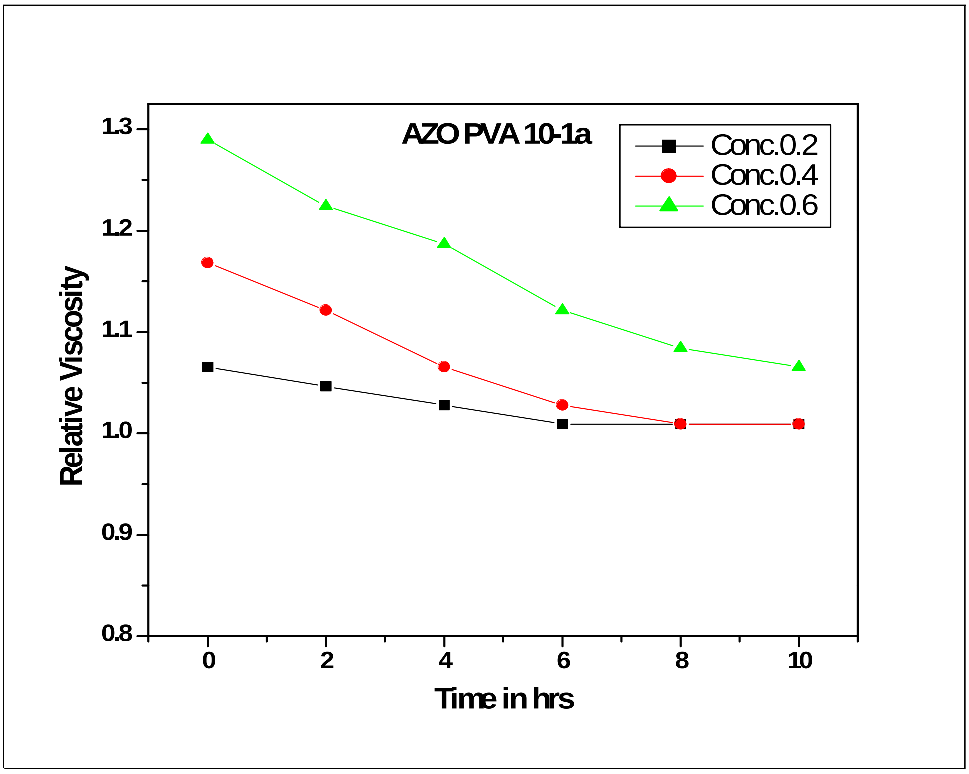


Fig. 4.11 (a) Relative dilute solution viscosity of polymer AZO PVA 10-1a in DMA during irradiation

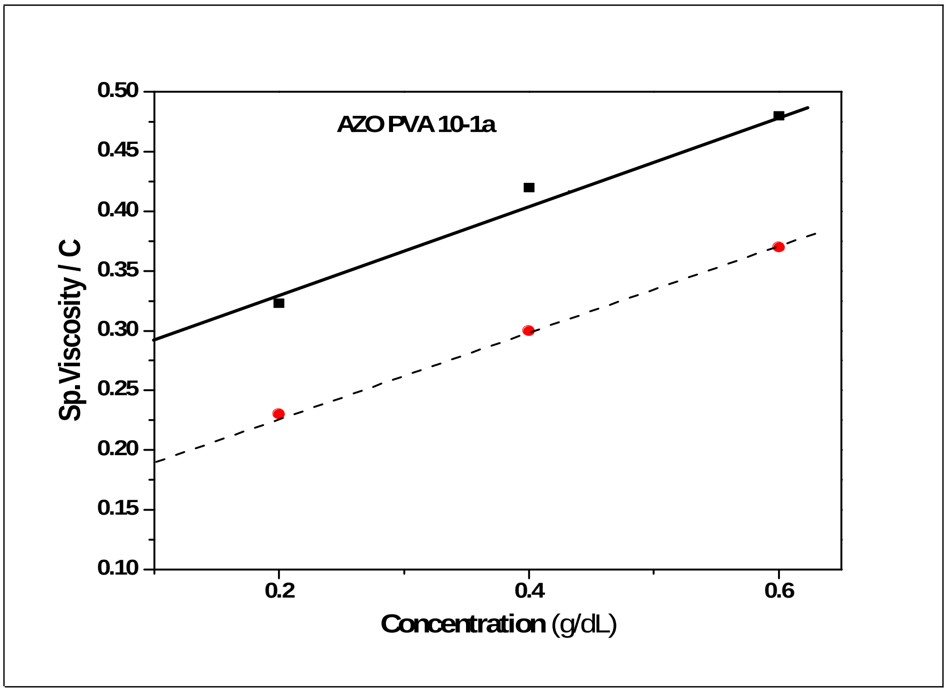


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Fig. 4.11 (b) Intrinsic viscosity of polymer AZO PVA 10-1a in DMA

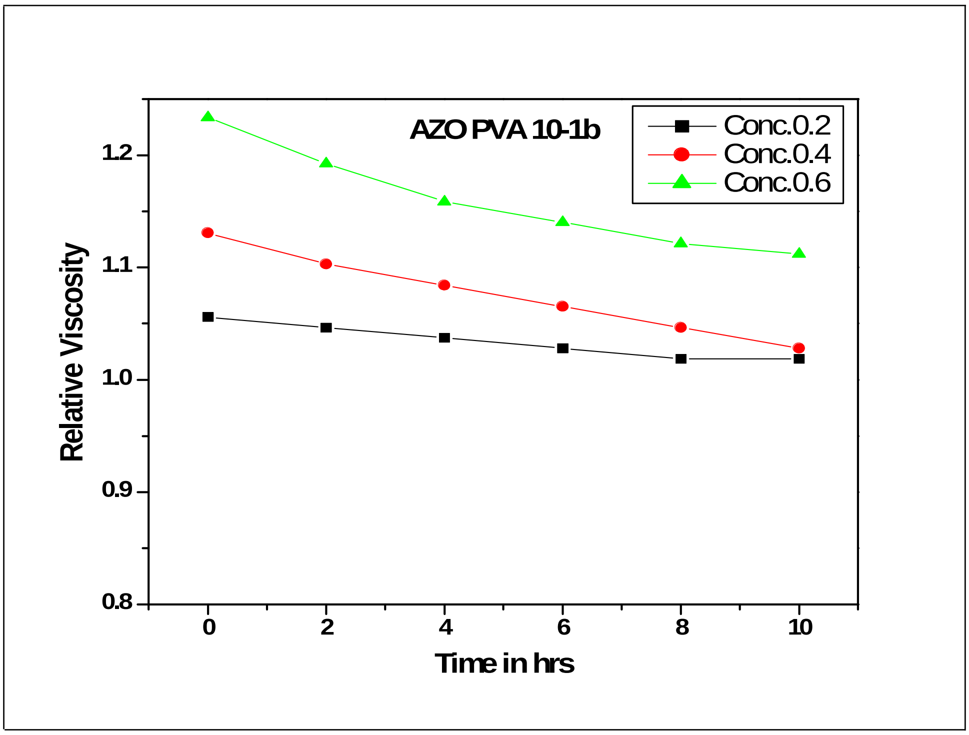

Fig. 4.12 (a) Relative dilute solution viscosity of polymer AZO PVA 10-1b in DMA during irradiation

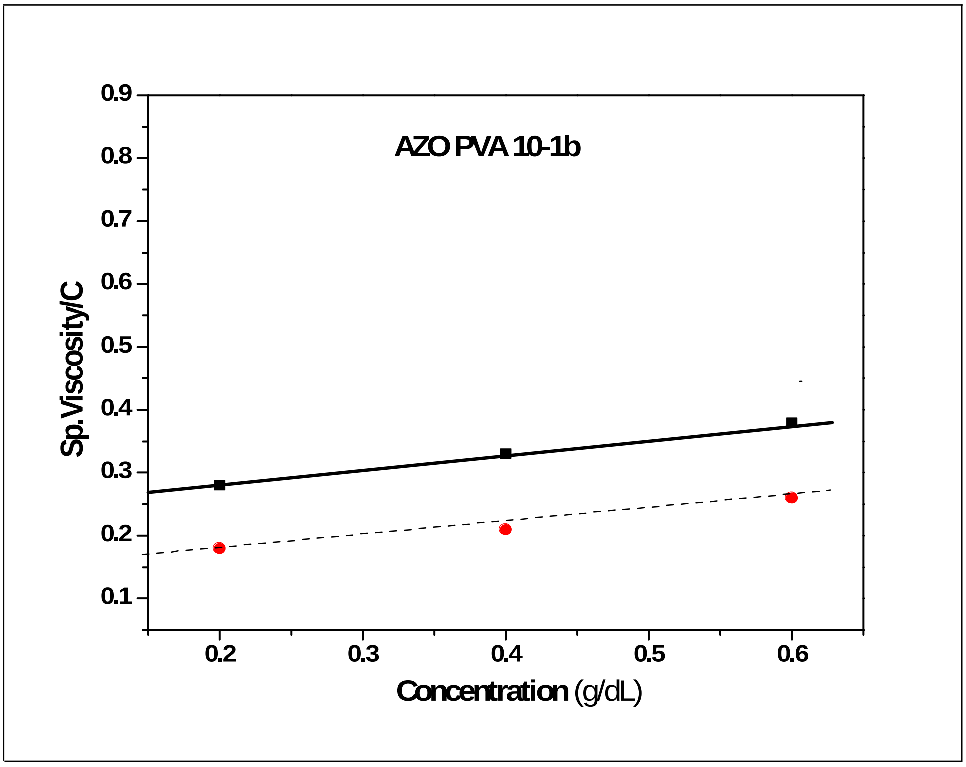

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Fig. 4.12 (b) Intrinsic viscosity of polymer AZO PVA 10-1b in DMA

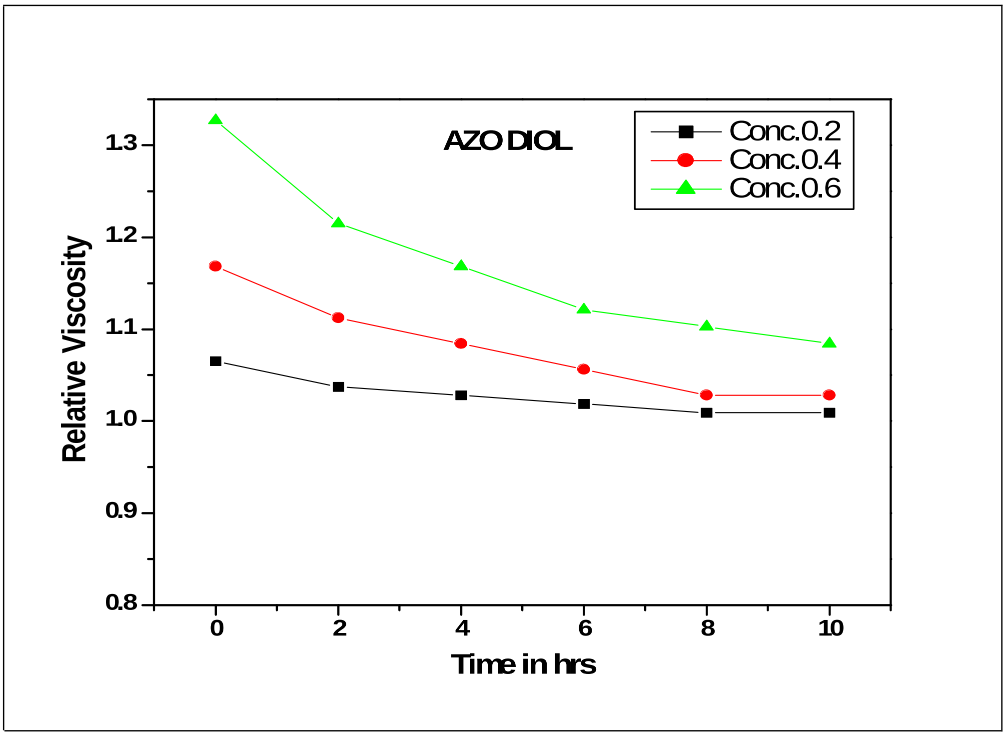
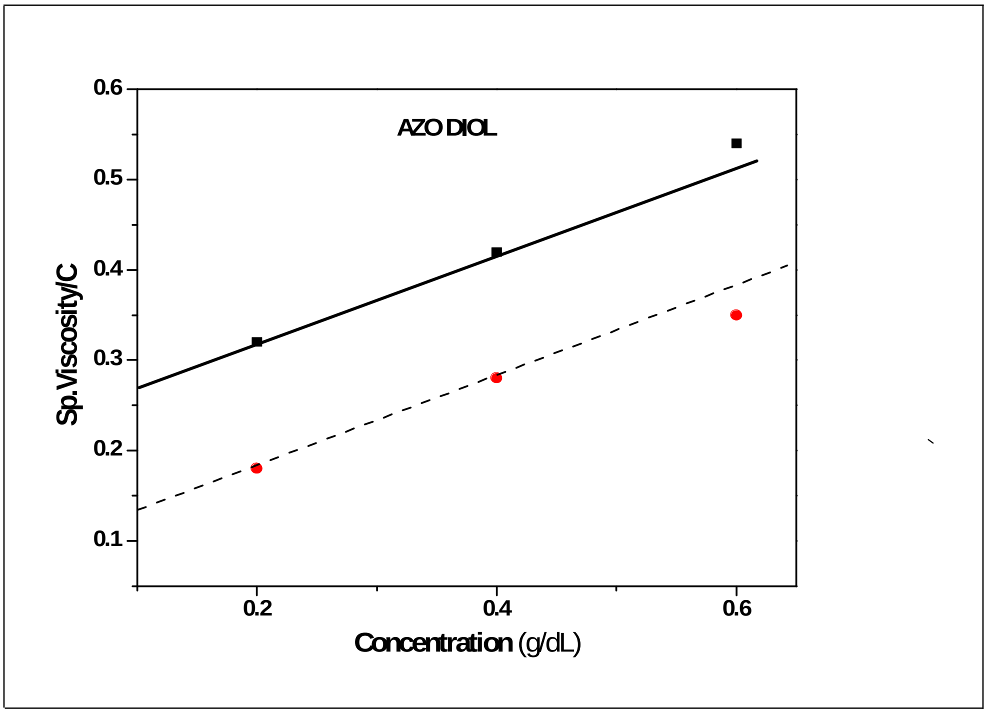


Fig. 4.13 (a) Relative dilute solution viscosity of polymer AZO DIOL in DMA during irradiation



— before irradiation, ----- after irradiation

Fig. 4.13 (b) Intrinsic viscosity of polymer AZO DIOL in DMA

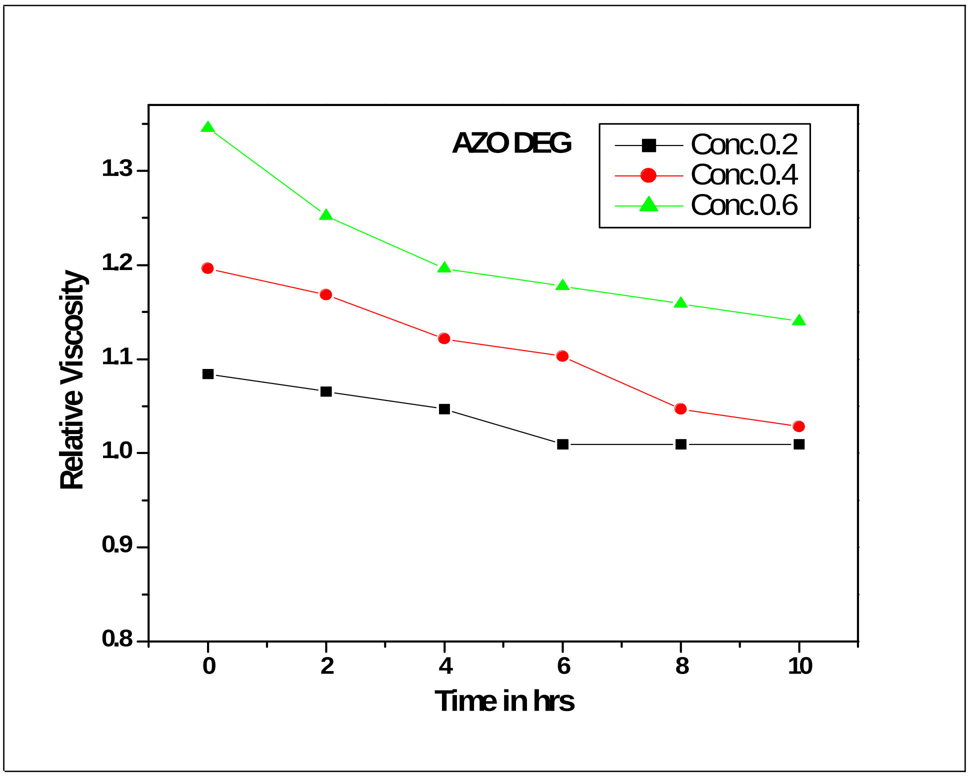
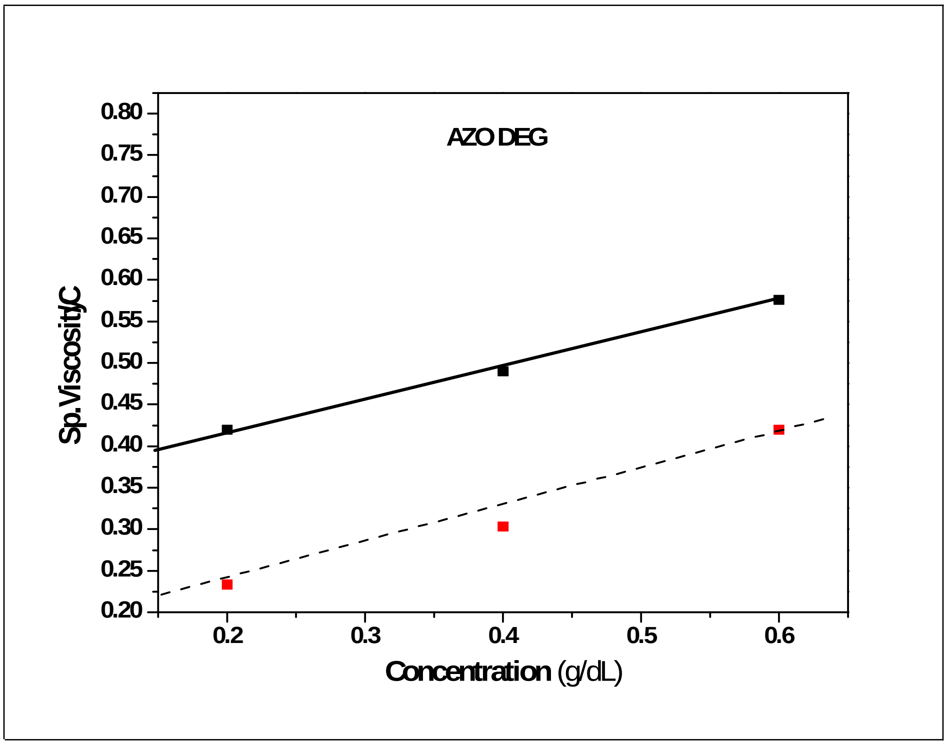


Fig. 4.14 (a) Relative dilute solution viscosity of polymer AZO DEG in DMA during irradiation



— before irradiation, ----- after irradiation

Fig. 4.14 (b) Intrinsic viscosity of polymer AZO DEG in DMA

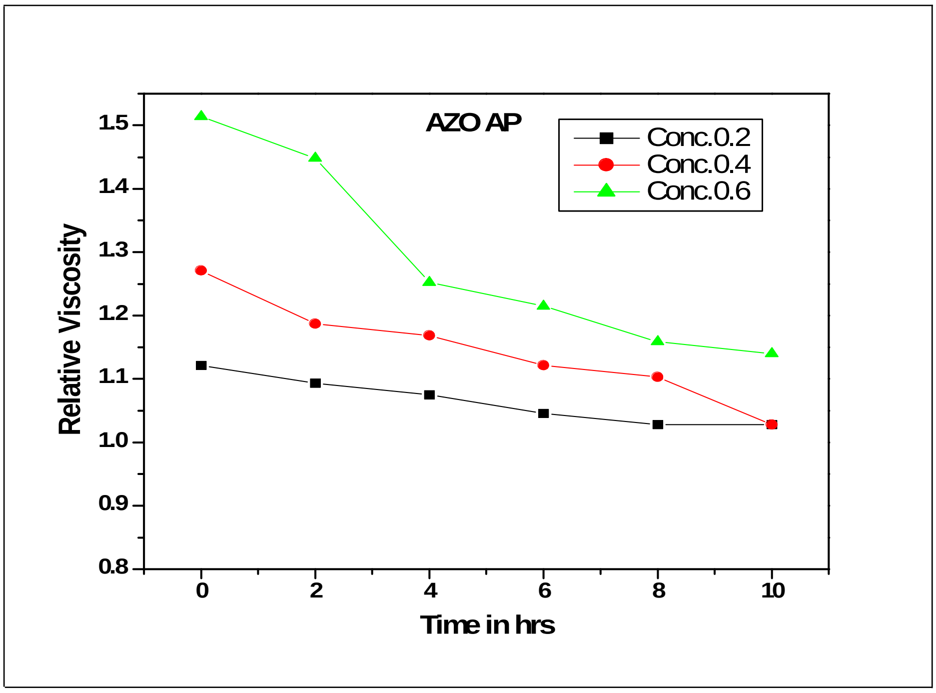
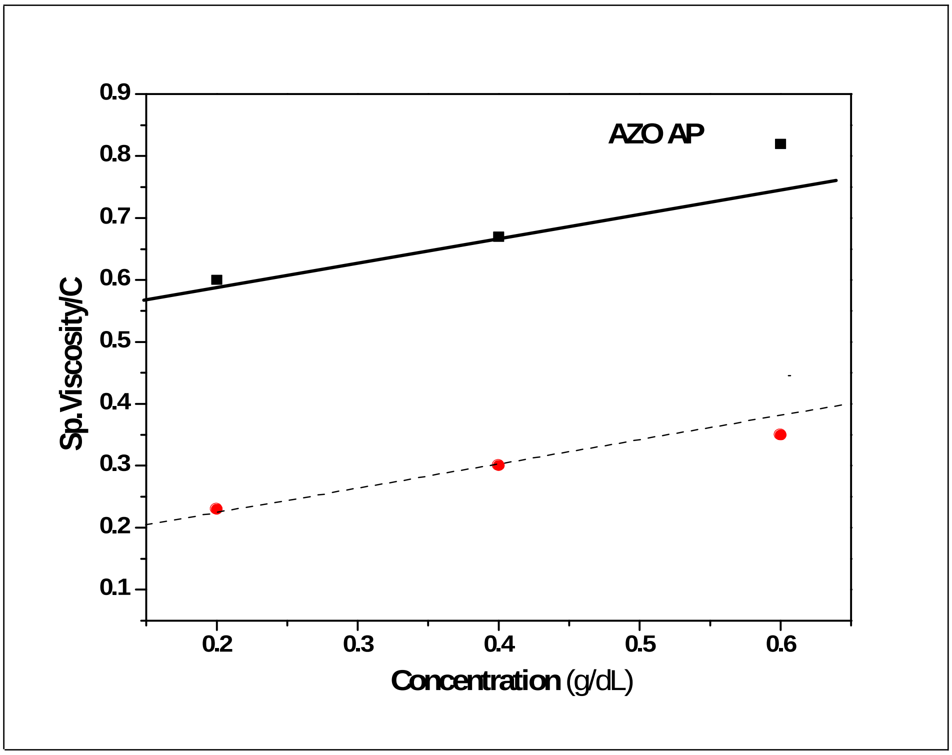


Fig. 4.15 (a) Relative dilute solution viscosity of polymer AZO AP in DMA during irradiation



— before irradiation, ----- after irradiation

Fig. 4.15 (b) Intrinsic viscosity of polymer AZO AP in DMA

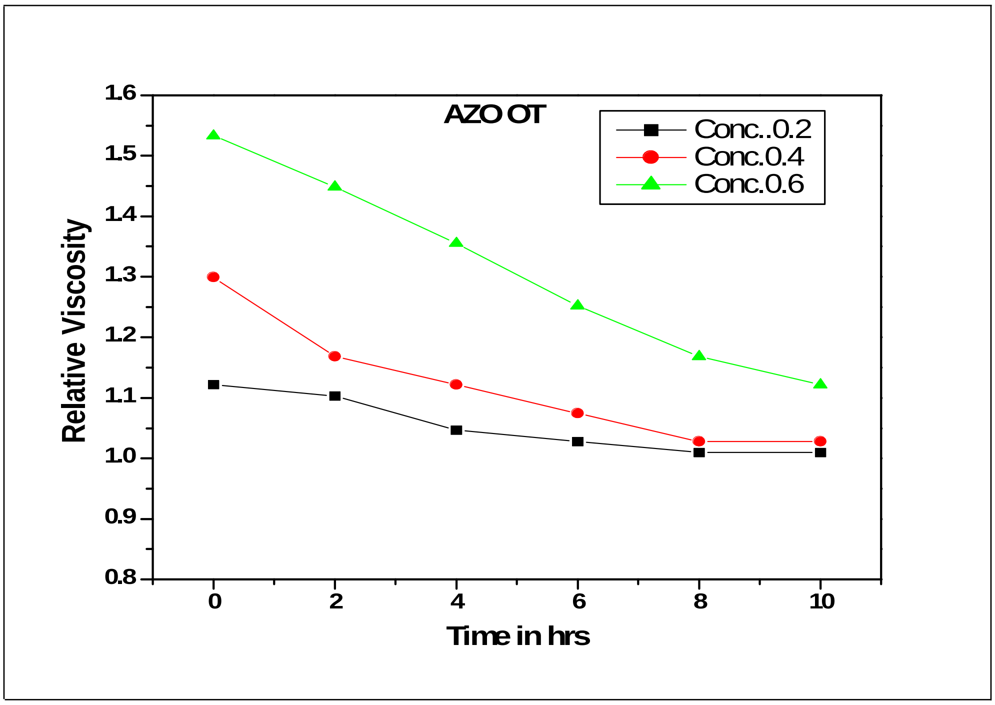
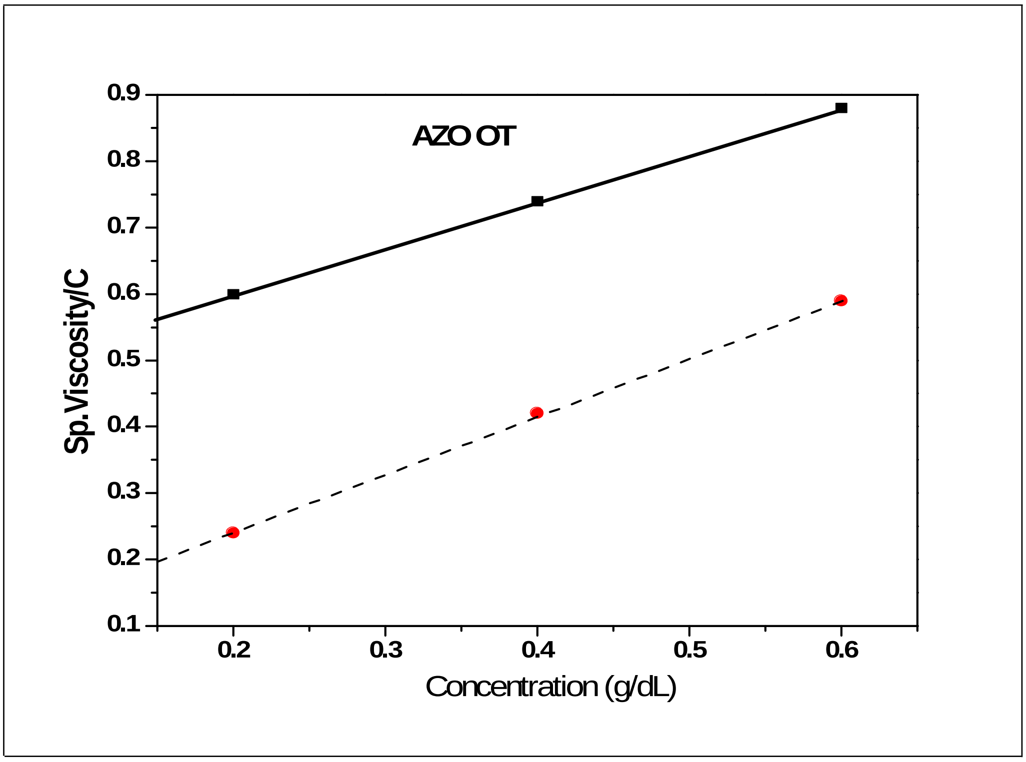


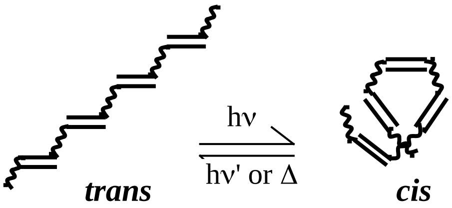
Fig. 4.16 (a) Relative dilute solution viscosity of polymer AZO OT in DMA during irradiation



— before irradiation, ----- after irradiation

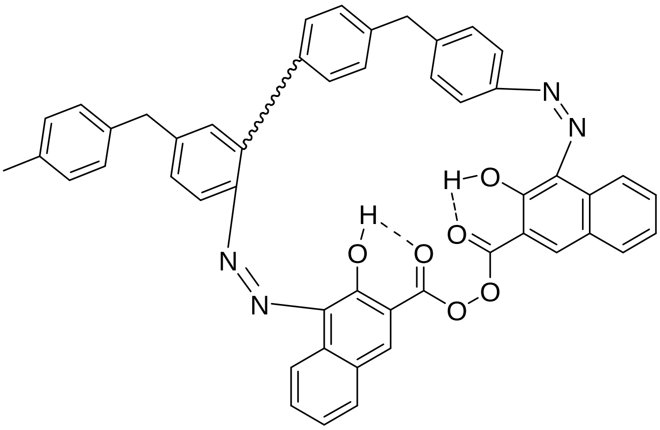
Fig. 4.16 (b) Intrinsic viscosity of polymer AZO OT in DMA

Analogues to the mechanism of reversible photoinduced viscosity changes of polyamides [54] or polyureas[56] and polyesters having azobenzene residues in the main chain and pendant groups,[203] light induced viscosity changes of polyesters with *ortho*-hydroxyazo aromatic group arise from the conformational change of the polymer chain. The polyester chain having *ortho*-hydroxyazo groups acts like a well know photochromic molecule, which may undergo the isomerisation from more thermodynamically stable *trans* to *cis* from during irradiation. The isomerisation from the *trans* to *cis* from during irradiation kinks the extended polymer chain resulting in compact conformation which can be schematically represented in (Scheme 4.1).



Scheme 4.1: Illustration of photoinduced conformational changes of polymer chains in solution

This is justifiable, because the *cis* isomer formed can still be stabilized via intramolecular hydrogen bonding and/by hydrophobic interaction as illustrated in Scheme 4.2.

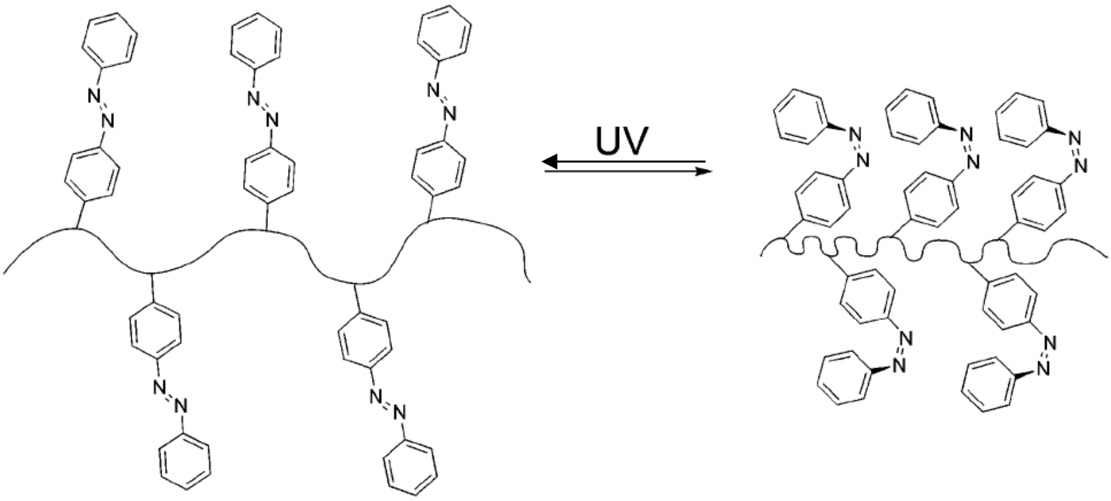


Scheme 4.2: Stabilisation of *cis*-conformation by intramolecular hydrogen bonding

The shrinkage of the extended conformation explains the photodecrease in viscosity, since the compact conformation returns to the original extended form after cutting of the light and keeping the solution in dark, the polymer regains their initial viscosity.

The change in the UV-visible spectra of the polysters during irradiation and the decrease/recovery cycles of the viscosity also supports the above proposition. Among the different *ortho*-hydroxyazo aromatic polyesters under investigation, highest viscosity changes were observed in the case of polymer AZO AP (65%) and AZO OT (66%) which contain stiff aromatic backbone with many photochromic moeties, whereas the other polymers having flexible methylene spacers show comparatively less photoinduced viscosity changes.

The intramolecular dipole-dipole interaction between neighbouring azobenzene chromophores plays a significant role in determining the photoviscosity effect which is another plausible molecular level interpretation. Under UV irradiation in the case of pendant azobenzene side chains unergo *trans* – *cis* isomerization inducing a dipole across the N=N bond. Neighbouring dipoles are believed to orient and attract each other, contracting the polymer backbone and hence decreasing the viscosity.[201] (Scheme 4.3). As the chromophore content increases, the distance between neighbouring chromophores decreases, resulting in more interaction, which could lead to a higher viscosity change as seen in AZO AP and AZO OT (Scheme 4.3).



Scheme 4.3

4.2.3. Photoinduced dilute solution conductivity changes of polymers with *ortho*-hydroxyazo aromatic groups

Photoinduced changes in conformation of polymers result not only to dilute solution viscosity but to other properties like conductivity[110]. Thus, photoinduced conductivity changes were studied using dilute polymer solution of AZO PVA 14-1a in N, N dimethyl acetamide at 28 ^{0}C. Here 0.6 g/ dL solution of AZO PVA 14-1a was irradiated with UV-visible light in a photochemical reactor. Changes in conductivities were recorded at definite intervals of irradiation. An increase in conductivity was the observed result. The conductivity value increased gradually with time of irradiation and it reached a constant value, after 8-10 h of irradiation. The solution regained their original conductivity after 14-16 h, when the irradiation was cut off and kept in dark. Irradiation followed by conductivity changes were measured using dilute solution of different concentration such as 0.4g/dL and 0.2g/dL. In both the dilutions increase in conductivity was observed and the changes were reversible. The result of the conductivity changes is graphically represented in Fig. 4.17. These photoinduced conductivity studies were also extended to other polymers AZO PVA 14-1b, AZO PVA 10-1a, AZO PVA 10-1b, AZO DIOL, AZO DEG, AZO AP, AZO OT and the results of all measurements are graphically shown in Fig. 4.18 – 4.24.

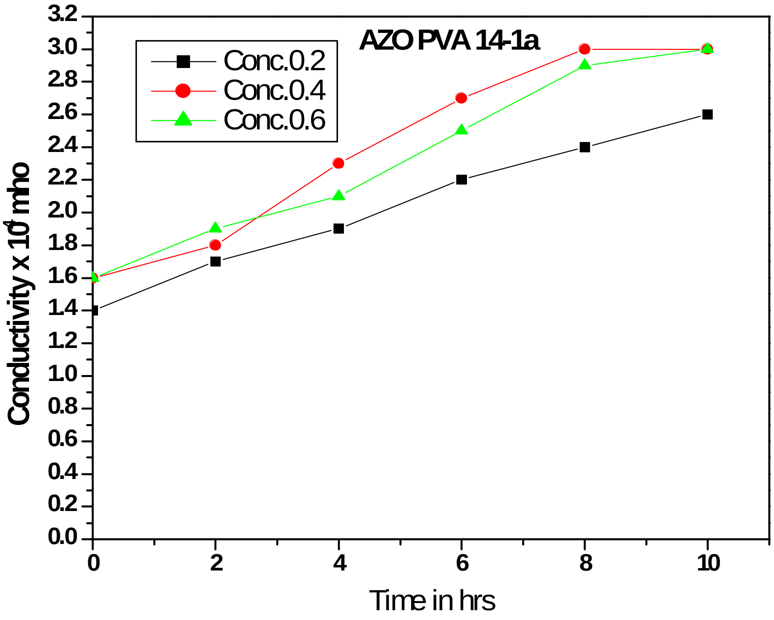


Fig. 4.17 Photoinduced conductivity changes of AZO PVA 14-1a in DMA

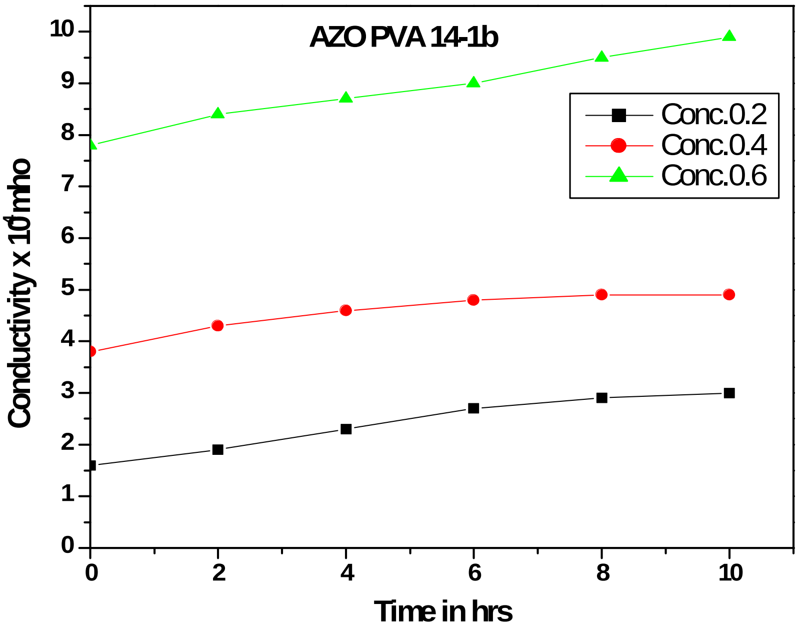


Fig. 4.18 Photoinduced conductivity changes of AZO PVA 14-1b in DMA

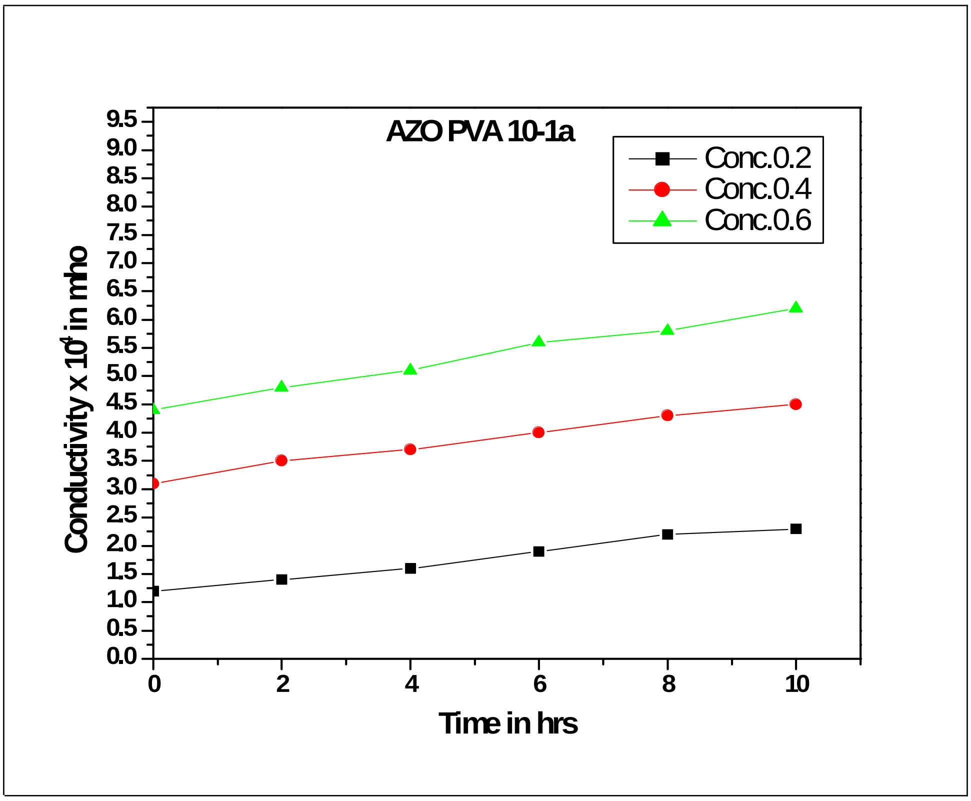


Fig. 4.19 Photoinduced conductivity changes of AZO PVA 10-1a in DMA

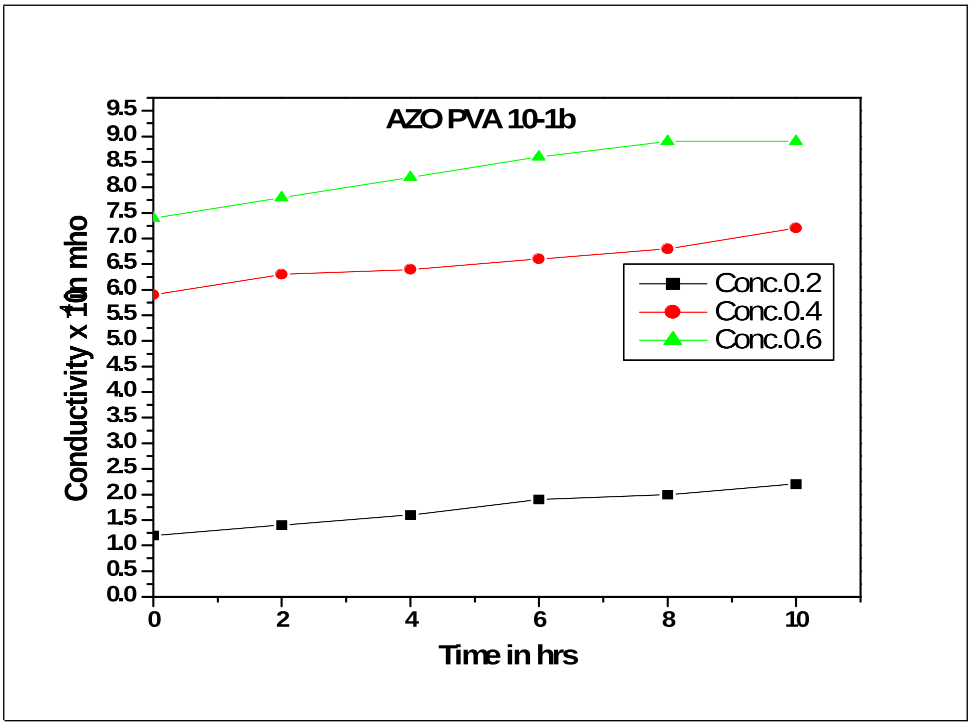


Fig. 4.20 Photoinduced conductivity changes of AZO PVA 10-1b in DMA

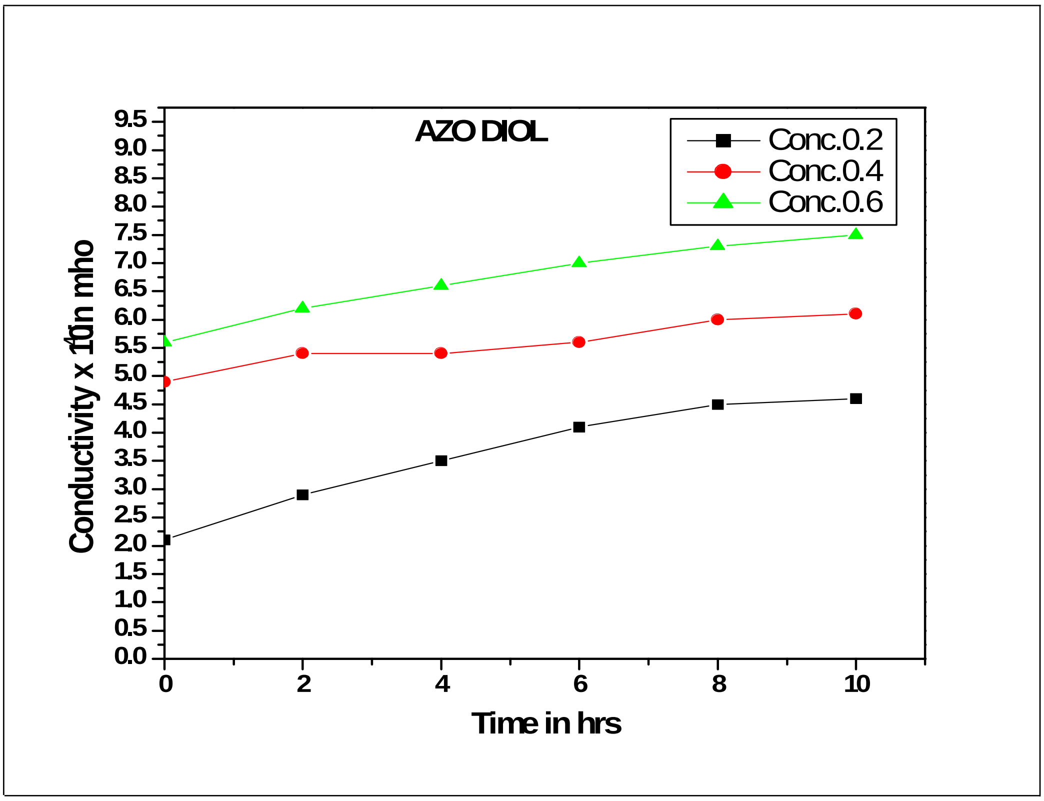


Fig. 4.21 Photoinduced conductivity changes of AZO DIOL in DMA

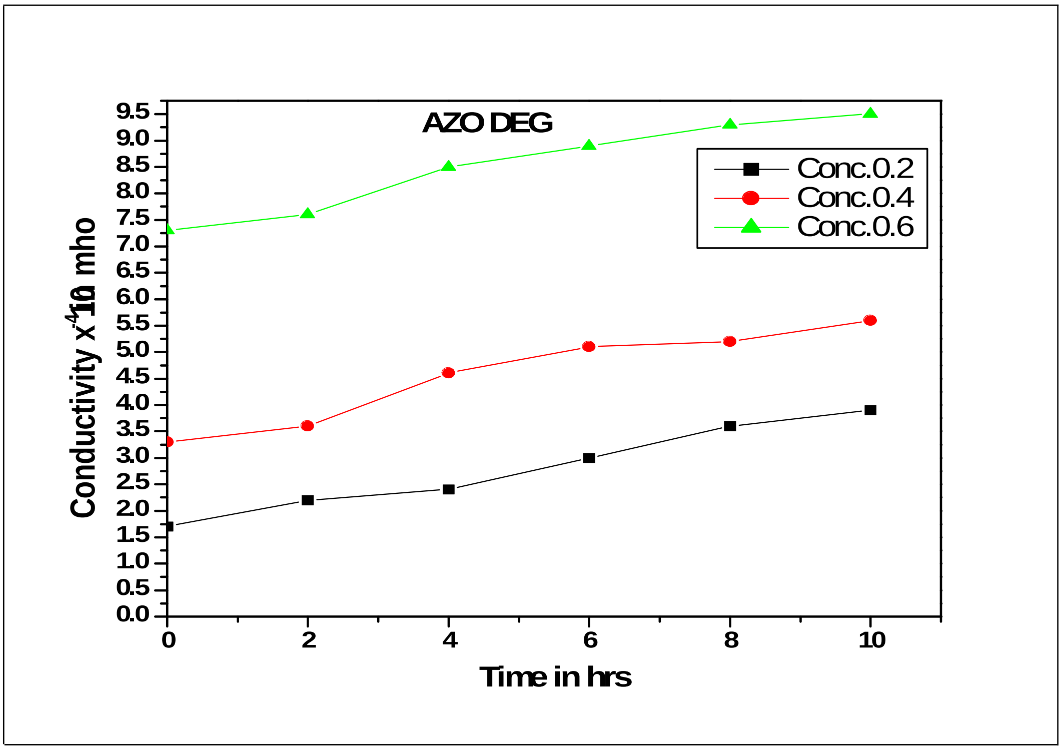


Fig. 4.22 Photoinduced conductivity changes of AZO DEG in DMA

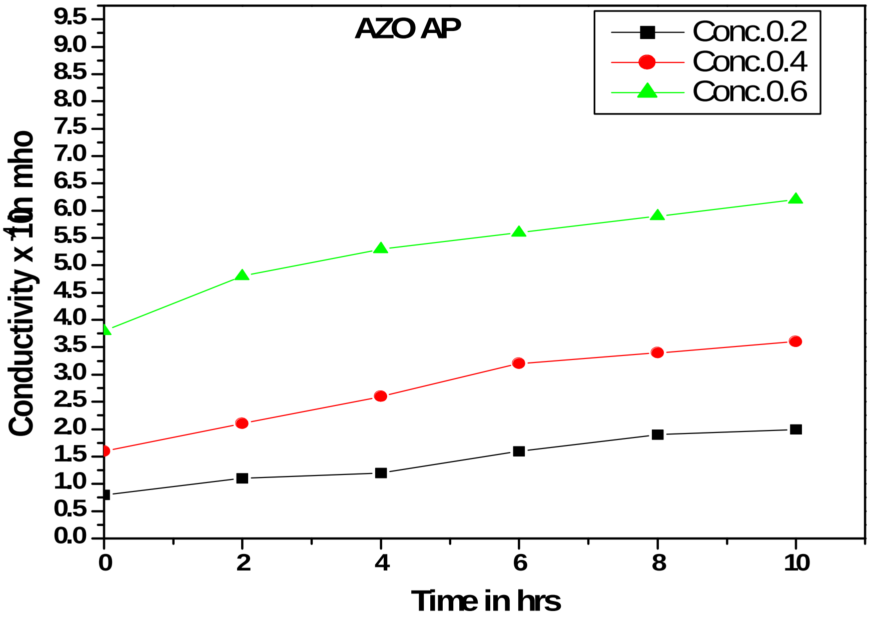


Fig. 4.23 Photoinduced conductivity changes of AZO AP in DMA

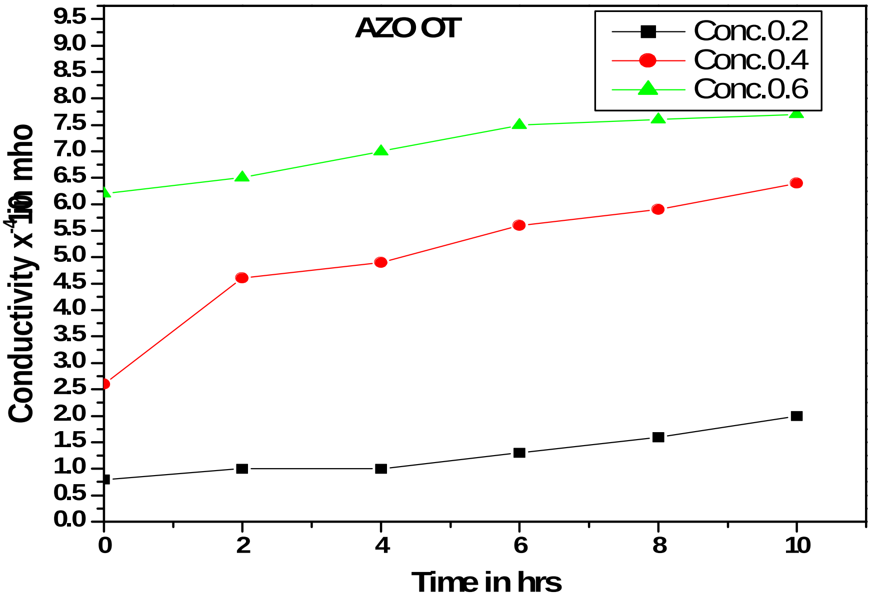


Fig. 4.24 Photoinduced conductivity changes of AZO OT in DMA

The details of the photoeffect on conductivities of the different *ortho*-hydroxyazo aromatic polymers as given in Table. 4.2.

TABLE 4.2

Conductivity changes of *ortho* –hydroxyazo aromatic polymers on irradiation

Sl. No	**Polymers**	**Before irradiation (10^{-4}mho)**	**After irradiation (10^{-4}mho)**	**Increase in conductivity (%)**
1.	AZO PVA 14-1a	1.6	3	46
2.	AZO PVA 14-1b	1.6	3	46
3.	AZO PVA 10-1a	1.2	2.3	48
4.	AZO PVA 10-1b	1.2	2.2	45
5.	AZO DIOL	2.1	4.6	54
6.	AZO DEG	1.7	3.9	56
7.	AZO AP	0.8	2	60
8.	AZO OT	0.8	2	60

The increase in conductivity during irradiation can also be explained in terms of photoisomerisation as envisaged in polyamides and polyesters having azo linkages in the backbone.[54] The dissociation equilibrium of polyesters having *ortho*-hydroxyazo groups is dependent on the change in the conformation of the polymer chain. Here, since only very few carboxylic acid groups are available for dissociation which permits the increase in the conductivity in more compact conformation, the explanation may not be completely based on dissociation of the acid groups. However, the more polar *cis* from in the compact conformation increases the dissociation of the chains, is more suitable explanation. Among the series of polyesters studied, AZO AP (60%) and AZO OT (60%) showed higher conductivity. Almost parallel observation encountered in viscosity changes, is a clear evidence for the isomerisation from *trans* to *cis* form.

SECTION 5

CONDUCTING PROPERTIES OF *ORTHO*-HYDROXYAZO POLYMERS IN SOLID STATE

5.1. INTRODUCTION

Photochromic materials have been attracting great deal of attention because of their potential technological applications in optical recording and for storage devices. Applying photochromic materials to practical applications, they may be used either in the form of solid film or pellet etc. Thus, photochromism in the solid state has become a subject of current interest. Extensive studies have been carried out on photochromism of polymers containing photochromic chromophores and composite polymer systems. Being in great demand as the organic photogenerating pigments, azo compound have been more extensively studied than phthalocyanin and perylene pigments. Therefore, any systematic work on organic photoconduction may find application in molecular electronic devices, where the phenomena of photoconductivity, charge generation and charge transport etc. are utilised.

Carlson's early invention of the organic photoconductors and their application to electrography have led to research in organic photoconductive materials as an active area. It was found that azo pigments derived from 2-naphthol exhibited moderate/good photoconductivity. The well known *ortho*hydroxyazo to ketohydrazone tautomerism both in solution and in solid state[24,25] is the reason attributed to the photoconducting behaviour. Moreover, the dilute solution conductivity of polymers having *ortho*-hydroxyazo groups in the polymeric backbone and also as pendant groups have been found to exhibit an increase in trend as a result of irradiation and that too reversible. Therefore, it is only appropriate to investigate the solid state conductivity of the synthesised polymers having *ortho*-hydroxyazo goups in the polymers, under irradiation conditions. Thus the present section describes the study of the conductivity changes of the synthesised polymers having *ortho*-hydroxyazo groups during UV irradiation.

5.2. RESULTS AND DISCUSSION

5.2.1. Solid state photoconductivity of *ortho*-hydroxyazo polymers as pellets on UV irradiation

Ortho-hydroxyazo polymers are practically insoluble in common organic solvents. In order to investigate the solid state conductivity, polymers were made into pellets approximately 10 mm in diameter and 1-2 mm thickness. The dimensional characteristics of pellets of different *ortho*-hydroxyazo polymers used for the solid state conductivity are given in Table 5.1. The whole experimental set up was irradiated using UV light, provided with cooling arrangements to prevent any increase in temperature during irradiation. Conductivity of AZO PVA 14-1a pellet was measured at definite intervals of time in minutes. It was observed that an increase in conductivity during irradiation and reached a constant value at about 30 minutes of irradiation. The original conductivity was regained after keeping it for some time in the dark. Increase in conductivity was plotted against time of irradiation and is represented in Fig. 5.1 . Similar solid state conductivity measurements were also carried out using AZO PVA 14-1b, AZO PVA 10-1a, AZO PVA 10-1b, AZO DIOL, AZO DEG, AZO AP and AZO OT. Graph of the conductivity changes show that the increase in conductivity is very feeble. However, the increasing conductivity of AZO AP and AZO OT are comparable (Fig. 5 .1 -5.4).

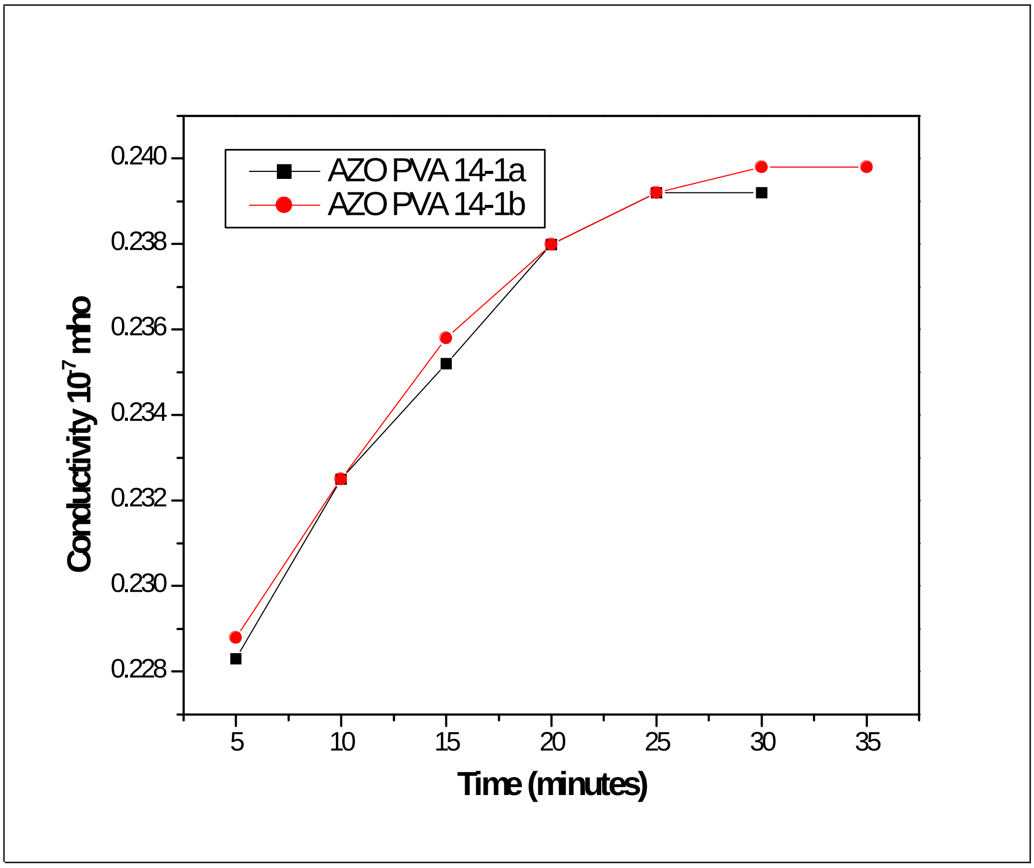


Fig. 5.1 Solid state conductivity of AZO PVA 14-1a and AZO PVA 14-1b

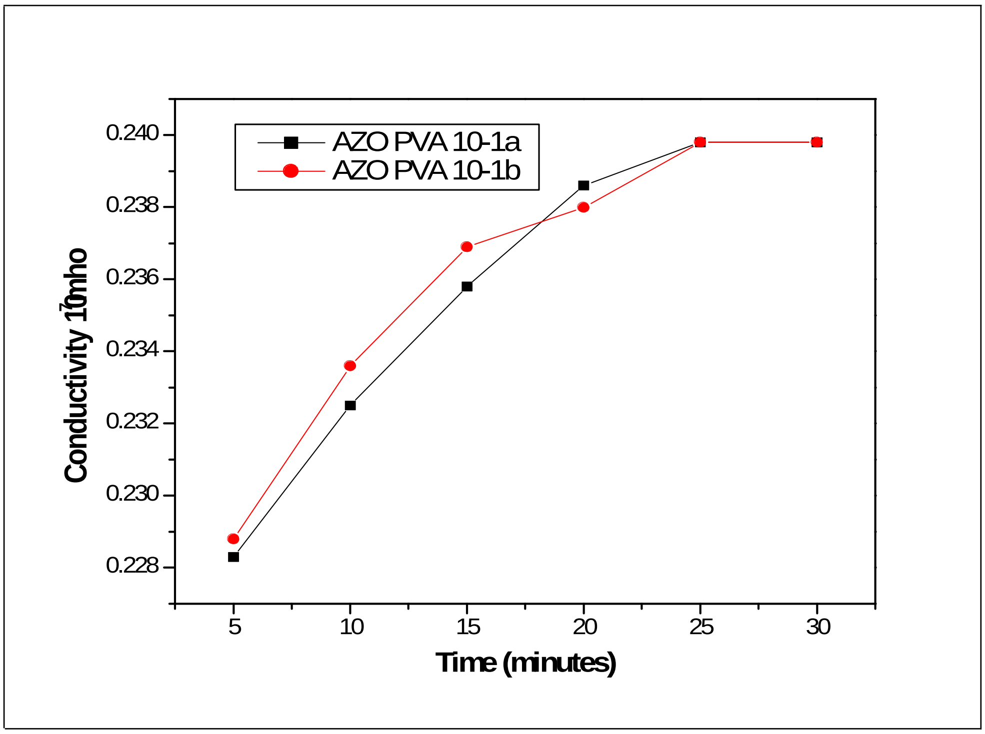


Fig. 5.2 Solid state conductivity of AZO PVA 10-1a and AZO PVA 10-1b

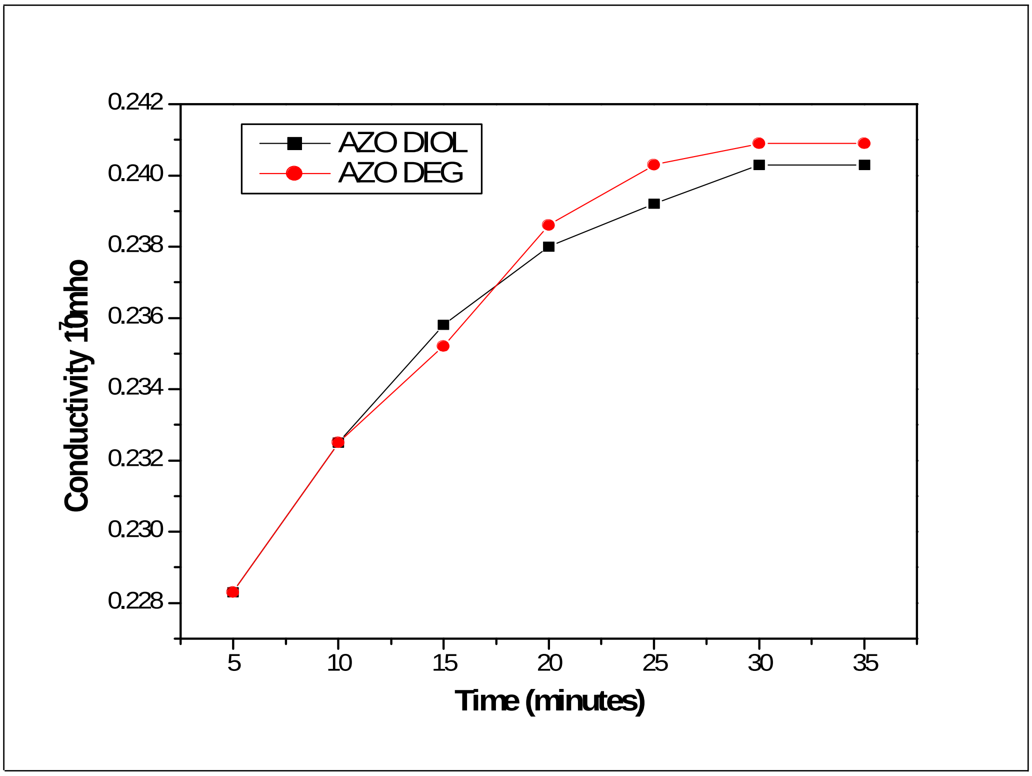


Fig.5.3 Solid state conductivity of AZO DIOL and AZO DEG

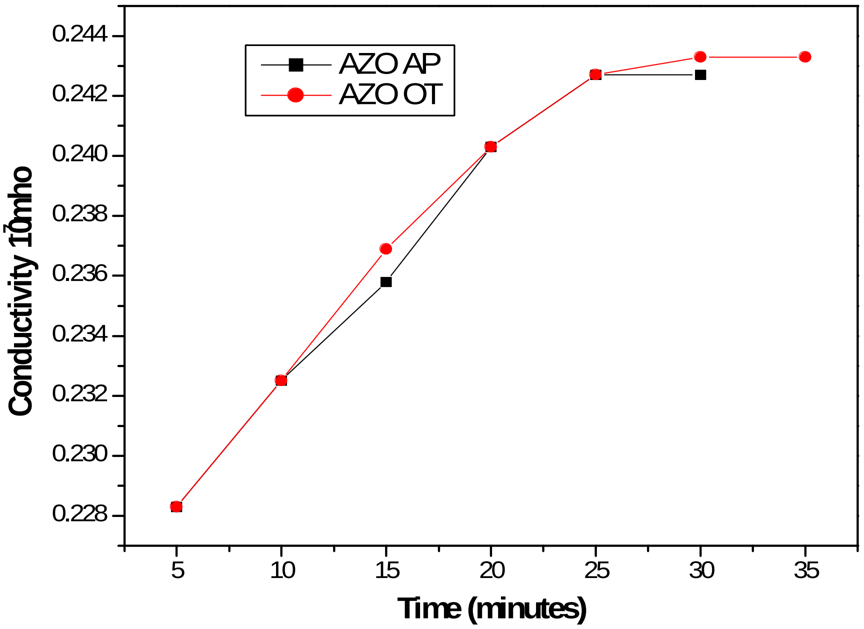


Fig. 5.4 Solid state conductivity of AZO APand AZO OT

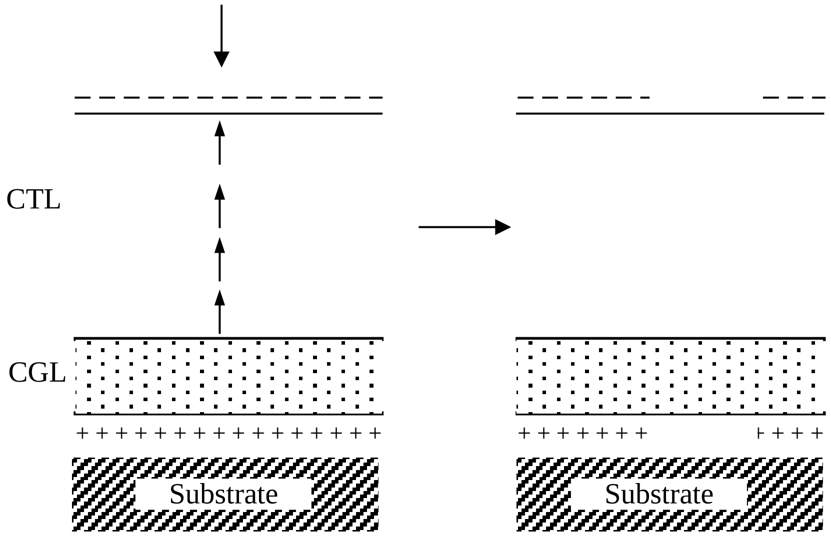
TABLE 5.1

Dimensional characteristics of *ortho*-hydroxyazo
aromatic polymer pellets used for UV irradiation conditions

Sl. No.	Polymer	Diameter (mm)	Thickness (mm)
1.	AZO PVA 14-1a	10.01	1.19
2.	AZO PVA 14-1b	10.04	1.63
3.	AZO PVA 10-1a	10.02	2.01
4.	AZO PVA 10-1b	10.01	1.42
5.	AZO DIOL	9.92	1.04
6.	AZO DEG	10.00	1.73
7.	AZO AP	10.05	1.00
8.	AZO OT	10.00	1.13

5.2.2. Mechanism of photoconductivity in the solid state of *ortho*-hydroxyazo aromatic polymers

The photoconductivity associated with *ortho*-hydroxyazo polymers may be attributed to the well illustrated hydroxyazo ketohydrazone in solids[204] and the substitutent in the anilde ring has no effect on the hydroxyazo to ketohydrazone tautomerism. Moreover, the absorption wave length is not sensitive to the structure of aromatic amine or the number of azo linkages. Considering these aspects, mechanism of solid state photoconduction in the above mentioned *ortho*-hydroxyazo groups containing polymers may be the charge generation from the ketohydrazone moiety followed by the charge transport through the e-h pair formation at the CGL/CLT interface[29], analogues to the photoconductivity behaviour of bisazo compound, 1,3,4-oxadiazole[49] as shown in Scheme 5.1.



Scheme 5.1: Diagrammatic representation of photoconductivity
CGL – Charge Generating Layer; CTL – Charge Transporting Layer

The conductivity of *ortho*-hydroxyazo polymers with increase in UV irradiatiion can be explained on the basis of excitation of valence electrons into the conduction band. From the observed results on photoconductivity of *ortho*-hydroxyazo polymers, it can be seen that only a feeble increase is noticed (on average 4-6%). This increase in conductivity is not so much significant. This points to the existence of very small percentage of ketohydrazone tautomer in the solid state of polymers, unlike azo pigments which have been found to exist a ketohydrazone in the predominant form. Alternatively, *ortho*-hydroxyazo form may be dominant both in solid and solution state. The predominance of azo form in solution which manifests in configuration and conformation and consequent photoinduced physical property changes like viscosity and conductivity has already been described in section 4.2.2 and 4.2.3.

SECTION 6

EXPERIMENTAL

6.1. GENERAL

The dihydroxy compounds used for polymer synthesis 1,3-propanediol, diethylene glycol, polyvinyl alcohol M.W. 10000, 14000 etc were synthetic grade chemicals (E. Merck, and Sigma Aldrich). Diphenyl methane, 2-hydroxy-3-carboxynaphathalene, *o*-tolidine, *p*-aminophenol were synthetic grade samples. Solvents used acetone, chloroform, N,N-dimethyl acetamide, N,N-dimethyl formamide were synthetically pure and further purified by double distillation.

Irradiation were carried out with a Philips 125W High Pressure Mercury vapour lamp in a quartz photochemical reactor of 500 mL and 250 mL capacity. The lamp was surrounded by a jacket containing the solution to be irradiated. Dilute solution viscosity measurements were performed at 28 ^{0}C with AVS 400 automatic viscometer with glass panelled thermostatic water bath. Conductivity measurements were done using a digital conductivity meter CE-M-890E and a conductivity cell. TG and DTA studies were conducted using STA 409 PC, NETZSCH. NMR Spectra were recorded using Brucker 300 MHz and 500 MHz instrument. IR spectra were recorded using Jasco FTIR spectrophotometer using KBr pellets.

DSC measurements were carried out using DSC.Q.100-3.5 build 175. XRD measurements of the polymer in the powdered form were conducted using Brucker – AXS, D-5005, W. Germany, SEM analysis was done with JEOL model JSM – 6390 instrument.

6.2. SYNTHESIS OF 4,4´-AZO*BIS*PHENYLMETHANE DI (2-HYDROXY -3-CARBOXY NAPHTHALENE)

This was carried out by the general tetrazotisation and coupling method. In a typical procedure cold concentrated hydrochloric acid (16 mL) was added to a stirred solution of, 4,4´–diaminodiphenylmethane in water (3.96 g, 0.02 mol), while cooling. A solution of sodium nitrite (2.76 g, 0.04 mol) was added to it. The presence of free nitrous acid was tested with potassium iodide and starch paper after 30 minutes. This was added to an ice cold solution of 3-carboxy-2-naphthol (7.5 g, 0.04 mol) in sodium hydroxide solution (5.6 g, 0.14 moles) over a period of 45 minutes. The mixture was continuously stirred for 90 minutes and the resulting suspension was acidified with dilute sulphuric acid. The product obtained was separated by filtration. Dried and recrystallised from freshly distilled chloroform to afford dark violet powder of 4,4´-azo*bis*phenylmethane di (2-hydroxy-3-carboxy naphthalene). Yield: 12 g (85%) mp. 210 ^{0}C. ^{1}H NMR in $CDCl_3$ (Fig 6.1).

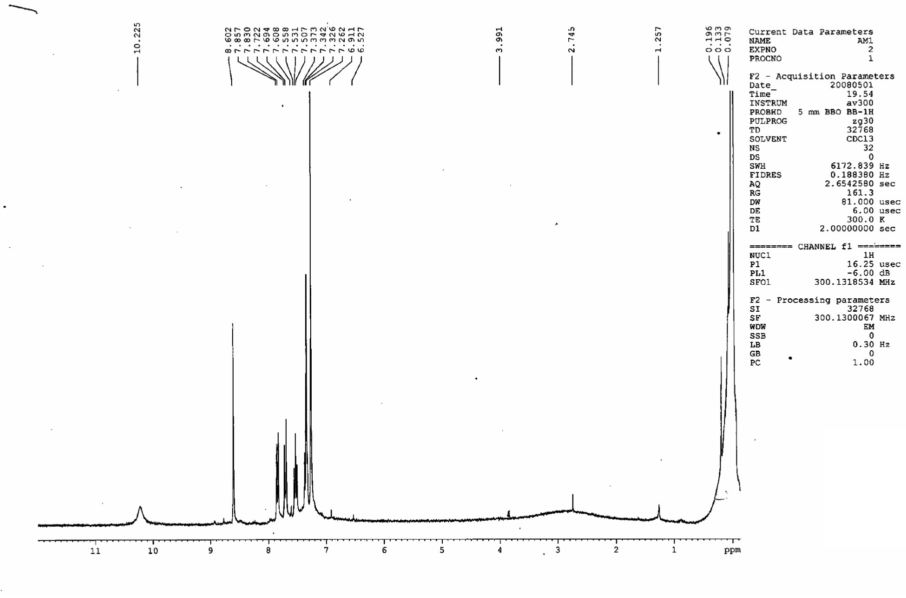


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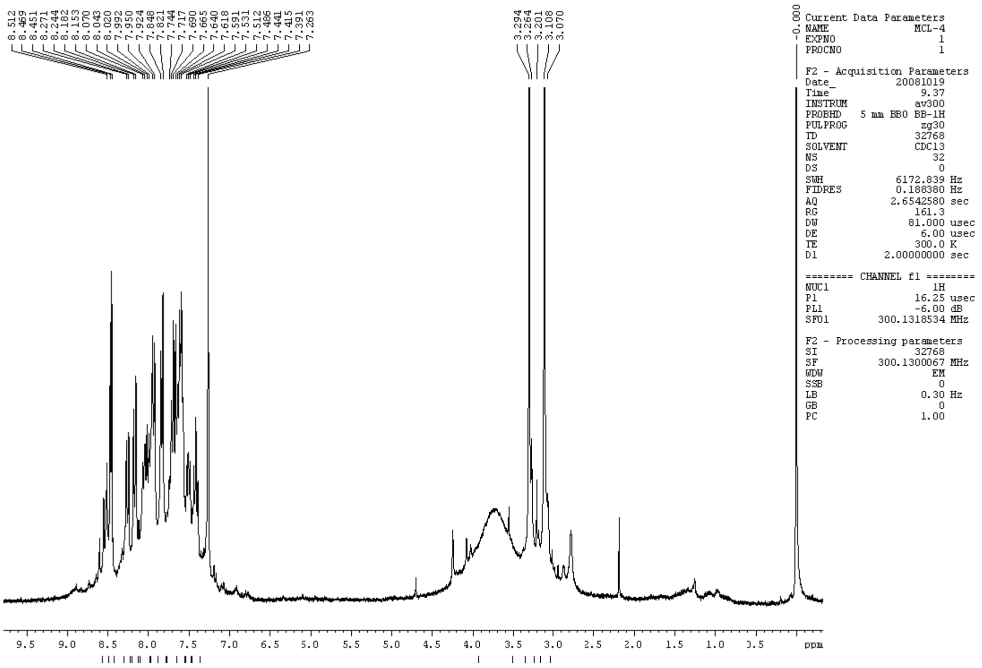
Fig. 6.1 ^{1}H NMR Spectrum of 3 in $CDCl_3$

6.3. SYNTHESIS OF 4,4′AZO*BIS*PHENYLMETHANE DI (2 HYDROXY-3- NAPHTHOYL CHLORIDE)

A mixture of thionyl chloride (30 mL) and, 4,4′-azo*bis*phenylmethane di (2-hydroxy–3-naphthoic acid) (2.5 g) was taken in a 250 mL R.B flask and refluxed for 3 h in presence of a few drops of DMF as catalyst. Excess of thionyl chloride was removed by distillation under reduced pressure. The residue obtained was extracted with freshly distilled chloroform, filtered and the filtrate concentrated by distillation. Traces of solvent was further removed by keeping it overnight, 4,4′–azo*bis*phenylmethane di (2-hydroxy-3-

naphthoyl chloride) (**4)** was obtained as reddish brown powder. Yield: 2 g (80 %) mp. 262 ^{0}C. Fig. 6.2. presents ^{1}H NMR spectrum of **4** in CDCl$_3$.



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PC                   1.00
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Fig. 6.2 ^{1}H NMR spectrum of 4 in CDCl$_3$.

6.4. PHOTO STIMULATED PROPERTY CHANGES OF AZO PVA 14-1a

6.4.1. Synthesis of AZO PVA-14 1a

Interfacial polycondemation method was adopted for the synthesis of polyester from polyvinyl alcohol (MW. 14000) and azo dicarbonyl chloride. In a typical procedure, PVA (0.96 g, 3 mmol) dissolved in water was stirred with 10% aqueous solution NaOH (30 mL) in presence of sodium sulphate. Azo dicarbonyl chloride (1.9 g, 3 mmol) dissolved in a mixture of chloroform and DMF (9:1, v/v) was then added to the solution of polyvinyl alcohol and stirred for 90 minutes in an atmosphere of nitrogen. The polymerised emulsion mixture was transferred into a separating funnel. The product washed several times with freshly distilled chloroform to remove impurities. The purified product was added to excess of freshly distilled acetone for coagulation and kept overnight to settle down. Filtered and the residue was allowed to dry in air. The product obtained washed with water and neutralised by adding a few drops of dil. HCl. The regenerated product was filtered, washed with distilled water and very dilute solution of DMSO. Dried in air oven to afford reddish brown crystals of polyester AZO PVA 14- 1a. Yield: 1g (36%) mp >300^{0}C, UV λmax (DMA): 296 nm, 372 nm, 468 nm; IR (KBr) spectrum of AZO PVA 14-1a is presented in Fig 6.3

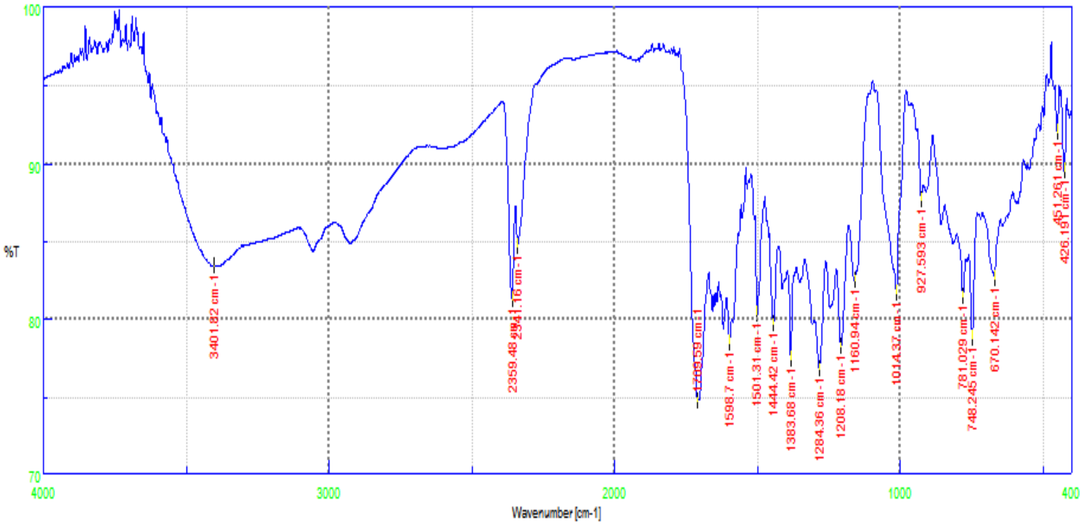

Fig. 6.3 IR (KBr) Spectrum of AZO PVA 14-1a

6.4.2. Photoinduced viscosity changes of AZO PVA 14-1a

A dilute solution of polymer AZO PVA 14-1a (0.2g/dL) in dimethyl acetamide was prepared by stirring it for 24 h. The intense reddish brown solution (300mL) was irradiated in a photochemical reactor with 125 W high pressure mercury arc lamp. The viscosity measurements was taken at definite intervals of irradiation time. After 10 h of irradiation the viscosity reached a constant value. The irradiated solution was kept under dark for 15 h to follow reversibility Irradiation followed by viscosity measurements and its reversibility was repeated with solutions of different concentration, 0.4g/dL, 0.6g/dL.

A graph was plotted with relative viscosity against time. In all three concentrations, the relative viscosity was found to decrease till it reached a constant value at 10 h. After 10 h of irradiation, the viscosity remained constant (Fig 4.9a). The intrinsic viscosities before and after irradiation were plotted against different concentration. It was found that there was 34% decrease in intrinsic viscosity after irradiation (Fig 4.9b)

6.4.3. Photoinduced conductivity changes of AZO PVA 14-1a

A dilute solution (0.2g/dL) of the polymer AZO PVA 14-1a in dimethyl acetamide was irradiated in a photochemical reactor with high pressure mercury quartz lamp and the lamp was surrounded with an external water jacket for cooling. The conductivity measurements were carried out at definite intervals of time of irradiation. It was found that the conductivities increased and reached a maximum at 10 h and remained constant. When the solution was kept under dark for 16 h, reversibility of the conductivity was observed.

Irradiation and conductivity measurements were repeated for other solutions of concentration 0.4g/dL, 0.6g/dL etc. The results of conductivity changes was plotted against time of irradiation (Fig 4.17). In all the three concentration, increase in conductivities (46%) and reversibility after cutting of the light was observed.

6.5. PHOTOSTIMULATED PROPERTY CHANGES OF AZO PVA 14-1b

6.5.1. Synthesis of AZO PVA 14-1b

Interfacial polycondensation method was followed for the synthesis of polymer AZO PVA-14-1b. Polyvinyl alcohol (MW 14000) (0.64g, 2m mol) dissolved in water was stirred with 10% aqueous sodium hydroxide (30 mL) in presence of sodium sulphate. Azo dicarbonyl chloride (0.64g, 1mmol) dissolved in freshly distilled chloroform DMF mixture (9:1, v/v) was then added to the solution of PVA and stirred for 90 minutes in an atmosphere of nitrogen. The polymerised emulsion mixture was then transferred into a separating funnel. The product was washed several times with freshly distilled $CHCl_3$ to remove all impurities. The purified product was added to freshly distilled acetone (excess) for coagulation and kept overnight to settle down. Filtered the residue and was allowed to dry in air. The product obtained was dissolved in water and neutralised by adding a few drops of dil. hydrochloric acid. The regenerated product was filtered, washed with distilled water, dried in air to afford reddish brown polyester AZO PVA 14-1b. Yield: 0.5g (40%) mp. >300^{0}C, UV λmax (DMA): 296 nm, 372 nm, 468 nm; IR (KBr) spectrum of AZO PVA 14-1b is presented in Fig 6. 4.

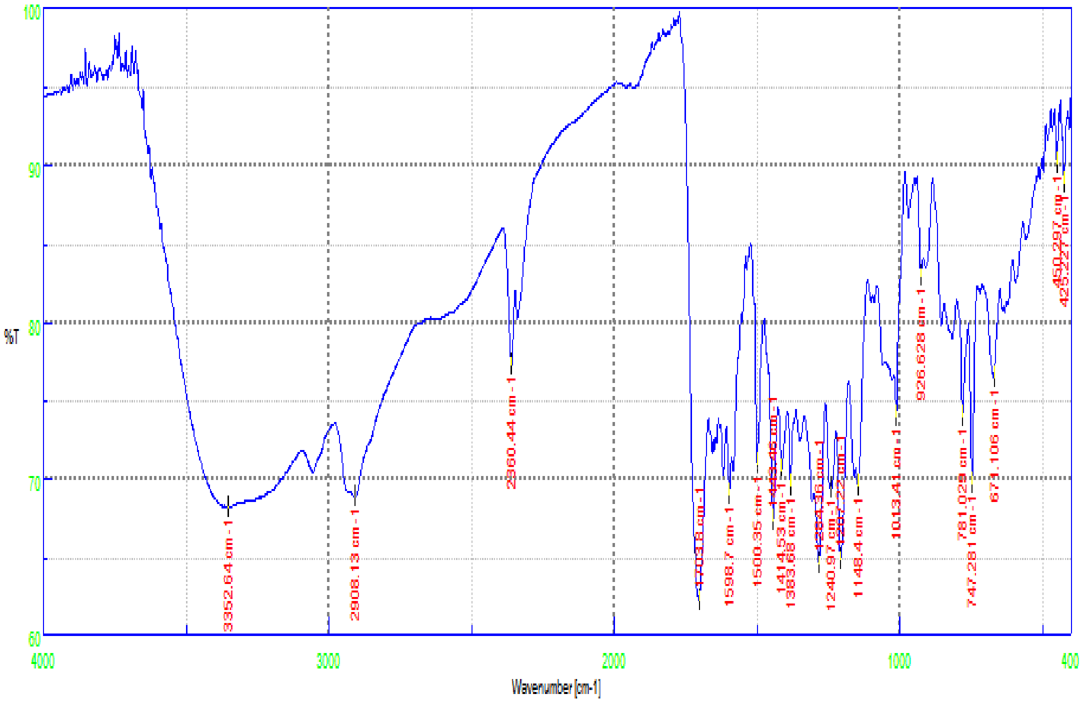

Fig 6.4 IR (KBr) Spectrum of AZO PVA 14-1b

6.5.2. Photoinduced viscosity changes of AZO PVA 14-1b

A dilute solution of AZO PVA 14-1b (0.2g /dL) in DMA was prepared by stirring for about 24 h. 300 mL of the reddish brown solution was irradiated in photochemical reactor. Viscosity measurements were done at definite intervals of time of irradiation (2,4,6,8 and10 h) till it reaches a constant value. The irradiated solutions was kept under dark for 15 h to follow reversibility. Irradiation followed by viscosity measurements and its reversibility were repeated with solution of different concentration (0.4g/dL, 0.6g/dL). From the time of flow, specific viscosities (η_{sp}) were calculated. η_{sp}/C values were plotted against concentrations (Fig 4.10b). The intrinsic viscosity of the solution before and after irradiation were computed and the percentage decrease in intrinsic viscosity of the polymer on photoirradiation was calculated. A 34% decrease in intrinsic viscosity was observed (Fig 4.10b).

6.5.3. Photoinduced conductivity changes of AZOPVA 14-1b

A dilute solution of the polymer AZO PVA 14-1b (0.2g/dL) was prepared in dimethyl acetamide by stirring it for 24 h. 300mL of the solution was irradiated using a UV-visible light in a photochemical reactor. At definite intervals of time (2,4,6,8 and 10 h)conductivities were measured. The change in conductivity against time of irradiation was plotted. It was found that conductivity increases up to 10 h. of irradiation and then remained constant. When the solution was kept in the dark for 16 h, the conductivity regained its initial value. The irradiations followed by conductivity measurements were repeated for solution of other concentrations 0.4g/dL. 0.6g/dL. In all the three concentrations, an increases in conductivities (46%) and reversibilities after cutting of the light was observed. (Fig 4.18)

6.6. PHOTOSTIMULATED PROPERTY CHANGES OF AZO PVA 10-1a AND AZO PVA 10-1b

6.6.1. Synthesis of AZO PVA 10-1a

Interfacial polycondensation method was followed for the synthesis of polymer AZO PVA 10-a. In a typical procedure, polyvinyl alcohol (MW.10000) 0 .47g (2 mmol) dissolved in water was stirred with 10% NaOH (20mL) in presence of sodium sulphate. Azo carbonyl chloride (1.27g, 2 mmol) dissolved in freshly distilled chloroform and DMF (9:1, v/v) was than added to the solution of the above PVA and stirred for 90 minutes in an atmosphere of nitrogen. The polymerised emulsion mixture was transferred into a separating funnel. The product was washed several times with freshly distilled chloroform to remove all the impurities. The purified product was added to freshly distilled acetone (in excess) for coagulation and kept overnight to settle down. The product was filtered and the residue allowed to dry in air. This was further dissolved in water and neutralised by adding a few drops of dil.HCl. The regenerated product was filtered, washed repeatedly with distilled water and very dilute solution of DMSO. Dried in air to afford the reddish brown polymer AZO PVA 10-1a. Yield: 0.7g (40%) mp. > 300 ^{0}C. UV λmax (DMA): 272 nm, 370 nm, 486 nm; IR (KBr) spectrum of AZO PVA 10-1a is presented in Fig 6.5

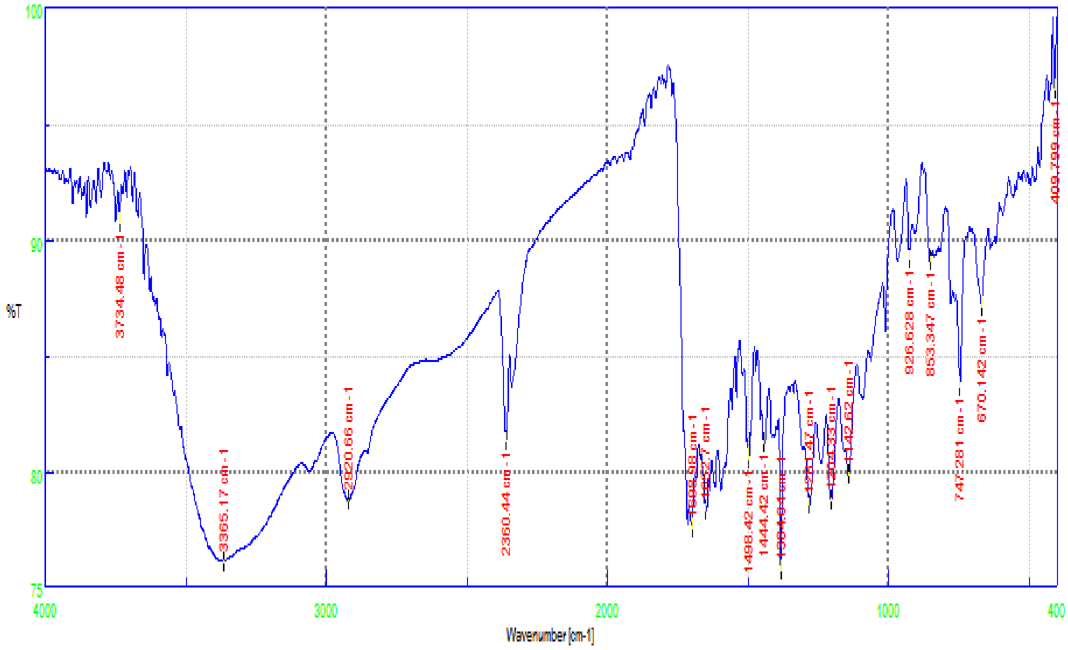

Fig 6.5 IR (KBr) Spectrum of AZO PVA 10-1a

6.6.2. Synthesis of AZO PVA 10-1b

The synthesis of polymer AZO PVA 10-1b was carried out by interfacial polycondensation method. Here PVA (MW.10000\) (0.47g, 2 mmol) dissolved in water was stirred with aqueous solution of 10% sodium hydroxide (20mL) in presence of sodium sulphate. Azo carbonyl chloride (0.65g, 1mmol) dissolved in a mixture of DMF and freshly distilled chloroform (1:9, v/v) was quickly added to a solution of PVA and stirred for 60 minutes in an atmosphere of nitrogen. The polymerised emulsion was transferred into a separating funnel. The product was washed several times with chloroform to remove impurities. The purified product was added to excess of freshly distilled acetone for coagulation and kept overnight to settle down. The product was filtered and the residue allowed to dry in air. This was then dissolved in water and neutralised by adding a few drops of dil. HCl. The regenerated product was further washed with water, dried in air to afford the reddish brown powder AZO PVA10-1b. Yield: 0.55g (51%), mp. > 300 ^{0}C, UV λmax (DMA): 270 nm, 374 nm, 482 nm; IR (KBr) spectrum of AZO PVA 10 -1b is presented in Fig 6.6.

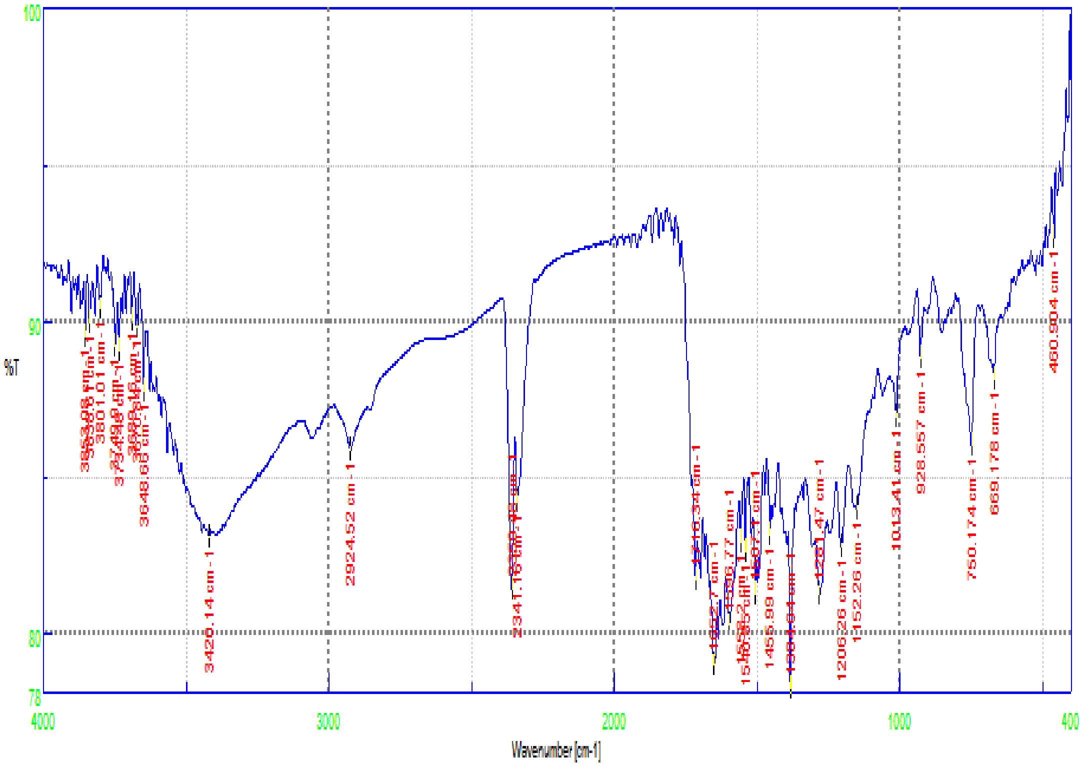

Fig. 6.6 IR (KBr) Spectrum of AZO PVA 10-1b

6.6.3. Photoinduced viscosity changes of AZO PVA 10-1a and AZO PVA 10-1b

A dilute solution (0.2g/dL) of the polymer (AZO PVA 10-1a or AZO PVA 10-1b) was prepared in freshly distilled dimethyl acetamide . About 300 mL of this solution was irradiated with a UV–visible light in a photochemical reactor. The viscosities were measured at definite intervals of time, till a constant value was reached. The viscosity of the solution was again measured after cutting off the light for 16 h. The viscosity measurements were repeated for different solutions of concentrations 0.4g/dL and 0.6g/dL etc. The values of viscosities were plotted against concentrations. From the graph, the decrease in intrinsic viscosity was calculated. Decrease in intrinsic viscosity was observed for both polymers (Fig 4.11b and 4.12b). The intrinsic viscosity changes of AZO PVA polymers are given in Table 6.1

TABLE 6.1

Intrinsic viscosity changes of AZO PVA polymers

Polymer	**Concentration (g/dL)**	**Intrinsic viscosity (η)**	
		Before irradiation	**After irradiation**
AZO PVA 14 -1a	0.2	0.3201	0.2184
	0.4	0.4195	0.3038
	0.6	0.4876	0.4022
AZO PVA 14-1b	0.2	0.2808	0.1860
	0.4	0.3319	0.2485
	0.6	0.3888	0.3094
AZO PVA 10-1a	0.2	0.3229	0.2269
	0.4	0.4189	0.2988
	0.6	0.4790	0.3671
AZO PVA 10-1b	0.2	0.2791	0.1834
	0.4	0.3333	0.2172
	0.6	0.3807	0.2637

6.6.4. Photoinduced conductivity changes of AZO PVA 10-1a and AZO PVA 10-1b

A dilute solution of the polymer AZO PVA 10-1a or AZO PVA 10-1b (0.2g/dL) was prepared in dimethyl acetamide by stirring it for 24 h. 300mL of the solution was irradiated using a UV-visible light in a photochemical reactor. Conductivities were measured at definite intervals of time (2,4,6,8, 10 h) of irradiation. The change in conductivity against time of irradiation was plotted. It was found that conductivity increase up to 10 h. of irradiation and then remained constant. When the solution was kept in the dark for 16 h, the conductivity regained its initial value. The irradiation followed by conductivity measurements were repeated for other solution of concentrations 0.4g/dL and 0.6g/dL. The result obtained was similar to that of 0.2 g/dL concentration. The conductivity changes of AZO PVA polymers on UV irradiation are given in Table 6.2

TABLE 6.2

Conductivity changes of AZO PVA polymers on UV irradiation

Polymer	**Concentration (g/dL)**	**Conductivity (10^{-4} mho) *vs* Time of irradiation (h)**					
		0	2	4	6	8	10
AZO PVA 14-1a	0.2	1.40	1.71	1.9	2.2	2.39	2.6
	0.4	1.6	1.8	2.3	2.7	3.0	3.0
	0.6	1.6	1.91	2.09	2.46	2.9	3.0
AZO PVA 14-1b	0.2	1.6	1.89	2.33	2.66	2.91	3.0
	0.4	3.83	4.29	4.57	4.79	4.88	4.88
	0.6	7.78	8.39	8.76	8.98	9.5	9.86
AZO PVA 10-1a	0.2	1.2	1.41	1.6	1.9	2.21	2.3
	0.4	3.09	3.5	3.73	4.01	4.30	4.50
	0.6	4.38	4.79	5.07	5.58	5.79	6.17
AZO PVA 10-1b	0.2	1.2	1.41	1.6	1.86	1.98	2.2
	0.4	5.91	6.28	6.41	6.59	6.76	7.20
	0.6	7.39	7.79	8.16	8.54	8.88	8.90

6.7. PHOTOSTIMULATED PROPERTY CHANGES OF AZO DIOL AND AZO DEG

6.7.1. Synthesis of AZODIOL

Interfacial poly condensation method was adopted for the synthesis of polyester from 1,3-propanediol and azo*bis*phenylmethane di (2-hydroxy-3-naphthoyl chloride). Azodicarbonyl chloride (1.9 g, 3 mmol) was dissolved in a mixture of DMF and freshly distilled chloroform (1:10 v/v). This was quickly added to an alkaline solution (10mL, 0.01N NaOH) of 1,3 diol (22 μL, 3 mmol) and stirred for 60 minutes in an atmosphere of nitrogen. The emulsified reaction mixture was transferred to a separating funnel and washed several times with freshly distilled chloroform to remove impurities. The purified emulsified mixture was then added to freshly distilled acetone (in excess) for coagulation. The coagulated polymer was settled by keeping overnight and the supernatant liquid was decanted. The product was allowed to dry in air. The powdered mass was further dissolved in minimum quantity of distilled water. The slightly alkaline solution was neutralized with a few drops of dilute HCl, so as to regenerate the polymer. Filtered, washed several times with distilled water and kept overnight to obtain rose red powder of polymer AZO DIOL. Yield: 1 g (47%) mp. >300 ^{0}C. The polymer obtained was insoluble in water, chloroform, methylene chloride etc, but soluble in DMA and DMSO UV λmax (DMA): 270 nm, 356 nm, 462 nm; The IR (KBr) Spectrum of AZO DIOL is presented in Fig 6.7.

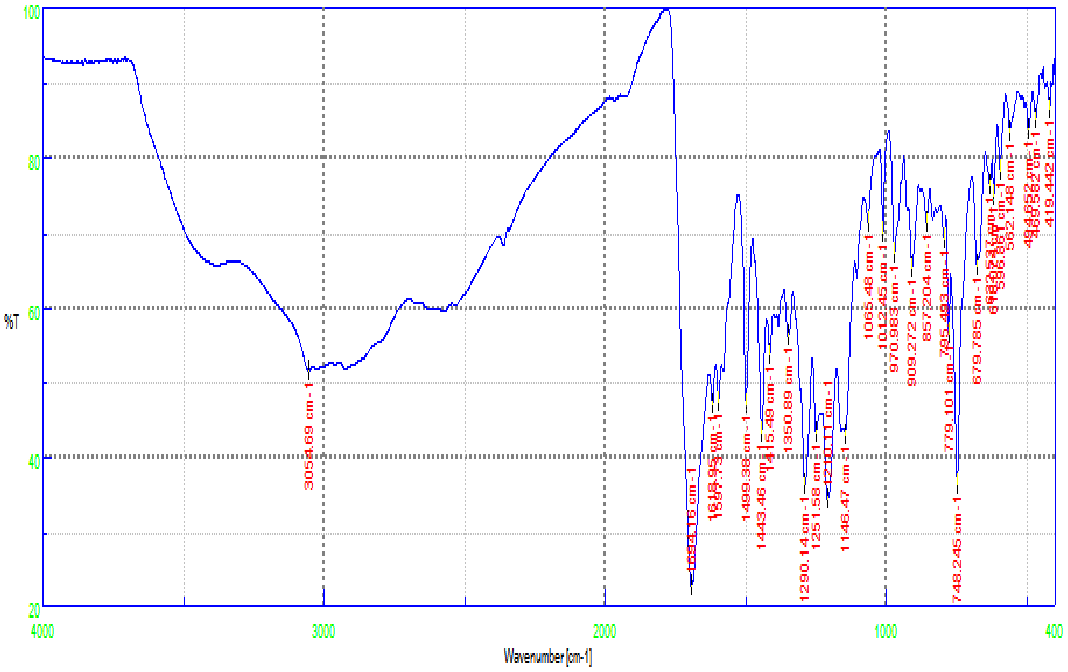

Fig 6.7 IR (KBr) Spectrum of AZO DIOL

6.7.2. Synthesis of AZO DEG

Diethylene glycol (28 µL, 3 mmol) was dissolved in 1% NaOH (10 mL). The azo dicarbonyl chloride (1.9 g, 3 mmol) dissolved in a freshly prepared mixture of DMSO and $CHCl_3$ (1:10 v/v) and quickly added to the solution of diethylene glycol together with Na_2SO_4 (1g) and stirred for 60 minutes in an atmosphere of nitrogen. The emulsified reaction mixture was transferred into a separating funnel. Washed repeatedly with freshly distilled chloroform to remove all the impurities. The purified product was added to excess of freshly distilled acetone for coagulation. Kept overnight to settle down the polymer. It was filtered and the residue was allowed to dry in air. The sodium salt of the product obtained was dissolved in distilled water. The regenerated product was filtered, washed repeatedly with distilled water and kept for air drying to obtain rose red polymer AZO DEG. Yield: 0.91g (42%) mp. 285 ^{0}C, UV λ max (DMA): 270 nm, 354 nm, 452 nm; IR (KBr) spectrum of AZO DEG is presented in Fig. 6.8.

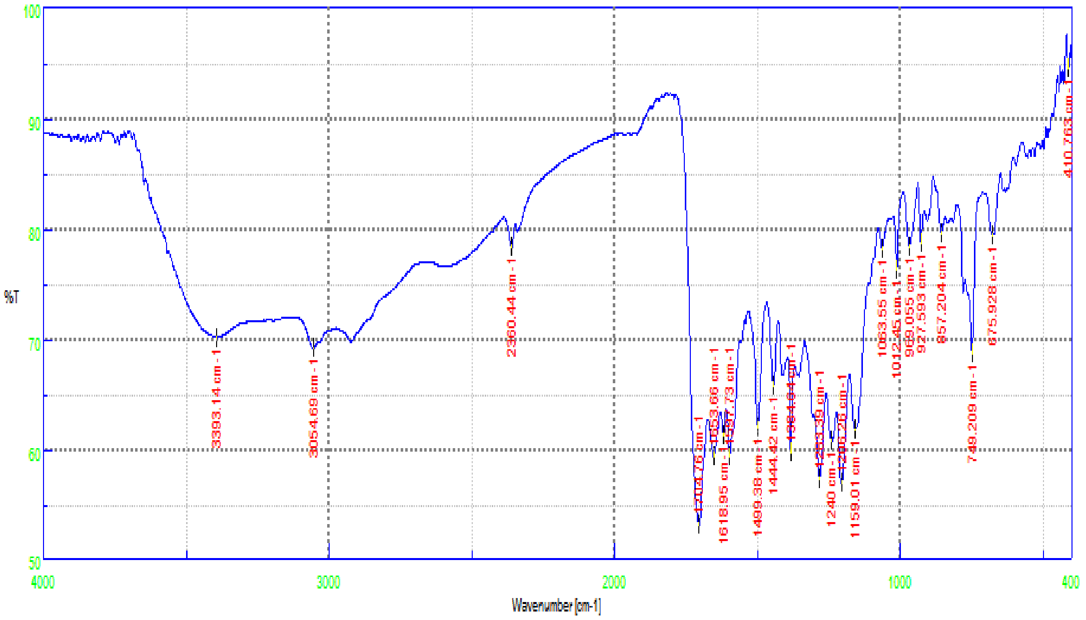

Fig 6.8 IR (KBr) Spectrum of AZO DEG

6.7.3. Photoinduced viscosity changes of AZO DIOL and AZO DEG

A dilute solution 0.2g/dL of polyester (AZO DIOL or AZO DEG) was prepared in freshly distilled dimethyl acetemide. 300 mL of the above solution was irradiated with a UV-visible light in a photochemical reactor. The viscosities were measured at definite intervals of time till a constant value was reached. The viscosity of the solution was measured after cutting off the light for 16 h. The viscosity measurements were also repeated for different solutions of concentration 0.4 g/dL and 0.6 g/dL. The specific viscosities were calculated. The values of viscosities were plotted against concentration.

From the graph, the decrease in intrinsic viscosity was calculated. A decrease in intrinsic viscosity was observed (Fig. 4.13b and 4.14b) for AZO DIOL and AZO DEG. The intrinsic viscosity changes of AZO DIOL and AZO DEG are given in Table 6.3.

TABLE 6.3

Intrinsic viscosity changes of AZO DIOL and AZO DEG

Polymer	Concentration (g/dL)	Intrinsic viscosity (η)	
		Before irradiation	After irradiation
AZO DIOL	0.2	0.3215	0.1826
	0.4	0.4191	0.2840
	0.6	0.5393	0.3522
AZO DEG	0.2	0.4197	0.2334
	0.4	0.4922	0.3059
	0.6	0.5782	0.4197

6.7.4. Photoinduced conductivity changes of AZO DIOL and AZO DEG

A dilute solution of the polymer, AZO DIOL or AZO DEG (0.2 g/dL) was prepared in dimethyl acetamide. The solution (300 mL) was irradiated using a UV-visible light in a photochemical reactor. At definite intervals of time, conductivities were measured. The changes in conductivities v/s time of irradiation was plotted. It was found that conductivity increases upto 10 h of irradiations and then remained constant. When the solution was kept in the dark for 16 h, the conductivity regained its initial value. The irradiations followed by conductivity measurements were repeated for other solutions of concentrations 0.4g/dL and 0.6g/dL and there reversibilities were studied. The conductivity changes of AZO DIOL and AZO DEG on UV irradiation are given Table 6.4.

TABLE 6.4

Conductivity changes of AZO DIOL and AZO DEG on UV irradiation

Polymer	**Concentration (g/dL)**	**Conductivity (10^{-4} mho) *vs* Time of irradiation (h)**					
		0	2	4	6	8	10
AZO DIOL	0.2	2.1	2.90	3.47	4.15	4.50	4.6
	0.4	4.89	5.35	5.35	5.58	5.97	6.13
	0.6	5.56	6.20	6.64	6.94	7.31	7.46
AZO DEG	0.2	1.70	2.21	2.42	2.93	3.61	3.9
	0.4	3.24	3.63	4.58	5.10	5.17	5.56
	0.6	7.31	7.56	8.46	8.77	9.26	9.42

6.8. PHOTOSTIMULATED PROPERTY CHANGES OF AZO AP AND AZO OT

6.8.1. Syntheses of 4, 4′-dihydroxyazobenzene

Concentrated HCl (12 mL, 0.14 mol) was added to a stirred solution of *p*. aminophenol. (4.36 g, 0.04 mol) in water (20 mL). The mixture was cooled in an ice bath and a solution of sodium nitrite (2.9g, 0.04 mol) was added to it. After 15 minutes this mixture was added to a stirred solution of phenol (4.7g, 0.05 mol) and NaOH (4.8 g, 0.12 mol) in ice cold water over a period of 30 minutes. The reaction mixture was stirred for 1h. The reddish brown suspension formed was acidified with dil.HCl while cooling. The precipitated product was filtered, dried and recrystallised from toluene to afford powder of 4,4′-dihydroxyazobenzene. Yield: 3.2 g (32%), mp. 215^0C. IR (KBr) and ^{1}H NMR spectra are given in fig. 6.9 and 6.10 respectively.

IR (KBr) cm^{-1}: 3215 (OH), 1565 (-N=N-); ^{1}H NMR (acetone d_6) , δ: 6.8-7.4 (Ar-H), 5.6 (OH)

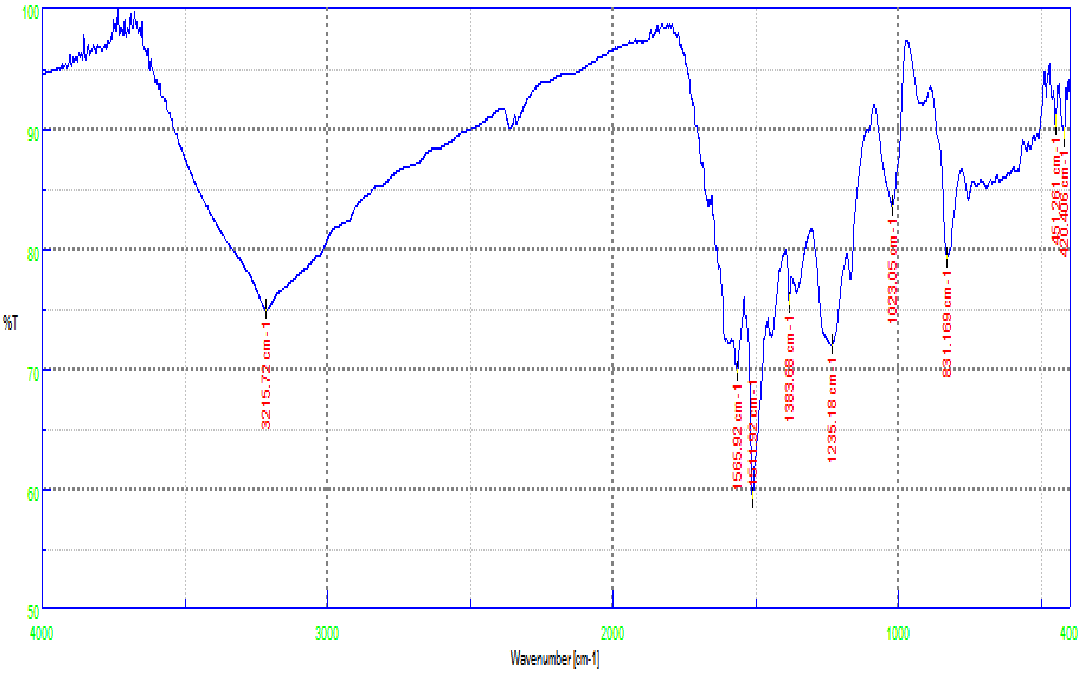

Fig 6.9 IR (KBr) Spectrum of 4,4′-dihydroxyazobenzene

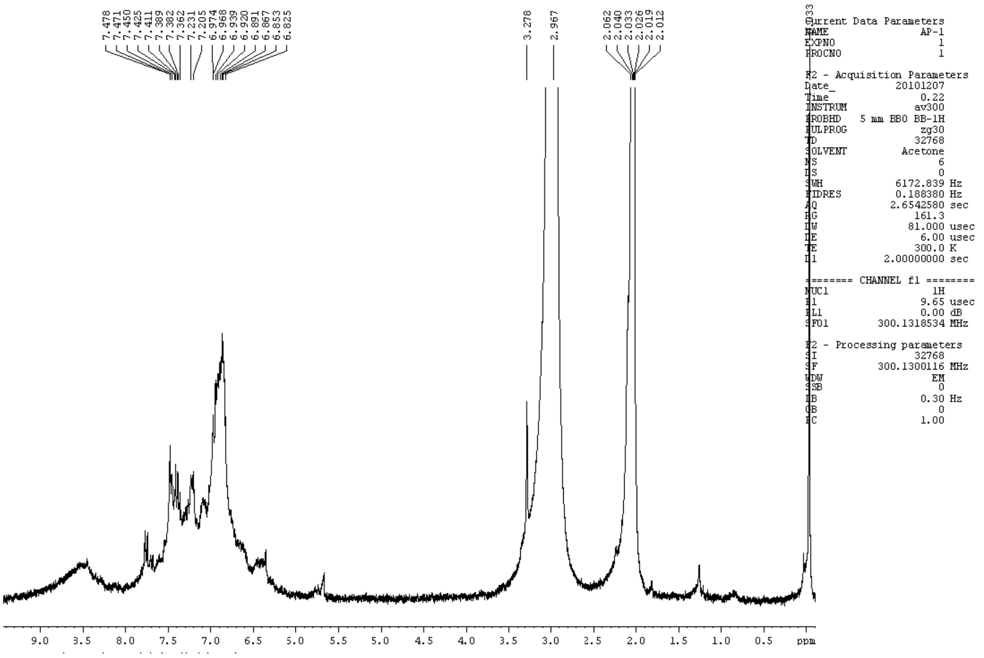

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Fig 6.10 ^{1}H NMR Spectrum of 4,4′-dihydroxyazobenzene

6.8.2. Synthesis of AZO AP

Interfacial polycondensation method was followed for the synthesis of polymer AZO AP. 4,4′-dihydroxyazobenzene (0.69g, 3 mmol) was stirred with 1% aqueous solution of NaOH (20 mL) for a few minutes. Azo dicarbonyl chloride (1.90 g, 3 mmol) dissolved in $CHCl_3$, DMF mixture (9:1, v/v) was then added to the above solution in the presence of sodium sulphate in an atmosphere of nitrogen for 60 minutes. The emulsified reaction mixture was taken in separating funnel and washed several times with freshly distilled $CHCl_3$ to remove all the impurities. The purified product was added to excess of acetone for coagulation. The coagulated polymer was kept to settle and the supernatant liquid was decanted. The residue was allowed to dry in air. The powdered mass was further dissolved in minimum quantity of distilled water. The slightly alkaline solution was neutralised with a few drops of dil. HCl, so as to regenerate the polymer. Filtered, washed several times with distilled water and kept for air drying to obtain brown polymer, AZO AP. Yield: 1.2g (46%) mp. 285^0C, λmax (DMA): 270 nm, 370 nm, 422 nm, 522 nm; IR (KBr) spectrum of AZO AP is presented in Fig. 6.11.

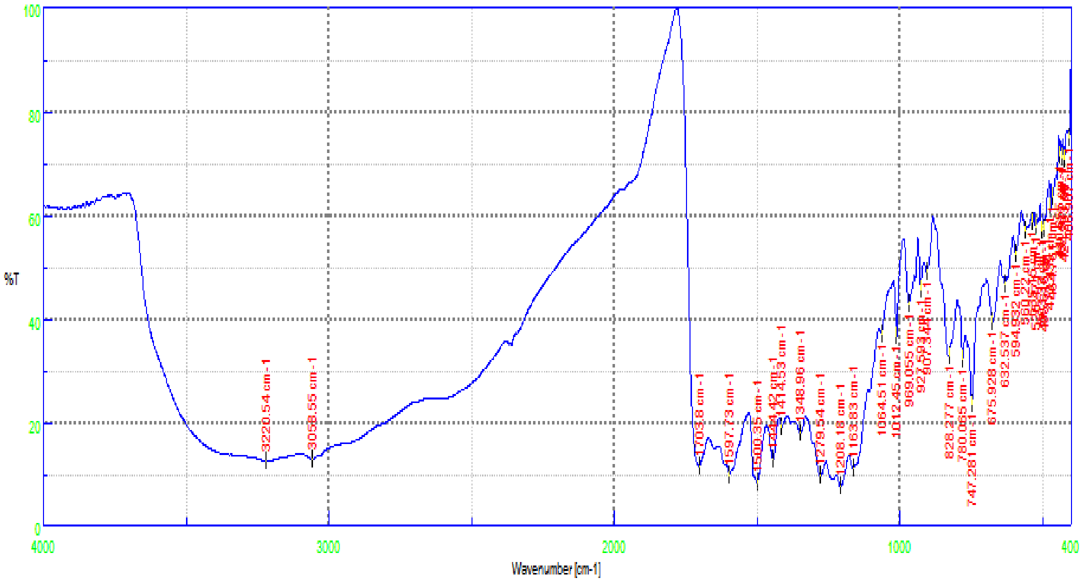

Fig 6.11 IR (KBr) Spectrum of AZO AP

6.8.3. Synthesis of *bis* (phenol-4-azo)-4, 4′-(3, 3′-dimethyl biphenyl)

Concentred HCl (16.8mL, 0.02 mol) was added to a stirred solution of *o*-tolidine (5.76g, 0.02 mol) in water. Cooled to room temperature and a solution of sodium nitrite (2.76 g, 0.04 mol) was added. The mixture was tested for the presence of free nitrous acid after 30 minutes. Phenol (3.8g, 0.04 mol) stirred with NaOH (4.8g, 0.12 mol) in ice cold water was added to the above mixture over a period of 45 minutes. Stirred for 60 minutes. The resulting suspension was acidified with dil. HCl. The product separated was filtered, dried and recrystallised from toluene to afford brown residue of *bis* (phenol-4-azo-) 4,4′-(3,3′-dimethyl-biphenyl) Yield: 6g (80%) mp.248 ^{0}C. IR (KBr) and ^{1}H NMR spectra are given in Fig. 6.12 and 6.13 respectively. IR (KBr) cm^{-1}: 3376 (OH), 1598 (-N=N-); ^{1}H NMR (DMSO d$_6$), δ: 10.31 (OH), 6.9-7.8 (Ar-H), 2.08-2.7 (CH$_3$)

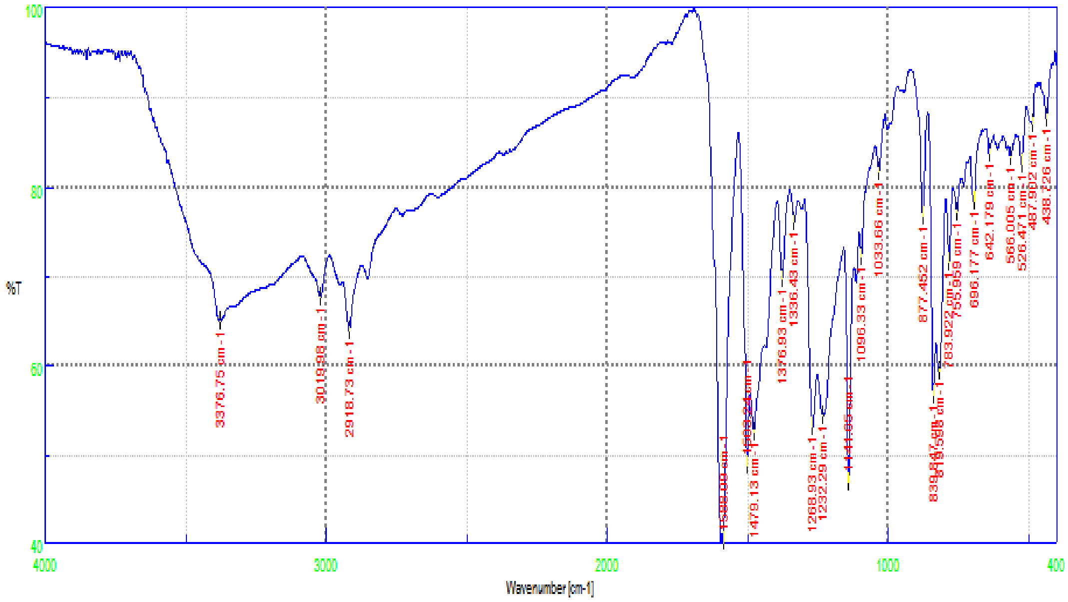

Fig 6.12 IR (KBr) spectrum of *bis* (phenol-4-azo-) 4,4′-(3,3′-dimethyl-biphenyl)

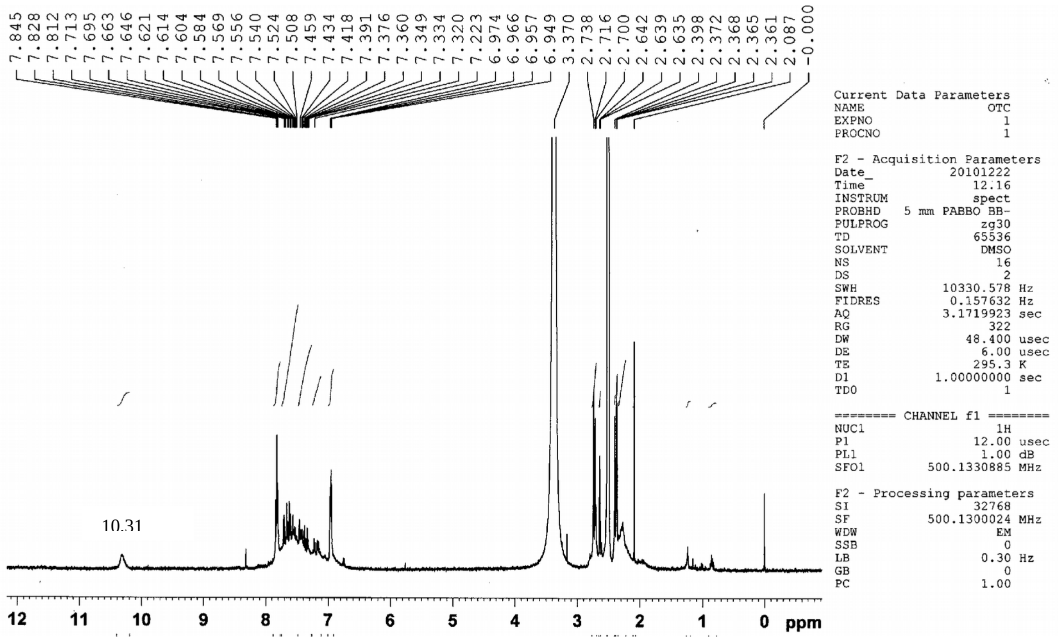

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Fig 6.13 ^{1}H NMR spectrum of *bis* (phenol-4-azo-) 4,4′-(3,3′-dimethyl-biphenyl)

6.8.4. Synthesis of AZO OT

Interfacial polycondensation method was used for the synthesis of AZO OT. *Bis*(phenol-4-azo)-4,4´-(3,3´-dimethylbiphenyl) (1.26g, 3 mmol) was stirred with 1% aqueous solution of NaOH (20 ml) for a few minutes. Azo carbonyl chloride (1.90g, 3 mmol) dissolved in $CHCl_3$, DMF mixture (9:1, v/v)was then added to the above solution in the presence of sodium sulphate. This was stirred for 60 minutes in an atmosphere of nitrogen at room temperature. The emulsified reaction mixture was taken in a separating funnel and washed several times with freshly distilled chloroform to remove all the impurities. The purified product was added to excess of acetone, for coagulation and kept overnight to settle down. The product filtered off, dissolved in distilled water and neutralised by adding a few drops of dil HCl. The regenerated product was filtered, washed repeatedly with distilled water, dried in air oven to afford brown colour polymer AZO OT. Yield: 1.6 g (51%) mp. 265^0C; UV λmax (DMA): 274 nm, 380 nm, 520 nm; IR (KBr) spectrum of AZO OT is presented in Fig 6.14

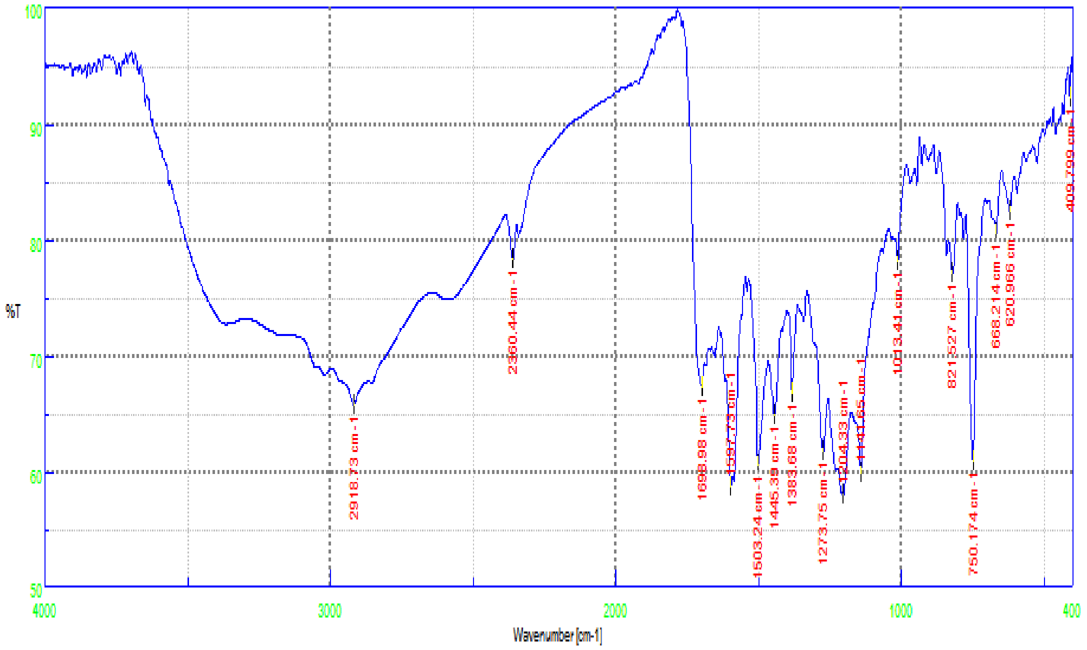

Fig 6.14 IR (KBr) spectrum of AZO OT

6.8.5. Photoinduced viscosity changes of AZO AP and AZO OT

A dilute solution of polymer [AZO AP or AZO OT (0.2g/dL)] in dimethyl acetamide were prepared by stirring for a few minutes. 300 mL of the intense brown solution was irradiated in a photochemical reactor with 125 W high pressure mercury arc lamp. The viscosity measurements were taken at definite intervals of irradiation time. After 10 h, the viscosity reached a constant value. The irradiated solution was kept under dark for 16 h to follow the reversibility. Irradiations followed by viscosity measurements and its reversibility, were repeated with other solution of different concentrations 0.4 g/dL and 0.6g/dL. A graph plotted with relative viscosity against time. In all three concentrations, the relative viscosity was found to decrease till it reached a constant value at 10 h. Above 10 h of irradiations, the viscosity remained constant. The intrinsic viscosities before and after irradiations were plotted against different concentrations. It was found that the decrease in viscosity after irradiation noticed for AZO AP and AZO OT (Fig 4.15b and 4.16b respectively in section 4). The intrinsic viscosity changes of AZO AP and AZO OT are given in Table 6.5

TABLE 6.5

Intrinsic viscosity changes of AZO AP and AZO OT

Polymer	Concentration (g/dL)	Intrinsic viscosity (η)	
		Before irradiation	After irradiation
AZO AP	0.2	0.5934	0.2298
	0.4	0.6698	0.3043
	0.6	0.8197	0.3488
AZO OT	0.2	0.600	0.2447
	0.4	0.7379	0.4176
	0.6	0.8790	0.5878

6.8.6. Photoinduced conductivity changes of AZO AP and AZO OT

A dilute solution (0.2g/dL) of the polymer AZO AP or AZO OT in dimethyl acetamide was irradiated with a high pressure mercury quartz lamp and the lamp was surrounded with an external water jacket for cooling. The conductivity measurements were carried out at definite intervals of time of irradiation. It was found that the conductivities increased and reached a maximum value at 10 h and remained constant after 10 h. When the solution was kept under dark for 16 h, reversibility of the conductivity was observed.

Irradiations and conductivity measurements were repeated for solutions of other concentrations 0.4g/dL and 0.6g/dL etc. The results of conductivity changes were plotted against time of irradiation (Fig 4.24). In all the three concentrations, an increase in conductivity (60%) and reversibility after cutting of the light were observed for both AZO AP and AZO OT. The conductivity changes of AZO AP and AZO OT on UV irradiation are given Table 6.6.

TABLE 6.6

Conductivity changes of AZO AP and AZO OT on UV irradiation

Polymer	**Concentration (g/dL)**	**Conductivity (10^{-4} mho) *vs* Time of irradiation (h)**					
		0	2	4	6	8	10
AZO AP	0.2	0.8	1.11	1.21	1.57	1.90	2.0
	0.4	1.57	2.19	2.63	3.22	3.42	3.58
	0.6	3.78	4.79	5.25	5.58	5.94	6.17
AZO DEG	0.2	0.8	0.98	1.03	1.34	1.60	2.0
	0.4	2.55	4.58	4.87	5.56	5.87	6.38
	0.6	6.22	6.45	7.02	7.41	7.62	7.67

6.9. Solid state conductivity of *ortho*-hydroxyazo polymers as pellets on UV irradiation .

Pellets of all the *ortho*-hydroxyazo polymers were prepared by 10 mm diameter and 1-2 mm in thickness. The dimensional characteristics of pellets of different polymers used for solid state conductivities are given in Table 5.1 (Section 5). Silver paste was applied on either side of these pellets and a copper wire is connected for good electrical conduction. The whole experimental set up was irradiated using UV light, at room temperature provided with cooling arrangements to prevent any increase in temperature during irradiation. Resistivity is measured at definite intervals of time in minutes. It was observed that a decrease in resistivity during irradiation reached a constant value at about 30 minutes of irradiation. Conductivities are calculated using resistivity values. Increase in conductivity was plotted against time of irradiation (Fig. 5.1, section 5). The conductivity values are given in Table 6.7.

TABLE 6.7

Solid state conductivity changes of *ortho*-hydroxyazo polymers on UV irradiation

Polymer	**Conductivity (10^{-7} mho) *vs* Time of irradiation (min)**							**Percentage increase in conductivity**
	5	**10**	**15**	**20**	**25**	**30**	**35**	
AZO PVA 14-1a	0.2283	0.2325	0.2352	0.2380	0.2392	0.2392		4.5
AZO PVA 14-1b	0.2288	0.2325	0.2358	0.2380	0.2392	0.2398	0.2398	4.5
AZO PVA 10-1a	0.2283	0.2325	0.2358	0.2386	0.2398	0.2398		4.7
AZO PVA 10-1b	0.2288	0.2336	0.2369	0.2380	0.2398	0.2398		4.6
AZO DIOL	0.2283	0.2325	0.2358	0.2380	0.2392	0.2403	0.2403	5.0
AZO DEG	0.2283	0.2325	0.2352	0.2386	0.2403	0.2409	0.2409	5.2
AZO AP	0.2283	0.2325	0.2358	0.2403	0.2427	0.2427		6
AZO OT	0.2283	0.2325	0.2369	0.2403	0.2427	0.2433	0.2433	6.1

SUMMARY AND OUTLOOK

The synthesis of some related polymers which are having light sensitive *ortho*-hydroxyazo chromophores were carried out with a view to systematically investigating the dependence of certain physical properties on macromolecular conformations and also to examine their photostimulated conductivity in the solid state. These different polymers are characteristic in that they contain azo groups capable of undergoing reversible photoinduced isomerisation and also *ortho*-hydroxyazo systems which can undergo ketohydrazone tautomerism.

The synthesised polymers were characterised by analytical and spectroscopic methods. Thermogravimetric studies were also conducted to find out the regions of stability and to determine the glass transition temperature. Polymers were subjected to photoirradiation in suitable solvents under different conditions. The resulting changes in physical properties like dilute solution viscosity and conductivity were measured. Solid state conductivities of polymeric pellets were also investigated. The results of these investigations can be summarised as follows.

- ❑ Interfacial condensation approach is used for the synthesis of polyesters. The polymers thus obtained are in high purity and are insoluble in common organic solvents.

- The UV-visible spectra of the polymers taken in suitable solvents suggest that *ortho*-hydroxyazo aromatic polyesters have there principal absorption bands. The intense absorption band around 280 nm, a weak band around 360 nm and a very weak absorption band around 480 nm.

- TG and DSC studies on different polyesters reveal that they are of moderate thermal stability. Polymers show a varied thermal profile indicating drastic morphological changes which depends on the microstructure of the polymer backbone, the chromophore and the extent of functionalistion

- Photoirradiation of *ortho*-hydroxyazo aromatic polyesters in DMA, DMSO etc results in decrease in the intrinsic viscosity which are reversible. This occurs as a result of the conformational change in the polymer chain. The isomerisation of the azo groups from *trans to cis* form shrinks the polymer chain leading to compact conformation.

- The spectral response is also in conformity with the *trans-cis* isomerisation. The increase in the intensity of the weak absorption and the decrease in the intensity of strong absorption and the shift towards shorter wavelength reagion during irradiation are attributed to the excitation in $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transition respectively.

- A reversible photodecrease in solution viscosity is exhibited by *ortho*-hydroxyazo aromatic polymers. The UV visible spectra of different polyesters are in agreement with the photoviscosity changes.

- Dilute solutions of polymers on irradiation followed by conductivity measurements show a reversible photoincrease in conductivity. The response of the conductivity correlates well with the isomerisation of azoaromatic residues in the polymer. Thus, the *trans-cis* isomerisation of the azoaromatic residues lead to an increase in conductivity in dilute solutions.

- Direct irradiation of *ortho*-hydroxyazo groups containing polyesters with UV irradiation in the solid state pellets show a mild photoincrease in conductivity which were also reversible. The feeble response of increase in photoconductivity can be explained on the basis of very small percentage of ketohydrazone tautomer of *ortho*-hydroxyazo residues in the polymer.

- The XRD measurements of the polyesters reveal their crystalline nature. The XRD patterns of all polyesters are well defined.

- SEM of these *ortho*-hydroxyazo polymers exhibits some crystalline morphology.

From the studies carried out on photoresponsive *ortho*-hydroxy azoaromtic polyesters, it can be concluded that properties like dilute solution viscosity, conductivity etc. specifically depend upon their conformation. Moreover, conformational change is brought about by the changes in geometrical structures of the chromophoric groups attached to the polymeric chain. Alternatively, the molecular level conformational changes can be manifested in the macromolecular level properties.

One of the thrust areas in the field of photochemical research is the energy resource problem. Though this problem cannot be fully tackled by the fundamentals of chemistry, any contribution in this direction will certainly minimize the technological and engineering problems. Polymer materials are still in pursuit of supporting materials for large scale energy conversion. Reversible photochemical deformation of polymer material is the principle of photochemical and mechanical energy conversion. Since *ortho*-hydroxyazo aromatic polyesters synthesised can easily cast into film, photoinduced dimensional changes which may occur in films could be investigated for its potential as “photoregulated switches”. The above systems also satisfy the requirement of materials which behave liquid crystalline properties.

REFERENCES

1. I.Y. Galaev and B. Mattiasson, *Trends Biotechnol*, **1999**, *17*, 335-340.

2. S.J. Kim., S.J. Park., S.M. Lee., Y.M. Lee., H.C. Kim and S.I. Kim, *J. Appl. Polym. Sci.*, **2003**, *89,* 890-894.

3. J. Raula, J. Shan, M. Nuopponen, A. Niskanen, H. Jiang, E.I. Kauppinen and H. Tenhu, *Langmuir*, **2003**, *19*, 3499-3504.

4. M. Yamato, M. Utsumi, A. Kushida, C. Konno, A. Kikuchi and T. Okano, *Tissue Eng*., **2001**, *7*,473-480.

5. K. Ageishi., T. Endo and M. Okasawa, *J. Poly. Sci. Polym. Chem*. Edn. **1981**, *19*,1085.

6. A. Altomare, C. Carlini, F. Ciardelli, R. Solaro, J.L. Houben and N. Rosato, *Polymers*, **1983**, *24*,95.

7. J.E. Guillet, In *Polymers Photophysics and Photochemistry*, *An Introduction to the Study of Photoprocesses in Macromolecules*, Cambridge University, New York, **1985**.

8. D. Phillips (Ed.), *Polymer Photophysics, Luminescence, Energy Migration and Molecular Motion in Synthetic Polymers*, Chapman and Hall, New York, **1985**.

9. M. Irie. In *Photophysical and Photochemical Tools in Polymer Science*, M.A. Winnik (Ed.), Reidel, Dordrecht, **1986**, P.*269*.

10. W. Marckwald. Z. *Physik*. *Chem*., **1989**, *30,*140.

11. T. Seiki, In *Handbook of Photochemistry and Photobiology*, Harisingh Nalwa (Ed)., American Scientific., **2003**, P.*435*.

12. H. Rau. In "Photochemistry and Photophysics", J.F. Rebeck (Ed.,), Vol. 2, CRC, F.L. Boca Raton, **1990**, P.*119.*

13. R.J. Gugliemetti, In *Photochromism Molecules and Systems,* H. Durr and H. Bour. Laurent (Ed.), Elsevier, Amsterdam, **1990**, P.*134*.

14. H. Rau, In *Photochromism Molecules and Systems*, H. Durr and H. Bour- Laurent (Ed.), Elsevier, Amsterdam, **1990**, P.*165*.

15. R.C. Bertelson, In *Organic and Thermochromic Compounds*, J.C Crano and R.J. Guglielmetti (Ed.), Plenum, New York, **1999**.

16. G.S. Kumar and D.C. Neckers, *Chem*. *Rev*. **1989**, *89*,1915.

17. M. Irie, *Adv*. *Polymer Sci.* **1990**, *94*,27.

18. H. Husy, E. Marian and G. Schetty, *Text*. *Res*. *J*, **1969**, *39*,94.

19. M. Irie and D. Kungwatchkun, *Macromolecules*, **1986**, *19*,2476.

20. Gigi Abraham and E. Purushothaman, *Indian J. Chem. Tech.* **2003**, *10*,175.

21. K.R. Girijan and E. Purushothaman, *Indian J. Chem. Tech,* **2008**, *15*,197-200.

22. H.S. Blair and C.B. McArdle, *Polymer*, **1984**, *25*, 1347.

23. M. Umeda and M. Hashimoto, *J. Appl. Phy.*, **1992**, *72*, 117.

24. P. Bull and C.H. Nicholls, *Dyes and Pigments*, **1982**, *3*, 5.

25. Y. Matsunga and N. Miyajima, *Bull. Chem. Soc.*, Japan, **1971**, *44*, 361.

26. J.E. Kudar, *Tetrahedron*, **1972**, *28*, 1973.

27. A.R. Monahan and J. B. Flannery, *Chem. Phy. Lett*, **1972**, *17*, 510.

28. K. J. Jiang, HZ. Chen., M. Wang, *Materials Science and Engineering*, **1999**, *B57 (2)*, 87-91.

29. K.Y. Law, *Organic Photoconductive Materials, Recent Trends and Developments, Chemical Reviews,* **1993**, *93* (1), 449-86.

30. H. Rau and B. Bunsengers, *Physikalische Chemie*, **1968**, *72* (7), 637.

31. R.B. Champ and M.D. Shattuck, *U.S. Patent*, **1975**, *3*, 898, 084.

32. K. Tautsui *U.S. Patent*, **1985**, *4*, 540, 643.

33. M. Ohta, M. Sasaki and M. Shoshi, *U.S. Patent*, **1986**, *4*, 567, 124.

34. M. Hashimoto, *U.S. Patent*, **1986**, *4*, 618, 672.

35. K.Y. Law and I. W Tarnawskyj, *U.S. Patent*, **1989**, *4*, 797, 337.

36. T. Fukagai, M. Kimura, M. Ohta and M. Hashimoto, *U.S. Patent*, **1989**, *4*, 830, 942.

37. M. Hashimoto, M. Ohta, A. Kozima, K. Sakai and M. Sasaki, *U.S. Patent*, **1984**, *4*, 426, 327.

38. M. Hashimoto, *U.S. Patent*, **1990**, *4*, 916,039.

39. T. Murayama, S. Ostuka and H. Nagasaka, *Res. Dev. Rev. Mitsubishi Chem.,* **1987**, *1*, 57.

40. K.Y. Law and I.W. Tarnawskyj, *J. Photochem. Photobiol, A. Chem.,***1991**, *57*, 217.

41. K. Ishihara, S. Kato and I. Shinohara, *J. Appl. Polym. Sci.,* **1982**, *27*, 4273.

42. T.Kitamura, S. Imamura and M. Kawamato, *J. Imaging Technol.,* **1988**, *14*, 136.

43. T. Kitamura and N. Ueda, *Electrophotography,* **1988**, *28,* 269.

44. K.Y. Law and F.C. Bailey, *Dyes and Pigments*, **1988**, *9*, 85.

45. K. Seki., Y. Susuki and H. Yamanami, SPSE *Proceedings, VIIth International Congress on Advances in Non-impact Printing Technologies*, **1990**, *60*.

46. O. Murakami, T. Uenaka, S.Otsuka and T. Murayama, IS and T *Proceedings, VIIth International Congress on Advances in Non-impact Printing Technologies*, **1991**, 318.

47. Y. Chen, C.K. Liao, T.Z .Wu, *Polymer,* **2002**, *43 (17)* 4545-55.

48. Y.J. Kim., W.M. Frederik., L.S. Charlotte., T.H. Joseph. *Inorganica Chimica Acta*, **2001**, *318 (1)*, 53-60.

49. J. Xue, S. Wang, L. Zhang, X. Li., *Dyes and Pigments*, **2007**, *75*, 369-372.

50. A. Ahluwalia, R. Piolanti, D.D Rossi, *Langmuir,* **1997**, *13* 5909-5913

51. R. Lovrien, *Proc. Natl. Acad. Sci.*, USA, **1967**, *57*, 236-242.

52. L. Matejka, K. Dusek, *Makromol. Chem.* **1981**, *182*, 3223-3226.

53. M. L. Hallensleben, H. Menzel, *Br. Polym. J.* **1990**, *23*, 199-204.

54. M. Irie. Y. Hirano, S. Hashimoto, K. Hayashi, *Macromolecules* **1981**, *14*, 262-267.

55. G.S. Kumar, P. DePra, D.C. Neckers, *Macromolecules*, **1984**, *17*, 1912-1917.

56. G.S. Kumar, P. DePra, K. Zhang, D.C. Neckers, *Macromolecules* **1984**, *17*, 2463- 2467.

57. K. Kimura, *Coord. Chem. Rev*. **1996**, *148*, 41.

58. H. Tokuhisa, M. Yokoyama and K. Kimura. *Chem. Mater*., **1993**, *5*, 989.

59. H. Tokuhisa. M, Yokoyama and K. Kimura, *Macromolecules* **1994**, *27*, 1842.

60. H. Tokuhisa, M. Yokoyama and K. Kimura, *Bull. Soc. Chem.* Jpn, **1996**, *69*, 2123

61. M.V. Voinova, M. Jonson, *Biosensors and Bioelectronics* **2004**, *20*, 1106-1110.

62. R.H. Berg, S. Havilsted P.S, Ramanujam, *Nature*, **1996**, *383*, 505.

63. R.H. Berg, P.H. Rasmussen, S. Hvilsted, P.S. Ramanujam, *Proceeding of the IVth European Conference on Molecular Electronics*, **1997**, Cambridge, pp.3-6.

64. J. Bredenbeck, J. Helbing, A. Sieg, T. Scrader, W. Zinth,C. Renner R. Behrendt, L. Moroder, J. Wachtveitl, P. Hamm, *Proc. Natl. Acad. Sci.* USA, **2003**, *100* 6452-6457.

65. M. Doi. S.F. Edwards, *The Theory of Polymer Dyanamics*, *Cladendon Press*, Oxford, **1998**.

66. B.L. Feringa, *Molecular Electronics*. Wiley VCH, GmbH, Weinheim, **2001**.

67. H.R. Hafiz, F. Nakanishi. *Nanotechnology* **2003**, *14,* 649-654.

68. E. Katz, B. Willner, I. Willner. *Biosens. Bioelectron*, **1997**, *12,* 703-719.

69. T. Shimoboji, E. Larenas, T. Fowler, S. Kulkarni, A.S. Hoffman, P.S. Stayton, *Proc. Natl. Acad. Sci.* USA, **2002**, *99 (26),* 16592-16596.

70. I. Willner, E. Katz, *Angew. Chem. Int.* Ed. **2000**, *39,* 1180-1218.

71. I. Willner. N. Lapidot. A. Riklin, R. Kasher, E. Zahavy, E. Katz. *J. Am. Chem. Soc.*, **1994**, *116*, 1428-1441.

72. C.L. Forber, E.C. Kelusky, M.C. Zerner and N.J. Bunce., *J. Am. Chem. Soc.,***1985**, *107,* 5884.

73. T. Seki, T. Tanaka and K.Ichimura, *Adv. Mater*, **1997**, *9,* 563.

74. T. Seki, T. Tanaka and K. Ichimura, *Polymer,* **1998**, *30*, 646.

75. T. Seki, K. Fukuda and K. Ichimura, *Langmuir,* **1999**, *15*, 5098.

76. A.M. Hor, C.K. Hsiao and Di Paola- Baranyi, *J. Imaging Sci.,* **1990**, *34*,224.

77. H. Kamogawa, M. Kato and H. Sugiyama, *J. Polym. Sci.,* **1968**, *6*, 2967.

78. M. Irie and H. Tanaka, *Macromolecules,* **1983**, *16,* 210.

79. J.L. Houben, O. Pieroni and A. Fissi, *Biopolymers,* **1978**, *17*, 799.

80. A. Ueno, K. Takahashi, J. Anzai and T. Osa, *J. Chem. Soc.*, **1981**, *103,* 6410.

81. J. Anzai, A. Ueno and T.Osa, *J. Chem. Soc., Perkin Trans*. II, **1987**, *67*.

82. H. Yamamato and A. Nishida, *J. Photochem. Photobiol.,* **1988**, *42*, 149.

83. A.Ueno, K. Adachi, J. Nakamura and T. Osa, *J. Polym. Sci. Poly. Chem.* Ed. **1990**, *28,* 1161.

84. A. Ueno, J. Anzai, T. Osa and Y. Kadoma, *Bull. Chem. Soc.* Japan, **1997**, *50*, 2995.

85. H.R. Maradiya, V. S. Patel, *Chemistry of Heterocyclic compounds* **2002**, *38* (11), 1324-30.

86. H.R. Maradiya, V.S. Patel, *Journal of the Serbian Chemical Society*, **2002**, *67* (1), 17-25.

87. H.R. Maradiya, *Turkish Journal of Chemistry*, **2001**, *25*, 441-50.

88. G. Hallas, A.D. Towns, *Dyes and Pigments* **1996**, *32 (3),* 135-49.

89. G. Hallas, A.D. Towns, *Dyes and Pigments*, **1997**, *35 (3)*, 219-37.

90. G. Hallas, A.D. Towns, *Dyes and Pigments*, **1997**, *33 (4),* 319-36.

91. G. Hallas, J-H Choi,. *Dyes and Pigments*, **1999**, *42*, 249-65.

92. H.S. Bhatti, S. Seshadri, *Dyes and Pigments*, **2004**, *62*, 83-92.

93. R.W. Sabnis, D.W. Rangnekar, *Dyes and Pigments*, **1989**, *10,* 295-302.

94. T.H. Afifi, A.Z. Sayed, *Journal of the Society of Dyers and Colourists,* **1997**, *113*, 256-8.

95. T.H. Afifi, *Advances in Colour Science and Technology*, **2003**, *6 (3)*, 63-72.

96. P.O. Astrand, P. Sommer- Larsen, S. Hvilsted. P.S. Ramanujam, K.L. Bak, S.P.A. Saver, *Chemical Physics Letters* **2000**, *325*, 115-9.

97. S.R. Selim, T.H. Afifi, *Advances in Colour Science and Technology*, **2001**, *4 (3)*, 82-8.

98. S. Alaa, A.E. Aziz, T.H. Afifi. *Dyes and Pigments*, **2006**, *70,* 8-17.

99. G. Hallas. J-H. Choi, *Dyes and Pigments*, **1999**, *40*, (2-3) 99-117.

100. G. Hallas. *Journal of the Society of Dyers and Colourists*, **1979**, *95*, 285-94.

101. K.L. Georgiadou, E.G. Tsatsaroni, *Dyes and Pigments*, **2002**, *53*, 73-8.

102. V.H. Patel, M.P.Patel, R.G. Patel, *Dyes and Pigments*, **2002**, *53*,191-8.

103. A. Higuchi, A. Hamamura, Y. Shindo, H. Kitamura, B.O. Yoon, T. Mori, T. Uyama and A. Umezawa, *Biomacromolecules,* **2004**, *5,* 1770.

104. J. Edahiro, K. Sumaru, Y. Tada, K. Ohi. T. Takagi, M. Kameda, T. Shinbo, T. Kanamori and Y. Yoshimi, *Biomacromolecules*, **2005**, *6*, 970.

105. G. Hayashi, M. Hagihara, C. Dohno and K. Nakatani, *J. Am. Chem. Soc.*, **2007**, *129*, 8678.

106. J. Auernheimer, C. Dahmen, U. Hersel, A. Bausch and H. Kessler, *J. Am. Chem. Soc.*, **2005**, *127*, 16107.

107. D. Person., A.J. Downard, A. Muscroft- Taylor and A.D. Abell. *J. Am. Chem. Soc.*, **2007**, *129*, 14862.

108. W. Stockenius., R.H. Lozier and R.A. Bogomolini, *Biochem Biophys. Acta.*, **1979**, *215*, 505.

109. V.D. Ermakova, V.D. Arsenov, M.I. Cherkashin and P.P. Kisilitsa, *Russ. Chem. Rev.*, **1977** *46*, 145.

110. M. Irie, A. Menju and K. Hayashi. *Macromolecules* **1979**, *12*, 1176.

111. D. Oesterhelt and B. Hess, *Eur. J. Biochem.*, **1973**, *37*, 316.

112. D.R. McCaslin and C. Tanford, *Biochem.*, **1981**, *20*, 5212.

113. H.B. Neori, P.A.G. Fortes and M. Montal, *Biochem.*, **1983**, *22*, 206.

114. U.A. Stewart, C.S. Johnson and D.A. Gabriel. *Macromolecules*, **1986**, *19*, 964.

115. Gigi Abraham and E. Purushothaman, *Indian J. of Chem. Tech.*, **1998**, *5*, 213.

116. C. H. Fan., K.W. Plaxco and A. J. Heeger, *Proc. Natl. Acad. Sci.* U.S.A., **2003**, *100*, 9134.

117. Y. D. Mao, C.X. Luo and Q. Ouyang, *Nucleic Acids Res*., **2003**, *31*,
e108.

118. F. Ricci, R.Y. Lai., A.J. Heeger, K.W. Plaxco and J.J. Sumner, *Langmuir*, **2007**, *23*, 6827.

119. C.E. Immoos, S. J. Lee and M.W. Grinstaff. *ChemBiochem.* **2004**, *5*, 1100.

120. U. Rant, K. Arinaga., S. Scherer., E. Pringsheim., S. Fujitha, N. Yokoyama., M. Tornow and G. Abstreiter, *Proc. Natl. Acad. Sci.* U.S.A., **2007**, *104*, 1110.

121. C.E. Immoos, S.J. Lee and M.W. Grinstaff, *J. Am. Chem. Soc.* **2004**, *126*, 10814.

122. Y. Xiao, A.A. Lubin, B.R. Baker, K.W. Plaxco and A.J. Heeger, *Proc. Natl. Acad. Sci.,* U.S.A, **2006**, *103*, 16677.

123. D.L. Huber., R.P. Manginell., M.A. Samara., B.I. Kim and B.C. Bunker, *Science*, **2003**, *301*, 352.

124. H. Yamanaka., K. Yoshizako., Y. Akiyama., H. Sota, Y. Hasegawa, Y. Shinohara, A. Kikuchi and T. Okano, *Anal Chem.* **2003**, *75*, 1658.

125. K. Yoshizako., Y. Akiyama., H. Yamanaka.,Y. Shinohara, Y. Hasegawa, E. Carredano, A. Kikuchi and T. Okano, *Anal. Chem.,***2002**, *74*, 4160.

126. K. Nagase, J. Kobayashi, A. Kikuchi, Y. Akiyama, H. Kanazawa and T. Okano, *Langmuir,* **2007**, *23*, 9409.

127. Y. Liu, L. Mu., B.H. Liu and J.L. Kong, *Chem. Eur. J.,* **2005**, *11*, 2622.

128. F. Zhou and W.T.S. Huck, *Phys. Chem. Chem. Phys.,* **2006**, *8*, 3815.

129. I.S. Choi and Y.S. Chi, *Angew. Chem, Intl.* Ed., **2006**, *45*, 4894.

130. P. Uhlmann, L. Ionov, N. Houbenov, M. Nitschke, K. Grundke, M. Motornov, S. Minko and M. Stamm, *Prog. Org. Coat.,* **2006**, *55*, 168.

131. C. Alexander and K. M. Shakesheff, *Adv. Mater.,* **2006**, *18*, 3321.

132. S.L. Gras, T. Mahmud, G. Rosengarten, A. Mitchell and K. Kalantar-Zadeh, *Chem Phy Chem.,* **2007**, *8*, 2036.

133. J.A. Howarter and J.R. Youngblood, *Adv. Mater.,* **2007**, *19*, 3838.

134. K. Ichimura, S.K. Oh and M. Nakagawa, *Science,* **2000**, *288,* 1624.

135. C.L. Feng., J. Jin. Y.J. Zhang., Y.L. Song., L.Y. Xie., G.R. Qu, Y. Xu and L. Jiang, *Surf. Interface Anal.,* **2001**, *32*, 121.

136. C.L. Feng., Y.J. Zhang. J. Jin, Y.L. Song, L.Y. Xie, G.R. Qu, L. Jiang and D. B. Zhu, *Langmuir*, **2001**, *17*, 4593.

137. C. Raduge, G. Papastavrou, D.G. Kurth and H. Motschmann, *Eur. Phys. J.E.,* **2003**, *10,* 103.

138. C.G.F. Cooper, J.C. MacDonald, E. Soto and W.G. McGimpsey. *J. Am. Chem. Soc.,* **2004**, *126*, 1032.

139. F. Hamelmamm., U. Heinzmann, U. Siemling, F. Bretthauer and J. V. derBruggen, *Appl. Surf. Sci.,* **2004**, *222*, 1.

140. R. Rosario, D. Gust, A. A. Garcia, M. Hayes, J. L. Taraci, T. Clement, J. W. Dailey and S.T. Picraux, *J. Phys. Chem. B.,* **2004**, *108,* 12640.

141. J. Berna, D.A. Leigh, M. Lubomska, S.M. Mendoza, E. M. Perez, P. Rudolf, G. Teobaldi and F. Zerbetto, *Nat. Mater*., **2005**, *4,* 704.

142. N. Delorme, J. F. Bardeau, A. Bulou and F. Poncin- Epaillard, *Langmuir*, **2005**, *21*, 12278.

143. W.H. Jiang, G.J. Wang, Y.N. He. X. G. Wang, Y.L. An, Y.L Song and L. Jiang, *Chem. Commun.*, **2005**, 3550.

144. N. Lake, J. Ralston and G. Reynolds, *Langmuir*, **2005**, *21*, 11922.

145. N.L. Abbott and G. M. Whitesides, *Langmuir*, **1994**, *10,* 1493.

146. J. A. M. Sondaghuethorst and L.G.J. Fokkink., *Langmuir*, **1994**, *10,* 4380.

147. X.M. Wang. A.B. Kharitonov, E. Katz and I. Willner, *Chem*. *Commun*., **2003**, 1542.

148. J. Lahann, S. Mitragotri, T.N. Tran, H. Kaido, J. Sundaram, I.S. Choi, S. Hoffer, G.A. Somorjai and R. Langer, *Science*, **2003**, *299*, 371.

149. E. Katz, O. Lioubashevsky and I. Willner, *J. Am. Chem. Soc.*, **2004**, *126*, 15520.

150. B. Zhao, W. J. Brittain, W.S. Zhou and S.Z.D. Cheng. *J. Am. Chem. Soc.,* **2000**, *122*, 2407.

151. D. Julthongpiput., Y.H. Lin., J. Teng. E.R. Zubarev., and V.V. Tsukruk, *J. Am. Chem. Soc.*, **2003**, *125*, 15912.

152. D. Julthongpiput, Y. H. Lin., J. Teng, E.R. Zubarev and V. V. Tsukruk, *Langmuir*, **2003**, *19*, 7832.

153. M. Motornov., S. Minko, K. J. Eichhorn, M. Nitschke, F. Simon and M. Stamm., *Langmuir*, **2003**, *19*, 8077.

154. Y.G. Takei, T. Aoki, K. Sanui, N. Ogata, Y. Sakurai and T. Okano, *Macromolecules*, **1994**, *27*, 6163.

155. G. B. Crevoisier, P. Fabre, J.M. Corpart and L. Leibler, *Science,* **1999**, *285*, 1246.

156. T.L. Sun, G.J. Wang, L. Feng, B.Q. Liu, Y.M. Ma, L. Jiang and D.B. Zhu., *Angew. Chem. Int*. Ed., **2004**, *43*, 357.

157. M.D. Wilson and G.M. Whitesides, *J. Am. Chem. Soc.*, **1988**, *110,* 8718.

158. H. Menzel and M.L. Hallensleben, *Polym. Bull*., **1991**, *27*, 89.

159. H. Menzel, *Macromolecules*, **1993**, *26*, 6226.

160. R. Lovrien, P. Pesheck and W. Tisel, *J. Am. Chem. Soc.*, **1974**, *96*, 244.

161. G. Vander Veen and W. Prins, *Photochem. Photobiol*., **1974**, *19*, 191.

162. G. Smets, *J. Polym. Sci. Polym. Chem.*(Ed.), **1975**, *13*, 2223.

163. E.S. Gil, S.M. Hudson., *Prog. Polym. Sci*. **2004**, *29*, 1173.

164. S. Fujishige, KKI. Ando., *J. Phy. Chem. A.,* **1989**, *93,* 3311.

165. J. C. Rodriguez- Cabello, J. Reguera, A. Girotti, M. Alonso, A.M. Testera, *Prog Polym. Sci.* **2005**, *30*,1119.

166. M. Alonso, V. Reboto, L. Guiscardo, A.S. Martin, J. C. Rodriguez- Cabello *Macromolecules* **2000**, *33*, 9480.

167. K. Kurata, A. Dobashi, *J. Macromole. Sci., Part A- Pure Appl. Chem*. **2004**, *41*, 143.

168. Y.B. Lim, S-A Han, H-U Kong, J-S Park, B. Jeong, S.W. Kim, *Biodegradable Polyesters, Pharm. Res*. **2000**, *17*, 811.

169. Y. Yu., M. Nakano and Y. Ikeda. *Nature.* **2003**, *425*, 145.

170. A. Lendlein, Y. Jiang, O. Juenger and R. Ianger. *Nature,* **2005**, *434*, 879-882.

171. Y. Zhao and J. He, *Soft Matter*, **2009**, *5*, 2686.

172. Q. Zeng, Z.A. Li, Z. Li, C. Ye, J.G. Qin and B.Z. Tang, *Macromolecules,* **2007**, *40*, 5634.

173. Z. Li, W. Wu, C. Ye, J. Qin and Z. Li. *Poly. Chem.,* **2010**, *1*, 78.

174. D.R. Wang, G. Ye, Y. Zhu and X.G. Wang, *Macromolecules*, **2009**, *42*, 2651.

175. W. H. Li, S. Nagano and T. Seki, *New. J. Chem.,* **2009**, *33*, 5019.

176. Y. Mutsunga and Niyajima, *Bull. Chem. Soc.* Jpn. **1971**, *44*, 361.

177. I. Y. Bershtein, O.F. Ginsburg, *Russ. Chem. Rev.,* **1972**, *41*, 97.

178. L.J. Guggenberger and G. Teuffer, *Acta Crystallogra.,* **1975**, *B31*, 785.

179. A. Whitaker, J. Soc. *Dyers Colourists,* **1978**, *94,* 431.

180. Von. D. Kobelt, E.F. Paulus and W. Kunstmann, *Acta Crystallogra,* **1972**, *B28,* 1319.

181. M. Hashimoto and M. Sasaki, *U.S. Patents,* **1990**, *4*, 916, 39, 4, 925, 758.

182. M. Hashimoto, M. Ohta, M. Kimura and T. Fukagai, *U.S. Patent*, **1989**, *4*, 830, 942.

183. S. Umehara and M. Matsumoto, T. Takiguchi and S. Ishikawa, *U.S. Patent,* **1989**, *4*, 830, 994.

184. D.H. Song, H.Y. Yoo, J.P. Kim., *Dyes and Pigments,* **2007**, *75,* 727-731.

185. G. Smets, *Advanced Polymer Science*, **1983**, *50*, 17.

186. R. Mani, C. Rangaswamy, K. Ramarajan and L. Ravikumar, *Macromol. Chem. Rapid Commun.* **1988**, *9,* 417.

187. C. Frenz, A. Fuchs, H.W. Schmidt, U. Theissen and D. Haarer, *Macromol. Chem. Phys.,* **2004**, *41*, 1246-1258.

188. T. Breiner, K. Kreger, R. Hagen, M. Hackel, L. Kador, A. H. E. Muller, E. J. Kramer and H.W. Schmidt, *Macromolecules*, **2007**, *40*, 2100-2108.

189. R. Sankar, W. Karo (Eds.), *Polymer Synthesis*, Vol. I. Academic, New York, **1974**.

190. E. L. Charsley and S. B. Warrington (Eds.) in *Thermal Analyses Techniques and Applications,* Cambridge, **1992**, P.*156.*

191. L. Contat- Rodrigo, A. Ribes- Greus and C.T. Imrie, *J. Appl. Polym. Sci.* **2002**, *86*, 174.

192. W.W. Wendlandt, *Thermal Methods of Analyses*, Wiley and Sons, New York, **1974**.

193. R.C. Mackenzie, *Thermochim. Acta.,* **1984**, *73*, 307.

194. W.Wm. Wendlandt, *Thermal Analysis,* III Edition, Wiley, New York, **1986**, *P.228*.

195. G.W.H. Hohne, H.K. Cammenga, W. Eysel, E. Gmelin and W. Hemminger, *Thermochim. Acta,* **1990**, *1*, 160.

196. K.R. Girijan, *Ph.D. Thesis*, Calicut University, Oct. **2006**.

197. H. P. Klug and L.E. Alexander, *X-ray Diffraction Procedures*, A Wiley Interscience Publication, **1974**, P.692-694.

198. J. S. Shelly, P. T. Mather and K.L. DeVaries, *Polymer*, **2001**, *43,* 5849.

199. A. Khan, C. Kaiser and Hecht, *Angew. Chem*., Int. Ed. **2006**, *45*, 1878.

200. C. J. Gabriel and J.R. Parquette, *J.Am. Chem. Soc.* **2006**, *128,* 13708.

201. M. Moniruzzaman, C. J. Sabey, and G.F. Fernando. *Macromolecules*, **2004**, *37*, 2572-2577.

202. H. Songawa, K. Terada, T. Masuda F. Sanda, *Polym. Bull,* **2009**, *63*. 803-813.

203. S. Sivaram (Ed.). *Polymer Science- Contemporary Themes*, Vol. 1. Tata McGraw Hill, New Delhi, India, **1991**, P.338.

204. M. Umeda, T. Nimi and M. Hashimoto, *Jpn, J. Appl. Phy.* **1990**, *29,* 2746.