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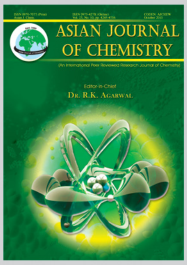

Photoinduced Viscosity Changes of Polyesters Containing *ortho*-Hydroxyazo Groups

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The synthesis and photoinduced changes in viscosity of polyesters having *ortho*-hydroxyazo groups in the polymer backbone are described. Reversible photodecrease in viscosity was observed in all cases. Isomerization from *trans* to *cis* form is responsible for the photodecrease in viscosity. The extended conformation in the *trans* form changes to the more compact *cis* form upon irradiation results in ultimate decrease in viscosity.

Key Words: Photoinduced viscosity, Synthesis, Polyesters.

INTRODUCTION

Photoresponsive macromolecules have attracted much interest and considerable progress has been achieved in this field over the past few decades. The incorporation of photochromic moieties into the polymer chain induce abrupt changes in the physical properties of the polymeric systems. A number of biologically active systems[1,2] and photochromic azo dyes which are covalently or non-covalently bound to the polymeric systems were found to control polymer conformation and to achieve photoregulation in membranes. Photocontrol in chiral recognition is another important phenomenon. The detailed investigation revealed that molecular level *cis-trans* isomerization[3] which ultimately leads to photochromic behaviour is the main justification attributed to the photoresponsiveness in azo group containing polymer. Changes in geometrical structure of the azobenzene residues incorporated in the polymer backbone or as pendant groups cause conformational changes of the polymer chain affecting solution properties, since the isomerization involves appreciable changes in polarity and geometrical structure. The viscosity of the dilute solution of the polymer system is a direct reflection of the polymer conformation. In solution, polymer with azoaromatic unit in the backbone is expected to behave like semiflexible rods and the major portion of them is in the *trans* conformation and the polymer chain is expected to be in the extended conformation. The extended shape of the semiflexible chain will form rather compact coils, when the configuration of constituent azoaromatic unit changes from *trans* to *cis*. The *cis* form can return to the *trans* form which is thermodynamically more stable[4,5]. Isomerization proceeds with the structural changes which is reflected from dipole moment measurements[6]. The conformational changes are manifested in physical properties like dilute solution conductivity[7-9] dilute solution viscosity[10,11], pH[12], *etc*. The photoisomerization responsible for photochromism of certain polyamides[13] and the photodecrease in viscosity shown by azo compounds[14] and the solid state photoconductivities[15] by *ortho*-hydroxyazo systems promoted to design more easily accessible photochromic polyester having *ortho*-hydroxyazo groups. Here the synthesis, characterization and the dilute solution viscosity changes of polyesters having *ortho*-hydroxyazo groups are described.

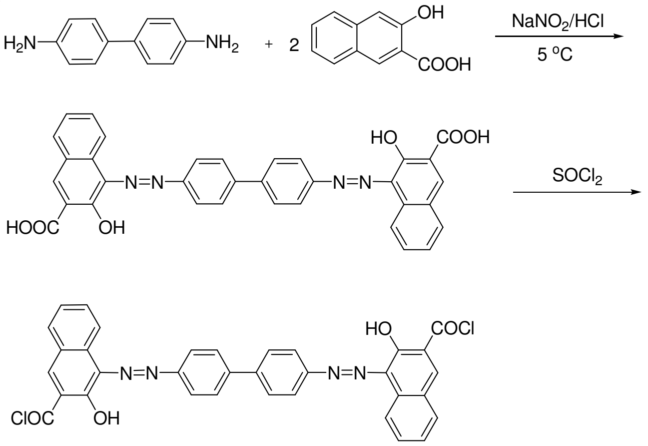
EXPERIMENTAL

Dicarboxylic acid containing *ortho*-hydroxyazo groups was prepared by tetrazotization of benzidine with $NaNO_2$ and HCl at 5 ºC followed by condensation with 2-hydroxy-3-carboxynaphthalene. The dicarboxylic acid was further converted to the corresponding dicarbonyl chloride by refluxing with molar excess of $SOCl_2$ in presence of DMF as catalyst.

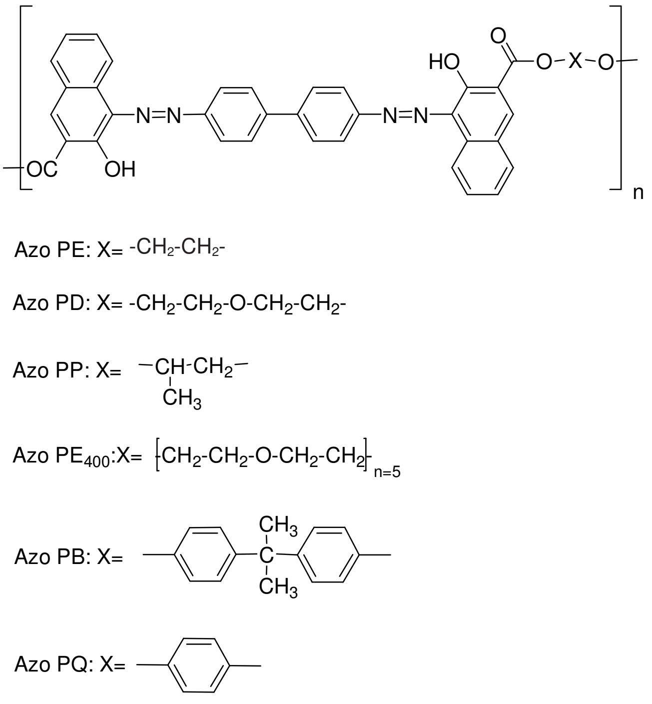
The polymers were synthesized by interfacial polycondensation method. In a typical procedure[16] azodicarbonyl chloride dissolved in $CHCl_3$ was quickly added to an alkaline solution of ethylene glycol. The emulsified mixture was added to excess of acetone. The coagulated polymer was separated by filtration and purification by repeated washings with distilled water and a very dilute solution of DMF, yielded a fibrous polymer.

RESULTS AND DISCUSSION

The interfacial polycondensation of ethylene glycol with 4,4'-azobisphenyl(di-2-hydrozy-3-napthoyl chloride) afforded the polymer azopoly-ethylene (AzoPE). The appearance of



stretching frequency around 1213 cm^{-1} with a shoulder at 1155 cm^{-1} shows the presence of C-O-C linkage. The C=O stretching frequency at 1693 cm^{-1} is characteristic of *ortho*-hydroxy esters which are hydrogen bonded. The stretching frequency at 2939 cm^{-1} is attributed to -OH group.



Scheme-I

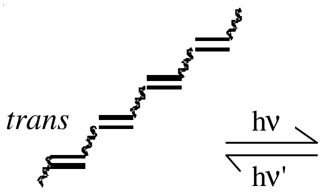
All the polymers (**Scheme-I**) synthesized exhibit approximately similar frequency (Table-1). The difference in the frequencies clearly indicate the formation of different polyesters. All the polymers were also characterized by DSC studies.

Photoinduced viscosity changes were measured using dilute solution of the polymer (0.6 g) in dimethyl acetamide. Irradiation were carried out with 125 W high pressure mercury vapour lamp in a quartz photochemical reactor of 250 mL capacity. Viscosity measurements were done using Ostwald's viscometer at 28 ºC in definite intervals of time. The viscosity value decreased gradually with time of irradiation (Table-2) and reached a minimum value after irradiation for 10 h. The solution regained its original viscosity after 16 h, when the irradiation source was cut off. Irradiation followed by viscosity measurements were performed using solution of concentration 0.4 and 0.2 g/dL. In all these cases, a decrease in viscosity was observed and the changes were reversible. The results of all the viscosity measurements at definite intervals of time are represented in Fig. 1a.

TABLE-2
EFFECT OF VISCOSITY ON IRRADIATION

Polymer	Intrinsic viscosity (η) (dL g^{-1})		Decrease in intrinsic viscosity (%)
	Before irradiation	After irradiation	
Azo PE	0.45	0.25	45
Azo PD	0.48	0.25	47
Azo PP	0.50	0.26	48
Azo PE_{400}	0.27	0.14	48
Azo PB	0.45	0.20	56
Azo PQ	0.25	0.10	60

The decrease in viscosities can be explained in terms of photoisomerization. On irradiation, the extended *trans* form changes to more compact *cis* form. This kind of *trans-cis*. conversion and the reversible photoinduced isomerization and consequent conformational change as extended conformation to more compact conformation (**Scheme-II**) has been reported earlier[17].



Scheme-II

Viscosity change of AzoPE can be correlated with spectral response. The UV-visible spectrum of polyester in dimethyl acetamide shows a strong band at 354 nm and a very weak band in the visible region at 510 nm. On irradiation, the intensity of π-π* absorption band is decreased while the intensity n → π* absorption band is increased (Fig. 2).

TABLE-1
ANALYTICAL AND SPECTRAL DATA OF POLYMERS SYNTHESIZED

Polymer	Solvent	m.p. (ºC)	λ_{max} (nm)	IR (KBr, n_{max}, cm^{-1})
Azo PE	DMAC	292	390, 415, 515	1155, 1213, 1693, 2939
Azo PD	DMAC	>300	370, 410, 510	1155, 1207, 1708, 3060
Azo PP	DMAC	284	370, 415, 495	1157, 1207, 1708, 2966
Azo PE_{400}	DMAC	>300	370, 420, 490	1155, 1209, 1708, 3062
Azo PB	DMAC	264	370, 415, 495	1178, 1217, 1706, 2968
Azo PQ	DMAC	272	380, 415, 505	1159, 1209, 1708, 2949

DMAC = Dimethyl acetamide.

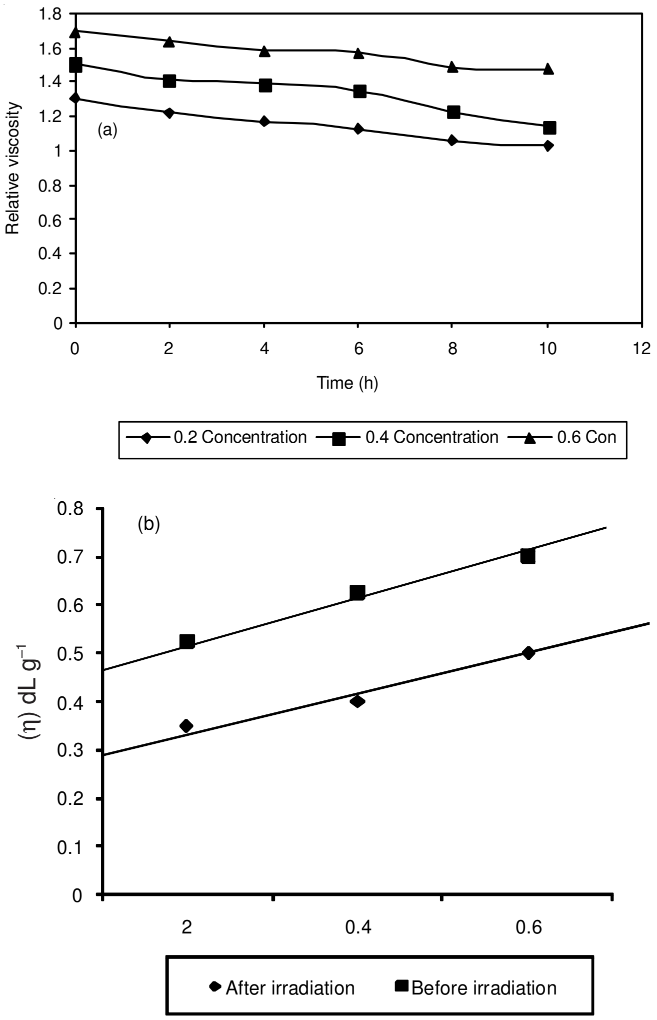


Fig. 1. (a) Relative dilute solution viscosity of polymer azo PE in dimethyl acetamide during irradiation (b) Intrinsic viscosity of polymer azo PE in dimethyl acetamide

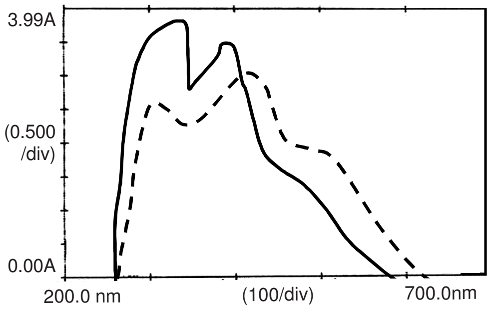
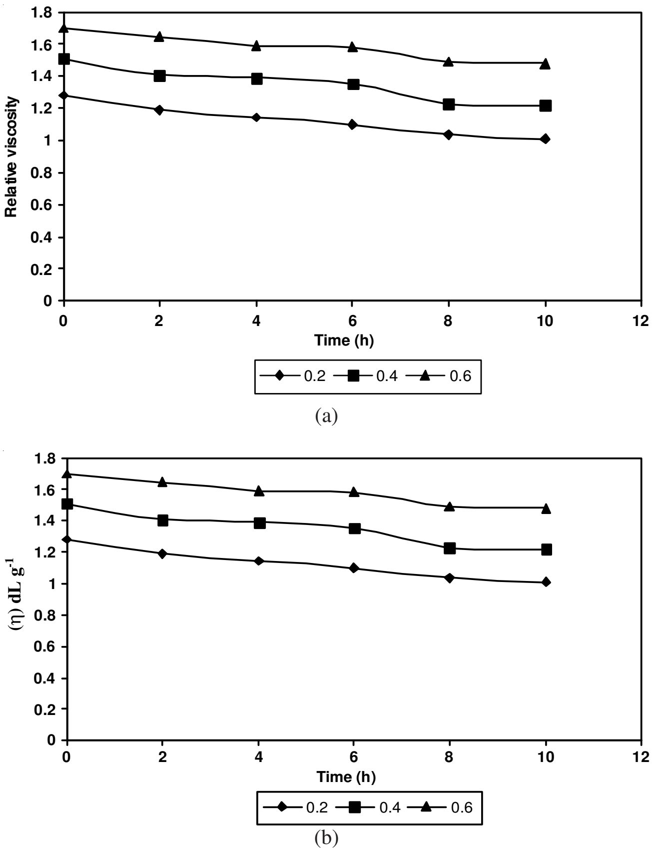


Fig. 2. UV-Visible spectrum of azo PE in dimethyl acetamide solution (—) before irradiation (......) after irradiation

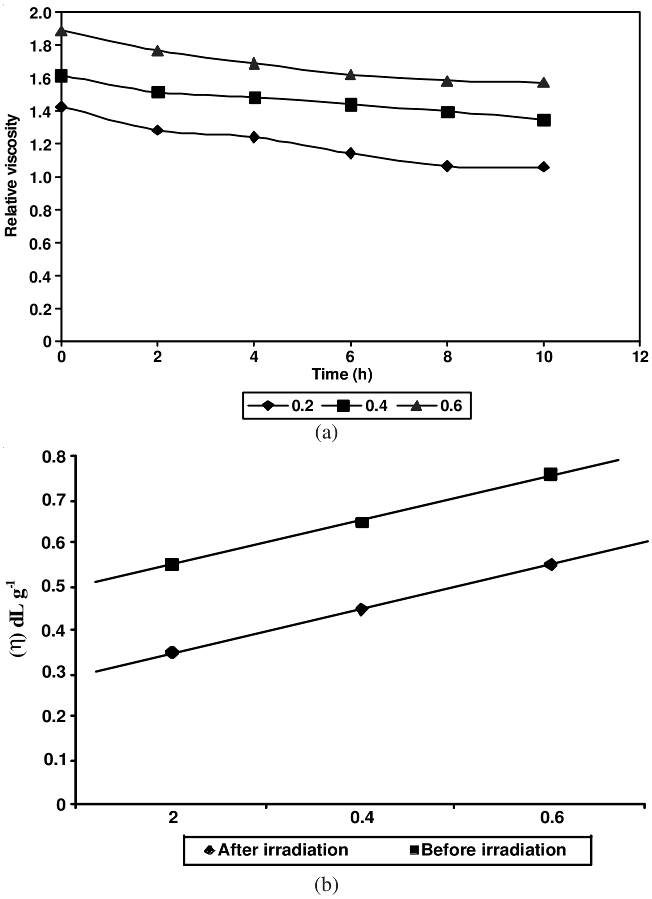
The changes in the intensity of the absorption bands are clear evidence of the photoisomerization of azobenzene residues. Analogues spectral changes were also reported[18]. Inorder to generalize the effect of irradiation on viscosity the photoviscosity changes and reversal studies were also carried out with different concentration of polymers Azo PD, Azo PP, Azo P400, AzoPB and AzoPQ. The decrease in intrinsic viscosity changes are graphically represented as Figs. 3-7. The decrease in percentage viscosity in dilute solutions of all the polymers are also given in Table-2.



(a)

(b)

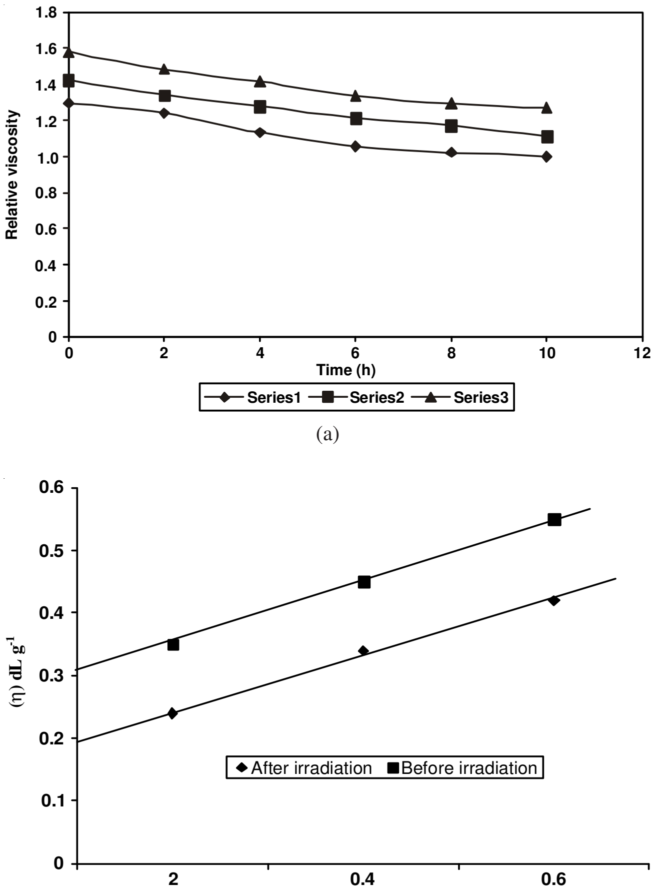
Fig. 3. (a) Relative dilute solution viscosity of azo PD in dimethyl acetamide during irradiation (b) Intrinsic viscosity of azo PD in dimethyl acetamide



(a)

(b)

Fig. 4. (a) Relative viscosity of azo PP in dimethyl acetamide during irradiation (b) Intrinsic viscosity azo PP in dimethyl acetamide

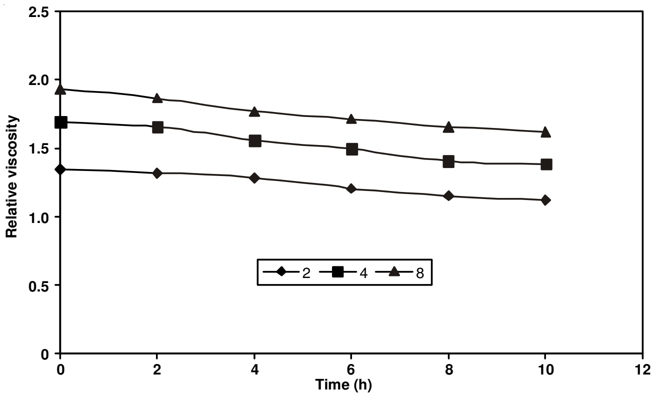


(a)

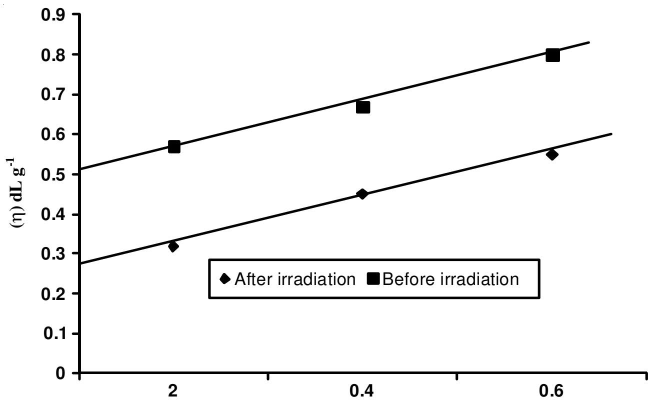
(b)

Fig. 5. (a) Relative viscosity of azo PE400 in dimethyl acetamide during irradiation 400 (b) Intrinsic viscocity of azo PE400 in dimethyl acetamide

The spectral response observed in the above series of polyesters also correlated well with the isomerization of the azo groups in the polymer backbone. It is clear from Table-2 that in azo PB and azo PQ, the polymers with stiff backbone showcomparatively high value in the percentage decrease in dilute solution viscosity during irradiation. The presence of stiff back bone makes the population of *cis* isomer much easily in the photostationary state, since *cis* to *trans* conversion in the photostationary equilibrium is suppressed to a great extent due to less stable *cis* transition state, is a reasonable explanation. Thus in all respects the observation in the viscosity change is a striking evidence for the isomerization from *trans* to *cis* form.

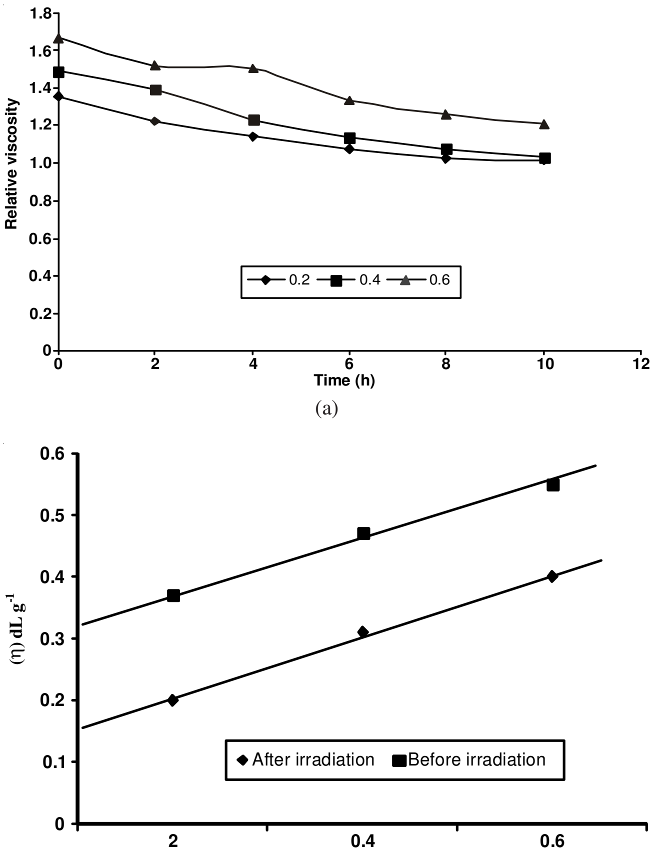


(a)



(b)

Fig. 6. (a) Relative dilute solution viscosity of azo PB in dimethyl acetamide during irradiation (b) Intrinsic viscocity of azo PB in dimethyl acetamide



(a)

(b)

Fig. 7. (a) Relative dilute solution viscosity of azo PQ in dimethyl acetamide during irradiation (b) Intrinsic viscocity of polymer azo PQ in dimethyl acetamide

Conclusion

Isomerization from *trans* to *cis* form is responsible for the decrease in viscosity. In the *trans* form the extended conformation changes to the more compact *cis* form as a result of irradiation which ultimately manifested in decrease in viscosity.

ACKNOWLEDGEMENTS

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