4. PHOTOSTIMULATED PROPERTY CHANGES OF AZO POLYMERS

Over the past ten years photoresponsive macromolecules have attracted much interest and considerable progress has been made in this field. The investigations reveal that cis-trans isomerisation\textsuperscript{142-143} which ultimately leads to photochromic behaviour, is the main justification attributed to the photoresponsiveness in azo groups containing polymers. Changes in geometrical structure of the azobenzene residues incorporated in the polymer backbone or as pendant groups cause conformational change\textsuperscript{28} of the polymer chain affecting solution properties since the isomerisation involves appreciable change of polarity and geometrical structure. The viscosity of a polymer system is a direct reflection of the polymer conformation. In solution, polymers with azoaromatic units in the backbone or as pendant groups are expected to behave like semiflexible rods. If each repeating unit of the polymer chain contains an azobenzene group and if a major portion of them is in the trans configuration, then the polymer chains will be in the extended conformation. The extended shape of the semiflexible chain will form rather compact coils, when the configuration of the constituent azobenzene units changes from trans to cis form. Photo-irradiation easily carry out this job without any fatigue to the polymer system. Eventually, this conformational change (Fig. 4.1) will be manifested in the viscosity of polymer solution.
Fig. 4.1. Schematic illustration of photo-induced conformational changes of polymer chains in solution

The present study deals with the systematic investigation of the photo-induced changes in:

i) viscosity of polyesters with azobenzene residues in the side chain
(ii) viscosity of polyesters with azobenzene residues in the backbone
(iii) conductivity of polyesters with azobenzene residues in the side chain
(iv) conductivity of polyesters having azobenzene groups in the backbone and
(v) dilution of polyesters with azobenzene crosslinks.

Results and Discussion

4.1. Photo-induced Viscosity Changes of Polyvinyl Esters (AZO PVE) with Pendant Azobenzene Groups

Polyvinyl esters with pendant azobenzene residues were synthesised and characterized as described in Chapter 3.1. A dilute solution of
the polymer AZO PVE$_{18}$ (20) in N,N-dimethylacetamide (0.6 g/dl) was irradiated with UV-visible light at 28°C in a photochemical reactor with quartz thimbles. Changes in viscosity were measured at definite time intervals of irradiation. A steady decrease in viscosity was resulted and after 8 hrs of irradiation no further decrease in viscosity was observed though the solution was subjected to irradiation continuously for 16 hrs. The observed change was found to be reversible since the solution regained the original viscosity after keeping the solution under dark for 15 hrs at 28 °C. Irradiations followed by the viscosity measurements at definite time intervals were repeated with solutions of different concentrations and similar reversible photodecrease in viscosities were observed. From a plot of concentration vs $\eta_{sp/C}$, the intrinsic viscosity, [$\eta$], of the solutions before and after irradiations were computed. The percentage decrease in intrinsic viscosity as a result of irradiation was found to be 60% (Fig. 4.2).

Analogous to the mechanism of reversible photo-induced viscosity changes of polyamides$^{26}$ or polyureas$^{144}$ having azobenzene residues in the main chain, the photodecrease in viscosity of polyvinyl esters pendant with azobenzene side chains arises from the conformational change of the polymer chain. The polyester chain having a number of side chain azo groups acts like a well-known photochromic molecule, which undergoes isomerisation from the trans to cis form during irradiation. The isomerisation from trans to the cis form kinks the extended polymer chain, resulting in compact conformation. The shrinkage
Fig. 4.2. Photo-induced viscosity changes of AZO PVE

- θ θ AZO PVE₁ₐ (20); □ □ AZO PVE₁ₖ (21);
- △ △ AZO PVE₃ₙ (22); ○ △ △: before irradiation;
- □ □ △: after irradiation

of the extended conformation explains the photodecrease in viscosity. Since the compact conformation returns to the original extended form after cutting off the light and keeping the solution in dark, the polymer regains their initial viscosity.
Azobenzene and nearly all its substituted derivatives are known to change their absorption spectrum when the configuration changes from \textit{trans} to the \textit{cis} form. Their principal absorption band ($\pi - \pi^*$) is in the UV region and their colour is caused by a weak $n-\pi^*$ absorption in the visible region. On conversion to the \textit{cis} isomer by photo-irradiation, a decrease in intensity of $\pi-\pi^*$ band with a shift to shorter wavelength region and an increase in the intensity of the $n-\pi^*$ absorption is observed. The reversible photo-induced viscosity change of AZO PVE$_{1a}$ as a result of photo-isomerisation can also be explained from its absorption spectrum. The absorption spectrum of AZO PVE$_{1a}$ was recorded in N,N-dimethylacetamide (Fig. 4.3). A strong band was observed in the UV region at 323 nm and a very weak band in the visible region.

Fig. 4.3. Photo-effect on the absorption spectrum of AZO PVE$_{1a}$ (20)
(-) before irradiation; (--) after irradiation
at 438 nm. The slight shift of the band position in comparison with unsubstituted azobenzene can be attributed to the substitution effect. On photo-irradiation of the polymer solution, the intensity of the \( \pi \rightarrow \pi^* \) absorption band decreased accompanied by a shift (318 nm) in absorption maximum, while the intensity of the band at 438 nm increased. The change in intensities of the bands is a clear evidence of the photoisomerisation of azobenzene residues.

The reversible photo-induced viscosity changes in AZO PVE\(_{1a}\) as a result of photo-isomerisation stimulated the interest in studying the behaviour of other polyvinyl esters having azobenzene residues in which the linkages are at meta or ortho positions. Thus dilute

![Graph showing absorption spectrum](image)

**Fig. 4.4. Photo-effect on the absorption spectrum of AZO PVE\(_{1b}\) (21):**

(-) before irradiation; (---) after irradiation
polymer solutions of AZO $\text{PVE}_{1\text{b}}$ (21) and AZO $\text{PVE}_{1\text{c}}$ (22) were irradiated. The details of the viscosity studies are shown in Fig. 4.2. AZO $\text{PVE}_{1\text{b}}$ showed a 68% decrease in intrinsic viscosity [$\eta$] after 8 hrs of irradiation, while AZO $\text{PVE}_{1\text{c}}$ showed only 66% decrease. In both cases the changes were reversible, and the original viscosity was regained after keeping the solution in the dark for 15 hrs.

The spectral responses were also in agreement with the viscosity changes. The spectra recorded in N,N-dimethylacetamide are given in Fig. 4.4 and Fig. 4.5.

Fig. 4.5. Photo-effect on the absorption spectrum of AZO $\text{PVE}_{1\text{c}}$ (22):

(-) before irradiation; (--) after irradiation
4.2. Photo-induced Viscosity Changes of Polyvinyl Esters (AZO PVE) with Pendant Azobenzene Groups in Presence of Protic or Lewis acids

In low molecular weight azo compounds a cyclised product was reported to be formed in presence of protic acids or Lewis acids. To correlate this observation with polyvinyl esters having pendant azobenzene groups, photo-induced viscosity studies were also carried out in presence

Fig. 4.6. Photo-induced viscosity changes of AZO PVE in presence of conc. sulphuric acid: ○ AZO PVE_{1a}; □ AZO PVE_{1b}; △ AZO PVE_{1c}
of sulphuric acid or Lewis acid. The results of the photo-irradiation using three polymer solutions AZO PVE1a (20), AZO PVE1b (21) and AZO PVE1c (22) show a gradual increase in relative viscosity upto 10 hrs and no further increase could be observed (Fig. 4.6 and Fig. 4.7). The changes were found to be irreversible in all the cases since the viscosity could not be regained even after keeping the solution under

Fig. 4.7. Photo-induced viscosity changes of AZO PVE in presence of anh. aluminium chloride: ○ AZO PVE1a; □ AZO PVE1b; ▲ AZO PVE1c
dark for more than 90 hrs. The UV-visible spectrum of the polymer AZO PVE_{1a} in the presence of a little sulphuric acid (Fig. 4.8) or anhydrous aluminium chloride (Fig. 4.9) before and after irradiation shows a hypsochromic shift of the n-% transition. The blue shift suggests that the lone pair is held up by protonation or by complexation.

\[ \text{Fig. 4.8. Photo-effect on the absorption spectrum of AZO PVE}_{1a} \text{ (20) in DMA in presence of conc. sulphuric acid: (--) before irradiation; (--) after irradiation.} \]

This results in a partial positive charge to the side chains. The repulsive interactions of the side chains induce a conformational change in the polymer chain which can be followed by the increase in viscosity. Similar type of photo-induced increase in viscosity has been encountered in spirobenzopyran to merocyanine isomerisation\textsuperscript{22,23,145}. Anyhow,
Fig. 4.9. Photo-effect on the absorption spectrum of AZO PVE\(_{1a}\) (20) in DMA in presence of anh. aluminium chloride: (-) before irradiation; (--) after irradiation.

The photo-induced increase in viscosity of polymer solutions in presence of protic solvents or Lewis acids depend on the extent of formation of a charged species. The irreversible nature of the photo-induced viscosity change can be explained on the basis of the generated protonated form or the complex species which ultimately leads to charged species\(^{146,147}\) as represented in Scheme 4.1.
Scheme 4.1. Mechanism of the cyclization of azobenzene in presence of protic acids or Lewis acids

4.3. Photo-induced Viscosity Changes of Polyesters (PE) with Azobenzene Groups in the Backbone

The light induced viscosity changes observed in the case of polyvinyl esters having azo linkages as pendant groups initiated to study the effect of photo-irradiation on polyesters with azoaromatic units in the backbone. The synthesis of azoaromatic polyesters are designed so as to have maximum number of photo-isomerisable groups. Moreover, the synthesised azoaromatic polyesters are characteristic in that they contain no flexible methylene spacer groups but only stiff phenelene or bipheneiene residues in the chain. The details of the synthesis and characterization are described already in Chapter 3.3.
When a dilute (0.6 g/dl) solution of the polymer PE$_{1a}$ (31) in N,N-dimethylacetamide was irradiated with UV-visible light followed by measuring the viscosities at definite time intervals, at 28 °C, the viscosity of the solution was found to be decreasing till it reaches a constant value, after 6 hrs of irradiation. Even after continuous irradiation, no further change in viscosity was observed. Moreover, the viscosity change was reversible and the initial viscosity was regained after keeping the solution in dark at 28 °C for 15 hrs. The viscosity

![Graph showing viscosity changes before and after irradiation.](image)

**Fig. 4.10.** Photo-induced viscosity changes in PE$_{1a}$ (31):

- ● before irradiation;
- ○ after irradiation
studies of the irradiated solutions were also carried out with solutions of other concentrations. From a graph of concentration plotted against $\eta_{sp/c}$, the intrinsic viscosities of the solutions were calculated (Fig. 4.10). Similar photo-induced viscosity studies were repeated with other polyesters $PE_{1b}$ (32) and $PE_{1c}$ (33) and of solutions with different concentrations (Fig. 4.11). The viscosity changes in all these

![Graph showing viscosity changes](image)

**Fig. 4.11.** Photo-effect on viscosities of polymers: ■ $PE_{1b}$; ▲ $PE_{1c}$ (before photo-irradiation), ◊ $PE_{1b}$; △ $PE_{1c}$ (after photo-irradiation)
polyesters were found to be completely reversible in 14 to 16 hrs, after the irradiation source was removed. In the case of polymer PE$_{1a}$ the intrinsic viscosity during irradiation is 40% less than the viscosity in the dark. The polyesters PE$_{1b}$ and PE$_{1c}$ showed a decrease in viscosity of 48% and 36% respectively. The UV-visible spectrum of the polymer PE$_{1a}$ in N,N-dimethylacetamide is shown in Fig. 4.12.

Fig. 4.12. Photo-effect on the absorption spectrum of polymer PE$_{1a}$: (-) before irradiation; (--) after irradiation

The figure showed a decrease in intensity of the peak at 346 nm, corresponding to the $\pi-\pi^*$ transition of the polymer, after irradiation for 6 hrs.
Polyesters PE$_{2a}$ (34), PE$_{2b}$ (35) and PE$_{2c}$ (36) synthesised from 1-(4-hydroxyphenyl)azo]-1-naphthol and different azobenzene dicarbonyl chlorides were subjected to irradiation in N-methylpyrrolidone followed by viscosity measurements. In all the three systems and at different concentrations, the photodecrease in viscosity continued until it reaches a constant value, after 8 hrs of irradiation. Here the initial viscosity was recovered after keeping the solutions in dark for 12-15 hrs. Fig. 4.13

![Graph showing the photo-effect on viscosities of polymers](http://example.com/graph)
shows the decrease in intrinsic viscosity, $\eta$, of the three polymers $\text{PE}_{2a}$, $\text{PE}_{2b}$ and $\text{PE}_{2c}$. The decrease was 40% for $\text{PE}_{2a}$ and 36% for $\text{PE}_{2b}$ after 10 hrs of irradiation. The decrease in $\text{PE}_{2c}$ was 40%. The UV-visible spectrum of $\text{PE}_{2a}$ was recorded in N-methylpyrrolidone. Fig. 4.14 shows the spectral changes on irradiation.

![Graph showing spectral changes](image)

**Fig. 4.14.** Photo-induced spectral changes in $\text{PE}_{2a}$:
(-) before photo-irradiation; (--) after photo-irradiation

Considerable viscosity changes were observed in the polyesters $\text{PE}_{3a}$, $\text{PE}_{3b}$ and $\text{PE}_{3c}$ synthesised from bis(phenol-4-azo)-4,4'-biphenyl and different azobenzenedicarbonyl chlorides (Fig. 4.15). Here a photodecrease in intrinsic viscosity of 40%, 46% and 40% were observed in the three polymers $\text{PE}_{3a}$, $\text{PE}_{3b}$ and $\text{PE}_{3c}$ respectively. In all the three cases,
the decrease in viscosity was maximum within 6 hrs of irradiation and the recovery of viscosity in 10-12 hrs of keeping the solutions in dark. Closely parallel to this observation, there was considerable change in the intensity of absorption after 6 hrs of irradiation. The UV-visible spectrum of polymer PE$_3a$ taken in morpholine, before and after 6 hrs of irradiation is given in Fig. 4.16.
Among the different polyesters under investigation, highest viscosity changes were observed in the case of polymers PE\textsubscript{4a} (40), PE\textsubscript{4b} (41) and PE\textsubscript{4c} (42). These polymers were synthesised from bis(phenol-4-azo-2-carboxy)-4,4'-biphenyl and different azobenzenedicarbonyl chlorides. The details of the synthesis and characterisation are already described in Chapter 3.3. Dilute solution viscosity measurements in N-methylpyrrolidone (Fig. 4.17) showed a 52\% photodecrease in intrinsic viscosity, $[\eta]$, for the polymer PE\textsubscript{4a}. In the case of PE\textsubscript{4b} a photodecrease of 55\% and in PE\textsubscript{4c} a photodecrease of 60\% in viscosity were the observed result. The changes in viscosity were complete within 5 hrs of irradiation and the reversibility occurs after 12-14 hrs of keeping the solution.
Fig. 4.17. Photo-induced viscosity changes of polymers: \( \bullet \) PE\(_{4a} \); \( \blacksquare \) PE\(_{4b} \); \( \blacktriangle \) PE\(_{4c} \) (before photo-irradiation), \( \bigcirc \) PE\(_{4a} \); \( \square \) PE\(_{4b} \); \( \blacktriangle \) PE\(_{4c} \) (after photo-irradiation)

in dark. These polymers also showed characteristic UV-visible spectra before and after irradiation. The UV-visible spectrum of PE\(_{4a} \) in N-methylpyrrolidone is shown in Fig. 4.18.
Fig. 4.18. Spectral changes in polymer PE₄₈: (−) before and (−−) after photo-irradiation

Photo-induced viscosity changes were also studied with polyesters prepared from bis(phenol-4-azo)-4,4′-(3,3′-dimethylbiphenyl) and azobenzene-diearboxyl chlorides in morpholine. The details of the synthesis are given in Chapter 3.3. The viscosity changes observed were comparatively low. Thus, the polymer PE₅₈ (43) showed a 40%, PE₅₉ (44) a 30% and PE₅₉ (45) a 36% decrease in viscosity on irradiation (Fig. 4.19). Moreover, constant viscosity values were attained within 6 hrs of irradiation and the original viscosity was regained after keeping the solution for 16-18 hrs in the dark. The UV-visible spectrum of PE₅₈
Fig. 4.19. Photo-effect on viscosities of polymers: ○ PE₅ₐ; ■ PE₅₅; ▲ PE₅₉ (before photo-irradiation), ○ PE₅₉; □ PE₅₉; △ PE₅₉ (after photo-irradiation)

recorded in morpholine is shown in Fig. 4.20, before and after 6 hrs of irradiation.

The investigations carried out on the different polyesters having
azo linkages in the polymer backbone suggest that the photodecrease in viscosity arises from the conformational change of the polymer chain and not from any interchain interactions. In analogy with the viscosity changes encountered in polyvinyl esters having azo linkages as pendant groups and the detailed mechanism suggested by Irie and co-workers in polyamides, the reason for the conformational change of the polymer chain can be attributed to the photo-induced trans-cis isomerisation of azobenzene residues. The change in UV-visible spectra of the polyesters during irradiation and the decrease/recovery cycles of the viscosity also supports the above proposition. On a close investigation of the viscosity studies done, it appears that the polyesters PE_{4(a-c)}
display higher viscosity changes. The presence of carboxy substituted diphenelene residues enhances the stiffness in the polymer chains. They behave as semiflexible rods in solution. The extended rod like shape of the semiflexible chain shrinks readily to a more compact structure, during the isomerisation from trans to cis form. However, polymer PE5(a-c) shows comparatively small decrease in photoviscosity showing that the formation of the cis content is hindered. This can also be explained in terms of photo-isomerisation. Though there is no unequivocal proof in the literature of the mechanism of photochemical isomerisation having N=N bond, the "inversion mechanism" is the most probable path for azobenzenes with electron withdrawing substituents. Isomerisation by the inversion mechanism may be slightly restricted, when the unshared electron pair in the azo nitrogen atoms are sterically opposed by the ortho-methyl groups. Thus transfer of unshared electron pair from sp² to p-orbital formed through "rehybridisation" and hence vibration in the plane of the molecule from one position to the other is somewhat reduced.

4.4. Photoeffect on Conductivity of Polymers

Photocontrol of macromolecular conformation, similar to reversible solution viscosity changes, also significantly affects the solution conductivity. The well illustrated trans-cis isomerisation is considered to be the key step in the photo-induced conductivity of polymers with azobenzene moieties. Only scant reports are available in the
literature\textsuperscript{26} making a correlation between the extent of photo-isomerisation and the solution conductivity of polymers. Thus, it is thought worthwhile to include the newly synthesised polyesters having azo groups in the backbone and as pendant groups also in the purview of the conductivity studies.

4.4.1 Photo-induced Conductivity Changes of Polyvinyl Esters (AZO PVE) with Pendant Azobenzene groups

The photo-induced conductivity changes were measured using dilute polymer solutions of AZO PVE\textsubscript{18} (20) in N,N-dimethylacetamide at 28 °C. Thus a 0.6 g/dl concentrated solution was irradiated with UV-visible light in a photochemical reactor. Changes in conductivity were recorded at definite time intervals of irradiation. An increase in conductivity was the observed result. The conductivity value increased gradually with time of irradiation (Fig. 4.21) and it reaches a constant value, after irradiation for 10 hrs. The solution regained their original conductivity within 15 hrs, when the irradiation was cut off. Irradiation followed by conductivity changes were also measured using dilute solutions (0.6 g/dl) of polymer AZO PVE\textsubscript{1b} (21) and AZO PVE\textsubscript{1c} (22). In both the cases increase in conductivity was observed and the changes were reversible. The results of the conductivity measurements at definite time intervals are graphically represented in Fig. 4.21. Similar type of photo-induced conductivity changes were also studied using a solution
Fig. 4.21. Photo-induced conductivity changes of polymers: ○ AZO PVE$_{1a}$; □ AZO PVE$_{1b}$; ▲ AZO PVE$_{1c}$, in DMA (conc. 0.6 g/dl)

of concentration 0.4 g/dl. The trend of the conductivity changes is shown in Fig. 4.22. The details of the photo-effect on conductivities of the polymers AZO PVE are given in Table 4.1.

The increase in conductivity can be explained in terms of photo-isomerisation. As envisaged in polyamides$^{26}$ having azo linkages in the backbone, the dissociation equilibrium of substituted esters having
azo groups is dependent on the change in conformation of the polymer chain. Here the dissociation of the side chain acid is increased in the more compact conformation. Alternatively, the extended conformation depresses the dissociation. The more polar cis form in the compact conformation increases the dissociation of the side chains, is another possible explanation.
Table 4.1. Photo-effect on conductivity of polymers AZO PVE in DMA

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<tr>
<th>Polymer</th>
<th>Concentration (g/dl)</th>
<th>Time of irradiation to attain constancy (hrs)</th>
<th>Time of reversibility (hrs)</th>
<th>Increase in conductivity (%)</th>
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4.4.2. Photo-induced Conductivity Changes of Polyesters (PE) with Azo Linkages in the Backbone

The light induced conductivity changes observed in polyvinyl esters with azo linkages as pendant groups were also extended to study the photo-effect on conductivity of polyesters with azo groups in the backbone. Thus, irradiation of a dilute solution (0.6 g/dl) of polymer PE$_{1a}$ (31) in N,N-dimethylacetamide with UV-visible light followed by conductivity measurements at definite intervals of time showed an increase in

![Graph showing conductivity changes over time](image)

**Fig. 4.23.** Photo-effect on conductivity of polymers: ○ PE$_{1a}$; □ PE$_{1b}$; ▲ PE$_{1c}$ in DMA (conc. 0.6 g/dl)
conductivity (Fig. 4.23). After 4 hrs of irradiation no further increase in conductivity was observed. The reversal of conductivity was followed by keeping the solution in dark for 17 hrs, when the original value was regained. Similar photo-induced conductivity changes and reversal studies were carried out with the other polymers PE_{1b} (32) and PE_{1c} (33) (Fig. 4.23). The photo-effect on conductivity followed at another concentration (0.4 g/dl) of the polymers is shown in Fig. 4.24.

Fig. 4.24. Photo-effect on conductivity of polymers: ○ PE_{1a}; □ PE_{1b}; △ PE_{1c}, in DMA (conc. 0.4 g/dl)
The generality of the photo-induced conductivity changes and reversal phenomena were studied by extending the conductivity measurements to other polymers having azo linkages in the backbone. Thus conductivity changes were recorded for dilute polymer solutions of PE$_{2a}$ (34), PE$_{2b}$ (35), PE$_{2c}$ (36), PE$_{3a}$ (37), PE$_{3b}$ (38), PE$_{3c}$ (39), PE$_{4a}$ (40), PE$_{4b}$ (41), PE$_{4c}$ (42), PE$_{5a}$ (43), PE$_{5b}$ (44) and PE$_{5c}$ (45) at definite intervals of time of irradiation. The trend in conductivity changes of different polymers are shown in Fig. 4.25 to Fig. 4.28. The details of irradiation and the percentage increase in conductivity are given in Table 4.2.

Similar photo-induced conductivity changes were observed for all the polyesters PE$_1$ (a-c) – PE$_5$ (a-c) when the investigations were carried out with the solutions of different concentrations. They are graphically represented in Fig. 4.29 to Fig. 4.32.

The response of the conductivity observed in the above series of polyesters correlates well with the isomerisation of the azobenzene residues in the polymer backbone. In the series PE$_1$ (a-c) $\rightarrow$ PE$_5$ (a-c), very good conductivity responses were observed in the polymers PE$_4$ (a-c). PE$_{4a}$ showed 37%, PE$_{4b}$ 36% and PE$_{4c}$ 33% increase in conductivity (Table 4.2). Parallel observation encountered in viscosity changes is a striking evidence for the isomerisation from trans $\rightarrow$ cis form and consequent increase in dissociation in the cis form.
Fig. 4.25. Photo-induced conductivity changes of polymers:
- PE$_{2a}$; PE$_{2b}$; PE$_{2c}$
in NMP (conc. 0.5 g/dl)

Fig. 4.26. Photo-induced conductivity changes of polymers:
- PE$_{3a}$; PE$_{3b}$; PE$_{3c}$
in morpholine (conc. 0.5 g/dl)
Fig. 4.27. Photo-induced conductivity changes of: ● PE$_{4a}$;  
■ PE$_{4b}$;  ▲ PE$_{4c}$ in NMP  
(conc. 0.5 g/dl)

Fig. 4.28. Photo-induced conductivity changes of: ● PE$_{5a}$;  
■ PE$_{5b}$;  ▲ PE$_{5c}$ in morpholine (conc. 0.5 g/dl)
Fig. 4.29. Photo-induced conductivity changes of: ○ PE_{2a}; □ PE_{2b}; ▲ PE_{2c}, in NMP (conc. 0.3 g/dl)

Fig. 4.30. Photo-induced conductivity changes of: ○ PE_{3a}; □ PE_{3b}; ▲ PE_{3c}, in morpholine (conc. 0.3 g/dl)
Fig. 4.31. Photo-induced conductivity changes of: ○ PE$_{4a}$; ― PE$_{4b}$  
△ PE$_{4c'}$ in NMP  
(concn. 0.3 g/dl)

Fig. 4.32. Photo-induced conductivity changes of: ○ PE$_{5a}$; ― PE$_{5b}$  
△ PE$_{5c'}$ in morpholine  
(concn. 0.4 g/dl)
Table 4.2. Photo-induced conductivity changes of polymers PE

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4.5. Photostimulated Dilation Changes in Polyvinyl Esters with Azobenzene Crosslinks

Photosensitive molecules having azo chromophores are known to be transformed under photo-irradiation into other isomers, which return to the initial state either thermally or photochemically. The isomerisations are always reflected in the physical and chemical properties. The property changes of the azo chromophores - a combination of dipole moment and geometrical structural changes - are considered to be the main driving force to induce conformational changes of the polymer chains in solution, when these chromophores are incorporated into the polymers. The conformational changes are finally manifested in the physical properties like solution viscosity and conductivity. Another important aspect as a result of photo-isomerisation of azobenzene chromophores into the polymer chain is the change in shape of polymer gels. Here the molecular level conformational changes of the polymer chains are reflected at the visible macro level. The use of structural changes of photo-isomerisable chromophores at the molecular level for the direct conversion of photon energy into mechanical work has been illustrated by Merian\textsuperscript{152}. Similarly, reversible photostimulated dilation of polyacrylamide gels by incorporating triphenylmethane leuco derivatives in the gel network has been investigated\textsuperscript{153}. No attempt has been made to study the photostimulated dilation behaviour of polymers having azobenzene crosslinks. Therefore, it is thought interesting to synthesise crosslinked polyvinyl esters having azobenzene linkages and carry out the photostimulated dilation studies.
The polyvinyl esters bound with azobenzene crosslinks were obtained by the interfacial condensation of PVA (MW 10000) with molar excess of azobenzene-4,4'-dicarboxyl chloride. The details of the synthesis are given in Chapter 3.2. This polymer was found to be highly insoluble in almost all organic solvents. Hence, it was not possible to carry out studies on the photo-induced solution property changes. However, the polymer was found to swell in solvents like chloroform, dichloromethane and water. The change in dilation was measured as the change in volume of swelled polymer.

The polymer AZO PVE$_{2a}$ (23) was allowed to swell in chloroform in a graduated pyrex glass vessel. The changes in volume at definite intervals of time were measured. The plot of the volume of swollen gel vs the time showed a gradual increase in volume (Fig. 4.33) and the equilibrium condition was attained on keeping it for 14 hrs. Photo-stimulated dilation changes were also carried out by irradiating the polymer swelled in chloroform with UV-visible light. The changes are represented in Fig. 4.33. The observed volume of the gel, after irradiation for 14 hrs was found to be 26% higher than those of the swollen gel kept for 14 hrs. Moreover, dilated gel deswelled in the dark to the initial equilibrium volume in 70 hrs. The observation suggests that the pore volume of the cross links in the polymer AZO PVE$_{2a}$ is increased by photochemical reaction of the azobenzene residues present in the network.
The swelling behaviour of the polymer AZO PVE$_{2a}$ and its photostimulated dilation changes were repeated with other solvents like dichloromethane and water. The observed swelling changes are represented in Fig. 4.33. Both the rate of swelling and the photostimulated dilations in different solvents were found to be in the order water $>$ dichloromethane $>$ chloroform.
The generality of the swelling and photostimulated dilation changes of polymer gel with azobenzene crosslinks were established by extending the studies to other polymers AZO PVE$_{2b}$ (24) and AZO PVE$_{2c}$ (25). These polymers were also allowed to swell in different solvents like chloroform, dichloromethane and water and the photo-induced dilation studies were carried out. The changes are graphically represented in Fig. 4.34 and Fig. 4.35.

![Graph showing photostimulated dilation changes in polymer AZO PVE$_{2b}$](image)

**Fig. 4.34.** Photostimulated dilation changes in polymer AZO PVE$_{2b}$:
- ● chloroform;
- □ water;
- ▲ dichloromethane;
(-) without irradiation; (--) with irradiation
Fig. 4.35. Photostimulated dilation changes in polymer AZO PVE$_{2c}$:
- chloroform;
- water;
- dichloromethane:
(-) without irradiation; (--) with irradiation

The details of the photo-irradiation and the dilation studies of
the polymers in different solvents are presented in Table 4.3.

A qualitative treatment on the mechanism of photostimulated
gel dilation of azobenzene crosslinked polymers can be given on the
basis of photo-isomerisation (Scheme 4.2). Before irradiation, polyvinyl
esters having azobenzene crosslinks are mainly in the trans configuration.
<table>
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<th>Polymer</th>
<th>Chloroform</th>
<th>Dichloromethane</th>
<th>Water</th>
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<tr>
<td></td>
<td>Time of irradiation to attain constancy (hrs)</td>
<td>Increase in volume (%)</td>
<td>Time of deswelling (hrs)</td>
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<tr>
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Scheme 4.2. Pathway for the photostimulated gel dilation

During photo-irradiation the cis content of the polymer gel increases. As a result of the photo-isomerisation, an increase in pore volume of the network polymer may be achieved. The reversal of photostimulated gel dilation and the effective recycling of dilation and deswelling supports the above view. The dilation studies carried out using solvents of different polarities reveal that the formation of the more polar cis configuration is assisted by polar solvents.

The investigations - viscosity, conductivity and dilation - carried out on the different polyesters derived from azobenzenedicarbonyl chlorides and various hydroxy compounds like polyvinyl alcohol and bis(phenols)
disclose that the above physical properties of the polyester can be photochemically controlled, since these properties are direct manifestations of macromolecular conformations. The polymeric systems studied are characteristic in that they contain photochromic azo moieties either in the polymer backbone or as pendant groups. The photochromic phenomenon of these polymers is mainly attributed to the isomerisation reaction. This leads to a configuration change in the chromophore which in turn induce an overall conformational change in the polymer molecule.
EXPERIMENTAL