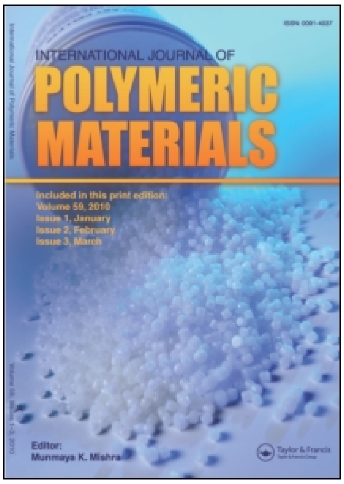

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Synthesis and Characterization of Photochromic Imidazolone Azopolycyanurates

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Photochromic imidazolone azopolycyanurates containing mercury dithizonate moiety have been prepared by interfacial polycondensation technique. All the azopolycyanurates have been characterized by their IR spectra, viscosity, molecular weight by GPC and thermogravimetry. The film of PMMA blended with photochromic imidazolone azopolycyanurate shows a very good photochromic effect on exposure to sunlight and regains its original colour on removal of sunlight. The change of return to the original colour have been measured using Beckman DK-2A Ratio Recording Spectrophotometer.

Keywords: Photochromic imidazolone azopolycyanurates; azopolycyanurates

INTRODUCTION

In continuation of our research work on photochromic polycyanurates/azopolycyanurates [1, 2], the present work comprises the synthesis and characterization of some novel photochromic imidazolone azopolycyanurates containing mercury dithizonate moiety. The photochromic behaviour of one of these azopolycyanurate blended with PMMA have been studied.

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*Corresponding author.

EXPERIMENTAL

Materials

Bisphenol-A and 2:7-dihydroxy naphthalene used were of commercial grade. They were further purified by crystallization. Other diols used were prepared by the method described earlier [3].

Synthesis of 2-phenyl-4-(4-hydroxybenzylidene)-5-oxazolone (I)

2-phenyl-4-(4-hydroxybenzylidene)-5-oxazolone was synthesized as described in literature [4].

Synthesis of 1-(4-aminophenyl)-2-phenyl-4-(4-hydroxybenzylidene)-5-imidazolone (II)

1-(4-aminophenyl)-2-phenyl-4-(4-hydroxybenzylidene)-5-imidazolone was synthesized as described in literature [5].

Synthesis of *p*-aminophenyl mercuric acetate (III)

p-aminophenyl mercuric acetate was synthesized as described in literature [6].

Synthesis of Dye (IV)

The dye (IV) was prepared by diazotizing the compound (III) and coupled with 1-(4-aminophenyl)-2-phenyl-4-(4-hydroxybenzylidene)-5-imidazolone (II) in the usual manner. The purity of the product was checked by tlc using DMF-chloroform (2 : 5) as solvent system and silica gel G as adsorbent.

Synthesis of Monomer (V)

Cyanuric chloride (1.84 g, 0.01 mol) in acetone (40 ml) was added with stirring to a solution of sodium bicarbonate (1.06 g) in distilled water (100 ml) at 0–5°C. To the resultant slurry, dye (IV) (7.17 g, 0.01 mol) was added. The mixture was stirred for two and half hour. The light brown product separated was filtered, washed with cold water and finally dried at room temperature, yield (82%), crystallized in benzene, m.p. 245–248°C (d). IR(KBr) : 3270–3390 cm^{-1} (—NH), 1700 cm^{-1} (C=O) 1450 cm^{-1} (—N=N—), 1600, 1570, 1480, 760 cm^{-1} (phenyl ring), 800–810 cm^{-1} (s-triazine ring) and 600–800 cm^{-1} (C—Cl).

Analysis: Found: C, 45.6%; H, 2.6%; N, 12.9%; Hg, 23.0%.

Calculated: C, 45.8%; H, 2.5%, N, 13.0%; Hg, 23.1%

for $C_{33}H_{22}N_8O_4Cl_2Hg$.

Synthesis of Azopolycyanurates (A)

A mixture of appropriate diol bisphenol-A (2.28 g, 0.01 mol), sodium hydroxide (0.8 g, 0.02 mol) and benzyl dimethyl hexadecyl ammonium bromide (0.15 g) in distilled water (25 ml) was charged in a three necked flask equipped with a stirrer, condenser and a thermometer and was allowed to stir vigorously at 40–45°C. To this, a solution of monomer (4.33 g, 0.005 mol) in chloroform (25 ml) was rapidly added and the emulsion was stirred vigorously for 5–6 hours at 40–45°C.

The contents were transferred in separating funnel and the aqueous layer was removed. The chloroform layer was washed with water and finally run into an excess of methanol. The polymers (A-1 – A-4) were precipitated out, filtered, washed thoroughly with water and finally with methanol and dried at room temperature. The physical properties of all the azopolycyanurates (A-1 – A-4) are presented in Table I.

Synthesis of Diphenylthiocarbazone (Dithizone)

Diphenylthiocarbazone (Dithizone) was synthesized as described in literature [7].

TABLE I Percentage yield, melting point and product appearance of azopolycyanurates (A)

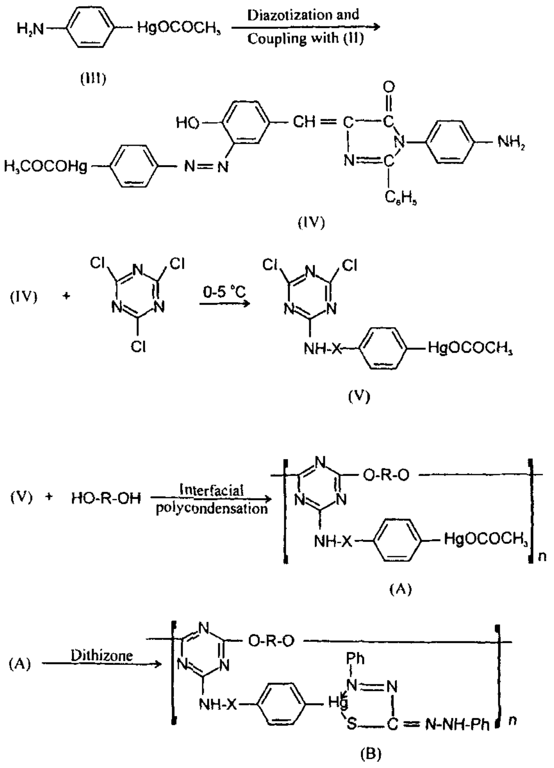
Azopolycyanurate (A)	*Aromatic diol*	*Yield (%)*	*m.p. (d)*	*Product appearance*
A-1	Bisphenol-A	82	315–20	Brown
A-2	Bisphenol-C	70	305–07	Brown
A-3	Methyl bisphenol-C	74	290–93	Brown
A-4	2:7-Dihydroxy naphthalene	79	296–99	Brownish red

Synthesis of Photochromic Imidazolone Azopolycyanurates (B)

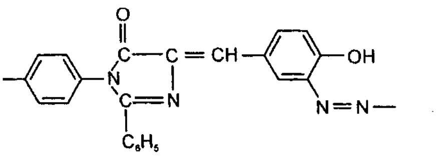
Azopolycyanurate A-1 (0.01 mol), dithizone (0.01 mol) and sodium carbonate (0.035 mol) were added to vigorously stirred mixture of water (100 ml) and chloroform (150 ml) at room temperature. The mixture was stirred vigorously for 3 hours and the resulting red coloured solution was evaporated under vacuum to obtain an orange-red coloured solid. The solid product was washed with water and dried. The physical properties of all the photochromic imidazolone azopolycyanurates (B-1 – B-4) are presented in Table II.

The general synthesis of the photochromic imidazolone azopolycyanurates is shown in Reaction Scheme 1.

REACTION SCHEME 1



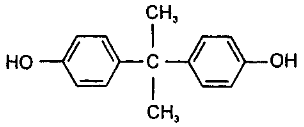
where X =



HO-R-OH represents various aromatic diols as listed in Table A.

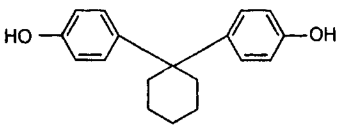
TABLE A

(a)



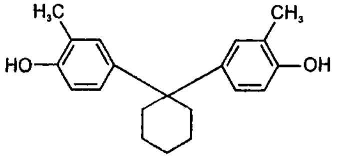
Bisphenol-A

(b)



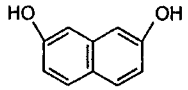
Bisphenol-C

(c)



Methyl bisphenol-C

(d)



2 : 7 - Dihydroxy naphthalene

TABLE II Percentage yield and physical properties of photochromic imidazolone azopolycyanurates (B)

Photochromic imidazolone azopolycyanurate (B)	*Yield (%)*	*m.p. (°C)*	*Absorption maxima*[a] *λ_{max} (nm)*	*Molecular weight ($\overline{Mn}$)*[b] *$\times 10^3$*	*Viscosity $[\eta]^c$ DL/G*	*Product appearance*
B-1	84	179–85	502	7.93	0.17	Red
B-2	76	210–17	504	6.60	0.14	Red
B-3	78	180–86	511	6.66	0.18	Red
B-4	81	187–92	509	7.92	0.14	Red

[a] Absorption spectra in chloroform.

[b] Gel permeation chromatography in THF based on polystyrene standards.

[c] Intrinsic viscosity in DMF at 36°C.

MEASUREMENTS

Spectral Analysis

Visible spectra were recorded on Shimadzu-160A UV/VIS Spectrophotometer. A Nicolet-400D FT-IR Spectrophotometer was used for infrared spectra of the samples in KBr pellets.

Viscometry

Intrinsic viscosity of the photochromic imidazolone azopolycyanurates were measured in DMF at $36 \pm 0.05°C$ with a Ubbelohde viscometer.

Molecular Weight

Number average molecular weights $(\overline{Mn})$ of the photochromic imidazolone azopolycyanurates were determined by Gel permeation chromatography (GPC) using Water's gel permeation chromatography station consisting of 600E multisolvent delivery system, ultrastyragel GPC columns packed with styrene-DVB porous copolymer beads of 10^3 A° and 10^6 A° pore size connected in series, 410-Differential Refractive Index detector and powermate 386/25 NEC data station with 820 maximum GPC software. THF was used as a mobile phase at 1.0 ml/mm flow rate. GPC system was calibrated with eight polystyrene standards of different molecular weight.

Thermogravimetric Analysis

The thermal stability of the azopolycyanurates were determined with a Du pont 951 thermogravimetric analyzer connected with a Dupont 990 thermal analyzer in static air at a heating rate of 10°C/min.

Kinetic Study

The photochromic behaviour was carried out using Beckman DK-2A, Ratio Recording Spectrophotometer using sunlight as an irradiation source.

Film (0.05 mm) of photochromic imidazolone azopolycyanurate blend was prepared by blending photochromic imidazolone azopolycyanurate sample B-1 (0.020 g) with polymethylmethacrylate (2.5 g) in dry chloroform (30 ml) and spreading it over a glass plate followed by evaporation of the solvent at room temperature. The film was elapsed for atleast overnight (24 hours) before measurement of photochromism. The film was exposed to natural bright sunlight in the summer season for 0.5 – 20 mins. and immediately placed in a Beckman DK-2A, Ratio Recording Spectrophotometer. The change of absorbance was recorded by scanning a spectrum at various time intervals at 37°C. Absorption spectra of infinite time was taken after several days.

RESULTS AND DISCUSSION

All the photochromic imidazolone azopolycyanurates were characterized by infrared spectra, visible spectra, intrinsic viscosity, gel permeable chromatography and thermogravimetric analysis.

Spectral Analysis

All the IR spectra (not shown) showed common characteristic absorption bands in the region 3200 – 3450 cm^{-1} due to O—H and N—H stretching vibration. Bands observed at 1690 cm^{-1} and 1630 cm^{-1} are due to C=O and C=N stretching vibration respectively. Bands at 1600, 1570 and 1490 cm^{-1} and 1630 cm^{-1} are due to aromatic C=C stretching vibrations. A weak band at 1550 – 1575 cm^{-1} is observed due to —N=N— stretching vibration. Bands observed in the region 1430 – 1670 cm^{-1} and 815 – 830 cm^{-1} may be attributed to in plane and out of plane vibration of s-triazine ring respectively, while in the region 1240 – 1300 cm^{-1} may be due to vibrations involving aryl ether linkage [8 – 10]. Bands around 1190 – 1200 (m), 1152 (m) cm^{-1} are due to N—C—S vibrations and around 690 – 725 (s) cm^{-1} (C—S) and 560 (w) cm^{-1} are due to N—M [11] stretching clearly indicates the presence of mercury (II) dithizonate moiety [12].

Other characteristic bands observed for a particular sample are as follows.

Bands at 1180 cm^{-1} and 550 cm^{-1} are due to vibration of propyl linkage (bisphenol-A) and sharp bands observed at 980 cm^{-1} and 520 cm^{-1} are due to the cyclohexane ring (bisphenol-C and methyl bisphenol-C).

Viscometry/Molecular Weight

The intrinsic viscosity and number average molecular weights ($\overline{Mn}$) of all the photochromic imidazolone azopolycyanurates are listed in Table II. The $\overline{Mn}$ data obtained from GPC measurements reveal that these photochromic imidazolone azopolycyanurates are of low molecular weight ranging from $6.6 \times 10^3 - 7.9 \times 10^3$.

Thermogravimetric Analysis

Thermogravimetric curves (not shown) were obtained at a scan rate of 10°C/min. for selected two azopolycyanurates and photochromic imidazolone azopolycyanurates.

The characteristic temperature for the assessment of relative thermal stability of polymer such as initial decomposition temperature T_0, temperature for 10% weight loss T_{10}, temperature for maximum rate of decomposition $T_{\max}$, integral procedure decomposition temperature IPDT and the activation energy E of the degradation process were calculated by Doyle's [13] and Broido's [14] method respectively. The data are summarized in Table III. All the azopolycyanurates and photochromic imidazolone azopolycyanurates degrade thermally in

TABLE III Temperature characteristics for thermal decomposition of azopolycyanurates (A) and photochromic imidazolone azopolycyanurates (B)

No.	T_0 (°C)	T_{10} (°C)	T_{max} (°C) Step-I	T_{max} (°C) Step-II	*IPDT* (°C)	*Activation energy (E) (KJ/mole)* Step-I	*Activation energy (E) (KJ/mole)* Step-II
A-1	250	275	425	487	368.88	30.31	23.42
B-1	175	210	450	575	373.75	15.22	32.11
A-3	213	257.5	392.5	540	383.40	28.42	22.19
B-3	187.5	215	497.5	595	383.05	16.08	34.84

T_0: Initial decomposition temperature.
T_{10}: Temperature for 10% weight loss.
$T_{\max}$: Temperature for maximum rate of decomposition.
IPDT: Integral procedure decomposition temperature.

two distinct steps. It is observed that azopolycyanurates have better thermal stability compared to the corresponding photochromic imidazolone azopolycyanurates.

Kinetic Study

(a) Spectral Change During Irradiation

The photochromic imidazolone azopolycyanurates PMMA-films on exposure to bright sunlight or a light source of suitable wavelength (500-W) tungsten lamp or 150-W Xenon lamp [15] showed very good photochromic effect. Figure 1 indicate the spectral change of a photochromic imidazolone azopolycyanurate (B-1)-PMMA film for different irradiation time at 37°C. A single peak at 465 nm is observed for before irradiation due to yellow orange colour. On exposure to bright sunlight a new peak appears at longer wavelength (580 nm) due to greyish blue colour, presumably because of photoinduced isomerization [16].

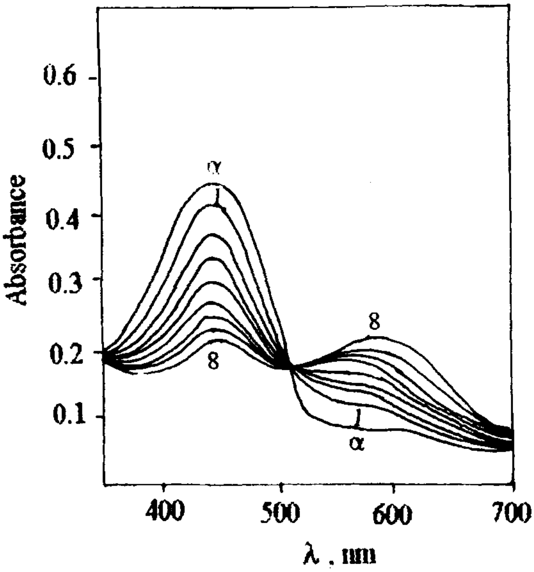


FIGURE 1 Spectral change of photochromic imidazolone azopolycyanurate (B-1)-PMMA film by irradiation at 37°C [(1) 30 sec. (2) 60 sec. (3) 120 sec. (4) 300 sec. (5) 420 sec. (6) 600 sec. (7) 900 sec. (8) 1200 sec. and (α) before irradiation].

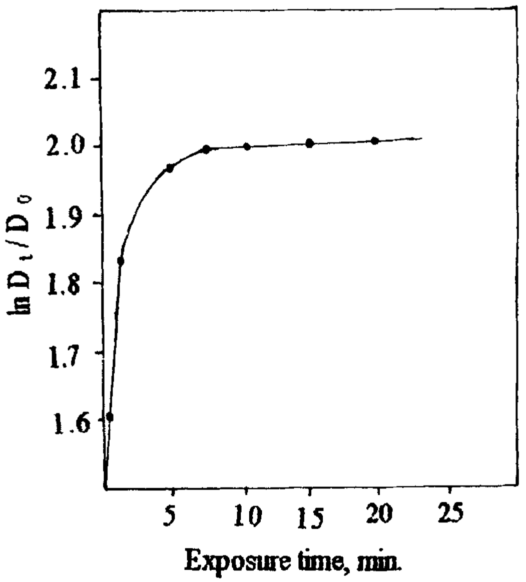


FIGURE 2 Relationship between ln D_t/D_o *vs.* t, where D_o and D_t denote the absorbance before and during irradiation respectively and t is the irradiation time at peak II.

It is observed that increasing the exposure time the intensity of the original peak decreased while that of the new peak increases. Table IV summarizes the results of the change in rate at different time intervals of the photochromic imidazolone azopolycyanurate (B-1)-PMMA film during irradiation. The first order rate constants k_1 and k_2 were determined by using the equation,

$$k_1 = \frac{2.303}{t} \log \frac{D_o}{D} \quad \text{and} \quad k_2 = \frac{2.303}{t} \log \frac{D}{D_o} \cdots\cdots \qquad (1)$$

where D_o and D denote absorbance before and during irradiation respectively, and t is an irradiation time.

(b) Spectral Recovery in the Dark

The spectral recovery in the dark is of thermal nature, the reverse process takes place rather slowly in the solid state such as film, at

TABLE IV Photochromic behaviour of polymeric blend of PMMA and photochromic imidazolone azopolycyanurate (B-1)

Irradiation time (sec.)	*Absorbance ratio light to dark*		*Isobestic point absorbance at 515 nm*	$k_1 \times 10^{-3,a}$ (*sec.*$^{-1}$)	$k_2 \times 10^{-3,b}$ (*sec.*$^{-1}$)
	Peak-I	*Peak-II*			
30	0.7357	3.7285	0.262	10.23	43.86
60	0.6915	4.4214	0.254	6.15	24.77
120	0.6615	4.6702	0.250	3.44	12.84
300	0.6479	4.6702	0.246	1.44	5.13
420	0.6190	5.3314	0.246	1.14	4.98
600	0.6104	5.3649	0.239	0.82	2.79
900	0.6000	5.6989	0.223	0.57	1.93
1200	0.5754	6.3286	0.207	0.46	1.54

[a] First order rate constant at peak-I (465 nm).
[b] First order rate constant at peak-II (580 nm).

ordinary temperatures. The rate of return to the original spectrum in the dark was measured by exposing the film to a bright sunlight for a fixed time (5 mins.) and recording the spectra after keeping for different time intervals in dark (1 min.. 45 mins... infinite). Typical spectra for film (B-1) are depicted in Figure 3. Compared to Figure 1 the reverse trend is observed *i.e.*, the intensity of peak I (465 nm) increases and peak II (580 nm) decreases with recovery time in the dark. A single isobestic point (Fig. 3) between active and normal forms indicates the absence of other reaction intermediates [16].

Figures 4 and 5 show the plots of absorbance versus returning time for different exposure time of peaks I and II respectively. The absorbance of peak I decreases while that of peak II increases with increasing exposure time. It is readily recognized that the return rate is rapid in the beginning which slows down after 5 mins. The rate of increase in intensity of peak I is less than the rate of decrease in intensity of peak II. The first order rate constant for the recovery of the photochromic imidazolone azopolycyanurate (B-1)-PMMA film was obtained from the expression [16],

$$k_2 \text{ obsd.} = \frac{2.303}{t} \log \frac{D_o}{D_t - D_\propto} \cdots\cdots \tag{2}$$

where D_o, D_t and $D_\propto$ refer to the absorbance at peak II, at the beginning of the run, at time t and after complete return respectively,

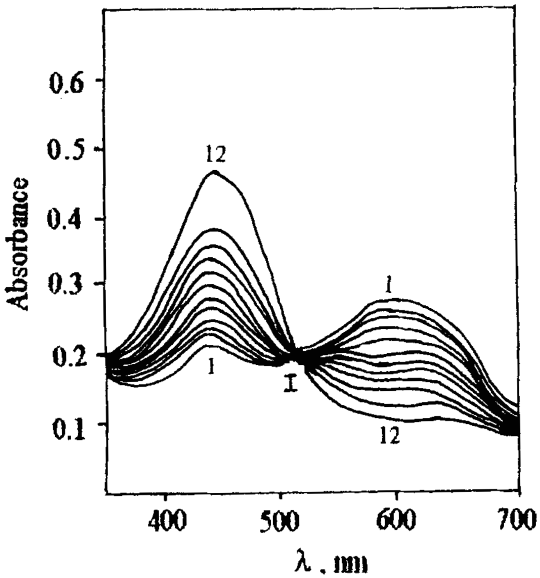


FIGURE 3 Visible spectrum of return reaction of the photochromic imidazolone azopolycyanurate (B-1)-PMMA film exposed to sunlight for 5 min. [(α) infinite time; (1) isobestic point, curve 1 – 12 shows 0, 1, 2, 3, 5, 7, 10, 20, 25, 30 min. after irradiation].

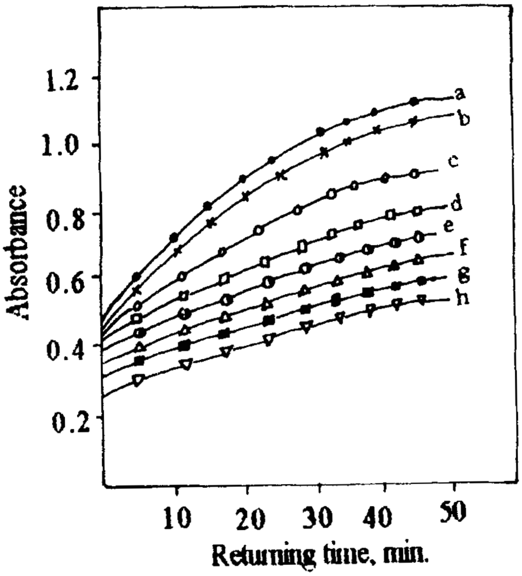


FIGURE 4 Relationship between the absorbance at (465 nm) with return reaction time in the dark at 37°C for the photochromic imidazolone azopolycyanurate (B-1)-PMMA film at different irradiation time [(a) 30 sec. (b) 60 sec. (c) 120 sec. (d) 300 sec. (e) 420 sec. (f) 600 sec. (g) 900 sec. and (h) 1200 sec.].

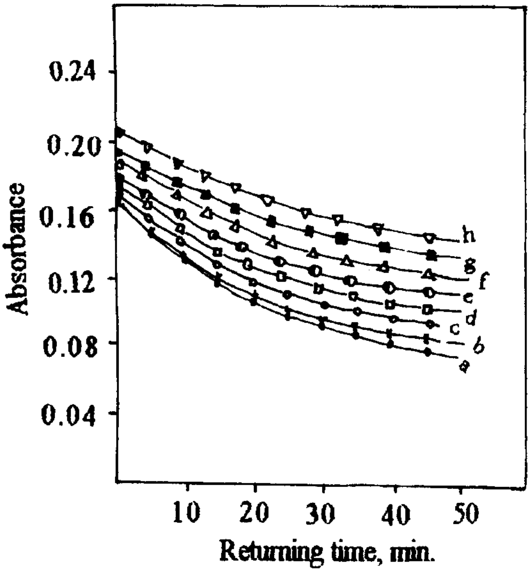


FIGURE 5 Relationship between the absorbance at (580 nm) with return reaction time in the dark at 37°C for the photochromic imidazolone azopolycyanurate (B-1)-PMMA film at different irradiation time [(a) 30 sec. (b) 60 sec. (c) 120 sec. (d) 300 sec. (e) 420 sec. (f) 600 sec. (g) 900 sec. and (h) 1200 sec.].

and the corresponding expression [16].

$$k_1 \text{ obsd.} = \frac{2.303}{t} \log \frac{D_\infty - D_o}{D_\infty - D_t} \cdots\cdots \qquad (3)$$

where D_o, D_t and D_∞ now refer to absorbance measured at peak I. Figure 6 shows a plot of ln $(D_o/D_t - D_\infty)$ *vs.* t at peak II and Figure 7 show a plot of ln $(D_\infty - D_o/D_\infty - D_t)$ *vs.* t at peak I for various exposure times. The rate constants k_1 and k_2 are calculated from the above plots. 50% recovery of the return absorbance in the dark at 580 nm was calculated from the terms $D_t/D_o \times 100$ (Fig. 8) where D_o and D_t denote the absorbance immediately after exposure time and returning time in the dark, respectively. Table V shows the results of recovery in the dark. It was found that the time for 50% recovery has been increased with increasing irradiation time. The rate constant k_1 and k_2 decrease with increasing in irradiation time. No regular trend is observed because of the experimental error.

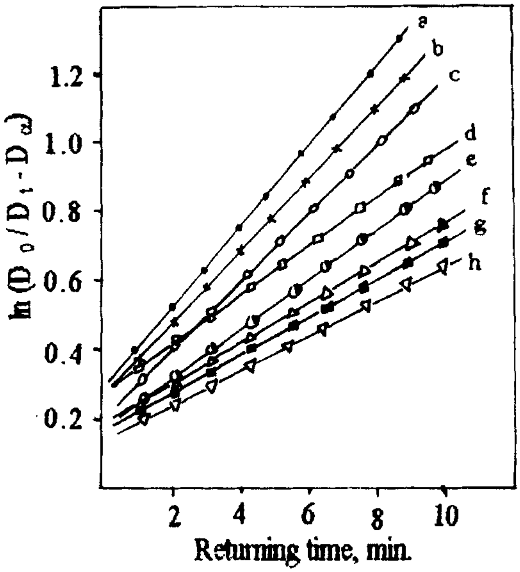


FIGURE 6 Relationship between ln $(D_o/D_t - D_{\alpha})$ *vs.* t, time of returning in the dark at peak II (580 nm) for the photochromic imidazolone azopolycyanurate (B-1)-PMMA film at different irradiation time [(a) 30 sec. (b) 60 sec. (c) 120 sec. (d) 300 sec. (e) 420 sec. (f) 600 sec. (g) 900 sec. and (h) 1200 sec.].

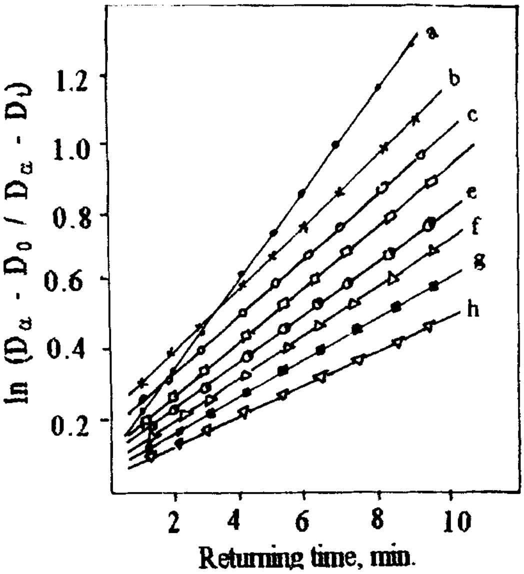


FIGURE 7 Relationship between ln $(D_{\alpha} - D_o/D_{\alpha} - D_t)$ *vs.* t, time of returning in the dark at peak I (465 nm) for the photochromic imidazolone azopolycyanurate (B-1)-PMMA film at different irradiation time [(a) 30 sec. (b) 60 sec. (c) 120 sec. (d) 300 sec. (e) 420 sec. (f) 600 sec. (g) 900 sec. and (h) 1200 sec.].

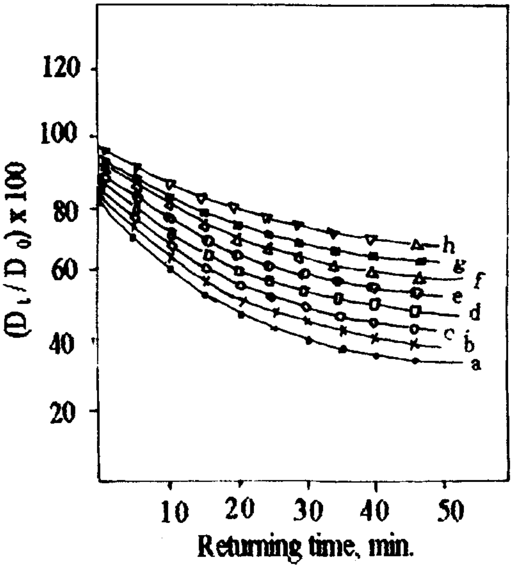


FIGURE 8 A plot of $(D_t/D_o)\times 100$ *vs.* t, where D_o and D_t denote the absorbance immediately after exposure time and returning time in the dark, respectively, t is returning time in min. [(a) 30 sec. (b) 60 sec. (c) 120 sec. (d) 300 sec. (e) 420 sec. (f) 600 sec. (g) 900 sec. and (h) 1200 sec.].

TABLE V Recovery in the dark, rate constant k_1 and k_2 for different irradiation time

Irradiation time (sec.)	*50% recovery time at peak II (min.)*	$k_1 \times 10^{-3,a}$ (*sec.*$^{-1}$)	$k_2 \times 10^{-3,b}$ (*sec.*$^{-1}$)
30	12	3.08	3.16
60	21	1.41	1.66
120	25	1.25	1.58
300	25	1.25	1.58
420	30	1.08	1.33
600	37	1.00	1.25
900	41	0.83	1.16
1200	45	0.75	1.10

[a] First order rate constant at peak-I (465 nm).
[b] First order rate constant at peak-II (580 nm).

CONCLUSIONS

All the photochromic imidazolone azopolycyanurates were obtained in good yield. The polymer blend with PMMA gives good photochromic effect. The thermograms of azopolycyanurates and photochromic imidazolone azopolycyanurates reveal that the simple azopolycyanurates are thermally more stable then the corresponding photochromic imidazolone azopolycyanurates.

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