Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Photochromic liquid-crystalline polymers. Main chain and side chain polymers containing azobenzene mesogens

A. S. Angeloni[a]; D. Caretti[a]; C. Carlini[a]; E. Chiellini[b]; G. Galli[b]; A. Altomare[b]; R. Solaro[b]; M. Laus[c]
[a] Dipartimento di Chimica Industriale e dei Materiali, Universitá di Bologna, Bologna, Italy [b] Dipartimento di Chimica e Chimica Industriale, Universitá di Pisa, Pisa, Italy [c] Dipartimento di Ingegneria Meccanica, Universitá di Brescia, Brescia, Italy

To cite this Article Angeloni, A. S. , Caretti, D. , Carlini, C. , Chiellini, E. , Galli, G. , Altomare, A. , Solaro, R. and Laus, M.(1989) 'Photochromic liquid-crystalline polymers. Main chain and side chain polymers containing azobenzene mesogens', Liquid Crystals, 4: 5, 513 — 527

To link to this Article: DOI: 10.1080/02678298908033186

URL: http://dx.doi.org/10.1080/02678298908033186

Liquid Crystals, 1989, Vol. 4, No. 5, 513–527

Photochromic liquid-crystalline polymers

Main chain and side chain polymers containing azobenzene mesogens†

by A. S. ANGELONI, D. CARETTI and C. CARLINI
Dipartimento di Chimica Industriale e dei Materiali, Universitá di Bologna,
Viale Risorgimento 4, 40136 Bologna, Italy

E. CHIELLINI‡, G. GALLI, A. ALTOMARE and R. SOLARO
Dipartimento di Chimica e Chimica Industriale, Universitá di Pisa,
Via Risorgimento 35, 56100 Pisa, Italy

and M. LAUS
Dipartimento di Ingegneria Meccanica, Universitá di Brescia, Via Valotti 9,
25060 Brescia, Italy

(*Received 28 October 1988; accepted 16 November 1988*)

Two classes of thermotropic polymers were synthesized containing the *trans*-azobenzene unit as both a mesogenic and a photochromic group. In the former class (**I**) the azobenzene unit is incorporated into the main chain of substituted polymalonates, while in the latter class (**II**) it is appended as a side chain substituent to a polyacrylate backbone. The liquid-crystalline properties of the polymers were studied as a function of the chemical structure. All of the prepared polymers **I** have smectic phases. Polymers **II** are nematic and/or smectic, or cholesteric when including a chiral residue *R'*. Polymers **I** and **II** when radiated at 348 nm in chloroform solution undergo *trans*-to-*cis* isomerization of the azobenzene moiety. The calculated rate constants are comparable with those of low molar mass model compounds, and indicate that the macromolecular structure does not significantly affect the photoisomerization rate.

1. Introduction

Polymers containing photochromic moieties which isomerize under U.V. irradiation may produce photo-induced conformational changes of the whole macromolecule, in terms of secondary and tertiary structures [1]. Such light effects have been invoked to explain many biological processes [2], and they have also been observed in optically active and achiral synthetic polymers both in solution [1, 3] and in the solid state [4, 5]. Recently liquid-crystalline polymers containing photochromic groups have been described [6–9]. In particular, the azobenzene moiety has been used as a photochromic mesogen in a variety of systems, comprising substituted polystyrenes and poly-α-methylstyrenes [10] and polyphosphazenes [11, 12]. In addition, potential applications of such materials in the field of optoelectronics [13], memory devices [14] and holography [15, 16] are attracting ever increasing interest.

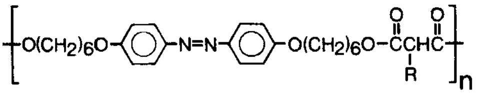
In this context two series of polymers have been prepared containing the *trans*-azobenzene unit placed in either the main chain or side chain (structures **I** and **II**) and

---

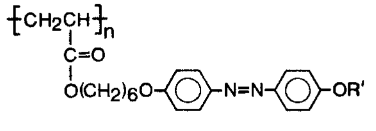
† Presented in part at the 8th A.I.M. Meeting, Milano, Italy, October 1987.

‡ To whom correspondence should be addressed.

their liquid-crystalline properties have been examined as a function of the structure of *R* and *R′*,



I (a–c)



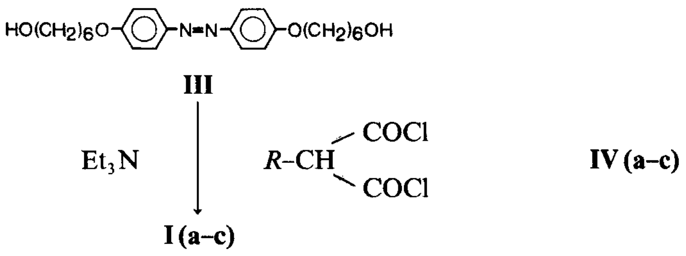
II (a–h)

In addition the photochromic behaviour of polymers **I** and **II** in solution has been investigated and compared with that of low molecular weight analogues in order to gain information about the influence of macromolecular structure on the *trans*-to-*cis* photomerization of the azobenzene moiety. Such an investigation is a prerequisite to the evaluation of the effects played by macromolecular connectivity and supermolecular structure on the photochromic behaviour of the polymers in bulk and stems from the combination of previous studies on the structure-property relationships in liquid-crystalline polymers [17–20] and on the light-induced conformational changes in synthetic polymers [21, 22].

2. Results and discussion

2.1. *Synthesis and liquid-crystalline properties*

Main chain azobenzene containing polymers **I** were prepared by homogeneous polycondensation reaction of 4,4′-bis(6-hydroxyhexyloxy)azobenzene (**III**) with different alkylmalonic acid dichlorides **IV (a–c)** as shown in Scheme 1.



I (a) $R = n\cdot C_3H_7$ (Pr)
I (b) $R = n\cdot C_4H_9$ (Bu)
I (c) $R = CH_2\text{-}CH^*\text{-}C_2H_5$ (2MB), with CH_3 on CH^*

Scheme 1

All the polymers prepared were characterized by F.T. I.R., ^{1}H N.M.R., ^{13}C N.M.R. (see the Experimental section) and G.P.C. analyses. Thermal and liquid-crystalline properties were investigated by combined differential scanning calorimetry (D.S.C.) and qualitative observation of the optical textures on the hot stage of a polarizing microscope. The values of phase transition temperatures as well as their

Table 1. Liquid-crystalline properties of polymers **I (a–c)** containing *trans*-azobenzene units in the main chain.

Polymer								
Sample	*R*†	[η]‡/dl g^{-1}	$\overline{\mathrm{Mn}}$§	T$_m$/K	T_{SI}/K	ΔH_{SI}/J mol^{-1}	ΔS_{SI}/J K^{-1}mol^{-1}	Mesophase
I (a)	Pr	0·53	16400	306	400	9600	23·9	S_A
I (b)	Bu	0·29	7200	337	402	8600	21·4	S_A
I (c)‖	2MB	0·38	14300	334	394	9800	24·9	S_A

† When $R = H$ (see [23]) T_m and T_{SI} values are 366 K and 421 K respectively.
‡ In chloroform at 30°C.
§ By G.P.C. in chloroform at 25°C.
‖ $[\alpha]_D^{25} = +5{\cdot}0$ (c = 1·6 g/dl, CHCl$_3$).

enthalpies and entropies (see table 1) were determined from the D.S.C. profiles of samples solidified from the isotropic melt at a cooling rate of 10 K/min.

The D.S.C. traces of all samples **I** show on heating a cold crystallization exotherm and two distinct endothermic transitions, the lower and higher temperature endotherm corresponding to melting and isotropization, respectively (see figure 1). On cooling, the latter transition shows a modest degree of supercooling (5–9 K), whereas this effect is rather pronounced for the former transition and a frozen mesophase is easily obtained and maintained at room temperature.

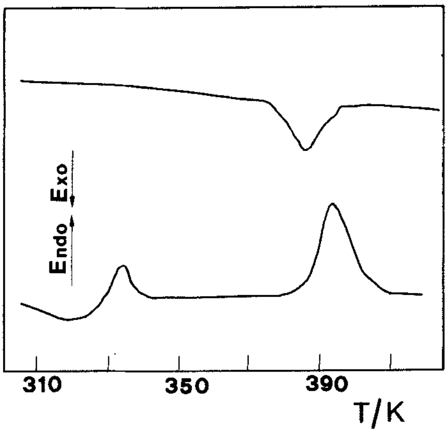
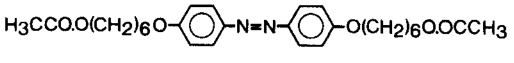


Figure 1. D.S.C. heating and cooling curves (10 K/min) for polymer **I (a)** (R = propyl).

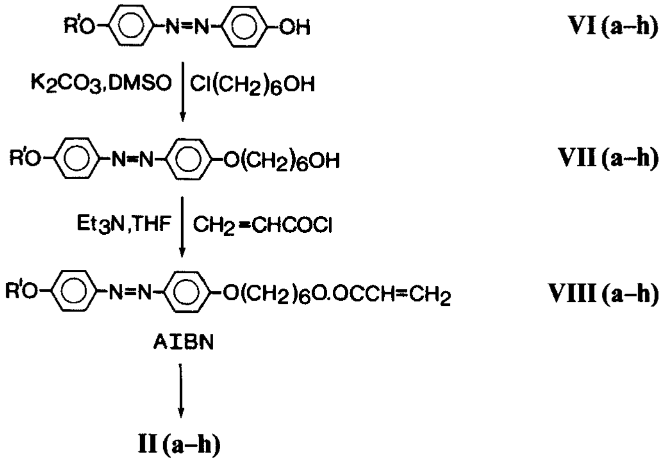
The rather high values of ΔH_i and ΔS_i (see table 1) and the optical observations of focal-conic textures indicate the formation of a smectic mesophase in these polymers. X-ray diffraction studies suggest the occurrence of S_A mesophases in all of them [24]. The replacement of a hydrogen atom by an alkyl group in the malonic residue of the repeating unit of **I** produces a decrease of both melting and isotropization temperature accompanied by an enlargement of the stability range of the mesophase (see table 1), as already reported for similar polymer systems [6]. This phenomenon is particularly evident when R = propyl (**I (a)**).

In contrast to what is observed for polymers **I**, the corresponding low molecular weight model compound **V** does not show any liquid-crystalline property, thus indicating that macromolecular structure favours the organization of the mesophase in such systems, as established for other thermotropic polymers [25, 26]



$T_m = 383\,K$ **V**

Side chain azobenzene containing polymers **II** were prepared from the corresponding acrylic monomers **VIII** by free radical polymerization, according to Scheme 2.



II (a) $R' = CH_3$ (Me) **II (e)** $R' = n \cdot C_5H_{11}$ (Pe)
II (b) $R' = C_2H_5$ (Et) **II (f)** $R' = n \cdot C_6H_{13}$ (He)
II (c) $R' = n \cdot C_3H_7$ (Pr) **II (g)** $R' = n \cdot C_{10}H_{21}$ (De)
II (d) $R' = n \cdot C_4H_9$ (Bu) **II (h)** $R' = C_5H_{11}*$ (2MB)

Scheme 2

Samples **VIII** were synthesized by reacting acryloyl chloride with the corresponding 4-alkyloxy-4′-(6-hydroxyhexyloxy)azobenzene (**VII**), as obtained from 4-alkyloxy-4′-hydroxyazobenzene (**VI**).

Spectroscopic analyses of polymers **II**, monomers **VIII**, as well as of the corresponding precursors **VI** and **VII** are in accord with the expected structures reported in Scheme 2 (see the Experimental section). Thermal and liquid-crystalline properties of precursors **VII**, acrylic monomers **VIII** and polymers made from these were investigated by combining D.S.C. measurements and optical observations of birefringent textures (see tables 2–4).

Precursors **VII** show a nematic phase, but when *R′* contains an odd number of carbon atoms monotropic transitions are observed, whereas enantiotropic transitions occur when the number of carbon atoms in *R′* is even with the only exception being **VII (g)** (see table 2).

For the acrylic monomers **VIII** no regular trend is observed for melting or isotropization temperatures. However, an enhancement of mesogenic propensity is observed on increasing the chain length of *R′* and the nature of the mesophase progressively changes from nematic to smectic (see table 3).

Table 2. Liquid-crystalline properties of the 4-alkyloxy-4′-(6-hydroxyhexyloxy)azobenzenes **VII (a–h)**†.

Sample	R'	T_m/K	T_{NI}/K	ΔH_{NI}/J mol^{-1}	ΔS_{NI}/J K^{-1}mol^{-1}
VII (a)	Me	309	(393)‡	1150	2·9
VII (b)	Et	396	408	1750	4·3
VII (c)	Pr	399	(391)‡	nd§	nd§
VII (d)	Bu	396	399	1800	4·5
VII (e)	Pe	393	(390)‡	1550	4·0
VII (f)	He	390	391	1750	4·4
VII (g)	De	391	(386)‡	nd§	nd§
VII (h)	2MB	363	—	—	—

† On heating, unless otherwise indicated.

‡ Detected at 10 K/min cooling rate, monotropic transition in parentheses.

§ D.S.C. overlapping peaks.

Table 3. Liquid-crystalline properties of the acrylic monomers **VIII (a–h)**†.

Sample	R'	T_m/K	$T_{\substack{\mathrm{NI}\\(\mathrm{SI})}}$ ‡/K	$\Delta H_{\substack{\mathrm{NI}\\(\mathrm{SI})}}$ /J mol^{-1}	$\Delta S_{\substack{\mathrm{NI}\\(\mathrm{SI})}}$ /J K^{-1}mol^{-1}	Mesophase
VIII (a)	Me	362§	—	—	—	—
VIII (b)	Et	366	367	950	2·7	N
VIII (c)	Pr	372	—	—	—	—
VIII (d)	Bu	369	(366)§	900	2·5	N
VIII (e)	Pe	363	(362)§	950	2·7	N
VIII (f)	He‖	358	368	1250	3·4	S, N
VIII (g)	De	347	368	8250	22·4	S
VIII (h)	2MB	366	—	—	—	—

† On heating, unless otherwise indicated.

‡ Detected at 10 K/min cooling rate, monotropic transition in parentheses.

§ By optical microscopy observation.

‖ Monotropic smectic–nematic transition at 358 K (ΔH_{SN} = 1400 J/mol and ΔS_{SN} = 4·0 J/K mol).

All polymers **II** display at least two phase transitions (see figure 2). The higher temperature process corresponds to the isotropization of the mesophase, while the lower temperature transition may be related to the transformation of a crystalline or ordered smectic phase into a different smectic or a nematic mesophase. Very limited degrees of supercooling (3–4 K) are observed on cooling from the isotropic melt. The liquid-crystalline properties of the polymers are summarized in table 4. A clear odd–even effect is detected for the isotropization temperature on varying the length of the alkyl substituent R', the members with even numbers n of alkyl chain carbon atoms showing higher values (see figure 3). The lower homologues (R' = methyl–propyl) possess a nematic phase, as evidenced by polarization microscopy and D.S.C. However, on increasing the chain length of R', an additional smectic phase is detected (R' = butyl, pentyl) (see figure 2), and eventually the polymers become purely smectic at $n > 6$ (see figure 3). Accordingly, the isotropization entropies vary in a substantial way from 2·0 J/K mol for **II (a)** (R' = methyl) to 19·1 J/K mol for **II (g)** (R' = decyl). Therefore, extension of the length of the terminal tail increases the smectogenic tendency of the polymer system, in agreement with low molar mass [27] and other polymer [28, 29] liquid crystals. The chiral polymer **II (h)** containing the

Table 4. Liquid-crystalline properties of the polymers **II (a–h)** containing *trans*-azobenzene units in the side chain.

Polymer											
Sample	*R′*	[η]†/dl g^{-1}	$\overline{\mathrm{Mn}}$‡	T_m/K	T_{SN}/K	T_i/K	ΔH_{SN}/J mol^{-1}	ΔH_i/J mol^{-1}	ΔS_{SN}/J mol^{-1} K^{-1}	ΔS_i/J mol^{-1} K^{-1}	Mesophase
II (a)	Me	0·06	38 000	370	—	403	—	800	—	2·0	N
II (b)	Et	0·13	370 000	360	—	430	—	950	—	2·2	N
II (c)	Pr	0·13	390 000	374	—	421	—	1250	—	2·9	N
II (d)	Bu	0·09	170 000	387	(384)§	427	900	1150	2·3	2·7	S, N
II (e)	Pe	0·07	79 000	378	402	416	1100	800	2·7	1·9	S, N
II (f)	He	0·09	99 000	373	—	420	—	4800	—	11·4	S
II (g)	De	0·10	130 000	363	—	444	—	8500	—	19·1	S
II (h)‖	2MB	0·07	170 000	374	—	380	—	1300¶	—	3·5	N*

† In chloroform at 30°C.
‡ By G.P.C. in chloroform at 25°C.
§ Monotropic transition.
‖ $[\alpha]_D^{25} = 6{\cdot}5$ ($c = 1{\cdot}3$ g/dl; $CHCl_3$).
¶ D.S.C. overlapping peaks.

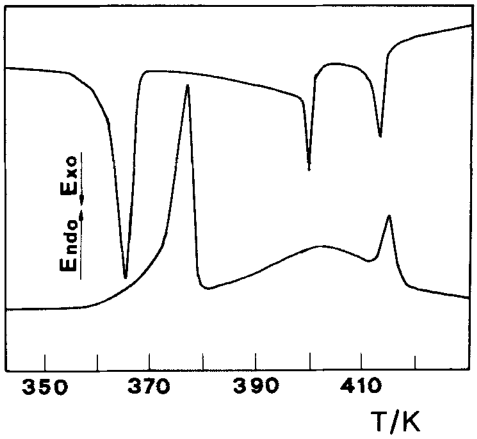


Figure 2. D.S.C. heating and cooling curves (10 K/min) for polymer **II (e)** (R' = pentyl).

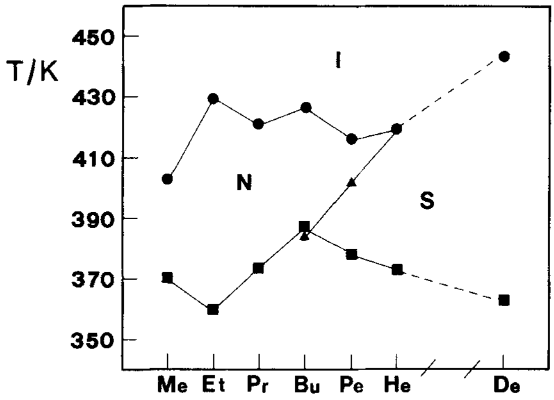
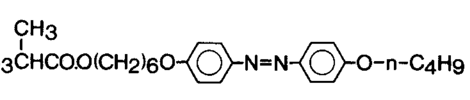


Figure 3. Phase transition temperatures for polymers **II (a–g)** as a function of the length of the *n*-alkyl substituent R': ■, T_m; ▲, T_{SN}; ●, T_i.

(S)-2-methylbutyl terminal substituent has a cholesteric phase of limited extent. A detailed investigation by X-ray diffraction of the structure of the mesophases and the phases below T_m is in progress [24].

Model compound **IX (d)** has an enantiotropic nematic phase of narrow persistence (5 K), while a monotropic smectic phase can be observed at 340 K. All of these results further demonstrate that incorporation of mesogenic monomers into a polymer backbone stabilizes the liquid-crystalline order and extends the mesophasic range [30, 31].


$$\mathrm{HC_3\overset{CH_3}{\overset{|}{C}}HCO.O(CH_2)_6O{-}C_6H_4{-}N{=}N{-}C_6H_4{-}O{-}n{-}C_4H_9}$$

$$T_m = 351\,\mathrm{K},\ T_{SN} = (340)\,\mathrm{K},\ T_{NI} = 356\,\mathrm{K}$$

$$\Delta H_{SN} = 400\,\mathrm{J/mol},\ \Delta H_{NI} = 1400\,\mathrm{J/mol}$$

IX (d)

2.2. *Photochromic behaviour in solution*

All *trans*-azobenzene containing polymers **I** and **II** as well as their related low molecular weight analogues **V** and **IX (d)** show, in chloroform solution, a strong U.V. absorption band centred at about 360 nm and a shoulder at around 440 nm (see table 5) attributed to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ electronic transitions of the *trans*-azobenzene chromophore [32], respectively. Within the limits of experimental error no simple correlation can be established between the molar extinction coefficient of the two bands and the polymer structure. However, for polymers **II**, the maximum position of the $\pi \rightarrow \pi^*$ electronic transition shifts to longer wavelengths with increasing length of the chain R' (see table 5).

Table 5. U.V. absorption properties and photochromism of polymers **I** and **II** and of some related low molecular weight analogs **V** and **IX (d)**† containing the *trans*-azobenzene unit

		$\pi \rightarrow \pi^*$		$n \rightarrow \pi^*$	Photoisomerization‡
Sample	R or R'	λ_{max}/nm	ε_{max}/l mol^{-1} cm^{-1}	ε_{440}/l mol^{-1} cm^{-1}	rate constant $\times 10^2$/s^{-1}
I (a)	Pr	358	25 000	2600	13·1
I (b)	Bu	358	25 000	2600	13·8
I (c)	2MB	358	24 500	2600	15·0
V	—	358	26 000	2700	14·6
II (a)	Me	356	26 500	2100	12·6
II (b)	Et	356	25 000	2200	13·1
II (c)	Pr	357	27 000	2300	14·0
II (d)	Bu	358	29 000	2200	14·9
II (e)	Pe	358	28 000	2400	12·6
II (f)	He	358	28 000	2300	12·4
II (g)	De	358	28 500	2100	11·6
II (h)	2MB	358	26 500	2100	13·5
IX (d)	Bu	360	26 000	2300	15·1

† In chloroform solution at room temperature.

‡ Rate constants normalized at the same lamp radiation intensity at 348 nm.

All samples undergo *trans*-to-*cis* photoisomerization of the azobenzene moiety upon irradiation at 348 nm in the $\pi \rightarrow \pi^*$ absorption region. The intensity of the U.V. absorption bands decreases with irradiation time in the 360 nm region but increases below 320 nm and above 425 nm. At the same time, the shoulder at about 440 nm gradually becomes more resolved giving rise at the photostationary state to an absorption band with a distinct maximum at 445 nm (see figure 4). The occurrence of two distinct isobestic points at 425 and 320 nm as well as the similarity of the U.V. spectra of the irradiated samples at the photostationary state with that of *cis*-azobenzene [32] indicate that only two absorbing species (*trans* and *cis* isomers) are present and no side reactions such as photocrosslinking or photodegradation occur.

In all cases ln $\{(A_0 - A_\infty)/(A_t - A_\infty)\}$, where A_0, A_t and A_∞ are the absorbances at 356 nm at zero time, t and infinite, respectively, shows a linear dependence on the irradiation time (see figure 5) as expected for first order kinetics [33].

Photoisomerization rate constants (see table 5) in all polymer samples **I** and **II** are very similar and of the same order of magnitude as those observed for the low

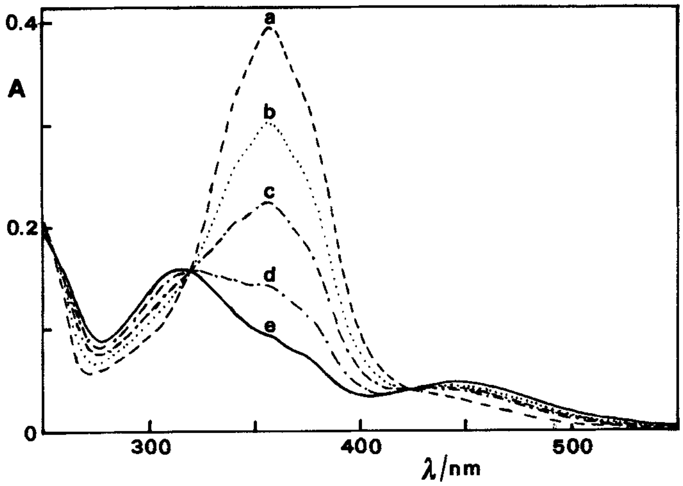


Figure 4. Variation of the U.V. absorption spectra of polymer **II (a)** (R' = methyl) in chloroform solution with irradiation time at 348 nm. Curves *a* to *e* refer to irradiation times of 0, 3, 7, 15 and 50 s, respectively.

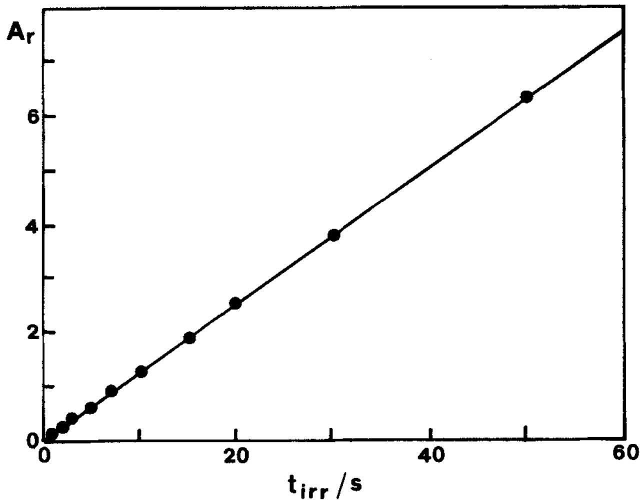


Figure 5. Plot of $A_r = \ln[(A_0 - A_\infty)/(A_t - A_\infty)]$ versus irradiation time for polymer **II (a)** (R' = methyl) in chloroform solution.

molecular weight analogs **V** and **IX (d)**. These results indicate that the macromolecular structure does not significantly affect the photoisomerization rate, probably due to the presence of the flexible hexamethylene spacers. However, within the limitations of the small variation range, the reported data seem to indicate that the photoisomerization rate increases for polymers **II** with increasing length of the alkyl substituent up to four carbon atoms and then progressively decreases (see table 5). Finally, the value of the rate constants of polymers **I** and **II** as well as of the related model compounds are one order of magnitude higher than those observed for homopolymers of 4-acryloxyloxy- or 4-methacryloyloxy-azobenzene [21, 34] suggesting that the 4,4′-dialkyloxy substituents on the azobenzene chromophore favour the *trans*-to-*cis* isomerization.

3. Experimental

3.1. *Materials*

3.1.1. *Main chain polymers* (**I**)

4,4′-bis-(6-hydroxyhexyloxy)azobenzene (**III**) was prepared as described elsewhere [35].

Alkylmalonic acid dichlorides **IV (a–c)** were synthesized by reacting the corresponding alkylmalonic acids with thionyl chloride as previously reported [36]. For this, commercial *n*-butylmalonic acid from Aldrich was used, whereas *n*-propyl- and (+)(*S*)-2-methylbutylmalonic acids were prepared [37] by alkaline hydrolysis with aqueous potassium hydroxide from the corresponding diethyl-alkylmalonates. These latter compounds were prepared by reacting diethylmalonate with the corresponding alkyl bromide or chloride by standard procedures [37, 38]. The purity of all precursors **IV (a–c)** was checked by F.T. I.R., ^{1}H N.M.R. and T.L.C. analyses.

Polymers **I (a–c)** were obtained by reacting, under dry nitrogen, **IV (a–c)** with an equimolar amount of **III** in 1,2-dichloroethane (DCE) solution and in the presence of excess triethylamine.

As a typical example the preparation of sample **I (a)** is described in detail. 0·571 g (1·38 mmol) of **III** was allowed to react with 0·296 g (1·38 mmol) of **IV (a)** in 20 ml of anhydrous DCE in the presence of 1 ml of triethylamine. The mixture was maintained at reflux under magnetic stirring for 2 h, and after removal of the solvent under vacuum it was treated with water, methanol and diethylether in that order. The crude polymer (yield 85 percent) was purified from oligomeric products by prolonged extraction in a Kumagawa apparatus [39] with boiling methanol until these fractions were completely removed, as checked by G.P.C. measurements.

The polymer sample was characterized by I.R. (typical bands at 3071, 2940, 2868, 1731, 1603, 1250, 844 cm^{-1}) and ^{13}C N.M.R. The assignments for the carbon atoms present in the structural unit of **I (a)** are listed in table 6.

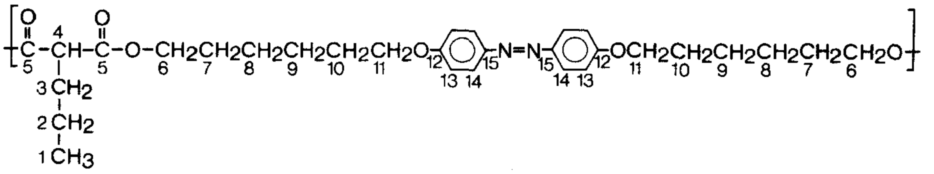
3.1.2. *Side chain polymers* (**II**)

4-alkyloxy-4′-hydroxyazobenzenes **VI (a–h)** were prepared starting from 4-nitrophenol via its etherification [40] with the appropriate alkyl bromide or chloride, successive reduction to 4-alkyloxyaniline by sodium borohydride in the presence of 10 per cent Pd/C as the catalyst [41], and finally by coupling reaction of the corresponding diazonium salt with phenol [42]. Whereas **VI (a)**, **VI (b)** and **VI (d)** were previously reported in the literature [43] the other members of the series were unknown.

All **VI (a–h)** samples and relevant precursors were characterized by F.T. I.R. and ^{1}H N.M.R. spectroscopy and their purity was also checked by T.L.C. analysis. Some details about reaction yields and purification of **VI (a–h)** are given in table 7.

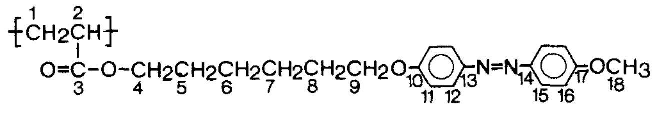
4-alkyloxy-4′-(6-hydroxyhexyloxy)azobenzenes **VII (a–h)** were prepared by reacting **VI (a–h)** with 6-chloro-1-hexanol (1 : 1·5 molar ratio) in DMSO solution and in the presence of excess anhydrous potassium carbonate. The reaction mixture was allowed to stay at 120°–130°C for about 2 h under vigorous stirring and then was poured into 10 per cent aqueous sodium hydroxide. The precipitated solid was filtered, washed several times with water, dried under vacuum and recrystallized. All the products were characterized by F.T. I.R., ^{1}H N.M.R. and T.L.C. analyses. Reaction yields, melting points and crystallization solvents for **VII (a–h)** are listed in table 7.

Table 6. ^{13}C–N.M.R. assignments for the carbon atoms present in the repeating unit of polymers **I (a)** and **II (a)**.



I (a)

II (a)



	II (a)			**I (a)**	
Carbon atom	δ calc./ppm	δ found/ppm	Carbon atom	δ calc./ppm	δ found/ppm
1	34·3	36·0	1	13·5	13·8
2	43·3	41·8	2	21·1	20·8
3	—	174·5	3	31·1	31·0
4	65·1	64·5	4	53·5	52·2
5–8	29·1	28.3	5	—	170·2
	29·2	25·5	6	65·1	65·5
	28·2	25·5	7–10	29·1	28·7
	31·1	29·0		29·2	25·8
9	72·1	68·1		28·2	25·9
10	161·9	161·3		31·1	29·3
11	114·1	114·2	11	72·1	68·4
12	123·7	124·4	12	161·9	161·7
13	145·0	147·2	13	114·1	115·1
14	145·0	147·3	14	123·7	124·8
15	123·7	124·4	15	145·0	147·6
16	114·1	114·8			
17	161·9	161·7			
18	55·5	55·4			

The 4-alkyloxy-4′-(6-acryloyloxyhexyloxy)azobenzene monomers **VIII (a–h)** were prepared by adding dropwise under dry nitrogen a slight excess of acryloyl chloride to the corresponding alcohol **VII (a–h)** dissolved in anhydrous THF at 0°C and in the presence of triethylamine. After stirring for about 1–2 h at room temperature, the reaction mixture was filtered, the solid washed with THF and the solvent was evaporated under vacuum to obtain a crude solid product. This last was generally crystallized at least twice from methanol until it was pure, as checked by T.L.C. analysis. All the **VIII (a–h)** samples were characterized by F.T. I.R. and ^{1}H N.M.R. spectroscopy. Details about reaction yields, melting points and crystallization solvents for **VIII (a–h)** are listed in table 7.

Polymers **II (a–h)** were prepared by free radical polymerization, at 60°C, of the corresponding monomers **VIII (a–h)** using 2,2′-azobis-isobutyronitrile (AIBN) (0·5 wt per cent with respect to the monomer) as a radical initiator.

Table 7. Characterization of acrylic monomers **VIII (a–h)** and their precursors **VII (a–h)** and **VI (a–h)**.

	VI			**VII**			**VIII**		
R′	Yield*/%	m.p./°C	Crystallization solvent	Yield†/%	m.p./°C	Crystallization solvent	Yield‡/%	m.p./°C	Crystallization solvent
Me	64	142	$H_2O/AcOH$	83	126	EtOH	60	89	MeOH
Et	87	125	$H_2O/EtOH$	59	123	EtOAc	56	93	MeOH
Pr	56	107	$H_2O/EtOH$	70	126	EtOAc	50	99	MeOH
Bu	73	109	$H_2O/EtOH$	78	123	C_6H_6	44	96	MeOH
Pe	95	104	C_6H_{12}	71	120	EtOAc	63	90	MeOH
He	92	99	C_6H_{12}	89	117	EtOAc	68	85	MeOH
De	81	105	MeOH	68	118	EtOAc	56	74	MeOH
2MB	47§	84	C_6H_{12}	58‖	90	C_6H_{12}	23¶	93	C_6H_{12}

* With respect to the corresponding 4-alkyloxyaniline.

† With respect to the corresponding **VI**.

‡ With respect to the corresponding **VII**.

§ $[\alpha]_D^{25} = +10{\cdot}4$ ($c = 0{\cdot}7$, $CHCl_3$).

‖ $[\alpha]_D^{25} = +7{\cdot}5$ ($c = 1{\cdot}9$, $CHCl_3$).

¶ $[\alpha]_D^{25} = +6{\cdot}9$ ($c = 1{\cdot}0$, $CHCl_3$).

As a typical example the synthesis of polymer **II (a)** is reported. 1 g (2·68 mmol) of **VIII (a)** dissolved in 5 ml of benzene, in the presence of 5 mg of AIBN, was introduced under nitrogen into a glass vial which was sealed under high vacuum after repeated freeze-thaw pump cycles. After 48 h the polymerization was stopped by pouring the reaction mixture into a large excess of methanol. The coagulated polymer **II (a)** was filtered and washed with hot methanol or diethylether several times until residual monomer and oligomers were completely removed, as checked by T.L.C. and G.P.C. analyses, respectively (yield 45 per cent). All the polymers were characterized by F.T. I.R., ^{1}H N.M.R., ^{13}C N.M.R. and G.P.C. analyses.

The F.T. I.R. spectrum of the polymer shows typical bands at 3073, 2942, 2867, 1733, 1600, 1251 and 843 cm^{-1}. In table 6 are listed ^{13}C N.M.R. assignments for the relevant carbons present in the polymer structural unit **II (a)**.

3.1.3. *Low molecular weight model compounds*

4,4′-bis-(6-acetyloxyhexyloxy)azobenzene (**V**) was prepared by adding dropwise 1·7 g (21·6 mmol) of acetyl chloride to a DCE solution of 3·0 g (7 mmol) of **III** in the presence of 2·2 g (21·6 mmol) of triethylamine, under vigorous stirring at −5° C. The mixture was allowed to rest for 1/2 h and then poured into cold water. The organic layer was separated, combined with ether extracts from aqueous phase and dried over anhydrous sodium sulphate. After removal of the solvent under vacuum and crystallization from ethylacetate 2·2 g of pure **V** (m.p. 110°C) was obtained as checked by T.L.C., ^{1}H N.M.R. and F.T. I.R. analyses (yield 63 per cent). (Typical I.R. bands at 3056, 2944, 2864, 1733, 1604, 1249 and 847 cm^{-1}).

4-butoxy-4′-(6-isobutyryloxyhexyloxy)azobenzene (**IX (d)**) was prepared by adding dropwise under stirring 1·3 g (12 mmol) of isobutyryl chloride in DCE solution to 1·5 g (4 mmol) of **VII (d)** dissolved in anhydrous DCE and in the presence of 1·2 g (12 mmol) of triethylamine. The reaction was allowed to proceed at room temperature for 2 h. After filtration and removal of the solvent under vacuum the residual solid was extracted with diethylether. After evaporation of ether and crystallization from ethanol, 1·0 g of pure **IX (d)** (m.p. 78°C) was obtained, as checked by T.L.C. ^{1}H N.M.R. and F.T. I.R. analyses (yield 59 per cent) (typical I.R. bands at 3074, 2955, 2943, 2864, 1723, 1602, 1241 and 843 cm^{-1}).

3.2. *Physicochemical measurements*

^{1}H and ^{13}C N.M.R. spectra were recorded at 200 MHz and 50·3 MHz, respectively, by using a Varian Gemini 200 spectrometer and solutions in $CDCl_3$.

I.R. spectra were recorded with a Perkin–Elmer model 1750 F.T. I.R. spectrophotometer on KBr pellets or cast films of the samples on KBr discs. Optical rotatory power measurements were carried out on $CHCl_3$ solutions at 25°C with a Perkin–Elmer 141 spectropolarimeter having a sensitivity of $\pm 0{\cdot}003°$.

Viscosity measurements were performed at 30°C on polymeric chloroform solutions by using an Ubbelohde dilution viscometer starting from a concentration of about 1 g/dl.

Number average molecular weights of polymer samples were determined in $CHCl_3$ solution by G.P.C. measurements with a 590 Waters chromatograph equipped with a Shodex column. Polystyrene standard samples were used for universal calibration.

Differential scanning calorimetry measurements were performed using a Perkin–Elmer DSC-7 apparatus under dry nitrogen flow at scanning rates of 10 K/min. The transition temperatures were taken as corresponding to the maximum and to the onset point of the enthalpic peaks for the polymer and the low molecular weight samples, respectively. The transition enthalpies were evaluated from the integrated area of the endothermic peaks using a reference indium sample as standard.

Optical microscopy observations were carried out with a Reichert Polyvar polarizing microscope equipped with a programmable hot stage. X-ray diffraction measurements were performed in a transmission mode with a conventional X-ray powder diffractometer; Ni-filtered CuK_α radiation ($\lambda = 1{\cdot}54$ Å) was used.

U.V. measurements in the 600–240 nm spectral region were performed at 25°C in $CHCl_3$ solution with a Jasco Uvidec 510 spectrophotometer. Irradiations were carried out with a halogen lamp (150 W) filtered with a 348 nm interference filter at 25°C on $CHCl_3$ solutions of the samples under stirring and in 1 cm path length quartz cuvette. The concentration of the solutions was adjusted to have an absorbance of about 0·4 at 358 nm.

The authors thank the Ministero della Pubblica Istruzione of Italy (Fondi 40 per cent) for support of this work.

References

[1] Ciardelli, F., Carlini, C., Solaro, R., Altomare, A., Pieroni, O., Houben, J. L., and Fissi, A., 1984, *Pure appl. Chem.*, **56**, 329.

[2] Erlanger, B. F., 1976, *Am. Rev. Biochem.*, **45**, 267.

[3] Irie, M., 1986, *Photophysical and Photochemical Tools in Polymer Science* (NATO ASI series C, Vol. 182), edited by M. A. Winnik (Reidel Publishing Co.), p. 269.

[4] Eisenbach, C. D., 1980, *Polymer*, **21**, 1175.

[5] Smets, G., 1983, *Adv. Polym. Sci.*, **50**, 17.

[6] Zentel, R., and Reckert, G., 1986, *Makromolek. Chem.*, **187**, 1915.

[7] Cabrera, I., Krongauz, V., and Ringsdorf, H., 1988, *Molec. Crystals liq. Crystals*, **155**, 221.

[8] Bualek, S., and Zentel, R., 1988, *Makromolek. Chem.*, **189**, 797.

[9] Tanaka, M., and Nakaya, T., 1988, *Makromolek. Chem.*, **189**, 771.

[10] Crivello, J. V., Deptolla, M., and Ringsdorf, H., 1988, *Liq. Crystals*, **3**, 235.

[11] Kim, C., and Allcock, H. R., 1987, *Macromolecules*, **20**, 1726.

[12] Singler, R. E., Willingham, R. A., Lenz, R. W., Furukawa, A., and Finkelmann, H., 1987, *Macromolecules*, **20**, 1727.

[13] Kaempf, G., 1987, *Polymer J.*, **19**, 257.

[14] Coles, H. J., and Simon, R., 1985, *Polymer*, **26**, 1801.

[15] Eich, M., and Wendorff, J. H., 1987, *Makromolek. Chem. rap. Commun.*, **8**, 467.

[16] Eich, M., Wendorff, J. H., Reck, B., and Ringsdorf, H., 1987, *Makromolek. Chem. rap. Commun.*, **8**, 59.

[17] Angeloni, A. S., Laus, M., Castellari, C., Galli, G., Ferruti, P., and Chiellini, E., 1985, *Makromolek. Chem.*, **186**, 977.

[18] Galli, G., Laus, M., Angeloni, A. S., Ferruti, P., and Chiellini, E., 1985, *Europ. polym. J.*, **21**, 727.

[19] Chiellini, E., and Galli, G., 1985, *Macromolecules*, **18**, 1652.

[20] Chiellini, E., Galli, G., Angeloni, A. S., Laus, M., and Pellegrini, R., 1987, *Liq. Crystals*, **2**, 529.

[21] Altomare, A., Carlini, C., Ciardelli, F., Solaro, R., and Rosato, N., 1984, *J. polym. Sci. polym. Chem. Ed.*, **22**, 1267.

[22] Altomare, A., Carlini, C., Ciardelli, F., Panattoni, M., Solaro, R., and Houben, J. L., 1985, *Macromolecules*, **18**, 729.

[23] Reck, B., and Ringsdorf, H., 1985, *Makromolek. Chem. rap. Commun.*, **6**, 291.

[24] Torquati, G., *et al.* (work in progress).

[25] Blumstein, R. B., Stickles, E. M., Gauthier, M. M., Blumstein, A., and Volin, F., 1984, *Macromolecules*, **17**, 177.

[26] Stevens, H., Rehage G., and Finkelmann, H., 1984, *Macromolecules*, **17**, 851.

[27] Gray, G. W., 1979, *The Molecular Physics of Liquid Crystals*, edited by G. R. Luckhurst and G. W. Gray (Academic Press), pp. 1, 263.

[28] Finkelmann, H., Happ, M., Portugall, M., and Ringsdorf, H., 1978, *Makromolek. Chem.*, **179**, 2451.

[29] Shibaev, V. P., and Plate, N. A., 1984, *Adv. Polym. Sci.*, **60/61**, 173.

[30] Finkelmann, H., Ringsdorf, H., and Wendorff, J. H., 1978, *Makromolek. Chem.*, **179**, 273.

[31] Finkelmann, H., and Rehage, G., 1984, *Adv. Polym. Sci.*, **60/61**, 99.

[32] Jaffe, H. H., and Orchin, M., 1962, *Theory and Application of Ultraviolet Spectroscopy* (Wiley).

[33] Altomare, A., Carlini, C., Ciardelli, F., Solaro, R., Houben, J. L., and Rosato, N., 1983, *Polymer*, **24**, 95.

[34] Altomare, A., Carlini, C., Ciardelli, F., and Solaro, R., 1988, *Polymer J.*, **20**, 801.

[35] Reck, B., and Ringsdorf, H., 1985, *Makromolek. Chem. rap. Commun.*, **6**, 291; 1985, *Ibid.*, **6**, 791 (correction).

[36] Linnel, W. H., and Khalifa, M., 1950, *J. chem. Soc.*, p. 1315.

[37] Vogel, A. I., 1987, *A Textbook of Practical Organic Chemistry* (*IV edition*) (Longman), pp. 491, 493.

[38] Zaugg, H. E., Dunigan, D. A., Michaels, R. J., Swett, L. R., Wang, T. S., Sommers, A. H., and De Net, R. W., 1961, *J. org. Chem.*, **26**, 644.

[39] Natta, G., Pino, P., and Mazzanti, G., 1957, *Gazz. chim. ital.*, **87**, 528.

[40] Allen, C. F. H., and Gates, J. W., Jr., 1955, *Organic Syntheses Collective*, Vol. 3, edited by E. C. Horning (Wiley), p. 140.

[41] Neilson, T., Wood, H. C. S., and Wylie, A. G., 1962, *J. chem. Soc.*, p. 371.

[42] Krause, M., 1899, *Berichte*, **32**, 124.

[43] Lecoin, D., Hochapfel, A., and Viovy, R., 1975, *Molec. Crystals liq. Crystals*, **31**, 233.