Azobenzene containing polymers: what is yet viable with aged liquid crystals

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Azobenzene containing polymers: what is yet viable with aged liquid crystals

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A Commentary on the paper "Photochromic liquid crystalline polymers. Main chain and side chain polymers containing azobenzene mesogens", by A. S. Angeloni, D. Caretti, C. Carlini, E. Chiellini, G. Galli, A. Altomare, R. Solaro and M. Laus. First published in *Liquid Crystals*, **4**, 513-527 (1989).

Liquid-crystalline polymers constitute a research area which has required an unusually wide range of background and multidisciplinary expertise. After the development and successful commercialisation of Kevlar, a lyotropic liquid crystal, in the mid 1960s, the 1970s also witnessed a tremendous upsurge of interest in liquid-crystalline thermoplastics; in the 1980s there was practically no major industrial firm which was not active in the field, even though hopes of a rapid return on investments meant that the subject tended to be oversold.

In those days of such blossoming innovation we initiated, in the early 1980s, studies aimed at the synthesis and characterisation of chiral liquid-crystalline polymers functionally amenable to self-assemble into supramolecular structures. Collaboration was soon enlarged to the groups at the Universities of Bologna (Angeloni and Caretti), and Brescia (Laus) and afterwards involved colleagues active in the area of photochromic and photoresponsive polymers (Altomare, Carlini, Solaro). The work on the photochromic liquid-crystalline polymers was, in fact, inspired by the findings that polypeptides carrying azobenzene side groups could undergo substantial photoinduced conformational transitions (secondary and tertiary) of the whole macromolecule under UV light illumination [2]. Accordingly, we envisioned the possibility of triggering photochemical and photophysical responses in the organised states of liquid-crystalline polymers, and started investigations into different classes of photochromic polymers containing the azobenzene mesogen in the main chain and the side chain [1].

Typical of liquid-crystalline side-group polymers, it was already a common observation that the state of order of a liquid-crystalline monomer is enhanced in the corresponding polymer in which a richer variety of mesophases, extending over wider temperature ranges, could often occur. Thus, it seemed a rule of thumb that a sufficiently anisometric but not mesogenic monomer would have provided a nematic, or even smectic, polymer of much higher clearing temperature. In reality, although the nematic phase can be viewed as most common for both low molar mass and polymeric liquid crystals, this fact is less common in side-group polymers. The nematic phase is more frequently observed in polymers where the length of the flexible spacer is short, normally between two and six methylene groups. A flexible tail at the end of the mesogenic group was also expected to play a role in favouring the formation of the nematic phase relative to the smectic of the azobenzene polyacrylates **1** (see figure 1). In fact, the lower homologues ($3 \leqslant n$) possessed one nematic phase, an additional smectic phase occurred in samples with intermediate values of n, while eventually the higher homologues ($n \geqslant 6$) became purely smectic. Furthermore, the polymers exhibited a distinct odd-even effect for the clearing temperature, the members with even values of n showing higher temperatures than adjacent members with odd n. One merit of the paper [1] was, therefore, to offer a sensible approach to the synthesis of photochromic polymers in which the mesophase behaviour, and specifically the formation of just one nematic phase, could be anticipated on a chemical basis. Even though those structure-property correlations could not warrant more general relevance in the preparation of liquid-crystalline polymers, as azobenzene has actually turned out to be a comparatively very effective nematogenic side group [3],

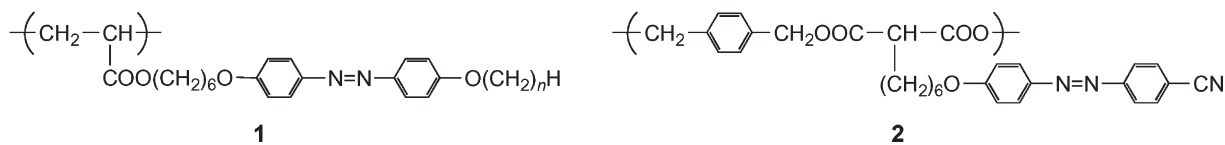*Email: gallig@dcci.unipi.it, emochie@dcci.unipi.it

Figure 1. Structures of liquid-crystalline polymers with azobenzene side groups for erasable optical data storage.

nonetheless they served later as proactive guideline specimens for the preparation of even more sophisticated and exotic photochromic polymers. Moreover, it was confirmed that the macromolecular structure does not significantly affect the *trans-cis* photoisomerisation rate (albeit only in solution at that time), owing to decoupling of the chromophores via the flexible spacer segments.

Azobenzene and its variously substituted analogues are special molecular cores in that they can act as both photochromic and mesogenic units. The more stable *trans* form of the azobenzene moiety, the *E* isomer, is linear or rod-like and supports the structure of the liquid-crystalline phase. By contrast, the photoinduced *cis* form, the *Z* isomer, has a bent shape which is not compatible with the liquid-crystalline phase, thereby destabilising it. The two forms can interconvert reversibly between each other by photoinduced isomerisation under appropriate UV-vis light illumination (π-π^* and n-π^* electronic transitions) as shown in figure 2.

In addition to the photochromism, the optical properties of azobenzene materials can be changed by illumination with polarised light, depending on the polarisation of the pump light.

At a molecular level, the photoisomerisation is only activated when the axis of the transition dipole moment of the chromophore has a component parallel to the linear light polarisation; the direction perpendicular is excluded from optical activation and so will become enriched in chromophores (see figure 2). Within the steady state of the *trans-cis* photoisomerisation, the azobenzene groups become oriented, via repeated angular dependent excitation of *trans-cis* photoisomerisation cycles, perpendicular to the polarisation of the incident light [4]. Indeed, the potential of a liquid-crystalline polymer with azobenzene side groups **2** (see figure 1) for reversible digital and holographic optical storage was disclosed by Wendorff and collaborators [5]. Even though the mechanism of photoorientation by a photoselection process was not recognised until a few years later [6], the breakthrough achievement conceptually evoked, or renewed [7], considerable interest in the area of optical storage, especially photoorientation, photoselection, and photoalignment in polymers, both liquid-crystalline and amorphous. Azobenzene moieties have become the most extensively studied chromophores in soft matter.

At a larger length scale, the nanodomains in the mesophase of azobenzene polymers can reorient under the action of polarised light. The strong driving force for selection of the chromophores enforces the alignment of the whole liquid-crystalline domain in a cooperative motion to a direction perpendicular to the light polarisation. As a result, an overall alignment of the different domains is created, while the orientational order parameter within the individual domains remains largely unaffected. This kind of motion has been found to give rise to intriguing consequences in azobenzene polymers, such as amplification of the degree of order by the combination of photoorientation and thermotropic self-organisation [8] and the use of azobenzene commanders of mesogenic soldiers [9], and photoinduced phase transitions [10]. In this last context, the nematic-isotropic phase transition that was photochemically induced in azobenzene polyacrylates, such as **3** shown in figure 3, may be an illustration. The time-resolved measurements showed that the *trans-cis* photoisomerisation occurred within 20 ns in the nematic phase, and the response time of the associated nematic-isotropic phase transition turned out to be 200 μs, that is essentially equal to that of the corresponding low molar mass model compounds [11]. Much more recently, the
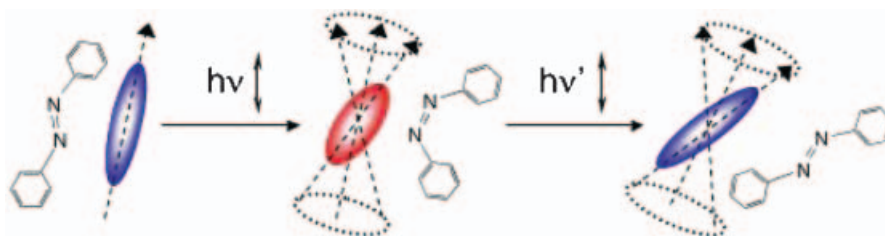

Figure 2. Schematic of molecular orientation during *trans-cis-trans* photoisomerisation.
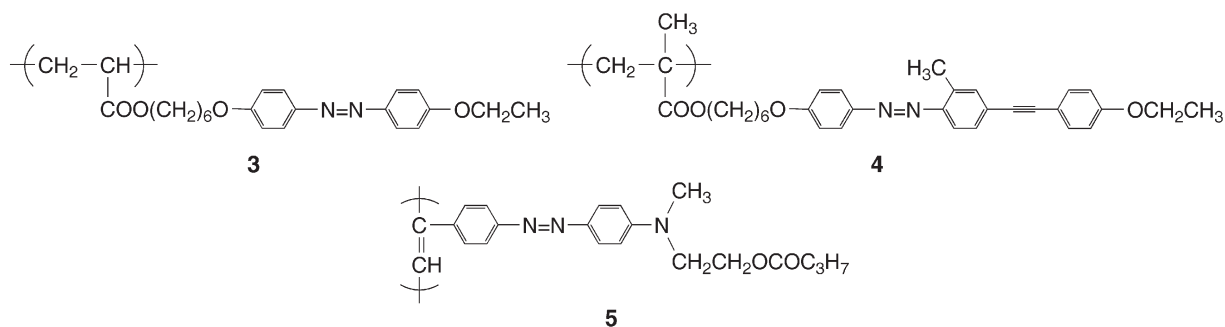
Figure 3. Structures of polymers with azobenzene side groups for photoinduced birefringence (nematic **3** and **4**) and nonlinear optics (amorphous **5**).

same phase transition in polymethacrylates, such as **4** shown in Figure 3, was exploited to effect a large change in birefringence (above 0.35 at 633 nm) [12]. Furthermore, the photoswitching behaviour of the polymer was tested at telecommunication wavelength of 1550 nm in the search for new materials for integrated photonic applications involving optical memory and optical switching. More unexpected was the discovery that chirality can be induced in both liquid-crystalline non-helical polymers with azobenzene side groups containing no stereogenic centres under illumination with circularly polarised light [13]. Moreover, reversible chiroptical switching has been described [14], which seems to entail control of the photoinduced enantiomeric supramolecular structure in the materials.

At an even larger scale of massive motion of azobenzene polymers, a modification of a film surface can occur. Irradiation of the azobenzene polymer film for a period longer than that required for photochemical alignment causes, in fact, mass transfer with the formation of Surface Relief Gratings, SRG, with a height in the micron range [15, 16]. Such a very surprising finding generated a huge literature because of the inherent issues of basic science and potential practical applications connected with it. The latter foresaw storing holographic images and coupling light in and out of waveguides, amongst other proposed applications. Several mechanisms have been suggested for SRG formation, but none of them seem to explain all of the complex phenomena observed. The driving forces here are the pressure gradients created by interfering light and unequal photoisomerisation patterns, or the electric field of the light, depending on which level the mechanism is looked at [17]. While the irradiation conditions have been optimised to some extent, the influence of the polymer structure on the SRG generation is still unknown [18, 19]. On the other hand, erasure of the inscriptions is difficult and various techniques are being explored, as for example, incoherent non-polarised light irradiation [20]. SRG structures could be generated in essentially any polymer incorporating azobenzene groups, but no other photosensitive or photochromic groups seem to be amenable to such inscription.

Stimulated by the extremely interesting developments of the azobenzene polymers, many more complex macromolecular structures and architectures have evolved from simple and straightforward incorporation of the chromophores into the polymer main chain or side chain. Currently available systems include various types of block copolymers, hyperbranched macromolecules and dendrimers, tethered molecules on surfaces, supramolecular self-assemblies, elastomers, monolayers and thin films. In one of the latest examples of side group polymers, an azobenzene polyacetylene, **5** shown in figure 3, has been synthesized and its optical properties studied [21]. It is suggested that direct conjugative linkage of the chromophore to the polyene main chain and the large π-electron delocalisation enhance the non-linear optical property, viz. $\chi^{(3)}$, and the optical limiting property of the polymer. Thus, the scope for the design and synthesis of azobenzene
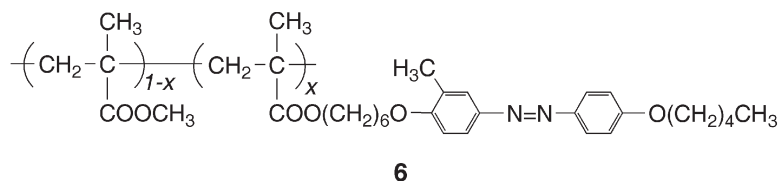
Figure 4. Structure of nematic polymethacrylates **6**, homopolymer ($x=1$) and copolymers ($x=0.5$–0.9), for optical nanowriting information storage.

polymers is still continuosly enlarging and even more possible novel applications remain unexplored.

In our own studies regarding erasable optical storage on azobenzene liquid-crystalline polymers we have focused on polymethacrylates **6** (see figure 4), and described examples of optical writing from mm to nm resolution [22]. The main crucial parameters for applications in data storage are bit stability, working temperature range and homogeneity at the molecular level. [22]. These first two parameters depend on the glass transition temperature and on a temperature at which spontaneous conformational rearrangements of the polymer main chain occur. Moreover, heterogeneities at the molecular level may seriously limit the effectiveness of the azobenzene polymer matrices as erasable storage devices at the nm length scale. Homogeneity of the polymeric matrix strongly depends on its thermal history and can be achieved by specific annealing procedures. The ultimate size of the obtainable optical-induced bit is not yet determined. A guess of such dimension would be of the order of the cooperativity and entanglement lengths, that is about 3–10 nm. In terms of data storage density this would correspond to about 1 Tbyte/cm^2 for our azobenzene polymethacrylates.

With the aim of pushing the resolution to such limits, we used near-field scanning optical microscopy (NSOM) to overcome the diffraction limit [22, 23]. This technique provides a tremendous improvement in the spatial resolution compared to conventional far-field techniques, such as confocal microscopy, by exploiting a nanometer scale sized light source, and imaging the sample within the near-field of the probe, i.e., at a much shorter distance than the light wavelength. The topography embossed bit (~45 nm) reached the intrinsic limit of the probe aperture only in a copolymer **6** ($x=0.7$) [23], as shown in figure 4, which corresponds in the most favourable case to an information density of 40 Gbyte/cm^2. This copolymer, in fact, provides the highest resolution substrate for optical nanowriting among those we considered so far, probably due to the reduced influence of the nematic orientational ordering potential. This poses again relevant questions when studying complex systems in restricted geometries and for applications to very high density optical memories. Indeed how does the role of the mesogenic potential change when the system becomes smaller than the coherence length of the liquid crystal? Or, when will the nematic potential cease to be an amplification factor, and become an obstacle, for the writing efficiency if nanometric resolution is the goal? A pure optical sub-wavelength writing/reading based on the birefringence of the azobenzene polymers was also developed (see
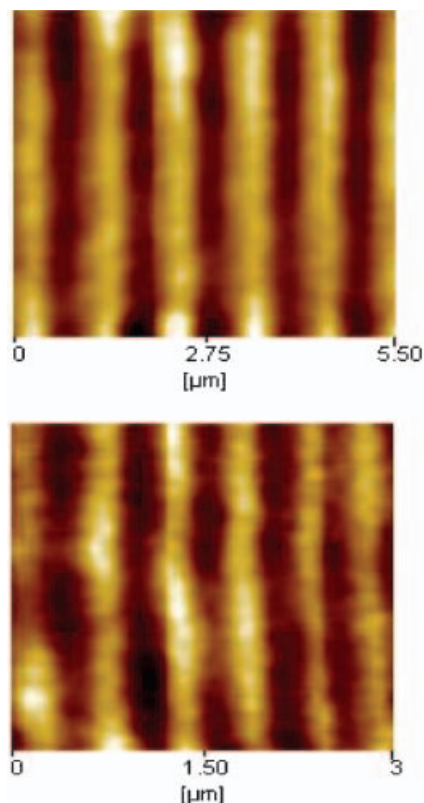
Figure 5. Birefringence NSOM images ($\lambda=690$ nm) of optical gratings produced by previously tracing parallel vertical lines with the NSOM probe ($\lambda=488$ nm, aperture ≈150 nm) on a copolymer **6** ($x=0.7$). The line spacings are 1000 nm (top), and 500 nm (bottom) [23].

figure 5). Here, the imaging quality was limited by the intrinsic resolution of aperture NSOM, so that the imprinted lines presented poor contrast and irregular cross section, as shown in figure 6. On the other hand, the optical properties appeared modified on a larger area
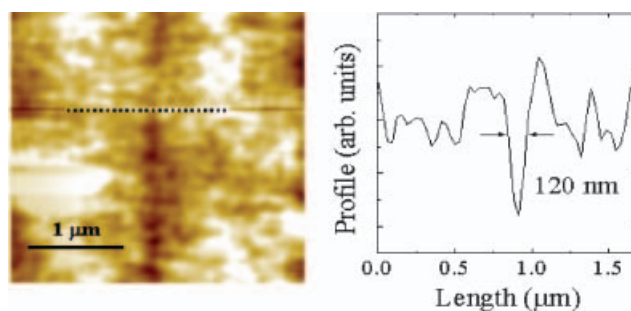

Figure 6. (Left) NSOM birefringence image ($\lambda=690$ nm) of a line produced by previous writing with the NSOM probe ($\lambda=488$ nm, aperture ≈100 nm) at the vertical position on a copolymer **6** ($x=0.7$). (Right) Line profile at the horizontal stroke in the left picture [23].

of several microns around the small feature (~120 nm). Likewise, the far field emitted by the NSOM probe is able to perform optical alignment, though diffraction limited. Further investigations of the ultimate bit size require optimization of the tip geometry, possibly including use of apertureless NSOM. This would allow systematic studies devoted to gain faster writing rates at the nm scale to be implemented in technological devices. Very recently, it has been shown that the structural phase of **6** polymers can be optically switched between the glassy, nematic and isotropic states [24]. The phase diagram that was determined reflected light-temperature equivalence to induce such phase transitions. It is claimed that the transition from the supercooled glass to the liquid-crystalline state represents a new writing mechanism in optical data storage.

In the present area of massive amounts of information and multimedia, the surface-storage technologies including CD and DVD optical disk devices are approaching fundamental limits that may be difficult to overcome. From the mid 1990s exploration of the next generation of data storage systems begun, and volume holographic devices appeared to be promising candidates for terabyte storage systems. The recent development of volume holographic optical storage memory has widely focused on the rewritable and photoaddressable polymers with azobenzene side groups [25] see for example Bayer AG.

During recent years, we became interested in the study of other features of liquid-crystalline azobenzene polymers and found out that they can exhibit behaviours of wide significance, in addition to the photochromic and photoaddressable response. These investigations included those of the nematic-nematic transition by ^{2}H NMR spectroscopy [26], the anisotropic nematic self-diffusion by forward recoil spectrometry (FRES) [27], and the heterogeneous dynamic regimes of spin-probe guests by non-linear [28] and linear [29, 30] electron spin resonance (ESR) spectroscopy. Whilst these special features once again may not be unique to azobenzene polymers, they have added special value to the comprehensive study of such fascinating materials.

References

[1] A.S. Angeloni, D. Caretti, C. Carlini, E. Chiellini, G. Galli, A. Altomare, R. Solaro, M. Laus. *Liq. Cryst.*, **4**, 513 (1989). Presented, in part, at the 8th National Meeting of the Italian AIM, Milan, October 1987.

[2] F. Ciardelli, C. Carlini, R. Solaro, A. Altomare, O. Pieroni, J.L. Houben, A. Fissi. *Pure Appl. Chem.*, **56**, 329 (1984).

[3] A.S. Angeloni, D. Caretti, M. Laus, E. Chiellini, G. Galli. *J. Polym. Sci., Polym. Chem.*, **29**, 1865 (1991).

[4] I. Zebger, M. Rutloh, U. Hoffman, J. Stumpe, H.W. Siesler, S. Hvilsted. *J. Phys. Chem. A*, **106**, 3454 (2002).

[5] M. Eich, J.H. Wendorff, B. Reck, H. Ringsdorf. *Makromol. Chem., Rapid Commun.*, **8**, 59 (1987).

[6] U. Wiesner, N. Reynolds, C. Boeffel, H.W. Spiess. *Makromol. Chem., Rapid Commun.*, **12**, 457 (1991).

[7] T. Todorov, L. Nikolova, N. Tomova. *Appl. Opt.*, **23**, 4309 (1984).

[8] J. Stumpe, L. Läsker, Th. Fischer, S. Kostromin. *J. Photochem. Photobiol. A: Chem.*, **80**, 453 (1994).

[9] K. Ichimura, Y. Suzuki, T. Seki. *Langmuir*, **4**, 1214 (1988).

[10] T. Ikeda, S. Horiuchi, D. Karanjit, S. Kurihara, S. Tazuke. *Macromolecules*, **23**, 42 (1990).

[11] O. Tsutsumi, T. Shiono, T. Ikeda, G. Galli. *J. Chem. Phys. B*, **101**, 1332 (1990).

[12] K. Okano, A. Shishido, Y. Ikeda. *Macromolecules*, **39**, 145 (2006).

[13] L. Nikolova, T. Todorov, M. Ivanov, F. Andruzzi, S. Hvilsted, P.S. Ramanujam. *Opt. Mater.*, **8**, 255 (1997).

[14] G. Iftime, F. Lagugné-Labarthet, A. Natansohn, P. Rochon. *J. Am. Chem. Soc.*, **122**, 12646 (2000).

[15] P. Rochon, E. Batalla, A. Natansohn. *Appl. Phys. Lett.*, **66**, 136 (1995).

[16] D.Y. Kim, S.K. Tripathy, L. Li, J. Kumar. *Appl. Phys. Lett.*, **66**, 1166 (1995).

[17] A. Natansohn, P. Rochon. *Chem. Rev.*, **102**, 4139 (2002).

[18] L. Andruzzi, A. Altomare, F. Ciardelli, R. Solaro, S. Hvilsted, P.S. Ramanujam. *Macromolecules*, **32**, 448 (1999).

[19] V. Börger, O. Kulikovska, K. G.-Hubmann, J. Stumpe, M. Huber, H. Menzel. *Macromol. Chem. Phys.*, **206**, 1488 (2005).

[20] N. Zettsu, Y. Seki. *Macromolecules*, **37**, 8692 (2005).

[21] S. Yin, H. Xu, M. Fang, W. Shi, Y. Gao, Y. Song. *Macromol. Chem. Phys.*, **206**, 1549 (2005).

[22] L. Andreozzi, M. Faetti, G. Galli, M. Giordano, D. Palazzuoli. *Macromol. Symp.*, **218**, 323 (2004).

[23] V. Likodimos, M. Labardi, L. Pardi, M. Allegrini, M. Giordano, A. Arena, S. Patanè. *Appl. Phys. Lett.*, **82**, 3313 (2003).

[24] P. Camorani, M.P. Fontana. *Phys. Rev. E*, **73**, 011703 (2006).

[25] O. Tsutsumi. *Macromol., Rapid Commun.*, **26**, 17 (2005).

[26] R. Muzzalupo, G.A. Ranieri, D. Catalano, G. Galli, C.A. Veracini. *Liq.Cryst.*, **19**, 367 (1995).

[27] E. Hall, C.K. Ober, G. Galli. *Liq. Cryst.*, **14**, 1351 (1993).

[28] L. Andreozzi, F. Cianflone, G. Galli, M. Giordano, D. Leporini. *Mol. Cryst. Liq. Cryst.*, **290**, 1 (1996).

[29] L. Andreozzi, M. Faetti, M. Giordano, D. Palazzuoli, G. Galli. *Macromolecules*, **34**, 7325 (2001).

[30] L. Andreozzi, C. Autiero, M. Faetti, G. Galli, F. Zulli, M. Giordano. *Mol. Cryst. Liq. Cryst.*, **450**, 163 (2006).

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Photochromic liquid-crystalline polymers
Main chain and side chain polymers containing azobenzene mesogens[†]

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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 their liquid-crystalline properties have been examined as a function of the structure of R and R',
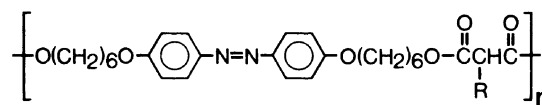
I (a–c)
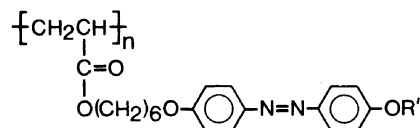
II (a–h)

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

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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.

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 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 endothem 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.

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]

H₃CCO.O(CH₂)₆O—⟨○⟩—N=N—⟨○⟩—O(CH₂)₆O.OCCH₃

$T_m =$ 383 K   V
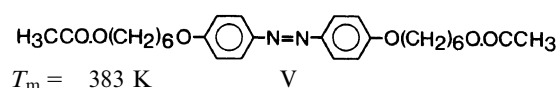
Side chain azobenzene containing polymers **II** were prepared from the corresponding acrylic monomers **VIII** by free radical polymerization, according to Scheme 2. Samples **VIII** were synthesized by reacting acryloyl chloride with the corresponding 4-alkyloxy-4′-(6-hydroxyhexyloxy)azobenzene (**VII**), 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).

HO(CH₂)₆O—⟨○⟩—N=N—⟨○⟩—O(CH₂)₆OH

III

Et₃N | R–CH⟨COCl COCl⟩   **IV (a–c)**

I (a–c)

I(a) $R = n \cdot C_3H_7$ (Pr)
I(b) $R = n \cdot C_4H_9$ (Bu)
I(c) $R = CH_2–CH^*–C_2H_5$ (2MB)
                    |
                  CH_3
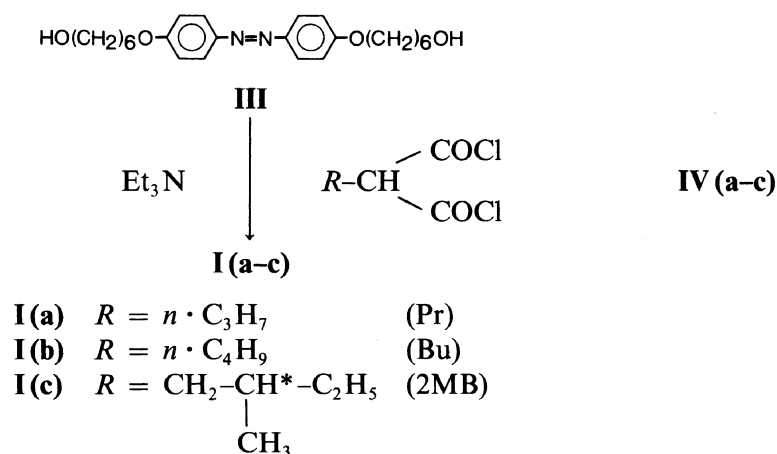
Scheme 1.

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

Polymer Sample	R†	$[\eta]$‡$/dl\,g^{-1}$	$\overline{M}n$§	T_m/K	T_{SI}/K	$\Delta H_{SI}/J\,mol^{-1}$	$\Delta S_{SI}/J\,K^{-1}\,mol^{-1}$	Mesophase
I(a)	Pr	0.53	16 400	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	14 300	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.
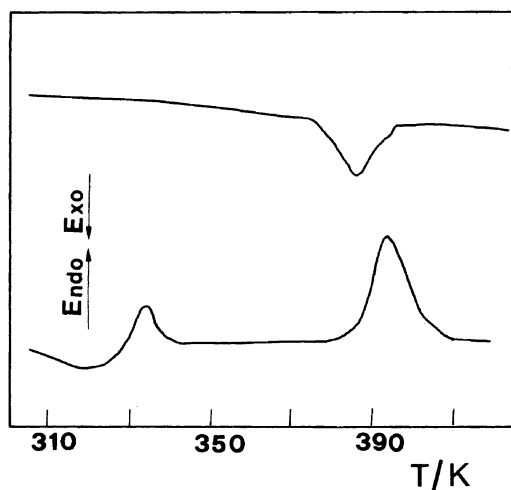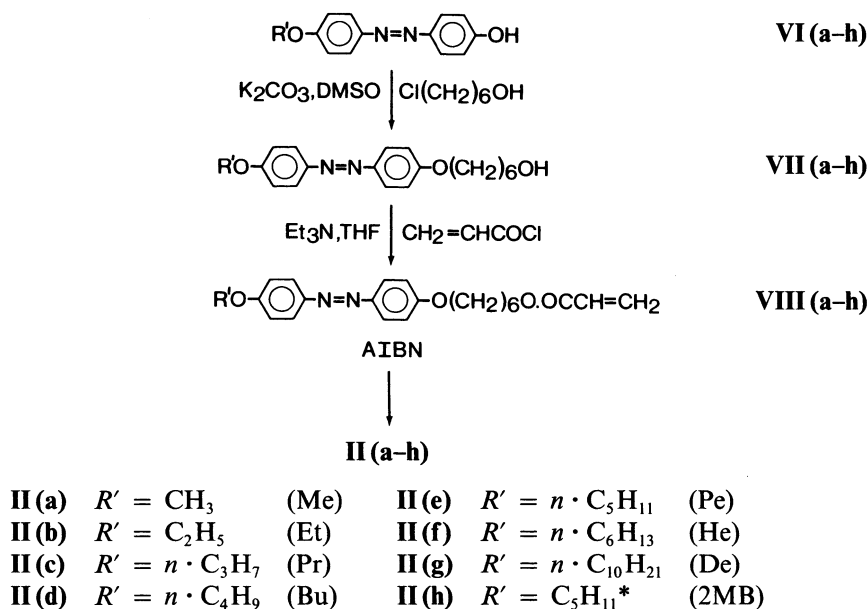‖ $[\alpha]_D^{25} = +5.0$ ($c=1.6$ g/dl, $CHCl_3$).

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

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).

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

$$RO\text{-}\langle\bigcirc\rangle\text{-}N{=}N\text{-}\langle\bigcirc\rangle\text{-}OH \qquad \textbf{VI (a–h)}$$

$$K_2CO_3, DMSO \;\Big|\; Cl(CH_2)_6OH$$

$$RO\text{-}\langle\bigcirc\rangle\text{-}N{=}N\text{-}\langle\bigcirc\rangle\text{-}O(CH_2)_6OH \qquad \textbf{VII (a–h)}$$

$$Et_3N, THF \;\Big|\; CH_2{=}CHCOCl$$

$$RO\text{-}\langle\bigcirc\rangle\text{-}N{=}N\text{-}\langle\bigcirc\rangle\text{-}O(CH_2)_6O.OCCH{=}CH_2 \qquad \textbf{VIII (a–h)}$$

$$AIBN$$

$$\textbf{II (a–h)}$$

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.

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_{NI}‡ (SI) / K	ΔH_{NI} (SI) / J mol^{-1}	ΔS_{NI} (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).

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 (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].

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

Polymer Sample	R'	$[\eta]$†/dl g^{-1}	$\overline{Mn}$‡	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	38000	370	—	403	—	800	—	2.0	N
II(b)	Et	0.13	370000	360	—	430	—	950	—	2.2	N
II(c)	Pr	0.13	390000	374	—	421	—	1250	—	2.9	N
II(d)	Bu	0.09	170000	387	(384)§	427	900	1150	2.3	2.7	S, N
II(e)	Pe	0.07	79000	378	402	416	1100	800	2.7	1.9	S, N
II(f)	He	0.09	99000	373	—	420	—	4800	—	11.4	S
II(g)	De	0.10	130000	363	—	444	—	8500	—	19.1	S
II(h)	2MB	0.07	170000	374	—	380	—	1300¶	—	3.5	N*

† In chloroform at 30°C. ‡ By G.P.C. in chloroform at 25°C. § Monotropic transition. $[\alpha]_D^{25}$=6.5 (c=1.3 g/dl; CHCl$_3$). ¶ D.S.C. overlapping peaks.
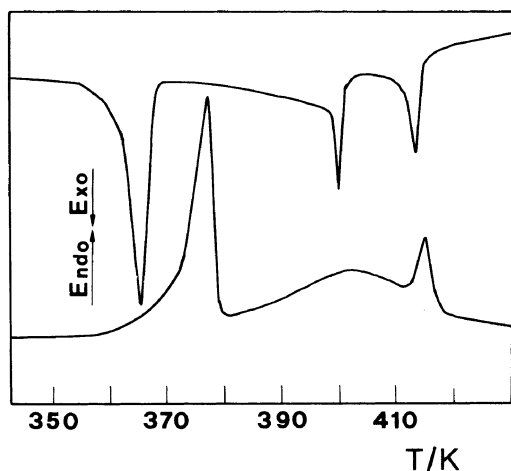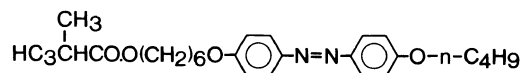
Figure 2.   D.S.C. heating and cooling curves (10 K/min) for polymer **II(e)** (R'=pentyl).

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).

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].

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 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 homo-polymers of 4-acryloyloxy- or 4-methacryloyloxy-azobenzene [21, 34] suggesting that the 4,4'-dialkyloxy substituents

$$HC_3CHCO.O(CH_2)_6O\!\!-\!\!\langle\bigcirc\rangle\!\!-\!\!N\!\!=\!\!N\!\!-\!\!\langle\bigcirc\rangle\!\!-\!\!O\text{-}n\text{-}C_4H_9$$

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

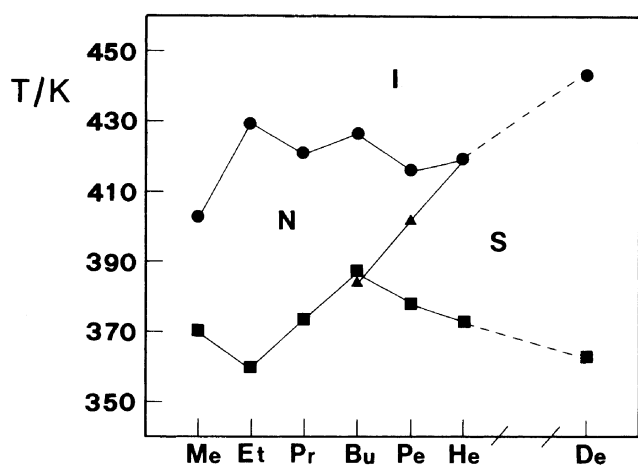$$\Delta H_{SN} = 400 \text{ J/mol}, \quad \Delta H_{NI} = 1400 \text{ J/mol}$$

IX (d)

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.

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.

Sample	R or R′	$\pi\rightarrow\pi^*$ λ_{max}/nm	$\pi\rightarrow\pi^*$ ε_{max}/1 mol^{-1} cm^{-1}	$n\rightarrow\pi^*$ ε_{440}/ 1 mol^{-1} cm^{-1}	Photoisomerization‡ 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.

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., ¹H 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
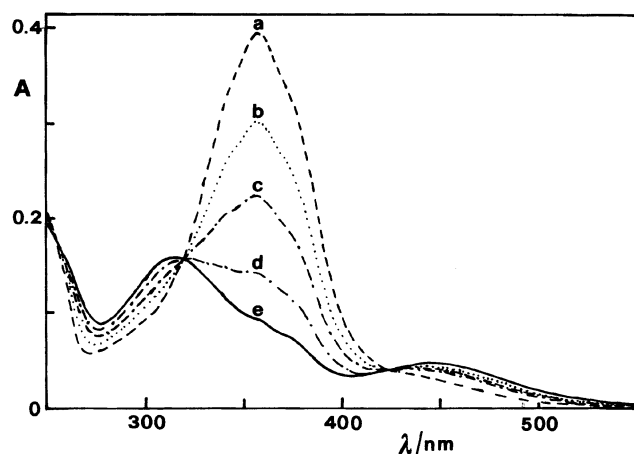
Figure 4. Variation of the U.V. absorption spectra of polymer **II(a)** (*R*′=methyl) in chloroform solution with irradiation time at 348 nm. Curves *a* to *e* refer to irradiation times of 0, 3, 7, 15 and 50 s, respectively.
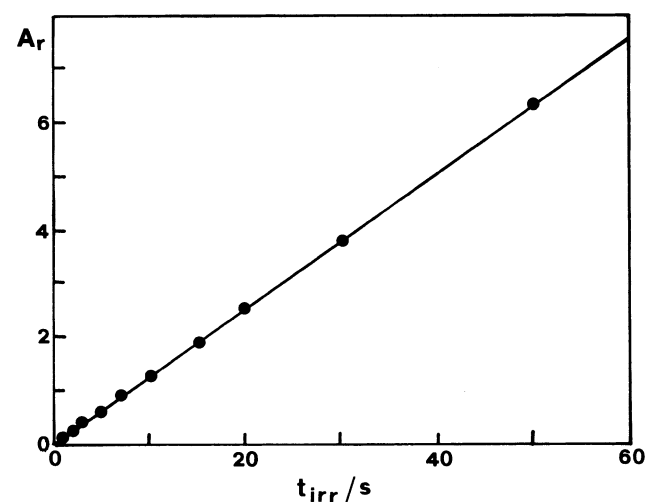
Figure 5. Plot of $A_t = \ln[(A_0 - A_\infty)/(A_t - A_\infty)]$ versus irradiation time for polymer **II(a)** (*R*′=methyl) in chloroform solution.

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-nitro-phenol 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-l-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.

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.

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 diethyl-ether. After evaporation of ether and crystallization from ethanol, 1.0 g of pure **IX(d)** (m.p. 78°C) was

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			

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$_2$O/AcOH	83	126	EtOH	60	89	MeOH
Et	87	125	H$_2$O/EtOH	59	123	EtOAc	56	93	MeOH
Pr	56	107	H$_2$O/EtOH	70	126	EtOAc	50	99	MeOH
Bu	73	109	H$_2$O/EtOH	78	123	C$_6$H$_6$	44	96	MeOH
Pe	95	104	C$_6$H$_{12}$	71	120	EtOAc	63	90	MeOH
He	92	99	C$_6$H$_{12}$	89	117	EtOAc	68	85	MeOH
De	81	105	MeOH	68	118	EtOAc	56	74	MeOH
2MB	47§	84	C$_6$H$_{12}$	58	90	C$_6$H$_{12}$	23¶	93	C$_6$H$_{12}$

* With respect to the corresponding 4-alkyloxyaniline. † With respect to the corresponding **VI**. ‡ With respect to the corresponding **VII**. § $[\alpha]_D^{25} = +10.4$ ($c=0.7$, CHCl$_3$). $[\alpha]_D^{25} = +7.5$ ($c=1.9$, CHCl$_3$). ¶ $[\alpha]_D^{25} = +6.9$ ($c=1.0$, CHCl$_3$).

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 $\pm 0.003°$.

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$_\alpha$ radiation ($\lambda = 1.54$ 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.

Acknowledgments

References

[1] F. Ciardelli, C. Carlini, R. Solaro, A. Altomare, O. Pieroni, J.L. Houben, A. Fissi. *Pure appl. Chem.*, **56**, 329 (1984).
[2] B.F. Erlanger. *Am. Rev. Biochem.*, **45**, 267 (1976).
[3] M. Irie. *Photophysical and Photochemical Tools in Polymer Science* (NATO ASI series C, Vol. 182), M.A. Winnik (Ed.). (Reidel Publishing Co.), p. 269 (1986).
[4] C.D. Eisenbach. *Polymer*, **21**, 1175 (1980).
[5] G. Smets. *Adv. Polym. Sci.*, **50**, 17 (1983).
[6] R. Zentel, G. Reckert. *Makromolek. Chem.*, **187**, 1915 (1986).
[7] I. Cabrera, V. Krongauz, H. Ringsdorf. *Molec. Crystals liq. Crystals*, **155**, 221 (1988).
[8] S. Bualek, R. Zentel. *Makromolek. Chem.*, **189**, 797 (1988).
[9] M. Tanaka, T. Nakaya. *Makromolek. Chem.*, **189**, 771 (1988).
[10] J.V. Crivello, M. Deptolla, H. Ringsdorf. *Liq. Crystals*, **3**, 235 (1988).
[11] C. Kim, H.R. Allcock. *Macromolecules*, **20**, 1726 (1987).
[12] R.E. Singler, R.A. Willingham, R.W. Lenz, A. Furukawa, H. Finkelmann. *Macromolecules*, **20**, 1727 (1987).
[13] G. Kaempf. *Polymer J.*, **19**, 257 (1987).
[14] H.J. Coles, R. Simon. *Polymer*, **26**, 1801 (1985).
[15] M. Eich, J.H. Wendorff. *Makromolek. Chem. rap. Commun.*, **8**, 467 (1987).
[16] M. Eich, J.H. Wendorff, B. Reck, H. Ringsdorf. *Makromolek. Chem. rap. Commun.*, **8**, 59 (1987).
[17] A.S. Angeloni, M. Laus, C. Castellari, G. Galli, P. Ferruti, E. Chiellini. *Makromolek. Chem.*, **186**, 977 (1985).
[18] G. Galli, M. Laus, A.S. Angeloni, P. Ferruti, E. Chiellini. *Europ. polym. J.*, **21**, 727 (1985).
[19] E. Chiellini, G. Galli. *Macromolecules*, **18**, 1652 (1985).
[20] E. Chiellini, G. Galli, A.S. Angeloni, M. Laus, R. Pellegrini. *Liq. Crystals*, **2**, 529 (1987).
[21] A. Altomare, C. Carlini, F. Ciardelli, R. Solaro, N. Rosato. *J. polym. Sci. polym. Chem. Ed.*, **22**, 1267 (1984).
[22] A. Altomare, C. Carlini, F. Ciardelli, M. Panattoni, R. Solaro, J.L. Houben. *Macromolecules*, **18**, 729 (1985).
[23] B. Reck, H. Ringsdorf. *Makromolek. Chem. rap. Commun.*, **6**, 291 (1985).
[24] G. Torquati, *et al.* (work in progress).
[25] R.B. Blumstein, E.M. Stickles, M.M. Gauthier, A. Blumstein, F. Volin. *Macromolecules*, **17**, 177 (1984).
[26] H. Stevens, G. Rehage, H. Finkelmann. *Macromolecules*, **17**, 851 (1984).
[27] G.W. Gray. *The Molecular Physics of Liquid Crystals*, G.R. Luckhurst, G.W. Gray (Eds). (Academic Press), pp. 1, 263 (1979).
[28] H. Finkelmann, M. Happ, M. Portugall, H. Ringsdorf. *Makromolek. Chem.*, **179**, 2451 (1978).
[29] V.P. Shibaev, N.A. Plate. *Adv. Polym. Sci.*, **60/61**, 173 (1984).
[30] H. Finkelmann, H. Ringsdorf, J.H. Wendorff. *Makromolek. Chem.*, **179**, 273 (1978).
[31] H. Finkelmann, G. Rehage. *Adv. Polym. Sci.*, **60/61**, 99 (1984).
[32] H.H. Jaffe, M. Orchin. *Theory and Application of Ultraviolet Spectroscopy* (Wiley) (1962).
[33] A. Altomare, C. Carlini, F. Ciardelli, R. Solaro, J.L. Houben, N. Rosato. *Polymer*, **24**, 95 (1983).

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

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

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

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

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

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

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

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

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

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