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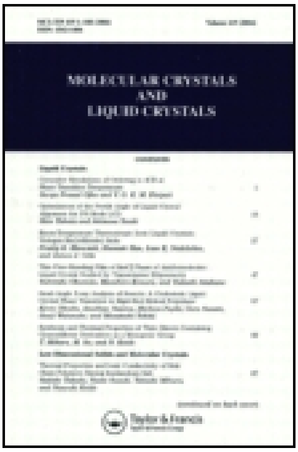

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Thermotropic and Solution Photoisomerization Properties of Side-Chain Liquid Crystalline Polymers Containing Methyl-Substituted Azobenzene Mesogens

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Version of record first published: 24 Sep 2006.

To cite this article: E. Chiellini , G. Galli , A. Altomare , R. Solaro , A. S. Angeloni , M. Laus , C. Carlini & D. Caretti (1992): Thermotropic and Solution Photoisomerization Properties of Side-Chain Liquid Crystalline Polymers Containing Methyl-Substituted Azobenzene Mesogens, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 221:1, 61-69

To link to this article: http://dx.doi.org/10.1080/10587259208037521

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Mol. Cryst. Liq. Cryst., 1992, Vol. 221, pp. 61–69
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Thermotropic and Solution Photoisomerization Properties of Side-Chain Liquid Crystalline Polymers Containing Methyl-Substituted Azobenzene Mesogens

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(Received January 25, 1991)

The thermotropic and solution photoisomerization properties of a class of polyacrylates containing differently methyl-substituted azobenzene groups are presented. Methyl-substitution inhibits the tendency to crystallize and causes a dramatic decrease in the stability of the established nematic phases. These effects result from a restriction of the packing capability of the mesogenic groups and a reduction of their length-to-breadth ratio. In dilute solution all polymeric samples undergo *trans*-to-*cis* photoisomerization of the azo group upon irradiation in the absorption region of the $\pi \rightarrow \pi^*$ electronic transitions. Photoisomerization rate constants are very similar and of the same order of magnitude as those observed for other polymeric systems containing the unsubstituted azobenzene chromophore.

INTRODUCTION

Thermotropic liquid crystalline side-chain polymers are currently attracting a great deal of interest in respect to their potential in practical applications.[1] These may include electro-optical data storage and display devices, waveguides in optical communications and selective optical filters and reflectors. Among the various mesogenic units, the photoresponsive azobenzene group appears particularly interesting because irradiation can cause the reversible *trans-cis* isomerization of the photochromic group simultaneously inducing a local phase transition.[2–7] Azobenzene moiety may also act as a convenient probe of polymer conformation, both in bulk and in solution.[8]

As a part of a program aimed at investigating the properties of azobenzene containing liquid crystalline polymers in relation to their molecular structures,[9–12]

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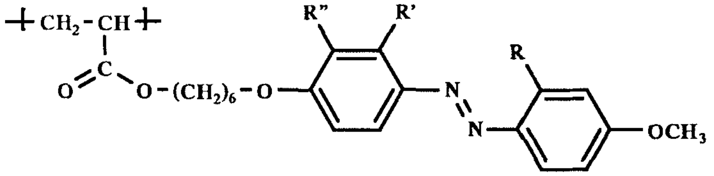
we became interested in producing new series of side-chain polymers with broad liquid crystalline phases and low transition temperatures by introducing methyl substituents. Substantial changes of the polymer properties are expected when substituents are introduced as lateral groups on mesogenic cores. However, very few studies have been performed in this respect,[13–16] and no systematic investigations are available on the effects of the introduction of several substituents in azobenzene-containing polymers.[12] In the present contribution we report on the synthesis and liquid crystalline properties of a class of polymers containing differently methyl-substituted azobenzene groups. Their chemical structures and relevant quotations are reported in Figure 1. In addition, the photochromic behaviour in solution of these polymers has been investigated and is discussed with reference to that of corresponding unsubstituted analogs.

EXPERIMENTAL PART

Acrylate monomers **9a–c** were prepared as previously described.[9,12] 4-Methoxy-2-methyl-4′-hydroxyazobenzene (**7d**), 4-methoxy-2-methyl-2′-methyl-4′-hydroxyazobenzene (**7e**) and 4-methoxy-2-methyl-3′-methyl-4′-hydroxyazobenzene (**7f**) were prepared by coupling diazotized 4-methoxy-2-methylaniline with phenol, *m*-cresol and *o*-cresol respectively, and purified by recrystallization from cyclohexane. Acrylate monomers **9d–f** were synthesized by reacting precursors **8d–f** with acryloyl



1 a-f

	R	R'	R"
a	H	H	H
b	H	H	CH_3
c	H	CH_3	H
d	CH_3	H	H
e	CH_3	CH_3	H
f	CH_3	H	CH_3

FIGURE 1 Representation of the structural formulas of the investigated methyl-substituted azobenzene containing polyacrylates.

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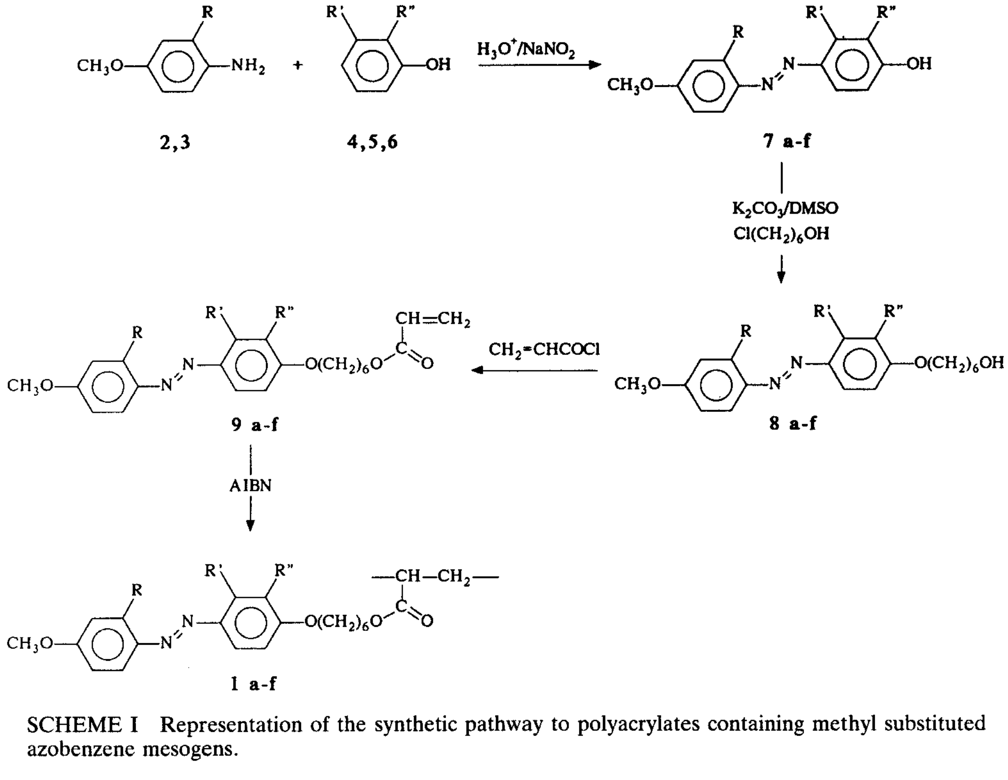
chloride. The general synthetic route is outlined in Scheme I. As a typical example, the synthesis of acrylate **9e** is reported.

4-Methoxy-2-methyl-2'-methyl-4'-hydroxyazobenzene (**7e**). A solution of 9.0 g (0.13 mol) of sodium nitrite in 30 ml of water was added dropwise with vigorous stirring to a solution of 13.7 g (0.10 mol) of 4-methoxy-2-methylaniline (**3**) in 150 ml of 3 M hydrochloric acid at 0–5°C. After 1 h the excess sodium nitrite was decomposed by addition of urea and the solution was slowly poured into a solution of 10.8 g (0.10 mol) of *m*-cresol (**6**) in 2 M sodium hydroxide. After 10 min, the solution was acidified with hydrochloric acid. The precipitate was isolated, washed with water and purified by recrystallization from cyclohexane/benzene (1:1 V:V); m.p. 149°C. Yield 72%. ^{1}H NMR ($CDCl_3$): δ (in ppm from TMS) = 7.8–7.6 (m, 2H, aromatic); 7.2 (bs, 1H, OH); 6.8–6.6 (m, 4H, aromatic); 3.8 (s, 3H, CH_3O); 2.7 (s, 3H, CH_3); 2.6 (s, 3H, CH_3). Intermediates **7d** (m.p. 121°C) and **7f** (m.p. 116°C) were crystallized from cyclohexane.

4-Methoxy-2-methyl-2'-methyl-4'-(6-hydroxyhexyloxy)azobenzene (**8e**). A mixture of 15.0 g (0.058 mol) of **7e**, 9.5 g (0.069 mol) of anhydrous potassium carbonate and 9.5 g (0.070 mol) of 6-chloro-1-hexanol in 50 ml of dimethylsulphoxide was stirred at 120°C for 2H, cooled to room temperature and poured into 100 ml of 1 M sodium hydroxide. The solid residue was filtered, washed several times with water and recrystallized from cyclohexane; m.p. 106°C. Yield 90%.



SCHEME I Representation of the synthetic pathway to polyacrylates containing methyl substituted azobenzene mesogens.

^{1}H NMR ($CDCl_3$): δ (in ppm from TMS) = 7.7 (d, 2H, aromatic); 6.9–6.7 (m, 4H, aromatic); 4.0 (t, 2H, CH_2O); 3.8 (s, 3H, CH_3O); 3.6 (t, 3H, CH_2O); 2.7 (s, 6H, CH_3); 2.2 (bs, 1H, OH); 1.9–1.3 (m, 8H, aliphatic).

Intermediates **8d** (m.p. 68°C) and **8f** (m.p. 90°C) were crystallized from cyclohexane.

4-Methoxy-2-methyl-2′-methyl-4′-(6-acryloyloxyhexyloxy)azobenzene (**9e**). A solution of 8.0 g (0.088 mol) of acryloyl chloride in 50 ml of anhydrous tetrahydrofuran was added dropwise with vigorous stirring to a solution of 13.0 g (0.036 mol) of **8e**, 9.1 g (0.090 mol) of triethylamine and 0.1 g of 2,6-di-*tert*-butyl-4-methylphenol in 50 ml of the same solvent at 0°C, while nitrogen was bubbled through the reaction mixture. After 30 min, the solution was filtered and the solvent evaporated under vacuum. The solid residue was recrystallized twice from methanol; m.p. 85°C. Yield 25%.

^{1}H NMR ($CDCl_3$): δ (in ppm from TMS) = 7.8 (d, 2H, aromatic); 6.9–6.7 (m, 4H, aromatic); 6.4-5.8 (m, 3H, vinyl); 4.2 (t, 2H, OCH_2); 4.0 (t, 2H, OCH_2); 3.8 (s, 3H, OCH_3); 2.7 (s, 6H, CH_3); 1.9–1.3 (m, 8H, aliphatic).

Monomers **9d** (m.p. 82°C) and **9f** (m.p. 59°C) were crystallized from methanol.

Polymerizations. In a typical experiment, a solution of 1.0 g of acrylate and 5.0 mg of 2,2′-azobis(2-methylpropionitrile) (AIBN) in 5.0 ml of anhydrous benzene was degassed by standard freeze/thaw techniques and heated in a sealed ampule under nitrogen at 60°C for 48 h. The resulting viscous solution was cooled and poured into 150 ml of methanol to precipitate the polymer as an amorphous yellow-orange solid. The polymer was purified by repeated precipitations from chloroform into methanol and was dried in vacuo at 80°C for 48 h. Reaction yields typically ranged between 30 and 40%.

Physicochemical characterizations. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Gemini 200 spectrometer. Average molecular weights were determined by size exclusion chromatography (SEC) in chloroform with a 590 Waters chromatograph equipped with a Shodex KF-804 column. Polystyrene standard samples were used for the universal calibration method. The thermal properties were investigated using a Perkin Elmer DSC-7 apparatus or a Mettler TA 4000 system. Samples of 5–10 mg were employed. The transition temperatures were taken, from the DSC traces of samples annealed by cooling from the isotropic melt, as corresponding to the maximum and to the onset point of the enthalpic peaks for polymers and low molar mass samples respectively, at a heating-cooling rate of 10 K · min^{-1}. Indium and tin standard samples were employed for temperature calibration and indium reference samples were used for the evaluation of the transition enthalpies. A Reichert Polyvar microscope equipped with a programmable Mettler FP 52 heating stage was used to examine the optical textures of the liquid-crystalline phases. UV measurements in the range 550–250 nm were performed in chloroform solution by a JASCO 7850 spectrophotometer connected in line to an AT type MS DOS computer. Irradiation experiments were carried out on chloroform solutions of the samples in a 1.0 cm path length quartz cuvette fitted with a hollow PTFE

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stopper and thermostatted at 25°C. The solution concentration was adjusted to an absorbance of about 0.4 at 366 nm. The light from a 150 W high pressure mercury lamp, filtered with a 366 narrow bandwidth interference filter was focussed on the top of the solution by a quartz optical fiber inserted in the cuvette stopper. The solution was kept under continuous magnetic stirring by a Hellma CUV-O-STIR model 333 microstirrer, while monitoring the 340 nm absorbance for at least 1200 sec. Best fit kinetic analyses of the collected data were performed by a commercial (Prati Elettronica s.r.l.) computer program.

RESULTS AND DISCUSSION

The synthetic route for the preparation of acrylate monomers **9a–f** and corresponding polyacrylates **1a–f** is summarized in Scheme I. 4-Methoxyaniline (**2**) or 4-methoxy-2-methylaniline (**3**) were diazotized and coupled with phenol (**4**) or *o*-cresol (**5**) or *m*-cresol (**6**) to prepare variously substituted azophenols **7a–f**. These were etherified with 6-chloro-1-hexanol and the resulting hydroxy-terminated intermediates **8a–f** were esterified with acryloyl chloride in the presence of a free-radical inhibitor to yield the acrylate monomers **9a–f**. The polyacrylates **1a–f** were synthesized by free radical polymerization of the corresponding monomers using AIBN as the initiator. The molecular weights of the polymers were characterized by analytical SEC relative to polystyrene standards using the universal calibration method. The average number molecular weights ($\overline{\mathrm{M}}$n) are comprised between 28000 and 85000 with first polydispersity index in the range 1.8–3.3 (Table I). According

TABLE I

Physico-chemical properties of liquid-crystalline polyacrylates **1a–1f**

Polymer	$\overline{\mathrm{Mn}}$(a)	$\overline{\mathrm{Mw}}/\overline{\mathrm{Mn}}$(a)	T_g (b)	T_{NI} (b)	ΔH_{NI} (b)	ΔS_{NI} (b)
			(K)	(K)	($Jmol^{-1}$)	($Jmol^{-1}K^{-1}$)
1a	38000	2.2	336(c)	403	810	2.0
1b	85000	3.1	n.d.	329	300	0.9
1c	70000	3.3	283	-(d)	-(d)	-(d)
1d	70000	3.0	300	351	740	2.1
1e	28000	1.8	291	340	440	1.3
1f	30000	2.0	304	-(d)	-(d)	-(d)

(a) By SEC, in chloroform.

(b) Glass transition temperature (Tg), nematic-isotropic transition temperature (T_{NI}), enthalpy (ΔH_{NI}) and entropy (ΔS_{NI}) by DSC.

(c) Melting temperature at 370 K.

(d) Not mesomorphic.

to previous findings,[17] we assume that the transitional properties of polymers **1** are substantially unaffected by their molecular weights. The mesomorphic behaviour of the samples was studied by DSC measurements coupled to polarizing microscopy observations. Representative DSC heating curves of thermotropic polyacrylates are reported in Figure 2. The identification of the liquid-crystalline phases was done by qualitative observations of the optical textures on the hot stage of a polarizing microscope. No liquid-crystalline behaviour was observed for monomers or intermediate compounds with the only exception of acrylate **9a** which displays a monotropic nematic mesophase (T_m = 409 K, T_{NI} = 393 K). Table I summarizes the molecular weight data and transitional properties of polymers **1**. All of the polymers, with the exceptions of **1c** and **1f**, show liquid-crystalline behaviour. Their DSC heating curves (see Figure 2) exhibit distinct glass transitions. In addition, one endothermic peak is detected which is assigned in all cases to the nematic-isotropic transition. Schlieren optical textures with typical disclinations of integer and half-integer order[18] are observed throughout the mesophase thermal interval. Only in the case of polymer **1a** could crystallization and subsequent melting processes be detected. For the other samples nematic glasses were obtained. Comparing the transitional features of polymers **1b–f** with those of polymer **1a**, it appears that lateral methyl substitution inhibits the tendency to crystallize and causes a dramatic decrease in the stability of the nematic phase as far as both transition temperatures and relevant thermodynamic quantities (enthalpy/entropy)

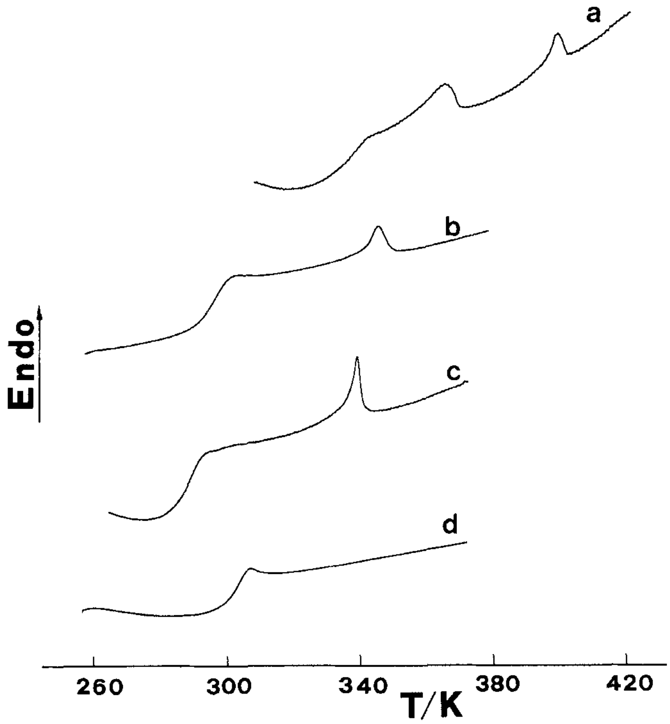

FIGURE 2 DSC second heating curves of liquid crystalline polyacrylates **1a** (a), **1d** (b), **1e** (c) and **1f** (d).

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are concerned. This latter effect is particularly noticeable for polymers **1c** and **1f** which do not exhibit any mesomorphic transitions. The glass transition is also affected by methyl substitution and is typically lower by 40 degrees for substituted polymers relative to the unsubstituted one. These combined effects, however, result in a nematic range of approximately 30 K in polymer **1a**, which in contrast is about 50 K in polymers **1d** and **1e**.

These results suggest that the introduction of the apolar methyl group at the azobenzene mesogen restricts its packing capabilities and diminishes its length-to-breadth ratio so diluting its anisotropic interactions responsible for liquid crystallinity.[19] It is not possible to anticipate relevant changes in the mesomorphic properties with substitution, i.e. placement and number of methyl groups, in azobenzene-containing polymers. We may speculate however that the introduction of one methyl group in the 2-position (outer phenyl ring) is less disruptive than any other one in the inner ring. On the other hand, disubstitution in the 2,2′-positions results in a rather extended mesophase possibly due to the interlocking of the two symmetrically placed methyl groups which helps stabilize the nematic phase. The influence of 2′- or 3′-substitution on the liquid crystalline properties of such polymers has been already investigated systematically[12] and is in general agreement with the present arguments.

Polyacrylate samples were also investigated for their UV absorption features and photoisomerization properties in solution. In chloroform, the absorption spectra of all polymers are characterized by an intense band at about 365 nm, associated with the lowest energy $\pi \rightarrow \pi^*$ electronic transition of the azobenzene chromo-

TABLE II

UV absorption and photoisomerization properties of photochromic polyacrylates **1a–f** in chloroform solution at 25°C

Polymer	UV absorption			Photoisomerization(a)	
	$\pi \rightarrow \pi^*$		$n \rightarrow \pi^*$	$10^3 k$	A_∞/A_0(b)
	λ_{max} (nm)	ε_{max} ($M^{-1}cm^{-1}$)	ε_{444} ($M^{-1}cm^{-1}$)	(s^{-1})	
1a	357	25,600	2,000	7.4	0.22
1b	361	25,300	2,350	7.0	0.39
1c	365	25,100	2,300	7.8	0.39
1d	364	24,500	2,400	7.3	0.47
1e	365	20,000	2,000	5.8	0.47
1f	366	22,000	2,400	5.5	0.38

(a) By irradiation at 366 nm.
(b) At 340 nm.

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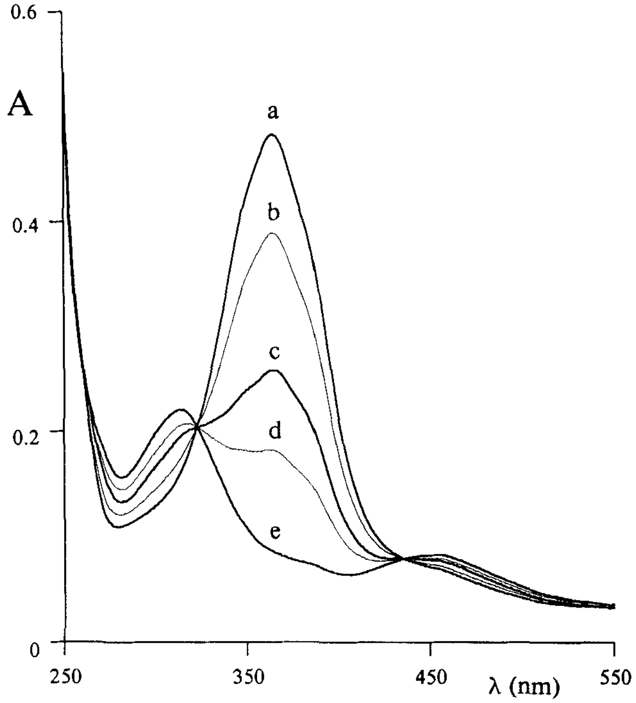

FIGURE 3 Variations of the UV absorption spectra of polymer sample **1e** in chloroform solution with irradiation time at 366 nm. Curves a–e refer to irradiation time 0, 50, 150, 240 and 660 s respectively.

phore, and a shoulder at about 450 nm associated with the $n \rightarrow \pi^*$ transition.[20] The molar extinction coefficients in correspondence of these electronic transitions are collected in Table II. Irradiation at 366 nm in the $\pi \rightarrow \pi^*$ absorption region produces the photoisomerization of the azo group from the thermodynamically stable *trans* configuration to the unstable, nonplanar, *cis* configuration. The intensity of the absorption bands between 550 and 435 nm and below 325 nm progressively increases with irradiation time while the intensity of the band in the 360 nm region decreases. As a typical example, the UV profiles in chloroform solution of sample **1e** at different irradiation times are reported in Figure 3. The similarity between the UV spectra at this photostationary state and that of *cis*-azobenzene[20] and the presence of two isosbestic points at about 430 nm and 320 nm indicate that only two absorbing species (*trans* and *cis* isomers) are present and no side reactions occur. In all cases, $\ln[A_0 - A_\infty)/(A_t - A_\infty)]$, where A_0, A_t and A_∞ are the absorbances at 340 nm at time 0, t, and ∞ respectively, shows a linear dependence on the irradiation time in agreement with a first-order photoisomerization kinetics.[21] The relevant kinetic constants ranged between $5.5 \cdot 10^{-3}$ and $7.8 \cdot 10^{-3}$ sec^{-1}, with the lower values being observed for the dimethyl substituted derivatives (Table II). This trend could be associated with a different role played by electronic effects in the structurally different azobenzene chromophores rather than with differences in molecular dynamics.

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