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

# Synthesis and thermotropic properties of new polyacrylates containing alkanoyl-substituted azobenzene mesogens

Giancarlo Galli[a]; Emo Chiellini[a]; Michele Laus[b]; Sante A. Angeloni[b]; Daniele Caretti[b]; Enzo Fanelli[c]; Giovanni Poeti[c]; Bernard Gallot[d]
[a] Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Pisa, Italy [b] Dipartimento di Chimica Industriale e dei Materiali, Università di Bologna, Bologna, ITALY [c] Dipartimento di Scienze Chimiche, Università di Camerino, Camerino, ITALY [d] Laboratoire des Materiaux Organiques, CNRS, Vernaison, France

**To cite this Article** Galli, Giancarlo , Chiellini, Emo , Laus, Michele , Angeloni, Sante A. , Caretti, Daniele , Fanelli, Enzo , Poeti, Giovanni and Gallot, Bernard(1994) 'Synthesis and thermotropic properties of new polyacrylates containing alkanoyl-substituted azobenzene mesogens', Liquid Crystals, 16: 1, 115 — 125

**To link to this Article: DOI:** 10.1080/02678299408036524

**URL:** http://dx.doi.org/10.1080/02678299408036524

LIQUID CRYSTALS, 1994, VOL. 16, NO. 1, 115–125

# Synthesis and thermotropic properties of new polyacrylates containing alkanoyl-substituted azobenzene mesogens

by GIANCARLO GALLI and EMO CHIELLINI*
Dipartimento di Chimica e Chimica Industriale, Università di Pisa,
Via Risorgimento 35, 56126 Pisa, Italy

MICHELE LAUS, SANTE A. ANGELONI and DANIELE CARETTI
Dipartimento di Chimica Industriale e dei Materiali, Università di Bologna,
Viale Risorgimento 4, 40136 Bologna, Italy

ENZO FANELLI and GIOVANNI POETI
Dipartimento di Scienze Chimiche, Università di Camerino,
Via S. Agostino 1, 62032 Camerino, Italy

and BERNARD GALLOT
Laboratoire des Materiaux Organiques, CNRS,
BP 24, 69390 Vernaison, France

(*Received 4 May 1993; accepted 20 July 1993*)

The synthesis and characterization of a series of new polyacrylates **1**, containing the azobenzene mesogen spaced from the backbone by a hexamethylene segment and substituted in the 4-position by an alkanoyl chain of variable length, together with those of the relevant precursors are reported. Optical and X-ray analyses provided evidence for the presence of a smectic A mesophase in a fairly broad range of temperature in both polymers and low molar mass compounds. In polyacrylates **1**, the side-chain substituents were fully interdigitated in a smectic $A_1$ structure. The comparison of the transition parameters of polymers **1** with those of another series of polyacrylates **7** containing the azobenzene unit substituted in the 4-position by an alkyloxy chain of variable length revealed that the replacement of an oxygen atom by a carbonyl group strongly enhanced the smectogenic character of the azobenzene group.

## 1. Introduction

The synthesis of liquid crystalline side-chain polymers has become an active research area because of their potential application in data storage systems, in ferroelectric and piezoelectric devices and in systems requiring non-linear optical characteristics [1]. With respect to widely used conventional materials, these polymers generally exhibit inferior or even comparable electro-optic properties, including molecular polarization and fast response to external electric and magnetic fields, but clear superiority with respect to dimensional stability, mechanical orientability, and ease of processing. These characteristics, coupled with the great versatility of structural design at both the molecular and bulk levels, are presently promoting more

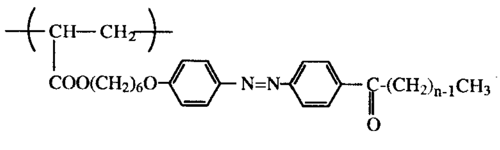
---

* Author for correspondence.

comprehensive understanding of the influence of the structural and molecular parameters on the liquid crystalline behaviour.

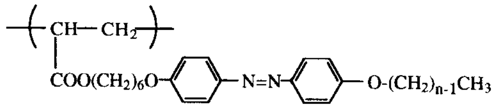
Among the various mesogenic groups that are being used in side-chain liquid crystalline polymers, a particular place is held by the azobenzene group. This group, when irradiated in the $\pi$–$\pi^*$ electronic transition region, undergoes a *trans-cis* configurational change that involves a local and substantially isothermal phase transition, due to the non-mesogenic character of the *cis*-form. The perturbation so generated in the matrix may be frozen-in, for example, by quenching, and can be retained even if the mesogenic group relaxes back to the *trans*-form. Accordingly, the photochemically-induced isothermal phase transition process can represent a very effective erasable, photoselective image fixation technique [2–7].

As a part of our containing investigations into the synthesis and properties of liquid crystalline polymers containing the photoresponsive azobenzene mesogen and their relationships to molecular structure [8–11], we have started to study the synthesis and properties of a series of new polyacrylates **1a–f**, as well as those of the relevant monomers and intermediates, containing the azobenzene unit substituted in the 4-position by an alkanoyl chain of variable length:



| **1** | **a** | **b** | **c** | **d** | **e** | **f** |
|---|---|---|---|---|---|---|
| *n* | 1 | 2 | 3 | 4 | 5 | 6 |

While the 4-alkanoylazobenzene mesogenic unit has been rather extensively studied in low molar mass liquid crystals [12–14], it has never been incorporated into the structure of polymer liquid crystals. It was anticipated that the introduction into the mesogenic molecular framework of the transverse dipole moment associated with the carbonyl group would considerably influence the liquid crystalline behaviour of the side-chain polymers, particularly their smectogenic tendency. It would also be pertinent to compare the mesomorphic properties of polymers **1a–f** with those of a previously investigated series of polymers **7a–f** containing the azobenzene mesogen substituted in the 4-position by an alkyloxy chain of variable length [8], in order to evaluate the effects of replacing the carbonyl group by an oxygen atom on the overall mesogenic character of the corresponding polymers:

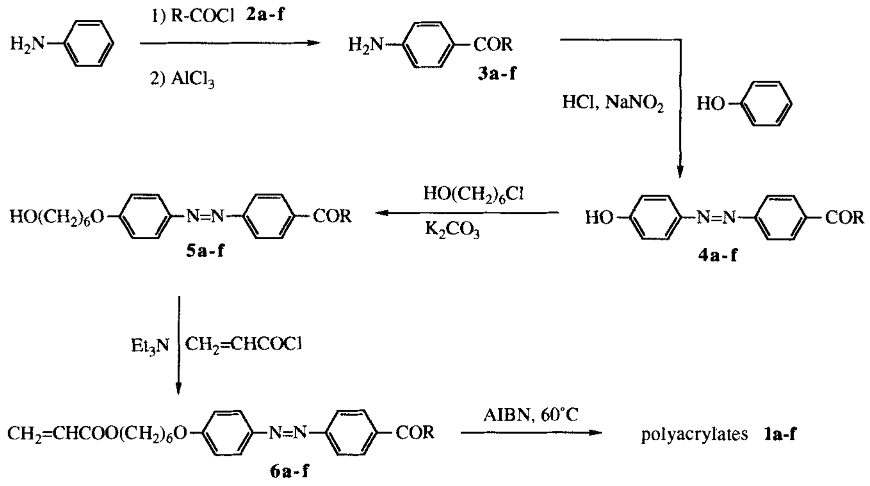


**7a–f**

## 2. Experimental

### 2.1. *Precursors and monomers*

Acrylate monomers **6a–f** were synthesized according to the general procedure outlined in the scheme. As a typical example, the synthesis of acrylate **6e** is reported in detail.



Scheme. Synthetic procedure for the preparation of acrylates **6a–f** and polyacrylates **1a–f**.

2.1.1. *4-Hexanoylaniline* (**3e**)

53·8 g (0·40 mol) of *n*-hexanoyl chloride (**2e**) were added under a nitrogen atmosphere in 2 h to a solution of 18·6 g (0·20 mol) of aniline in 220 ml of $CS_2$ at room temperature. After 4 h, 53·4 g (0·40 mol) of finely ground, anhydrous $AlCl_3$ were added portionwise in 2 h at room temperature. After 12 h reaction at 50°C, 13·5 ml of 10 per cent HCl were added and the mixture was left to react for an additional 10 h. The mixture was then shaken with diethyl ether and the water phase, after addition of 70 ml of 20 per cent HCl, was heated to reflux for 12 h. After cooling to room temperature and neutralization with 40 per cent aqueous NaOH, the water phase was shaken with diethyl ether. The extract was distilled under vacuum and crystallized twice from water/methanol (1 : 1 vol/vol): mp 83–84°C; yield 19·9 g (53 per cent).

2.1.2. *4-Hexanoyl-4′-hydroxyazobenzene* (**4e**)

A solution of 12·0 g (0·17 mol) of $NaNO_2$ in 30 ml of water was added dropwise at 0–5°C with vigorous stirring to 26·7 g (0·14 mol) of **3e** dissolved in 150 ml of 3 M HCl. After 1 h, the excess of $NaNO_2$ was decomposed by addition of urea and the solution was slowly poured into a solution of 13·6 g (0·14 mol) of phenol in 150 ml of 2 M aqueous NaOH. After 10 min, the solution was acidified with HCl and the solid precipitated was washed with water, dried and finally crystallized from cyclohexane: mp 133–135°C, yield 19·5 g (47 per cent).

2.1.3. *4-Hexanoyl-4′-(6-hydroxyhexyloxy)azobenzene* (**5e**)

A mixture of 3·7 g (27 mmol) of 6-chlorohexan-1-ol, 4·0 g (13·5 mmol) of **4e** and 3·7 g (27 mmol) of anhydrous $K_2CO_3$ in 50 ml of dry dimethylsulphoxide was heated at 110°C for 2 h. It was then poured into 200 ml of cold water with vigorous stirring and the precipitated solid was filtered off, washed several times with 1 M aqueous NaOH and water, and finally crystallized twice from cyclohexane: mp 112–114°C; yield 4·1 g (76 per cent).

2.1.4. *4-Hexanoyl-4′-(6-acryloyloxyhexyloxy)azobenzene* (**6e**)

A solution of 1·6 g (18 mmol) of acryloyl chloride in dry tetrahydrofuran was added dropwise with vigorous stirring under dry nitrogen to a solution of 3·5 g (8·8 mmol) of

**5e**, 2·7 g (26 mmol) of triethylamine and 0·1 g of 2,6-di-*t*-butyl-4-methylphenol in 100 ml of the same solvent at 0°C. After 30 min the solution was filtered and the solid washed with tetrahydrofuran and the filtrates were evaporated under vacuum. The solid crude product was crystallized twice from ethanol: mp 91–92°C yield 2·5 g (63 per cent).

$^1$HNMR ($CDCl_3$): $\delta$ (in ppm from tetramethylsilane (TMS)) = 8·1–7·8 (m, 6 H, aromatic); 7·0 (dd, 2 H, aromatic); 6·5–5·8 (m, 3H, vinyl); 4·2 (t, 2 H, $CH_2$); 4·1 (t, 2 H, $CH_2$); 3·0 (t, 2 H, $CH_2CO$); 1·8–1·2 (m, 14 H, aliphatic); 0·9 (t, 3 H, $CH_3$).

Details about reaction yields and the purifications of compounds **5** and **6** are given in tables 1 and 2 respectively.

### 2.2. *Polymers*

In a typical polymerization reaction, 1·0 g of acrylate was dissolved in 5 ml of dry benzene in the presence of 5·0 mg of 2,2′-azobis-isobutyronitrile (AIBN). The reaction mixture was introduced into a Pyrex glass ampoule, thoroughly freeze–thaw degassed and sealed under vacuum. After a reaction time of 48 h at 60°C, the polymer was recovered by addition of 100 ml of methanol and purified by extraction with boiling methanol in a Kumagawa extractor. The polymeric product was then dried in vacuum for 16 h. Reaction yields typically ranged from 20 to 30 per cent.

### 2.3. *Physicochemical characterizations*

$^1$HNMR spectra were recorded using a Varian Gemini 200 spectrometer. Average molecular weights were determined by size exclusion chromatography (SEC) using chloroform solutions and a 590 Waters chromatograph equipped with a Shodex KF-804 column. Polystyrene standard samples were used for the universal calibration method. Differential scanning calorimetric (DSC) analyses were carried out under a dry nitrogen flow with a Perkin–Elmer DSC 7 apparatus. Samples of 5–10 mg were

Table 1. Characterization of intermediates **5a–f**.

| Sample | Crystallization solvent | Yield/per cent | $T_m$/K | $T_i$/K | $\Delta S_i$/J mol$^{-1}$ K$^{-1}$ |
|---|---|---|---|---|---|
| **5a** | Ethanol | 73 | 394 | 421 | 17·0 |
| **5b** | Cyclohexane | 53 | 366 | 421 | 18·2 |
| **5c** | Ethanol | 58 | 391 | 409 | 17·3 |
| **5d** | Ethanol | 66 | 388 | 410 | 19·0 |
| **5e** | Cyclohexane | 76 | 387 | 393 | 17·5 |
| **5f** | Ethanol | 60 | 390 | 401 | 19·6 |

Table 2. Characterization of monomers **6a–f**.

| Sample | Crystallization solvent | Yield/per cent | $T_m$/K | $T_i$/K | $\Delta S_i$/J mol$^{-1}$K$^{-1}$ |
|---|---|---|---|---|---|
| **6a** | Methanol | 53 | 380 | —† | —† |
| **6b** | Ethanol | 46 | 363 | 381 | 11·5 |
| **6c** | Methanol | 50 | 379 | —† | —† |
| **6d** | Methanol | 53 | 368 | 377 | 17·1 |
| **6e** | Ethanol | 63 | 365 | —† | —† |
| **6f** | Methanol | 60 | 361 | 378 | 18·9 |

† Not mesomorphic.

employed. The temperature scale was calibrated against the melting temperature of indium. For the determination of the transition enthalpy, indium was used as a standard material. The transition temperatures were taken from the DSC traces of samples annealed by cooling from the isotropic melt, as corresponding to the maxima and to the onset points of the enthalpic peaks for the polymers and low molar mass samples respectively, at a heating rate of $10\,\mathrm{K\,min^{-1}}$. Optical microscopy observations were performed on polymer films mounted between glass slides using a Reichert Polyvar microscope equipped with a programmable Mettler FP 52 heating stage at a scanning rate of $10\,\mathrm{K\,min^{-1}}$. X-ray diffraction measurements were performed in transmission mode, from room temperature up to the isotropization point, using a powder Guinier camera equipped with a bent quartz monochromator giving well-focused and monochromatic X-rays ($\mathrm{CuK}_{\alpha 1}$ $\lambda = 1{\cdot}54\,\mathrm{\AA}$).

## 3. Results and discussion

### 3.1. *Synthesis*

Monomers **6a–f** were synthesized according to the general procedure outlined in the scheme. Briefly, aniline was converted by acid chlorides (**2a–f**) into the corresponding anilides which, without isolation, were submitted to an acid-catalysed Fries transposition reaction to the 4-alkanoylanilines (**3a–f**) [14, 15]. Their diazonium salts were then transformed into 4-alkanoyl-4′-hydroxyazobenzenes (**4a–f**) by coupling with phenol. 4-Alkanoyl-4′-(6-hydroxyhexyloxy)azobenzenes (**5a–f**) were prepared by etherification with 6-chlorohexan-1-ol of phenols **4a–f** in the presence of anhydrous $K_2CO_3$. The final reaction between hydroxylated compounds **5a–f** and acryloyl chloride was performed in the presence of triethylamine and a small amount of free radical inhibitor. Polyacrylates **1a–f** were prepared by free radical polymerization in solution with 2,2′-azobis-isobutyronitrile (AIBN) as the initiator (0·5 per cent by weight) at 60°C. Purification of the polymeric products was accomplished by precipitation from chloroform solution into methanol followed by continuous extraction with boiling methanol. Polymerization yields were fairly low, ranging between 20 and 30 per cent. Indeed, similar reaction yields were observed [8–10] in the polymerization of other acrylic monomers containing the azobenzene unit. In contrast, the polymerization of methacrylic monomers containing the same mesogenic group afforded the corresponding polymethacrylates in practically quantitative yield [11]. At present, we have no explanation of this peculiar behaviour. The molecular weight characteristics of the polyacrylates were determined by SEC and are given in table 3. The number average molecular weight ($M_n$) ranged from 18 000 to 27 000 with a first polydispersity index ($M_w/M_n$) between 1·5 and 1·7. For related liquid crystalline

Table 3. Physicochemical properties of polyacrylates **1a–f**.

| Polymer | $M_n$† | $M_w/M_n$† | $T_m$/K | $T_i$/K | $\Delta S_i/\mathrm{J\,mol^{-1}\,K^{-1}}$ |
|---|---|---|---|---|---|
| **1a** | 25000 | 1·6 | 343 | 465 | 1·0 |
| **1b** | 18000 | 1·5 | 354 | 454 | 7·7 |
| **1c** | 25000 | 1·6 | 353 | 453 | 8·8 |
| **1d** | 27000 | 1·7 | 355 | 448 | 10·7 |
| **1e** | 27000 | 1·5 | 343 | 422 | 9·7 |
| **1f** | 26000 | 1·6 | 365 | 441 | 12·2 |

† By SEC, in chloroform.

polymethacrylates it has been claimed [16] that the mesophase phase transition parameters become nearly independent of the polymer molecular weight above a degree of polymerization of about ten. By applying this to the present polymer system, we conclude that although the molecular weights of the polymers **1** are relatively low, the relevant phase transition parameters should not be affected by differences in their molecular weights.

### 3.2. *Mesomorphic behaviour of precursors* **5** *and monomers* **6**

The phase transition behaviour of the monomers and intermediate compounds was studied by DSC and polarizing microscopy. The transition parameters of precursors **5a–f** are given in table 1. All samples **5a–f** showed one enantiotropic mesophase identified as smectic A by the optical microscopic observation of focal-conic fans. X-ray diffraction spectra on unoriented samples were also recorded. They confirmed the existence of a smectic A phase with a measured interlayer spacing *d* varying from 25·6 Å for **5b** to 29·0 Å for **5f**. The dependence of the transition temperatures on the number *n* of carbon atoms, excluding the carbonyl moiety, of the terminal alkyl tail is illustrated in figure 1. The smectic–isotropic or isotropization temperatures ($T_i$) decreased regularly with increasing *n* in a typical alternating fashion in which samples possessing an alkyl tail with even *n* exhibited higher transition temperatures than adjacent homologues with odd *n*. This even–odd effect was more pronounced as the series was ascended. In contrast, there was no regular dependence of the melting temperature ($T_m$) on *n*. Thus the mesomorphic range was 55 K for **5b**, but as narrow as 6 K for **5e**. The trend of the smectic–isotropic entropy ($\Delta S_i$) as a function of the number *n* is represented in figure 2. $\Delta S_i$ increased with increasing *n* with a regular odd–even alternation in which members comprising substitutents with an even number of carbon atoms exhibited higher values.

A completely different mesophasic behaviour was shown by the acrylate monomers **6a–f** (table 2). In this series, the samples possessing an alkyl tail with an even number *n* exhibited an enantiotropic mesophase which was identified as smectic by observation of focal-conic textures. Unfortunately, the extensive decomposition of the acrylates at temperatures within the mesophasic range, prevented a final phase assignment by X-ray diffraction. In contrast, the acrylate samples possessing odd values of *n* displayed

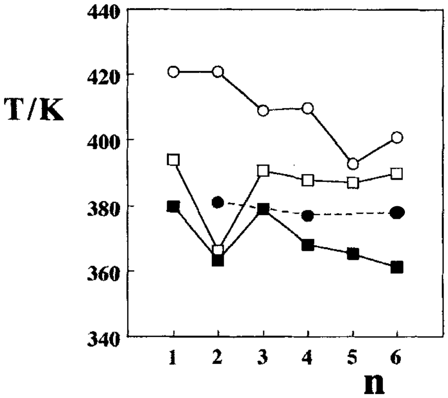


Figure 1. Trends of the isotropization (●, ○) and melting (■, □) temperatures as a function of the number *n* of carbon atoms of the terminal alkyl tail for intermediates **5a–f** (open symbols) and acrylates **6a–f** (full symbols).

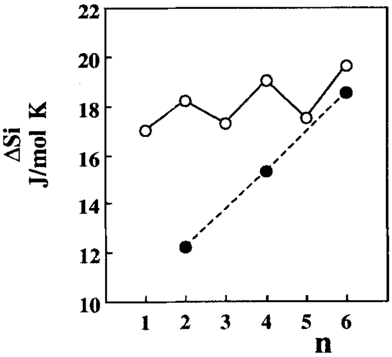


Figure 2. Trends of the isotropization entropy (●, ○) as a function of the number *n* of carbon atoms of the terminal alkyl tail for intermediates **5a**–**f** (open symbols) and acrylates **6a**–**f** (full symbols).

no mesomorphic properties even in the supercooled state. The trends of the melting and isotropization temperatures as functions of the number *n* of carbon atoms in the alkyl tail of acrylates **6a**–**f** are also represented in figure 1. $T_m$ decreased with a slightly pronounced odd–even alternation with increasing *n*, whereas the $T_i$ of the acrylates with even *n* were nearly constant. The largest mesomorphic range (18 K) was detected for **6b**. $\Delta S_i$ for acrylates with even *n* (figure 2) increased in a linear fashion with increasing *n*. By comparing the phase transition parameters of samples **5** with those of acrylates **6**, it appears that both the isotropization temperatures and entropies of samples **5** are consistently higher than the corresponding values for the acrylates **6**. This effect is probably due to the occurrence of intermolecular hydrogen bonding interactions that greatly enhance the stability of the smectic phase of samples **5** with respect to that of the acrylates **6**.

### 3.3. *Mesomorphic behaviour of polyacrylates* 1

The mesomorphic behaviour of the polyacrylates **1** was investigated by DSC and polarizing microscopy, and by X-ray diffraction on unoriented specimens of polymers **1b** to **1d** and **1f**. All the as-prepared polymers were characterized by a very low degree of crystallinity ($\approx 10$ per cent) as evaluated by DSC experiments. However, no crystallinity was detected by X-ray diffraction on sample **1f**. All the polymers showed one enantiotropic mesophase. On cooling from the isotropic liquid, crystallization occurred for polymer **1b** only, and the mesophase was locked-in at room temperature for polymers **1c**, **1d**, and **1f** as also revealed by X-rays. The relevant phase transition parameters are collected in table 3. In all cases, the nature of the mesophase was identified as smectic by observation of distinct fan-shaped textures and confirmed by X-ray diffraction. As a typical example, figure 3 shows the X-ray diffraction spectrum of an unoriented sample **1d** at 391 K. It consists of a small angle (inner region), sharp reflection and a wide angle (outer region) diffuse halo typical of a disordered smectic mesophase. The smectic interlayer spacing was $d = 30{\cdot}4$ Å and the average intermolecular distance between the side-chain mesogenic groups was $D \approx 4{\cdot}3$ Å. Neither the crystalline small angle spacing ($d_k$) nor the smectic interlayer spacing changed with temperature (figure 4). The value of the smectic interlayer spacing of polymers was in each case equal to or slightly longer than the length ($L$) of the polymer repeating unit in the fully extended conformation as evaluated from CPK models; this value increased from $L = 26 \pm 1$ Å for **1b** to $L = 31 \pm 1$ Å for **1f**. This suggests the presence of an

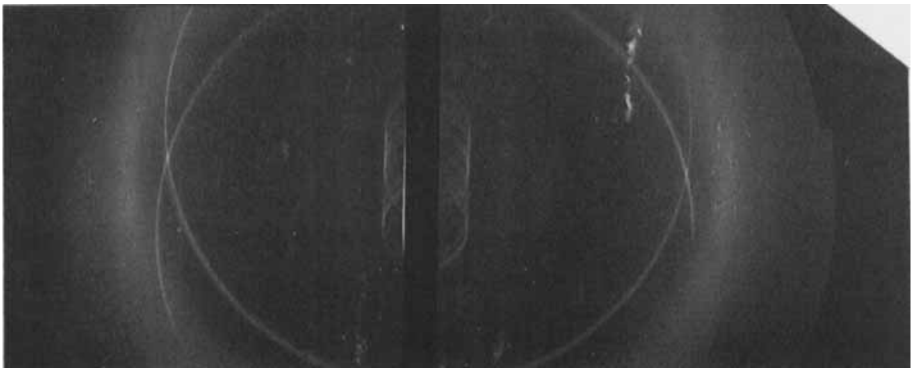


Figure 3. X-ray diffraction pattern of the unoriented smectic mesophase of polyacrylate **1d** at 391 K.

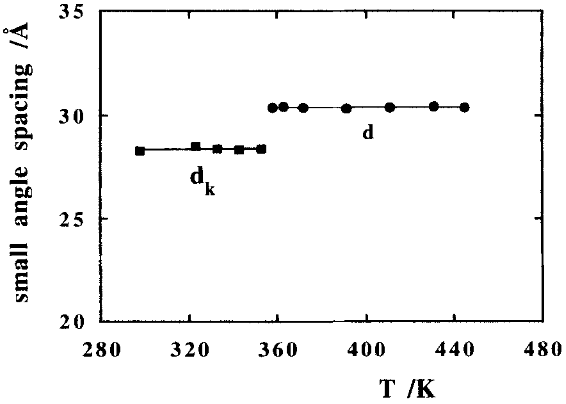


Figure 4. Variation of the crystalline ($d_k$) and smectic ($d$) small angle spacing as a function of temperature for polyacrylate **1d**.

orthogonal disordered smectic mesophase, such as the smectic $A_1$ phase. The X-ray diffraction patterns of unoriented **1b**, **1c** and **1f** samples were very similar to that of sample **1d** and in all cases the smectic interlayer spacing was unaffected by temperature throughout the mesophase range. The X-ray data for polyacrylates **1b–d** and **1f** are collected in table 4. Surprisingly, the values of $d$ for samples **1b–d** and **1f** were practically identical, in spite of the different lengths of the alkanoyl substituent on the azobenzene mesogen. A simple structural model for the smectic mesophase of polymers **1**, consistent with these findings and able to account for the insensitivity of the interlayer smectic spacings to the length of the terminal alkyl chains, is sketched in figure 5. This structure consists of a fully interdigitated smectic $A_1$ mesophase ($d \approx L$) in which the terminal alkyl chain on a mesogenic group is associated side by side with the flexible spacer of adjacent pendent mesogenic groups within the smectic layer. As the length of the flexible spacer in all the samples studied was greater or roughly equal to that of the terminal alkyl chain, the variation in the latter should result in a limited influence on the lateral chain packing of the mesogenic groups in the smectic mesophase. This structure should be stabilized by the dipolar interactions between adjacent mesogenic

Table 4. Small angle spacing of the semicrystalline ($d_k$) and smectic $A_1$ ($d$) phases of representative polyacrylates.

| Polymer | $d_k$/Å | $d$†/Å |
|---|---|---|
| **1b** | 26·7 | 30·0 |
| **1c** | 27·6 | 29·4 |
| **1d** | 28·4 | 30·4 |
| **1f** | nd‡ | 31·5 |

† Measured 20 K below the smectic–isotropic transition temperature.
‡ Amorphous sample by X-ray diffraction.

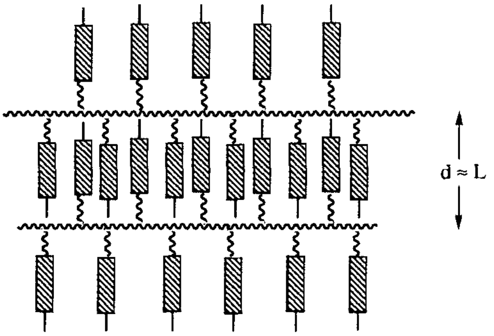


Figure 5. Schematic representation of the structural arrangement of the smectic $A_1$ mesophase of the polymers **1**.

groups, as has been observed for other side-chain liquid crystalline polymers [17–19]. The trends in the melting and smectic–isotropic transition temperatures for polymers **1** as a function of the number $n$ is illustrated in figure 6. While $T_m$ increased with increasing $n$, $T_i$ decreased. Accordingly, wider mesophasic ranges occurred for homologues with lower values of $n$, namely 122 K for **1a** ($n = 1$). Figure 7 shows the dependence of the smectic–isotropic transition entropy on the length of the terminal alkyl substituent. $\Delta S_i$ strongly increased with increasing $n$, with a pronounced odd–even alternation, with the even numbered polymer samples having the higher values. There was a marked increase in $\Delta S_i$ in passing from **1a** to **1b** and the others, which suggests that the smectic A phase of the former polyacrylate may differ in its degree of order.

The mesophase properties of polymers **1a–f** are in marked contrast to those of the previously described series of polymers **7a–f**, based on the azobenzene unit substituted in the 4-position by a linear alkyloxy chain containing a variable number $n$ of carbon atoms. The lower homologues ($n = 1$–$3$) of the latter polymer series exhibited one nematic mesophase, while on further increasing $n$ ($n = 4, 5$) an additional smectic phase formed; the polymers became purely smectic for $n \geq 6$. Comparison of the transition temperatures of both polymer series (figure 6) reveals that the polymers **1** possess a greater propensity to give rise to stable and persistent smectic mesophases than do the polymers **7**, thus indicating that the replacement of an oxygen atom by a carbonyl group strongly enhances the smectogenic character of the azobenzene group in side-chain polymers.

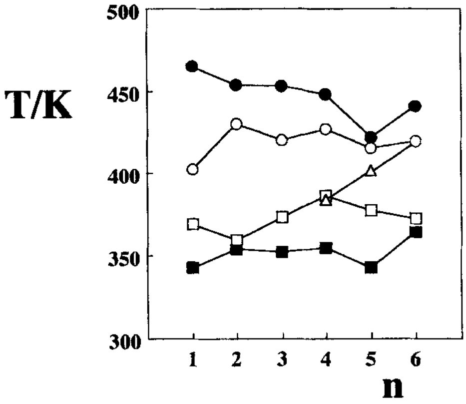


Figure 6. Trends of the isotropization (●, ○) smectic–nematic (Δ) and melting (■, □) transition temperatures as a function of the number *n* of carbon atoms of the terminal alkyl tail for polyacrylates **1** (full symbols) and **7** (open symbols).

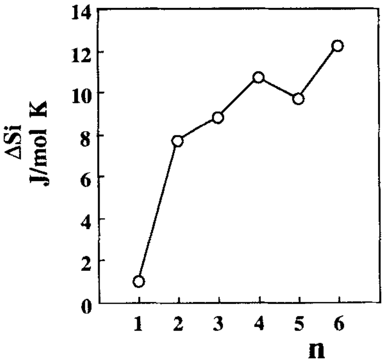


Figure 7. Trend of the isotropization entropy as a function of the number *n* of carbon atoms of the terminal alkyl tail for polyacrylates **1**.

## 4. Conclusion

A new series of side-chain liquid crystalline polyacrylates based on the photo-responsive azobenzene mesogenic unit spaced from the backbone by a hexamethylene spacer and substituted in the 4-position by an alkanoyl chain of variable length were synthesized and studied in respect of their mesomorphic behaviour. Evidence was provided of the formation of smectic mesophases in a fairly broad range of temperature for both polymers and relevant low molar mass precursors. The analysis of the X-ray diffraction spectra of the polymers suggested the presence of a completely inter-digitated smectic $A_1$ mesophase. In both low molar mass compounds and polymers, the smectic–isotropic phase transition parameters were characterized by distinct odd–even alternations. A comparison of the transition parameters of the polymers with those of a closely related polyacrylate series containing the azobenzene unit substituted in the 4-position by an alkyloxy chain of variable length revealed that the replacement of an oxygen atom by a carbonyl group strongly enhanced the smectogenic character of the azobenzene group. This effect is probably due to the increased polarizability of the mesogenic group parallel to its long molecular axis and the introduction of an additional dipole moment perpendicular to it.

Financial support from the Interuniversity Consortium of Condensed Matter of Italy (INFM) and CNR-Progetti Bilaterali is gratefully acknowledged.

## References

[1] Percec, V., and Pugh, C., 1989, *Side Chain Liquid Crystal Polymers*, edited by C. B. McArdle (Blackie & Sons).

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

[3] Seki, T., Tamaki, T., Suzuki, Y., Kawanishi, K., Ichimura, K., and Aoki. K., 1989, *Macromolecules*, **22**, 3505.

[4] Ortler, R., Brauchle, C., Miller, A., and Riepl, G., 1989, *Makromolek. Chem. rap. Commun.*, **10**, 189.

[5] Ikeda, T., Horiukchi, S., Karanjit, D. B., Kurihara, S., and Tazuke, S., 1990, *Macromolecules*, **23**, 36; 1990, *Ibid.*, **23**, 42.

[6] Ivanov, S., Yakovlev, I., Kostromin, S., Shibaev, V., Läsker, L., Stumpe, J., and Keysig, D., 1991, *Makromolek. Chem. rap. Commun.*, **12**, 709.

[7] Wiesner, U., Reynolds, N., Boeffel, C., and Spiess, H. W., 1991, *Makromolek. Chem. rap. Commun.*, **12**, 457.

[8] Angeloni, A. S., Caretti, D., Carlini, C., Chiellini, E., Galli, G., Altomare, A., Solaro, R., and Laus, M., 1989, *Liq. Crystals*, **4**, 513.

[9] Angeloni, A. S., Campagnari, I., Caretti, D., Carlini, C., Altomare, A., Chiellini, E., Galli, G., Solaro, R., and Laus, M., 1990, *Gazz. chim. ital.*, **120**, 171.

[10] Angeloni, A. S., Caretti, D., Laus, M., Chiellini, E., and Galli, G., 1991, *J. polym. Sci. polym. Chem. Ed.*, **29**, 1865.

[11] Chiellini, E., Galli, G., Angeloni, A. S., Laus, M., and Caretti, D., 1992, *Macromolecular Assemblies in Polymeric Systems*, edited by P. Stroeve and A. C. Balazs, ACS Symp. Ser. No. 493, 280.

[12] Poeti, G., Fanelli, E., and Braghetti, M., 1978, *Molec. Crystals liq. Crystals*, **45**, 145.

[13] Albertini, G., Fanelli, E., Guillon, D., Melone, S., Poeti, G., Rustichelli, F., and Torquati, G., 1983, *J. chem. Phys.*, **78**, 2013.

[14] Fanelli, E., Poeti, G., Francescangeli, O., and Torquati, G., 1988, *Nuovo Cim.*, **10D**, 1373.

[15] Clifford, D. R., Dais, R. N., and Woodcock, R., 1960, *J. chem. Soc.*, p. 5097.

[16] Percec, V., Tomazos, D., and Pugh, C., 1989, *Macromolecules*, **22**, 3259.

[17] Chiellini, E., Galli, G., Cioni, F., Dossi, E., and Gallot, B., *J. mater. Chem.* (in the press).

[18] Esselin, S., Bosio, L., Noel, C., Decobert, G., and Dubois, J. C., 1987, *Liq. Crystals*, **2**, 50.

[19] Hardouin, F., Achard, M. F., Destrade, C., and Tinh, N. G., 1984, *J. Phys., Paris*, **45**, 765.