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Liquid Crystals

Publication details, including instructions for authors and subscription information:

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Online publication date: 11 November 2010

To cite this Article Patel, Pratik R. and Dave, Jayrang S.(2003) 'The synthesis and mesogenic properties of side chain polymethacrylates with terminal branched groups', *Liquid Crystals*, 30: 6, 691 – 696

To link to this Article: DOI: 10.1080/0267829031000707734

URL: <http://dx.doi.org/10.1080/0267829031000707734>

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The synthesis and mesogenic properties of side chain polymethacrylates with terminal branched groups

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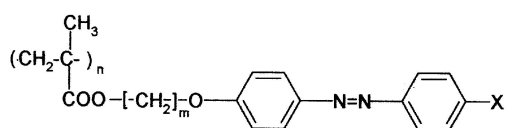
(Received 6 December 2002; accepted 3 February 2003)

The synthesis is described of six polymethacrylates attached through oxytetramethylene and oxyhexamethylene spacers to an azobenzene moiety consisting of branched terminal *iso*-butoxy, *iso*-amyloxy and *n*-amyloxy groups. The monomers show a nematic mesophase while their polymers show an additional higher order smectic C phase. The effects of the terminal branched alkoxy group and the spacers on mesomorphic properties are discussed. The phase characteristics, thermal stabilities and molecular masses of the polymers were investigated by DSC, XRD, TGA and GPC. The polymers were also characterized by UV-vis, IR and NMR spectroscopy.

1. Introduction

The increased interest in synthesis and structural investigations of side chain liquid crystalline polymers with an azo group in the mesogenic units is due to their potential applications in the fields of non-linear optics, in optical storage and in electro-optical displays [1–7]. The photo-responsive azobenzene group appears particularly interesting because irradiation can cause *trans*–*cis* isomerization of the photochromic group, so inducing a local phase transition [8–13]. Additionally, the azo-containing mesogenic group may act as a convenient photo-responsive probe of polymer conformation, both in the bulk and in solution [14]. Polymers with a methacrylate backbone offer excellent optical properties and a high permanent dipole moment, both are necessary for efficient NLO structures [15].

In this context, we have synthesized six polymethacrylate polymers containing a *trans*-azobenzene pendant group; these have varying flexible spacers with branched *iso*-butoxy, *iso*-amyloxy and *n*-amyloxy terminal groups. The polymers investigated were:



| polymer | P ₁ | P ₂ | P ₃ | P ₄ | P ₅ | P ₆ |
|----------|--------------------|--------------------|---------------------|---------------------|-------------------|-------------------|
| <i>m</i> | 4 | 6 | 4 | 6 | 4 | 6 |
| <i>X</i> | <i>iso</i> -butoxy | <i>iso</i> -butoxy | <i>iso</i> -amyloxy | <i>iso</i> -amyloxy | <i>n</i> -amyloxy | <i>n</i> -amyloxy |

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2. Experimental

2.1. Characterization

Microanalysis of the monomers was carried out using a Coleman USA CHN-analyser. The spectroscopic data of the monomers and polymers were obtained on a Perkin-Elmer FTIR spectrometer, a Jeol FX 100 spectrophotometer (NMR), and a Hitachi U-2000 double beam spectrophotometer (UV-vis). The molecular mass and polydispersity ratios for the polymers were determined using a Perkin-Elmer (Series 200) HPLC apparatus, using polystyrene standards and tetrahydrofuran eluent. The textures of the liquid crystalline phases exhibited by the polymers were studied using a Leitz 'laborlux' polarizing microscope provided with a Kofler hot stage. Thermal properties were investigated by differential scanning calorimetry (DSC Mettler TA-4000 system). The thermal stabilities of the polymers were examined on a high resolution Mettler TGA 2950 instrument at heating rates of 10°C min⁻¹ under N₂.

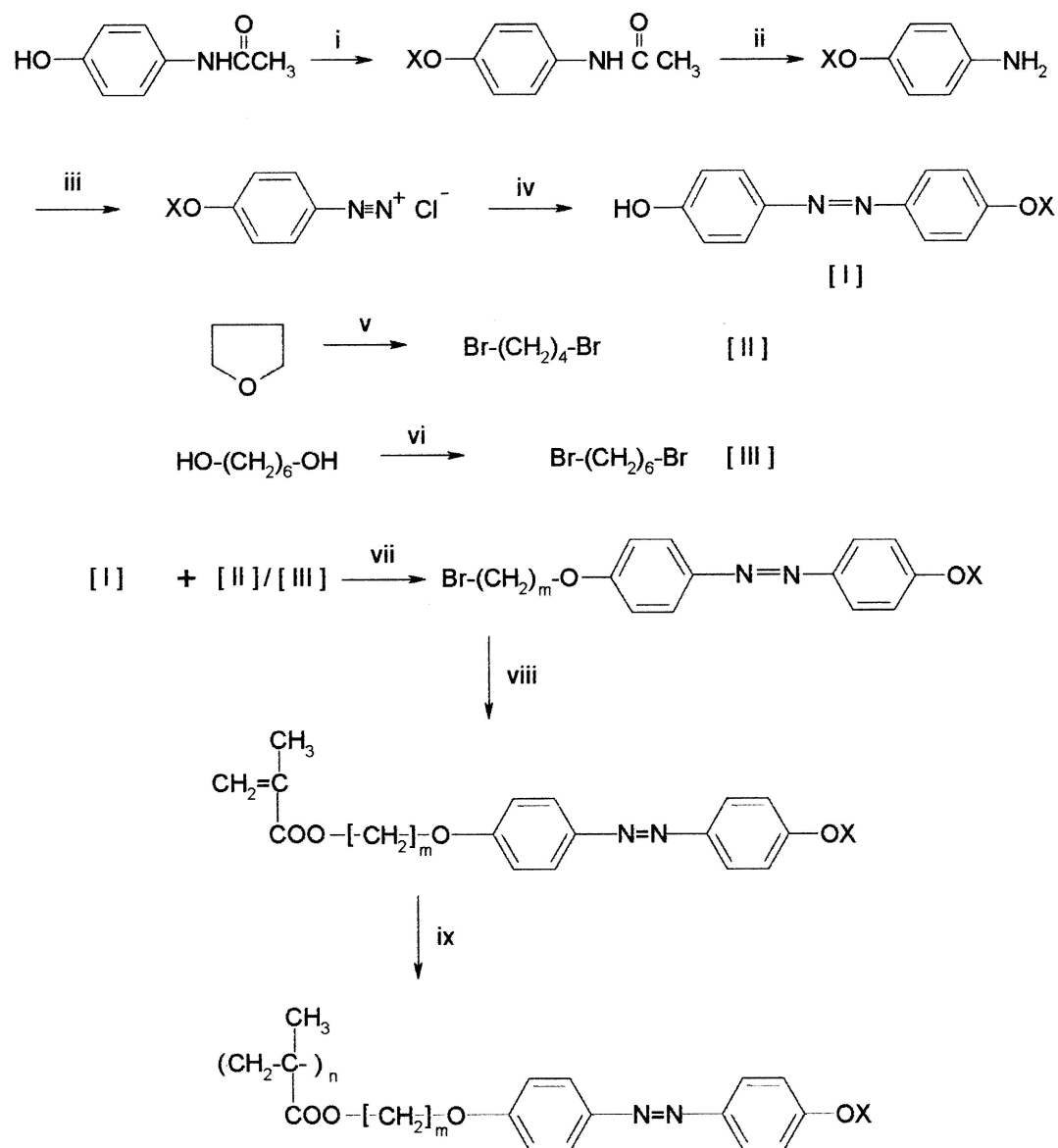
2.2. Materials

4-Hydroxyacetanilide, *iso*-butylbromide *iso*-amylbromide, *n*-amylbromide, tetrahydrofuran, methacrylic acid and 1,6 hexanediol were obtained from Merck Ltd. and used as received. Toluene, which was used in the polymerization reaction, was heated at reflux over sodium and then distilled under nitrogen.

The Polymers were prepared by the reactions shown in the scheme.

2.2.1. 4-*iso*-butoxyaniline, 4-*iso*-amyloxyaniline and 4-*n*-amyloxyaniline

These were synthesized by reported methods [16, 17].



Scheme. $m = 4,6$; $X = \text{iso-butyl, iso-amyl or } n\text{-amyl}$. (i) Anhyd. K_2CO_3 , *iso*-butylbromide, *iso*-amylbromide or *n*-amylbromide, dry acetone; (ii) H_2O , HCl ; (iii) HCl , NaNO_2 , $0-5^\circ\text{C}$; (iv) phenol, aq. NaOH , $0-10^\circ\text{C}$; (v) H_2SO_4 , HBr ; (vi) H_2SO_4 , HBr ; (vii) anhyd. K_2CO_3 , dry acetone; (viii) DMF , KHCO_3 , methacrylic acid; (ix) toluene, AIBN , 70°C .

2.2.2. *4-Hydroxyphenylazo-4'-iso-butoxybenzene, 4-hydroxyphenylazo-4'-iso-amylxybenzene and 4-hydroxyphenylazo-4'-n-amylxybenzene*
These were prepared by known procedures [18].

2.2.3. 1,4-Dibromobutane

This was prepared from tetrahydrofuran following standard procedures [18].

2.2.4. 1,6-Dibromohexane

This was prepared from 1,6-hexanediol by a reported method [18].

2.2.5. α -Bromo- ω -(4-alkoxyazobenzene-4'-oxy)alkanes

These were synthesized by the method described by Crivello *et al.* [19]. FTIR (KBr cm^{-1}): 1276 (CH_2Br). ^1H NMR: (CDCl_3 , 300 MHz, δ ppm, standard TMS) (*iso*-butoxy) 0.95 (6H, d, $2 \times -\text{CH}_3$), 1.2–2 (m, alkyl chain), 2.1 (1H, m, $-\text{CH}(\text{CH}_3)_2$), 3.9 (2H, d, $-\text{OCH}_2-\text{CH}(\text{CH}_3)_2$), 4.00 (2H, t, $-\text{OCH}_2-\text{CH}_2$), 6.95 (2H, d, H^2), 7.9 (2H, d, H^6); (*iso*-amylxy) 0.9 (6H, d, $2 \times -\text{CH}_3$), 1.2–1.75 (m, alkyl chain), 1.85 (1H, m, $-\text{CH}(\text{CH}_3)_2$), 4.1 (4H, t, $2 \times -\text{OCH}_2$), 6.95 (2H, d, H^2), 7.9 (2H, d, H^6); (*n*-amylxy) 0.95 (3H, t, $-\text{CH}_3$), 1.2–2 (m, alkyl chain), 3.5 (2H, t, $-\text{OCH}_2$ alkyl chain), 4 (2H, t, $-\text{OCH}_2-\text{Br}$), 7 (2H, d, H^1), 7.85 (2H, d, H^2).

2.2.6. Monomers M_1 – M_6

These were prepared by the method of Tamaki *et al.* [20]. FTIR (KBr cm^{-1}): 1721 (C=O), 1640 (C=C). ^1H NMR: (CDCl_3 , 300 MHz, δ ppm, standard TMS) (*iso*-butoxy) 0.95 (6H, d, $2 \times -\text{CH}_3$), 1.2–1.5 (m, alkyl chain), 1.6 (3H, s, CH_3-C), 2.1 (1H, m, $-\text{CH}(\text{CH}_3)_2$), 3.5 (2H, s, $\text{CH}_2=\text{C}$), 3.9 (2H, d, $-\text{OCH}_2-\text{CH}(\text{CH}_3)_2$), 4.00 (2H, t, $-\text{OCH}_2-\text{CH}_2$), 7.0 (2H, d, H^2), 7.9 (2H, d, H^6); (*iso*-amyloxy) 0.9 (6H, d, $2 \times -\text{CH}_3$), 1.2–1.55 (m, alkyl chain), 1.6 (3H, s, CH_3-C), 1.85 (1H, m, $-\text{CH}(\text{CH}_3)_2$), 3.5 (2H, s, $\text{CH}_2=\text{C}$), 4.1 (4H, t, $2 \times -\text{OCH}_2$), 6.5 (2H, d, H^2), 6.9 (2H, d, H^6); (*n*-amyloxy) 0.95 (3H, t, $-\text{CH}_3$), 1.2–2 (m, alkyl chain), 1.65 (3H, s, CH_3-C), 3.6 (2H, s, $\text{CH}_2=\text{C}$), 4.1 (4H, t, $2 \times -\text{OCH}_2$), 7 (2H, d, H^1), 7.85 (2H, d, H^2).

2.2.7. Polymerization

Preparation of the polymethacrylates was carried out by free radical polymerization. A toluene solution of the monomer (10% wt/vol) was polymerized under a nitrogen atmosphere for 24 h at 70°C, with 2,2'-azobisisobutyronitrile (AIBN, 0.5 mol %) as initiator. After reaction, the polymer was precipitated by adding to an excess of cold methanol and the crude polymer was filtered. It was then purified by dissolving in chloroform and reprecipitating from cold methanol.

3. Results and discussion

In order to study the influence of the ratio of spacer length to length of terminal chain, we have synthesized six polymethacrylates by radical polymerization using 2,2'-azobis(*iso*-butyronitrile) as initiator. The elemental analysis of the monomers is given in table 1.

3.1. Molecular mass determination

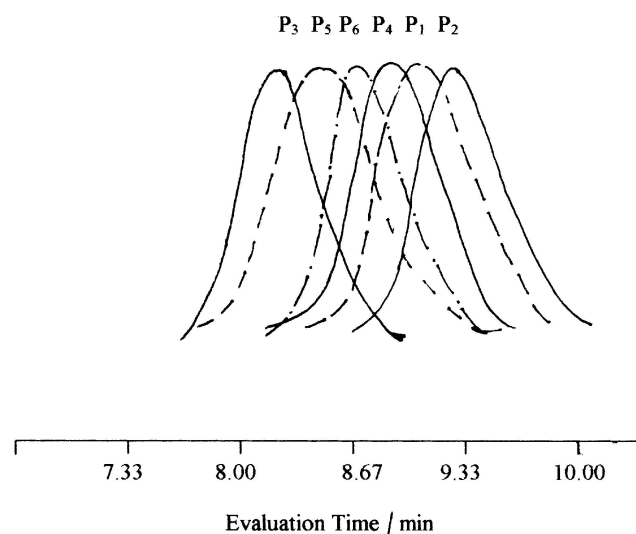
Molecular mass of the polymers was evaluated by gel permeation chromatography; the data obtained are collected in table 2. The GPC plot for polymers P_1 – P_6 shown in figure 1 indicates single peaks with average molecular mass (M_w) in the range 8349–24453 (as compared with polystyrene standards). Molecular mass distributions—as indicated by the ratio of the weight-

Table 1. Elemental analysis (%) of the monomers.

| Monomer | Found | | | Calculated | | |
|---------|-------|------|------|------------|------|------|
| | C | H | N | C | H | N |
| M_1 | 70.29 | 7.36 | 6.79 | 70.24 | 7.32 | 6.83 |
| M_2 | 71.25 | 7.78 | 6.32 | 71.23 | 7.76 | 6.39 |
| M_3 | 70.79 | 7.58 | 6.56 | 70.75 | 7.55 | 6.60 |
| M_4 | 71.69 | 7.99 | 6.12 | 71.68 | 7.96 | 6.19 |
| M_5 | 70.76 | 7.57 | 6.58 | 70.75 | 7.55 | 6.60 |
| M_6 | 71.69 | 7.98 | 6.16 | 71.68 | 7.96 | 6.19 |

Table 2. Weight average molecular mass and polydispersity indices of the polymers.

| Polymer | M_w | M_n | M_w/M_n Polydispersity |
|---------|--------|--------|--------------------------|
| P_1 | 8349 | 5056 | 1.65 |
| P_2 | 9321 | 5789 | 1.61 |
| P_3 | 18 799 | 13 601 | 1.63 |
| P_4 | 9219 | 5810 | 1.58 |
| P_5 | 24 453 | 10 400 | 2.3 |
| P_6 | 11 774 | 7135 | 1.65 |

Figure 1. GPC curves of the homopolymers P_1 , P_2 , P_3 , P_4 , P_5 and P_6 .

average to number-average molecular weight M_w/M_n (polydispersity)—were obtained in the range 1.58–2.3. It was observed that a high M_w sample has a higher molecular mass distribution than those of low M_w samples, which is in agreement with results reported by Heitz and Niessner [21].

3.2. Thermal analysis

Thermal properties of the monomers and polymers were investigated by DSC and polarizing optical microscopy (POM); see tables 3 and 4. Monomer M_1 , with an *iso*-butoxy terminal group and tetramethylene $-(\text{CH}_2)_4-$ spacer, exhibits an enantiotropic nematic mesophase at

Table 3. Transition temperatures (°C) of the monomers.

| Monomer | Nematic | Isotropic |
|---------|---------|-----------|
| M_1 | 66 | 86 |
| M_2 | | 95 |
| M_3 | (59) | 61 |
| M_4 | | 100 |
| M_5 | 62 | 81 |
| M_6 | (87) | 90 |

Table 4. Transition temperatures ($^{\circ}\text{C}$) of the polymers.

| Polymers | Smectic | Nematic | Isotropic | $\Delta H/\text{J g}^{-1}$ |
|----------------|---------|---------|-----------|---|
| P ₁ | 76 | | 132 | Cr-SmC 6.0 SmC-I 2.4 |
| P ₂ | | | 105 | |
| P ₃ | 100 | | 142 | Cr-SmC 8.6 SmC-I 2.9 |
| P ₄ | 72 | | 105 | Cr-SmC 5.6 SmC-I 1.5 |
| P ₅ | 101 | | 152 | Cr-SmC 2.4 SmC-I 8.0 |
| P ₆ | 86 | 119 | 128 | Cr-SmC 0.091 SmC-N 0.017 N-I 1.01 |

66°C ; however, with an increase in spacer length from $-(\text{CH}_2)_4-$ to $-(\text{CH}_2)_6-$ in monomer M_2 , no liquid crystal properties were observed on heating or cooling. Monomer M_3 , with the *iso*-amyloxy terminal group and $-(\text{CH}_2)_4-$ spacer, melts at 61°C on heating; on cooling, a nematic phase appears at 59°C in monotropic condition. However, monomer M_4 with a hexamethylene, $-(\text{CH}_2)_6-$, spacer is non-mesogenic, showing no liquid crystal character on heating or cooling. Monomer M_5 , with the *n*-amyloxy terminal group and $-(\text{CH}_2)_4-$ spacer, shows an enantiotropic nematic phase at 62°C ; however, monomer M_6 with the same terminal group and a $-(\text{CH}_2)_6-$ spacer shows a monotropic nematic phase at 86°C . The experimental results indicate that the type of mesophase formed by monomers with the same terminal group depends on the spacer length; it is observed that with increase in the spacer length from $-(\text{CH}_2)_4-$ to $-(\text{CH}_2)_6-$, the mesophase property is either eliminated (M_2 , M_4) or obtained in the monotropic condition (M_6).

All the polymers except P_2 show a higher order smectic C phase. DSC curves (figure 2) of all the polymers

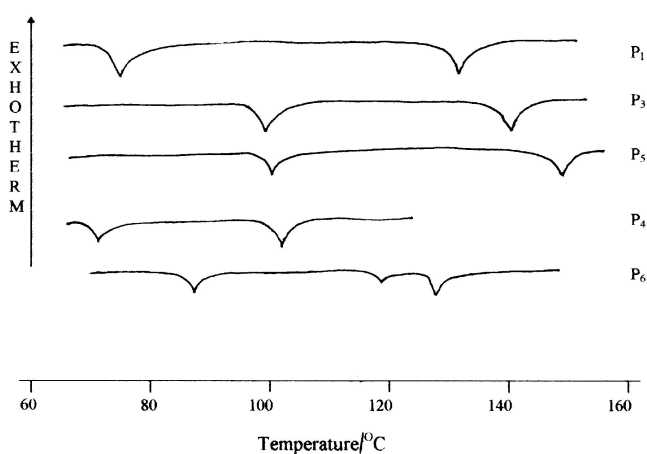


Figure 2. DSC curves of the homopolymers P_1 , P_3 , P_4 , P_5 and P_6 .

except P_2 show two endotherms on heating, related to solid-smectic and smectic-isotropic transitions.

It has been observed by Wolff *et al.* [22] that the closer to unity the ratio of spacer length to length of terminal chain, the higher the probability of finding only smectic phases. For example, polymer P_2 with the $-(\text{CH}_2)_6-$ spacer and *iso*-butoxy chain shows no liquid crystalline properties, perhaps because this ratio deviates considerably from 1. In the case of polymers P_1 , P_3 , P_4 , P_5 , P_6 , where the ratio of spacer length to length of terminal chain is closer to 1, smectic phases are seen. When comparing pairs of polymers, e.g. P_3 , P_5 (spacer $-(\text{CH}_2)_4-$) and P_4 , P_6 (spacer $-(\text{CH}_2)_6-$), each pair has the same spacer length but different terminal groups; polymer P_5 has an *n*-amyloxy terminal group, whereas polymer P_3 has a branched *iso*-amyloxy terminal group. Similarly polymer P_6 has an *n*-amyloxy terminal group whereas polymer P_4 has a branched *iso*-amyloxy terminal group. It is observed that the clearing temperatures and LC phase range of polymers with branched terminal groups (P_3 , P_5) are lower than those of the *n*-terminal groups (P_4 , P_6).

When comparing polymers P_1 and P_3 , with the same spacer length $-(\text{CH}_2)_4-$ but different terminal groups, it is observed that both mesophase transition and clearing temperatures of P_3 with an *iso*-amyloxy terminal group are higher than P_1 with an *iso*-butoxy terminal group. It has been pointed out by Gray [23] that in low molar mass mesogens, when branching occurs at the first carbon atom of the chain, liquid crystal phase stability is affected the most, as there is an increase in steric hindrance in the system due to acoplanarity; but movement of the point of branching towards the end of the chain causes the transition temperatures to rise again. We observed here a similar trend in the transition temperatures of polymers P_1 and P_3 , showing that P_3 has a higher transition temperature than P_1 .

Attard *et al.* presented a molecular field model applicable to side chain polymers in an attempt to highlight the physics that underlies the formation of liquid crystalline phases in these systems [24]. This led to the proposal of another molecular model [24], with which to rationalize the behaviour of the smectic polymers: the virtual trimer model, in which for the first time a section of the backbone is considered to be an integral part of the mesogenic species. Accordingly, as the spacer chain length is increased, the heat capacity associated with the glass transition temperature (T_g) becomes increasingly weaker and hence uncertainties in T_g become larger [25]. As the T_g values of the polymers were very broad, they could not be determined on DSC thermograms. Moreover the DSC traces show no baseline shift, a characteristic of glass transitions, indicating that the polymers could be crystalline.

3.3. Thermogravimetric analysis

All the liquid crystalline polymers were subjected to thermal analysis (figure 3). The initial decomposition of the polymers, showing a weight loss in the range 45–55%, occurs during the first decomposition step. Polymers P₃ and P₅ undergo one-stage decomposition, while polymers P₁, P₄, P₆ undergo two-stage decomposition. The thermal stability of the polymethacrylates, on the basis of T_{\max} for the first step of decomposition, is in the decreasing order P₆ > P₃ > P₅ > P₁ > P₄. The activation energy E_a for the polymers has been calculated by Broido's method and is listed in table 5:

$$E_a = \frac{\ln[\ln(1/y_{55\%})] - \ln[\ln(1/y_{80\%})]}{1/T_{55\%} - 1/T_{80\%}} \cdot R$$

where y = % of polymer undecomposed, $R = 8.314 \text{ cal mol}^{-1}$, T is in °C.

3.4. X-ray diffraction

The results of WAXD patterns confirmed the presence of the smectic phase; figure 4 shows typical temperature-dependent WAXD patterns of P₃ and P₆ at phase temperature. At room temperature the diffraction pattern in the small angle regions has a periodicity of $d_{001} = 43 \text{ \AA}$ for P₃ and 31 \AA for P₆ (table 6), which indicates the molecular length. The d_{001} layer spacing is a little shorter than the length of the fully extended monomer molecule.

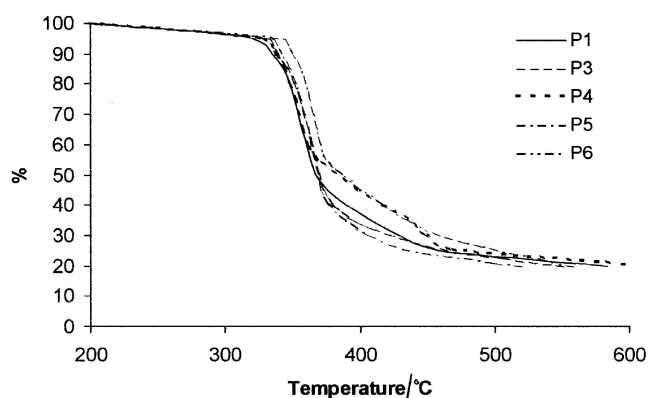


Figure 3. TGA curves of the homopolymers P₁, P₃, P₄, P₅ and P₆.

Table 5. Thermogravimetric analysis of the polymers.

| Polymer | $T_{55\%}/^{\circ}\text{C}$ | $T_{80\%}/^{\circ}\text{C}$ | $E_a \times 10^3 \text{ kcal mol}^{-1}$ |
|----------------|-----------------------------|-----------------------------|---|
| P ₁ | 363 | 347.84 | 213.4 |
| P ₃ | 366.86 | 350.93 | 205.3 |
| P ₄ | 368.32 | 348.18 | 162.1 |
| P ₅ | 365.98 | 352.55 | 243.8 |
| P ₆ | 374.6 | 359.76 | 226.2 |

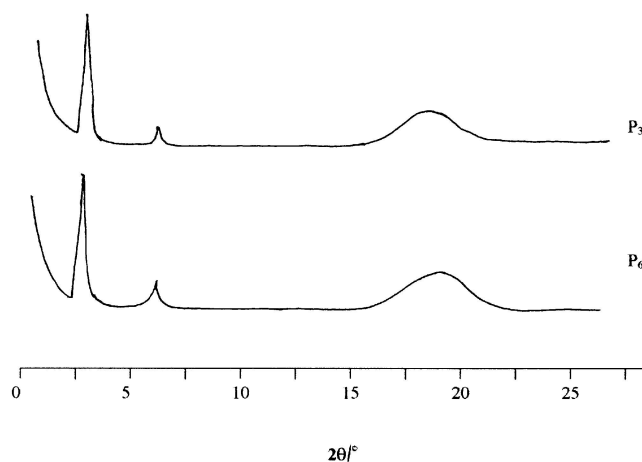


Figure 4. Temperature dependent wide angle X-ray powder diffractograms of P₃ and P₆ at 25 and 100°C.

Table 6. X-ray diffraction data for polymers P₃ and P₆.

| | Sr. No. | 2θ | $d/\text{\AA}$ |
|----------------|---------|-----------|----------------|
| P ₃ | 1 | 2.025 | 43.58 |
| | 2 | 3.683 | 23.97 |
| | 3 | 19.673 | 4.509 |
| P ₆ | 1 | 2.826 | 31.23 |
| | 2 | 3.688 | 23.94 |
| | 3 | 11.565 | 7.64 |
| | 4 | 20.448 | 4.33 |

3.5. UV spectroscopy

All *trans*-azobenzene-containing polymers in chloroform solution show a strong U.V. absorption band centred at about 360 nm, and a shoulder at about 440 nm attributed to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ electronic transitions of the *trans*-azobenzene chromophore respectively [26].

4. Conclusions

A decrease in the clearing temperatures of polymers with increasing number of methylene groups in the flexible spacer was found in the pairs of polymers P₁ and P₂, P₃ and P₄, P₅ and P₆. The closer the ratio of spacer length to terminal chain is to 1, the higher the probability of finding only smectic phases (P₁, P₃, P₄, P₅, P₆). Polymer P₃ (*iso*-amyloxy) has higher mesophase transition and clearing temperatures than polymer P₁ (*iso*-butoxy) with same spacer $-(\text{CH}_2)_4-$ length. This may be due to the movement of the branching point away from the first carbon of the chain in the terminal group. The polymers with an *n*-amyloxy terminal group (P₅, P₆) show higher transition temperatures than those with the branched *iso*-amyloxy terminal group (P₃, P₄).

Authors thank Dean, Prof. S. G. Shah and Head for providing research facilities. P.R.P. is grateful to CSIR for the award of a Senior Research Fellowship.

References

- [1] MCARDLE, C. B. (editor), 1989, *Side Chain Liquid Crystal Polymers* (Blackie), p. 357.
- [2] RINGSDORF, H., and ZENTEL R., 1982., *Makromol. Chem.*, **183**, 1245.
- [3] EICH, M., WENDORFF, J. H., RINGSDORF, H., and SCHMIDT, H. W., 1985, *Makromol. Chem.*, **186**, 2639.
- [4] ANDERLE, K., BIRENHEIDE, R., EICH, M., and WENDORFF, J., 1989. *Makromol. Chem. rapid Commun.*, **10**, 477.
- [5] ANGELONI, A. S., CARETTI, D., CARLINI, C., CHIELLINI, E., GALLI, G., ALTOMARE, A., SOLARO, R., and LAUS, M., 1989, *Liq. Cryst.*, **4**, 513.
- [6] STUMPE, J., MULLER, L., KREYSIG, D., HAUCK, G., KOSWIG, H., RUHMANN, R., and RUBNER J., 1991, *Makromol. Chem. rapid Commun.*, **12**, 81.
- [7] ANGELONI, A. S., CARETTI, D., LAUS, M., CHIELLINI, E., and GALLI, G. J., 1991, *Polym. Sci. polym. Chem. Ed.*, **29**, 1865.
- [8] RINGSDORF, H., and SCHMIDT, H. W., 1984, *Makromol. Chem.*, **185**, 1327.
- [9] EICH, M., WENDORFF, J. H., RECK, B., and RINGSDORF, H., 1987, *Makromol. Chem. rapid Commun.*, **8**, 59.
- [10] EICH, M., and WENDORFF, J. H., 1987, *Makromol. Chem. rapid Commun.*, **8**, 467.
- [11] SEKI, T., TAMAKI, T., SUZUKI, Y., KAWANISHI, Y., ICHIMURA, K., and AOKI, K., 1989, *Macromolecules*, **22**, 3505.
- [12] ORTLER, R., BRAUCHLE, C., MILLER, A., and RIEPL, G., 1989. *Makromol. Chem. rapid Commun.*, **10**, 189.
- [13] IKEDA, T., HORIUKCHI, S., KARANJIT, D. B., KURIHARA, S., and TAZUKE, S., 1990, *Macromolecules*, **23**, 36.
- [14] CIARDELLI, F., CARLINI, C., SOLARO, R., ALTOMARE, A., PIERONI, O., HOUBEN, J. L., and FISSI, A., 1984, *Pure appl. Chem.*, **56**, 329.
- [15] AMANO, M., and KAINO, T., 1990, *Electron. Lett.*, **26**, 981.
- [16] VYAS, G. M., and SHAH, N. N., 1963. *Org. Synth. Cl.* Vol. VI (Revised Edn of Annual Vol. 30–39) (New York: John Wiley), p. 836.
- [17] GISWELL, T. R., KLANDERMANN, B. H., and BATESKEY, B. C., 1973, *Mol. Cryst. liq. Cryst.*, **22**, 211.
- [18] *Vogel's Textbook of Practical Organic Chemistry*, IVth Edn, 1989, revised by B. S. Furniss, A. J. Hannford, P. W. G. Smith and A. R. Tatchell Longman (Singapore Publishers), pp. 649, 563.
- [19] CRIVELLO, J. V., DEPTOLLA, M., and RINGSDORF, H., 1988, *Liq. Cryst.*, **3**, 235.
- [20] TAMAKI, N., TSUYOSHI, H., and OKAMOTA, Y., 1993, *Macromolecules*, **26**, 5494.
- [21] HEITZ, W., and NIESSNER, N., 1990, *Makromol. Chem.*, **191**, 225.
- [22] WOLFF, D., CACKOVIC, H., KRUGER, H., RUBNER, J., and SPRINGER, J., 1993, *Liq. Cryst.*, **14**, 917.
- [23] GRAY, G. W., 1974 *Liquid Crystals and Plastic Crystals*, Vol. 1 (Ellis Horwood), p. 138.
- [24] ATTARD, G. S., DAVE, J. S., WALLINGTON, A., IMRIE, C. T., and KARASZ, F. E., 1991, *Makromol. Chem.*, **192**, 1495.
- [25] ATTARD, G. S., IMRIE, C. T., and KARASZ, F. E., 1993, *Macromolecules*, **26**, 545.
- [26] ANGELONI, A. S., CARETTI, CARLINI, C., and CHIELLINI, E., 1989, *Liq. Cryst.*, **4**, 513.