Synthesis and Characterization of Amorphous-Liquid Crystalline Poly(Vinyl Ether) Block Copolymers

İ. Ersin SERHATLI & Müge SERHATLI

İstanbul Technical University, Department of Chemistry
80626 Maslak, İstanbul - TURKEY

A new series of amorphous-liquid crystalline poly(vinyl ether) block copolymers was synthesized using living cationic polymerization and free-radical polymerization techniques. Vinyl ether monomer was polymerized using a trifluoromethane sulfonic acid and methyl triflouoromethanesulfonate/tetrahydrothiophene initiator system in dichloromethane at -18°C, and quantitatively terminated with labile azo compounds in order to obtain poly(vinyl ether) with well-defined molecular weight and end groups. This polymer was used in a subsequent blocking step in which azo groups were decomposed at 80°C in the presence of methyl methacrylate and styrene monomer.

In both copolymers, blocks of different chemical composition were segregated in the solid and melt-phase transitions. The mesophase-transition temperatures of the liquid-crystalline blocks were found to be very similar to those of the corresponding homopolymers.

Introduction

In recent years, graft and block copolymers have attracted increasing interest owing to their ability to form microphase-separated systems. In particular, copolymers containing liquid crystalline (LC) segments may have important applications in various high-tech fields such as electrooptics[1] and the compatibilization of polymer blends[2].

For these applications, it is essential that polymeric materials be developed with reproducible molecular parameters and consistent mesomorphic behavior.

Living-polymerization techniques have been largely adopted since they are very effective methods for preparating polymers with reproducible molecular characteristics. Of these techniques, particular attention should be given to anionic[3] and cationic[4] living polymerization. Living cationic polymerization enables control of the molecular-weight distribution and end groups in the resulting polymer. Matyjaszewski and Webster[5-6] have reported a new initiating system for the synthesis of living alkyl vinyl ether polymers. In this system, a mixture of a strong protonic acid (trifluoromethanesulfonic acid or methyl triflouoromethanesulfonate) and a Lewis base (tetrahydrothiophene), which stabilizes the active chain ends, produces the living polymerization.

Goethals et.al.[7] have used this system in order to obtain macromonomers by end-capping living polymers with tertiary amines or alcohols. According to the literature, alkyl vinyl ether block copolymers

have also been prepared using other methods[8].

The potenial application of polymeric materials containing azobenzene in order to produce photo- and thermo-addresset devices for data storage has been investigated by various authors[9−10].

Investigated here are the coupling reactions of side-chain liquid-crystalline living poly(vinyl ether) initiated by the methyl trifluoromethane sulfonate/tetrohydrothiophene system, yielding AB- and ABA-type block copolymers. This paper describes the preparation and properties of related monomer and copolymer with different chemical compositions.

Experimental

Preparation of liquid-crystalline monomer;
4,'ethoxy-4-(6-vinyloxyhexyloxyl)azobenzene (VE1);
A mixture of 10.0 g (45.1 mmol) 4'-ethoxy-4-hydroxyazobenzene, 7.33 g (45.1 mmol) 1-chloro-6-vinyloxyhexane and 12.5 g (90.2 mmol) dry potassium carbonate in 70 ml anhydrous dimethyl sulfoxide was heated at $90°$ C for 2h. The mixture was then poured into 100 ml of cold water, stirred vigorously and filtered. The solid residue was washed with 1N sodium hydroxide, water and then crystallized from 95% ethanol to give 8.2 g 4,'ethoxy-4-(6-vinyloxyhexyloxyl) azobenzene[11].

The yield was 51%, m.p; 96-97$°$C.

^{1}*H-NMR Results (CDCl$_3$):*
7.9 (d, 4H, Arom); 7.0 (d, 4H, Arom); 6.4 (dd, 1H, H$_2$C = C $\underline{H}$); 4.2 (d, 1H, H $\underline{H}$C = CH); 4.1-3.9 (m, 5H, $\underline{H}$HC = CH−2 and ArOCH$_2$); 3.7 (t, 2H, OCH$_2$); 1.9-1.3 (m, 11H, (CH$_2$)$_4$ and CH$_3$).

Preparation of Polyvinylether;

All polymerizations were carried out in a dry nitrogen atmosphere in a two-necked reaction flask equipped with a magnetic stirrer and constant-temperature bath.

2 ml of freshly distilled dichloromethane, 212 mg VE1 (0.6 mmol) and 15 μl (0.17 mmol) tetrahydrothiophene were injected into a two-necked reaction flask and stirred in a nitrogen atmosphere. The open neck of the flask was capped with a rubber septum and the nitrogen inlet was closed. 5 μl of methyl trifluoromethanesulfonate (0.044 mmol) was then syringed into the system while stirring continued. The reaction was allowed to continue for 10 minutes. Then a solution of 30 mg (0.12 mmol) azo compound and 4.4' azobis(4-cyano pentanol) (ACP)[12] in 2 ml dichloromethane was prepared separately and syringed into the reaction mixture followed by 70 μl 2,6-lutidine. Stirring was continued for 2h.

Synthesis of Block Copolymers;

Block copolymers were prepared following the general procedure previously described in the literature[13,14,15]. In a typical copolymerization reaction, the required amounts of relevant monomer styrene (St) or methylmethacrylate (MMA) and macroinitiator poly(vinylether) (PVE1) having an azo functional group were dissolved in 3 ml DMF. The reaction mixture was placed in a pyrex glass ampule, thoroughly freeze-thaw degassed and then sealed in a vacuum. After reacting for various time periods at $80°$C, the copolymers were precipitated by the addition of a ten-fold excess of methanol, filtered and purified by extraction using boiling methanol, benzene and cyclohexane, respectively. The copolymers were then dried in vacuo for 24 h.

Instruments

^{1}H-NMR spectra were performed with a Varian Gemini 200 MHz spectrometer. Average molecular weights were determined using size-exclusion chromatography (SEC) of the THF solutions with a setup consisting of

a Waters pump (model 600E), a Hewlett Packard column (Mixed-C,PL gel 5μ), THF being used as the eluent at a flow rate of 1 ml min^{-1} and a Waters differentials refractometer (model 410). Narrow molecular-weight polystyrene standards were used for calibration.

The thermal and liquid-crystalline properties of the polymers were determined using differential scanning calorimetry (DSC) (Perkin Elmer DSC-6 Model at a scanning rate of $10°$C min^{-1}) and polarized light microscopy (Reichart Polyvar Microscope equipped with a programmable Mettler FP52 stage at a scanning rate of $10°$C min^{-1}).

Results and Discussions

Amorphous-liquid-crystalline poly(vinyl ether) block copolymers were synthesized via a two-step procedure involving a living cationic polymerization and free-radical polymerization system.

The whole polymerization mechanism can be represented as follows;

Scheme
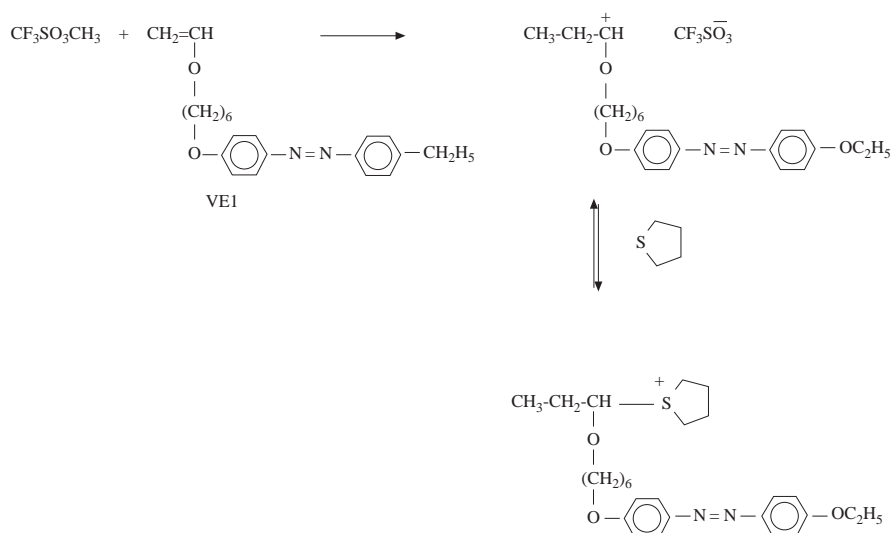
After polymerization and end-capping, the reaction mixture was allowed to warm to room temperature.

Consequently, liquid-crystalline poly(vinyl ether) possessing one reactive azo group in the main chain was obtained. Subsequently, this polymeric radical source was used to generate PVE1 macroradicals through the thermal decomposition of the azo group at $80°$C, which in turn initiated the free-radical polymerization of different vinyl monomers, such as methylmethacrylate (MMA), styrene (St).

In each experiment, an azomacroinitiator PVE1, $M_n = 6600$ and $M_w/M_n = 1.2$ was used. Typical results are shown in Table 1.
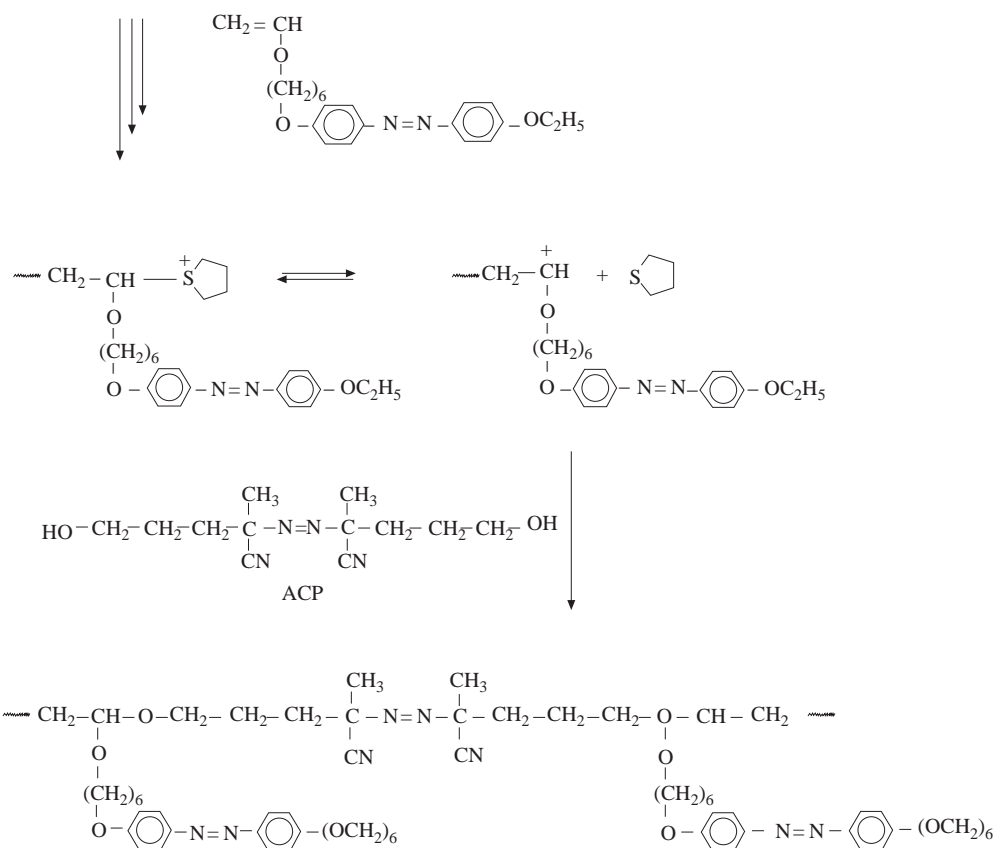
Table 1. Polymerization conditions of VE1 by cationic mechanism

Sample	Monomer (mol.l^{-1})	m_0/i_0 [a]	Reaction Time (h)	Conversion (%)	M_n [b]
PVE1	0.285	13	2	85	6600

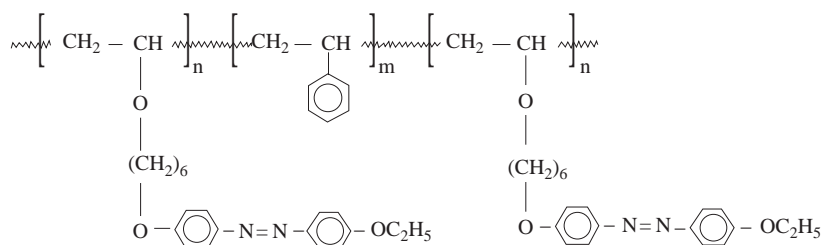[a] Mole ratio, monomer/initiator

[b] Obtained from (SEC), based on PSt standards

Temperature: -18$°$C, in dichloromethane

$$CH_2 = CH$$
$$O$$
$$(CH_2)_6$$
$$O - \langle \bigcirc \rangle - N = N - \langle \bigcirc \rangle - OC_2H_5$$

$$\sim CH_2 - CH - \overset{+}{S} \rangle \quad \rightleftharpoons \quad \sim CH_2 - \overset{+}{CH} \quad + \quad S \rangle$$
$$\qquad\qquad O \qquad\qquad\qquad\qquad O$$
$$\qquad (CH_2)_6 \qquad\qquad\qquad (CH_2)_6$$
$$O - \langle \bigcirc \rangle - N = N - \langle \bigcirc \rangle - OC_2H_5 \qquad O - \langle \bigcirc \rangle - N = N - \langle \bigcirc \rangle - OC_2H_5$$

$$\qquad\qquad CH_3 \qquad CH_3$$
$$HO - CH_2 - CH_2 - CH_2 - C - N = N - C - CH_2 - CH_2 - CH_2 - OH$$
$$\qquad\qquad\qquad CN \qquad CN$$

ACP

$$\sim CH_2 - CH - O - CH_2 - CH_2 - CH_2 - \overset{CH_3}{\underset{CN}{C}} - N = N - \overset{CH_3}{\underset{CN}{C}} - CH_2 - CH_2 - CH_2 - O - CH - CH_2 \sim$$
$$O \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad O$$
$$(CH_2)_6 \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (CH_2)_6$$
$$O - \langle \bigcirc \rangle - N = N - \langle \bigcirc \rangle - (OCH_2)_6 \qquad O - \langle \bigcirc \rangle - N = N - \langle \bigcirc \rangle - (OCH_2)_6$$

Scheme

$$\sim \Big[CH_2 - CH \Big]_n \sim \Big[CH_2 - CH \Big]_m \sim \Big[CH_2 - CH \Big]_n \sim$$
$$\qquad\quad O \qquad\qquad\qquad\qquad\qquad\qquad O$$
$$\qquad (CH_2)_6 \qquad\qquad\qquad\qquad\qquad\quad (CH_2)_6$$
$$O - \langle \bigcirc \rangle - N = N - \langle \bigcirc \rangle - OC_2H_5 \qquad O - \langle \bigcirc \rangle - N = N - \langle \bigcirc \rangle - OC_2H_5$$

ABA Block Copolymer

$$\sim \Big[CH_2 - CH \Big]_n \sim \Big[CH_2 - \overset{CH_3}{\underset{\underset{OCH_3}{C=O}}{C}} \Big]_m \sim$$
$$\qquad\quad O$$
$$\qquad (CH_2)_6$$
$$O - \langle \bigcirc \rangle - N = N - \langle \bigcirc \rangle - OC_2H_5$$
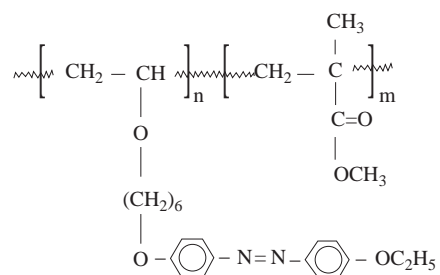
AB Block Copolymer

Scheme

Block copolymers, PVE1-*b*-PMMA and PVE1-*b*-PSt, were obtained with different compositions and conversions using different monomer ratios in the feed mixture. It should be pointed out that the termination mode of the vinyl monomer used in the second stage plays an important role in the structure of the resultant block copolymers.

A block of ABA type is obtained if the termination of macroradicals consisting of vinyl monomers occurs by combination, as in the case of styrene. On the contrary, block copolymers of the AB type will be formed if the termination of macroradicals occurs by disproportionation, as in the case of MMA.

Table 2. Polymerization conditions and results of LC Block Copolymers

Sample	Monomer (mol.1^{-1})	PVE1 (g.1^{-1})	Reaction Time (h)	Conversion (%)	M_n	M_w/M_n	Mol [a] content (%)
PVE1-*b*-PMMA	MMA 2.34	12.5	5	69	70000	1.2	1.5 PVE1 98.5 PMMA
PVE1-*b*-St	St 2.9	12.5	5	37	70000	1.2	30 PVE1 70 PSt

[a] Determined from ^{1}H-NMR measurements

Temperature: 80°C, in DMF

The structure of the prepolymer and copolymers was determined through ^{1}H-NMR spectroscopy. A typical ^{1}H-NMR spectrum of an azo containing PVE1 exhibits signals in the range 7.9-7.0 ppm (8H, aromatic); 4.0 ppm (4H, ArOCH$_2$); 2.0-1.0 ppm (13H, CH$_2$ and CH$_3$). Figure 1.
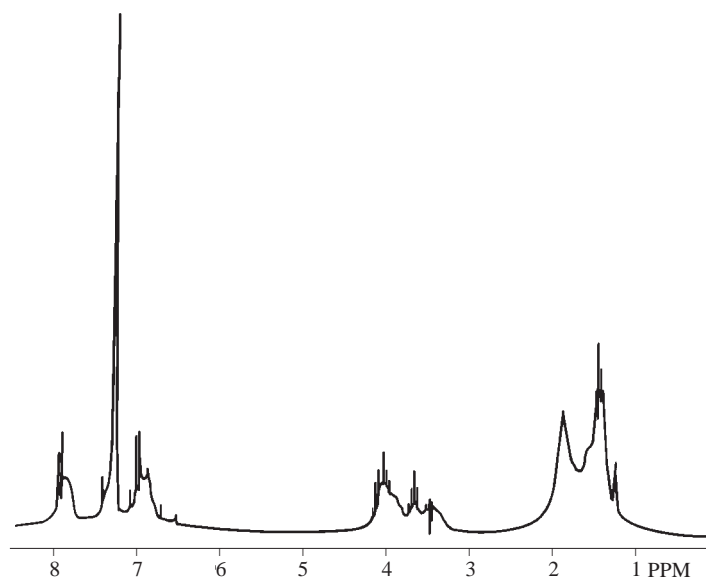

Figure 1.

The polymerization time was deliberately kept short so that polymers with low molecular weight and narrow polydispersities were obtained. The structure of the copolymers was also deduced from ^{1}H-NMR

measurements. The signals of the protons in the OCH$_3$ group at 3.6 ppm and at 6.4-7.4 ppm (aromatic H) indicate the existence of both PMMA and PS segments, respectively. (Fig. 2 and 3). As can be seen in Table 2, significant increase in the composition of the PVE1 was observed with the styrene monomer. This can be explained by the higher polymerizability of the MMA monomer with respect to the styrene monomer. Clear proof of the block copolymer formation was also obtained by SEC with dual detection of the refractive index and ultraviolet recordings.
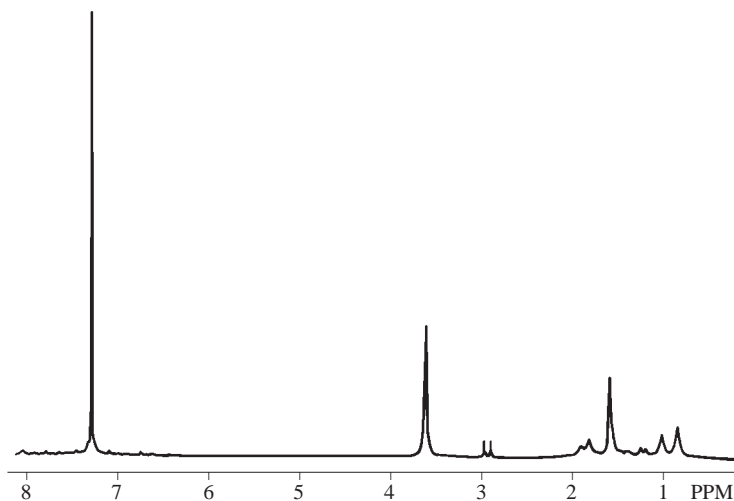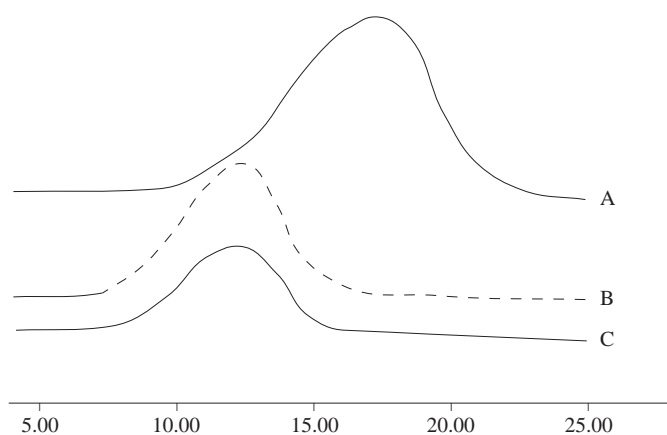

Figure 2.
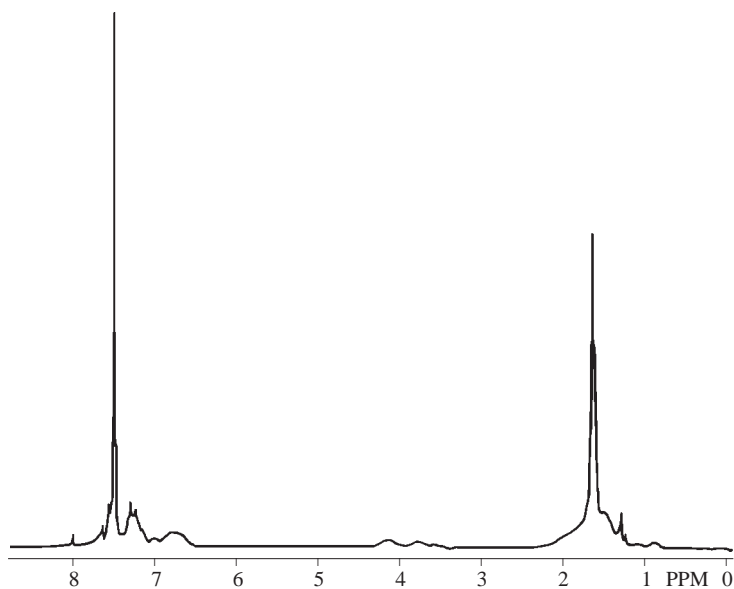
Figure 3.

Chromatograms of the prepolymer and block copolymers are shown in Figure 4.

Figure 4.

There are three peaks; one at high elution volume due to prepolymer and the other two peaks at low elution volume, due to block copolymers.

The thermal behavior of monomer and block copolymers was studied with DSC and polarizing microscopy.

The phase-transition temperatures are listed in Table 3.

Table 3. Thermal behavior of the liquid-crystal monomer and polymers.

Sample[a]	T_m(°C)	T_i(°C)[b]	T_c(°C)
VE1	95	117	-
PVE1	138	131[c]	109
PVE1-*b*-PMMA	151	146[c]	120
PVE1-*b*-PSt	151	149[c]	120

[a] Melting T_m, Isotropization T_i, Crystallization T_c temperatures,
[b] Cooling (10°C min^{-1})
[c] Obtained only during cooling

The liquid-crystalline properties of PVE1 prepolymer obtained from the living cationic polymerization of monomer (VE1) have already been described[16].

The producing LC polymers with reproducible molar-mass characteristics are represented by polymer-analogous reactions between monodisperse polymer matrices and mesogenic molecules containing functional groups, even though quantitative conversions of the functional groups have to yet be obtained.

The DSC cooling curves of VE1 monomer, PVE1 and block copolymers are shown in Fig. 5. In the heating curve of VE1, two endothermic peaks occur at 95 and 117 K, corresponding to melting and the enantiotropic-nematic mesaphase.
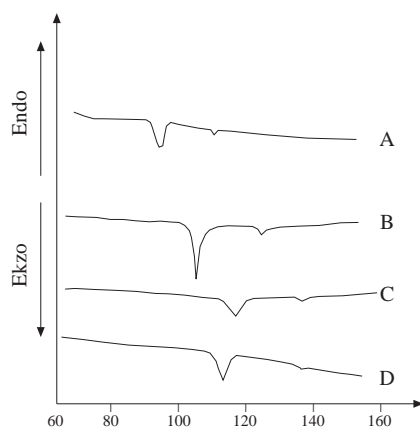
Figure 5.

In the poly(VE1) sample, the nematic mesophase was formed upon cooling of the isotropic melt and was, therefore, monotropic or metastable. Accordingly, the isotropic-nematic transition was taken from the DSC cooling alone. For a microphase-separated block copolymer, we should be able to identify the glass transitions of both blocks from DSC measurements. Unfortunately, the glass transition of the PMMA phase, which usually takes place at temperatures between $110\,^\circ$C and $125\,^\circ$C, was not revealed by the DSC experiment (Fig. 5). The DSC curve for the corresponding block copolymer with PSt reveals the glass transition of the PSt phase at $105\,^\circ$C, whereas the T_g of the LC phase was not observed. For this reason, polarized optical microscopy was performed on the block copolymers in order to detect direct evidence of a microphase-separated structure.
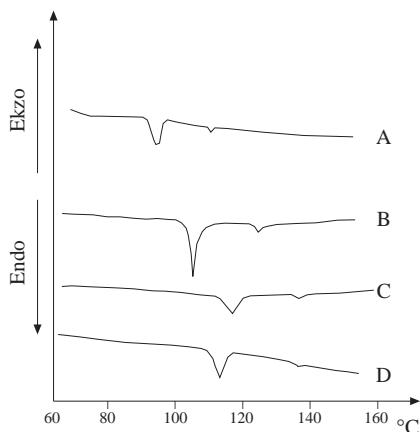
Figure 6.

The melting T_m, isotropic-nematic T_i and crystallization T_c temperatures increased with an increase in the molar mass of the block copolymers[17].

It is well known that the present poly(vinyl ether)s tend to have a more stable crystalline phase than the structurally analogous polyacrylates.

Conclusion

This paper has described the synthesis and investigation of a novel kind of block copolymers comprising both amorphous and liquid-crystalline blocks within the same polymer structure. Thermal and spectroscopic data show that the two blocks of different chemical composition are at least partly phase-separated in the glassy and LC phases and undergo distinct transitions which were also observed through optical-microscopy measurements.

References

1. V. Percec and C. Pugh, **"Side-Chain Liquid-Crystal Polymers"**, edited by C.B. McArdle (Blakie & Sons), 1989.

2. L. Kwolek, P.W. Morgan and J.R. Schaefgen in H.F. Mark, N.N. Bikales, C.G. Overberger and G. Menges (Eds.), **"Encyclopedia of Polymer Science and Engineering"**, Vol.9, 2nd edn., John Wiley, New York, pp.1-61, 1985.

3. Szwarc, J.Jagur-Gdodzinski, in **"Ions and Ion Pairs in Organic Reactions"** M. Szwarc, Ed., Wiley, New York, Vol.2, 1974.

4. J. P. Kennedy, B. Ivan, **"Designed Polymers by Carbocationic Macromolecular Engineering"**, Hanser, Munich 1992.

5. H. Lin, K. Matyjaszewski, **Polym. Prepr. Am. Chem. Soc., Div. Polym. Chem.**, 31(1), 599 (1990).

6. C.G. Cho, A. Feit, O.W. Webster, **Macromolecules 23**, 1918 (1980).

7. E.J. Goethals, N.H. Haucourt, A.M. Verheyen, J. Habimana, **Makromol. Chem., Rapid Commun. 11**, 623-627 (1990).

8. M. Sawamato, **Prog. Polym. Sci., 16**, 111 (1991).

9. T. Ikeda, S. Horiukchi, D.B. Karanjit, S. Kurihara, S. Tazuka, **Macromolecules 23**, 36 and 42 (1990).

10. S. Ivanov, I. Yakovlev, S. Konstromin, V. Shibaev, L. Lasker, J. Stumpe, D. Keysig, **Makromol. Chem., Rapid Commun., 12**, 709 (1991).

11. E. Chiellini, G. Galli, M.C. Bignozzi, A.S. Angeloni, M. Fagnani, M. Laus, **Macromol. Chem. Phys., 196**, 3187-3196 (1995).

12. C.H. Bamford, A.D. Jenkins, R.P. Wayne, **Trans. Faraday 56**, 932 (1960).

13. G. Galli, E. Chiellini, E.I. Serhatlı, Y. Yağcı, M. Laus, A.S. Angeloni, **Makromol Chem., Rapid Commun., 14**, 185 (1993).

14. E. Chiellini, G. Galli, E.I. Serhatlı, Y. Yağcı, M. Laus, A.S. Angeloni, **Ferroelectrics, 148**, 311 (1993).

15. I.E. Serhatlı, G. Galli, Y. Yağcı, E. Chiellini, **Polym. Bull. (Berlin), 34**, 539 (1995).

16. V. Percec, D. Tomazos, **Adv. Mater., 4**, 548 (1992).

17. M. Portugall, H. Ringsdorf and R. Zentel, **Makromol. Chem., 183**, 2311 (1982).