Polymer Vol. 36 No. 16, pp. 3127–3134, 1995
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0032-3861/95/$10.00+0.00

Random thermotropic elastomers: effect of hard/soft-segment lengths on the properties of liquid-crystalline copoly(ether ester)s*

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(Received 3 November 1993; revised 15 July 1994)

Random segmented copoly(ether ester)s were synthesized by reacting terephthaloyl chloride sequentially with poly(oxytetramethylene) glycol ($\bar{M}_n = 250$, 650, 1000, 2000 g mol^{-1}) and hydroquinone via melt condensation. A series of copolymers were obtained by maintaining a constant weight ratio of hard to soft segments, which results in simultaneous variation of hard/soft-segment lengths. The properties of these copolymers with oxy-1,4-phenyleneoxycarbonyl-1,4-phenylenecarbonyl hard segments and polyoxytetramethylene soft segments were studied for solubility behaviour, X-ray diffraction, infra-red spectroscopy, differential scanning calorimetry and polarizing microscopy. Thermal properties were found to vary with the hard-segment length. All copoly(ether ester)s are elastomeric at room temperature (25°C). Polarizing microscopic observations are indicative of highly ordered smectic mesophases, which owe their origin to the hard segments.

(Keywords: segmented copoly(ether ester)s; thermotropic elastomer; thermal properties)

INTRODUCTION

Self-organizing thermotropic main-chain liquid-crystalline polymers[1,2], composed of a flexible spacer and a rigid mesogen (the moiety that causes liquid crystallinity), have been investigated extensively in the past few years. The high degree of molecular orientation and order lead to materials with superior mechanical strength when processed from the liquid-crystalline melt. An additional advantage is the lower melt viscosity of the liquid-crystalline state vis-à-vis the isotropic state, which originates from molecules sliding past one another within domains as well as from domain–domain motion. In turn, this property makes these materials highly shear-dependent. this behaviour of liquid crystallinity can be coupled with another class of polymers, thermoplastic elastomers[3,4], comprised of alternating hard and soft segments. At use temperature, the lower glass transition temperature T_g of the soft blocks imparts elastomeric properties, while the rigid hard blocks serve as physical crosslinks and reinforcement sites, which are responsible for mechanical performance. Above the melting/glass transition temperature of the hard segments, thermoplastic elastomers can be processed similarly to conventional thermoplastics. However, incompatibility between the hard and soft blocks in the thermoplastic elastomers results in higher melt viscosity, generating difficulties while processing. Replacing such thermoplastic hard blocks with liquid-crystalline hard blocks will result in polymers that can be easily processed owing to their lower viscosity. In addition, these thermotropic elastomers would exhibit an unusual combination of properties originating from rubber-like elasticity coupled to the directional properties of the mesogen.

The synthesis and properties of side-chain liquid-crystalline elastomeric systems have been well studied[5–8]. Main-chain liquid-crystalline elastomers with alkylene 4,4′-bibenzoate as mesogenic hard segment have been reported recently[9]. We have synthesized previously[10] such systems based on oxy-2-methyl-1,4-phenyleneoxycarbonyl-1,4-phenylenecarbonyl/oxy-2-chloro-1,4-phenyleneoxycarbonyl-1,4-phenylenecarbonyl with substitution in the core of the hard segment. In this paper we report main-chain thermotropic elastomeric systems having polyoxytetramethylene and oxy-1,4-phenyleneoxycarbonyl-1,4-phenylenecarbonyl as soft and hard segments, respectively. The length of the hard as well as the soft segments was varied by maintaining a constant weight ratio of hard to soft segments (68 : 32). The thermal properties and thermotropic character of these polymers were described in relation to variation in length of hard/soft segments.

EXPERIMENTAL

Materials

Terephthalic acid (TA), hydroquinone (HQ) and poly(oxytetramethylene) glycol ($\bar{M}_n = 250$, 650, 1000, 2000) (POTMG) were obtained from Aldrich Chemical Co. Inc., USA. POTMG was dried overnight using activated 4 Å and 3 Å molecular sieves. HQ was

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recrystallized using hot water. Terephthaloyl chloride (TPC) was synthesized from TA and thionyl chloride in petroleum ether containing a catalytic amount of dimethylformamide. All apparatus was flame-dried prior to use.

Polymer synthesis

Freshly recrystallized TPC was reacted with POTMG ($\bar{M}_n = 250$, 650, 1000, 2000) by slowly raising the reaction temperature from room temperature to 90°C over a period of 3 h under a dry, pure nitrogen atmosphere with stirring to form oligo(ether ester) with acid chloride end-groups. Hydrogen chloride (by-product) liberated was scrubbed through aqueous alkali traps. Then HQ was added to the reaction mixture containing oligo(ether ester) and unreacted terephthaloyl chloride and the temperature of the reaction mixture was raised gradually to 200°C over 3 h under a dry, pure nitrogen blanket with stirring and maintained at this temperature for a period of 30 min. The polymer obtained was purified by extraction with petroleum ether, washed sequentially with 5 wt% aqueous sodium bicarbonate, water and methanol, and dried to constant weight. Synthesis of each polymer is repeated three times. The mole ratio of TPC/POTMG/HQ was varied with the change in number-average molecular weight of POTMG (250, 650, 1000 and 2000) such that the weight ratio of hard to soft segments remains constant (68 : 32) as shown in *Table 1*. Explanation of the sample codes in *Table 1* is as follows: 'T' denotes terephthaloyl chloride; 'B1', 'B2', 'B3', 'B4' denote POTMG of number-average molecular weight 250, 650, 1000 and 2000, respectively; 'H' denotes hydroquinone; and numbers following 'H' denote mole percentage of hydroquinone in the feed ratio. For example, sample code TB1H77 designates the copolymer containing terephthaloyl chloride, POTMG 250 and 77 mol% hydroquinone.

Polymer characterization

The intrinsic viscosity $[\eta]$ of polymer solutions in 4-chlorophenol at 50°C was measured using an Ubbelohde viscometer. Infra-red spectral measurements were made using potassium bromide (KBr) discs with a Shimadzu IR-470 spectrophotometer. X-ray diffraction measurements were carried out using a Philips PW 1730 X-ray diffractometer with Cu K_α target and nickel filter. Differential scanning calorimetric analyses were conducted using a Mettler-4000 thermal analyser and DSC-30 cell. Temperature calibration was made by using an indium–lead–zinc standard and that of heat flow by using an indium standard. All thermal analyses were run at a rate of 10°C min^{-1} under dry nitrogen. The sample mass was between 5 and 7 mg. Samples were analysed within two temperature ranges: from −75 to 50°C for soft-segment glass transition temperature, and between 50 and 375°C for hard-segment transitions. Glass transition temperatures were read at the middle of the change in the heat capacity. The thermal transitions were reported as the maxima and minima of their endothermic or exothermic peaks, respectively. Polarizing microscopic studies were conducted under crossed polarized light with a Leitz 350 hot stage coupled to a Leitz Laborlux 12 Pol S microscope. Photographs were taken using a Leica Wild MP S52/46 Photoautomat system.

RESULTS AND DISCUSSION

The properties of liquid-crystalline copolyesters are greatly dependent on the molecular structure of the components and the manner in which they are assembled. The low-temperature solution polycondensation route and well defined mesogen length lead to ordered copolymers[11]; whereas chemically disordered copolymers (random copolymers) are synthesized usually via the high-temperature transesterification reaction[12] as well as via the staged addition technique without isolation/purification of intermediate species[13]. The origin of randomness is due to the presence of molecules with varying mesogen length and/or to random orientation of head-to-tail sequences. Another way of introducing chemical disorder is to employ chain segments with a distribution in lengths of flexible spacers rather than a single persistence length[14]. Random copolymers show substantially lower thermal transitions as compared to the corresponding ordered homologues[15]. However, it has been observed that, while the ordered polymer fails to display liquid crystallinity, the random homologues do so[16]. With this view, the random copoly(ether ester)s dealt with here are synthesized via staged addition melt condensation employing a poly(oxytetramethylene) glycol (POTMG) spacer having a narrow but distinct distribution of lengths.

Thermoplastic elastomers have been studied in respect of variation in hard- and soft-segment lengths[17–19]. Higher hard-segment lengths are preferred for better mechanical properties. In ordered liquid-crystalline polymers[20] containing polyoxyethylene spacer, mesophase stability decreases with increase in spacer length at constant mesogen length, and finally liquid crystallinity disappears with 13 oxyethylene units. An increase in length of mesogen, at constant spacer length, enhances both melting and clearing temperatures[21]. However, above a critical length, the rigid blocks tend to induce infusibility. This was indeed observed by us for a series of such polymers with POTMG ($\bar{M}_n = 250$) as flexible spacer[22]. This differential effect of increase in mesogen length on thermal properties can be moderated considerably by simultaneously increasing spacer length. With this concept, we have synthesized copoly(ether ester)s by reacting terephthaloyl chloride first with flexible poly(oxytetramethylene) glycol. The resulting prepolymer was reacted thereafter with hydroquinone. The weight ratio of hard to soft segments was kept constant so as to have polymers with simultaneous variance in hard/soft-segment lengths. Pale yellow polymers are obtained with high yields (95–98%). The global structure of hard and soft segments is as shown in *Figure 1*. Polymers are crystalline as suggested from percentage crystallinity (above 40%) obtained from wide-angle X-ray diffraction (*Table 1*). The concentration of hard-segment blocks was chosen such that they have sufficient length to provide tie points necessary for 'rubbery' character while retaining liquid crystallinity. For the polymer containing POTMG of number-average molecular weight 250[22], further increase in mole percentage of soft segment results in loss of liquid crystallinity, whereas such an increase for polymer

Table 1 Synthesis and thermal data of copoly(ether ester)s obtained from terephthaloyl chloride, poly(oxytetramethylene) glycol and hydroquinone

	Sample code			
	TB1H77	TB2H87	TB3H91	TB4H95
Composition[a]	1:0.23:0.77	1:0.125:0.875	1:0.09:0.91	1:0.05:0.95
POTMG $\bar{M}_n$	250	650	1000	2000
Weight ratio (hard:soft)	68:32	68:32	68:32	68:32
Crystallinity (%)[b]	41.4	41.4	48.9	40.1
T_g[c] (°C)	−47.0	−48.0	−43.0	−50.0
ΔC_p[d] ($J\,mol^{-1}\,K^{-1}$)	231.16	120.00	169.76	147.27
T[e] (°C) (ΔH ($kJ\,mol^{-1}$))	236.3 (2.45); 294.6 (2.61); 343.0 (1.35)	243.6 (4.31); 294.6 (1.23)	255.0 (8.33); 295.2 (0.48)	243.4 (5.39); 297.1 (1.54)
T_{c1}[f] (°C) (ΔH_{c1} ($kJ\,mol^{-1}$))	230.3 (3.33)	220.4 (4.31)	247.4 (9.00)	235.3 (5.05)
T_{c2}[g] (°C) (ΔH_{c2} ($kJ\,mol^{-1}$))	245.0; 281.9 (0.36)	203.7 (2.28); 222.3 (0.31); 277.2 (2.18)	229.6 (8.10); 286.5 (1.89)	203.2 (2.41); 232.3 (0.47); 278.9 (1.44)

[a] Molar ratio of terephthaloyl chloride:poly(oxytetramethylene) glycol:hydroquinone

[b] Calculated from room-temperature X-ray diffraction

[c] Soft-segment glass transition temperature

[d] Heat-capacity change corresponding to glass transition

[e] Peak temperatures and corresponding enthalpy changes obtained during second heating

[f] Peak temperature and enthalpy change of crystallization obtained during second cooling when samples were heated just beyond low-melting transition during second heating

[g] Peak temperature and enthalpy change of crystallization obtained during second cooling when samples were heated just beyond high-melting transition during second heating

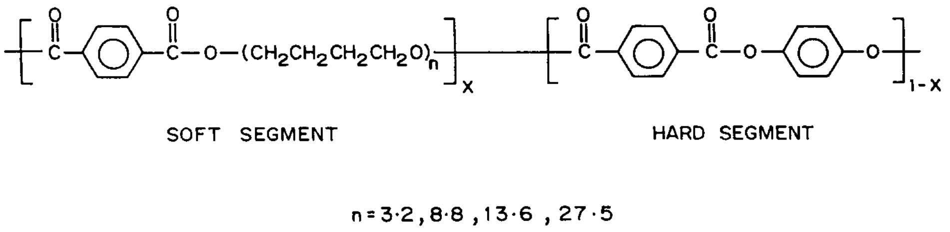

Figure 1 Global structure of copoly(ether ester)

containing POTMG of number-average molecular weight 2000 leads to waxy polymers.

The synthesized copoly(ether ester)s were thoroughly investigated for their solubility characteristics. All the polymers were found to be insoluble in common organic solvents. However, all the polymers could be solubilized in 4-chlorophenol when heated at 80°C for 3 h. Intrinsic viscosity determined in 4-chlorophenol was very low ($0.10\,dl\,g^{-1}$). Such low values are due to solvent-induced hydrolytic slicing of polymers arising from the rigorous conditions employed for their solubilization. The infra-red spectrum of copolymer solution in 4-chlorophenol indicates multiple carbonyl peaks (1715 and $1683\,cm^{-1}$) in addition to the original ester carbonyl peak at $1725\,cm^{-1}$ (*Figure 2b*). The infra-red spectrum of the above polymer reprecipitated from 4-chlorophenol solution by using methanol also shows such multiple carbonyl peaks (*Figure 2c*). The amplified carbonyl region of *Figure 2c* is reproduced in *Figure 2d*. This clearly indicates molecular-weight degradation due to solvolysis. Owing to this difficulty, molecular weights of the polymers could not be estimated. In order to find the molecular weights of polymers indirectly, another synthesis was carried out using terephthaloyl chloride, POTMG 2000 and bisphenol A in place of hydroquinone. The polymer obtained readily solubilizes in chloroform. It shows an intrinsic viscosity of $0.25\,dl\,g^{-1}$ in chloroform at 27°C with number-average molecular weight 16 840 as determined from vapour pressure osmometry. Even though this value is lower, it compares well with intrinsic viscosity values of copolymers (0.10 to $0.30\,dl\,g^{-1}$) containing poly(oxyalkylene) glycols prepared by the acid chloride route[11,20]. Also, all the copolymers in this paper were synthesized using identical methodology, so that their molecular weights should be similar for comparison of their thermal characteristics. The thermal properties of all these copoly(ether ester)s discussed later do show fairly regular variations as a function of composition rather than molecular weight.

A typical infra-red spectrum of the copoly(ether ester) recorded from a KBr disc is shown in *Figure 2a*. The absorptions at 2960 and $2880\,cm^{-1}$ (aliphatic C–H stretching) correspond to methylene groups. Formation of an ester linkage in copoly(ether ester) is indicated by a peak at $1725\,cm^{-1}$ corresponding to ester carbonyl. Peaks between 1600 and $1500\,cm^{-1}$ correspond to aromatic C=C stretching, whereas those between 1300 and $1100\,cm^{-1}$ correspond to skeletal –C–O–C– stretchings in ester/ether linkages.

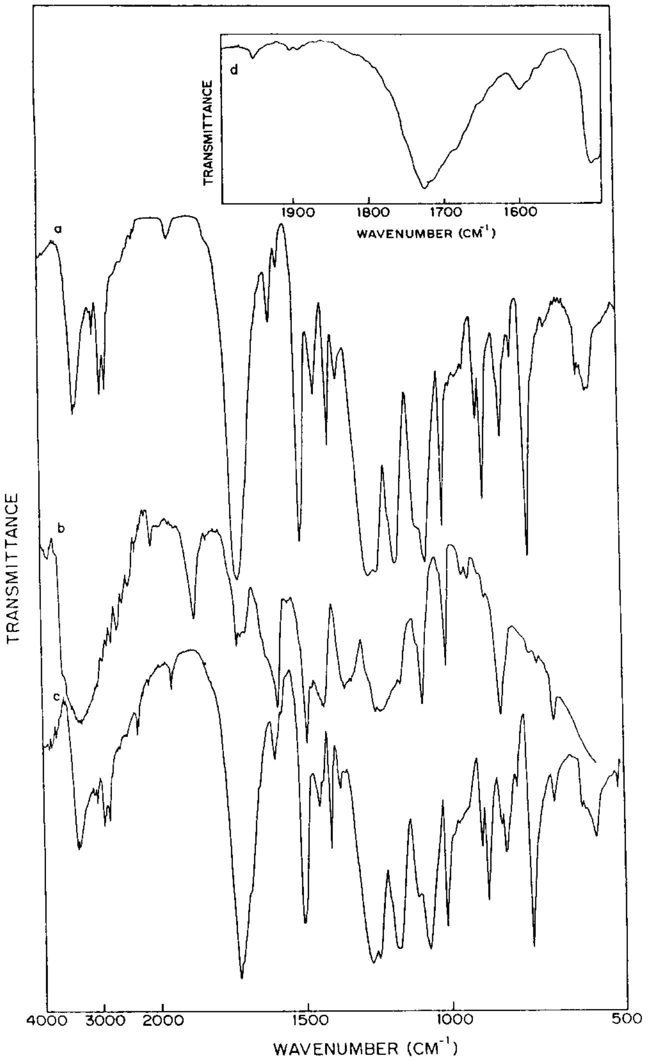

Figure 2 Infra-red spectra of (a) virgin copoly(ether ester), (b) copoly(ether ester) solution in 4-chlorophenol, (c) reprecipitated copoly(ether ester) from 4-chlorophenol and (d) amplified carbonyl region of (c)

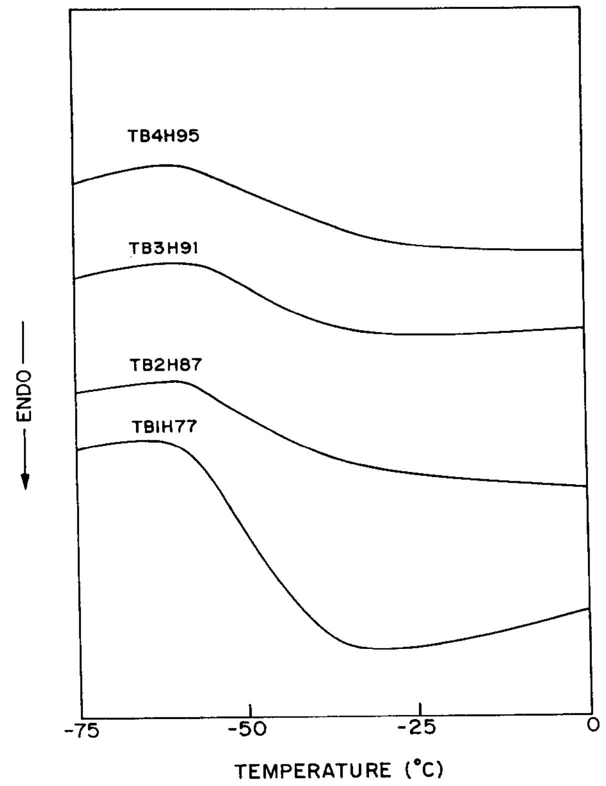

Figure 3 Soft-segment glass transition curves of copoly(ether ester)s

Differential scanning calorimetric (d.s.c.) study shows a second-order glass transition (T_g) below room temperature (*Table 1*) pertaining to soft segments as shown in *Figure 3*. The T_g value obtained is similar to that for a thermoplastic elastomer like Hytrel[23]. The hard segment exhibits multiple first-order transitions. These will be designated further as low-temperature and high-temperature peaks. In order to have a uniform thermal history and to compare the thermal properties of different copoly(ether ester)s, samples were heated (a) just beyond the first major melting peak and (b) just beyond the high-temperature peak. Subsequent second heating and second cooling curves obtained after heating samples just beyond the first major melting transition are shown in *Figure 4* and *Figure 5* respectively. For polymers TB1H77, TB2H87 and TB4H95, the appearance of a small shoulder on the low-temperature endotherm was due to imperfect crystallites. This was confirmed by the absence of such a shoulder after annealing the sample. With increase in hard-segment length, along the series, the melting temperature (T_m), enthalpy change of melting (ΔH) as well as enthalpy change of crystallization (ΔH_{c1}) corresponding to the low-temperature peak increase as shown in *Table 1*. A drop in T_m, ΔH and ΔH_{c1} was observed for polymer TB4H95. This is not a consequence of its molecular weight. Low-molecular-weight polymer containing a longer spacer (POTMG 2000) should be soluble in the usual organic solvents. Such solubility is not observed for polymer TB4H95. Thus, the drop in T_m, ΔH and ΔH_{c1} for this polymer may be a consequence of its 'randomness', which arises due to POTMG 2000 chains having a large distribution of their lengths. According to comonomer inclusion theory[24] of flexible random copolymers, the crystalline phase is a solid solution of crystallizable hard segments and amorphous soft-segment units. These amorphous units produce defects in the crystalline lattice of hard segments. Such 'imperfect crystallites' show a lower melting temperature than the corresponding hard segments of homopolymer. Such a dependence of the thermal properties on the distribution of spacer length (poly(oxyethylene) glycol 200 with $DP = 4.1$) and not on polymer molecular weight has already been reported for random copolymers[20].

When samples were heated beyond the high-temperature peak, the subsequent cooling cycle displays multiple exotherms as shown in *Figure 6*. The crystallization temperature (T_{c2}) and ΔH_{c2} corresponding to the lower-temperature transition are compared with earlier cooling data (T_{c1}, ΔH_{c1}) (*Table 1*). Lower values of ΔH_{c2} and/or T_{c2} suggest the possible degradation of the polymer at temperatures above the high-temperature transition. Degradation was observable visually on opening the d.s.c. sample pan. The presence of ether units in the polymer promotes such degradation.

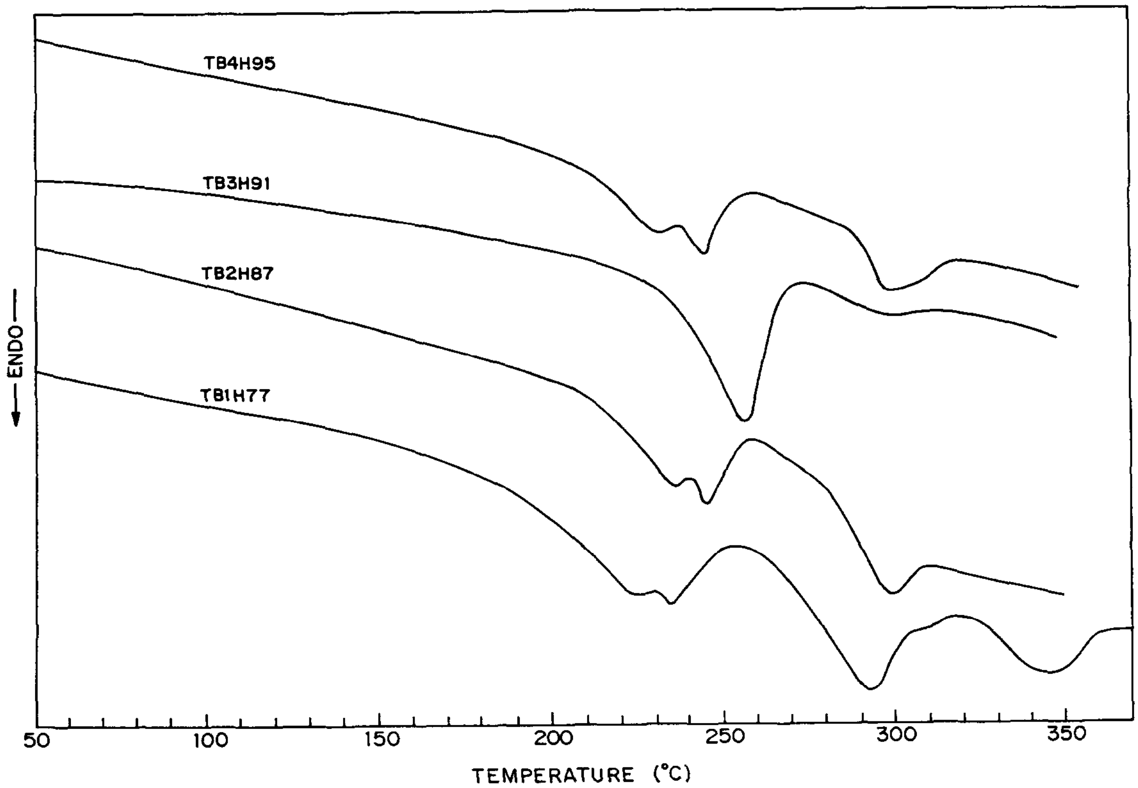

Figure 4 D.s.c. second heating curves of copoly(ether ester)s

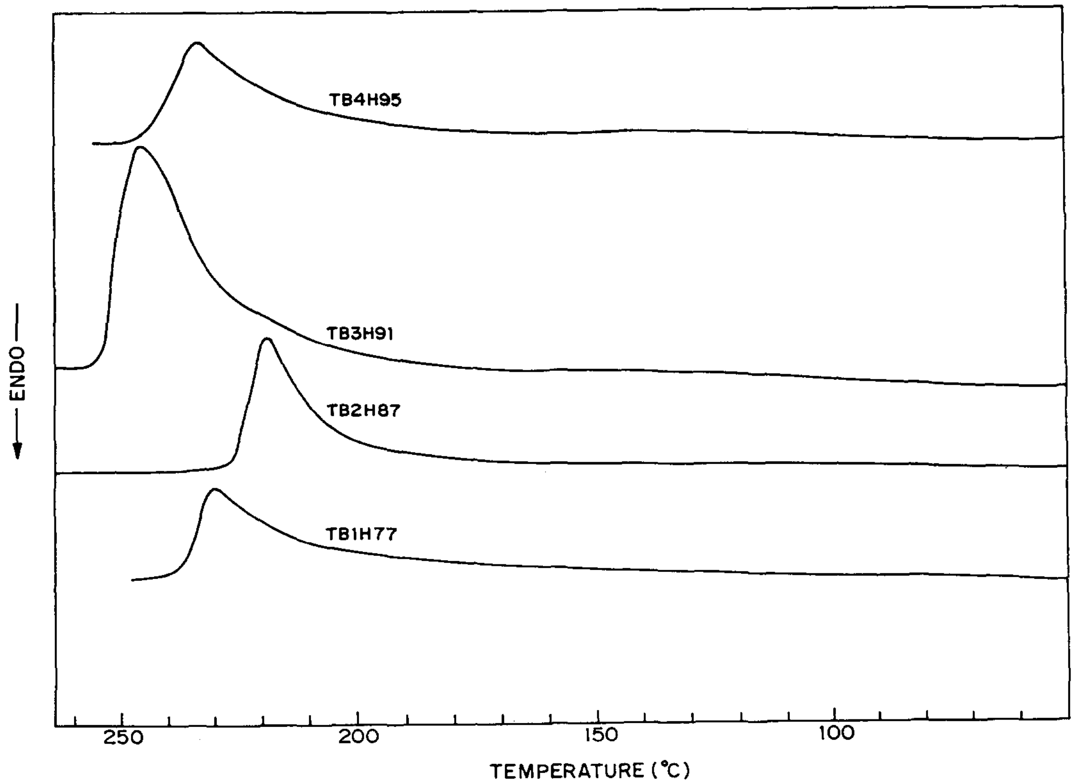

Figure 5 D.s.c. second cooling curves of copoly(ether ester)s

Multiple endotherms have been observed in copolyesters[25,26]. These arise from one or a combination of reasons such as differing crystal type/structure and perfection, molecular-weight distribution and crystal reorganization. Annealing treatment as well as different heating rates do not alter multiple endotherms in the present system. This indicates that these peaks are not a consequence of molecular-weight distribution or crystal

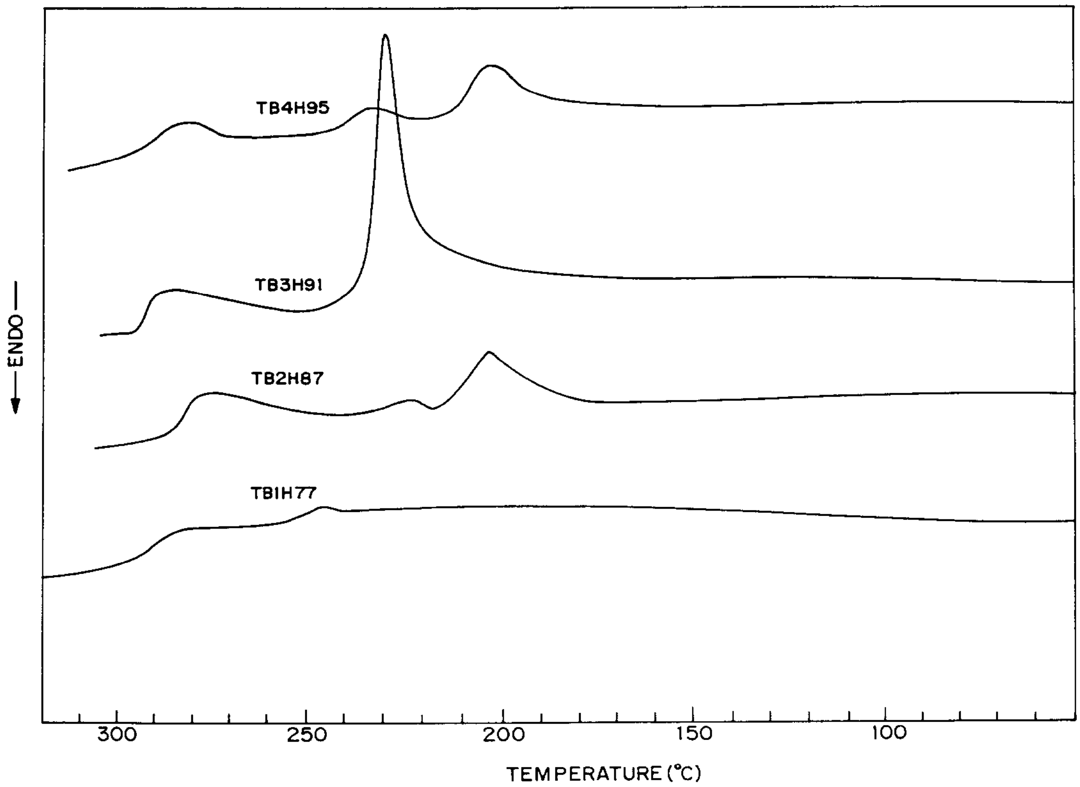

Figure 6 D.s.c. second cooling curves of copoly(ether ester)s after samples were heated just beyond high-melting transition during second heating

reorganization/perfection. The occurrence of a high-temperature endotherm may be due to rigid crystallites, which arise from hard segments having a length longer than the statistical average length. The flexible spacer in the copolymer will negligibly influence the thermal properties of such rigid crystallites. This was revealed from the very small shift in the peak temperature corresponding to the high-temperature endotherm along the series (*Table 1*). In contrast, a remarkable shift in peak temperature pertaining to the lower-temperature endotherm was observed as average hard/soft-segment length increases along the series.

All copoly(ether ester)s were observed for their liquid-crystalline behaviour on a polarizing microscope coupled with a hot stage. Below the melting temperature of the hard segments, crystallites originating from them could be observed embedded in an elastomeric matrix. All polymers show a highly viscous birefringent melt above the melting temperature of the hard segment. For developing identifiable liquid-crystalline texture from such a viscous melt, samples need to be kept isothermally at the desired temperature for several hours or days[27]. However, the susceptibility of our samples to degradation forced us to limit isothermal observations to no more than an hour. For polymer TB1H77, coloured texture was observed, particularly at the edges of the specimen (*Figure 7*); whereas for polymer TB4H95, oval-shaped structures embedded in small granular areas were observed as presented in *Figures 8a* and *8b*. For polymer TB2H87, small bright objects resembling batonnets[14,27,28] were observed as shown in *Figure 9*. Similar objects were also seen for polymer TB1H77 when the sample was sheared between coverslip and glass plate. For polymer TB3H91, bright bands were observed on shearing that resemble banded texture (*Figure 10*). Such textures induced by shearing have been reported for many thermotropic liquid-crystalline systems[29,30]. Even though the exact type of mesophase could be found out only from high-temperature X-ray diffraction studies, preliminary microscopic observations do suggest the possibility of highly ordered smectic mesophases for our copoly(ether ester)s. Longer spacers in our copolymers possibly permit higher degree of freedom for the mesogenic units, thereby resulting in smectic layers. No change in morphology was observed visually near the vicinity of the high-temperature peak maxima. This may be due to a small proportion of rigid crystallites as explained earlier as well as to limitations of isothermal observations as discussed earlier. However, such peaks may even originate from solid-to-solid transition of rigid

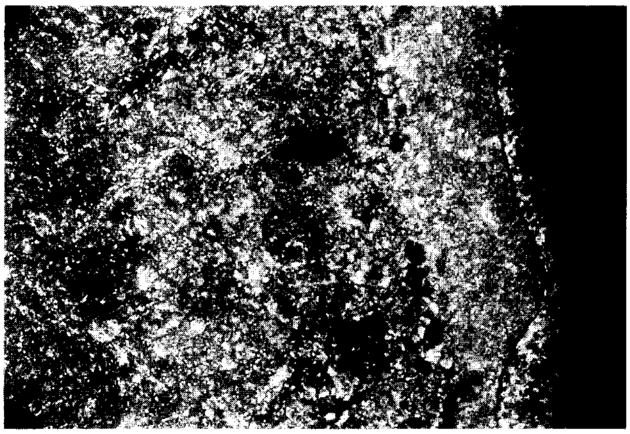

Figure 7 Photograph of copoly(ether ester) TB1H77 at 292°C (original magnification: ×320)

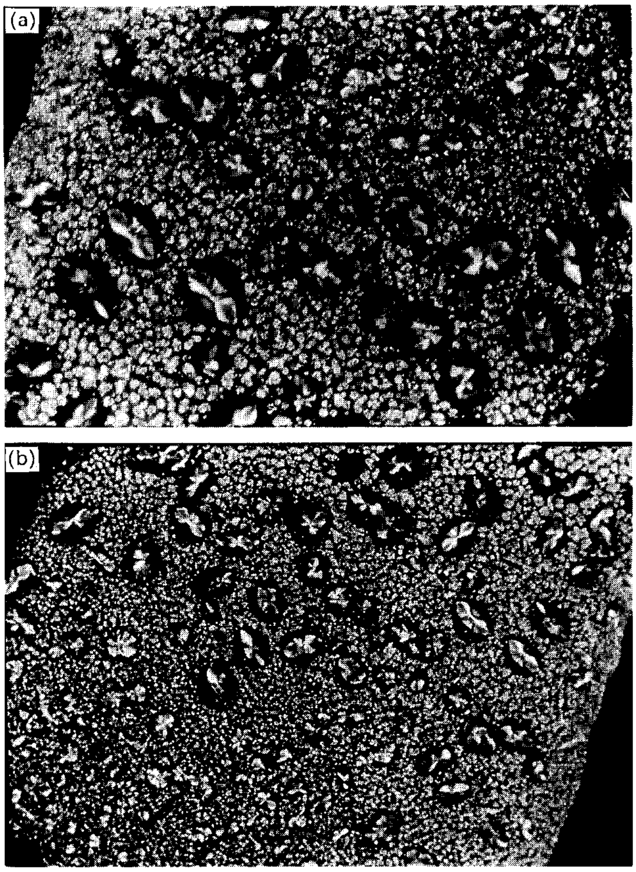

Figure 8 Photographs of copoly(ether ester) TB4H95 at (a) 274°C (original magnification: ×320) and (b) 280°C (magnification: ×200)

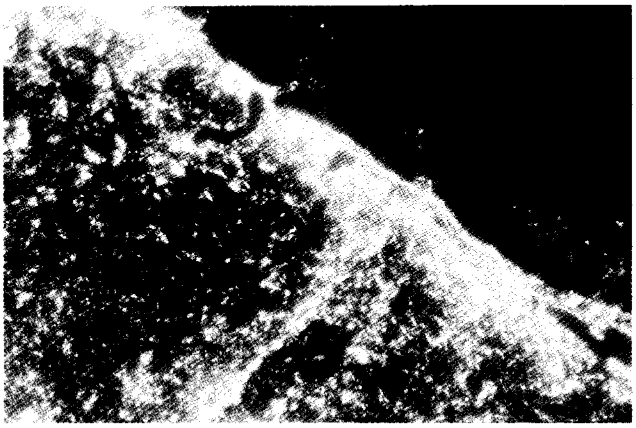

Figure 9 Photograph of copoly(ether ester) TB2H87 at 286°C (original magnification: ×320)

crystallites. No isotropization temperature for any of the polymers could be detected, as observations at high temperature are hampered by thermal degradation.

CONCLUSIONS

Random segmented copoly(ether ester)s of varying hard/soft-segment lengths were synthesized by increasing the number-average molecular weight of POTMG. All copolymers are crystalline at ambient temperature, as observable from room-temperature X-ray diffraction.

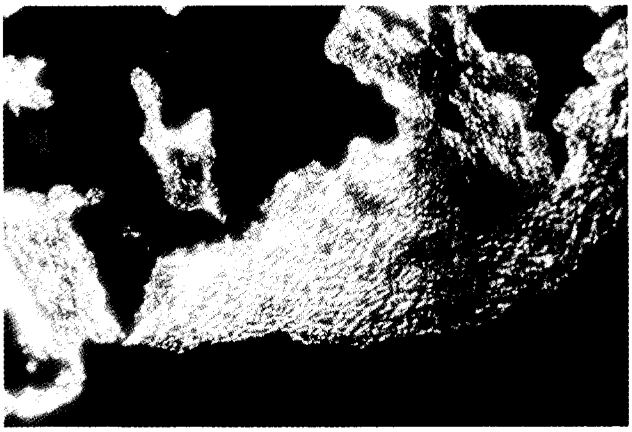

Figure 10 Photograph of copoly(ether ester) TB3H91 at 285°C (original magnification: ×320)

The segmented nature of copoly(ether ester)s was inferred from d.s.c. thermograms through the observation of a low-temperature (−40 to −50°C) glass transition pertaining to soft segments and high-temperature (above 200°C) melting endotherms corresponding to hard segments. Variance in lengths of hard/soft segments does not influence the glass transition originating from the soft segments. This, however, alters the melting transition of the hard segments. All copoly(ether ester)s exhibit highly ordered smectic mesophase due to the hard blocks. Isotropization could not be detected in these copoly(ether ester)s due to degradation prior to this transition. These copoly(ether ester)s can be aptly described as segmented thermotropic liquid-crystalline elastomers.

ACKNOWLEDGEMENTS

We thank Mme C. Noel, PCSM, ESPCI, France, for very fruitful discussions, and Dr J. P. Jog, National Chemical Laboratory, Pune, for providing the POM facility. One of us (MMS) would like to thank UGC, New Delhi, for a Research Fellowship.

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