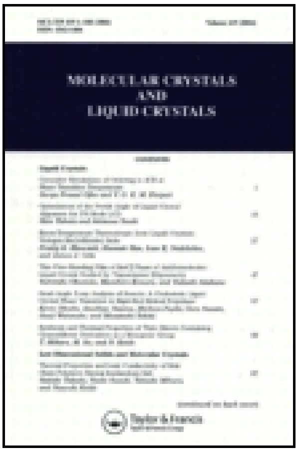

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Hybrid Liquid-Crystalline Block Copolymers with Polystyrene and Polyester Blocks

G. Galli [a] , E. Chiellini [a] , M. Laus [b] , A. S. Angeloni [b] , M. C. Bignozzi [b] & O. Francescangeli [c]

[a] Dipartimento di Chimica e Chimica Industriale, University of Pisa Via Risorgimento 35, 56126, Pisa, Italy

[b] Dipartimento di Chimica Industriale e dei Materiali, University of Bologna Viale Risorgimento 4, 40136, Bologna, Italy

[c] Dipartimento di Scienze dei Materiali e della Terra, University of Ancona Via Brecce Bianche, 60131, Ancona, Italy

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HYBRID LIQUID-CRYSTALLINE BLOCK COPOLYMERS WITH POLYSTYRENE AND POLYESTER BLOCKS

G. GALLI[1], E. CHIELLINI[1], M. LAUS[2], A. S. ANGELONI[2], M. C. BIGNOZZI[2], and O. FRANCESCANGELI[3]

[1]Dipartimento di Chimica e Chimica Industriale, University of Pisa
Via Risorgimento 35, 56126 Pisa, Italy
[2]Dipartimento di Chimica Industriale e dei Materiali, University of Bologna
Viale Risorgimento 4, 40136 Bologna, Italy
[3]Dipartimento di Scienze dei Materiali e della Terra, University of Ancona
Via Brecce Bianche, 60131 Ancona, Italy

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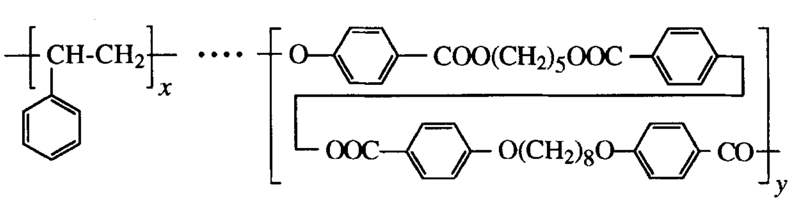
Abstract The synthesis and some thermal and dynamic-mechanical properties of four series of liquid-crystalline block copolymers, comprising polystyrene and polyester blocks, are described. Within each series, the smectic C-nematic and nematic-isotropic transition temperatures of the polyester block were constant throughout the whole composition range, and the enthalpies of both phase transitions were directly proportional to the composition. The two blocks were incompatible in the glass and melt phases and underwent their individual phase transitions.

INTRODUCTION

Very recently, diverse synthetic efforts have produced the first examples of liquid-crystalline (LC) block copolymers[1-10]. Different approaches to the preparation of block copolymers containing LC blocks have included i) polymer-analog reactions on preformed block copolymers with narrow dispersity of block lenghts[1,3]; ii) polymerization of mesogenic monomers by ring-opening metathesis[5], group-transfer[2], and living anionic[4] methods; and iii) condensation of telechelics bearing functional end groups[6]. These synthetic procedures have the evident advantages of involving well defined and controlled polymer structures with rather narrow molecular weight dispersities. However, the above methods have also some shortcomings, when, for instance, a sequence of multiple post-reactions is required on polymers which may not be highly selective with quantitative yields thus resulting in various structural irregularities of the eventual LC copolymers. Living polymerizations are applied within a somewhat limited choice of chemical structures, in which functional groups typical of most mesogens are not tolerated and interfere severely with the active species in the polymer growing process. Furthermore, materials with blocks of very short lengths have only been achieved inherent in the polymerization method applied.

We have adopted a complementary synthetic approach based on the use of azo macroinitiators and have developed new LC block copolymer structures in which either one or both of the block components were mesomorphic in themselves[7-10]. Quite analogous to the closely related initiator AIBN, 4,4'-bis(4-cyanopentanoyl chloride) can initiate the free-radical polymerization of a large number of monomers. Incorporation of such radical source into polymeric structures provides various azo macroinitiators that in turn can be employed for the preparation of block copolymers[11]. Most recent applications of such macroinitiators have yielded to a variety of polymer compositions with blocks of very different chemical and physical characters[12-14]. Therefore, using these functional azo initiators will allow preparation of a diversity of LC block copolymer architectures due to the great versatility of the free-radical polymerization. Possible effects of the molecular weight and molecular weight polydispersities on the phase structure and transitions of the polymers could also be assessed.

Following our continuing interest in developing novel LC polymeric materials, this paper reports on the synthesis and some thermal and dynamic-mechanical properties of four series of block copolymers **1**, with the following simplified structure:



1(m,n)

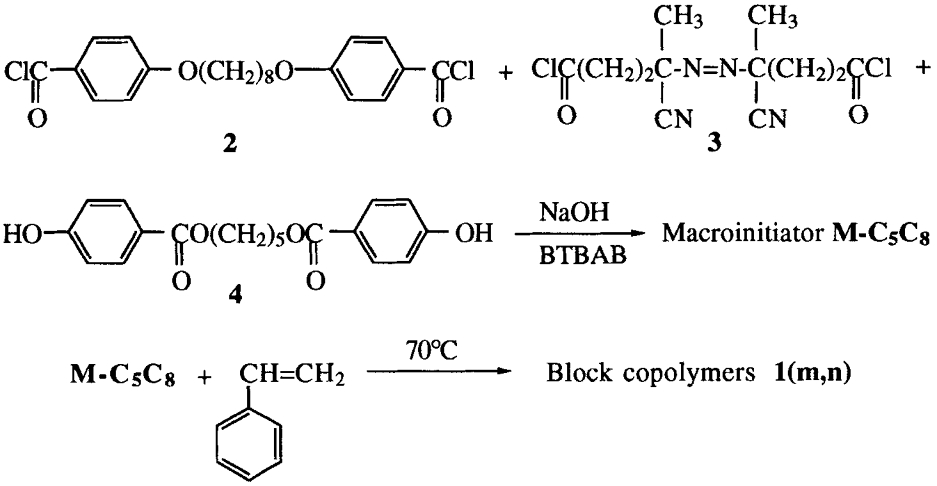
These copolymers consisted of polystyrene and LC polyester blocks and, accordingly, were amorphous-LC copolymers. The latter block was shown to form smectic C and nematic mesophases[15,16]. The block copolymers are designated with the general acronym **1(m,n)**, where **m** (**m**=a-d) represents the series mark relating to the different macroinitiator and **n** (**n**=1-4) refers to the molar concentration of styrene in the feed mixture. The synthesis and properties of copolymers **1(a,n)** have already been described[8], but they are reconsidered here for comparison.

EXPERIMENTAL SECTION

Materials

4,4'-Octamethylene dioxydibenzoyl chloride (**2**) and pentamethylene di(4-hydroxybenzoate) (**4**) were prepared according to ref.15. 4,4'-Azobis(4-cyanopentanoyl chloride) (**3**) was prepared from 4,4'-azobis(4-cyanopentanoic acid) following the procedure described in ref.17.

Synthesis of Macroinitiators. In a typical polymerization reaction, 1.75 g (4.14 mmol) of **2** and 0.14 g (0.46 mmol) of **3** were dissolved in 30 mL of dichloroethane and the solution was transfered into an appropriate flask containing 1.58 g (4.6 mmol) of **4**, 0.48 g (12.0 mmol) of NaOH and 0.20 g (0.56 mmol) of benzyl tributylammonium bromide (BTBAB) in 50 mL of water at 0-5°C. The mixture was vigorously stirred for 2 min and then poured into 300 mL of methanol. The precipitated macroinitiator **M-C_5C_8(b)** was purified by repeated precipitations from chloroform solution into methanol and dried 24 h in vacuo at room temperature. Yield 2.3 g (66%).



SCHEME 1. Synthesis of block copolymers **1**.

TABLE I. Reaction conditions, molecular weight and composition data of macroinitiators **M-C_5C_8(a)-(d)**, polyesters **C_5C_8(a)-(d)**, and block copolymers **1(m,n)**.

Sample	F[a] of **3** (mol-%)	[Sty][b] (M)	Sty convn. (%)	**C_5C_8**[c] (wt.-%)	Mn[d]	Mw/Mn[d]	Azo group[e]
M-C_5C_8(a)	13.0	-	-	100	6100	2.3	1.1
C_5C_8(a)	-	-	-	100	3500	2.1	-
1(a,1)	-	5.2	13	32	69000	4.6	-
1(a,2)	-	3.5	15	38	36000	5.3	-
1(a,3)	-	1.7	13	59	33000	3.2	-
1(a,4)		0.6	11	84	22000	2.6	-
M-C_5C_8(b)	10.0	-	-	100	11000	2.4	1.5
C_5C_8(b)	-	-	-	100	5000	2.2	-
1(b,1)	-	5.2	12	23	160000	2.3	-
1(b,2)	-	3.5	14	33	49000	3.3	-
1(b,3)	-	1.7	13	43	45000	3.3	-
1(b,4)	-	0.6	10	74	24000	3.7	-
M-C_5C_8(c)	6.0	-	-	100	6500	2.3	0.5
C_5C_8(c)	-	-	-	100	5400	1.8	-
1(c,1)	-	5.2	11	22	62000	5.0	-
1(c,2)	-	3.5	13	41	61000	3.0	-
1(c,3)	-	1.7	14	60	44000	2.5	-
1(c,4)	-	0.6	12	83	16000	3.7	-
M-C_5C_8(d)	2.5	-	-	100	6100	2.3	0.2
C_5C_8(d)	-	-	-	100	3600	2.0	-
1(d,1)	-	5.2	14	48	59000	5.8	-
1(d,2)	-	3.5	12	59	47000	5.3	-
1(d,3)	-	1.7	14	76	36000	4.1	-
1(d,4)	-	0.6	15	85	27000	2.9	-

[a]Composition of **3** in the feed mixture. [b]Molar concentration of styrene in the feed mixture. [c]Polyester block **C_5C_8**. [d]By SEC, in chloroform at 25°C. [e]Average number of active azo groups per macroinitiator polymer chain.

Four different macroinitiators were prepared using different mol-% compositions (F) of **3**, with respect to the total diacid chloride content, in the feed mixture: F= 13%, **M-C_5C_8(a)**; F= 10%, **M-C_5C_8(b)**; F= 6%, **M-C_5C_8(c)**; F= 2.5%, **M-C_5C_8(d)**.

Synthesis of Block Copolymers. In a typical copolymerization reaction, the required amount of styrene and 0.5 g of the macroinitiator **M-C_5C_8** were dissolved in anhydrous and peroxide-free tetrahydrofuran to a total solution volume of 15 mL. The reaction mixture was introduced into a Pyrex glass ampoule, thoroughly freeze-thaw degassed and then sealed under vacuum. After reacting for 20 h at 70°C, the copolymer was recovered by addition of a ten-fold excess of methanol and purified from polystyrene by extraction with boiling cyclohexane in a Kumagawa extractor. The copolymer was then dried in vacuo for 24 h. The styrene conversion was in the 10-15% range.

All copolymers **1(m,n)** were synthesized by the above procedure, starting from macroinitiators **M-C_5C_8(a)-(d)**, using different amounts of styrene ([S]) in the feed mixture: [S]= 5.2 M, **n**=1; [S]= 3.5 M, **n**=2; [S]= 1.7 M, **n**=3; [S]=0.6 M, **n**=4.

Physicochemical Characterization

^{1}H NMR and ^{13}C NMR spectra were recorded on polymer solutions in $CDCl_3$ with a Varian Gemini 200 spectrometer. The composition of the copolymers was determined from the ^{1}H NMR spectra.

Molecular weight characteristics (Mn, Mw/Mn) were determined by size exclusion chromatography (SEC) of chloroform solutions with a 590 Waters chromatograph equipped with refractive index detector using a Shodex KF-804 column. While Mn and Mw/Mn of copolymers **1** were evaluated relative to polystyrene standard samples, they were determined by the universal calibration method using polystyrene standard samples for macroinitiators **M-C_5C_8** and polyesters **C_5C_8**.

Differential scanning calorimetry (DSC) analyses were carried out under dry nitrogen flow with a Perkin-Elmer DSC 7 apparatus. The transition temperatures were taken from the DSC traces of samples annealed by cooling from the isotropic melt, as corresponding to the maximum/minimum of the enthalpic peaks at a heating/cooling rate of 10 K min^{-1}. Dynamic-mechanical measurements were performed with a Perkin Elmer DMA-7 analyzer (scanning rate of 4 $Kmin^{-1}$) at 1 Hz frequency. Samples were compression molded at 380 K for 15 min to form ~1 mm thick sheets and the three point bending geometry was used.

X-ray diffraction patterns were recorded on oriented samples produced by drawing fibers out of the mesophase with a pair of tweezers. X-ray diffraction photographs were taken on a Rigaku-Denky RV300 rotating anod generator equipped with a pin-hole flat camera. Ni-filtered $CuK_{\alpha I}$ radiation was used.

RESULTS AND DISCUSSION

Synthesis

Block copolymers **1(m,n)** were synthesized via the two-step procedure illustrated in Scheme 1. It consisted of two successive polycondensation and free-radical polymerization processes. In the first reaction stage, the macroinitiator **M-C_5C_8**,

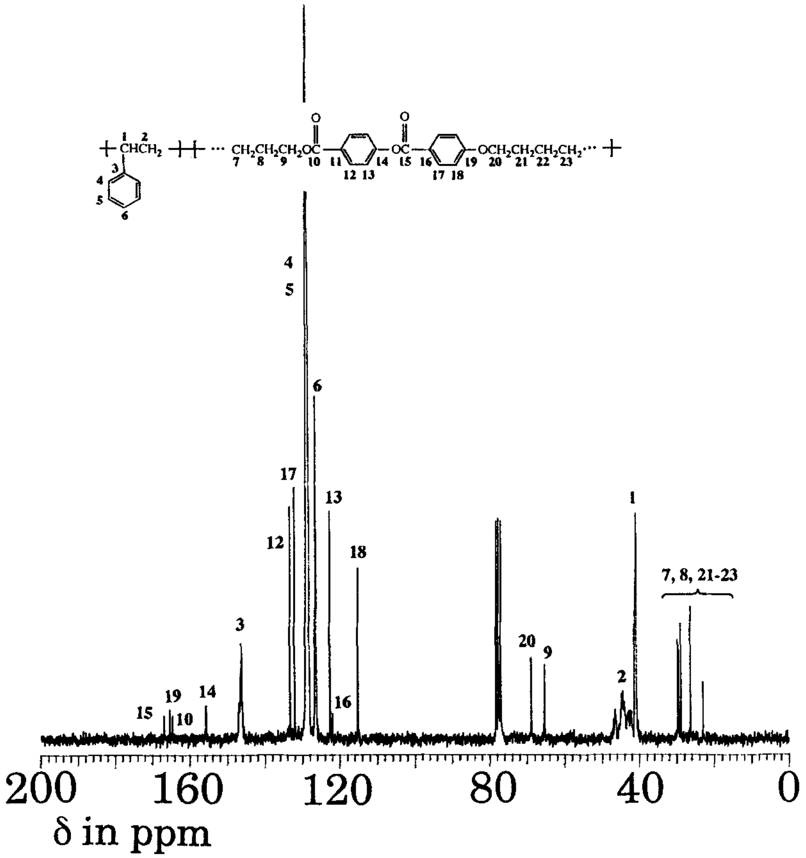


FIGURE 1. ^{13}C NMR spectrum of block copolymer **1(b,2)** (in $CDCl_3$).

possessing reactive azo groups in the main chain, was prepared by reacting in equimolar amounts the pentamethylene di(4-hydroxybenzoate) (**4**) sodium salt and the mixture of 4,4'-azobis(4-cyanopentanoyl chloride) (**3**) and 4,4'-octamethylene dioxydibenzoyl chloride (**2**) in the presence of a catalytic amount of a phase transfer agent (BTBAB). The macroinitiator **M-C$_5$C$_8$** was then used as free-radical source to initiate the polymerization of styrene through the thermal decomposition of the azo group at 70°C. The resulting polymeric products were purified by repeated precipitations from chloroform solution into methanol and by fractionation with boiling cyclohexane to extract the polystyrene homopolymer. Minute amounts of polystyrene were obtained in all cases thus clearly indicating that chain transfer processes were negligible.

Four copolymer series were prepared starting from four macroinitiators containing 2.5, 6, 10 or 13 mol-% of 4,4'-azobis(4-cyanopentanoyl chloride) with respect to the total diacid chloride content, and using within each series different mole concentrations of styrene (5.2 to 0.6 M) in the feed mixture (Table I).

The structure of the copolymers was established by ^{13}C NMR and ^{1}H NMR spectroscopy. Figure 1 reports as a typical example, the ^{13}C NMR spectrum of **1(b,2)**, together with the relevant assignments. Carbons 2 and 3 displayed structured resonance signals arising from different stereochemical sequences typical of essentially heterotactic polystyrene. Polyester block composition, as evaluated from ^{1}H NMR spectra, ranged from 22 to 85 wt.-% (Table I), corresponding to 5 to 50 mol-%. In addition, all the macroinitiators **M-C_5C_8(a)-(d)** were thermally decomposed at 70°C in the presence of a large amount of a free radical inhibitor, to avoid or at least to reduce the incidence of radical recombination reactions, and the resulting polymers **C_5C_8(a)-(d)** were taken as models for the polyester block in the relevant copolymers. The number average molecular weight (Mn) and the first polydispersity index (Mw/Mn) of the macroinitiators **M-C_5C_8**, were evaluated by SEC using the universal calibration method and ranged from 11000 to 6100 and from 2.4 to 2.3 respectively, whereas those of polymers **C_5C_8** ranged from 5400 to 3500 and from 2.2 to 1.8. The values of Mn of polymers **C_5C_8**, as calculated under the hypotheses that 4,4'-azobis(4-cyanopentanoyl chloride) reacted in a quantitative manner and distributed randomly along the polymer chain, resulted 2900 for **C_5C_8(a)**, 4300 for **C_5C_8(b)**, 4200 for **C_5C_8(c)**, and 5000 for **C_5C_8(d)**. They were in reasonable agreement with the experimental values (Table I), thus substantiating the above hypotheses and indicating that the molecular weight of the polyester block in the copolymers may be rather accurately controlled by adjusting the concentration of the azo groups in the macroinitiator.

Figure 2 reports collectively the SEC curves of the four block copolymer series. It is interesting to note that the SEC curves of series **1(a,n)**, **1(b,n)** and **1(c,n)** are monomodal with minor tailing on the low molar mass side, whereas those of series **1(d,n)** display two well defined maxima. As the latter series was prepared from the macroinitiator with the lowest amount of azo groups, the bimodal distribution likely reflects the presence of a substantial amount of polyester homopolymer. Within each series, the SEC curves of the block copolymers are shifted toward lower values along the elution volume scale as the concentration of the styrene monomer in the feed mixture, and therefore of the polystyrene block content in the relevant copolymer, increased. This result confirms previous observations[9] that the polystyrene block length in the relevant copolymers was effectively controlled by the styrene monomer concentration in the feed mixture.

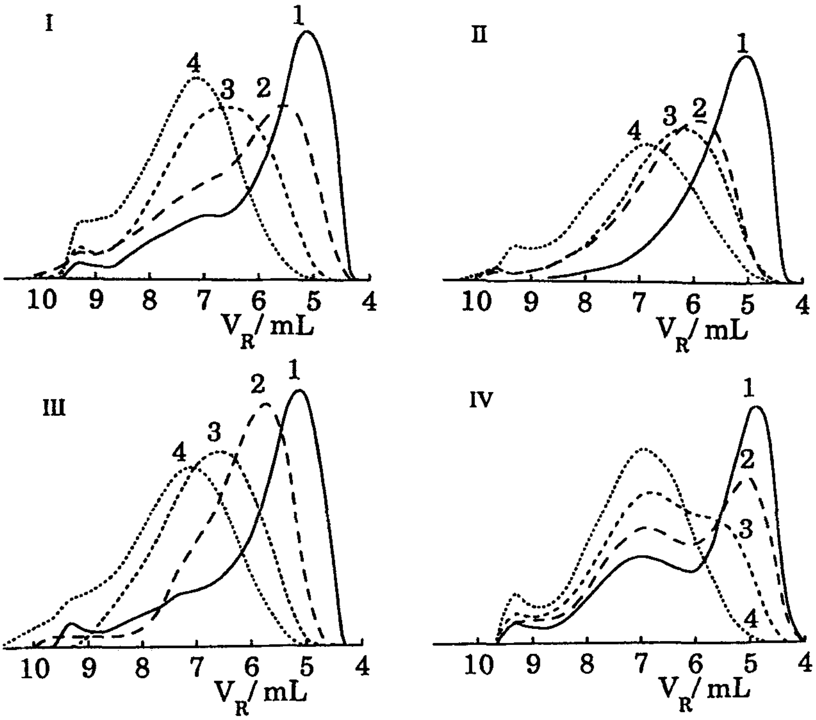


FIGURE 2. SEC curves of block copolymers **1(m,n)**: I, **1(a,n)**; II, **1(b,n)**; III, **1(c,n)**; IV, **1(d,n)**. The numbers on the curves correspond to **n**.

Accordingly, the molecular characteristics of the polystyrene block can be effected by appropriately choosing the styrene monomer concentration at any fixed concentration of macroinitiator. The values of Mn and Mw/Mn of the block copolymers **1**, estimated by SEC using the polystyrene calibration curve, ranged from 16000 to 160000 and from 2.6 to 5.8 respectively (Table I). However, as the polyester and polystyrene blocks constituting the copolymers must have different configurational characteristics in solution and interactions with the solvent, the molecular weight data for the block copolymers are only indicative.

The free-radical polymerization of styrene predominantly terminates by a combination termination[18,19] and, therefore, in the present polymerization system triblock (polyester-polystyrene-polyester) copolymers from macroinitiator chains containing one reactive azo group and multiblock (polyester-polystyrene) copolymers from macroinitiator chains containing more than one reactive azo group are expected to form.

Dynamic-mechanical Behavior

The glass and sub-glass transitions of block copolymers were studied by DMA in the linear viscoelasticity range (Table II). As a typical example, Figure 3 shows the trends of the dynamic storage modulus (G') and the loss tangent (tan δ) at 1 Hz as a function of temperature for block copolymers **1(c,n)**. G' of all samples was about $4 \cdot 10^9$ Pa at 150 K and decreased steadily with increasing temperature. A drop of G' and a corresponding increase in tan δ were observed in the 170-230 K region. This relaxation was associated primarily with local mode processes of relatively short chain segments of the polyester block.

Table II. Physicochemical and liquid-crystalline properties of polyesters **C_5C_8(a)-(d)** and block copolymers **1(m,n)**.

sample	Tg^B [a,c] (K)	Tg^A [a,d] (K)	T_{SN}^B [b,c] (K)	Ti^B [b,c] (K)	ΔH_{SN}^B [b,c] (Jg^{-1})	ΔHi^B [b,c] (Jg^{-1})
C_5C_8(a)	304	-	397	447	9.2	1.4
1(a,1)	306	381	400	451	2.3	0.3
1(a,2)	306	377	401	451	3.5	0.8
1(a,3)	305	368	402	451	5.8	1.0
1(a,4)	304	365	399	451	8.0	1.3
C_5C_8(b)	305	-	396	445	8.1	1.6
1(b,1)	305	370	394	443	1.3	0.3
1(b,2)	305	376	396	443	1.8	0.4
1(b,3)	305	373	394	443	3.3	0.6
1(b,4)	305	357	395	444	6.1	0.9
C_5C_8(c)	307	-	395	445	8.2	1.8
1(c,1)	307	373	394	446	2.0	0.3
1(c,2)	307	377	396	446	3.1	0.8
1(c,3)	308	375	394	446	5.1	1.3
1(c,4)	308	366	394	445	7.1	1.5
C_5C_8(d)	307	-	398	452	9.1	1.9
1(d,1)	308	375	399	455	3.5	0.7
1(d,2)	307	372	401	456	5.5	1.0
1(d,3)	307	365	399	455	7.3	1.5
1(d,4)	307	363	399	455	8.3	1.6

[a]By DMA, at 1 Hz and 4 $Kmin^{-1}$ scanning rate. [b]By DSC, at 10 $Kmin^{-1}$ scanning rate. [c]B: polyester block C_5C_8. [d]A: polystyrene block.

In addition, two main dispersion phenomena occurred at about 300 and 380 K, with peaks in the relevant tan δ curves, correlated to the complex loss behavior at the glass transitions of the polyester and polystyrene blocks respectively. Above 400 K, all the samples lost their dimensional stability.

The decrease of G' with two definite steps at the glass transition of both polyester and polystyrene blocks was directly related to their weight fraction in the copolymer. This phenomenology is very similar to the one previously described[8] for block copolymers **1(a,n)** and reflects the existence of a microphase separation between the

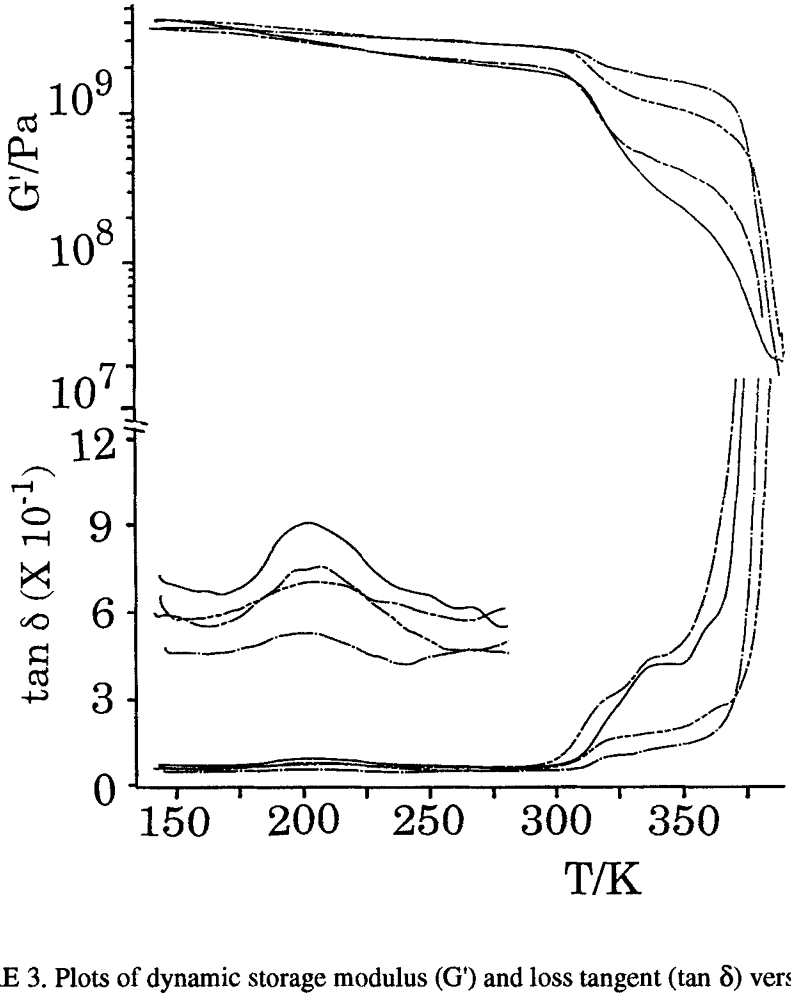


FIGURE 3. Plots of dynamic storage modulus (G') and loss tangent (tan δ) versus temperature for block copolymers **1(c,n)** at 1 Hz:
1(c,1), _._; **1(c,2)**, _ _ _ _; **1(c,3)**, _ _ _ ; and **1(c,4)**, ____.
(inset figure magnified × 5).

two phases in agreement with a substantial incompatibility of the two chemically different blocks in the glassy state. It is interesting to observe that, within each polymer series, the glass transition temperature (Tg) of the polyester block was practically constant, whereas the glass transition temperature of the polystyrene block decreased regularly from samples with **n**=1 to samples with **n**=4. This closely related to the parallel decrease of the molecular weight of the polystyrene block in the relevant copolymers[9,20].

Thermal Behavior

The LC behavior of block copolymers was studied by DSC measurements, polarizing microscopy and X-ray diffraction. Polymers **C_5C_8(a)-(d)** were also studied as models for the polyester block in the relevant block copolymer series. The transition temperatures and thermodynamic parameters are collected in Table II. The DSC traces of all block copolymers were qualitatively similar to those of **1(c,1)** which are illustrated in Figure 4. The glass transition of the polystyrene block at about 370 K preceded two endothermic transitions attributed to smectic-nematic and nematic-isotropic transitions respectively. Both transitions were reversed on cooling with a supercooling of a few degrees.

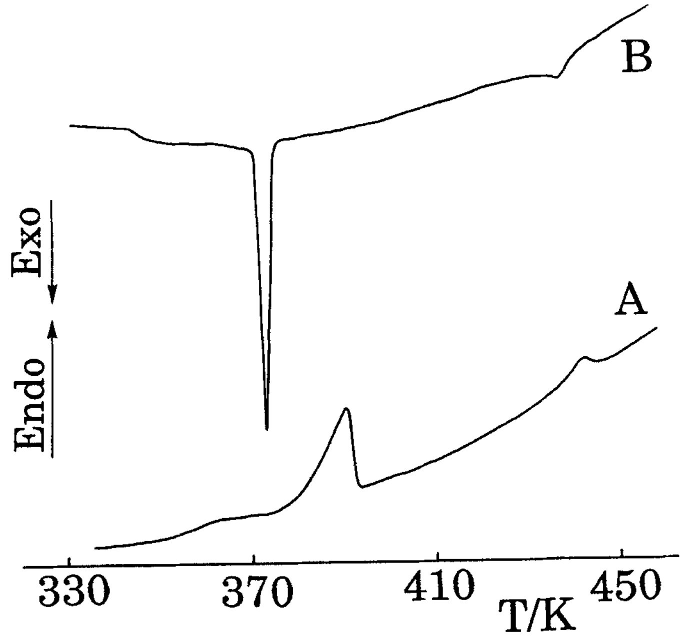


FIGURE 4. DSC heating (A) and cooling (B) curves of block copolymer **1(c,1)**.

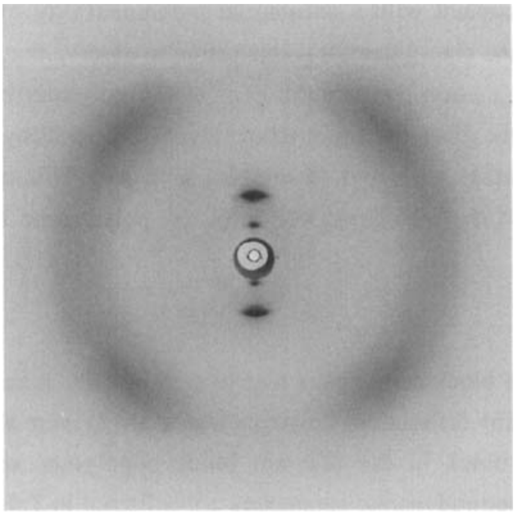


FIGURE 5. Fiber X-ray diffraction pattern of the smectic phase of block copolymer **1(c,1)** (vertical fiber axis).

The nature of the smectic mesophase was identified by X-ray diffraction on oriented specimens produced by drawing fibers out of the mesophase (Figure 5). The anisotropy shown in the X-ray patterns of the oriented samples clearly demonstrated that a high degree of molecular orientation can be achieved by drawing fibers from the mesophases. The diffraction pattern consisted of small angle sharp reflections and wide angle diffuse crescents in keeping with the presence of a disordered smectic phase with unstructured liquid-like layers. The four diffuse crescents were roughly equidistant from the origin and formed pairs on a straight line making an angle $\beta = 18°$ with respect to the equator. Therefore, the rigid mesogenic groups were tilted by the angle β with respect to the director of the layer planes in a smectic C phase very similar to the one observed for the LC polyesters $\mathbf{C_5C_m}$.[16] In this unconventional smectic C phase[21,22] the mesogens are tilted and the spacer segments are parallel to the layer normal. This result clearly indicates that in the present copolymer system the presence of the polystyrene block has no influence on the nature of the mesophases generated by the polyester block.

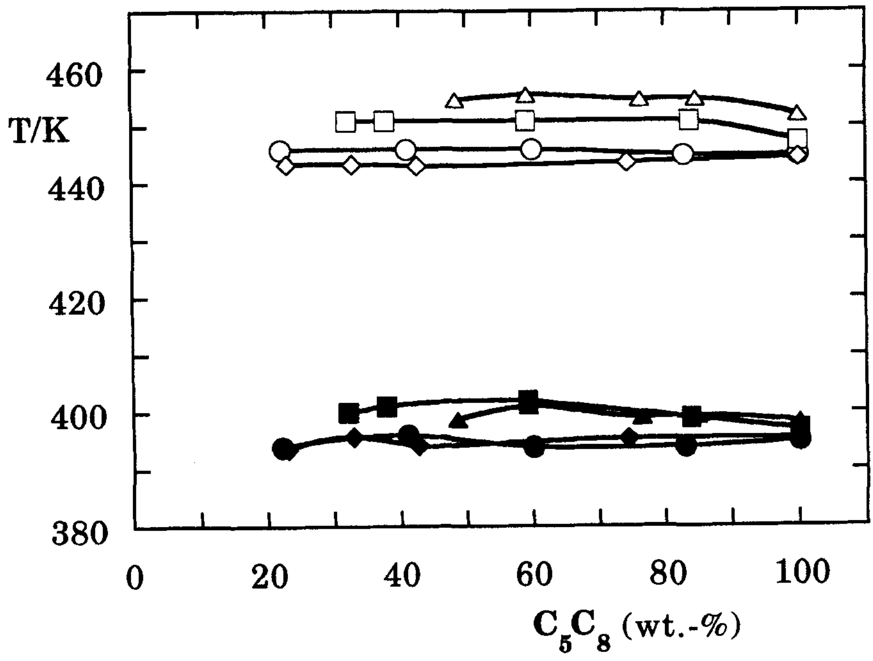


FIGURE 6. Trends of the smectic C-nematic (full symbols) and nematic-isotropic (open symbols) transition temperatures of block copolymers **1** as a function of the weight fraction of the polyester block C_5C_8: **1(a,n)**, ■,□; **1(b,n)**, ◆,◊; **1(c,n)** ●,○; **1(d,n)** ▲,△.

Figure 6 illustrates collectively the trends of the smectic C-nematic and nematic-isotropic transition temperatures for the four block copolymer series as a function of the polyester block content in the relevant copolymers. Within each block copolymer series, the phase transition temperatures are constant throughout the whole composition range and very similar to those of the relevant homopolymers C_5C_8.

The trends of the smectic C-nematic and nematic-isotropic transition enthalpies for the four block copolymer series as a function of the polyester block content are shown in Figure 7. The enthalpy changes associated to both the smectic C-nematic and nematic-isotropic phase transitions are directly proportional to the weight of the LC polyester block, and the normalized enthalpies are equal to those of the respective homopolymers C_5C_8. Therefore, within the above ranges of composition and molecular weight, the mesophase transition parameters of the polyester block are not influenced by the presence of the polystyrene block, and the two chemically different blocks appear to be strongly phase-separated within their glassy and melt states.

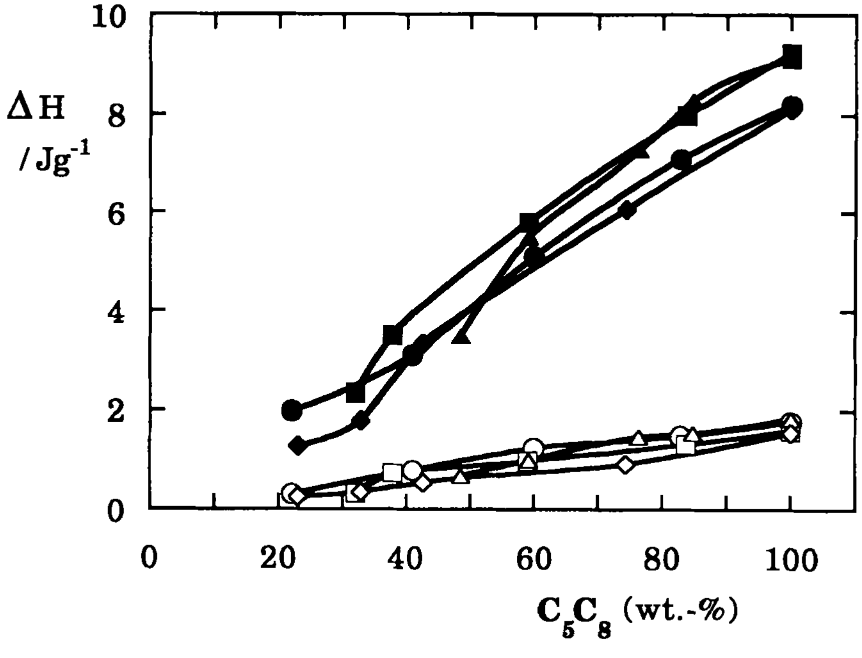


FIGURE 7. Trends of the smectic C-nematic (full symbols) and nematic-isotropic (open symbols) transition enthalpies of block copolymers **1** as a function of the weight fraction of the polyester block C_5C_8: **1(a,n)**, ■,□; **1(b,n)**, ◆,◇; **1(c,n)** ●,○; **1(d,n)** ▲,△.

CONCLUSIONS

Four series of block copolymers, consisting of polystyrene and LC polyester blocks were prepared by a synthetic route that involved the preparation of a polyester macroinitiator and its subsequent thermal decomposition in the presence of styrene. Therefore, hybrid polymeric materials were obtained in that the described copolymers are constituted by blocks of monomeric units typically polymerizable by stepwise and chain growth processes, respectively. In addition, segments having completely different bulk configurational characters are part of the same macromolecular structure. While one block (coil) is amorphous throughout the whole temperature range, the other one (rod-like) is able to form both smectic and nematic phases with increasing temperature above the glass transition. The block length and composition could be tuned and predetermined reasonably well on a structural basis, thus allowing design and production of tailor-made block copolymers. The combined thermal and dynamic-mechanical analyses indicate that the chemically different blocks are phase-separated and their phase structure and transitions are unaffected with respect to the corresponding homopolymers. The prepared hybrid copolymers can be considered examples of glassy polymeric materials with variable thermoplastic features.

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