Polymer Bulletin 31, 387–392 (1993)

Polymer Bulletin

Hybrid liquid-crystalline block copolymers based on polystyrene and polyester blocks

A. S. Angeloni[1], M. C. Bignozzi[1], M. Laus[1], E. Chiellini[2,]* and G. Galli[2]

[1]Dipartimento di Chimica Industriale e dei Materiali, Università di Bologna, I-40136 Bologna, Italy

[2]Dipartimento di Chimica e Chimica Industriale, Università di Pisa, I-56126 Pisa, Italy

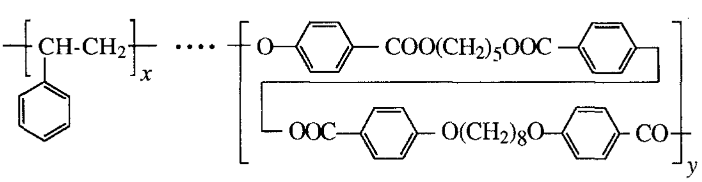
Summary

The synthesis and some thermal and dynamic-mechanical properties of a novel class of hybrid block copolymers comprised of polystyrene and liquid-crystalline polyester blocks are reported. The two blocks appear to be incompatible in the solid and melt phases and undergo distinct thermal transitions. The mesophase transition temperatures of the block copolymers are constant within all the composition range. The mesophase transition enthalpies are directly proportional to the weight fraction of the liquid-crystalline polyester block.

Introduction

Liquid-crystalline polymers and block copolymers are two examples of polymeric systems that can exhibit noncrystalline order and give rise to structured fluid phases and phase separation phenomena. In turn, these features are expected to result in specific physical, rheological, and mechanical properties (*1*). Combining the above characteristics in one single polymer structure would be of obvious interest. However, the synthesis of liquid-crystalline block copolymers appears rather difficult by the conventional polymerization procedures especially due to the complex functional nature of mesogenic monomers (*2-4*). We are developing novel liquid-crystalline block copolymer structures with a new synthetic approach, and in the present contribution we wish to report on the synthesis and some thermal and dynamic-mechanical properties of a new class of block copolymers **1a-d**.

They are constituted by amorphous polystyrene blocks (blocks A) and liquid-crystalline polyester blocks (blocks B) in different weight proportions. The latter consist of two mesogenic *p*-oxybenzoyl diads interconnected in an antiparallel fashion by two linear aliphatic chains of five and eight methylene groups through two ester and ether linking groups respectively. The relevant homopolyester had been shown to form smectic C and nematic mesophases (*5*).



1a-d

Figure 1. Schematic structure of block copolymers **1a-d**.

---

*Corresponding author

Experimental

Materials. 4,4'-Octamethylene dioxydibenzoyl chloride (**2**) and pentamethylene di(4-hydroxybenzoate) (**4**) were prepared according to (*5*). 4,4'-Azobis(4-cyanopentanoyl chloride) (**3**) was prepared from 4,4'-azobis(4-cyanopentanoic acid) following the procedure described in (*6*). Block copolymers **1a-d** were prepared according to the synthetic route illustrated in Scheme 1.

Synthesis of the macroinitiator **5**: In a typical polymerization reaction, 1.75 g (4.14 mmol) of **2** and 0.20 g (0.62 mmol) of **3** were dissolved in 30 ml of dichloroethane and the solution was transferred into an appropriate flask containing 1.64 g (4.76 mmol) of **4**, 0.48 g (12.0 mmol) of NaOH and 0.2 g (0.56 mmol) of benzyltributylammonium bromide 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 separated macroinitiator **5** was purified by repeated precipitations from chloroform solution into methanol. Yield: 72%.

Synthesis of block copolymers **1**: For the copolymerization reaction, the required amount of styrene and 0.5 g of the macroinitiator **5** were dissolved in anhydrous tetrahydrofuran to a total volume of 15 ml. The solution was then introduced into a Pyrex glass ampoule, that after freeze-thaw degassing was sealed under vacuum. After reacting for 20 h at 70°C, the copolymer **1** 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 styrene conversion was in the 11-15% range.
All copolymers **1** were synthesized by the above procedure using different amounts of styrene in the feed mixture: **1a**, 78.5 mmol; **1b**, 52.4 mmol; **1c**; 26.2 mmol; **1d**, 8.7 mmol.

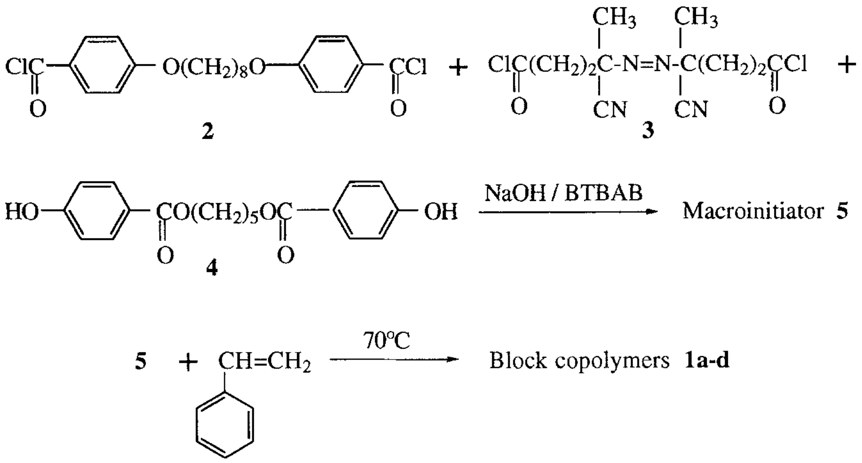
Hydrolysis of block copolymers **1**: In a typical hydrolysis reaction, 0.5 g (2.4 mmol of ester group) of **1d** were suspended in 70 ml of methanol and 3.5 g (87.5 mmol) of NaOH and the reaction mixture was refluxed for 2 h. The suspension was then cooled to room temperature, filtered and the residue was washed with 2x50 ml of water, 3x50 ml of methanol and dried. Yield: 90%.

Physicochemical characterization. Average molecular weights were determined by SEC of chloroform solutions with a 590 Waters chromatograph equipped with refractive index detector using a Shodex KF-804 column calibrated with polystyrene or polyester standard samples. The liquid-crystalline properties of the polymers were studied by a combination of differential scanning calorimetry (Perkin Elmer DSC-7 at a scanning rate of 10 Kmin^{-1}) and polarized light microscopy (Reichert Polyvar microscope equipped with a programmable Mettler FP52 heating stage at a scanning rate of 10 Kmin^{-1}). Dynamic-mechanical measurements were performed with a Dynamic Mechanical Thermal Analyzer (Perkin Elmer DMTA-7 at a 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.

Results and discussion

Block copolymers **1a-d** were synthesized by a two-step procedure as illustrated in Scheme 1. In the first stage, the macroinitiator **5**, possessing reactive azo groups in the main chain, was prepared by a polycondensation reaction under phase transfer conditions between the sodium diphenolate of **4** and the stoichiometric amount of a mixture of the diacid chlorides **2** and **3** in the presence of a catalytic amount of benzyltributylammonium bromide (BTBAB) as the catalyst. A 13 mol-% of **3**, with respect to the total diacid chloride content, was employed in the feed mixture. Subsequently, **5** was used to initiate the free-radical polymerization of styrene through the thermal decomposition of the azo group at 70°C.
Four samples of copolymers were prepared by using different concentrations of styrene ([S]) in the feed mixture ([S]=5.2 M, **1a**; [S]=3.5 M, **1b**; [S]=1.7 M, **1c**; [S]=0.6 M, **1d**) at a

Scheme 1. Synthetic procedure for the preparation of block copolymers **1a-d**.



constant concentration of macroinitiator (33.3 gl^{-1}). The styrene conversion ranged from 11 to 15%. The block copolymers were fractionated by extraction with boiling cyclohexane to eliminate small amounts of polystyrene homopolymer. The polystyrene content, evaluated by ^{1}H NMR, ranged from 16 to 68 wt.-% (Tab.1). An Mn=6100 and an Mw/Mn=2.3 were determined for the macroinitiator **5** by SEC using polyester standard samples for calibration. **5** was also thermally decomposed at 70°C in the presence of a large excess of the free-radical inhibitor 2,6-di-*tert*-butyl-4-methylphenol, to avoid or at least reduce the radical recombination reaction, and an Mn=3500 and an Mw/Mn=2.1 were evaluated for the resulting polyester **6**. Under the assumptions that the 4,4'-azobis(4-cyanopentanoyl chloride) precursor reacted quantitatively and was statistically inserted along the polymer chain an Mn=2900 can be calculated for **6**. This value is smaller but in reasonable agreement with the experimental one and indicates that the macroinitiator contained on average one active azo group per polymer chain. In addition, to gain more information about the polystyrene block, copolymers **1a-d** were subjected to complete alkaline cleavage and the residual polymeric products **7a-d**, consisting of the polystyrene blocks present in the respective copolymers, were recovered and analyzed by SEC. Mn values ranging from 206000 (**7a**) to 25000 (**7d**) with relatively narrow molecular weight distribution (Mw/Mn ≈ 1.7) were determined. The free-radical polymerization of styrene terminates principally by a recombination mechanism and, therefore, due to the reaction scheme and stoichiometry adopted, the copolymer structure in Fig.1 is a simplified one. The actual copolymer product should have a BAB triblock structure, including also AB multiblock sequences. The question of the block copolymer structure and molecular weight will be addressed better in a more comprehensive paper (7).

The glass and sub-glass transitions of the block copolymers were studied by DMTA in the linear viscoelasticity range at 1 Hz frequency, while their liquid-crystalline behavior was analyzed by DSC and polarizing microscopy. Polymer **6** was studied as a model for the polyester block in the copolymers. The transition temperatures and relevant thermodynamic parameters are collected in Tab.1. The dynamic modulus G' of all samples at 150 K was about $4 \cdot 10^9$ Pa and decreased progressively with increasing temperature with however two major drops at 305 and about 370 K, with associated peaks in the relevant tan δ curves, attributed to the glass transition temperatures of blocks B and A respectively (Fig.2). Above 400 K, all the samples lost their dimensional stability. The decrease in modulus at the glass transition temperature of block B is directly related to the wt.-% of this block in the copolymer. The glass

Table 1. Thermal properties of block copolymers **1** and modified polymer **6**.

sample	styrene (wt.-%)	T_g[a] (K)	T_g[b] (K)	T_{SN}[c] (K)	T_{NI}[c] (K)	ΔH_{SN}[c] (J/g)	ΔH_{NI}[c] (J/g)
1a	68	306	381	400	451	2.3	0.3
1b	62	306	377	401	451	3.5	0.8
1c	41	305	368	402	451	5.8	1.0
1d	16	304	365	399	451	8.0	1.3
6	0	304	--	397	447	9.2	1.4

[a] Glass transition temperature of the polyester block B, by DMTA (4 $\mathrm{Kmin^{-1}}$ scanning rate). [b] Glass transition temperature of the polystyrene block A, by DMTA (4 $\mathrm{Kmin^{-1}}$ scanning rate). [c] Smectic-to-nematic (SN) and nematic-to-isotropic (NI) transition temperature and enthalpy, by DSC (10 $\mathrm{Kmin^{-1}}$ scanning rate).

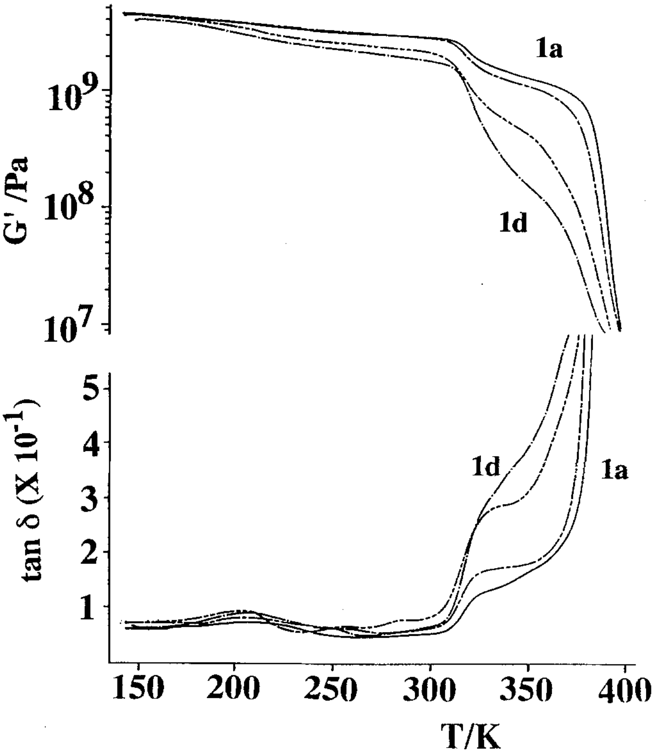


Figure 2. Dynamic storage modulus (G') and tan δ versus temperature plots for block copolymers **1a-d** at 1 Hz: **1a**, ——— ; **1b**, — — — ; **1c**, — — — —; **1d**, —·— .

transition temperature of block B is practically the same in all the block copolymers synthesized, whereas the glass transition temperature of block A decreases regularly from **1a** to **1d**. This decrease is probably due to the combined effects of a decrease in molecular weight of the polystyrene block and the parallel growth of a diffuse interdomain region between the different blocks (*8*). The occurrence of two distinct glass transition temperatures and the close correspondence between the dynamic-mechanical properties and the compositional characteristics of the block copolymers undoubtedly indicate phase separation with minor, if any, interaction between the two blocks.

The thermal properties at temperatures above 390 K were delineated by DSC. The DSC heating and cooling traces of block copolymers and polymer **6** are qualitatively similar. On heating, two endothermic transitions at 397 and 447 K are associated to the smectic C-to-nematic and nematic-to-isotropic transitions of block B, in agreement with (*5*). Interestingly, a melting endotherm, with relatively low enthalpy content, is observed for **6** at 374 K with no counterpart in the DSC of any block copolymer **1**, indicating a decrease in the crystallization propensity of the polyester block in the copolymers. Figs.3 and 4 illustrate the trends of the phase transition temperatures and the enthalpies associated to the smectic C-to-nematic and nematic-to-isotropic phase transitions of block copolymers **1** as functions of the weight fraction of block B. Both mesophase transition temperatures are practically constant within all the investigated composition range and very similar to those of polyester **6**. Furthermore, their enthalpies are directly proportional to the wt.-% of the liquid-crystalline block B, possible deviation being observed at the lowest polyester contents only. These data suggest that the two blocks are segregated also at temperatures above their glass transitions and that the mesophase transitions of block B are not influenced by the presence of the polystyrene block A.

In conclusion, by the synthetic procedure described in the present work it was possible to obtain new block copolymers composed by liquid-crystalline polyester and polystyrene blocks.

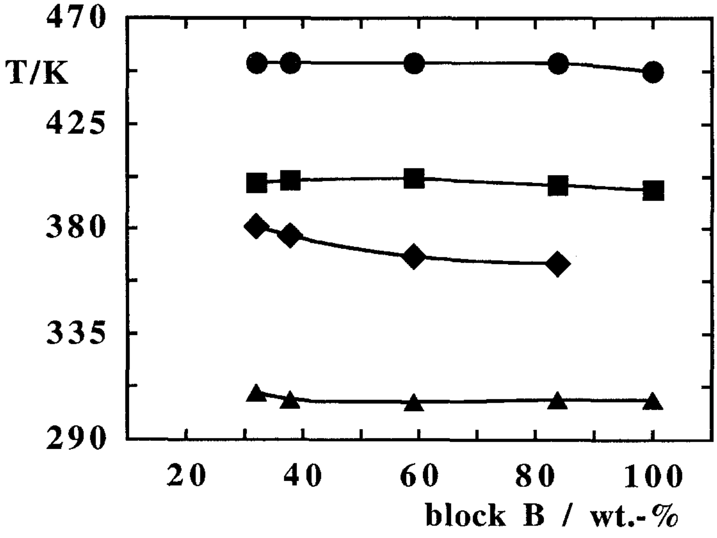


Figure 3. Glass transition (▲) of block B, glass transition (◆) of block A, smectic C-to-nematic (■), and nematic-to-isotropic (●) temperatures of block copolymers **1a-d** as functions of the weight fraction of block B.

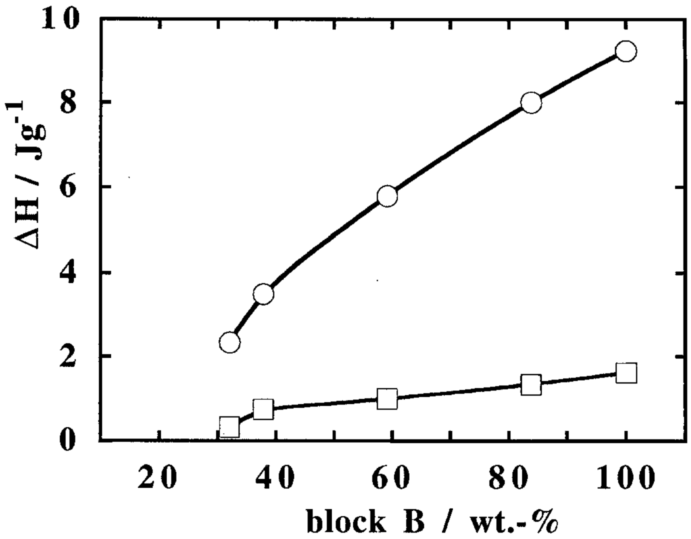


Figure 4. Smectic C-to-nematic (○), and nematic-to-isotropic (□) enthalpies of block copolymers **1a-d** as functions of the weight fraction of block B.

They can be classified as hybrid block copolymers in that the former block was prepared by a step-wise reaction, while the latter block was prepared by a chain reaction. The two blocks appear to be strongly incompatible in the solid and melt phases and undergo distinct thermal transitions. While the precise block structure of the copolymers remains to be elucidated better, it is anticipated that this experimental procedure is extremely versatile and can be used to prepare a great variety of block copolymers comprising main-chain polyester blocks and polyvinyl blocks from various mesogenic monomers.

Acknowledgment

This work was partially supported by the National Research Council (CNR) of Italy, Progetto Chimica Fine 2 - Sottoprogetto Materiali Polimerici.

References

1. Adams J, Gronski W (1990) in: Weiss RA, Ober CK (eds) *Liquid-Crystalline Polymers* (ACS Symposium Series No 435 p 174)
2. Auman BC, Percec V (1988) *Polymer* **29**: 938
3. Zaschke B, Frank W, Fischer H, Schmutzler K, Arnold M (1991) *Polym.Bull.(Berlin)* **27**: 1
4. Galli G, Chiellini E, Yagci Y, Serhatli E I, Laus M, Angeloni A S, Bignozzi M C (1993) *Makromol.Chem., Rapid Commun.* **14**: 185
5. Chiellini E, Galli G, Laus M, Angeloni A S, Francescangeli O, Yang B (1992) *J. Mater. Chem.* **2**: 449
6. Yagci Y (1985) *Polymer Commun.* **26**: 7
7. Chiellini E, Galli G, Angeloni AS, Bignozzi MC, Laus M (1993) *Makromol. Chem., Macromol. Symp.*, in press
8. Kraus G, Rollmann W (1976) *J. Polym. Sci., Polym. Phys Ed.* **14**: 1133.

Accepted August 3, 1993 C