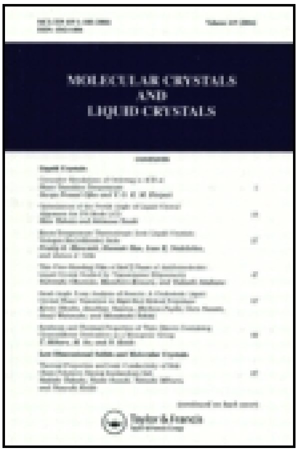

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Dynamic-Mechanical Behavior of Hybrid Thermotropic Liquid Crystalline Block Copolymers

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DYNAMIC-MECHANICAL BEHAVIOR OF HYBRID THERMOTROPIC LIQUID CRYSTALLINE BLOCK COPOLYMERS

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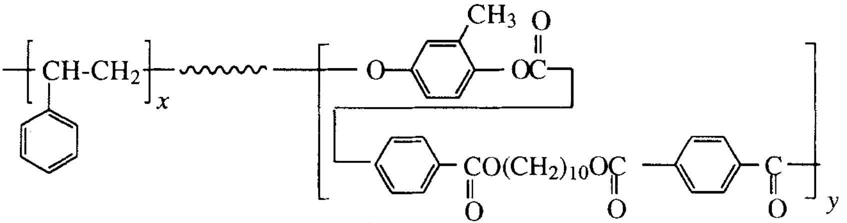
Abstract. The preparation and the dynamic-mechanical behavior of a novel class of liquid crystalline block copolymers is described. In a first step, hydroxyl terminated oligoesters were obtained by polycondensation reaction of methylhydroquinone and 4,4'-dicarboxy-1,10-dibenzoyloxydecane in pyridine solution in the presence of tosyl chloride and dimethylformamide. Hydroxyl terminated oligoesters were then further polymerized with 4,4'-azo-bis(4-cyanopentanoyl chloride) and, in a third step, the macroinitiators obtained were employed in the free-radical polymerization of styrene. The DMA analysis showed that the two different blocks were only partly compatible in the glassy and melt phases and underwent distinct phase transitions. The nematic-isotropic transition temperature of the polyester block was constant throughout the whole composition range and the phase transition enthalpy was directly proportional to the percent of the polyester block.

INTRODUCTION

Block copolymers are multicomponent polymer systems of great practical relevance because their multiphase structure often allows for non-linear and self mutuating behavior[1,2]. Their use to extend the utilization range of engineering resins and to form high performance blends is well assessed. A precise design of the macromolecular structure of block copolymers, including the block length and block length distribution, leads to potentially valuable components susceptible of modifying the interfacial characteristics and the cohesion properties between the matrix and the dispersed phase. This facilitates the production of uniformly dispersed microdomain structures with inherently stabilized morphology.

In this respect, block copolymers containing mesomorphic blocks represent[3] new and valuable materials to finely modulate the mechanical properties of engineering thermoplastic and thermosetting polymer blends. In fact, the intimate coupling between the intrinsic microphase incompatibility, typical of block copolymers, with the self-ordering characteristics of the LC phases may lead not only to a synergistic enhancement of the thermo-mechanical properties, but also may help to improve the processing of polymer blends. In addition, block copolymers containing mesomorphic blocks can help to clarify some fundamental aspects of polymer physics such as the equilibrium relations between the dimension and shape of the domain structure, including also the relevant interfacial contributions, and the molecular dimensions and interactions of the different blocks.

Within this general framework, the present paper reports on the thermal and dynamic-mechanical behavior of three samples of a block copolymer consisting of amorphous polystyrene (PS) and semiflexible LC polyester based on aromatic bis terephthaloyloxy-1,4-methylphenylene triads (TmPT) sequentially interconnected by an α,ω-decamethylene dioxy segment. The general structure of the block copolymer samples indicated as **1a**, **1b** and **1c**, as differentiated on compositional basis, is represented as follows:



1a-c

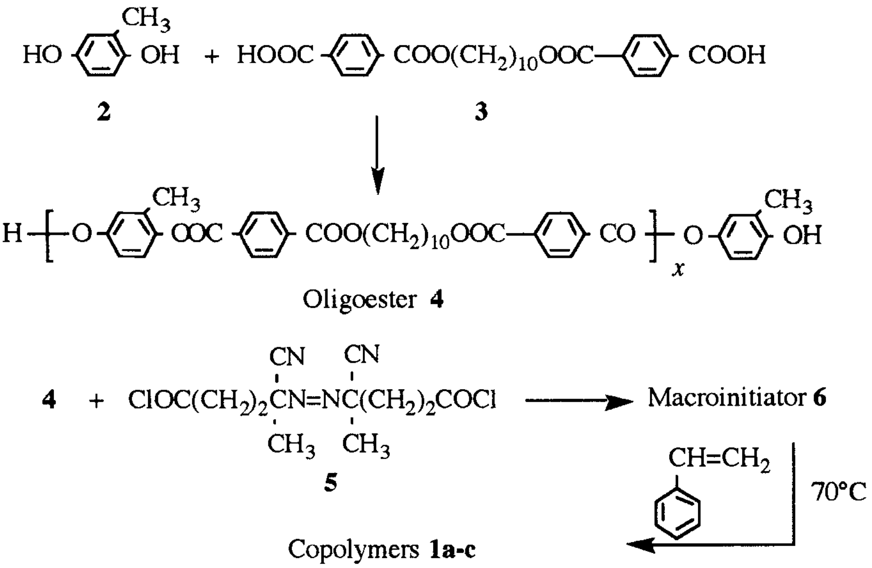
The structurally analogous homopolyester of (TmPTC10)n proved to be semicrystalline and to form a nematic mesophase. These features are maintained in the investigated copolymers that can therefore be classified as amorphous-liquid crystalline hybrid block copolymers.

EXPERIMENTAL PART

Copolymer Samples (Scheme 1)

Methylhydroquinone (**2**) was purified by crystallization in toluene. 4,4'-Decamethylene dioxydibenzoic acid chloride (**3**) and 4,4'-azo-bis(4-cyanopentanoic acid) chloride (**5**) were prepared according to refs. 4 and 5 respectively. Methyl phenylene dioxy terminated oligoester (**4**) was prepared according to ref. 6, by using a molar excess of methylhydroquinone in order to adjust the molar mass of the polycondensation products.

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



Macroinitiator **6** was prepared by extension of **4** with **5** in the presence of triethylamine in chloroform solution. Block copolymers **1a-c** were prepared by dissolving the macroinitiator **6** in THF together with the styrene in a glass ampoule outgassed and sealed after nitrogen purge[6]. After reacting for 20 h at 70°C, the copolymers were 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 10-15% range. Three block copolymers were prepared using different amounts of styrene ([S]) in the feed mixture: [S]= 1.0 M, **1a**; [S]= 1.5 M, **1b** and [S]= 3.0 M, **1c**.

All the block copolymers were hydrolyzed with NaOH in boiling methanol/water to give the polystyrene homopolymers **7a-c**.

Characterization

Molar mass values were determined by SEC in THF, by using an LC10 Perkin-Elmer liquid chromatograph equipped with a Jasco 830-RI refractive index detector and 10^3 Å and 10^4 Å Waters ultrastyragel columns. Monodisperse polystyrene standards were used for calibration. Copolymer composition and structure were characterized by IR using a Perkin-Elmer 1600 FTIR spectrophotometer, and by ^{1}HNMR with a Varian Gemini 200 spectrometer. Thermal properties and mesophase behavior were studied with a Mettler DSC30 calorimeter and a Reichert polarizing optical microscope equipped with a Mettler FP52 hot stage. Thermal stabilities were checked by thermogravimetric analyses with a Mettler TG50. Dynamic-mechanical measurements were performed with a dynamic-

Table I. Physico-chemical characteristics of oligoester **4**, block copolymers **1a-c** and polystyrene homopolymers **7a-c**.

Sample	Polyester (wt-%)	M_w[a]	Mw/Mn[a]
4	100	4500	1.61
1a	39	21000	2.22
1b	29	54500	1.52
1c	16	110500	1.48
7a	-	17500	1.73
7b	-	28500	1.71
7c	-	69500	1.63

[a] By SEC, in chloroform at 25°C.

mechanical analyzer (Perkin Elmer DMA-7, at a scanning rate of 4 $Kmin^{-1}$ and 1 Hz frequency) using the three point bending geometry. The powder polymer sample was introduced into a rectangular mould. The entire assembly was placed between press plates with a nominal pressure of 5 $tonn/cm^2$ and let to stand at room temperature for 20 min. The temperature was then raised to 120°C, the pressure released to 0.5 $tonn/cm^2$. The sample was let to cool at room temperature and recovered as a rectangular 18x5x1 mm sheet.

RESULTS AND DISCUSSION

Synthesis

The synthetic procedure adopted for the preparation of the liquid crystalline block copolymers **1** is illustrated in Scheme 1. The hydroxyl-terminated oligoester **4** was prepared[6] by polycondensation between diacid **3** and methylhydroquinone **2**, using a molar excess of the latter, in order to adjust the molar mass value and provide phenolic end-groups. Oligoester **4** was successively reacted with the diacyl chloride **5** to produce macroinitiator **6** incorporating thermal labile azo groups at both ends. The macroinitiator **6** was then used to initiate the free-radical polymerization of styrene through the thermal decomposition of the azo group at 70 °C. Three block copolymers **1a-c** were prepared using different mole concentrations of styrene in the feed mixture (Table I). Block copolymers **1a-c** were purified by repeated precipitations from chloroform solution into

TABLE II. Glass transition temperatures[a)] and LC phase transition parameters[b)] of block copolymers **1**, oligoester **4** and polystyrene samples **7a-c**.

Sample	T_{g1} (K)	T_{g2} (K)	T_m (K)	$T_{n\text{-}i}$ (K)	$\Delta H_{n\text{-}i}$ (J/g)
4	279	-	400	414	9.6
1a	280	344	407[c)]	407[c)]	9.3[c)]
1b	282	346	401	413	2.9
1c	283	349	403	413	1.8
7a	-	355	-	-	-
7b	-	359	-	-	-
7c	-	365	-	-	-

[a)] By DMA, at 1 Hz and 4 $Kmin^{-1}$ scanning rate. [b)] By DSC, at 10 $Kmin^{-1}$ scanning rate. Melting (m) and nematic-isotropic (n-i) transitions. [c)] Single broad peak for melting and isotropization.

methanol and by fractionation with boiling cyclohexane to extract the polystyrene homopolymer. The structure of the copolymers was established by ^1H NMR and ^{13}C NMR spectroscopy. The content of the main-chain block, as evaluated by ^1H NMR, ranged from 16 to 39% (Table I).

The weight average molar mass (Mw) and the first polydispersity index (Mw/Mn) of the macroinitiator, as evaluated by SEC resulted 4500 and 1.61, respectively. The values ranged from 21000 to 110500 and from 1.5 to 2.2 respectively. To gain more information about the polystyrene block, copolymers **1a-c** were subjected to complete alkaline cleavage. The residual polystyrene homopolymers, taken as molecular analogues to the polystyrene blocks present in the respective copolymers, were analyzed by SEC. Mw values ranging from 17500 (**7a**) to 69500 (**7c**) with relatively narrow molar mass 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 above reported copolymer structure is a simplified one. The actual copolymer product should be more appropriately represented by a blend of ABA triblock and (AB)n multiblock type macromolecular species.

Thermal and dynamic-mechanical properties

The glass transition behavior of block copolymers **1**, polyester **4** and polystyrenes **7** was studied by DMA in the linear viscoelasticity range (Table II). Figures 1 and 2 show the trends of the dynamic storage modulus (G') and loss tangent (tan δ) respectively at 1 Hz as a function of temperature for block copolymers **1a-c** together with the one of

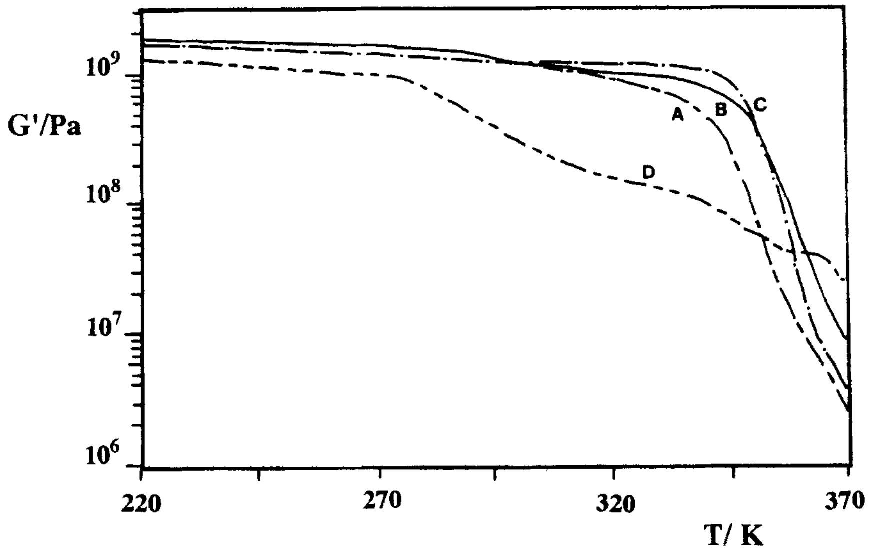


FIGURE 1. Plots of dynamic storage modulus (G') versus temperature for block copolymers **1a** (A), **1b** (B), **1c**, (C) and polyester **4** (D) at 1 Hz.

polyester **4** taken as a model for the main-chain block in the block copolymers. G' of all samples was about 2 10^9 Pa at 230 K and decreased steadily with increasing temperature. Two main dispersion phenomena occurred at about 300 and 380 K. Comparison of the DMA curves of copolymers **1a-c** with the one of polyester **4** clearly reveals that the

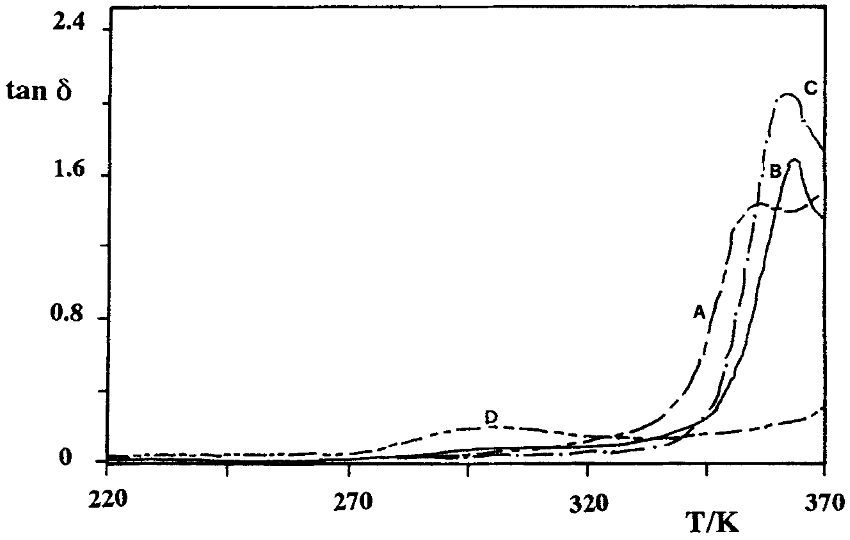


FIGURE 2. Plots of loss tangent (tan δ) versus temperature for block copolymers **1a** (A), **1b** (B), **1c**, (C) and polyester **4** (D) at 1 Hz.

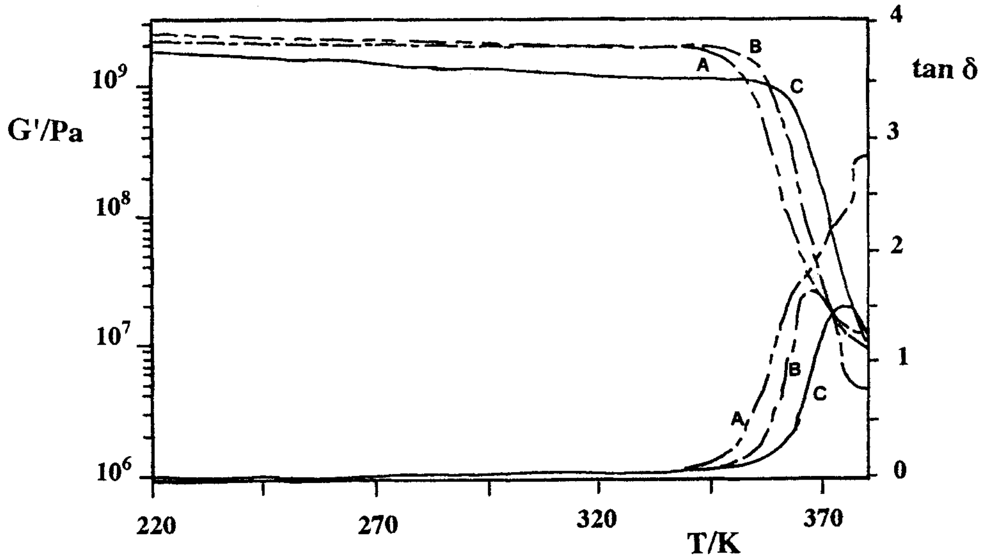


FIGURE 3. Plots of dynamic storage modulus (G') and loss tangent (tan δ) versus temperature for polystyrene samples **7a** (A), **7b** (B) and **7c**, (C) at 1 Hz.

above dispersion phenomena are correlated to the complex loss behavior at the glass transitions of the polyester and polystyrene blocks respectively. The glass transition temperature of the polyester block (Tg1) was practically constant, whereas the glass transition temperature of the polystyrene block (Tg2) regularly increased from 344 to 349 K on going from **1a** to **1c**. The occurrence of two distinct glass transition regions undoubtedly indicates a phase separation between the two blocks even in the amorphous state.

Figure 3 illustrates the trends of G' and tan δ at 1 Hz as a function of temperature for the polystyrene samples **7a-c**. In these samples, the glass transition process is located in the 355-365 K region, that is well above the glass transition region of the polystyrene blocks in the corresponding block copolymers. The glass transition temperature increases from **7a** to **7c**. The trend of the glass transition temperature for the polystyrene block in the block copolymers and the polystyrene homopolymers as a function of the relevant molar mass values is illustrated in Figure 4. The increase in the glass transition temperature is clearly related to the parallel increase of the polystyrene molar mass, as previously observed[7-8] for another class of structurally related block copolymers. However, the increase in the glass transition temperature as the molar mass increases is more marked for polystyrene homopolymers **7a-c** than for the corresponding polystyrene blocks in the copolymers **1a-c**. In addition, the glass transition temperatures of the polystyrene blocks are definitely lower than the ones of the corresponding polystyrene homopolymers. The decrease of the glass transition temperature of the polystyrene

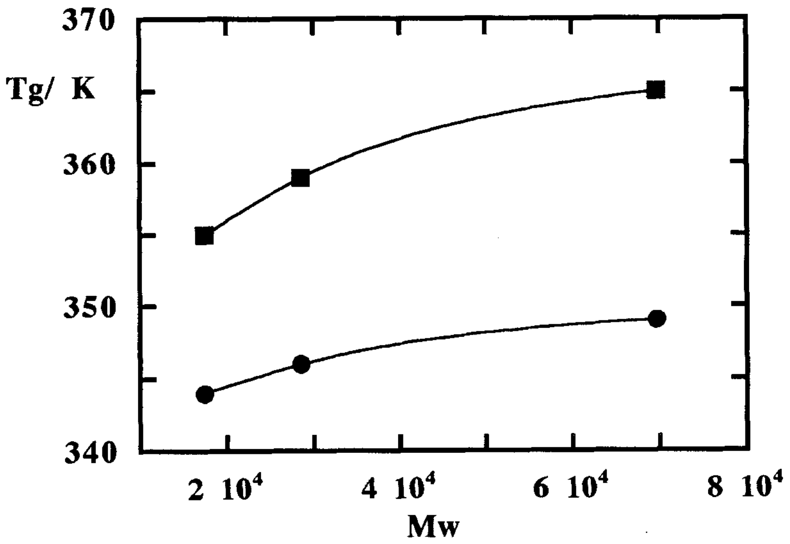


FIGURE 4. Trends of the glass transition temperatures of the polystyrene block in block copolymers **1** (●) and of the polystyrene homopolymers **7** (■) as a function of the weight average molar mass.

component with decreasing concentration of its blocks was reported in a variety of systems[9] and explained either by considering that the properties of the finely dispersed microphase are not the same as those of the polymer in bulk, or by supposing partial mixing of segregated phases. The presence of an intermediate peak, or a pronounced low temperature shoulder, below that corresponding to the polystyrene block glass transition was sometimes observed and attributed to glass transition relaxation of the intermixed phase. Indeed, such a shoulder has been revealed also in the present block copolymer systems. This observation, coupled to the different molar mass dependence of the glass transition temperature of the polystyrene homopolymers and the polystyrene blocks, are likely to indicate the existence of a partial miscibility between the polyester and the polystyrene blocks.

The LC behavior of block copolymers was studied by DSC measurements, polarizing microscopy and X-ray diffraction. The transition temperatures and thermodynamic parameters are collected in Table II. The DSC traces of all block copolymers were very similar. The glass transition of the polystyrene block preceded two endothermic transitions, attributed to the melting and nematic- isotropic transition of the polyester block. The phase transition temperatures of both endothermic transitions are constant throughout the whole composition range and very similar to those of the relevant homopolymer **4**. The enthalpy change associated to the nematic-isotropic phase transition is directly proportional to the weight of the LC polyester block, and the normalized enthalpies are very similar to those of homopolymer **4**. Therefore, within the reported ranges of composition and molecular weight, the mesophase transition parameters of the polyester block are apparently not influenced by the presence of the polystyrene block.

CONCLUSIONS

A series of block copolymers, consisting of polystyrene and LC polyester blocks prepared from a LC macroradical polyester initiatior was analyzed by combined thermal and dynamic-mechanical techniques. The results so far obtained indicate that the chemically different blocks are partly miscible in the solid state depending on the molar mass value of the polystyrene block. However, the nature of the liquid crystalline mesophase generated by the polyester block and the relevant phase transition characteristics are unaffected with respect to the corresponding homopolymers. The prepared hybrid copolymers can be considered examples of polymeric materials with variable thermoplastic features.

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