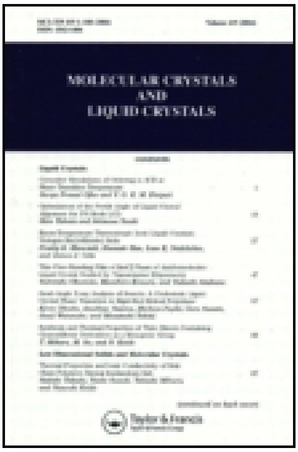

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LC Block Copolymers Containing Side-Chain and Main-Chain Blocks

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LC BLOCK COPOLYMERS CONTAINING SIDE-CHAIN AND MAIN-CHAIN BLOCKS

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Abstract The synthesis and some thermal properties of a new type of block copolymers comprising both main-chain and side-chain liquid-crystalline (LC) blocks in the same macromolecular structure are described. The former block is a semiflexible LC polyester (block A), and the latter is a LC polymethacrylate (block B). The two structurally different blocks were at least partly phase-separated within the glassy and LC states and underwent distinct phase transitions. Significant deviations of the thermodynamic parameters observed relative to those of the corresponding homopolymers suggest the occurrence of a more or less diffuse interphase.

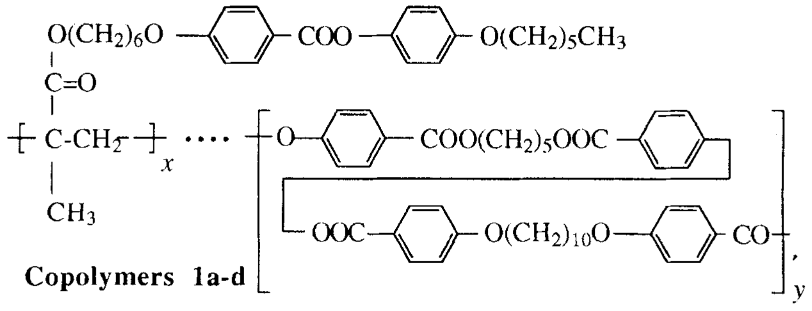
INTRODUCTION

Very recently, great attention has been addressed to the synthesis and physical properties of block copolymers containing LC segments[1]. These new materials can be key factors in assessing specific aspects of polymer physics. In fact, block copolymers with LC segments are ideal models for semicrystalline block copolymers and new opportunities can be envisaged to obtain equilibrium relations between geometrical and topological patterns, such as the dimension and shape of the domain structure, and the macromolecular dimensions and interactions of the different blocks. In addition, these materials can be valuable in elucidating the influence exerted by the boundary conditions and finite domain size on the onset, nature and stability of the LC phases.

From a more applicative point of view, these copolymers can be employed as highly versatile interfacially active additives and viscosity improvers potentially capable of providing enhanced optimization of material performance.

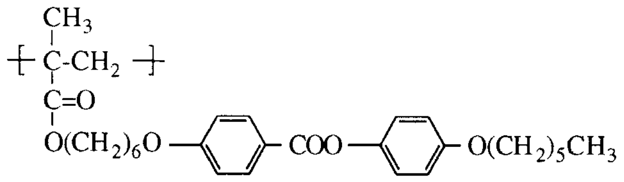
By a synthetic procedure involving the use of azo macroinitiators[2], we have started to prepare and study new block copolymers consisting of semicrystalline/side-chain LC blocks[3], amorphous/main-chain LC blocks[4-6], and very recently the first examples of block copolymers comprising both main-chain and side-chain LC blocks[7]. For the first two copolymer systems, the chemically different blocks appeared mutually immiscible thus producing multidomain structures in which the two blocks were strongly segregated. For the last class of block copolymers, the thermal and dynamic-mechanical data also shows that the two chemically different blocks were partially phase-separated in the glassy and LC phases. However, the glass transition behavior and the substantial deviations of the smectic-nematic and nematic-isotropic phase transition parameters of the main-chain block from those expected from the structurally analogous homopolymer suggested the existence of selective interactions between the main-chain and side-chain blocks.

To gain a better insight into the influence of the macromolecular architecture on the observed behavior, the present work was aimed at investigating the synthesis and properties of a new class of block copolymers **1a-d** comprising both main-chain and side-chain LC blocks, with the following structure:



Copolymers 1a-d

Block copolymers **1a-d** are constituted by a side-chain LC polymethacrylate block, containing a side-chain mesogenic unit, and a main-chain LC polyester block made up by two mesogenic *p*-oxybenzoyl diads alternatively interspaced by aliphatic chains of five and ten methylene groups and connected to the mesogenic cores by two ester and ether linking groups respectively. The side-chain polymethacrylate homopolymer **2**,



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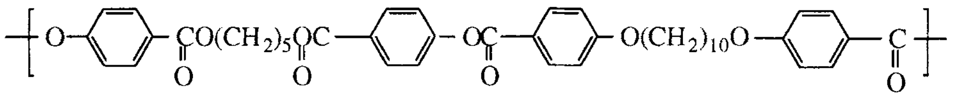
structurally analogous to the side-chain block, exhibited a smectic A mesophase[8]. The main-chain polyester homopolymer C_5C_{10},



C_5C_{10}

structurally analogous to the main-chain block, formed nematic and smectic C mesophases[9,10]. The block copolymers are designated with the general acronym **1a-d**, where **a-d** refer to the different weight amount of the methacrylate monomer in the feed mixture.

EXPERIMENTAL SECTION

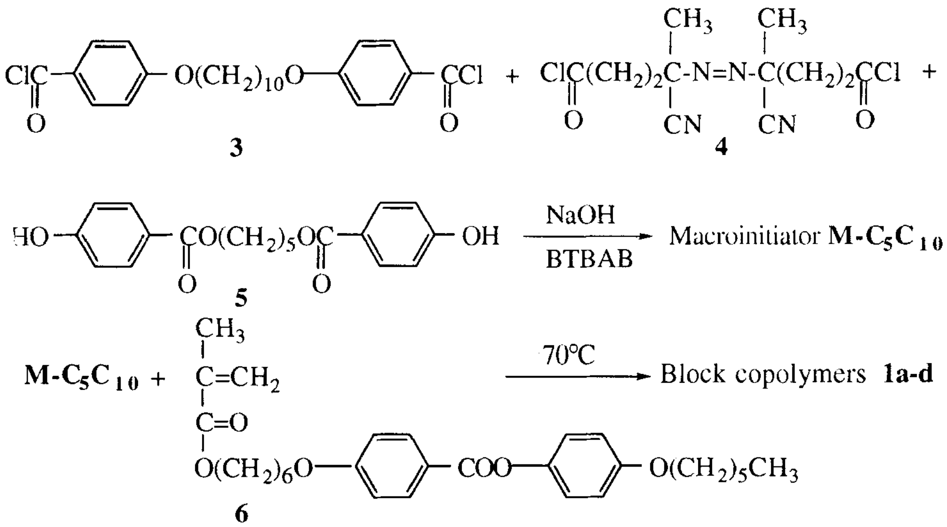
Materials

4-Hexyloxyphenyl 4((6-(methacryloyloxy) hexyl)oxy)benzoate (**6**) was prepared by a literature procedure[8]. 4,4'-decamethylene dioxydibenzoyl chloride (**3**) and pentamethylene di(4-hydroxybenzoate) (**5**) were prepared according to literature[10]. 4,4'-Azobis(4-cyanopentanoyl chloride) (**4**) was prepared from 4,4'-azobis(4-cyanopentanoic acid) following the procedure described in ref. 11. Macroinitiator **M-C_5C_{10}** and block copolymers **1a-d** were prepared according to the synthetic route illustrated in Scheme 1.

Synthesis of the Macroinitiator. 1.70 g (4.10 mmol) of **3** and 0.13 g (0.410 mmol) of **4** were dissolved in 30 ml of chloroform and the solution was transferred into an appropriate flask containing 1.553 g (4.51 mmol) of **5**, 0.36 g (9.5 mmol) of NaOH and 0.2 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_{10}** was purified by repeated precipitations from chloroform solution into methanol and dried 24 h in vacuo at room temperature. Yield 2.4 g (70%).

Synthesis of Block Copolymers. In a typical copolymerization reaction, the required amount of **6** and 0.4 g of the macroinitiator **M-C_5C_{10}** were dissolved in 10 ml of anhydrous THF. The reaction mixture was introduced into a Pyrex glass ampoule, 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 oligomers by extraction with boiling methanol in a Kumagawa extractor. The copolymer was then dried in vacuo for 24 h. The copolymerization yield was in the 60-70% range.

Four copolymer samples were synthesized by the above procedure leaving constant the amount of the macroinitiator (0.4 g) and using different quantities of 4-hexyloxyphenyl 4((6-(methacryloyloxy)hexyl)oxy)benzoate (**6**) in the feed mixture: 0.3 g, **1a**; 0.7 g, **1b**; 1.0 g, **1c**; 2.0 g, **1d**.



SCHEME 1. Synthesis of block copolymers **1a-d**.

Physicochemical Characterization

^1H 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 ^1H NMR spectra. Molar mass characteristics (Mn, Mw/Mn) were determined by size exclusion chromatography (SEC) of chloroform solutions with a 590 Waters chromatograph equipped with a Perkin Elmer UV detector using a 10^4 Å

TABLE I. Reaction conditions, molar mass and composition data of macroinitiator **M-C_5C_{10}**, polyester **C_5C_{10}**, and block copolymers **1a-d**

Sample	[**6**][a] (g)	**C_5C_{10}**[b] (wt.-%)	Mn[c]	Mw/Mn[c]
M-C_5C_{10}	-	100	11500	2.3
C_5C_{10}	-	100	4800	1.9
1a	0.3	72	28000	2.4
1b	0.7	47	36100	2.2
1c	1.0	28	34400	2.7
1d	2.0	19	50000	3.0

[a]Weight of methacrylate **6** in the feed mixture at a constant weight (0.4 g) of **M-C_5C_{10}**. [b]Polyester block **C_5C_{10}**, by ^{1}H NMR. [c]By SEC, in chloroform at 25°C.

Polymer Laboratories column. While Mn and Mw/Mn of copolymers were evaluated relative to polystyrene standard samples, they were determined by the universal calibration method using polystyrene standard samples for macroinitiator **M-C_5C_{10}** and polyester **C_5C_{10}**.

Differential scanning calorimetry (DSC) analyses were carried out under dry nitrogen flow with a Perkin-Elmer DSC 7 apparatus. The transition temperatures of the samples were taken from the DSC traces on cooling from the isotropic melt, as corresponding to the minimum of the enthalpic peaks at a cooling rate of 10 K min^{-1}. X-ray diffraction photographs were taken on a Rigaku-Denky RV300 rotating anod generator equipped with a pin hole flat camera. Ni-filtered CuK$_\alpha$ radiation was used.

RESULTS AND DISCUSSION

Synthesis

Block copolymers **1a-d** were synthesized via two sequential polycondensation and free-radical polymerization processes as illustrated in Scheme 1. The macroinitiator polyester **M-C_5C_{10}** was prepared by reacting equimolar amounts of the sodium salt of pentamethylene di(4-hydroxybenzoate) (**5**) and the mixture of the diacid chlorides of 4,4'-azobis(4-cyanopentanoic acid) (**4**) and 4,4'-decamethylene dioxydibenzoic acid (**3**) in the presence of a catalytic amount of a phase transfer agent (BTBAB). A 10 mol-% of **4**, with respect to the total diacid chloride content, was used in the feed mixture. Subsequently, the macroinitiator **M-C_5C_{10}** was used as free-radical source to initiate the polymerization of methacrylate **6** through the thermal decomposition of the azo group at 70°C. Four block copolymers **1a-d** were prepared using different weight concentrations of methacrylate in the feed mixture (Table I). The resulting polymeric products were purified by repeated precipitations from chloroform solution into methanol and by extraction with boiling methanol to eliminate unreacted monomers. The structure of the copolymers was established by ^{1}H NMR and ^{13}C NMR spectroscopy. The content of the main-chain block, as evaluated by ^{1}H NMR, ranged from 19 to 72 wt. % (Table I).

In addition, a sample of **M-C_5C_{10}** was thermally decomposed at 70°C in the presence of a large amount of 2,6-di-*tert*-butyl-4-methylphenol, as a radical scavenger, to avoid or at least reduce the free radical recombination reaction. The resulting polyester **C_5C_{10}** was also studied as a model of the main-chain block in copolymers **1a-d**. The molecular characteristics of the polymers and copolymers were studied by SEC. Mn= 11500 and Mw/Mn= 2.3 for **M-C_5C_{10}**, while Mn= 4800 and Mw/Mn =1.9 for **C_5C_{10}** were found using the universal calibration method (Table I). We estimate that macroinitiator **M-C_5C_{10}** contained on average one reactive azo group per polymer. Mn in the 28000 to 50000 range and Mw/Mn comprised between 2.2 and 3.0 were evaluated for block copolymers **1a-d**, by SEC using the polystyrene calibration curve (Table I). Therefore, the molecular characteristics of the polymethacrylate block could be varied in a broad range by appropriately choosing the relative methacrylate monomer content.

It is well established that the free-radical polymerization of methacrylate monomers terminates[12] by a disproportionation process which, in the present polymerization system with a macroinitiator containing one reactive azo group, resulted in the formation of AB diblock copolymers. However, any incidence of termination by a combination mechanism and the presence of more than one azo group in the polymer chain of the macroinitiator **M-C_5C_{10}** would yield triblock and multiblock copolymer structures.

Thermal Behavior

The LC behavior of block copolymers **1a-d** was studied by DSC measurements, polarizing microscopy and X-ray diffraction. Their phase transition temperatures and enthalpies are collected in Table II, along with those of polyester **C_5C_{10}** and polymethacrylate **2** for comparison. Polymethacrylate **2** was amorphous and formed a smectic A mesophase. Polyester **C_5C_{10}** was also amorphous and exhibited smectic C and nematic mesophases.

TABLE II. Liquid-crystalline properties of polyester C_5C_{10} and block copolymers **1a-d**.

Sample	polymethacrylate block $T_{I\text{-}Sa}$[a] (K)	$\Delta H_{I\text{-}Sa}$[a,b] (Jg^{-1})	$T_{N\text{-}Sc}$[a] (K)	polyester block $T_{I\text{-}N}$[a] (K)	$\Delta H_{N\text{-}Sc}$[a,b] (Jg^{-1})	$\Delta H_{I\text{-}N}$[a,b] (Jg^{-1})
C_5C_{10}	-	-	411	430	4.7	2.9
1a	380	9.8	408	426	3.2	1.8
1b	385	15.3	409	428	3.2	1.7
1c	385	13.6	410	427	3.3	1.2
1d	386	15.3	410	426	2.7	0.9
2	388	15.5	-	-	-	-

[a] By DSC, at 10 Kmin^{-1} scanning rate. [b] Normalized phase transition enthalpies.

The DSC traces of all block copolymers are illustrated in Figure 1 along with those of polyester C_5C_{10} and polymethacrylate **2**. On account of the better resolution of the transition peaks, the thermal behavior of the block copolymers was delineated considering only the DSC cooling curves. In the DSC cooling curve of polyester C_5C_{10} (Fig. 1A), two exothermic peaks at 430 and 411 K corresponded to the isotropic-nematic and nematic-smectic C transitions, respectively. Polymethacrylate **2** showed one exothermic peak at 388 K (Fig. 1F) due to the isotropic-smectic A transition. The DSC cooling curves (Figure 1B-E) of block copolymer **1a-d** showed three exothermic transitions. Comparison of these curves with the ones of macroinitiator C_5C_{10} and polymethacrylate **2** suggests that the two higher temperature exotherms are associated to the isotropic-nematic and nematic-smectic C transitions of the main-chain block, whereas the low temperature exotherm is associated to the isotropic-smectic A transition of the side-chain block. The above attribution is further substantiated by X-ray diffraction analysis. As a typical example, Figure 2 reports the X-ray powder patterns of **1a** at different temperatures, after annealing by cooling from the isotropic melt. At room temperature, the X-ray diagram (Figure 2C) consists of two rather broad small angle reflections, that correspond to periodicities (d) of 27 and 20 Å, and a wide angle signal at D= 4.6 Å. Very similar spectra were recorded for samples **1b**, **1c** and **1d**. The former periodicity at small angles corresponds exactly to the periodicity of the smectic A mesophase of polymethacrylate **2**, and the latter to that of the smectic C mesophase of polyester C_5C_{10}. Therefore, the main-chain and the side-chain blocks were phase-separated and gave rise to two coexisting smectic mesophases (C and A) with different layer periodicities.

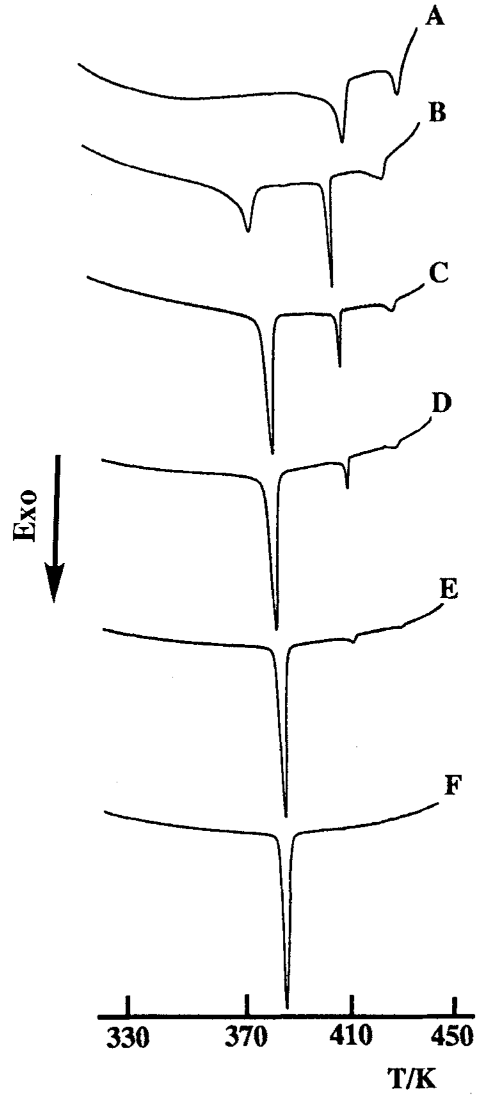


FIGURE 1. DSC cooling curves of homopolymers C_5C_{10} (A), **2** (F) and block copolymers **1a** (B), **1b** (C), **1c** (D) and **1d** (E).

On heating (Figure 2B), the two small angle reflections sharpen thus indicating a longer correlation of the smectic layers. The small angle peak corresponding to d=27 Å disappeared above 370 K at the smectic A-isotropic transition of the side-chain block, corresponding to the temperature relevant to the lower temperature DSC transition. The spectrum was then constituted (Figure 2A) only by one peak and a diffuse wide angle halo, consistent with the presence of the smectic C mesophase of the main-chain block.

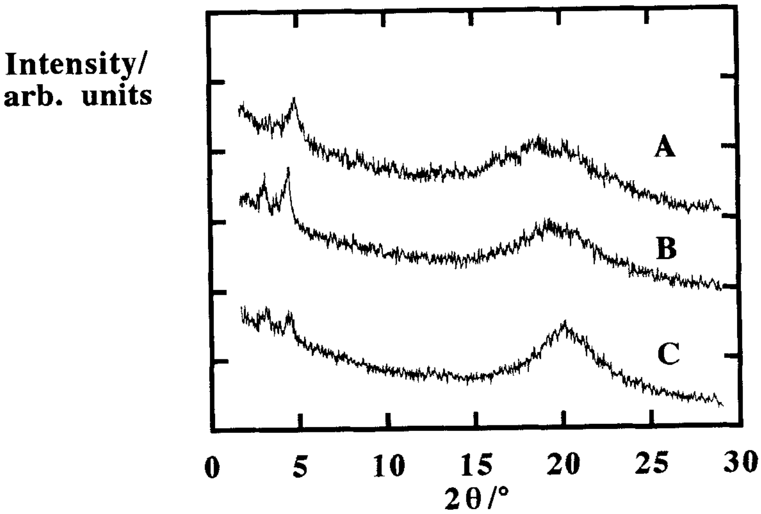


FIGURE 2. X-ray diffraction diagrams for block copolymer **1a** at 300 (C), 340 (B) and 380 K (A).

At approximately 400 K, the small angle peak corresponding to d= 20 Å disappeared thus indicating the transition to the nematic mesophase of the main-chain block.

Figure 3 illustrates the trends of the nematic-smectic C and isotropic-nematic transition temperatures ($T_{N\text{-}Sc}$ and $T_{I\text{-}N}$) of the polyester block, as well as of the isotropic-smectic A transition temperature ($T_{I\text{-}Sa}$) relevant to the polymethacrylate block as a function of the polyester block content in the relevant copolymers **1a-d**. The phase transition temperatures of the main-chain block are quite constant whereas the phase transition temperature of the side-chain block sligtly decreases as the main-chain block content increases. This decrease is probably connected to the decrease of the side-chain block length.

The trends of the normalized transition enthalpies of block copolymers **1a-d** as a function of the polyester block content are shown in Figure 4. The isotropic-smectic A transition enthalpy ($\Delta H_{I\text{-}Sa}$) of the side-chain block decreases with increasing amount of the LC polyester block, whereas the enthalpy changes associated to the isotropic-nematic and nematic-smectic C transitions ($\Delta H_{I\text{-}N}$ and $\Delta H_{N\text{-}Sc}$) of the main-chain block increase regularly. These results indicate the existence of a certain degree of miscibility between the two chemically different blocks. In previous papers[2-6], we have shown that in various LC block copolymer systems containing LC and non-LC blocks neither the temperature nor the enthalpy of different mesophase transitions

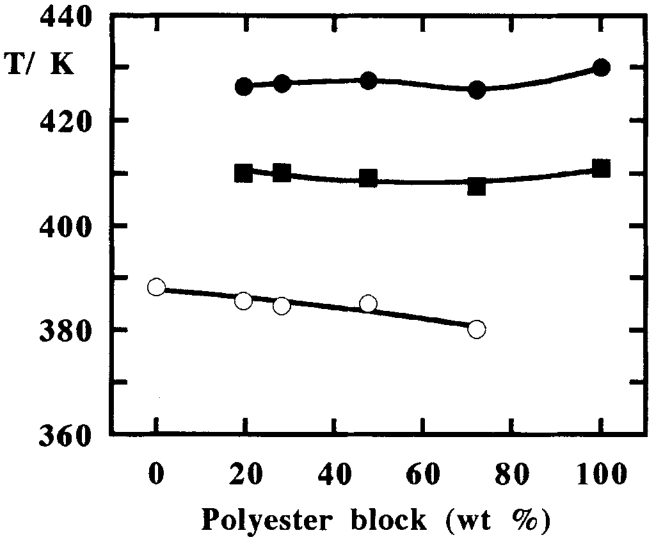


FIGURE 3. Trends of the isotropic-nematic (●) and nematic-smectic C (■) transition temperatures of the polyester block and of the isotropic-smectic A (○) transition temperature of the polymethacrylate block of block copolymers **1a-d**.

were affected to any appreciable extent by block copolymer composition in agreement with the mainly incompatible nature of the two blocks that underwent their individual phase behavior practically independent of each other. In contrast, in block copolymers comprising both main-chain and side-chain LC blocks the thermal, dynamic-mechanical, and X-ray diffraction data indicated[7] that the two structurally different blocks were at least partly phase-separated within the glassy and LC states. This was reflected in significant deviations of the thermodynamic parameters relative to those of the corresponding homopolymers especially as far as the main-chain block was concerned. In fact, the nematic-isotropic phase transition temperature of the main-chain block was definitely lower than that of the relevant homopolymer. Moreover, the smectic C-nematic and nematic-isotropic transition enthalpies of the main-chain block were substantially lower than those expected on the basis of the chemical composition. The partial compatibility of the two chemically different blocks observed in the present main-chain/side-chain block copolymers matches the behavior detected in the previously investigated copolymer system[7]. However, in the present block copolymer system, a sligthly pronounced stability decrease of the smectic C and nematic mesophases of the main-chain block is observed contrary to the stability increase detected for the previous series[7].

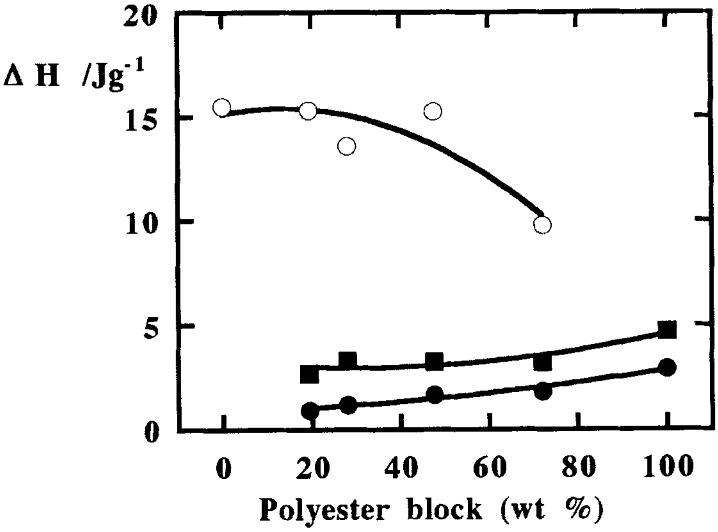


FIGURE 4. Trends of the normalized isotropic-nematic (●) and nematic-smectic C (■) transition enthalpies of the polyester block and of the isotropic-smectic A (○) transition enthalpy of the polymethacrylate block of block copolymers **1a-d**.

CONCLUSIONS

We have synthesized and studied a series of new block copolymers comprising both main-chain and side-chain LC blocks within the same polymer structure. Thermal data show that the two chemically different blocks are partly phase-separated and undergo distinct transitions, which could also be monitored by X-ray diffraction measurements. However, significant deviations of the phase transition parameters of both blocks from those expected from the structurally analogous homopolymers suggest the existence of a substantial interphasic region between the main-chain and side-chain blocks.

In contrast to the behavior observed for other main-chain/side-chain block copolymers[7] in which an increase in the stability of the LC phase generated by the main-chain block was detected, in the present block copolymer system the stability of the LC phases of both the main-chain and side-chain blocks is lower than the one of the corresponding homopolymers. Accordingly, no general statements can be made so far on the role of the block length and block length distribution or on the nature and stability of the relevant LC phases in determining the compatibility and phaseseparation propensity of the chemically different blocks within the glassy and LC phases and their influence on the onset and stability of the relevant mesophases.

ACKNOWLEDGMENT

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