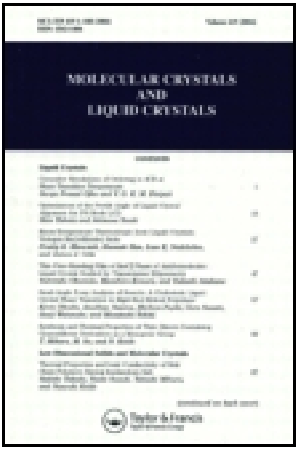

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Mesophase Behavior of Polyester-Polymethacrylate Liquid Crystal Block Copolymers

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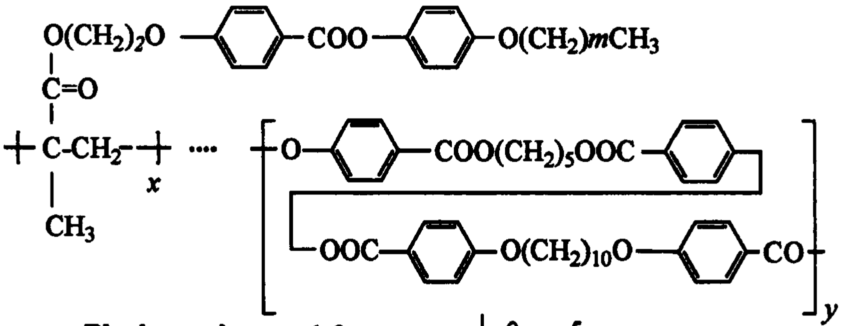
The synthesis and properties of two series of main chain and side chain LC block copolymers constituted by a side chain LC polymethacrylate block and a main chain LC polyester block were described. The two chemically different blocks are phase segregated. The trend of the thermodynamic phase transition parameters suggests that the smectic phase of the side chain blocks provides less favourable boundary conditions than the isotropic phase of the side chain blocks and decreases the stability of both the nematic and smectic mesophases of the main chain block.

Keywords: Polyester-polymethacrylate; liquid crystals; block copolymers

INTRODUCTION

In recent work [1–5], we have synthesized and studied several series of block copolymers comprising both main chain and side chain LC blocks within the same polymer structure. In general, thermal and dynamic-mechanical data showed that the two chemically different blocks are at least partly phase-separated in the glassy and LC phases. However, the significant deviations of the phase transition parameters of both blocks from those expected from the structurally analogous homopolymers indicate the existence of partial miscibility between the main chain and side chain blocks thus possibly producing an interphasic region. Moreover, when the main chain and side chain blocks gave rise to two coexisting smectic domains (A and C) with different layer periodicities, the relative orientations of the chains and the smectic planes differed in the various samples. The orientation of the smectic domains was correlated to the length [4] of the main chain and side chain blocks. For short side chain blocks, the smectic planes of the side chain block were forced to orient parallel to those of the main chain. In contrast, when the side chain block was sufficiently long it imposed its own orientation characteristics on the main chain block. In this case, the smectic planes of the main chain block were parallel to those of the side chain block. For intermediate chain lengths, both the chemically different blocks can impose their own orientation characteristics. Accordingly, the smectic planes of the side chain and main chain blocks are perpendicular to each other and perpendicular and parallel respectively to the fiber axis.

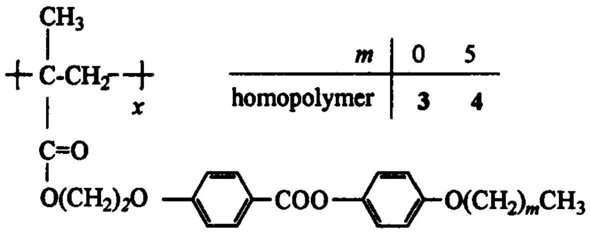
To further elucidate the influence exerted by the macromolecular architecture on the peculiar phase transition behavior of this class of block copolymers, in the present contribution we report on the synthesis and properties of two series of main chain and side chain LC block copolymers **1** and **2**, with the following general structure:



Block copolymers 1-2

m	0	5
series	**1**	**2**

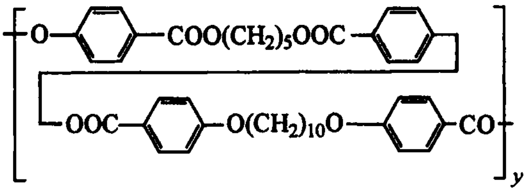
These block copolymers are constituted by a side chain LC polymethacrylate block and a main chain LC polyester block made up by two mesogenic *p*-oxybenzoyl diads alternatively interspaced by aliphatic chains of five and ten methylene groups connected to the mesogenic cores by two ester and ether linking groups, respectively. The side chain polymethacrylate homopolymers [6] **3** and **4**, structurally analogous to the side chain block, exhibited a nematic mesophase (**3**) and a smectic A mesophase (**4**). The



m	0	5
homopolymer	**3**	**4**

Polymethacrylates 3 and 4

main chain polyester homopolymer [7, 8] C_5C_{10}, structurally analogous to the main chain block, formed nematic and smectic C mesophases. Within each series, the block copolymers are designated with a letter from **a** to **d** referring to the different amount of the methacrylate monomer in the feed mixture.



C_5C_{10}

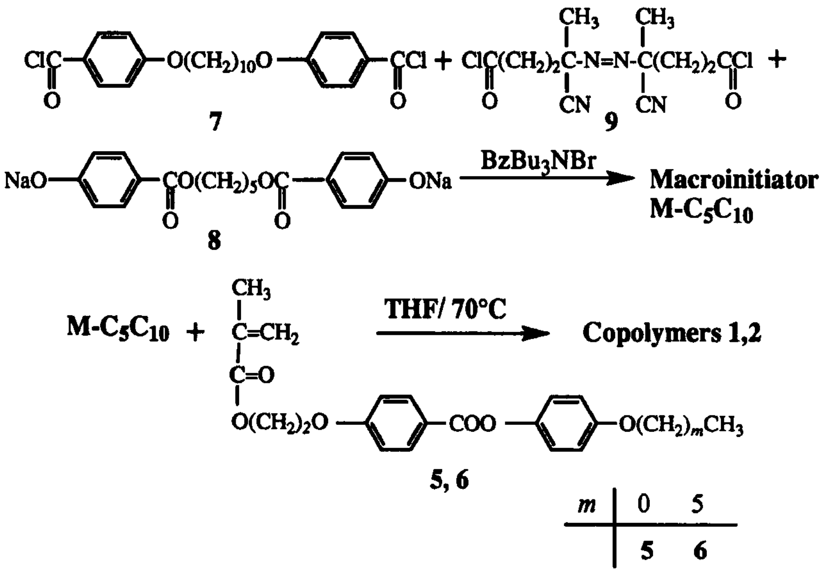
EXPERIMENTAL PART

Materials

Methacrylate monomers **5** and **6**, 4,4′-decamethylene dioxydibenzoic acid chloride (**7**) and pentamethylene di(4-hydroxybenzoate) (**8**) were prepared according to literature [6–7]. 4,4′-Azobis(4-cyanopentanoyl chloride) (**9**) was prepared from 4,4′-azobis(4-cyanopentanoic acid) following the procedure described in ref. 1.

Macroinitiator **M-C_5C_{10}** and block copolymers **1–2** were prepared [3] according to the synthetic route illustrated in Scheme 1.

Four copolymer samples for each methacrylate monomer were synthesized by keeping constant the amount of the macroinitiator (0.4 g) and using different quantities of the methacrylate in the feed mixture. According to the different quantities of the methacrylate, the block copolymers were identified by the letters **a**, **b**, **c** and **d** to which methacrylate quantities of 0.3, 0.7, 1.0 and 2.0 g correspond.



Scheme 1

Physicochemical Characterization

^{1}H NMR and ^{13}C NMR spectra were recorded with a Varian Gemini 200 spectrometer. The composition of the copolymers was determined from the ^{1}H NMR spectra. Molar mass characteristics 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 Polymer Laboratories column. Differential scanning calorimetry (DSC) analyses were carried out under dry nitrogen flow with a Perkin-Elmer DSC 7 apparatus. X-ray diffraction photographs were taken on a Rigaku-Denki RU300 rotating anod generator equipped with a pin hole flat camera. Ni-filtered CuK$_\alpha$ radiation was used.

RESULTS AND DISCUSSION

Synthesis

The synthesis of block copolymers **1–2** is very similar to the one previously described [3] and is schematically illustrated in Scheme 1. It involves first the preparation of the macroinitiator M-C$_5$C$_{10}$, possessing reactive azo groups in the main chain, by a polycondensation reaction between equimolar amounts of the sodium salt of the pentamethylene di(4-hydroxybenzoate) and the 4, 4′-azobis(4-cyanopentanoyl chloride) and 4, 4′-decamethylene dioxydibenzoic acid chloride in the presence of a catalytic amount of benzyl tributylammonium bromide, and then the thermal decomposition of the azo groups of the macroinitiator **M-C_5C_{10}** at 70°C to initiate the free-radical polymerization of methacrylates **5–6**, leading to the two block copolymer series **1–2**. Each series consisting of four samples were prepared from the same macroinitiator by using different amounts of the relevant methacrylate in the feed mixture.

The content of the main chain block, as evaluated by ^1H NMR, ranged from 28 to 78 wt.%. The number average molar mass (Mn) and the first polydispersity index (Mw/Mn) were determined by size exclusion chromatography (Tab. I). Mn and Mw/Mn result respectively 55000 and 2.7 for the macroinitiator **M-C_5C_{10}**.

For the block copolymers **1** and **2**, within each series, the number average molar mass increases as the concentration of methacrylate monomer increases. These results are qualitatively similar to those previously reported [3] for analogous series of block copolymers containing liquid crystalline blocks.

Liquid Crystalline Behavior

The phase transition temperatures and relevant thermodynamic parameters of the block copolymer series **1** and **2** are collected in Tables II and III.

TABLE I Composition and molar mass data of macroinitiator **M-C_5C_{10}**, polyester C_5C_{10}, and block copolymers **1–2**

Sample	*5 or 6*[a] *(g)*	*C_5C_{10}*[b] *(wt.-%)*	*M_n*[c]	*M_w/M_n*[c]
M-C_5C_{10}	–	100	55000	2.7
C_5C_{10}	–	100	12000	2.5
1a	0.3	65	19800	3.3
1b	0.7	43	19800	3.3
1c	1.0	37	24400	2.8
1d	2.0	28	20300	2.7
2a	0.3	78	20300	2.7
2b	0.7	60	26900	2.6
2c	1.0	51	36700	2.3
2d	2.0	40	38000	2.9

[a]Weight of methacrylates **5** or **6** in the feed mixture. [b]Content of polyester block C_5C_{10}, by ^1H NMR. [c]By SEC, in chloroform at 25°C.

TABLE II Liquid-crystalline properties[a] of polyester C_5C_{10}, block copolymers **1a–d** and polymethacrylate **3**

Sample	*Side Chain Block*		*Main Chain Block*			
	T_{I-N} *(K)*	ΔH_{I-N} *(Jg^{-1})*	T_{I-N} *(K)*	T_{N-Sc} *(K)*	ΔH_{I-N} *(Jg^{-1})*	ΔH_{N-Sc} *(Jg^{-1})*
C_5C_{10}	–	–	430	411	2.9	4.7
1a	391	1.3	427	409	2.3	3.5
1b	392	1.4	427	409	2.4	3.2
1c	393	1.5	426	409	2.1	3.7
1d	395	1.7	426	409	2.4	4.0
3	395	2.3	–	–	–	–

[a] By DSC, at $-10\,\mathrm{Kmin^{-1}}$ scanning rate.

TABLE III Liquid-crystalline properties[a] of polyester C_5C_{10}, block copolymers **2a–d** and polymethacrylate **4**

Sample	*Side Chain Block*		*Main Chain Block*			
	T_{I-S} *(K)*	ΔH_{I-S} *(Jg^{-1})*	T_{I-N} *(K)*	T_{N-Sc} *(K)*	ΔH_{I-N} *(Jg^{-1})*	ΔH_{N-Sc} *(Jg^{-1})*
C_5C_{10}	–	–	430	411	2.9	4.7
2a	444	6.4	421	402	2.2	2.6
2b	451	17.0	420	402	1.3	1.8
2c	452	17.7	419	400	1.6	1.9
2d	454	18.3	417	400	0.9	1.4
4	456	18.0	–	–	–	–

[a] By DSC, at $-10\,\mathrm{Kmin^{-1}}$ scanning rate.

Polymethacrylates **3–4** were amorphous and formed a nematic mesophase (**3**) and a smectic A mesophase (**4**). Polyester C_5C_{10} was also amorphous and exhibited smectic C (Sc) and nematic mesophases.

Figure 1 illustrates the DSC cooling curves of the samples of series **1** as a typical example. Three exothermic transitions occur for all the block copolymers **1a–d**. In each curve, the peak at the lowest temperature corresponds to the isotropic-nematic transition of polymethacrylate block, while the other two peaks at 409 and 427 K are characteristic of nematic-smectic C and isotropic-nematic transitions of the polyester block respectively. This clearly shows that the two blocks are microphase separated. An analogous behavior was detected for copolymers **2a–d**, but in that case the isotropic-smectic transition of the side chain block occurred at much higher temperature ($\approx$450 K) than both the isotropic-nematic ($\approx$420 K) and nematic-smectic ($\approx$400 K) transitions of the main chain block. The above

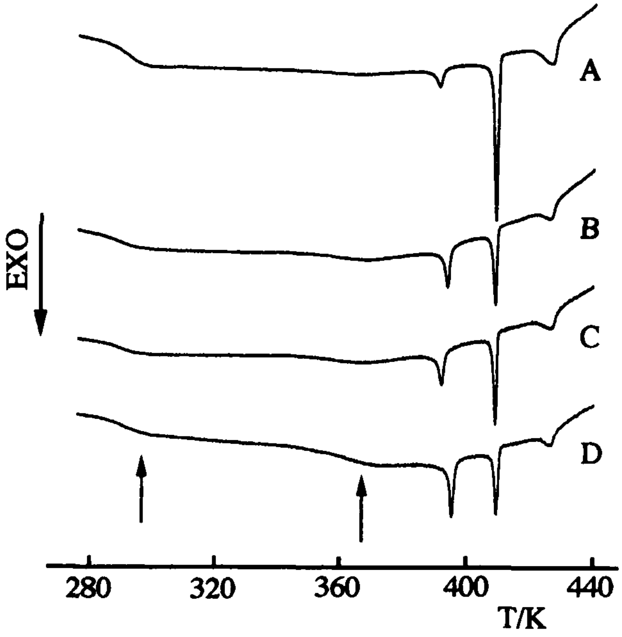


FIGURE 1 DSC second cooling curves (10 Kmin^{-1}) for block copolymer series 1: **1a** (A); **1b** (B); **1c** (C) and **1d** (D). Arrows indicate the glass transition regions.

attribution is confirmed by X-ray diffraction analysis on oriented mesophases produced by drawing fibers at temperatures in the range where the smectic C mesophase of the polyester block coexisted with either the isotropic phase or the smectic A mesophase of the polymethacrylate block, and cooling them in air at room temperature. As an example Figure 2A shows the X-ray diffraction pattern of the fiber sample of copolymer **2c**. To better visualize the features of this pattern, the contours at constant intensity in the small-angle region are reported in Figure 2B. The anisotropy of the pattern clearly shows that a high degree of molecular orientation can be achieved by drawing fibers from the mesophase. Two pairs of sharp reflections located at right angles to each other are clearly visible in the small-angle region of the spectrum, which correspond to periodicities (d_1 and d_2) of 20.0 and 25.0 Å, respectively. The former periodicity is equal to the layer spacing of the smectic C mesophase of the polyester $\mathbf{C_5C_{10}}$ whereas the latter is equal to that of the smectic A mesophase of the polymethacrylate **4**. Therefore, the phase-separated polyester and polymethacrylate blocks give rise to two coexisting smectic phases. The reflection corresponding to 25.0 Å

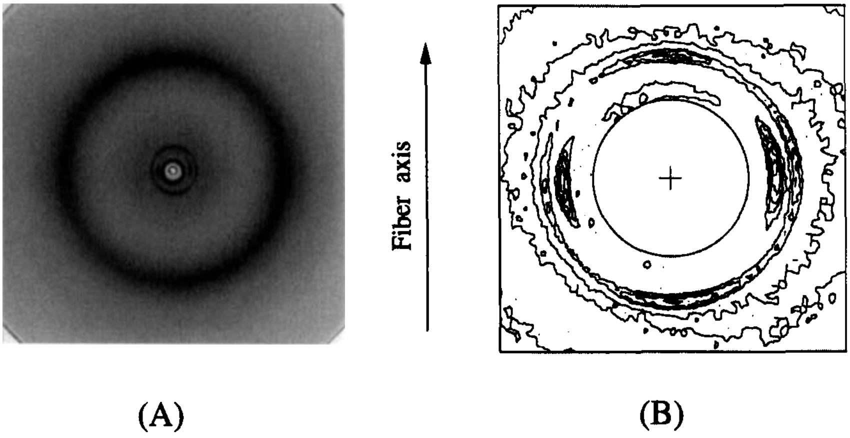


FIGURE 2 (A) Fiber X-ray diffraction pattern of block copolymer **2c**. The sample to film distance is 75 mm. (B) Contours at constant intensity in the small-angle region of the pattern. (See Color Plate VIII).

appears as a sharp peak with maximum localized along the equatorial line while the contribution of the reflection at 20.0 Å is a ring of not uniform intensity distribution where the intensity is mainly distributed along the meridional line. Accordingly, in copolymer **2c** the planes of the smectic domain of the polyester block are oriented normally to the fiber axis whereas the planes of the smectic domain of the polymethacrylate block are parallel to the fiber axis. In the wide-angle region a rather diffuse halo is detected due to the liquid-like arrangement of the mesogens within the smectic (A or C) layers (intermolecular distance $D \approx 4.6$ Å). However, because of the overlapping signals of the two different blocks in this angular region, it is not possible to identify the different contribution of the two smectic mesophases. For the other copolymers **2**, X-ray diffraction analysis showed that the relative orientations of the smectic planes in the distinct domains with respect to the fiber axis were different in samples with different compositions.

In the DSC curve of copolymer **1d** two slightly inflections at about 293 and 373 K are well evident corresponding to the glass transition temperatures (Tg) of the main chain and side chain blocks respectively. The Tg of methacrylate block becomes less evident as the series is ascended on going from sample **1a** (35% of side chain block) to sample **1d** (72% of side chain block) whereas the Tg of the polyester block shows the opposite trend.

The phase transition temperatures, relevant to the liquid crystalline transitions, of both the main chain and the side chain blocks in the two series as functions of the main chain block content are collectively represented in Figure 3.

The transition temperatures of the polymethacrylate blocks are almost constant throughout all the compositional range. The transition temperatures of the main chain block in series **1** are slightly higher than those in series **2**. The environment surrounding the main chain block domains in the former case is constituted by the isotropic phase of the side chain blocks, whereas in the latter case it is constituted by the smectic phase of the side chain block. Therefore the lower transition temperatures observed in series **2** may suggest that the smectic phase of the side chain blocks provides less favourable boundary conditions than the isotropic phase thus decreasing the stability of both the nematic and smectic C mesophases of the main chain block in series **2**. This explanation is also consistent with the trend of the normalized transition enthalpies of the main chain blocks as function of the main chain block content (Fig. 4). The normalized phase transition enthalpies of block copolymer series **1** increase only sligthly as the main chain block content increases. In contrast, a pronounced increase in the nor-

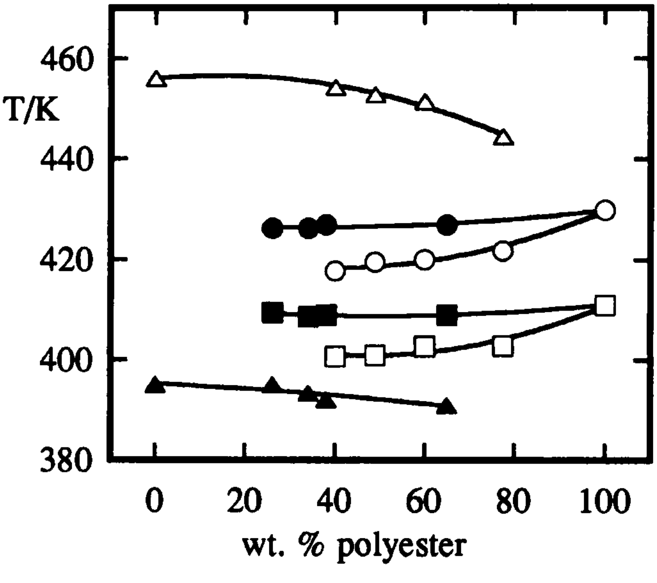


FIGURE 3 Trends of the smectic C-nematic (■, □) and nematic-isotropic (●, ○) transition temperatures of the polyester block of block copolymer series **1** (full symbols) and **2** (open symbols) as well as of the nematic-isotropic (▲) and smectic A-isotropic (△) transition temperatures of the polymethacrylate block of block copolymers **1** and **2** respectively as a function of the wt.% content of polyester block.

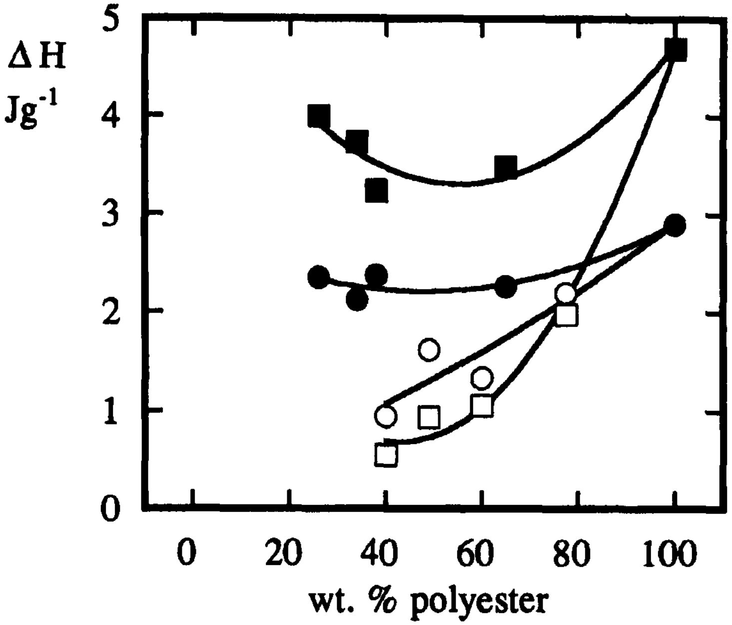


FIGURE 4 Trends of the smectic C-nematic (■, □) and nematic-isotropic (●, ○) normalized transition enthalpies of the polyester block of block copolymer series 1 (full symbols) and 2 (open symbols) as a function of the wt. % content of polyester block.

malized phase transition enthalpies of block copolymer series **2** is observed thus further indicating that the boundary conditions provided by the smectic phase of the side chain decreases the degree of order of the main chain block in series **2**. In addition, the smectic-nematic transition enthalpy of the main chain homopolymer C_5C_{10} as well as the one of the block copolymer series **1** is greater than the normalized nematic-isotropic transition enthalpy of the block copolymer series **2**. This indicates that the presence of the smectic mesophase, generated by the side chain block of series **2**, has a substantial influence on the liquid crystalline mesophases of the main chain block domain.

The normalized enthalpies relevant to the side chain blocks as a function of the main chain block content are reported in Figure 5. ΔH_{N-I} of the polymethacrylate block in series **1** decreased sligthly with increasing content of the polyester block in the copolymers. In contrast, a strong decrease was detected for the enthalpies of the smectic-isotropic transition of the polymethacrylate block in the copolymers **2**. This decrease could indicate [9] a change in the smectic-isotropic transition nature from first to second order with decreasing the size of the side chain domains.

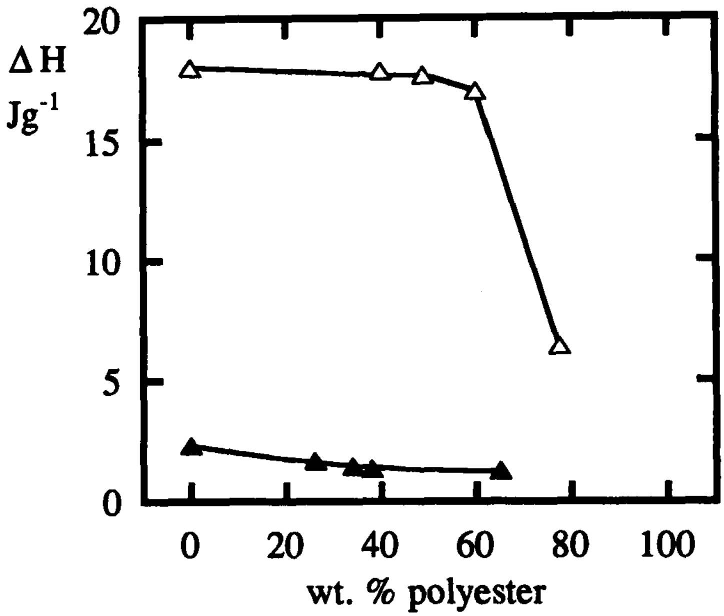


FIGURE 5 Trends of the nematic-isotropic (▲) and smectic A-isotropic (Δ) normalized transition enthalpies of the polymethacrylate block of block copolymer series **1** (full symbols) and **2** (open symbols) as a function of the wt. % content of polyester block.

CONCLUSIONS

The synthesis and properties of two series of main chain and side chain LC block copolymers constituted by a side chain LC polymethacrylate block and a main chain LC polyester block have been studied. Distinct phase transitions corresponding to the chemically different blocks were observed thus clearly indicating that the two blocks are phase segregated. The environment surrounding the main chain block domains at temperatures within the liquid crystalline transitions of this block, in block copolymers **1** is constituted by the isotropic phase of the side chain blocks whereas in block copolymers **2** is constituted by the smectic phase of the side chain block. The lower transition temperatures relevant to the main chain block transitions observed in series **2** coupled with transition enthalpy values lower than expected suggest that the smectic phase of the side chain blocks provides less favourable boundary conditions than the isotropic phase and decreases the stability of both the nematic and smectic C mesophases of the main chain block domain.

Acknowledgment

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