Hybrid Liquid-Crystalline Block Copolymers I. Synthesis and Mesomorphic Behavior of Polyester–Polymethacrylate Block Copolymers

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ABSTRACT: A new type of block copolymers comprising both main-chain and side-chain liquid-crystalline (LC) blocks in the same macromolecular structure was synthesized and studied. The former was a semiflexible LC polyester block, and the latter was an LC polymethacrylate block. Thermal, dynamic-mechanical, and X-ray diffraction data indicated that the two structurally different blocks were partly phase-separated in the glassy and LC states. Significant deviations of the transition temperatures and enthalpies were observed relative to those of the corresponding homopolymers.

KEY WORDS Block Copolymer / Liquid-Crystalline Copolymer / Polyester
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Very recently, great attention has been devoted to the synthesis and physical properties of liquid-crystalline (LC) block copolymers.^{1–12} Interest in these copolymers is basically related to their potential use as highly versatile interfacially active additives and melt-viscosity reducers potentially capable of providing enhanced optimization of materials performance. In addition, from a more fundamental standpoint, due to the equilibrium nature of the LC transitions, these new materials can be helpful in assessing specific aspects of polymer physics. On the one hand, block copolymers with LC segments may be model systems for semicrystalline block copolymers and new opportunities can be envisaged to obtain equilibrium relations between gross geometrical and topological patterns such as the dimension

and shape of the domain structure, including also the relevant interfacial contributions, and the molecular dimensions and interactions of the different blocks. On the other hand, 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.

Different approaches to the preparation of block copolymers containing LC blocks include i) polymer-analog reactions on pre-formed block copolymers with narrow dispersity of block lengths^{1,3}; ii) copolymerization of mesogenic monomers with non-mesogenic monomers by living or quasi-living techniques, such as the ring-opening metathesis,⁵ group-transfer,² anionic,^{4,12} and cationic¹¹ polymerizations; iii) condensation of telechelics

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

bearing functional end groups⁶; and iv) the use of azo macroinitiators.⁷⁻¹⁰

By this last procedure, we have developed new block copolymers consisting of semi-crystalline/side-chain LC blocks,⁷ amorphous/main-chain LC blocks,^{8,9} or a combination of both main-chain and side-chain LC blocks.¹⁰ For the former two copolymer systems, the chemically different blocks appeared mutually immiscible thus producing multidomain structures in which the two blocks were strongly segregated. Even in the latter class of block copolymers, the 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 interactions between the main-chain and side-chain blocks like in a partially compatible system.

To extend the macromolecular architecture of this class of block copolymers and to further elucidate the peculiar role of the block length and block length distribution in determining the compatibility and phase-separation propensities of the chemically different blocks within the glassy and LC phases, this paper illustrates the synthesis and properties of a new class of block copolymers **1a-d** comprising both main-chain and side-chain LC blocks (Figure 1). They were constituted by a main-chain LC polyester block (block A) and a side-chain LC polymethacrylate block (block B). The main-chain polyester homopolymer **2** exhibited nematic and smectic C meso-

phases.^{13,14} The side-chain polymethacrylate homopolymer **3** formed nematic and smectic A mesophases.¹⁵

Therefore, one could anticipate finding enhanced interactions among the LC blocks in copolymers **1a-d** incorporating simultaneously main-chain and side-chain blocks in one single macromolecule. In this paper we report on the synthesis and general mesophase behavior of block copolymers **1a-d**. Their rather unique mesophase structure will be described in a following paper.¹⁶

EXPERIMENTAL

Materials

Decamethylene dioxydibenzoyl chloride¹³ (**4**), 4, 4'-azobis(4-cyanopentanoyl chloride)¹⁷ (**5**), pentamethylene di(4-hydroxybenzoate)¹³ (**6**), and 4-butoxyphenyl 4-(6-(methacryloyloxy)hexyloxy)benzoate¹⁵ (**7**) were prepared according to literature procedures. Macroinitiator **M-C₅C₁₀** and block copolymers **1a-d** were prepared according to the synthetic route illustrated in Scheme 1.

Macroinitiator M-C₅C₁₀: 1.85 g (4.10 mmol) of **4** and 0.13 g (0.410 mmol) of **5** were dissolved in 30 ml of dichloroethane and the solution was

transferred into an appropriate flask containing 1.55 g (4.51 mmol) of **6**, 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-C₅C₁₀** was purified by repeated precipitations from chloroform solution into methanol and dried 24 h *in vacuo* at room temperature. Yield: 64%.

Block Copolymers 1a–d: In a typical copolymerization reaction, the required amount of **7** and 0.4 g of the macroinitiator **M-C₅C₁₀** were dissolved in 10 ml of anhydrous tetrahydrofuran. 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 yield of copolymerization was in the 60–70% range.

Four copolymer samples were synthesized by the above procedure keeping constant the concentration of the macroinitiator and using different amounts of **7** in the feed mixture: 0.3 g, **1a**; 0.7 g, **1b**; 1.0 g, **1c**; 2.0 g, **1d**.

Characterization

¹H NMR and ¹³C NMR spectra were recorded on a Varian Gemini 200 spectrometer. The composition of the copolymers was determined from the relevant ¹H NMR spectra. Average molecular weights were determined by size exclusion chromatography (SEC) of chloroform solutions with a 590 Waters chromatograph equipped with a Perkin Elmer UV detector using a Shodex KF-804 column. Polystyrene standard samples were employed for the SEC calibration. 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. Optical microscopy observations were performed on polymer films between glass slides by means of a Reichert Polyvar microscope equipped with a programmable Mettler FP52 heating stage at a scanning rate of 10 K min⁻¹. Dynamic-mechanical measurements were performed with a dynamic-mechanical analyzer (Perkin Elmer DMTA 7 at a scanning rate of 4 K min⁻¹) at 1 Hz frequency. Samples were compression molded at 400 K for 15 min to form ~1 mm thick sheets, and the three point bending geometry was used. X-ray diffraction measurements on powder samples were performed using the Inel CPS 120 powder diffractometer, equipped with a position sensitive detector covering 120° in the scattering angle 2θ, with an angular resolution of 0.018° in θ. Ge(111) monochromatized Cu-K_α radiation was used. The sample, ~1 mm thick, was placed between two thin Al sheets, fixed to an Al sample holder. Heating was achieved by a hot stage whose temperature was controlled within ±0.1°C by an automatic temperature regulator. X-Ray diffraction patterns were recorded from room temperature up to the isotropization point.

RESULTS AND DISCUSSION

Synthesis

Block copolymers **1a–d** were synthesized via two successive polycondensation and free-radical polymerizations as outlined in Scheme 1. The polyester macroinitiator **M-C₅C₁₀** was prepared by reacting equimolar amounts of the sodium salt of pentamethylene di(4-hydroxybenzoate) (**6**) and a mixture of 4,4'-decamethylene dioxydibenzoyl chloride (**4**) and 4,4'-azobis(4-cyanopentanoyl chloride) (**5**) (10:1 by mol) in the presence of a catalytic amount of a phase transfer agent (BTBAB). Subsequently, the macroinitiator **M-C₅C₁₀** was used as a

Scheme 1. Synthetic route for the preparation of block copolymers **1a–d**.

free-radical source to initiate the polymerization of methacrylate **7** through the thermal decomposition of the azo groups at 70°C. Four block copolymers **1a–d** were prepared using different concentrations of the methacrylate monomer in the feed mixture (Table I). They were purified by repeated precipitations from chloroform solution into methanol and by extraction with boiling methanol to eliminate oligomers and unreacted monomers. The content of the polyester block ranged from 21 to 65 wt% (Table I). In addition, a sample of **M-C₅C₁₀** 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 recombination of the primary macroradicals generated. The resulting polyester **2** was taken as a model of the main-chain block in the copolymers.

The molecular weight characteristics of the polymers and copolymers were studied by SEC. All the SEC curves had a similar shape, but while the curve of **2** was shifted toward higher values along the elution volume scale with respect to that of macroinitiator **M-C₅C₁₀**, those of copolymers **1a–d** were shifted toward

Table I. Composition and molecular weight data of block copolymers **1a–d**, macroinitiator **M-C₅C₁₀** and polyester **2**

Sample	M_n^b	M_w/M_n^b	Polyester block ^a	Polymethacrylate block	M_n^b
			wt%	wt%	
1a	18000	1.7	65	35	14000
1b	21000	1.8	41	59	18000
1c	24000	2.0	33	67	21000
1d	33000	3.4	21	79	30000
M-C₅C₁₀	5400 ^c	2.4 ^c	100	—	—
2	3400 ^c	2.0 ^c	100	—	—

^aContent of polyester block in copolymers, homopolymer, or macroinitiator (by ¹H NMR). ^bBy SEC, with polystyrene calibration, unless indicated otherwise. ^cBy SEC, with universal calibration.

lower values (Figure 2). $M_n=5400$ and $M_w/M_n=2.4$ for **M-C₅C₁₀**, and $M_n=3400$ and $M_w/M_n=2.0$ for **2** were found using the universal calibration method (Table I). An M_n of 3200 was calculated for polyester **2** under the hypotheses that 4,4'-azobis(4-cyanopentanoyl chloride) (**5**) reacted quantitatively in the polycondensation reaction and distributed statistically along the polymer chain.⁹ This

Figure 2. SEC curves of block copolymers **1a** (A), **1b** (B), **1c** (C), **1d** (D), macroinitiator **M-C₅C₁₀** (E), and polyester **2** (F).

value is consistent with the experimental one. Accordingly, we estimate that macroinitiator **M-C₅C₁₀** contained on average one reactive azo group per polymer chain. Values of M_n in the range 18000 to 33000 and M_w/M_n comprised between 1.7 and 3.4 were evaluated for block copolymers by SEC using the polystyrene calibration curve (Table I). The molecular weight of the polyester block was constant (3400) throughout the series, while the molecular weight of the polymethacrylate block increased from 14000 for **1a** to 30000 for **1d**.

It is well established that the free-radical polymerization of methacrylate monomers terminates^{18,19} by a disproportionation mechanism which, in the present polymerization system and from macroinitiator chains containing one reactive azo group, resulted in the formation of polyester (block A)/polymethacrylate (block B) AB diblock copolymers. However, any preference for a combination termination mechanism and the presence of more than one azo group in the polymer chain of the macroinitiator **M-C₅C₁₀** would yield ABA triblock and (AB)_n multiblock copolymer structures.

Dynamic-Mechanical Behavior

The glass and subglass transitions of block copolymers **1a–d** were studied by dynamic-mechanical analysis (DMA) in the linear vis-

Table II. Transition temperatures^a of block copolymers **1a–d**, polyester **2**, and polymethacrylate **3**

Sample	Polyester block (block A)			Polymethacrylate block (block B)		
Type	Block A /wt%	T_g^b /K	T_{S-N}^c /K	T_{N-I}^c /K	T_g^b /K	T_{S-N}^c /K
1a	65	304	397	419	365	nd ^d
1b	41	317	401	421	363	364
1c	33	326	403	423	360	367
1d	21	329	404	424	362	372
2	100	296	411	430	—	—
3	0	—	—	—	366	372

^a g, glassy; S, smectic (A or C); N, nematic; I, isotropic.

^b By DMA, at 1 Hz and 4 K min⁻¹ scanning rate. ^c From the DSC cooling curve, at 10 K min⁻¹ scanning rate. ^d Not detected by DSC.

Figure 3. Trend of the dynamic storage modulus (G') with temperature for block copolymers **1a** (A), **1b** (B), **1c** (C), and **1d** (D) at 1 Hz (arrows indicate the glass temperatures of **1a**).

coelasticity range at 1 Hz frequency. The transition temperature of the relaxation processes was taken at the maximum of the relevant loss tangent peaks (Table II). The trends of the dynamic storage modulus (G') (Figure 3) and loss tangent ($\tan \delta$) (Figure 4) as a function of temperature are very similar for all block copolymers. G' was about 4×10^9 Pa at 150 K for all samples and decreased progressively with increasing temperature. One minor relaxation was detected in the 170–230 K region,

primarily due to local modes of relatively short chain segments of both main-chain and side-chain blocks. A marked drop of G' , with a prominent peak in the relevant $\tan \delta$ curve, was observed between 290 and 310 K due to the glass transition of the main-chain block. In addition, a gradual decrease of the modulus in the temperature region between 330 and 370 K was due to the glass transition of the side-chain block. Above 380 K, all the samples lost their dimensional stability.

The decrease of G' in two definite steps at the glass transitions of the polyester and polymethacrylate blocks was related to their weight fraction in the copolymer. The T_g of the polyester block decreased, whereas that of the

polymethacrylate block remained practically constant with a slight increase as the amount of the main-chain block in the block copolymers increased (Figure 5). Thus, the evolution of the glass transition of the main-chain block with copolymer composition seemed a reliable monitor of the existence of interactions among the different blocks in the amorphous state. The occurrence of two distinct glass transition regions indicates a phase separation between the blocks. However, the width of the glass transition region of both main-chain and side-chain blocks and the variations in the relevant T_g reflect a certain degree of compatibility between the chemically different blocks. This should result in the formation of a somewhat diffuse interphase. The practical insensitivity of the T_g of the polymethacrylate block to copolymer composition may be attributed to two compensating opposite contributions, that is an increase due to an increase in M_n of this block (Table I) and an anticipated decrease because of enhanced compatibility with the polyester block.

Mesomorphic Behavior

The phase transition temperatures and enthalpies of the block copolymers are collected in Tables II and III, along with those of polyester **2** and polymethacrylate **3** homopolymers

Figure 4. Trend of the loss tangent ($\tan \delta$) with temperature for block copolymers **1a** (A), **1b** (B), **1c** (C), and **1d** (D) at 1 Hz (arrows indicate the glass temperatures of **1a**).

Figure 5. Trends of the glass transition temperatures of the polyester block ($\blacktriangle$) and polymethacrylate block ($\triangle$) in block copolymers **1a**–**d** as a function of the wt% content of polyester block (block A).

Table III. Transition enthalpies^a of block copolymers **1a**–**d**, polyester **2**, and polymethacrylate **3**

Sample		Polyester block (block A)		Polymethacrylate block (block B)	
Type	block A /wt%	ΔH_{S-N}^a /J g ⁻¹	ΔH_{N-I}^a /J g ⁻¹	ΔH_{S-N}^a /J g ⁻¹	ΔH_{N-I}^a /J g ⁻¹
1a	65	1.1	0.3	nd ^b	1.1
1b	41	1.2	0.4	0.5	1.7
1c	33	1.3	0.5	0.7	1.8
1d	21	2.0	0.7	1.5	2.7
2	100	4.7	2.9	—	—
3	0	—	—	3.0	2.8

^aBy DSC, at 10 K min⁻¹ scanning rate. S, smectic (A or C); N, nematic; I, isotropic. ^bNot detected by DSC.

for comparison. The thermal behavior of block copolymers **1a–d** was derived from the DSC cooling curves, on account of the better resolution of the transition peaks. In each copolymer, they were qualitatively similar to those that are illustrated in Figure 6 for **1c**. Polyester **2** was amorphous and exhibited an isotropic-nematic transition at 430 K and a nematic-smectic C transition at 411 K (Figure 6A). Polymethacrylate **3** was also amorphous and underwent isotropic-nematic and nematic smectic A transitions at 382 and 372 K, respectively (Figure 6B). The DSC cooling curve (Figure 6C) of copolymer **1c** showed four exothermic peaks centered at 423, 403, 388, and 367 K. Comparison of this curve with those of **2** and **3** suggests that the former two transitions were due to the mesophase transitions of the main-chain block, whereas the latter two were associated to the mesophase transitions of the side-chain block.

The above attribution was also confirmed by X-ray diffraction analysis. As a typical example, Figure 7 reports the X-ray powder patterns of **1a** at different temperatures, after the sample had been annealed by cooling from the isotropic melt. At room temperature, the X-ray diagram (Figure 7B) consisted of two small-angle reflections, originated from layer periodicities of 20.0 Å (d_1) and 29.0 Å (d_2), and a wide-angle signal corresponding to a mean intermolecular distance (D) of 4.6 Å. Very similar spectra were recorded for **1b**, **1c**, and **1d**, for which only slight differences in the intensity ratios of the two small-angle reflections were noted, without modifications of the angular peak positions. No correlation exists between the signals with periodicities d_1 and d_2 . The former corresponds exactly to the layer spacing of the smectic C mesophase of polyester **2** (Figure 7E), and the latter to the layer spacing of the smectic A mesophase of polymethacrylate **3** (Figure 7A). Therefore, the main-chain and the side-chain blocks were at least partly phase-separated and gave rise to two coexisting disordered smectic (A or C)

mesophases with different layer periodicities. The small-angle peak at d_2 disappeared at temperatures above 370 K at the smectic-nematic transition of the side-chain block, and the diagram was then consistent with the presence of the smectic mesophase of the main-chain block (Figure 7C). Above 400 K, the small-angle peak at d_1 also vanished (Figure 7D), indicating the transition to the nematic mesophase of the main-chain block. The above trend of the X-ray diffraction patterns was completely reproducible in successive heating and cooling cycles. Detailed X-ray diffraction studies on mechanically and magnetically oriented samples are in progress to characterize

Figure 6. DSC second cooling curves (10 K min^{-1}) for polyester **2** (A), polymethacrylate **3** (B), and block copolymer **1c** (C).

Figure 7. X-Ray diffraction diagrams for polymethacrylate **3** at 300 K (A), block copolymer **1a** at 298 K (B), 373 K (C), and 403 K (D), and polyester **2** at 376 K (E).

the fine structure of the two smectic mesophases. When observed at the polarizing microscope, the copolymer samples did not exhibit specific optical textures and no information on their mesophase nature could be gained by this technique.

Figure 8 illustrates the trends of various mesophase transition temperatures of the polyester and polymethacrylate blocks as a function of the polyester block content in the copolymers. The transition temperatures of the main-chain block displayed a minimum at a composition of about 70 wt%, whereas a not very pronounced maximum in the transition temperatures of the side-chain block was observed at a composition of about 20 wt%.

The enthalpies of both the smectic–nematic and nematic–isotropic transitions of the polymethacrylate block, after normalization for the copolymer composition, decreased gradually with increasing content of the polyester block in the copolymers (Figure 9). However, well defined minima in the normalized enthalpies of both the smectic–nematic and nematic–isotropic transitions of the polyester block were detected at a polyester composition of about 50 wt%. These results suggest the existence of partial miscibility between the two chemically different blocks. In addition, mutual disordering effects of the blocks might also contribute to lowering the transition enthalpies.

In previous papers,^{7–9} we have shown that in various LC block copolymers containing LC and non-LC blocks neither the temperature nor the enthalpy of the different mesophase transitions were affected to any significant extent by block copolymer composition in agreement with an essentially incompatible nature of the two blocks. They in fact underwent their individual phase transitions practically independent of each other. In contrast, in block copolymers comprising both main-chain and side-chain LC blocks the two structurally different blocks were partly phase-separated within the glassy and LC states.¹⁰ In particular, the nematic–isotropic transition temperature

of the main-chain block was definitely higher than that of the relevant homopolymer. Moreover, the smectic–nematic and nematic–isotropic transition enthalpies of the main-chain block were substantially lower than those computed on the basis of the chemical composition of the copolymer. The partial compatibility of the two chemically different blocks observed in the present main-chain side-chain block copolymers matches the one of the previous copolymer system. However, in the present block copolymers, a decrease of stabil-

Figure 8. Trends of the transition temperatures of block copolymers **1a–d** as a function of the wt% content of polyester block (block A): smectic–nematic (■) and nematic–isotropic (●) (polyester block); smectic–nematic (□) and nematic–isotropic (○) (polymethacrylate block).

Figure 9. Trends of the normalized transition enthalpies of block copolymers **1a–d** as a function of the wt% content of polyester block (block A): smectic–nematic (■) and nematic–isotropic (●) (polyester block); smectic–nematic (□) and nematic–isotropic (○) (polymethacrylate block).

ity of the smectic and nematic mesophases of the main-chain block is observed in contrast to the increase in the mesophase stability detected for the previous series.

CONCLUSIONS

We have synthesized and studied a series of block copolymers comprising both main-chain and side-chain LC blocks within the same polymer structure. Thermal and dynamic-mechanical data show that the two chemically different blocks are at least partly phase-separated in the glassy and LC phases and undergo distinct transitions, which could also be monitored by X-ray diffraction measurements. 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. The stability of the LC phase of both the main-chain and side-chain blocks is lower than that of the corresponding homopolymers. This is in contrast to the behavior observed for other main-chain/side-chain block copolymers¹⁰ in which an increase in the stability of the LC phase generated by the main-chain block was detected. Therefore, no general statements may yet be made on the role of the block length and block length distribution as well as of the nature and stability of the LC phases in determining the compatibility and phase-separation propensity of the chemically different blocks within the glassy and LC phases, or their influence on the onset and stability of the relevant mesophases. A systematic investigation on similar main-chain/side-chain block copolymer systems, by keeping constant the main-chain block structure and changing the chemical structure and length of the side-chain block, is presently under way.

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REFERENCES

1. a) J. Adams and W. Gronski, *Makromol. Chem., Rapid Commun.*, **10**, 553 (1989); b) J. Adams, J. Sanger, C. Tefehne, and W. Gronski, *Macromol. Chem., Rapid Commun.*, **15**, 879 (1994).
2. M. Hefft and J. Springer, *Makromol. Chem., Rapid Commun.*, **11**, 397 (1990).
3. a) B. Zschke, W. Frank, H. Fischer, K. Schmutzler, and M. Arnold, *Polym. Bull. (Berlin)*, **27**, 1 (1991); b) M. Arnold, S. Poser, H. Fischer, W. Frank, and H. Utschick, *Macromol. Chem., Rapid Commun.*, **15**, 487 (1994).
4. T. Kodaira and K. Mori, *Makromol. Chem.*, **193**, 1331 (1992).
5. Z. Komiya and R. R. Schrock, *Macromolecules*, **26**, 1387 (1993).
6. L. H. Radzilowski, J. L. Wu, and S. I. Stupp, *Macromolecules*, **26**, 879 (1993).
7. G. Galli, E. Chiellini, Y. Yagci, E. I. Serhatli, M. Laus, A. S. Angeloni, and M. C. Bignozzi, *Makromol. Chem., Rapid Commun.*, **14**, 185 (1993).
8. A. S. Angeloni, M. C. Bignozzi, M. Laus, E. Chiellini, and G. Galli, *Polym. Bull. (Berlin)*, **31**, 387 (1993).
9. E. Chiellini, G. Galli, A. S. Angeloni, M. Laus, M. C. Bignozzi, Y. Yagci, and E. I. Serhatli, *Macromol. Symp.*, **77**, 349 (1994).
10. G. Galli, E. Chiellini, M. Laus, M. C. Bignozzi, A. S. Angeloni, and O. Francescangeli, *Macromol. Chem. Phys.*, **195**, 2247 (1994).
11. a) V. Percec and M. Lee, *J. Macromol. Sci., Pure Appl. Chem.*, **A29**, 723 (1992); b) G. Galli, E. Chiellini, M. C. Bignozzi, A. S. Angeloni, and M. Laus, Preprints, 35th IUPAC International Symposium on Macromolecules, Akron, OH (U.S.A.), 1994, p 270.
12. R. Bohnert and H. Finkelmann, *Macromol. Chem. Phys.*, **195**, 689 (1994).
13. E. Chiellini, G. Galli, M. Laus, A. S. Angeloni, O. Francescangeli, and B. Yang, *J. Mater. Chem.*, **2**, 449 (1992).
14. O. Francescangeli, B. Yang, G. Albertini, A. S. Angeloni, M. Laus, E. Chiellini, and G. Galli, *Liq. Cryst.*, **3**, 353 (1993).
15. R. Zentel and H. Ringsdorf, *Makromol. Chem., Rapid Commun.*, **5**, 393 (1984).
16. O. Francescangeli, M. Laus, M. C. Bignozzi, A. S. Angeloni, G. Galli, and E. Chiellini, *Polym. J. (Jpn.)*, in press; cf. following paper, Part 2.
17. Y. Yagci, *Polym. Commun.*, **26**, 7 (1985).
18. W. Heitz, *Makromol. Chem., Macromol. Symp.*, **10/11**, 297 (1987).
19. G. C. Eastmond, *Makromol. Chem., Macromol. Symp.*, **10/11**, 71 (1987).