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DESIGN AND PREPARATION OF LIQUID CRYSTALLINE BLOCK COPOLYMERS

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Abstract The design and preparation of liquid crystalline (LC) block copolymers by use of azo-macroinitiators are outlined. This approach is very versatile and makes it possible to realize diverse architectures of block copolymers, including non-LC/side-chain, non-LC/main-chain and side-chain/main-chain block copolymers. The different blocks were phase separated and underwent their individual phase transitions. In side-chain/main-chain block copolymers different LC mesophases coexisted in equilibrium.

INTRODUCTION

Multicomponent polymer systems are of relevant practical importance because their unique multiphase structure often allows for non-linear and synergistic behavior. Block copolymers containing liquid crystalline (LC) polymer block(s) represent the latest development in architectures of such materials[1,2]. They can combine within one polymer structure distinctive features of order at a molecular level, typical of liquid crystals, and at a supramolecular length scale, characteristic of block copolymers. In fact, block copolymers consisting of incompatible polymer blocks tend to phase separate into the individual components. However, because of the chemical bond(s) linking together the polymer blocks, phase separation is impossible at a macroscopic level and, as a result, mesoscopic lattices are formed. The phase behavior of diblock copolymers consisting of one block A and one block B is essentially determined by the overall degree of polymerization, the overall volume fraction, and the temperature expressed in terms of the segment-segment interaction parameter χ_{AB}[3]. Traditional morphologies with periodically arranged spheres, cylinders, or lamellae occur corresponding to a decreasing mean curvature of the interphase boundary. Other, more complex periodic structures have also been described where both separated phases are continuous and interpenetrate each other[4].

In LC block copolymers, the concomitant orders at different length scales can affect the phase behavior substantially, and the morphologies of these materials are expected to be greatly influenced by different structuring effects that would likely operate in tandem. In this case, on the one hand, the immiscibility of the polymer blocks drives a microphase separation, and, on

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the other hand, the ordering field typical of the LC mesophases facilitates a spontaneous organization of the mesogens in a microseparated phase. It is intuitively anticipated that the LC character of one component of the copolymer will enhance the incompatibility of the blocks. However, several new questions arise relating, for example, to how the morphology and the mesophase interact in reaching their respective equilibrium states, or to what correlations can be established between the nature and stability of the mesophase of the LC block and the overall topological characteristics of the block copolymer.

In addition to the fundamental interest related to these materials, a number of practical applications can be envisaged, including their use as highly versatile interfacially active components for the engineering of polymer blends with high performance polymers.

In principle, the combination of side-chain LC, main-chain LC and non-LC blocks leads to five basic LC block copolymers: side-chain/non-LC (class I), main-chain/non-LC (class II), side-chain/main-chain (class III), main-chain/main-chain (class IV) and side-chain/side-chain (class V). Some of them have already been prepared, whereas others must still be prepared and studied[1,2]. Block copolymer architectures with finely controlled structural parameters can be prepared following different synthetic strategies, e.g. by i) living cationic[5-7], anionic[8-10], or ring-opening metathesis[11,12] polymerizations, ii) polymer analogous reactions[13-15], and iii) use of macroinitiators[16-22].

In this paper, we outline the synthetic procedures that have been developed in our group in the last few years and specifically addressed to the preparation of block copolymers containing LC blocks via the use of macroinitiators (Fig.1).

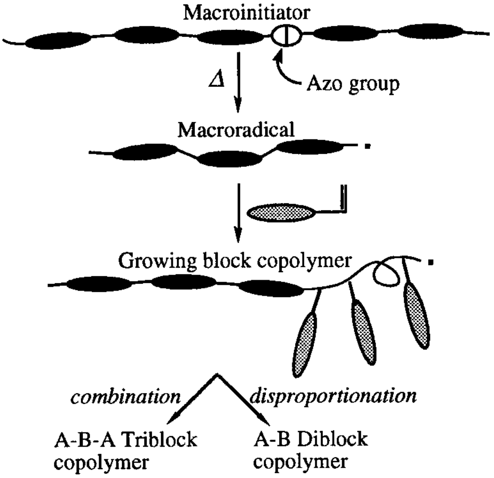
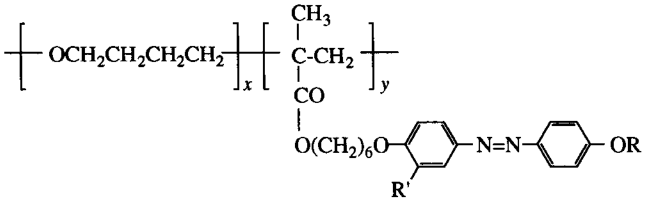


Fig.1. Synthetic scheme for the preparation of LC block copolymers of class III containing both main-chain and side-chain blocks.

Macroinitiators are polymers which incorporate photo- or thermal-labile group(s), such as azo groups. As these reactive groups form part of the polymer backbone, their decomposition leads to a simultaneous fragmentation of the macroinitiator. The radical terminated polymer fragments initiate the polymerization of a suitable monomer and become part of the block copolymer. Finally, according to the specific termination mechanism of the latter monomer used, A-B diblock or A-B-A triblock copolymers are formed. $(A\text{-}B)_n$ multiblock copolymers can also be obtained from macroinitiators containing more than one functional group per polymer chain.
By following this general synthetic approach we prepared three different classes (I, II and III) of block copolymers.

Class I: Side-chain/non-LC block copolymers

The structure of representative samples belonging to this class of block copolymers is the following:



1a : R = CH_3; R' = H
1b : R = $(CH_2)_5CH_3$; R' = CH_3

These A-B diblock copolymers **1a,b** are constituted by one polytetrahydrofuran (*p*-THF) block and one LC polymethacrylate block. The latter is built up from either one of two methacrylate monomers containing variously substituted azobenzene mesogens which have proved to form nematic (N) or smectic (S) and nematic mesophases below the isotropic (I) phase in the relevant homopolymers[16]. The block copolymers were synthesized via a two-step procedure consisting of two successive cationic and free-radical initiation processes starting from a bifunctional low molar mass initiator containing one azo central group and two acyl chloride end groups (Fig.2). The 4,4'-azobis(4-cyanopentanoic acid chloride) (**2**) when reacted with a silver salt having low nucleophilic ions in the presence of tetrahydrofuran produces the diacyl cation **3** which is able to polymerize tetrahydrofuran at both ends by an addition mechanism. Accordingly, in this reaction stage the macroinitiator **4** is obtained based on polytetrahydrofuran and possessing one reactive azo group in the main chain. Subsequently, the macroinitiator **4** (M_n = 27000 $gmol^{-1}$) is used to initiate the free-radical polymerization of the methacrylate monomers **6a** or **6b** through the thermal decomposition of the azo group at 70 °C.

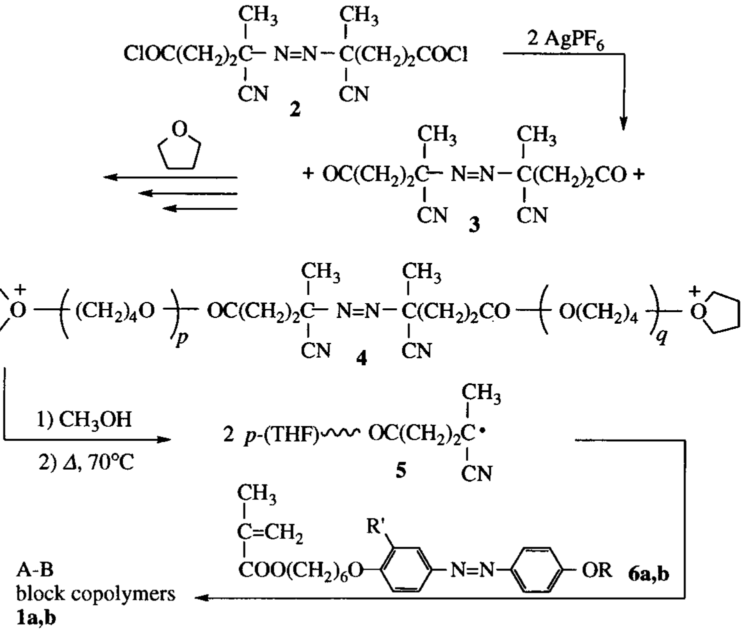


Fig.2. Synthetic scheme for the preparation of side-chain/non-LC block copolymers **1a,b**.

The mesophase transition temperatures ($T_{N\text{-}S}$, $T_{N\text{-}I}$) of the block copolymers **1a** (M_n = 41000 gmol^{-1}) and **1b** (M_n = 97000 gmol^{-1}) are very similar to those of the corresponding homopolymers thus suggesting that the polytetrahydrofuran and polymethacrylate blocks are strongly segregated and undergo distinct transitions. Furthermore, the isotropization enthalpy ($\Delta H_{N\text{-}I}$) of the polymethacrylate blocks is directly proportional to the polymethacrylate content thus indicating that the presence of the polytetrahydrofuran blocks does not affect in a significant way the isotropization transition of the polymethacrylate blocks[16].

Class II: Main-chain/non-LC block copolymers

The second class of block copolymers **7** was synthesized by the two-step procedure reported in Figure 3.

In the first reaction stage, a polyester macroinitiator **10** containing azo groups is prepared by a polycondensation reaction between equimolar amounts of the diacid chlorides **2** and **8** and the sodium salt of the diphenol **9** in the presence of a catalytic amount of a phase transfer agent[17].

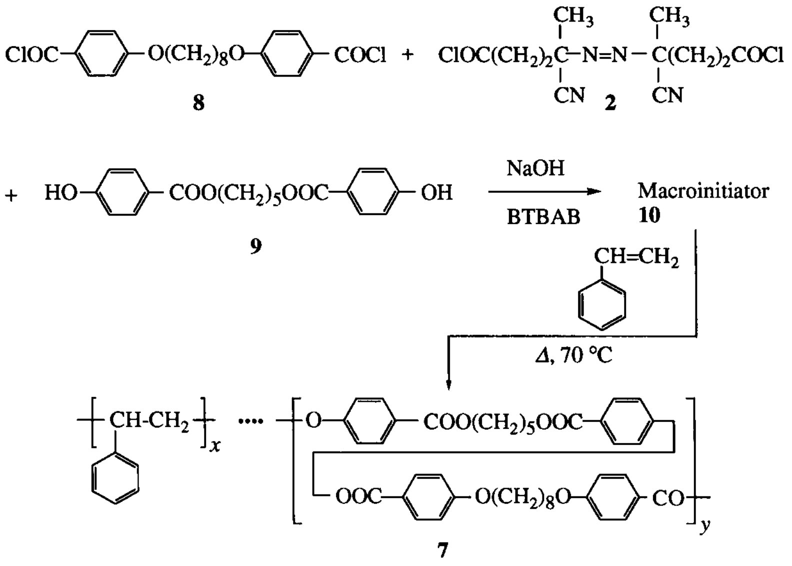


Fig.3. Synthetic scheme for the preparation of main-chain/non-LC block copolymers **7**.

The macroinitiator is then used as a free-radical source for the polymerization of styrene through the thermal decomposition of the azo group at 70 °C leading to A-B-A triblock copolymers **7**, with polystyrene being the central B block.

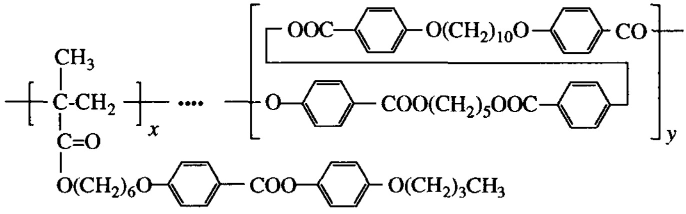
Minor amounts of polystyrene homopolymer were obtained in all cases, thus clearly indicating a negligible occurrence of chain transfer processes.

Various copolymer series were prepared by starting from macroinitiators containing different amounts of reactive azo groups and using within each series different concentrations of styrene in the feed mixture. Several samples of macroinitiators **10** were prepared with M_n = 6000-11000 $gmol^{-1}$ that were used to produce block copolymers with polystyrene blocks of varying molar mass (M_n = 25000-250000) and composition (20-85 wt.%).

The basic LC behavior of the polyester homopolymer, which displays nematic and smectic C mesophases is maintained in the various block copolymers. In particular, the smectic C-nematic and nematic-isotropic transition temperatures are constant within the whole compositional range and in addition, the smectic C-nematic and nematic-isotropic phase transition enthalpies are directly proportional to the content of the main-chain LC block. Therefore, the two chemically different blocks are strongly segregated within the solid and melt phases, and the mesophase transition parameters (T, ΔH) of the main-chain block are not influenced by the presence of the polystyrene block[17].

Class III: Main-chain/side-chain block copolymers

The third class of block copolymers was obtained by naturally combining the first two classes, that is by reacting a main-chain macroinitiator with mesogenic side-chain methacrylates[18,19]. Accordingly, the copolymers incorporate one side-chain LC polymethacrylate block and one main-chain LC polyester block. The structure of a representative example of these A-B diblock copolymers **11** is as follows:



11

The relevant polyester homopolymer formed smectic C and nematic mesophases, while the polymethacrylate homopolymer structurally analogous to the side-chain block exhibited smectic A and nematic mesophases.

Several block copolymer samples **11** (M_n = 18000-50000 gmol^{-1}) were prepared by reacting various polyester macroinitiators (M_n = 5400-26000 gmol^{-1}) with different proportions of the methacrylate monomer in the feed mixture[19,20], following a reaction scheme similar to that summarized in Figure 3 for copolymers **7**.

Figure 4 illustrates the DSC cooling trace of one example block copolymer **11** (M_n = 43000 gmol^{-1}) consisting of 32 wt.% polyester block. Four enthalpic transitions are observed. The two higher temperature peaks are due to the isotropic-nematic and nematic-smectic transitions of the main-chain block, while the two lower temperature peaks are due to the isotropic-nematic and nematic-smectic transitions of the side-chain block. This result is also confirmed by X-ray diffraction studies (Fig.4). In fact, a small-angle signal at 20 Å appears below 390 K for the smectic structure of the main-chain block, whereas at 340 K two small-angle signals start to be detected at 20 and 29 Å, due to the coexisting smectic structures of the main-chain and side-chain blocks, respectively. Thus, the main-chain and the side-chain blocks are phase-separated and give rise to two equilibrium smectic mesophases with different layer periodicities[22].

The trends of the various mesophase transition temperatures of the polyester and polymethacrylate blocks as a function of the polyester block content in copolymers **11** are shown in Figure 5.

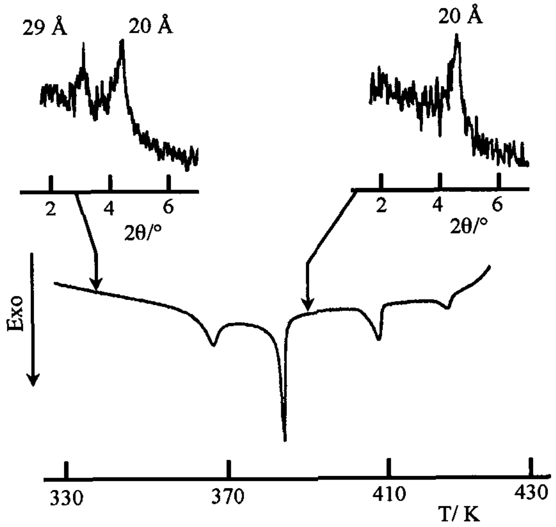


Fig.4. DSC cooling trace and small-angle X-ray diffraction spectra at different temperatures for one example main-chain/side-chain block copolymer **11**.

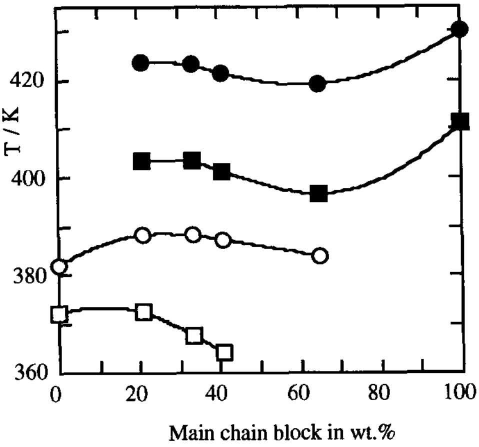


Fig.5. Trends of the smectic-nematic (■) and nematic-isotropic (●) transition temperatures of the polyester block, and of the smectic-nematic (□) and nematic-isotropic (○) transition temperatures of the polymethacrylate block of block copolymers **11** as a function of composition.

The transition temperatures ($T_{S\text{-}N}$, $T_{N\text{-}I}$) of the main-chain block display a minimum at a composition of about 70 wt.%, whereas those of the side-chain block seem to reach a not very pronounced maximum at a composition of about 20 wt.%. The normalized enthalpies of both the smectic-nematic ($\Delta H_{S\text{-}N}$) and nematic-isotropic ($\Delta H_{N\text{-}I}$) transitions of the polymethacrylate block decrease gradually with increasing content of the polyester block in the copolymers (Fig.6). However, well defined minima in the enthalpies of both the smectic-nematic and nematic-isotropic transitions of the polyester block are detected at a polyester composition of about 50 wt.%. These results suggest the existence of partial miscibility between the two chemically different blocks[19].

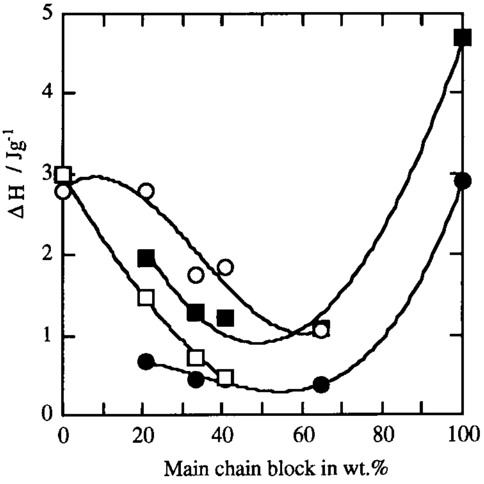


Fig.6. Trends of the smectic-nematic (■) and nematic-isotropic (●) transition enthalpies of the polyester block, and of the smectic-nematic (□) and nematic-isotropic (○) transition enthalpies of the polymethacrylate block of block copolymers **10** as a function of composition.

CONCLUSIONS

The synthetic approach to new LC architectures based on macroinitiators seems stimulating in that it allows the creation of a huge diversity of LC block copolymers, owing to an essentially unlimited choice of combinations of free-radically polymerizable monomers with macroinitiators prepared by chain-growth or step-growth polymerizations. A drawback associated with this procedure is that a modest control can be exerted on the polymerization process and, consequently, blocks of varying molar mass dispersities are normally produced.

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