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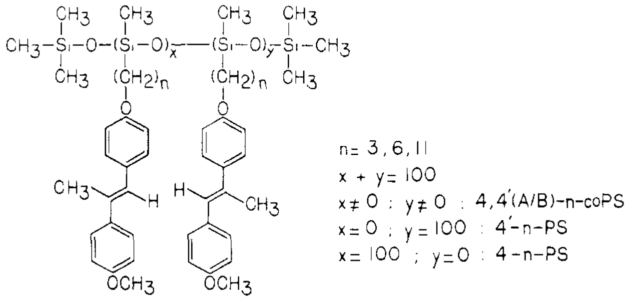
Transformation of a Monotropic Mesophase into an Enantiotropic Mesophase by Copolymerization of the Parent Polymers' Monomer Pair Containing Constitutional Isomeric Mesogenic Side Groups

In a series of publications from our laboratory,[1-3] we have suggested that copolymerization of monomer pairs containing mesogenic units which are constitutional isomers should depress the tendency toward side-chain crystallization of polymers containing long, flexible spacers and simultaneously provide qualitative information about the degree of decoupling. The previous experiments were performed with side groups based on 4-methoxy-4′-hydroxy-*trans*-α-methylstilbene (4-MHMS) and 4-hydroxy-4′-methoxy-*trans*-α-methylstilbene (4′-MHMS) constitutional isomers. However, all comonomer compositions were directly synthesized as mixtures of constitutional isomers by the monomethylation of 4,4′-dihydroxy-*trans*-α-methylstilbene.[1-3] Although the molar ratio between the two consitutional isomeric side groups was determined by spectroscopic methods, no information about the behavior of each of the two individual homopolymers based only on one individual constitutional isomer was available. Meanwhile we have synthesized and characterized the homopolymers based on 4-MHMS[4] and 4′-MHMS[5] individual isomers.

This paper describes the first quantitative results concerning the influence of copolymer composition on the phase transitions of thermotropic liquid-crystalline poly(methylsiloxanes) containing 4-MHMS (4-*n*-PS), 4′-MHMS (4′-*n*-PS), and different ratios between these two constitutional isomeric mesogenic side groups [4,4′(*A*/*B*)-*n*-coPS] attached to the polymer backbone through flexible spacers containing 3, 6, and 11 methylenic units (Scheme I). Ratio *A*/*B* refers to the molar ratio between 4-MHMS and 4′-MHMS constitutional isomeric side groups in the copolymer.

The synthesis and characterization of these homopolymers and copolymers were performed according to general procedures used in our laboratory.[3-6] Copolymers based on several different ratios between the two individually synthesized isomeric monomers[4,5] were synthesized. Phase transitions were assigned by a combination of differential scanning calorimetry (DSC) (20 °C/min) and thermal optical microscopy. DSC curves of all polymers were perfectly reproducible and independent of the heating or cooling scans that they were recorded from.

Scheme I
Poly(methylsiloxanes) and Copoly(methylsiloxanes) Containing 4-MHMS- and 4′-MHMS-Based Mesogenic Side Groups and Different Spacer Lengths



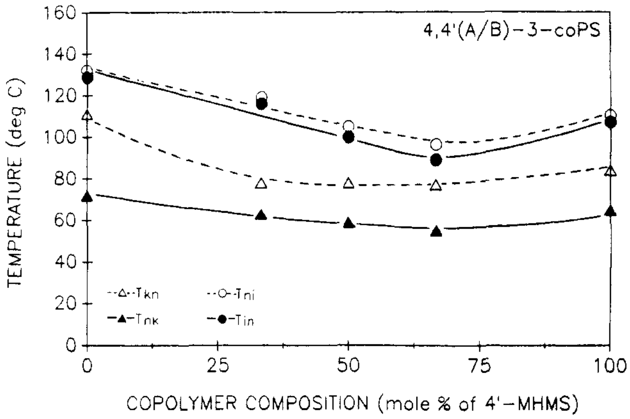


Figure 1. Dependence between (Δ, Tkn) crystalline–nematic, (▲, Tnk) nematic–crystalline, (O, Tni) nematic–isotropic, and (●, Tin) isotropic–nematic transition temperatures and the 4,4′-(*A*/*B*)-3-coPS copolymer composition.

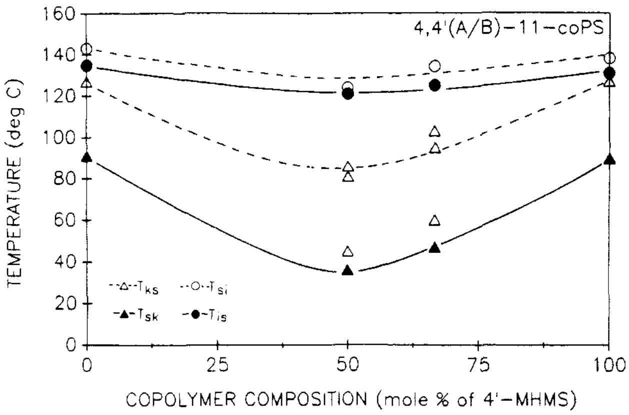


Figure 2. Dependence between (Δ, Tks) crystalline–smectic (▲, Tsk) smectic–crystalline, (O, Tsi) smectic–isotropic, and (●, Tis) isotropic–smectic transition temperatures and the 4,4′(*A*/*B*)-11-coPS copolymer composition.

Figure 1 presents the phase diagram of the copolymer system 4,4′(*A*/*B*)-3-coPS. Both homopolymers exhibit an enantiotropic nematic mesophase and side-chain crystallization.[4,5] The use of different ratios of these two constitutional isomeric side groups in the structure of 4,4′-(*A*/*B*)-3-coPS depresses to approximately equal extent both the nematic–isotropic and the crystalline–nematic (as well as their revers) phase transition temperatures. The enthalpy changes associated with the mesomorphic–isotropic and the reverse phase transitions of the homopolymers 4′-*n*-PS are equal to those of 4-*n*-PS (n = 3, 6, 11) and within experimental error are equal to those of their copolymers. For polymers with n = 3, ΔH_{in} = 0.10 kcal/mru, for polymers with n = 6, ΔH_{in} = 0.09 kcal/mru, and for polymers with n = 11, ΔH_{is} = 0.75 kcal/mru.

Figure 2 presents the phase diagram of the copolymer system 4,4′(*A*/*B*)-11-coPS. Both 4-11-PS and 4′-11-PS present an enantiotropic smectic mesophase and side-chain crystallization.[4,5] The resulting copolymers exhibit a strongly depressed crystalline melting transition temperature and a slightly lowered smectic–isotropic transition

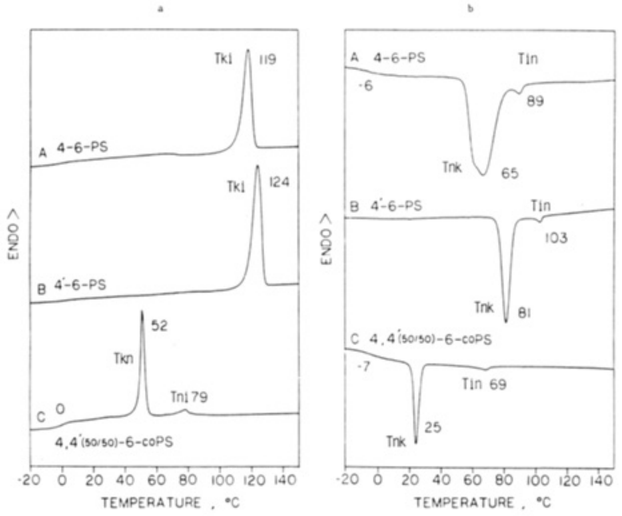


Figure 3. (a) Normalized DSC second heating scan traces (20 °C/min) of (A) 4-6-PS, (B) 4′-6-PS, and (C) 4,4′(50/50)-6-coPS and (b) normalized DSC first cooling scan traces (20 °C/min) of (A) 4-6-PS, (B) 4′-6-PS, and (C) 4,4′(50/50)-6-coPS.

temperature. As a consequence, copolymerization of the two constitutional isomeric–mesogenic groups with long spacers enlarges the thermal stability of the mesophase. Interestingly, 4,4′(*A*/*B*)-11-coPS copolymers display three meltings, which, as previously speculated, can be definitively assigned to the meltings of each of the two constitutional isomers and to their eutectic mixture, respectively.[3] These independent meltings demonstrate a higher degree of decoupling of the side groups attached to the polymer backbone through long, flexible spacers than that observed for copolymers with similar groups attached through short spacers.

Figure 3 presents DSC curves describing the phase behavior of the most interesting copolymer: 4,4′(50/50)-6-coPS. 4-6-PS (Figure 3a, curve A; and Figure 3b, curve A) and 4′-6-PS (Figure 3a, curve B; and 3b, curve B) homopolymers each display a monotropic–nematic mesophase. Upon copolymerization, both the crystalline phase and the nematic mesophase are strongly depressed (Figure 3a, curve C; and Figure 3b, curve C). However, as with 4,4′(*A*/*B*)-11-coPS, the crystalline phase is suppressed more than the liquid-crystalline phase. Consequently, in this particular situation, copolymerization of the two constitutional isomeric monomers transforms the monotropic mesophase into an enantiotropic one. This last copolymer example demonstrates that constitutional isomeric–mesogenic side groups drastically affect mesomorphic phase transitions in side-chain liquid-crystalline copolymers. A representative optical polarization micrograph showing the crystallization from the Schlieren nematic–monotropic mesophase of 4′-6-PS is shown in Figure 4a. Figure 4b presents the Schlieren nematic texture of the enantiotropic mesophase displayed by 4,4′(50/50)-6-coPS.

Transformation of a monotropic mesophase into an enantiotropic mesophase by copolymerization is well documented in the case of main-chain liquid-crystalline copolymers.[7] The same effect was also observed upon increasing the main-chain liquid-crystalline polymer molecular weight.[7] In the case of side-chain liquid-crystalline polymers, transformation of virtual or monotropic mesophases into enantiotropic mesophases was mostly observed upon increasing the polymer molecular weight[8] or on changing the nature of the polymer backbone.[3-5] This dependence between mesomorphic phase transition and copolymer composition does not yet elucidate a general relationship or trend in the case of the side-chain liquid-crystalline copolymers.[9] In most cases and as in the examples detailed here, mesomorphic transitions are strongly depressed upon copolymerization.[9,10] This is in contrast to main-chain liquid-crystalline polymers were mesomorphic phase transitions and the corresponding thermodynamic parameters are weight-averaged values of the corresponding parameters of the parent homopolymers.[11]

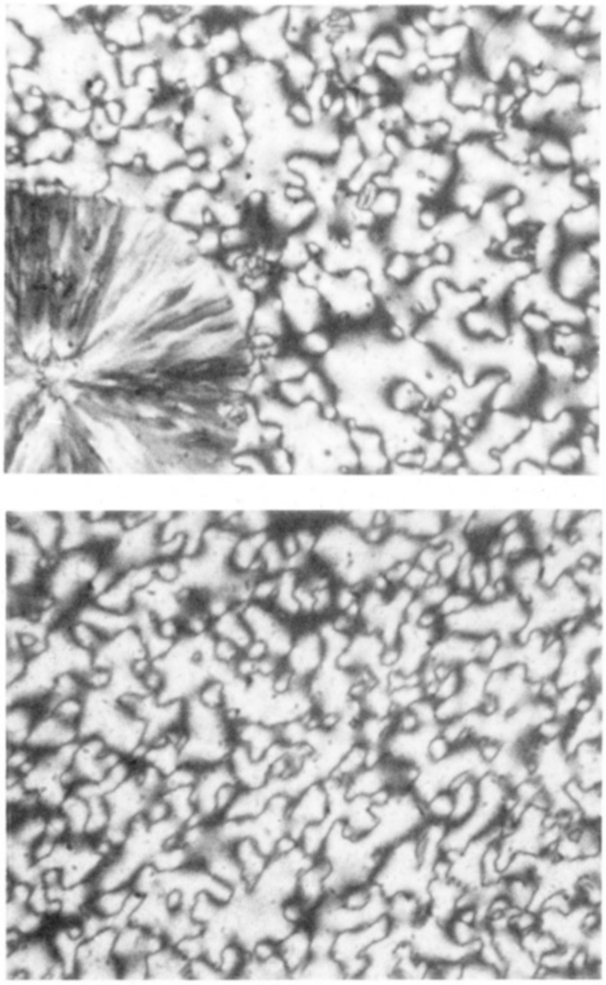


Figure 4. Representative optical polarized micrographs (70×) of (a, top) 4′-6-PS after 3 min of annealing at 105 °C on cooling from the isotropic phase and (b, bottom) 4,4′(50/50)-6-coPS after 3 min of annealing at 69 °C on the cooling scan.

In conclusion, although copolymerization of side-chain liquid-crystalline mesogenic monomers still provides an open subject of research, the experiments described in this communication demonstrate the ability to tailor mesomorphic phase transitions using copolymers based on constitutional isomeric mesogenic units.

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