of melting of the lower melting form, 1.0 kcal/mol of C_4H_6 units,[6] to recast the melting enthalpy of our samples as a nominal percent crystallinity (Table III).

Discussion of Results

The final melting temperature T_m is practically independent of molecular weight. We assume that the value obtained, $T_m = -26 \pm 1$ °C, is thermodynamic in origin and that it depends primarily on the concentration of trans sequences which exceed some critical length. Judged by the constancy in overall composition of the samples (Table I) and the virtually identical diad content of low and high molecular weight samples (Table II), the sequence distribution probably does not change very much with molecular weight. It is mildly surprising, however, to find such a weak molecular weight effect on T_m even for sample A in which the number of monomer units per chain (DP) is only 21; perhaps the very slight trend in trans content offsets the chain-end effect. Melting transitions have been observed dilatometrically for polybutadienes from free radical polymerization.[7,8] The values of T_m reported—37, 23, and 0 °C at 81%, 73%, and 64% 1,4-trans contents—extrapolate to values that are in reasonable accord with our result of $T_m = -26$ °C at 57% trans.

The amount of crystallinity obtained during the 30-min interval at −53 °C decreases rapidly with increasing molecular weight. We assume this behavior is primarily kinetic in origin, although equilibrium effects associated with the chain length certainly cannot be ruled out. Crystallizable sequences in the longer chains are likely to be less mobile, so it is not unexpected to find that the extent of crystallization decreases with increasing molecular weight for a fixed supercooling and incubation period. For the thermal history employed here, the calorimetric evidence for crystallinity disappears into the noise beyond $M = 40 \times 10^3$.

Low-frequency viscoelastic measurements should be extremely sensitive to traces of crystallinity, especially for long chains where even minute amounts would convert the liquid to a network. Crystallization is almost certainly the cause of our problems with viscoelastic measurements below −25 °C for the low molecular weight samples. No such effects were encountered in viscoelastic measurements on samples of similar microstructure but higher molecular weight (samples E and F, Table I). Conventional polymer liquid behavior was observed down to −75 °C for those samples, even with typical holding times (for purposes of temperature equilibration and data acquisition) of several hours between −75 and −25 °C.

Conclusions

We have shown that the final melting temperature T_m for the typical representatives of mixed-microstructure polybutadiene examined here is near −26 °C and that T_m for microstructures in this range is insensitive to chain length. Even well below −26 °C the degree of crystallinity is vanishingly small for modest holding times (on the order of hours) when the molecular weight exceeds $M = 50 \times 10^3$.

These observations are relevant to a recent discussion about crystallinity in mixed-microstructure polybutadienes[9] and the possible influence of crystallization on the mechanical properties of polybutadiene networks at 25 °C.[10] It now seems clear that the theoretical estimates of T_m for mixed-microstructure polybutadienes presented there[9] are much too high. This is not surprising since, for example, the contribution of crystallite surface energies was not considered, and that contribution is usually rather large in copolymers.[11] Estimates of T_m ranging from 30 to 60 °C were given for mixed-microstructure polybutadienes of the sort examined here,[9] it seems from our work that the true value for such polymers must lie well below 0 °C. This judgment is supported by calorimetry on Phillips Trans-4 polybutadiene (93% trans units). For that polymer we obtained $T_m \sim 57$ °C (at scan rates of 1.25 and 5 °C/min) and ~60% crystallinity. According to the theoretically estimated behavior presented in Figure 1 of ref 9, T_m of Trans-4 should have been nearly 90 °C. In view of the results presented here, the large values of initial (small strain) modulus at 25 °C in mixed-microstructure polybutadiene networks relative to classical network predictions[10] cannot reasonably be attributed to crystallinity.

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Registry No. polybutadiene, 9003-17-2.

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Polymerization and Characterization of Liquid Crystalline Poly(hexyl isocyanate)/Styrene Solutions

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In recent years, interest in preparing molecular composites composed of rigid-rod and random coil polymers has escalated owing to the potential these unique polymer blends have for exhibiting combinations of desirable features, including high strength, toughness, and processibility. In general, it has been difficult to prepare homogeneous blends of high molecular weight polymers. This has been particularly true for polymers possessing significantly different conformations. Several approaches have been developed recently, however, which are relatively

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effective in molecularly dispersing rigid-rod polymers in random coil matrices.[1-11]

Through careful examination of ternary solutions of rigid-rod poly(*p*-phenylenebenzobisthiazole) (PPBT) and flexible-coil poly-(2,5(6*H*) benzimidazole) (ABPBI) or poly(2,5(6*H*)-benzothiazole) (ABPBT) in methanesulfonic acid, Helminiak et al. were able to prepare homogeneous molecular composites.[1-4] Solution concentration was found to be a critical variable in controlling phase separation. At concentrations slightly less than the liquid crystalline–isotropic critical concentration (C^*), homogeneous molecular composites resulted. At concentrations above C^*, solutions phase separated into domains containing nearly exclusively rigid-rod polymer in a continuous phase consisting of random coil and rigid-rod polymers. At concentrations significantly below C^*, sufficient chain mobility was present to enable phase separation of the incompatible polymers to occur.

Tsutsui et al. have found that in situ free radical polymerization of binary solutions of helical polypeptides in vinyl monomer solvents yielded homogeneous molecular composites.[6-11] Furthermore, when solution concentrations greater than C^* were employed, the liquid crystallinity present in the starting solutions was maintained in the final molecular composites. This approach can be envisioned to provide the versatility of preparing molecular composites with isotropic or anisotropic orientations of the liquid crystalline polymer by proper choice of solution concentration prior to polymerization.

The present investigation was undertaken as a first step in an effort to extend the in situ polymerization technique to other classes of liquid crystalline polymers. Liquid crystalline poly(hexyl isocyanate) (PHIC) was chosen as the first system for investigation owing to its well-characterized liquid crystalline properties and to its solubility in a variety of common organic solvents.[12-22] The solubility and liquid crystallinity of PHIC in common organic monomers will be described along with preliminary results of the in situ polymerizations.

Experimental Section

PHIC with $M_w = 59\,900$ was prepared by sodium cyanide initiated polymerization of hexyl isocyanate in dimethyl formamide/toluene (50:50) solution at −78 °C. The polymer, which was isolated by precipitation into methanol, exhibited a small amount of insoluble gel particles on dissolution in chloroform. These were removed by filtering the solution and reprecipitating the polymer into methanol prior to use. The weight-average molecular weight was calculated from the equation of Bur and Fetters[23]

$$[\eta] = (7.58 \times 10^{-4}/M_0^{3})M_w^{2.0}$$

Solubility studies were conducted by mixing 10 wt % PHIC with 14 common commercially available monomers (Table I). Of these, only styrene and vinylidene chloride solubilized PHIC completely. Since literature reports indicated that at least 15 wt % PHIC solutions would be required to achieve liquid crystallinity, only styrene and vinylidene chloride offered any potential for achieving the necessary concentrations.[15] While both of these monomers were found to readily yield PHIC solutions of greater than 40 wt %, styrene was chosen for further study. PHIC/styrene solutions possessing up to 55 wt % PHIC could be prepared at room temperature.

Characterization of all solutions was conducted with crossed polarized light on a Leitz polarizing microscope equipped with a Mettler hotstage accurate to ±0.2 °C. Observatons were made at 200×. A specially designed glass slide possessing a circularly ground moat was employed to ensure constant sample concentration in the viewing area. Slides were prepared by placing a solution drop in the center of the viewing area, depressing the drop with a coverslip to spread the solution through the moat to the coverslip edge, and sealing the coverslip with epoxy prior to observation to ensure constant concentration during experiments.

Microscope slide polymerizations were conducted with solutions containing 2 wt % AIBN on the Leitz polarizing microscope at 50 °C. The solutions were prepared identically with those above utilizing styrene possessing 2 wt % AIBN. The liquid crystallinity was monitored with crossed polarized light throughout the polymerizations, which typically required approximately 2 h. Polymerizations were generally run for 24 h, however, to ensure the most complete conversion possible. Larger scale polymerizations were conducted similarly in sealed vials and polymerized for 24 h.

Thermal stability studies of liquid crystalline molecular composites were conducted at heating rates of 10 °C/min on the Mettler hotstage of the Leitz polarizing microscope. Composites prepared in the polymerization studies were used as is, and the liquid crystallinity was monitored with crossed polarized light.

Results and Discussion

Characterization of PHIC/Styrene Solutions. PHIC/styrene solutions ranging in concentration from 15.0 to 55 wt % were prepared in sealed glass vials that were allowed to stand at least 24 h prior to use. Solutions possessing concentrations of 20 wt % or less were completely isotropic at 25 °C. The 25 wt % solutions were biphasic with liquid crystalline domains in a continuous isotropic phase. The 30 wt % solution exhibited a phase inversion yielding isotropic domains in a continuous liquid crystalline phase. At 35 wt % and above, all solutions were completely liquid crystalline at 25 °C. The occurrence of a wide biphasic interval is well documented for PHIC and typically results in the partitioning of the high molecular weight molecules into the liquid crystalline phase.[12-17]

To determine a convenient temperature at which to conduct free radical polymerizations with both biphasic and liquid crystalline solutions, the effect of temperature on liquid crystallinity was studied. Temperature was found to have a considerable effect on the liquid crystallinity of the solutions at all concentrations. Anisotropic solutions were examined at 40, 50, and 60 °C. Solutions were allowed to equilibrate at each temperature for 15 min before observations to allow relaxation to occur. The 25 wt % solutions maintained a small degree of liquid crystallinity at 40 °C but became completely isotropic at 50 °C. The 30 and 35 wt % solutions exhibited an increase in their isotropic phases, but both remained biphasic up to 60 °C with continuous liquid crystalline phases. The 40 and 45 wt % solutions became biphasic at 40 and 50 °C, respectively, with only very small isotropic domains being visible at 60 °C in the 45 wt % sample (Figure 1). The 50 wt % solution exibited a small texture change on heating to 60 °C but had no observable isotropic domains (Figure 2).

Polymerization of Liquid Crystalline PHIC/Styrene Solutions. Biphasic 45 wt % solutions and liquid crystalline 50 wt % solutions were polymerized on microscope slides as described above to determine the ability of the polymerizing styrene chains to "lock-in" the original orientation of the PHIC chains via an interpenetrating network mechanism. The polymerization of 50 wt % PHIC/styrene occurred with virtually complete reten-

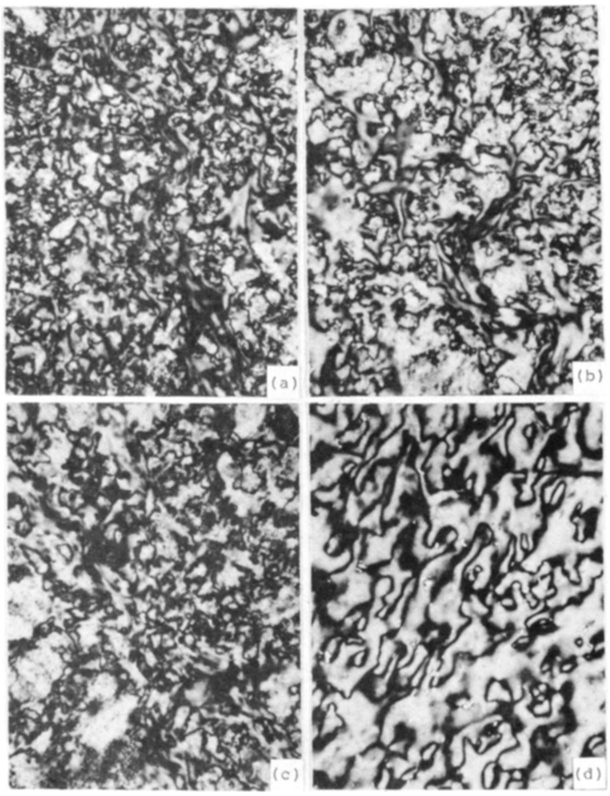

Figure 1. Liquid crystalline 45 wt % PHIC/styrene solutions at (a) 25 °C, (b) 40 °C, (c) 50 °C, and (d) 60 °C. Magnification, 110×.

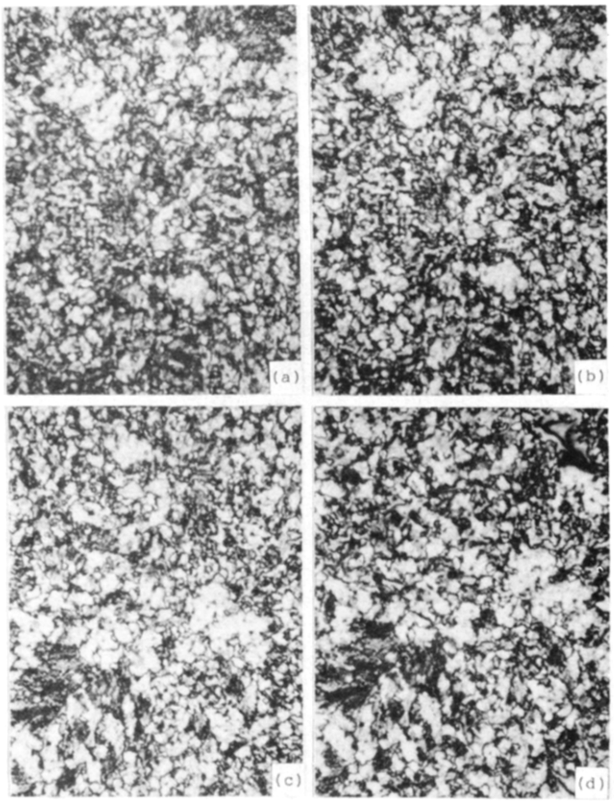

Figure 2. Liquid crystalline 50 wt % PHIC/styrene solutions at (a) 25 °C, (b) 40 °C, (c) 50 °C, and (d) 60 °C. Magnification, 110×.

tion of the original crossed polarized light texture (Figure 3). Polymerization was essentially complete after 2 h and remained unchanged on further heating to 19 h. Polymerization of PHIC/styrene solutions to PHIC/polystyrene (PS) composites occurred more readily than phase separation under these conditions.

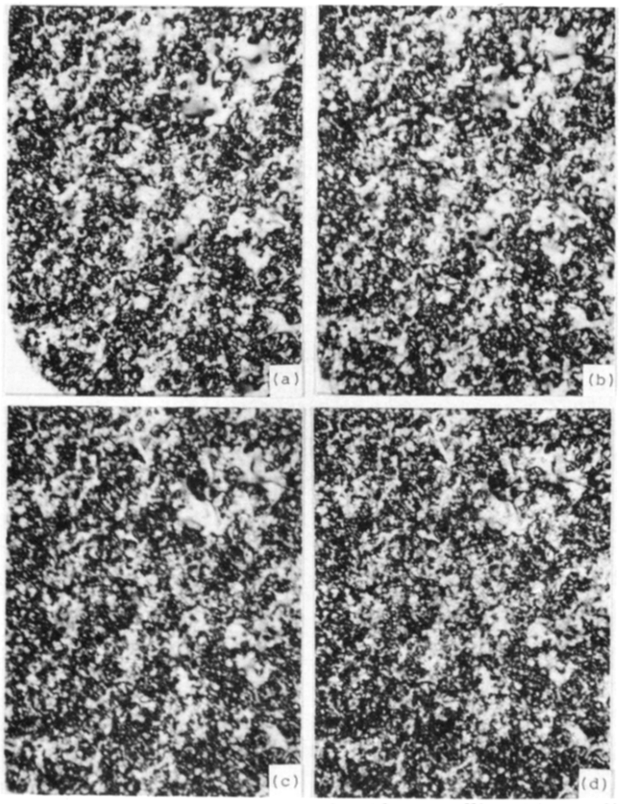

Figure 3. Polymerization of liquid crystalline 50 wt % PHIC/styrene solutions containing 2 wt % AIBN at (a) $t = 0$, (b) $t = 45$ min, (c) $t = 120$ min, and (d) $t = 1140$ min. Magnification, 110×.

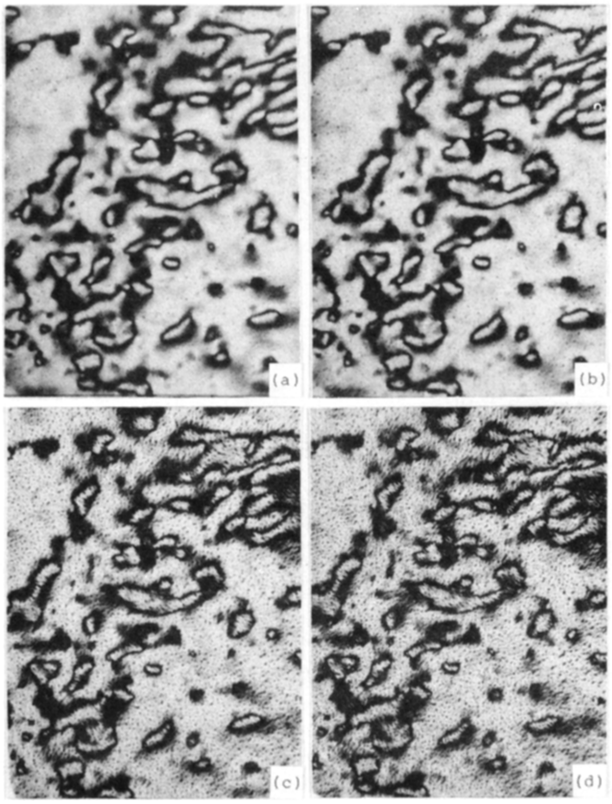

Figure 4. Polymerization of biphasic liquid crystalline 45 wt % PHIC/styrene solutions containing 2.0 wt % AIBN at (a) $t = 0$, (b) $t = 30$ min, (c) $t = 150$ min, and (d) $t = 210$ min. Magnification, 110×.

Table I
Solubility of PHIC (10 wt %) in Some Common Vinyl Monomers

monomer	solubility[a]
acrylic acid	−
acrylonitrile	−
butyl acrylate	−
N,*N*-dimethylacrylamide	−
ethyl acrylate	−
2-hydroxyethyl methacrylate	−
methyl acrylate	−
methyl methacrylate	−
methyl vinyl ketone	−
styrene	+
vinyl acetate	−
vinylidene chloride	+
4-vinylpyridine	−
N-vinyl-2-pyrrolidinone	−

[a] (+) indicates complete solubility at 10 wt % PHIC, and (-) indicates incomplete solubility at 10 wt % PHIC.

Polymerization of biphasic 45 wt % PHIC/styrene solutions yielded polymer blends with crossed polarized light textures similar to those of the starting solutions (Figure 4). The only noticeable changes were the slight increase in the size of the isotropic domains during the initial hour of polymerization and the very modest texture change. It is likely that the minor increase in isotropic domain size is attributable to relaxation of the solution as a consequence of phase equilibration at 50 °C and not to phase separation of PHIC and polymerizing styrene. Slight increases in isotropic domain size were seen with time in control 45 wt % solutions inhibited with *N*-phenylnaphthylamine when equilibrated at 50 °C. On cooling back to room temperature, the inhibited solutions relaxed back to their original texture.

The morphologies of both 45 and 50 wt % PHIC/PS molecular composites were stable on heating at 10 °C/min on the microscope hotstage up to approximately 190 °C. Neither showed any change in texture on heating when observed under crossed polarized light until 190 °C, when the field quickly grew dark and the material began to flow. On cooling back to room temperature, the material remained isotropic. The loss in properties near 190 °C corresponds to the rapid onset decomposition of PHIC, which is reported to occur between 180–200 °C.[13,24]

When polymerizations were performed on a larger scale in sealed glass vials at 50 °C, both the 45 and 50 wt % PHIC/styrene solutions slowly turned white. The resulting phase-separated white solids appeared nearly completely isotropic when observed under crossed polarized light. This suggests that the polymerization of styrene around PHIC to a homogeneous interprenetrating network molecular composite is in competition with phase separation of these inherently incompatible polymers. When the polymerizations are run on a larger scale over longer times, rigid-rod PHIC and random coil PS have more time to migrate and phase separate. This result is not surprising in light of the theory developed by Flory, which predicts that ternary solutions of rigid-rod and random coil polymers will phase separate when the concentration of random coil polymer increases above a negligible amount.[25]

Conclusions

PHIC was sufficiently soluble in both styrene and vinylidene chloride to exhibit liquid crystallinity. Microscope slide polymerizations of 45 and 50 wt % PHIC/styrene solutions occurred with retention of the original solution crossed polarized light texture, suggesting that the polymerizing polystyrene chains effectively "locked-in" the orientation of the starting PHIC/styrene solutions. This technique was also successful in preparing molecular composites with anisotropic and isotropic regions by starting with biphasic PHIC/styrene solutions. Polymerizations conducted on larger scales over longer times resulted in gross phase separation for both 45 and 50 wt % solutions at 50 °C.

Polymerization of solutions of monomer solvents and lyotropic liquid crystalline polymers above the critical concentration can result in molecular composites with crossed polarized light textures similar to the starting solutions. To prepare molecular composites, it is necessary for the polymerization of the solvent to be faster than the phase separation of the inherently incompatible polymers. Use of this approach for the preparation of a variety of molecular composites should be possible with a range of monomers, liquid crystalline polymers, and polymerization mechanisms. Recent work in our laboratory has shown that large-scale homogeneous poly(acrylic acid)/cellulose diacetate molecular composites can be prepared conveniently by this technique.

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Registry No. PHIC (homopolymer), 26746-07-6; PS (homopolymer), 9003-53-6; acrylic acid, 79-10-7; acrylonitrile, 107-13-1; butyl acrylate, 141-32-2; *N*,*N*-dimethylacrylamide, 2680-03-7; ethyl acrylate, 140-88-5; 2-hydroxyethyl methacrylate, 868-77-9; methyl acrylate, 96-33-3; methyl methacrylate, 80-62-6; methyl vinyl ketone, 78-94-4; styrene, 100-42-5; vinyl acetate, 108-05-4; vinylidene chloride, 75-35-4; 4-vinylpyridine, 100-43-6; *N*-vinyl-2-pyrrolidinone, 88-12-0.

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