creased; however, as the surfactant was increased to 1.5 wt %, the particle diameters increased. Because of this threshold, the surfactant concentration of 1 wt % was proposed for the suspension polymerization technique.

In addition to the effect on particle size, surfactant concentration had a significant effect on the monodispersity of the particles, as indicated by the standard deviations calculated for the number-average diameters. As surfactant concentration increased, the deviation from the average diameter decreased. This result suggests that the surfactant provides better control of the surface tension of the monomer droplets in the silicone oil.

The equilibrium degree of swelling for the microspheres was calculated from the radii data. This analysis resulted in an equilibrium degree of swelling of 8.0 at pH 4.75 and of 13.2 at pH 7.40.

**Conclusion.** P(MAA-*g*-EO) can be prepared in the form of microspheres by means of a free-radical suspension polymerization. These particles have a water-swollen diameter ranging from 10 to 60 μm and were found to be stable in pHs ranging from 4.75 to 7.4. In addition, increasing the concentration of the surfactant, P(DMS-*b*-EO) caused a decrease in the polydispersity of the particle size distributions.

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**Registry No.** (MMA)(EO)(TEGDMA) (graft copolymer), 122093-19-0; (MMA)(TEGDMA)(M(1000)G) (graft copolymer), 122093-21-4.

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# Stabilization of a Liquid-Crystalline Phase through Noncovalent Interaction with a Polymer Side Chain

Liquid-crystalline polymers have great potential as functional materials, in applications as varied as electrooptic devices or high-strength fibers.[1] It is well-known that molecular interactions have a significant influence on the ordering of liquid-crystalline states. The proper combination of the shape of a molecule and the magnitude as well as the orientation of its interactions with neighboring species contributes to the liquid crystallinity of the molecule. In the case of some liquid-crystalline carbohydrates[2] or poly(ester amides),[3] intermolecular hydrogen bonds are present and contribute to the overall order of their mesophases.

The objective of this study was to determine if a polymer containing a side-chain group capable of hydrogen bonding could be used to stabilize and enhance the mesomorphicity of a mesogenic small molecule with which it could interact through formation of hydrogen bonds. Clearly, the geometry of the two components would be critical as H bonding should occur along the long molecular axis of the two interacting species. Since H-bonding interactions are much stronger than those resulting from the more usual dipole–dipole interaction, any stabilizing influence would likely be of unusual magnitude.

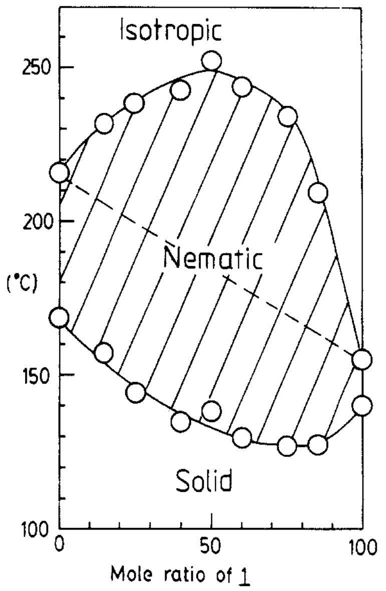
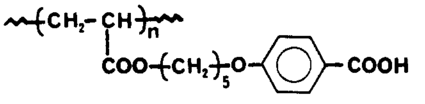


**Figure 1.** Phase diagram for the binary mixtures of polymer 1 and stilbazole 2.

In a first approach, the interacting moieties used were the carboxylic acid side chain of polymer 1 and the pyridine ring of a low molecular weight liquid-crystalline compound 2. Polymer 1 is a polyacrylate[4] containing in its side chain a pentamethylene spacer group terminated with a 4-oxybenzoic acid unit. Due to the formation of hydrogen bonds between its pendant pentoxybenzoic acid groups, polyacrylate 1 exhibits mesomorphicity with a nematiclike phase observed between 140 and 155 °C. Compound 2[5] is a *trans*-stilbazole ester moiety with nitrogen at the para position; 2 exhibits a nematic state between 168 and 216 °C.[6] Binary mixtures of these two components were examined since intermolecular hydrogen bonding between them should allow the complex to retain overall linearity thereby forming a new, longer rodlike mesogenic structure. In order to ensure that a regular 1:1 complex of two species is obtained, the binary mixture of 1 and 2 was prepared by slow evaporation from pyridine solution. This technique, which involves the use of an interacting solvent to break self-hydrogen bonding, has been used successfully by our laboratory in previous experiments[7,8] exploring the formation of homogeneous polymer blends with H-bond donor and acceptor polymers such as poly(4-hydroxystyrene)[7] or poly(4-vinylbenzoic acid)[8] with poly(4-vinylpyridine). As a result of H-bond formation, such polymer blends are compatible and show single $T_g$ values appreciably higher than those of either of the individual components of the mixture because of the formation of the hydrogen-bonded complexes.



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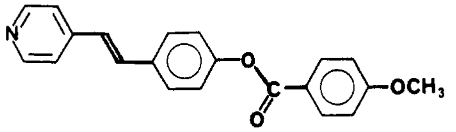

2

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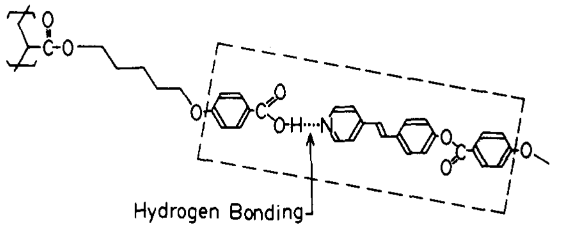

**Figure 2.** Extended mesogen resulting from mixing of polymer 1 and stilbazole 2.

Once the mixtures of the interacting liquid-crystalline components were prepared, their mesophases were examined by hot-stage (Mettler FP-52) polarizing microscopy. Polymer 1 and stilbazole ester 2 are miscible over the whole range of composition. Figure 1 shows the phase diagram[9] of the binary mixture of 1 and 2. For this system, the mixing of 1 and 2 causes a remarkably strong enhancement of the mesophase. This observation is interesting since the isotropization temperatures of binary mixtures usually occur between those of the two individual components.[10] In our case, the mesophase–isotropic transition curve shows a very significant positive deviation from the normal behavior of binary mixtures. For example, the equimolar mixture (1:1 mole ratio of 1/2) displays a mesophase extending from 140 to 252 °C whereas each of the individual components, 1 and 2, shows a transition to isotropic phase at 155 and 216 °C, respectively. The mesomorphic range of the 1:1 mixture is 112 °C while the corresponding ranges for individual components 1 and 2 are 15 and 48 °C, respectively. Even a mixture with only 15 mol % of polymer 1 and 85 mol % of compound 2 shows enhanced mesophase stability to 233 °C.

The mesophase obtained from the 1:1 equimolar mixture was stable to the highest temperature as shown in Figure 1. It is likely that this strong enhancement of the mesophase is in fact caused by the *formation of a new and extended mesogenic unit* involving the hydrogen-bonded complex shown in Figure 2. If this were not the case and no strong interaction existed between polymer 1 and stilbazole ester 2, the mesophase–isotropic transition curve would be expected to lie close to the dashed straight line in Figure 1.

FT-IR measurements strongly support the existence of the H-bonded complex. The band at 1685 cm$^{-1}$ observed for 1, which was due to carboxylic acid dimers of polymer 1, is greatly diminished in the 1:1 equimolar mixture, and the band at 1704 cm$^{-1}$, which appears in its place, seems attributable to the complex formed between the pyridine unit of 2 and the carboxylic acid units of polymer 1.

Homogeneous mesophases possessing similar threaded-type textures were observed for all molar ratios of 1 and 2 in the mixture. These binary mixtures likely form a nematic phase since it is observed that nonstoichiometric mixtures with a high content of 2 (75 or 85 mol %) still form homogeneous mesophases, suggesting that the excess of 2, which, itself, forms a nematic phase, is miscible with the hydrogen-bonded complex of 1 and 2.

Similar effects of mesophase stabilization through intermolecular hydrogen bonding have also been observed by us[11] for mixtures in which both components are of low molecular weight such as binary mixtures of an alkoxybenzoic acid and stilbazole ester 2. For example, a 1:1 mixture of 4-butoxybenzoic acid (nematic, 147–160 °C) and stilbazole ester 2 (nematic, 168–216 °C) exhibits a nematic texture up to 237 °C.

*p*-Alkoxybenzoic acid dimer is known to form a mesophase[12] through the hydrogen bonding of carboxylic acid tail groups. However, our system is significantly different from the simple acid dimer system since alkoxybenzoic acids always exist as dimers in *both* the crystalline state and the mesophase, and thus the alkoxybenzoic acid dimer is considered as a single-component mesogen. In our system, it is the mixing of two independent liquid-crystalline components that leads to the formation of a new mesogen through formation of a regular hydrogen-bonded complex. Mesophase stabilization of this magnitude has not been observed for conventional binary mixtures of mesogens. This type of interaction also has great potential in the area of miscibility of liquid-crystalline blends and in the design of novel host–guest liquid-crystalline system.

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**Registry No.** 1 (homopolymer), 122408-80-4; 2, 122408-78-0.

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## High Flux X-ray Scattering of Polydiacetylene P4BCMU in Dilute Solution

Polydiacetylenes are prototype conducting polymers. They have many interesting properties, such as a high third-order susceptibility and a high photoconductivity.[1] Applications of polydiacetylenes in materials science and electronics have become significant and have resulted in several commercial products.[2] Potential uses in polydiacetylenes as an optical memory and information pro-