differences in the specific cation solvation properties of the two solvent systems, and this analytical technique is very sensitive to small changes in solute–solvent interactions.

## Experimental Section

**Polymers.** Various salts of partially sulfonated polystyrene were prepared at the Exxon Research and Engineering Co. For the preparation, polystyrene was reacted with acetyl sulfate as the sulfonating agent in acetic anhydride.[1,9] After neutralization of the products with either aqueous sodium hydroxide or tri-*n*-butylamine solutions, sodium poly(styrenesulfonate) (NaPSS) or the tri-*n*-butylammonium poly(styrenesulfonate) (APSS) was obtained. The degree of sulfonation of the investigated samples was between 1 and 7 mol %, as indicated in Table I.

**GPC Characterization.** GPC measurements were made on a Waters 201 instrument having a high-pressure solvent delivery system and a refractive index detector. A set of five $\mu$-Styragel columns ($10^6$, $10^5$, $10^4$, $10^3$, 500) purchased from Waters Associates was used, and the instrument was operated at ambient temperature. Four solvent systems were used in these studies at polymer concentrations of 0.1% w/v: (1) tetrahydrofuran (THF); (2) tetrahydrofuran + 2 g/L $LiNO_3$ (THF/$LiNO_3$); (3) 10:1 tetrahydrofuran/dimethyl formamide (THF/DMF); (4) 10:1 tetrahydrofuran/dimethyl formamide + 2 g/L $LiNO_3$ (THF/DMF/$LiNO_3$). The flow rate was kept at 1.45 mL/min, and calibrations were made with commercially available, narrow-distribution polystyrene standards purchased from Waters Associates. Generally 0.1 mL of the polymer solution was used for the analysis. The molecular weight averages in the Table I are average values of two or three measurements, and their reproducibility was within 5%.

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# Notes

## Poly(2,6-dimethyl-1,4-phenylene oxide)–Polystyrene Interpenetrating Polymer Networks

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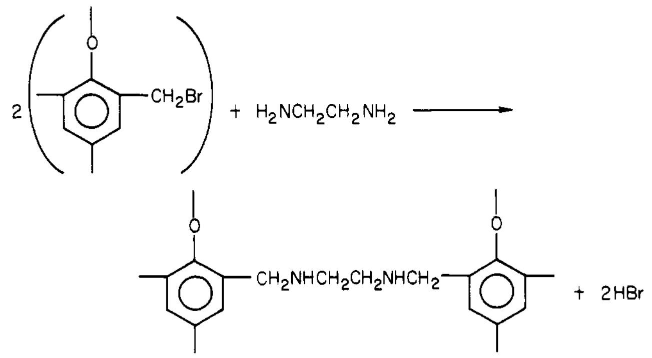
Interpenetrating polymer networks (IPN's) are a novel polyblend composed of two or more permanently entangled (catenated) chemically dissimilar, cross-linked polymers. True IPN's should be essentially free of covalent bonds between the different cross-linked, component networks (i.e., grafting) and be homogeneous blends. Most of the IPN's reported to date have involved heterogeneous systems,[1-9] usually with one rubbery phase and one glassy phase. This combination of rubbery and glassy polymers often results in a synergistic effect in properties,[3,6,7] particularly mechanical properties. Either high-impact plastics or reinforced rubbers result, depending on the morphology (i.e., phase continuity). The only instances in which apparently homogenous morphology has resulted are with IPN's in which grafting between the component polymer networks was a distinct possibility.[10-13] In this note we described IPN's which we believe approximate true IPN's with a single-phase morphology and no grafting between the distinct polymer networks. This was achieved by forming IPN's from polymers with known complete compatability by well-controlled cross-linking reactions.

Scheme I



Thus, IPN's, pseudo-IPN's (PDIPN's—only one polymer cross-linked), and linear blends of polystyrene (PS) incorporating poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) (whose compatability has been reviewed elsewhere[14]) were prepared, using for the IPN's and PDIPN's the simultaneous interpenetrating network (SIN) technique. The polystyrene was cross-linked by incorporating divinylbenzene. Several methods have been reported for synthesizing cross-linked PPO: for example, materials such as polysulfonazides and (hydroxymethyl)diphenyl oxide[15,16] have been used. However, these methods were found to be difficult to employ for simultaneous IPN's in which these two polymer networks are formed in situ at about the same time. In this study the PPO was first brominated and subsequently cross-linked with diethylamine (Scheme I).

Solubility studies and elemental analyses were performed to confirm that cross-linking did indeed occur. The cured polymers did not dissolve in either tetrahydrofuran or trichloroethane (both good solvents for PPO); however, swelling did occur to about twice the initial dimensions.

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Table I
Glass Transition Temperature ($T_g$) of the PPO/PS Blends by DSC and Rheovibron (°C)

| | wt % PPO/PS | | | | |
|---|---|---|---|---|---|
| | 100/0 | 75/25 | 50/50 | 25/75 | 0/100 |
| FIPN's (CPPO/CPS)[a] | 226 (232)[b] | 172 | 149 (145) | 120 | 83 (82) |
| PDIPN's-1 (CPPO/LPS) | 226 (232) | 266 | 234 (235) | 113 | 75 |
| PDIPN's-2 (LPPO/CPS) | 213 (222) | 162 | 138 (142) | 117 | 83 (82) |
| linear blends (LPPO/LPS) | 213 (222) | 152 | 130 (128) | 99 | 75 |

[a] C = cross-linked; L = linear. [b] Measured by Rheovibron.

The elemental analyses (N, Br) (Schwarzkopf) showed that only 10% of the bromine in PPO was involved in the cross-linking reactions, the remaining bromine being inactive (most likely as aromatic bromine). On the basis of the amount of bromine reacted, the number-average molecular weight between two cross-link sites ($\bar{M}_c$) in PPO was 17 000. The theoretical $\bar{M}_c$ of the cross-linked polystyrene was 7260. After the IPN's, both types of PDIPN's (one with linear PS and one with linear brominated PPO), and linear blends were formed as described in the Experimental Section, they were studied by electron microscopy, by measurements of the ultimate tensile stress (TS), by dynamic mechanical spectroscopy (Rheovibron), and by differential scanning calorimetry (DSC).

The electron micrographs of all the IPN's, PDIPN's, and linear blends showed the presence of only one phase. The pure brominated PPO phase appears darker in these electron micrographs (due to either extra staining by osmium tetraoxide or the presence of the bromine) than the lighter pure PS phase. The electron micrographs in all cases did not show any domains of either component.

The $T_g$'s of the full IPN's (FIPN's), PDIPN's, and linear blends are listed in Table I. The two glass transition temperatures measured by DSC and Rheovibron are within experimental error. In all cases one single broad $T_g$ was observed, indicating complete segmental mixing of the two polymers, in agreement with electron microscopy. The glass transition temperature in all cases varied systematically with the composition. The FIPN's showed higher $T_g$'s than the PDIPN's and the linear blends at the corresponding compositions. This is undoubtedly due to the higher $T_g$'s of the pure (cross-linked) components and does not relate to the morphology differences. The maximum of the difference in absolute value of the measured FIPN $T_g$ from the corresponding weight average of the pure polymer networks occurs at 75:25 (brominated) PPO/PS. It is believed that this indicates[13] that near that composition the greatest extent of additional chain entanglement occurs. This is confirmed by the behavior of the ultimate tensile strengths (TS) of the FIPN's. These are shown in Figure 1 together with the data on the PDIPN's and linear blends. The FIPN's showed an enhancement in the TS (presumably due to the extra entanglement) with a maximum at or near 25% PS (75% brominated PPO). The PDIPN's and linear blends of the brominated PPO and PS do not exhibit any maximum. The TS of the pure PS is somewhat lower than expected from the theoretical degree of cross-linking. The tensile strengths of the FIPN's are higher than those of the PDIPN's and the linear blends at the same composition. There is no significant difference in the tensile strength, in general, between the PDIPN's and linear blends. The enhancement in tensile strength is most likely due to the permanent chain entanglements in the FIPN's. In the case of PDIPN's and linear blends, the entanglements are only temporary and "untangling" can occur at large deformations because one or both polymers are linear (topological constraints do not exist).

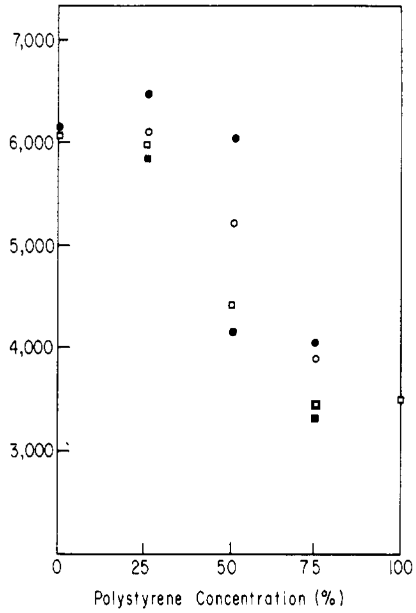

**Figure 1.** Tensile strength vs. polystyrene concentration: (●) CPPO/CPS; (○) CPPO/LPS; (□) LPPO/GPS; (■) LPPO/LPS.

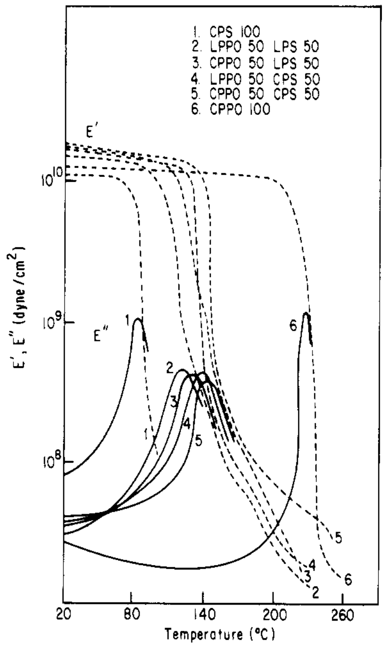

**Figure 2.** Temperature dependence of storage ($E'$) and loss ($E''$) moduli: (1) pure CPS; (2) 50:50 LPPO/LPS; (3) 50:50 CPPO/LPS; (4) 50:50 LPPO/CPS; (5) 50:50 CPPO/CPS; (6) pure CPPO.

The storage modulus $E'$ of FIPN, PDIPN's, and linear blends with 50% PS as a function of temperature is shown in Figure 2. From room temperature up to the respective $T_g$'s, the moduli of all the IPN's are higher than those of the pure components, with the modulus of the FIPN being the greatest. This synergism in modulus has been noted before in compatible PPO–PS blends[17] and has been ascribed to an increase in packing density due to blending. One would therefore expect the FIPN's to exhibit the greatest increase in modulus, since there should be a greater amount of permanent chain entanglements between the two networks which would result in a greater increase in packing density. The moduli sharply decrease near the $T_g$'s of each blend, respectively, as usual. The loss modulus $E''$ of this sample as a function of temperature is also shown in Figure 2. The loss modulus data show a single $T_g$, indicating extensive phase mixing. The $T_g$'s, however, are broader than those of the pure components.

## Experimental Section

**A. Preparation of Polymers and Polymer Blends. 1.** The PPO was brominated by direct bromination of poly(phenylene oxide) in solution. One liter of *s*-tetrachloroethane and 125.0 g (1.04 mol) of PPO ($\eta$ = 0.55 dL/g) were combined in a 3-L round-bottomed, three-necked flask equipped with a stirrer, thermometer, dropping funnel, and condenser. The reaction mixture, maintained under a nitrogen atmosphere and illuminated with a sun lamp, was stirred and heated to incipient reflux (136 °C). Bromine (7.86 g, 0.0492 mol) was added dropwise. Copious evolution of HBr carried off some of the bromine, so another equal amount of bromine was added. The reaction was maintained at 136 °C for 1 h and then cooled, and chloroform was added. The brominated PPO was precipitated by slow addition of methanol, filtered, and washed with methanol. The material was dissolved in chloroform and reprecipitated. The collected material was broken up in a Waring blender, filtered, washed well, and dried in vacuo at 60 °C overnight. A master batch of PPO (containing 4.75% bromine) was prepared by dissolving in toluene (20% by weight).

**2. Linear Blends.** The PPO solution and styrene monomer (inhibitor removed) were mixed with 1% azobis(isobutyronitrile) (AIBN) catalyst. The mixture was poured between glass plates with a Teflon spacer and subsequently polymerized at 70 °C for 24 h. The glass plate mold was kept in a horizontal position so that an even-thickness sheet could be obtained. Combinations of 75, 50, and 25% PPO by weight were made.

**3. Pseudo-IPN's (PDIPN's).** Two types of pseudo-IPN's were prepared, one from cross-linked PPO (CPPO)/linear polystyrene (LPS) (PDIPN-1) and the other from a linear PPO (LPPO)/cross-linked polystyrene (CPS) (PDIPN-2). The former PDIPN's were prepared from a mixture of PPO solution with ethylenediamine (cross-linking agent) and styrene monomer with AIBN. Ethylenediamine (1.4 g) was added to 40 g of PPO. The mixture of PPO solution and styrene monomer admixed with divinylbenzene and AIBN resulted in PDIPN-2. The curing conditions and compositions were the same as those for the linear blends.

**4. Full IPN's (FIPN's).** FIPN's (both polymers cross-linked) were prepared from the mixture of the PPO solution with ethylenediamine and stryene monomer with divinylbenzene and AIBN. The curing conditions and compositions were the same as those for the linear blends.

**B. Measurements. 1. Electron Micrographs.** The samples were prepared according to Kato's osmium tetraoxide staining technique[18] and a two-step sectioning method. The electron micrographs were taken at a magnification of 95 000 with an AEI 6B and a Philips 300 transmitting electron microscope.

**2. Differential Scanning Calorimetry.** The glass transition temperatures ($T_g$'s) were determined on a DSC-2 Perkin-Elmer differential scanning calorimeter. Measurements were carried out from 300 to 500 K under nitrogen at a scanning rate of 10 °C/min. Specimen sizes were on the order of 20 mg.

**3. Ultimate Properties.** The tensile strengths were determined on an Instron tensile tester at room temperature at a crosshead speed of 2 in./min, using dumbbell-shaped specimens (0.08 in. × 0.25 in. × 2 in.).

**4. Rheovibron.** Dynamic viscoelastic properties were measured on a Model DDV-II Rheovibron dynamic viscoelastometer (Toyo Instrument Co.). A frequency of 110 Hz and a heating rate of 2 °C/min were used in taking measurements over a temperature range of 20–260 °C. Nitrogen gas was purged through the sample chamber to avoid oxidation at high temperature.

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# Oxyluminescence of Random and Block Copolymers of Styrene and Butadiene

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In two previous studies of chemiluminescence of polymers, it was found that the oxyluminescence vs. temperature curve of a polymer exhibited a sharp inflection as the mechanism of the oxidation reaction changed with temperature.[1,2] The study was also extended to polymer mixtures. The luminescence curve of an incompatible mixture retained the characteristics of the component polymers,[2] but only one inflection was observed if the two polymers formed a compatible pair.[1] Furthermore, the inflection temperature of the compatible mixture changed systematically with composition. These results suggest that the proximity of the two different macromolecular chains plays an important role in the luminescent behavior of mixtures.

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