and the value of the reduced temperature at the volume transition is smaller.

On the basis of Figure 4, the phenomena observed in this study can be qualitatively understood by assuming that the reduced temperature (or the free energy, ΔF, of contact between polymer segments) is not a monotonic function of the percent Me_2SO. The reduced temperature must be high in both pure Me_2SO and pure water and has a minimum of negative value at approximately 70% Me_2SO. In this case the phase diagram is formed by replacing the lower half of Figure 4 with a mirror image of the upper half. The swelling curves then become a set of reentrant curves. The two transitions for larger amounts of ionizable group show larger volume changes and occur at closer values of percent Me_2SO.

The nonmonotonic dependence of the reduced temperature (or the free energy of contact ΔF) on percent Me_2SO may be interpreted in the following way. The copolymer gels (*N*,*N*-diethylacrylamide–sodium acrylate and *N*-isopropylacrylamide–sodium acrylate) are swollen in both pure Me_2SO and pure water. This behavior indicates that attractive interactions between polymer chain and solvent molecule dominate over the attraction between polymer chains. When Me_2SO and water are mixed, the two solvents have an attractive interaction resulting in an increase of free energy, ΔF, for polymer–polymer contact and in a decrease in reduced temperature. The increase in the affinity among polymer segments would induce the collapse of the polymer network. Therefore, the gels are collapsed in the intermediate range of mixtures of Me_2SO and water.

The volume change should be the same for the upper and the lower transitions if ΔF depends only on percent Me_2SO, but the volume changes observed experimentally at the two transitions are not identical. The volume change occurring at the lower Me_2SO concentration is usually larger than the one at the higher Me_2SO concentration. This difference can be explained by the dependence of the degree of ionization of sodium acrylate groups on the Me_2SO concentration, and probably due to the difference between the molar volumes of two solvent. In solutions with a higher Me_2SO concentration, ionization may be depressed because of the lower polarizability of Me_2SO than of water; thus the volume change at the upper transition is smaller.

V. Conclusion

The reentrant phenomenon has been observed for the first time in polymer gels. It will be of particular interest to study the behavior of a polymer network as the area of the closed-loop instability diminishes. Our preliminary experiments have shown that the size of closed-loop area can be changed by varying the network structure of the gel. Also to be studied is the situation where the reduced temperatures at which the two discontinuous transitions occur are brought to coincide. The kinetics of the reentrant phase transition at this special situation is of particular interest when temperature or solvent change involves two phase transitions simultaneously.

The phase transition in gels, marked by a discrete volume collapse, appears to be a universal phenomenon which can be observed by choosing appropriate combinations of polymers and solvents. Theoretical considerations also support this view. In addition to the scientific merit, it is important to study and understand the specific roles played by the chemical constituents in order to develop technology that employs polymer gels. The reentrant phenomenon seems to widen the possible application of the phase transition in gels to switches, memories, sensors, and mechanochemical transducers.

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Preparation of Deuterated Poly(2,6-dimethyl-1,4-phenylene oxide)

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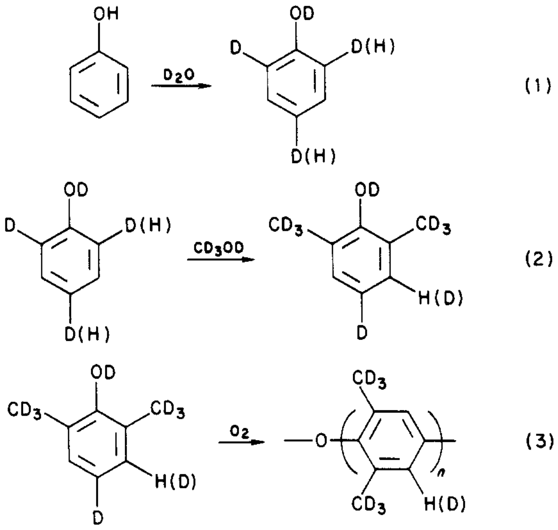
ABSTRACT: Phenol has been deuterated in the ortho and para positions with deuterium oxide using sodium deuterioxide catalysis and then has been methylated with perdeuteriomethanol over a magnesium oxide catalyst at 450 °C. A sample of 99.9% 2,6-dimethylphenol has been isolated from the reaction mixture and then oxidatively coupled to form poly(2,6-dimethyl-1,4-phenylene oxide). The deuterium content of the 2,6-dimethylphenol was 5.54 methyl and 1.33 aryl deuteriums per molecule and that of the polymer was 5.53 methyl and 0.36 aryl deuteriums per repeating unit.

Introduction

Neutron scattering studies on blends containing poly(2,6-dimethyl-1,4-phenylene oxide) required samples of the polymer with approximately 75% of the hydrogen replaced with deuterium.[1] The preparation of the monomer, deuterated 2,6-dimethylphenol, and such a polymer by reactions 1, 2, and 3 are described in this paper.



Experimental Section

Deuterium contents were determined by ^1H NMR spectroscopy on a Varian EM-390 spectrometer. Monomer purity was measured by gas chromatography with a Varian Model 3700 FID gas chromatograph using a 6-ft SE-30 column and calibrated with authentic samples of anisole, *o*-cresol, 2,6-dimethylphenol, 2,4-dimethylphenol, and 2,4,6-mesitol. The solvents and phenol were reagent grade. The amines in the catalyst for the polymerization were freshly distilled before use.

Deuteration of Phenol. Sodium metal (1.0 g, 0.043 g-atom) was added in several portions to phenol (75 g, 0.80 mol) and deuterium oxide (99.8 atom %; 43 g, 2.15 mol) in a 250-mL flask equipped with a reflux condenser and a heating mantle and maintained under a nitrogen atmosphere. The mixture was heated at reflux for 1 h and then a distillation head was attached. For the next 1.5 h 44 g of volatiles was distilled over in two fractions. As the second fraction cooled, phase separation occurred and the phenol-rich phase was collected in a pipette and transferred back to the flask. An additional 40 g (2.00 mol) of deuterium oxide was added to the flask, the mixture was heated at reflux for 0.5 h, 37 g of volatiles was distilled over, 40 g of deuterium oxide was added, the mixture was heated at reflux for 0.5 h, and 40 g of volatiles was distilled over. The reaction flask was cooled to 25 °C and sufficient carbon dioxide was introduced to convert any phenoxide to phenol. The distillation was continued; after a forecut (15 g, bp range 103–178 °C), 45 g of deuterated phenol was collected (bp 178 °C). The material contained 3.15 deuterium atoms per phenol. The distribution of deuterium on the aromatic ring positions based on the ^1H NMR spectrum corresponded to approximately a 1:2:1 molar ratio of 2,4- to 2,6- to 2,4,6- di- and trisubstituted rings: ^1H NMR ($CDCl_3$ vs. Me_4Si) 7.24 (*m*-H, s with adjacent D's, d (J = 9 Hz) with adjacent *p*-H), 6.89 (*p*-H, t (J = 9 Hz); *o*-H, d (J = 9 Hz)), 5.9 ppm (OH, ca. 0.1 per phenol).

Alkylation of Deuterated Phenol with Perdeuteriomethanol. A stainless-steel hot-tube reactor[2] containing a magnesium oxide catalyst[3] was preconditioned by passing deuterium oxide through it at a temperature of 450 °C. A solution of 40 g of the deuterated phenol (above), 50 g of perdeuteriomethanol (99.5 atom %), and 20 mL of deuterium oxide was introduced via a syringe pump into the reactor at a rate that provided a spatial velocity of 0.5 mL/(mL catalyst bed/h). Nitrogen was used as a carrier gas. The products were collected in a trap at 0 °C. GC analysis showed the following composition, in order of elution in weight percent: anisole, 0.2; phenol, 0.7; *o*-cresol, 16; *p*-cresol, 0.3; 2,6-xylenol, 63; 2,4-xylenol, 2.5; 2,4,6-mesitol, 16.

The reaction mixture was combined with a second reaction mixture from an identical alkylation reaction and then fractionally distilled at atmospheric pressure through a Vigreux column. Six fractions of ca. 15 g each were collected with a boiling point range between 190 and 210 °C. Each fraction was dissolved in pentane and cooled to 0 °C. The crystals that formed and the corresponding filtrates were analyzed by gas chromatography and then combined with other fractions of similar composition whenever possible. Repeated crystallizations were performed. The temperature for crystallization was increased to ca. 17 °C as purities approached 90% to achieve more efficient fractionation. When the purity of the xylenol reached 97–98%, further purification by medium-pressure liquid chromatography (MPLC) on silica gel with 25% ether–75% *n*-hexane as eluent gave 99.9% pure deuterated xylenol. With less pure samples (less than 90% xylenol), MPLC was much less effective in providing additional purification. The purification was carried out until approximately 6 g of deuterated 2,6-xylenol with 99.9% purity was obtained: ^1H NMR ($CDCl_3$ vs. Me_4Si) 7.02 (s, 1.7 *m*-H's), 5.0 (s, 0.67 H, OH), 2.20 ppm (s, 0.46 H, Me).

Polymerization. To a 50-mL three-necked Morton flask equipped with a mechanical stirrer, an oxygen inlet tube, and a thermometer were added 8 mL of toluene, 2.00 g of deuterated 2,6-xylenol (15.5 mmol), 1.00 mL of a solution containing 0.628 w/v % *N,N'*-di-*tert*-butylethylenediamine (0.0365 mmol) and 7.34 w/v % butyldimethylamine (0.726 mmol), and 0.020 mL of a 10 w/v % solution of Adogen 464 (tricaprylmethylammonium chloride). Oxygen was bubbled in at a flow rate of 0.3 SCFH, stirring was started, and 0.0110 mL of a solution of 1.18 g of cuprous oxide in 10 mL of 48% hydrobromic acid (0.009 mg-atom of Cu and 0.047 mg-atom of Br) was added. The temperature of the reaction mixture was maintained at 35–40 °C with a water bath. After 34 min, the reaction mixture was diluted with toluene and the polymer was precipitated by slowly adding 10 volumes of methanol. The polymer was separated by suction filtration, washed with methanol, and dried at 60 °C in a vacuum oven overnight: yield, 1.58 g (79%); intrinsic viscosity (chloroform, 25 °C), 0.57 dL/g; molecular weight by GPC (chloroform containing 0.5% ethanol, poly(2,6-dimethyl-1,4-phenylene oxide) calibration) M_w = 46 000, M_n = 19 400 (with a polystyrene calibration M_w = 68 500 and M_n = 28 900); ^1H NMR (deuteriochloroform vs. Me_4Si with *sym*-trioxane as internal standard) 2.07 (s, 0.47 H, Me), 6.48 ppm (s, 1.64 H, meta); glass transition temperature (midpoint by DSC) 225 °C (identical with an undeuterated polymer with a similar molecular weight).

Results and Discussion

In the first step of the preparation of the deuterated polymer, some of the hydrogen on phenol was exchanged with deuterium (reaction 1) to minimize hydrogen/deuterium exchange reactions in the alkylation step (reaction 2) which can occur at the oxygen and at the ortho and para positions. In the presence of sodium deuterioxide, reaction 1 proceeded rapidly at the reflux temperature. Distillation removed the water and a small portion of the phenol. After the first distillation, the phenol that had separated from the aqueous phase was returned to the remaining phenol in the distillation flask and then subjected to a second exchange. As before, distillation removed most of the water and a small amount of phenol. A third exchange with fresh deuterium oxide, followed by neutralization of the catalyst with carbon dioxide and the fractional distillation of the reaction mixture, produced a high boiling fraction of deuterated phenol. The composition of the mixture was estimated by ^1H NMR analysis to consist of ca. 50% 2,6-, 25% 2,4-, and 25% 2,4,6-deuteration. In all of these compounds the hydroxyl group was almost quantitatively deuterated.

The conversion of phenol to 2,6-xylenol (reaction 2) was carried out by a procedure similar to one used for alkylations described in the literature.[3] The heated column reactor which contained a magnesium oxide catalyst was first preconditioned by running the reaction with nondeuterated reactants. Next, deuterium oxide was passed through the heated column and then the reaction was carried out with the deuterated phenol and perdeuteriomethanol. The reaction products were a mixture of deuterated phenols (2,6-xylenol, 68%; *o*-cresol, 16%; 2,4,6-mesitol, 16%; 2,4-xylenol, 2%; phenol, 0.7%; *p*-cresol,

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0.4%) and a trace of anisole (0.2%). The 2,6-xylenol was separated from the mixture by fractional distillation, followed by multiple recrystallizations and then medium-pressure liquid chromatography. The purity of the final product was determined by gas chromatography to be 99.9%.

The quantity and location of the deuterium in the 2,6-xylenol were determined by ^{1}H NMR spectroscopy. The spectrum was measured in the presence of an internal standard (*sym*-trioxane). The quantity of methyl protons (0.46 at 2.20 ppm) showed that 92 atom % substitution of deuterium on the methyl groups had occurred. No para-substituted hydrogen was observed, indicating complete deuteration at that site. Some of the meta hydrogens (15%) were also absent (1.70 H's at 7.02 ppm). Apparently under the extreme conditions of the alkylation reaction, slow exchange also occurred at this relatively unreactive position. A peak at 5 ppm, due to 0.67 hydroxyl hydrogen, was indicative of exchange at the hydroxyl during the isolation and purification.

The polymerization (reaction 3) was carried out with a copper/diamine catalyst.[4] High molecular weight (intrinsic viscosity in chloroform, 0.57 dL/g; M_w from GPC using poly(phenylene oxide) standards, 43 800 daltons) polymer was obtained in the same reaction time required for polymerization of the nondeuterated monomer. Thus, there is no discernible isotope effect in the polymerization.

The ^{1}H NMR spectrum of the deuterated polymer was measured with *sym*-trioxane present as an internal standard. A weak resonance at 2.05 ppm corresponded to 0.47 methyl H per repeat (92 atom % deuterium on the methyls)—identical with the value for the methyl groups in the monomer. The intensity of the resonance for the aryl hydrogens at 6.48 ppm corresponded to 1.64 hydrogens per repeat unit (18 atom % deuterium on the rings). An increase in deuterium on the ring was expected based on a suggestion[5] that an NIH shift[6] during 2,6-xylenol polymerization can result in a transfer of the hydrogen in the 4-position of monomer to the 3-position of the repeat unit in the polymer.

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Temperature Dependence of Neutron Scattering Behavior and Resultant Thermodynamics of Mixing of Poly(2,6-dimethyl-1,4-phenylene oxide) in Polystyrene[†]

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ABSTRACT: Small-angle neutron scattering (SANS) measurements have been carried out as a function of temperature on blends of polystyrene with poly(2,6-dimethyl-1,4-phenylene oxide). From the temperature dependence of the interaction parameter, χ_{12}, a negative heat of mixing consistent with calorimetry values and a negative local entropy of mixing are derived. A Θ temperature of 345 °C has been estimated. The spinodal has been simulated from the thermodynamic data and Flory's equation-of-state theory and has been compared with the position of the spinodal estimated from the SANS measurements. Phase separation is predicted to occur above 350 °C.

Introduction

During the past few years a great deal of interest has been shown in the thermodynamics and physical and mechanical properties of polymer blends. It was thought that high molecular weight polymers were basically immiscible but many polymers have now been shown to be miscible.[1]

There is increasing evidence that polymer miscibility can be effected by specific interactions between the polymers. These specific interactions give rise to favorable heats of mixing which dominate any unfavorable noncombinatorial entropy contributions which may arise. One such miscible blend which is of considerable interest is that of polystyrene (PS) with poly(2,6-dimethyl-1,4-phenylene oxide), trivially named poly(xylenyl ether) (PXE), which forms the basis of a set of engineering thermoplastics. All the evidence indicates that PS/PXE blends are miscible in all proportions and over a considerable range of molecular weights.[2-4] Phase separation has not been observed for the pure PS/PXE blends but the addition of a sufficient amount of one of the halogens[5-8] to either the phenyl group of the PS or the phenylene ring of the PXE will cause phase separation. PS/PXE blends have a negative heat of mixing[9] and also a negative volume of mixing,[10] both of which are indicative of a favorable specific interaction. The actual nature of the specific interaction has not been completely elucidated but there is some evidence of an interaction between the phenyl and phenylene rings[3] and

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