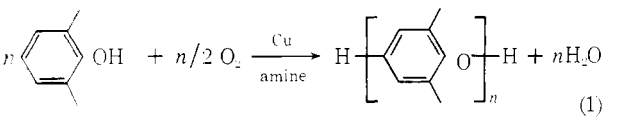
Communications to the Editor

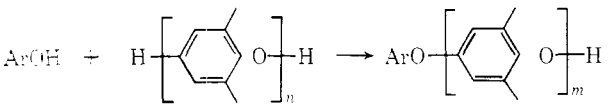
Block Copolymers by Oxidative Coupling of Phenols

The oxidative coupling of 2,6-disubstituted phenols, usually accomplished by reaction with oxygen in the presence of a copper–amine complex catalyst, yields poly(arylene ethers).[1] Copolymers, presumably of



(1)

random structure, have been reported from the oxidation of mixtures of phenols.[2] The possibility of forming block copolymers by sequential oxidation of two or more phenols appeared unlikely, in view of the rapid redistribution reaction which accompanies the polymerization; addition of a monomeric phenol to a polymerizing mixture has been shown to cause a rapid decrease in solution viscosity as redistribution converts the polymer already formed to a mixture of low oligomers.[3,4]



$m = 1, 2 \ldots$ (2)

We have found that block copolymers of 2,6-dimethylphenol (I) and 2,6-diphenylphenol (II) can be obtained by polymerizing the diphenylphenol, adding dimethylphenol, and continuing polymerization. The reverse procedure, addition of II to the growing polymer from I, results in randomization. Oxidation of a mixture of the two phenols simultaneously, as expected, produces random copolymer. Formation of block copolymers requires an active polymerization catalyst, such as tetramethylbutanediamine–cuprous bromide. With this catalyst the oxidative coupling of I at 25° is much faster than its redistribution with the polymer from II.

A mixture of 0.288 g (0.002 mol) of cuprous bromide, 0.284 g of N,N,N′,N′-tetramethyl-1,3-butanediamine, and 5.0 g of anhydrous magnesium sulfate was stirred at 25° in 140 ml of benzene, with a vigorous stream of oxygen introduced near the bottom of the flask. After 5 min 9.9 g (0.04 mol) of 2,6-diphenylphenol and 4.9 g (0.04 mol) of 2,6-dimethylphenol were added and the oxidation was continued for 5 hr. The mixture was filtered and the polymer was isolated in 92% yield by precipitation in methanol; the composition, determined by integration of the methyl and aromatic protons in the nmr spectrum, was 49 mol % I and 51% II.

A second polymer was prepared in the same way but with only the diphenylphenol added initially.

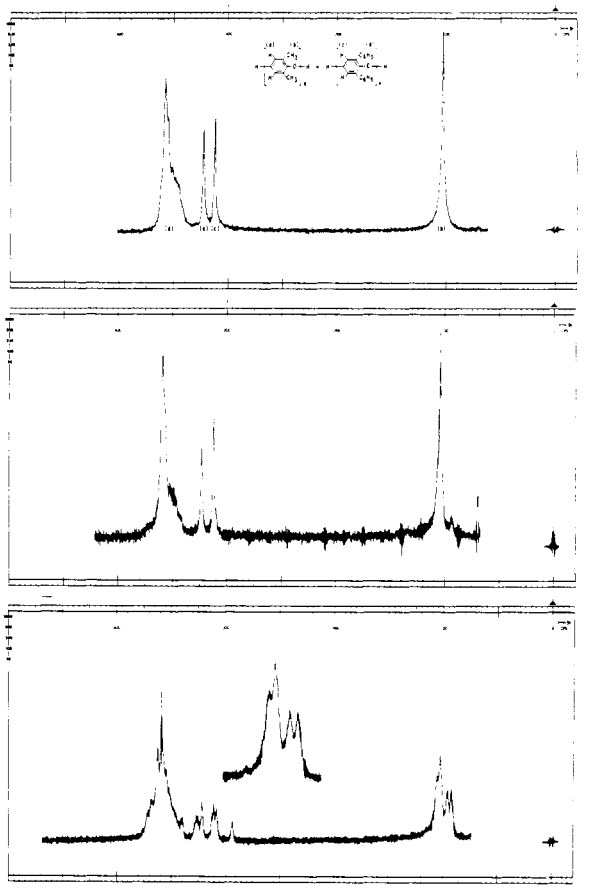


Figure 1. Proton nmr spectra of dimethylphenol–diphenylphenol copolymers. Top, mixture of homopolymers; center, block copolymer; bottom, random copolymer.

After 3 hr the dimethylphenol was added and polymerization was continued for 50 min more. The polymer was obtained in 90% yield and contained 45 mol % I and 55% II.

The random structure of the polymer obtained by simultaneous oxidation of both monomers is apparent from its nmr spectrum (Figure 1), most clearly shown in the methyl region, which has four peaks, at δ 2.13, 2.08, 1.95, and 1.87 ppm, corresponding to the four possible environments of the methyl protons. A methyl-substituted ring may be between two methyl-substituted rings (M*M*M), between two phenyl-substituted rings (P*M*P), or between one of each type. In this last case the phenyl-substituted ring may lie toward the "head" of the chain (M*M*P) or in the opposite direction (P*M*M). From an examination of the effect of substituting phenyl for methyl in model compounds, the expected values of the chemical shift are M*M*P, 2.17 ppm; M*M*M, 2.08 ppm; P*M*P, 1.94 ppm; P*M*M, 1.85 ppm.[5]

The copolymer obtained by adding I to the growing polymer from II clearly has a block structure. Positions of the peaks due to the aromatic backbone protons are identical with those of the two homopoly-

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(2) A. S. Hay and D. M. White, *Polym. Preprints*, **10**, 92 (1969).
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(4) G. D. Cooper, *Ann. N. Y. Acad. Sci.*, **159**, 278 (1969).
(5) G. D. Cooper, and J. G. Bennett, unpublished work.

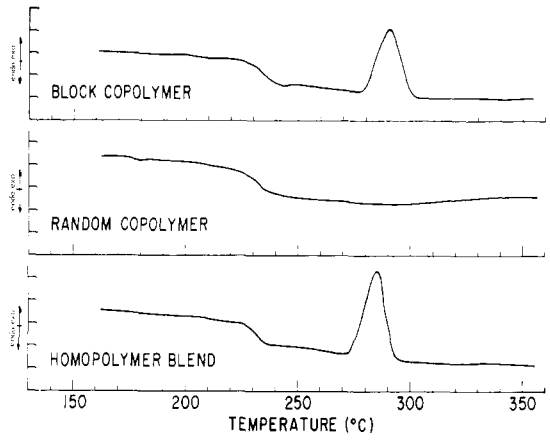

Figure 2. Differential scanning calorimetry traces of dimethylphenol–diphenylphenol copolymers.

mers, while the methyl protons are almost exclusively of the M*M*M type; a small peak at δ 1.86 ppm (P*M*M) presumably corresponds to a juncture between blocks. The absence of dimethylphenol homopolymer is established by the fact that a 20% solution of the copolymer in methylene chloride is stable indefinitely; dimethylphenol homopolymer, even of very low molecular weight, precipitates from methylene chloride as a crystalline polymer–CH_2Cl_2 complex.[6]

Both the random and block copolymers are amorphous as initially obtained and show a single glass transition at 227° (Figure 2). The glass transitions of the homopolymers are too close (225° for dimethylphenol polymer[7] and 230° for diphenylphenol homopolymer[8]) to permit the observation of separate transitions in the block copolymer. Diphenylphenol homopolymer crystallizes when heated above the glass transition and then melts at 480°.[8] The diphenylphenoxy portion of the block copolymer crystallized at 290°, as does the homopolymer, but melting could not be observed because of the onset of decomposition at approximately 450°.

Acknowledgment. The authors are indebted to R. A. Kluge for assistance in the interpretation of dsc and nmr results.

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Study of Crystallinity in Polymers by the Use of "Molecular Probes"

Recent experiments in our laboratories[1,2] have shown that the technique of gas chromatography can be utilized to obtain information about polymer structure and interactions in the solid phase. Although it might appear reasonable to apply the name "gas chromatography of polymers" to such experiments, the terminology is misleading in that the polymer is obviously not in the gas phase, nor is it undergoing a chromatographic separation. The terms glpc (gas–liquid partition chromatography) and gspc (gas–solid partition chromatography) appear to be equally inapplicable. In fact the nature of the experiment has more in common with the molecular beam technique for gas reactions and we prefer therefore to refer to these as studies on polymers using "molecular probes."

In essence, the experiment involves sending a pulse of molecules along a narrow tube which has a thin coating of the polymer to be investigated covering the inner wall or dispersed on an inert support. The probe molecules will undergo random diffusional motion in all directions, upon which is superimposed a velocity U in the forward direction maintained by a flow of inert carrier gas. In general each of the probe molecules will have a velocity component U_p perpendicular to the flow direction which will cause it to impinge on the polymer surface at the wall. If there is no interaction with the polymer there will be no alteration in the component of velocity U_f in the forward direction. On the other hand, any interaction will result in a retardation of the net translational velocity of the probe molecules along the tube direction. The nature of the interaction can be deduced from this change in velocity by application of rather simple theoretical considerations.

In the previous studies[1,2] we showed that the "molecular probe" technique could be used to study glass transitions and thermodynamic interactions in polymer systems. In the present communication we wish to report preliminary studies which indicate that this technique may also represent a powerful new method for studying crystallinity in macromolecules.

The first suggestion that crystallinity in polymers might be studied by gas chromatography is due to Alishoev, Berezkin, and Mel'nikova,[3] who used powdered polyethylene and polypropylene (1%) mechanically mixed in a column of glass beads. Using tetradecane and hexadecene as probe molecules they showed a relatively sharp transition in the retention volume and peak width at a temperature corresponding to the melting point of the polymer. They suggested that the method might be used to estimate the degree of crystallinity in the polymer but gave no further indication of how this could be done. Further they stated that the transition virtually disappeared when the polymer was coated from solution onto the support, which is not confirmed in the present work.

Experimental Section

A Microtek Model DSS-162 gas chromatograph with dual hydrogen flame detectors was modified to include an accurate flow control and pressure gauge on the carrier gas inlet. Oven temperatures were measured to the nearest $^1/_{10}$° using a precision mercury thermometer which was inserted through a 0.25-in. hole drilled through the oven wall. Polyethylene and polypropylene were coated on Chromo-

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