Curing Partially Brominated Poly(isobutylene-*co*-4-methylstyrene) Elastomers with Phenolic Resins: Mechanistic Investigation

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Received 19 November 1998; accepted 24 May 2000

ABSTRACT: The crosslinking of partially brominated poly(isobutylene-*co*-4-methylstyrene) elastomer **1** by phenolic resin crosslinkers was investigated. The curing was modeled using small molecule analogs of the elastomer and the phenolic resin. In order to mimic the conditions that prevail within the highly aliphatic rubber, the study was carried out in isooctane using catalysts such as coated ZnO that are compatible with such low polar media. *In situ* NMR analysis was used to probe the reaction between the molecular analogs. *p*-Isopropyl benzyl bromide was used as the elastomer analog and hydroxymethyl phenols were used as the resin analogs. Isotopic labeling allowed for independent yet simultaneous monitoring of the reactivity of the elastomer and resin analogs. The resin analog reacted with the elastomer analog via an electrophilic aromatic substitution, leading to the formation of a dibenzyl type ether and benzyl-phenyl type ethers as reaction intermediates. At lower temperatures the elastomer analog reacted with itself in a competing "self-cure" process that may be suppressed by increasing the homogeneity of the reaction mixture or by increasing the temperature of the reaction. The applicability of the mechanism was confirmed by successful model cure experiments involving a low molecular weight sample of elastomer **1** and the phenolic resin analog. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 680–685, 2001

Key words: bromination; poly(isobutylene-*co*-4-methylstyrene); elastomer; phenolic resin

INTRODUCTION

Although the crosslinking chemistry of elastomers has been widely investigated,[1] the development of new elastomers such as the recently introduced copolymers of isobutylene and *p*-methylstyrene requires that new curing processes or conditions be established. Of particular interest are crosslinking chemistries that involve not only the *p*-methylstyrene moieties of this copolymer but also derivatives thereof, such as the partially brominated polymer **1**. The presence of benzylic bromide and aromatic moieties confer on this new elastomer its unique reactivity and affords new avenues for postmodification of the elastomer and its curing through novel crosslinking pathways. The classical crosslinking mechanism associated with the reactivity of the allylic hydrogens in common unsaturated elastomers is not applicable

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Contract grant sponsor: U.S. Department of Energy Division of Materials Sciences (to J.M.J.F.); contract grant number: DE-AC03-76SF00098.

Journal of Applied Polymer Science, Vol. 80, 680–685 (2001)

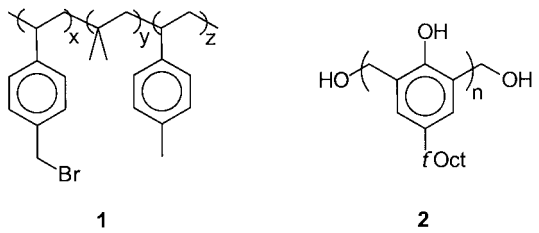

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Figure 1 Brominated poly(isobutylene-*co*-4-methylstyrene) and phenolic resin.

to this new type of elastomer. The presence of benzylic halide and aromatic moieties suggest that the well-understood electrophilic aromatic substitution reaction may be the most attractive crosslinking pathway involving the formation of highly stable carbon–carbon bonds. Although the polymerization of benzylic halides is well documented,[2–5] it has remained of little practical value because of the lack of precise control over the process. As a result, this polymerization is not attractive as a crosslinking pathway for elastomers **1**.

In an earlier study we used model compounds such as *p*-isopropylbenzyl halides to model the crosslinking of brominated poly(isobutylene-*co*-4-methylstyrene) using a variety of organic and inorganic zinc salts.[6] These model studies proved to be directly applicable to predicting the mechanism of crosslinking of the elastomer and helped develop improved conditions for its curing. In related systems involving novel resist materials, which were also based on cationically crosslinked benzylic species, similar model studies proved invaluable in the optimization and commercialization of both the approach and the materials.[7–9]

Phenolic resins are often used as cure promoters with halogenated elastomers, and the detailed mechanism of their action has remained elusive. We now report on the mechanistic insight we acquired for the novel cure of partially brominated poly(isobutylene-*co*-4-methylstyrene) **1** and a phenolic resin crosslinker **2** in the presence of Zn salts[10] using small molecule analogs as model compounds (Fig. 1).

p-Isopropylbenzylbromide (PIBB) **3** and *o*-hydroxybenzyl alcohols **4** and **5** (Fig. 2) were chosen as model compounds for the partially brominated poly(isobutylene-*co*-4-methylstyrene) **1** elastomer and the phenolic resin crosslinker **2**, respectively; Zn salts,[10] and more particularly coated ZnO, were selected as the catalysts. Isooctane was used as the solvent to simulate the nonpolar environment found within the largely aliphatic brominated poly(isobutylene-*co*-4-methylstyrene) copolymers. Resin analogs **4** and **5** were deuterated at the benzylic position in order to differentiate them from the elastomer analog. Isotopic labeling allows the reaction of the resin analog to be monitored by ^{2}H-NMR while the reaction of the elastomer analog may be monitored by ^{1}H-NMR.

EXPERIMENTAL

Materials

p-Isopropyltoluene (PIPT), *p*-isopropylbenzyl alcohol (PIBA), 2,4-dimethyl phenol, and *p*-octylphenol were purchased from Aldrich and used without further purification. Coated ZnO (Kadox) was obtained from the Zinc Corporation of America. The solvents used for the NMR study, isooctane (Fisher Scientific) and isooctane-d_{18} (Isotec), were also used without further purification. In the following text deuterated compounds are indicated by the italic letter *d*.

Methods

Preparation of PIBB

The PIBA (11.27 g, 75 mmol) was dissolved in 50 mL of dry benzene and cooled in an ice bath. Phosphorus tribromide (7.04 g, 26 mmol) was added to the mixture and stirred for 2 h. The mixture was then quenched with 2 mL of water to destroy unreacted PBr_3. The solvent was removed *in vacuo* and the residue was extracted with chloroform, dried over $MgSO_4$, filtered, and removed *in vacuo*. The product was purified by distillation under a vacuum (bp 82°C at 1 mmHg). The PIBB had spectral characteristics consistent with the literature data.[11]

Preparation of Deuterated 2-Hydroxy-3,5-dimethylbenzyl Alcohol-d_2

2,4-Dimethyl phenol (3.1 g, 25 mmol) was mixed with deuterated paraformaldehyde-d_2 (1.6 g, 50

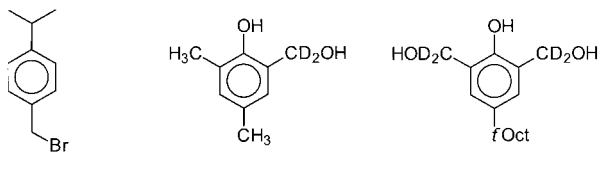

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Figure 2 Small molecule analogs of the elastomer and the phenolic resin.

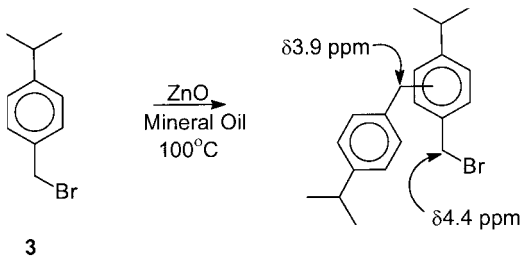

Figure 3 The reaction of PIBB in the presence of ZnO.

mmol), K_2CO_3 (5.3 g, 40 mmol), and 45 mL of water. This mixture was stirred at 50°C for 4 h. After allowing the reaction mixture to cool to room temperature, the reaction mixture was saturated with carbon dioxide by adding dry ice. The resulting solution was extracted with ethyl acetate. The organic layer was separated and dried over $MgSO_4$, and the solvent was removed *in vacuo*. The crude product was purified by column chromatography on silica gel using 15% ethyl acetate in hexanes as the eluent to yield the pure product as a white solid (2.8 g, 18 mmol, 73% yield). The PIBB had spectral characteristics consistent with the literature data.[12]

*Preparation of Deuterated 4-(t-*Octyl)-2,6-bis(hydroxymethyl)phenol-d_4

4-(*t*-Octyl)phenol (2.7 g, 13 mmol) was mixed with deuterated paraformaldehyde-d_2 (1.6 g, 50 mmol), K_2CO_3 (5.3 g, 40 mmol), and 25 mL of water. This mixture was stirred at 50°C for 8 h. After allowing the reaction mixture to cool to room temperature, it was saturated with carbon dioxide by adding dry ice. The resulting solution was extracted with ethyl acetate. The organic layer was separated and dried over $MgSO_4$, and the solvent was removed *in vacuo*. The crude product was purified by column chromatography on silica gel using 20% ethyl acetate in hexanes as the eluent to yield the pure product as a white

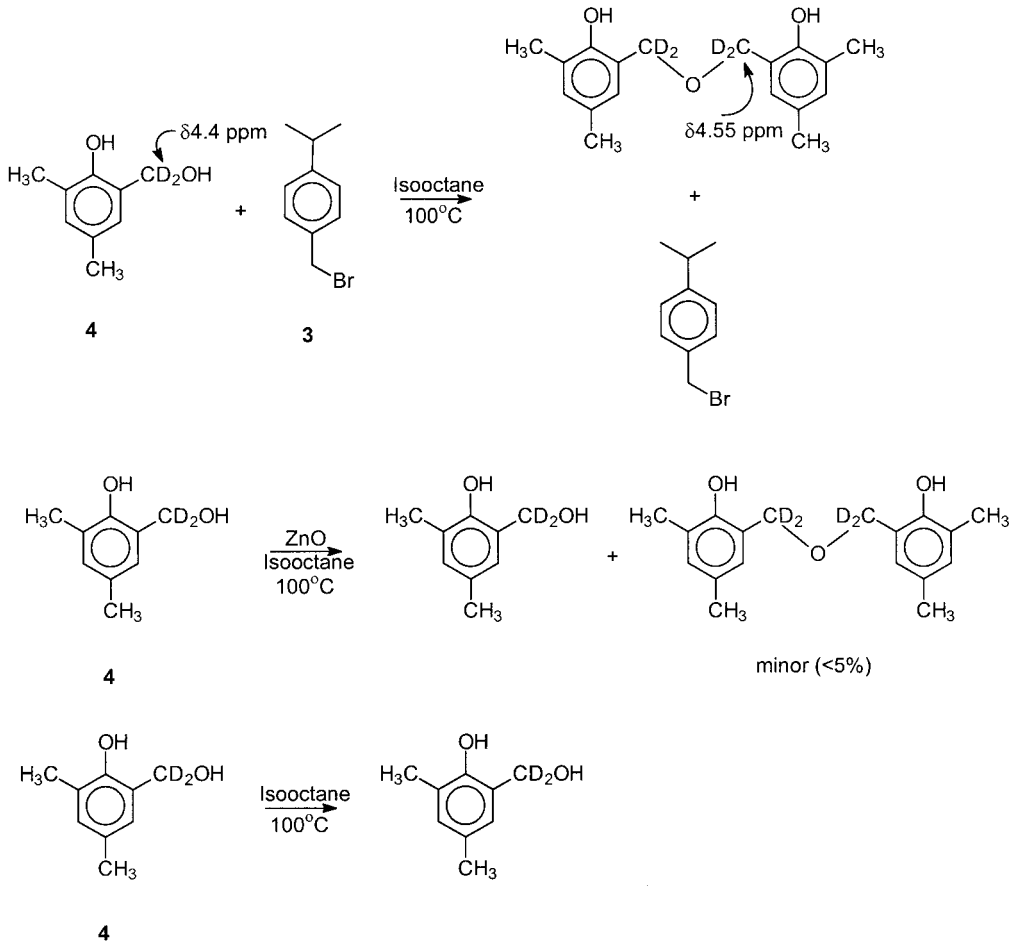

Figure 4 Control experiments among PIBB, resin analog **4**, and ZnO.

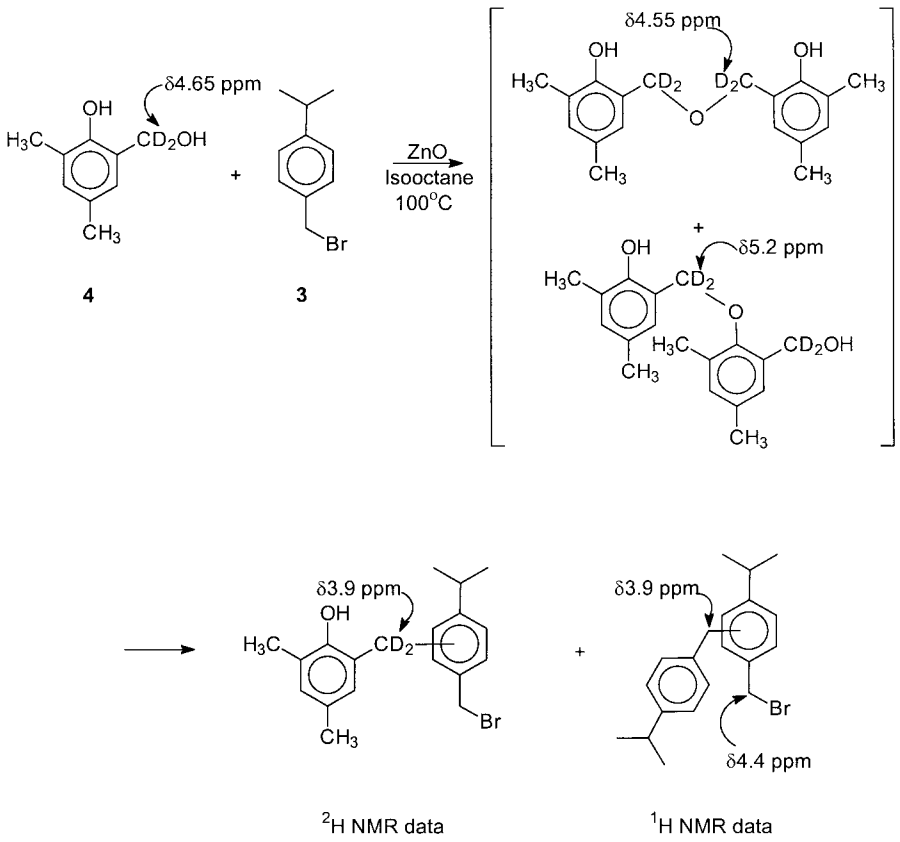

Figure 5 The reaction between PIBB and resin analog **4** at 100°C in the presence of ZnO.

solid (1.2 g, 4.5 mmol, 34% yield). The PIBB had spectral characteristics consistent with the literature data.[12]

Model Studies

The model studies were carried out by dissolving 0.25 mmol of the model compounds in 1 mL of isooctane followed by the addition of the desired powdered catalyst, coated ZnO (Kadox). This dispersion was then transferred to an NMR tube and the progress of the reaction was monitored by recording ^{2}H- and ^{1}H-NMR spectra over time at 80 and 100°C.

RESULTS AND DISCUSSION

PIBB is known to react with itself in a nonpolar medium in the presence of ZnO via electrophilic aromatic substitution.[13] The resulting oligomeric products show a new benzylic resonance at $\delta = 3.9$ ppm, as well as the original benzylic bromide resonance at $\delta = 4.4$ ppm, in the ^{1}H-NMR spectrum. It was proposed that this electrophilic aromatic substitution that occurs at elevated temperatures is catalyzed by a ZnBrX species, which is generated *in situ* by the reaction between PIBB and ZnO (Fig. 3).[14]

The following control experiments were carried out (Fig. 4). Resin analogs by themselves were found to remain unchanged when heated in isooctane at 100°C over a period of 2 h. In the presence of an equivalent amount of ZnO, a small amount of the resin analog (<5%) was converted to the corresponding dibenzyl ether. In the presence of an equivalent amount of PIBB, the resin analog was quantitatively converted to the corresponding dibenzyl ether while the PIBB remained unchanged. These observations indicated that there was no significant reaction between the resin analog and PIBB in the absence of ZnO and between the resin analog and ZnO in the absence of PIBB.

When the model study was carried out by mixing equimolar amounts of resin analog **4**, PIBB, and ZnO in isooctane at 100°C (Fig. 5), three new

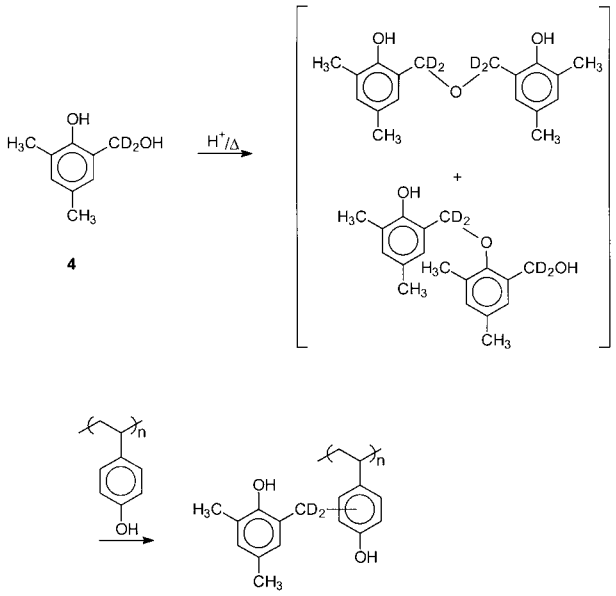

Figure 6 The reactivity of the resin analog under acidic conditions.

peaks were observed in the ^{2}H-NMR spectrum at δ = 5.2, 4.55, and 3.9 ppm, as was a peak at δ = 4.65 ppm that corresponded to starting material **4**. As the reaction proceeded the peak at δ = 3.9 ppm grew while all three other peaks diminished. Monitoring the same system by ^{1}H-NMR showed a new peak at δ = 3.9 ppm, while the peak δ = 4.4 ppm corresponding to the benzylic bromide remained as the major peak until the end of the reaction.

The above observations were rationalized as follows. In the ^{2}H-NMR spectrum the new peaks at δ = 5.2 and 4.55 ppm indicated the formation of benzyl-phenyl ether and dibenzyl ether linkages,

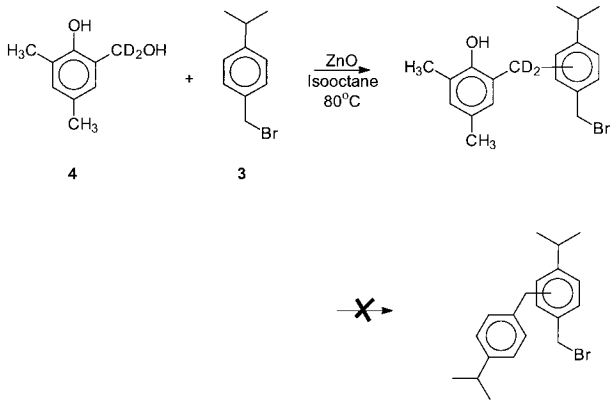

Figure 7 The reaction of PIBB with resin analog **4** at 80°C.

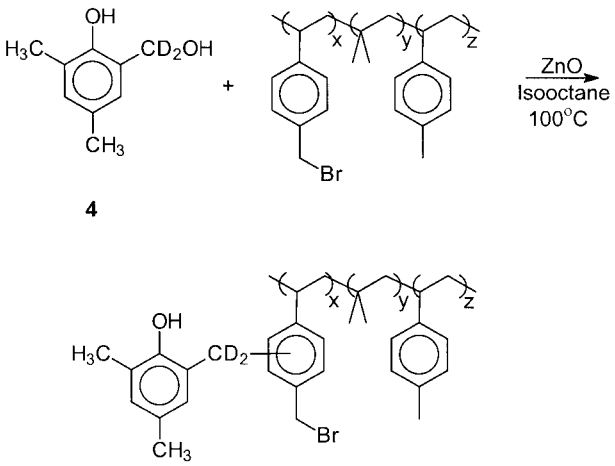

Figure 8 The reaction of EXXPRO® **1** with resin analog **4** in the presence of ZnO.

respectively. The peak at δ = 3.9 ppm corresponded to the desired "cure" product formed by electrophilic aromatic substitution of the resin analog on PIBB. This reaction of the resin analog with PIBB is referred to as the desired cure reaction. Data from the ^{1}H-NMR spectrum further indicated that the PIBB was reacting with itself via a competing "self-cure" process. The observed reaction pattern of resin analog **4** was consistent with its earlier known behavior under acidic conditions (Fig. 6).

When the above-mentioned model study was carried out at 80°C instead of 100°C (Fig. 7), the reaction of the resin analog with the elastomer analog (PIBB) was observed while the competing reaction of PIBB with itself was suppressed completely. Thus, the kinetics of the desired cure reaction were clearly more favorable than those of the self-cure process and temperature may be used as a tool in promoting the desired cure reaction over the self-cure of the elastomer. This is particularly significant in view of the importance of cure temperature in commercial processes.

Similar results were obtained when the model studies were carried out at 100°C using resin analog **5** instead of **4**, although two significant differences were observed. The rate of the desired cure reaction was higher with compound **5**, and the reaction of PIBB with itself was minimized. The above observations can be attributed to the higher solubility of **5** in the reaction medium when compared to **4**. Another significant point was that the desired cure process involving reaction of the resin analog with PIBB was faster than the self-cure reaction of PIBB itself. Thus, the

nature of the crosslinks was probably dictated by the homogeneity of the system and may well be diffusion controlled.

In order to test the validity of the proposed crosslinking pathway in the polymeric system, the model studies were repeated with the actual elastomer in place of the PIBB. These experiments were carried out at 100°C by first dissolving partially brominated poly(isobutylene-*co*-4-methylstyrene) in isooctane, then mixing it with resin analog **4** and ZnO (Fig. 8). The results from this experiment were analogous to those with PIBB. The data from the ^{2}H-NMR spectrum indicated that resin analog **4** reacted with the elastomer via electrophilic aromatic substitution, although the reaction observed in the polymer system was slower than that with the PIBB model system. This can be rationalized by the increase in viscosity and the resulting decrease in mobility that occurred when polymer **1** was used instead of its low molecular weight analog.

In conclusion, the model studies carried out with the deuterated analogs of phenolic cure agents demonstrated the power of model experiments in understanding crosslinking processes that, by their very nature, are extremely difficult to monitor by currently available direct techniques. This study sheds light on the chemical nature of the crosslinks between brominated poly(isobutylene-*co*-4-methylstyrene) and these phenolic resins. The results also show possible ways to control the curing using the reaction temperature and homogeneity of the formulation. While mechanistic studies relying largely on model compounds cannot replace the experimentation that is carried out on the elastomers themselves,[15] it is expected that the information they provide will be invaluable in understanding the actual cure processes and therefore enhance the process of cure optimization.

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