Amine Substitution Reactions of Brominated Poly(isobutylene-*co*-isoprene): New Chemical Modification and Cure Chemistry

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ABSTRACT: Nucleophilic substitution reactions of brominated poly(isobutylene-*co*-isoprene) (BIIR) with amines are characterized through studies of a model compound, brominated 2,2,4,8,8-pentamethyl-4-nonene (BPMN), and analysis of BIIR cure rheology. Nucleophilic amines do not accelerate HBr elimination from the allylic bromide within BIIR but readily engage in N-alkylation reactions with this functional group. N-Alkylation and accompanying proton-transfer reactions are shown to be reversible, and the distribution of allylic bromide, ammonium bromide salts, and their corresponding amines is dictated by equilibrium thermodynamics. *N*,*N*-Dimethyloctylamine and *N*-methyloctadecylamine undergo a single N-alkylation reaction with BPMN, while octylamine forms bis-N-alkylation products that can be used to generate stable cross-linked BIIR networks.

Introduction

Bromination of poly(isobutylene-*co*-isoprene) to generate BIIR yields an elastomer that has the air impermeability required for tire inner liner applications and the cure reactivity required to generate adhesion between the tire inner liner and its carcass. While superior sulfur vulcanization kinetics are known to originate from the exo-allylic bromide structure of BIIR, the cure chemistry of this commercially important elastomer is poorly understood.[1] The allylic bromide functionality of the elastomer responds to standard cure accelerators in an anomalous manner, and it is susceptible to isomerization and elimination reactions at elevated temperature that can detract from end-use performance.[2] Our current interest is in understanding the intrinsic reactivity of the material, especially substitution reactions of BIIR with amines. As will be demonstrated, it is possible to cross-link BIIR with an appropriate choice of amine; it is also possible to chemically modify BIIR with an appropriate amine without cross-linking the elastomer.

The low level of reactive functionality within BIIR (1−2% allylic bromide) complicates attempts to characterize its reaction products, especially where reaction leads to excessive cross-linking. We have therefore studied a low molecular weight model compound, brominated 2,2,4,8,8-pentamethyl-4-nonene (BPMN, **1**), whose reaction products are amenable to chromatographic separation as well as characterization by NMR and mass spectroscopy. This model compound approach has been applied by others for the study of IIR structure[3] and halogenation chemistry,[1,4] and we have recently employed this methodology to detail the thermal stability of BIIR.[5] These studies have demonstrated consistency in the product distributions derived from BIIR and BPMN, thereby providing confidence in the model's ability to reflect the behavior of the polymeric system.

In this report we demonstrate a range of nucleophilic substitution reactions of BIIR with 1°, 2°, and 3° amines through studies of BPMN reactivity and by cure rheometry on the polymer. Substitution reactions of the allylic bromide and accompanying proton-transfer reactions are defined and rationalized on the basis of thermodynamic equilibria.

Experimental Section

Materials. Brominated 2,2,4,8,8-pentamethyl-4-nonene (BPMN, **1**) was prepared as described previously.[5] The following reagents were used as received from Sigma-Aldrich (Oakville, Ontario): octylamine (97%), *N*-methyloctadecylamine (98%), *N*,*N*-dimethyloctylamine (95%), 1,8-bis(dimethylamino)naphthalene (Proton-Sponge), and hydrobromic acid (48% in water, 99.999%). BIIR (Bayer BB2030) was used as supplied by Bayer Inc. (Sarnia, Ontario).

Synthesis and Isolation of (*E*/*Z*)-*N*,*N*-Dimethyl-*N*-octyl-6,6-dimethyl-2-(2,2-dimethylpropyl)hept-2-enylammonium Bromide (5a). A solution of BPMN (0.135 g, 0.492 mmol), *N*,*N*-dimethyloctylamine (0.077 g, 0.492 mmol), and dodecane (0.2 mL) was heated at 100 °C for 4 h, yielding a brown solid. The reaction mixture was filtered and washed with hexanes, and the solid residue was dissolved in Et_2O and washed with distilled water (2 × 10 mL), saturated $KHCO_3$ (2 × 10 mL), and saturated NaCl (2 × 10 mL). The organic phase was isolated, and the mixture was concentrated in vacuo. Volatile components were removed by Kugelrohr distillation (P = 0.6 Torr, T = 80 °C) to give the residue, **5a**. High-resolution MS analysis; required for $C_{24}H_{50}N^+$ *m*/*e* 352.3943, found *m*/*e* 352.3943. ^{1}H NMR ($CDCl_3$): δ 0.8−2.2 (m, 52.63H, 2 × $-C(CH_3)_3$, 3 × $-CH_2-$, $-(CH_2)_6CH_3$), 3.28 (s, 2.61H, $-CH_3$), 3.29 (s, 3.28H, $-CH_3$), 3.47 (t, 0.90H, $-C-CH_2$), 3.65 (t, 1.19H, $-C-CH_2$), 4.05 (s, 0.99H, $=C-CH_2$), 4.09 (s, 0.98H, $=C-CH_2$), 5.87 (t, 0.60H, $=C-H$), 6.09 (t, 0.40H, $=C-H$).

Synthesis and Isolation of (*E*/*Z*)-*N*-Methyl-*N*-octadecyl-6,6-dimethyl-2-(2,2-dimethylpropyl)hept-2-enylamine (6b). A solution of BPMN (0.090 g, 0.328 mmol),

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N-methyloctadecylamine (0.093 g, 0.328 mmol), and dodecane (0.2 mL) was heated at 100 °C for 4 h. The crude product was dissolved in Et_2O and washed with distilled water (2 × 10 mL), saturated $KHCO_3$ (2 × 10 mL), and saturated NaCl (2 × 10 mL). The organic phase was isolated, and the mixture was concentrated in vacuo. Traces of residual BPMN were removed by Kugelrohr distillation (P = 0.6 Torr, T = 80 °C) to yield the residue, **6b**. High-resolution MS analysis; required for $C_{33}H_{67}NH^+$ *m/e* 478.5352, found *m/e* 478.5354. ^{1}H NMR ($CDCl_3$): δ 0.8−2.05 (m, 69.04H, 2 × $-C(CH_3)_3$, 3 × $-CH_2-$, $-(CH_2)_{16}CH_3$), 2.07 (s, 1.14H, $-CH_3$), 2.08 (s, 1.77H, $-CH_3$), 2.24 (t, 2.00H, $-C-CH_2$), 2.79 (s, 0.70H, $=C-CH_2$), 2.84 (s, 1.13H, $=C-CH_2$), 5.26 (t, 0.60H, $=C-H$), 5.36 (t, 0.40H, $=C-H$).

Synthesis and Isolation of (*E*/*Z*)-*N*-Octyl-6,6-dimethyl-2-(2,2-dimethylpropyl)hept-2-enylamine (6c) and (*E*/*Z*)-*N*-Octyl-bis(6,6-dimethyl-2-(2,2-dimethylpropyl)hept-2-enyl)amine (8). A solution of BPMN (0.018 g, 0.066 mmol) and octylamine (0.013 g, 0.10 mmol) was heated at 100 °C for 2 h. The resulting brown solid was dissolved in Et_2O and washed with distilled water (2 × 10 mL), saturated $KHCO_3$ (2 × 10 mL), and saturated NaCl (2 × 10 mL). The organic phase was isolated, and the product was concentrated in vacuo. The crude mixture was separated by normal-phase HPLC using a Waters model 400 instrument equipped with UV−vis and refractive index detectors (hexanes eluent, Supelcosil PLC-Si column). Aliquots containing **6c** were concentrated in vacuo and characterized by high-resolution MS; required for $C_{22}H_{45}N^+$ *m/e* 323.3552, found *m/e* 323.3540. ^{1}H NMR ($CDCl_3$): δ 0.8−2.05 (m, 59.27H, 2 × $-C(CH_3)_3$, 3 × $-CH_2-$, $-(CH_2)_6CH_3$), 2.51 (t, 1.98H, $-CH_2-$), 3.13 (s, 0.60H, $=C-CH_2$), 3.16 (s, 1.24H, $=C-CH_2$), 5.22 (t, 0.85H, $=C-H$), 5.38 (t, 0.15H, $=C-H$).

Aliquots containing **8** were concentrated in vacuo and characterized by high-resolution MS; required for $C_{36}H_{71}N^+$ *m/e* 517.5587, found *m/e* 517.5573. ^{1}H NMR ($CDCl_3$): δ 0.8−2.05 (m, 68.20H, 4 × $-C(CH_3)_3$, 6 × $-CH_2-$, $-(CH_2)_6CH_3$), 2.19 (t, 1.96H, $-CH_2-$), 2.76 (s, 0.77H, $=C-CH_2$), 2.8 (s, 3.09H, $=C-CH_2$), 5.23 (t, 1.63H, $=C-H$), 5.34 (t, 0.36H, $=C-H$).

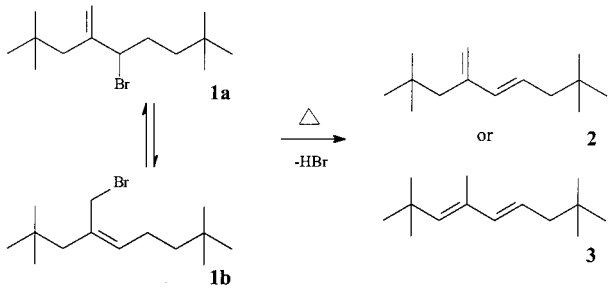
Synthesis and Isolation of Quaternary Ammonium Salts 5b, 5c, and 7. As required, **6b**, **6c**, or **8** was dissolved in $CDCl_3$ and washed with HBr (48 wt % in water), dried over sodium sulfate, and filtered to generate **5b**, **5c**, and **7**, respectively. Found for **5b**: ^{1}H NMR ($CDCl_3$): δ 0.9−2.30 (m, 91.74H, 2 × $-C(CH_3)_3$, 3 × $-CH_2-$, $-(CH_2)_{16}CH_3$), 2.62 (s, 3.22H, $-CH_3$), 2.90 (m, 2.13H, $=C-CH_2$), 3.56 (m, 2.04H, $=C-CH_2$), 5.66 (t, 0.60H, $=C-H$), 5.84 (t, 0.40H, $=C-H$). Found for **5c**: ^{1}H NMR ($CDCl_3$): δ 0.8−2.05 (m, 68.32H, 2 × $-C(CH_3)_3$, 3 × $-CH_2-$, $-(CH_2)_6CH_3$), 2.80 (t, 1.95H, $-CH_2-$), 3.55 (s, 0.46H, $=C-CH_2$), 3.63 (s, 1.44H, $=C-CH_2$), 5.58 (t, 0.66H, $=C-H$), 5.77 (t, 0.34H, $=C-H$). Found for **7**: ^{1}H NMR ($CDCl_3$): δ 0.8−2.0.05 (m, 81.56H, 4 × $-C(CH_3)_3$, 6 × $-CH_2-$, $-(CH_2)_6CH_3$), 3.00 (t, 1.94H, $-CH_2-$), 3.62 (s, 1.96H, $=C-CH_2$), 3.63 (s, 1.85H, $=C-CH_2$), 5.68 (t, 1.62H, $=C-H$), 5.95 (t, 0.38H, $=C-H$).

Kinetics of BPMN-Amine Substitutions. To a dry NMR tube a 1 molar equivalent of the required amine was added to a 0.073 M solution of BPMN in toluene-d_8. The tube was sealed, and the contents were mixed prior to placing it in a silicone oil bath maintained at 100 °C. ^{1}H NMR spectra were recorded at 0,1, 2, and 6 h. Normalized ^{1}H NMR integration of the following peaks was used to provide the relative concentration of the compounds: δ 4.9 ppm (**1a**, 1H, s), 3.9 ppm (**1b**, 2H, s), 3.0 ppm (**5c** + **6c**, 2H, s), 3.3 ppm (**7** + **8**, 4H, s), 3.0 ppm (**5b** + **6b**, 2H, s), 3.5 ppm (**5a**, 6H, s), 6.1 ppm (**3**, 1H, s).

BIIR-Amine Substitutions. Compounds of BIIR and amines were prepared using a Haake Polylab R600 internal batch mixer. The reaction of BIIR (45.0 g) with *N*,*N*-dimethyloctylamine (9.87 g, 0.063 mol) was carried out at 140 °C for 10 min. The product was purified by dissolution/precipitation (hexane/methanol) and dried in vacuo. ^{1}H NMR analysis was conducted in $CDCl_3$ with selective presaturation of solvent and upfield aliphatic proton signals.

Compounds for cross-linking studies were mixed at 50 °C for 5 min. Cross-linking reactions were conducted at 160 ± 1 °C within a TechPro oscillating disk rheometer (ODR). The torque required to oscillate a biconical disk embedded in the sample through a 5° arc at 1.6 Hz was recorded with a resolution of ±0.1 dNm. Given that this measurement represents the low-frequency elastic modulus of the material, cross-linking kinetics can be inferred from the difference of instantaneous and minimum torque measurements.

Scheme 1. Thermal Stability of BPMN and BIIR



Analysis. NMR spectra were recorded with a Bruker AM-400 spectrometer (400.13 MHz ^{1}H, 100.62 MHz ^{13}C) in $CDCl_3$ or toluene-d_8, with chemical shifts referenced to tetramethylsilane. Low-resolution mass spectra were recorded with a Fisons VG Quattro triple-quadrupole instrument with chemical ionization (i-C_4H_{10}). High-resolution MS was performed using a Kratos MS-50 TCTA instrument operating with chemical ionization (i-C_4H_{10}) at the University of Montreal.

Results and Discussion

Bromination of 2,2,4,8,8-pentamethyl-4-nonene and poly(isobutylene-*co*-isoprene) with 1,3-dibromo-5,5-dimethylhydantoin or Br_2 yields a kinetically favored exo allylic bromide (**1a**)[6] that upon heating rearranges to give an equilibrium distribution of exo (**1a**) and E,Z-endo structures (**1b**) which at 140 °C exists as a 1:5 ratio of **1a**:**1b** (Scheme 1).[5] HBr elimination occurs concurrently to yield two principal conjugated dienes (**2** and **3**). Furthermore, β-scission of allyl cation intermediates creates a range of low molecular weight dienes and alkyl bromides. Since HBr accelerates both isomerization and β-scission processes, these reactions are inhibited by a neutral acid scavenger such as 1,2-epoxydodecane.[5]

Given the propensity of **1** to eliminate HBr to form elimination and fragmentation products, it is conceivable that amines may support both substitution and elimination pathways. We found that HBr elimination from BPMN was not accelerated by the nonnucleophilic base 1,8-bis(dimethylamino)naphthalene (Proton-Sponge). Exposure of **1** to 1.8 equiv of Proton-Sponge at 100 °C yielded no fragmentation products, and although elimination and isomerization were observed at 140 °C (Figure 1), the reaction rates were comparable to those observed in experiments employing 1,2-epoxydodecane.[5] Removal of acid from solution through the formation of ammonium bromide salts stabilizes the allylic bromide **1** with respect to HBr-accelerated elimination and fragmentation. Subsequent experiments (vide infra) with nucleophilic amines showed no increased propensity for elimination to conjugated diene during the course of the substitution reactions. This suggests that in this system elimination is predominantly an E_1 process.

Tertiary Amine Reactivity. Steric hindrance imposed by the unique arrangement of *N*-methyl substituents in Proton-Sponge limits the nucleophilicity of this base,[7] and no evidence of N-alkylation by **1** was found in this system. However, **1** reacted readily with *N*,*N*-dimethyloctylamine (**4a**) to produce (E,Z)-endo isomers

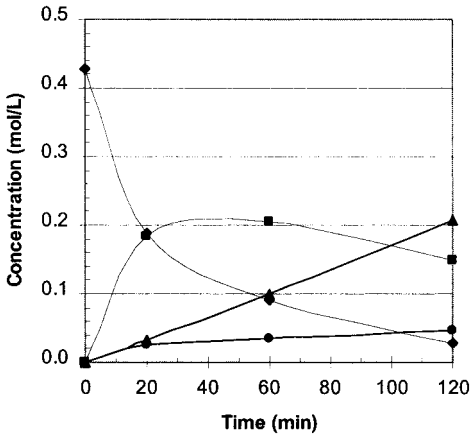


Figure 1. Thermal stability of **1** (0.43 M; dodecane, 140 °C) with 1.8 equiv of Proton-Sponge: ◆, **1a**; ■, **1b**; ▲, **2**; ●, **3**.

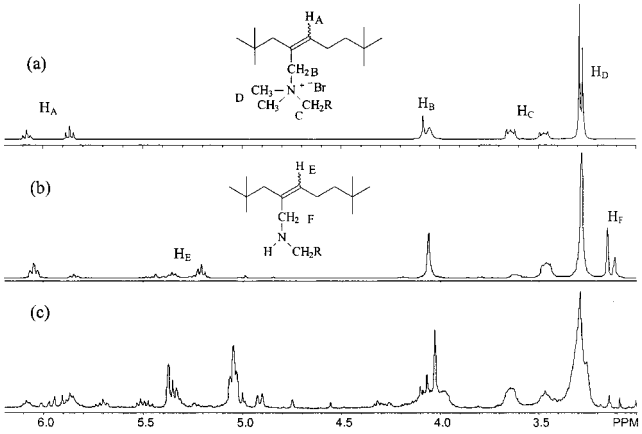
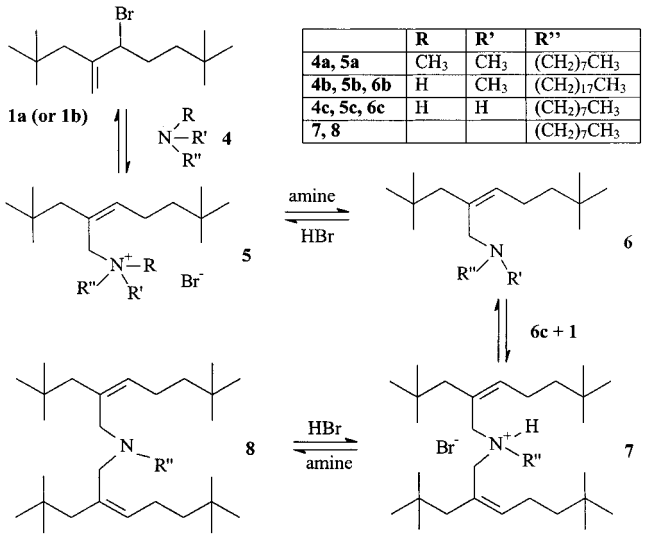


Figure 2. Downfield region of the ^{1}H NMR spectra ($CDCl_3$) of (a) **5a**, (b) **5a** heated with 1.0 equiv of **4c** (2 h, 100 °C), and (c) BIIR heated with **4a** (10 min, 140 °C). All compounds are a mixture of E/Z isomers.

Scheme 2. Amine Substitution Reactions of BIIR



	R	R'	R''
4a, 5a	CH_3	CH_3	$(CH_2)_7CH_3$
4b, 5b, 6b	H	CH_3	$(CH_2)_{17}CH_3$
4c, 5c, 6c	H	H	$(CH_2)_7CH_3$
7, 8			$(CH_2)_7CH_3$

of the quaternary ammonium salt, **5a** (Scheme 2). No evidence of an exo substitution product could be found by ^{1}H NMR (Figure 2a). This is consistent with the findings of Young et al. regarding the reactivity of butenyl chlorides.[8,9] They report that triethylamine reacts with 3-chloro-1-butene in benzene to produce the internal olefin product (*(E/Z)-N,N,N*-triethylbut-2-enyl-ammonium chloride) exclusively and attributed this apparent selectivity to the operation of an S_N2' mechanism.[8] In our case, a rapid **1a**−**1b** rearrangement precludes us from assigning a bimolecular mechanism (S_N2 vs S_N2') and a unimolecular process (S_N1 or S_N1') cannot be ruled out without more detailed kinetic data.

We note that the preference for endo substitution products in our system may not be a product of substitution kinetics, but rather of thermodynamic stability. It is well established that very significant stabilization of alkenes results from a higher extent of alkyl substitution.[10] Furthermore, we expect that steric effects imposed by adjacent *tert*-butyl substituents will also favor the observed endo products. That thermodynamic stability and not kinetic selectivity results in the observed isomeric products implies that **5a** is capable of rearrangement, and we will present evidence later to demonstrate the reversibility of the N-alkylation process.

Complete conversion of **1** to **5a** is achieved at 100 °C using reagent concentrations where the solubility limit of the salt is exceeded, leading to the precipitation of the product. Under these reaction conditions we observed no evidence of the conjugated dienes (**2**, **3**) generated by HBr elimination, suggesting that nucleophilic substitution is more rapid than elimination. Nevertheless, HBr elimination products can be observed in reactions carried out in dilute solution, for reasons discussed later.

Secondary Amine Reactivity. The reaction of **1** with *N*-methyloctadecylamine (**4b**) at 100 °C yielded a mixture of the ammonium salt **5b**, its conjugate base **6b**, and *N*-methyloctadecylammonium bromide (Scheme 2). The latter originated from the deprotonation of **5b** by **4b**, given that conjugated dienes (**2**, **3**) derived from direct HBr elimination from **1** were not observed in the reaction mixture. As was the case in the tertiary amine system only (E,Z)-endo isomers were formed, and high reagent concentrations resulted in the precipitation of ammonium salts.

While the quaternization of the tertiary amine **6b** by **1** is conceivable, we did not observe any evidence of such a reaction. This is contrary to the BPMN/*N,N*-dimethyloctylamine system in which rapid N-alkylation of the tertiary amine was noted. We assume that steric bulk imposed by the pentamethylnonene substituent of **6b** hinders this process, whereas the relatively unencumbered nitrogen in *N,N*-dimethyloctylamine is more reactive. This result suggests that tertiary amine derivatives of BIIR can be produced from secondary amines without concern for polymer cross-linking through a subsequent quaternization reaction.

Proton transfer between **4b** and **5b** generates complexity in the product distribution of secondary amine reactions that is not present in the tertiary amine system. Given that *N*-methyloctadecylamine acts as a nucleophile and base, it undergoes N-alkylation to generate BPMN substitution products as well as proton transfer to generate its hydrobromide salt. Amine consumed by proton transfer is incapable of nucleophilic substitution, and quantitative conversion of **1** to substitution product therefore requires an excess of this reagent. Furthermore, ^{1}H NMR analysis of the reaction mixture is complicated by proton exchange that is rapid on the NMR time scale, resulting in coalesced signals with chemical shifts intermediate between those of **5b** and **6b** (Figure 3).

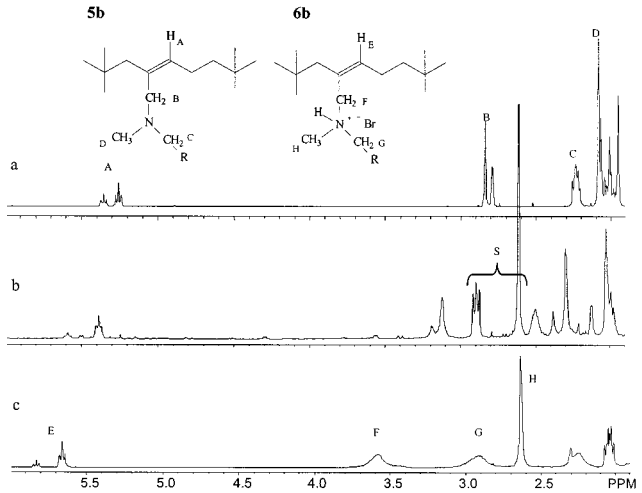


Figure 3. Downfield region of the ^{1}H NMR spectra ($CDCl_3$) of (a) **5b**, (b) **6b** + 1 equiv of *N*-methyloctadecylamine, and (c) **6b**; S = *N*-methyloctadecylammonium bromide. All compounds are a mixture of E/Z isomers.

Primary Amine Reactivity. The chemistry of the BPMN-primary amine system is considerably more complex, given that bis-N-alkylation products are formed readily. Reaction of BPMN with 1.0 molar equivalent of octylamine at 100 °C produced (E,Z)-endo monosubstitution and disubstitution products as salts (**5c**, **7**) and their corresponding amines (**6c**, **8**). The process summarized in Scheme 2 involves N-alkylation of octylamine by **1** to produce **5c**, followed by deprotonation by unreacted amine to produce **6c**. N-Alkylation of **6c** yields the dimer **7** that is converted to **8** by unreacted amine. A quaternary product derived from **8** was not observed.

Substitution/Elimination Reaction Yields. Preliminary kinetic data were acquired for the purposes of determining the relative rates of substitution and elimination reactions and defining limiting reaction conversions. Reactions were conducted in dilute toluene-d_8 solutions (to avoid exceeding product solubility limits) at 100 °C within a NMR tube and monitored periodically by ^{1}H NMR. Rapid proton exchange complicated our attempts to quantify the concentration of **5** relative to **6** as well as the concentration of **7** relative to **8**. Therefore, only the total concentration of a given substitution product (**5** + **6**, **7** + **8**) is reported.

The *N*,*N*-dimethyloctylamine/BPMN system proved to be the least reactive with respect to both substitution and elimination (Figure 4). The conversion of **1** to **5a** over 6 h at 100 °C was limited to 24%, over which time the rate of substitution exceeded that of HBr elimination. Reaction products in the *N*-methyloctadecylamine system evolved much faster (Figure 5), as a constant ratio of **1** to N-alkylation products **5b** + **6b** was reached within 1 h. This apparent limiting conversion existed despite the availability of free amine and allylic bromide. HBr elimination continued throughout the test period, but the relative amounts of allylic bromide and substitution products remained unchanged. The behavior of the octylamine/BPMN system was complicated by the variety of available N-alkylation and proton-transfer reaction pathways. Figure 6 demonstrates a rapid formation of the intermediates **5c** and **6c** that are capable of further N-alkylation to produce **7** and **8**. Once again, the system produced a static product distribution that contained starting materials.

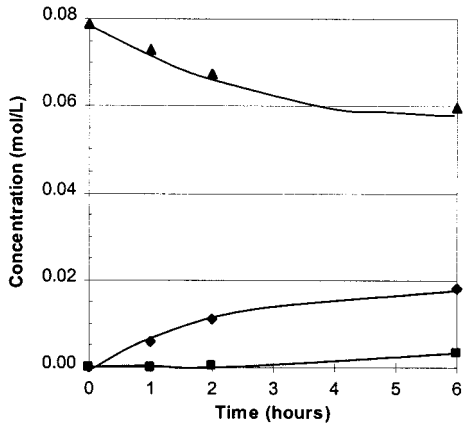


Figure 4. Substitution/elimination kinetics of BPMN/*N*,*N*-dimethyloctylamine (100 °C, toluene-d_8): ▲, (**1a** + **1b**); ◆, **5a**; ■, (**2** + **3**).

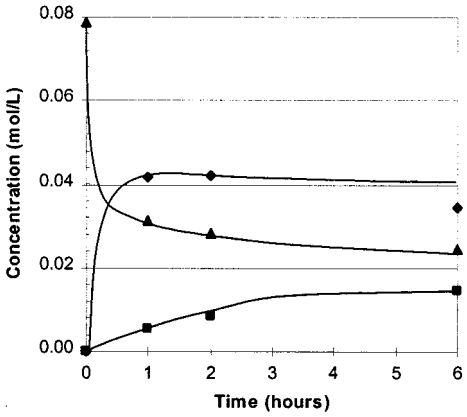


Figure 5. Substitution/elimination kinetics of BPMN/*N*-methyloctadecylamine (100 °C, toluene-d_8): ▲, (**1a** + **1b**); ◆, (**5b** + **6b**); ■, (**2** + **3**).

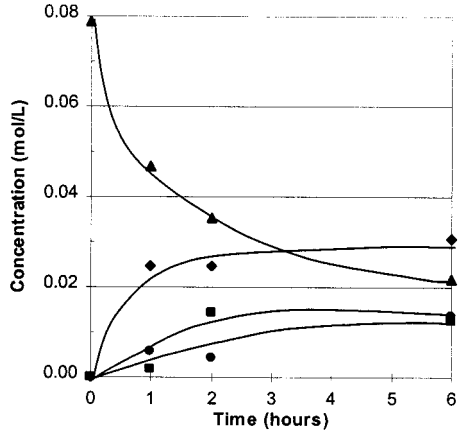


Figure 6. Substitution/elimination kinetics of BPMN/octylamine (100 °C, toluene-d_8): ▲, (**1a** + **1b**); ◆, (**5c** + **6c**); ■, (**2** + **3**); ●, (**7** + **8**).

Although substitution products were prepared in good yield by using reagent concentrations high enough to lead to ammonium salt precipitation, full conversion could not be achieved under conditions of complete solubility. This limit to BPMN-amine reaction extent can be rationalized on the basis of equilibrium thermodynamics, wherein a dynamic equilibrium of reversible proton transfer and N-alkylation reactions is established. Scheme 2 depicts all reactions as reversible, in which case a static product distribution containing starting compounds **1** and **4** as well as substitution

products is anticipated. However, continuous HBr elimination by **1** is expected to consume all BPMN-derived products to yield the more stable conjugated dienes **2** and **3**.

The reversibility of *N*,*N*-dimethyloctylamine quaternization by **1** was confirmed by heating an isolated sample of **5a** to 100 °C for 1 h in toluene-d_8. ^{1}H NMR confirmed the presence of **5a**, **4a**, and **1b** in the mixture (Figure 2) and revealed no evidence of conjugated dienes **2** and **3**. Similarly, the decomposition of **5b** to generate small amounts of **1b**, *N*-methyloctadecylamine (**4b**), and conjugated dienes **2** and **3** were found upon heating a sealed NMR tube to 165 °C for 90 min.

Tong et al. have demonstrated that a carboxylate anion can act as a nucleophile in an exchange reaction with onium ions at 140 °C,[11] and alkyl group displacements from quaternary ammonium halides by amine nucleophiles have been well documented.[12] We have similarly observed the ability of amines to participate in alkyl exchange with BPMN-derived compounds. Upon heating a solution of **5a** with approximately 0.25 equiv of octylamine to 100 °C for 2 h and washing with base, ^{1}H NMR revealed the presence of residual **5a** along with the single N-alkylation product **6c** (Figure 2b). Analogously, heating a solution of **5b** with a large excess of octylamine to 100 °C for 2 h produced the single N-alkylation product **6c** in high yield. These exchange reactions, combined with evidence of the reversibility of both proton exchange and N-alkylations, support our assertion that limiting reaction conversions result from thermodynamic equilibrium conditions. Furthermore, this result suggests that amine substitution reactions of BIIR can be reversed upon treatment with an appropriate nucleophile.

BIIR-Amine Substitution Reactions. The reaction of amines with BIIR can be accomplished without solvent using conventional rubber compounding equipment. Shown in Figure 2c is the ^{1}H NMR spectrum of BIIR heated with excess *N*,*N*-dimethyloctylamine to 140 °C for 10 min. Clear evidence of an N-alkylation product analogous to **5a** is apparent, thereby supporting the use of the model compound in structural studies of BIIR reactions. Also evident in this spectrum is the presence of structures analogous to allylic bromide (**1a,b**) and conjugated dienes **2** and **3**.[5] These structures are expected, given the kinetic measurements of rearrangement, substitution, and HBr elimination reactions of the model compound (Figure 4).

The bis-N-alkylation reaction demonstrated for the octylamine/BPMN system can be used to cross-link the polymer efficiently using a primary amine as the sole curing agent. Master batches of BIIR containing various concentrations of octylamine (expressed as molar equivalents of amine relative to allylic bromide within BIIR) were cured at 160 °C to generate the cross-linking profiles shown in Figure 7. Cross-link densities greater than the baseline (0 equiv of octylamine) were reached rapidly, and stable torque plateaus indicated that the network structure did not deteriorate with time.

It is interesting to note that the highest cross-link density was produced with 1.0 molar equivalents of octylamine relative to allylic bromide. Whereas 0.5 equiv of amine satisfy the stoichiometric requirement for allylic bromide conversion to disubstitution product, amine base is needed to regenerate nucleophilic character by proton transfer from the first N-alkylation product, **5c** (Scheme 2). As a result, an excess of

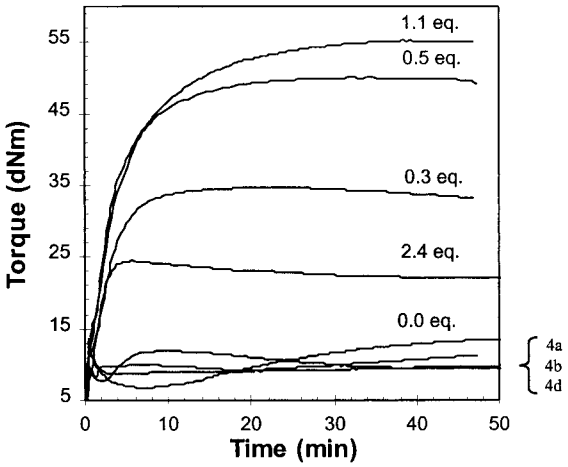


Figure 7. Cross-linking kinetics of BIIR reacting with octylamine (**4c**) and 1 equiv of *N*,*N*-dimethyloctylamine (**4a**), *N*-methyloctadecylamine (**4b**), and Proton-Sponge (**4d**) (160 °C).

octylamine is required to facilitate the second N-alkylation that produces a cross-link. It should also be noted that a large excess of amine creates conditions where allylic bromide is the limiting reagent, thereby arresting the process in a state dominated by structures **5c** and **6c** as opposed to disubstitution products **7** and **8**. This was observed in the 2.4 amine equivalent reaction (Figure 7) that produced the lowest cross-link density of the series.

In a manner that is consistent with the model compound, BIIR did not cross-link to a significant extent in the presence of 1.0 equiv of Proton-Sponge, *N*,*N*-dimethyloctylamine, and *N*-methyloctadecylamine (Figure 7). This suggests that amine derivatives of BIIR can be prepared without cross-linking, thereby facilitating graft copolymer synthesis using amino-functionalized reagents.

Conclusions

The allylic bromide functionality within BIIR undergoes substitution with amine nucleophiles without acceleration of concurrent HBr elimination. Substitution products, comprised exclusively of E,Z-endo isomers, include single N-alkylation products for *N*,*N*-dimethyloctylamine and *N*-methyloctadecylamine, and bis-N-alkylation products for primary amines. Substitution and proton-transfer reactions are reversible, leading to an equilibrium distribution of reaction products. Whereas secondary amines can be used to prepare derivatives of BIIR without cross-linking, bis-N-alkylation of primary amines with BIIR can generate stable cross-linked polymer networks.

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