Cross-Linking of Brominated Poly(isobutylene-*co*-isoprene) by N-Alkylation of the Amidine Bases DBU and DBN

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ABSTRACT: An unusual cross-linking of brominated poly(isobutylene-*co*-isoprene), BIIR, has been shown to occur in the presence of the normally nonnucleophilic amidine bases 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN). Model compound studies using brominated 2,2,4,8,8-pentamethyl-4-nonene (BPMN) have provided structural information which indicates that this cross-linking most likely occurs through a sequence of reactions which involves the following: (1) N-alkylation of the amidine base to an amidinium salt, (2) hydrolysis of the salt to an ammonium lactam, (3) deprotonation of the ammonium lactam to an amino-lactam, and (4) a second amine N-alkylation. The ability of DBU and DBN to undergo N-alkylation with BIIR has been confirmed by reaction of BIIR in solution with an excess of each of these bases to give N-alkylation products that have been characterized spectroscopically.

Introduction

Poly(isobutylene-*co*-isoprene), butyl rubber,[1] is a widely used elastomer that is valued for its oxidative stability and high impermeability to gases. As a consequence, it has found common use in inner tubes for tires and related applications. The development of halogenated poly(isobutylene-*co*-isoprene), halobutyl rubbers, has expanded the scope of applications for this material for two reasons. First, halobutyl rubbers have an expanded array and rates of cross-linking chemistry. For example, bromobutyl rubber (BIIR) can be cross-linked with sulfur alone, zinc oxide alone, sulfur plus zinc oxide, or sulfur plus zinc oxide and an accelerator.[2] This has led to further applications that range from inner liners of tires, where covulcanization with highly unsaturated elastomers occurs, to pharmaceutical grade rubber with minimal leachates. Second, the allylic halogen functionality provides excellent reactivity for chemical modification by, for example, sulfur, nitrogen, and phosphorus nucleophiles to produce chemically modified polymers.[3−5]

One of the consequences of the allylic halogen functionality in halobutyl rubber is thermal instability due to elimination of hydrogen halides.[6] This is problematic since free acid can cause degradation of the elastomer as an undesirable side reaction. To circumvent this problem, nonbasic acid scavengers such as epoxides (e.g., epoxidized soy bean oil) are commonly used as stabilizers. Additionally, controlled dehydrohalogenation can be carried out in the presence of bases (e.g., CaO) to produce conjugated-diene butyl rubber,[7] which can subsequently be characterized by solution techniques such as NMR.[8] Recently, we have examined the effects of the amidine bases 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) on the stability of BIIR and were surprised to observe slow cross-linking behavior at room temperature, which became rapid at elevated temperatures (100−160 °C). DBU and DBN have frequently been described in the literature[9] as nonnucleophilic bases which are effective dehydrohalogenating reagents. We have therefore sought an explanation for this unusual cross-linking behavior with the assistance of model compound chemistry.

Cross-linked elastomers are generally insoluble materials; this leads to greater difficulty in structural characterization of the chemistry of cross-linking since solution analytical and spectroscopic techniques cannot be used. Model compounds have therefore been frequently used to assist in elucidating the structural features of processes such as the vulcanization of natural rubber,[10−13] EPDM,[14] and poly(butadiene),[13,15] the halogenation of butyl rubber,[16] and the zinc oxide cure of bromobutyl rubber.[17,18] In this specific instance, we have used brominated 2,2,4,8,8-pentamethyl-4-nonene (BPMN) as a model for bromobutyl rubber. In this report we describe the reaction products of BPMN with both DBU and DBN and correlate these structures with the products obtained from chemical modification of bromobutyl rubber with excess DBU and DBN. On the basis of these structural characterizations, a scheme for the cross-linking behavior of BIIR by these amidine bases is proposed.

Experimental Section

Instrumentation. NMR spectra were recorded with a Bruker AVANCE-600 spectrometer (600.17 MHz ^{1}H, 150.92 MHz ^{13}C) in $CDCl_3$, with chemical shifts referenced to tetramethylsilane. 1D and 2D spectra (COSY, HMBC, HSQC) were obtained for all BPMN derivatives, while 1D ^{1}H NMR spectra were obtained for all modified BIIR samples. FT-IR spectra were recorded using a Nicolet Avatar ESP 360 instrument at a resolution of 4 cm^{-1}. Low-resolution MS (electrospray) was performed using a Waters ZQ Single Quad instrument equipped with an ESI/APcI multiprobe and a Waters 2695XE HPLC system, equipped with a photodiode array and a fluorescence detector setup.

Compounding was done using a Haake Polylab R600 internal batch mixer. Cross-linking reactions were carried out,

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and rheological properties were measured using an Advanced Polymer Analyzer from Alpha Technologies with biconical plates (3 deg of arc and 100 cpm).

Materials. Brominated 2,2,4,8,8-pentamethyl-4-nonene (BPMN) was prepared as described previously.[6] The following reagents were used as received from Sigma-Aldrich (Oakville, Ontario): 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) 98%, 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) 98%. BIIR (LANXESS BB2030) was used as supplied by LANXESS Inc. (Sarnia, Ontario).

Synthesis and Isolation of BPMN/DBU Bromide Salt (1). A solution of BPMN (100 μL, 0.33 mmol, 90 mg) and DBU (25 μL, 0.166 mmol) in toluene (0.5 mL) was heated at 75 °C for 1 h. Upon cooling the mixture to room temperature, a white salt precipitated from solution. After separation by filtration, the white salt was found to be a mixture of a DBU−HBr salt and a BPMN−DBU salt by ^{1}H NMR, while the liquid layer contained unreacted BPMN. The BPMN−DBU salt was isolated by dissolution in dichloromethane and then filtration to remove the undissolved DBU−HBr salt. The dichloromethane was removed in vacuo to give an orange oil (60 mg, 42%) that was characterized by NMR, IR, and MS. Low-resolution MS analysis: *m/z* 347.24 (M^+); $C_{23}H_{43}N_2$ requires 347.34. IR (CH_2Cl_2): 1616 cm^{-1} (C=N). ^{1}H NMR ($CDCl_3$): δ 0.88 (s, 18H, two $-C(CH_3)_3$), 1.75 (s, 2H, $(CH_3)_3C-$**CH_2**$-C=$), 5.48 (t, 1H, =**CH**$-CH_2-$), 2.04 (m, 2H, $=CH-$**CH_2**$-$), 1.21 (m, 2H, $=CH-CH_2-$**CH_2**$-$), 4.2 (s, 2H, $=C-CH_2-N=$), 3.55 (t, 2H, $=N-$**CH_2**$-CH_2-$), 2.12 (q, 2H, $=N-CH_2-$**CH_2**$-$), 3.71 (t,2H, $=N-CH_2-CH_2-$**CH_2**$-N$), 3.76 (t, 2H, $N-$**CH_2**$-$), 1.8 (bs, 2H, $N-CH_2-$**CH_2**$-$), 1.8 (bs, 2H, $N-CH_2-CH_2-$**CH_2**$-$), 1.75 (bs, 2H, $N-CH_2-CH_2-CH_2-$**CH_2**$-$), 2.96 (m, 2H, $N-CH_2-CH_2-CH_2-CH_2-$**CH_2**$-C=N$). ^{13}C NMR: δ 29.5, 32.3, 46.1, 128.7, 137.5, 23.5, 44.2, 30.1, 29.3, 54.0, 46.1, 20.2, 49.6, 55.9, 26.2, 28.5, 23.1, 28.9, 167.6 (C=N). Predominantly the Z-isomer (>90%) by NOESY.

Synthesis and Isolation of BPMN/DBU Lactam (3). BPMN−DBU bromide salt (**1**, 35 mg, 81.8 μmol), excess KOH, and D_2O (0.5 mL) were added to a NMR tube and heated 4.5 h at 80 °C. The product (orange layer) was extracted with dichloromethane and then dried under high vacuum to give the lactam **(3)** as an oil (30 mg, 100%). Low-resolution MS: *m/z* 367.27 ($M-H^+$); $C_{23}H_{43}D_2N_2O_1$ requires 367.37. IR (CH_2Cl_2): 1636 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$): δ 0.84 (s, 9H, $-C(CH_3)_3$), 0.86 (s, 9H, $-C(CH_3)_3$), 1.9 (s, 2H, $(CH_3)_3C-$**CH_2**$-C=$), 5.22 (t, 1H, =**CH**$-CH_2-$), 1.98 (m, 2H, $=CH-$**CH_2**$-$), 1.18 (m, 2H, $=CH-CH_2-$**CH_2**$-$), 3.15 (s, 2H, $=C-$**CH_2**$-NH$), 2.52 (t, 2H, $-NH-$**CH_2**$-CH_2-$), 1.65−1.7 (m, 2H, $-NH-CH_2-$**CH_2**$-$), 3.4 (t, 2H, $NH-CH_2-CH_2-$**CH_2**$-N$), 3.31 (m, 2H, $O=C-N-CH_2-$), 1.57−1.63 (m, 2H, $O=C-N-CH_2-$**CH_2**$-$), 1.65−1.7 (m, 2H, $O=C-N-CH_2-CH_2-$**CH_2**$-$), 1.57−1.63 (m, 2H, $O=C-N-CH_2-CH_2-CH_2-$**CH_2**$-$), 2.48 (m, 0.56H, $-CH_2-$**CH_2**$-C=O$, 72% deuterium). ^{13}C NMR ($CDCl_3$): δ 29.8, 31.8, 48.5, 135.1, 132.6, 23.4, 44.8, 30.4, 29.2, 49.8, 46.7, 28.7, 46.1, 49.8, 28.8, 30.1, 23.4, 37.2, 175.8 (C=O).

Synthesis and Isolation of DBU Bisalkylation Product (4). Dideuterated DBU lactam (**3**, 10 mg, 27.4 μmol), toluene (0.5 mL), and BPMN (7.5 mg, 27.4 μmol) were added to a Wheaton vial and then sealed and heated 1 h at 75 °C. The solvent was evaporated, and the resulting orange oil was characterized. Low-resolution MS: *m/z* 561.45 ($M-H^+$); $C_{37}H_{69}D_2N_2O_1$ requires 561.57. IR (CH_2Cl_2): 1642 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$): δ 0.84−0.92 (s, 36H, four $-C(CH_3)_3$), 1.92 (s,4H, two $(CH_3)_3C-$**CH_2**$-C=$), 5.22 (t, 2H, two =**CH**$-CH_2-$), 2.05 (m, 4H, two $=CH-$**CH_2**$-$), 1.19 (m, 4H, two $=CH-CH_2-$**CH_2**$-$), 2.8 (s, 2H, two $=C-$**CH_2**$-NH$), 2.24 (t,2H, $-N-$**CH_2**$-CH_2-$), 1.58−1.65 (m, 2H, $-N-CH_2-$**CH_2**$-$), 3.43 (t, 2H, $N-CH_2-CH_2-$**CH_2**$-N$), 3.28−3.35 (m, 2H, $O=C-N-$**CH_2**), 1.58−1.65 (m, 2H, $O=C-N-CH_2-$**CH_2**$-$), 1.68−1.7 (m, 2H, $O=C-N-CH_2-CH_2-$**CH_2**$-$), 1.58−1.65 (m, 2H, $O=C-N-CH_2-CH_2-CH_2-$**CH_2**$-$), 2.49 (m, 0.56H, $CO-$**CH_2** 72% deuterium). ^{13}C NMR: δ 30.0, 31.8, 48.1, 134.2, 133.2, 23.3, 44.7, 30.5, 29.5, 54.5, 51.2, 26.4, 45.8, 49.7, 28.7, 30.1, 23.4, 37.8, 177.2 (C=O).

Synthesis and Isolation of BPMN/DBN Bromide Salt. A solution of BPMN (100 μL, 0.33 mmol), DBN (20 μL, 0.165 mmol), and toluene (0.5 mL) was heated at 75 °C for 1 h. The solvent was evaporated, and the resulting oil was purified by column chromatography (alumina). Elution with hexanes gave unreacted BPMN. Elution with methanol gave a mixture of BPMN−DBN salt and DBN−HBr salt. Additional of chloroform to a methanol solution of the salts precipitated the DBN−HBr salt, which was removed by filtration. Evaporation of the solvent gave the BPMN−DBN salt as a dark orange oil (65 mg, 49%). Low-resolution MS: *m/z* 319.31 (M^+); $C_{21}H_{39}N_2$ requires 319.31. IR (CH_2Cl_2): 1670 cm^{-1} (C=N). ^{1}H NMR ($CDCl_3$): δ 0.83 (s, 18H, two $-C(CH_3)_3$), 1.71 (s, 2H, $(CH_3)_3C-$**CH_2**$-C=$), 5.48 (t, 1H, =**CH**$-CH_2-$), 2.01 (m, 2H, $=CH-$**CH_2**$-$), 1.17 (m, 2H, $=CH-CH_2-$**CH_2**$-$), 4.04 (s, 2H, $=C-$**CH_2**$-N$), 3.31 (t, 2H, $-N-$**CH_2**$-CH_2-$), 2.2 (q, 2H, $-N-CH_2-$**CH_2**$-$), 3.54 (t, 2H, $N-CH_2-CH_2-$**CH_2**$-N$), 3.84 (t, 2H, $-N-$**CH_2**), 2.09 (q, 2H, $-N-CH_2-$**CH_2**$-$), 3.13 (t, 2H, $-N-CH_2-CH_2-$**CH_2**$-C=N$). ^{13}C NMR ($CDCl_3$): δ 29.6, 32.1, 46.7, 127.6, 138.6, 23.5, 44.2, 30.2, 29.0, 52.9, 42.9, 18.4, 42.8, 54.6, 19.2, 31.6, 165.2 (C=N).

Synthesis and Isolation of DBN Lactam. BPMN−DBN bromide salt (30 mg, 75.1 μmol), excess KOH, distilled water (0.1 mL), and $CDCl_3$ (0.5 mL) were added to a NMR tube and heated for 6 h at 140 °C. The product was extracted with CH_2Cl_2, and then the solvent was evaporated under high vacuum to yield an orange oil (25 mg). MS: *m/z* 337.32 $(M + H)^+$; $C_{21}H_{41}N_2O_1$ requires 337.32. IR (CH_2Cl_2): 1670 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$): δ 0.84 (s, 9H, $-C(CH_3)_3$), 0.86 (s, 9H, $-C(CH_3)_3$), 1,89 (s, 2H, $(CH_3)_3C-$**CH_2**$-C=$), 5.24 (t, 1H, =**CH**$-CH_2-$), 1.98 (m, 2H, $=CH-$**CH_2**$-$), 1.18 (m, 2H, $=CH-CH_2-$**CH_2**$-$), 3.15 (s, 2H, $=C-$**CH_2**$-NH$), 2.51 (t, 2H, $-NH-$**CH_2**$-CH_2-$), 1.67 (qv, 2H, $-NH-CH_2-$**CH_2**$-$), 3.3 (t, 2H, $-NH-CH_2-CH_2-$**CH_2**$-N-$), 3.35 (t, 2H, $O=C-N-$**CH_2**), 1.98 (m, 2H, $O=C-N-CH_2-$**CH_2**$-$), 2.34 (t, 2H, **CH_2**$-CO$). ^{13}C NMR: δ 30.1, 31.9, 48.7, 135.4, 132.6, 23.4, 44.8, 30.5, 29.3, 49.8, 46.7, 27.9, 40.7, 47.4, 18.1, 31.2, 175.2 (C=O).

Synthesis and Isolation of DBN Bisalkylation Product. DBN lactam (10 mg, 29.7 μmol), toluene (0.5 mL), and BPMN (8.17 mg, μmol) were added to a Wheaton vial, sealed, and heated for 2 h at 75 °C. The solvent was evaporated, and the product was characterized. MS: *m/z* 531.61; $C_{35}H_{67}N_2O_1$ requires 531.53. IR (CH_2Cl_2): 1691 cm^{-1}(C=O). ^{1}H NMR ($CDCl_3$): δ 0.84−0.91 (s, 36H, four $-C(CH_3)_3$), 1.93 (s, 2H, two $(CH_3)_3C-$**CH_2**$-C=$), 5.25 (t, 1H, two =**CH**$-CH_2-$), 2.01 (m, 2H, two $=CH-$**CH_2**$-$), 1.17 (m, 2H, two $=CH-CH_2-$**CH_2**$-$), 2.81 (s, 2H, two $C-$**CH_2**$-N$), 2.34 (t, 2H, $-N-$**CH_2**$-CH_2-$), 1.97 (q, 2H, $-N-CH_2-$**CH_2**$-$), 3.33 (t, 2H, $N-CH_2-CH_2-$**CH_2**$-$), 3.23 (t, 2H, $C=N-$**CH_2**), 1.66 (q, 2H, $C=N-CH_2-$**CH_2**$-$), 1.39 (t, 2H, $C=N-CH_2-CH_2-$**CH_2**$-C-N$). ^{13}C NMR ($CDCl_3$): δ 30.2, 31.7, 47.9, 138.2, 133.3, 23.2, 44.7, 32.0, 29.5, 54.5, 31.2, 18.5, 47.4, 41.3, 38.9, 23.9, 176.6 (C=O).

BIIR Reaction with Excess DBU in Solution. BIIR (2 g, 0.4 mmol allylic bromide) was dissolved in toluene (50 mL), and then DBU (0.47 mL, 3.2 mmol) was added to the flask. The mixture was reacted at 110 °C for 2 h. The polymer was purified twice by dissolution/precipitation (toluene/acetone), dried in vacuo, and characterized: IR (CH_2Cl_2): 1650 cm^{-1} (C=O). ^{1}H NMR downfield region ($CDCl_3$): δ 5.05 ppm (t, 1H, $-CMe=$**CH**$-$, residual butyl rubber), 5.22 (t, 1H, =**CH**$-CH_2-$, H5), 3.41 (t, 2H, $NH-CH_2-CH_2-$**CH_2**$-$, H13), 3.31 (m, 2H, $O=C-N-$**CH_2**$-$, H14), 3.18 (s, 2H, $=C-$**CH_2**$-NH$, H10), 2.52 (t, 2H, $-NH-$**CH_2**$-CH_2-$, H11), 2.48 (m, 2H, $-CO-$**CH_2**$-$, H18).

BIIR Reaction with Excess DBN in Solution. BIIR (1 g, 0.2 mmol allylic bromide) was dissolved in toluene (50 mL), and then DBN (0.2 mL, 1.6 mmol) was added to the flask. The mixture was heated at 110 °C for 1.5 h in a thermostated oil bath, and then the polymer was purified twice by dissolution/precipitation (toluene/acetone), dried in vacuo, and characterized: IR (CH_2Cl_2): 1665 cm^{-1} (C=N). ^{1}H NMR downfield region ($CDCl_3$): δ 5.05 ppm (t, 1H, $-CMe=$**CH**$-$, residual butyl rubber), 5.47 (t, 1H, =**CH**$-CH_2-$, H5), 4.06 (s, 2H, $=C-$**CH_2**$-N$, H10), 3.86 (t, 2H, $-N-$**CH_2**, H14), 3.54 (t, 2H, $=N-CH_2-CH_2-$**CH_2**$-N$, H13), 3.31 (t, 2H, $=N-$**CH_2**$-CH_2-$, H11), 3.22 (t, 2H, $-N-CH_2-CH_2-$**CH_2**$-C=N$, H16).

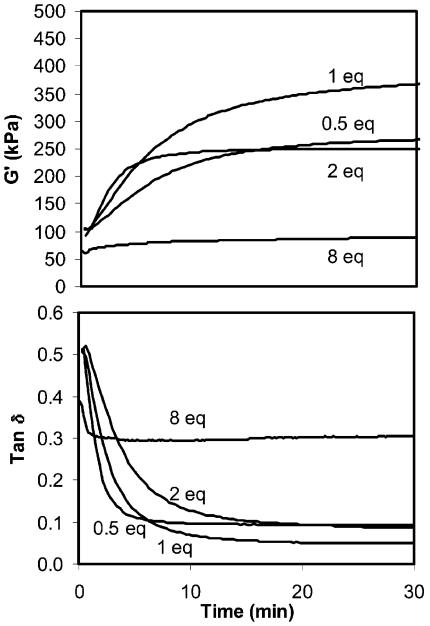


Figure 1. Storage modulus and loss tangent for different ratios of DBU to BIIR at 140 °C.

Solvent Free Reactions of BIIR with DBU and DBN. Compounds were mixed at 23−35 °C for 10 min (60 rpm) in the batch mixer and then reacted for 60 min at 140 °C in the cavity of the APA.

BIIR (50 g, 0.01 mol allylic bromide) was reacted with different equivalents of DBU: 0.5 equiv (0.74 mL, 0.005 mol), 1 equiv (1.5 mL, 0.01 mol), 2 equiv (3 mL, 0.02 mol), and 8 equiv (11.9 mL, 0.08 mol). Torque profiles are shown in Figure 1.

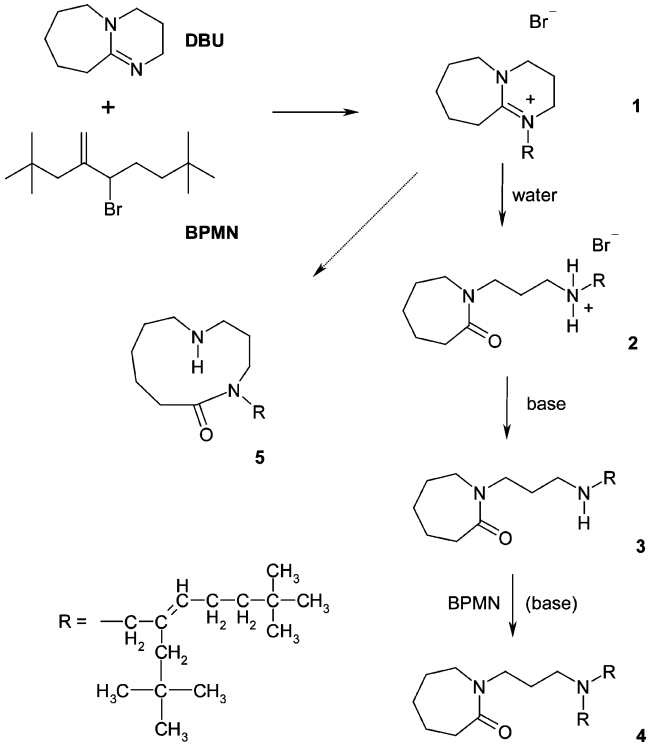
BIIR (50 g, 0.01 mol allylic bromide) was reacted with different equivalents of DBN: 0.5 equiv (0.61 mL, 0.005 mol), 1 equiv (1.23 mL, 0.01 mol), 2 equiv (2.46 mL, 0.02 mol).

Results and Discussion

Typical cross-linking behavior of BIIR in the presence of DBU is shown in Figure 1. Ratios of DBU to allylic bromide functionality in BIIR were varied from 0.5 to 8 equiv. The rubber and amidine base were mixed at low temperature (23−35 °C, 10 min, batch mixer) prior to cross-linking at elevated temperature (140 °C, 60 min, rheometer). Under these conditions, maximum cross-link density was obtained with 1 equiv of DBU. Similar results (not shown) were obtained with DBN; however, the maximum extent of cross-linking was lower as indicated by a storage modulus of 173 kPa, significantly less than the value of 383 kPa obtained with 1 equiv of DBU. The insolubility of the cross-linked BIIR in polar and nonpolar solvents (and their mixtures) indicated that cross-linking was due to covalent bonding rather than ionic aggregation.[5]

To elucidate the nature of the interaction of DBU with BIIR, reactions were carried out in solution between DBU and BPMN. As shown in Scheme 1, the initial reaction product obtained (toluene, 75 °C, 60 min) was the N-alkylation product (**1**) rather than a dehydrobromination product. Although DBU is well-known as a dehydrohalogenating reagent,[9] N-alkylation of DBU is also known to occur in some instances, particularly with primary[19,20] and benzylic halides.[21] This amidine salt (**1**) (as well as all subsequent model compound adducts) was fully characterized by IR and NMR (COSY, HMBC, HSQC) spectroscopy and mass spectrometry. Substitution by allylic rearrangement is expected in the BPMN

Scheme 1. Mono- and Bisalkylation of DBU with BPMN



system,[3−5] giving a trisubstituted alkene as the presumably thermodynamically more stable product. The C=N functional group gave an IR absorption at 1616 cm^{-1} and a ^{13}C NMR chemical shift of 167.6 ppm; the alkene was determined to be predominantly (>90%) the Z-isomer by NMR (NOESY).

Hydrolysis of the amidinium salt (**1**) in the presence of base (KOH, D_2O) occurred readily to give the seven-membered amino-lactam (**3**), dideuterated α to the carbonyl group due to isotope exchange through reversible base-catalyzed enolization. Formation of 11-membered lactams has also been reported[20] to occur in some instances; however, no product corresponding to compound **5** was observed in this instance. Complete ^1H and ^{13}C NMR assignments for lactam **3** are summarized in Table 1. The carbonyl group of the lactam gave an IR absorption at 1636 cm^{-1} and a ^{13}C NMR chemical shift of 175.8 ppm. Subsequent reaction of the amino-lactam with BPMN (toluene, 75 °C) gave the anticipated bisalkylation product (**4**) with the carbonyl group giving an IR absorption of 1642 cm^{-1} and a ^{13}C NMR chemical shift of 177.2 ppm.

Verification of this sequence of reactions can be confirmed in part by reactions of DBU with BIIR. First, reaction of the polymer in solution (toluene, 110 °C) with an excess of DBU gave an un-cross-linked, modified polymer that was purified by precipitation. Characterization of the material by IR showed a broad carbonyl absorbance at 1649 cm^{-1}, consistent with an amide, while ^1H NMR (Figure 2) shows signals in the 2.5−3.5 ppm region and at 5.22 ppm consistent with an N-alkylation product analogous to lactam **3**; BIIR would appear to contain sufficient residual moisture for the direct hydrolysis of the initially formed amidinium salt under catalysis by excess DBU. Furthermore, there is no NMR evidence for the formation of conjugated-diene butyl rubber, which typically shows signals in the 4.7−6.0 ppm range,[6,8] as the product of dehydrohalogenation.

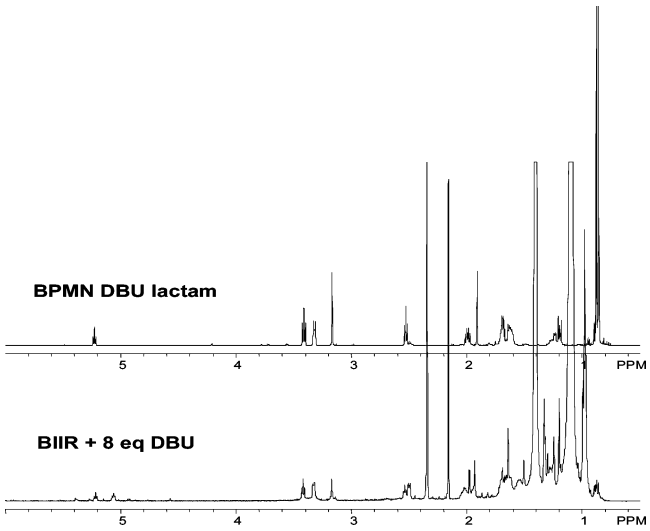
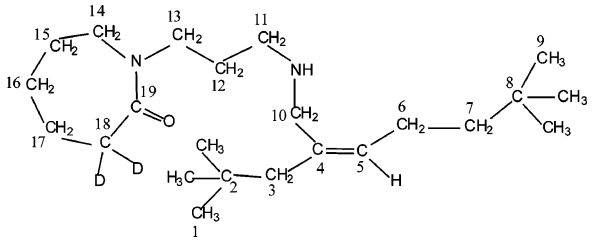


Figure 2. ^{1}H NMR spectra ($CDCl_3$) of BIIR reacted with 8 equiv of DBU (lower spectrum) and of BPMN−DBU lactam (**3**) (upper spectrum); lower spectrum shows residual butyl rubber at 5.05 ppm.

Table 1. ^{1}H and ^{13}C NMR Chemical Shift Assignments for the DBU−BPMN−Lactam (3)



position no.	^{1}H (ppm) and multiplicity	^{13}C (ppm)
1	0.84 (s)	29.8
2		31.8
3	1.9 (s)	48.5
4		135.1
5	5.22 (t)	132.6
6	1.98 (m)	23.4
7	1.18 (m)	44.8
8		30.4
9	0.86 (s)	29.2
10	3.15 (s)	49.8
11	2.52 (t)	46.7
12	1.67 (m)	28.7
13	3.40 (t)	46.1
14	3.31 (m)	49.8
15	1.60 (m)	28.8
16	1.69 (m)	30.1
17	1.62 (m)	23.4
18		37.2
19		175.8

Second, a sample of BIIR was cross-linked with 1 equiv of DBU, and then the insoluble material was examined by ATR-IR; a broad carbonyl absorption at 1650 cm^{-1} was observed, consistent with lactam formation in the cross-linked rubber.

A similar sequence of reactions has been demonstrated to occur upon reaction of DBN with BPMN, though with one small but significant difference—hydrolysis of the BPMN N-alkylation product of DBN was slower than that of the DBU amidinium salt (**1**). This is probably due to differences in ring strain in the two systems and the effects of ring strain upon kinetic reactivity. The consequence of this difference in hydrolytic reactivity is that reaction of BIIR with an excess of DBN leads to the formation of a rubber modified with an amidinium salt, as evidenced by ^{1}H NMR (not shown), rather than a lactam. The cross-linking of BIIR with DBN has been found to be less effective than with DBU (vide supra). This is consistent with the slower rate of hydrolysis since this reaction must occur before cross-linking through bisalkylation can occur.

With both DBU, as shown in Figure 1, and DBN, maximum cross-link density was obtained when 1 equiv of amidine base was used. This stoichiometry is consistent with the reaction sequence shown in Scheme 1. A 2:1 stoichiometry of BIIR to DBU is required to form a cross-link analogous to structure **4** or its hydrobromide salt. However, a second equivalent of DBU is required for the transformation analogous to **1** → **3** in Scheme 1 for neutralization of the hydrobromide salt (**2**). Thus, the reaction sequence shown in Scheme 1 is consistent with the cross-linking behavior shown in Figure 1. BIIR is produced industrially by bromination of butyl rubber in solution (hexanes) followed by steam stripping of the solvent. The residual water content in BIIR seems to be sufficiently high for hydrolysis of amidinium salts to occur.

DBU and DBN are widely described in the literature as nonnucleophilic bases and are commonly used for promoting dehydrohalogenation reactions; these reactions are described as proceeding "under mild conditions and without side reaction".[23] This present work has shown that there are clearly situations in which amidine bases are nucleophilic. In particular, as is shown by NMR in Figure 2, treatment of BIIR with DBU in toluene solution proceeds predominantly by N-alkylation, with no evidence of dehydrohalogenation to conjugated-diene butyl rubber. This atypical reactivity has led to the development of an unusual and efficient procedure for cross-linking BIIR which differs substantially from current methodologies[2] used to vulcanize halobutyl rubber.

Conclusions

It has been demonstrated that the amidine bases DBU and, to a lesser extent, DBN can cross-link BIIR. It has been shown through the use of the model compound BPMN that this can be accounted for by a very unusual but precedented series of reactions that involve the following: (1) N-alkylation to form an amidinium salt, (2) hydrolysis to an ammonium lactam, (3) deprotonation to an amino-lactam, and (4) a second N-alkylation to generate a cross-link structure. This cross-linking behavior is similar to that previously reported for primary amines[3] and for diamines.[22] DBU and DBN are, in essence, serving as latent primary amines.

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Supporting Information Available: Storage modulus and loss tangent for cross-linking of BIIR with DBN; COSY and HMBC spectra for DBU−BPMN lactam (**3**) and DBN−BPMN lactam; ^{1}H and ^{13}C NMR assignments for DBN−BPMN lactam. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Webb, R. N.; Shaffer, T. D.; Tsou, A. H. In *Kirk-Othmer Encyclopedia of Chemical Technology,* 4th ed.; John Wiley & Sons: New York, 2004.

(2) Hopkins, W.; von Hellens, W.; Koski, A.; Rausa, J. Rubber Expo 2001, Fall Technical Program, 160th, Cleveland, OH, Oct 16−20, 2001, pp 1854−1875.
(3) Parent, J. S.; White, G. D. F.; Whitney, R. A.; Hopkins, W. *Macromolecules* **2002**, *35*, 3374−3379.
(4) Parent, J. S.; White, G. D. F.; Whitney, R. A. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2937−2944.
(5) Parent, J. S.; Penciu, A.; Guillen Castellanos, S.; Liskova, A.; Whitney, R. A.; *Macromolecules* **2004**, *37*, 7477−7483.
(6) Parent, J. S.; Thom, D. J.; White, G.; Whitney, R. A.; Hopkins, W. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 2019−2026.
(7) Baldwin, F. P.; Malatesta, A. U.S. Patent 3,965,213, 1976.
(8) Tipnis, S. J. M.Sc. Thesis, Queen's University, Kingston, Canada, 2003.
(9) Oediger, H.; Moeller, F.; Eiter, K. *Synthesis* **1972**, 591−8.
(10) Lautenschlaeger, F. K. *Rubber Chem. Technol.* **1979** *52*, 213−31.
(11) McSweeney, G. P.; Morrison, N. J. *Rubber Chem. Technol.* **1983**, *56*, 337−43.
(12) Morrison, N. J. *Rubber Chem. Technol.* **1984**, *57*, 97−103.
(13) Skinner, T. D. *Rubber Chem. Technol.* **1972**, *45*, 182−92.
(14) Winters, R.; Heinen, W.; Verbruggen, M. A. L.; Lugtenburg, J.; van Duin, M.; de Groot, H. J. M. *Macromolecules* **2002**, *35*, 1958−1966.
(15) Gregg, E. C., Jr.; Lattimer, R. P. *Rubber Chem. Technol.* **1984**, *57*, 1056−97.
(16) Vukov, R. *Rubber Chem. Technol.* **1984**, *57*, 275−83.
(17) Vukov, R. *Rubber Chem. Technol.* **1984**, *57*, 284−90.
(18) Kuntz, I.; Zapp, R. L.; Pancirov, R. J. *Rubber Chem. Technol.* **1984**, *57*, 813−25.
(19) Alder, R. W.; Sessions, R. B. *Tetrahedron Lett.* **1982**, *23*, 1121−4.
(20) Hori, Y.; Nagano, Y.; Tanaka, K.; Taniguchi, H. *Chem. Express* **1986**, *1*, 491−4.
(21) Shi, M.; Shen, Y.-M. *Helv. Chim. Acta* **2002**, *85*, 1355−1363.
(22) Ivan, G.; Tavaru, E.; Giurginca, M.; Nicolescu, D. N. *Rev. Roum. Chim.* **1989**, *34*, 1017−28.
(23) Savoca, A. C. 1,8-Diazabicyclo[5.4.0]undec-7-ene. In *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Ed.; J. Wiley and Sons: New York, 1995.

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