# Polar, Functionalized Diene-Based Materials. 2. Free Radical Copolymerization Studies of 2-Cyanomethyl-1,3-butadiene with Styrene and Acrylonitrile

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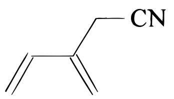
*Received February 8, 2000; Revised Manuscript Received May 30, 2000*

ABSTRACT: The solution free radical copolymerizations of 2-cyanomethyl-1,3-butadiene (CMBD) with styrene and acrylonitrile were studied. Traditional free radical polymerization kinetics were observed, giving copolymers with $\langle M_n \rangle$ values of $20 \times 10^3$−$60 \times 10^3$ g/mol and polydispersities typically near 1.5. The reactivity ratios of CMBD and styrene of 3.0 and 0.23 and CMBD and acrylonitrile of 1.5 and 0.4 indicated that the cyano monomer was more reactive than styrene or acrylonitrile. The copolymerization behavior was consistent with the reactivity ratios measured, giving nonideal, nonazeotropic copolymerizations, where the copolymers were always richer in cyano monomer than in styrene or acrylonitrile. All of the copolymers showed only one glass transition temperature that agreed well with the theoretical values calculated by the Gordon−Taylor equation. Finally, the cyano diene units incorporated into the copolymers maintained a similar microstructure seen in the homopolymers of approximately 95% 1,4 and 5% 4,3 structure.

## Introduction

The synthesis and utilization of functionalized polymeric materials have aroused continuing research interest due to the possibility of introducing the properties of a functional group to high molecular weight materials.[1] Despite the numerous potential applications in the rubber industry, only limited research has focused on the functionalized dienes and even less has focused on their copolymers with commercially available monomers, like styrene or acrylonitrile.[2−5] The reason is probably due to the relatively difficult synthesis of functionalized dienes. Stadler's group reported the copolymerization of (*N*,*N*-dialkylamino)isoprene with styrene and 1,3-butadiene.[5,6] Their research was focused on the anionic polymerization and the copolymer structural characterization. Penelle's group reported the free-radical polymerizations of several siloxy−butadiene derivatives with styrene and methyl methacrylate.[4] Their research included the reactivity ratios and NMR microstructural analysis.

Our group has synthesized functionalized diene derivatives with cyano, amino, and ester groups.[7] In this paper, the specific functionality incorporated is the cyano group. The monomer, 2-cyanomethyl-1,3-butadiene (CMBD), is shown below. Our interest is not only in synthesizing new, polar diene-based elastomers but also in modifying existing materials. Specifically, it is anticipated that poly(2-cyanomethyl-1,3-butadiene), poly(CMBD), will be a useful additive to improve the compatibility and mechanical properties of polymer blends. It is also anticipated that the incorporation of the polar monomer as a covalently bound modifier in diene-based materials will aid in cross-linking or in tailoring existing properties. For example, in nitrile rubber (NBR), the higher the acrylonitrile content, the higher the resistance to hydrocarbons, impermeability to gases, and thermal resistance, but the lower the resilience, the temperature flexibility, and solution viscosity.[8,9] In other words, the oil resistance and low-temperature flexibility are mutually incompatible. The cyano-substituted monomer could provide an ideal solution to this problem. It could be introduced covalently into NBR or styrene−butadiene rubber (SBR) as a third comonomer, taking advantage of the good solvent and oil resistance properties accompanying the cyano groups without decreasing the flexibility of the copolymer.



2-cyanomethyl-1,3-butadiene (CMBD)

We previously reported the successful synthesis of the homopolymer of CMBD via bulk, solution, and emulsion polymerization.[10] Below we present the synthesis of poly(2-cyanomethyl-1,3-butadiene-*co*-styrene) and poly(2-cyanomethyl-1,3-butadiene-*co*-acryonitrile) by solution free radical polymerization. The comonomers were chosen due to the potential applications mentioned above.

## Experimental Section

**Materials**. Bromine was purchased from Alfa. All other reagents were purchased from Aldrich. Benzoyl peroxide (BPO) was purified by recrystallization from methylene chloride. Tetrahydrofuran (THF), acetonitrile ($CH_3CN$), styrene, *o*-methylstyrene, and allyl cyanide were purified by distillation using calcium hydride or potassium. All other chemicals were used as received.

**Monomer Synthesis and Purification. 2-Cyanomethyl-1,3-butadiene.** The synthetic procedure utilized was described in our previous preprint and paper.[10] The monomer purification was accomplished in two steps. A 300 mL stainless steel Parr reactor was used for step one. The vessel was precooled before loading by placing it in an acetone/dry ice bath. When the temperature was below −10 °C, it was charged with CMBD (30 g), liquid sulfur dioxide (30 L), methanol (10 mL), and hydroquinone (0.25 g). The vessel was sealed quickly, slowly

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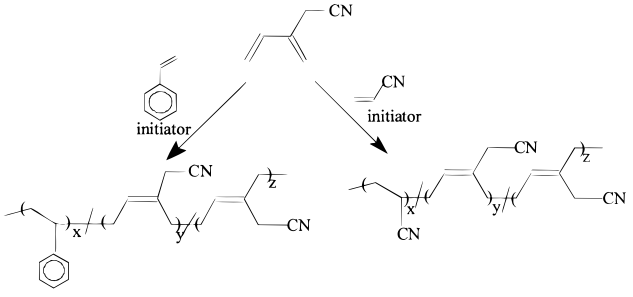
10.1021/ma0002287 CCC: $19.00

**Scheme 1. Copolymerization of CMBD with Styrene and Acrylonitrile**



heated to 85 °C, and maintained at that temperature for 4 h. After cooling to room temperature, the resulting product, 2-cyanomethyl-1,3-butadienesulfone, was filtered, washed with cold methanol, and dried in a vacuum oven. The yield of this step is approximately 35%. The product is a green crystal with a molecular weight of 157 g/mol. The structure was verified by $^1$H NMR. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 6.20 (s, 1H), 3.91 (s, 2H), 3.79 (s, 2H), 3.30 (s, 2H). To a round-bottom flask, 2-cyanomethyl-1,3-butadienesulfone (10 g) was added, stirred, and heated to 150 °C. A water aspirator, equipped with a cold trap, was used to collect the clear liquid product, CMBD. The yield of this step is approximately 85%. The structure was verified by GC-MS and high-resolution mass spectrometry (HR-MS). The theoretical mass was calculated to be 93.057 849 2 g/mol; HR-MS showed a measured mass of 93.057 853 54 g/mol with a deviation of 0.05 ppm. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 6.46 (dd, 1H, J1 = 12 Hz, J2 = 8 Hz), 5.47 (s, 1H), 5.33 (s, 1H), 5.24 (d, 1H, $J$ = 8 Hz), 5.19 (d, 1H, $J$ = 12 Hz), 3.27 (s, 2H). $^{13}$C NMR (300 MHz, $CDCl_3$): $\delta$ 119.66, 135.30, 136.37, 115.07, 20.67, 117.27 ppm.

**Polymer Synthesis**. A typical copolymerization reaction follows. The specific example given is for the synthesis of poly(2-cyanomethyl-1,3-butadiene-*co*-acrylonitrile). CMBD (0.80 g, 8.60 mmol), acrylonitrile (0.11 g, 2.07 mmol), THF (0.91 g, 12.60 mmol), and BPO (26.02 mg, 0.11 mmol) were added to a 20 mL ampule. After three cycles of freeze−pump−thaw, the ampule was sealed under vacuum and heated to 75 °C for 12 h. A stabilizer, 1,6-di-*tert*-butyl-4-methylphenol (7.02 mg, 0.032 mmol), was added at the end of the reaction. The polymer was precipitated in methanol (20 mL) and dried in a vacuum oven overnight at room temperature. The conversion was calculated on the basis of the amount of unreacted monomers as determined by GC or $^1$H NMR.

**Polymer Characterization.** NMR examination was performed with a Varian VXR-300 and VXR-400 in deuterated chloroform or acetonitrile at room temperature. COSY and NOESY experiments were performed to elucidate the polymer microstructures. Molecular weights of the polymers were determined with a Waters gel permeation chromatograph using polystyrene standards and tetrahydrofuran (THF) as the solvent. The glass transition temperatures ($T_g$) were determined with Perkin-Elmer Pyris differential scanning calorimeter at a heating rate of 10 °C from −130 to 100 °C with nitrogen purge. Glass transition temperatures were reported on the basis of the second heating.

## Results and Discussion

**Copolymerization**. The monomer, CMBD, was synthesized under reasonably mild conditions and in greater than 99% purity after a two-step purification. Copolymers of CMBD with styrene and acrylonitrile were synthesized via solution free radical polymerization in THF using BPO as the initiator (Scheme 1). The conversions and the copolymer compositions were monitored by NMR or GC.

The results of poly(2-cyanomethyl-1,3-butadiene-*co*-styrene) (CMBD−styrene) are listed in Table 1. As can be seen, when the CMBD feed composition increased from 15% to 85%, the copolymer composition increased from 28% to 94% within 12 h. The number-average molecular weight of the copolymers s1−s5 increased from 17.7 × $10^3$ to 29.6 × $10^3$ g/mol, which was close to the number-average molecular weight of poly(CMBD) synthesized under the same polymerization conditions. In each run, the CMBD composition in the copolymer is always higher than the CMBD feed composition. This suggested a higher reactivity ratio of CMBD compared to that of styrene. This behavior is consistent with our measured reactivity ratios for the monomer pair, which will be illustrated later in this paper. When the CMBD unit percentage in the copolymer increased from 28% to 94%, the copolymer appearance changed from a white solid to a viscous, tacky solid. All the copolymers were soluble in chloroform, but not completely soluble in the more polar solvent, acetonitrile. This contradicts the results of poly(CMBD), which was soluble in acetonitrile and not completely soluble in chloroform. This is easily understood because the less polar styrene unit contained in the copolymer decreased the solubility parameter of the copolymer compared to the case of the homopolymer.

Table 2 shows the kinetic results over a 24 h period of one copolymerization starting with 50:50 feed ratio. As the polymerization proceeded, the conversions of CMBD and styrene increased. The CMBD composition in the copolymer dropped from 97% to 73% from 4 to 8 h and then decreased slowly to 68% when the reaction was stopped at 24 h. The number-average molecular weight of the copolymers s6−s11 held constant near 20 × $10^3$ g/mol as expected. The corresponding polydispersities of copolymers s6−s11 increased from 1.74 to 3.37 with the polymerization time, suggesting an increasing in polymer branching. Polymerization with a lower initiator concentration, 0.1% BPO, was also carried out (s12). Compared to copolymer s11, a relatively high molecular weight ($\langle M_n \rangle = 64.3 \times 10^3$ g/mol) was obtained with a lower yield.

A similar series of poly(2-cyanomethyl-1,3-butadiene-*co*-acrylonitrile)s (CMBD−acrylonitrile) a1−a11 were synthesized in THF, and their results are shown in Table 3 and in Table 4. When the CMBD feed composition was lower than or equal to 35% (a1 and a2), the conversion of CMBD reached 100% within 12 h. Since the homopolymer of acrylonitrile or copolymer with a high percentage of acrylonitrile is not soluble in THF, precipitation of polymer a1 and a2 from the solvent was observed, and the polymerization reaction mixture became heterogeneous. Therefore, no data were reported for examples a1 and a2. For copolymers a3−a5, similar polymerization behavior was observed compared to s1−s5. The CMBD composition was always higher than the feed composition, indicating a higher reactivity than that of acrylonitrile. Within 12 h, the CMBD unit percentage in the copolymers increased from 65% to 84% when CMBD feed composition increased from 50% to 80%. It was also noticed that the differences between the feed and actual compositions in the copolymers in CMBD/acrylonitrile system were not as large as in the CMBD/styrene system. For example, the difference in polymer s3 in Table 1 was 23% while the difference in polymer a3 in Table 3 was 15%.

The kinetics of the copolymerization of CMBD with acrylonitrile was similar to that with styrene (Table 4). The conversions of CMBD and acrylonitrile increased with time, and the CMBD composition in the corre-

**Table 1. Copolymerization of CMBD with Styrene[a]**

| example no. | feed composition (c)[b] | conv (%) (c)[c] | conv (%) (s)[d] | copolymer composition (c)[e] | $\langle M_n\rangle$[f] (×$10^{-3}$) | PDI[f] | $T_g$ (°C)[g] |
|---|---|---|---|---|---|---|---|
| s1 | 0.15 | 80 | 37 | 0.28 | 17.7 | 1.58 | 60.6 |
| s2 | 0.25 | 70 | 22 | 0.51 | 18.7 | 1.77 | 45.7 |
| s3 | 0.53 | 64 | 17 | 0.77 | 21.6 | 1.97 | 13.6 |
| s4 | 0.75 | 62 | 16 | 0.92 | 25.8 | 2.08 | 2.7 |
| s5 | 0.85 | 64 | 23 | 0.94 | 29.6 | 2.10 | −2.9 |

[a] Polymerization conditions: solution free-radical polymerization, 75 °C, 1% BPO as the initiator, 1:1 THF as the solvent, 12 h. [b] Content of CMBD in the feed. [c] Percentage conversion of CMBD. [d] Percentage conversion of styrene. [e] Content of CMBD in the copolymer. [f] Data obtained by GPC. [g] Data obtained by DSC.

**Table 2. Copolymerization of CMBD with Styrene[a]**

| example no. | initiator (%) | time (h) | conv (%) (c)[b] | conv (%) (s)[c] | conv (%) (t)[d] | copolymer composition (c)[e] | $\langle M_n\rangle$[f] (×$10^{-3}$) | PDI[f] |
|---|---|---|---|---|---|---|---|---|
| s6 | 1 | 4 | 32 | 5 | 18 | 0.97 | 20.7 | 1.74 |
| s7 | 1 | 8 | 54 | 20 | 37 | 0.73 | 19.9 | 1.91 |
| s8 | 1 | 12 | 77 | 26 | 52 | 0.75 | 21.7 | 2.33 |
| s9 | 1 | 16 | 84 | 29 | 56 | 0.74 | 21.9 | 2.52 |
| s10 | 1 | 20 | 91 | 37 | 64 | 0.71 | 20.6 | 2.90 |
| s11 | 1 | 24 | 94 | 45 | 70 | 0.68 | 20.2 | 3.37 |
| s12 | 0.1 | 24 | 55 | 18 | 37 | 0.76 | 64.3 | 1.71 |

[a] Polymerization conditions: solution free-radical polymerization, 75 °C, BPO as the initiator, 1:1 THF as the solvent, CMBD:styrene feed ratio = 50:50. [b] Percentage conversion of CMBD. [c] Percentage conversion of styrene. [d] Total conversion. [e] Content of CMBD in the copolymer. [f] Data obtained by GPC.

**Table 3. Copolymerization of CMBD with Acrylonitrile[a]**

| example no. | feed[b] composition (c) | conv (%) (c)[c] | conv (%) (a)[d] | copolymer composition (c)[e] | $\langle M_n\rangle$[f] (×$10^{-3}$) | PDI[f] | $T_g$ (°C)[g] |
|---|---|---|---|---|---|---|---|
| a1 | 0.25 | –[h] | – | – | – | – | – |
| a2 | 0.35 | – | – | – | – | – | – |
| a3 | 0.50 | 87 | 47 | 0.65 | 16.4 | 1.54 | 9.2 |
| a4 | 0.65 | 83 | 52 | 0.75 | 24.3 | 1.76 | 5.0 |
| a5 | 0.80 | 76 | 57 | 0.84 | 29.5 | 2.48 | −0.2 |

[a] Polymerization conditions: solution free-radical polymerization, 75 °C, 1% BPO as the initiator, 1:1 THF as the solvent, 12 h. [b] Content of CMBD in the feed. [c] Percentage conversion of CMBD. [d] Percentage conversion of acrylonitrile. [e] Content of CMBD in the copolymer. [f] Data obtained by GPC. [g] Data obtained by DSC. [h] Not available.

**Table 4. Copolymerization of CMBD with Acrylonitrile[a]**

| example no. | initiator (%) | time (h) | conv (%) (c)[b] | conv (%) (a)[c] | conv (%) (t)[d] | copolymer composition (c)[e] | $\langle M_n\rangle$[f] (×$10^{3}$) | PDI[f] |
|---|---|---|---|---|---|---|---|---|
| a6 | 1 | 3 | 34 | 8 | 21 | 0.80 | 16.8 | 1.50 |
| a7 | 1 | 6 | 64 | 27 | 45 | 0.71 | 16.3 | 1.50 |
| a8 | 1 | 9 | 87 | 49 | 67 | 0.65 | 13.5 | 1.64 |
| a9 | 1 | 12 | 87 | 47 | 67 | 0.65 | 16.4 | 1.54 |
| a10 | 1 | 15 | –[g] | – | – | – | – | – |
| a11 | 0.1 | 12 | 38 | 25 | 0.60 | 0.60 | 23.6 | 1.43 |

[a] Polymerization conditions: solution free-radical polymerization, 75 $^{o}$C, BPO as the initiator, 1:1 THF as the solvent. [b] Percentage conversion of CMBD. [c] Percentage conversion of acrylonitrile. [d] Total conversion. [e] Content of CMBD in the copolymer. [f] Data obtained by GPC. [g] Not available.

sponding copolymers decreased from 80% to 65% within 12 h. The number-average molecular weights of the copolymers a6–a9 were all near 16 × $10^3$ g/mol. However, the increasing polydispersities were not observed as in the CMBD/styrene system. The PDI of copolymer a6–a9 remained constant near 1.5. The copolymerization matrix became heterogeneous within 12–15 h. The polymer precipitated from a10 was not completely soluble in THF, but was soluble in more polar solvents, such as acetone. Therefore, it was reasonable to conclude that the reason for precipitation during polymerization was not due to cross-linking but was due to the poor solubility of CMBD–acrylonitrile containing a high percentage of acrylonitrile. All of the CMBD–acrylonitrile copolymers were viscous, tacky solids due to the amount of CMBD incorporated. The solubility of CMBD–acrylonitrile was close to that of the homopolymer of CMBD. All were soluble in acetone, acetonitrile, and THF and not completely soluble in chloroform. Therefore, the $CD_3CN$ was used as the solvent in all NMR spectra of CMBD–acrylonitrile shown later. Polymerization with a lower initiator concentration, 0.1% BPO, was also carried out (a11). Compared to that of copolymer a9, a higher molecular weight ($\langle M_n\rangle = 23.6 \times 10^3$ g/mol) was obtained with a lower yield.

**Reactivity Ratios**. Since a copolymer's composition and monomer sequence distribution are mainly dependent on the concentration of the monomers and the reactivity of the monomers relative to the propagating chain ends, it is crucial to investigate the reactivity ratios of monomer pairs in a copolymerization system. Two methods have been used to determine reactivity ratios in the previous literature on copolymerization.[11,12] One is based on the data of copolymer composition/conversion, and the other is obtained from the information about monomer sequence distribution, typically gained from the copolymer NMR. The second method has some limitations, such as instrumental discrimina-

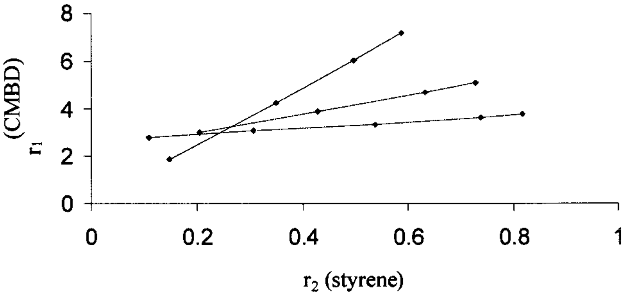


**Figure 1.** Reactivity ratios of CMBD and styrene.

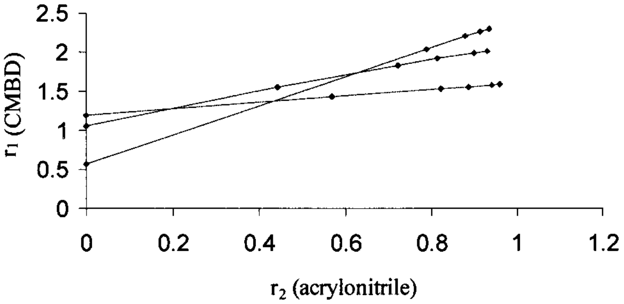


**Figure 2.** Reactivity ratios of CMBD and acrylonitrile.

**Table 5. Radical Reactivities (1/*r*) of Monomers with Various Polymer Radicals**

| | polymer radical | |
|---|---|---|
| monomer | styrene | acrylonitrile |
| 1,3-butadiene | 1.72 | 21.7 |
| isoprene | 1.95 | 33.3 |
| 2-TMSBD | 1.56 | *a* |
| 2-TBMSBD | 1.01 | |
| CMBD | 4.35 | 2.5 |

[a] Not available.

**Table 6. Values of $r_1r_2$ in Free-Radical Copolymerizations**

| | styrene | acrylonitrile |
|---|---|---|
| 1,3-butadiene | 0.81 | 0.017 |
| isoprene | 0.99 | 0.014 |
| 2-TMSBD | 0.77 | –[a] |
| 2-TBMSBD | 0.70 | – |
| CMBD | 0.69 | 0.60 |

[a] Not available.

tion, ambiguous assignment of NMR signals to monomer sequences, etc. Thus, it has been used in few cases to calculate reactivity ratios directly. In this paper, the first method was utilized. Instead of the most traditional way which usually needs the determination of copolymer composition at conversions close to zero (at least lower than 5%), a slightly different approach was taken, which involved the use of the Mayo−Lewis equation. The Mayo−Lewis equation, an integration equation derived from the copolymer composition differential equation, is compatible in cases with relatively higher conversions (higher than 10%). In the CMBD/styrene system, several copolymerizations with various feed ratios were performed. The polymerizations were stopped at conversions lower than 30% and were monitored by GC. The internal standards chosen, *o*-methylstyrene and allyl cyanide, were proven to have good correlations with styrene and CMBD, respectively. The values of data points plotted in Figure 1 were obtained using the Mayo−Lewis equation. The intersection circle showed that $r_1$(CMBD) is 3.0 ± 0.1 and $r_2$(styrene) is 0.23 ± 0.03. In the CMBD/acrylonitrile system, similar polymerizations were carried out. Because of the inability to detect the acrylonitrile using the GC, NMR techniques were used instead to quantify the conversions. The calculations were based on the NMR integration ratio of the unreacted monomers and the internal standard. A similar $r_1/r_2$ plot was drawn and is shown in Figure 2. Because of the higher instrumental error of the NMR technique than the GC, the lines in the $r_1/r_2$ graph did not intersect in a circle as small as the CMBD/styrene system. The $r_1$ (CMBD) is 1.5 ± 0.3 and $r_2$ (acrylonitrile) is 0.4 ± 0.2. The *Q*−*e* scheme was also tried to determine the reactivity ratios of CMBD and acrylonitrile. The *Q*−*e* values for styrene and acrylonitrile were obtained from literature, and those for CMBD were derived from the measured reactivity ratio with styrene mentioned earlier ($Q = 2.67$, $e = -0.191$).[12] The calculation results showed that $r_1$(CMBD) is 4.2 and $r_2$ (acrylonitrile) is 0.03. These data are less reliable compared to that from an $r_1/r_2$ plot due to the limited accuracy of *Q*−*e* parameters and the reliability of the Price−Alfrey equation assumption. Nonetheless, the data obtained from the NMR and *Q*−*e* techniques for the CMBD/AN case indicate that the CMBD is more reactive than acrylonitrile.

Table 5 shows various monomer reactivities with polymeric styrene and acrylonitrile radicals.[7,12−13] As can be seen from the first column, CMBD had the highest monomer reactivity with the styrene radical. Because of the polar electron-withdrawing cyano group, it was more reactive than isoprene. The value is higher than butadiene due to the polarity in addition to the electron-withdrawing group. CMBD was much more reactive than 2-(dimethylsiloxy)-1,3-butadiene (2-TMSBD) and 2-(*tert*-butyldimethylsiloxy)-1,3-butadiene (2-TBSMBD) because of the electron-withdrawing group of cyano instead of the electron-donating siloxy groups and the steric hindrance of the silicon-containing side groups. With the acrylonitrile radical, the trend is vague, probably due to the strong alternating tendency between acrylonitrile and butadiene or isoprene.

The values of $r_1r_2$ for various monomer pairs are shown in Table 6.[7,12,13] The greater the difference of the two monomer polarities, the lower the $r_1r_2$ value and the stronger tendency to form alternating copolymers instead of random copolymers. The polarity of CMBD is between styrene and acrylonitrile, and the polarity of butadiene and isoprene is close to that of styrene. The value of CMBD is the lowest in the first column because CMBD is the most polar monomer, and the polarity difference with styrene is the highest. Similarly, the value of CMBD is the highest in the second column because its polarity difference with acrylonitrile is the smallest.

The determined reactivity ratios for the two copolymerizations are consistent with the polymerization behavior observed and can be used to explain copolymer composition, monomer sequence distribution, etc. For example, the reactivity ratio of CMBD is higher than the other monomer in both copolymerization systems, which indicates a higher reactivity of it compared to that of styrene or acrylonitrile. Since $r_1 > 1$, $r_2 < 1$, and $r_1r_2 < 1$ in both systems, the two copolymerization systems could be represented by two curved lines that do not intersect with the diagonal in a *F*/*f* graph (see Figure 3, $F$ = instantaneous copolymer composition and $f$ = monomer feed composition). Both of the systems belong to a nonideal nonazeotropic copolymerization. According

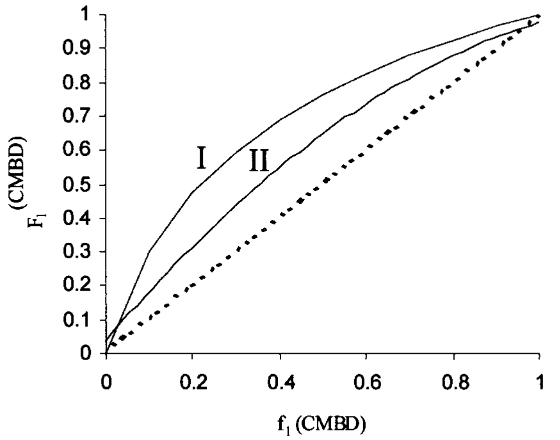


**Figure 3.** Dependence of the instantaneous copolymer composition $F_1$ on the initial comonomer feed composition $f_1$: curve I, CMBD/styrene; curve II, CMBD/acrylonitrile.

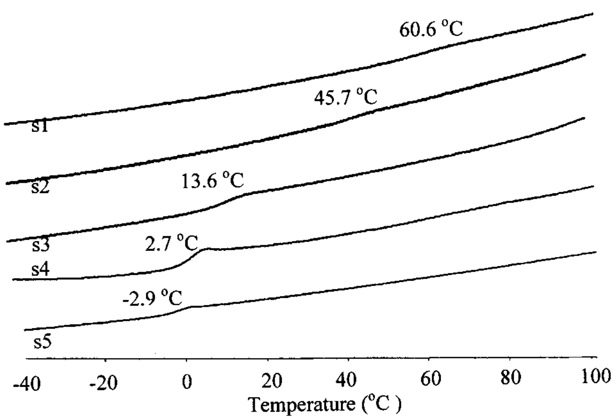


**Figure 4.** DSC data of the copolymers s1–s5.

to the plot, the copolymer will always be richer in CMBD than in styrene or acrylonitrile, which is consistent with what we observed. Under the exact same polymerization conditions including the monomer feed ratio, the difference between the copolymer composition and the initial monomer feed composition was always higher in the CMBD/styrene system than in the CMBD/acrylonitrile one. This is supported by the fact that curve I is further away from the diagonal than curve II in the *F*/*f* plot (Figure 3), with the diagonal representing the ideal azeotropic copolymerization where the copolymer composition will be equal to the monomer feed ratio.

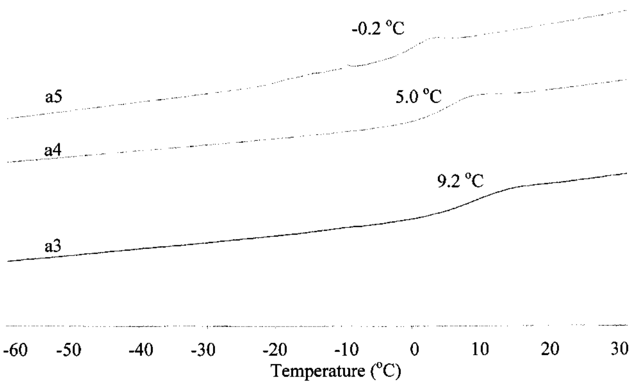


**Figure 5.** DSC data of the copolymers a3–a5.

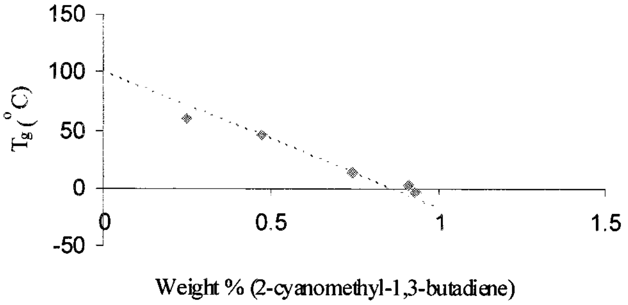


**Figure 6.** Copolymers s1–s5: glass transition temperature ($T_g$) as a function of the weight of CMBD in the copolymer.

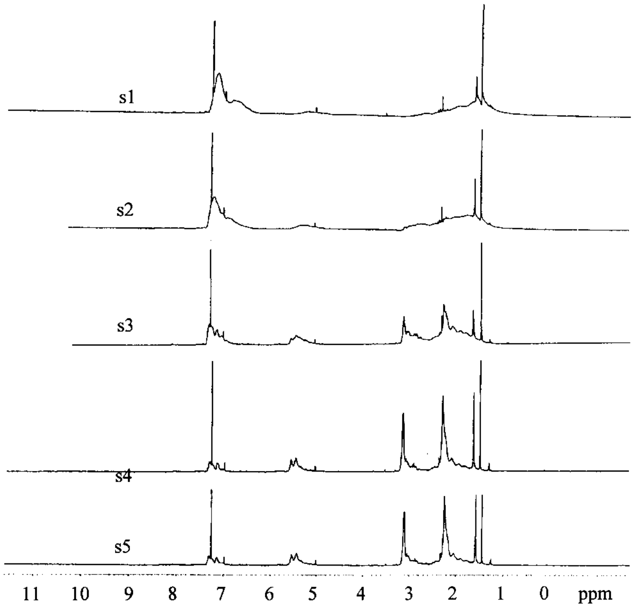


**Figure 7.** $^1$H NMR spectra of the copolymers s1–s5. $CDCl_3$ as the solvent.

**Thermal Properties.** The glass transition temperatures ($T_g$) of the copolymers s1–s5 are shown in Figure 4, and those of a3–a5 are shown in Figure 5. All of the copolymers showed only one glass transition temperature, characteristic of a random copolymer. From Figure 4, it can be seen that the higher the CMBD in copolymer, the lower the glass transition temperature. The $T_g$ decreased from 60.6 to −2.9 °C when the percentage of CMBD increased from 25% to 94%. A similar tendency was observed in Figure 5. When the CMBD composition in copolymer increased from 65% to 84%, the $T_g$ dropped from 9.2 to −0.2 °C. Figure 6 illustrates the dependence of the glass transition temperature of the copolymers on the s1–s5 weight percentage of CMBD in the copolymers. The theoretical line was obtained from the Gordon–Taylor equation, which usually fits the noncrystalline, random copolymer and was previously used successfully in the styrene–butadiene system. It can be seen that the data points for CMBD–styrene fit the equation very well. Although not shown, the copolymers a3–a5 also fit the Gordon–Taylor equation.

**NMR Characterization of the Copolymers.** The $^1$H NMR spectra of the copolymers s1–s5 are shown in Figure 7. By comparing to the $^1$H NMR spectra of the homopolymers, poly(CMBD) (Figure 8) and polystyrene, the signals of the copolymer spectra were easily assigned. The peaks attributed to the methylene protons next to the cyano group appeared at 3.12 ppm with the upfield shoulders at 2.8–3.0 ppm possibly due to the presence of the hetero sequence. The signals at 1.0–

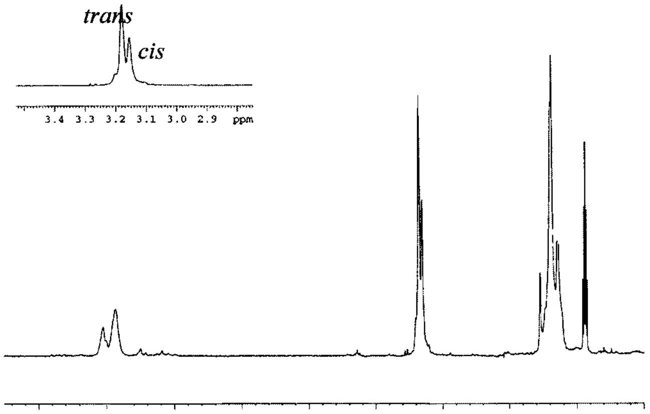


**Figure 8.** $^1$H NMR spectrum of poly(CMBD). $CD_3CN$ as the solvent.

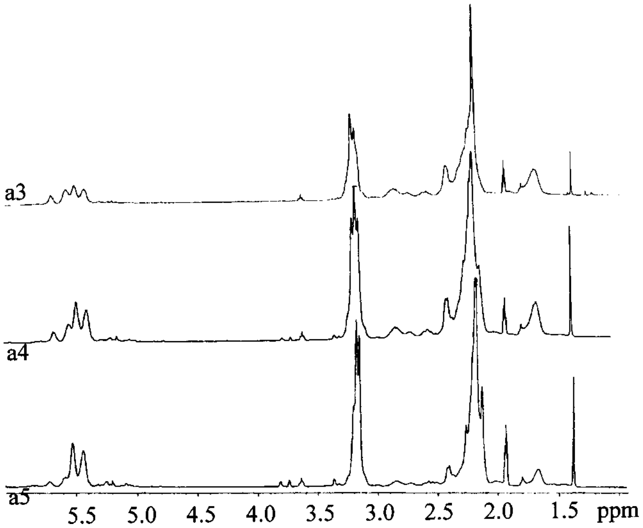


**Figure 9.** $^1$H NMR spectra of the copolymers a3−a5. $CD_3CN$ as the solvent.

2.5 ppm were attributed to methylene and methine protons along the backbone. The signals around 5.5 ppm corresponded to the vinyl protons in the 1,4 structure of the CMBD unit in the copolymer. A small amount of 4,3 structure (<5%) was observed, as determined by the characteristic vinyl proton peak at approximately 5.0 ppm, upfield from the 1,4 hydrogens. No obvious 1,2 structure was seen. The two signals at approximately 5.5 ppm were assigned to the *cis*- and *trans*-1,4 structure as indicated in the homopolymer spectrum (Figure 8). This pattern was only observed in the copolymer s3−s5 but not in s1−s2. This could be due to the equivalence of the *cis* and *trans* vinyl protons in the copolymer with a short CMBD sequence length. Therefore, it was reasonable to conclude that the CMBD sequence length increased from the copolymer s1 to s5, which was consistent with the CMBD composition increasing from s1 to s5. The aromatic protons in the styrene unit appeared from 6.9 to 7.4 ppm, and the chemical shifts of the *ortho* protons are further downfield than the chemical shifts of the *meta* and *para* protons. The integration ratio of the aromatic protons and the vinyl signals can be used to determine the copolymer composition. The results were consistent with what was calculated previously.

The $^1$H NMR spectra of the copolymers a3−a5 are shown in Figure 9. As can be seen, the vinyl proton signals were further split compared to the NMR spectra of the poly(CMBD) (Figure 9). Two new signals at 5.72 and 5.60 ppm appeared, and the amount of the two new peaks increased with the acrylonitrile composition of the copolymer. It is reasonable to assign the two new peaks to the hetero sequence of CMBD. Therefore, the CMBD sequence length increased with its composition in the copolymer, from a3 to a5. This was consistent with the splitting of the methylene proton signals around 3.2 ppm. In addition to the two signals, 3,16 and 3.18 ppm, which appeared in the spectra of the homopolymer, two new signals appeared at 3.21 and 3.25 ppm and followed the same decreasing trend as the sequence length of CMBD increased from the copolymer a3−a5. Similar to the homopolymer and CMBD−styrene, only a small amount of 4,3 structure was observed near 5.0 ppm, and no obvious 1,2-structure was seen. The signals from 2.4 to 2.9 ppm were attributed to the methine proton next to the cyano group in the acrylonitrile unit. The signals from 1.3 to 2.4 ppm correspond to the different methylene protons along the copolymer backbone.

## Conclusion

Poly(2-cyanomethyl-1,3-butadiene-*co*-styrene) and poly(2-cyanomethyl-1,3-butadiene-*co*-acrylonitrile) have been successfully synthesized via free radical solution polymerization, and the copolymerization behavior was investigated. The reactivity ratios of CMBD with styrene and acrylonitrile were determined by the Mayo−Lewis equation. The cyano-substituted monomer, CMBD, had a higher reactivity than styrene and acrylonitrile. Compared to butadiene, isoprene, 2-TMSBD, and 2-TBMSBD, CMBD had the highest monomer reactivity with the styrene or acrylonitrile radical. The resulting copolymers' glass transition temperatures were dependent on the copolymer composition and fit the Gordon−Taylor equation. The copolymer composition was mainly controlled by the monomer feed ratio. All the copolymers obtained were random, noncrystalline polymers, which showed only one $T_g$ on DSC.

Although the results focus on copolymerizations incorporating two monomers, they imply that CMBD can be used potentially as a third comonomer in existing materials, such as SBR or NBR. Advantage can be taken of CMBD's high reactivity as well as the good solvent and oil resistance properties accompanying the cyano groups, without decreasing the flexibility of the copolymers.

**Acknowledgment.** We gratefully acknowledge financial support from the National Science Foundation Faculty Early Career Development Award (Div. of Mat. Res.), Dupont Young Faculty Award, 3M Young Faculty Award, and Iowa State University Start-up Funds.

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MA0002287