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Polar, Functionalized Diene-Based Materials. 1. Bulk, Solution, and Emulsion Free Radical Polymerization of 2-Cyanomethyl-1,3-butadiene

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ABSTRACT: The bulk, solution, and emulsion free radical polymerizations of 2-cyanomethyl-1,3-butadiene were studied. Traditional bulk free radical polymerization kinetics were observed, giving polymers with $\langle M_n \rangle$ values of 20×10^3−60×10^3 g/mol and polydispersities near 1.5. In solution polymerization, the highest molecular weight (82×10^3 g/mol at 53% conversion) was obtained in tetrahydrofuran, with a broader polydispersity attributed to chain transfer to the solvent. In these two types of polymerizations, the Diels−Alder side product yield was affected by initiator concentration, solvent concentration, and polymerization time. Emulsion polymerization gave the highest molecular weight of poly(2-cyanomethyl-1,3-butadiene) to date of 128×10^3 g/mol in significantly shorter reaction time than bulk or solution reactions. Finally, the polymer microstructure of approximately 95% 1,4 and 5% 4,3 structure was determined, with the percent *cis*-1,4 (36−45%) varying with the polymerization temperatures. The glass transition temperature of poly(2-cyanomethyl-1,3-butadiene) is near −18 °C, based on the molecular weight and the microstructure.

Introduction

Synthesis and utilization of functionalized polymeric materials has long sparked research interest because of the potential applications as compatibilizing agents in polymer blends, additives to increase mechanical properties, drug delivery reagents, etc. In this area, considerable attention has been given to various styrene-based materials.[1] However, except for a few commercially interesting alkyl- and halogen-substituted butadienes, functionalized dienes have been studied far less.[2] A few silicon-containing butadiene derivatives with functional groups at the C-2 position, including trialkylsilyl, trialkoxysilyl, and *N*,*N*-dialkylaminosilyl, have been examined, mainly with a focus on anionic polymerization.[3−7] Other butadiene derivatives with amino side groups have also been described. Stadler's group reported the anionic and free radical polymerization of dialkylaminoisoprenes and copolymerizations with styrene and 1,3-butadiene.[8−11] Our research has mainly focused on diene derivatives with polar functional groups, such as cyano, ester, and amino.[12,13] To introduce these functional groups into polymers, 1,3-butadiene monomers with specific groups were synthesized and polymerized. Compared to another popular route to introduce functionality, chemical modification of nonfunctionalized polymer, this strategy has many advantages. For example, side reactions accompanying modification are avoided, and the distribution of functionality is far more controlled.

In this paper, 2-cyanomethyl-1,3-butadiene was synthesized and polymerized by free radical polymerization. The specific functional group was chosen because of the interest in investigation of the polar effects of the cyano group on the monomer reactivity, polymer microstructure, and final properties. It is anticipated that the cyano group could be converted to different functional groups, making the monomer or the resulting polymer precursors in the synthesis of other functionalized diene polymers. Furthermore, after hydrogenation, the synthesis of polar, functionalized polyolefins with an ethylene cyanoethylene type repeating unit could be obtained. Potential applications for poly(2-cyanomethyl-1,3-butadiene) include the use as an additive to improve the compatibilities and mechanical properties of polymer blends. The monomer could serve as a comonomer in existing materials to aid in cross-linking or to alter existing properties. An example of the latter includes the introduction of the cyano diene into styrene−butadiene rubber (SBR) or acrylonitrile−butadiene rubber (NBR) to improve oil and solvent resistance as well as adhesive properties.

Previously, the cyano functionality has been introduced into butadiene at the C-1 or C-2 positions.[2,14] However, the key steps of the synthesis of these two monomers involved a pyrolysis process at temperatures greater than 500 °C. Moreover, 2-cyano-1,3-butadiene displayed a strong tendency to form Diels−Alder dimers. Herein, we report the synthesis of 2-cyanomethyl-1,3-butadiene, in which the cyano functionality was introduced under milder and more controlled conditions. Our initial work has been in the free radical polymerization of this new monomer. Therefore, in addition to monomer synthesis, the subsequent bulk, solution, and emulsion polymerizations and the initial structural and thermal characterization are discussed.

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. All solvents, tetrahydrofuran (THF), acetone, dioxane, nitromethane, and acetonitile, were purified by distillation using calcium hydride or potassium. All other chemicals were used as received.

Monomer Synthesis. 2-Cyanomethyl-1,3-butadiene (III). The monomer III was made in three steps. Bromine (159.82 g, 1 mol) was added dropwise to isoprene (68.12 g, 1 mol) in a two- or three-necked round-bottom flask which was cooled using a dry ice/acetone bath. The reaction temperature was monitored internally and was maintained below −20 °C. The yield of this step is almost 100%. The product, 1,4-dibromo-

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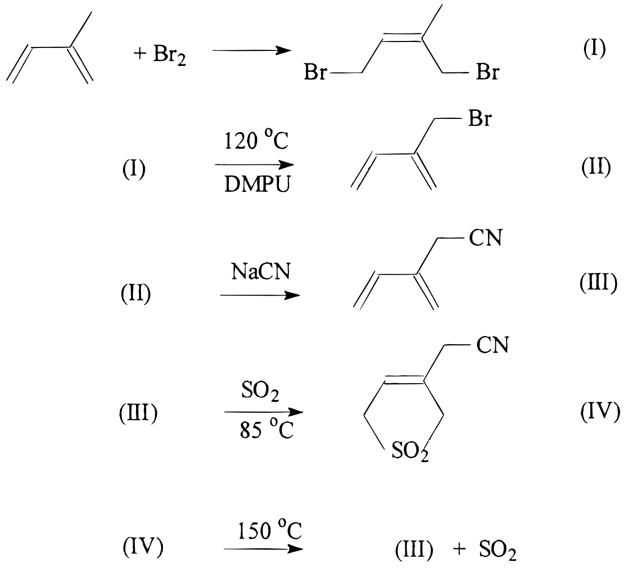
2-methyl-2-butene (I), is a yellow liquid. Mass spectrometry: $m/e = 228$ g/mol. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.91 (t, 1H), 3.96 (m, 4H), 1.88 (s, 3H). Compound I was used in the second step without further purification. 1,3-Dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU) was added to a stirred solution of compound I using 2:1 v/v ratio. The solution was heated until the temperature reached 120 °C. Vacuum was applied using an aspirator, and 2-bromomethyl-1,3-butadiene (II) was collected. The product is a light yellow liquid. Mass spectrometry: $m/e = 147$ g/mol. Compound II was used in the third step without further purification. Crude compound II from the last step, sodium cyanide (73.3 g, 1.5 mol), acetonitrile (500 mL), and tetrabutylammonium chloride (2 g) were added together and stirred at room temperature for 48 h. The resulting mixture was quenched with water, extracted with ether twice, and washed with saturated sodium chloride solution. After distillation, 34 g of compound III was obtained. The overall yield for step 2 and step 3 is 35%. The product, 2-cyanomethyl-1,3-butadiene (III), was verified by ^{1}H NMR and GC-MS. Mass spectrometry: $m/e = 93$ g/mol.

Monomer Purification. 2-Cyanomethyl-1,3-butadiene (III). The monomer purification was completed 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 compound III (30 g), liquid sulfur dioxide (30 mL), methanol (10 mL), and hydroquinone (0.25 g). The vessel was sealed quickly, slowly 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 (IV), was filtered, washed with cold methanol, and dried in a vacuum oven. A 17.8 g sample of compound IV was obtained after being dried. The yield of this step is 35%. The product is a green crystalline product with a molecular weight of 157 g/mol. The structure was verified by ^{1}H NMR. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.20 (s, 1H), 3.91 (s, 2H), 3.79 (s, 2H), 3.30 (s, 2H). Compound IV (10 g) was added to a round-bottom flask, stirred, and heated to 150 °C. A water aspirator, equipped with a cold trap, was used to collect the clear liquid product, compound III (5 g). The yield of this step is 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, $CDCl_3$): δ 6.46 (dd, 1H, $J_1 = 12$ Hz, $J_2 = 8$ 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, $CDCl_3$): δ 119.66, 135.30, 136.37, 115.07, 20.67, 117.27 ppm.

Bulk and Solution Polymerization. Poly(2-cyanomethyl-1,3-butadiene). The monomer, solvent, and initiator were added to an ampule. After three cycles of freeze−pump−thaw, the ampule was sealed under vacuum and heated to the desired temperature. A stabilizer, 2,6-di-*tert*-butyl-4-methylphenol, was added at the end of the reaction. The polymer was precipitated in methanol and dried in a vacuum oven. ^{1}H NMR (300 MHz, CD_3CN): δ 5.52, 5.53 (1H), 3.18, 3.16 (2H), 2.1−2.4 (4H). The theoretical weight percents are 77.38% C, 7.58% H, and 15.04% N. Elemental analysis showed 76.58% C, 7.92% H, and 14.02% N. After each polymerization, ^{1}H NMR spectroscopy of the polymerization mixture was performed. The conversion was calculated based on the integration ratio of the remaining monomer to the polymer from the proton NMR spectrum. The most characteristic proton signals used in the calculations were the C-5 methylene proton peaks in the monomer (3.27 ppm) and in the polymer (3.16−3.18 ppm).

Emulsion Polymerization. Poly(2-cyanomethyl-1,3-butadiene). The monomer (1 g), potassium persulfate ($K_2S_2O_8$, 12 mg), sodium dodecyl sulfate (SDS, 40 mg), sodium bicarbonate ($NaHCO_3$, 12 mg), and water (7.2 g) were added to a 50 mL three-necked round-bottom flask. The flask was supplied with N_2 (via a mineral oil bubbler) through a gas inlet adapter. The solution was degassed for half an hour before it was heated to 50 °C. After the desired reaction time, the vessel was cooled to room temperature. Saturated NaOH solution (2 mL) or acetone (2 mL) was added to destroy the emulsion. The polymer was precipitated in MeOH. The polymer was dissolved in THF containing a stabilizer, 2,6-di-*tert*-butyl-4-methylphenol, and reprecipitated in MeOH. The polymer was dried in a vacuum oven. The yield was based on the polymer weight.

Scheme 1. Synthesis and Purification of 2-Cyanomethyl-1,3-butadiene (III)



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 using a Waters gel permeation chromatography using polystyrene standards. The glass transition temperatures (T_g) were determined with a Perkin-Elmer Pyris differential scanning calorimeter (DSC) 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

Synthesis and Purification of 2-Cyanomethyl-1,3-butadiene (Scheme 1). The limited study of polymerization of substituted 1,3-butadienes is mostly due to the difficulty in synthesizing and purifying the corresponding monomers. Our group first utilized a two-step synthesis to yield an important substituted 1,3-butadiene precursor, 2-bromomethyl-1,3-butadiene (II), starting from isoprene. The first step, 1,4-addition of bromine to isoprene, gave 1,4-dibromo-2-methyl-2-butene (I) in nearly quantitative yield.[15] Low reaction temperatures (<−20 °C) were necessary to avoid the production of other isomers. Subsequent dehydrobromination using 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU) gave compound II. Other side products included isomers of compound II and other bromides based on the GC-MS spectrum. Because of the similarities of structures, all attempts to purify compound II using normal physical separation methods, distillation or flash chromatography, from the product mixture failed. Therefore, the mixture from the last step was directly used to proceed to the substitution reaction with sodium cyanide. This led to the desired 2-cyanomethyl-1,3-butadiene (III). Because of high polymerization reactivity of compound III, high temperatures were avoided, and a phase transfer reagent, tetrabutylammonium chloride, was used to shorten the reaction time. Again, it was almost impossible to purify compound III using normal physical separation methods.

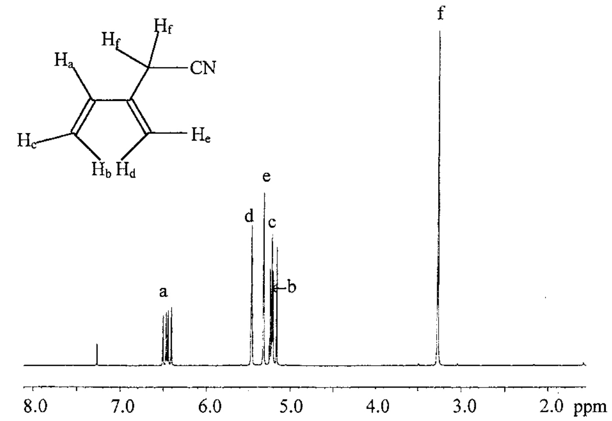


Figure 1. ^{1}H NMR spectrum of 2-cyanomethyl-1,3-butadiene (III).

Table 1. Bulk Free Radical Polymerization of III at 75 °C

example	initiator[a]	time (min)	$\langle M_n \rangle$ ($\times 10^{-3}$)[b]	PDI	conv (%)	DA yield (%)[c]	*cis*/*trans*[d]
1	1% BPO	120	39.2	2.11	44	1	40:60
2	1% AIBN	20	20.3	1.50	10	<1	*e*
3	1% AIBN	40	20.7	1.47	22	1	44:56
4	1% AIBN	60	21.4	1.42	33	1	41:59
5	1% AIBN	80	25.9	1.50	40	2	43:57
6	1% AIBN	100	25.7	1.71	53	2	41:59
7	1% AIBN	120	37.2	1.93	71	2	41:59
8	1% AIBN	140	33.9	3.37	80	3	40:60

[a] Mole percentage. [b] $\langle M_n \rangle$ is based on GPC calibrated with polystyrene. [c] Diels–Alder dimer yield. [d] The *cis*/*trans* ratio in 1,4 structure. [e] Not available.

Table 2. Bulk Free Radical Polymerization of III at 60 and 45 °C

example	% initiator[a]	temp (°C)	time (h)	$\langle M_n \rangle$ ($\times 10^{-3}$)[b]	PDI	conv (%)	DA yield (%)[c]	*cis*/*trans*[d]
1	1	60	2	27.6	1.53	12	1	36:64
2	1	60	3	27.6	1.55	19	1	36:64
3	1	60	4	27.6	1.64	27	2	36:64
4	1	60	5	33.7	1.57	34	3	37:63
5	1	60	6	35.8	1.61	38	4	36:64
6	0.5	60	5	37.0	1.55	24	3	36:64
7	0.25	60	5	45.3	1.55	17	3	37:63
8	1	45	22	62.0	1.86	17	<1	32:68

[a] AIBN, mole percentage. [b] $\langle M_n \rangle$ is based on GPC calibrated with polystyrene. [c] Diels–Alder dimer yield. [d] The *cis*/*trans* ratio in 1,4 structure.

Therefore, a two-step chemical purification using sulfur dioxide was used. The reactions of sulfur dioxide with dienes was first reported by Frank et al.[16] The dienes utilized were limited to 1,4-butadiene, isoprene, and 2,3-dimethyl-1,3-butadiene. To our knowledge, this report is the first to detail the synthesis of a dienesulfone starting from a diene with a polar substituent. No peak other than 2-cyanomethyl-1,3-butadiene was observed by GC-MS. The proton NMR of compound III is shown in Figure 1.

Synthesis of Homopolymer. Three free radical polymerization methods: bulk, solution, and emulsion were used to synthesize the homopolymer of 2-cyanomethyl-1,3-butadiene (III). The results of bulk free radical polymerization of III are listed in Table 1 and in Table 2. Benzoyl peroxide (BPO) and 2,2′-azobis(isobutyronitrile) (AIBN) were used as the initiators in the bulk polymerization studies. Several observations were made. First, under the exact same polymerization conditions, AIBN repeatedly gave polymers with higher yields, but with similar molecular weights as BPO initiated polymers (Table 1, examples 1 and 7). Consequently, AIBN was used in further bulk polymerizations. Second, in a kinetic study of the bulk polymerization (75 °C, 1% AIBN, Table 1, examples 2–8), it was observed that with increased polymerization time the conversion increased from 10% to 80% with no obvious autoacceleration seen. The number-average molecular weight was nearly constant at approximately 20×10^3 g/mol during the first hour and increased at longer times. Within 2 h, $\langle M_n \rangle$ reached 37×10^3 g/mol. The polymer did cross-link if the polymerization time exceeded 3 h. The polydispersities of the resulting materials followed the same increasing tendency as the $\langle M_n \rangle$. The increasing PDI and $\langle M_n \rangle$ could be due to the onset of branching, especially in example 8 (Table 1) with a PDI of 3.37. This explanation is consistent with the well-known fact that branching increases with conversion and may be a precursor to cross-linking.[22]

Bulk polymerizations were also performed at lower temperatures, 60 °C, using the same amount of initiator, 1% AIBN. The results are shown in Table 2 (examples 1–5). As expected, the lower the polymerization temperature, the lower the propagation rate, as evidenced by significantly lower conversion at equivalent times (Table 1, example 7; Table 2, example 1). The polydispersities were all near 1.5–1.6, showing no obvious change with time. This could be due to a decreased likelihood of branching at the lower 60 °C temperature. Polymerizations using lower AIBN concentrations, 0.5% and 0.25%, were also performed (Table 2, examples 6 and 7). As the concentration of initiator decreased, the molecular weight increased and the conversion decreased. Bulk polymerizations were also performed at an even lower temperature, 45 °C (Table 2, example 8). As expected, the highest molecular weight ($\langle M_n \rangle = 62 \times 10^3$ g/mol) was obtained at this temperature, compared to those experiments at higher temperatures with similar conversions (Table 1, example 3; Table 2, example 2). Obviously, a longer reaction time was needed to reach similar yields due to the slower propagation rate at the lower temperature. In summary, homopolymers of III with $\langle M_n \rangle$ from 20×10^3 to 62×10^3 g/mol have been synthesized, and the bulk polymerization behavior followed the traditional free radical polymerization theory.

In free radical polymerization, polarity has the major effect on the overall rate of addition. In diene type systems, the corresponding radicals are nucleophilic and electron-withdrawing substituents facilitate the addition of the nucleophilic radicals. Therefore, the reactivity of 2-cyanomethyl-1,3-butadiene should be larger than that of isoprene and 5-(*N*,*N*-dialkylamino)isoprene. Our experiments have confirmed this prediction. Under the same polymerization conditions in Table 1 (1% AIBN, 75 °C), isoprene afforded less than a 5% yield after 2 h and 35% yield after 24 h. The 5-(*N*,*N*-dialkylamino)isoprenes, other polar monomers examined in the Sheares group, also showed this effect, providing 50–60% yield (dimethyl, 52%; diethyl, 58%; di-*n*-propyl, 56%; diisopropyl, 60%; di-*n*-butyl, 60%) after 24 h. Isoprene is not readily polymerized under free radical conditions in bulk presumably due to the high mutual termination of growing radicals.

The results of solution radical polymerizations of 2-cyanomethyl-1,3-butadiene are shown in Table 3. To

Table 3. Solution Free Radical Polymerization of III at 75 °C

example	initiator[a]	solvent	ratio[b]	time (h)	$\langle M_n \rangle$ ($\times 10^{-3}$)[c]	PDI	conv (%)	DA yield[d]	*cis*/*trans*[e]
1	1% BPO	dioxane	3:1	24	25.9	1.82	80	*f*	
2	1% BPO	dioxane	5:1	24	15.9	1.44	85		
3	1% BPO	THF	2:1	18	18.3	1.92	60	1	
4	1% AIBN	THF	2:1	18	9.4	1.78	65	<1	
5	1% BPO	THF	1:1	12	32.6	2.28	72	3	47:53
6	1% BPO	THF	2:1	12	20.6	1.60	45	1	50:50
7	1% BPO	THF	3:1	12	16.1	1.58	40	1	51:49
8	0.1% BPO	THF	1:1	12	59.0	1.75	34	5	48:52
9	0.1% BPO	THF	1:1	24	66.2	1.89	40	6	46:54
10	0.05% BPO	THF	1:1	24	68.8	1.73	27	10	47:53
11	0.01% BPO	THF	1:1	24	81.2	1.73	17	12	48:52
12	0.1% BPO	THF	0.5:1	24	82.1	2.28	53	12	45:55
13	0.05% BPO	THF	0.5:1	24	78.0	1.94	39	15	45:55
14	0.01% BPO	THF	0.5:1	24	87.3	1.86	29	16	48:52
15	1% BPO	acetone	1:1	12	36.6	4.50	78		
16	1% BPO	acetonitrile	1:1	12	28.6	2.66	57		
17	1% BPO	nitromethane	1:1	12		*g*	82		

[a] Mole percentage. [b] Solvent/monomer volume. [c] $\langle M_n \rangle$ is based on GPC calibrated with polystyrene. [d] Diels−Alder dimer yield ratio. [e] The *cis/trans* ratio in 1,4 structure. [f] Not available. [g] Very broad.

examine the influence of solvent polarity, solubility, chain transfer, etc., on the polymerizations, the solvents chosen were dioxane, THF, acetone, acetonitrile, and nitromethane. Using dioxane as the solvent (Table 3, examples 1 and 2), two layers were observed during polymerization, indicating the precipitation of the polymers. Therefore, dioxane was not further studied as it is a poor solvent for poly(2-cyanomethyl-1,3-butadiene). Using THF as the solvent and identical polymerization conditions, BPO gave polymers with higher molecular weight than AIBN initiated polymers (Table 3, examples 3 and 4). This could be a result of BPO having a longer half-life than AIBN at the same temperature. BPO was therefore chosen as the initiator for the remaining solution polymerizations. Various concentrations of initiator and amounts of THF were examined. The results are shown in Table 3, examples 5−14. The polymerization behavior followed traditional free radical polymerization theory. The higher the amount of solvent used, the lower the conversion and the lower the molecular weight of the resulting polymers due to the chain transfer to solvent. With a lower concentration of initiator, higher molecular weights were accompanied by lower yields. The highest $\langle M_n \rangle$ obtained was 87×10^3 g/mol, using the lowest amount of initiator and the lowest solvent/monomer ratio (Table 3, example 14). Using varying amounts of THF (Table 3, examples 5−7), the chain transfer constant in THF was calculated to be 1.15×10^{-3}, assuming the solvent is the main chain transfer agent. Other polar solvents, acetone, acetonitrile, and nitromethane, were also used (Table 3, examples 15−17). In each case, polymers with polydispersities larger than 2.6 were obtained. This is due to the high degree of chain transfer to these solvents that have acidic hydrogens.

A very interesting aspect of the polymerization of 1,3-butadienes is the tendency to form Diels−Alder dimers. Although reported in several references, this behavior is not observed in every case.[14,17−20] Small amounts of the Diels−Alder dimers of 2-cyanomethyl-1,3-butadiene were observed in both the bulk and solution polymerizations. The dimers were separated, and the structure was proven by GC-MS using the chemical ionization method. The yields of the dimers (DA yield) are listed in Tables 1−3. As can be seen, the yield of dimers typically increased with polymerization time, decreasing concentration of initiator, and decreasing amount of solvent used. To test this theory, a polymerization was run, optimizing the potential contributing factors (no initiator, bulk, 75 °C). Indeed, this reaction yielded more Diels−Alder dimers than 1,4- and 3,4-addition products combined. It was concluded that the Diels−Alder reaction is a competitive process to the normal addition polymerization reactions, and the degree to which it occurs is significantly influenced by the above-mentioned factors.

Table 4. Emulsion Polymerization of III at 50 °C[a]

example	time (h)	conv (%)	$\langle M_n \rangle$ ($\times 10^{-3}$)[a]	PDI
1	1	22	128	2.46
2	1.5	42	cross-linked	
3	2	56	cross-linked	

[a] Recipe (by weight): monomer 25, water 180, SDS 10, potassium persulfate 0.3, sodium bicarbonate 0.3. [b] $\langle M_n \rangle$ is based on GPC calibrated with polystyrene.

Emulsion polymerization was also used to synthesize poly(2-cyanomethyl-1,3-butadiene). The advantages of the technique are well-known, including good thermal control and the use of water instead of organic solvent. Moreover, increasing molecular weight with increasing polymerization rate becomes possible. Various conditions were examined. The recipe used in a few examples and the results obtained are shown in Table 4. High molecular weight polymer was obtained in an hour (conversion = 22%, $\langle M_n \rangle = 128 \times 10^3$ g/mol, PDI = 2.46, *cis/trans* in 1,4 structure = 34:66). However, due to the high molecular weight and the existence of active cyano groups along the backbone, the polymer cross-linked at higher conversions (>40%). Though it appears not to be practical to synthesize the homopolymer of compound III using emulsion polymerization techniques, the monomer could be used in small percentages as a potential third comonomer in emulsion copolymerizations. For example, it could be incorporated into commercial NBR or SBR, taking advantage of the high reactivity and the good solvent and oil resistance properties accompanying the cyano groups, without decreasing the flexibility of the copolymer.

Thermal Characterization of Poly(2-cyanomethyl-1,3-butadiene). The glass transition temperatures of poly(2-cyanomethyl-1,3-butadiene) were measured by DSC. The T_g of example 7 in Table 1 ($\langle M_n \rangle = 37.2 \times 10^3$ g/mol, *cis*:*trans* = 41:59) is −18 °C, which as expected is much higher than the T_g of polyisoprene due

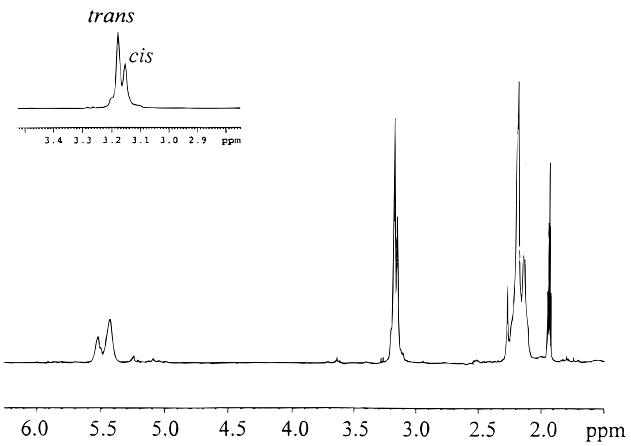
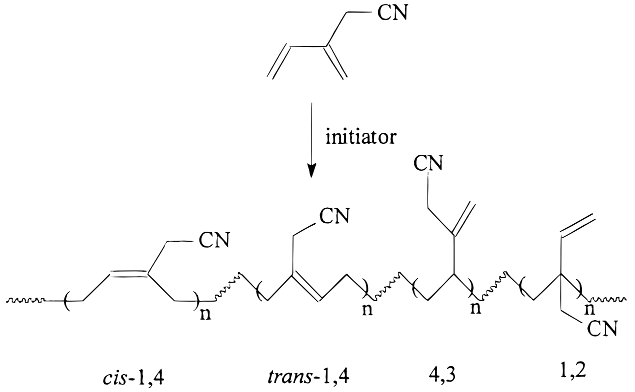


Figure 2. ^{1}H NMR spectrum of poly(2-cyanomethyl-1,3-butadiene).

Scheme 2. Polymerization of 2-Cyanomethyl-1,3-butadiene (III)



to the polar cyano substituent. The T_g of example 4 in Table 2 ($\langle M_n \rangle = 33.7 \times 10^3$ g/mol, *cis:trans* = 37:63) is −15 °C, slightly higher than −18 °C due to the higher percentage of *trans* microstructure. The T_g of example 14 in Table 3 ($\langle M_n \rangle = 87.3 \times 10^3$ g/mol, *cis:trans* = 48:52) is −15 °C, also higher than −18 °C though it has a lower *trans* microstructure. The reason is due to its much higher molecular weight than example 7 in Table 1.

Polymer Microstructure. Because of the close relationship between microstructure and polymer properties, the elucidation of the polymer microstructure is not only interesting but also crucial in establishing structure/property relationships. There are four possible microstructures, as shown in Scheme 2: *cis*-1,4, *trans*-1,4, 4,3, and 1,2.

The ^{1}H NMR spectrum of poly(2-cyanomethyl-1,3-butadiene) in CD_3CN is shown in Figure 2. As can be seen, there are two signals at 5.52 and 5.43 ppm, which correspond to vinyl protons in 1,4 structures. 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 peak attributed to the C-5 methylene protons next to the cyano group appeared as one peak at 3.12 ppm in $CDCl_3$ and was split into two peaks at 3.18 and 3.16 ppm in CD_3CN. The signals at 2.1−2.4 ppm were attributed to the methylene protons along the polymer backbone. The integration ratio of peak areas at 5.5, 3.2, and 2.2 was close to 1:2:4, respectively, which verified the polymer microstructure was almost all 1,4 structure.

To elucidate the designation of *cis* and *trans* microstructure in the proton NMR spectrum, COSY and NOESY experiments were performed. Similar experiments were utilized previously to distinguish the microstructures of other substituted dienes.[9] Figure 3 shows the COSY spectrum of poly(2-cyanomethyl-1,3-butadiene) using CD_3CN as the solvent. Cross-peaks at (2.2, 5.4) and (2.2, 5.5) correspond to the coupling between vinyl protons and methylene protons along the polymer backbone. Only in the *cis*-1,4 microstructure is long distance coupling seen between the vinyl proton and the C-5 methylene protons. In the *trans* structure, this coupling does not exist and is not seen. Therefore, the existence of a cross-peak at (3.16, 5.5) and the absence of a cross-peak at (3.18, 5.4) was strong evidence for the designation of the *cis* and *trans* vinyl protons in the ^{1}H NMR spectrum. Using $CHCl_3$ as the solvent, the same behavior was observed. Similar evidence was also obtained in the NOESY experiment. Since the short distance contacts between the vinyl protons and C-5 protons are only expected in the *cis* structure, it was easy to distinguish *cis* from *trans* in the spectrum. The cross-peak pattern was very similar to that of COSY. Cross-peaks at (2.2, 5.5) and (2.2, 5.4) were both observed. This was easily explained as the short distance contacts between vinyl protons and methylene protons along the polymer backbone. A cross-peak at (3.16, 5.5) was observed; there was no sign of a cross-peak at (3.18, 5.4). This nicely supported our previous designation of vinyl protons in the ^{1}H NMR spectrum. Because of the short distance between the C-5 methylene peaks in the proton spectrum and small chemical shifts in the two-dimensional NMR spectra, there is no direct evidence for distinguishing the C-5 protons in different microstructures from the experimental results described previously. However, logical assignments can be made by correlating the methylene hydrogens and the vinyl hydrogens. For example, an increase in the peak area at 3.16 ppm with the increase of *cis*/*trans* ratio was always observed. Therefore, it is reasonable to attribute the peak at 3.16 ppm as the C-5 protons in the *cis* microstructure and the peak at 3.18 ppm as the *trans* microstructure. The integration ratios were also consistent with our conclusion.

On the basis of the previous assignments of polymer microstructure, the ratio of *cis* and *trans* microstructures in the obtained polymers was determined on the basis of the integration ratio of peaks at 3.16 and 3.18 ppm. The results of various polymers obtained under different polymerization conditions were compared. The most obvious factor that was found to influence the microstructure was the polymerization temperature. In bulk or solution polymerizations, at the same temperature, polymers with almost the same microstructure ratios were obtained (Tables 1−3). It is well-known that temperature affects the microstructure distributions of diene polymers in free radical polymerization. For polyisoprene or polychloroprene, the higher the temperature, the higher the percentage of *cis* structure.[21] Similar tendencies were observed in poly(2-cyanomethyl-1,3-butadiene). The *cis*/*trans* ratio increased from approximately 32% to 36% to 45%, as the polymerization temperature was increased from 45 to 60 to 75 °C. It seemed that no obvious relationship existed between microstructure and the type of the initiator, the concentration of the initiator, and the reaction time. At the same 75 °C temperature, the *cis*/*trans* ratios in

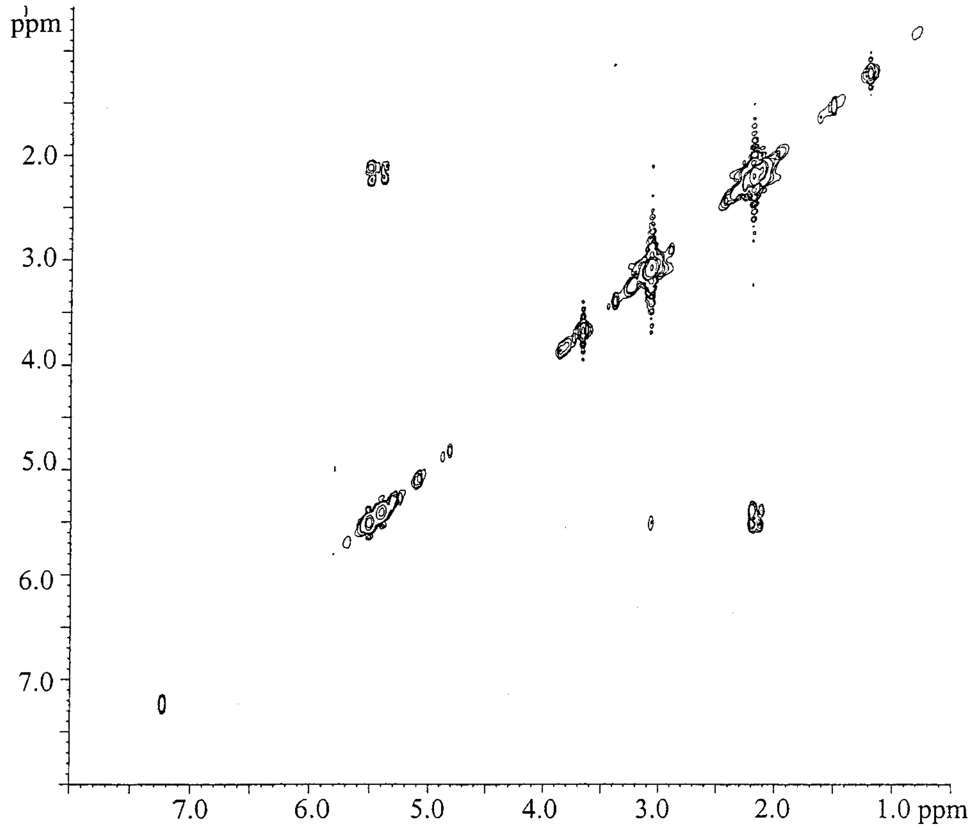


Figure 3. ^{1}H COSY spectrum of poly(2-cyanomethyl-1,3-butadiene).

Table 5. Microstructure of Various Butadiene Derivatives

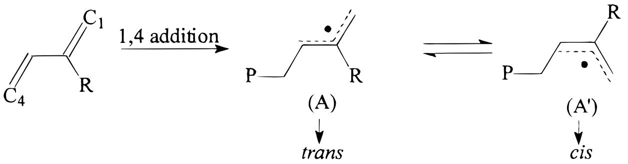
polymer	T (°C)	% cis ratio in 1,4-structure
poly(2-cyanomethyl-1,3-butadiene)	45	32
	60	36
	75	42−48
polyisoprene	75	18
poly[5-(*N*,*N*-dimethylamino)isoprene]	75	74
poly[5-(*N*,*N*-diisopropylamino)isoprene]	75	95
poly(TMSBD)[a,7]	60	39
	90	43
poly(TBSMBD)[b,7]	60	56
	90	66

[a] 2-(Trimethylsiloxy)butadiene. [b] 2-(*tert*-Butyldimethylsiloxy)-butadiene.

bulk polymerization were consistently slightly lower than those in solution polymerization. This may be some indication that the microstructure could also be dependent on the polymerization method as well.

As can be seen in Table 5, at the same temperature 75 °C, the *trans*-1,4 structure is favored over the *cis*-1,4 structure in poly(2-cyanomethyl-1,3-butadiene) and polyisoprene, and the contrary is observed for poly[5-(*N*,*N*-dialkylamino)isoprene]. These observations can be rationalized by arguments similar to those used by Penelle's group to explain the mictrostructures of poly-(TMSBD) and poly(TBMSBD).[7] Scheme 3 shows the main polymerization addition route for butadiene derivatives, 1,4 addition. Two radicals A and A′ are formed and in equilibrium. The radical A will result in the *trans* structure, and A′ will result in the *cis* structure. In the equilibrium A is usually favored over A′ to avoid the interaction between the terminal allyl hydrogen atom in the rigid system and the CH_2 group on the other side. Once the side group's size becomes bulky, the equilibrium shifts to the right side due to the steric hindrance. This can explain the *cis* structure series in Table 5: poly[5-(*N*,*N*-dialkylamino)isoprene] > poly(2-cyanomethyl-1,3-butadiene) > polyisoprene. If the side group is very bulky, the *cis* structure will predominate. For example, poly[5-(*N*,*N*-isopropyl)isoprene] has 95% *cis* structure.

Scheme 3. The 1,4-Addition of Butadiene Derivatives



Conclusion

This fundamental study of the free radical polymerization of 2-cyanomethyl-1,3-butadiene and its final polymer properties is an extension of our initial work on other polar, functionalized butadienes. Herein, it has been demonstrated that the monomer can be produced under reasonable conditions and in >99% purity, making subsequent polymerizations feasible. Polymers were successfully made through traditional bulk, solution, and emulsion free radical polymerization techniques. It was determined that the amount of Diels−Alder dimers was effected by initiator concentration, solvent concentration, and polymerization time. The final polymers, with glass transition temperatures around −18 °C, are potential candidates after cross-linking for functionalized elastomers. Although these results focus on the homopolymerization behavior, they imply that the monomer has potential as a comonomer in commercially available polymers such as styrene−butadiene and nitrile rubber. Hence, our interest now is in the incorporation of the cyano monomer in copolymers with the purpose of exploiting its high reactivity and the potential properties associated with the cyano functionality.

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