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Polar, Functionalized Diene-Based Materials. 4. Polymerization Studies of 2,3-Bis(4-ethoxy-4-oxobutyl)-1,3-butadiene and Copolymerization with Styrene

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ABSTRACT: New ester and acid functionalized diene-based polymers were successfully synthesized by bulk and solution homopolymerizations and copolymerizations with styrene. The ester-containing diene chosen, 2,3-bis(4-ethoxy-4-oxobutyl)-1,3-butadiene, followed typical free-radical kinetics. For the bulk polymerizations, number-average molecular weights of $13 \times 10^3 - 80 \times 10^3$ g/mol and polydispersities of 2.0−4.0 were seen. Solution polymerizations did not exhibit a chain transfer to solvent effect, but rather showed a dependence on chain transfer to monomer, with the highest molecular weight of 96×10^3 g/mol obtained in cumene. Copolymerizations with styrene led to random copolymers, with the expected increase in the glass transition temperature as the styrene concentration increased. Functional modification of the homopolymer from a diester to a diacid was obtained in quantitative yields via saponification in tetrahydrofuran and water. This modification elevated the glass transition temperature of the polymer from −37 °C (diester) to 67 °C (diacid). The diacid polymer was only soluble in highly polar solvents (DMSO, THF) but was soluble in water while in the carboxylate form. All polymers exhibited 100% 1,4-microstructure as determined by ^{1}H NMR.

Introduction

Incorporation of functionality into the backbone of a diene-based polymer, either by synthesizing a monomer with the functionality already covalently bound or by chemical reaction after the polymerization, has been a major goal for many research groups. The purpose of incorporating the functionality has been to tailor diene-based elastomer properties. Nakahama utilized the first method to synthesize several silyl-functionalized butadienes. These monomers were polymerized via anionic methods. The monomers included trialkylsilyl, trialkoxysilyl, and *N*,*N*-dialkylaminosilylbutadienes.[1−6] Penelle also polymerized trialkylsilyl-substituted derivatives as well as utilized the reactivity of the silyl functionality after polymerization to do further modification.[7,8] Stadler et al. produced several non-silicon-containing *N*,*N*-dialkyl-2-aminomethyl-1,3-butadiene polymers and copolymers using mostly anionic techniques.[9−12] Our research group has focused on *N*,*N*-dialkyl-2-aminomethyl and 2-cyanomethyl-1,3-butadienes for polymerization using free-radical techniques.[13,14] The *N*,*N*-dialkyl-2-aminomethyl derivatives were used to study the effect of varying alkyl groups on the polymerization kinetics, microstructure, and thermal and adhesion properties. The cyanomethyl derivatives were synthesized to alter solvent resistance and adhesion characteristics. For both functional groups, the results of the bulk, solution, and emulsion polymerizations were studied.

The research previously described focused primarily on substitution at the C-2 position, with a few exceptions. Nakahama produced poly(2,3-diphenyl-1,3-butadiene)[15] and Prud'homme synthesized poly(2,3-dimethyl-1,3-butadiene).[16] The work presented here describes a 2,3-disubstituted ester-containing diene, which was polymerized via free-radical techniques and was functionally modified to the acid-containing diene polymer. This polymer is unique structurally because it combines the polar functionality found in our monosubstituted dienes with 2,3-disubstitution, thereby doubling the polar functionality per repeat unit.

The ester group was chosen because of its polarity and ease of modification to many other groups. The ester can potentially be modified to the acid, amide, or alcohol, altering the thermal and mechanical properties. The polarity of the group should alter the adhesion, solubility, and processability of the resulting polymers compared to isoprene- and butadiene-containing materials. This functionality on every repeat unit could also be exploited to produce graft copolymers, with potential utility as blend compatibilizers. Additionally, the two bulky pendant groups attached at the 2- and 3-positions are likely to contribute to the production of a very stable tetrasubstituted double bond. This stability should translate into enhanced thermal and oxidative stability.

Within this paper are several fundamental studies. First, the concentration effects of several initiators are analyzed in bulk polymerization. Second, solvent effects on chain transfer are examined for solution polymerization. Third, the copolymerization of 2,3-bis(4-ethoxy-4-oxobutyl)-1,3-butadiene with styrene is investigated. Finally, the reactivity of the functionality along the polymer backbone is examined. In each case, the structural and thermal properties of the resulting materials are determined.

Experimental Section

Materials. Styrene (99%), ethyl 4-chlorobutyrate (98%), and 1,4-dichlorobutyne (99%) were purchased from Aldrich and were distilled prior to use to obtain a clear liquid. The functionalized monomer was purified by column chromatography until the ^{1}H NMR spectrum corresponded to the expected structure.

Monomer Synthesis. 2,3-Bis(4-ethoxy-4-oxobutyl)-1,3-butadiene (I). a. Ethyl δ-Iodobutyrate. Acetone (700 mL)

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and sodium iodide (90 g, 600 mmol) were added to a one-necked, 1.0 L round-bottom flask, equipped with a water condenser. Ethyl δ-chlorobutyrate (14 mL, 100 mmol) was then added and the mixture refluxed overnight. The solution was cooled and concentrated under vacuum. Approximately 100 mL of water was added to dissolve the salt, and the organic layer was extracted twice with ether (150 mL). The extracts were concentrated and distilled over copper powder under reduced pressure to provide the liquid product (23.5 g, 98% yield). ^{1}H NMR ($CDCl_3$): δ 1.25 (t, 3H; $J = 6$ Hz, $-CH_3$) 2.10 (dd, 2H; $J = 6$ and 9 Hz, $-CH_2$), 2.45 (t, 2H; $J = 9$ Hz, $-CH_2-CO_2$), 3.22 (t, 2H; $J = 6$ Hz, $-CH_2I$), 4.14 (q, 2H; $J = 6$ Hz, $-OCH_2$). High-resolution mass spectrometry: theoretical mass 241.9797, measured mass 241.9799, deviation 1.1 ppm.

b. 2,3-Bis(4-ethoxy-4-oxobutyl)-1,3-butadiene (I). Zinc granules (30 mesh, 26 g, 400 mmol) and 80 mL of tetrahydrofuran (THF) were added to an argon-purged three-necked, 250 mL round-bottom flask. The zinc was activated by refluxing in 8 mL of 1,2-dibromoethane. Ethyl δ-iodobutyrate (24 g, 100 mmol) was added and heated to 50 °C for 24 h. Before the next step, the alkyl zinc iodide solution was cooled to room temperature. Lithium chloride (8.5 g, 200 mmol) was added to a two-necked, 500 mL round-bottom flask. The flask was evacuated and flame-dried several times to remove all water from the salt and from the surface. After purging with argon, copper cyanide (9.0 g, 100 mmol) was added to the flask under a strong flow of argon. The flask was then evacuated and purged with argon. After the addition of 80 mL of THF, the solution was cooled to −30 °C and the alkyl zinc iodide solution was added. The solution was warmed to 0 °C, held at that temperature for 10 min, and cooled to −78 °C. This was followed by the dropwise addition of 1,4-dichloro-2-butyne (4.4 mL, 45 mmol). The solution was stirred for 24 h as it warmed to room temperature. The flask was opened, and its contents were poured into a saturated ammonium chloride solution to quench any residual cuprate. The organic layer was extracted twice with 150 mL of ether, washed with brine, and finally washed with saturated sodium thiosulfate in order to remove any iodide ions from the solution. The organic layer was dried over magnesium sulfate, filtered, and concentrated to provide a crude oil. The product was purified on a silica gel column. The eluent was a 15% ethyl acetate/hexanes mixture. Yield: 82%. ^{1}H NMR ($CDCl_3$): δ 1.26 (t, 6H; $J = 6$ Hz, $-CH_3$), 1.80 (q, 4H; $J = 9$ Hz, $-CH_2$), 2.28 (t, 4H; $J = 9$ Hz, $-CH_2-CO_2$), 2.30 (t, 4H; $J = 9$ Hz, $-CH_2-C{=}$), 4.12 (q, 4H; $J = 6$ Hz, $-OCH_2$), 4.96 (d, 2H, $-CH{=}C$), 5.11 (d, 2H, $-CH{=}C$). ^{13}C NMR ($CDCl_3$): δ 174 ($-CO_2$), 146 ($-C{=}CH_2$), 113 ($CH_2{=}C$), 60 ($-OCH_2$), 34 ($-CH_2-C{=}$), 33 ($-CH_2-CO_2$), 24 ($-CH_2$), 14 ($-CH_3$). High-resolution mass spectrometry: theoretical mass 282.183 109, measured mass 282.183 144, deviation 0.12 ppm.

Polymer Synthesis. Poly[2,3-bis(4-ethoxy-4-oxobutyl)-1,3-butadiene] (II). A specific example of a typical polymerization follows. 2,3-Bis(4-ethoxy-4oxobutyl)-1,3-butadiene (1.0 g, 3.55 mmol), THF (0.45 g, 0.5 mL, 6.62 mmol), and 2,2′-azobis(isobutyronitrile) (2.9 mg, 0.0178 mmol) were added to an ampule. After three cycles of freeze−pump−thaw, the ampule was sealed under vacuum and heated to 75 °C for 24 h. An inhibitor, 2,6-di-*tert*-butyl-4-methylphenol, was added to end the reaction. The polymer was dissolved in 3 mL of acetone and precipitated into 50 mL of hexanes. The polymer was then dried under vacuum for 24 h. ^{1}H NMR ($CDCl_3$): δ 1.25 (t, 6H, $-CH_3$), 1.68 (m, 4H, $-CH_2$), 2.05 (t, 4H, $-CH_2-CO_2$), 2.09 (t, 4H, $-CH_2-C{=}$), 2.29 (t, 4H, $-CH_2-C{=}$), 4.12 (q, 4H, $-OCH_2$). IR: (CO) 1730 cm^{-1}. ^{13}C NMR ($CDCl_3$): δ 174 ($-CO_2$), 133 ($-C{=}C$), 60 ($-OCH_2$), 34 ($-CH_2-C{=}$), 31.5 ($-CH_2-C{=}$), 31 ($-CH_2-CO_2$), 14 ($-CH_3$). Elemental analysis: theoretical % C = 68.06, % H = 9.28; experimental % C = 68.02, % H = 9.79.

Copolymer Synthesis. Poly[2,3-bis(4-ethoxy-4-oxobutyl)-1,3-butadiene-*co*-styrene]. A specific example of a typical polymerization follows. 2,3-Bis(4-ethoxy-4-oxobutyl)-1,3-butadiene (1.0 g, 3.55 mmol), benzene (1.94 g, 2.22 mL), styrene (1.11 g, 10.65 mmol), and 2,2′-azobis(isobutyronitrile) (11.7 mg, 0.0712 mmol) were added to an ampule. After three cycles of freeze−pump−thaw, the ampule was sealed under vacuum and heated to 75 °C for 24 h. An inhibitor, 2,6-di-*tert*-butyl-4-methylphenol, was added to end the reaction. The polymer was dissolved in 3 mL of acetone and precipitated into 50 mL of hexanes. The polymer was then dried under vacuum for 24 h. ^{1}H NMR ($CDCl_3$): δ 1.22 (t, 6H, $-CH_3$), 1.58 (m, 2H, $-CH_2-CHPh$), 1.68 (m, 4H, $-CH_2$), 1.9 (m, 1H, $-CHPh$), 2.05 (t, 4H, $-CH_2-CO_2$), 2.09 (t, 4H, $-CH_2-C{=}$), 2.29 (t, 4H, $-CH_2-C{=}$), 4.12 (q, 4H, $-OCH_2$), 6.55 (d 2H, Ar−H), 7.0 (d, 3H, Ar−H). Elemental analysis: theoretical % $C_S = 92.26$, % $C_M = 68.06$; experimental % $C_S = 82.15$, % $W_S = 58$; % $M_S = 79.1$. GPC: $\langle M_n \rangle = 20.1 \times 10^3$ g/mol; $T_g = 44$ °C.

Polymer Modification. Poly[2,3-bis(4-hydroxy-4-oxobutyl)-1,3-butadiene] (III). Lithium hydroxide (0.091 g, 3.8 mmol) and a stir bar were added to a 100 mL Schlenk flask. The flask was evacuated and purged with argon before adding 20 mL of water. The polymer (0.60 g, 3.5×10^4 g/mol) was dissolved in 20 mL of THF and was added by syringe into the reaction flask. The solution was stirred for 2 days. Dilute hydrochloric acid was added, and the polymer was extracted with a 50:50 solution (40 mL) of THF and diethyl ether twice. The sample was concentrated and placed in a vacuum oven at 100 °C overnight. The yield of the reaction was quantitative by NMR. ^{1}H NMR (CD_3SOCD_3): δ 1.50 (m, 4H, $-CH_2$), 2.0 (t, 4H, $-CH_2-CO_2$), 2.0 (t, 4H, $-CH_2-C{=}$), 2.15 (t, 4H, $-CH_2-C{=}$), 11.9 (s, 2H, $-CO_2H$). IR: (CO) 1705 cm^{-1}. Elemental analysis: theoretical % C = 63.70, % H = 8.02; experimental % C = 63.23, % H = 7.85.

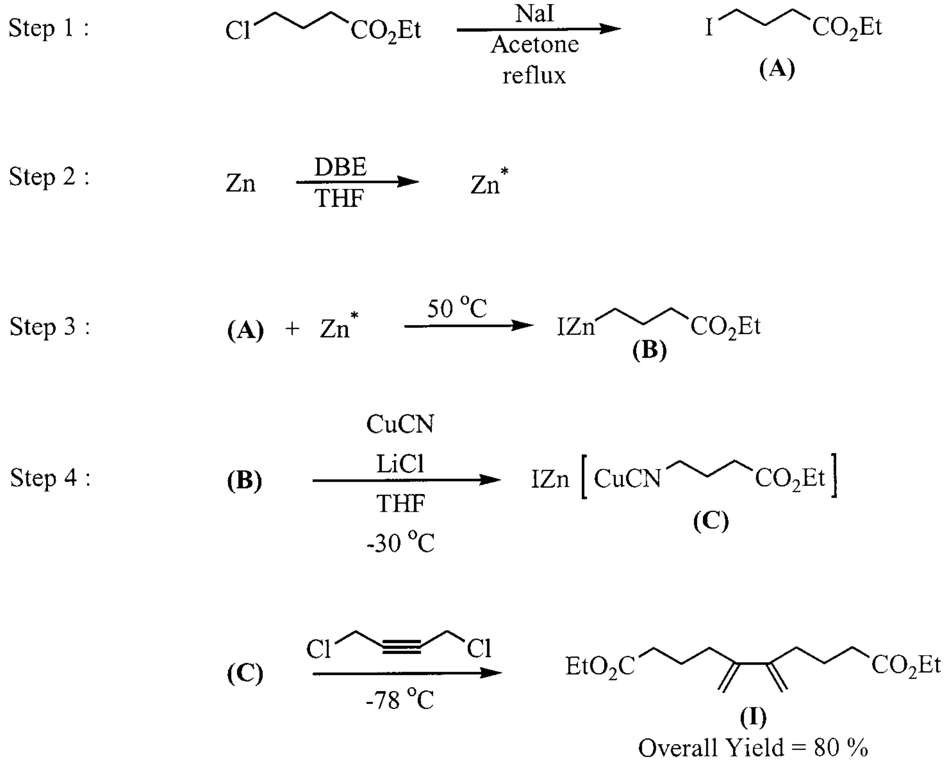
Monomer and Polymer Characterization. The ^{1}H NMR and ^{13}C NMR spectra were measured in $CDCl_3$, CD_3SOCD_3, or CD_3COCD_3 with a Varian Unity spectrometer at 300 and 75.5 MHz, respectively. Polymer molecular weights were determined by gel permeation chromatography (GPC) using a Waters gel permeation system (410 refractive index detector). The chromatography system was equipped with three Waters Styragel columns [(HR 1 (100 Å), 2 (500 Å), 4 (10^4 Å), and 5 (10^5 Å)], and measurements were made at 40 °C, with THF as the eluent, at a flow rate of 1.0 mL/min. Molecular weights were calculated using a calibration plot constructed from polystyrene standards. Polymer glass transition temperatures were determined with a Perkin-Elmer Pyris 1 differential scanning calorimeter (DSC) at a heating rate of 10 °C/min with nitrogen purge. Glass transition temperatures were reported as the inflection point of the change in heat capacity during the second heat. Thermogravimetric analysis (TGA) was obtained with a Perkin-Elmer TGA 7 thermogravimetric analyzer at a heating rate of 10 °C/min under nitrogen atmosphere or air. IR spectra were taken in a Nicolet Magna-IR spectrometer.

Results and Discussion

Synthesis of 2,3-Bis(4-ethoxy-4-oxobutyl)-1,3-butadiene (I). The S_N2' reaction[17] of a cuprate and 1,4-dichloro-2-butyne provided an efficient and clean process to produce the functionalized monomer. Using this chemistry, a number of different cuprates can be utilized to react with the alkynyl substrate to generate the corresponding functionalized butadienes in high purity and yield. The monomer is also more stable to light and heat than other diene monomers.[18]

The synthesis of compound **I** is shown in Scheme 1. Starting the reaction with ethyl δ-chlorobutyrate and performing a halogen exchange to ethyl δ-iodobutyrate (A) provided substantially higher reactivity when inserting the zinc in the next step. After the addition of dibromoethane (DBE) to zinc powder in THF, ethyl δ-iodobutyrate was added to form the zinc inserted product (B). The cuprate (C) was formed by addition of copper cyanide and lithium chloride. Once the complex was formed, 1,4-dichloro-2-butyne was added to initiate the S_N2' insertion and to form the final product. The product was purified by column chromatography with an overall yield of 80%. Because of the ease of purifica-

Scheme 1. Synthesis of 2,3-Bis(4-ethoxy-4-oxobutyl)-1,3-butadiene



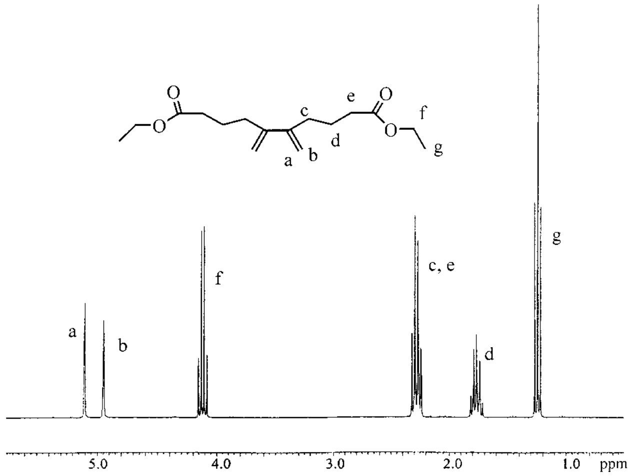


Figure 1. ^{1}H NMR spectrum of 2,3-bis(4-ethoxy-4-oxobutyl)-1,3-butadiene (**I**).

tion, the monomer was scaled up to produce approximately 80 g of polymer-grade monomer per experiment. This allowed for all of the polymers described herein to be synthesized from one batch of monomer. The proton NMR spectrum of compound **I**, shown in Figure 1, depicts the olefinic hydrogens near 5.0 ppm and the methylene protons of the ester at approximately 4.2.

Bulk Polymerization of 2,3-Bis(4-ethoxy-4-oxohdbutyl)-1,3-butadiene (I). The reaction data for the bulk polymerization of compound **I** are listed in Table 1. The 2,2′-azobis(isobutyronitrile) initiated polymerizations at 75 °C followed expected free-radical polymerization trends.[1] As the initiator concentration was increased from 0.5 to 3 mol %, the molecular weight decreased from 32 × 10^3 to 14 × 10^3 g/mol with a corresponding increase in conversion from 33 to 62%. The polymerizations initiated by *tert*-butyl peracetate (TBPA) and *tert*-butyl hydroperoxide (TBHP) at 100 and 125 °C, respectively, also followed typical free-radical kinetics. However, the number-average molecular weights did not decrease below approximately 60 × 10^3 g/mol for TBPA and 45 × 10^3 g/mol for TBHP when the initiator concentration was above 0.5%. The leveling off of these molecular weights along with the simultaneous increases in the polydispersity suggested that a different mechanism was contributing to the polymerization.

Table 1. Bulk Free Radical Polymerization of Compound I[a]

initiator	initiator (%)[b]	conv[c]	$\langle M_n \rangle \times 10^{-3}$ [d] (g/mol)	PDI[d]
AIBN	0.5	33	32	2.08
AIBN	1	44	23	2.09
AIBN	2	54	18	2.05
AIBN	3	62	14	2.01
TBPA	0.5	58	81	2.17
TBPA	1	64	64	2.35
TBPA	2	61	62	2.69
TBPA	3	64	60	2.80
TBHP	0.5	58	61	2.57
TBHP	1	63	48	2.84
TBHP	2	59	42	3.39
TBHP	3	77	45	3.94

[a] Reactions were performed for 24 h at 75, 100, and 125 °C for AIBN, TBPA, and TBHP, respectively. [b] Mole percent. [c] Percent conversion by weight after precipitation. [d] Values obtained by GPC using polystyrene standards.

It was thought that thermal polymerization took place at high viscosities and/or temperatures greater than or equal to 100 °C. In most cases, higher initiator concentrations and therefore higher conversions led to increased viscosity and what appears to be chain branching. The broadening of the polydispersity supported this. Moreover, increasing the polymerization temperature increased the rate at which the thermal mechanism appeared to operate, as indicated by the larger polydispersities in the 125 °C TBHP reactions. Because of the lower temperature and viscosities in the AIBN initiated

Table 2. Bulk Polymerization of Compound I with No Initiator Present

temp (°C)	time (h)	conv[a]	$\langle M_n \rangle \times 10^{-3}$ [b] (g/mol)	PDI[b]
75	24	1	39	2.09
100	24	8	74	2.03
125	24	20	80	2.84
125	4	2.5	96	2.49
125	8	6	106	2.70
125	12	7	94	3.25
125	16	13	102	2.99
125	20	15	132	2.66

[a] Percent conversion by weight after precipitation [b] Values obtained by GPC using polystyrene standards

Table 3. Kinetic Data for the Polymerization of Compound I in Bulk Using 0.5 %[a] TBHP at 125 °C

time (min)	conv[b]	$\langle M_n \rangle \times 10^{-3}$ [c] (g/mol)	PDI[c]
5	0	0	0
10	1	29	1.47
15	3.5	32	1.47
20	5	30	1.58
25	6	33	1.59
30	11	30	1.61
60	9	29	1.96
90	22	34	1.69
120	25	37	2.04
150	28	37	1.78
180	28	45	2.22
210	40	39	2.02
240	38	46	2.30
480	51	51	3.07
720	53	60	2.95
960	65	58	2.78
1200	64	55	3.04

[a] Mole percent. [b] Percent conversion by weight after precipitation. [c] Values obtained by GPC using polystyrene standards.

polymerizations, these effects were not seen. To further confirm that thermal polymerization was taking place, reactions were repeated using the same temperatures and times, but in the absence of initiator. It is possible that impurities in the polymerization reaction could act as the initiator in the absence of added initiator. The first three entries in Table 2 confirmed that polymer was formed by thermal polymerization and that the conversion was increased as the reaction temperature was raised. At 125 °C, further experiments were performed, monitoring conversion with time to the start of the thermal polymerization and the degree to which it affected the polydispersity of the sample. The thermal polymerization mechanism started at approximately 4 h (2.5% conversion). Indeed, these data correlated well with the kinetic data of the TBHP-initiated polymerizations in Table 3. For the first 3 h of polymerization, the number-average molecular weight and the polydispersity remained under control. However, beyond the same 4 h mark at which the reactions without initiator began to show evidence of high molecular weight polymer with broad dispersity, the $\langle M_n \rangle$ values and the polydispersities of the TBHP reactions began to rise. It appears then that although this thermal product is produced, it can be minimized by control of the reaction temperature, time, and viscosity.

Because of the thermodynamic stability of a tetrasubstituted double bond, the polymerization took place even with the steric hindrance of the pendant groups. Generation of the stable double-bond formation was also responsible for the complete 1,4-chain growth. To date, we have not determined the cis/trans microstructure due to the symmetry of the polymer (Figure 2). The microstructure of the previously published poly(2,3-dimethyl-1,3-butadiene) was ascertained via X-ray crystallography. This is not a possibility for this amorphous polymer. However, due to the bulky pendant groups on the backbone, the polymer structure is likely to be trans-1,4. To determine whether this hypothesis is correct or not, the use of isotope labeling is necessary and will be pursued in future studies. The structure of compound **I** also favored disproportion over combination termination due to the steric hindrance of the pendant groups.

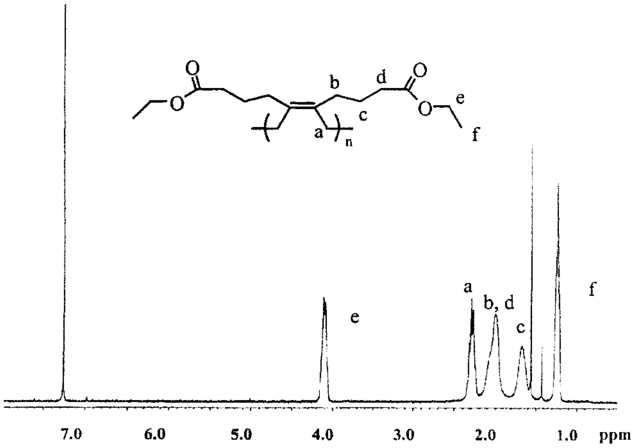


Figure 2. ^1H NMR spectrum of poly[2,3-bis(4-ethoxy-4-oxobutyl)-1,3-butadiene] (**II**).

Solution Polymerization of 2,3-Bis(4-ethoxy-4-oxobutyl)-1,3-butadiene (I). The five solvents used for the experiments were benzene, tetrahydrofuran, ethyl acetate, bromobenzene, and cumene. These solvents were chosen on the basis of the variation in their boiling points and chain transfer behavior. Benzene, tetrahydrofuran, and ethyl acetate were employed for AIBN-initiated polymerizations at 75 °C to determine the effects of solvent chain transfer (861:313:1 difference between Cs values at 60 °C for the polymerization of styrene in ethyl acetate, THF, and benzene).[18] The chain transfer constants of these solvents were measured (relative to monomer) for the nonpolar styrene. Differences, nonetheless, in their behavior during polymerization, as well as changes in the molecular weight, polydispersity, and conversion of our final polymers were anticipated. Similar assumptions were made for bromobenzene and cumene that were used not only for AIBN-initiated polymerizations but also for TBPA and TBHP reactions. For each solvent, the solubility of the monomer and the final polymer was verified to ensure that no precipitation of the polymer occurred during the polymerizations.

Solution polymerizations in THF and benzene were compared with respect to changing monomer-to-solvent ratios (Table 4). As the amount of solvent was decreased, the molecular weight increased as expected for equal polymerization times. The polydispersity remained constant near 1.75, which suggested a mixture of disproportionation and combination termination. These results were mirrored between the two solvents. This was not expected because THF has a significantly higher chain transfer tendency due to its acidic hydrogens. The calculated chain transfer constants for these polymerizations in THF and benzene are 1.8×10^{-3} and 2.1×10^{-3}, respectively.[19] These results showed that the solvent had no distinguishing effect on the polymerization of this monomer.

Table 4. Solution Polymerization of Compound I Using AIBN[a]

solvent	solvent (%)[b]	conv[c]	$\langle M_n \rangle \times 10^{-3}$ [d] (g/mol)	PDI[d]
THF	50	9	15	1.85
THF	43	15	20	1.71
THF	33	19	25	1.71
THF	20	24	29	1.67
benzene	50	10	14	1.72
benzene	43	18	21	1.71
benzene	33	20	25	1.68
benzene	20	26	28	1.85
ethyl acetate	50	11	16	1.87
ethyl acetate	43	11	16	1.91
ethyl acetate	33	15	20	1.86
ethyl acetate	20	17	25	2.07
cumene	50	10	15	1.89
cumene	43	13	15	2.04
cumene	33	13	18	2.00
cumene	20	13	23	2.02
bromobenzene	50	15	15	1.97
bromobenzene	43	16	16	2.16
bromobenzene	33	20	17	2.00
bromobenzene	20	16	25	2.01

[a] All reactions were performed at 75 °C for 24 h using 0.5% initiator. [b] Volume-to-volume ratios of solvent to monomer. [c] Percent conversion by weight after precipitation. [d] Values obtained by GPC using polystyrene standards.

Table 5. Solution Polymerization of Compound I TBPA and TBHP[a]

initiator	solvent	solvent (%)[b]	conv[c]	$\langle M_n \rangle \times 10^{-3}$ [d] (g/mol)	PDI[d]
TBPA	Cm	50	27	32	1.73
TBPA	BB	50	35	30	1.93
TBHP	Cm	50	27	48	2.02
TBHP	Cm	43	31	60	2.04
TBHP	Cm	33	41	72	2.19
TBHP	Cm	20	50	96	2.64
TBHP	BB	50	25	63	2.08
TBHP	BB	43	31	65	2.24
TBHP	BB	33	36	90	2.29
TBHP	BB	20	51	65	3.15

[a] TBPA polymerizations were performed at 100 °C for 24 h with 0.5 mol % initiator concentration. TBHP polymerizations were performed at 125 °C for 24 h with 0.5 mol % initiator concentration. Cm = cumene. BB = bromobenzene. [b] Mole percent. [c] Conversion by weight after precipitation. [d] Values obtained by GPC using polystyrene standards.

Ethyl acetate, bromobenzene, and cumene were also tested using AIBN as the initiator at 75 °C (Table 4). These three solvents produced similar results to the previous two solvents with calculated chain transfer constants of 3.5×10^{-3}, 4.4×10^{-3}, and 6.2×10^{-3} for ethyl acetate, bromobenzene, and cumene, respectively. The molecular weight and conversion increased as the solvent concentration was decreased. These data provided more evidence that the chain transfer to solvent is not the controlling factor in the solution polymerization of this monomer.

Cumene and bromobenzene were then investigated using two additional initiators, TBPA and TBHP. The solvents were used because of their high boiling points and the relative difference in their chain transfer constants (85:1 difference at 60 °C in the polymerization of ethyl methacrylate).[18] TBPA was analyzed first at 100 °C using 50 mol % cumene and bromobenzene (Table 5). Because of the increased temperature, the polymerization rate increased, which led to molecular weights and conversions greater than those in the AIBN-initiated reactions. The two solvents had no effect on the molecular weight or polydispersity, as was seen previously with benzene, THF, and ethyl acetate.

Table 6. Solution Copolymerization of Compound I with Styrene[a]

initiator[b]	$\langle M_n \rangle \times 10^{-3}$ [c] (g/mol)	PDI[c]	conv[d]	T_g (°C)	styrene feed ratio[e]	styrene incorp[f]
AIBN	16	1.92	28	−25	25	33
AIBN	18	1.94	31	1	50	54
AIBN	20	1.91	45	44	75	81

[a] All reactions were run in an equal volume of benzene at 75 °C for 24 h. [b] 0.5 mol %. [c] Values obtained by GPC using polystyrene standards. [d] Conversion by weight after precipitation. [e] Mole percent. [f] Percent calculated by ^{1}H NMR spectral integration.

TBHP was then investigated, and similar data were recorded (Table 5). Increased molecular weights and conversions were obtained as the solvent concentration decreased. However, the polydispersity did increase as expected due to the elevated temperature. The experiments with the least amount of solvent in both cumene and bromobenzene gave higher polydispersity than the other samples. This was likely due to the higher viscosity of these two experiments, leading to more branching.

After analyzing the data of the solution polymerizations, all of the evidence at 75, 100, and 125 °C suggests that chain transfer to solvent is not the controlling factor in the final molecular weight or polydispersity. Several of these solvents have higher chain transfer constants than benzene and should lower the molecular weight and increase the polydispersity. One explanation for this phenomenon would be chain transfer to monomer. The acidic, methylene hydrogens alpha to the carbonyls have a higher likelihood of chain transfer than do the solvents. Chain transfer to initiator is also possible in this scenario but is not as likely due to the concentrations utilized.

Thermal Characteristics of Poly[2,3-bis(4-ethoxy-4-oxobutyl)-1,3-butadiene] (II). The glass transition temperature, −37 °C, for polymer **II** was characteristic of a material with a flexible backbone and large side groups along the backbone, not conducive to crystalline behavior. The 61×10^3 g/mol polymer (Table 1, example 0.5% TBHP) has a 10% weight loss temperature of 349 and 352 °C for oxygen and nitrogen, respectively. This was a little unexpected as diene-based materials with a low T_g are not typically associated with high thermal and thermooxidative stability. Polydienes also have a tendency to undergo cross-linking upon heating, but polymer **II** remained stable up to 320 °C without any evidence of cross-linking.[14]

Copolymerization of Compound I with Styrene. Copolymers of dienes and styrene have been utilized for various applications and products due to the combined thermal and mechanical properties.[2] The results of the copolymerizations of compound **I** and styrene are shown in Table 6. The feed ratios of styrene to diene (1:3, 1:1, 3:1) were based on molar amounts. The conversion and the molecular weight increased as the styrene feed ratio increased. The incorporation of styrene also increased as the feed ratio increased, with a higher percentage of styrene in the polymer than in the feed. These results show a higher reactivity rate of styrene than the diene. This is contrary to the reactivity of butadiene versus styrene under similar reaction conditions (1.4−0.58 reactivity ratios).[1] One potential reason for this reversal of reactivity is the steric effect of the disubstituted butadiene.

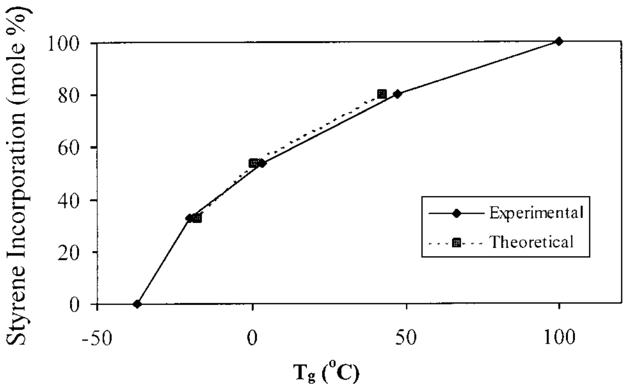
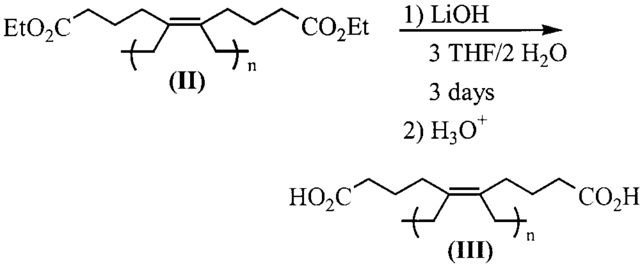


Figure 3. Graph of experimental versus theoretical glass transition temperatures calculated by the Gordon−Taylor equation.

Scheme 2. Functional Modification of Poly[2,3-bis(4-ethoxy-4-oxobutyl)-1,3-butadiene]



The differential scanning calorimetry data for these three copolymers showed only one glass transition temperature per polymer, suggesting a random copolymer structure. The theoretical values were calculated using eq 1.

$$T_g = (W_1T_{g1} + kW_2T_{g2})/(W_1 + kW_2) \tag{1}$$

This equation was chosen because of its utility in calculating theoretical glass transition temperatures for other butadiene and styrene copolymers. Equation 1, the Gordon−Taylor equation ($k = 0.87$, W_1 = weight percent of compound **I** incorporated, W_2 = weight percent of styrene incorporated), is useful because it provides theoretical glass transition temperatures of copolymers whose homopolymer glass transitions are significantly different.

Figure 3 shows the experimental and theoretical glass transition temperature values versus the percent styrene incorporation. There is an excellent correlation between the two sets of data. The glass transition values follow an increasing pattern as expected due to the increase in styrene content.

Functional Modification of Poly[2,3-bis(4-ethoxy-4-oxobutyl)-1,3-butadiene] (II). Functional modification of this polymer will alter the thermal and the mechanical properties, as well as provide the possibility of a diene backbone for graft copolymerization. The modification of the preformed polymer was achieved by saponification of the esters to acids (Scheme 2). Most post-polymerization reactions do not proceed to 100% conversion, but this transformation was quantitative. The diacid **III** was insoluble in acetone and chloroform, with only THF readily dissolving the polymer and DMSO slightly dissolving the polymer. The modified polymer was also soluble in water in the carboxylate form. Upon conversion of the esters to acids, the T_g increased by 104 deg to 67 °C. This increase was expected due to the hydrogen-bonding capacity of the acid functionality. The thermal stability decreased slightly with a 10% weight loss at 345 and 348 °C in oxygen and nitrogen, respectively. The IR spectrum shown in Figure 4 further verifies the change from the ester to the acid functionalized polymer. The change in the carbonyl absorption and the addition of the O−H absorption depicts this modification.

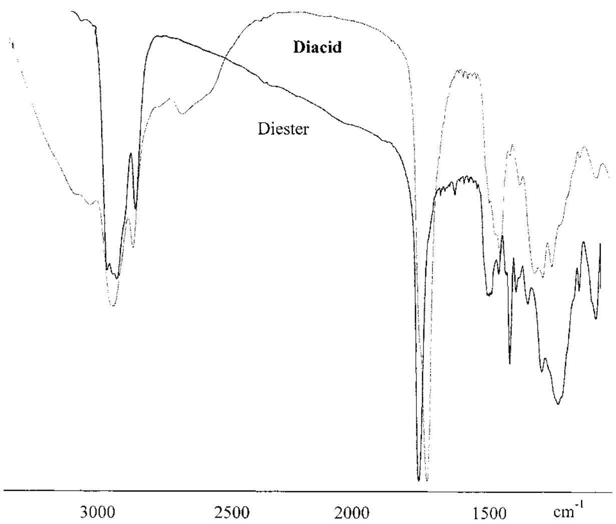


Figure 4. Infrared spectra of poly[2,3-bis(4-ethoxy-4-oxobutyl)-1,3-butadiene] (**II**) and the diacid modified polymer (**IV**).

Conclusion

The synthesis of 2,3-bis(4-ethoxy-4-oxobutyl)-1,3-butadiene and polymerization via free-radical bulk and solution polymerization as well as the copolymerization with styrene and the functional modification to the acid have been successfully achieved. The monomer is potentially synthetically feasible with an 80% yield after purification on an 80 g scale. The free-radical methods used were all successful, producing a clear, viscous liquid with molecular weights as high as 96×10^3 g/mol. The polymer exhibited a high thermal and thermo-oxidative stability compared to other materials with subambient glass transition temperatures. The polymer also degraded prior to cross-linking upon thermal treatment. This is also rare considering that most diene materials cross-link upon heating. Functional modification was easily achieved leading to the quantitative production of the acid derivative. The high solubility of the acid derivative polymer in organics and the aqueous solubility of the carboxylate modified polymer provide several options when processing this material. The ester-containing polymer exhibited potentially interesting adhesive properties when in contact with glass, metal, and plastic surfaces. These adhesive properties are still under investigation. All of these described factors make this polymer and its acid derivatized copolymers potentially useful in applications such as membranes, coatings, adhesives, and surfactants.

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