Available online at www.sciencedirect.com

ScienceDirect

Polymer 48 (2007) 105–109

polymer

www.elsevier.com/locate/polymer

Synthesis of disubstituted amine-functionalized diene-based polymers

Yue Yang, Valerie V. Sheares*

Department of Chemistry, University of North Carolina at Chapel Hill, Venable Hall 15-26, Chapel Hill, NC 27599-3290, USA

Received 24 May 2006; received in revised form 25 September 2006; accepted 30 September 2006
Available online 20 November 2006

Abstract

Diene-based polymers with two amine groups within each repeat unit were successfully synthesized by bulk and solution free radical polymerization techniques. All polymers have exclusive 1,4-microstructure. The number average molecular weights of the materials obtained were in the range of 30–52 × 10^3 g/mol using 2,2′-azobisisobutyronitrile (AIBN), *t*-butyl peracetate (*t*-BPA), or *t*-butyl hydroperoxide (*t*-BHP) as the initiators. The highest molecular weight achieved was 72 × 10^3 g/mol when *t*-butyl peroxide (*t*-BPO) was used as the initiator. Quantitative quaternization was achieved yielding hydrophilic water soluble polymers. Prior to quaternization, the polymers are hydrophobic and dissolve in most organic solvents.

Keywords: Amine; Functionalized; Polyisoprene

1. Introduction

There has been considerable interest in incorporating functional groups into diene-based polymers because of their commercial importance and wide range of applications. The annual production of polydienes in the United States is over four billion pounds of elastomers and approximately two billion pounds of plastics [1]. Styrene–butadiene rubber (SBR), nitrile rubber (NBR) and acrylonitrile–butadiene–styrene rubber (ABS) are widely used in automotive products, belting, hose, flooring, electrical insulation, and housewares.

Functional groups that have been incorporated into the polydienes include silyl, phenyl, nitrile, ester, amine and amide groups [2–10]. The Sheares group began devoting its effort to the investigation of functionalized diene-based polymers in 1998. A number of functional groups such as nitriles, amines and esters were incorporated into the polymers [5–7,9,11]. Amine groups were incorporated into the polymers due to their adhesive properties. The Sheares group has studied the polymerization of 2-[(*N*,*N*-dialkylamino)methyl]-1,3-butadiene with methyl, ethyl and *n*-propyl substituents via free radical polymerizations [9]. Later, homopolymers and copolymers made from an unsymmetrical monomer, 2-[(*N*-benzyl-*N*-methylamino)methyl]-1,3-butadiene, were prepared [11]. Due to the similarity in structure, these polymers have high compatibility with polystyrene, polyisoprene and polybutadiene. Therefore, these materials have the potential to be used in the modification of commercially available materials such as styrene–butadiene rubber, either as a third comonomer or as a polar additive.

The amine-functionalized diene monomers are of great interest due to their chemical and structural versatilities. Moreover, ionomers and polyelectrolytes can be obtained by partially or completely quaternizing the amine-functionalized polymers. These types of materials have a wide range of applications in waste water treatment [12], ion exchange resins [13], phase transfer catalysis [14], chemical sensors [15], and biomedical applications such as drug delivery and gene delivery [16–18]. Herein we reported the synthesis and polymerization of 2,3-bis(dimethylaminomethyl)-1,3-butadiene. With two amine groups within each repeat unit, we can double the functionality without doubling the degree of polymerization.

---

* Corresponding author. Tel.: +1 919 962 3663; fax: +1 919 962 2388.
E-mail address: ashby@email.unc.edu (V.V. Sheares).

0032-3861/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2006.09.064

2. Experimental

2.1. Materials

All reagents were purchased from Aldrich. AIBN was recrystallized from methanol. Benzoyl peroxide was recrystallized from diethyl ether. Solvents for solution polymerization were dried over sodium and distilled before use. All other reagents were used without further purification.

2.2. Characterization

NMR spectra were obtained on a Varian VXR-300 in deuterated chloroform. Molecular weights were determined using a Waters size exclusion chromatograph using THF as the solvent and polystyrene standards. Thermogravimetric analysis (TGA) was performed using a Perkin–Elmer thermogravimetric analyzer with a heating rate of 10 °C/min in a N_2 atmosphere. Glass transition temperatures were determined with a Perkin–Elmer–Pyris differential scanning calorimeter, using a heating rate and cooling rate of 10 °C/min. Elemental analysis was performed by Atlantic Microlab, Inc.

2.3. Synthesis of 2-bromo-3-(N,N-dimethylamino)propene (*I*)

To a solution of dimethylamine (45 g, 1 mol) in ether was added 2,3-dibromopropene (100 g, 0.5 mol) dropwise at 0 °C. The reaction mixture was allowed to slowly warm to room temperature and stirred for 16 h. The solution was extracted twice with diethyl ether, washed once with brine, and dried over anhydrous sodium sulfate. After evaporation of the solvent, the residue was distilled to give 2-bromo-3-(*N*,*N*-dimethylamino)propene in quantitative yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.79 (s, 1H), 5.56 (s, 1H), 3.09 (s, 2H), 2.26 (s, 6H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 131.60 ($CH_2{=}\mathit{C}BrCH_2$), 119.12 ($\mathit{C}H_2{=}CBrCH_2$), 68.20 ($\mathit{C}H_2N$), 45.14 [$N(\mathit{C}H_3)_2$].

2.4. Synthesis of 2,3-bis(dimethylaminomethyl)-1,3-butadiene (*II*) [19]

A Grignard reagent, readily prepared from **I** (32.8 g, 0.20 mol) and magnesium (5.76 g, 0.24 mol), was added dropwise to **I** (32.8 g, 0.20 mol) in the presence of dichloro[1,3-bis(diphenylphosphino)propane]nickel (4.3 g, 0.008 mol) in THF at 0 °C. The reaction mixture was allowed to slowly warm to room temperature. After refluxing for 4 h, the reaction mixture was quenched with saturated sodium chloride, extracted with diethyl ether three times, washed once with brine, and dried over anhydrous sodium sulfate. After evaporation of the solvent, the residue was distilled to give 2,3-bis(dimethylaminomethyl)-1,3-butadiene in 30% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.29 (s, 2H), 5.06 (s, 2H), 3.03 (s, 4H), 2.18 (s, 12H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 143.54 ($CH_2\mathit{C}{=}\mathit{C}CH_2$), 113.35 ($\mathit{C}H_2{=}CCH_2$), 62.21 ($\mathit{C}H_2N$), 43.27 [$N(\mathit{C}H_3)_2$]. Elem. Anal. Calcd.: C, 71.37%; H, 11.98%; N, 16.65%. Found: C, 71.46%; H, 12.22%; N, 16.35%.

2.5. Bulk and solution polymerizations of 2,3-bis(dimethylaminomethyl)-1,3-butadiene (*II*)

The following general procedure was used for all polymerizations. Monomer **II**, initiator and solvent were added to a 20 mL ampoule with a magnetic stir bar. Since the total volume of reaction mixture was less than 1 mL, this gave plenty of space for the vapor produced in the reaction. Therefore, safety is not an issue while using the reaction apparatus. After three cycles of freeze–pump–thaw, the ampoule was sealed under vacuum and placed in an oil bath preheated to the desired temperature. After the required polymerization time, the reaction was stopped by adding 1 mg of the inhibitor 2,6-di-*tert*-butyl-4-methylphenol. ^{1}H NMR was taken for a small sample of the reaction mixture immediately after the polymerization and the conversion was calculated based on the integration ratio of the characteristic polymer peak at 2.92 ppm to the remaining monomer vinylic peaks at 5.29 ppm and 5.06 ppm. The polymer was precipitated twice in acetone and dried under vacuum for 48 h. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.92 (s, 4H), 2.05–2.30 [b, 16H, 12 from $N(CH_3)_2$, 4 from polymer backbone]. ^{13}C NMR (300 MHz, $CDCl_3$): δ 135.56 ($CH_2\mathit{C}{=}\mathit{C}CH_2$), 60.01 and 59.03 ($\mathit{C}H_2N$), 45.53 [$N(\mathit{C}H_3)_2$], 30.08 ($\mathit{C}H_2CCH_2N$). Elem. Anal. Calcd.: C, 71.37%; H, 11.98%; N, 16.65%. Found: C, 70.85%; H, 12.08%; N, 16.47%.

2.6. Quaternization

Polymer (0.10 g) was dissolved in 3 mL methanol. Dimethyl sulfate (1.3 to 1 mole ratio of dimethyl sulfate to amine moiety) was added and the reaction was allowed to stir at room temperature for 3 h. The resulting white precipitate was collected and dried under vacuum for 48 h.

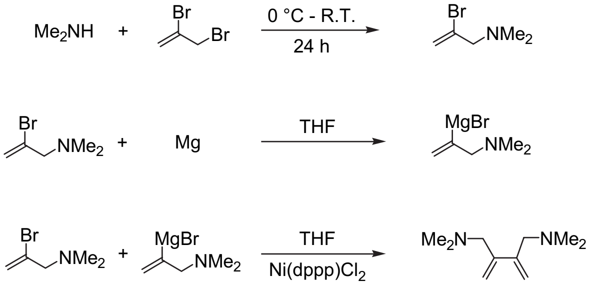
3. Results and discussion

3.1. Synthesis of monomers

Our interest in monomer **II** was the incorporation of two amine functional groups per repeat unit of the resulting polymers (Scheme 1). An S_N2 reaction followed by a nickel-catalyzed Grignard homocoupling reaction gave the desired monomer with high purity (100% purity by GC–MS). Attempts to prepare other amine-functionalized butadienes by this approach using diethyl amine, *n*-dipropyl amine and diisopropyl amine were made. However, once the side group is larger than a methyl group, the nickel coupling reaction does not proceed due to steric problems.

3.2. Free radical polymerization of 2,3-bis(dimethylaminomethyl)-1,3-butadiene

Different initiators were chosen in order to find the optimal polymerization conditions. The reaction temperature was



II

Scheme 1. Synthesis of 2,3-bis(dimethylaminomethyl)-1,3-butadiene by nickel coupling chemistry.

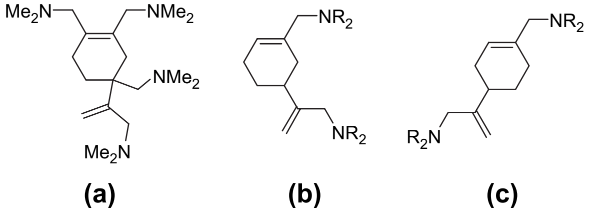


Fig. 1. Structures of Diels–Alder dimers.

chosen according to the half life of the initiators with complete decomposition after approximately 24 h. No vinylic peak was observed in the range of 5.0–6.0 ppm in ^{1}H NMR spectrum, indicating that all polymers were exclusively composed of 1,4-microstructure. The conversion from monomer to polymer generally increased as the reaction temperature was increased. Polymers with molecular weights in the range of 30–52 × 10^3 g/mol were synthesized as shown in Table 1. After reprecipitation, polydispersities were in the range of 1.2–1.5, indicating that the polymerization was most likely terminated by combination. The polydispersity was less than 1.5 as a result of fractionation during the purification step. Generally, no crosslinking or side reactions were observed when the reaction was carried out below 175 °C.

When the reaction was initiated using *t*-BHP at 175 °C, a Diels–Alder dimer side product was obtained (Fig. 1a). ^{1}H NMR showed vinylic peaks at 5.2 ppm and 5.0 ppm in a 1:1 ratio. In previous studies, Diels–Alder side products (Fig. 1b and c) were obtained in the free radical polymerization of 2-(*N*,*N*-dialkylamino)methyl-1,3-butadiene at temperatures as low as 75 °C [9]. In the polymerization of 2,3-bis(dimethylaminomethyl)-1,3-butadiene, the temperature at which the side reaction occurred was 100 °C higher. This is likely due to the much larger steric hindrance of the disubstituted monomer, making it more difficult for the Diels–Alder reaction to occur.

The preliminary polymerization study showed that in general the conversion was low in the system. This may be due to some chain transfer reactions to the monomer, which lead to less active chains. The conversion increased as the reaction temperature increased. However, side products were obtained when the reaction temperature was as high as 175 °C. To achieve higher conversion without producing any side products, polymerization reactions were carried out at 130 °C using *t*-BPO as the initiator. Table 2 summarizes the reaction conditions and the results. Although no side products were observed, higher conversion was not achieved. The conversion from monomer to polymer was only 19% after 24 h. Nonetheless, polymers of the highest molecular weight were obtained (72 × 10^3 g/mol) using this initiator. Increasing the reaction time from 24 h to 48 h resulted in an increase of the conversion from 19% to 30% without increasing the molecular weight. An increase in the initiator concentration from 0.5% to 1% increased the conversion from 30% to 42% after 48 h, but with a molecular weight decrease to 58 × 10^3 g/mol. When the monomer was stirred at 130 °C in the absence of initiators, no polymer was obtained after 24 h, indicating that no thermal polymerization occurred.

Solution free radical polymerizations were also investigated. Interesting results were obtained when polymerization reactions were carried out in solution using *t*-BPO as the initiator at 130 °C. Table 3 summarizes the results when THF was used as the solvent. It was found that adding small amounts of solvent to the reaction system greatly increased the conversion from 19% in bulk to 71% when the monomer to THF ratio (v/v) was 4:1. As the ratio of monomer to THF decreased from 4:1 to 1:1, the conversion after 24 h decreased from 71% to 46%, and the conversion after 48 h decreased from 82% to 60%. Conversion after 48 h was always slightly higher than conversion after 24 h. In addition, the molecular weight was reduced to about half of that obtained in bulk. The polymer started to crosslink once the conversion reached 70%. Therefore, no GPC data was obtained for these materials.

Generally, conversion for a typical solution free radical polymerization reaction is lower than that for bulk polymerization. The unusual higher conversion in solution than in bulk obtained here were initially thought to be due to chain transfer

Table 1
Bulk free radical polymerization of 2,3-bis(dimethylaminomethyl)-1,3-butadiene

Initiator (0.5%)	Temperature (°C)	Time (h)	Conversion[a] (%)	$\langle M_n \rangle$[b] ($\times 10^{-3}$ g/mol)	PDI[b]
AIBN	70	24	19	27.8	1.26
AIBN	70	48	26	32.4	1.30
t-BPA	105	24	44	52.5	1.53
t-BHP	175	24	55	33.2	1.47

[a] Determined by ^{1}H NMR.
[b] Determined by GPC.

Table 2
Bulk free radical polymerization using *t*-BPO as initiator at 130 °C

Initiator ratio (%)	Time (h)	Conversion[a] (%)	$\langle M_n \rangle$[b] ($\times 10^{-3}$ g/mol)	PDI[b]
0.5	24	19	71.6	1.38
0.5	48	30	71.7	1.52
1	48	42	58.3	1.51
None	24	0	–	–

[a] Determined by ^{1}H NMR.
[b] Determined by GPC.

Table 3
Solution free radical polymerization using *t*-BPO as initiator at 130 °C

Monomer:THF (v/v)	Time (h)	Conversion[a] (%)	$\langle M_{\text{n}} \rangle$[b] ($\times 10^{-3}$ g/mol)	PDI[b]
1:1	24	46	33.1	1.62
2:1	24	64	43.7	1.55
4:1	24	71	NA	NA
1:1	48	60	35.4	1.74
2:1	48	79	NA	NA
4:1	48	82	NA	NA

[a] Determined by ^{1}H NMR.
[b] Determined by GPC.

reactions to the various solvents. To test this hypothesis, several solvents with different chain transfer constants were examined (Table 4). The conversions were all higher than in bulk reactions and increased as the reaction time increased. No autoacceleration was observed. Molecular weights were in the range of 30–40 × 10^3 g/mol with polydispersities in the range of 1.5–1.8. However, the results were the same for all solvents chosen regardless of the chain transfer constants indicating that other side reactions occurred in the polymerization, possibly chain transfer to the initiator.

In order to investigate if the same unusual behavior existed when other initiators were used, solution polymerization was carried out using *t*-BPA as the initiator. The results showed that the reaction behavior follows the traditional free radical polymerization theory (Table 5).

Table 6 shows that the conversion from monomer to polymer decreased from 71% to 38% as the amount of *t*-BPO decreased from 0.5% to 0.1%, but the molecular weight did not increase as expected in traditional free radical polymerization. Instead, the molecular weight remained unchanged. This is likely due to the chain transfer reactions also. However, the details of the reaction mechanism are still not completely understood.

Table 4
Solution radical polymerization using *t*-BPO as initiator at 130 °C, monomer:solvent (v/v) = 4:1

Solvent	Time (h)	Conversion[a] (%)	$\langle M_{\text{n}} \rangle$[b] ($\times 10^{-3}$ g/mol)	PDI[b]
THF	6	37	30.4	1.63
THF	12	56	31.7	1.74
THF	18	65	38.0	1.55
THF	24	71	NA	NA
Toluene	6	32	37.2	1.52
Toluene	12	47	34.9	1.50
Toluene	18	54	33.9	1.50
Toluene	24	67	28.9	1.56
Cyclohexane	6	42	37.6	1.62
Cyclohexane	12	56	39.4	1.58
Cyclohexane	18	62	33.5	1.60
Cyclohexane	24	67	29.5	1.79
Ethyl acetate	6	35	30.4	1.55
Ethyl acetate	12	56	31.1	1.65
Ethyl acetate	18	65	34.0	1.59
Ethyl acetate	24	70	37.1	1.52

[a] Determined by ^{1}H NMR.
[b] Determined by GPC.

Table 5
Free radical polymerization using *t*-BPA as initiator at 105 °C

Solvent	Conversion[a] (%)	$\langle M_{\text{n}} \rangle$[b] ($\times 10^{-3}$ g/mol)	PDI[b]
Monomer:cyclohexane (v/v) = 4:1	25	30.1	1.60
None	44	52.5	1.53

[a] Determined by ^{1}H NMR.
[b] Determined by GPC.

Table 6
Solution radical polymerization using *t*-BPO as initiator at 130 °C for 24 h, monomer:THF (v/v) = 4:1

t-BPO (%)	Conversion[a] (%)	$\langle M_{\text{n}} \rangle$[b] ($\times 10^{-3}$ g/mol)	PDI[b]
0.50	71	38.0[c]	1.55
0.25	55	37.6	1.55
0.10	38	38.6	1.48

[a] Determined by ^{1}H NMR.
[b] Determined by GPC.
[c] After 24 h, the polymer was partially crosslinked and no GPC data was available. Molecular weight of a sample obtained after running the polymerization reaction for 18 h was used here for comparison.

3.3. Anionic polymerization of 2,3-bis(dimethylaminomethyl)-1,3-butadiene

Anionic polymerization was attempted using *sec*-butyllithium as the initiator. The reaction temperature was 10 °C when toluene or cyclohexane was used as the solvent, and −78 °C when THF was used. However, no polymer was obtained in all cases even after 48 h. One possible explanation is that the two amine groups in the monomer or THF can strongly chelate to the lithium after the initiation as shown in Fig. 2, preventing the addition of monomers.

3.4. Thermal and solubility properties of poly[2,3-bis(dimethylaminomethyl)-1,3-butadiene]

The homopolymer of 2,3-bis(dimethylaminomethyl)-1,3-butadiene had a 5% weight loss at 300 °C and a 10% weight loss at 336 °C under nitrogen, which is comparable to the other functionalized diene polymers synthesized by the Sheares group. The glass transition temperature of poly[2,3-bis(dimethylaminomethyl)-1,3-butadiene] was 41 °C, much higher than the glass transition temperatures seen for the other diene-based materials previously studied, which had glass transition temperatures lower than room temperature (Fig. 3). Compared to polymer **III**, poly[2,3-bis(dimethylaminomethyl)-1,3-butadiene] has only one methylene group

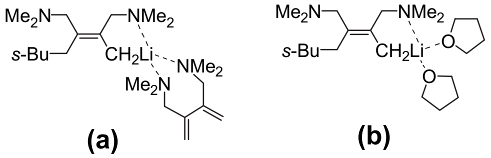


Fig. 2. Chelate structure of 2,3-bis(dimethylaminomethyl)-1,3-butadiene and lithium.

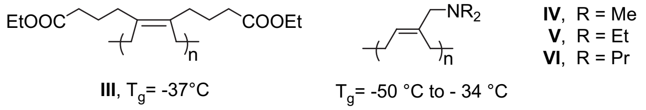


Fig. 3. Glass transition temperature of functionalized diene-based polymers.

between the functional group and the butadienyl skeleton. Shorter side chains allow less flexibility and conformational rotation, resulting in a higher glass transition temperature. Moreover, compared to polymers **IV**, **V** and **VI**, poly[2,3-bis(dimethylaminomethyl)-1,3-butadiene] has two amine groups within each repeating unit, which leads to significant inter- and intramolecular interactions, and a higher glass transition temperature.

Poly[2,3-bis(dimethylaminomethyl)-1,3-butadiene] was soluble in common organic solvents such as chloroform, THF, methanol, ethyl acetate, diethyl ether and hexane. It was not soluble in water, but was soluble in acidic water. The quaternization reaction proceeded quantitatively resulting in a white crystalline material that was completely soluble in water and was not soluble in any of the above organic solvents.

3.5. Hydrogenation of 2,3-bis(dimethylaminomethyl)-1,3-butadiene

Attempts to hydrogenate the obtained poly[2,3-bis(dimethylaminomethyl)-1,3-butadiene] were carried out using 10% palladium on carbon as the catalyst at 1500 psi and 150 °C. As expected, the double bond in the polymer was very stable and no hydrogenation occurred even after 48 h. The polymer is stable at room temperature for at least one year.

4. Conclusion

Amine-functionalized diene-based polymers with two amino groups in each repeat unit were successfully synthesized by bulk and solution free radical polymerization techniques. The amine-functionalized polymers can be used as a polar additive to increase the adhesive property of the polymer blends. They can also be used as coatings where a strong chelation of the polymer to various metals is desired. Quaternization of the polymer was successfully carried out with 100% conversion, leading to a final material that was water soluble. This can be used in various areas such as ion exchange resins, phase transfer catalysis, waste water treatment and biomedical applications.

Acknowledgement

The authors thank financial support from the National Science Foundation (Division of Materials Research) under Grant Number 0418499.

References

[1] Odian G. In: Principle of Polymerization. 3rd ed. New York: Wiley-Interscience; 1991.

[2] Takenaka K, Hirao A, Hattori T, Nakahama S. Macromolecules 1987;20:2034.

[3] Hirao A, Sahano Y, Takenaka K, Nakahama S. Macromol Chem Phys 1998;31:9141.

[4] Yaegashi T, Yodoya S, Nakamura M, Takeshita H, Takenaka K, Shiomi T. J Polym Sci Part A Polym Chem 2004;42:999.

[5] Jing Y, Sheares VV. Macromolecules 2000;33:6255.

[6] Jing Y, Sheares VV. Macromolecules 2000;33:6262.

[7] Beery MD, Rath MK, Sheares VV. Macromolecules 2001;34:2469.

[8] Petzhold C, Morschhäuser R, Kolshorn H, Stadler R. Macromolecules 1994;27:3707.

[9] Sheares VV, Wu L, Li Y, Emmick TK. J Polym Sci Part A Polym Chem 2000;38:4070.

[10] Takenaka K, Hanada K, Shiomi T. Macromolecules 1999;32:3875.

[11] Wu L, Sheares VV. J Polym Sci Part A Polym Chem 2001;39:3227.

[12] Ravikumar RA, Hussain RK. J Appl Polym Sci 2002;92:1501.

[13] Henry WD, Zhao D, SenGupta AK, Lange C. React Funct Polym 2004;60:109.

[14] Petzhold CL, Stefens J, Monteavaro LL, Stadler R. Polym Bull 2000;44:477.

[15] Greene NT, Morgan SL, Shimizu KD. Chem Commun 2004;10:1172.

[16] Wolfert MA, Dash PR, Nazarova O, Oupicky D, Seymour LW, Smart S, Strohalm J, Ulbrich K. Bioconjugate Chem 1999;10:993.

[17] Shenoy D, Little S, Langer R, Amiji M. Mol Pharm 2005;2:357.

[18] Ogris M, Brunner S, Schuller S, Kircheis R, Wagner E. Gene Ther 1999;6:595.

[19] Akira T, Toshiyuki M, Yoshinori T, Makoto H. Bull Chem Soc Jpn 1991;64:1051.