

SYNTHESIS OF HYDROXYL-TERMINATED POLYBUTADIENE POSSESSING HIGH CONTENT OF 1,4-UNITS VIA ANIONIC POLYMERIZATION*

Ji-ming Chen^{a, b}, Zai-jun Lu^{a**}, Guang-qin Pan^b, Yong-xin Qi^b, Jian-jun Yi^b and Hai-jian Bai^b

^a School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, China

^b Institute of Lanzhou Petrochemical Company, Petrochina, Lanzhou 730060, China

Abstract The hydroxyl-terminated polybutadiene (HTPB) possessing high content of 1,4-units was synthesized by anionic polymerization of butadiene, using alkylolithium containing silicon-protected hydroxyl group as initiator and cyclohexane as solvent. The polymers were characterized by GPC, IR and ¹H-NMR. The mechanical properties of cured films were also evaluated. The results show that the content of 1,4-units for HTPBs made by anionic polymerization reaches up to 90%. The molecular weight distribution is very narrow (≤ 1.05). The functionality of hydroxyl groups approaches 2. Compared with free radical HTPB, the elongation at break of anionic HTPB films increased by 70%, while the tensile strength remained nearly unchanged. This new HTPB can be very useful in solid propellant.

Keyword: Hydroxyl-terminated polybutadiene; Anionic polymerization; 1,4-Unit; Mechanical properties.

INTRODUCTION

Hydroxyl-terminated polybutadiene (HTPB) is a telechelic liquid rubber containing hydroxyl groups. It was widely used as the binder for solid propellant of missiles and rockets^[1] due to its good mechanical properties after curing^[2]. Recently, the synthesis of high performance HTPB is highly desired because the shooting range of missiles has been progressively enhanced. It is well-known that the performance of HTPBs is greatly affected by their chain microstructures. For example, with increasing the content of 1,4-units, the glass transition temperature (T_g) of polybutadienes decreases, exhibiting a rubbery state^[3]. By contraries, polybutadienes exhibit a plastic state with decreasing the content of 1,4-units. In order to obtain high performance HTPB, the high content of 1,4-units is considered as one of the important molecular parameters.

HTPB made by traditional radical polymerization (abbreviated as radical HTPB) has a maximum 1,4-unit content of 79%^[4, 5] and a broad molecular weight distribution. In addition, its ill-defined hydroxyl distribution easily causes the nonuniform cross-linking network and worse mechanical properties. Although the living radical polymerization was extensively developed recently^[6–8], the content of 1,4-units was still not improved. On the contrary, HTPB made by anionic polymerization (abbreviated as anionic HTPB) can give high 1,4-unit content of 90%, narrow molecular weight distribution and well-defined hydroxyl distribution in principle. These characteristics are very useful in improving the performance of HTPB. Therefore, the synthesis of anionic HTPB has attracted much attention.

Typical anionic HTPB is prepared using naphthalene lithium as difunctional initiator in THF solvent. Its microstructure is mainly 1,2 configuration due to the use of polar solvent^[9, 10]. To obtain the high content of

* This work was financially supported by the Lanzhou Petrochemical Company.

** Corresponding author: Zai-jun Lu (鲁在君), E-mail: z.lu@sdu.edu.cn

Received August 17, 2009; Revised October 2, 2009; Accepted October 16, 2009

doi: 10.1007/s10118-010-9121-y

1,4-units, difunctional initiators soluble in non-polar solvents, such as 1,3-bis(1-lithio-methylhexyl)benzene, has been developed^[3, 11, 12]. However, the association of diinitiators and the addition of polar additives affected the polymerization process and polymer microstructure^[13]. It seems that the best method is to choose the monofunctional initiator containing a protected hydroxyl group. Schuls^[14] synthesized anionic HTPB using hydroxyl-carrying mixed acetals as protected monofunctional initiator, but the solubility of formed initiator is not good in hydrocarbon solvent.

More recently, our group^[15] reported the synthesis of hydroxyl-terminated polyisoprene (HTPI) with 90% of 1,4-unit content by anionic polymerization, using a novel protective monofunctional initiator with good solubility in hydrocarbon solvent. To our knowledge, this is the highest content of 1,4-units among the reported HTPIs. In this article, our aim is to extend this method to synthesize the anionic HTPB, whose properties can meet the urgent requirements in advanced solid propellant.

EXPERIMENTAL

Materials

Tert-butyldimethylsilyloxy propyllithium $(\text{CH}_3)_3\text{CSi}(\text{CH}_3)_2\text{O}(\text{CH}_2)_3\text{Li}$ (BPL) was synthesized according to the reported method^[16]. Butadiene (Qilu petrochemical company) was purified by distillation over CaH_2 . Cyclohexane (Sinopharm Shanghai Chemical Reagent Co. Ltd.) was dried and distilled over CaH_2 twice. Ethylene oxide (Sinopharm Shanghai Chemical Reagent Co. Ltd.) was distilled over KOH. Radical HTPB (Lanzhou Petrochemical Company) has hydroxyl value 0.5238 mmol/g, $M_n = 8100$ (GPC), 4400 (VPO), and $M_w/M_n = 1.55$. Toluenediisocyanate (TDI) (Aldrich, 2,4- 80% and 2,6- 20%) was used as received.

Synthesis of Anionic Polymerized HTPB

To a 5 liter reactor charged with argon, 2500 mL cyclohexane, 500 mL butadiene and 96.4 mL BPL (0.80 mol/L) were added. The reaction was carried out at 50°C for 2.5 h. Subsequently, 23.0 mL ethylene oxide was added and reaction was continued for 1 h. 17.5 mL degassed methanol was injected to terminate the reaction. After acidic hydrolysis with HCl, the viscous polymer was isolated with ethanol and dried under vacuum. ¹H-NMR (CDCl_3 , δ): 5.0 (1,2-unit $=\text{CH}_2$), 5.40 (1,2-unit $-\text{CH}=\text{}$), 1.3 (1,2-unit $-\text{CH}_2-$), 5.38 (1,4-unit $-\text{CH}=\text{}$), 2.03, 2.12 (1,4-unit $-\text{CH}_2-$), 3.6 (CH_2OH), 0.90 ($(\text{CH}_3)_3\text{C}-\text{Si}$), 0.04 ($(\text{CH}_3)_2\text{Si}-$). IR (KBr, cm^{-1}): 3300–3500 ($-\text{OH}$), 725 (*cis*-1,4), 966 (*trans*-1,4), 911 (vinyl 1,2).

Preparation of Cured Films

To a 500 mL reactor, 200 g (0.05 mol) HTPB and 9.25 g (0.053 mol) TDI were added and stirred for 1 h. Subsequently, the mixture was poured into a mould. After reaction at room temperature for 72 h, a film with 2 mm thickness was obtained.

Measurements

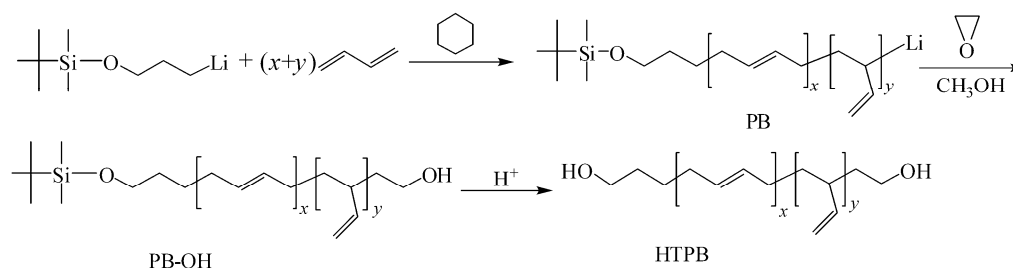
¹H-NMR spectra were recorded on a Bruker AV400 spectrometer with CDCl_3 as solvent and without addition of the internal reference. IR spectra were recorded on a Nicolet 560 with KBr pellets. GPC measurements were carried out in THF (1 mL/min) at 35°C with a Waters 515 pump equipped with three styragel columns and a refractive index detector. Monodisperse PS samples were used as standards for calibration. Mechanical property measurements were performed on an RG-300 electronic universal testing machine (Shenzhen Reger instrument co.) with a crosshead speed of 100 mm/min at 25°C. The sample standard distance was 40 mm. Hydroxyl group value was determined by acetylation reagent titration method according to GJB 1327A-2003.

RESULTS AND DISCUSSION

Synthesis and Characterization of Anionic HTPB

It is well-known that the microstructure of polybutadiene prepared anionically is determined mainly by polarity of the solvent. When nonpolar solvents are used, high 1,4-units content is obtained. The BPL was used as initiator because it can be fully soluble in nonpolar solvents such as hexane, cyclohexane and benzene. This

makes it possible to perform anionic polymerization of butadiene in nonpolar solvents and obtain high content of 1,4-units. Meanwhile, BPL is also a kind of monofunctional initiator. It can avoid the “pseudo-gel” phenomena which often occurred in difunctional initiator systems. Scheme 1 illustrates the synthetic route of anionic HTPB. In the presence of cyclohexane solvent, butadienes were initiated by BPL and polymerized to produce living polybutadiene (PB). Living PB was subsequently capped with ethylene oxide and terminated with methanol to form PB-OH. In order to improve the hydroxyl group yield, the ethylene oxide was purified by butyllithium. After removal of silicon protecting group by acid, anionic HTPB was obtained.



Scheme 1 Synthetic route of anionic HTPB

Figure 1 shows the GPC curves of anionic HTPB and radical HTPB. The curve of anionic HTPB shows a single sharp peak, indicating a narrow molecular weight distribution ($M_w/M_n = 1.03$, $M_n = 8400$), while the peak of radical HTPB is broad, indicating the polydisperse distribution ($M_w/M_n = 1.55$). This is because the living anionic polymerization proceeded without chain transfer and chain termination reactions in comparison with radical polymerization. This led to the narrow molecular weight distribution and good control on the molecular weight.

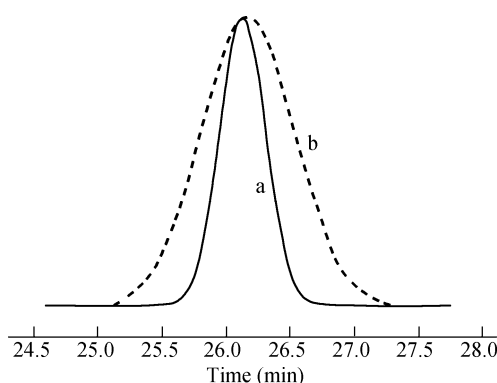


Fig. 1 GPC curves of anionic HTPB (a) and free radical HTPB (b)

Figure 2 shows $^1\text{H-NMR}$ spectra of anionic HTPB at different reaction stages. For PB, two peaks at $\delta = 0.90$ and 0.04 due to protons of *tert*-butyl $((\text{CH}_3)_3\text{C}-\text{Si})$ and methyl $((\text{CH}_3)_2-\text{Si})$ groups were clear observed. After end-capping with ethylene oxide, a new peak at $\delta = 3.6$ appeared (see Fig. 2 PB-OH and HTPB), indicating the formation of β -hydroxyl groups. After acidic hydrolysis, the peaks at $\delta = 0.90$ and 0.04 disappeared (see Fig. 2 HTPB), which suggested that the protective groups were removed completely and α -hydroxyl groups were exposed.

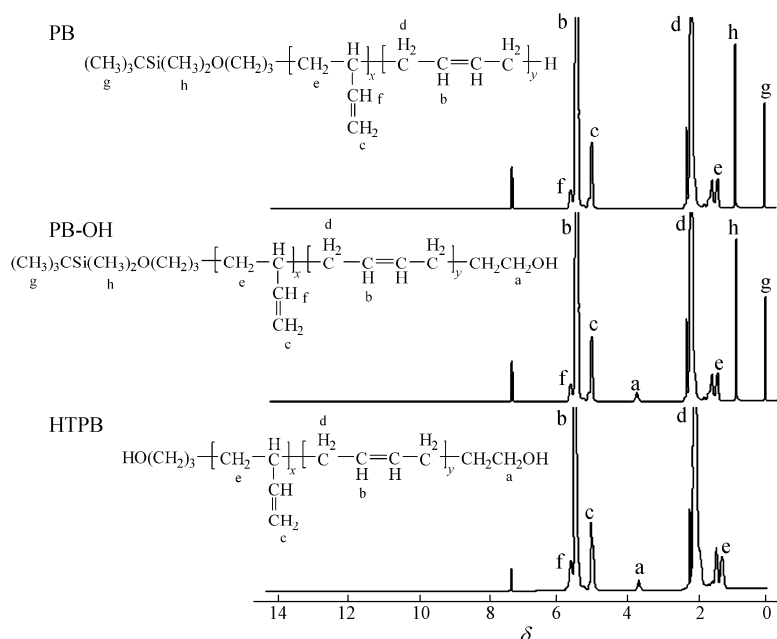


Fig. 2 ^1H -NMR spectra of PB, PB-OH, and HTPB

Figure 3 shows the FT-IR spectrum of anionic HTPB. The peaks at 3300–3500 cm^{-1} confirmed the existence of hydroxyl groups. The characteristic peaks due to microstructures of polybutadiene chains were also observed at 725 cm^{-1} (*cis*-1,4), 966 cm^{-1} (*trans*-1,4) and 911 cm^{-1} (vinyl 1,2), respectively.

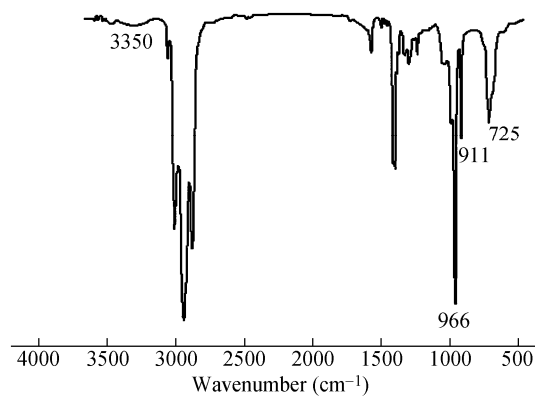


Fig. 3 FT-IR spectrum of anionic HTPB

Table 1. Microstructure characterization of anionic HTPB and radical HTPB

Samples ^a	M_n^b	Hydroxyl value ^c (mmol/g)	$C_{cis-1,4}$ (%)		$C_{trans-1,4}$ (%)		$C_{1,2}$ (%)	
			IR ^d	^1H -NMR ^e	IR	^1H -NMR	IR	^1H -NMR
HTPBA	4200	0.4810	35.15	35.09	54.83	54.52	10.02	10.39
HTPBR	4400	0.5238	20.96	20.56	57.60	57.45	21.44	21.99

^a HTPBA: synthesized by anionic polymerization using BPL in cyclohexane at 50°C for 2 h., HTPBR: synthesized by radical polymerization using H₂O₂ in ethanol at 117°C for 3 h; ^b Measured by VPO; ^c Determined by acetylation reagent titration method; ^d $C_{cis-1,4} = 17667A_{725}/(17667A_{725} + 3674A_{911} + 4741A_{966})$, $C_{trans-1,4} = 4741A_{966}/(17667A_{725} + 3674A_{911} + 4741A_{966})$, $C_{1,2} = 3674A_{911}/(17667A_{725} + 3674A_{911} + 4741A_{966})$, where A_{725} , A_{911} and A_{966} are areas of characteristic absorption peaks, respectively; ^e $2C_{1,2}/[C_{1,2} + 2(1-C_{1,2})] = I_{4.81-5.01}/I_{5.38}$, $C_{trans-1,4}/(1-C_{1,2}-C_{trans-1,4}) = I_{2.03}/I_{2.12}$, where I is the integral area of corresponding absorption peak.

The microstructure content of HTPBs can be calculated from IR and ^1H -NMR spectra, and the results were summarized in Table 1. The data calculated from IR spectra was in good agreement with those from ^1H -NMR spectra. The 1,4-unit content of anionic HTPB reached *ca.* 90%, which was *ca.* 12% higher than that of radical HTPB.

The hydroxyl value and average functionality of HTPBs are listed in Table 2. The functionality of anionic HTPB (f_n) approached to 2. This was in good agreement with the theoretical value assuming each HTPB had two hydroxyl groups at both chain ends. The functionality of radical HTPB was bigger than 2. The reason is radical HTPB is a mixture containing a variety of polybutadienes of varying number and site of hydroxyl groups.

Table 2. Hydroxyl value and average functionality of anionic HTPBs and radical HTPB

Samples	M_n		M_w/M_n^c	Hydroxyl value ^d (mmol/g)	f_n^e
	Theor. ^a	Meas. ^b			
HTPBA1	3000	3100	1.05	0.6211	1.92
HTPBA2	4000	4200	1.03	0.4810	1.93
HTPBA3	5000	5100	1.04	0.3804	1.94
HTPBR		4400	1.55	0.5238	2.30

^a M_n theor. = weight of monomer/mole number of initiator; ^b Measured by VPO; ^c determined by GPC;

^d Determined by acetylation reagent titration method; ^e Number average functionality, $f_n = M_n \times \text{hydroxyl value}/1000$ ^[17]

Influence of Solvent Composition on Microstructure of Anionic HTPB

Table 3 shows the influence of mixed solvent composition on microstructure of anionic HTPB. The total contents of 1,4-units decreased from 89.98% to 7.20% with increasing the volume ratio of THF to cyclohexane. Therefore, we can control the microstructure content by the polarity of mixed solvents.

Table 3. The influence of solvent composition on microstructure of anionic HTPB

Samples ^a	THF/Cyclohexane ^b	<i>Cis</i> -1,4 ^c (%)	<i>Trans</i> -1,4 (%)	Vinyl-1,2 (%)
HTPBA4	0/100	35.15	54.83	10.02
HTPBA5	25/75	22.97	3.66	73.37
HTPBA6	50/50	7.26	6.57	86.17
HTPBA7	75/25	4.34	7.89	87.77
HTPBA8	100/0	0	7.20	92.80

^a HTPBA: synthesized by anionic polymerization using BPL in corresponding mixed solvent composition at 50°C for 2 h; The butadiene volume was 500 mL, the BPL volume was 96.4 mL, the mixed solvent composition volume was 2500 mL, the ethylene oxide volume was 23.0 mL and the degassed methanol volume was 17.5 mL; ^b Volume ratio; ^c Calculated from FT-IR

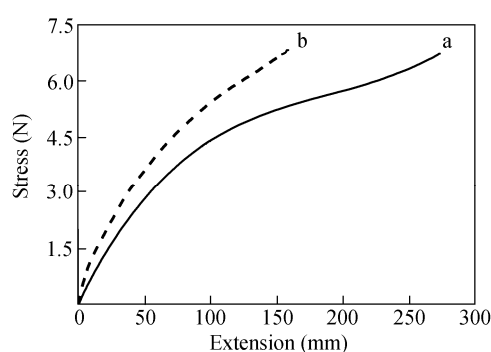


Fig. 4 Stress-extension curves of cured films based on (a) anionic HTPB and (b) radical HTPB

Mechanical Properties of HTPB Films

Figure 4 shows the stress-strain curves of cured films based on anionic and radical HTPBs. The tensile strengths of these two kinds of cured films were 0.56 MPa and 0.57 MPa, respectively. However, the elongation at break of the anionic HTPB film was 687.5%, increasing by 70% compared with that of the radical HTPB film. The reason may be that the narrow molecular weight distribution of anionic HTPB led to the formation of uniform cross-linking network, which facilitated the transport and dispersion of the stress. However, radical HTPB had the broad molecular weight distribution and ill well-defined hydroxyl groups. The cross-linking network was nonuniform after curing. This easily caused stress concentration and low elongation at break.

CONCLUSIONS

In conclusion, HTPB with high 1,4-unit content of 90% has been successfully synthesized *via* anionic polymerization using alkyllithium with silicon-protected hydroxyl group as initiator and cyclohexane as solvent. The polymer exhibited narrow molecular weight distribution ($M_w/M_n \leq 1.05$) and controllable molecular weight and microstructure. Its functionality approached 2. Compared with radical HTPB, the cured film based on anionic HTPB retained the tensile strength, but increased the elongation at break by 70%. This is very useful to develop the high performance binder for solid propellant.

ACKNOWLEDGEMENTS We greatly thank Ms. Jing Yu, Mr. Yaoheng Zhang, and Mr. Ying Huang for good suggestion and measurements.

REFERENCES

- 1 Karabeyoglu, M.A., Altman, D. and Cantwell, B.J., *J. Propul. Power*, 2002, 18(3): 610
- 2 Sekkar, V., Gopalakrishnan, S. and Devi, K.A., *Eur. Polym. J.*, 2003, 39(6): 1281
- 3 Jou, C.D., Hsieh, H.C. and Tsiang, R.C., *Polymer*, 1997, 38(23): 5873
- 4 Vilar, W.D., Menezes, S.M.C. and Akcelrud, L., *Polym. Bull.*, 1994, 33: 563
- 5 Vilar, W.D., Menezes, S.M.C. and Akcelrud, L., *Polym. Bull.*, 1995, 35: 481
- 6 Sarbu, T., Lin, K., Spanswick, J., Gil, R.R., Siegwart, D.J. and Matyjaszewski, K., *Macromolecules*, 2004, 37: 9694
- 7 Karavia, V., Deimede, V. and Kallitsis, J.K.J., *Macromol. Pure Appl. Chem.*, 2004, 41(2): 115
- 8 Coessens, V. and Matyjaszewski, K., *Macromol. Rapid Commun.*, 2005, 26(24): 1022
- 9 Halasa, A.F., *Rubber Chem. Technol.*, 1981, 54: 627
- 10 Moton, M. and Fetters, L.J., *Rubber Chem. Technol.*, 1975, 48: 359
- 11 Almeida, C.L. and Akcelrud, L.C., *Polym. Int.*, 1998, 47: 497
- 12 Hargis, G.I., Fabris, H.J., Wilson, J.A. and Livigni, R.A., 1991, U.S. Pat., 5,063,190
- 13 Fetters, L.J., Kamienski, C.W., Morrison, R.C. and Young, R.N., *Macromolecules*, 1979, 12(2): 344
- 14 Schulz, D.N., Halasa, A.F. and Oberster, A.E., *J. Polym. Sci., Part A: Polym. Chem.*, 2003, 41(1): 153
- 15 Sun, Q.Q., Lu, Z.J., Zhang, L., Zhang, K. and Luo, X., *Acta Chim. Sinica*(in Chinese), 2008, 66(1): 117
- 16 Lu, Z.J., Li, M.S. and Sun, Q.Q., 2006, CN Pat., 200610069832
- 17 Cao, Y. and Jin, G.T., *China Elastomerics*(in Chinese), 1996, 6(4): 34 5