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Investigation on cationic ring-opening polymerization of 1,5,7,11-tetraoxaspiro [5,5] undecane in the presence of low molecular weight tetraols

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Abstract

A new four-armed tetraol, poly(1,5,7,11-tetraoxaspiro [5,5] undecane) tetraol (poly(TOSU)), was prepared by the cationic ring-opening polymerization of TOSU using $BF_3\cdot OEt_2$ as initiator. Its structure was characterized by ^1H, ^{13}C NMR and FTIR spectra. GPC curves showed that the polymer obtained had two fractions with higher and lower molecular weights; however, each had a relatively narrow molecular weight distribution. The molecular weights of the polycarbonate tetraols were controlled by the molar ratio of TOSU consumed to initial BHDU. The mechanism of the polymerization was discussed. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Four-armed tetraol; 1,5,7,11-Tetraoxaspiro [5,5] undecane; Cationic ring-opening polymerization

1. Introduction

Spiro orthocarbonates (SOCs) undergo double ring-opening polymerization with an expansion in volume [1–4]. This unique property has attracted the interest of polymer chemists [5,6]. The polymerization of 1,5,7,11-tetraoxaspiro [5,5] undecane (TOSU) using $BF_3\cdot OEt_2$ as initiator was first reported by Bailey et al. [7]. The poly(TOSU) obtained is biocompatible, and has been examined as a key component of a potential dental composite material [8].

Although the cationic ring-opening polymerization of SOCs has been investigated extensively, only a low molecular weight (MW) polymer was obtained and the MW cannot be controlled. Recently, a cationic zirconocene complex was used in the initiation and polymerization of TOSU [9]. The low polydispersity index ($PDI \leq 1.2$) of the polymer produced suggests that the polymerization exhibited "living" characteristics, which was explained in terms of the stabilization of the propagating cations by the bulky counter anion. However, two fractions of the polymer were isolated based on their solubility in methanol: an insoluble one in low yield and a soluble one in high yield. There was no detailed explanation for this phenomenon.

It was reported [10] that the polyurethane prepared from poly(SOC) glycol had excellent hydrolysis-resistant properties in comparison with the corresponding polyurethane made from a polyester glycol, although the latter had better mechanical properties. However, the mechanical properties could be improved when star-shaped polyether polyols were used [11]. It is very important to control the polymerization of SOCs, especially to study the synthesis and characterization of well-defined star-shaped poly(SOC) polyol for its application in polyurethane, modification of epoxy resins, etc. There have been a number of reports on the preparation of hydroxyl-terminated polyethers or polyacetals with well-controlled structures in the presence of an alcohol compound [12–14]. For these systems, two competitive mechanisms of propagation were proposed: (1) an activated monomer mechanism (AM) and (2) an active chain end mechanism (ACE) [13] (see Scheme 1). Cyclics were formed via the ACE mechanism with an intramolecular chain transfer reaction (Eqs. (2) and (3) in Scheme 1), and only linear polydiols could be formed via the AM mechanism. When the monomer was added into the mixture of diols and initiator at a rate equal to the rate of monomer consumption, polymerization proceeded via the AM mechanism. As a result, the MW of the polymer could be controlled by the mole ratio of monomer consumed to the initial diols, and the MW distribution was narrow. In addition, the amount of cyclic oligomers in the products was reduced drastically [13]. When the monomer, initiator and diols were mixed together, the proportion of ACE mechanism was reduced and the cyclics were also suppressed [14].

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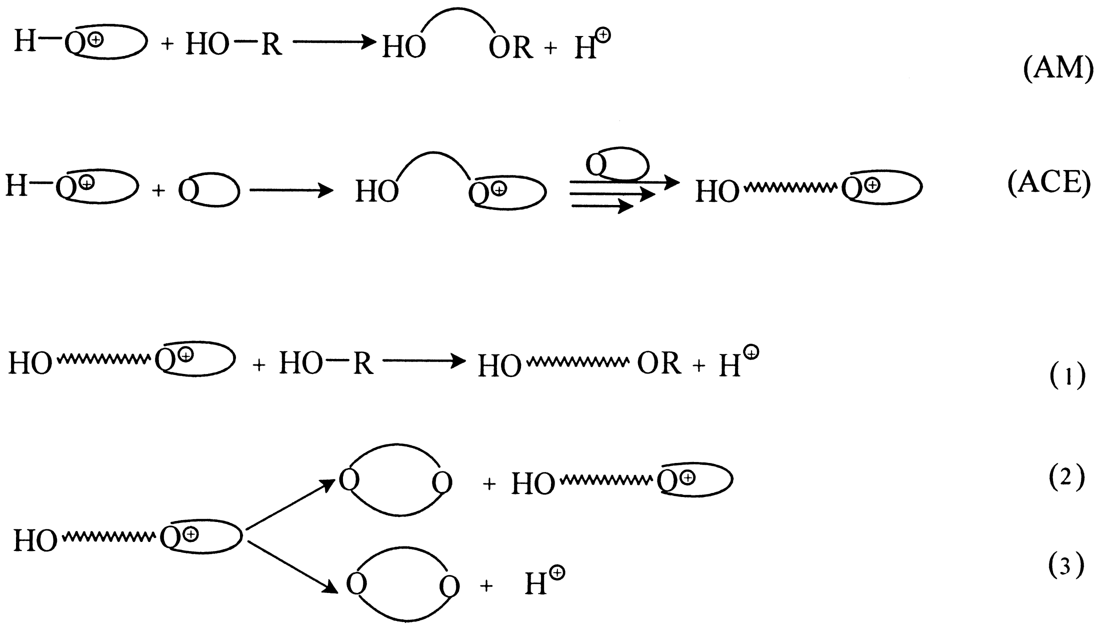


Scheme 1.

Generally, star-shaped polymers can be prepared by the chain transfer reaction of a living precursor with a multifunctional reagent, such as polyalcohol compounds [15,16]. Here, we report the preparation of poly(TOSU) tetraol by the cationic ring-opening polymerization of TOSU initiated by $BF_3 \cdot OEt_2$ in the presence of 6,6-bis(5-hydroxy-2-oxapentyl)-4,8-dioxaundecanediol-1,11 [$C(CH_2OCH_2CH_2CH_2CH_2OH)_4$, BHDU].

2. Experimental

2.1. Materials

TOSU was synthesized by a modification of the method described by Sakai [17] and purified first by recrystallization from toluene, and then by double sublimation. The melting point of the product was 141°C (lit. [7], 141°C). BHDU was prepared according to our published method [16]. The ^1H, ^{13}C NMR and FTIR data of compound BHDU are as follows:

^1H NMR ($CDCl_3$): δ 1.79 (q, 8H, $CH_2CH_2CH_2$); 3.39 (s, 8H, C–CH_2O); 3.47 (s, 4H, OH); 3.58 (t, 8H, OCH_2CH_2); 3.73 (t, 8H, CH_2OH) ppm. ^{13}C NMR ($CDCl_3$): δ 31.82 ($CH_2CH_2CH_2$); 44.69 (^4C); 61.18 (CH_2OH); 70.18 (OCH_2); 70.84 (C–CH_2O) ppm. FTIR (neat): ν 1109.6; 1054.8 (C–O) cm^{-1}.

Tetrahydrofuran (THF) was distilled from the constant deep-green solution of sodium-benzophenone under a nitrogen atmosphere. Methylene chloride was purified by distillation over calcium hydride. $BF_3 \cdot OEt_2$ was distilled under reduced pressure just before use. $LiAlH_4$, petroleum ether

Table 1
Conditions and results of cationic ring-opening polymerization of 1,5,7,11-tetraoxaspiro [5,5] undecane in the presence of BHDU (polymerization conditions: $[TOSU]_0 = 2.0$ mol l^{-1}; $[BF_3 \cdot OEt_2]_0 = 0.01$ mol l^{-1}; temperature, 25°C; reaction time, 24 h)

No.	$[BHDU]_0$ (mol l^{-1})	Conv. (%)[a]	Yield (%)[b]		M_n(VPO)[c]		M_n(NMR)[d]	$M_n(t)_1$[e]	$M_n(t)_2$[f]	M_w/M_n(GPC)	
			2b	**2a**	**2b**	**2a**	**2a**	**2a**		**2b**	**2a**
1	0.125	94	21	72	18 750	2850	2810	2780	2830	1.33	1.30
2	0.100	93	16	75	16 870	3310	3290	3350	3390	1.33	1.29
3	0.080	94	13	79	15 010	4060	4090	4130	4150	1.36	1.32
4	0.067	91	10	80	14 120	4690	4720	4760	4780	1.42	1.37
5	0.057	94	9	85	13 390	5540	5640	5650	5640	1.43	1.38
6	0.050	90	6	83	11 070	6010	6090	6130	6150	1.48	1.38

[a] Conversion was determined by ^1H NMR spectra.
[b] Polymers **2a** and **2b** are, respectively, calculated according to the weights of the dried polymer and the monomer added.
[c] Obtained from vapor pressure osmometer.
[d] Calculated according to Eq. (10) based on ^1H NMR data.
[e] Calculated using Eq. (11), where N is from Eq. (13).
[f] Calculated using Eq. (11), where N is from Eq. (14a).

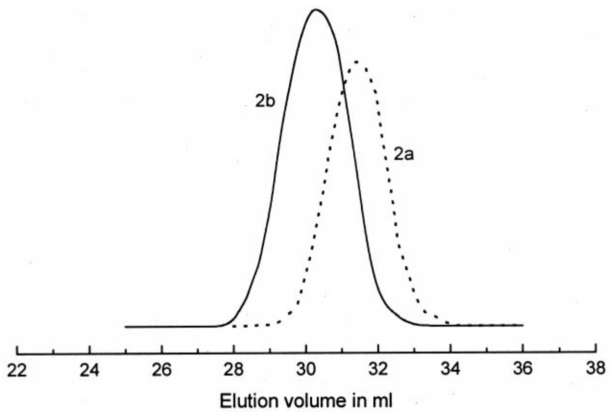


Fig. 1. GPC curves of poly(TOSU) (No. 3 in Table 1), insoluble (**2b**) and soluble (**2a**) in methanol.

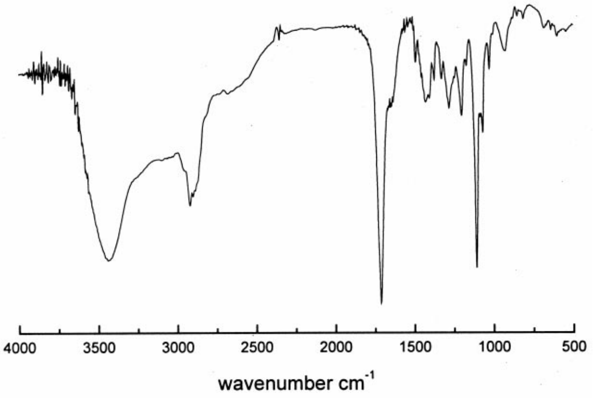


Fig. 2. FTIR spectra of poly(TOSU) (No. 3, **2a** in Table 1).

and di(*n*-Bu)SnO were used as received. Pentaerythritol (PE), ethanol, acetonitrile, and toluene were of analytical grade and used without further purification.

2.2. Typical polymerization procedure

A two-necked, round-bottom flask fitted with a magnetic bar was evacuated and purged with pure nitrogen three times, into which TOSU, methylene chloride and BHDU were added. The catalyst was injected with a syringe and the polymerization was carried out at a preset temperature. When the polymerization was completed, samples for determining the conversion of monomer were taken out and measured by ^1H NMR spectra. Adding excess distilled water stopped the polymerization. The mixture was washed with distilled water until neutralization, and the polymer was precipitated by adding the mixture into methanol, and collected by filtration. The filtrate was distilled under vacuum to afford another part of the polymer. The two parts of the polymer were dried at 40°C/0.2 Torr for 12 h.

2.3. Characterization

^1H and ^{13}C NMR spectra were measured on a Bruker DMX-500 nuclear magnetic resonance (NMR) instrument with $CDCl_3$ as solvent and tetramethylsilane (TMS) as standard. IR spectrum was recorded on a Vector-22 FTIR instrument. The MW and MW distribution of the polymers were determined by a Waters 150C gel permeation chromatograph (GPC) equipped with a microstyragel column (500, 10^3 and 10^4 Å) and polystyrene as standards, THF was used as eluent at a flow rate of 1.0 ml/min. The number average MWs, M_n (VPO), were determined in chloroform at 37°C on a QX-08 vapor pressure osmometer.

Table 2
The amount of BHDU in high MW poly(TOSU) (prepared with the same conditions as listed in Table 1)

	Number					
	1	2	3	4	5	6
$[OH]_0/[I]_0$ [a]	50	40	32	26.8	22.8	20
N_{NMR} [b]	6.99	5.48	3.85	3.32	2.33	1.96
N_{VPO} [c]	6.58	5.10	3.70	3.01	2.42	1.84

[a] Equivalent ratio of hydroxy to initiator.
[b] Calculated using Eq. (14a).
[c] Calculated using Eq. (13).

3. Results and discussion

3.1. Cationic ring-opening polymerization of 1,5,7,11-tetraoxaspiro [5,5] undecane

The polymerization of TOSU was carried out at different conditions summarized in Table 1. Two parts of the polymer were isolated based on its solubility in methanol. The polymers, soluble (**2a**) and insoluble (**2b**) in methanol, were obtained, respectively, in high yield and in relatively low yield. Similar results were observed when the polymerization of the derivatives of SOCs was carried out using a Lewis acid catalyst [4,9].

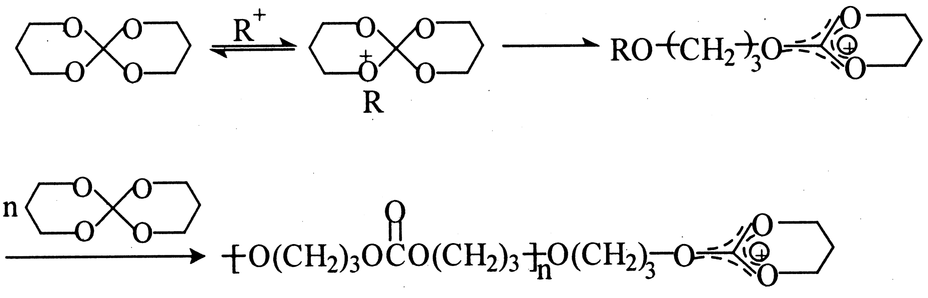
Typical GPC curves of the two polymer fractions, one soluble and another insoluble in methanol, are shown in Fig. 1a and b, respectively. The symmetrical peaks shown in Fig. 1 indicate that the cyclic oligomers produced in the polymerization could be neglected.

Since two fractions of the polymer based on their solubility in methanol were obtained, the polymerization mechanism of SOCs must differ from that of cyclic ether or cyclic acetal initiated by the same catalyst.

3.2. Polymerization mechanism

The polymerization mechanism of TOSU, firstly discussed by Sakai et al. [18], suggested that the attack of cationic species on the monomer opened its first ring to form a carbocation, successively the second ring was opened by the attack of the monomer as shown in Scheme 2.

When the alcohol compound was used as a chain transfer



Scheme 2.

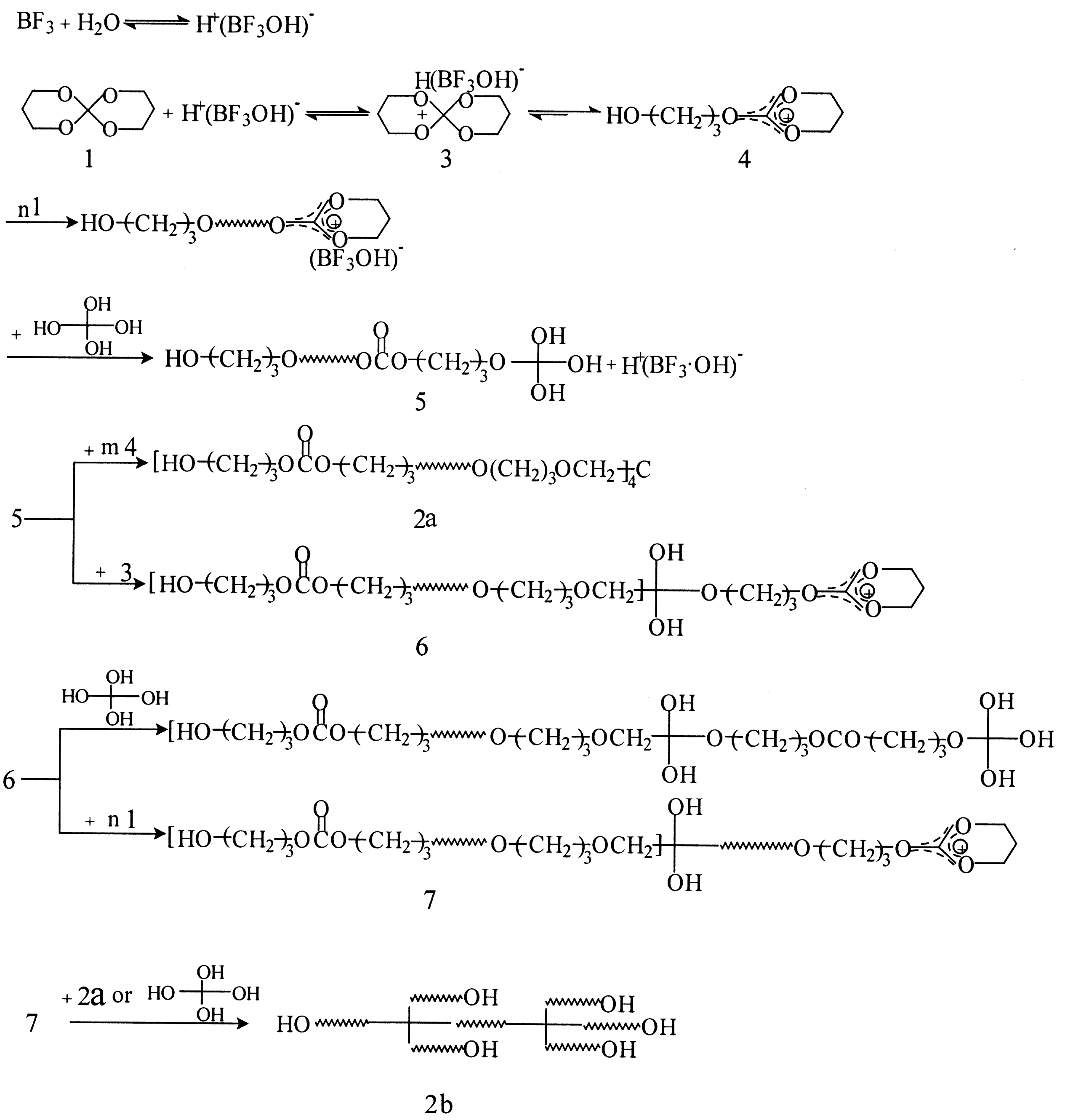
agent, the chain transfer reaction of the alcohol compound with two active species, oxonium and carbocation, might occur. Therefore, we suggest the polymerization mechanism of TOSU in the presence of the alcohol compound as shown in Scheme 3.

It is generally accepted that the initiation process for boron trifluoride and water proceeds according to reaction (4). The initiator attacked the monomer and the oxonium species **3** formed opened its first ring to afford carbocation **4** in Scheme 3. The carbocation center was stabilized by the interaction with the three adjacent oxygens. When the hydroxyl group of BHDU or poly(TOSU) polyol reacted with **4**, polymer **5** was formed. If the successive propagation continued according to this mechanism, it is impossible to produce a polymer having more than one unit of BHDU, only four-armed hydroxy-terminated poly(TOSU) with one unit of BHDU (**2a**) was produced (see reaction (6)). Its structure was verified by ^{1}H and ^{13}C NMR spectra, which will be discussed later. When the hydroxyl group of BHDU or poly(TOSU) reacted with oxonium species **3**, the carbocation **6** was formed. Different results were obtained when **6** was attacked by the following hydroxyl groups: (1) By the hydroxyl group of BHDU to form poly(TOSU) containing two units of BHDU. (2) By the hydroxyl group in the same macromolecule, the cyclic oligomer was formed. No cyclics were found in the GPC curves of Fig. 1, indicating that the intramacromolecular chain transfer reaction can be neglected. (3) By the hydroxyl group in another macromolecule containing one or more units of BHDU, the newly formed macromolecule contained two or more branched units, which propagated to form a high MW polymer. Therefore, the molar ratio of high MW poly(TOSU) to low MW poly(TOSU) was determined by the ratios of oxonium/carbocation and BHDU/initiator. As the molar ratio of BHDU/initiator increased, the possibility of chain transfer reaction of polyols with oxonium species **3** increased. So more polymer chain carbocations **6** were formed according to reaction (7), the yield of polymer **2b** increased, which was observed in Table 1. The higher the molar ratio of BHDU/initiator, the more units of BHDU the polymer obtained contained and the higher the yield of polymer **2b**. It is interesting to note that with the increase of the molar ratio of BHDU/initiator, the MW of high-MW polymer **2b** increased, contrary to the result observed for low-MW polymer **2a** (see Table 1). The probably reason is as follows: at a higher ratio of BHDU/initiator, the propagating chain with more branched units produced the polymer with higher MW. As a result, the polymers with one branched unit were produced from less monomer; the lower MW polymer **2a** was formed. After BHDU was completely consumed and once cationic center **6** was formed, the propagation proceeded successively according to reaction (6). Compared toh oxonium **3**, carbocation **4** is more stable. Therefore, the equilibrium between **3** and **4** favors carbocation **4**. It is reasonable that the yield of the low-MW polymer was much higher than that of the high-MW polymer (see Table 1), because the chain transfer reaction of **4** with a hydroxyl compound cannot produce a polymer with two and more branched units.

3.3. Structural analysis of poly(TOSU)

In order to confirm the polymerization mechanism proposed in Scheme 3, the polymers formed were characterized by FTIR spectrum as well as ^{1}H and ^{13}C NMR spectra. The typical IR spectrum of **2a** is shown in Fig. 2. The presence of carbonate group (C=O) in the polymer backbone is supported by the strong absorption peak at $\nu = 1745.9\ \mathrm{cm}^{-1}$, and the two peaks at $\nu = 1262.4$ and $1115.6\ \mathrm{cm}^{-1}$ were ascribed to ester (CO(C=O)OC) and ether linkage (COC), respectively.

Fig. 3a is a typical ^{1}H NMR spectrum of polymer **2a**. Compared with the ^{1}H NMR spectrum of BHDU, the signals at 3.35 and 3.73 ppm correspond to two methylene groups: one next to the quaternary carbon in BHDU and another adjacent to the hydroxyl group at the end of the polymer. The agreement of integral values of the peaks at 3.35 and 3.73 ppm indicates that all hydroxyl groups of BHDU participated in the chain transfer reaction. In order to confirm this result, trifluoroacetic anhydride (TFA) was directly added into the NMR tube before measurement, the ^{1}H NMR spectrum after esterification is shown in Fig. 3b. Only one new peak at 4.40 ppm, assigned to the methylene protons next to the end-standing ester group, indicates that poly(TOSU) had only one kind of end-standing hydroxyl group. If one macromolecule contains one BHDU unit on average, the integral values of the peak at 4.40 and 3.35 ppm should be equal. This result was verified by the ^{1}H NMR data in Fig. 3b.



Scheme 3.

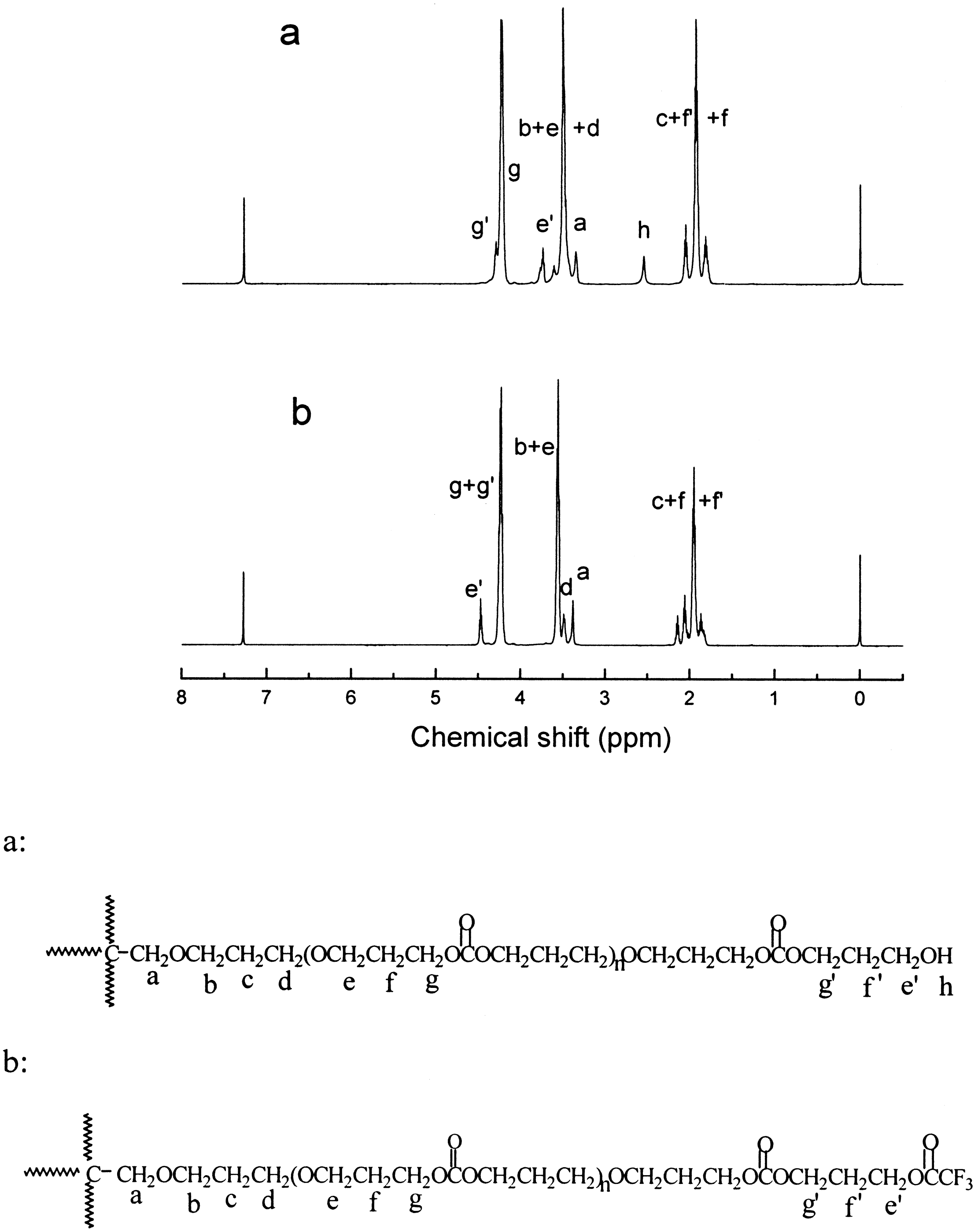


Fig. 3. ^{1}H NMR spectrum of poly(TOSU) (No. 3, **2a** in Table 1) before (a) and after (b) esterification with $(CF_3CO)_2O$.

A typical ^{13}C NMR spectrum of the polymer **2a** is shown in Fig. 4. The peaks at 155.3, 67.2, 65.3 and 29.2 ppm correspond to the carbonyl carbon of the carbonate group, the carbon adjacent to the carbonate ester group, the carbon adjacent to ether oxygen, and the middle carbon of the trimethylene group in the TOSU unit, respectively. The small peak at 45.4 ppm is attributed to the quaternary carbon of BHDU. The peak at 61 ppm corresponding to the methylene carbon adjacent to the end hydroxyl group in BHDU was completed absent in Fig. 4, demonstrating that no hydroxyl group from BHDU stood at the end of poly(TOSU) tetraol, and the four-armed poly(TOSU) tetraol was formed.

The ^{1}H NMR spectrum of **2b** is similar to the ^{1}H NMR spectrum of **2a**, which showed that **2b** had the same structure as **2a**. Different from that of **2a**, the integral value of the peak at 4.40 ppm in the ^{1}H NMR spectrum of **2b** is smaller

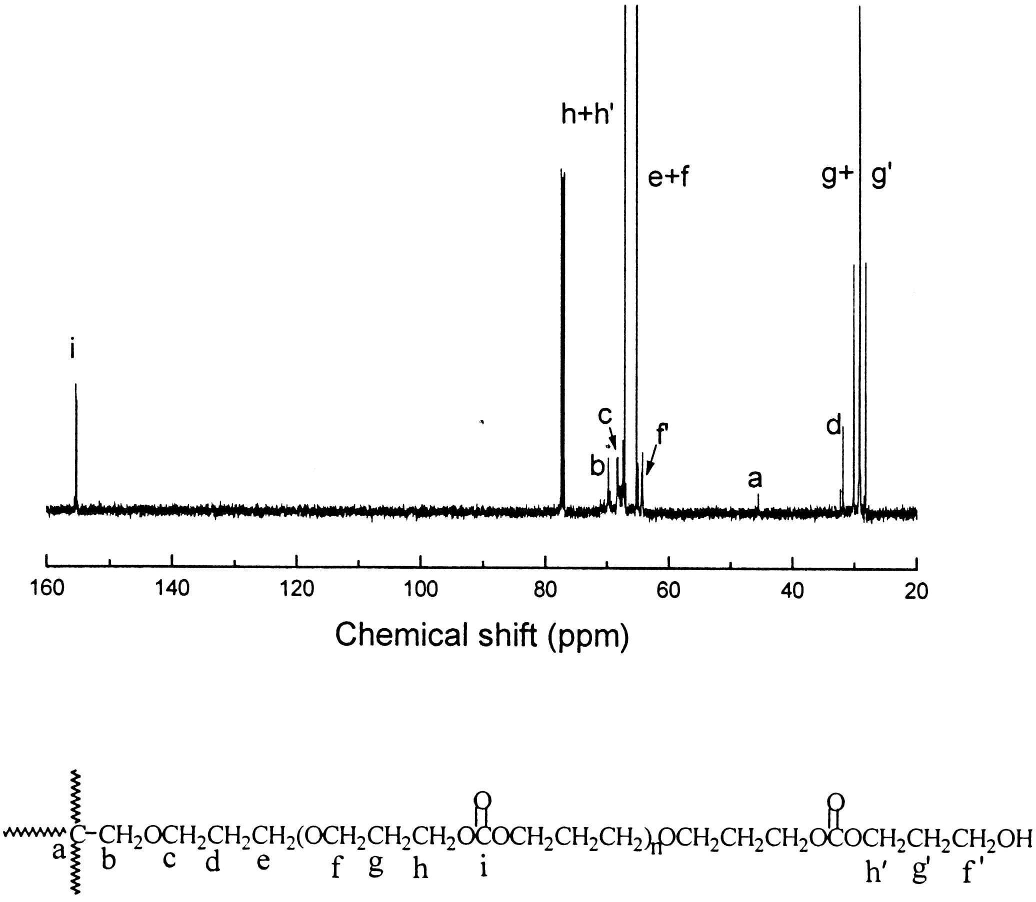


Fig. 4. ^{13}C NMR spectrum of poly(TOSU) (No. 3, **2a** in Table 1).

than that at 3.35 ppm, indicating that each macromolecule of **2b** contained more than one BHDU unit. This is different from cationic ring-opening polymerization of cycloethers or cycloacetals.

Concerning the polymer **2a**, assuming that the four-armed poly(TOSU) was formed and each macromolecule contains one BHDU unit, the number-average MW, M_n(NMR), could be calculated by Eq. (10):

$$M_n(\mathrm{NMR}) = [(I_{4.2}/2)/(I_{1.8} - I_{4.2})] \times 4 \times 160 + 368 \qquad (10)$$

where $I_{1.8}$ and $I_{4.2}$ are the integral values of the peaks at 1.79–2.15 and 4.22–4.30 ppm, respectively; 4 means the branch number of each macromolecule; 160 and 368 are the MWs of the monomer and BHDU. At the same time, providing that each macromolecule contains one BHDU unit, the theoretical number average MW, M_n(th), can be calculated according to Eq. (11):

$$M_n(\mathrm{th}) = \{[\mathrm{SOC}]_0 \times y_l/[\mathrm{BHDU}]_{l0}\} \times 160 + 368 \qquad (11)$$

where y_l is the yield of the low-MW polymer **2a**, $[\mathrm{SOC}]_0$ are the initial molar concentration of TOSU, and $[\mathrm{BHDU}]_{l0}$ the molar concentration of BHDU in polymer **2a**, and it can be calculated by Eq. (12):

$$[\mathrm{BHDU}]_{l0} = [\mathrm{BHDU}]_0\{(y_l/M_l - 368)/[y_h \cdot N/(M_h - N368) + y_l/(M_l - 368)]\} \qquad (12)$$

where M_l and M_h are the MWs of **2a** and **2b**, respectively, which were obtained from VPO, y_h is the yield of **2b**. Providing that each arm in all the macromolecules has the same propagation rate, i.e. has the same MW, the amount of BHDU unit in each macromolecule of **2b**, N_{VPO}, could be calculated by Eq. (13):

$$N_{\mathrm{VPO}} = M_h/M_l. \qquad (13)$$

Assuming that the stylization is negligible, N_{NMR} can also be got from ^{1}H NMR data according to Eq. (14):

$$(2 + 2N_{\mathrm{NMR}})/4N_{\mathrm{NMR}} = I_{4.40}/I_{3.35}. \qquad (14)$$

Simplifying Eq. (14), Eq. (14a) was obtained

$$N_{\mathrm{NMR}} = 1/(2I_{4.40}/I_{3.35} - 1) \qquad (14a)$$

where $I_{4.40}$ and $I_{3.35}$ are the integral values of the peaks at 4.37–4.47 and 3.35–3.38 ppm, respectively; $2 + 2n$ means the amount of branches in each polymer **2b** containing *N* BHDU.The calculated values of N_{NMR} and N_{VPO} are listed in Table 2. The almost similar values of N_{NMR} and N_{VPO} verified that the polymers produced (**2b** with high MW and **2a** with low MW) are ascribed to the chain transfer reaction of polyalcohol with oxonium and carbocation species, and the propagation mechanism proceeded according to Scheme 3. The MWs for those branches connected to each other were in fact lower than that for free branches, it is reasonable for the results listed in Table 2 that N_{VPO} is slight lower than N_{NMR}; especially in the case of **2b** with more BHDU units, the difference is bigger.

4. Conclusions

1,5,7,11-Tetraoxaspiro [5,5] undecane underwent double ring-opening polymerization in the presence of 6,6-bis(5-hydroxyl-2-oxapentyl)-4,8-dioxaundecanediol-1,11, using $BF_3 \cdot OEt_2$ as initiator. Although the polymers obtained could be isolated as two fractions: one soluble and another insoluble in methanol, they had the same structure. The only difference was the MW; the polymer with low MW was soluble in methanol. The formation of the two polymers was due to the chain transfer of polyalcohol, respectively, with oxonium and carbocation species. The transfer reaction with carbocation species afforded only poly(TOSU) tetraol with low MW and that with oxonium species formed poly(TOSU) polyols with high MW. The yield, MWs and the amount of BHDU unit in each macromolecule increased as the molar ratio of BHDU/initiator increased, because polymer chain with more branched units has more possibilities to propagate. For low MW poly(TOSU), the MW of poly(TOSU) tetraols could be controlled by the molar ratio of monomer consumed to initiator BHDU. ^1H and ^{13}C NMR results of the polymers obtained support that all of BHDU and every hydroxyl group of BHDU participated in the chain transfer reactions.

Acknowledgements

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