Radical Ring-Opening Polymerization of Five-Membered Cyclic Vinyl Sulfone Using *p*-Toluenesulfonyl Halides

Shimon Tanaka, Yoshio Furusho, Takeshi Endo

Molecular Engineering Institute, Kinki University, Fukuoka 820-8555, Japan
Correspondence to: T. Endo (E-mail: tendo@moleng.fuk.kindai.ac.jp)

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ABSTRACT: Radical ring-opening polymerizations of a five-membered cyclic vinyl sulfone monomer, 2-vinylthiolane-1,1-dioxide (VTDO), was carried out by using *p*-toluenesulfonyl iodide (TosI) and bromide (TosBr) as radical initiators, and the corresponding ring-opened polymer (PVTDO) was obtained. Both TosI and TosBr were found to work as the radical initiators for the polymerization of VTDO in bulk. The use of TosI gave PVTDOs with a broad, multimodal distribution of molecular weight in low yields. When 10 mol % of TosBr was employed, the isolated yield of PVTDO reached 49%, and the obtained PVTDO had a relatively narrow, monomodal molecular weight distribution of 1.8 with an M_n of 4100. © 2012 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 51: 222–227, 2013

KEYWORDS: cyclic vinyl sulfone; heteroatom-containing polymers; living polymerization; polyolefin sulfone; polyolefins; *p*-toluenesulfonyl halide; radical polymerization; radical ring-opening polymerization

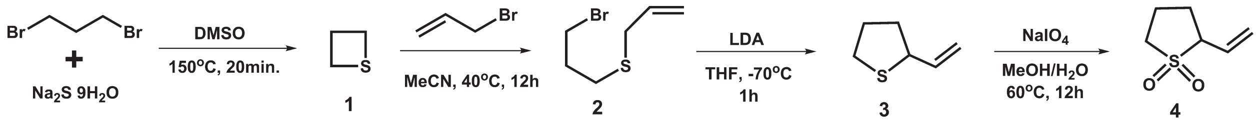
INTRODUCTION Polysulfones are defined as the polymers that include sulfonyl groups connected to aliphatic or aromatic groups in main chain.[1] Aromatic polysulfones, an important class of engineering plastics, are prepared by polycondensation and are used in a wide range of applications. Aliphatic polysulfones such as polyolefin sulfone and polyalkylene sulfone contain weak sulfur–carbon bond in the main chain that is readily cleaved under extreme ultraviolet irradiation, so that they have been utilized as resist material.[2,3] In general, polyolefin sulfones have been synthesized by the radical copolymerization of olefins with sulfur dioxide.[4–9] Another synthetic method of polyolefin sulfones is radical ring-opening polymerization of cyclic vinyl sulfone monomers, which is quite attractive from viewpoint of polymer synthesis as well as material science, because it permits copolymerization with various vinyl monomers, allowing a wide range of design of polysulfones so as to meet various requirements.[10–12] The radical ring-opening polymerization produces polymers with functional groups, such as ether, esters, amides, and carbonates, incorporated into the backbone of the polymer chains, which cannot be achieved by the conventional radical polymerization of vinyl monomers.[13]

Aryl- and alkylsulfonyl halides undergo bond homolysis,[14] and the resulting sulfonyl radicals are subsequently added to substituted and unsubstituted olefins.[15–24] Percec pointed out that the homolysis of the sulfonyl halide can be initiated thermally.[25] Edwards reported radical addition of *p*-toluenesulfonyl iodide (TosI) to unsaturated alcohols and ethers.[26] The addition of TosI to the unsaturated alcohols in acetonitrile occurs readily at room temperature under argon atmosphere to give 1:1 adducts, β-iodosulfones. Percec reported that metal-catalyzed living radical polymerization of common vinyl monomers, such as methacrylates and styrenes, can be realized by using the systems composed of *p*-toluenesulfonyl halides, cupper halides, and bipyridines.[27–29] The initiation step of the metal-catalyzed polymerization of these vinyl monomers using tosyl halides is the attack of a sulfonyl radical to the vinyl group of a monomer, and the resulting carbon radical works as a propagating radical that is in equilibrium with a dormant halide species. On the other hand, sulfonyl radical works as a propagating radical in the ring-opening polymerization of cyclic vinyl sulfone monomers. Based on this mechanism in combination with the fact that TosI is radically added to olefins, we hypothesized that TosI *per se* could operate as radical initiator without any other reagents, leading to the radical ring-opening polymerization of cyclic vinyl sulfones. In this article, we report the radical ring-opening polymerization of a five-membered cyclic vinyl sulfone, 2-vinylthiolane-1,1-dioxide (VTDO), using *p*-toluenesulfonyl halide initiators.

EXPERIMENTAL

Materials

1,3-Dibromopropane, sodium sulfide nonahydrate, allyl bromide, diisopropylamine, sodium periodate, sodium *p*-toluenesufinate tetrahydrate, and iodine were purchased from Wako Pure Chemical Industries (Japan). *p*-Toluenesulfonyl hydrazide, *p*-toluenesulfonyl chloride, and bromine were purchased



SCHEME 1 Synthesis of 2-vinylthiolane-1,1-dioxide (**4**, VTDO).

from Tokyo Chemical Industry (Japan). *n*-Butyllithium (1.57 M in hexane) was purchased from Kanto Chemical (Japan). Dimethyl sulfoxide (DMSO), acetonitrile, tetrahydrofuran (THF), and *N, N*-dimethylformamide (DMF) were purchased from Wako Pure Chemical Industries and distilled before use. 2,2-Azobisisobutyronitrile (AIBN) was purchased from Wako Pure Chemical Industries (Japan) and recrystallized from acetone. VTDO was prepared according to the literature (Scheme 1).[10,30,31] *p*-Toluenesufonyl bromide (TosBr) and TosI were prepared according to the literature.[27,28]

Measurements

^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-ECS400 (400 and 100 MHz for ^{1}H and ^{13}C, respectively, with tetramethylsilane as an internal standard). Number average molecular weight (M_n) and weight average molecular weight (M_w) were estimated by size exclusion chromatography (SEC) using DMF solution of lithium bromide (10 mM) as an eluent at a flow rate of 0.6 mL/min at 40 °C, performed on a Tosoh chromatograph model HLC-8220 system equipped with three consecutive polystyrene gel columns (Super-AW4000, Super-AW3000, and Super-AW2500) and a refractive index detector at 40 °C. The molecular weight calibration curve was obtained with polystyrene standards. Thermogravimetric analysis (TGA) was conducted with a Seiko Instruments. TG/DTA6200 at a heating rate of 10 °C/min under nitrogen flow (20 mL/min).

Monomer Synthesis

Synthesis of Thietane (1)[30]

Sodium sulfide nonahydrate (60.1 g, 250 mmol) was added to a solution of 1,3-dibromopropane (50.5 g, 250 mmol) in DMSO (100 mL) in small portions at 5 °C. Then, steam was introduced to the mixture, which was heated at 150 °C for 20 min with vigorous stirring and the steam distillate was collected. The aqueous layer of the distillate was saturated with NaCl, and the organic layer was separated, dried, and distilled to give pure thietane (**1**) (10.3 g, 139 mmol, 56%). Bp 96–98 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 2.92–2.99 (m, 2H; $CH_2—CH_2—CH_2$), 3.25 (t, 4H; $S—CH_2$); ^{13}C NMR ($CDCl_3$, 100MHz): δ (ppm) 26.0 ($CH_2—CH_2—CH_2$), 27.86 ($S—CH_2$).

Synthesis of Allyl 3-Bromopropyl Sulfide (2)[31]

To a solution of thietane (**1**) (23.6 g, 318 mmol) in acetonitrile (120 mL) was added allyl bromide (38.5 g, 318 mmol) at room temperature. The mixture was stirred at 40 °C for 12 h. The solvent was evaporated at reduced pressure, and the residue was distilled to give **2** (52.6 g, 270 mmol, 85%). Bp 60–63 °C (4 mmHg).

^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 2.10 (m, 2H; $Br—CH_2—CH_2$), 2.61 (t, 2H; $Br—CH_2$), 3.13 (d, 2H; $S—CH_2—CH{=}CH_2$), 3.51 (t, 2H; $S—CH_2—CH_2$), 5.10–5.14 (m, 2H; $CH{=}CH_2$), 5.76–5.82 (m, 1H; $CH{=}CH_2$); ^{13}C NMR δ (ppm) 28.79 ($Br—CH_2—CH_2$), 32.05 ($Br—CH_2$), 32.17 ($S—CH_2—CH_2$), 34.73 ($S—CH_2—CH{=}CH_2$), 117.2 ($CH{=}CH_2$), 134.2 ($CH{=}CH_2$).

Synthesis of 2-Vinylthiolane (3)[31]

To diisopropylamine (5.8 mL, 41 mmol) was added dropwise to a hexane solution of *n*-butyllithium (1.57 M, 26 mL, 41 mmol) at −70 °C. An argon stream was maintained throughout the experiment. Dry THF (30 mL) was added. To this rapidly stirred solution was then added dropwise a solution of **2** (4.6 mL, 31 mmol) in THF (20 mL) over a 30-min period. Stirring was continued at −70 °C for a further 1 h, and the mixture was then quenched with water. After the mixture had warmed to room temperature, it was washed with 5% HCl and then with saturated $NaHCO_3$ aqueous solution, dried over Na_2SO_4, and filtered. The hexane was removed at atmospheric pressure and the residue was distilled under reduced pressure to give **3** (2.97 g, 26 mmol, 84%). Bp 55–58 °C (16 mmHg).

^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 1.6–2.2 (m, 4H; $CH—CH_2—CH_2—CH_2$), 2.94 (m, 2H; $S—CH_2$), 3.92 (m, 1H; $S—CH$), 4.9—5.2 (m, 2H; $CH{=}CH_2$), 5.7–5.9 (m, 1H; $CH{=}CH_2$); ^{13}C NMR δ (ppm) 30.87 ($CH_2—CH_2—CH_2$), 33.27 ($CH_2—CH_2—CH$), 38.01 ($S—CH_2$), 51.63 ($S—CH$), 114.6 ($CH{=}CH_2$), 140.3 ($CH{=}CH_2$).

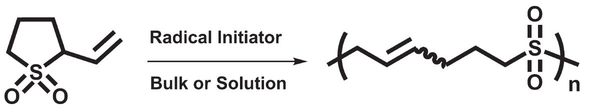
Synthesis of 2-Vinylthiolane-1,1-dioxide (4, VTDO)[10]

To a solution of sodium periodate (14.0 g, 65.5 mmol) in distilled water (130 mL) and methanol (100 mL), a solution of **3** (3.26 mL, 28.5 mmol) in methanol (30 mL) was added dropwise over a 30-min period. The mixture was stirred for a further 12 h at 60 °C. The precipitated solid was removed by filtration and then methanol was evaporated under reduced pressure. The aqueous solution was extracted with dichloromethane. The extract was dried over $MgSO_4$, and the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography (eluent: dichloromethane) to afford crude **4**, which was distilled under reduced pressure in the presence of active carbon and hydroquinone to give pure **4** (2.46 g, 16.8 mmol, 59%) as a light yellow liquid. Bp 110–113 °C (4 mmHg).

^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 2.0–2.4 (m, 4H; $CH_2—CH_2—CH_2—CH$), 3.0–3.25 (m, 2H; $SO_2—CH_2—CH_2$), 3.61 (m, 1H; $CH—CH{=}CH_2$), 5.40–5.47 (m, 2H; $CH—CH{=}CH_2$), 5.75–5.85 (m, 2H; $CH{=}CH_2$); ^{13}C NMR δ (ppm) 24.81 ($CH_2—CH_2—CH_2$), 30.12 ($CH_2—CH_2—CH$), 51.0 ($SO_2—CH_2$), 65.0 ($SO_2—CH$), 122.8 ($CH{=}CH_2$), 128.5 ($CH{=}CH_2$).

Polymerization of VTDO

The following procedure is a typical method for the polymerization of VTDO (Scheme 2). A mixture of VTDO (0.52 g, 3.6



SCHEME 2 Radical ring-opening polymerization of VTDO.

mmol) and TosBr (84 mg, 0.36 mmol) in a glass ampoule was degassed through three freeze–pump–thaw cycles. The ampoule was sealed under vacuum and heated at 100 °C for 24 h. The polymerization was quenched by rapid cooling with liquid nitrogen and an excess of methanol was added to the reaction mixture. A polymeric product was washed with methanol for several times, collected by suction filtration, and dried under vacuum at 60 °C. The polymer yield was gravimetrically determined from the weight of the methanol-insoluble product.

RESULTS AND DISCUSSION

Free Radical Ring-Opening Polymerization of VTDO and Hydrogenation of PVTDO

First, the free radical ring-opening polymerization of VTDO was carried out by using AIBN (4 mol % to monomer) as a radical initiator at 60 °C for 25 h in DMF according to the literature.[10–12] The PVTDO was obtained in 88% yield and the number average molecular weights (M_n) of obtained VTDO were estimated by means of SEC to be 31,000 with a molecular weight distribution (M_w/M_n) of 2.5. The ^{1}H NMR spectrum of the PVTDO prepared using AIBN initiator at 60 °C in DMF (measured in DMSO-d_6 at 90 °C) is shown in Figure 1. The NMR result indicated that the radical polymerization of VTDO proceeded clearly via a ring-opening process. The obtained PVTDO was soluble in polar organic solvents such as DMF, dimethylacetamide (DMAc), DMSO, and nitroxide-mediated polymerization (NMP) in low polymer concentration (about 0.1 wt %) above 80 °C.

The hydrogenation of the carbon–carbon double bond in PVTDO was carried out by using *p*-toluenesulfonyl hydrazide in DMF at 100 °C.[6] The TGA data showed that the 5% weight-loss temperature (T_{d5}) of the pristine PVTDO was 241 °C, indicating that the PVTDO is not thermally stable probably because of the C=C bond in the main chain [Fig. 2(a)]. A drastic increase in the thermal decomposition temperature was observed for the hydrogenated PVTDO [Figure 2(b, c)] of which the T_{d5} values were 308 and 336 °C for the hydrogenated PVTDO samples obtained by 2 and 12 h of hydrogenation, respectively. The hydrogenated PVTDOs were insoluble in most common organic solvents, such as DMF, DMAc, DMSO, and NMP, so that the hydrogenation conversion could not be determined by ^{1}H NMR. Figure 3 shows DSC thermograms of the pristine PVTDO and the hydrogenated PVTDO (12-h hydrogenation). The pristine PVTDO showed endothermic peaks above 150 °C, which suggested partial crystallinity of the pristine PVTDO. However, as shown in Figure 2, thermal decomposition of the pristine PVDTO began near the onset temperature of the endothermic peak, thus hampering further investigation. On the other hand, the hydrogenated PVTDO exhibited endothermic peaks in a higher temperature range from 180 to 220 °C, which were attributable to the melt of the crystalline region. Furthermore, a slope change of the DSC curve owing to the glass transition of amorphous region was not observed. Thus, the DSC results of the hydrogenated PVTDO suggested that hydrogenated PVTDO consisted mainly of crystalline region and the insolubility of the hydrogenated PVTDO in organic solvents was owing to the high crystallinity. Matsumoto and coworkers[5] examined the solubility of some polydiene sulfones and pointed out that a symmetric polymer chain structure is favored for partial crystallization, resulting in the poor solubility of the polydiene sulfones. By the same token,

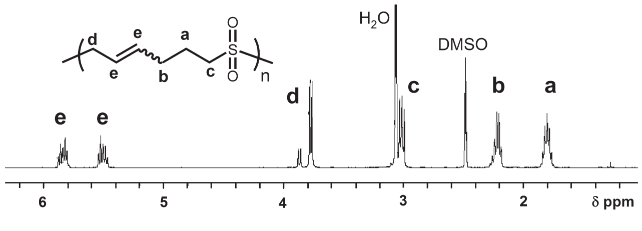


FIGURE 1 ^{1}H NMR spectrum of PVTDO synthesized from AIBN at 60 °C in DMF.

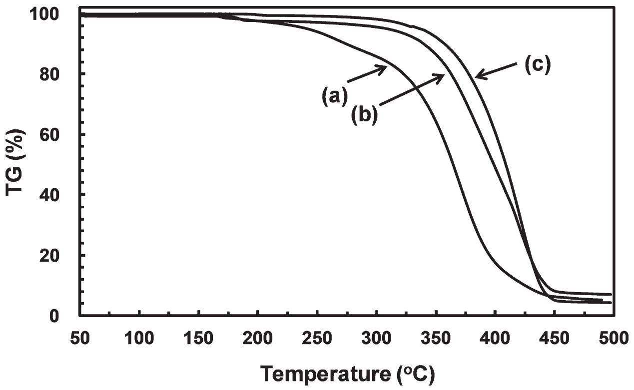


FIGURE 2 TG curves for the pristine PVTDO (a: T_{d5} = 241 °C) and the hydrogenated PVTDO (b: T_{d5} = 308 °C (2-h hydrogenation)), (c T_{d5} = 336 °C (12-h hydrogenation)).

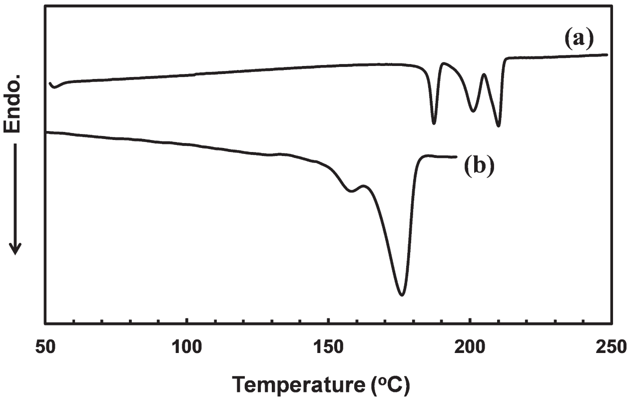


FIGURE 3 DSC thermographs for the hydrogenated PVTDO (a: 12-h hydrogenation, 5 K/min heating, first scan) and the pristine PVTDO (b: 10 K/min heating, first scan).

TABLE 1 Results of Polymerization of VTDO Using TosI

Run	TosI (mol %)	Temp. (°C)	Time (h)	Yield (%)	M_n[a] (g/mol)
1	2	80	2	28	3,100, 1,000
2	2	60	2	15	4,300, 1,000
3	2	40	2	9	3,100, 1,000
4	0.5	80	3	16	6,500
5	1	80	3	29	5,400, 900
6	10	80	2	26	2,500, 900

[a] Measured by means of SEC using polystyrene standards in DMF (LiBr, 10 mM).

the hydrogenated PVTDO had more crystallinity as well as less solubility than the pristine PVTDO that contained a mixture of *cis*- and *trans*-olefin units as evidenced by the ^{1}H NMR spectrum shown in Figure 1.

Polymerization of VTDO Using *p*-Toluenesulfonyl Halides

We investigated the ring-opening polymerization of VTDO using *p*-toluenesulfonyl halides, such as TosI and TosBr, as initiators. Under the conditions studied herein, no polymerization of VTDO proceeded without the tosyl halide initiator. The experimental conditions and the results with TosI initiator are summarized in Table 1. When 2 mol % of TosI was used, polymerization of VTDO proceeded at the reaction temperatures above 40 °C to afford the polymeric products after 2 h (Runs 1–3). However, the yields of PVTDO remained low as 9–28% and could not be increased by prolongation of the time or elevating the temperature above 80 °C. Similarly, the PVTDO yield did not exceed 30% when the amount of TosI was changed from 0.5 to 10 mol % (Runs 4–6). In all cases, the unreacted monomer was recovered in filtrates after purification of PVTDO. This suggests that the polymerization was terminated by combination of two active chain ends or radical disproportionation.

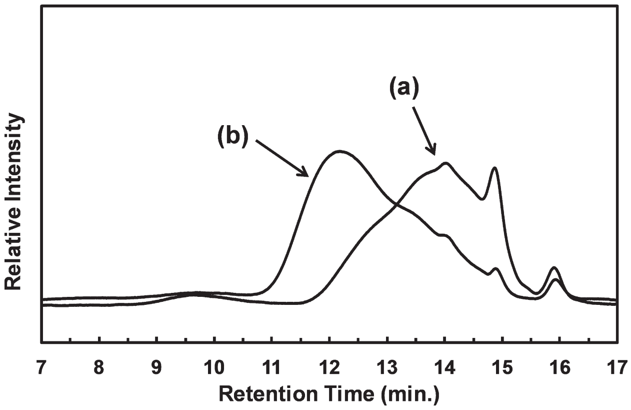


FIGURE 4 SEC profiles of PVTDO prepared using TosI (a: 2 mol %; b: 0.5 mol %) at 80 °C.

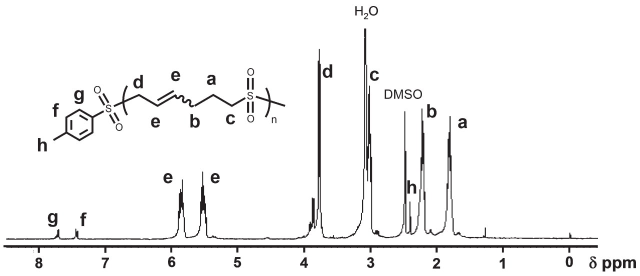


FIGURE 5 ^{1}H NMR spectrum of PVTDO prepared from 2 mol % of TosI initiator at 80 °C in bulk.

Figure 4 shows the SEC curves of PVTDO synthesized using TosI initiator (Runs 1 and 4, Table 1). Both curves exhibited broad, multimodal distributions of molecular weight. The two refractive intensity peaks at high and low-molecular-weight part of the PVTDO prepared with 2 mol % of TosI were estimated to be 3100 and 1000, respectively [Fig. 4(a)]. The use of a smaller amount of TosI (0.5 mol %) increased the M_n to 6500. However, the molecular weight distribution of the PVTDO remained broad [Fig. 4(b)].

The ^{1}H NMR spectrum of the PVTDO prepared using TosI initiator at 80 °C (Run 1, Table 1) is shown in Figure 5. The spectral pattern was quite similar to that of the PVTDO prepared using AIBN initiator shown in Figure 1, except for the tosyl region. The characteristic proton signals of the tosyl group at the polymer chain ends were observed at 7.4 and 7.8 ppm for the aromatic protons and 2.4 ppm for the methyl protons. The NMR result suggested that TosI operated as a radical initiator and the polymerization of VTDO proceeded via ring-opening process. The polymerization of VTDO with TosI was inhibited in the presence of a radical scavenger, 2,2,6,6-tetramethylpiperidinyl-oxy radical (TEMPO). This inhibition strongly supported the radical mechanism of the ring-opening polymerization.

We have thus confirmed our working hypothesis that the polymerization initiated by thermal dissociation of TosI at elevated temperature to generate the toluenesulfonyl and halide radicals, which attack the vinyl group in VTDO monomer and form an open-chain sulfonyl radical via the ring opening, which further attacks the vinyl group of another monomer to constitute the propagation step of the polymerization.

We next examined the polymerization of VTDO using TosBr. The polymerization conditions and the results are summarized in Table 2. When compared with the TosI cases, longer reaction time and higher reaction temperature were needed for polymerizing VTDO with TosBr, as can be expected from the lower reactivity of TosBr. When the polymerization was conducted with 2 mol % of TosBr at 100 °C for 24 h, PVTDO was obtained in 38% yield (Run 1, Table 2). The M_n and M_w/M_n of the obtained polymer were estimated to be 5300 and 2.5, respectively. The isolated yield of PVTDO reached 49% when 10 mol % of TosBr was employed, and its M_n and M_w/M_n were determined to be 4100 and 1.8, respectively (Run 2, Table 2). The yield value could not be increased on prolonging the polymerization time to 48 h and elevating the temperature up to 120 °C. As a whole, the isolated yields of PVTDO using TosBr were higher than those with TosI. It should be noted here that the polymerization

TABLE 2 Results of Polymerization of VTDO Using *p*-Toluenesulfonyl Halides

Run	TosBr (mol %)	TosI (mol %)	Temp. (°C)	Time (h)	Yield (%)	M_n[a] (g/mol)	M_w/M_n[a]
1	2	–	100	24	38	5,300	2.5
2	10	–	100	24	49	4,100	1.8
3	2	2	80	24	30	4,600	1.7
4	5	5	80	24	32	2,600	1.6
5	3	1	80	16	23	4,100	1.7

[a] Measured by means of SEC using polystyrene standards in DMF (LiBr, 10 mM).

using 10 mol % of TosBr afforded PVTDO with an M_n of 4100 (Run 2, Table 2), which exhibited a relatively narrow, monomodal molecular weight distribution of 1.8 (Fig. 6). We also examined the mixed initiator systems of TosBr and TosI (Runs 3–5, Table 2), which afforded PVTDO in lower yields around 30%. The molecular weight distributions were as narrow as those with 10 mol % of TosBr although the SEC curves showed some small peaks and shoulders in the low-molecular-weight part.

Based on the results thus obtained, we speculate the plausible mechanism of the radical ring-opening polymerization of VTDO using the sulfonyl halides as initiators as shown in Scheme 3 although quantitative discussion is impossible as the produced PVTDO was separated from the polymerization mixture during the polymerization owing to its poor solubility as already mentioned. The polymerization is initiated by the thermal homolysis of the S—X bond of TosX (X = Br and I)[14] to give the sulfonyl and halogen radicals. The sulfonyl radical first attacks the vinyl group of the VTDO monomer, forming a carbon radical, which rearranges immediately to the more stable open-chain sulfonyl radical as the propagating radical via ring opening, which further attacks the vinyl groups of another monomer to constitute the propagating step of the polymerization (path a). Besides recombination and disproportionation of the propagating sulfonyl radical, a possible termination reaction could be the 1,2-radical addition of the sulfonyl halides on the vinyl groups of the VTDO, resulting in formation of the *β*-iodosulfone (path b).[26] The C—X bond is sufficiently stable at the temperatures examined in this study, thereby undergoing no dissociation of the C—X bond in the absence of amines[32] or metal catalysts[28] and constituting a termination step. The halogen radical could also initiate the polymerization, rendering the polymerization mechanism complicated (path c). Last but not least, it is worth mentioning that this could be developed as a living radical polymerization system if the side reactions such as the 1,2-addition are sufficiently suppressed somehow or other.

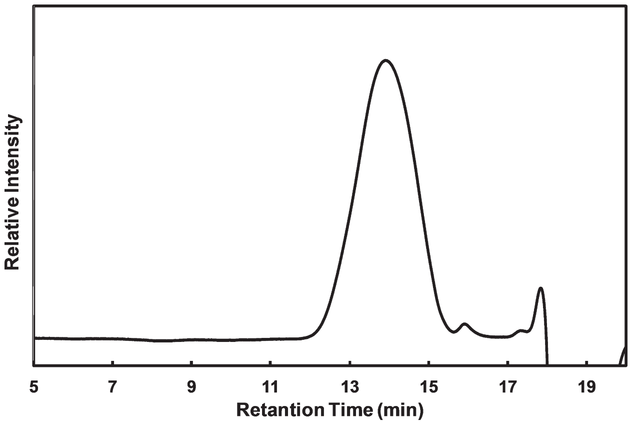
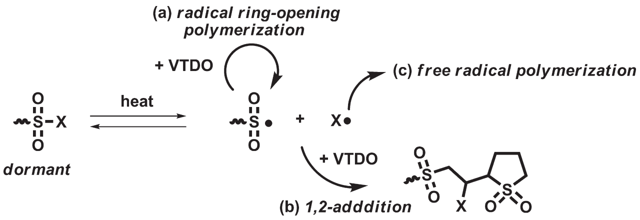


FIGURE 6 SEC curve of the PVTDO prepared with 10 mol % of TosBr at 100 °C for 24 h.



SCHEME 3 Plausible mechanism for the radical ring-opening polymerization of VTDO.

CONCLUSIONS

The polyolefin sulfone (PVTDO) was prepared by the radical ring-opening polymerization of VTDO with *p*-toluenesulfonyl halides as an initiator in bulk. When TosI was employed, polymeric products with a broad, multimodal distribution of molecular weight were obtained in low yields. The ^{1}H NMR analysis of the PVTDO synthesized with TosI along with the inhibition of the polymerization with TEMPO indicated that TosI operated as a radical initiator and the polymerization proceeded via ring-opening process. In contrast to TosI, the use of TosBr as an initiator resulted in high yields up to 49%. Furthermore, the PVTDO synthesized with TosBr initiator had a monomodal distribution of molecular weight of 1.8 with an M_n of 4100. To the best of our knowledge, this is the first example of *p*-toluenesulfonyl halides (TosI and TosBr) initiated radical ring-opening polymerization of cyclic vinyl sulfone monomer instead of common radical initiators such as AIBN and benzoyl peroxide. Another hypothesis concerning this system is that a controlled radical polymerization would be achieved if the propagating sulfonyl radical is stabilized as a dormant species and the side reactions are sufficiently suppressed by changing the polymerization conditions, such as use of solvents or metal complexes,[33–35] which is ongoing in our group.

ACKNOWLEDGMENT

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REFERENCES AND NOTES

1 Elial, H. G. Macromolecules: Industrial Polymer and Syntheses; Wiley-VCH: Weinheim, Germany, **2007;** Vol. 2, pp 436–441.

2 Lawrie, K.; Blakey, I.; Blinc, J.; Gronheid, R.; Jack, K.; Pollentier, I.; Leeson, M. J.; Younkin, T. R.; Whittaker, A. K. *Rad. Phys. Chem.* **2011,** *80*, 236–241.

3 Lawrie, K. J.; Blakey, I.; Blinco, J. P.; Cheng, H. H.; Gronheid, R.; Jack, K. S.; Pollentier, I.; Leeson, M. J.; Younkin, T. R.; Whittaker, A. K. *J. Mater. Chem.* **2011,** *21*, 5629–5637.

4 Tanaka, N.; Sato, E.; Matsumoto, A. *Macromolecules* **2011,** *44*, 9125–9137.

5 Kitamura, T.; Tanaka. N.; Mihashi, A.; Matsumoto, A. *Macromolecules* **2010,** *43*, 1800–1806.

6 Tanaka, N.; Sato, E.; Matsumoto, A. *Org. Biomol. Chem.* **2011,** *9*, 3753–3758.

7 Florjańczyk, Z. *Prog. Polym. Sci.* **1991,** *16*, 509–560.

8 Soares, B. G. *Prog. Polym. Sci.* **1997,** *22*, 1397–1430.

9 Ramazanov, G. A.; Shakhnazarova, R. Z.; Guliev, A. M. *Russian J. Appl. Chem.* **2005,** *78*, 1695–1698.

10 Cho, I.; Kim, S. K.; Lee, M. H. *J. Polym. Sci. Polym. Symp.* **1986,** *74*, 219–226.

11 Cho, I.; Lee, M. H. *J. Polym. Sci. Part C: Polym. Lett.* **1987,** *25*, 309–311.

12 Cho. I.; Choi, S. Y. *Macromol. Chem. Rapid Commun.* **1991,** *12*, 399–402.

13 Sanda, F.; Endo T. *J. Polym. Sci. Part A: Polym. Chem.* **2001,** *39*, 265–276.

14 Bertrand, M. P. *Org. Prep. Proc. Int.* **1994,** *26*, 257–290.

15 Asscher, M.; Vofsi, D. *J. Chem. Soc.* **1964,** 4962–4971.

16 Sinnreich, J.; Asscher, M. *J. Chem. Soc. Perkin Trans. 1* **1972,** 1543–1545.

17 Orochov, A.; Asscher, M.; Vofsi, D. *J. Chem. Soc. Perkin Trans. 2* **1973,** 1000–1002.

18 da Silva Corrêa, C. M. M.; Waters, W. A. *J. Chem. Soc. C* **1968,** 1874–1879.

19 Kamigata, N.; Sawada, H.; Kobayashi, M. *J. Org. Chem.* **1983,** *48*, 3793–3796.

20 Kamigata, N.; Ozaki, J.; Kobayashi, M. *J. Org. Chem.* **1985,** *50*, 5045–5050.

21 Kharasch, M. S.; Zavist, A. F. *J. Am. Chem. Soc.* **1951,** *73*, 964–967.

22 Amiel, Y. *Tetrahedron Lett.* **1971,** *12*, 661–663.

23 Amiel, Y. *J. Org. Chem.* **1974,** *39*, 3867–3870.

24 Truce, W. E.; Heuring, D. L.; Wolf, G. C. *J. Org. Chem.* **1974,** *39*, 238–244.

25 Percec, V.; Barboiu, B.; Kim. H. J. *J. Am. Chem.* **1998,** *120*, 305–316.

26 Edwards, G. L.; Walker, K. A. *Tetrahedron Lett.* **1992,** *33*, 1779–1782.

27 Grigoras, C.; Percec, V. *J. Polym. Sci. Part A: Polym. Chem.* **2005,** *43*, 319–330.

28 Percec, V.; Grigoras, C. *J. Polym. Sci. Part A: Polym. Chem.* **2005,** *43*, 3920–3931.

29 Percec, V.; Asandei, A. D.; Asgarzadeh, F.; Barboiu, B.; Holerca, M. N.; Grigoras, C. *J. Polym. Sci. Part A: Polym. Chem.* **2000,** *38*, 4353–4361.

30 Nagasawa, K.; Yoneta, A. *Chem. Pharm. Bull.* **1985,** *33*, 5048–5052.

31 Vedejs, E.; Hagen, J. P.; Roach, B. L.; Spear, K. L. *J. Org. Chem.* **1978,** *43*, 1185–1190.

32 Goto, A.; Suzuki, T.; Ohfuji, H.; Tanishima, M.; Fukuda, T.; Tsujii, Y.; Kaji, H. *Macromolecules* **2011,** *44*, 8709–8715.

33 Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001,** *101*, 2921–2990.

34 Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001,** *101*, 3689–3745.

35 Rosen, B. M.; Percec, V. *Chem. Rev.* **2009,** *109*, 5069–5119.