Novel Radical Ring-Opening Polymerization of Vinyloxirane Derivatives: Synthesis and Polymerization of 2-Vinyl-1-oxaspiro[2.5]octanes

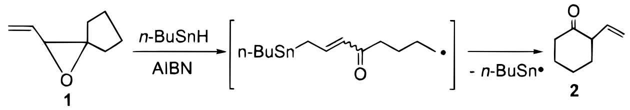
Toshio Koizumi,* Takanori Ando, Takakazu Kojima, and Takeshi Endo[†]

Department of Chemistry, The National Defense Academy,
Hashirimizu, Yokosuka 239, Japan, and
Research Laboratory of Resources Utilization,
Tokyo Institute of Technology, Nagatsuta-cho,
Midori-ku, Yokohama 226, Japan

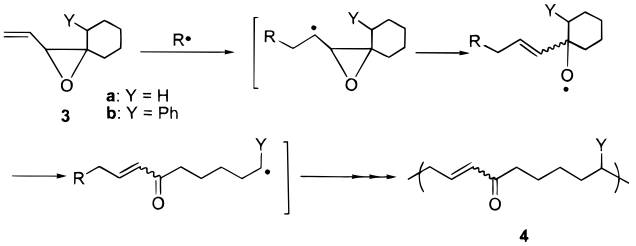
Received May 13, 1998
Revised Manuscript Received August 19, 1998

Cyclic compounds that undergo radical ring-opening polymerization are important for the synthesis of functional polymers having various groups such as ethers, esters, ketones, and carbonates in the main chain.[1] We have recently reported that vinyloxirane derivatives bearing a phenyl group as a radical stabilizing group undergo complete ring opening with selective cleavage of the carbon−carbon bond of the oxirane ring, contrary to the ionic ring-opening polymerization of oxiranes, to afford the corresponding polymers containing a vinyl ether moiety in the backbone.[2] A simple vinyloxirane, 2-epoxy-3-butene, can barely be polymerized by radical initiators; only a viscous liquid was obtained in very low yield.[3] Most of oxirane cleavages have involved carbon−oxygen bond scission under ionic or radical conditions. Kim et al. reported that alkoxy radicals generated by a radical ring-opening reaction of oxirane **1** in the presence of tri-*n*-butyltin hydride underwent β-scission to produce a carbon-centered radical followed by a ring-closure reaction to afford the one-carbon expanded product **2** (Scheme 1).[4] This result prompted us to explore the possibility of double radical ring-opening polymerization of vinyloxirane derivatives because the carbon-centered radical could attack the vinyl group of another vinyloxirane if tri-*n*-butyltin hydride was not used (Scheme 2). In this paper, we report the radical polymerization behavior of vinyloxiranes carrying a spiro moiety (2-vinyl-1-oxaspiro[2.5]octane (**3a**) and 2-vinyl-4-phenyl-1-oxaspiro[2.5]octane (**3b**)).

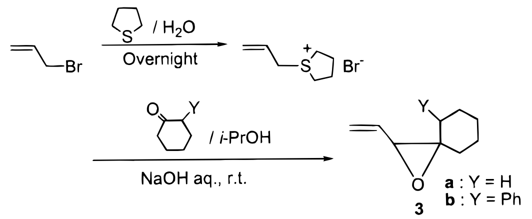
Scheme 1



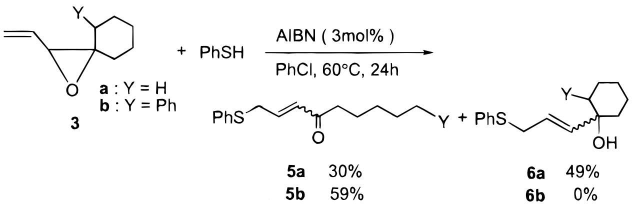
Scheme 2



Scheme 3



Scheme 4



Vinyloxiranes **3** were synthesized by the method reported previously, starting from allyl bromide, tetrahydrothiophene, and the corresponding cycloalkanones (Scheme 3).[5] First, we examined the radical polymerization behavior of **3a**, and these results are summarized in Table 1 (runs 1−6).[6] The yields of the resulting polymers were low when the polymerization was conducted in bulk at 60 and 80 °C using azobis(isobutyronitrile) (AIBN) and benzoyl peroxide (BPO), respectively (run 1 and 2). Although the polymerization of **3a** in a concentrated solution at 120 °C using di-*tert*-butyl peroxide (DTBP) resulted in the formation of a gelled polymer (run 3), a solvent-soluble polymer could be obtained in runs 4−6. The polydispersity of the polymers tended to decrease as the amount of the solvent was increased. The large polydispersity values were observed in runs 2 and 4 probably due to cross-linking that occurred to some extent on the carbon−carbon double bond of the resulting polymers. To clarify the structure of the polymers, the radical addition of **3a** with benzenethiol was carried out in the presence of AIBN at 60 °C as a model reaction. In this reaction two kinds of products were formed: one of them was the expected product (**5a**) bearing an enone moiety and the other was an alcohol (**6a**) (Scheme 4). Any cyclized products were not isolated from the reaction mixture, in contrast to the reaction of oxirane **1** using tri-*n*-butyltin hydride and AIBN. The structure of the polymer obtained was examined by comparison with ^{1}H NMR and IR spectra of model compound **5a**. The ^{1}H NMR spectrum of polymer **4a** (run 6) was similar to that of **5a** (Figure 1). Signals corresponding to the vinylic protons were observed around 6.0 and 6.8 ppm in both the spectra. However, other vinylic signals were present in the region of 5.3 to 5.8 ppm in the ^{1}H NMR of **4a**. In the IR spectrum of the polymer characteristic absorptions based on the carbonyl group and vinylic C−H bond were observed around 1700 and 3200 cm^{-1}, respectively. No absorption due to the oxirane around 900 cm^{-1} was observed. However, a weak absorption was also observed around 3500 cm^{-1} due to a hydroxy group. These spectral data suggest that the polymer includes an alcohol substructure bearing the hydroxy groups which is similar to that of model compound **6a**. This product is probably due to hydrogen abstraction by the alkoxy radical prior to ring opening of the cyclohexane ring of

---

[†] Tokyo Institute of Technology.

10.1021/ma9807668 CCC: $15.00

Table 1. Radical Polymerization of 3a and 3b

run	monomer	init (mol %)	solvent[a]	temp (°C)	time (h)	yield (%)[b]	M_n[c]	M_w/M_n[c]
1	3a	AIBN (3)	bulk	60	24	7	3480	3.05
2	3a	BPO (3)	bulk	80	48	13	5500	8.10
3	3a	DTBP (3)	PhCl (1)	120	24	24[d]		
4	3a	DTBP (3)	PhCl (3)	120	24	18	6190	5.28
5	3a	DTBP (3)	PhCl (4)	120	48	26	6640	2.70
6	3a	DTBP (5)	PhCl (6)	120	48	31	5970	2.00
7	3b	BPO (3)	bulk	80	48	1	4120	2.17
8	3b	DTBP (3)	bulk	120	24	54[d]		
9	3b	DTBP (5)	PhCl (3)	120	48	30	5970	4.06

[a] Numbers in parentheses are molar ratio (PhCl/**3**). [b] Insoluble in *n*-hexane. [c] Estimated by GPC (based on polystyrene). [d] A gelled polymer was obtained.

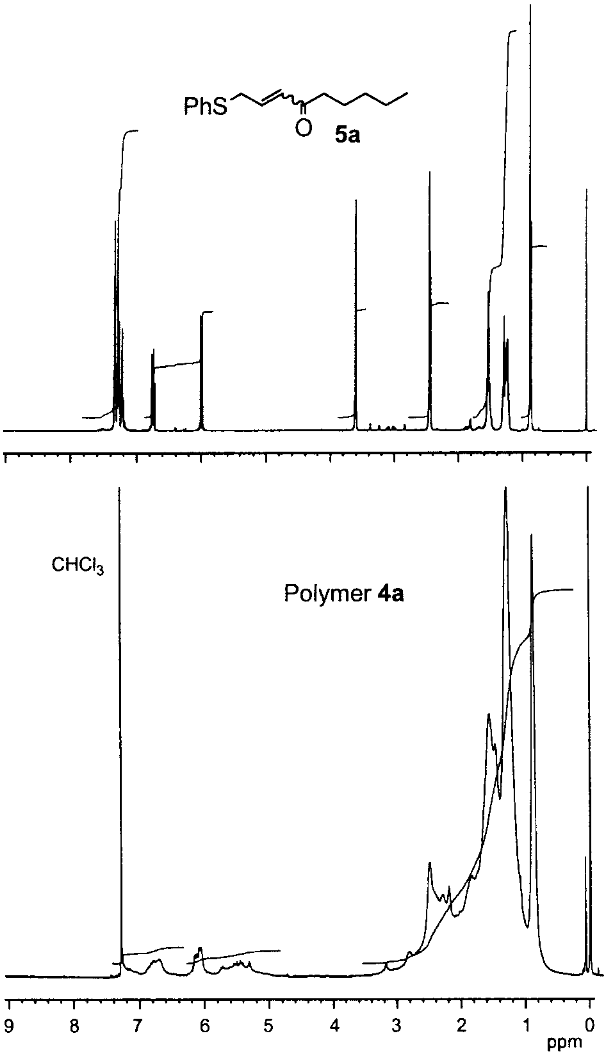


Figure 1. ^{1}H NMR spectra of **5a** and polymer **4a** ($CDCl_3$, 500 MHz).

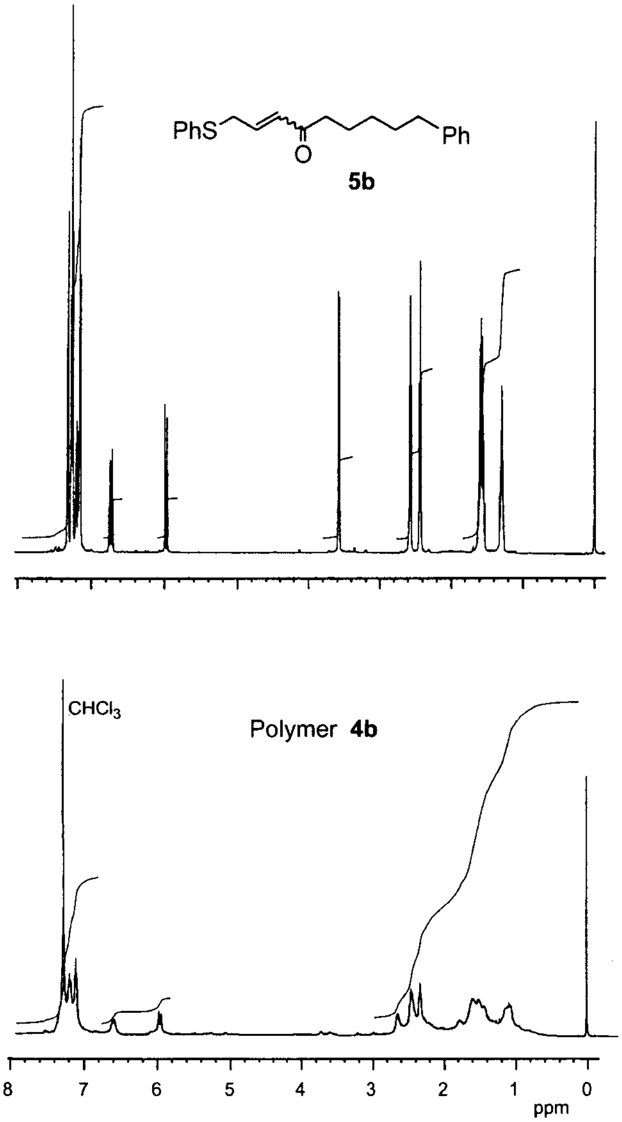


Figure 2. ^{1}H NMR spectra of **5b** and polymer **4b** ($CDCl_3$, 500 MHz).

3a (Scheme 2). The olefin content of polymer **4a** estimated by ^{1}H NMR was very low (about 35%). This result indicates that attack of the propagating species onto the carbon−carbon double bond of the resulting polymer is somewhat easy.

Next, the polymerization of **3b** having a phenyl group as a radical stabilizing group was examined. Radical addition of **3b** with benzenethiol at 60 °C using AIBN gave only an adduct **5b** having an enone moiety, in contrast to that of **3a**. Any cyclized products were not isolated, similarly to the case of **3a**. This fact implies that the phenyl group is able to accelerate the β-scission of the alkoxy radical to a stabilized carbon-centered radical. Therefore, **3b** was expected to afford a polymer having only an enone unit. As shown in Table 1 (runs 7−8), although a gelled polymer was obtained by polymerization at 120 °C in bulk (run 8), the radical polymerization of **3b** was conducted in chlorobenzene at 120 °C for 48 h using DTBP to yield the expected polymer in moderate yield (run 9). The structure of the polymer was confirmed by ^{1}H NMR and IR spectra. The ^{1}H NMR spectra of the obtained polymer (run 9) was compatible with that of model compound **5b** (Figure 2). In the ^{1}H NMR of polymer **4b**, characteristic signals based on the vinyl protons around 6.0 and 6.6 ppm and methylene protons adjacent to the carbonyl group in the region of about 2.3 to 2.6 ppm were observed. The presence of vinylic signals, which were observed in the region of 5.3 to 5.8 ppm in the ^{1}H NMR of **4a**, was negligible. In the IR spectrum of polymer **4b**, the OH absorption was almost disappeared compared to the IR spectrum of polymer **4a**, and the presence of a carbonyl group was confirmed around 1700 cm^{-1} in both polymers. The olefin content of polymer **4b** was estimated to be about 50% by ^{1}H NMR and was increased compared to that of polymer **4a**. The phenyl group of **4b** was found to be able to suppress attack of the propagating species onto the carbon−carbon double bond of the resulting polymer. Thus, we have found that the desired radical ring-opening polymerization proceeded successfully using **3b**. The phenyl group as a radical stabilizing group was required for the efficient ring-opening of the alkoxy radical intermediate.

This is the first example of double radical ring-opening polymerization of vinyloxirane derivatives. Further studies on this new radical ring-opening polymerization using other vinyloxirane derivatives are now in progress.

References and Notes

(1) (a) Endo, T.; Yokozawa, T. In *New Methods for Polymer Synthesis*; Mijs, W. J., Ed.; Plenum Press: New York, 1992; p 155. (b) Bailey, W. J.; Chen, P. Y.; Chen, S.-C.; Chiao, W.-B.; Endo, T.; Gapud, B.; Kuruganti, V.; Lin, Y.-N.; Ni, Z.; Pan, C.-Y.; Shaffer, S. E.; Sidney, L.; Wu, S.-R.; Yamamoto, N.; Yamazaki, N.; Yonezawa, K.; Zhou, L.-L. *Makromol. Chem., Macromol. Symp.* **1986**, *6*, 81.

(2) (a) Cho, I.; Kim, J.-B. *J. Polym. Sci. Polym. Lett. Ed.* **1983**, *21*, 433. (b) Endo, T.; Kanda, N. *J. Polym. Sci. Polym. Chem. Ed.* **1985**, *23*, 1931. (c) Endo, T.; Suga, K.; Orikasa, Y.; Kojima, S. *J. Appl. Polym. Sci.* **1989**, *37*, 1815. (d) T. Koizumi, Y. Nojima, and T. Endo, *J. Polym. Sci. Polym. Chem. Ed.* **1993**, *31*, 3489.

(3) Murata, K. *J. Polym. Sci. Polym. Chem. Ed.* **1972**, *10*, 3673.

(4) Kim, S.; Lee, S. *Tetrahedron Lett.* **1991**, *32*, 6575.

(5) Rosenberger, M.; Newkom, C.; Aig, E. A. *J. Am. Chem. Soc.* **1983**, *105*, 3656.

(6) A typical procedure: **3a** or **3b** (2 mmol), initiator, and chlorobenzene were placed in an ampule tube. The tube was degassed and sealed under reduced pressure. The polymerization was carried out for 24 or 48 h. The reaction mixture was poured into a plenty of *n*-hexane to precipitate polymer. The resulting polymer was filtered, washed with *n*-hexane, and dried in vacuo. (The detailed reaction conditions are shown in Table 1.)

MA9807668