Synthesis and Radical Ring-Opening Polymerization Behavior of Bifunctional Vinylcyclopropane Bearing a Spiroacetal Moiety

Tadashi Okazaki, Fumio Sanda, and Takeshi Endo*

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Nagatsuta-cho, Midori-ku, Yokohama 226, Japan

Received March 20, 1995; Revised Manuscript Received June 19, 1995®

ABSTRACT: Synthesis and radical ring-opening polymerization of bifunctional vinylcyclopropane having a spiroacetal moiety, 1,10-bis(vinyl)-4,8,12,15-tetraoxatrispiro[2.2.2.2.2.2]pentadecane (**1**), were carried out. **1** was prepared by the reaction of 1,1-dichloro-2-vinylcyclopropane and pentaerythritol in DMF in the presence of a base. **1** was isolated by column chromatography as a highly viscous pale yellow transparent oil. Radical polymerization of **1** was carried out in the presence of an appropriate initiator (3 mol % vs **1**) at 60, 80, and 120 °C in degassed sealed ampules for 20 h. The polymerization mixtures were homogeneous during the polymerizations. Poly(**1**) was isolated by reprecipitation into ether with a small amount of triethylamine to avoid hydrolysis of the polymer. The crude polymerization mixtures were soluble in chlorobenzene, DMF, and chloroform; however, the polymers after isolation were insoluble in common organic solvents. An incomplete single ring-opening polymerization was confirmed from the analyses of the ^{1}H- and ^{13}C-NMR and IR spectra of the polymer. A double ring-opened unit was not contained in the polymer. The volume shrinkage on the polymerization of **1** with AIBN at 60 °C was 4.7%.

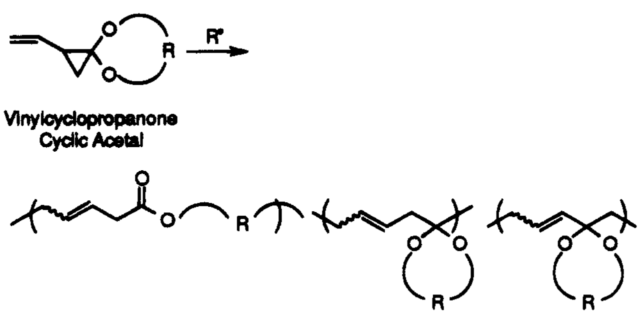
Introduction

Cyclic monomers that undergo ring-opening polymerization are important in the field of precision materials, adhesives, and so on, since they show low shrinkage or sometimes expansion in volume on polymerization.[1] Generally, many monomers and materials undergo polymerization and curing via a radical process. Since vinyl polymerization is commonly accompanied by volume shrinkage larger than ring-opening polymerization, monomers and materials that show low shrinkage or some expansion in volume through radical ring-opening polymerization are particularly useful. In the course of the study of the radically polymerizable cyclic monomers that show low shrinkage on polymerization, we have examined the radical polymerization behavior of vinylcyclopropanone cyclic acetals[2] (Scheme 1). The volume shrinkages of the monomers were relatively small because of the double ring-opening effect. Meanwhile, monomers bearing spirocyclic acetal moieties are expected to show useful properties such as low viscosity and thermo setting that can be applicable to painting materials and so on.[3] Now we have designed a novel monomer consisting of bifunctional vinylcyclopropanone spirocyclic acetal moiety, 1,10-bis(vinyl)-4,8,12,15-tetraoxatrispiro[2.2.2.2.2.2]pentadecane (**1**). In this paper, the synthesis and radical polymerization behavior of **1** are disclosed. This is the first report of radical ring-opening polymerization behavior of bifunctional vinylcyclopropane bearing a spiroacetal moiety.

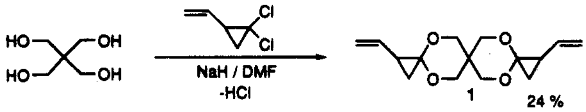
Results and Discussion

The new monomer **1** was preparated by the reaction of 1,1-dichloro-2-vinylcyclopropane with tetraalkoxide obtained from pentaerythritol and 4 equiv of sodium hydride in DMF in 24% yield (Scheme 2). 1,1-Dichloro-2-vinylcyclopropane was prepared according to the previously reported method.[2,4] Since the solubility of pentaerythritol in DMF was very low, the low yield of **1** should be caused by a heterogeneous reaction. **1** was obtained as a highly viscous pale yellow transparent oil by column chromatographic isolation. The structure of **1** was determined by ^{1}H- and ^{13}C-NMR and IR spectra besides elemental analysis. ^{1}H- and ^{13}C-NMR spectra of **1** are shown in Figures 1 and 2.

Scheme 1



Scheme 2



Radical polymerization of **1** was carried out in the presence of an appropriate radical initiator (3 mol % vs **1**) in chlorobenzene or DMF in a degassed sealed ampule for 20 h. The polymerization proceeded homogeneously after 20 h in any condition. Isolation of the obtained polymers was carried out with reprecipitation into ether with a small amount of triethylamine to avoid hydrolysis of the polymer. Pale yellow transparent solid polymers were obtained by the reprecipitation. The crude polymerization mixtures were soluble in chlorobenzene, DMF, and chloroform, but the polymers after the reprecipitation were insoluble in common organic solvents. The solubility of the crude polymerization mixture might come from the low degree of cross-linking of the polymer and/or solvation of the cross-linked polymer by the solvent as well as unreacted monomer. Once the cross-linked polymer was isolated, the polymer might not be sufficiently solvated any more.

The conditions and results of the polymerization of **1** are summarized in Table 1. The conversion of **1** in the

---

* To whom all correspondence should be addressed.

® Abstract published in *Advance ACS Abstracts,* August 1, 1995.

0024-9297/95/2228-6026$09.00/0

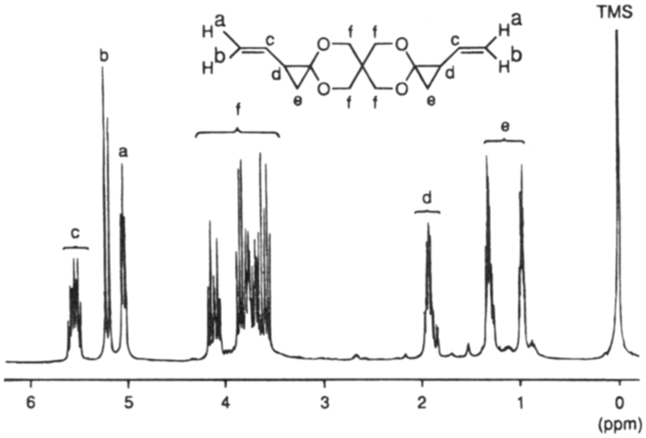


Figure 1. ^{1}H-NMR spectrum of **1** (solvent $CDCl_3$, 400 MHz).

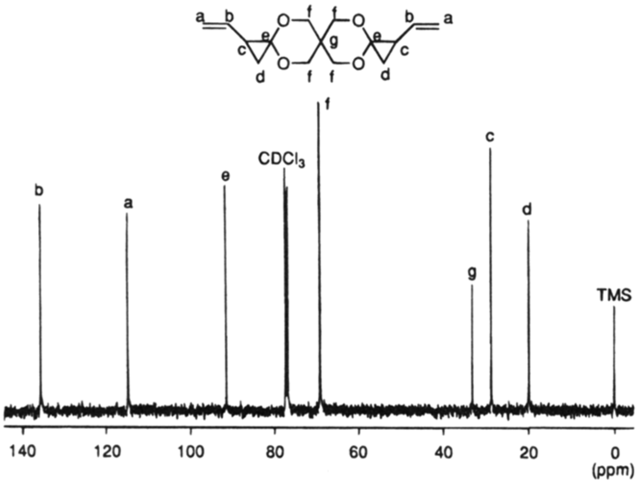


Figure 2. ^{13}C-NMR spectrum of **1** (solvent $CDCl_3$, 100 MHz).

Table 1. Radical Polymerization of 1[a]

run	initiator[b]	temp (°C)	solvent (1 M)	conv[c] (%)	yield[d] (%)	$\bar{M}_n$ ($\bar{M}_w/\bar{M}_n$)[e]
1	AIBN	60	chlorobenzene	23	20	22000 (2.05)
2	BPO	80	chlorobenzene	5	3	6700 (1.63)
3	DTBP	120	chlorobenzene	0	0	
4	AIBN	60	DMF	21	18	8800 (2.52)
5	BPO	80	DMF	5	4	8700 (1.48)
6	DTBP	120	DMF	2	2	3200 (1.02)

[a] Conditions: **1**, 3 mmol; initiator, 3 mol % vs **1**; 20 h. [b] AIBN, 2,2′-azobis(isobutyronitrile); BPO, benzoyl peroxide; DTBP, di-*tert*-butyl peroxide. [c] Determined by ^{1}H-NMR. [d] Ether-insoluble part. [e] Estimated by GPC based on polystyrene standards, eluent LiBr in DMF (5.8 mM).

polymerization was relatively small, 2−23% in any condition, which was almost equal to the yield of the polymer. No polymerization proceeded with DTBP in chlorobenzene at 120 °C (run 3 in Table 1). The bulk polymerization could not be performed because of the high viscosity of **1**. The molecular weight of the polymer decreased while the molecular weight distribution increased as the polymerization temperature rose. Relatively high molecular weight polymer ($\bar{M}_n$ 22 000) was obtained in the polymerization in chlorobenzene at 60 °C (run 1 in Table 1).

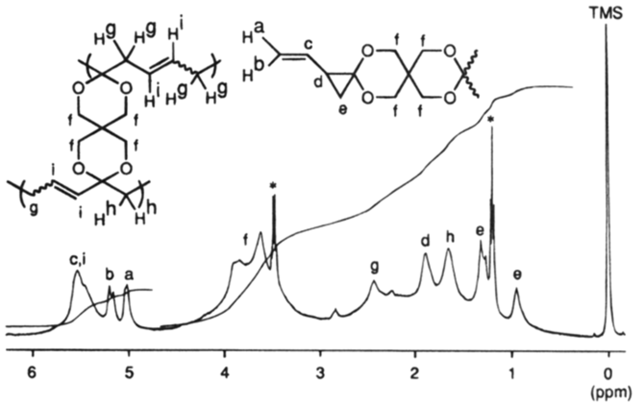


Figure 3. ^{1}H-NMR spectrum of poly(**1**) (solvent $CDCl_3$, 400 MHz). Polymerization conditions: 3 mol % AIBN in chlorobenzene (1 M), 60 °C, 20 h (run 1 in Table 1). *: Signals derived from ether contamination.

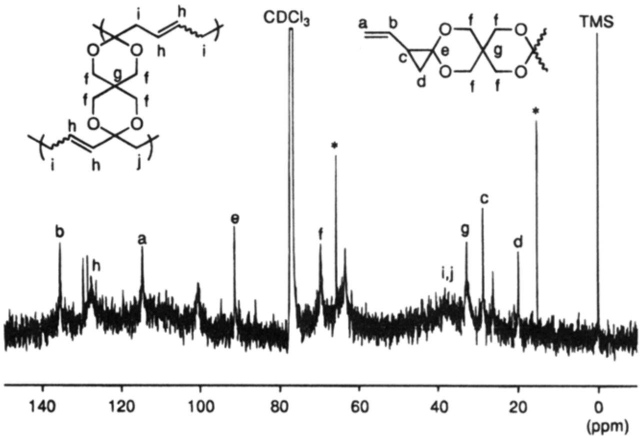
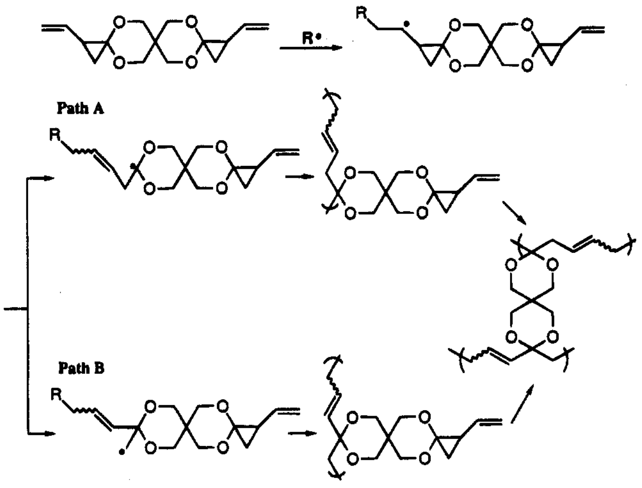


Figure 4. ^{13}C-NMR spectrum of poly(**1**) (solvent $CDCl_3$, 100 MHz). Polymerization conditions: 3 mol % AIBN in chlorobenzene (1 M), 60 °C, 20 h (run 1 in Table 1). *: Signals derived from ether contamination.

The structure of the obtained polymer was determined by the ^{1}H-NMR, solid state ^{13}C-NMR, and IR spectra. Since the isolated polymer was not completely soluble in $CDCl_3$ but swelled in the solvent, the NMR spectra of the polymer could be measured although the resolution was not sufficient enough. The presence of signals based on cyclopropane ring protons (0.9−1.0, 1.2−1.3, and 1.8−2.0 ppm) in the ^{1}H-NMR spectrum of the obtained polymer confirmed that the cyclopropane ring structure was included in the polymer (Figure 3). From the integration ratio of the signals assigned to cyclopropane ring protons toward other signals, the content of the cyclopropane unit was estimated to be 43%. Since no signal at 3 ppm based on methylene protons α to the ester carbonyl group was observed, no ester group formed by double ring-opening was contained in the polymer.[2] No absorption at 1740 cm^{-1} in the IR spectrum also confirmed the absence of an ester group. A small absorption at 1730 cm^{-1} based on the carbonyl group of polyketone which should be formed by the hydrolysis of the acetal unit of the polymer was observed. The signals of the ^{13}C-NMR could be assigned as shown in Figure 4 in comparison with that of **1** (Figure 2). The vinylcyclopropane structure was maintained without ring-opening in the polymer since the signals at 19.9, 28.9, 91.5, 114.7, and 135.5 ppm assigned to the protons of the vinylcyclopropane moiety were observed. Signals around 175 ppm were not observed, which indicated the absence of an ester group formed by the ring-opening of the cyclic acetal moiety. The solid state ^{13}C-NMR spectrum of the polymer showed an approximately similar pattern with the ^{13}C-NMR spectrum measured in $CDCl_3$. The tendency of single ring-opening is almost equal to the behavior of the monofunctional five-membered vinylcyclopropanone cyclic acetal.[2] The ring strain of the six-membered dioxane moiety should be as small as that of the five-

Scheme 3



membered dioxolane moiety. The plausible mechanism of the polymerization of **1** is illustrated as Scheme 3.

The volume change on the polymerization of **1** was determined by the comparison of the densities of **1** (d = 1.11 g/cm^3) and poly(**1**) (d = 1.16 g/cm^3), which were measured by the density gradient tube method at 25 °C. The volume shrinkage on the radical polymerization of **1** was 4.7%, which was slightly smaller than that of other usual ring-opening monomers.[2] The glass transition temperature and 10 % weight loss temperature in nitrogen of poly(**1**) obtained in the polymerization at 60 °C in chlorobenzene (run 1 in Table 1) were 85 and 360 °C, respectively.

Conclusion

In this study, the synthesis and radical ring-opening polymerization behavior of bifunctional vinylcyclopropane bearing a spiroacetal moiety, 1,10-bis(vinyl)-4,8,12,15-tetraoxatrispiro[2.2.2.2.2.2]pentadecane (**1**), were examined. The novel monomer **1** was prepared by the reaction of 1,1-dichloro-2-vinylcyclopropane and pentaerythritol. Radical polymerization of **1** initiated with AIBN was carried out in chlorobenzene or DMF. The crude polymerization mixtures were soluble in chlorobenzene, DMF, and chloroform; however, the polymers after isolation were insoluble in common organic solvents. The structure of the polymer was the unit containing the spirocyclic moiety formed by the ring-opening of the vinylcyclopropane moiety. The degree of ring-opening was 57%. The incomplete ring-opening behavior should cause the ambiguous solubility of the polymer. The volume shrinkage on the radical polymerization of **1** was rather small (4.7%).

Experimental Section

Measurement. ^{1}H- and ^{13}C-NMR spectra of **1** and poly(**1**) were measured at 27 °C on JEOL JNM-EX-90 and JNM-EX-400 spectrometers, using tetramethylsilane (TMS) as an internal standard in deuteriochloroform. The solid state ^{13}C-NMR spectrum (CP-MAS) of poly(**1**) was measured at 27 °C on a JEOL JNM-GX-270 using adamantane as an external standard. FT-IR spectra were obtained with a JASCO FT/IR-5300 at 25 °C. Molecular weight and its distribution ($\bar{M}_w/\bar{M}_n$) were determined by gel permeation chromatography (GPC) on a TOSOH HLC-8020 system with a data processor equipped with four polystyrene gel columns (TSK gel G6000H, G5000H, G4000H, and G2500H), using LiBr in *N,N*-dimethylformamide (DMF) solution (5.8 mM) as an eluent (flow rate 1.0 mL/min), polystyrene calibration, and refractive index (RI) and ultraviolet (UV) detectors. Thermal analyses were performed on Seiko Instruments TG/DTA220 and DSC220C. The glass transition temperature (T_g) by differential scanning calorimetry (DSC) was taken as an inflection point on a trace at a heating rate of 10 °C/min. The 10% weight loss temperature (T_{d10}) was determined by thermogravimetric analysis (TGA) at a heating rate of 10 °C/min under a nitrogen atmosphere. Densities of **1** and poly(**1**) were measured by the density gradient tube method at 25 °C with a Shibayama Scientific Co., Ltd. Model A.

Materials. Chlorobenzene and DMF were used after purification by the usual methods. Initiators 2,2′-azobis(isobutyronitrile) (AIBN, Tokyo Kasei Kogyo Co., Ltd.), benzoyl peroxide (BPO, Nacalai Tesque, Inc.), and di-*tert*-butyl peroxide (DTBP, Nacalai Tesque, Inc.) were used as received.

Synthesis of 1. To a mixture of sodium hydride (2.63 g, 110 mmol) in DMF (80 mL) were added pentaerythritol (2.98 g, 21.9 mmol) and then a solution of 1,1-dichloro-2-vinylcyclopropane (6.00 g, 43.8 mmol) in DMF (20 mL) at 0 °C. The addition was followed by stirring at room temperature for 15 h. After the reaction, water (100 mL) was added carefully at room temperature. The mixture was extracted with ether (120 mL), and the organic layer was washed with a saturated solution of sodium hydrogen carbonate. The organic layer was dried over anhydrous magnesium sulfate and evaporated. The residue was purified by column chromatography (eluent, ethylacetate/*n*-hexane = 1/20 with 5% triethylamine) to obtain a viscous liquid **1**, 1.37 g (24%): ^{1}H-NMR ($CDCl_3$) δ 0.98 (m, 2 H), 1.27–1.34 (m, 2 H), 1.90–2.94 (m, 2 H), 3.53–4.17 (m, 2 H), 5.01–5.57 (m, 6 H); ^{13}C-NMR ($CDCl_3$) δ 19.91, 19.97, 28.80, 33.27, 69.11, 69.29, 91.50, 114.73, 114.81, 135.40; IR (neat) 3082, 2957, 2908, 2860, 2044, 1896, 1809, 1738, 1637, 1446, 1352, 1267, 1174, 1047, 960, 904, 872, 817, 708, 689, 655, 513 cm^{-1}. Anal. Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 67.73; H, 7.82.

Polymerizations of 1. General Procedure. To a monomer (3 mmol) in a polymerization tube was introduced an initiator. The tube was cooled, degassed, sealed off, and heated at a set temperature for 20 h. The polymer was isolated from the resulting mixture by reprecipitation into ether with 5% triethylamine and dried *in vacuo* at 50 °C.

References and Notes

(1) Takata, T.; Endo, T. In *Expanding Monomers: Synthesis, Characterization, and Application*; Sadhir, R. K., Ed.; CRC Press: Boca Raton, FL, 1992; Chapter 3.
(2) Sanda, F.; Takata, T.; Endo, T. *Macromolecules* **1994**, *27*, 1099.
(3) (a) Baillet, C.; Gandi, S.; Breant, P.; Delfosse, L. *Polym. Degrad. Stab.* **1992**, *37*, 149. (b) Takiyama, E.; Haniuda, T. *Nihon Secchaku Kyoukaishi* **1977**, *13*, 330. (c) Schulze, T.; Klemm, E. *Polym. Bull.* **1993**, *31*, 409. (d) Grijpma, D. W.; Kroeze, E.; Nijenhuis, A. J.; Pennings, A. J. *Polymer* **1993**, *34*, 1496. (e) Ing, V. D. *Angew. Chem.* **1952**, *64*, 544. (f) Bailey, W. J.; Ni, Z.; Wu, S.-R. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 3021.
(4) Sanda, F.; Takata, T.; Endo, T. *Macromolecules* **1993**, *26*, 1818.

MA950375I