1284 Macromolecules 1994, 27, 1284-1285

Communications to the Editor

Novel Radical Ring-Opening Polyaddition of Dithiols to Bis(isopropenylepoxyethyl)benzene

Toshio Koizumi,[†] Nobukazu Yoshikawa, and Takeshi Endo*

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Nagatsuta-cho, Midori-ku, Yokohama 227, Japan

Received October 13, 1993
Revised Manuscript Received January 5, 1993

Radical ring-opening polymerization has attracted interest for incorporation of various functional groups such as ether, ester, ketone, and carbonate into the backbones of polymers.[1] Recently, it has been reported that vinyloxirane 1 (R = H) bearing a phenyl group as a radical stabilizing group undergoes complete ring opening with selective cleavage of the carbon–carbon bond of the oxirane ring to afford the corresponding polymer containing a vinyl ether moiety in the backbone[2–4] (Scheme 1). When the radical polymerization of 1 (R = H) was carried out at higher temperature (>120 °C) in bulk, only a gelled polymer could be obtained probably due to cross-linking on the vinyl ether group of the resulting polymer. We have found that vinyloxirane 2 (R = Me), which has a methyl group at the α-position of the vinyl group of 1, undergoes radical ring-opening polymerization to afford the corresponding soluble polymer even in bulk at 120 °C.[5]

In order to clarify the structure of the polymer obtained from 1, the radical addition of 1 with benzenethiol as a model reaction was carried out in the presence of radical initiator to obtain the corresponding 1:1 adduct having vinyl ether and sulfide groups via carbon–carbon bond cleavage of the oxirane ring[2] (Scheme 2). These results prompted us to develop a new type of radical polyaddition of bifunctional vinyloxiranes and dithiols accompanying ring-opening reaction of the oxirane ring. This radical polyaddition may be regarded as "radical ring-opening polyaddition". Although there are a lot of reports on ionic and radical polyadditions, the radical ring-opening polyaddition has not been reported so far.

In this paper, we report that the radical polyaddition of dithiols to bifunctional vinyloxirane can lead to the formation of the polymer having vinyl ether and sulfide groups via carbon–carbon bond cleavage of the oxirane ring (Scheme 3).

In the radical ring-opening polymerization of **2**, we have found the good results in which **2** cannot undergo cross-linking of the resulting polymer as a radical side reaction because of the formation of hindered olefin by the methyl group in the main chain.[5] Therefore, 1,4-bis(isopropenylepoxyethyl)benzene (**3**) as a bifunctional vinyloxirane was synthesized by the phase-transfer reaction of a methallyldimethylsulfonium salt with terephthalaldehyde according to the method reported in our previous paper[3] (Scheme 4).

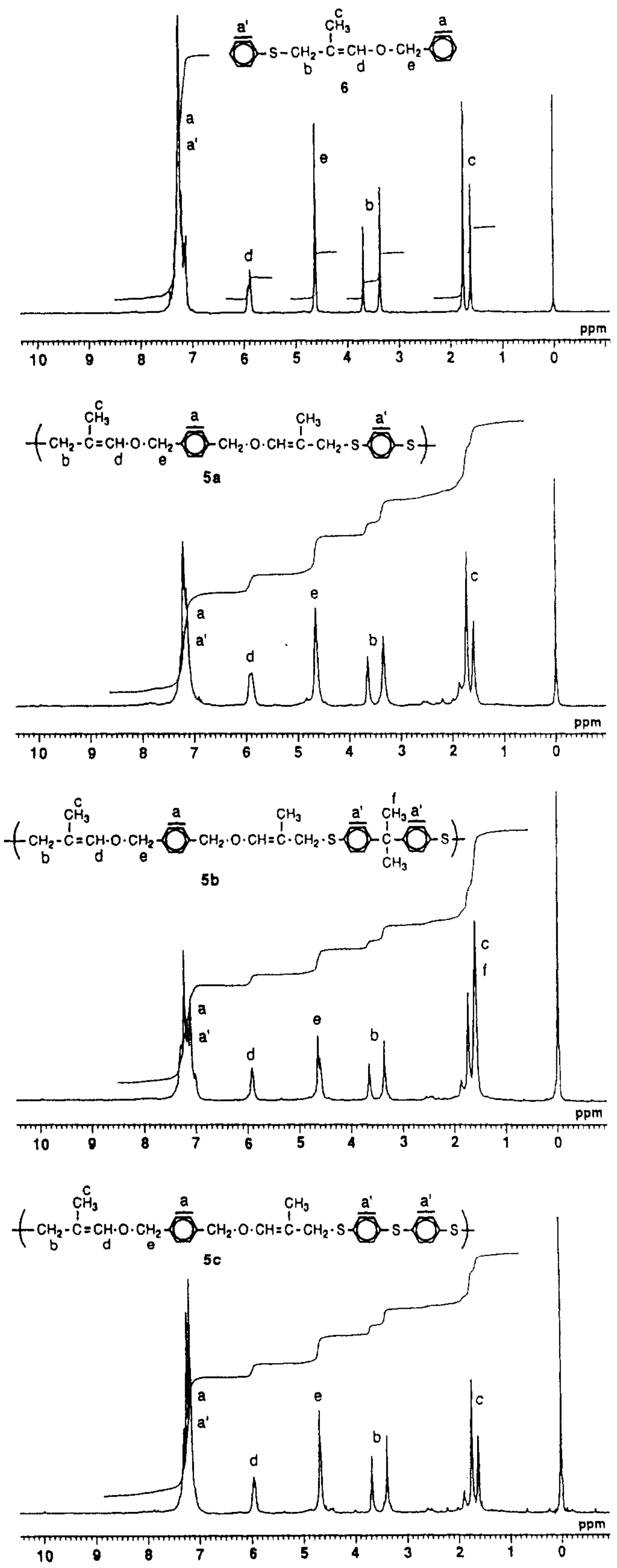
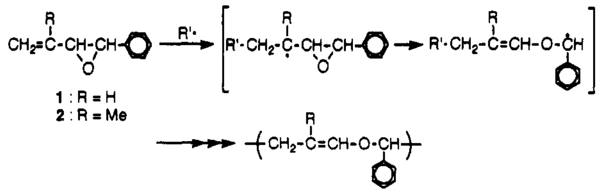


Figure 1. ^{1}H NMR spectra of **6** and **5a–c** (solvent, $CDCl_3$, 90 MHz).

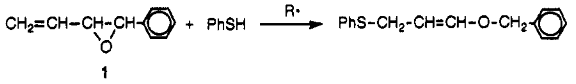
[†] Present address: Department of Chemistry, The National Defense Academy, Hashirimizu, Yokosuka 239, Japan.

0024-9297/94/2227-1284$04.50/0 © 1994 American Chemical Society

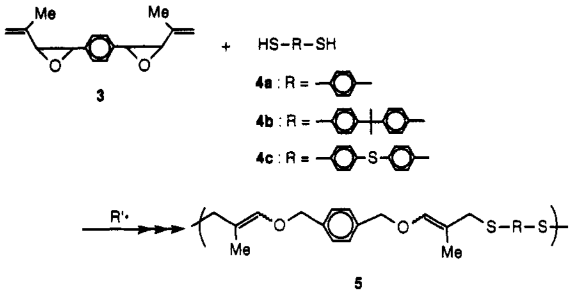
Scheme 1



Scheme 2



Scheme 3



Scheme 4

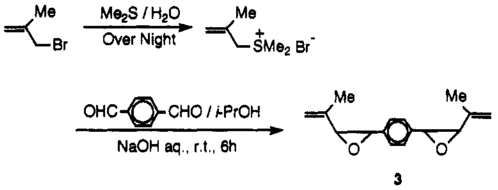


Table 1. Radical Ring-Opening Polyaddition of Dithiols to 3

run	initiator[a]	dithiol	solvent	temp (°C)	yield (%)[c]	$\overline{M}_n$[d]	$\overline{M}_w/\overline{M}_n$[d]
1	AIBN	**4a**	PhCl	60	99	5980	2.95
2	DTBP	**4a**	PhCl	120	95[e]		
3	UV[b]	**4a**	$PhCH_3$	20	85	3720	2.01
4	AIBN	**4b**	PhCl	60	100	8590	3.53
5	UV[b]	**4b**	$PhCH_3$	20	87	7690	3.69
6	AIBN	**4c**	PhCl	60	100	7430	2.33

[a] 6 mol % for **3**. [b] High-pressure Hg lamp. [c] Insoluble in hexane. [d] Estimated by GPC (based on polystyrene). [e] Gelled polymer was only obtained.

The radical polyadditions of dithiols [1,4-benzenedithiol (**4a**), 4,4′-isopropylidenedithiophenol (**4b**), and bis(4-mercaptophenyl) sulfide (**4c**)] to **3** were carried out in sealed tubes for 24 h under various conditions, and their results are summarized in Table 1.

Although the polyaddition of **3** and **4a** in the presence of di-*tert*-butyl peroxide (DTBP) at 120 °C resulted in the formation of a gelled polymer (run 2), the desired polymers (**5a–c**) could be obtained quantitatively when the polyadditions were conducted at 60 °C for 24 h in the presence of azobis(isobutyronitrile) (AIBN) in chlorobenzene (runs 1, 4, and 6). The structure of the polymers was confirmed by IR and ^1H NMR spectra. In both the IR spectra of the obtained polymers and the corresponding model compound **6** which was obtained by the radical addition of benzenethiol to **2** in the presence of AIBN in benzene at 60 °C for 24 h,[6] strong absorption could be observed around 1680 cm^{-1} based on the vinyl ether group. The ^1H NMR spectra of the polymers were very similar to that of **6** as shown in Figure 1. In all the ^1H NMR spectra, the signals due to vinyl and benzyl protons were observed around 5.9 and 4.6 ppm, respectively. The vinyl and benzyl protons formed by carbon–carbon bond cleavage of the oxirane ring were present. These spectral data suggested that the radical polyaddition of **4** to **3** successfully proceeded through the selective cleavage of two oxirane rings of **3** to afford the polymers possessing vinyl ether and sulfide groups.

The polyaddition of dithiols (**4a** and **4b**) to **3** also proceeded under photoirradiation at 20 °C to afford the corresponding polymers of which the structure was the same as that of the polymers obtained by the radical polyaddition. However, the molecular weight of the polymers was lower than that of the polymers obtained with AIBN (runs 3 and 5).

From these results described above, we found that the radical polyaddition of **4** to **3** could give the corresponding polymers quantitatively in the presence of AIBN in chlorobenzene at 60 °C for 24 h, and may demonstrate the first example of radical ring-opening polyaddition as a novel polymerization method. Further studies on the application of the novel polymerization are now in progress.

We thank Sumitomo Seika Co. for a generous gift of 1,4-benzenedithiol and bis(mercaptophenyl) sulfide.

References and Notes

(1) (a) Endo, T.; Yokozawa, T. *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) Cho, I.; Kim, J.-B. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 433.

(3) Endo, T.; Kanda, N. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 1931.

(4) Endo, T.; Suga, K.; Orikasa, Y.; Kojima, S. *J. Appl. Polym. Sci.* **1989**, *37*, 1815.

(5) Koizumi, T.; Nojima, Y.; Endo, T. *J. Polym. Sci., Polym. Chem. Ed.*, in press.

(6) Yoshikawa, N.; Koizumi, T.; Endo, T. 61st National Meeting of the Chemical Society of Japan, 1C2 16, Yokohama, Japan, 1991.