

NOTES

Radical Ring-Opening Polymerization Behavior of Halogenated Phenyl-3-vinyloxiranes

Toshio KOIZUMI,^{*,†} Osamu MORIYA,^{*} Yoshikiyo URATA,^{*} Yoshiaki NOJIMA,^{**} and Takeshi ENDO^{**†}

^{*}Department of Chemistry, The National Defense Academy, Hashirimizu, Yokosuka 239, Japan

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

(Received December 28, 1994)

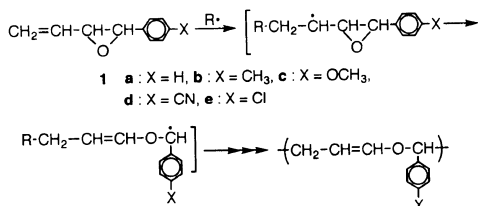
KEY WORDS Radical Polymerization / Radical Ring-Opening Polymerization / Polymerization Behavior / Vinyloxirane / Halogenated Phenyl-3-vinyloxirane /

Radical ring-opening polymerization is important for the synthesis of polymers having functional groups such as ester, ether, ketone, and carbonate in the main chain.¹ Recently, we reported that *p*-substituted 2-phenyl-3-vinyloxirane derivatives (**1**) underwent complete ring-opening polymerization *via* selective cleavage of the carbon-carbon bond of the oxirane ring to give the polymers bearing a vinyl ether moiety in the backbone (Scheme 1).²

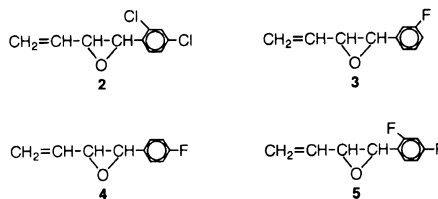
Cho *et al.* reported that when the radical polymerization of **1a** (X=H) was carried out at 120°C in bulk, only a gelled polymer was obtained probably due to crosslinking on the vinyl ether group of the resulting polymer.³ On the other hand, we have found that 2-isopropenyl-3-phenyloxirane, which has a methyl group at the α -position of the vinyl group of

1a, cannot undergo crosslinking of the resulting polymer even by radical polymerization at 120°C in bulk because of the formation of a hindered olefin by the methyl group in the main chain.⁴ The molecular weight ($\bar{M}_n = 1500$ —3200) of these polymers obtained from 2-phenyl-3-vinyloxirane derivatives **1** is comparatively low.^{2,4} Vinyloxiranes giving polymers with higher molecular weight have not been reported so far.

In this paper, we report that the radical ring-opening polymerization of fluorinated phenyl-3-vinyloxirane derivatives (**3—5**) can lead to the formation of higher molecular weight polymers having a vinyl ether moiety, whereas chlorinated phenyl-3-vinyloxirane derivatives (**1e** and **2**) afford polymers with low molecular weight under the same polymerization conditions.



Scheme 1.



Monomers 2—5

* To whom correspondence should be addressed.

EXPERIMENTAL

Synthesis of 2-(m-Fluorophenyl)-3-vinyloxirane (3)

A mixture of allyl bromide (13.7 g, 0.11 mol) and dimethylsulfide (7.8 g, 0.13 mol) in 10 ml of water was stirred at room temperature overnight. After removal of unreacted dimethyl sulfide at reduced pressure, *m*-fluorobenzaldehyde (11.9 g, 0.10 mol) in 10 ml of isopropyl alcohol was added to the aqueous solution containing allyldimethylsulfonium bromide and subsequently sodium hydroxide (4.5 g, 0.11 mol) in 10 ml of water was added dropwise at room temperature while stirring vigorously. After stirring for 6 hours, the resulting dimethyl sulfide was removed and the solution was extracted with ether three times. The combined organic layer was washed successively with water and brine and dried over anhydrous magnesium sulfate. After removal of ether, the residue was distilled *in vacuo* to obtain 9.8 g (yield 62%) of 2-(*m*-fluorophenyl)-3-vinyloxirane **3**: bp 89–91°C/9 mmHg. IR (neat): 3090, 2990, 1645, 1620, 1595, 1495, 1230, 990, 930, 890, 865 cm⁻¹. ¹H NMR (CDCl₃): 3.23–4.31 (2H, m), 5.14–6.00 (3H, m), 6.83–7.57 (5H, m) ppm. ¹³C NMR (CDCl₃): 58.08, 58.18, 59.48, 59.59, 62.79, 112.79, 114.09, 115.01, 115.50, 119.67, 121.34, 122.00, 129.48, 129.75, 130.13, 131.54, 134.62, 139.66, 139.99, 157.21, 157.59, 168.56, 168.48 ppm. *Anal.* Calcd for C₁₀H₉FO: C, 73.16%; H, 5.53%. Found: C, 73.06%; H, 5.72%.

Synthesis of 2-(p-Fluorophenyl)-3-vinyloxirane (4)

4 was synthesized similarly to **3** as mentioned above, bp 54–56°C/0.5 mmHg; yield 74%. IR (neat): 3090, 2990, 1645, 1610, 1515, 1290, 1225, 990, 930, 880, 835 cm⁻¹. ¹H NMR (CDCl₃): 3.20–4.26 (2H, m), 5.14–5.97 (3H, m), 6.86–7.57 (4H, m) ppm. ¹³C NMR (CDCl₃): 58.13, 59.54, 62.68, 114.52, 114.90, 115.50, 115.88, 119.45, 121.78, 126.93, 127.26, 127.85, 128.18, 130.78, 131.75, 132.84, 134.79,

156.84, 157.21, 167.78 ppm. *Anal.* Calcd for C₁₀H₉FO: C, 73.16%; H, 5.53%. Found: C, 72.91%; H, 5.80%.

Synthesis of 2-(o,p-Difluorophenyl)-3-vinyloxirane (5)

5 was synthesized similarly to **3** as mentioned above, bp 84–85°C/9 mmHg; yield 67%. IR (neat): 3090, 2990, 1620, 1510, 1285, 1230, 985, 965, 930, 875 cm⁻¹. ¹H NMR (CDCl₃): 3.20–4.40 (2H, m), 5.17–6.06 (3H, m), 6.63–7.51 (3H, m) ppm. ¹³C NMR (CDCl₃): 53.96, 54.12, 54.34, 59.05, 61.92, 102.44, 103.64, 104.77, 110.30, 111.00, 111.11, 111.92, 119.89, 121.95, 126.93, 127.04, 128.88, 128.99, 131.32, 134.46, 155.53, 157.27, 166.64, 167.72 ppm. *Anal.* Calcd for C₁₀H₈F₂O: C, 65.93%; H, 4.43%. Found: C, 65.79%; H, 4.53%.

Synthesis of 2-(o,p-Dichlorophenyl)-3-vinyloxirane (2)

2 was synthesized similarly to **3** as mentioned above, bp 73–74°C/2 mmHg; yield 46%. IR (neat): 3090, 2990, 1645, 1595, 1475, 1380, 1240, 985, 930, 880 cm⁻¹. ¹H NMR (CDCl₃): 3.11–4.34 (2H, m), 5.06–6.03 (3H, m), 7.11–7.46 (3H, m) ppm. ¹³C NMR (CDCl₃): 56.94, 57.21, 59.16, 62.14, 120.05, 121.89, 126.71, 127.31, 127.42, 128.77, 128.88, 128.99, 131.05, 131.97, 133.59, 133.76, 134.03, 134.30 ppm. *Anal.* Calcd for C₁₀H₈Cl₂O: C, 55.84%; H, 3.75%. Found: C, 55.48%; H, 3.74%.

Synthesis of 2-Phenyl-3-vinyloxirane (1a)

1a was synthesized by the method reported previously.² Yield 76%, bp 67–69°C/3.5 mmHg (lit.² 99–100°C/16 mmHg), ¹H NMR (CDCl₃): 3.25–4.30 (2H, m), 5.10–5.80 (3H, m), 7.10–7.45 (5H, m) ppm.

Synthesis of 2-(p-Chlorophenyl)-3-vinyloxirane (1e)

1e was synthesized as previously shown.² Yield 50%, bp 135°C/15 mmHg (lit.² 135°C/15 mmHg), ¹H NMR (CDCl₃): 3.17–4.26 (2H, m), 5.11–5.96 (3H, m), 7.00–7.43 (4H, m)

ppm.

Radical Polymerization of **1a**, **1e**, and **2–5**

A typical procedure is as follows: after the monomer (3 mmol), radical initiator (3 mol%), and chlorobenzene (PhCl) (12 mmol) were placed in a glass ampoule, the mixture was degassed and sealed *in vacuo*. Polymerization was carried out at a set temperature for 48 hours as shown in Table I. The polymer was isolated by pouring the reaction mixture into methanol. The spectral data of the polymers (Run 9–12 in Table I) are as follows:

Polymer from **2**. IR (KBr): 3050, 2920, 1660, 1385, 1350, 1195, 1080, 1045 cm^{-1} , ^1H NMR (CDCl_3): 1.29–3.00 (br, $-\text{CH}_2-\text{C}=\text{C}-$), 3.54–5.43 (br, $-\text{CH}=\text{C}-\text{O}-$ and $-\text{O}-\text{CH}(\text{Ar})-$), 5.50–6.29 (br, $-\text{C}=\text{CH}-\text{O}-$), 6.59–8.43 (br, Ar-H) ppm, ^{13}C NMR (CDCl_3): 30.61, 34.18, 78.99, 100.66, 101.52, 127.47, 128.77, 131.97, 132.67, 133.43, 133.54, 136.99, 137.55, 145.30, 145.46, 146.54, 146.70, 146.81 ppm.

Polymer from **3**. IR (KBr): 3050, 2900, 1665, 1400, 1350, 1060 cm^{-1} , ^1H NMR (CDCl_3): 1.23–3.00 (br, $-\text{CH}_2-\text{C}=\text{C}-$), 3.49–5.14 (br, $-\text{CH}=\text{C}-\text{O}-$ and $-\text{O}-\text{CH}(\text{Ar})-$), 5.60–6.14 (br, $-\text{C}=\text{CH}-\text{O}-$), 6.29–8.22 (br, Ar-H) ppm, ^{13}C NMR (CDCl_3): 32.13, 35.86, 79.53, 80.88, 82.67, 101.20, 101.69, 112.63, 112.74, 113.71, 114.74, 121.19, 121.95, 129.53, 129.80, 143.94, 144.32, 145.03, 145.30, 157.27, 168.16 ppm.

Polymer from **4**. IR (KBr): 3050, 2900, 1660, 1350, 1060 cm^{-1} , ^1H NMR (CDCl_3): 1.20–3.03 (br, $-\text{CH}_2-\text{C}=\text{C}-$), 3.40–5.20 (br, $-\text{CH}=\text{C}-\text{O}-$ and $-\text{O}-\text{CH}(\text{Ar})-$), 5.45–6.11 (br, $-\text{C}=\text{CH}-\text{O}-$), 6.29–8.29 (br, Ar-H) ppm, ^{13}C NMR (CDCl_3): 32.40, 36.19, 37.54, 38.63, 56.99, 63.49, 101.36, 101.74, 114.69, 115.23, 115.66, 128.01, 128.34, 136.79, 137.49, 145.51, 146.76, 156.84, 167.78 ppm.

Polymer from **5**. IR (KBr): 3060, 2920, 1660, 1360, 1060 cm^{-1} , ^1H NMR (CDCl_3): 1.26–3.14 (br, $-\text{CH}_2-\text{C}=\text{C}-$), 3.49–5.39 (br, $-\text{CH}=\text{C}-\text{O}-$ and $-\text{O}-\text{CH}(\text{Ar})-$), 5.57–6.09 (br, $-\text{C}=\text{CH}-\text{O}-$), 6.17–8.14 (Ar-H) ppm,

^{13}C NMR (CDCl_3): 31.04, 34.56, 74.22, 76.17, 101.47, 103.26, 104.39, 104.50, 110.68, 111.55, 123.52, 128.72, 145.04, 156.35, 156.84, 164.85, 167.78 ppm.

RESULTS AND DISCUSSION

Halogenated phenyl-3-vinyloxiranes (**2–5**) were synthesized in good yields as reported previously.²

Radical polymerizations of vinyloxiranes **2–5** were carried out in PhCl or bulk for 48 hours in the presence of azobisisobutyronitrile (AIBN) or di-*t*-butylperoxide (DTBP) (3 mol% for vinyloxirane) in sealed tube. Radical polymerizations of **1a** (X=H) and **1e** (X=Cl) were also performed under the same conditions for comparison with the results of **2–5**. The polymers were isolated by pouring the reaction mixture into methanol. The results are summarized in Table I. **1a** and chlorinated phenyl-3-vinyloxiranes **1e** and **2** gave the corresponding polymers with molecular weights (\bar{M}_n) 2400–3400 by polymerization in bulk at 60°C (Runs 1–3). The molecular weight of the polymer obtained from 2-(*m*-fluorophenyl)-3-vinyloxirane **3** was essentially the same as that of the polymer from **1a** (Run 4), whereas **4** and **5** gave polymers with molecular weights twice those of the polymers obtained from **1a**, **1e**, **2**, and **3** in polymerization in bulk at 60°C (Runs 5 and 6).

The radical polymerizations of **1a**, **1e**, and **2–5** were also carried out in PhCl at 120°C to afford the corresponding polymers having a vinyl ether moiety in the backbone *via* cleavage of the carbon–carbon bond of the oxirane ring. The molecular weights of the polymers obtained from fluorinated phenyl-3-vinyloxiranes **3–5** were higher than those obtained from **1a**, **1e**, and **2**. 2-(*p*-Fluorophenyl)-3-vinyloxirane **4** afforded the polymer with high molecular weight ($\bar{M}_n=11800$) (Run 11). The polymer obtained from 2-(*p*-chlorophenyl)-3-vinyloxirane **1e** had lower molecular weight ($\bar{M}_n=3200$) (Run 8). The same was observed in the radical

polymerization of 2-(*o,p*-difluorophenyl)-3-vinylloxirane **5** and 2-(*o,p*-dichlorophenyl)-3-vinylloxirane **2**. The molecular weights of the polymers obtained from **5** and **2** were 9300 and 1600, respectively (Runs 9 and 12). The polymer obtained from **4** bearing a fluorine atom at *p*-position had higher molecular weight than that from **3** bearing a fluorine atom at *m*-position (Runs 10 and 11). In a comparison of the radical polymerizations of **1a**, **1e**, and **2**, molecular weights of the polymers decreased in the following order: **1a** > **1e** > **2** (Runs 7–9). Thus, fluorinated phenyl-3-vinylloxiranes **3–5** gave higher molecular weight polymers than **1a** and chlorinated phenyl-3-vinylloxiranes **1e** and **2**.

The structures of the obtained polymers were confirmed by IR and ^1H NMR spectra. Cho *et al.* reported that the structure of the polymer from **1a** was confirmed by IR and ^1H NMR by a comparison with that of a model compound obtained by the radical addition of benzenethiol to **1a**. IR and ^1H NMR data of the model compound were compatible with those of polymers from **1e** and **2–5**. In the IR spectra of the starting vinylloxiranes and the obtained polymers, absorption around 880 cm^{-1} due to the oxirane disappeared completely and absorption around 1660 cm^{-1} due to the vinyl ether group was observed after rad-

ical polymerization. All ^1H NMR spectra of the polymers were very similar to that of the polymer from **1a**, and showed very broad signals at *ca.* 1.3–3.0 ($-\text{CH}_2-\text{C}=\text{C}-$), 3.5–5.4 ($-\text{CH}=\text{C}-\text{O}-$ and $-\text{O}-\text{CH}(\text{Ar})-$), 5.5–6.2 ($-\text{C}=\text{CH}-\text{O}-$), and 6.3–8.2 (Ar-H), respectively. ^{13}C NMR spectra of the polymers from **1a**, **1e**, and **3–5** showed that signals around 54.0–63.0 corresponding to the oxirane carbons disappeared completely. These spectral data give indication that the radical ring-opening polymerizations (1,5-polymerization) of **1a**, **1e**, and **3–5** proceed through cleavage of the carbon-carbon bond of the oxirane as also reported by Cho *et al.*³ and Endo *et al.*^{2,4} In the ^{13}C NMR of the polymer from **2**, very small signals (56.99, 57.21, and 59.21 ppm) possibly due to the oxirane carbons were observed. The radical polymerization of **2** would thus appear to be 1,5-polymerization accompanied by a small amount of 1,2-polymerization (vinyl polymerization).

The reason why **3** and **4** lead to the formation of the polymer with higher molecular weight is not clear at present. In the radical polymerizations of *p*-substituted styrenes, the rate constant (k_p) for propagation increases as the Hammett substituent constant (σ_p) increases [k_p : H < F ($\sigma_p = 0.062$) < Cl ($\sigma_p = 0.227$) < Br ($\sigma_p = 0.232$)] and the rate constant

Table I. Radical polymerizations of **1a**, **1e**, and **2–5**

| Run | Oxirane | Solvent | Initiator | Temp/ $^{\circ}\text{C}$ | Yield/% ^a | \bar{M}_n^b | \bar{M}_w/\bar{M}_n^b |
|-----|-----------|---------|-----------|--------------------------|----------------------|---------------|-------------------------|
| 1 | 1a | Bulk | AIBN | 60 | 10 | 3400 | 1.84 |
| 2 | 1e | Bulk | AIBN | 60 | 12 | 2800 | 1.81 |
| 3 | 2 | Bulk | AIBN | 60 | 14 | 2400 | 2.25 |
| 4 | 3 | Bulk | AIBN | 60 | 8 | 3400 | 1.65 |
| 5 | 4 | Bulk | AIBN | 60 | 11 | 6100 | 1.67 |
| 6 | 5 | Bulk | AIBN | 60 | 10 | 6600 | 1.65 |
| 7 | 1a | PhCl | DTBP | 120 | 36 | 4200 | 7.91 |
| 8 | 1e | PhCl | DTBP | 120 | 32 | 3200 | 3.07 |
| 9 | 2 | PhCl | DTBP | 120 | 29 | 1600 | 2.61 |
| 10 | 3 | PhCl | DTBP | 120 | 32 | 6800 | 2.81 |
| 11 | 4 | PhCl | DTBP | 120 | 43 | 11800 | 8.70 |
| 12 | 5 | PhCl | DTBP | 120 | 39 | 9300 | 3.68 |

^a Insoluble in MeOH. ^b Estimated by GPC (based on PSt).

(k_t) for termination increases in the following order: Br < Cl < H < F.⁵ The molecular weights of the polymers obtained from **1a** (*p*-H), **1e** (*p*-Cl), and **4** (*p*-F) increased as k_t increased (Runs 1, 2, 4, 7, 8, and 11). It is reported that propagating radicals from styrene and *p*-chlorostyrene terminate entirely by coupling.^{6,7} The mode of termination may be coupling in the polymerization of vinyloxiranes, since the propagating radicals (benzyl radical) from vinyloxiranes are the same as those from styrenes. It is assumed that differences in k_t may cause different results in the radical polymerizations of **1a**, **1e**, and **2–5**. Also the electronic effect of fluorine atom presumably may possibly lead to easy cleavage of the carbon–carbon bond of the oxirane ring and inhibit side reactions such as chain transfer, since **4** and **5** having weak electron-withdrawing group (F: $\sigma_p=0.026$) gave higher molecular weight polymers than **1e**, **2**, and **3**

having strong electron-withdrawing group (F: $\sigma_m=0.337$, Cl: $\sigma_p=0.227$) except for **1a**.

REFERENCES

1. (a) T. Endo and T. Yokozawa, "New Methods for Polymer Synthesis," W. J. Mijis, Ed., Plenum Press, New York, 1992, p 155; (b) W. J. Bailey, P. Y. Chen, S.-C. Chen, W.-B. Chiao, T. Endo, B. Gapud, V. Kuruganti, Y.-N. Lin, Z. Ni, C.-Y. Pan, S. E. Shaffer, L. Sidney, S.-R. Wu, N. Yamamoto, N. Yamazaki, K. Yonezawa, and L.-L. Zhou, *Makromol. Chem., Macromol. Symp.*, **6**, 81 (1986).
2. T. Endo and N. Kanda, *J. Polym. Sci., Polym. Chem. Ed.*, **23**, 1931 (1985).
3. I. Cho and J.-B. Kim, *J. Polym. Sci., Polym. Lett. Ed.*, **21**, 433 (1983).
4. T. Koizumi, Y. Nojima, and T. Endo, *J. Polym. Sci., Polym. Chem. Ed.*, **31**, 3489 (1993).
5. M. Imoto, M. Kinoshita, and M. Nishigaki, *Macromol. Chem.*, **86**, 212 (1965).
6. J. C. Bevington and H. W. Melville, *J. Polym. Sci.*, **12**, 449 (1952).
7. G. Ayrey, F. G. Levitt, and R. J. Mazza, *Polymer*, **6**, 157 (1965).