Macromolecules **1992,** *25,* 6719–6721 **6719**

Selective Radical Ring-Opening Polymerization of α-Cyclopropylstyrene

Fumio Sanda, Toshikazu Takata, and Takeshi Endo*

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

Received July 14, 1992
Revised Manuscript Received September 28, 1992

Cyclic monomers which 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. Many monomers and materials polymerize and cure via a radical process. Since generally vinyl polymerization is accompanied by larger volume shrinkage than ring-opening polymerization, monomers and materials that show lower shrinkage through radical polymerization as a major mode of vinyl polymerization are especially useful. Cyclic monomers bearing a vinyl group such as vinylcyclopropane and vinyloxirane have been reported to undergo radical ring-opening polymerization.[1] 1,1-Disubstituted 2-vinylcyclopropanes (1) undergo radical ring-opening polymerization to give polymers bearing not only unit 2 (Scheme I) but also other units such as a cyclobutane-containing unit.[2]

The incomplete selectivity in the radical polymerization of 1 probably comes from the instability of radical intermediate 1′ (Scheme I). Thus the introduction of a radical-stabilizing group into vinylcyclopropane would increase the selectivity of the polymerization. In this paper, the selective radical polymerization of α-cyclopropylstyrenes (3) is disclosed. Cationic polymerization of 3 has been reported to afford polymers bearing three possible units (4, 5, and 6) (Scheme II).[3]

The monomers, **3a** (X = OMe), **3b** (X = H), and **3c** (X = Cl), were prepared by Wittig reaction of the corresponding cyclopropyl ketones (Scheme III),[4] and their structures were determined by spectral and analytical data.

Radical polymerization of 3 was carried out in the presence of an appropriate initiator (3 mol % vs monomer) in bulk for 20 h. Both methanol-insoluble and soluble polymers were obtained as colorless transparent viscous oils. Results and conditions are summarized in Table I. Radical polymerizability decreased in the following order: **3c** > **3b**, **3a**. The molecular weight of the polymer decreased while the conversion increased at higher temperature.

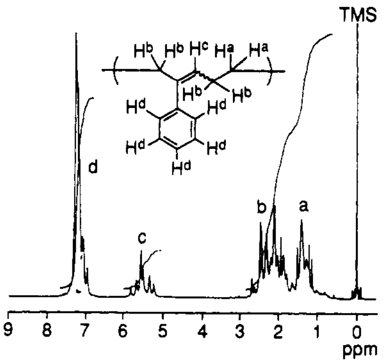


Figure 1. ^{1}H NMR spectrum of poly(**3b**) (run 6 in Table I, solvent CDCl$_3$, 500 MHz).

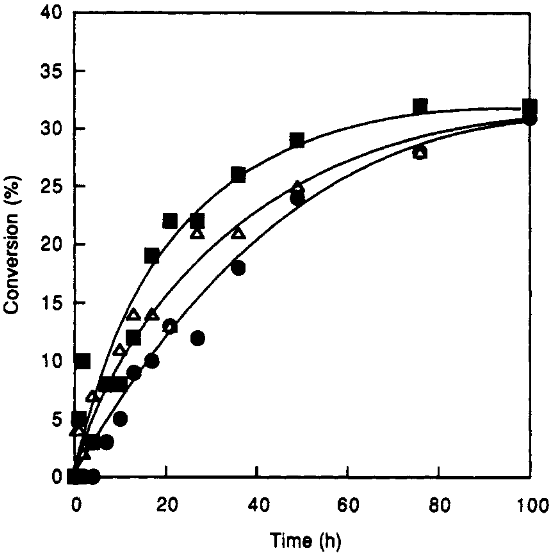
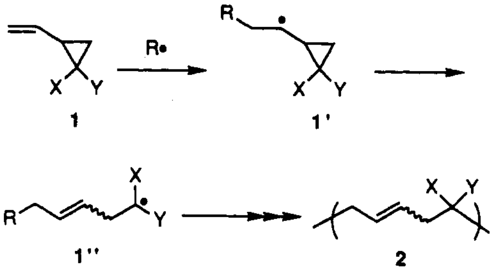


Figure 2. Time–conversion curves in the polymerizations of **3a**, **3b**, and **3c** estimated by ^{1}H NMR (60 MHz): (Δ) **3a**; (●) **3b**; (■) **3c** (DTBP 3 mol %, C$_6$D$_6$ 4 equiv, 120 °C).

Scheme I



The ^{1}H NMR spectrum of poly(**3b**) obtained in run 6 (Table I) is shown in Figure 1. Poly(**3b**) obtained in runs 4 and 5 (Table I) showed spectra similar to that of poly(**3b**) from run 6. The vinyl proton appeared around 5.6 ppm, and its integration ratio was exactly consistent with the proposed polymer structure which would be formed

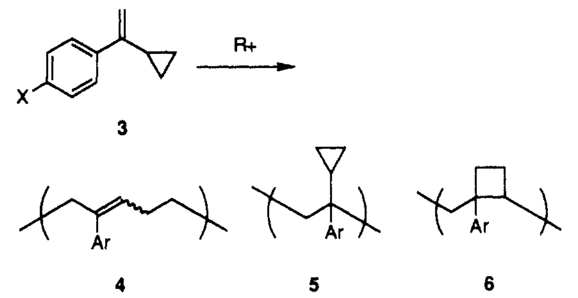
Table I
Radical Polymerization of 3a, 3b, and 3c[a]

run	monomer	init[b]	temp (°C)	conv[c] (%)	yield[d] (%) insol	yield[d] (%) sol	$\bar{M}_n$ ($\bar{M}_w/\bar{M}_n$)[e] insol	$\bar{M}_n$ ($\bar{M}_w/\bar{M}_n$)[e] sol
1	**3a**	AIBN	60	25	14	8	3300 (1.9)	2100 (2.0)
2	**3a**	BPO	80	16	4	4	1700 (1.6)	920 (1.8)
3	**3a**	DTBP	120	47	31	10	1400 (1.7)	500 (1.2)
4	**3b**	AIBN	60	32	23	5	3600 (2.0)	2300 (1.4)
5	**3b**	BPO	80	28	19	6	2400 (2.0)	1000 (1.5)
6	**3b**	DTBP	120	47	35	6	1400 (2.0)	300 (1.3)
7	**3c**	AIBN	60	24	16	7	7100 (1.7)	4100 (1.9)
8	**3c**	BPO	80	38	23	7	4100 (1.9)	2400 (1.8)
9	**3c**	DTBP	120	52	43	7	2500 (1.7)	1300 (1.2)

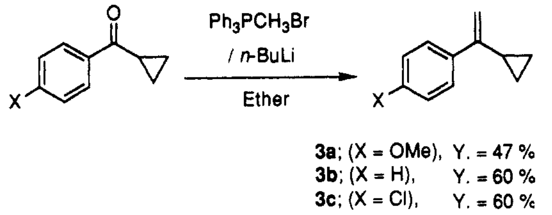
[a] Conditions: bulk, monomer 3 mmol, 20 h. [b] Initiator 3 mol %; AIBN = 2,2′-azobis(isobutyronitrile), BPO = benzoyl peroxide, DTBP = di-*tert*-butyl peroxide. [c] Estimated by ^{1}H NMR. [d] Methanol-insoluble and soluble parts. [e] Estimated by GPC (based on PSt.).

0024-9297/92/2225-6719$03.00/0 © 1992 American Chemical Society

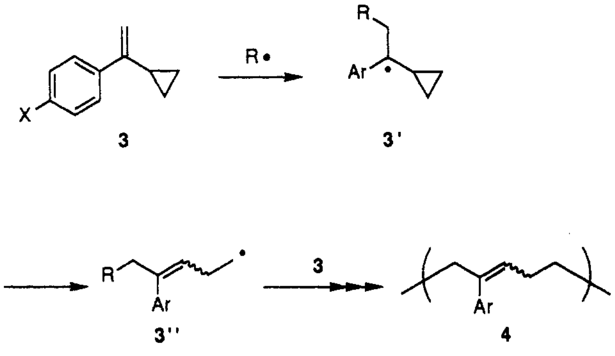
Scheme II



Scheme III



Scheme IV



via clean 1,5-ring-opening polymerization. Allylic (b) and main-chain methylene (a) protons appeared in a good integration ratio around 1.0–2.8 ppm. The cyclopropane ring was not observed in the NMR of the polymer, in which there was no signal corresponding to the cyclopropane protons at 0.5–0.9 ppm. Strong infrared absorptions at 3060 (**3a** and **3b**) and 3075 cm^{-1} (**3c**) due to the cyclopropane ring observed in the IR spectra of the monomers disappeared in the IR spectra of the corresponding polymers. Therefore, the structure of the obtained polymer was determined as **4**, which was undoubtedly formed by selective 1,5-ring-opening polymerization. The vinyl polymerization unit **5** and the cyclobutane-containing unit **6**, which were reported in the cationic polymerization of **3b**,[3] were not confirmed.

The ratio of the observed rates of the polymerizations of **3a–c** was estimated to be **3c**:**3a**:**3b** = 2.0:1.6:1 from time–conversion curves (Figure 2). The conversion was estimated by the integration ratio of the vinyl proton of the monomer in the ^1H NMR spectrum. Each measurement was carried out in a degassed sealed NMR tube. The effect of the para substituent on the rate of the polymerization is not the same as that of para-substituted styrenes,[5] probably because the para substituent affects the reactivity of monomers **3** and primary radical **3′** much more than it does the reactivity of the propagating homoallyl end radical **3″** (Scheme IV). Isomerization from **3′** to **3″** in Scheme IV should be very fast, since the rate of the rearrangement of cyclopropylmethyl radical to 3-butenyl radical is very high.[6,7] Consequently, only **4** was formed. Therefore, the rate-determining step of the polymerization would be the addition of **3″** to **3**, supporting the above assumption. A possible mechanism for the polymerization is illustrated in Scheme IV.

Table II
Volume Change on Radical Polymerization of 3a, 3b, and 3c

	density[a]		
monomer	monomer	polymer	vol change[b] (%)
3a	1.010	1.083[c]	-7.23
3b	0.958	1.040[d]	-8.56
3c	1.090	1.173[e]	-7.61

[a] Measured by density gradient tubes at 25 °C. [b] [Density(monomer) − density(polymer)]/density(monomer) × 100. [c] Run 3 in Table I. [d] Run 6 in Table I. [e] Run 9 in Table I.

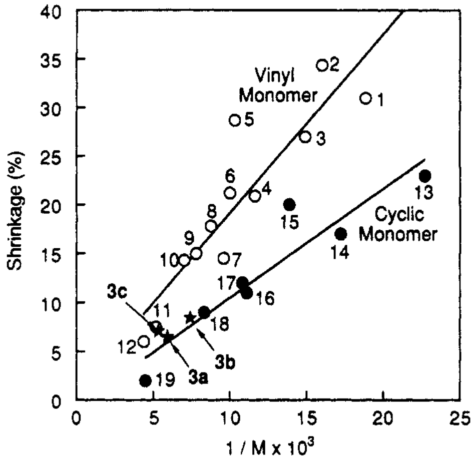


Figure 3. Relationship between volume shrinkage on polymerization and molecular weight (M): 1, acrylonitrile; 2, vinyl chloride; 3, methacrylonitrile; 4, vinyl acetate; 5, vinylidene chloride; 6, methyl methacrylate; 7, styrene; 8, ethyl methacrylate; 9, *n*-propyl methacrylate; 10, *n*-butyl methacrylate; 11, *N*-vinylcarbazole; 12, 1-vinylpyrene; 13, ethylene oxide; 14, propylene oxide; 15, 2,2-dimethylethylene oxide; 16, 1,3,5-trioxane; 17, epichlorohydrin; 18, styrene oxide; 19, hexamethylcyclotrisiloxane.

Generally, ring-opening polymerization occurs with a volume shrinkage smaller than that of vinyl polymerization. The volume change during the polymerization of **3** was evaluated from the densities of the monomers and the polymers obtained in the radical polymerization. The results are summarized in Table II.

The relationship between volume shrinkage on polymerization and the reciprocal of the molecular weight of **3** is shown together with those of several cyclic and vinyl monomers[8] in Figure 3.

Both cyclic and vinyl monomers show a linear relationship between the volume shrinkage on polymerization and the reciprocal of the molecular weight of the monomer.[8] The larger the molecular weight of the monomer becomes, the smaller the shrinkage becomes. Shrinkage of vinyl monomers is about 2 times larger than that of ring-opening monomers. The difference in degree of volume shrinkage between cyclic and vinyl monomers can be explained by the difference in changes of bond length and distance between molecules on polymerization.[9] **3a**, **3b**, and **3c** showed some shrinkage similar to that observed in ordinary cyclic monomers. It is significant that this radical polymerization causes a rather low shrinkage in volume. This result is caused by **3a**, **3b**, and **3c**.

References and Notes

(1) Endo, T.; Yokozawa, T. *New Method for Polymer Synthesis*; Mijs, W. J., Ed.; Plenum Press: New York, 1992; p 155.
(2) Sanda, F.; Takata, T.; Endo, T. *63rd National Meeting of the Chemical Society of Japan*, 1992, 1A1 12, Osaka.
(3) Ketley, A. D.; Berlin, A. J.; Fisher, L. P. *J. Polym. Sci., Part A-1* **1967**, *5*, 227.

(4) Okamoto, T.; Kobayashi, K.; Oka, S.; Tanimoto, S. *J. Org. Chem.* **1988**, *53*, 4897.

(5) Imoto, M.; Kinoshita, M.; Nishigaki, M. *Makromol. Chem.* **1965**, *86*, 217.

(6) House, H. O. *Acc. Chem. Res.* **1976**, *9*, 59.

(7) *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; John Wiley & Sons: New York, 1968–1976; Vols. 1–5.

(8) Endo, T.; Ogasawara, T. *Netsukoukaseijushi* **1984**, *5*, 30.

(9) Takata, T.; Endo, T. *Expanding Monomers: Synthesis, Characterization, and Application*; Sadhir, R. K., Luck, R. M., Eds.; CRC Press: Boca Raton, FL, 1992; Chapter 3.