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Radical Ring-Opening Polymerization of α-Cyclopropylstyrenes. Polymerization Behavior and Mechanistic Aspects of Polymerization by the Molecular Orbital Method

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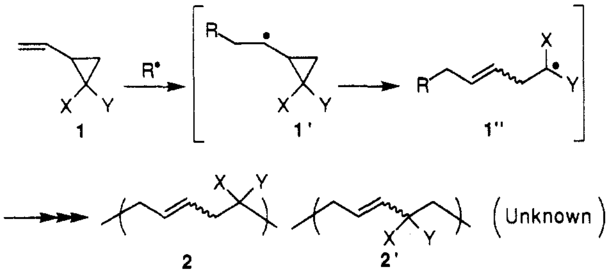
ABSTRACT: Synthesis and radical polymerization of substituted α-cyclopropylstyrenes [1-(4-substituted phenyl)-1-cyclopropylethylene; **3a** (X = OMe), **3b** (X = H), and **3c** (X = Cl)] were carried out. **3a–c** were prepared by the Wittig reaction of the corresponding cyclopropyl aryl ketones. The radical polymerization of **3** was performed in the presence of an appropriate radical initiator (3 mol % vs monomer) at 60–120 °C. The molecular weight of the polymer obtained decreased while the conversion of the monomer increased, as the polymerization temperature rose. The structure of the polymer was determined to consist only of the unit formed by selective 1,5-ring-opening polymerization. The ratio of the observed rates of polymerization was estimated to be **3c**:**3a**:**3b** = 2.0:1.6:1. The effect of a para substituent on the rate of polymerization was not the same as that of para substituted styrenes. The electron density of vinyl β-carbon of **3** decreased in the following order: **3a** > **3b** > **3c**, being the same as that of para substituted styrenes from ^{13}C NMR analysis and molecular orbital calculation. The rate of polymerization was suggested to be affected by the polarity of the monomers (**3**). The dipole moment as an index of polarity well explained the order of the rate of polymerization. **3** showed shrinkage similar to those of common cyclic monomers with similar molecular weights; 7.23–8.56%. This value was consistent with the occurrence of the selective radical ring-opening polymerization of **3**. T_g of the polymers (**4**) obtained was lower by 94–102 °C than corresponding poly(para-substituted styrene)s.

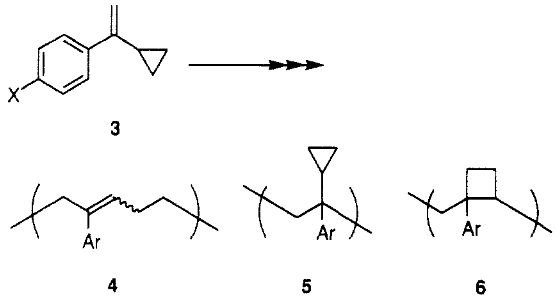
Introduction

Cyclic monomers which undergo ring-opening polymerization are important in the field of materials such as precision materials, adhesives, and so on, since they show low shrinkages or sometimes expansion in volume on polymerization.[1] Many monomers and materials polymerize and cure via a radical process. Since generally vinyl polymerization is accompanied by volume shrinkage larger than ring-opening polymerization, monomers and materials that show lower shrinkage through radical polymerization as the major mode of polymerization are especially useful. Some cyclic monomers bearing vinyl groups such as 1,1-disubstituted 2-vinylcyclopropanes (**1**) have been reported to undergo radical ring-opening polymerization.[2] Recently, it has been clarified that a few units other than units **2** and/or **2′** obtained by 1,5-ring-opening polymerization are involved (Scheme I).[2c]

Scheme I



Scheme II



The incomplete selectivity in the radical polymerization of **1** comes probably from the instability of radical intermediate **1′** (Scheme I). If this is the actual reason, the introduction of a radical-stabilizing group such as a phenyl group into the radical position of **1′** would increase the selectivity of the polymerization. Recently, we have found that when a phenyl group is introduced to the vinyl carbon α to the cyclopropane ring of **1**, selective radical 1,5-ring-opening polymerization is attained.[3] In this paper, synthesis and radical polymerization behavior of α-cyclopropylstyrenes **3**, the elucidation of the effect of a substituent on the polymerization on the basis of polarity, the volume change during the polymerization of **3**, and thermal properties of polymers obtained are described in detail. α-Cyclopropylstyrenes **1** can be regarded as one of the α-substituted styrenes like α-methylstyrene of which cationic, anionic, and radical polymerizations are extensively studied. As for **3**, only cationic polymerization of **3** has been reported to afford a polymer bearing three possible units (**4–6**; Scheme II).[4]

Experimental Section

Measurements. ^{1}H and ^{13}C NMR spectra of monomers and polymers were recorded on JEOL JNM-EX-90 and JNM-GX-500 spectrometers operating in the pulsed FT modes, using tetramethylsilane (TMS) as internal standard in deuteriochloroform at 27 °C. FT-IR spectra were obtained with a Jasco FT/IR-3 at 25 °C. Molecular weight and its distribution (MWD; $\bar{M}_w/\bar{M}_n$) were estimated by gel permeation chromatography (GPC) on a Tosoh HPLC CCP & 8000 system with a data processor, equipped with three polystyrene gel columns (TSK gel, G2000H, G2500H, and G3000H), using tetrahydrofuran as eluent, a flow rate of 1.0 mL/min, polystyrene calibration, and refractive index

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Table I. Radical Polymerization of 3a–c[a]

							yield (%)[d]		$\bar{M}_n$ ($\bar{M}_w/\bar{M}_n$)[e]	
run	monomer	init[b]	chlorobenzene (M)	temp (°C)	time (h)	conv[c] (%)	insol	sol	insol	sol
1	**3a**	AIBN	none	60	20	25	14	8	3300 (1.9)	2100 (2.0)
2	**3a**	BPO	none	80	20	16	4	4	1700 (1.6)	920 (1.8)
3	**3a**	DTBP	none	120	20	47	31	10	1400 (1.7)	500 (1.2)
4	**3a**	DTBP	none	120	40	66	46	18	2400 (1.6)	500 (1.8)
5	**3b**	AIBN	none	60	20	32	23	5	3600 (2.0)	2300 (1.4)
6	**3b**	AIBN	2.8	60	40	26	14	9	2300 (1.4)	700 (1.8)
7	**3b**	BPO	none	80	20	28	19	6	2400 (2.0)	1000 (1.5)
8	**3b**	BPO	2.8	60	40	30	11	9	1900 (1.4)	600 (1.3)
9	**3b**	DTBP	none	120	20	47	35	6	1400 (2.0)	300 (1.3)
10	**3b**	DTBP	none	120	40	71	40	30	2800 (1.8)	900 (2.7)
11	**3b**	DTBP	2.8	80	40	37	9	21	1100 (1.5)	400 (1.5)
12	**3c**	AIBN	none	60	20	24	16	7	7100 (1.7)	4100 (1.9)
13	**3c**	BPO	none	80	20	38	23	7	4100 (1.9)	2400 (1.8)
14	**3c**	DTBP	none	120	20	52	43	7	2500 (1.7)	1300 (1.2)
15	**3c**	DTBP	none	120	40	72	34	35	2600 (1.7)	1000 (2.2)

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

(RI) and ultraviolet (UV) detectors. Thermal analyses were performed on Seiko Instruments TG/DTA220 and DSC220C. A 10% weight loss temperature by thermogravimetric analysis (TGA) was determined at a heating rate of 10 °C/min under a nitrogen atmosphere. The glass transition temperature (T_g) by differential scanning calorimetery (DSC) was taken as the inflection point on the trace.

Measurement of Density. Densities of **3** and poly(**3**) were measured by density gradient tubes at 25 °C with a Shibayama Kagaku Seisakusho Model A.

Molecular Orbital Calculations. All computations were done on an Apple Macintosh IIfx with use of MOPAC version 6.00 (QCPE No. 455) revised as version 6.02 for Apple Macintosh.[5] The calculations were carried out by the restricted Hartree–Fock (RHF) method and the PM3 Hamiltonian. The starting geometries were obtained by a Cambridge Scientific Computing, Inc., Chem 3D Plus version 3.0. All calculations were done with full optimization of all geometrical variables (bond length, bond angles, and dihedral angles).

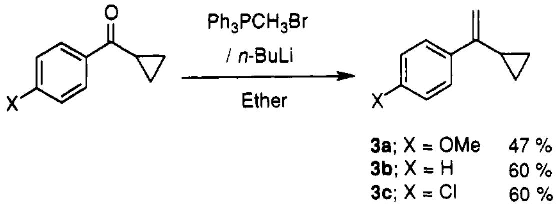
Materials. Initiators 2,2′-azobis(isobutyronitrile) (Tokyo Kasei Kogyo Co.), benzoyl peroxide (Kosoh Chemical, Co.), and di-*tert*-butyl peroxide (Nacalai Tesque, Inc.) were used as received. Chlorobenzene was dried and distilled by the usual method and stored over molecular sieves (4A).

Synthesis of 3a. To a mixture of methyltriphenylphosphonium bromide (101 g, 284 mmol) and ether (670 mL) was added dropwise at 0 °C *n*-butyllithium (1.6 M solution in *n*-hexane, 204 mL, 327 mmol). To the resulting mixture was added dropwise at 0 °C a solution of cyclopropyl 4-methoxyphenyl ketone (50.0 g, 284 mmol) in ether (330 mL). After stirring at room temperature for 3 h, the reaction mixture was washed with water (800 mL). The organic layer was separated, dried over anhydrous sodium sulfate, and evaporated. The residual oil was distilled: yield 23.1 g (47%); bp 96 °C (1.0 mmHg) [lit.[6] bp 116 °C (50 mmHg)]; ^1H NMR ($CDCl_3$) δ 0.46–0.66 (m, 2 H), 0.71–0.91 (m, 2 H), 1.47–1.80 (m, 1 H), 3.79 (s, 3 H), 4.84 (s, 1 H), 5.18 (s, 1 H), 6.77–6.93 (m, 2 H), 7.45–7.61 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 6.5, 15.7, 55.3, 107.4, 113.5, 127.2, 134.2, 148.6, 159.2; IR (neat) 3060, 2990, 2810, 1941, 1605, 1506, 1490, 1241, 1175, 1030, 829 cm^{-1}.

Synthesis of 3b. 3b was prepared from cyclopropyl phenyl ketone similarly to **3a**: yield 60%; bp 104 °C (27 mmHg) [lit.[6] bp 107 °C (25 mmHg)]; ^1H NMR ($CDCl_3$) δ 0.53–0.78 (m, 2 H), 0.81–0.93 (m, 2 H), 1.53–1.78 (m, 1 H), 4.97 (s, 1 H), 5.31 (s, 1 H), 7.26–7.41 (m, 3 H), 7.54–7.69 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 6.7, 15.6, 109.0, 126.1, 127.4, 128.1, 141.7, 149.4; IR (neat) 3060, 2995, 1942, 1880, 1798, 1670, 1620, 1567, 1490, 1441, 1380, 1257, 1019, 883, 770, 699 cm^{-1}.

Synthesis of 3c. 3c was prepared from cyclopropyl 4-chlorophenyl ketone similarly to **3a**: yield 60%; bp 70 °C (0.4 mmHg); ^1H NMR ($CDCl_3$) δ 0.49–0.69 (m, 2 H), 0.73–0.95 (m, 2 H), 1.47–1.77 (m, 1 H), 4.96 (s, 1 H), 5.26 (s, 1 H), 7.22–7.36 (m, 2 H), 7.46–7.61 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 6.6, 15.6, 109.6, 127.4, 128.3, 133.2, 140.1, 148.3; IR (neat) 3075, 2999, 1900, 1620, 1590, 1489, 1087, 1010, 890, 828, 738 cm^{-1}. Anal. Calcd for $C_{11}H_{11}Cl$: C, 73.95; H, 6.21. Found: C, 73.61; H, 6.44.

Scheme III



Polymerization of 3. General Procedure. To a monomer (**3**; 3 mmol) in a polymerization tube was introduced a radical initiator and subsequently dry solvent, if required. The tube was cooled, degassed, sealed off, and heated at a set temperature for 20 h. The resulting mixture was diluted with methylene dichloride (2 mL), and the mixture was poured into methanol (50 mL) to precipitate the polymer. Centrifugal separation followed by removal of solvent by decantation afforded the insoluble part. ^1H NMR and IR spectra of the insoluble part were measured. The methanol-soluble part was concentrated under reduced pressure to afford a mixture of monomer **3** and lower molecular weight polymer.

Results and Discussion

1. Synthesis of Monomer. The monomers (**3**) were prepared by the Wittig reaction of the corresponding cyclopropyl aryl ketones in moderate yields, according to the previously reported method (Scheme III).[7] **3** could be purified by distillation under reduced pressure, while a small amount of polymeric residue was obtained in any case. Thermal polymerizability of **3** was suggested to be lower than styrene.

2. Radical Polymerization of 3. Polymerization of **3** was carried out under some different radical conditions. The results and conditions are summarized in Table I. Both the conversion of the monomers and the yield of the polymers in the bulk polymerization with BPO at 80 °C were lower than those with AIBN at 60 °C (runs 1, 2, 5, and 7). Since the order of the conversions in solution polymerization was reversed (runs 6 and 8), incomplete solubility of BPO in the monomers would result in the low conversion in the bulk polymerization compared to that with AIBN. Both the conversion and the yield in the bulk polymerization of **3b** were higher than those of the solution polymerization (runs 10 and 11). The ratio of the yield of the methanol-soluble poly(**3b**) to that of the methanol-insoluble part in the solution polymerization was larger than that of the bulk polymerization at any temperature

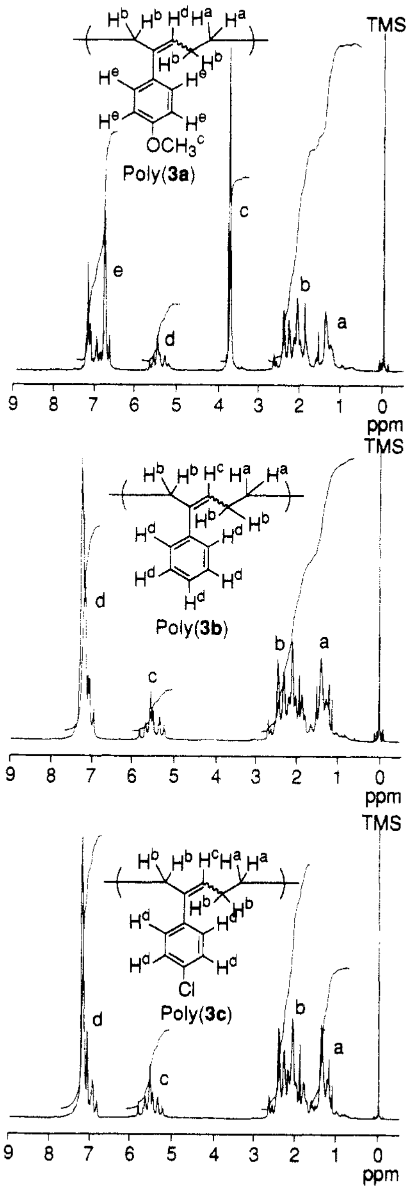


Figure 1. ^{1}H NMR spectra (solvent, CDCl$_3$; 500 MHz) of poly(**3a**) (run 3 in Table I), poly(**3b**) (run 9 in Table I), and poly(**3c**) (run 14 in Table I).

(runs 5–11). The molecular weight of the polymer formed decreased as the polymerization temperature rose in both the bulk and the solution polymerizations. The molecular weight of the polymer obtained by the bulk polymerization was higher than that of the solution polymerization (runs 5–11). The conversion of the monomers, the yield, and the molecular weight of the polymers increased as the polymerization time was prolonged (runs 3, 4, 9, 10, 14, and 15).

^{1}H NMR spectra of poly(**3a**), poly(**3b**), and poly(**3c**) are shown in Figure 1. Vinylic proton signals appeared around 5.6 ppm, and their integration ratio was exactly consistent with the polymer structures which would be formed via a clean 1.5-ring-opening polymerization. Allylic (b) and main-chain methylene (a) protons appeared around 1.0–2.8 ppm with an agreeable integration ratio. No cyclopropane ring proton signal was observed in the NMR spectra of the polymers, in which signals of the cyclopropane protons of the monomers (0.5–0.9 ppm) disappeared completely. Similar ^{1}H NMR spectra were obtained independent of the polymerization conditions in any case. Meanwhile, strong 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 those of the corresponding polymers. From these data, the structure of the obtained polymer was determined as **4**, which was undoubtedly formed by the selective 1,5-ring-opening polymerization. Neither vinyl polymerization unit **5** nor cyclobutane-containing unit **6**, which have been reported to be formed in the cationic polymerization of **3b**,[4] could be confirmed in any polymer.

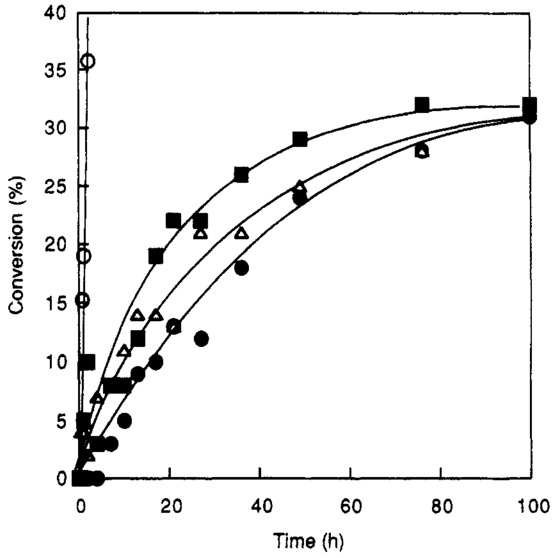
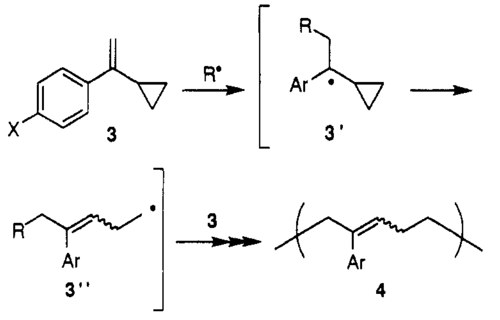


Figure 2. Time–conversion curves of the polymerizations of **3a–c** and styrene which were obtained by monitoring by ^{1}H NMR (60 MHz): (△) **3a**; (●) **3b**; (■) **3c**; (○) styrene. DTBP, 3 mol %; C$_6$D$_6$, 2.8 M, 120 °C.

Scheme IV



The ratio of the observed rates of polymerization of **3a–c** was estimated to be **3c**:**3a**:**3b** = 2.0:1.6:1 from the time–conversion curves (Figure 2). The effect of a para substituent on the rate is not the same as that of para-substituted styrenes,[8] probably because the para substituent little affects the reactivity of the propagating homoallyl end radical of **3″** as easily understood from its structure but only affects the reactivity of both the monomers **3** and primary radical **3′** (Scheme IV). Isomerization of **3′** to **3″** should be very fast, since the rate of the rearrangement of a cyclopropylmethyl radical to a 3-butenyl radical is very large.[9] Consequently, only **4** was formed. Therefore, the rate-determining step of the polymerization would be the addition of **3″** to **3**, like the cases of the usual vinyl polymerizations. The observed rates of the polymerizations of **3a–c** were fairly smaller than that of styrene (1/3.5 to 1/7) (Figure 2). The absence of a group that stabilizes the propagating homoallyl end radical of **3″** would lower the rate of the polymerization compared to styrene, which polymerizes via the stabilized propagating benzyl radical.

To obtain some information on the substituent effect, ^{13}C NMR analysis of **3** was carried out. The relationship between Hammett's substituent constant value (σ_p) and the ^{13}C NMR chemical shift of the vinylic β-carbon in the

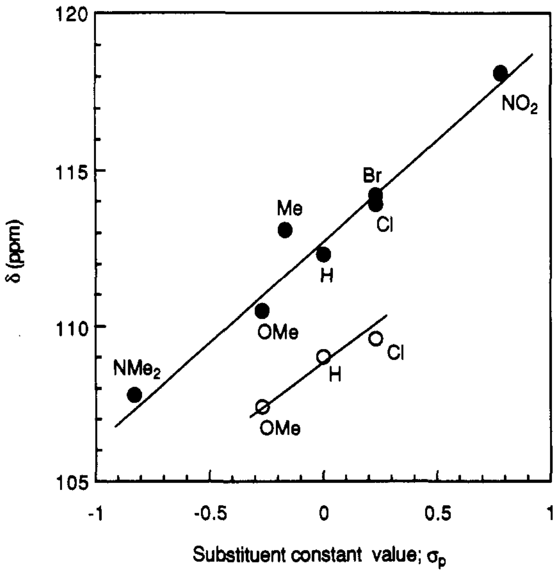


Figure 3. Plots of the ^{13}C NMR chemical shift of the vinylic β-carbon of α-cyclopropylstyrenes and para-substituted styrenes vs Hammett's constant (σ): (○) para-substituted α-cyclopropylstyrenes; (●) para-substituted styrenes (solvent, $CDCl_3$; 22.5 MHz).

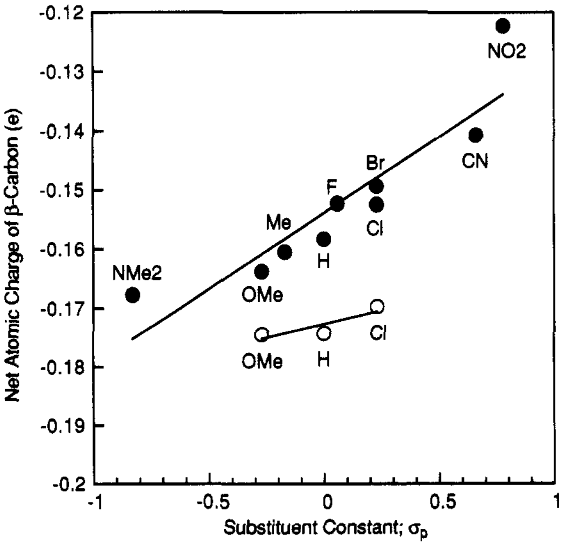
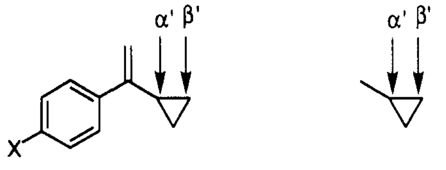


Figure 4. Calculated electron density of para-substituted α-cyclopropylstyrenes and styrenes: (○) para-substituted α-cyclopropylstyrenes; (●) para-substituted styrenes.

^{13}C NMR spectra of para-substituted styrenes and α-cyclopropylstyrenes is shown in Figure 3. A linear relationship is observed in both a series of para-substituted styrenes and that of α-cyclopropylstyrenes. The larger the σ_p value becomes, the larger the ^{13}C NMR chemical shift value of the vinylic β-carbon becomes. This result seems to suggest that the order of the electron density of the vinylic β-carbons of **3a–c** is as the same as that of para-substituted styrenes. The electron density calculated by the molecular orbital method well agrees with this result (Figure 4). The details of the calculation are described later in this paper. The signals of the vinylic β-carbon of **3** shift to ca. 4 ppm higher field than those of para-substituted styrenes which have the same substituents (Figure 3). Since the ^{13}C NMR chemical shift of the vinylic β-carbon of α-methylstyrene is just the same as that of styrene and the difference in the chemical shift of β-carbon between **3** and methylcyclopropane is only ca. 1 ppm (Table II), this shift toward higher field observed for **3** should be caused by a shielding effect resulting from the ring current of the cyclopropane.

Table II. ^{13}C NMR Chemical Shift of the Ring Carbon of Cyclopropanes of 3a–c and Methylcyclopropane



X=OMe; 3a, H; 3b, Cl; 3c Methylcyclopropane

compound	^{13}C NMR chemical shift[a] (ppm) α′-C	β′-C
3a	15.664	6.530
3b	15.643	6.682
3c	15.556	6.639
methylcyclopropane	4.9[b]	5.6[b]

[a] Solvent, $CDCl_3$; 22.5 MHz. [b] Reported data.[10]

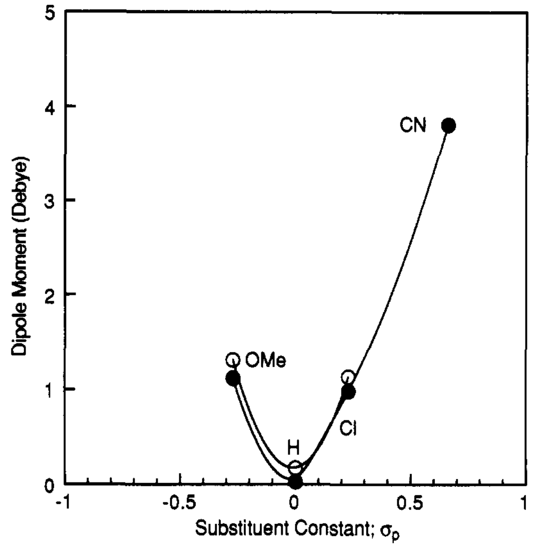


Figure 5. Relationship between substituent constant σ_p and the dipole moment of para-substituted α-cyclopropylstyrenes and styrenes: (○) para-substituted α-cyclopropylstyrenes; (●) para-substituted styrenes.

It has been reported that the charge-transfer complex is formed in the transition state of radical polymerization of para-substituted styrene.[8] So, the polarity of the polymerization system would affect the rate of polymerization of **3** like in cationic polymerization of *p*-methoxystyrene.[11] The relationship between the calculated dipole moment which is thought to be an index of the polarity of the system and the substituent constant is shown for α-cyclopropylstyrenes and para-substituted styrenes in Figure 5. The calculation of the dipole moment was carried out by the semiempirical molecular orbital method (PM3). The dipole moment of **3b** is the smallest of the three monomers. As we mentioned previously, a styrene having a more electron-withdrawing group exhibits a larger rate in the radical polymerization of **3**. As shown in Figure 6 plots of the rate of the radical polymerization vs Hammett's substituent constant of **3** show a U-shape curve which is clearly different from the linear relationship of the styrenes. The U-shape curve, however, is similar to that of the dipole moment (Figure 5). It has been reported that the rate of radical polymerization of butyl acrylate in chlorobenzene and anisole is larger than that in benzene,[12] indicating a positive effect of the polarity on the rate. Namely, the rate of polymerization is accelerated in the polar solvent. Similarly to this report, the polarity of the monomers would affect the radical polymerization

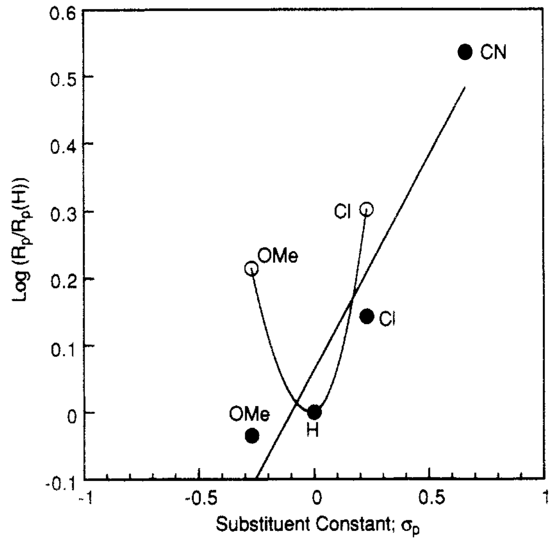
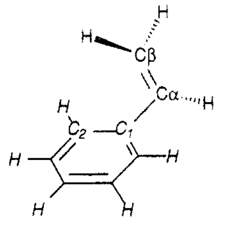


Figure 6. Relationship between substituent constant σ_p and $\log(R_p(X)/R_p(H))$ of para-substituted α-cyclopropylstyrenes and styrenes: (○) para-substituted α-cyclopropylstyrenes; (●) para-substituted styrenes.



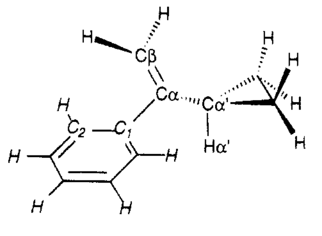
Φ=dihedral angle for C_2-C_1-C_α-C_β

Figure 7. Dihedral angle of styrene between the benzene ring and the vinyl group.

of 3 rather than the electronic effect, consequently giving the different behavior from the styrenes.

3. Conformation of 3 for Molecular Orbital Calculation. To calculate the electron densities and dipole moments mentioned above, it is necessary to decide the conformation of 3 which is required for the molecular orbital calculation of 3. Prior to working with 3, we examined the reported data for styrene. π-Conjugation between the benzene ring and the vinyl group shows the largest efficiency in the planer conformation. However, their steric hindrance is smaller in the twisted conformation than in the planar one. Owing to this conflicting factor, the most stable conformation of styrene cannot be simply determined (Figure 7).

Since styrene is liquid at room temperature, it is impossible to decide its conformation by X-ray analysis. The various experimental and theoretical dihedral angles (Φ) and rotational barriers of styrene have been reported by the methods of statistical thermodynamics,[13a,b] Raman spectroscopy,[13b] fluorescence,[13c,e] microwave spectroscopy,[13e] IR,[14] UV,[15] photoelectron,[16] NMR,[13f,g] molecular rotatory polarization,[17] calorimetric[13a] and molecular refractometric studies,[18] molecular mechanics calculation,[13h] and semiempirical and ab initio molecular orbital calculations (Table III).[13i–r] Although the most stable conformation of styrene has not been clearly decided yet, the planar structure seems to be most likely judging from the data reported. Moreover, the difference in the formation energy between the two conformations at Φ = 0° and 15–24° (presented to be the most stable conformation by ab initio calculation[13q,r]) is only 0.1 kcal/mol.



Φ_1=dihedral angle for C_2-C_1-C_α-C_β

Φ_2=dihedral angle for C_β-C_α-$C_{\alpha'}$-$H_{\alpha'}$

Figure 8. Dihedral angles of **3b**: Φ_1 (C_2–C_1–C_α–C_β) formed between the benzene ring and the vinyl group and Φ_2 (C_β–C_α–$C_{\alpha'}$–$H_{\alpha'}$) formed between vinyl and cyclopropyl groups.

Table III. Reported Experimental and Theoretical Dihedral Angles (Φ) for C_2–C_1–C_α–C_β and Rotational Barriers of Styrene

method	Φ (deg)	rotational barrier (kcal/mol)	ref
statistical thermodynamics	0	2.2	13a,b
Raman spectroscopy	0	1.78	13b
fluorescence	0	3.27	13c
fluorescence and Raman	0	3.06	13d
microwave spectroscopy	0	3.29	13e
NMR		1.6	13f
NMR	16.5	4.0	13g
MM2		1.5	13h
MOMM	16	3.2	13i
(5,2/2) contracted		3.9	13j
CNDO/2		4.3	13k
INDO		3.0	13l
C-INDO		3.65	13m
AM1	18	1.39	13n
AM1	20	1.4	13o
ab initio			
HF/minimal basisset	0	3.9	13j
HF/STO-3G		4.4	13p
HF/STO-3G	0	3.89	13q
HF/4-21G	24	2.29	13q
HF/4-31G	18	2.81	13q
HF/6-31G	0	3.13	13r
HF/6-31G*	15.02	2.88	13r

Since 3 is a liquid similarly to styrene at room temperature, it is also impossible to decide the conformation by X-ray analysis. In this work the conformational analysis of 3 by semiempirical molecular orbital calculation was carried out as follows. In the case of **3b**, the calculation was performed considering a dihedral angle which is formed between vinyl and cyclopropyl groups in addition to that formed between the benzene ring and the vinyl group. Formation energies of 74 conformers of **3b**, of which dihedral angles Φ_1 (C_2–C_1–C_α–C_β) and Φ_2 (C_β–C_α–$C_{\alpha'}$–$H_{\alpha'}$) (Figure 8) were fixed as shown below, were calculated. Dihedral angle, bond length, and bond angle except for Φ_1 and Φ_2 were optimized.

Φ_1: 0, 15, 30, 45, 60, 75, and 90°.

Φ_2: −180, −150, −120, −90, −60, −30, 0, 30, 60, 90, 120, 150, and 180°.

The result of the calculation is shown in Figure 9. Among the 74 conformers of **3b**, the most stable one had Φ_1 = 15°, Φ_2 = 150°, and a formation energy of 59.389 525 kcal/mol. The fully optimized conformer starting from this one after removing the constraint of Φ_1 and Φ_2 was calculated to have Φ_1 = 14.85°, Φ_2 = 150.02°, and a formation energy of 59.380 251 kcal/mol.

Similarly, the fully optimized conformer obtained from the conformer which had Φ_1 = 0° and Φ_2 = 180° showed Φ_1 = 0°, Φ_2 = 180°, and a formation energy of 59.762 175 kcal/mol. The difference in the formation energy between

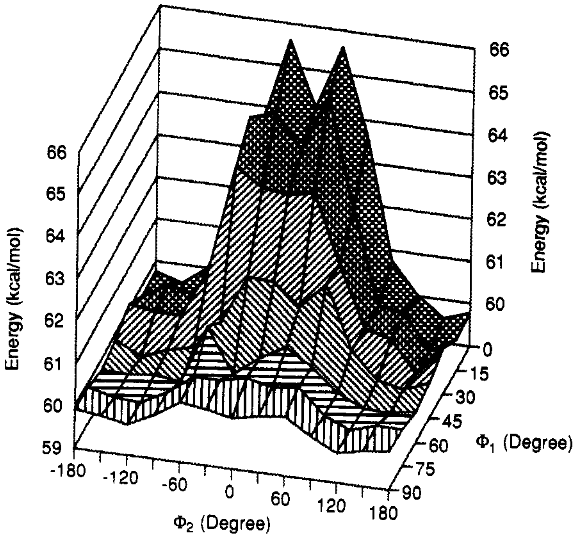


Figure 9. Relationship between the formation energy and dihedral angles Φ_1 (C_2–C_1–C_α–C_β) and Φ_2 (C_β–C_α–$C_{\alpha'}$–$H_{\alpha'}$) of **3b**.

Table IV. Thermal Analysis of Poly(3)

polymer	T_g[a] (°C)	10% weight loss temp[b] (°C)
poly(**3a**)[c]	11	369
poly(**3b**)[d]	0	356
poly(**3c**)[e]	16	350

[a] Measured by DSC. [b] Measured by TGA, under N_2. [c] Run 4 in Table I. [d] Run 10 in Table I. [e] Run 15 in Table I.

these two most stable conformers was only 0.38 kcal/mol. In addition to that, there is no rotational barrier between these conformers judging from Figure 9. So, it would cause no problem to adopt the conformer of which $\Phi_1 = 0°$ and $\Phi_2 = 180°$. In this paper, therefore, we used this conformer for the molecular orbital calculation.

4. Thermal Analysis of Poly(3). The glass transition temperatures of poly(**3a**), poly(**3b**), and poly(**3c**) obtained by the polymerization with DTBP at 120 °C were 11, 0, and 16 °C, respectively. T_g of poly(**3**) was much lower than that of corresponding poly(para-substituted styrene)s [poly(*p*-methoxystyrene), 113 °C; poly(styrene), 100 °C; poly(*p*-chlorostyrene), 110 °C] in any case.[19] Introduction of *p*-methoxy and *p*-chloro groups into poly(**3b**) enhanced the T_g by 11–16 °C, similar to the cases of poly(para-substituted styrene)s. The distance between aromatic groups of poly(**3**) longer than that of poly(para-substituted styrene) should increase the flexibility of the main chain of the polymer and lower its T_g. The 10% weight loss temperature of the polymers under nitrogen was 350–369 °C (Table IV).

5. Volume Change on Polymerization. Generally, ring-opening polymerization is accompanied by volume shrinkage smaller than that of vinyl polymerization.[20] The volume change during the polymerization of **3** was evaluated from densities of the monomers (**3**) and the polymers [poly(**3**)]. The results are summarized in Table V.

Both cyclic and vinyl monomers show a linear relationship between volume shrinkage on polymerization and the reciprocal of molecular weight.[20] The larger the molecular weight of the monomer gets, the smaller the shrinkage becomes. Shrinkage of the vinyl monomers is about 2 times larger than that of the ring-opening monomers. The difference in the 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.[1] **3a–c** showed some shrinkage (7.23–8.56%) which is smaller than that reported for the vinyl monomers and similar to that observed in the ordinary cyclic monomers. It is interesting that this radical polymerization causes rather low shrinkage in volume. This result strongly supports that **3a–c** unambiguously undergo radical polymerization through the clean 1,5-ring-opening process as the above-mentioned spectral data suggest.

Table V. Volume Change on the Radical Polymerization of 3a–c

monomer	density[a] monomer	density[a] polymer	volume 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 9 in Table I. [e] Run 14 in Table I.

Conclusion

In this work, first radical polymerization of α-cyclopropylstyrenes (**3**) was carried out and selective radical 1,5-ring-opening polymerization was achieved. The different substituent effect on the rate of polymerization from para-substituted styrenes was observed. From the studies by the ^{13}C NMR and the molecular orbital calculation, the polarity of the monomers (**3**) was suggested to affect the rate of polymerization of **3** rather than the electron density of the vinylic β-carbon of **3**. The volume shrinkage on polymerization of **3** was smaller than those of vinyl monomers and similar to those of cyclic monomers.

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