

Synthesis of Substituted Polymethylenes from Acenaphthylene by Radical Polymerization and Copolymerization

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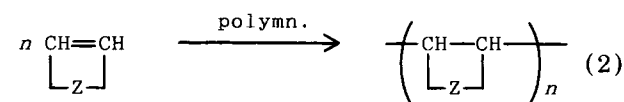
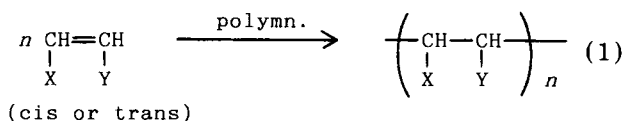
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SYNOPSIS

Radical polymerization of acenaphthylene (Ace) as a 1,2-disubstituted ethylene was investigated. It was found that the polymerization rate (R_p) was expressed as follows: $R_p = k[\text{Ace}]^{1.0}[\text{AIBN}]^{0.68}$, and that the overall activation energy was 113 kJ/mol for polymerization with 2,2'-azobisisobutyronitrile (AIBN) in benzene at 50–70°C. Poly(Ace) obtained was characterized by NMR spectroscopy and GPC. Some substituted copolymethylenes were also prepared by radical copolymerization of Ace with other 1,2-disubstituted ethylenes, that is, maleic anhydride, diisopropyl fumarate, and *N*-cyclohexylmaleimide. The monomer reactivity ratios were determined from comonomer–copolymer composition curves.

INTRODUCTION

We have reported on synthesis of substituted polymethylenes by radical high polymerization of fumaric and maleic derivatives.^{1–11} The substituted polymethylenes produced from linear (acyclic) and cyclic 1,2-disubstituted ethylenes are represented as follows, respectively²:



The polymerization of fumarates (or maleates)^{1–4} and their amide derivatives^{5–8} belongs to the linear and those of *N*-substituted maleimides^{9–11} do to the cyclic. Acenaphthylene (Ace), which is one of the cyclic 1,2-disubstituted ethylenes as well as male-

imides, maleic anhydride,¹² and vinylene carbonate,^{13–15} is well known to polymerize by radical,^{16–25} cationic,^{26–28} and anionic^{22,29} initiators. For example Romani and Weale²¹ reported in 1966 on the radical polymerization kinetics of Ace under high pressure. Recently Springer and coworkers^{23,24,30–33} have reported on synthesis, solution properties, and photodecomposition of the poly(Ace). However, there is no study on synthesis of substituted polymethylenes from Ace as a 1,2-disubstituted ethylene. In this article, radical polymerization and copolymerization of Ace and characterization of the resulting polymethylenes are described.

EXPERIMENTAL

Materials

Ace was purified by recrystallization from benzene, followed by sublimation, and indene was distilled under reduced pressure after they were passed through an alumina column with benzene as an eluent. Styrene (St), maleic anhydride (MAN), diisopropyl fumarate (DiPF), and *N*-cyclohexylmaleimide (CHMI) were purified by distillation or recrystallization after ordinary purification. Other re-

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Table I Radical Polymerization of Ace and Indene in Bulk or in Benzene

Monomer (mol/L)	Initiator ^a (mol/L)	Temp. (°C)	Time (h)	Conversion (%)	$M_n \times 10^{-4}$	\bar{M}_w / \bar{M}_n
Ace (bulk)	ACN (3 mol %)	90	4	64.6	7.5	3.1
Ace (bulk)	ACN (3 mol %)	100	2	71.0	5.5	3.5
Ace (bulk)	DTBP (3 mol %)	100	10	65.7	17.5	3.8
Ace (bulk)	DTBP (3 mol %)	120	5	77.7	14.2	—
Ace (bulk)	None	90	53	3.7	18.0	—
Ace (3.0)	AIBN (0.01)	60	3	4.2	2.7	1.7
Ace (3.0)	AIBN (0.03)	60	3	7.8	1.3	1.6
Ace (3.0)	AIBN (0.05)	60	6.5	24.0	1.1	1.4
Indene (bulk)	ACN (0.13)	90	10	17.5	0.1	2.3
Indene (bulk)	AIBN (0.03)	50	10	4.4	0.2	1.6
Indene (2.1)	AIBN (0.06)	60	10	1.0	0.2	1.6
Indene (bulk)	AIBN (0.05)	0 ^b	26.5	~0	—	—

^a ACN: 1,1'-Azobiscyclohexane-1-carbonitrile; DTBP: di-*tert*-butyl peroxide; AIBN: 2,2'-azobisisobutyronitrile.

^b With UV irradiation.

agents and solvents were purified by ordinary methods.

2,2'-Azobisisobutyronitrile (AIBN) and 1,1'-azobiscyclohexane-1-carbonitrile (ACN) were recrystallized from methanol. Di-*tert*-butyl peroxide (DTBP) was used as received without further purification.

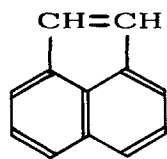
Polymerization

Polymerization was carried out in a sealed glass tube. The polymer produced was precipitated with a large amount of methanol, was filtered, and was then dried under vacuum. Copolymerization was carried out similarly. The copolymer with maleic anhydride was precipitated into dry diethyl ether.

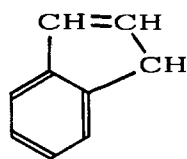
The composition of copolymers was determined by ¹H NMR spectroscopy or elemental analysis. Monomer reactivity ratios were calculated by the nonlinear, least-squares procedures.³⁴

Measurements

Number- and weight-average molecular weights (\bar{M}_n and \bar{M}_w , respectively) were determined by gel per-



Acenaphthylene
(Ace)



Indene

Scheme 1

meation chromatography (GPC) in THF (Tosoh 8000 series GPC system), and were calibrated with standard polystyrenes. ¹H and ¹³C NMR spectra were taken on a JEOL GX-400 or a FX-60Q, with deuteriochloroform as a solvent.

RESULTS AND DISCUSSION

Radical Polymerization of Ace

The results of radical polymerization of Ace under the various polymerization conditions are shown in Table I, in which the results of the polymerization of indene are also included. Indene is also one of the cyclic β -substituted styrene derivatives along with Ace (Scheme 1). Polymers with a high molecular weight, greater than 10^4 , were obtained readily from bulk or solution polymerization of Ace in a high yield. It was found that the polymerization of Ace hardly proceeded in the absence of a radical initiator, although St is known to polymerize spontaneously with heating.

It has been found that indene has a lower polymerization reactivity than Ace, that is, a high molecular weight polymer could not be obtained, even in bulk polymerization, because of the allyl hydrogen that may be abstracted degradatively.

Kinetic studies of radical polymerization were carried out. Figure 1 shows the time-conversion relationship for polymerization of Ace in benzene with AIBN at the temperature range of 50–70°C. An apparent, overall activation energy for this polymerization was determined to be 113 kJ/mol from an Arrhenius plot (Fig. 2) of polymerization rates (R_p),

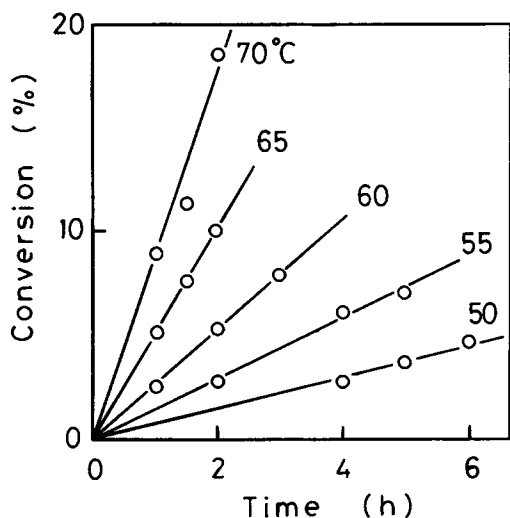


Figure 1 Time-conversion relationships for radical polymerization of Ace in benzene with AIBN: (Ace) = 3 mol/L, (AIBN) = 0.3 mol/L.

calculated from each of the initial slopes of the curves in Figure 1. The activation energy obtained is larger than those for polymerizations of common vinyl monomers such as St, and is similar to other 1,2-disubstituted ethylenic monomers, for example, *N*-substituted maleimides and vinylene carbonate.²

In Figures 3 and 4, the dependences of AIBN and Ace concentrations on R_p are shown, respectively. The reaction orders with respect to AIBN and Ace concentrations are 0.68 and 1.0, respectively, that is, R_p can be expressed as follows:

$$R_p = k[\text{AIBN}]^{0.68}[\text{Ace}]^{1.0} \quad (3)$$

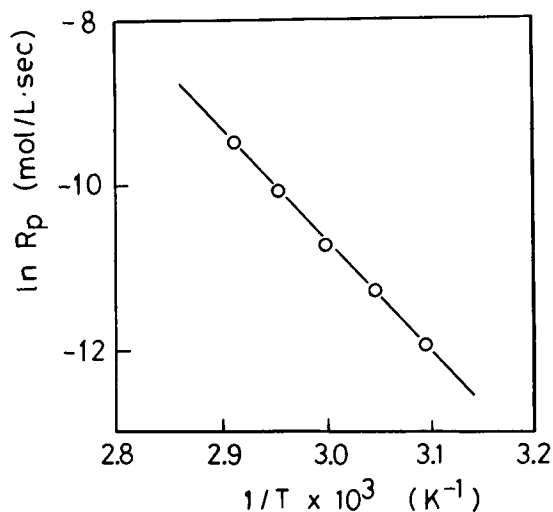


Figure 2 Arrhenius plot of polymerization rate (R_p) for radical polymerization of Ace.

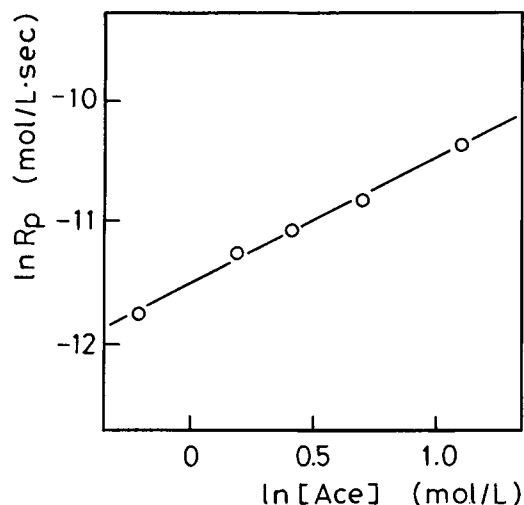


Figure 3 Effect of the concentration of Ace on R_p .

The order, with respect to the monomer concentration, is normally unity, but that on the initiator concentration is larger than that expected for bimolecular termination. A similar high reaction order has also been reported by Romani and Weale.²¹ The polymerization system is homogeneous during polymerization. Thus, it is not ascribed to unimolecular termination of the polymer radical. At present, the reason for the high order is not clear.

Characterization of Poly(Ace)

Figure 5 shows ¹³C NMR spectra of Ace and poly(Ace). In the spectrum of the polymer, a peak, based on the vinylene carbon in the five-membered ring of Ace at δ 129.2, is absent, and a broad peak,

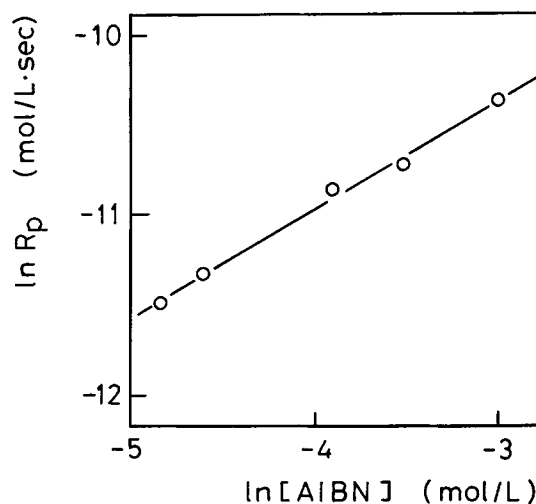


Figure 4 Effect of the concentration of AIBN on R_p .

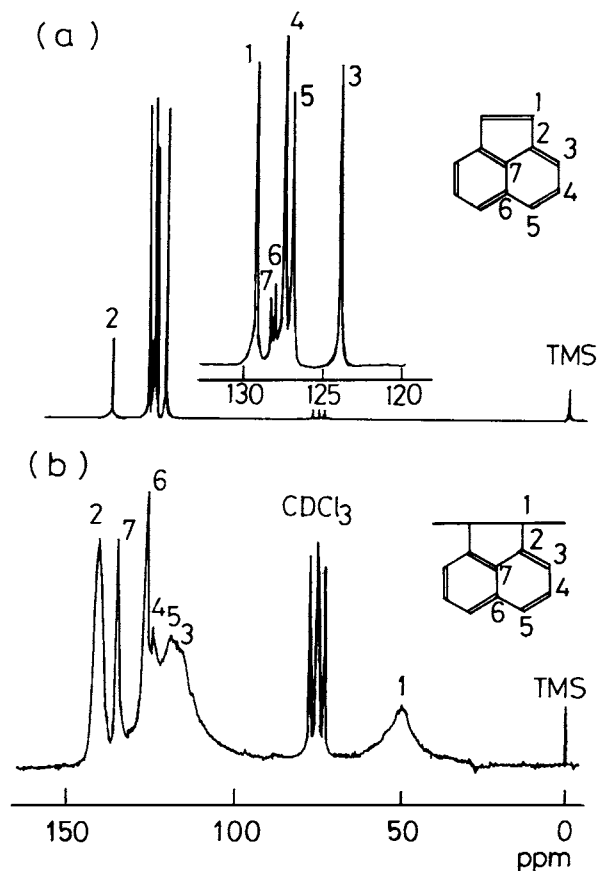
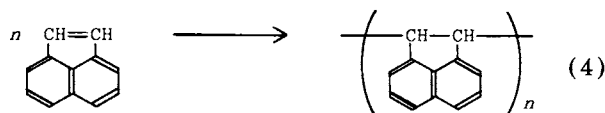


Figure 5 ^{13}C NMR spectra of (a) Ace and (b) poly(Ace) in CDCl_3 .

due to a methine carbon, is observed around δ 50. Similar results were also obtained from ^1H NMR spectroscopy, that is, it was confirmed that the peak at δ 7.1 of Ace monomer disappeared upon polymerization, although the ^1H NMR spectrum of poly(Ace) was more broad and complicated, the CH region was at δ 1.5–3.5, and the aromatic region was at δ 4.5–7.5. These results indicate that polymerization proceeds via an opening of the double bond out of the naphthalene ring to give substituted polymethylene as shown in eq. (4).



Poly(Ace) obtained is colorless powder, but the color was found to change to yellow or brown when stored for a long time. In the dark, the polymer is stable, even in air. Therefore the degradation of poly(Ace) under irradiation of UV light was examined. The GPC elution curves of poly(Ace) re-

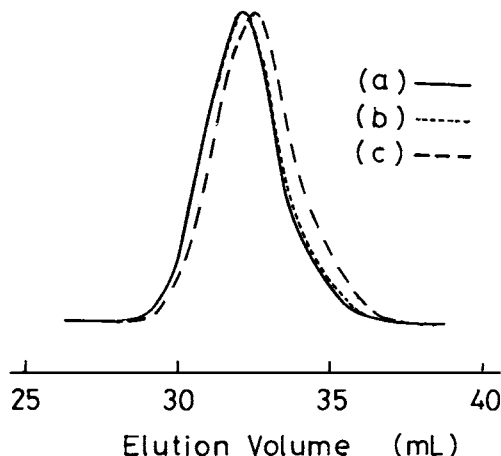


Figure 6 GPC elution curves of poly(Ace): (a) original, (b) after UV irradiation in nitrogen atmosphere, and (c) after UV irradiation in air.

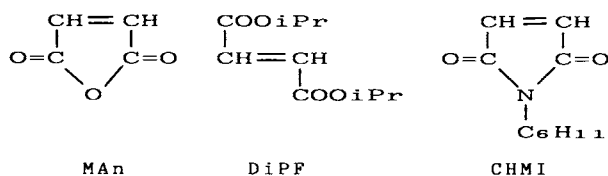
covered after being irradiated with a high-pressure mercury lamp (100 W) in nitrogen or in air are shown in Figure 6. The molecular weight decreased by the irradiation in air, whereas the polymer in nitrogen did not change, suggesting that some photo-oxidative degradation might occur in the presence of both oxygen and light.

Copolymerization with Other 1,2-Disubstituted Ethylenes

It is expected that substituted polymethylenes are obtained from radical copolymerization with other 1,2-disubstituted ethylenes. The copolymerizations of Ace (M_1) with some electron-accepting, 1,2-disubstituted ethylenes (M_2), that is, MAn, DiPF, and CHMI, as shown in Scheme 2, were performed with AIBN in benzene at 60°C .

The comonomer-copolymer composition curves for these copolymerizations are shown in Figures 7–9. The monomer reactivity ratios determined are summarized in Table II.

In copolymerization with MAn, the monomer reactivity ratios were calculated to be $r_1 = 0.46$ and $r_2 = 0.02$, agreeing well with the values reported (r_1



Scheme 2

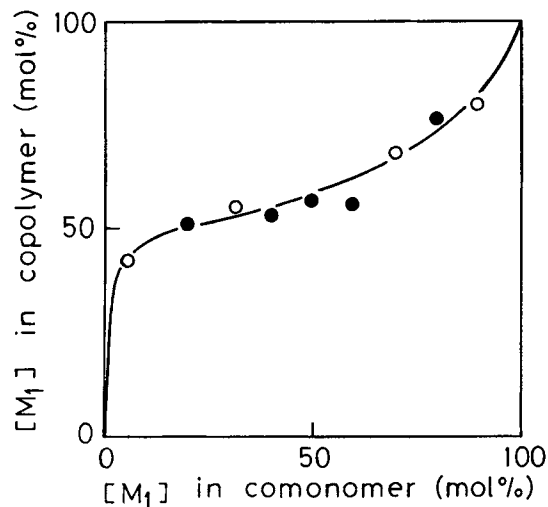


Figure 7 Comonomer-copolymer composition curves for radical copolymerization of Ace (M_1) with MAn (M_2) in benzene at 60°C: (O) from elemental analysis, (●) from ^1H NMR spectroscopy after methylation.

= 0.43 and $r_2 = 0.07$ in acetic anhydride at 60°C).³⁵ An alternating copolymer, bearing a structure shown in eq. (5), was formed similar to the alternating copolymerization of St with MAn.³⁷ However, considerable deviations from an equimolar composition in the copolymer ($M_1 = M_2 = 50$ mol % in copolymer) were observed in the actual composition of the copolymers obtained from a high Ace content in feed in Figure 7, indicating that an alternating tendency is not as high as the copolymerization of St with MAn.

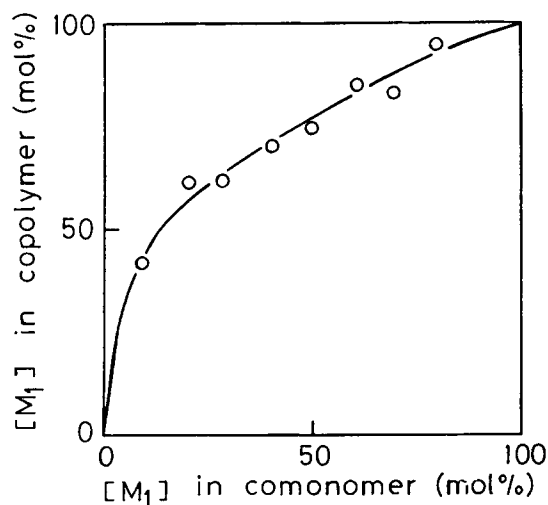


Figure 8 Comonomer-copolymer composition curves for radical copolymerization of Ace (M_1) with DiPF (M_2) in benzene at 60°C.

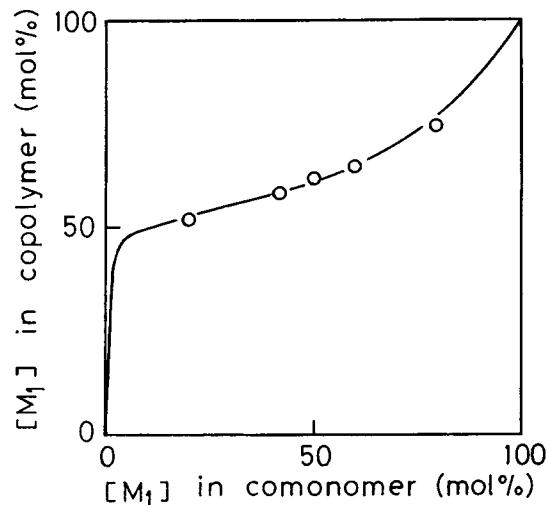
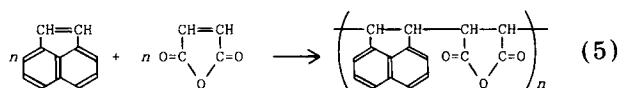
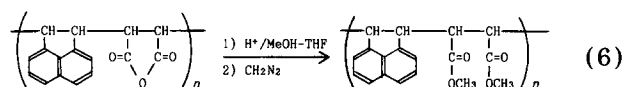


Figure 9 Comonomer-copolymer composition curves for radical copolymerization of Ace (M_1) with CHMI (M_2) in benzene at 60°C.



This alternating copolymer was refluxed in a mixture of methanol and THF in the presence of an acidic catalyst, followed by the reaction with diazomethane (eq. 6).



The compositions of Ace and dimethyl fumarate (or maleate) units in the copolymers methylated were determined from the NMR spectra. The plot of the copolymer composition was also shown in Figure 7, indicating that methylation of this polymer pro-

Table II Monomer Reactivity Ratios for Radical Copolymerization of Ace or St (M_1) with Several 1,2-Disubstituted Ethylenes (M_2) in Benzene at 60°C

M_1	M_2	r_1	r_2	Reference
Ace	MAn	0.46	0.02	This work
		0.43	0.07	35
	DiPF	2.57	0.06	This work
St	CHMI	0.57	0.11	This work
	St	2.3	0.27	36
	MAn	0.01	0	37
St	DiPF	0.40	0.06	38
	CHMI	0.11	0.02	39

Table III Radical Copolymerization of Ace (M_1) with 1,2-Disubstituted Ethylenes (M_2) in Benzene at 60°C^a

M_2	Time (h)	Yield (%)	(M_1) in Copolymer (mol %)
MAN	2	16.2	55.8
DiPF	8	4.5	75.2
DiPF ^b	8	29.2	99.0
DiPF ^c	8	4.7	72.8
CHMI	2	7.5	62.2

^a (M_1) = (M_2) = 1 mol/L, (AIBN) = 0.05 mol/L.

^b In the presence of SnCl₄ (1 mol/L).

^c In the presence of ZnCl₂ (1 mol/L).

ceeded quantitatively, that is, the alternating copolymer of Ace and the fumarate was produced.

On the other hand, an alternating copolymer of Ace and fumarates was not obtained from a direct copolymerization of Ace with fumarates. For example, in the copolymerization with DiPF (M_2), the monomer reactivity ratios were as follows: $r_1 = 2.57$, $r_2 = 0.06$. The copolymerization rate was also much lower than that of MAN, as shown in Table III. These results are different from the fact that fumarates undergo readily alternating copolymerization with St.³⁸ This may also be due to steric hindrance of the 1,2-disubstituted ethylene structure of both Ace and DiPF. It has been reported³⁶ that Ace has a higher monomer reactivity than St in the copolymerization of Ace (M_1) with St (M_2); $r_1 = 2.3$ and $r_2 = 0.27$. The high reactivity of Ace also seems to decrease the alternating tendency.

It is known that the addition of a Lewis acid to polar vinyl monomers, such as methyl methacrylate and acrylonitrile, changed their apparent monomer reactivities.⁴⁰ Therefore, the effect of the addition of SnCl₄ and ZnCl₂ on the copolymerization system of Ace and DiPF was examined. The copolymerization rate and the copolymer composition were reflective in both cases of the presence and absence of ZnCl₂. But, it was found that the addition of SnCl₄ gave a copolymer consisting of the predominant St unit of more than 99%. This was different from the fact that an alternating copolymer was produced with a higher yield in the copolymerization of St with MMA in the presence of a Lewis acid, such as SnCl₄. From GPC analysis, the copolymer of Ace and DiPF, produced during copolymerization in the presence of SnCl₄, was revealed to have bimodal molecular weight distribution, suggesting that two active sites of polymerization existed in this system:

one radical and the other cationic. The facile cationic homopolymerization of Ace was considered to occur in the polymerization system.²⁶⁻²⁸

It was also observed that Ace readily copolymerized with CHMI ($r_1 = 0.57$, $r_2 = 0.11$), as shown in Figure 9, but the alternating tendency was slightly lower than the copolymerization of St with CHMI, $r_1 = 0.11$ and $r_2 = 0.02$.³⁹ This was interpreted by the sterically hindered structures and highly reactive Ace, as well as by copolymerization of Ace with MAN or DiPF, as mentioned above.

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Received July 9, 1991

Accepted September 4, 1991