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Yukio Imanishi[a]; Kazuo Hara[a]; Shinzo Kohjiya[a]; Seizo Okamura[a]
[a] Department of Polymer Chemistry, Kyoto University, Kyoto, Japan

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Cationic Polymerization of Cyclic Dienes. VI. Cationic Copolymerization of Cyclopentadiene and α-Methylstyrene

YUKIO IMANISHI, KAZUO HARA, SHINZO KOHJIYA, and
SEIZO OKAMURA

Department of Polymer Chemistry
Kyoto University
Kyoto, Japan

SUMMARY

The cationic copolymerizations of α-methylstyrene and cyclopentadiene were carried out and the monomer reactivity ratios were determined. It was found that cyclopentadiene was more reactive than α-methylstyrene, and that the effect of solvent polarity on the monomer reactivity ratio was small. It was deduced from the pK_{BH^+} values of cations pertinent to the present investigation that there is little difference between the stabilities of cyclopentenyl cation and cumyl cation. The present experiment seems to be the first example showing that there is little solvent effect even in the copolymerization between monomers of dissimilar structures, if the stabilities of cations are similar.

Copolymers whose intrinsic viscosity were higher or near unity were produced.

INTRODUCTION

The effect of solvent polarity on the monomer reactivity ratio in the cationic copolymerization has been a subject of current interest. It has been reported that although the solvent effect is not marked in the copolymerization between styrene derivatives [1], it is quite important in the copolymerization between structurally dissimilar monomers such as isobutene-styrene derivatives [2, 3], styrenes-alkyl vinyl ethers [4], and cyclopentadiene-isobutene [5]. Several investigations with cyclic dienes have been carried out in our laboratory to solve the problem on the relationship between the structure and the reactivity of cyclic dienes.

In the present investigation, the reactivity of cyclopentadiene was compared with that of α-methylstyrene. The copolymerization was carried out in a few solvents of different polarity to investigate the solvent effect on the copolymerization between a diene and an arylic monomer. Another purpose of this investigation was to obtain a high molecular weight copolymer of cyclopentadiene.

EXPERIMENTAL

Procedure

In a 100-ml flask flashed with nitrogen, known amounts of solvent and monomer were charged with a syringe through a self-sealing rubber cap. The flask was chilled in liquid nitrogen and the air in the flask was completely exchanged with nitrogen under vacuum manipulation. Thereafter the flask was transferred into a dry ice-methanol bath and after a thermal equilibrium was reached the catalyst solution was added with syringe to initiate the copolymerization. After a suitable time for the conversion not to exceed 20%, methanol was added to stop the copolymerization. When the copolymerization is conducted in n-hexane, a precooled monomer mixture was added to a mixture of solvent and catalyst because the polymer is insoluble. The copolymer was washed with methanol repeatedly and dried in vacuum. As polycyclopentadiene is known to be oxidized quickly [6], 4, 4′-thiobis(6-t-butyl-3-methylphenol) was used as an antioxidant to avoid the oxidation of copolymer.

Analysis of Copolymer Composition

The elementary composition of poly(α-methylstyrene) (C % = 91.53) is very similar to that of polycyclopentadiene (C % = 90.91) Hence the elementary analysis of copolymer composition is not suitable. The copolymer composition was analyzed by infrared spectroscopy, as will be described subsequently. The infrared spectra of poly(α-methylstyrene) and polycyclopentadiene were measured as carbon disulfide solution or potassium bromide disk. An absorption at 2930 cm^{-1} due to a methylene group appeared in both polymers. Two absorptions at 1030 and 700 cm^{-1} due to a phenyl group appeared only in poly-α-methylstyrene. These three absorption bands were employed as key band to analyze the copolymer composition.

The mixtures of poly(α-methylstyrene) and polycyclopentadiene of various molar compositions were made and their infrared spectra were measured as 2.5% carbon disulfide solution or as potassium bromide disk. The optical density ratios $D_{1030}\ cm^{-1}/D_{2930}\ cm^{-1}$ and $D_{700}\ cm^{-1}/D_{2930}\ cm^{-1}$ are calculated and plotted in Fig. 1 as

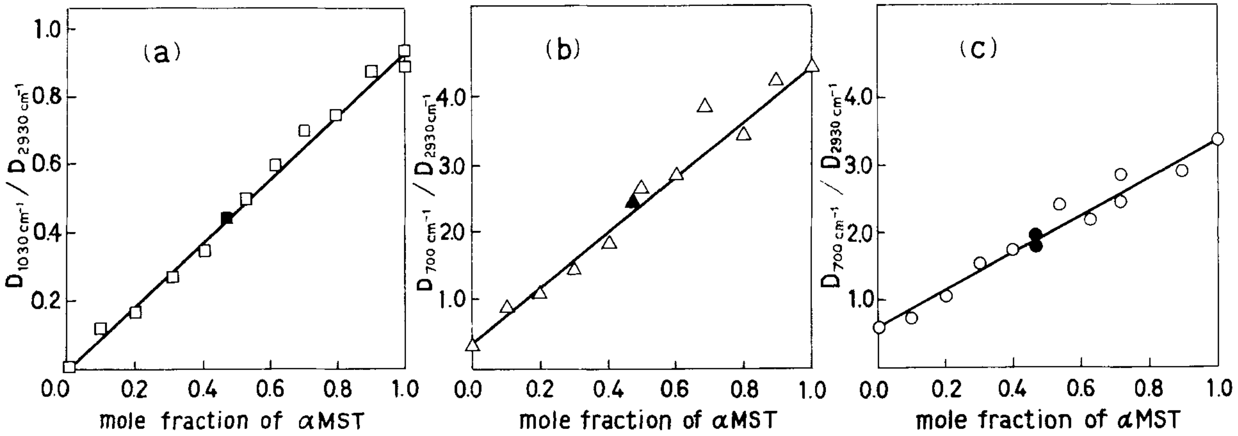

Fig. 1. Calibration lines for the determination of copolymer composition. (a) CS_2 solution, D_{1030} cm^{-1}/D_{2930} cm^{-1} versus mole fraction of α-methylstyrene; (b) CS_2 solution, D_{700} cm^{-1}/D_{2930} cm^{-1} versus mole fraction of α-methylstyrene; (c) KBr disk, D_{700} cm^{-1}/D_{2930} cm^{-1} versus mole fraction of α-methylstyrene.

a function of the mole fraction of α-methylstyrene in the polymer mixture. Straight lines were obtained and these were used as calibration lines for the analysis of copolymer composition. In this procedure an assumption was made that the molar extinction coefficient of a key band of copolymer is the same as that of the polymer mixture. To support the assumption, a mixture of α-methylstyrene (mole fraction 0.471) and cyclopentadiene (mole fraction 0.529) was copolymerized up to 100% conversion. The resultant copolymer was subjected to infrared spectroscopy. If the assumption is correct, the copolymer composition analyzed by infrared spectroscopy should be equal to the composition of the feed monomer, and this was the case. The results of the test experiment are shown in Fig. 1 as black points. They very nearly form the straight lines.

With methods (a) and (b) the compositions of copolymers produced in toluene were analyzed at different concentrations in carbon disulfide solution (2.5 and 5%). The change in concentration was found not to affect the determination.

The compositions of three copolymers were analyzed by nuclear magnetic resonance spectroscopy as well as infrared spectroscopy. The results are compared in Table 1. It is seen that the analyses are in fairly good agreement. Thus the validity of the use of infrared spectroscopy was again revealed.

Table 1. Analyses of Copolymer Composition by Infrared Spectroscopy and Nuclear Magnetic Resonance Spectroscopy

Sample	F_1[a] by IR (mean value)	F_1[a] by NMR (integral curve)	F_1[a] by NMR (area ratio of phenyl proton)
A	0.470	0.473	0.49_4
B	0.886	0.921	0.96_2
C	0.322	0.535	0.41_7

[a] F_1, mole fraction of α-methylstyrene in copolymer.

Identification of the True Copolymerization

To identify that the true copolymerization took place, fractionation of the copolymerization product was carried out. About a 1% toluene solution of the copolymerization product was made, and a small amount of methanol as a precipitant was added successively. The copolymerization product was divided into five fractions, and with each fraction the composition and the viscosity were measured. Some low molecular weight fraction was lost, mainly during the process of filtration. As is seen in Table 2, in going from fraction 1 to fraction 5, the intrinsic viscosity decreases but the copolymer composition was almost unchanged.

Next, the homopolymers of α-methylstyrene and cyclopentadiene were produced under the same conditions as the copolymerization, and they are mixed and fractionated in the way as described above. The results are shown in Table 3. In going from fraction 1 to frac-

Table 2. Fractionation of Copolymerization Product[a]

Fraction	Weight %	[η], dl/g	F_1[b]
Original		0.399	0.385
1	18.9	0.699	0.396
2	16.0	0.496	0.375
3	16.3	0.432	0.427
4	10.5	0.161	0.452
5	3.7	—	0.436

[a] Copolymerization condition, solvent toluene, catalyst $BF_3 \cdot O(C_2H_5)_2$, temperature −78°C.

[b] Mole fraction of α-methylstyrene in copolymer.

Table 3. Fractionation of the Mixture of Poly(α-methylstyrene) and Polycyclopentadiene[a]

Fraction	Weight %	[η], dl/g	F_1[b]
Original		0.716	0.440
1	11.2	1.451	0.098
2	6.48	1.325	0.173
3	15.1	0.594	0.293
4	25.7	0.501	0.555
5	6.57	0.150	0.578

[a] Polymerization condition, solvent toluene, catalyst BF_3 $O(C_2H_5)_2$, temperature −78°C.

[b] Mole fraction of α-methylstyrene in copolymer.

tion 5 the intrinsic viscosity decreased but F_1 increased. This is because the low molecular weight poly(α-methylstyrene) precipitates later. Hence, if poly(α-methylstyrene) is formed at all in the copolymerization condition, it should come out later, when fractionated. This was not observed actually, and the formation of true copolymer was confirmed.

Viscosity

The viscosity of copolymer was measured in toluene solution at 30°C.

Materials

α-Methylstyrene, cyclopentadiene, methylene chloride, toluene, n-hexane, and borontrifluoride etherate were purified as reported previously [7, 8].

Table 4. Analysis of the Composition of Copolymer Obtained in Methylene Chloride

		F_1			
Run No.	f_1	Method (a)	Method (b)	Method (c)	Mean
200	0.000	0.000	0.000	0.000	0.000
201	0.060	—	0.0268	0.0484	0.0376
202	0.126	0.102	0.0945	0.0550	0.0838
203	0.198	—	—	0.159 0.131	0.145
204	0.276	—	0.177	0.215 0.176	0.189
205	0.366	0.306	0.306	0.264 0.291	0.292
206	0.471	0.348	0.400	0.296 0.330	0.344
207	0.571	0.507	0.548	0.465 0.464	0.496
208	0·697	0.547	0.682	0.558	0.596
209	0.839	0.780	—	0.780	0.780
210	1.000	1.000	1.000	1.000	1.000

RESULTS

The copolymerizations of α-methylstyrene (M_1) and cyclopentadiene (M_2) were carried out in methylene chloride, toluene, or n-hexane as solvent with boron trifluoride etherate as catalyst. All copolymerizations were carried out at −78°C with the initial total monomer concentration 20 vol. % and the initial catalyst concentration 50 mmoles/liter.

Copolymer Composition

The copolymer composition was analyzed by infrared spectroscopy as potassium bromide disk or as carbon disulfide solution. The monomer reactivity ratios were determined by the cross-section method.

The analysis of copolymer composition produced in methylene chloride is shown in Table 4. The mole fraction of α-methylstyrene in copolymer (F_1) was determined by averaging three F_1 values determined by three different ways.

The compositions of copolymers obtained in methylene chloride, toluene, and n-hexane were plotted as a function of the fraction of α-methylstyrene in the monomer feed in Figs. 2, 3, and 4, respectively. The limit of variation in F_1 is also shown in the figures. The copolymer composition curves in the figures correspond to the monomer reactivity ratios determined by the cross-section method using mean values of F_1: $r_1 = 0.67 \pm 0.29$, $r_2 = 1.53 \pm 0.18$ in methylene chloride, $r_1 = 0.66 \pm 0.25$, $r_2 = 1.62 \pm 0.36$ in toluene, $r_1 = 0.47 \pm 0.27$, $r_2 = 1.23 \pm 0.22$ in n-hexane.

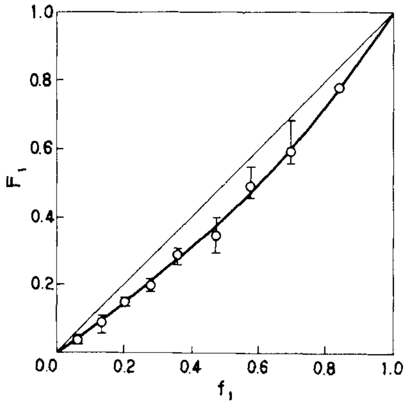

Fig. 2. Copolymer composition curve. Copolymerization of α-methylstyrene (M_1) and cyclopentadiene (M_2) in methylene chloride.

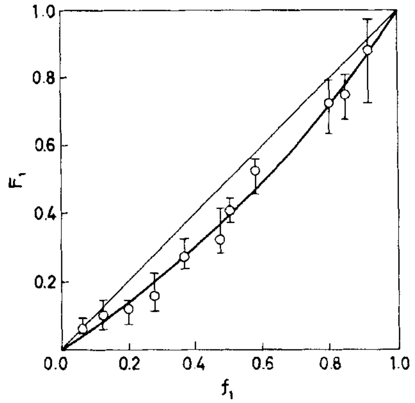

Fig. 3. Copolymer composition curve. Copolymerization of α-methylstyrene (M_1) and cyclopentadiene (M_2) in toluene.

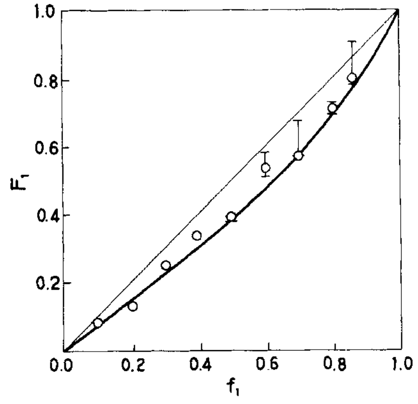

Fig. 4. Copolymer composition curve. Copolymerization of α-methylstyrene (M_1) and cyclopentadiene (M_2) in n-hexane.

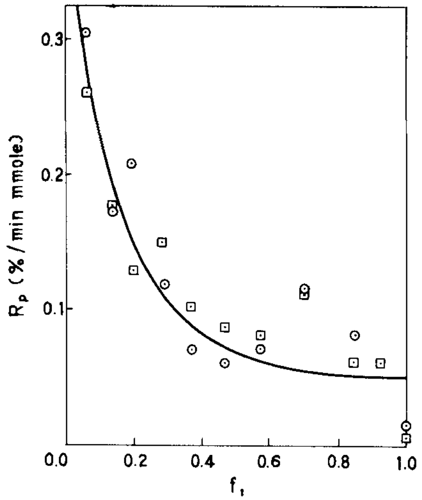

Fig. 5. Copolymerization rate and composition of feed monomer. Copolymerization of α-methylstyrene (M_1) and cyclopentadiene (M_2) with $BF_3 \cdot O(C_2H_5)_2$ at −78°C: ○, in methylene chloride; □, in toluene.

Copolymer Yield

The per cent yield of copolymer per unit time per unit catalyst concentration was calculated as a measure of the copolymerization rate R_p. R_p (%/min-mmole) was plotted against f_1 in Fig. 5. It was found that R_p decreased with increasing f_1, the content of α-methylstyrene. It was also found that the solvent polarity did not affect R_p significantly.

As the copolymer was insoluble in n-hexane, R_p in n-hexane was not investigated.

Viscosity of Copolymer

The intrinsic viscosities of the copolymers were measured in toluene solution at 30°C and is shown in Figs. 6, 7, and 8 as a function of f_1. The cyclopentadiene-rich copolymers produced in methylene chloride and in n-hexane were not completely soluble in toluene. Intrinsic viscosities of these copolymers were determined only with the toluene-soluble part. It was found that the copolymerizations in toluene and in methylene chloride yielded copolymers, the intrinsic viscosities of which were higher than or near unity. In the copolymerizations in n-hexane and in methylene chloride the intrinsic

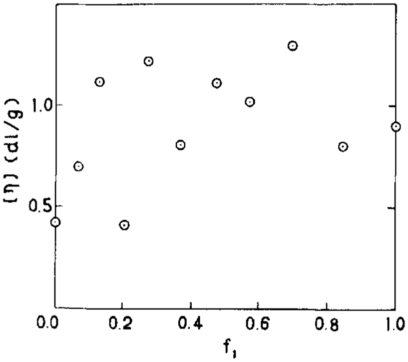

Fig. 6. Intrinsic viscosity of copolymer and composition of feed monomer. Copolymerization of α-methylstyrene (M_1) and cyclopentadiene (M_2) in methylene chloride.

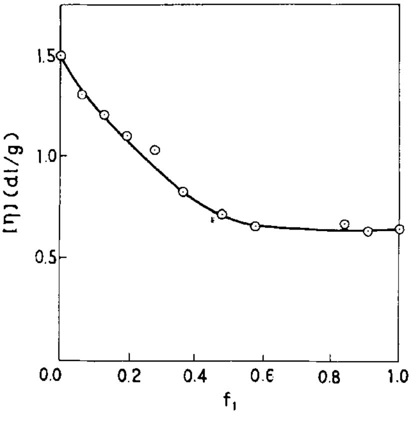

Fig. 7. Intrinsic viscosity of copolymer and composition of feed monomer. Copolymerization of α-methylstyrene (M_1) and cyclopentadiene (M_2) in toluene.

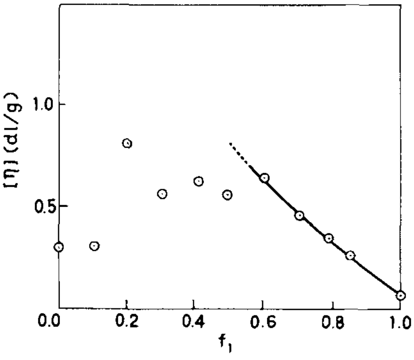

Fig. 8. Intrinsic viscosity of copolymer and composition of feed monomer. Copolymerization of α-methylstyrene (M_1) and cyclopentadiene (M_2) in n-hexane.

viscosity of copolymer tended to decrease with increasing α-methylstyrene content in the feed monomer. It is of particular interest that the viscosity of copolymer was not extremely lower than those of homopolymers, because a very marked decrease of copolymer viscosity was observed with isobutene-styrene [9] or α-methylstyrene [10] copolymerization.

Oxidation of Copolymer

The autooxidation of α-methylstyrene-cyclopentadiene copolymer was investigated by infrared spectroscopy. It has been known that polycyclopentadiene is oxidized by air very rapidly, and that with oxidation the infrared absorption due to a carbonyl group at 1700 cm^{-1} increases its intensity but the absorption due to a double bond at 3050 cm^{-1} is unchanged [6]. The change of the infrared spectrum of the film of the α-methylstyrene-cyclopentadiene copolymer on standing in air is shown in Fig. 9. The ratio of optical density D_{1700} cm^{-1}/D_{3050} cm^{-1} was calculated and its variation with time was recorded with several samples in Table 5. It was found that oxidation by air can be avoided by the addition of antioxidant, and that the copolymer, which contains more α-methylstyrene, is oxidized more slowly. Because the oxidation rate is roughly proportional to the content of cyclopentadiene, it is safe to say that only a cyclopentadiene unit in the copolymer affects the oxidation, and that the resistance to the oxidation of polycyclopentadiene is not improved by copolymerizing other monomers.

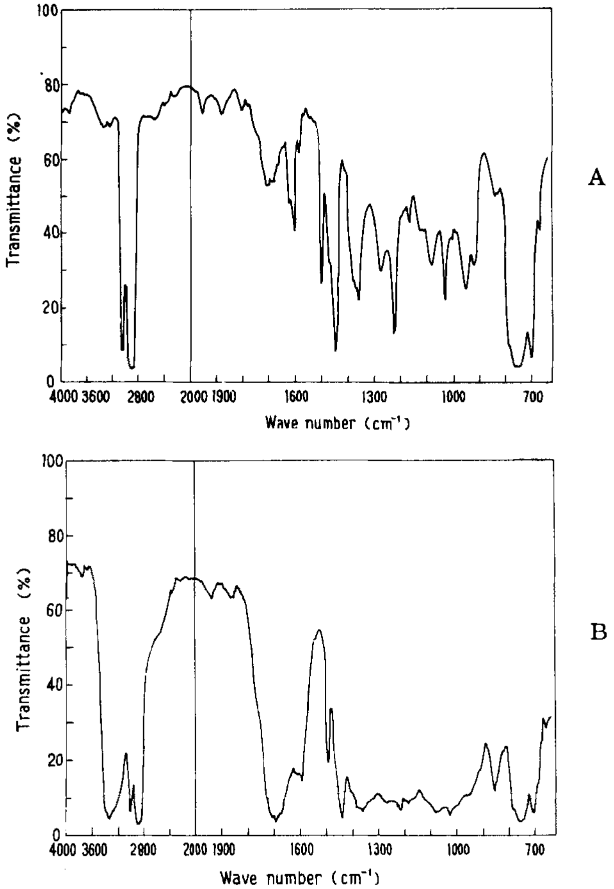

Fig. 9. Change of infrared spectrum of α-methylstyrene-cyclopentadiene copolymer on oxidation. Copolymer produced in toluene with $BF_3 \cdot O(C_2H_5)_2$ at −78°C. $F_1 = 0.06$. A, soon after a film was cast; B, after 108 days.

Table 5. Oxidation Rate of the Film of α-Methylstyrene (M_1)-Cyclopentadiene (M_2) Copolymer[a]

Sample		Time, days	$D_{1700}\ cm^{-1}/D_{3050}\ cm^{-1}$
1, $F_1 = 0.06$	Without antioxidant	0	0.16
		11	0.31
		32	0.66
		49	0.89
		108	1.17
	With antioxidant	0	0.13
		7	0.13
		15	0.14
		28	0.14
		45	0.15
		104	0.14
2, $F_1 = 0.49$	Without antioxidant	0	0.07
		7	0.06
		28	0.11
		45	0.12
		104	0.13
	With antioxidant	0	0.02
		7	0.04
		28	0.02
		45	0.02
		104	0.04

[a] Copolymerization condition, solvent toluene, catalyst $BF_3 \cdot O(C_2H_5)_2$, temperature −78°C.

Table 6. Copolymerization of Cyclopentadiene

M_1	M_2	r_1	r_2	Solvent	Catalyst	Solvent effect	Ref.
Isobutene	Cyclopentadiene	0.60	4.5	Toluene	$BF_3 \cdot OEt_2$	Large	[5]
		0.73	1.86	Methylene chloride			
		0.21	6.3	Toluene	$SnCl_4$		
		0.80	1.55	Methylene chloride			
α-Methylstyrene	Cyclopentadiene	0.47	1.23	n-Hexane	$BF_3 \cdot OEt_2$	Little	Present paper
		0.66	1.62	Toluene			
		0.67	1.53	Methylene chloride			

DISCUSSION

Monomer Reactivity Ratio

The cationic copolymerizations of α-methylstyrene and cyclopentadiene were carried out and the monomer reactivity ratios were determined. It was found that cyclopentadiene was more reactive than α-methylstyrene, and that the effect of solvent polarity on the monomer reactivity ratio was small.

The monomer reactivity ratios for the copolymerizations of cyclopentadiene so far obtained are listed in Table 6. It is seen that the effect of solvent polarity on the monomer reactivity ratio is more important in isobutene-cyclopentadiene than in α-methylstyrene-cyclopentadiene.

In cationic polymerization the reactivity of monomer may be determined by either the nucleophilicity of the double bond or the stability of the resulting cation. The nucleophilicity of the double bond may not be affected significantly by the nature of solvent. On the other hand, the stability of the resulting cation is strongly affected by the nature of solvent. An aliphatic cation such as t-butyl cation from isobutene is least resonance stabilized. It will be quite unstable in a nonpolar solvent such as n-hexane, but will gain a lot of solvation stabilization in a polar solvent such as methylene chloride. On the other hand, an arylic cation such as 1-phenyl ethyl cation from styrene is highly resonance stabilized. It will be stable even in a nonpolar solvent and will not gain as much stabilization energy in a polar solvent. In this respect, the reactivity of aliphatic olefins will be affected very much by the solvent polarity, and that of arylic olefins will be affected only a little. It follows that the increase of solvent polarity results in a greater increase of the reactivity of the monomer, which gives a less stable ion. On this basis, a large solvent effect on the isobutene-styrene copolymerization and a small solvent effect on the copolymerization between styrene derivatives have been interpreted [3].

Turning to the cationic copolymerization of cyclic dienes, the stability of cycloalkenyl cation is important to explain the experimental results. The stability of cation could be discussed in terms of the pK_{BH^+} value of Eq.(1) proposed for a base-protonated base ($B—BH^+$) equilibria.

$$B + H^+ \rightleftharpoons BH^+ \qquad H_0 = pK_{BH^+} + \log C_B/C_{BH^+} \tag{1}$$

pK_{BH^+} values of cations pertinent to the present investigation have not been determined directly but can be calculated from the values of the related cations on the basis of a reasonable assumption [11].

pK_{BH^+} of t-butyl cation (isobutene) —15.5 [11]

pK_{BH^+} of cyclopentenyl cation (cyclopentadiene)	−8.7 [12]
pK_{BH^+} of cumyl cation (α-methylstyrene)	−7.4 [13]*

A large difference in cation stability between isobutene and cyclopentadiene is reflected in the large solvent effect on the monomer reactivity ratio of isobutene-cyclopentadiene copolymerization (see Table 6).

On the other hand, there is little difference between pK_{BH^+} values of cyclopentenyl cation and cumyl cation. And, expectedly, the α-methylstyrene-cyclopentadiene copolymerization was little affected by the solvent polarity.

So far it has been generally accepted that the solvent effect emerges more or less in the copolymerization between monomers of dissimilar structures. However, the present experiment is the first example showing that this is not the case if the stabilities of cations are similar.

Viscosity of Copolymer

The intrinsic viscosity of α-methylstyrene-cyclopentadiene copolymer was higher than that of styrene-cyclopentadiene copolymer [15]. The intrinsic viscosity of the present copolymer was not extremely lower than those of homopolymers. This is in marked contrast to isobutene-styrene copolymer [9], where the intrinsic viscosity of copolymer was extremely low. This may be explained in terms that there is little difference between cation stabilities in the present case, so that the cross-transfer reaction is not important.

α-Methylstyrene-cyclopentadiene copolymer having an intrinsic viscosity higher than unity was obtained. The molecular weight of poly(α-methylstyrene) was controlled by changing the solvent [16]. The intrinsic viscosity of polycyclopentadiene obtained by antimony

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*This is a value reported for 2, 4, 6-trimethylcumyl cation, but methyl groups on the phenyl group do not seem to affect pK_{BH^+} value so much [13]. Deno et al. have recommended the use of

$$H_R - \log a_{H_2O} = pK'_{R^+} + \log C_{ol}/C_{R^+}$$

instead of Eq. (1) for mono- or diaryl olefin-protonated olefin equilibria when the olefin is produced by an acid-catalyzed dehydration of alcohol in situ, and reported a pK'_{R^+} value of cumyl cation to be −12.2 [13]. However, Eq. (1) seems to be applicable to describe the equilibria, too [14]. In the present paper, for the comparison with pK_{BH^+} values of t-butyl cation and cyclopentenyl cation Eq. (1) was used to calculate pK_{BH^+} of cumyl cation on the basis of Deno's experimental data.

trichloride was as high as 2 [17]. Therefore, it will be possible to produce α-methylstyrene-cyclopentadiene copolymer of much higher molecular weight by a suitable choice of polymerization conditions.

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