Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Copolymerization and Charge-Transfer Interaction of Methyl Isopropenyl Ketone Cyclodimer with Maleic Anhydride and Maleimide

Hitoshi Tanaka[a]; Takayuki Otsu[a]
[a] Department of Applied Chemistry Faculty of Engineering, Osaka City University, Osaka, Japan

To cite this Article Tanaka, Hitoshi and Otsu, Takayuki(1977) 'Copolymerization and Charge-Transfer Interaction of Methyl Isopropenyl Ketone Cyclodimer with Maleic Anhydride and Maleimide', Journal of Macromolecular Science, Part A, 11: 9, 1663 — 1676

To link to this Article: DOI: 10.1080/00222337708063083

URL: http://dx.doi.org/10.1080/00222337708063083

J. MACROMOL. SCI.-CHEM., A11(9), pp. 1663-1676 (1977)

Copolymerization and Charge-Transfer Interaction of Methyl Isopropenyl Ketone Cyclodimer with Maleic Anhydride and Maleimide

HITOSHI TANAKA and TAKAYUKI OTSU

Department of Applied Chemistry
Faculty of Engineering
Osaka City University
Sugimotocho, Sumiyoshi-ku
Osaka 558, Japan

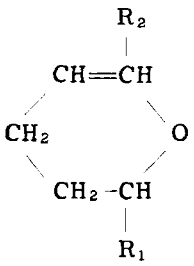
ABSTRACT

The copolymerizations of methyl isopropenyl ketone cyclodimer(MIPKD: 2-acetyl-2,5,6-trimethyl-2,3-dihydropyran) with maleic anhydride (MAn) and with maleimide (MI) in the presence of α,α'-azobisisobutyronitrile were investigated at 60 and 80°C. It was found that the copolymerizations were performed in both systems to give rather low molecular weight copolymers consisting of less than 50% MIPKD units. It was also observed from IR and NMR spectral determinations of the systems of MIPKD with MAn and with MI that 1:1 charge-transfer complexes with a small equilibrium constant were formed. Formation of these complexes seemed to affect the copolymerizations. Finally, the copolymerization of MIPKD with MAn was studied kinetically. The mechanism of copolymerization is discussed.

INTRODUCTION

Maleic anhydride (MAn), which is a strong electron-accepting monomer and hardly homopolymerizes, readily undergoes alternating copolymerization with various electron-donating monomers such as olefins, dienes, vinyl ethers, and vinyl sulfides [1]. In most of these copolymerizations, the charge-transfer (CT) complex formed between the two monomers has been found to play an important role in the formation of alternating copolymer.

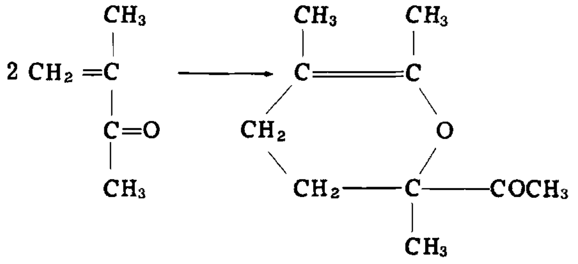
It has also been reported that some unsaturated cyclic ethers such as p-dioxene [2] and 2,3-dihydropyran derivatives (I) and (II) [3-5] copolymerize with MAn to give 1:1 alternating copolymers.



I : $R_1 = R_2 = H$
II: $R_1 = COCH_3$, $R_2 = CH_3$

In general, cyclic olefins are copolymerized more easily than the corresponding α,β-disubstituted olefins. One of the reasons has been considered to be a reflection of the restriction of mobility due to the substituents [6], and the relaxation of such a strain from olefinic bond to paraffinic bond seems to affect the copolymerization reactivtiy [7]. Therefore, it is of interest to study the copolymerization behavior of cyclic monomers with α,β-disubstituents(tetrasubstituted monomer). Sterically hindered α,β-multisubstituted olefins do not undergo homopolymerization, but sometimes, if electron-donating substituents are introduced, they can enter into copolymerization with MAn [8, 9].

In the previous paper [10], methyl isopropenyl ketone (MIPK) was found to easily convert to a cyclodimer (MIPKD), 2-acetyl-2,5,6-trimethyl-2,3-dihydropyran(III), through a Diels-Alder reaction [Eq. (1)].



(1)

MIPKD (III)

MIPKD is tetrasubstituted monomer; its formation has been described in the patent literature [11, 12], but its polymerization behavior has not been investigated. The present paper will describe the results of radical copolymerization of MIPKD with MAn in connection with the CT complex formation. For comparison, the radical copolymerization and CT interaction behavior of MIPKD with maleimide (MI) were also studied.

EXPERIMENTAL

Preparation of MIPKD

MIPKD was prepared from MIPK which was synthesized by reaction of methyl ethyl ketone with paraformaldehyde according to the method of White et al. [12]. The MIPK containing a small amount of hydroquinone was refluxed (98-99°C) for 10 hr in a nitrogen atmosphere in the absence of light. After reaction, MIPKD was obtained in quantitative yield by a fractional distillation under reduced pressure in a stream of nitrogen. The purity of MIPKD was confirmed from gas chromatography, and its structure was identified by IR, NMR, and mass spectroscopy; bp 60-61°C/6 Torr; n_D^{20} 1.4592; IR showed absorptions at $\nu_{C=O}$ 1715 and $\nu_{C=C}$ 1690 cm^{-1}; NMR showed (TMS in CCl_4) δ 1.23, 1.57, 1.78, 2.09 (singlet, four CH_3), 1.20-2.40 ppm (multiplet, $-CH_2-CH_2-$); the mass spectrum (m/e): M^+ 168.

Other Reagents

MAn and MI were purified by recrystallization from benzene and cyclohexane, respectively. α,α'-Azobisisobutyronitrile (AIBN) was recrystallized from ethanol. The solvents and precipitants were used after conventional purifications.

Copolymerization Procedure

The copolymerization of MIPKD with MAn was carried out in a sealed tube in the presence of AIBN with shaking in a thermostat maintained at 60 or 80° C. After copolymerization, the contents of the tube were poured into a large amount of diethyl ether to precipitate the copolymer. The compositions of the copolymers which were reprecipitated from dioxane solution into diethyl ether, were determined by elementary analysis for carbon and nitrogen. The copolymerization of MIPKD with MI was performed similarly, except that tetrahydroduran was used as a reprecipitation solvent.

Spectral and Molecular Weight Measurements

To determine the composition and the equilibrium constant of the CT complexes between MIPKD and MAn or MI, the UV and NMR spectra of these mixtures were measured at 25° C in benzene and carbon tetrachloride, respectively.

A Knauer vapor pressure osmometer was employed to determine the number-average molecular weight of the copolymers of MIPKD with MAn and with MI at 45° C in acetone and tetrahydrofuran, respectively.

RESULTS AND DISCUSSION

Formation of CT Complex

When MIPKD was mixed with MAn in benzene, a yellow coloration was observed, indicating the formation of a CT complex. UV spectral measurement was applied to this system in benzene at 25° C. The results of continuous variation are shown in Fig. 1, from which it is found that an absorbance maximum is observed at a 1:1 molar mixture. The absorption maximum due to this complex is observed at 360 nm. This indicates the formation of a 1:1 CT complex of MIPKD with MAn. A similar result was also obtained from NMR spectral measurements.

Figure 2 shows, for an example, the NMR spectral change of this system under Benesi-Hildebrand conditons [14], i.e., [MIPKD]

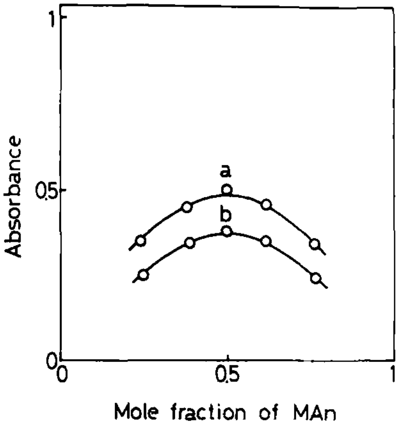


FIG. 1. Continuous variation for the CT complex formation of MIPKD with MAn in benzene at 25°C: (a) at 360 nm, (b) at 380 nm. [MAn] = [MIPKD] = 1 mole/liter.

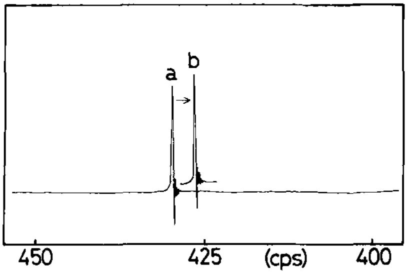


FIG. 2. Variation of NMR spectra of the mixture of MAn (0.1 mole/liter with MIPKD. (A) [MIPKD] = 1.52 mole/liter; (B) [MIPKD] = 5.53 mole/liter; in carbon tetrachloride.

$\gg$ [MAn]. It is clear that the absorption of the MAn protons shifts to a high magnetic field. From these observations, the equilibrium constant K for complex formation was determined according to the Benesi-Hildebrand equation [14] [Eq. (2)]:

$$\frac{1}{[\mathrm{MIPKD}]} = (1/\Delta_{obs})\, K\, \Delta_c - K \qquad (2)$$

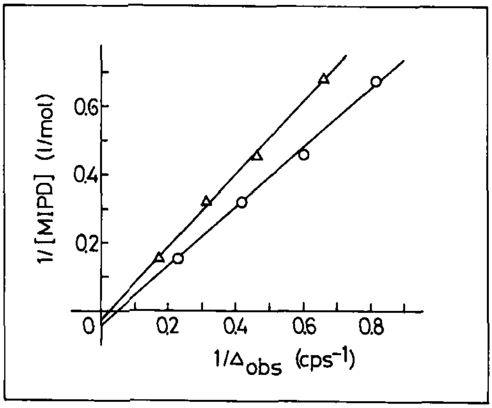


FIG. 3. Plots by Eq. (2): (○) MIPKD-MAn system; (△) MIPKD-MI system ([MI] = 0.1 mole/liter).

where $\Delta_{obs} = \delta_f^A - \delta_{obs}^A$ and $\Delta_c = \delta_f^A - \delta_c^A$. δ_f^A and δ_c^A are the chemical shifts of free and complexed MAn, respectively, and δ_{obs}^A is the observed chemical shift based on MAn which is expressed by Eq. (3).

$$\delta_{obs}^A = \delta_f^A \frac{[\mathrm{MAn}]}{[\mathrm{MAn}] + [\mathrm{complex}]} + \delta_c^A \frac{[\mathrm{complex}]}{[\mathrm{MAn}] + [\mathrm{complex}]} \qquad (3)$$

The plot of Eq. (2) is shown in Fig. 3, in which a similar plot for MIPKD-MI system is also shown. For this system, 1:1 CT complex formation was also confirmed from UV and NMR measurements. From Fig. 3 plots according to Eq. (2) give straight lines, and the K values are calculated as 0.03 and 0.02 l/mole for the MIPKD-MAn and MIPKD-MI system, respectively. From the observed small K values, both 1:1 CT complexes seem to be weak or of the contact type, similar to that of methyl vinyl ketone cyclodimer with MAn [5].

The shift of protons in MAn to high magnetic field (Fig. 2) may also be due to the magnetic anisotropy of carbon-carbon double bond in MIPKD, in which two double bonds of MIPKD and MAn are expected to approach in parallel with each other. Such a shift was also observed in the MIPKD-MI system. Therefore the formation of the complex seems to be favorable to the copolymerization, since the overlap of the reacting π orbitals of both monomers is possible.

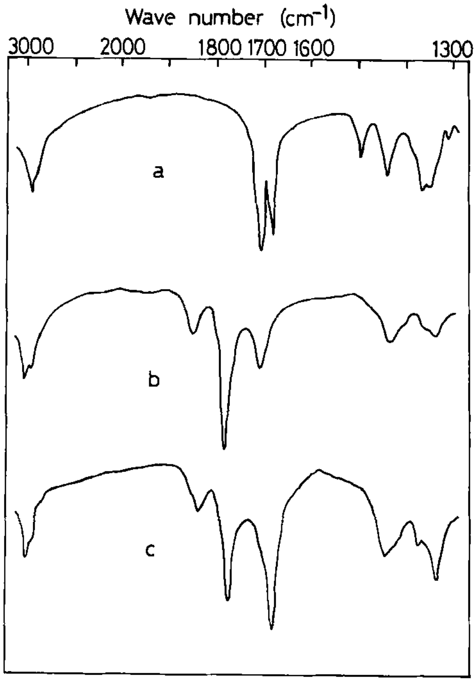


FIG. 4. IR spectra of MIPKD, MIPKD-MAn copolymer and MIPK-MAn copolymer: (a) MIPKD (neat liquid); (b) MIPKD-MAn copolymer (film); and (c) MIPK-MAn copolymer (film).

Copolymerization of MIPKD with MAn

MIPKD does not homopolymerize at 60 and 80°C with AIBN as an initiator. However MIPKD can copolymerize with MAn to give a colorless, powderlike copolymer which is soluble in dioxane and acetone. Figure 4 shows the IR spectrum of the resulting copolymer together with that of MIPKD and the MIPK-MAn copolymer.

The MIPKD-MAn copolymer (Fig. 4b) shows the characteristic peaks of MIPKD and MAn, i.e., at 1717 cm^{-1} for C=O group of MIPKD unit, and at 1798 and 1848 cm^{-1} for the anhydride group of MAn. Therefore it is clear that the resulting polymer is a copolymer of MIPKD and MAn. Comparison of the two spectra (Fig. 4a, 4b) shows also that the MIPKD copolymerizes with MAn through its internal double bond, since the absorption band due to the double bond at 1690 cm^{-1} observed in MIPKD disappears in the copolymer obtained.

TABLE 1. Copolymerization of MAn (M_1) with MIPKD (M_2)[a]

Temperature (°C)	[M_2] in feed (mole %)	Reaction time (hr)	Yield (%)	Elementary analyses: Carbon (%)	Elementary analyses: Nitrogen (%)	[M_2] in copolymer (mole %)[b]
60	19.1	4	1.3	59.69	0.77	30.9
	30.5	4	1.2	60.76	0.54	36.3
	41.8	4	1.0	61.13	0.61	37.4
	50.0	4	1.0	60.54	0.64	36.1
	65.2	4	0.6	61.22	0.62	37.7
	76.8	4	0.4	61.42	0.74	38.1
80	19.1	2	4.5	58.07	0.83	26.5
	30.5	2	4.0	59.71	0.77	31.0
	41.8	2	3.9	60.85	0.77	35.4
	50.0	2	3.2	60.53	0.87	33.7
	65.2	2	2.3	59.82	0.84	31.1
	76.8	2	1.8	60.52	0.97	33.1

[a] Reaction conditions: [MAn] + [MIPKD] = 3.14 mole/liter; [AIBN] = 5×10^{-2} mole/liter, in benzene.

[b] These values were calculated by considering the amount of initiator fragment at copolymer end from a nitrogen content.

Moreover, the difference of 20 cm^{-1} in wavenumber due to the carbonyl groups in MIPKD-MAn and MIPK-MAn copolymers (Figs. 4b, 4c) is far from the consideration that MIPKD converts into MIPK prior to polymerization and then reacts with MAn to give copolymer.

Table 1 shows the results of radical copolymerization of MIPKD with MAn at 60 and 80°C. It is noted that the compositions of the copolymers obtained does not change appreciably with feed monomer composition; they remain almost constant in the range from 30 to 40 mole % of MIPKD units (Fig. 5).

The relationships between the MAn concentration in the monomer feed and the rate of copolymerization R_p, and the number-average

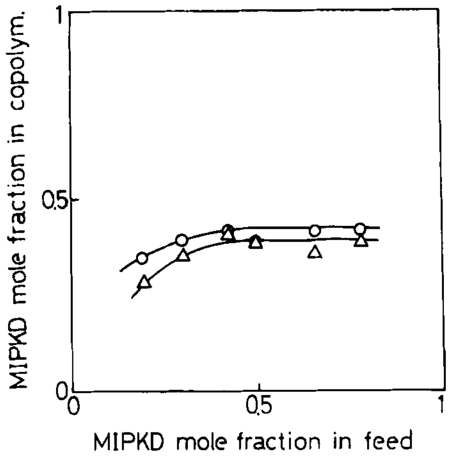


FIG. 5. Copolymer composition curves for the copolymerizations of MIPKD with MAn: (○) at 60°C; (△) at 80°C.

molecular weight $\overline{M}_n$ of the resulting copolymers are shown in Fig. 6. Both R_p and $\overline{M}_n$ are observed to increase with increasing of the feed MAn concentration. It is also found that the relationship between R_p and MAn concentration is first order. A similar dependence was also observed in radical copolymerization of N-vinylcarbazole with diethyl fumarate [15].

Figure 6 shows that the resulting copolymers are of low molecular weight. The combination of this with the result that the copolymers obtained consist of the MAn-rich composition strongly suggests that the chain transfer reaction of the growing MAn and radical to the free MIPKD and/or its complexed monomer is important.

This is also supported by the analysis of initiator fragments in the copolymers. The kinetic chain length, determined from the content of the initiator fragments which are calculated from carbon and nitrogen contents in Table 1, is several times larger than the observed degree of polymerization. In radical copolymerization of olefins having allylic hydrogen atoms with MAn, the importance of the abstraction reaction of these labile hydrogens by growing radical has been pointed out by several workers [1, 16, 17]. Since MIPKD has such labile hydrogen atoms and its reacting double bond is deactivated by tetrasubstituents, this type of chain-transfer reaction seems to play an important role in the copolymerization.

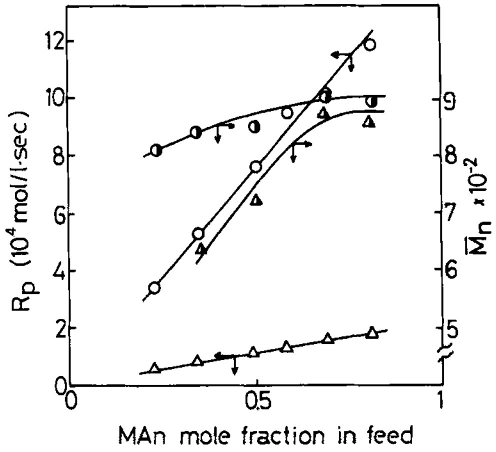


FIG. 6. Plots of (○, △) copolymerization rate R_p and (◑, ▲) number-average molecular weight $\overline{M}_n$ of the copolymers with the MAn mole fraction in the monomer feed: (△, ▲) at 60°C; (○, ◑) at 80° C.

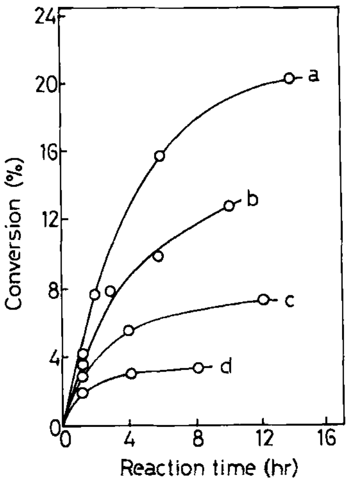


FIG. 7. Time-conversion curves for the copolymerization of MIPKD with MAn in the presence of various AIBN concentrations; (a) 0.1 mole/liter; (b) 0.07 mole/liter; (c) 0.03 mole/liter; (d) 0.01 mole/liter; at 80° C ([MIPKD] = [MAn] = 1.57 mole/liter).

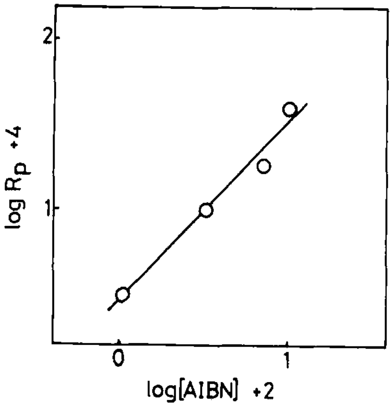


FIG. 8. Dependence of the AIBN concentration with the rate of copolymerization R_p at 80°C; [MIPKD] = [MAn] = 1.57 mole/liter.

Figure 7 shows the time-conversion curves for the copolymerization of MIPKD with MAn initiated by AIBN. From this figure, the R_p rates of polymerization are determined from the initial slopes of these time-conversion curves, and these R_p are found to be proportional to the first order with respect to the AIBN concentration as shown in Fig. 8. Therefore, the degradative chain transfer to free MIPKD and/or its complexed monomer seems to occur in a striking manner.

To confirm the copolymerization mechanism further, the apparent activation energy was estimated. As can be seen from the Arrhenius plot of Fig. 9, the apparent activation energy for the copolymerization of MIPKD with MAn initiated by AIBN is evaluated to be 92 kjoule/mole. This value is in good agreement with those (96.3 and 92.1 kjoule/mole) for the copolymerizations of MAn with vinyl sulfide [18] and with p-dioxene [19], respectively.

In addition, this copolymerization is not performed in the absence of AIBN under the conditions: [MIPD] = [MAn] = 1.57 mole/liter in benzene at 80 and 90°C for 2 hr. Therefore, no initiating radical formation from the CT complex occurs, contrary to the results of thermal initiation of the systems, MAn and strong electron-donating monomers such as styrene, p-dioxene [19], and vinyl sulfides [18].

As can be seen from the structure III, MIPKD is a tetra-substituted ethylenic monomer, and the steric effect of the substituents is important for the copolymerization. In fact, Murahashi and Nozakura [9] found that tetramethylethylene did not copolymerize with MAn, but

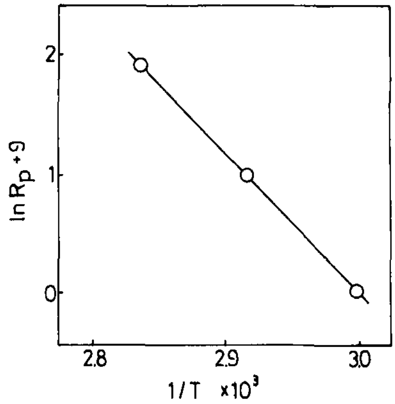


FIG. 9. Plots of ln R_p with 1/T for the copolymerization of MIPKD with MAn at 60, 70, and 80° C; [MIPKD] = [MAn] = 1.57 mole/liter; [AIBN] = 5×10^{-2} mole/liter.

trimethylethylene copolymerized readily. Therefore, the difference in reactivities between tetramethylethylene and MIPKD seems to be due to the cyclic structure of the latter, which reduces the steric effect. They also showed that the strain in internal olefins might affect their copolymerization reactivities with MAn, and the increase in such strain increased the reactivities [7].

From IR spectral determination, MIPKD shows an absorption band due to its double bond at 1690 cm^{-1}. This band is somewhat higher than those of methyl vinyl ketone cyclodimer (1680 cm^{-1}) and chloromethyl vinyl ketone cyclodimer (1670 cm^{-1}) [10]. Such a difference seems to depend not only on the polar effect, but also on the strain, and hence increased strain in MIPKD seems to relax its steric hindrance.

Copolymerization of MIPKD with MI and other Monomers

To clarify the behavior of MAn in its copolymerization with MIPKD, the copolymerizations of MIPKD with various monomers were carried out. Under similar conditions, the electron-accepting monomers with similar Q and e values to MAn, such as maleic acid, diethyl fumarate and fumaronitrile are found not to copolymerize with

TABLE 2. Copolymerization of MI (M_1) with MIPKD (M_2)[a]

[M_2] in feed (mole %)	Reaction time (min)	Yield (%)	Nitrogen by elementary analysis (%)	[M_2] in copolymer (mole %)	$\overline{M}_n$
19.1	10	9.4	11.81	11.4	3090
30.5	10	7.2	11.55	12.6	-
41.8	10	4.8	11.36	13.5	-
50.0	10	4.0	11.34	13.6	2740
65.2	10	2.2	10.61	17.2	2600
76.8	10	1.5	9.79	21.5	-

[a] Polymerization conditions: [MIPKD] + [MI] = 3.14 mole/liter; [AIBN] = 5×10^{-2} mole/liter; in dioxane at 80°C.

MIPKD. However, it was found that MI gave a copolymer with MIPKD which is a colorless powder and soluble in tetrahydrofuran but insoluble in benzene. Such difference seems to originate from the fact that MI consists of a cyclic structure, in addition to the ability of MI to participate in CT complex formation with MIPKD, as mentioned above.

Table 2 shows the results of the copolymerization of MIPKD with MI. It is found that the resulting copolymer which composed of the MI unit-rich composition are of higher molecular weight than those of MIPKD with MAn. Such a difference may reflect the higher homopolymerization ability of MI compared to MAn [20].

From these facts, it is concluded that the stereochemical structure relating steric hindrance of the comonomer used, as well as its electronic character, also affects the radical copolymerization reactivity with MIPKD. In addition, the CT complex formation in the ground state seems to be a dominant factor, since the formation of a CT complex with MIPKD with maleic acid, diethyl fumarate, and fumaronitrile is not observed.

REFERENCES

[1] T. Otsu, M. Taniyama, and M. Imoto, Mem. Fac. Eng. Osaka City Univ., 10, 165 (1968).

[2] T. Tomono, S. Iwatsuki, and Y. Yamashita, Kogyo Kagaku Zasshi, 70, 566 (1967).

[3] R. D. Kimbrough, Jr., W. P. Dickson, and J. M. Wilkerson, III, J. Polym. Sci. B, 2, 85 (1964).

[4] K. Fujimori, J. Macromol. Sci.–Chem., A9, 495 (1975).

[5] A. Tamura, S. Morita, K. Kakimoto, M. Tanaka, and J. Murata, Kogyo Kagaku Zasshi, 73, 217 (1970).

[6] S. Iwatsuki, S. Iguchi, and Y. Yamashita, Kogyo Kagaku Zasshi, 68, 2463 (1965).

[7] S. Murachashi, S. Nozakura, and K. Yasufuku, Bull. Chem. Soc. Japan, 38, 2082 (1965).

[8] C. C. Price, J. Polym. Sci., 1, 83 (1946).

[9] S. Murahashi and S. Nozakura, Bull. Chem. Soc. Japan, 39, 1338 (1966).

[10] H. Tanaka and T. Otsu, J. Macromol. Sci.–Chem., A11, 231 (1977).

[11] D. L. Stearns and W. E. Heinz, U. S. Pat. 2,851,497 (1958).

[12] W. Grimme and F. Eugelhardt, Ger. Pat. 1,004,807 (1957).

[13] T. White and R. N. Haward, J. Chem. Soc., 1943, 25.

[14] H. A. Benesi and J. H. Hildebrand, J. Amer. Chem. Soc., 71, 2703 (1949).

[15] Y. Shirota, M. Yoshimura, A. Matsumoto, and H. Mikawa, Macromolecules, 7, 4 (1974).

[16] M. M. Martin and N. P. Jensen, J. Org. Chem., 27, 1201 (1962).

[17] S. Nozakura and Y. Inaki, Progr. Polym. Sci. Japan, 2, 109 (1971).

[18] H. Inoue and T. Otsu, Makromol. Chem., 153, 21 (1972).

[19] S. Iwatsuki, Y. Tanaka, and Y. Yamashita, Kogyo Kagaku Zasshi, 67, 1467 (1964).

[20] Y. Nakayama and G. Smets, J. Polym. Sci. A-1, 5, 1619 (1967).

Accepted by editor March 30, 1977
Received for publication April 22, 1977