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Ternary Molecular Complex in the Alternating Copolymerization of Methyl Methacrylate with Styrene Using Stannic Chloride

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ABSTRACT

The equimolar alternating copolymerization of methyl methacrylate (MMA) with styrene (St) in the presence of stannic chloride in toluene (Tl) is investigated kinetically. The concentrations of the ternary molecular complexes, [$SnCl_4$·MMA····St] and [$SnCl_4$·MMA····Tl], are calculated by use of the formation constants of the ternary molecular complexes. The rates of copolymerization under photoirradiation and with tri-n-butyl boron—benzoyl peroxide as an initiator are proportional to the 1.5th order and 1.0th order, respectively, of the concentration of the ternary molecular complex [$SnCl_4$·MMA····St]. The alternating copolymerization precedes the homopolymerization of the methyl methacrylate charged in excess. The alternating regulation of the copolymerization is ascribed to the homopolymerization of the ternary molecular complex from the kinetic results. The magnitudes of the shifts for the four groups of protons in the coordinated methyl methacrylate on the ternary molecular complex formation are kept in a specific ratio which indicates a specific time-averaged orientation of benzene ring to the coordinated methyl methacrylate. A charge transfer absorption band and the thermodynamic parameters for the formation of the ternary molecular complex are also discussed.

INTRODUCTION

Several kinetic studies have revealed the various complicated features of the equimolar alternating copolymerization of polar vinyl monomer with donor monomer in the presence of metal halide. On the copolymerization of methyl methacrylate (MMA) with styrene (St) in toluene using ethylaluminum sesquichloride, the rate order with respect to the concentration of the ternary molecular complex $[AlEt_{1.5}Cl_{1.5}\cdot MMA\cdots St]$ varied between 1.0 and 2.0 with the charged concentration of alkylmetal halide, and the reaction did not attain steady-state conditions [1]. The rate of copolymerization of methyl acrylate with styrene in the presence of ethylaluminum sesquichloride was proportional to the concentration of the ethylaluminum sesquichloride-methyl acrylate complex, being independent of both the concentrations of free methyl acrylate and styrene [2]. The copolymerization of methyl methacrylate and butadiene using an $AlEtCl_2$-$VOCl_3$ catalyst proceeded by a rapid initiation followed by stepwise propagation, and the rate did not depend on the charged concentrations of either methyl methacrylate and butadiene [3]. Whether these kinetic features are essential for the alternating regulation or not is a significant problem for elucidation of the alternating copolymerization mechanism.

In our previous paper [4], the equilibrium constants (K_{A1}, K_{A2}) for the complex formation between stannic chloride and methyl methacrylate were determined at several different temperatures by use of the absorbance in the 355 nm region, e.g., $K_{A1} = 65$ and $K_{A2} = 12$ liter/mole at -50°C in toluene. The continuous variation plots using the ^{1}H-chemical shifts revealed a 1:1 interaction between the methyl methacrylate coordinated to stannic chloride and styrene or toluene (Tl) [5-7]. Furthermore, the equilibrium constants (K_{St}, K_{Tl}) for the formation of the ternary molecular complex have been determined in n-hexane at the temperature range -50 to +20°C by use of the chemical shift [5-7].

In the alternating copolymerization solution of methyl methacrylate with styrene in the presence of stannic chloride in toluene, consequently, there exist four equilibria:

$$SnCl_4 + MMA \overset{K_{A1}}{\rightleftharpoons} SnCl_4(MMA) \tag{1}$$

$$SnCl_4(MMA) + MMA \overset{K_{A2}}{\rightleftharpoons} SnCl_4(MMA)_2 \tag{2}$$

$$SnCl_4 \cdot MMA + St \overset{K_{St}}{\rightleftharpoons} [SnCl_4 \cdot MMA \cdots St] \tag{3}$$

$$SnCl_4 \cdot MMA + Tl \overset{K_{Tl}}{\rightleftharpoons} [SnCl_4 \cdot MMA \cdots Tl] \tag{4}$$

where $SnCl_4 \cdot MMA$ represents the methyl methacrylate coordinated to stannic chloride, and $[SnCl_4 \cdot MMA \cdots St]$ and $[SnCl_4 \cdot MMA \cdots Tl]$ are the ternary molecular complexes of the coordinated methyl methacrylate with styrene and toluene, respectively.

In this paper the alternating copolymerizations of methyl methacrylate with styrene in the presence of stannic chloride, both under photoirradiation and with an initiator, are kinetically investigated on the basis of the concentration of the ternary molecular complex in the polymerization mixture, which can be calculated by use of the equilibrium constants. Furthermore, the ternary molecular complex formation is examined by the ^1H-chemical shift, the charge transfer absorption band, and the thermodynamic parameters.

EXPERIMENTAL

Materials

The monomers and the solvents were purified and thoroughly dehydrated in the usual manner. Stannic chloride was stored under an atomosphere of nitrogen after distillation from phosphorous pentoxide and led directly into a polymerization ampule by distillation in vacuo.

Copolymerization

The copolymerization solution in toluene in a Pyrex glass ampule, which cut off the light shorter than 300 nm, was irradiated at -50°C with a 500-W high-pressure mercury lamp. The charged molar ratio of methyl methacrylate to stannic chloride was kept at 2.4. The alternating regularity of the resulting polymer was confirmed by the same procedure as described in the previous paper [8]. The rate of the alternating copolymerization (R_p) is expressed as the copolymer yield per unit volume of the solution in 0.5 hr. All the conversions were kept below 7.5%, and the variations of the concentrations of the ternary molecular complexes with the progress of polymerization were neglected.

The copolymerization was also conducted using a radical initiator, tri-n-butyl boron–benzoyl peroxide (2:1 molar ratio), instead of photoirradiation. The copolymerization rate (R_p) represents the copolymer yield per unit volume of the solution in 2 hr. All other conditions were the same as described above.

Spectrometry

Absorption spectra were obtained in methylene chloride at -70 ± 1°C by a Shimazu MPS-50L spectrophotometer using a cell of 1 cm path length set in a transparent quartz Dewar vessel with a Dry Ice-methanol coolant.

^{1}H-NMR spectra were run on a 100 MHz JEOL spectrometer using tetramethylsilane as internal standard.

RESULTS

Molecular Complex Formation

The formation constants of the ternary molecular complex between the coordinated methyl methacrylate and styrene or toluene in n-hexane were determined more precisely in consideration of the equilibriums of Eqs. (1) and (2) by use of the ^{1}H-chemical shifts according to the previous reports [5-7]. For the $SnCl_4(MMA)_2$ complex-aromatic donor system, the charged concentrations of methyl methacrylate and stannic chloride were 0.20 and 0.04 mole/liter, respectively, in order to suppress the dissociation of the $SnCl_4(MMA)_2$

TABLE 1. Thermodynamic Parameters for the Molecular Complex Formation in n-Hexane

System	Δ_{AD}[a] (ppm)	K[b] (liter/mole)	-ΔH (kcal/mole)	-ΔS (eu)
$SnCl_4(MMA)_2$-St	0.67	0.75	2.4 ± 0.1	11.2 ± 0.6
$SnCl_4(MMA)_2$-Tl	0.74	1.65	3.3 ± 0.2	13.8 ± 0.8
$SnCl_4$(MMA)-St	0.74	0.99	2.7 ± 0.2	12.3 ± 0.8
$SnCl_4$(MMA)-Tl	0.74	1.29	3.1 ± 0.2	13.4 ± 0.8
MMA-St	0.42	0.27	1.5 ± 0.1	9.4 ± 0.4
MMA-Tl	0.46	0.33	1.8 ± 0.1	10.2 ± 0.4

[a] Chemical shift change of the methoxy protons for the formation of pure molecular complex.

[b] Equilibrium constant at -50°C.

complex [7]. For the $SnCl_4$(MMA) complex-aromatic donor system, those of methyl methacrylate and stannic chloride were 0.05 and 0.30 mole/liter, respectively, in order to prevent the formation of the $SnCl_4(MMA)_2$ complex. The resulting equilibrium constants at -50°C and the thermodynamic parameters obtained from those at four different temperatures are listed in Table 1.

The copolymerization conditions where the charged stannic chloride exclusively forms the 1:2 complex with methyl methacrylate can be chosen in order to simplify the population of the complex species in the copolymerization solution. Under the conditions where the molar ratio of the charged methyl methacrylate to stannic chloride is 2.4 ([MMA] = 4.80, [$SnCl_4$] = 2.00 mole/liter) in toluene and at -50°C, the concentrations of the 1:2 stannic chloride-methyl methacrylate complex, the 1:1 stannic chloride-methyl methacrylate complex, and free methyl methacrylate in the copolymerization solution are estimated to be 1.84, 0.16, and 0.96 mole/liter respectively, by the use of $K_{A1} = 65$ and $K_{A2} = 12$ liter/mole.

Accordingly, the kinetic investigations have been conducted on the copolymerization in toluene at -50°C with a [MMA]/[$SnCl_4$] molar ratio of 2.4.

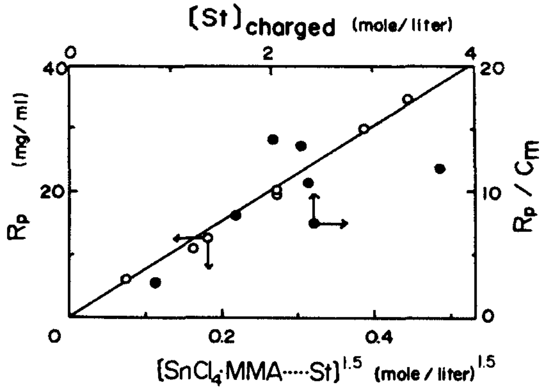


FIG. 1. Rate of alternating copolymerization vs concentration of ternary molecular complex at -50°C in toluene under photoirradiation. R_p is expressed as the yield per unit volume in 0.5 hr.

Copolymerization under Photoirradiation

As shown in Fig. 1, the rate of the alternating copolymerization under photoirradiation depends clearly on the 1.5th order of the concentration of the ternary molecular complex [$SnCl_4$·MMA····St] calculated by the use of K_{St} and K_{T1} in Table 1 [9]. Plotting either the rate (R_p) itself or the rate normalized by the concentration of the coordinated methyl methacrylate (R_p/C_m) against the charged concentration of styrene cannot give a good correlation (see Fig. 1).

The conversion increases proportionally to the polymerization time, while the intrinsic viscosity of the resulting copolymer remains constant throughout the polymerization period, as shown in Fig. 2. These results indicate that the present copolymerization process is in a steady state.

As shown in Fig. 3, the copolymerization rate is proportional to the square root of the intensity (I) of the incident light, which was controlled by variation of the distance between the lamp and the ampule.

Copolymerization with Initiator

The rate of the alternating copolymerization using tri-n-butylboron–benzoyl peroxide (2:1 molar ratio) as an initiator depends

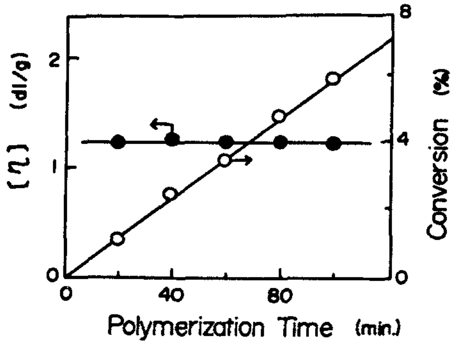


FIG. 2. Intrinsic viscosity and conversion vs polymerization time; [η] obtained in toluene at 30°C. Copolymerization conditions: photoirradiation at -50°C in toluene; [MMA] = 2.76, [St] = 1.63, [$SnCl_4$] = 1.15 mole/liter.

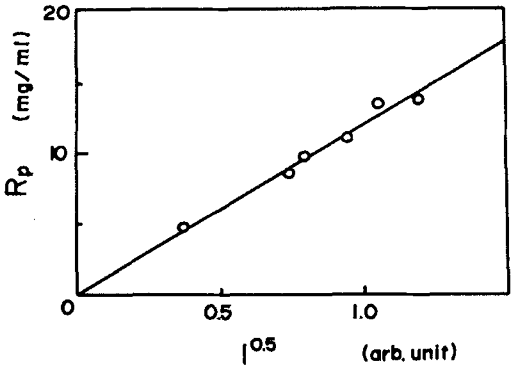


FIG. 3. Rate of alternating copolymerization vs intensity of incident light. Copolymerization conditions: photoirradiation at -50°C in toluene; [MMA] = 2.00, [St] = 1.00, [$SnCl_4$] = 0.83 mole/liter.

primarily on the first order of the concentration of the ternary molecular complex, as shown in Fig. 4. There is a poor correlation between the rate (R_p), even normalized (R_p/C_m), and the charged concentration of styrene.

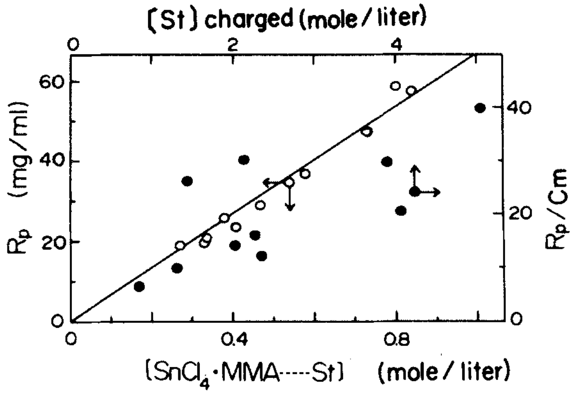


FIG. 4. Rate of alternating copolymerization vs concentration of ternary molecular complex at -50°C in toluene using $B(n\text{-}Bu)_3$–BPO initiator. R_p is expressed as the yield per unit volume in 2 hr.

The conversion is proportional to the polymerization time, and the intrinisc viscosity is independent of the time. This is similar to the results under photoirradiation (Fig. 2).

The rate is proportional to the concentration of tri-n-butyl boron used as the initiator of $B(n\text{-}Bu)_3 \cdot (BPO)_{0.5}$. The copolymerization of methyl methacrylate with styrene in the absence of stannic chloride in toluene at 30°C was also carried out using the same initiator, and the rate was found to be proportional to the concentration of tri-n-butyl boron as well. In this case the result was a random copolymer similar to that obtained by the conventional radical mechanism with a biomolecular termination.

Other Features of the Copolymerization

When methyl methacrylate is used in excess ([MMA] = 3.84, [St] = 0.36 mole/liter) for the alternating copolymerization under photoirradiation at -20°C, the rate becomes very small and almost negligible, leaving the excess methyl methacrylate unreacted after the charged styrene is consumed entirely by the alternating copolymerization, as shown in Fig. 5.

All the above copolymerizations proceeded entirely homogenously throughout the reaction time. A concurrent occurrence of cationic

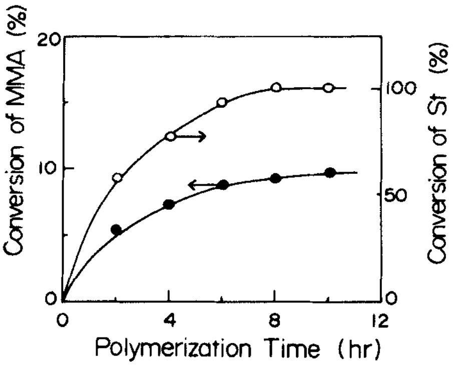
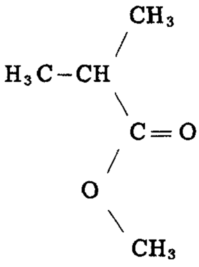


FIG. 5. Conversion vs polymerization time using the charged methyl methacrylate in excess. Copolymerization conditions: photo-irradiation at -20°C in toluene; [MMA] = 3.84, [St] = 0.36, [$SnCl_4$] = 1.60 mole/liter.

homopolymerization of styrene was not observed. When drying of the materials, expecially of stannic chloride, was insufficient, however, the copolymerization behavior changed remarkably. The appearance of white precipitates or gelation often occurred in the course of the polymerization, resulting in a mixture of the alternating copolymer and polystyrene. Moreover, the intrinsic viscosity of the alternating copolymer increased with the polymerization time.

Ternary Molecular Complex

The absorption spectrum of the $SnCl_4(MMA)_2$ complex-styrene system in methylene chloride at -70°C gives a new absorption in the 315 nm region which cannot be associated with either of the component, as shown in Fig. 6. The charge-transfer bands of the solution of the complex-aromatic donor or butadiene systems are listed in Table 2. In the cases of the free methyl methacrylate, the methyl isobutylate (1) complex and the 3-butenyl methyl ketone (2) complex-aromatic donor systems, no new band could be observed.



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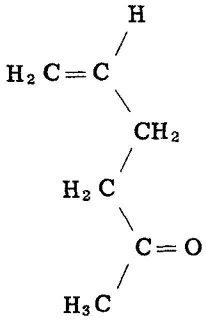

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Table 3 collects the relative ratios of the shifts for each of the groups of proton to the shift for the methoxy protons of methyl methacrylate on the molecular complex formation with styrene or toluene. The absolute limiting values of the shift (Δ_{AD}) for the methoxy protons are given in Table 1. Both the 1:2 complex-styrene and toluene systems exhibit the magnitudes of the shifts for methoxy, trans-vinyl, cis-vinyl, and α-methyl protons in a ratio of approximately 1.0:0.9: 0.5:0.5. On the other hand, both the free methyl methacrylate-styrene and toluene systems exhibit the magnitudes in a ratio of

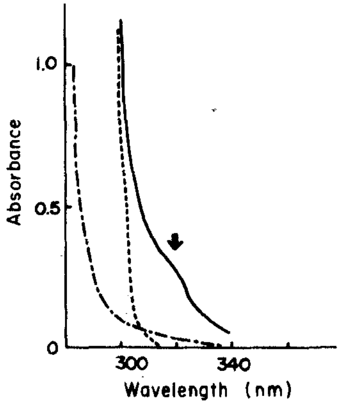

FIG. 6. Absorption spectrum of the $SnCl_4(MMA)_2$ -styrene system in methylene chloride at -70°C. (—): [MMA] = 0.26, [St] = 0.19, [$SnCl_4$] = 0.11 mole/liter. (– ·): [MMA] = 0.26, [$SnCl_4$] = 0.11 mole/liter. (- -) [St] = 0.19 mole/liter.

TABLE 2. Absorption Bands on the Molecular Complex Formation in Methylene Chloride at -70°C

System[a]		New band (λ_{max}, nm)
Acceptor	Donor	
$SnCl_4(MMA)_2$	St	+ (315)
	Tl	+
	Ms	+ (340)
	BD	+
MMA	St	-
	Ms	-
$SnCl_4(MIB)_2$	St	-
	Ms	-
$SnCl_4(BMK)_2$	St	-

[a] Ms, Mesitylene; BD, butadiene; MIB, methyl isobutyrate; BMK, 3-butenyl methyl ketone.

TABLE 3. Relative Ratios of the Shifts for the Protons in Methyl Methacrylate to That for the Methoxy Protons on the Molecular Complex Formation

System	trans-H	cis-H	α-CH_3
$SnCl_4(MMA)_2$ -St	0.91	0.55	0.49
$SnCl_4(MMA)_2$ -Tl	0.92	0.51	0.51
MMA-St	1.06	0.04	0.28
MMA-Tl	0.97	0.01	0.28

approximately 1.0:1.0:0.0:0.3. The difference between the effects of styrene and toluene on the ratios is very small.

DISCUSSION

Mechanism of the Alternating Copolymerization

From the kinetic results stated above, the scheme of the present alternating copolymerization can be proposed as follows:

1. Using photoirradiation,

$$[SnCl_4 \cdot MMA \cdots St] \xrightarrow{h\nu} [SnCl_4 \cdot MMA \cdots St]^* \longrightarrow 2R\cdot \tag{5}$$

$$R\cdot + [SnCl_4 \cdot MMA \cdots St] \xrightarrow{k_p} M\cdot \tag{6}$$

$$2M\cdot \xrightarrow{k_t} \text{polymer} \tag{7}$$

where $[SnCl_4 \cdot MMA \cdots St]^*$, R·, and M· represent the ternary molecular complex in the excited state, the initiation radical, and the propagating radical, respectively.

Under the steady-state conditions,

$$2fI[SnCl_4 \cdot MMA \cdots St] = 2k_t[M\cdot]^2 \tag{8}$$

where 2f is the quantum yield.

Generally,

$$R_p = k_p[M\cdot][SnCl_4 \cdot MMA \cdots St] \tag{9}$$

From Eqs. (8) and (9),

$$R_p = k_p(f/k_t)^{0.5} I^{0.5} [SnCl_4 \cdot MMA \cdots St]^{1.5} \tag{10}$$

2. Using initiator,

$$[B(n\text{-}Bu)_3 \cdot BPO_{0.5}] \xrightarrow{k_d} 2R\cdot \tag{11}$$

$$R\cdot + [SnCl_4\cdot MMA\cdots St] \xrightarrow{k_p} M\cdot \tag{12}$$

$$2M\cdot \xrightarrow{k_t} \text{polymer} \tag{13}$$

Under the steady-state conditions,

$$2fk_d[B(n\text{-}Bu)_3][BPO] = 2k_t[M\cdot]^2 \tag{14}$$

where f is the initiator efficiency.

Under the experimental conditions,

$$[BPO] = \frac{1}{2}[B(n\text{-}Bu)_3] \tag{15}$$

From Eqs. (9), (14), and (15),

$$R_p = k_p\,(fk_d/2k_t)^{0.5}\,[B(n\text{-}Bu)_3][SnCl_4\cdot MMA\cdots St] \tag{16}$$

Equations (10) and (16) can reasonably explain all of the experimental results.

Consequently, it can be concluded that the present alternating copolymerization proceeds through radical homopolymerization of the ternary molecular complex in the steady state.

The ternary molecular complex may be excited by the light absorption using the charge-transfer band in the 310 to 340 nm range.

As shown in Fig. 1, the concentration of the $[SnCl_4\cdot MMA\cdots St]$ complex is far less than the charged concentration of monomers, but still the ternary molecular complex governs the process of alternating copolymerization. The reactivity of the $[SnCl_4\cdot MMA\cdots St]$ complex should be overwhelmingly larger than those of the free monomers and other molecular complexes under alternating copolymerization.

Figure 5 indicates that alternating copolymerization precedes homopolymerization of the monomer charged in excess. This fact also reflects the greater reactivity of the ternary molecular complex.

Ternary Molecular Complex

The new band which appeared in the $SnCl_4(MMA)_2$ complex-donor system shifted to the longer wavelength with the lower ionization

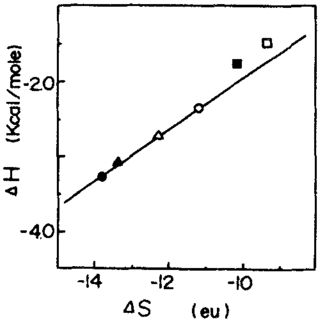

FIG. 7. Relation between enthalpy change and entropy change for the molecular complex formation: (○) $SnCl_4(MMA)_2$-styrene, (△) $SnCl_4$(MMA)-styrene, (□) MMA-styrene, (●) $SnCl_4(MMA)_2$-toluene, (■) $SnCl_4$(MMA)-toluene, and (▲) MMA-toluene.

potentials of donors; absorption shoulders were observed for styrene (I_p = 9.00 eV [10]) and mesityrene (I_p = 8.74 eV [10]) at 317 and 340 nm, respectively. These red shifts support the assignment of the band to the charge-transfer band. The modification of the acceptor monomer, as shown in Table 2, indicates that both the coordination to the Lewis acid and the conjugation of the polar group with the vinyl group are essential for the appearance of the charge-transfer band.

Figure 7 exhibits a linear relationship between enthalpy changes (ΔH) and entropy changes (ΔS) in Table 1 for the ternary molecular complex formation. This fact indicates that the same kind of interaction force functions in common with the ternary molecular complex. The values of ΔH and ΔS for the free methyl methacrylate systems seem to indicate another linear relationship. The variations of ΔH and ΔS suggest that the ternary molecular complex formation is governed by the enthalpy factor.

A specific time-averaged orientation of benzene ring to methyl methacrylate was indicated by the ratio of the shifts for methoxy, trans-vinyl, cis-vinyl, and α-methyl protons in common with the coordinated methyl methacrylate system (1.0:0.9:0.5:0.5) and with the free methyl methacrylate system (1.0:1.0:0.0:0.3), as shown in Table 3.

The binding force of methyl methacrylate with the benzene ring may be ascribed mainly to the dispersion force and to the interaction between the dipole of the carbonyl group of methyl methacrylate and the quadrupole of the benzene ring, and partly to the charge-transfer interaction of methyl methacrylate and the aromatic compound.

REFERENCES

[1] N. G. Gaylord and B. Matyska, J. Macromol. Sci.—Chem., A4, 1519 (1970).

[2] M. Hirooka, Paper Presented at the 23rd IUPAC Congress, Boston, 1971, Preprint p. 311.

[3] J. Furukawa, E. Kobayashi, Y. Iseda, and Y. Arai, Polymer J., 1, 442 (1970).

[4] H. Hirai and M. Komiyama, J. Polym. Sci., Polym. Lett. Ed., 10, 925 (1972).

[5] H. Hirai, M. Komiyama, and N. Toshima, J. Polym. Sci., B, 9, 883 (1971).

[6] H. Hirai, M. Komiyama, and N. Toshima, Ibid., 9, 789 (1971).

[7] H. Hirai and M. Komiyama, J. Polym. Sci., Polym. Chem. Ed., 12, 2701 (1974).

[8] T. Ikegami and H. Hirai, J. Polym. Sci., A-1, 8, 463 (1970).

[9] H. Hirai and M. Komiyama, J. Polym. Sci., Polym. Lett. Ed., 12, 673 (1974).

[10] G. F. Crable and G. L. Kearns, J. Phys. Chem., 66, 436 (1962).