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

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Tsutomu Oishi[a]; Masayuki Moriwaki[a]; Masaaki Momoi[a]; Minoru Fujimoto[a]
[a] Department of Industrial Chemistry, Technical College Yamaguchi University, Yamaguchi, Japan

**To cite this Article** Oishi, Tsutomu , Moriwaki, Masayuki , Momoi, Masaaki and Fujimoto, Minoru(1989) 'Reactivities of *N*-(4-Substituted Phenyl)-α-Chloromaleimide in Radical Copolymerization with Styrene or Methyl Methacrylate', Journal of Macromolecular Science, Part A, 26: 6, 861 — 876

**To link to this Article: DOI:** 10.1080/00222338908052016

**URL:** http://dx.doi.org/10.1080/00222338908052016

J. MACROMOL. SCI.–CHEM., A26(6), pp. 861-876 (1989)

# REACTIVITIES OF *N*-(4-SUBSTITUTED PHENYL)-$\alpha$-CHLOROMALEIMIDE IN RADICAL COPOLYMERIZATION WITH STYRENE OR METHYL METHACRYLATE

TSUTOMU OISHI, MASAYUKI MORIWAKI, MASAAKI MOMOI,
and MINORU FUJIMOTO

Department of Industrial Chemistry
Technical College
Yamaguchi University
2557 Tokiwadai, Ube, Yamaguchi 755, Japan

## ABSTRACT

Radical copolymerizations of *N*-(4-substituted phenyl)-$\alpha$-chloromaleimide (RPhClMI: 1, R = H; 2, R = Cl; 3, R = $OCH_3$; 4, R = $CH_3$; 5, R = $COOC_2H_5$) ($M_1$) with styrene (ST) ($M_2$) or methyl methacrylate (MMA) ($M_2$) in tetrahydrofuran at 60°C were performed with azobisisobutyronitrile as initiator. This report explores the polymerization behavior of RPhClMI and the substituent effects in copolymerizations. The following reactivity ratios were determined: $r_1$ = 0.008-0.02, $r_2$ = 0.056-0.11 in the RPhClMI-ST system and $r_1$ = 0.021-0.11, $r_2$ = 0.55-0.63 in the RPhClMI-MMA system. It was found that the relative reactivities ($1/r_2$) of RPhClMI toward a polystyryl radical was not correlated to the resonance-substituent constant ($E_R$), but it was correlated to the polar-substituent constant ($\sigma$) in the modified Hammett equation ($\log (1/r_2) = \rho\sigma + \gamma E_R$). The $\bar{M}_n$ in the RPhClMI-ST copolymer was 6 000 to 49 000; that of the RPhClMI-MMA copolymer was 2 100 to 9 700.

## INTRODUCTION

In order to obtain detailed information on the polymerization behavior of an unsaturated dibasic acid and its derivatives, we conducted studies on *N*-(4-substituted phenyl)isomaleimide [1], *N*-substituted maleimide [2], *N*-substituted citraconimide [3, 4], *N*-substituted itaconimide [5, 6], alkyl *N*-(4-substituted phenyl)itaconate [7], dialkyl mesaconate [8], dialkyl dithiol mesaconate [9], dialkyl citraconate [10], and *N*-(4-substituted phenyl)-isocitraconimide [11]. In a previous paper [3] we reported that the relative reactivities ($1/r_2$) of *N*-(4-substituted phenyl)citraconimides toward a polystyryl radical are correlated only with the polar-substituent constant ($\sigma$) of the alkyl group in the modified Hammett equation [12]:

$$\log(1/r_2) = \rho\sigma + \gamma E_R, \tag{1}$$

where $E_R$ is the resonance-substituent constant, and the reaction constants $\rho$ and $\gamma$ are 1.08 and zero, respectively.

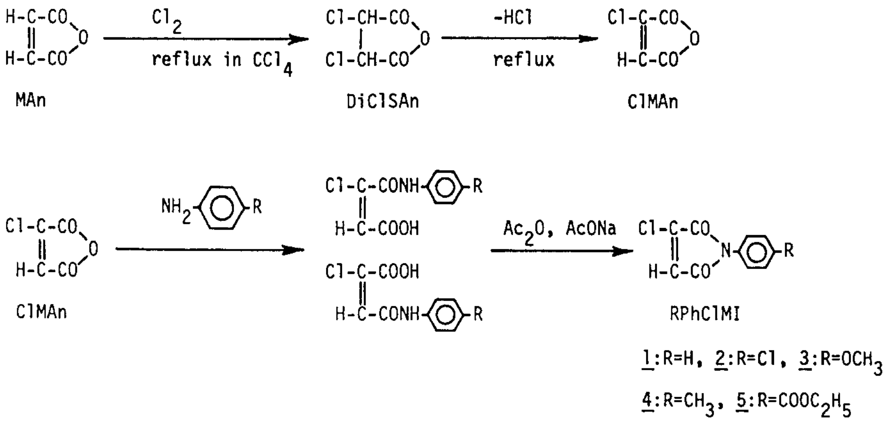
This article describes our investigation of the ($1/r_2$) values for *N*-(4-substituted phenyl)-α-chloromaleimide (RPhClMI) toward a polystyryl radical or a poly(methyl methacrylate) (MMA) radical, according to Eq. (1). Some of the RPhClMI compounds have been synthesized before [13], but never copolymerized with common vinyl monomers.

## EXPERIMENTAL

### Synthesis of RPhClMI Monomers

Five different RPhClMI monomers were prepared, as shown in Scheme 1, according to the method reported by Pyriadi et al. [13] with some modification.

*N-(4-Substituted Phenyl)-α-Chloromaleamic Acid (RPhClMA).* A solution of a primary arylamine in dry benzene was added dropwise to a dry benzene solution of α-chloromaleic anhydride [14] with vigorous stirring over a period of 30 min at 0-5°C in a three-necked flask. After stirring for 3 h, the crude product had precipitated and was filtered and purified by recrystallization from methanol. The product, obtained in about 80% yield, seemed to consist of the isomers shown in Scheme 1.



SCHEME 1.

*N-(4-Substituted Phenyl)-α-Chloromaleimide (RPhClMI).* A mixture of 0.1 mol RPhClMA, 5 g anhydrous sodium acetate, and 150 mL acetic anhydride was heated with stirring at about 95°C for 1.5 h. After cooling, the reaction mixture was poured into ice water and stirred for about 4 h. Free acid was neutralized with $NaHCO_3$ to obtain the crude RPhClMI, which was extracted with benzene. The benzene solution was dried over magnesium sulfate, filtered, and evaporated to give RPhClMI, which was recrystallized repeatedly from cyclohexane/ethanol. Yields, melting points, elemental analysis, and $^1$H-NMR data are shown in Table 1.

## Materials

Styrene (ST), methyl methacrylate (MMA), α,α'-azobisisobutyronitrile (AIBN), tetrahydrofuran (THF), and methanol were purified by the usual methods.

## Copolymerization Procedure

Radical copolymerizations were performed in the presence of AIBN in sealed glass tubes at 60°C. After the required amounts of RPhClMI monomer, comonomer (ST or MMA), and THF solution containing a constant

TABLE 1. Properties of the *N*-(4-Substituted Phenyl)-α-Chloromaleimides

| RPhClMI | | | Elemental analysis | | | | | | Chemical shift δ in ppm from $Me_4Si$ (TMS)[b] | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Yield,[a] | Calculated | | | Found | | | | | |
| 4-substituent | mp, °C | % | C | H | N | C | H | N | H–C=C | N–Ph–R | –Ph–R |
| 1 H | 160-162 | 58 | 57.9 | 2.9 | 6.7 | 57.7 | 2.9 | 6.4 | 6.65 (s) 1H | 7.25 (m) 5H | |
| 2 Cl | 154-156 | 45 | 49.6 | 2.1 | 5.8 | 49.4 | 2.1 | 5.7 | 7.10 (s) 1H[c] | 7.44 (m) 4H[c] | |
| 3 $OCH_3$ | 142-144 | 56 | 55.6 | 3.4 | 5.9 | 55.6 | 3.3 | 5.8 | 6.65 (s) 1H | 7.03 (m) 4H | 3.75 (s) 3H |
| 4 $CH_3$ | 153-155 | 41 | 59.6 | 3.6 | 6.3 | 59.7 | 3.6 | 6.3 | 6.65 (s) 1H | 7.15 (m) 4H | 2.34 (s) 3H |
| 5 $COOC_2H_5$ | 117-119 | 48 | 55.8 | 3.6 | 5.0 | 55.6 | 3.6 | 5.1 | 6.68 (s) 1H | 8.05-7.25 (m) 4H | 4.31 (q) 2H, 1.36 (t) 3H |

[a] Based on *N*-(4-substituted phenyl)chloromaleamic acids.

[b] Solvent $CDCl_3$.

[c] Solvent $CD_3COCD_3$.

amount of AIBN were placed in the tube, it was degassed under vacuum (0.01 torr) by freezing-thawing, Nitrogen was introduced, and then the tube was sealed off. The copolymerizations were accomplished while shaking the mixture in a thermostat bath at 60°C. After the desired period of time, the contents were poured into a large amount of methanol to precipitate the copolymer. The resulting copolymer was purified by reprecipitation from the THF solution into a large amount of methanol. The precipitate was filtered, thoroughly washed with methanol, and dried under reduced pressure to obtain the copolymer.

### Measurements

IR and NMR spectra, thermal, and elemental analyses were done with the same instruments as reported previously [15]. The molecular weights of the copolymers were measured by gel-permeation chromatography (GPC) by the same procedure reported in the previous paper [16].

## RESULTS AND DISCUSSION

### Homopolymerization of RPhClMI

Attempts at radical polymerization of RPhClMI in THF in the presence of AIBN (10, 30, and 100 mmol/L) at 60°C for 48 h produced no homopolymer. A similar tendency was noted for *N*-alkyl-α-chloromaleimide (RClMI) [17]. This may be attributable to steric hindrance by the α-chloro group in RPhClMI.

### Copolymerization of RPhClMI with ST

Copolymerizations of RPhClMI with ST (Table 2) proceeded homogeneously throughout. A typical copolymer composition curve is shown in Fig. 1. Other composition curves are similar to this. Table 2 shows that the conversions are highest with the monomers at about 50 mol% in the feed. In addition, Fig. 1 suggests that the copolymerization is of the alternating type. These results may be attributable to the formation of a charge-transfer (CT) complex between RPhClMI and ST, but this could not be proved experimentally. Though for the copolymerization of ST with maleic anhydride the solution becomes colored, when the monomers were mixed and the formation of a CT complex was indicated by the UV spectra [18], such phenomena were not observed in this study.

The monomer reactivity ratios, $r_1$ and $r_2$, were determined from the results

TABLE 2. Radical Copolymerizations of RPhClMI ($M_1$) with ST ($M_2$) in THF at 60°C[a]

| Monomer RPhClMI, $M_1$ | $M_1$ in monomer, mol% | Polymerization time, min | Conversion, % | N analysis, % | $M_1$ in copolymer, mol% |
|---|---|---|---|---|---|
| 1 | 18.2 | 20 | 5.2 | 4.11 | 43.9 |
| | 39.4 | 20 | 6.9 | 4.24 | 45.9 |
| | 49.8 | 20 | 7.0 | 4.27 | 46.4 |
| | 59.7 | 20 | 6.4 | 4.39 | 48.3 |
| | 80.6 | 20 | 3.0 | 4.61 | 52.0 |
| 2 | 19.9 | 10 | 5.6 | 3.81 | 45.3 |
| | 39.2 | 10 | 7.4 | 3.82 | 45.5 |
| | 49.2 | 10 | 7.9 | 3.90 | 47.1 |
| | 59.4 | 10 | 5.6 | 3.92 | 47.5 |
| | 79.9 | 10 | 3.1 | 4.12 | 51.5 |

| | | | | | |
|---|---|---|---|---|---|
| 3 | 20.8 | 10 | 4.0 | 3.72 | 42.8 |
| | 39.0 | 10 | 4.6 | 3.89 | 46.0 |
| | 49.7 | 10 | 6.2 | 3.99 | 47.9 |
| | 58.9 | 10 | 3.8 | 4.05 | 49.0 |
| | 77.8 | 10 | 2.5 | 4.35 | 55.2 |
| 4 | 19.7 | 10 | 3.0 | 3.92 | 43.4 |
| | 40.0 | 10 | 4.3 | 3.96 | 44.1 |
| | 49.5 | 10 | 6.3 | 4.19 | 48.0 |
| | 60.2 | 10 | 6.0 | 4.28 | 49.6 |
| | 79.2 | 10 | 3.1 | 4.40 | 51.8 |
| 5 | 20.3 | 10 | 5.0 | 3.47 | 45.6 |
| | 40.0 | 10 | 6.2 | 3.54 | 47.3 |
| | 49.0 | 10 | 8.0 | 3.60 | 48.8 |
| | 60.3 | 10 | 5.8 | 3.68 | 50.8 |
| | 77.6 | 10 | 3.0 | 3.69 | 51.0 |

[a] [AIBN], 10 mol/L; THF, 8 mL; $M_1 + M_2 = 2.0$ g.

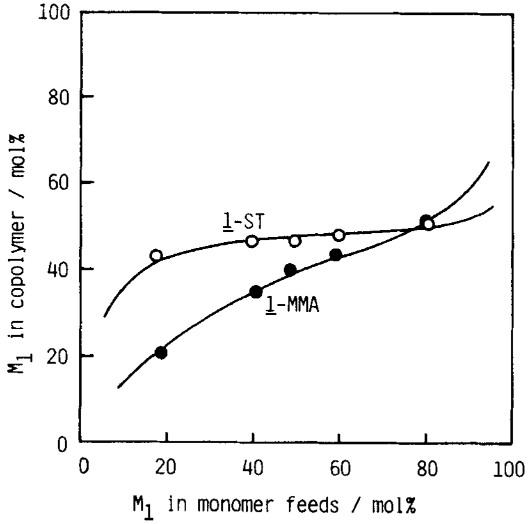


FIG. 1. Copolymer-composition curves for (○) RPhClMI (R = H) ($M_1$)-ST($M_2$) and (●) RPhClMI (R = H) ($M_1$)-MMA($M_2$) systems in THF at 60°C.

in Table 2 by the Fineman-Ross method [19] and were refined by an iterative curve-fitting method. Alfrey-Price [20] $Q_1$ and $e_1$ values were then calculated by assuming that $Q_2 = 1.0, e_2 = -0.8$ for ST [21]. All these results are shown in Table 3.

As shown in Fig. 2, plots according to Eq. (1) give a linear relation with $\rho$ equal to 0.39 (with 0.05 standard deviation). Plots of $[\log(1/r_2) - 0.39\sigma]$ against $E_R$ give an almost linear relationship, with $\gamma$ equal to 0.0 (with 0.1 standard deviation, see Fig. 3). This strongly suggests that the relative reactivities of RPhClMI toward a polystyryl radical are affected only by the polar character of the substituent R. It is very difficult to explain why the reactivity depends only on the polar character of the monomer molecule. However, this might be attributable to the conjugated structure of RPhClMI, i.e., the reacting double bond is completely conjugated with the substituent R, as illustrated in Scheme 2.

## Copolymerization of RPhClMI with MMA

Results of radical copolymerizations of RPhClMI with MMA are summarized in Table 4. The conversions tend to decrease with increasing concentra-

TABLE 3. Monomer-Reactivity Ratios for RPhClMI ($M_1$) and ST ($M_2$) or MMA ($M_2$), and $Q_1$, $e_1$ Values for the Monomer

| RPhClMI | Monomer reactivity ratios | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | $M_2$ = ST | | $M_3$ = MMA | | | | | |
| ($M_1$) | $r_1$ | $r_2$ | $r_1$ | $r_2$ | $Q_1$[a] | $e_1$[a] | $\sigma$[b] | $E_R$[b] |
| 1 | 0.015 ± 0.04 | 0.080 ± 0.04 | 0.054 ± 0.04 | 0.61 ± 0.04 | 1.57 | 1.79 | 0.00 | 0.00 |
| 2 | 0.008 ± 0.04 | 0.070 ± 0.04 | 0.021 ± 0.03 | 0.56 ± 0.04 | 1.60 | 1.94 | 0.23 | 0.10 |
| 3 | 0.062 ± 0.05 | 0.11 ± 0.06 | 0.11 ± 0.05 | 0.63 ± 0.05 | 1.52 | 1.43 | -0.27 | 0.11 |
| 4 | 0.020 ± 0.03 | 0.097 ± 0.04 | 0.071 ± 0.04 | 0.64 ± 0.05 | 1.42 | 1.68 | -0.17 | 0.03 |
| 5 | 0.020 ± 0.04 | 0.056 ± 0.05 | 0.052 ± 0.04 | 0.55 ± 0.06 | 2.22 | 1.81 | 0.45 | 0.20 |

[a] Calculated by assuming that $Q_2$ and $e_2$ of ST were 1.0 and -0.8, respectively; see Ref. 21.

[b] The constants $\sigma$ and $E_R$ from the modified Hammett equation (Eq. 1).

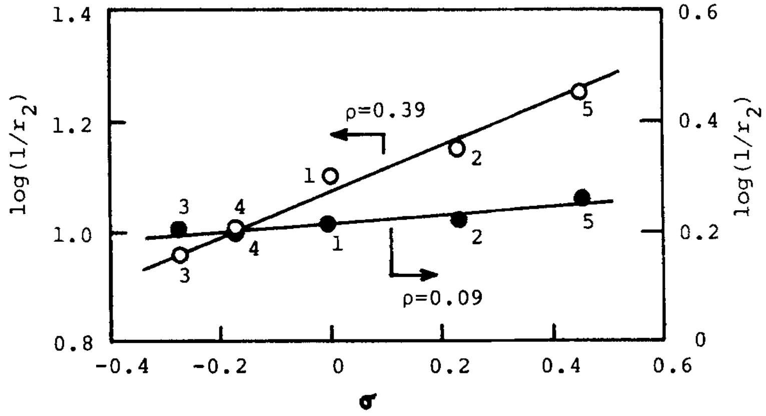


FIG. 2. Correlations between the relative reactivities ($1/r_2$) of RPhClMI ($M_1$) toward an attack by (○) a polystyryl radical or by (●) a poly(MMA) radical and the $\sigma$ constants for the substituents: 1, R = H; 2, R = Cl; 3, R = $OCH_3$; 4, R = $CH_3$; 5, R = $COOC_2H_5$.

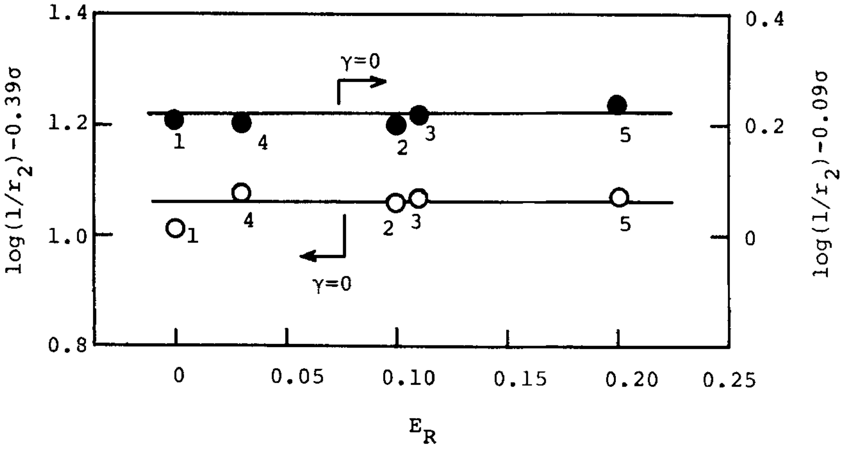
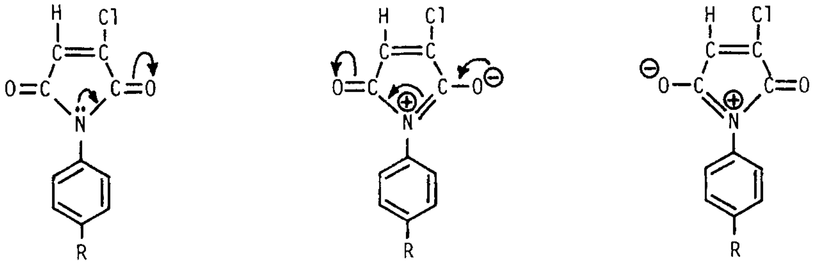


FIG. 3. Correlations between the relative reactivities ($1/r_2$) toward an attack by (○) a polystyryl radical or by (●) a poly(MMA) radical and the $E_R$ constants for the substituents: 1, R = H; 2, R = Cl; 3, R = $OCH_3$; 4, R = $CH_3$; 5, R = $COOC_2H_5$.



SCHEME 2.

tion of RPhClMI in the monomer feed. The copolymerization proceeded homogeneously throughout, as in the RPhClMI-ST system. A typical copolymer-composition curve of 1-MMA system is shown in Fig. 1. The RPhClMI content in the copolymer tends to increase with increasing RPhClMI concentration in the monomer.

Plots of log $(1/r_2)$ against the $\sigma$ constants show a good linear relationship, with $\rho$ equal to 0.09 (with 0.03 standard deviation), as shown in Fig. 2. In addition, plots according to Eq. (1) are also linear, with $\gamma$ equal to 0.0 (with 0.08 standard deviation), as shown in Fig. 3. This suggests that the reactivity depends only on the polar character of the monomer molecule, but not on the resonance character. It is interesting to note that the substituents may slightly affect the reacting double bond in RPhClMI. These phenomena can also be observed in other imides containing a five-membered ring [1-6, 11], perhaps due to the mobile lone electron-pair of the nitrogen atom in RPhClMI, as described previously [3, 4]. The conjugated system in RPhClMI may become longer owing to the mobile lone electron-pair on the nitrogen atom, as can be understood from the resonance structure illustrated in Scheme 2.

The reason for the difference between the $\rho$ values (0.39 for RPhClMI-ST and 0.09 for RPhClMI-MMA) may be as follows: 1) It can be thought that the electron density of the reacting double bond in RPhClMI is highly positive, that is, the $e_1$ values for RPhClMI are highly positive, as shown in Table 3. The ST attacking radical, which has a more nucleophilic nature than MMA, could attack the double bond of RPhClMI easily. 2) There is no large difference between the $Q$ values of ST (1.0) and MMA (0.74) [21]. Accordingly, copolymerization with ST may be more influenced by the polar character of the substituent than copolymerization with MMA.

In both the RPhClMI-ST and the RPhClMI-MMA systems, the $\gamma$ values

TABLE 4. Radical Copolymerizations of RPhClMI ($M_1$) with MMA ($M_2$) in THF at 60°C[a]

| RPhClMI, $M_1$ | $M_1$ in monomer, mol% | Polymerization time, h | Conversion, % | N analysis, % | $M_1$ incopolymer, mol% |
|---|---|---|---|---|---|
| 1 | 19.7 | 1.0 | 5.7 | 2.34 | 20.4 |
| | 40.1 | 1.0 | 5.0 | 3.55 | 34.9 |
| | 48.9 | 1.0 | 3.1 | 3.96 | 40.7 |
| | 59.0 | 1.0 | 2.0 | 4.22 | 44.6 |
| | 79.8 | 2.0 | 1.1 | 4.57 | 50.3 |
| 2 | 20.9 | 1.0 | 6.1 | 2.51 | 24.1 |
| | 40.4 | 1.0 | 4.1 | 3.32 | 35.8 |
| | 49.1 | 1.0 | 3.2 | 3.56 | 39.8 |
| | 60.1 | 1.0 | 2.1 | 3.96 | 42.1 |
| | 77.5 | 2.0 | 1.2 | 4.01 | 48.3 |

| | | | | | |
|---|---|---|---|---|---|
| 3 | 20.1 | 1.0 | 5.7 | 2.69 | 26.1 |
| | 40.5 | 1.0 | 4.6 | 3.31 | 35.0 |
| | 50.0 | 1.0 | 3.1 | 3.40 | 36.5 |
| | 59.7 | 1.0 | 2.6 | 3.95 | 46.1 |
| | 79.3 | 2.0 | 1.6 | 4.41 | 55.6 |
| 4 | 20.0 | 1.0 | 7.3 | 2.71 | 25.3 |
| | 39.2 | 1.0 | 5.8 | 3.37 | 34.0 |
| | 49.2 | 1.0 | 3.2 | 3.51 | 36.1 |
| | 59.4 | 1.0 | 1.5 | 4.01 | 43.9 |
| | 77.1 | 2.0 | 1.0 | 4.45 | 51.8 |
| 5 | 19.4 | 1.0 | 8.1 | 2.58 | 27.5 |
| | 38.4 | 1.0 | 6.0 | 2.95 | 33.9 |
| | 48.3 | 1.0 | 4.3 | 3.15 | 37.8 |
| | 57.7 | 1.0 | 4.0 | 3.35 | 42.0 |
| | 76.4 | 2.0 | 3.0 | 3.73 | 51.1 |

[a] [AIBN], 10 mol/L; THF, 8 mL; $M_1 + M_2 = 2.0$ g.

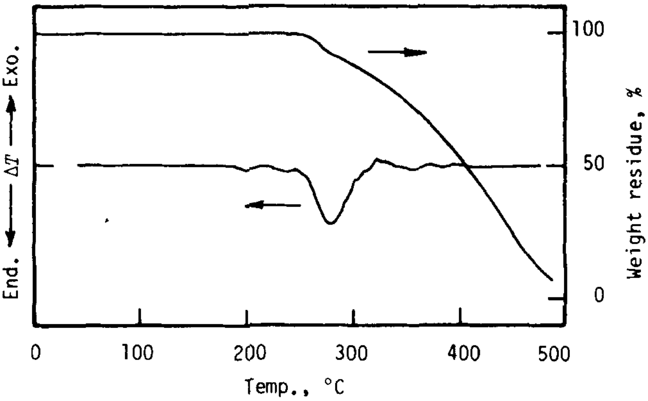


FIG. 4. TGA and DSC curves of RPhClMI (R = H)-ST copolymer (obtained from 50 mol% of RPhClMI (R = H) in monomer feed) at a heating rate of 10°C/min in a nitrogen atmosphere.

were zero. That is, there is little contribution from the resonance character of the substituents in RPhClMI. This is very difficult to explain. However, the steric hindrance of the α-chloro group in RPhClMI may be more important than the resonance character of the substituents.

It is known that the *e* values for vinyl monomers are proportional to the $\sigma$ constants of their substituents [22]. In our study, there was no linear relationship between the $e_1$ values for RPhClMI and the $\sigma$ constants. This may be according to the *Q-e* theory of Alfrey-Price [20], in which steric hindrance is neglected completely. It can be thought that the chloride group in our monomer, RPhClMI, may play an important role on the copolymerizations from the standpoint of steric hindrance.

## Properties of the Copolymers

The number-average molecular weight, $\bar{M}_n$, the weight-average molecular weight, $\bar{M}_w$, and the polydispersity were calculated as 6 000 to 49 000, 34 000 to 410 000, and 1.5 to 8.9 in the RPhClMI-ST system; 2 100 to 9 700, 6 800 to 87 000, and 1.2 to 8.0 in the RPhClMI-MMA system, respectively.

TGA and DSC curves for the RphClMI-ST copolymer are shown in Fig. 4, and the corresponding curves for the other copolymers were of similar shapes. It was found that the copolymers obtained are stable to heat to about 250°C. The weight loss of each copolymer at 400°C in a nitrogen atmosphere was between 46 and 62%.

The copolymers are all white powders and soluble in such organic solvents as THF, *N,N*-dimethylformamide, chloroform, dimethylsulfoxide, and *N,N*-dimethylacetamide.

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Received February 16, 1988
Revision received June 27, 1988