

Syntheses and Thermostabilities of N-Substituted Maleimide Copolymers. III. N-Isopropylmaleimide, N-sec-Butylmaleimide and N-tert-Butylmaleimide

Tsutomu OISHI*, Masaaki MOMOI*, Minoru FUJIMOTO*,
and Kazunori DOIUCHI**

(Received July 15, 1988)

Abstract

The objective of this study is to improve the thermostabilities of common vinyl polymers : poly[styrene (ST)] and poly[methyl methacrylate (MMA)], by using *N*-substituted maleimide (RMI) [*N*-substituent (R), R=isopropyl (IPMI), *sec*-butyl (SBMI), *tert*-butyl (TBMI)] as a comonomer. IPMI, SBMI and TBMI were copolymerized with ST or MMA in the presence of azobisisobutyronitrile in benzene at 60°C. The thermostabilities of copolymers were investigated by thermal gravimetric (TG) analysis and differential scanning calorimetric (DSC) measurements. Softening points, initial degradation temperatures, and glass transition temperatures of copolymers rose with increasing the contents of RMI in copolymers.

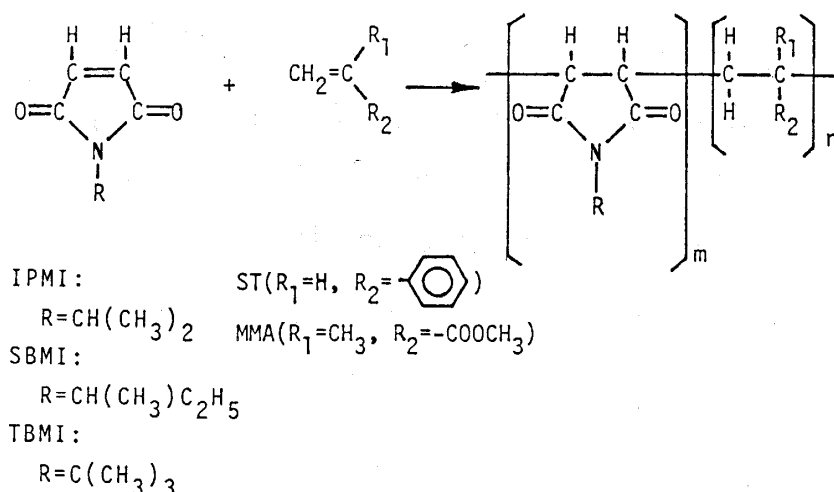
1. Introduction

It has been reported that the thermostabilities of copolymers obtained from *N*-cyclohexylmaleimide (CHMI) and *N*-benzylmaleimide (BZMI) with styrene (ST), methyl methacrylate (MMA), and vinyl acetate (VAC) in previous papers^{1,2)}. It was found that softening points (T_m), initial degradation temperatures (T_d), and glass transition temperatures (T_g) of copolymers rose with increasing the contents of CHMI or BZMI in copolymers. In this article, we describe copolymerizations of *N*-isopropylmaleimide (IPMI), *N*-*sec*-butylmaleimide (SBMI), and *N*-*tert*-butylmaleimide (TBMI) with ST, MMA, and thermostabilities of the copolymers.

There have been many reports on the polymerization reactivity of *N*-substituted maleimide (RMI)³⁾. However, no systematic studies on the thermostabilities of RMI copolymers, especially on T_g determined by TG-DSC, have been carried out.

*Department of Industrial Chemistry, Technical College.

**Nippon Oil & Fats Co., Ltd.



Scheme 1

2. Experimental

2.1 Monomers

Method A. IPMI, SBMI and TBMI were prepared from maleic anhydride (MAN) and the corresponding primary amine according to the method reported by Searle⁴.

Method B. Methanesulfonic acid was used as a dehydration reagent instead of acetic anhydride.

Boiling points, yields, and data of NMR spectra are as follows :

IPMI : yield 27.8% (method A) ; 15.1% (method B), bp 54-55°C/2mmHg, [lit.⁵ bp 75°C/10mmHg] [lit.⁶ bp 65°C/7.5mmHg].

SBMI : yield 37.6% (method A) ; 45.0% (method B), bp 58-60°C/2mmHg.

TBMI : yield 30.2% (method A), 22.5% (method B), bp 58°C/4mmHg, [lit.⁵ 104°C/18mmHg], [lit.⁶ 63°C/1.5mmHg]

ST, MMA, α, α' -azobisisobutyronitrile (AIBN) and benzene were purified by the usual methods. Commercial methanol was used as a precipitant without further purification.

2.2 Copolymerizations

Radical copolymerizations of RMI with ST or MMA were performed in the presence of AIBN as an initiator in benzene in a sealed glass tube at 60°C. After copolymerization for a given time, the tube was opened and its contents were poured into a large amount of methanol to precipitate copolymer, using the same techniques as described in previous papers^{1,2}.

2.3 Measurements

Molecular weights of copolymers were measured by gel permeation chromatographic (GPC) analysis by using the same techniques as described in an earlier paper¹. IR and ¹H-NMR spectra were obtained, and thermal and elemental analyses were achieved by using the same instruments as reported previously¹.

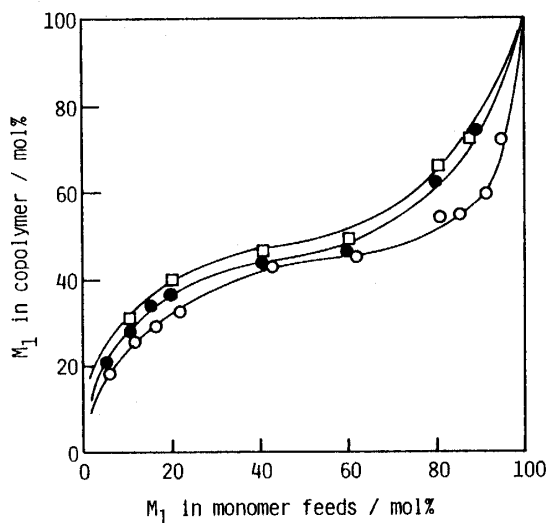


Fig. 1 Copolymer-composition curves for (○) : IPMI (M_1)–ST (M_2), (●) : SBMI (M_1)–ST (M_2), and (□) : TBMI (M_1)–ST (M_2) systems.

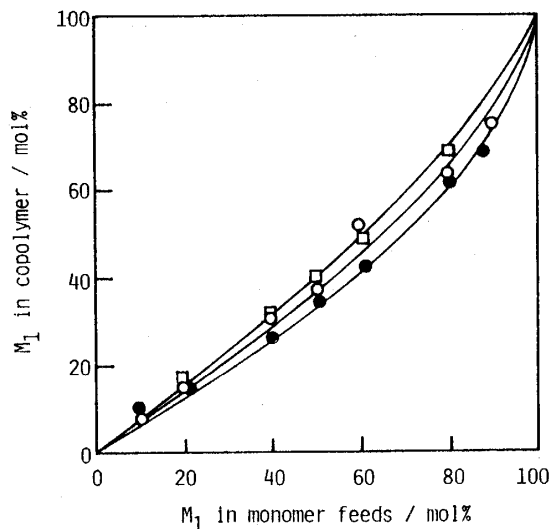


Fig. 2 Copolymer-composition curves for (○) : IPMI (M_1)–MMA (M_2), (●) : SBMI (M_1)–MMA (M_2), and (□) : TBMI (M_1)–MMA (M_2) systems.

3. Results and Discussion

3.1 Copolymerizations

Results of copolymerizations of IPMI (M_1), SBMI (M_1) and TBMI (M_1) with ST (M_2) are summarized in Table I, II, and III. All copolymerizations proceeded homogeneously throughout. Viscosity of a solution became high with the elapse of time. It can be seen from Table I, II, and III that yields are the best in about 50 mol% of monomer feeds among three systems. This tendency was also recognized in other RMI-ST systems, which suggests the formation of charge-transfer complex between RMI and ST. All copolymers were white powders. The composition of copolymer was determined from nitrogen analysis. Fig.1 gives composition curves for three systems. The order of the copolymerizability was TBMI > SBMI > IPMI. That is, substituent effects were observed in the reactivity of RMI with ST. These effects have been reported in detail previously⁶. It is generally accepted that copolymerizations of RMI with ST are alternating one⁶⁻⁸) and that each monomer reactivity ratio is practically zero. But since polymerization time is very long in this experiment, copolymerizations were not compatible with the alternating type. The reason for this may be that one of monomers is consumed completely because of long polymerization time. Copolymers were obtained quantitatively when the concentration of RMI in monomer feeds was more than 50mol%. This tendency was recognized in CHMI-ST¹⁾, BZMI-ST²⁾ systems. However, in homopolymerizations of IPMI, SBMI and TBMI, yields were less than those of CHMI, and BZMI in the same time. As shown in Table I, II, and III, the yields in 12 hrs were quantitative, but in 5 hrs were about 5.9 to 27.3%. The viscosity in polymerization system became very high, consequently the rate of polymerization increased with the elapse of time. It is thought that the Gel Effect, i.e., the Autoacceler-

Table 1 Radical Copolymerizations of IPMI(M_1) with ST(M_2) in Benzene(4mL) at 60 C^a.

run No	M_1 in monomer		Polymeriza- tion time h	Yield wt%	N-Analy- ses/%	M_1 in copolymer mol%	$M_n^{b)}$ $\times 10^{-4}$	$M_w/M_n^{b)}$
	wt%	mol%						
17-1	7.4	6.3	12.0	30.2	2.36	18.2	1.7	7.5
17-2	13.2	11.5	12.0	38.8	3.30	25.8	2.6	10.0
17-3	19.1	16.4	12.0	53.8	3.76	29.6	3.0	11.6
17-4	25.2	21.9	12.0	53.8	4.14	32.8	3.8	10.3
17-5	47.6	43.1	12.0	81.7	5.31	42.9	5.1	10.2
17-6	66.6	62.4	5.0	78.9	5.55	45.0	4.4	28.5
17-7	84.8	81.8	5.0	52.7	6.54	53.9	6.3	19.4
17-8	88.5	86.4	5.0	47.8	7.12	59.3	2.6	34.1
17-9	92.6	91.3	5.0	23.5	6.63	54.7	5.3	18.1
17-10	95.7	94.9	5.0	37.6	8.46	72.0	3.8	31.0
17-0	100.0	100.0	5.0	24.5	—	—	3.0	9.7
17-0-1	100.0	100.0	12.0	62.8	—	—	2.8	8.8

a) $[AIBN]=1.0 \times 10^{-2}$ mol/L ; $M_1 + M_2 = 1.0$ g.

b) Estimated by GPC.

Table 2 Radical Copolymerization of *N*-s-Butyl maleimide (SBMI, M_1) with Styrene (ST, M_2) in Benzene (4mL) at 60 C^a.

run No	M_1 in monomer		Polymeriza- tion time h	Yield wt%	N-Analy- ses/%	M_1 in copolymer mol%	$M_n^{b)}$ $\times 10^{-4}$	$M_w/M_n^{b)}$
	wt%	mol%						
18-1	7.2	5.0	5.0	17.9	2.61	21.4	2.0	9.0
18-2	14.6	10.0	5.0	26.0	3.39	28.6	2.3	10.5
18-3	20.5	14.9	5.0	38.0	3.95	34.1	3.0	11.1
18-4	26.2	19.4	5.0	39.5	4.20	36.6	4.7	10.8
18-5	49.7	40.2	5.0	60.6	4.92	44.2	4.0	12.7
18-6	68.4	59.6	5.0	74.7	5.13	46.5	3.7	14.9
18-7	85.0	79.4	5.0	56.8	6.53	62.9	4.4	12.7
18-8	92.3	89.0	5.0	45.6	7.40	74.2	2.7	15.1
18-0	100.0	100.0	5.0	5.9	—	—	3.9	13.4
18-0-1	100.0	100.0	19.0	65.9	—	—	1.6	12.1

a) $[AIBN]=1.0 \times 10^{-2}$ mol/L ; $M_1 + M_2 =$ about 1.0g.

b) By GPC.

Table 3 Results of Radical Copolymerization of *N*-*t*-Butyl maleimide (TBMI, M_1) with Styrene (ST, M_2) in Benzene(4mL) at 60 C^a.

run No	M_1 in monomer		Polymerization time h	Yield wt%	N-Analyses/%	M_1 in copolymer mol%	$M_n^{b)}$ $\times 10^{-4}$	Mw/ $M_n^{b)}$
	wt%	mol%						
19-2	14.1	10.1	5.0	28.8	3.68	31.4	3.3	9.2
19-4	26.8	19.9	5.0	41.3	4.61	40.9	6.0	7.9
19-5	49.8	40.3	5.0	65.3	5.16	46.8	6.2	11.9
19-6	68.6	59.8	5.0	81.2	5.36	49.1	3.9	20.3
19-7	85.6	80.1	5.0	69.9	6.77	56.9	4.1	20.7
19-8	91.8	88.3	5.0	64.9	7.38	73.9	3.7	20.0
19-0	100.0	100.0	5.0	27.3	—	—	3.6	8.4
19-0-1	100.0	100.0	12.0	61.3	—	—	3.8	7.9

a) $[AIBN] = 1.0 \times 10^{-2} \text{ mol/L}$; $M_1 + M_2 = \text{about } 1.0\text{g}$.

b) Estimated by GPC.

Table 4 Radical Copolymerization of IPMI (M_1), SBMI (M_1), TBMI (M_1) with MMA (M_2) in Benzene (4mL) at 60 C^a.

run No	M_1 in monomer		Polymerization time h	Yield wt%	N-Analyses/%	M_1 in copolymer mol%	$M_n^{b)}$ $\times 10^{-4}$	Mw/ $M_n^{b)}$
	wt%	mol%						
20 ($M_1 = \text{IPMI}$)								
20-1	13.7	10.2	19.0	77.7	1.07	7.9	2.2	9.0
20-2	25.2	19.5	19.0	78.4	1.97	15.0	2.6	8.7
20-3	47.9	39.8	19.0	85.3	3.83	30.7	2.5	10.4
20-4	58.4	50.2	19.0	86.3	4.56	37.3	1.5	24.6
20-5	67.7	60.2	19.0	85.1	6.40	52.0	3.8	13.0
20-6	84.7	79.9	19.0	83.8	7.14	63.7	2.4	29.2
20-7	92.4	89.7	19.0	83.5	8.12	75.1	1.6	56.4
21 ($M_1 = \text{SBMI}$)								
21-1	14.4	9.9	19.0	75.8	1.36	10.2	2.7	8.6
21-2	29.6	21.5	19.0	75.4	1.84	14.1	2.5	6.6
21-3	50.7	40.2	19.0	77.5	3.22	26.2	1.8	11.8
21-4	61.4	51.0	19.0	76.6	4.06	34.3	1.8	11.2
21-5	70.7	60.8	19.0	75.8	4.89	42.9	1.3	14.3
21-6	86.2	80.4	19.0	72.9	6.56	62.3	1.0	29.0
21-7	91.8	88.0	19.0	71.2	7.03	68.5	1.6	16.0
22 ($M_1 = \text{TBMI}$)								
22-1	27.4	19.8	25.0	81.7	2.19	17.1	1.2	33.6
22-2	50.1	39.6	25.0	54.5	3.76	31.4	1.6	19.1
22-3	60.2	49.7	25.0	85.8	4.67	50.5	1.8	18.4
22-4	69.3	60.3	25.0	86.2	5.41	48.6	1.9	14.5
22-5	86.0	80.1	25.0	87.3	7.03	68.5	1.8	13.6

a) $[AIBN] = 1.0 \times 10^{-2} \text{ mol/L}$; $M_1 + M_2 = \text{about } 1.0\text{g}$.

b) Estimated by GPC.

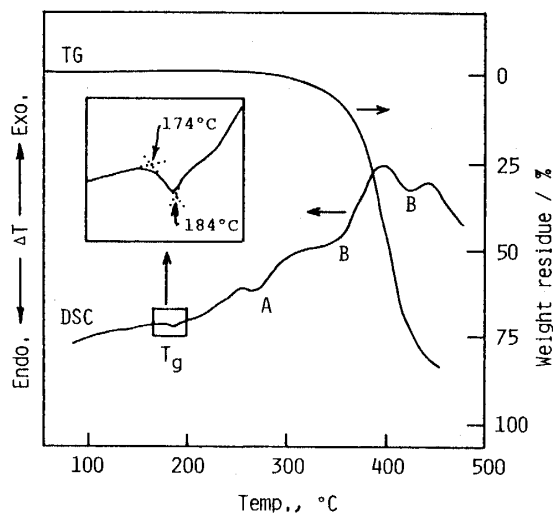


Fig. 3 TG and DSC curves for poly (IPMI-*co*-ST) [run17-5] at a heating rate of 10°C/min in nitrogen.

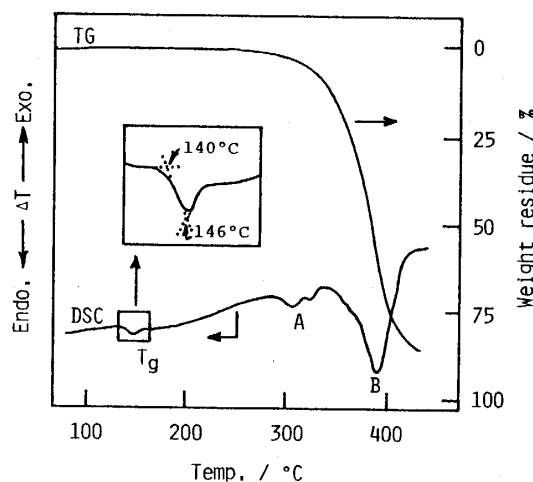


Fig. 4 TG and DSC curves for poly (SBMI-*co*-MMA) [run 21-3] at a heating rate of 10°C/min in nitrogen.

ation (Trommsdorff) Effects took place.

Results of copolymerizations of IPMI, SBMI and TBMI are summarized in Table IV. Copolymerizations proceeded homogeneous throughout as well as ST system. The rise of viscosity of the reaction system was observed. Copolymer composition curves are shown in Fig. 2. Three types of composition curves were similar and were in accord with types of an ideal copolymerization, which proceeded along an azeotropic line. A more detailed description gives the order of copolymerization reactivity as follows: TBMI-MMA > IPMI-MMA > SBMI-MMA systems. Radical reactivity of RMI in copolymerization with MMA was also influenced by *N*-substituents. Yields of copolymers were about 70 to 85 wt% in 19 hrs.

The number average molecular weights (\overline{M}_n), the weight average molecular weights (\overline{M}_w) and the polydispersity ($\overline{M}_w/\overline{M}_n$) for copolymers are as follows: $\overline{M}_w=1.7 \times 10^4$ to 6.2×10^4 , $\overline{M}_n=1.3 \times 10^5$ to 8.2×10^5 , and $\overline{M}_w/\overline{M}_n=7.5$ to 34.1 for the RMI-ST systems; $\overline{M}_n=1.0 \times 10^4$ to 3.8×10^4 , $\overline{M}_w=1.7 \times 10^5$ to 4.9×10^5 , and $\overline{M}_w/\overline{M}_n=6.6$ to 56.4. The polydispersities of copolymers in this experiment were very large, compared with those of copolymers obtained in shorter polymerization time.

All copolymers were white powders and soluble in such organic solvents as THF, chloroform, dioxane, benzene, toluene, dimethyl sulfoxide (DMSO), *N,N*-dimethyl formamide, and *N,N*-dimethyl acetamide.

3.2 Thermostabilities of Copolymers

Typical TG and DSC curves for RMI-ST copolymers are shown in Fig.3. A TG curve for poly (IPMI-*co*-ST) revealed that an initial degradation of copolymer was observed at about 292°C. In poly (IPMI-*co*-ST), three endothermic peaks were observed owing to a glass transition point (T_g), a melting point (T_m) (A in Fig.3), and decomposition (B in Fig. 3). TG and DSC curves for other poly (RMI-*co*-ST)s were similar patterns to those of poly (IPMI-*co*-ST). However, T_g of copolymers could not

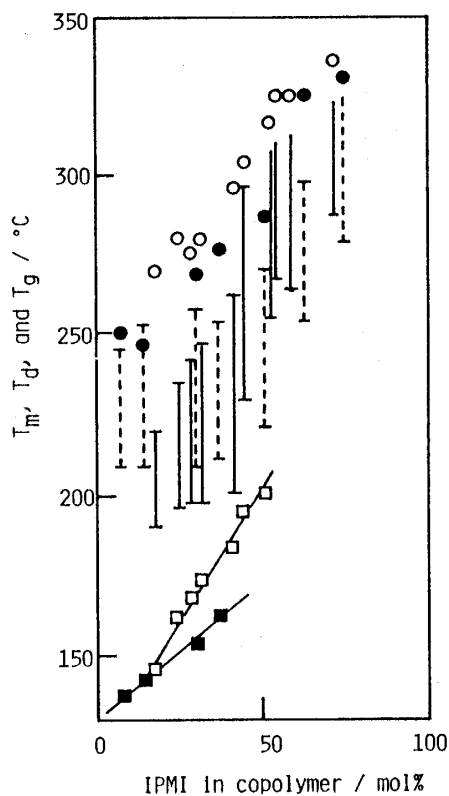


Fig. 5 Relationships between contents of IPMI in copolymer and T_m , T_d , and T_g : T_m (—), T_d (○), and T_g (□); poly (IPMI-*co*-MMA): T_m (·····), T_d (●) and T_g (■).

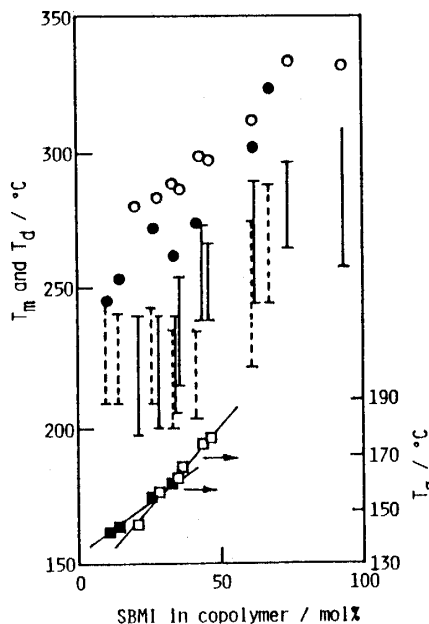


Fig. 6 Relationships between contents of SBMI in copolymer and T_m , T_d , and T_g : poly (SBMI-*co*-ST)s: T_m (—), T_d (○), and T_g (□); poly (SBMI-*co*-MMA): T_m (·····), T_d (●) and T_g (■).

be observed when concentrations of RMI in copolymer were over about 50 mol%. Homopolymers did not exhibit appreciable T_g peaks in DSC curves.

Typical TG and DSC curves for RMI-MMA copolymers are shown in Fig. 4. TG and DSC curves for other poly (RMI-*co*-MMA)s were similar patterns to those of poly (SBMI-*co*-MMA)s. However, no T_g could be observed when the concentration of RMI in copolymers were over about 30 mol%. A TG curve for poly (SBMI-*co*-MMA) shows that an initial degradation appeared at about 270°C. In addition, a DSC curve in Fig. 4 exhibits that three endothermic peaks were observed based on a T_g , a T_m (A in Fig. 4) and decomposition (B in Fig. 4). A problem is that copolymers start on decomposition while melting.

Initial degradation temperatures (T_d), T_m , and T_g of copolymers are shown in Fig. 5, 6, and 7. In both poly (IPMI-*co*-ST)s and poly (IPMI-*co*-MMA)s, all T_d , T_m and T_g became higher with an increase of the concentrations of IPMI in copolymers. These tendencies were also detected in poly (SBMI-*co*-ST)s, poly (SBMI-*co*-MMA)s, poly (TBMI-*co*-ST)s, and poly (TBMI-*co*-MMA)s, as shown in Fig. 6 and 7. Compared with T_g in the constant contents of RMI in three copolymer systems, the order of T_g was as follows: poly (IPMI-*co*-ST)s > poly (TBMI-*co*-ST)s > poly (SBMI-*co*-ST)s. In addition, the order of slopes of T_g was as follows: poly (IPMI-*co*-ST)s = poly (TBMI-

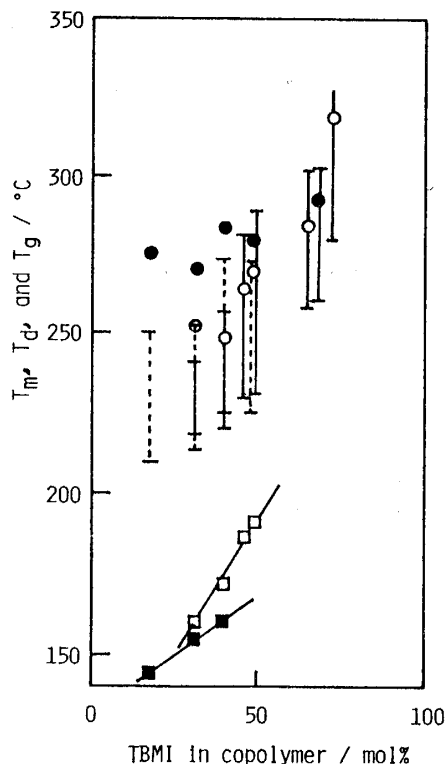


Fig. 7 Relationships between contents of TBMI in copolymer and T_m , T_d , and T_g : poly (TBMI-*co*-ST) : (—), T_d (○) and T_g (□); poly (TBMI-*co*-MMA) : T_m (·····), T_d (●) and T_g (■).

co-ST)s > poly (SBMI-*co*-ST)s. As described above, no T_g could be observed when the contents of RMI were over about 50 mol%. The reason for this may be associated with disappearance of T_g in RMI homopolymers.

On the other hand, T_g of RMI-MMA copolymers became higher with increasing the contents of RMI in copolymers. The slopes of T_g in each poly (RMI-*co*-MMA) were almost equal.

When compared with T_g of poly (BZMI-*co*-ST)s²⁾ and poly (BZMI-*co*-MMA)s,²⁾ T_g of all copolymers in this experiment were much greater with increasing the content of RMI in copolymer. That is, the slopes of T_g is greater than those of poly (BZMI-*co*-ST)s. This fact is also recognized in the MMA systems.

4. Conclusion

- (1) Three types of *N*-substituted maleimide (RMI), i. e., IPMI, SBMI and TBMI are found very useful for the improvement of T_g (80 to 90 °C)⁹⁾ of poly (ST).
- (2) As expected, these monomers, IPMI, SBMI and TBMI are useful for the improvement of T_g [38°C (isotactic) ; 105°C (syndiotactic)⁹⁾ of poly (MMA).
- (3) T_g , T_d and T_m linearly rise with increasing the contents of RMI in copolymers. This fact was recognized in both RMI-ST and RMI-MMA systems.
- (4) The greatest problem is to prepare IPMI, SBMI, and TBMI monomers since the

yields are very low. To make matters worse, these monomers have irritating smell.

References

- 1) T. Oishi, M. Momoi, M. Fujimoto, K. Sumida, and K. Doiuchi, *Memories of the Faculty of Engineering Yamaguchi Univ.*, **39**(1), 127 (1988).
- 2) T. Oishi, M. Momoi, M. Fujimoto, K. Katoh and Y. Koinuma, *Memories of the Faculty of Engineering Yamaguchi Univ.*, **39**(1), 135 (1988).
- 3) For examples : T. Oishi and T. Kimura, *Kobunshi Ronbunshu*, **33**, 685 (1976) ; T. Oishi and T. Kimura, *Kobunshi Ronbunshu*, **36**, 751 (1979).
- 4) N. E. Searie, U.S. Patent, **7**, 444, 536 (1948).
- 5) R. C. P. Cubbon, *Polymer*, **6**, 419 (1966).
- 6) I. Takase, S. Fukushima, H. Aida, and M. Yamada, *Kobunshi Kagaku*, **30**, 632 (1973).
- 7) T. Oishi, and T. Kimura, *Kobunshi Ronbunshu*, **32**, 380 (1975).
- 8) T. Oishi, and T. Kimura, *Kobunshi Ronbunshu*, **33**, 141 (1976).
- 9) J. Brandrup and E. H. Immergut, *Polymer Handbook*, John Wiley and Sons Interscience, N. Y., (1974), PP. V-51 to V-59, and P. III-139.