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Polymerization of *N*-Substituted Maleimides Initiated by Thiophenol

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ABSTRACT: Thiophenol initiated the polymerization of *N*-substituted maleimides such as *N*-phenylmaleimide (N-PMI) and *N*-ethylmaleimide (N-EMI) without oxidant. The SEC spectrum of poly(N-PMI) was multimodal; however, it changed to unimodal in the presence of hydroquinone and polymerization was partially inhibited. The results indicated that the polymerization proceeded *via* both radical and non-radical reactions. The radical polymerization was initiated by radical species yielded from a charge–transfer complex of thiophenol with N-PMI, and the non-radical process was assumed to be an anionic one in which the Michael addition of thiophenol to N-PMI initiated the polymerization.

KEY WORDS *N*-Phenylmaleimide / *N*-Ethylmaleimide / Michael Addition / Radical Polymerization / Anionic Polymerization /

The radical polymerization of *N*-substituted maleimides is well known and a large number of papers has been published[1-4]; however, only limited research groups have reported on anionic polymerization.[5-7] Recently Oishi *et al.* showed an interesting method for the preparation of optically active polymaleimides using an anionic initiator combined with a chiral base.[8] On the other hand, some step-reaction polymerizations of bismaleimides have been reported: diamines[9-11] and dithiols[12] add to bismaleimides forming polymers. We previously reported a polymerization of methyl methacrylate (MMA) initiated by thiophenol, in which the Michael addition of thiophenol to the monomer forms an initiating anionic species and the propagating chain end adds to additional monomers yielding poly(MMA).[13] We further examined various monomers having α,β-unsaturated carbonyl groups for the Michael addition-initiated polymerization and have found that *N*-substituted maleimides such as *N*-phenylmaleimide (N-PMI) and *N*-ethylmaleimide (N-EMI) are polymerized by thiophenol. No report on the polymerization of maleimides initiated by thiophenol has been published. In this paper we discuss the mechanism of polymerization, in which both radical and ionic processes proceed.

EXPERIMENTAL

Materials

N-PMI and N-EMI were recrystallized from cyclohexane and petroleum ether, respectively. MMA and styrene were purified by distillation according to conventional methods. Thiophenol was distilled under nitrogen and stored while being protected from atmospheric oxygen. DMF and acetonitrile were distilled over calcium hydride and phosphorous pentoxide, respectively. Other special grade reagents and solvents were used without further purification.

Polymerization

Typical reaction conditions are as follows:

A *N*-substituted maleimide (7.5 mmol) and a solvent (2 ml) were placed in a glass tube, which was stoppered with a rubber septum and cooled in an ice bath. After nitrogen was bubbled into the mixture using two needles through the septum for 30 min, the tube was set in a bath thermostated at 40°C, and then thiophenol was injected to start the polymerization. At certain time intervals the reaction solution was poured into methanol to precipitate the polymer. The conversion was gravimetrically determined. The polymerization was carried out in the dark because the reaction was affected even by scattered light in the room.

SEC Measurements

SEC spectra of poly(N-PMI) were obtained on a TOYOSODA HCL-802A with a column of TSK-G3000 (solvent: DMF); oligo (N-PMI), poly(N-EMI), and copolymers were on a JASCO TRI ROTAR-III with a column of KF-802.5 (solvent; THF). Polystyrene standards, supplied by Toyosoda Manufacturing Co., Ltd., were used for the molecular weight calibration.

RESULTS AND DISCUSSION

Thiophenol polymerized *N*-substituted maleimide without oxidant. Table I shows the results with N-PMI and N-EMI. The polymerization proceeded fast in tetrachloroethane; similar solvent effect was observed in the thiophenol-initiated polymerization of MMA.[13] The solvent seems therefore to facilitate this type of polymerization. Figure 1 shows the time–conversion profile of the polymerization of N-PMI in tetrachloroethane. The polymerization at an early stage was rather fast but the rate decreased markedly in time. The first order plots of monomer consumption was found to consist of two linear parts (Figure 2), indicating that polymerization proceeded *via* two different processes, one predominating at initial stage and the other at a latter stage.

Table I. Polymerization of *N*-substituted maleimides[a]

Solvent	Conversion/%	
	N-PMI[b]	N-EMI[c]
Benzene	13.9	—
Tetrachloroethane	70.0	28.1
DMF	5.7	15.0[d]
Acetonitrile	3.8[d]	20.8
DMSO	1.7	13.4[d]

[a] Monomer 7.5 mmol; thiophenol 0.075 mmol; solvent 2 ml, 40°C.
[b] Reaction time, 2 d.
[c] Reaction time, 4 h.
[d] Polymer precipitated during the reaction.

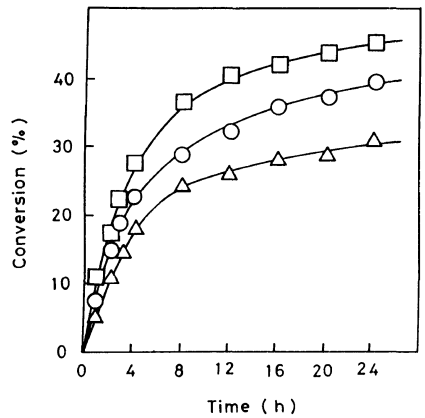


Figure 1. Polymerization of N-PMI with thiophenol in tetrachloroethane. N-MPI 7.5 mmol; thiophenol (△) 0.038 mmol, (○) 0.075 mmol, (□) 0.113 mmol; tetrachloroethane 2 ml; 40°C.

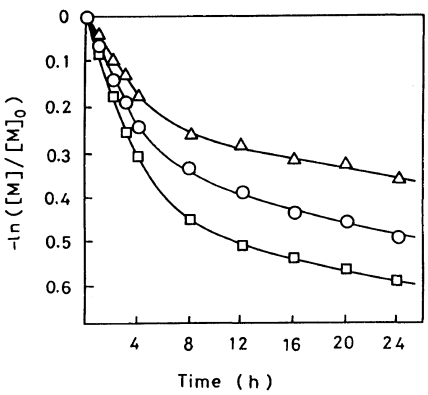


Figure 2. First-order plot of monomer consumption. The data were taken from Figure 1.

Further increase of thiophenol concentration depressed the initial polymerization rate as shown in Figure 3. This indicates that thiophenol takes part not only in the initiation but also termination. The SEC spectra of the polymer are shown in Figure 4. At a higher thiophenol concentration, 5 mol% to the monomer, the spectrum was unimodal with a quite narrow molecular weight distribution (b), whereas a bimodal spectrum was obtained when the concentration of thiophenol was relatively low: 0.5 mol%, in which the peak of the highest molecular weight was due to exclusion limit of the column. These results suggest two concurrent processes proceeding at the lower thiophenol concentration, while only one process seems to predominate at higher concentration. When thiophenol was increased to 25 mol%, the Michael adduct of thiophenol to N-PMI and oligomers composed of more than three N-PMI units were detected (Figure 5). Based on these results, one polymerization process which is predominant at higher thiophenol concentrations is presumed to include the Michael addition as Scheme 1 shows:

The ionic intermediate of the Michael reaction adds to additional N-PMI molecules to form a polymer before the propagation of the anionic chain end is terminated by proton from thiophenol. Therefore, the chain length depends on the ratio of their concentrations. Since the increase of thiophenol results in increase of the termination, the rate of

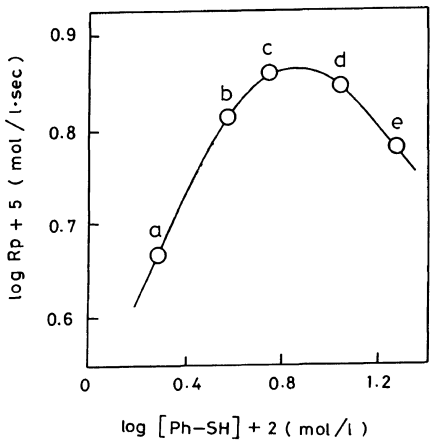
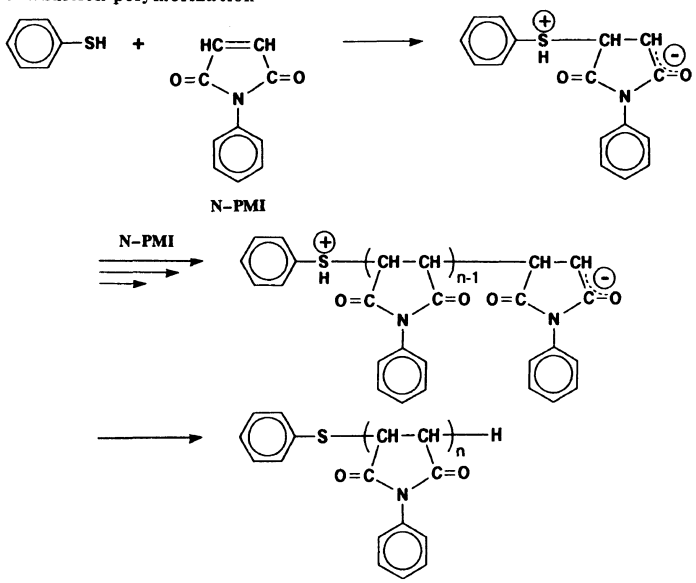


Figure 3. Dependence of the initial rate on thiophenol concentration in the polymerization of N-PMI. N-PMI 7.5 mmol; thiophenol (mol% to N-PMI) (a) 0.5, (b) 1.0, (c) 1.5, (d) 3.0, (e) 5.0; 40°C.

Michael addition polymerization



Scheme 1.

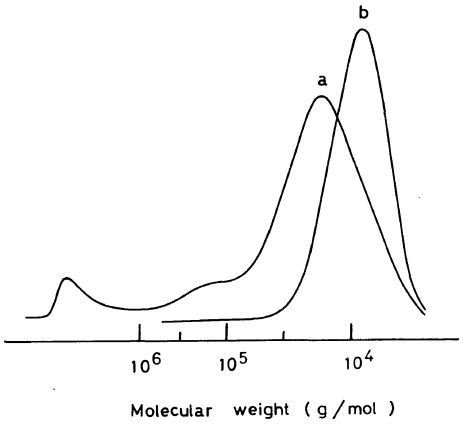


Figure 4. SEC analysis of poly(N-PMI) polymerized in tetrachloroethane. Polymerization: N-PMI 7.5 mmol; thiophenol (mol% to N-PMI) (a) 0.5, (b) 5.0; 40°C; 3 h.

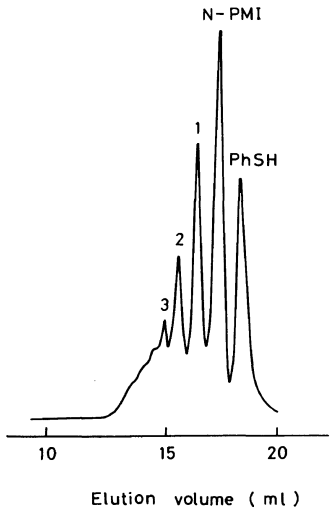


Figure 5. SEC analysis of the Michael adduct of thiophenol to N-PMI and oligo(N-PMI). Reaction: N-PMI 7.5 mmol; thiophenol 1.875 mmol (25 mol%); 20°C; 24 h. The figures on the top of peaks denote the number of monomer unit in the oligomers: 1 corresponds to the Michael adduct.

polymerization decreases at higher concentrations, showing a maximum as seen in Figure 3.

Both the initiation of dipole–dipole reaction and propagation of ion–dipole reaction must be accelerated in polar solvents. The depressed conversion in polar solvents such as DMF and DMSO, seen in Table I, can therefore be

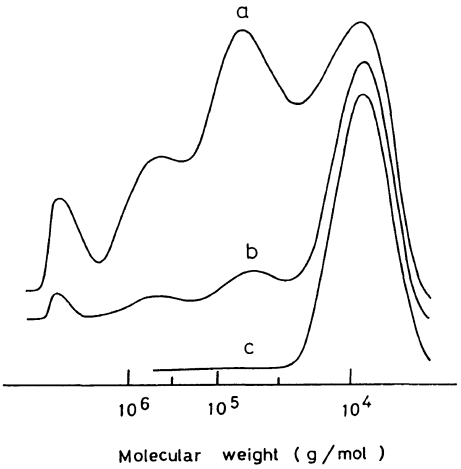


Figure 6. SEC analysis of poly(N-PMI) polymerized in DMF. Polymerization: N-PMI 7.5 mmol; thiophenol 0.075 mmol; 40°C; (a) 48 h, (b) 24 h, (c) 24 h (hydroquinone 0.075 mmol).

explained as follows: the accelerated propagation was exceeded by the simultaneously accelerated termination. The thiophenol-initiated polymerization of MMA does not take place in such polar solvents because of accelerated termination.[13] The polymerization rate reflects balance between propagation and termination; therefore, the enhanced rate in tetrachloroethane may be due to appropriate polarity for the balance.

The SEC spectra of the polymers obtained in much polar DMF were trimodal with an additional peak due to an exclusion limit (Figure 6). The peaks of higher molecular weight polymers increased with reaction time (a, b) and disappeared in the presence of hydroquinone (c). The remaining unimodal peak in the lower molecular weight region is therefore of the polymer formed by non-radical mechanism. The higher molecular weight polymers formed by radical polymerization had bimodal molecular weight distribution as seen in the figure. Otsu *et al.* showed a bimodal SEC spectrum of poly(*N*-cyclohexylmaleimide) polymerized with AIBN.[14] During the early stage of polymerization, the concentration of thiophenol being relatively high, the non-

radical process initiated by the Michael addition is predominant because of the greater initiation rate. As the polymerization proceeds and concentration of thiophenol decreases, the radical process becomes predominant at the latter stage as seen in Figure 6(a). This mechanism of two processes is consistent with the results in tetrachloroethane as shown above.

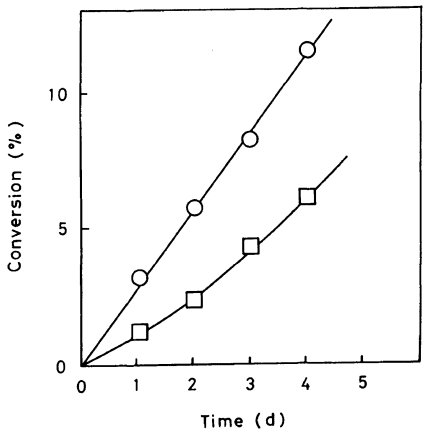
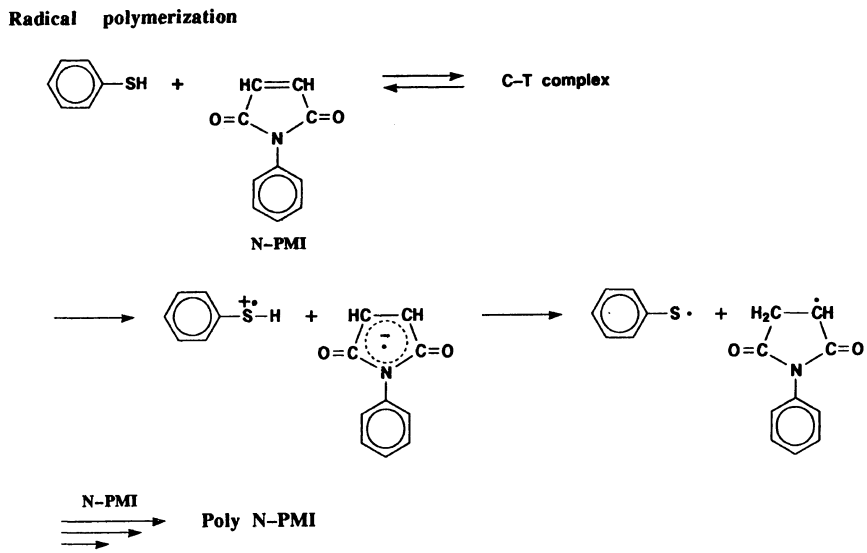


Figure 7. Polymerization of N-PMI with thiophenol in DMF in the presence of hydroquinone. N-PMI 7.5 mmol; thiophenol 0.075 mmol; DMF 2 ml; (○) in the absence of hydroquinone, (□) in the presence of hydroquinone (0.075 mmol).

The time–conversion plot in the presence of hydroquinone is shown in Figure 7. Although the polymerization was partially inhibited in DMF, no induction period was observed. This is clear evidence for the predominant non-radical process during the early stage. Hydroquinone had no effect on the thiophenol-initiated polymerization of MMA, and acetic acid accelerated the polymerization by catalytic activation of the monomer.[13] However, in the case of N-PMI, acetic acid retarded the polymerization in contrast to the case of MMA. This indicates that termination by protons is more sensitive to the polymerization of N-PMI than to that of MMA. Hydroquinone may therefore inhibit not only partially proceeding radical polymerization but also the Michael addition polymerization because of termination by its phenolic proton.

Kuramoto *et al.* reported a radical copolymerization of maleic anhydride with styrene using *p*-thiocresol, in which an initiating radical species, yielded from the complex of maleic anhydride with *p*-cresol, is assumed.[15] The radical process inhibited by hydroquinone in our case will take place similarly as shown in Scheme 2.



Scheme 2.

Polymerization was accelerated even by scattered light in the room probably because the photoreaction of the charge–transfer complex generates initiating radical species; hence, polymerization was carried out in the dark.

As seen in Table I, N-EMI is more reactive than N-PMI. Figure 8 shows the time–conversion profile of the polymerization of N-EMI. In this range of conversion, the SEC spectra of the polymers obtained were unimodal, in which there was no peak of the higher molecular weight polymer. The radical process is therefore negligible during the early stage of the polymerization of N-EMI. Molecular weight and dispersion of the polymer formed predominantly *via* the non-radical process are shown in Figure 9. The number average molecular weight was almost constant in the range shown and its distribution widened gradually with conversion. The inhibition effect of hydroquinone for this monomer is summarized in Table II. The conversion decreased in the presence of this inhibitor but no complete inhibition was observed even with sufficient amount. Since hydroquinone is much less soluble in tetrachloroethane, it is difficult to examine the

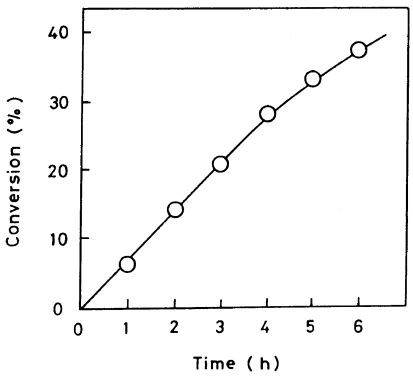


Figure 8. Polymerization of N-EMI with thiophenol in tetrachloroethane. N-EMI 7.5 mmol; thiophenol 0.075 mmol; tetrachloroethane 2 ml; 40°C.

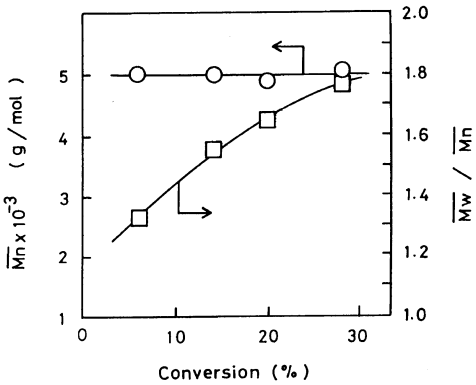


Figure 9. Molecular weight and dispersion of poly(N-EMI) shown in Figure 8.

Table II. Effect of hydroquinone on the polymerization of N-EMI[a]

Solvent (ml)	N-EMI mmol	Hydroquinone mmol	Conversion %
CH_3CN (2)	7.5	—	12.7
CH_3CN (2)	7.5	0.075	4.3
CH_3CN (4)–TCE (1.5)[b]	15	—	45.5
CH_3CN (4)–TCE (1.5)[b]	15	0.15	36.3
DMF (4)	15	—	14.2[c]
DMF (4)	15	0.15	7.2[c]

[a] Thiophenol 0.075 mmol, 40°C, 4 h.
[b] TCE, tetrachloroethane.
[c] Polymer precipitated during the reaction.

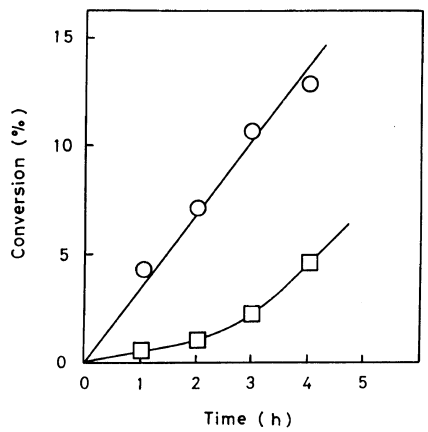


Figure 10. Polymerization of N-EMI with thiophenol in acetonitrile in the presence of hydroquinone. N-EMI 7.5 mmol; thiophenol 0.075 mmol; acetonitrile 2 ml; (○) in the absence of hydroquinone, (□) in the presence of hydroquinone (0.075 mmol).

inhibition effect in the solvent. When some tetrachloroethane was added to acetonitrile the conversion increased and less inhibition of hydroquinone was observed. This will be explained in terms of acceleration of the non-radical process. In DMF, the polymer precipitated during polymerization; hence, the time-conversion profile in the presence of hydroquinone was checked in acetonitrile (Figure 10). In spite of the unimodal SEC spectrum of poly(N-EMI), indicative of the predominant non-radical process, polymerization was retarded effectively by hydroquinone. This can be ascribed to inhibition by phenolic protons as discussed above, because the higher reactivity of N-EMI is due to the more reactive propagating end, which is therefore more susceptible to protonation.

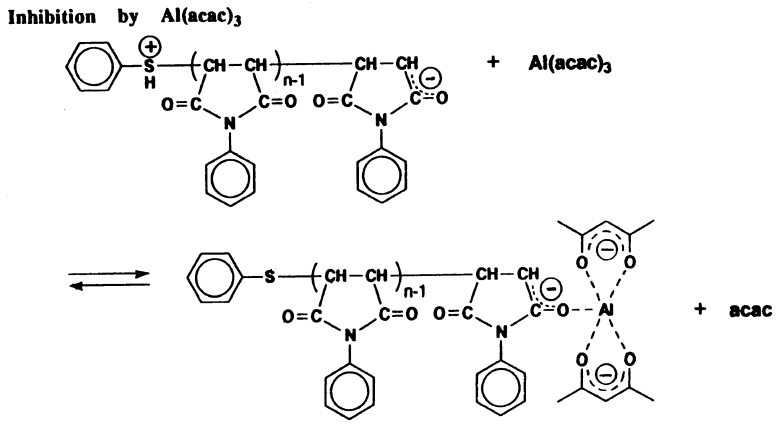
Since the properties of the anionic propagating chain end interest us, the effects of some metal complexes were examined. As the results in Table III show, aluminium acetylacetonate, which has no effect on the ordinary radical polymerization of vinyl monomers below 60°C, retarded the polymerization of both N-MPI and N-EMI. That the aluminium complex controls the polymerization provides important information on the mechanism. The most likely mechanism is shown in Scheme 3, in which coordination of the propagating enolate end to aluminium retards the propagation. This aluminium complex enhanced the rate of the thiophenol-initiated polymerization of MMA presumably because the coordination protects the end from termination, while an another aluminium complex such as methylaluminium bis-β-naphtoxide inhibits the polymerization.[13] The detailed mechanism is still unknown but the effect of the aluminium complex is the evidence in support of the non-radical mechanism.

Copolymerization usually serves to elucidate the reaction mechanism; therefore, MMA and styrene were examined as comonomers. The results are summarized in Table IV. In the copolymerization with styrene, both maleimides gave copolymers of equimolar composition; the results are similar to those of radical polymerization. However, SEC spectra of all copolymers were unimodal, though the

Table III. Inhibition by aluminium acetylacetonate[a]

Monomer	Al (acac)$_3$	Time	Conversion
	mmol	h	%
N-PMI	—	48	13.9
N-PMI	0.075	48	4.8
N-EMI	—	24	39.2
N-EMI	0.075	24	7.3

[a] Monomer 7.5 mmol; thiophenol 0.075 mmol; benzene 2 ml; 20°C.



Scheme 3.

Table IV. Copolymerization of *N*-substituted maleimides with styrene or MMA[a]

Monomer		Time	Conversion	Copolymer	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
M_1	M_2	h	%	$M_1:M_2$[b]	$g\,mol^{-1}$	
N-PMI	Styrene	0.5	41.2	50:50	12600	2.34
N-PMI	MMA	3	38.1	31:69	10800	3.44
N-EMI	Styrene	3	22.0	50:50	6500	1.92
N-EMI	MMA	3	28.0	29:71	1170	2.23
—	Styrene	3	0	—	—	—

[a] Monomer 7.5 mmol; thiophenol 0.075 mmol; tetrachloroethane 2 ml; 40°C.
[b] Calculated from elemental analysis.

number average molecular weight increased a little and its distribution widened. Moreover, as described above, the polymerization of N-EMI proceeds predominantly via the non-radical mechanism. Accordingly, the radical mechanism seems unlikely for the copolymerization of N-EMI with styrene. It should also be noted that styrene alone does not polymerize with thiophenol but easily forms only the Michael reaction adduct, indicating that termination by protons is too fast for the styrene end to propagate. On the basis of all these results, one possible mechanism is as follows: thiophenol adds to styrene in its complex with N-EMI to form the propagating maleimide end. This non-radical mechanism will apply to the case of N-PMI, also, because SEC analysis of the copolymer gave an unimodal spectrum lacking the peak of higher molecular weight polymer formed by a radical mechanism observed in the homopolymerization of N-PMI. Complex formation between the monomers in alternative copolymerization has been controversial. In our case, however, since the styrene end cannot propagate to form polymer, the complex formation seems essential for the copolymerization with styrene to always form the maleimide end as described above. The copolymerization of N-PMI with styrene was faster than that of N-EMI with the comonomer (Table IV), whereas the former maleimide was less reactive than the latter in the polymerization initiated by thiophenol (Table I). This reversed reactivity must come form the complex formation. Nevertheless, the composition of the copolymer of N-PMI with MMA was very similar to that of the copolymer formed by radical polymerization.[16] Furthermore, a typical anionic copolymerization of N-PMI with styrene using organozinc compounds gives a copolymer whose composition is much different from that of the copolymer polymerized by thiophenol.[6] We have now no definitive evidence for the mechanism of the copolymerization.

CONCLUSIONS

N-Substituted maleimides were polymerized by thiophenol. The polymerization of N-PMI proceeds *via* concurrent radical and non-radical processes; the radical process was inhibited by hydroquinone. In the case of N-EMI, a non-radical process is predominant. The non-radical process is assumed to be the Michael addition; the effect of aluminium complex on the polymerization supports the anionic mechanism. Copolymerization with styrene gave polymers of equimolar composition for both maleimides, suggesting that the Michael addition of thiophenol to the charge-transfer complex of the maleimide with styrene initiates the copolymerization. The mechanism of the copolymerization with MMA is unclear. This thiophenol-initiated polymerization is useful to polymerize monomers having α,β-

unsaturated carbonyl groups, especially to prepare polymers of relatively low molecular weight and narrow molecular weight distribution.

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