

# Studies on the Copolymerization of Methyl Methacrylate and N-Aryl maleimides

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## SYNOPSIS

This article describes the synthesis and characterization of copolymers of methyl methacrylate (MMA) and N-4-chlorophenyl maleimide (PC)/N-3-chlorophenyl maleimide (MC). The copolymers were synthesized by varying the mole fraction of N-aryl maleimides from 0.1 to 0.5 in the initial feed using azobisisobutyronitrile (AIBN) as an initiator and tetrahydrofuran (THF) as the solvent. The copolymer composition was determined from the  $^1\text{H-NMR}$  spectra by taking the ratio of proton resonance signals due to methoxy protons ( $\delta = 3.59$  ppm) of MMA and aromatic protons ( $\delta = 7.2\text{--}7.4$  ppm) of N-aryl maleimides. The reactivity ratios for MMA-PC and MMA-MC copolymers were found to be 0.952 ( $r_1$ ), 0.029 ( $r_2$ ) and 0.833 ( $r_1$ ) and 0.033 ( $r_2$ ), respectively. Thermal characterization of the copolymers was done using differential scanning calorimetry (DSC) and dynamic thermogravimetry. Initial decomposition temperature and glass transition temperature increased with increasing mole fraction of N-aryl maleimide content in the copolymers. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

The copolymerization of vinyl monomers with N-aryl maleimides using free radical initiators have been reported in the past.<sup>1-5</sup> The introduction of rigid polar maleimide groups in the methyl methacrylate (MMA) backbone increases the rigidity and intra- and intermolecular interactions. Such structural modifications are expected to affect the thermal behavior of the copolymers.

In our previous articles<sup>6,7</sup> we reported the copolymerization behavior of N-(2- and 4-tolyl) maleimide/N-(4-carboxyphenyl) maleimide with MMA. The effect of the introduction of these monomers on the copolymerization behavior, thermal behavior, and mechanical properties has been reported. Copolymerization resulted in an increase in  $T_g$  and thermal stability. The position of substituent (methyl group at *ortho* or *para*) affected the copolymerization behavior. However, it showed no effect

on  $T_g$ . The presence of electron withdrawing group at *para* position ( $-\text{COOH}$ ) resulted in a marked increase in the glass transition temperature. The present studies were, therefore, undertaken with an aim to investigate the effect of introduction of electron withdrawing group and their position (i.e., the presence of chloro group at *meta* or *para* position) in N-aryl maleimides on the copolymerization and thermal behavior of the copolymers.

## EXPERIMENTAL

### Materials

Maleic anhydride (Loba Chemie), *p*-chloroaniline (National chemicals) and methanol (Qualigens) were used as supplied. *m*-Chloroaniline (National chemicals) and acetic anhydride (Sisco chemicals) were distilled before use. Acetone (Qualigens) was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and then distilled. Anhydrous sodium acetate (CDH) was obtained by fusion.

Methyl Methacrylate (CDH) was purified by washing with 10% NaOH solution till the sodium

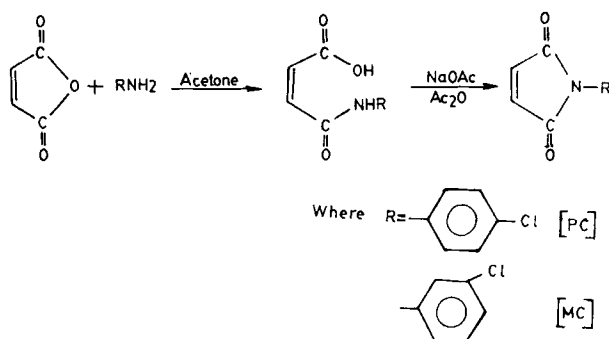
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hydroxide layer became colourless. Then it was washed repeatedly with distilled water until neutral. The washed monomer was dried over anhydrous  $\text{Na}_2\text{SO}_4$  then distilled under reduced pressure. Azobisisobutyronitrile (AIBN) (High Polymer labs) was recrystallized from chloroform. The solvent THF (Qualigens) was dried by immersing sodium wire in it and then distilled.

### Preparation of N-Aryl Maleimide Monomers

The preparation of N-3-/4-chlorophenyl maleimide monomers was carried out according to the procedure reported by Searle<sup>8</sup> using acetone as a solvent.

The reaction scheme is described as follows:



N-4-chlorophenyl maleimide (PC) monomer was prepared by dissolving 98 g (1 mol) of maleic anhydride in 250 mL of acetone taken in a 1 liter round-bottom flask equipped with a magnetic stirrer, nitrogen inlet and a condenser. 127.5 g (1 mol) of *p*-chloroaniline dissolved in 300 mL acetone was added slowly to this solution with vigorous stirring. The temperature was kept constant between 20–25°C for 2 h. The reaction mixture was then treated with 82 g of anhydrous sodium acetate and 350 mL of acetic anhydride and the solution was refluxed for 4 h. The contents were cooled and poured over crushed ice. The precipitated PC thus obtained was washed with water until neutral (Yield ~ 93%). Purification was done by passing a chloroform solution of the monomer through silica gel column and then precipitated by adding hexane. Recrystallization was done from methanol. Similar method of synthesis was used for the preparation of N-3-chlorophenyl maleimide (MC) (Yield 90–95%).

The monomers prepared were characterized by DSC, FTIR,  $^1\text{H-NMR}$ , and elemental analysis. In the DSC scans of the maleimide monomers an endothermic transition due to melting was observed. The melting points noted from the endothermic peak

positions were found to be 96 and 110°C for MC and PC respectively. The results of elemental analysis in MC and PC were as follows:

Experimental:

(MC) C = 56.86%, H = 3.11%, N = 7.15%

(PC) C = 57.33%, H = 3.07%, N = 6.49%

Theoretical:

$\text{C}_{10}\text{H}_6\text{ClNO}_2$ : C = 57.83%, H = 2.89%, N = 6.75%.

The experimental values agree well with the theoretical values. In the IR spectrum of the monomers, the characteristic peak due to carbonyl stretching of imide group was observed at 1712 and 1751  $\text{cm}^{-1}$  and the  $-\text{C}=\text{C}-$  stretch was observed at 1615  $\text{cm}^{-1}$ . In the  $^1\text{H-NMR}$  spectra of N-aryl maleimide monomers the proton resonance signals due to aryl group was observed at  $\delta = 7.2\text{--}7.4$  ppm while the olefinic protons appeared at  $\delta = 6.85$  ppm as a singlet (s). The integration was used to calculate the number of protons.

### Copolymerization of Methylmethacrylate with N-Aryl Maleimides

Copolymerization of MMA with N-aryl maleimide monomers was carried out in THF using AIBN as an initiator at 60°C in a nitrogen atmosphere. The mole fraction of the N-aryl maleimide monomer in the initial feed was varied from 0.1 to 0.5. A 20% solution of monomers in THF was placed in a three-necked round-bottom flask equipped with a reflux condenser, a  $\text{CaCl}_2$  drying tube, and a nitrogen gas inlet tube. The whole assembly was placed in a thermostatted oil bath and stirred using a magnetic stirrer. Nitrogen was passed through the reaction mixture and the temperature was raised to 60°C. The polymerization was initiated by adding 1% (w/w) AIBN. The reaction was stopped at low conversion ( $\leq 15\%$ ) by pouring the contents of the flask into a large excess of methanol. The precipitated polymer was washed repeatedly with hot methanol and then dried in a vacuum oven. The polymer samples have been designated by adding a prefix P to the letter designation of the N-aryl maleimide monomers and a numerical suffix indicating the mole fraction of the N-aryl maleimide in the initial feed multiplied by 10. For example, a copolymer prepared by taking 0.1 mol fraction of N-4-chlorophenyl maleimide [PC] has been designated as PPC-1.

## Characterization

$^1\text{H-NMR}$  spectra of the monomers and the copolymers were recorded on a JEOL-JNM-FX100 FT-NMR spectrometer using  $\text{CDCl}_3$  as solvent and tetramethylsilane as an internal standard. FTIR spectra of the monomers and polymers was recorded in KBr pellets using Biorad Digilab FTS-40 spectrophotometer. Molecular characterization of the samples was done by measuring the intrinsic viscosities of the samples in chloroform at  $30 \pm 0.1^\circ\text{C}$  using an Ubbelohde suspension level viscometer.

A DuPont 9900 thermal analyzer having a 910 DSC module and a 951 TG module was used for the thermal characterization of monomers and copolymers. DSC scans were recorded in a static air atmosphere at a heating rate of  $10^\circ\text{C}/\text{min}$  by using  $7 \pm 1$  mg of powdered samples. In order to have a same thermal history, the samples were first heated in a DSC cell from  $50$ – $200^\circ\text{C}$  followed by cooling in the DSC cell to room temperature. The same sample was reheated (second heating cycle) from  $50$ – $250^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$  to record the DSC traces.

TG/DTG traces were recorded in nitrogen atmosphere (Flow rate— $60 \text{ cm}^3/\text{min}$ ). A heating rate of  $10^\circ\text{C}/\text{min}$  and a sample size of  $10 \pm 1$  mg was used in each experiment.

## RESULTS AND DISCUSSION

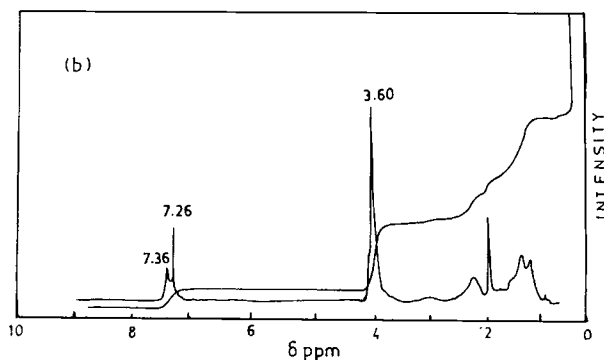
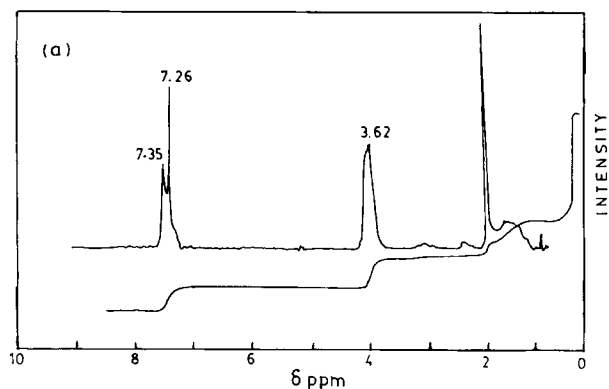
In the copolymerization of MMA with N-aryl maleimide the presence of electron withdrawing group at *p*-position (MMA-PC copolymers) did not affect

the percent conversion per unit time. However an increase in percent conversion per unit time was observed in the case of MMA-MC copolymers with increasing mole percent of MC in the feed (Table I). Intrinsic viscosity  $[\eta]$  values were obtained from the plots of reduced viscosity vs. concentration as the intercept by extrapolating the plots to zero concentration. Intrinsic viscosities of the copolymers were found to decrease with increasing amount of N-aryl maleimide in the initial feed (Table I). Intrinsic viscosity is a measure of hydrodynamic volume and is dependent on molecular weight as well as on polymer-solvent interactions. In the IR spectrum of the copolymers, absorption peaks due to carbonyl stretching of imide group at  $1712$  and  $1751 \text{ cm}^{-1}$  were obtained. All other characteristic bands of methyl methacrylate were also present. No absorption band was observed at  $1615 \text{ cm}^{-1}$ , indicating the absence of double bond.

$^1\text{H-NMR}$  spectra of the copolymers are shown in Figure 1. Resonance signals due to methoxy protons of MMA and aromatic protons of N-aryl maleimides were observed at  $\delta = 3.6$  ppm and  $\delta = 7.2$ – $7.4$  ppm, respectively in the  $^1\text{H-NMR}$  spectra of copolymers. The other characteristic proton resonance signal observed in  $^1\text{H-NMR}$ , due to the MMA was at  $0.8$ – $1.2$  ppm ( $\text{CH}_3$  group) and  $1.8$ – $2.00$  ppm ( $\text{CH}_2$  group). The intensity of signal due to aromatic protons increased with increasing amount of N-aryl maleimide in the copolymers. The ratio of the intensity of signals due to methoxy protons of MMA and aromatic protons of N-aryl maleimide was used to calculate the mole fractions of monomers in the copolymer (Table I).

**Table I** Copolymerization of MMA with N-Aryl Maleimide Monomers: Reaction Conditions, Copolymer Composition, and Intrinsic Viscosity

Sample Designation	Mole Fraction of N-Aryl Maleimide		% Conv./min	$[\eta]$ (mL/g)
	Feed	Copolymer		
PPC-1	0.100	0.110	0.13	24.9
PPC-2	0.200	0.167	0.11	15.6
PPC-3	0.299	0.264	0.11	14.8
PPC-4	0.398	0.278	0.12	12.3
PPC-5	0.500	0.333	0.14	10.1
PMC-1	0.100	0.106	0.13	24.5
PMC-2	0.200	0.186	0.13	19.3
PMC-3	0.300	0.252	0.17	17.2
PMC-4	0.400	0.319	—	9.7
PMC-5	0.530	0.386	0.20	8.4

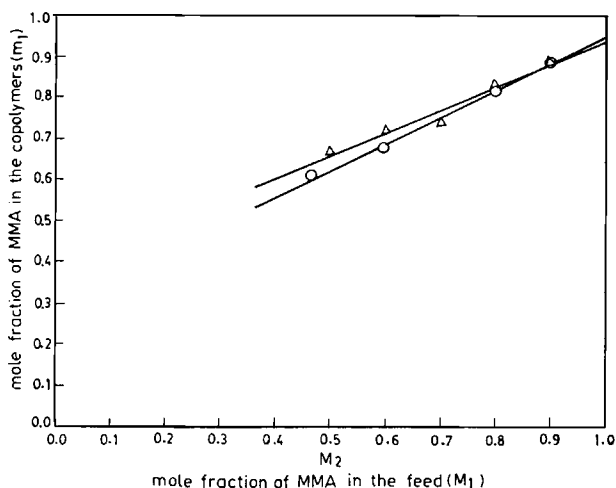


**Figure 1**  $^1\text{H-NMR}$  spectra of (a) PMC-5 and (b) PMC-2 in  $\text{CDCl}_3$ .

In the copolymerization of MMA ( $M_1$ ) with N-aryl maleimide ( $M_2$ ) an increase in  $M_1$  resulted in an increase in  $m_1$  thereby indicating that these monomers undergo a random copolymerization (Fig. 2).

The reactivity ratios of the monomers were determined using Fineman-Ross method.<sup>9</sup> The values of  $r_1$  (MMA) and  $r_2$  (N-aryl maleimide) were found to be 0.833 ( $r_1$ ) and 0.033 ( $r_2$ ) for MMA-MC and 0.952 ( $r_1$ ) and 0.029 ( $r_2$ ) for MMA-PC. These results show a higher reactivity ratio of MMA as compared to N-aryl maleimide comonomers. The copolymer is richer in the more reactive monomer with random placement. In this case, the copolymer will have a tendency to contain more MMA than N-aryl maleimide.

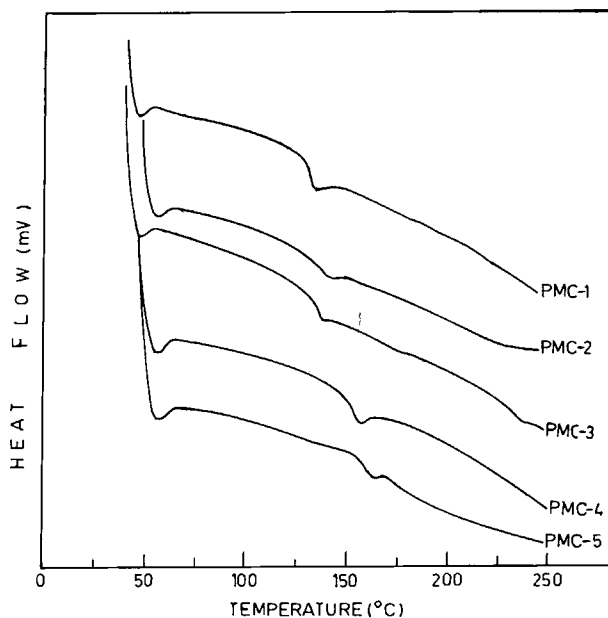
The  $Q$  and  $e$  values for N-aryl maleimide monomers were also calculated using the Alfrey-Price equation. The  $Q_1$  and  $e_1$  values for MMA were taken from the literature.<sup>10</sup> The  $Q$  and  $e$  values for MMA-



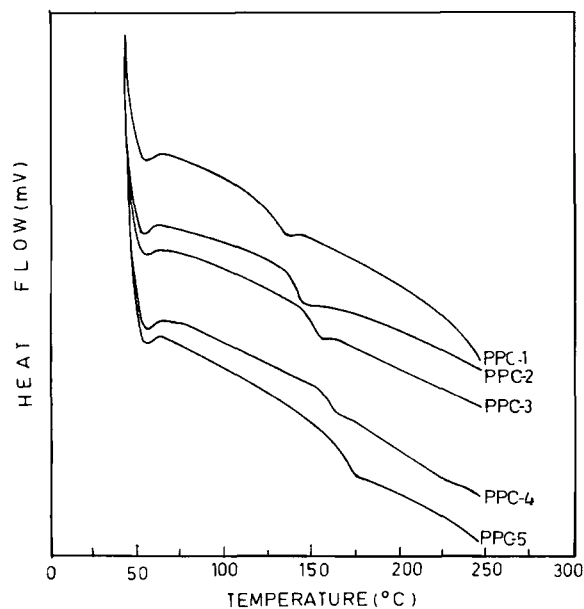
**Figure 2** Plot of mole fraction of MMA in the feed ( $M_1$ ) vs. mole fraction of MMA in copolymers ( $m_1$ ): (O) MMA-MC ( $\Delta$ ) MMA-PC.

MC and MMA-PC copolymer were found to be 1.97 ( $Q_2$ ) and 2.3 ( $e_2$ ) and 1.75 ( $Q_2$ ) and 2.29 ( $e_2$ ), respectively. The  $e_2$  values, which depend on electronic requirement of substituent, were similar in MC and PC, whereas  $Q_2$  values were slightly different.

DSC scans of various copolymers were recorded to study the effect of copolymer structure and composition on the glass transition temperature of the copolymers (Figs. 3 and 4). The glass transition re-



**Figure 3** DSC scans of MMA-MC copolymers (heating rate  $10^\circ\text{C}/\text{min}$ ).



**Figure 4** DSC scans of MMA-PC copolymers (heating rate 10°C/min).

gion was characterized by noting the following temperatures:

$T_e$  = extrapolated onset temperature

$T_g$  = midpoint temperature (inflection point)

$T_f$  = extrapolated end set temperature.

The results of DSC traces are summarized in Table II. The glass transition values of the copolymers increased with an increasing concentration of the N-aryl maleimide content in the backbone. This is due to the introduction of rigid imide group, which hinders the rotation of the backbone. The position of the substituent (4-/3-chloro) in the N-aryl maleimide also affected the  $T_g$ . Comparison of MMA-PC copolymers with MMA-MC copolymers having equal mole fraction of N-aryl maleimides, showed higher  $T_g$  values in the presence of PC as compared to MC (Table II).

Thermal stability of the copolymers was determined by recording TG/DTG traces in nitrogen atmosphere. From these traces, the initial decomposition temperature ( $T_i$ ), temperature of maximum rate of weight loss ( $T_{max}$ ) and final decomposition temperature ( $T_f$ ) were noted down. Percent weight loss was also determined. These results are summarized in Table III. A typical TG/DTG trace for PPC-5 is shown in Fig. 5. All the copolymers showed a single step decomposition except PMC-3, which

**Table II Results of DSC Scans of Copolymers (Heating Rate 10°C/min)**

Sample Designation	$T_e$ (°C)	$T_g$ (°C)	$T_f$ (°C)
PPC-1	130	133	137
PPC-2	140	145	150
PPC-3	148	153	157
PPC-4	156	164	167
PPC-5	166	171	175
PMC-1	130	132	133
PMC-2	131	134	139
PMC-3	133	135	135
PMC-4	149	155	156
PMC-5	152	158	161

showed about 4.3% weight loss in the temperature range of 135–162°C.

A comparison of the TG traces of PMMA with those for copolymers showed a significant change in the thermal behavior. In PMMA, a three-step decomposition was observed.<sup>6</sup> The three stages in PMMA degradation<sup>11-14</sup> are due to: (i) scission of head-to-head linkages (157–250°C); (ii) chain end initiated decomposition (250–335°C); (iii) random main chain scission (335–427°C).

In the copolymers a single step degradation was observed that occurred above 365°C, which is even higher than the initiation temperature for random chain scission of PMMA chain. It can be seen that even a low mole fraction of N-aryl maleimide is suf-

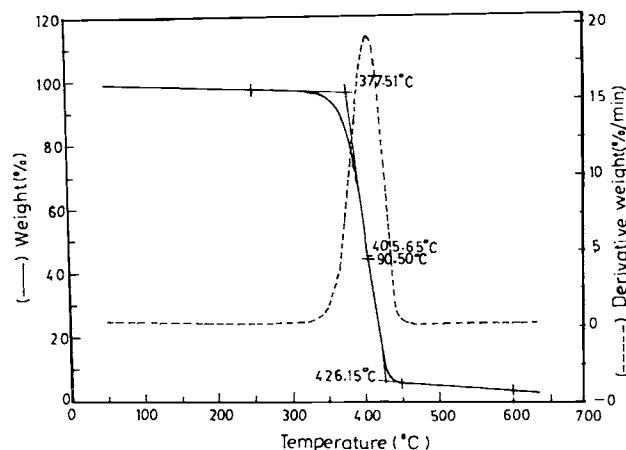
**Table III Results of Thermogravimetric Analysis in N<sub>2</sub> Atmosphere (Heating Rate 10°C/min)**

Sample Designation	$T_i$ (°C)	$T_{max}$ (°C)	$T_f$ (°C)	% Weight Loss at 500°C
PPC-1	365	394	416	91
PPC-2	374	402	421	92
PPC-3	362	389	412	93
PPC-4	378	406	425	92
PPC-5	378	406	426	90
PMC-1	367	399	422	96
PMC-2	370	397	419	96
PMC-3	135	156	162	5
	382	409	427	90
PMC-4	378	404	424	93
PMC-5	370	398	419	98

$T_i$  = Initial decomposition temperature.

$T_{max}$  = Temperature of maximum rate of weight loss.

$T_f$  = Final decomposition temperature.



**Figure 5** TG and DTG trace of PPC-5 in nitrogen atmosphere (heating rate = 10°C/min).

ficient to stop the H—H or chain end-initiated degradation, and such a low mole fraction of N-aryl maleimide is not expected to affect the other useful properties of PMMA. Once a random chain scission has been initiated in copolymers, further degradation proceeds by a Zipper mechanism and weight loss from 91–98% was observed.

## CONCLUSION

Incorporation of even low mole fractions of N-aryl maleimides in the backbone of PMMA resulted in a significant increase in  $T_g$ . The presence of chloro group at *p*-position in N-aryl maleimide (MMA–PC copolymer) was more effective in increasing  $T_g$  as compared to MMA–MC copolymers. Copolymerization of MMA with N-aryl maleimides resulted in an increase in the thermal stability. The position of substituent [4-, 3-chloro] did not affect the thermal stability.

These monomers have also been used to cast sheets using varying mole fraction of MMA. Further studies on mechanical, optical, and long-term performance of these copolymer sheets are in progress.

## REFERENCES

1. I. M. Barrales-Rienda, J. I. G. DeLa Campa, and I. Gonzalez Ramos, *J. Macromol. Sci. Chem.*, **A11**, 267 (1977).
2. J. D. Patel and M. R. Patel, *J. Polym. Sci., Polym. Chem. Ed.*, **21**, 3027 (1983).
3. M. Z. Elsabee, M. W. Sabaa, and S. Mokhtar, *Polym. J.*, **15**, 429 (1983).
4. L. Choudhary, D. S. Varma, I. K. Varma, and F. W. Wang, *J. Thermal Anal.*, **39**, 633 (1993).
5. M. Bezdek and F. Hrabak, *J. Polym. Sci., Polym. Chem. Ed.*, **17**, 2857 (1979).
6. R. Bharel, V. Choudhary, and I. K. Varma, *J. Appl. Polym. Sci.*, **54**, 2165 (1994).
7. R. Bharel, V. Choudhary, and I. K. Varma, *J. Appl. Polym. Sci.*, **49**, 31 (1993).
8. N. E. Searle, U.S. Pat. 2,444,536 (July 1948).
9. M. Fineman and S. D. Ross, *J. Polym. Sci.*, **5**, 269 (1950).
10. R. Z. Greenley, in *Polymer Handbook*, 3rd ed., J. Brandrup and E. H. Immergut, Eds., Wiley-Interscience, New York, 1989, pp. II/267–274.
11. T. Kashiwagi, A. Inaba, and J. E. Brown, *Macromolecules*, **18**, 131 (1985).
12. T. Kashiwagi, A. Inaba, J. E. Brown, K. Hatada, T. Kitayama, and E. Masuda, *Macromolecules*, **19**, 2160 (1986).
13. T. Hirata, T. Kashiwagi, and J. E. Brown, *Macromolecules*, **18**, 1410 (1985).
14. L. E. Manning, D. Y. Sogah, and G. M. Cohen, *Macromolecules*, **22**, 4652 (1989).

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