Preparation, Characterization, and Thermal Behavior of MMA-N-Aryl Maleimide Copolymers

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SYNOPSIS

The work describes the synthesis and characterization of copolymers of methyl methacrylate (MMA) and N-o-tolyl maleimide (MO)/N-p-tolyl maleimide (MP)/4-maleimido benzoic acid (MB). The copolymers were synthesized by varying the mol fraction of N-aryl maleimides from 0.1 to 0.5 in the initial feed using azobisisobutyronitrile (AIBN) as an initiator and tetrahydrofuran as the solvent. The copolymer composition was determined from the ^{1}H-NMR spectra by taking the ratio of proton resonance signals due to $-OCH_3$ of MMA ($\delta = 3.59$ ppm) and the aromatic protons ($\delta = 7.0–7.3$ ppm) of N-aryl maleimides. The monomer reactivity ratios of MMA–MP were $r_1 = 0.926 \pm 0.001$ and $r_2 = 0.47 \pm 0.03$ and MMA–MO were $r_1 = 1.37 \pm 0.005$ and $r_2 = 0.31 \pm 0.01$. The initial decomposition temperature of copolymers and glass transition temperatures increased with increasing N-aryl maleimide content in the backbone. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The copolymerization of alkyl (methacrylates) with N-aryl maleimides, using free radical initiators, is well documented in the literature.[1-5] Considerable work has been done in order to understand polymerization behavior and substituent effects in copolymerization and determination of monomer reactivity ratios of N-aryl maleimide–vinyl monomer pairs. The copolymers formed were found to be richer in methyl methacrylate (MMA) than N-aryl maleimides. This is principally because of the higher tendency of N-aryl maleimides to react with MMA.

Some studies have also been carried out for evaluating the effect of the structure of these copolymers on thermal behavior. The introduction of rigid maleimide units in the MMA backbone reduces flexibility. The introduction of polar imido groups in the side chains may lead to enhanced intra- and intermolecular interactions. These structural modifications are, therefore, expected to influence the thermal behavior of the copolymers.

The present study was undertaken to evaluate the effect of substituent in N-aryl maleimides on the copolymerization reaction and thermal behavior of the copolymers.

EXPERIMENTAL

Materials

Maleic anhydride (G.S. Chemical Allied Industries), p-aminobenzoic acid (Riedel), sodium bicarbonate (Qualigens), and methanol (E. Merck) were used as supplied. o-Toluidine (Fluka AG) and acetic anhydride (Qualigens) were distilled before use, while p-toluidine (E. Merck) was recrystallized from hexane. Acetone (Qualigens) was dried over anhydrous Na_2SO_4, then refluxed for 0.5 h and distilled.

Methyl methacrylate (Fluka AG) was purified by washing with 10% NaOH solution to remove the inhibitor followed by repeated washing with water until neutral. The monomer was dried over anhydrous sodium sulfate and distilled under reduced pressure. The solvent, tetrahydrofuran (THF) (Qualigens) was dried by immersing sodium wire in it and then distilled. Anhydrous sodium acetate (Sarabhai M. Chemicals) was obtained by fusion. Azobisiobutyronitrile (AIBN) (Hema Lab. Chem.) was recrystallized from chloroform.

Preparation of N-Aryl Maleimide Monomers

N-aryl maleimide monomers were prepared according to the procedure reported by Searle[6] using acetone as a solvent. The basic reaction scheme involved can be described as follows:
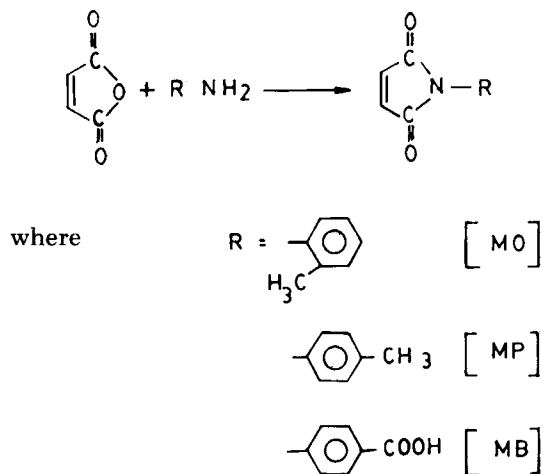
Scheme 1

N-4-tolyl maleimide (MP) was prepared by dissolving p-toluidine, 49 g (0.5 mol), in 98 mL of dry acetone in a three-necked 1-L round-bottomed flask fitted with a reflux condenser. The contents of the flask were heated to 60°C and stirred using a magnetic stirrer. N_2 gas was bubbled through the solution and then maleic anhydride, 53.5 g (0.5 mol), dissolved in 160 mL of acetone was added over a period of half an hour. The reaction was carried out for 4 h. Anhydrous sodium acetate, 41 g (0.5 mol), and acetic anhydride (205 mL) were added and the solution was refluxed for 3 h. The contents were cooled and poured over crushed ice. The precipitated N-4-tolyl maleimide (MP) thus obtained was washed with dilute sodium bicarbonate solution and then with water until neutral. Recrystallization was done from ethanol and further purification was done by passing a chloroform solution of the monomer through a silica gel column and then precipitated by adding petroleum ether. Similar method of synthesis was used for the preparation of other N-aryl maleimides. The yield of recrystallized N-aryl maleimides was in the range of 45–65%. Lowest yield of 45% was observed in N-o-tolyl maleimide (MO). In the differential scanning calorimetry (DSC) scans of the maleimide monomers an endothermic transition due to melting was observed. The melting points noted from the endothermal peak positions were at 77 (MO), 152 (MP), and 242°C (MB).

Copolymerization of Methyl Methacrylate with N-Aryl Maleimides

Copolymerization of MMA with N-aryl maleimide monomers was carried out in THF using AIBN as an initiator. The general method used for the preparation of copolymers is now described.

A 20% solution of monomers in THF was placed in a three-necked round-bottomed flask equipped with a magnetic stirrer, reflux condenser, and a nitrogen inlet tube. 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 to the contents of the flask. The reaction was terminated at low conversion ($\leq 10\%$) by precipitation using methanol as a nonsolvent. The precipitated polymer was washed with methanol several times and then dried in a vacuum oven.

Several copolymer samples were prepared by changing the mole fraction of N-aryl maleimide monomers from 0.1 to 0.5 in the initial feed. These samples have been designated by adding a prefix P to the letter designation of the N-aryl maleimide and a suffix indicating the mole fraction of the N-aryl maleimide in the initial feed (multiplied by 10). For example, a copolymer of MP with MMA prepared by taking 0.1 mole fraction of MP in the initial feed has been designated as PMP-1.

Characterization

A Nicolet 5 PC FT-IR spectrophotometer was used for recording IR spectra of the monomers and the copolymers by making KBr pellets of the samples

Table I Composition of MMA and N-Aryl Maleimide Copolymers and Their Intrinsic Viscosity at 30.0 ± 0.1°C in $CHCl_3$

Sample Designation	Mole Fraction of N-Aryl Maleimide		$[\eta]$ dL/g
	Feed	Copolymer	
PMP-1	0.100	0.134	0.410
PMP-2	0.201	0.193	0.361
PMP-3	0.297	0.273	0.296
PMP-4	0.401	0.323	0.260
PMP-5	0.495	0.366	0.202
PMO-1	0.101	0.079	0.428
PMO-2	0.200	0.140	0.354
PMO-3	0.302	0.188	0.284
PMO-4	0.396	0.280	0.222
PMO-5	0.478	0.353	0.164

in the powder form. A JeoL-JNM-FX-100 FT-NMR or Brucker-ACP-300 MHz FT-NMR spectrometer was used for recording the ^{1}H-NMR spectra of monomers and copolymers using $CDCl_3$ as a solvent and tetramethylsilane as an internal standard. The intrinsic viscosity was measured in chloroform at $30 \pm 0.1°C$ using Ubbelohde viscometer.

A DuPont 9900 thermal analyzer having a 910 DSC module was used for thermal characterization of the monomers and copolymers. A sample size of 10 ± 1 mg and a heating rate of $10°C/min$ was used.

A DuPont 1090 thermal analyzer having a 951 TG module was used for evaluating the thermal behavior of the monomers and the copolymers in nitrogen atmosphere (flow rate $= 60$ cm^3/min). A sample size of 10 ± 1 mg and heating rate of $10°C/min$ was used.

composition was determined by taking the ratio of methoxy proton and aromatic proton resonance signals. The results of copolymer composition thus determined are summarized in Table I.

A plot of M_1 (mole fraction of MMA in the feed) vs. m_1 (mole fraction of MMA in copolymers) is shown in Figure 2. In the copolymerizations of MMA with N-aryl maleimides, an increase in M_1 resulted in an increase in m_1.

The reactivity ratios of the monomers were calculated from a knowledge of copolymer composition using Fineman–Ross and Kelen Tüdos methods. Values of r_1 (MMA) and r_2 (N-aryl maleimide comonomer) are given in Table II. These results show a higher reactivity ratio of MMA as compared to N-aryl maleimide comonomer. This indicates that MMA is more reactive (i.e., $k_{11} > k_{12}$ and $k_{21} > k_{22}$).

RESULTS AND DISCUSSION

Copolymerization of MMA with *N*-Aryl Maleimides

In the copolymerization of MMA with N-aryl maleimides the presence of electron-withdrawing and electron-donating groups as well as their position (*o*- or *p*-) affected the yield of the copolymer. For example, in the copolymerization of MMA with MP ($—CH_3$ at *p*-position) higher conversion per unit time was obtained as compared to when MO ($—CH_3$ at *o*-position) monomer was taken. This may be attributed to the steric hindrance of $—CH_3$ at ortho position. In case of MMA–MB copolymers lower conversion per unit time was obtained as compared to MMA–MO and MMA–MP copolymers, which may be due to the electron-withdrawing $—COOH$ group.
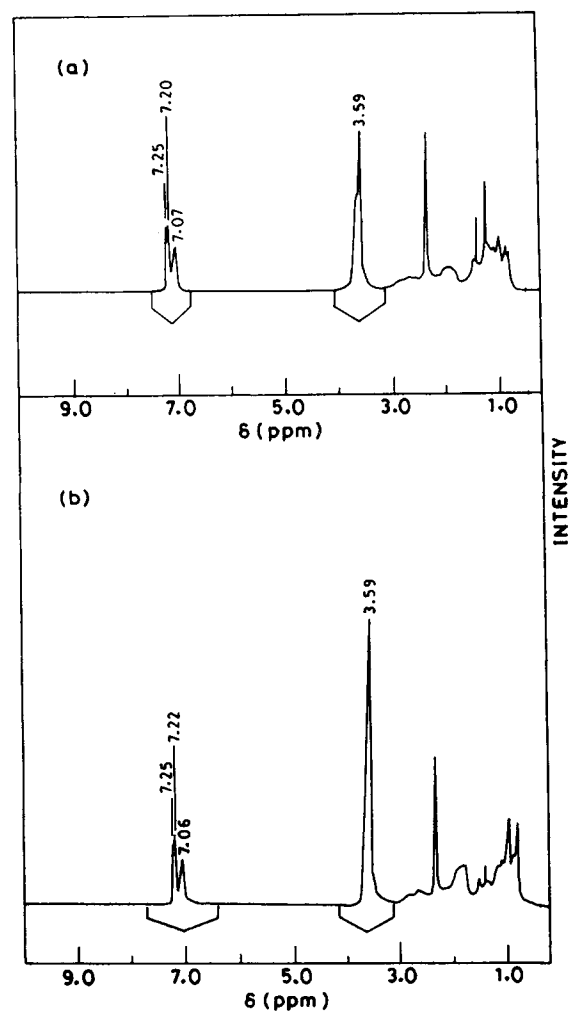
The values of intrinsic viscosity [η] are given in Table I. Intrinsic viscosity is a measure of hydrodynamic volume and depends on molecular weight as well as on the size of the polymer coil in a given solution. In MMA–N-aryl maleimide copolymers, an increase in the N-aryl maleimide content resulted in a decrease in the [η] values. MMA–MB copolymers were insoluble in chloroform, so their intrinsic viscosity measurements could not be carried out.

^{1}H-NMR spectra of the copolymers are shown in Figure 1. The resonance signals due to the $—OCH_3$ protons of the MMA and aromatic protons of N-aryl maleimides were present at $\delta = 3.59$ ppm and at $\delta = 7.0–7.3$ ppm, respectively. The intensity of the signal due to aromatic protons increased with increasing N-aryl maleimide content. The copolymer

Figure 1 ^{1}H-NMR spectra of (a) PMP-4 and (b) PMP-3 in $CDCl_3$.

Table II Reactivity Ratios of MMA (r_1) and N-Aryl Maleimides (r_2) Comonomers

Method	MMA–MP		MMA–MO	
	r_1	r_2	r_1	r_2
Fineman–Ross	0.926	0.500	1.364	0.30
Kelen Tudos	0.925	0.443	1.375	0.32
Avg.	0.926 ± 0.001	0.47 ± 0.03	1.370 ± 0.005	0.31 ± 0.01
Q	0.78[a]	1.121	0.78[a]	0.824
e	0.40[a]	1.310	0.40[a]	1.330

[a] Represents the values for MMA taken from the literature.

The Q and e values for the N-aryl maleimide monomers were also calculated using the Alfrey and Price equation.[7] The Q value for MO is lower as compared to MP monomer. The e values, which depend on the electronic requirement of the substituent, were similar in MO and MP.

The DSC scans of various copolymers were recorded primarily to study the effect of copolymer structure on T_g of copolymers. The DSC scans of MMA–MO copolymers recorded at a heating rate of 10°C/min in static air are shown in Figure 3. In the glass transition region, instead of the expected shift in the baseline, an endothermic peak was observed in most of the samples, which may be due to bulk stress relaxation. In order to have a similar thermal

history of various copolymers, it was decided to heat the samples to 200°C and allow them to cool in the DSC pan to room temperature. A rerun of such samples gave better results in the T_g region (Fig. 4). To fully characterize the glass transition region, four temperatures were noted:

T_0 = temperature of first deviation from baseline

T_e = extrapolated onset temperature

T_g = midpoint temperature (inflection point)

T_f = extrapolated end set temperature

The results of these studies are summarized in Table III. The glass transition values of the copolymers increased with an increase in the concentration of the N-aryl maleimide in the backbone. This is due
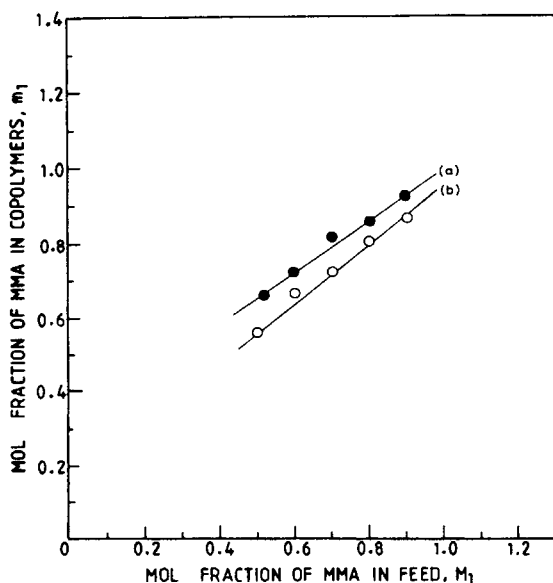
Figure 2 Plots of mole fraction of MMA in the feed (M_1) vs. mole fraction of MMA in copolymers (m_1): (a) MMA–MP and (b) MMA–MO copolymers.
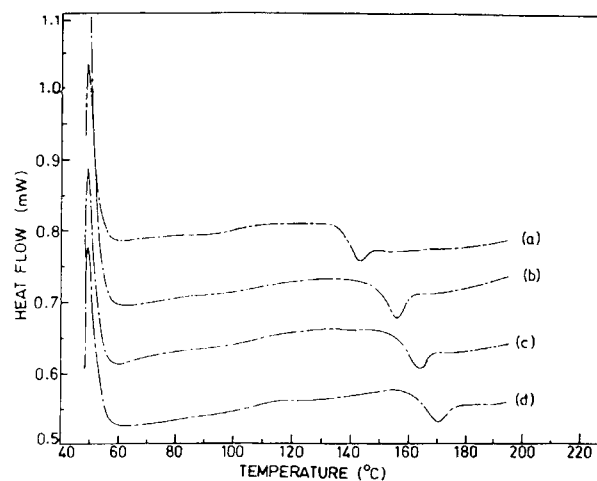
Figure 3 DSC scans of copolymers (first heating cycle): (a) PMO-1, (b) PMO-3, (c) PMO-4, and (d) PMO-5 (heating rate 10°C).
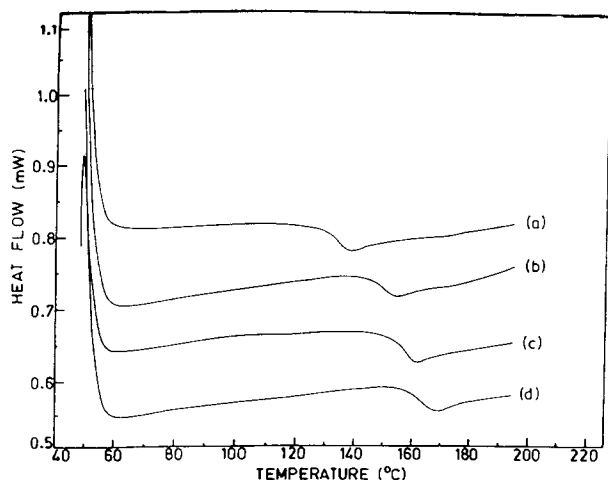
Figure 4 DSC scans of copolymers (second heating cycle): (a) PMO-1, (b) PMO-3, (c) PMO-4, and (d) PMO-5 (heating rate 10°C).

Table III Results of DSC Scans of Copolymers of MMA and N-Aryl Maleimides

Sample Designation	T_0 (°C)	T_e (°C)	T_g (°C)	T_f (°C)
PMMA	105	112	118	125
PMP-1	125	130	135	138
PMP-2	137	143	147	151
PMP-3	142	150	155	159
PMP-4	154	160	165	170
PMP-5	165	169	176	182
PMO-1	128	129	134	137
PMO-2	128	135	138	141
PMO-3	139	144	149	153
PMO-4	145	152	156	159
PMO-5	151	157	162	167
PMB-1	131	135	140	145
PMB-2	151	156	162	166
PMB-3	157	167	179	187
PMB-4	192	198	203	207

to the introduction of rigid and polar imide groups, which hinders the rotation of the backbone. The position of the methyl substituent in N-aryl maleimide monomer (ortho or para) did not affect the glass transition temperature. The presence of the carboxyl group at the para position resulted in the higher values of glass transition temperature.

The relative thermal stability of the polymers was assessed by comparing initial decomposition temperature (T_i), final decomposition temperature (T_f), and temperature of maximum rate of weight loss (T_{max}). The results of the thermal behavior of copolymers are summarized in Table IV.

In poly-MMA (PMMA), a three-step decomposition was observed. The first step (157–250°C) is believed to be initiated by scission of head-to-head (H-H) linkages. Chain-end unsaturation is perhaps the contributing factor for the second step of degradation (250–335°C), while the third step (335–427°C) is attributed to random chain scission of the polymer.[8-11]

Incorporation of N-aryl maleimide in the PMMA backbone influenced the degradation behavior and major decomposition occurred in a single step. It can be seen that even a low mole fraction of N-aryl maleimide is sufficient 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. With further increase in N-aryl maleimide content (0.1–0.5 mole fraction) no increase in the initial decomposition temperature was observed. The structure of N-aryl

maleimide (i.e., presence of CH_3 at o- or p- or COOH group at p-position) did not affect the thermal stability of the copolymers. Once a random scission has been initiated (i.e., above 358°C) in MMA–MP and MMA–MB copolymers, further degradation proceeds by a zipper mechanism and weight loss

Table IV Thermal Behavior of Copolymers

Sample Designation	T_i (°C)	T_{max} (°C)	T_f (°C)	Weight Loss (%)
PMP-1	358	394	422	95
PMP-2	365	393	420	91
PMP-3	366	395	420	91
PMP-4	367	394	420	93
PMP-5	373	400	430	92
PMO-1	365	392	414	83
	456	515	595	10
PMO-2	365	395	429	88
	465	525	590	9
PMO-3	367	399	420	82
	465	546	581	10
PMO-4	372	405	433	93
	480	525	610	3
PMO-5	380	408	428	83
	465	523	562	9
PMB-1	366	391	427	93
PMB-2	371	397	419	88
PMB-3	376	396	422	91
PBM-4	378	396	424	87

from 90 to 95% is observed in a narrow temperature range of approximately 60–70°C. In MMA–MO copolymers about 80–85% weight loss is observed in the first step followed by a second step showing $\approx$ 10% weight loss.

CONCLUSION

1. A significant increase in T_g of PMMA is observed by the incorporation of even low mole fraction of N-aryl maleimides. The position of $-CH_3$ group (o- or p-) in N-aryl maleimides did not affect T_g. However, the presence of the $-COOH$ group at p-position in N-aryl maleimides was more effective in increasing T_g.
2. Copolymerization of MMA with N-aryl maleimides resulted in an increase in the thermal stability of copolymers. However, the structure of N-aryl maleimides (i.e., the presence of CH_3 at o- or p- or $-COOH$ group at p-position) did not affect the thermal stability.

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