Copolymerization and Copolymers of Acrylonitrile with Some Brominated Phenylmaleimides

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ABSTRACT

Acrylonitrile (AN) was copolymerized with N-(4-bromophenyl)-maleimide (BPMI) or N-(2,4,6-tribromophenyl)maleimide (TBPMI) in toluene solution using azobisisobutyronitrile as the free radical initiator. The monomer reactivity ratios were found to be for BPMI (M_1)–AN (M_2), $r_1 = 0.44 \pm 0.082$ and $r_2 = 1.82 \pm 0.125$, and for TBPMI (M_1)–AN (M_2), $r_1 = 0.053 \pm 0.051$ and $r_2 = 4.71 \pm 0.275$. The e and Q values were also calculated. The course of copolymerization to high conversion is characterized by a remarkable decrease of the initial reaction rate as well as of overall conversion as the fraction of brominated monomer in the monomer mixture is increased. However, these values are somewhat higher when BPMI is used as a comonomer. The resulting copolymers show a higher thermal stability than that of polyacrylonitrile, and the glass transition temperature increases markedly with increasing BPMI or TBPMI content.

INTRODUCTION

In our previous papers [1–3] the results of the study of the copolymerization of some brominated N-phenylmaleimides with styrene, methyl acrylate, or methyl methacrylate by free radical initiation were described. It was found that their polymerization reactivity strongly depends on the polarity of the comonomer used and on the number and position of the bromine substituents. The same was found for other N-substituted phenylmaleimides [4]. Some work dealing with N-(2,4,6-tribromophenyl)maleimide (TBPMI) polymerization showed that TBPMI does not homopolymerize and forms only oligomers [5]. These polymers are characterized by their rigid structure leading to high thermal stability, and their brominated derivatives have attracted special attention because they can be used for the improvement of flammability characteristics [6, 7].

The present report deals with the copolymerization kinetics of N-(4-bromophenyl)maleimide (BPMI) and TBPMI with acrylonitrile (AN) at low and high conversions. The measurements of some characteristic properties of the copolymers, particularly their thermal stabilities, were also undertaken.
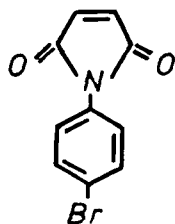
BPMI TBPMI
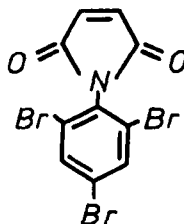
EXPERIMENTAL

Materials

Acrylonitrile and solvents were purified by distillation prior to use. N-(4-Bromophenyl)maleimide was prepared in a two-stage synthesis from maleic anhydride and 4-bromoaniline [2, 8] and was recrystallized from ethanol, mp 116°C. N-(2,4,6,-Tribromophenyl)maleimide (Dead Sea Bromine Co., Israel) was recrystallized from ethanol, mp 142.5°C. 2,2'-Azobis(isobutyronitrile) was recrystallized from methanol.

Measurements

Thermogravimetric analyses (TGA, DTA) were carried out with a DuPont 2000 and DCS-7 instrument in a helium atmosphere and at a heating rate of 10°C/min. The compositions of the copolymers were established by bromine and carbon analyses.

The molecular weights of the copolymers were measured by gel permeation chromatography (GPC) carried out on an Aerograph 8500 Varian instrument fitted with a UV detector. Styragel columns (Waters Associates) were used at a flow rate of 1 mL/min of degassed tetrahydrofuran. Retention times were calculated as polystyrene equivalents.

Polymerization Procedures

Solution polymerization to low conversion for the determination of the monomer reactivity ratios in toluene (50 mL solutions) of monomers (0.025 mol) with AIBN (0.082 g) as the initiator at 60°C were carried out under a constant stream of nitrogen in a 100-mL, double-jacketed glass reactor equipped with a magnetic stirrer. After an appropriate time interval (20–100 minutes), when a withdrawn sample precipitated in methanol, the whole reaction mixture was poured into methanol and the polymer was isolated by filtration, dissolved in toluene, reprecipitated, and dried at 60°C and 0.1 mm.

Rates of copolymerization were measured dilatometrically. Dilatometers (about 20 mL) filled with the toluene solution of monomer mixture and initiator (AIBN) were connected to a high vacuum line and freed of oxygen by three freezing-thawing cycles. The dilatometers were then placed in a thermostat bath and the volume contraction was recorded as a function of time. The reaction was terminated by vacuum suction of the contents and precipitation in excess cold methanol. The conversion was determined gravimetrically.

RESULTS AND DISCUSSION

Copolymerization Reaction

The free radical copolymerization of acrylonitrile (AN) with N-(4-bromophenyl)maleimide (BPMI) or N-(2,4,6-tribromophenyl)maleimide (TBPMI) was performed in toluene solution using AIBN as the initiator. The influence of the molar fraction of AN in the initial monomer mixture (f) on the composition (F) and some properties of the resulting copolymers obtained at low conversions are summarized in Table 1 for BPMI–AN and in Table 2 for TBPMI–AN systems. In

TABLE 1. Copolymerization of N-(4-Bromophenyl)maleimide (BPMI) (M_1) and Acrylonitrile (M_2) in Toluene at 60°C with AIBN as Initiator[a]

f_1	Conversion, %	Br, %	F_1	BPMI, wt%	$\overline{M}_w \times 10^{-3}$ [b]	$\overline{M}_n \times 10^{-3}$ [b]	T_g,[c] °C
0.1	6.5	7.59	0.062	23.9			106.8
0.2	7.3	12.10	0.115	38.1	134.9	16.2	
0.3	6.1	16.25	0.181	51.2			138.1
0.4	8.3	19.59	0.253	61.7	29.8	15.3	161.0
0.5	6.4	22.54	0.340	71.0			173.2
0.6	4.9	24.42	0.411	76.9	25.3	12.8	194.9
0.7	6.9	26.51	0.516	83.5			219.0
0.8	11.8	28.70	0.665	90.4	12.2	6.0	
0.9	6.6	31.35	0.821	95.6			

[a]Polymerization conditions: Toluene solutions (50 mL) of monomers (0.025 mol) and AIBN (0.0829 g), 60°C.

[b]Determined by GPC.

[c]Determined by DSC.

TABLE 2.   Copolymerization of *N*-(2,4,6-Tribromophenyl)maleimide (TBPMI) (M_1) and Acrylonitrile (M_2) in Toluene at 60°C with AIBN as Initiator[a]

f_1	Conversion, %	Br, %	F_1	TBPMI, wt%	$\overline{M}_w \times 10^{-3}$ [b]	$\overline{M}_n \times 10^{-3}$ [b]	T_g,[c] °C
0.1	9.7	11.22	0.023	8.5			
0.2	5.6	14.25	0.045	26.7	21.2	9.9	110.8
0.3	5.9	24.58	0.085	41.8			
0.4	5.3	29.03	0.113	49.6	20.8	10.1	136.7
0.5	8.0	35.00	0.162	60.0			59.5
0.6	7.1	38.00	0.192	64.8	13.6	4.7	172.7
0.7	10.8	43.85	0.279	74.9			198.6
0.8	5.4	47.64	0.362	81.4	13.7	5.5	220.3
0.9	4.1	53.68	0.590	91.8			

[a]Polymerization conditions: Toluene solutions (50 mL) of monomers (0.025 mol) and AIBN (0.082 g), 60°C.
[b]Determined by GPC.
[c]Determined by DSC.

both cases the plots of instantaneous monomer–copolymer mol fraction composition (Fig. 1) show a marked tendency toward a random copolymerization reaction, the BPMI or TBPMI content being lower in the copolymer. By using the Kelen-Tüdös equation [9], the monomer reactivity ratios and the confidence intervals were calculated and have been related to the polarity (*e*) and the resonance effect (*Q*) in the Alfrey-Price scheme (Table 3), assuming the value for AN given in the literature [10]. Acrylonitrile is thus more reactive than BPMI or TBPMI toward both types of propagating species, and the resulting copolymers are therefore richer in AN than the monomer mixtures. The same type of pattern has been found in the copolymerization of BPMI and TBPMI with methyl acrylate or methyl methacrylate [3, 11, 12]. The initial reaction rates, R_p, for different monomer feed ratios, but at a constant total monomer concentration (1 mol/L), are plotted in Fig. 2. They were determined by dilatometry at low conversion and they give straight lines in both cases, decreasing as the content of brominated monomer in the monomer mixture increased from 0.1 to 0.7 mol fraction. This influence is somewhat stronger with TBPMI as a comonomer. The decrease of the initial rate of monomer consumption with the mole fraction of brominated maleimide, as well as the limiting conversion observed in experiments with a higher mole fraction of these monomers, arise from the fact that maleimide diads cannot be easily formed due to steric hindrance, particularly with TBPMI monomer. Some influence of degradative chain transfer [13] may be an additional reason for such a course of reactions since it is a general tendency in free radical polymerization of bromine-containing monomers that chain transfer reactions, either from a monomer or from the polymer chain, would easily take place [14].

The course of polymerization to high conversion in toluene is represented by the integrated time–conversion curves with BPMI (Fig. 3) and TBPMI (Fig. 4) as comonomers. For both systems a temperature of 70°C and a higher initiator
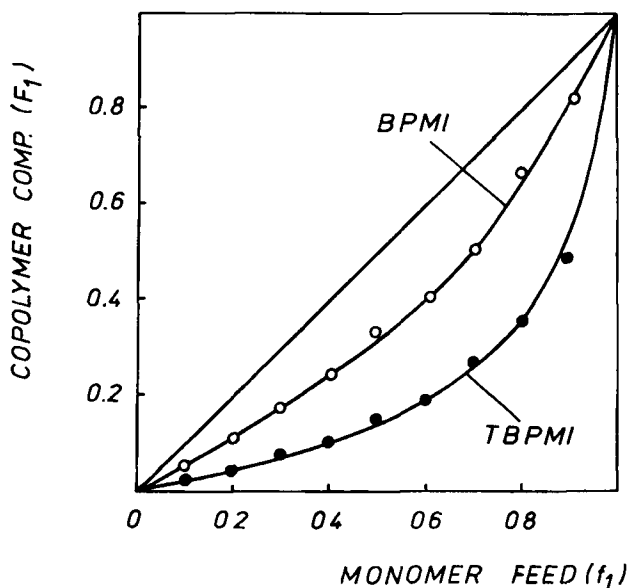
FIG. 1. Monomer–copolymer composition curves for the copolymerization of N-(4-bromophenyl)maleimide (BPMI) (M_1) or N-(2,4,6-tribromophenyl)maleimide (TBMPMI) (M_1) with acrylonitrile (M_2) in toluene at 60°C with AIBN. Experimental (○); calculated by r_1 and r_2 (——).

concentration ([AIBN] $= 2 \times 10^{-2}$ mol/L) were necessary to obtain an appreciable conversion. It is of interest to note that in dimethylformamide (DMF), the usual solvent for acrylonitrile free radical polymerization, the reaction does not take place under the identical conditions, probably due to strong complex formation between TBPMI and DMF. The familiar pattern of the curves shows a decrease of conversion as the mol fraction of brominated phenylmaleimide increases in the monomer mixture. Comparison of the examined polymerization systems shows that higher conversions were obtained with BPMI as a comonomer for the same reaction time. It is also well documented that the polymerization of acrylonitrile in bulk or in an aromatic solvent like benzene or toluene proceeds in a heterogeneous condition owing to precipitation of the polymer formed [15]. In such a system an accelerated polymerization rate was observed. This phenomenon could have the same influence

TABLE 3.   Copolymerization Parameters for Free Radical Copolymerization of N-(4-Bromophenyl)maleimide (BPMI) (M_1) or N-(2,4,6-Tribromophenyl)maleimide (TBPMI) (M_1) with Acrylonitrile (M_2)

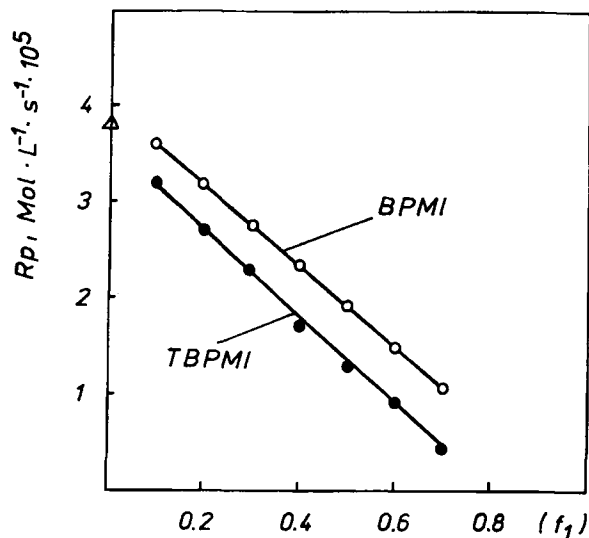| M_1	r_1	r_2	e_1	Q_1
BPMI	0.440 ± 0.082	1.82 ± 0.125	0.73	1.77
TBPMI	0.053 ± 0.051	4.71 ± 0.275	2.11	2.38

FIG. 2.   Dependence of the initial reaction rates (R_p) on monomer feed composition (f_1) in the copolymerization of N-(4-bromophenyl)maleimide (BPMI) (M_1) or N-(2,4,6-tribromophenyl)maleimide (TBPMI) (M_1) with acrylonitrile (M_2) at a total monomer concentration of [M] = 1 mol/L, [AIBN] = 1 × 10^{-2} mol/L in toluene at 60°C.
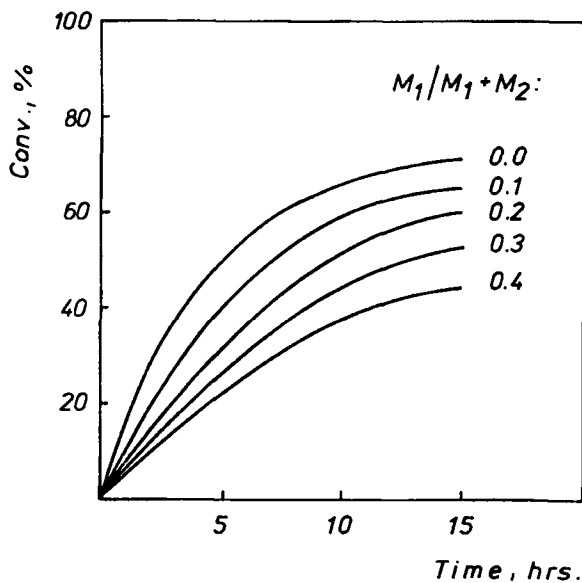
FIG. 3.   Influence of the monomer mixture composition on conversion versus reaction time in the copolymerization of N-(4-bromophenyl)maleimide (M_1) and acrylonitrile (M_2) at 70°C, [M] = 1 mol/L, [AIBN] = 2 × 10^{-2} mol/L in toluene.
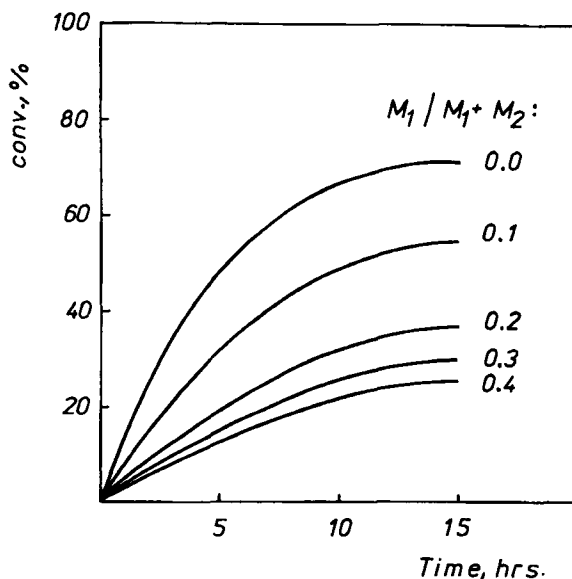
FIG. 4. Influence of the monomer mixture composition on conversion versus reaction time in the copolymerization of N-(2,4,6-tribromophenyl)maleimide (M_1) and acrylonitrile (M_2) at 70°C, [M] = 1 mol/L, [AIBN] = 2 × 10^{-2} mol/L in toluene.

on the course of both copolymerization reactions using BPMI or TBPMI as the comonomer because a higher reaction rate was obtained at a higher acrylonitrile content. Also, the limiting conversion of copolymerization arises in the first place from the relatively long polymerization time when the concentration of the initiator has become rather small due to the fast decomposition rate of AIBN at 70°C [16].

Copolymer Properties

The molecular weight measurements ($\overline{M}_w$ and $\overline{M}_n$) on the copolymers obtained at low conversions (Tables 1 and 2) for both systems were found to be in the 12–35 × 10^3 range and tend to decrease as the brominated phenylmaleimide mole fraction is increased in the monomer mixture. This tendency is probably due to chain transfer reactions, as was mentioned before [14].

The thermal properties of both types of copolymers were determined by TGA and DTA measurements in a helium atmosphere. Typical thermograms of copolymers of similar composition for BPMI-AN (41 mol% BPMI) and TBPMI-AN (52 mol% TBPMI) are shown in Figs. 5 and 6, respectively. They show similar decomposition curves and also a somewhat higher stability of BPMI copolymer, probably due to the higher steric hindrance influence in the TBPMI copolymer. Some residue at the end of the fast decomposition region indicates that depolymerization did not go to completion, the usual characteristic of both halogenated N-phenylmaleimide [17] and acrylonitrile-based polymers [18].

The glass transition temperatures (T_g), determined by DSC measurements over a wide range of copolymer compositions, are shown in Tables 1 and 2. By using the Gordon–Taylor equation [19], a plot of T_g against ($T_g - T_{g2})W_2/W_1$ gave a straight
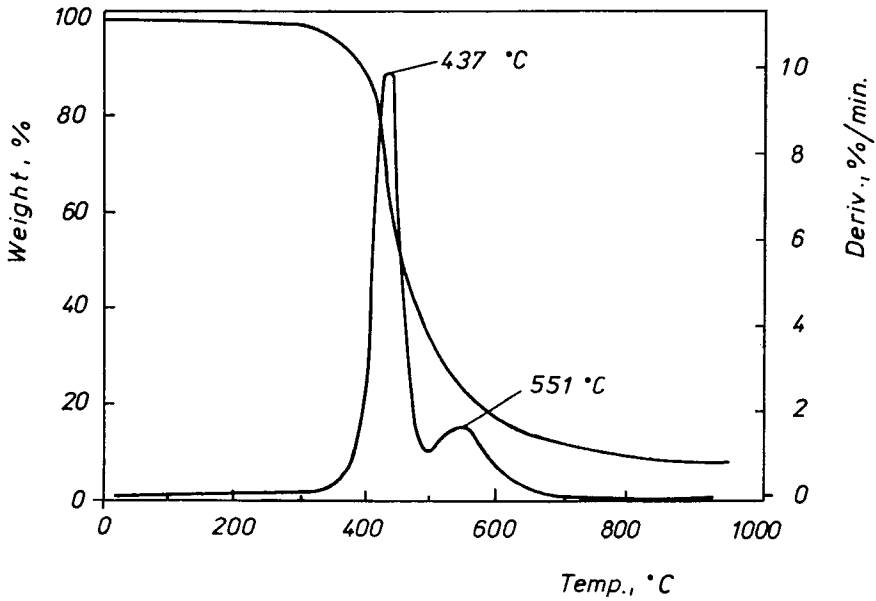
FIG. 5.   Thermogravimetric analysis of the copolymer of N-(4-bromophenyl)malei-
mide and acrylonitrile (molar ratio 41/59) in helium.
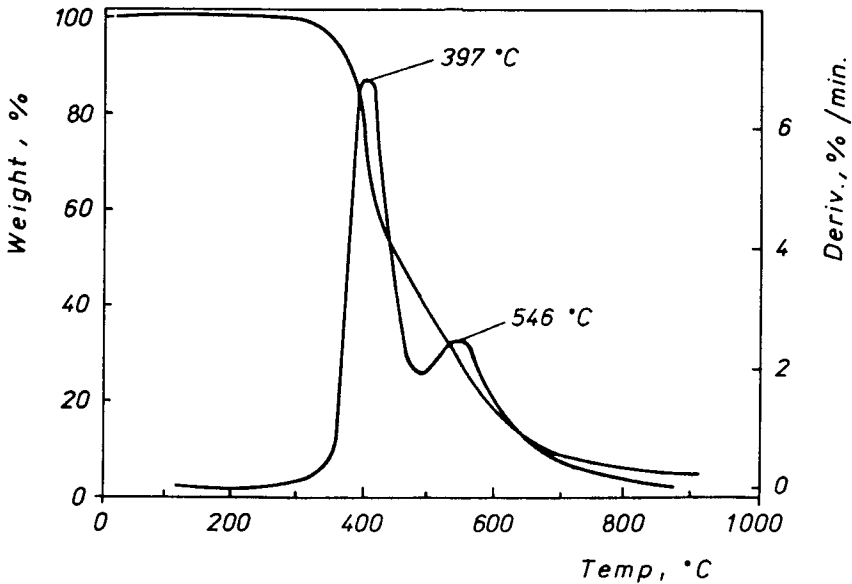

FIG. 6.   Thermogravimetric analysis of the copolymer of N-(2,4,6-tribromophenyl)-
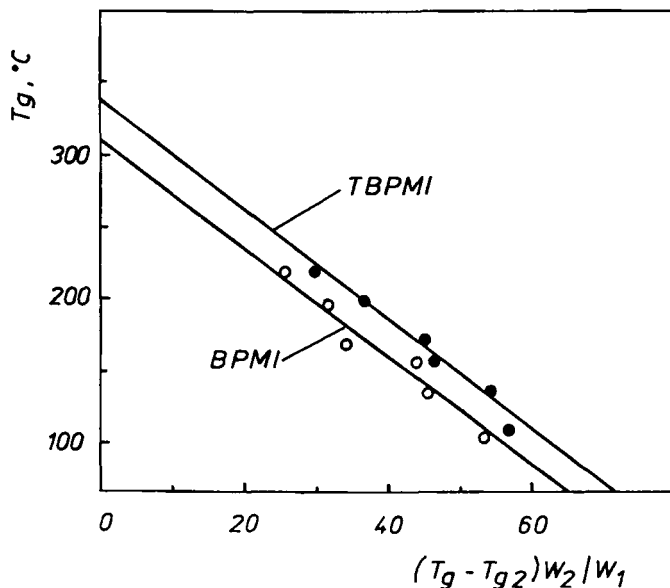maleimide and acrylonitrile (molar ratio 52/48) in helium.

FIG. 7. Relation of glass transition temperature (T_g) to composition for a series of copolymers of N-(4-bromophenyl)maleimide (BPMI) or N-(2,4,6-tribromophenyl)maleimide (TBPMI) (M_1, W_1) with acrylonitrile (M_2, W_2) prepared by free-radical copolymerization in toluene at 60°C with AIBN as initiator.

line for both types of copolymers, as presented in Fig. 7. Here, T_{g2} marks the glass transition temperature of polyacrylonitrile and is taken to 90°C [10], and W_1 and W_2 are the weight fractions of BPMI or TBPMI and AN in the copolymers, respectively. The intercept obtained by the least-square method of the lines, when the weight fraction of the comonomers falls to zero, gave a value of 337°C for T_{g1} of poly(N-2,4,6-tribromophenylmaleimide), which is in good agreement with the earlier result [3], and a value of 311°C for poly(N-4-bromophenylmaleimide). These values are far above the 248°C found for poly(N-phenylmaleimide) [20], which is a good indication of the influence of Br substitution on the glass transition temperatures of their polymers.

ACKNOWLEDGMENTS

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