Copolymerization and Copolymers of Styrene N-(2,4,6-Tribromophenyl) Maleimide with Styrene

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COPOLYMERIZATION AND COPOLYMERS OF N-(2,4,6-TRIBROMOPHENYL) MALEIMIDE WITH STYRENE

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ABSTRACT

Kinetic studies of the free radical copolymerization of N-(2,4,6-tribromophenyl) maleimide (TBPMI) with styrene in solution were carried out. The thermal and flammability characteristics of the resulting polymers were also investigated. The monomer reactivity ratios were found to be $r_1 = 0.006 \pm 0.0026$ (TBPMI) and $r_2 = 0.086 \pm 0.0023$, and the activation energy of the copolymerization reaction was $E_a = 73.6$ kJ/mol. The resulting copolymers showed an alternating structure regardless to the monomer feed composition. The molecular weights of the copolymers obtained are rela-

tively high and gradually increase by increasing the TBPMI fraction in the feed, whereas the T_g's showed similar values (540 K) for the equimolar ratio of the comonomers. The course of copolymerization up to high conversion was followed by microcalorimetry and is characterized by a remarkable increase of the initial reaction rate as the fraction of TBPMI was increased; it is also higher at higher total monomer concentrations. However, the overall conversion decreases when the fraction of TBPMI is higher than the equimolar ratio. The thermal stability of the alternating copolymers is higher than that of polystyrene, and their mixture showed appreciable flame-retardant properties, as demonstrated by a limiting oxygen index measurement.

INTRODUCTION

Free radical copolymerization of N-substituted maleimides with other vinyl monomers have been reported, and it was shown that their reactivity strongly depends on the polarity of the comonomer used [1-4]. In all cases with styrene a nearly alternating copolymerization took place, leading to copolymers with great structural stiffness and high thermal stability [1-6]. Recently, copolymers of brominated phenyl maleimides have attracted special attention because they can be used for the improvement of flammability characteristics, as claimed in the patent literature [7, 8]. Some work dealing with N-(2,4,6-tribromophenyl) maleimide (TBPMI) polymerization noted that TBPMI did not homopolymerize and formed only oligomers [9] but readily formed copolymers with styrene and butadiene [10]. However, no adequate attention has been paid to the kinetics of the reactions or to the properties of the copolymers obtained.

This paper details the copolymerization of TBPMI with styrene at low and high conversion by following the course of the reactions by microcalorimetry. The measurements of some characteristic properties of the copolymers, particularly their thermal and flammability behaviors in mixtures with polystyrene, were also undertaken.

EXPERIMENTAL

Materials

Styrene was washed with aqueous sodium hydroxide solution, dried, and distilled under nitrogen at 10 mm before use. N-(2,4,6-Tribromophenyl) maleimide (Dead Sea Bromine Co., Israel) was twice recrystal-

lized from ethanol, mp 142.5°C. The ^{1}H-NMR spectrum in CDCl$_3$ showed a singlet at 7.85 ppm (phenyl) and at 6.9 ppm (maleic). Azobisisobutyronitrile was recrystallized from methanol. Solvents were purified in the usual manner.

Measurements

Thermogravimetric analyses (TGA, DTG) were carried out with a Perkin-Elmer TGS-2 and DSC-2 instrument in a nitrogen or air atmosphere and at a heating rate of 10°C/min. ^{1}H-NMR spectra were measured on a 90-MHz Varian EM-90 Spectrometer in deuterated chloroform with TMS as the internal standard. 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. Limiting oxygen index (LOI) measurements were carried out with a Stanton-Redcroft FTA instrument on films cast from dichloromethane solution (20 wt%) onto a glass plate.

Polymerization Procedures

Solution polymerizations up to low conversion in benzene (50 mL solutions) of monomers (0.025 mol) with AIBN (0.082 g) as the initiator at 50°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 (10–100 min), when a withdrawn sample precipitated in methanol, the whole reaction mixture was poured into methanol, and the polymer was isolated by filtration, dissolved in benzene, reprecipitated, and dried at 60°C and 0.1 mm. The copolymer composition was established by bromine and carbon analyses.

Polymerization up to high conversion was performed in toluene solutions in an Calvet-type microcalorimeter (SETARAM, France), and the overall conversion was established gravimetrically after each measurement. The course of the reaction was followed by the recorded electromotive force expressed in microvolts, which is proportional to the heat of the polymerization reaction. From the ratio of the segmental area under the curves to the total area at a particular time, the conversion at that instant was determined. It was previously shown that by following the course of styrene polymerization, the calorimeter we used makes

stable and accurate measurements [11]. Its resolution at isothermal conditions is 50 μW and 0.043 cal/h respectively. In other words, when the rate of styrene polymerization is measured, a resolution of 0.0025% can easily be achieved, which is far better than that obtained by using the point-by-point method.

RESULTS AND DISCUSSION

Copolymerization Reaction

The free radical copolymerization of N-(2,4,6-tribromophenyl) maleimide (TBPMI) with styrene (St) was performed in benzene or toluene solutions by using AIBN as the initiator. The influence of the molar ratios of the initial monomer mixture (f) on the composition (F) and some properties of the resulting copolymers obtained at low conversions are shown in Table 1. The plot of comonomer–copolymer mol fraction composition for TBPMI (M_1) (Fig. 1) shows a strong tendency toward alternating copolymerization. The same type of alternation is noticed in

TABLE 1. Copolymerization of N-(2,4,6-Tribromophenyl) Maleimide (M_1) and Styrene (M_2) in Benzene at 50°C with AIBN as Initiator[a]

f_1	Conversion, %	Br, %	F_1	$\overline{M_w}^{b} \times 10^{-3}$	$\overline{M_n}^{b} \times 10^{-3}$	$T_g,^{c}$ °C
0.10	5.4	40.07	0.355			
0.20	8.4	43.76	0.426	48.2	23.4	242
0.30	6.9	44.88	0.454			
0.35	7.3	45.27	0.464	75.5	29.7	252
0.40	5.5	45.56	0.471			
0.50	8.7	45.96	0.481	87.2	42.3	267
0.60	8.2	46.30	0.489	97.8	46.2	265
0.70	7.7	46.56	0.496			
0.80	9.4	46.86	0.504	120.9	65.6	270
0.85	9.2	47.55	0.523			

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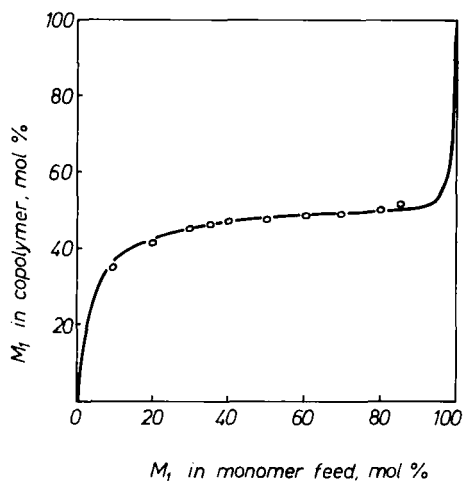[b]Determined by GPC.
[c]Determined by DSC.

FIG. 1. Monomer–copolymer composition curve for the copolymerization of *N*-(2,4,6-tribromophenyl) maleimide (M_1) with styrene (M_2) in benzene at 50°C with AIBN as initiator: experimental (○), calculated by r_1 and r_2 (——).

the copolymerization of styrene and a number of *N*-substituted malei-mides including *N*-phenyl maleimide, because the maleimides are electron-acceptor monomers. [1–6].

By using the Kelen-Tüdös equation, the monomer reactivity ratios [12] and the confidence interval [13] were calculated from the results in Table 1 and are also presented graphically in Fig. 2. The values $r_1 = 0.006 \pm 0.0026$ (M_1 = TBPMI) and $r_2 = 0.086 \pm 0.0023$ were ob-tained and agree fairly well with those reported earlier [10]. The reactiv-ity ratios found were related to the polarity (*e*) and to the resonance effect (*Q*) in the Alfrey–Price scheme for TBPMI as follows: $Q = 1.34$ and $e = 1.85$. It is well documented that monomers presenting such a large *e* value possess electron-acceptor properties, and in combination with electron-donor monomers, of which styrene is a typical example, they readily form alternating copolymers in conventional free-radical polymerization [14]. The tendency to form an alternating TBPMI/St copolymer was also confirmed by measuring the glass transition temper-atures (T_g) of the copolymers, as shown in Fig. 3. Small differences in the T_g (which is about 265°C), in spite of large differences in the mono-mer feed composition, suggests that the copolymerization is indeed nearly alternating. The course of the polymerization reactions up to high
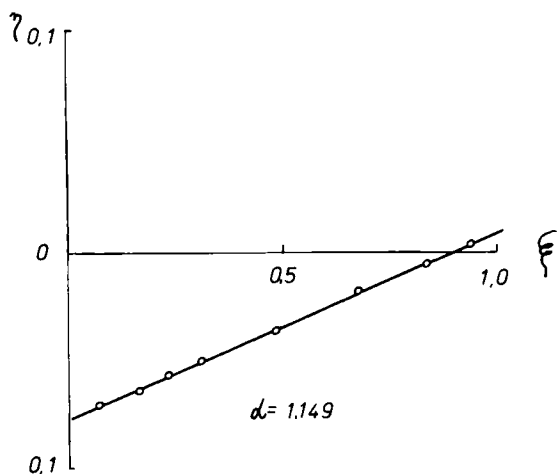
FIG. 2. Kelen–Tüdös diagram for the calculation of monomer reactivity ratios for the system N-(2,4,6-tribromophenyl) maleimide (M_1)–styrene (M_2) in benzene.
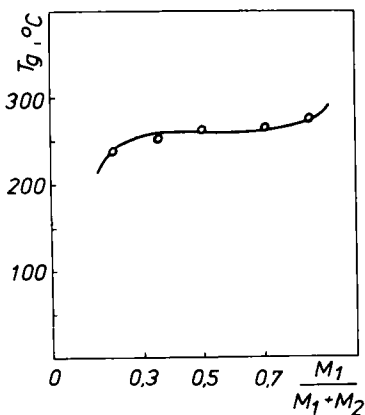

FIG. 3. Relation of glass transition temperature (T_g) of copolymers to composition of the monomer feed in the low conversion copolymerization of N-(2,4,6-tribromophenyl) maleimide (M_1) and styrene (M_2) in benzene.

conversions in a homogeneous environment in toluene solutions was followed by the microcalorimetric method. The integrated time–conversion curves were calculated, and they are presented in Fig. 4. It is clearly evident that in those cases where the mol fraction of TBPMI in the monomer mixture was higher than 0.5, not only was the reaction rate increased, but also after a certain time polymerization practically stopped. The conversion at this stage was as much lower as the amount of TBPMI was higher. In the case where the molar fraction of TBPMI was 0.6, conversion stopped at about 88%, but the conversion was only about 48% when the molar fraction of TBPMI was 0.8.
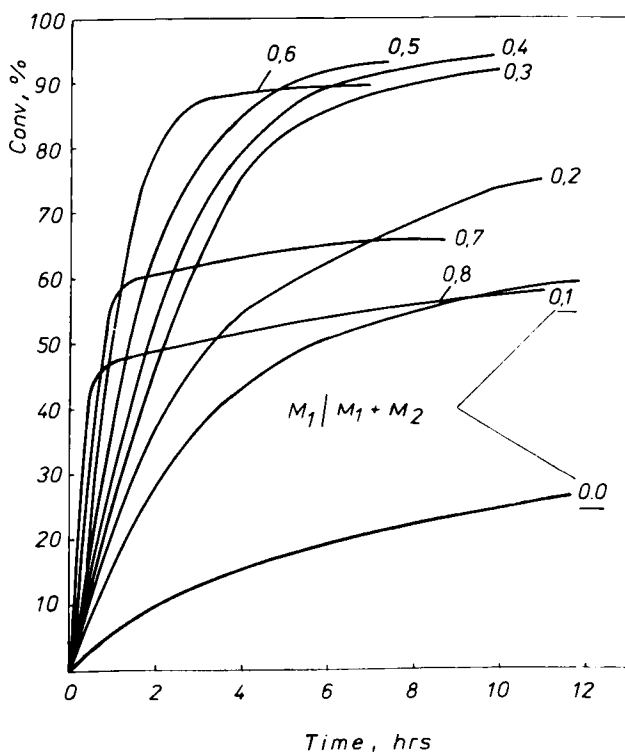

FIG. 4. Influence of the monomer mixture composition on the conversion versus reaction time in the copolymerization of N-(2,4,6-tribromophenyl) maleimide (M_1) and styrene (M_2) at 65°C: [M] = 1 mol/L, [AIBN] = 1 × 10^{-2} mol/ L, in toluene.

The dependence of the initial copolymerization rate R_p on the mono-mer composition at different feed ratios but at constant total monomer concentrations of 1 and 3 mol/L is plotted in Fig. 5. These initial rates were determined by microcalorimetry at low conversions, and they give straight lines in both concentrations. The R_p of copolymerization in-creases linearly as the TBPMI mol fraction in the monomer mixture is increased. The observed variations in polymerization rates are probably caused not only by the rates of propagation reactions but also by chang-ing the initiation rate with the composition of the monomer feed. As expected, much higher reaction rates are obtained by increasing the total monomer concentration. Figure 6 shows that the initial rate of copoly-merization was proportional to the square root of the initiator (AIBN) concentration, thus indicating bimolecular termination. The intercept, which is somewhat above the zero point, is presumable due to the contri-
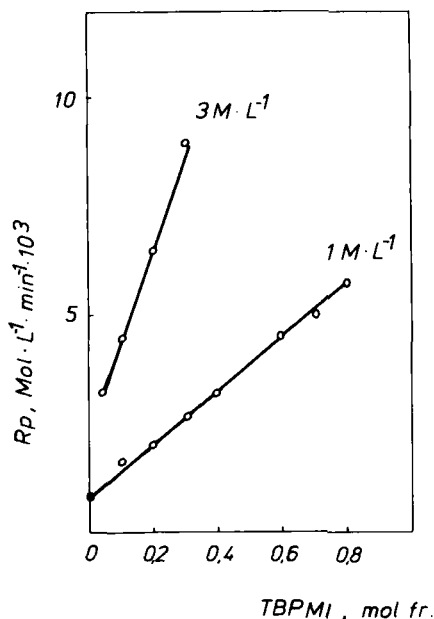

FIG. 5. Initial copolymerization rates versus monomer feed molar ratios in copolymerization of N-(2,4,6-tribromophenyl) maleimide and styrene of total monomer concentration of 1 and 3 mol/L at 65°C, [AIBN] = 1 × 10^{-2} mol/ L, in toluene.
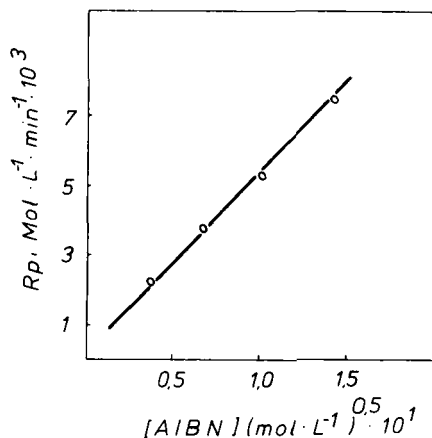
FIG. 6. Initial rate of copolymerization (R_p) of N-(2,4,6-tribromophenyl) maleimide (M_1) and styrene (M_2) versus $[AIBN]^{0.5}$, at 65°C: total $[M] = 1$ mol/L, $[M_1] = 0.1$ mol/L, in toluene.

bution of the thermal initiation process. The temperature dependence of conversion was established in toluene at 55, 65, and 75°C for a TBPMI/St (0.1/0.9) mixture with a total concentration of 3 mol/L. Overall rate constants were determined as slopes of straight lines from a plot of ln $[M_0]/[M_t]$ against time, and they gave the values $k_{55} = 1.21 \times 10^{-5}$ s^{-1}, $k_{65} = 2.90 \times 10^{-5}$ s^{-1}, and $k_{75} = 6.01 \times 10^{-5}$ s^{-1}, respectively. The overall energy of activation for the given monomer feed composition calculated from Fig. 7 was found to be $E_a = 73.6$ kJ/mol. This value is rather high in comparison to the styrene–maleic anhydride system when the polymerization reaction was performed in a homogeneous environment as well as in acetone ($E_a = 57.8$ kJ/mol) [15] and dioxane ($E_a = 59.2$ kJ/mol) [16]. This difference is probably caused by the higher steric effect when TBPMI is used as a comonomer.

Copolymer Properties

The molecular weight measurements (Table 1) showed a significant increase of $\overline{M}_w$ and $\overline{M}_n$ of the copolymers when the TBPMI content in the monomer mixture was increased (Fig. 8). This finding is opposite to the normal behavior of bromine-containing monomers in radical polymerizations due to the presence of chain transfer reactions [17, 18].
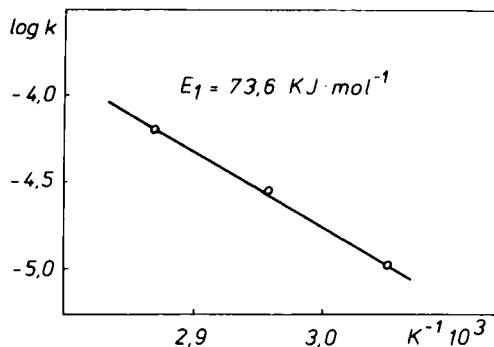
FIG. 7. Arrhenius plot of copolymerization of N-(2,4,6-tribromophenyl) maleimide (M_1) and styrene (M_2): total [M] $= 3$ mol/L, $[M_1] = 0.3$ mol/L, [AIBN] $= 1 \times 10^{-2}$ mol/L, in toluene.

The thermal stabilities of TBPMI–St alternating copolymers were determined by TGA and DTA measurements in nitrogen and air atmospheres (Fig. 9). They show that the copolymers start to decompose spontaneously ($T_{5\%}$) in nitrogen at 394°C and in air at 370°C, which is about 30°C above the decomposition temperature of polystyrene [17].
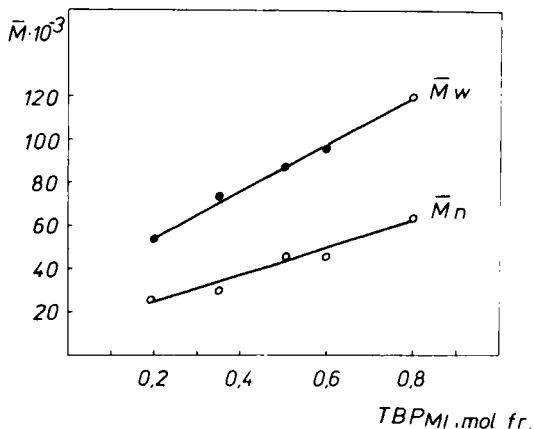

FIG. 8. Relation of molecular weights of copolymers to the composition of the monomer feed in the low conversion copolymerization of N-(2,4,6-tribromophenyl) maleimide and styrene in benzene.
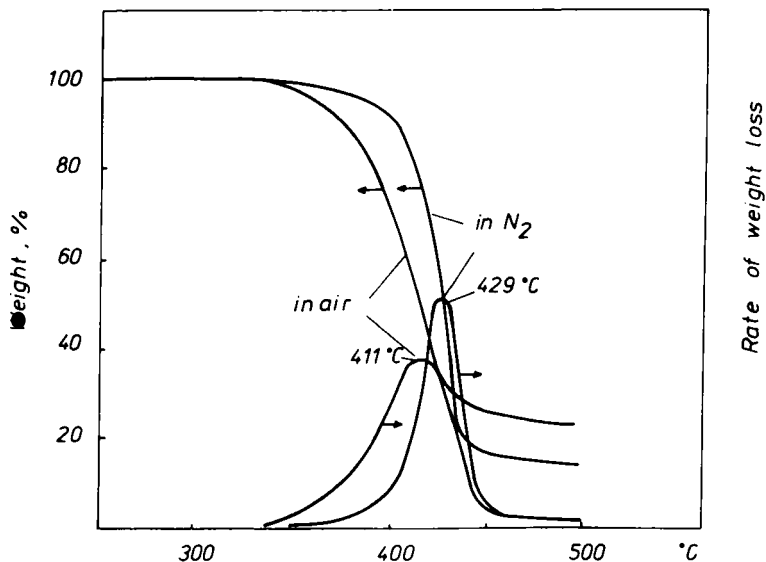
FIG. 9. Thermogravimetric analysis of alternating copolymer of N-(2,4,6-tribromophenyl) maleimide and styrene in nitrogen and air atmospheres.
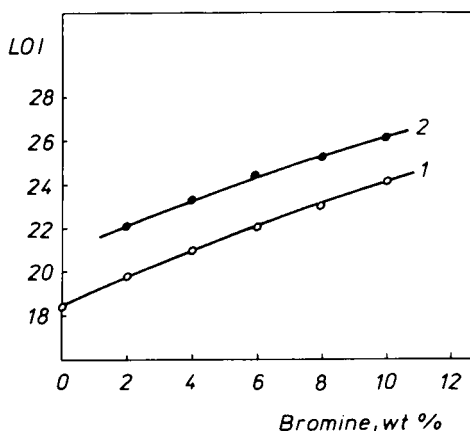

FIG. 10. Influence of the content of brominated monomer (Br, wt%) on the limiting oxygen index of the mixture of polystyrene and copolymer of N-(2,4,6-tribromophenyl) maleimide with styrene without Sb_2O_3 (1) and in the presence of Sb_2O_3 (Br/Sb = 3/1) (2).

Some residue (20% in nitrogen) at the end of the fast decomposition region indicated that depolymerization to volatile products did not go to completion, the usual characteristic of halogenated N- phenyl maleimide copolymers [19].

The flammability properties of poly(TBPMI-alt-St) and its mixture with polystyrene were determined by limiting oxygen index (LOI) measurements and are shown in Fig. 10. Its values are an approximately linear function of the weight percent of bromine in the polymer. The values of LOI increase when Sb_2O_3 is added to the polymer (Br/Sb = 3/1). Sb_2O_3 is a very well known synergist for Br compounds [20].

From these results we conclude that TBPMI is an efficient flame retardant for styrene copolymers, and it compares favorably with other brominated but low molecular weight compounds [20].

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