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HIGH CONVERSION COPOLYMERIZATION OF α-METHYLSTYRENE WITH *N*-METHYLMALEIMIDE OR *N*-PHENYLMALEIMIDE

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ABSTRACT

High conversion copolymerization of α-methylstyrene (α-MeSt) with *N*-methylmaleimide (NMeMI) or *N*-phenylmaleimide (NPhMI) was performed in a Calvet differential microcalorimeter under different ratios of monomer-to-monomer in the feed by using 2,2-azobis(isobutyronitrile) (AIBN) as the initiator. From a tracing of the electric signal of the calorimeter it was observed that in the presence of an excess of NMeMI or NPhMI, alternating copolymerization was the first reaction, and homopolymerization started only after the copolymerization was finished. The calorimetric method is therefore a convenient procedure for the preparation of blends of alternating copolymers with homopolymers of NMeMI or NPhMI of predetermined composition. Preliminary experiments indicate that based on a single T_g criterion, blends prepared within this work are miscible.

INTRODUCTION

Previous papers described that in the free-radical-initiated copolymerization of α-methylstyrene (α-MeSt) with *N*-methylmaleimide (NMeMl) [1] or *N*-phenylmaleimide (NPhMl) [2], there is a high tendency for the formation of alternating copolymers regardless of the ratio of comonomers in the feed. Studies on the mechanism of copolymerization performed in toluene or chloroform with 2,2-azobis(isobutyronitrile) (AIBN) as initiator, up to conversions not exceeding 10%, indicate that the copolymerization of α-MeSt with NMeMl or NPhMl proceeds under the participation of charge-transfer complexes, as proposed by Shirota and coworkers [3, 4].

In a continuation of this work, the copolymerization of α-MeSt with NMeMl and MPhMl, respectively, was performed in a Calvet differential microcalorimeter up to high conversion following a previously described procedure [5]. The Calvet microcalorimetry is very sensitive to all changes in the termination reaction, and it is convenient for studying relatively slow reactions.

EXPERIMENTAL

Physicochemical Measurements

The copolymer composition was determined by NMR spectroscopy on a Varian EM 390 spectrometer. Differential scanning calorimetry (DSC) was carried out on Perkin-Elmer models DSC-2 and DSC-7, using a scanning rate of 20°C/min, with a sample size of 15 mg. The only distinctive feature of the DSC thermograms was the glass transition temperature, which was taken as the temperature at which the midpoint of the heat capacity change at transition was achieved.

Materials

α-Methylstyrene was a 99% purity commercial product (Aldrich Europe, Belgium). A freshly distilled fraction boiling at 50°C at 13 kPa (10 mmHg) was used in the copolymerization reactions. *N*-Methylmaleimide (Aldrich Europe, Belgium) was recrystallized from ether and dried in high vacuum, mp 91–92°C (literature mp 90–92°C [6]). *N*-Phenylmaleimide was a commercial product (Aldrich Europe, Belgium) recrystallized from cyclohexane at mp 90°C (literature mp 90°C [7]).

Polymerization Procedure

Copolymerizations were performed up to high conversion in a differential microcalorimeter Calvet Setaram Instrument, Lyon, France. The calorimeter consists of two cylindrical cells, 20 × 80 mm, with a maximum usable volume of 10 mL. α-MeSt was copolymerized with NPhMI in toluene or chloroform as the solvent, while the copolymerization with NMeMI was performed in chloroform only because the monomers are not soluble at 60°C in toluene. The copolymerizations were performed at different monomer-to-monomer ratios in the feed but at a constant total monomer concentration in the feed: 1 mol/L^{-1}, 2 mol/L^{-1}, and 3 mol/L^{-1}, respectively.

Example of copolymerization: Into a mixture of 0.2832 g (0.0024 mol) α-MeSt and 1.6608 g (0.0096 mol) NPhMI was added 0.0057 g (0.3 wt%) AIBN dissolved in 2.2 mL toluene. A solution of comonomers was placed into a glass ampule, cooled in an ice bath, and filled with nitrogen. The ampule was heated to slightly below 60°C and placed into the measuring cell of the calorimeter adjusted to 60°C. The electromotive force in μV was recorded. After 14 h, when the electric signal remained unchanged for 1 h, the copolymer solution was diluted with 4 mL chloroform, and added dropwise into 100 mL methanol. The precipitate was filtered off, washed with methanol, and dried overnight in vacuum at 60°C. Yield: 1.913 g (98.43%) of white powder.

RESULTS AND DISCUSSION

Copolymerization of α-MeSt with NPhMI or NMeMI is a slow reaction, so the rate of copolymerization can be conveniently followed by a Calvet differential calorimeter. Figure 1 presents a tracing of the electromotive force of the calorimeter and the conversion of copolymerization of α-MeSt with NPhMI in toluene at a 1 to 1 molar ratio of the comonomers.

The maximum tracing of the electromotive force is the point where the system reaches 60°C, which usually takes 5 to 10 min. The conversion is

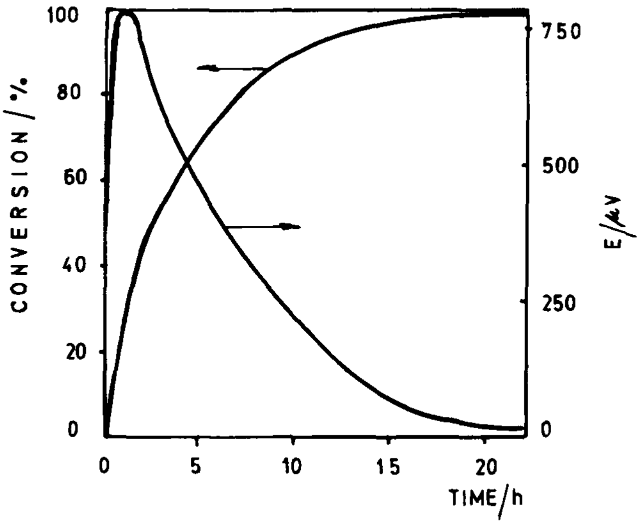

FIG. 1. Calvet microcalorimeter tracing and conversion against time in the copolymerization of α-MeSt with NPhMI at a molar ratio of 0.5 to 0.5 in toluene, 0.3% AIBN at 60°C; total monomer concentration 1 mol/L.

determined from the segmental area under the electric signal curve at a specific time divided by the total area under the electric signal curve.

Different results were obtained in the copolymerization of the same comonomers at nonequimolar ratios in the feed. The tracing of the electromotive force of the calorimeter and the conversion against time for the copolymerization of α-MeSt with NMeMI at molar ratios of 0.2 to 0.8 are shown in Fig. 2. It is evident that after the predetermined temperature of 60°C is reached, the tracing shows the expected pathway up to the point which corresponds to a conversion of 38%, where a minimum is formed. After about 15 min the electric signal passes through another maximum, and from this point the electromotive force decreases to zero. It is of interest to note that conversion at the minimum electric signal closely corresponds to the theoretically possible yield of alternating copolymer of 36%.

Similar data were also obtained in the copolymerization of α-MeSt with NPhMI at various ratios of electron donor and electron acceptor monomers in the feed, as shown in Fig. 3. As shown, the theoretical and experimental yields of alternating copolymers are in good agreement.

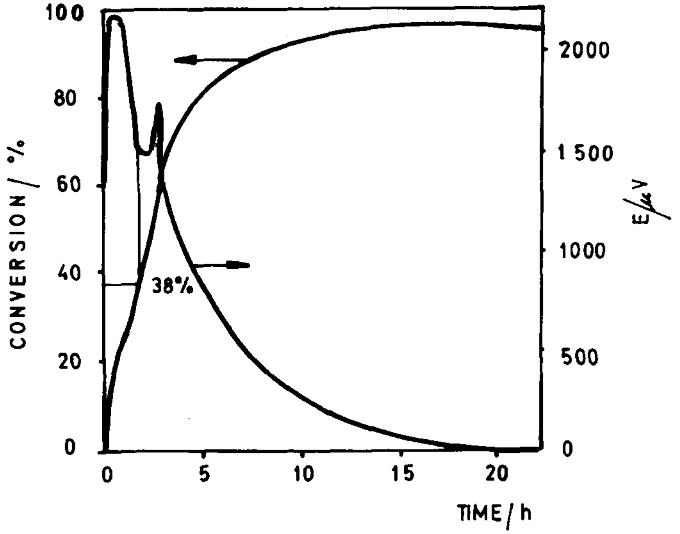

FIG. 2. Calvet microcalorimeter tracing and conversion against time in the copolymerization of α-MeSt with NMeMI at a molar ratio of 0.2 to 0.8 in $CHCl_3$; 0.3% AIBN at 60°C; total monomer concentration 3 mol/L.

Molar fraction of NPhMI in feed, experimental/theoretical yield of alternating copolymers, %: 0.9, 17/17.3; 0.8, 40/36; 0.7, 55/56; 0.6, 81/78; 0.4, 83/83.4; 0.3, 61/65. It should be emphasized that since α-MeSt does not homopolymerize under the applied experimental conditions, copolymerization stops after the theoretical yield of alternating copolymer is reached in the case of an excess of α-MeSt.

Figures 4 and 5 summarize the experimental yields of alternating copolymers determined from the electric signal of a Calvet microcalorimeter in the copolymerization of α-MeSt with NPhMI or NMeMI at various ratios of comonomers in the feed and at different comonomer concentrations. These data are compared with theoretical yields of alternating copolymers which are represented by solid lines in Figs. 4 and 5. It is evident that the theoretical yields of alternating copolymers are in good agreement with the experimental data, thus indicating that alternating copolymerization of α-MeSt with NMeMI or NPhMI and homopolymerization of homopolymerizable electron acceptor monomers are not simultaneous but are consecutive reactions—homopolymerization starts only after the completion of alternating copolymerization.

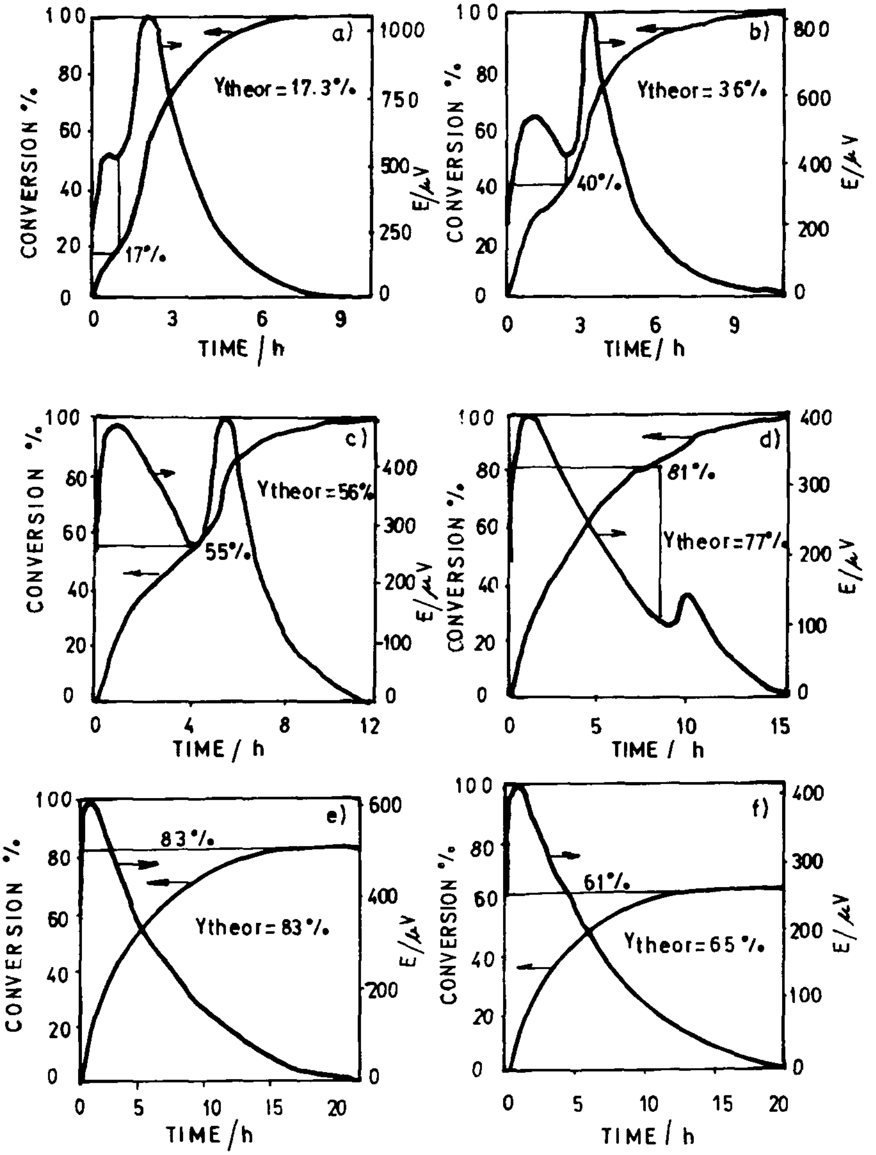

FIG. 3. Calvet microcalorimeter tracing and conversion against time in the copolymerization of αMeSt with NPhMI at molar ratios of a) 0.1 to 0.9, b) 0.2 to 0.8, c) 0.3 to 0.7, d) 0.4 to 0.6, e) 0.6 to 0.4, and f) 0.7 to 0.3; in toluene at 60°C; 0.3% AIBN; total monomer concentration 1 mol/L; Y_{theor} = theoretical yield of alternating copolymer.

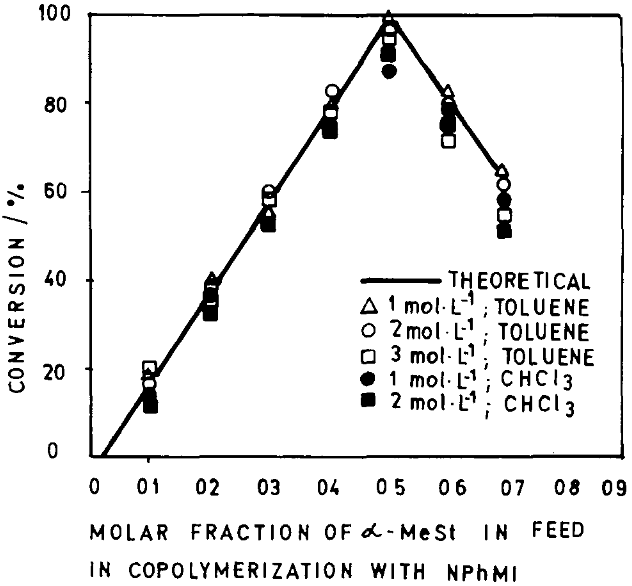

FIG. 4. A comparison of theoretical (solid line) and experimental yields of alternating copolymers in the copolymerization to high conversion of α-MeSt with NPhMI at different monomer-to-monomer ratios in feed at various total monomer concentrations in toluene.

It is of interest to mention that the mechanism of consecutive copolymerization and homopolymerization represents a convenient method for the preparation of polymer blends of alternating copolymers with predetermined amounts of homopolymers directly from the calorimeter reactor without a subsequent mixing of components.

Preliminary results of our studies on the miscibility of blends of alternating copolymers prepared in this work with corresponding homopolymers of NPhMI or NMeMI, based on a single T_g as the criterion, are illustrated in Figs. 6 and 7.

Figure 6 shows the DSC thermograms of poly(α-MeSt-*co*-NMeMI) blends with various amounts of poly-NMeMI. It is evident that in all blends, regardless of the ratio of copolymers to homopolymers, there is only one T_g, the values of which increase from 499 K for alternating copolymer to 548 K for poly-NMeMI. Similar results are also obtained with blends prepared in high conversion copolymerizations of α-MeSt

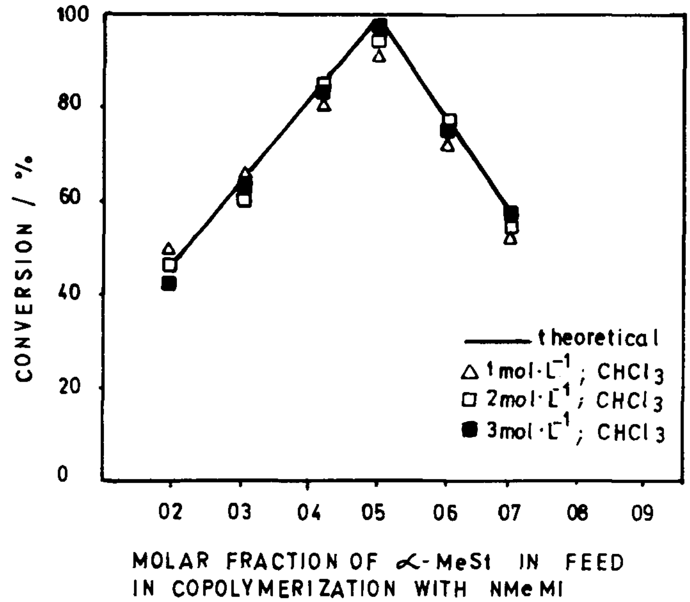

FIG. 5. A comparison of theoretical (solid line) and experimental yields of alternating copolymers in the copolymerization to high conversion of α-MeSt with NMeMl at different monomer-to-monomer ratios in feed at various total monomer concentrations in $CHCl_3$.

with NPhMl at various monomer-to-monomer ratios in feed (Fig. 7). The data in Fig. 7 indicate that T_g's of blends of poly(α-MeSt-*co*-NPhMl) with poly-NPhMl could be easily detected from DSC thermograms even in blend containing 83% homopolymer. However, the T_g of poly-NPhMl could not be determined by the DSC method since homopolymer decomposes in the range of the expected T_g.

As is evident from Figs. 6 and 7, all blends studied in this work show one T_g, thus indicating that according to the single T_g criterion, the blends of alternating copolymers of α-MeSt with NMeMl or NPhMl with the corresponding homopolymers are miscible.

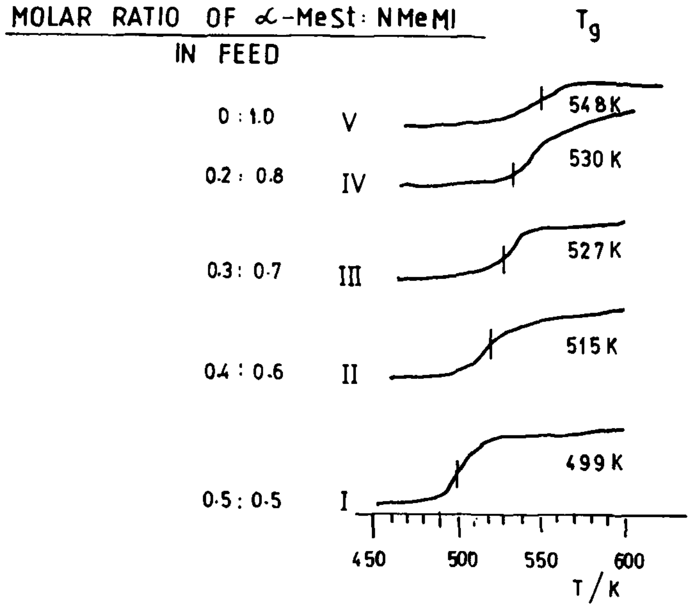

FIG. 6. DSC curves of blends of poly(α-MeSt-*co*-NMeMl) (a) with poly-NMeMl (b): I, a) 100%, b) 0%; II, a) 85.6%, b) 14.4%; III, a) 64.6%, b) 35.4%; IV, a) 43.3%, b) 56.7%; V, a) 0%, b) 100%.

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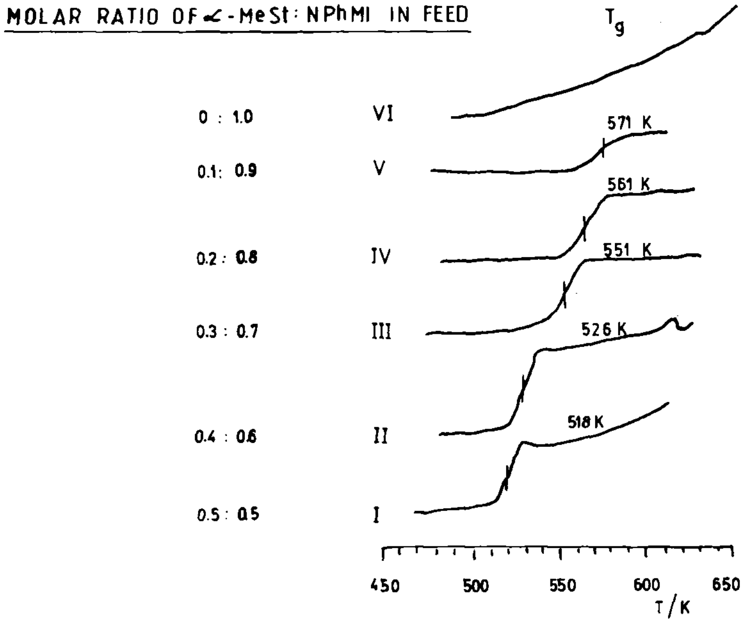

FIG. 7. DSC curves of blends of poly(αMeSt-*co*-NPhMI) (a) with poly-NPhMI (b): I, a) 100%, b) 0%; II, a) 77.5%, b) 22.5%; III, a) 55.93%, b) 44.07%; IV, a) 35.9%, b) 64.1%; V, a) 17.3%, b) 82.7%; VI, a) 0%, b) 100%.

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