

## High conversion polymerization of $\alpha$ -methylstyrene with maleimide at different monomer-to-monomer ratios in the feed

F. Ranogajec<sup>1</sup>, D. D. Fleš<sup>2\*</sup>, R. Vuković<sup>3</sup>, and D. Fleš<sup>3</sup>

<sup>1</sup>Institute "Ruđer Bošković", Zagreb, Yugoslavia

<sup>2</sup>Department of General and Inorganic Chemistry, Faculty of Technology, Zagreb, Yugoslavia

<sup>3</sup>INA-Research and Development, Zagreb, Yugoslavia

### SUMMARY

High conversion polymerization of  $\alpha$ -methylstyrene ( $\alpha$ -MeSt) with maleimide (Ml) was performed in Calvet differential microcalorimeter under different monomer-to-monomer ratios in the feed using AIBN as initiator. From the calorimetric curve it was observed that in the presence of an excess of Ml, alternating copolymer is quantitatively formed prior to the formation of poly(Ml).

### INTRODUCTION

In the previous papers from our laboratories it was shown that in the copolymerization of  $\alpha$ -methylstyrene ( $\alpha$ -MeSt) with N-phenylmaleimide (NPhMl) (1) or N-methylmaleimide (NMeMl) (2) there is a strong tendency to alternation regardless to the ratio of comonomers in the feed. It was further shown that charge-transfer complex participates in copolymerization reaction, and that in the copolymerization to high conversion in the presence of an excess of homopolymerizable NPhMl or NMeMl the alternating copolymerization is preceding the homopolymerization of N-substituted maleimides (3).

In this communication, the high conversion copolymerization of  $\alpha$ -MeSt with maleimide (Ml) is described. The copolymerization was carried out in Calvet microcalorimeter following procedure previously described for the copolymerization of  $\alpha$ -MeSt with NPhMl or NMeMl.

\*To whom offprint requests should be sent

## EXPERIMENTAL

### Materials

$\alpha$ -MeSt was commercial product (Aldrich Europe, Belgium) 99% purity; fraction boiling at 50°C/1.3 kPa was used. MI (Aldrich Europe, Belgium) 99% purity was recrystallized from a mixture of  $\text{CHCl}_3$  and hexane to m.p. 93-94°C.

### Polymerization procedure

Polymerization was performed to high conversion in differential microcalorimeter Calvet Setaram Instrument, Lyon, France. Cell volume (20x80 mm) was 10 ml. Polymerization in  $\text{CHCl}_3$  at 60°C was initiated with 0.3 wt/% of AIBN at different monomer-to-monomer ratio in the feed. Due to the insolubility of polymers in  $\text{CHCl}_3$  the reaction could not be carried out over 80%. The reaction mixture was diluted with  $\text{CHCl}_3$  and poured into methanol. The precipitate was removed by filtration, washed with methanol and dried in vacuum overnight at 60°C.

Differential scanning calorimetry (DSC) was carried out on a Perkin Elmer model DSC-2, using a scanning rate of 20°C/min., with a sample size of 15 mg. The only distinctive feature of the DSC thermograms was glass transition temperature which was taken as the temperature at which the midpoint of the heat capacity change at transition, was achieved.

## RESULTS AND DISCUSSION

The electric signal of Calvet microcalorimeter and conversion in the copolymerization of  $\alpha$ -MeSt with MI at equimolar ratio of comonomers and with an excess of electron acceptor (MI) are shown in Figure 1. It is evident that in copolymerization carried out with an excess of MI, the electric signal of calorimeter shows a minimum at the conversion which closely corresponds to the value of theoretical yield of alternating copolymer, as shown in Table 1 where the numerical data of theoretical and experimentally determined yields of alternating copolymers are presented. The same results were also obtained in the copolymerization of  $\alpha$ -MeSt with NMeMI and NPhMI, respectively (3).

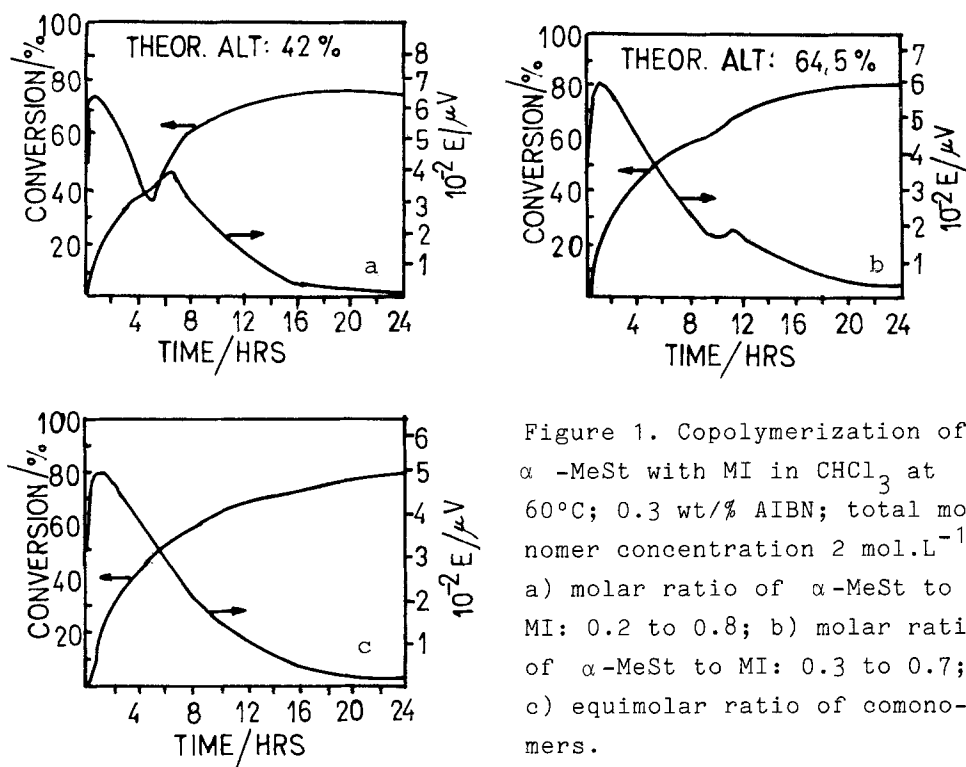


Figure 1. Copolymerization of  $\alpha$ -MeSt with MI in  $\text{CHCl}_3$  at  $60^\circ\text{C}$ ; 0.3 wt/% AIBN; total monomer concentration  $2 \text{ mol.L}^{-1}$ ; a) molar ratio of  $\alpha$ -MeSt to MI: 0.2 to 0.8; b) molar ratio of  $\alpha$ -MeSt to MI: 0.3 to 0.7; c) equimolar ratio of comonomers.

Table 1. Comparison of theoretical and experimental conversion of alternating copolymer of  $\alpha$ -MeSt with MI at  $60^\circ\text{C}$  in  $\text{CHCl}_3$ ; 0.3 wt/% AIBN; total monomer concentration  $2 \text{ mol.L}^{-1}$ .

Molar ratio		Conversion of alternating copolymer/%	
$\alpha$ -MeSt	MI	Theoretical	Experimental
0.2	0.8	42.0	41.5
0.3	0.7	64.5	64.0
0.5	0.5	100.0	79.9 <sup>1)</sup>

1) At conversion of 79.9% copolymer precipitates.

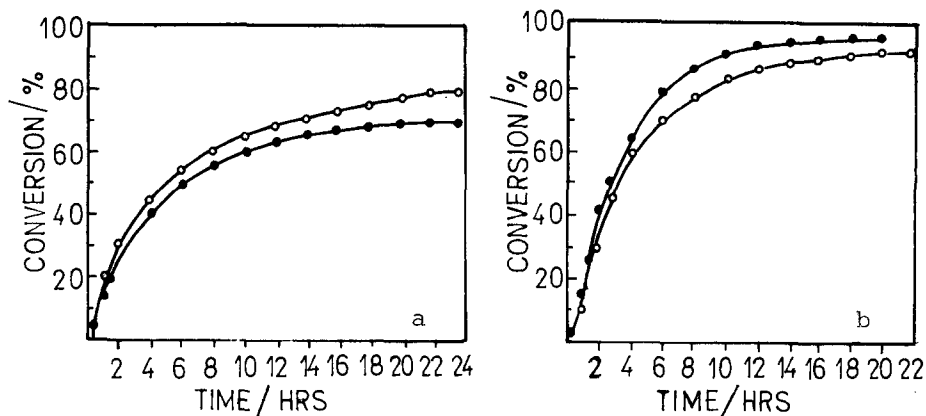


Figure 2. Comparison of the rate of conversion in alternating copolymerization and homopolymerization: a) copolymerization of  $\alpha$ -MeSt with MI (molar ratio 1 to 1) (o); homopolymerization of MI (●); b) copolymerization of  $\alpha$ -MeSt with NPhMI (molar ratio 1 to 1) (o); homopolymerization of NPhMI (●).

In Figure 2 is shown that the rate of conversion of alternating copolymerization of  $\alpha$ -MeSt with MI, at equimolar ratio of comonomers and the rate of conversion of homopolymerization of MI are not significantly different. The same was also found in the copolymerization and homopolymerization of  $\alpha$ -MeSt with NPhMI (Figure 2b), thus indicating that the formation of alternating copolymers prior to homopolymerization cannot be explained on the bases of difference of the rate of copolymerization and homopolymerization reaction. The competitive character of the copolymerization and homopolymerization reaction can, however, be explained as a consequence of the participation of the charge-transfer complex in the copolymerization reaction. It is well known that  $\alpha$ -MeSt as a strong electron donor forms stable CT-complexes with electron acceptors like maleic anhydride (MAN) (5) and maleimides, respectively.

During the course of our studies on the mechanism of alternating copolymerization of  $\alpha$ -MeSt with MAN, NPhMI and NMeMI, it was found that the rate of formation of  $\alpha$ -MeSt free radicals is much faster than the rate of formation of electron acceptors free radicals. Since, however, in all cases alternating

copolymer are formed regardless to the ratio of comonomers in the feed, it indicates that the addition of  $\alpha$ -MeSt is preferentially done through CT-complex, and as long as  $\alpha$ -MeSt is present in the feed, the alternating copolymers are formed through the addition of CT-complex. Only after  $\alpha$ -MeSt disappears from the reaction mixture, the free radical initiation of electron acceptor starts.

The composition of blends was calculated from the time-conversion curves in Figure 1. Based on single  $T_g$  as a criterion of miscibility, it was found that all blends of alternating poly( $\alpha$ -MeSt-co-MI) with poly(MI) show one  $T_g$  and are therefore miscible.  $T_g$  of alternating copolymers is 567K; blend which contains 80% of alternating copolymer has  $T_g$  580K; blend with 56.2% of alternating copolymer has  $T_g$  587K while poly(MI) decomposes on heating above 600K without any indication of  $T_g$ .

In conclusion it is of interest to note, that high conversion copolymerization of electron donor-acceptor monomers in the presence of an excess of homopolymerizable electron acceptor is interesting not only from the theoretical point of view, but it also represents a simple method for the preparation of alternating copolymer-homopolymer blends with predetermined composition.

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