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COPOLYMERIZATION AND COPOLYMERS OF 2,4,5-TRIBROMOSTYRENE WITH METHYL ACRYLATE AND METHYL METHACRYLATE

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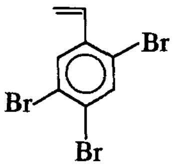
ABSTRACT

2,4,5-Tribromostyrene (TBSt) was copolymerized with methyl acrylate (MA) or methyl methacrylate (MMA) in a toluene solution using 2,2'-azobisisobutyronitrile as free radical initiator. The copolymerization reactivity ratios were found to be for the system TBSt / MA $r_1 = 7.4 \pm 1.2$ (TBSt) and $r_2 = 0.1 \pm 1.4$ (MA) and for the system TBSt / MMA $r_1 = 1.8 \pm 0.2$ (TBSt) and $r_2 = 0.1 \pm 0.2$ (MMA). The **e** and **Q** values were also calculated. The initial rate of copolymerization, as well as molecular weight of the obtained copolymers for both system linearly increase as the content of TBSt in the monomer mixture increases. Similar behavior has also been established for the course of the copolymerization reactions to high conversions. The resulting copolymers rapidly decompose at temperatures 20-800°C above the decomposition of corresponding (metha)crylate hompolymers. However, the glass transition temperature increases markedly with increasing TBS content.

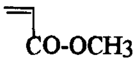
INTRODUCTION

Free radical homopolymerization and copolymerization of bromine substituted styrenes with vinyl monomers have been described in several papers [1-5]. It was shown that an increase in styrene bromination results in an increase in the rate of polymerization and in the values of copolymerization reactivity ratios, except in the case of pentabromostyrene where steric hindrance effect predominate. Also, the NMR spectra indicate that free radical synthesized polymers possess an atactic configuration [6]. The influence of o-, m- or p-bromostyrene isomers on the polymerization reaction has been studied as well and was found that there is large difference among the overall polymerization rate following the order o > m > p as a results of mutual polar, steric and resonance effect interactions [1]. Some work dealing with miscibility behavior of polystyrene and bromostyrene copolymers has been reported [7, 8]. Recently, copolymerization of brominated styrenes, particularly dibromo- and tribromostyrene, have attracted special attention, because they can be used as the reactive monomeric brominated flame retardants for thermoplastics [8, 9].

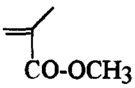
In an earlier article, we described the copolymerization kinetics of TBSt with styrene (St) or acrylonitrile (AN) [10] and some properties of the copolymers obtained. The present report deals with the copolymerization kinetics of TBSt with methyl acrylate (MA) and methyl methacrylate (MMA) at low and high conversions, as determined by dilatometry. Measurements of some characteristic properties of the copolymers, particularly their thermal stability, were also under-taken.



TBSt



MA



MMA

EXPERIMENTAL

Materials

Methyl acrylate and methyl methacrylate were freed from the inhibitor by washing with sodium hydroxide solution followed by several washings with water. They were dried over anhydrous sodium sulfate before used. 2,4,5-Tribromostyrene (Bromine Compounds, Ltd., Israel) was recrystallized several times from methanol, m. p. 67, 5°C. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Solvents were purified in the usual manner.

Measurements

Thermogravimetric analyses (TGA, DTA) were carried out with a DuPont

2000 and DCS-7 instrument in helium atmosphere and with a heating rate of 10 °C/min. The composition of copolymers were established by bromine analyses.

The molecular weight 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. Molecular weights were calculated as polystyrene equivalents.

Polymerization Procedures

Solution polymerization to low conversion for the determination of the monomer reactivity ration 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 precipetated 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 the 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 precipatation in excess methanol. The conversion was determined gravimetrically at the end of the each dilatometric experiment.

RESULTS AND DISCUSSION

Copolymerization Reaction

The free radical copolymerization of 2,4,5-tribromostyrene (TBSt), with methyl acrylate (MA) or methyl methacrylate (MMA) were performed in toluene solution using 2,2'-azobisisobutyronitrile (AIBN) as the initiator. The influence of the mole fraction of TBSt in the initial monomer mixture (f_1) on the composition (F_1) and some properties of the copolymers obtained for low conversions are summarized in Table 1 for the system TBSt/MA, and in Table 2 for the system TBSt/MMA. In both cases, the plots of instantaneous copolymer composition (Figure 1) show a marked tendency toward random copolymerization, the TBSt

TABLE 1. Copolymerization of 2,4,5-Tribromostyrene (TBSt, M_1) and Methyl Acrylate (M_2) in Solution at Low Conversions[a]

f_1[b)]	Conv. in %	Contents of Br in wt%	F_1[c)]	$10^{-3}\cdot M_w$[d)]	$10^{-3}\cdot M_n$[e)]	$T_{5\%}$[f)] °C	T_g[g)] °C
0.05	3.44	41.28	0.264				
0.1	3.48					343.0	76.0
0.2	18.10	62.89	0.681			357.0	
0.3	9.84	65.10	0.760	13.24	6.83		127.0
0.4	27.45	67.04	0.838				
0.5	15.36	68.00	0.880	23.78	10.64		166.0
0.6	13.27	68.60	0.910	35.62	15.56		
0.7	12.10	69.20	0.938	37.22	15.02		

[a)] Polymerization conditions: toluene solution (50 ml) of monomers (0.025 mol) and 2,2'-azobisisobutyronitrile (0.082 g), 60°C.

[b)] Mole fraction of TBSt in the initial monomer mixture.

[c)] Mole fraction of TBSt in copolymer.

[d)] Weight-average molecular weight determined by means of gel-permeation chromatography (solvent tetrahydrofuran).

[e)] Number-average molecular weight determined by means of gel-permeation chromatography (solvent tetrahydrofuran).

[f)] Temperature of the beginning of rapid decomposition at 5% weight loss, determined by means of differential scanning calorimetry.

[g)] Glass transition temperature determined by means of differenatial scanning calorimetry.

content being higher, however, in the copolymers. By using the Kelen-Tüdõs equation [11], the copolymerization 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 MA and MMA toward both types of propagating species, and the resulting copolymers are therefore richer in TBSt than the corresponding monomer mixtures. The same type of pattern has been found in the copolymerization of TBSt with styrene and acrylonitrile [10].

TABLE 2. Copolymerization of 2,4,5-Tribromostyrene (TBSt, M_1) and Methyl Methacrylate (M_2) in Solution at Low Conversions$^{a)}$

$f_1^{b)}$	Conv. in %	Contents of Br in wt%	$F_1^{c)}$	$10^{-3}\cdot M_w^{d)}$	$10^{-3}\cdot M_n^{e)}$	$T_{5\%}^{f)}$ °C	$T_g^{g)}$ °C
0.1	9.34	40.16	0.282			331.0	
0.15	15.86	47.45	0.379				134.5
0.2	14.30	52.48	0.464			337.0	
0.3	33.42	57.80	0.575	18.42	9.08		150.1
0.4	25.46	61.00	0.656	27.09	14.65		
0.5	33.02	62.42	0.699	39.63	20.95		
0.6	16.68	64.46	0.764	55.44	28.28		178.3
0.7	20.40	66.28	0.826				
0.8	16.81	67.44	0,.873				

$^{a-g)}$ See corresponding footnotes in Table 1.

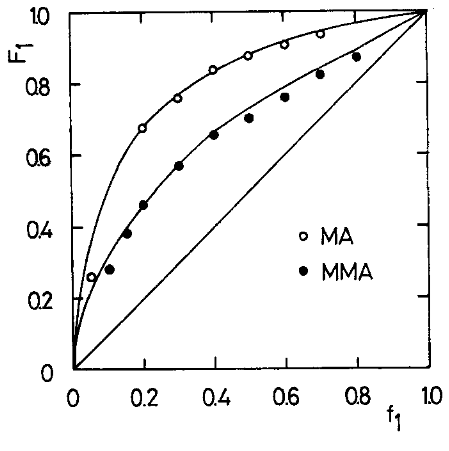


Figure 1. Monomer-copolymer composition curves for the copolymerization of 2,4,5-tribromostyrene (M_1) with methyl acrylate (MA, M_2) and methyl methacrylate (MMA, M_2) in toluene, at 60°C, with 2,2'-azobisisobutyronitrile as initiator. (Mole fraction of M_1 in copolymer F_1 vs. mole fraction of M_1 in initial monomer mixture f_1).

TABLE 3. Copolymerization Reactivity Ratios **r** and **Q, e** Values for Free-radical Copolymerization of 2,4,5-Tribromostyrene (M_1) with Methylacrylate (M_2) or Methyl Methacrylate (M_2)

M_2	r_1	r_2	Q_2	e_2	Q_1	e_1
Methyl acrylate	7.4±1,2	0.1±1,4	0.42	0.60	6.6	1.24
Methyl methacrylate	1.8±0,2	0.1±0,2	0.74	0.40	8.18	1.56

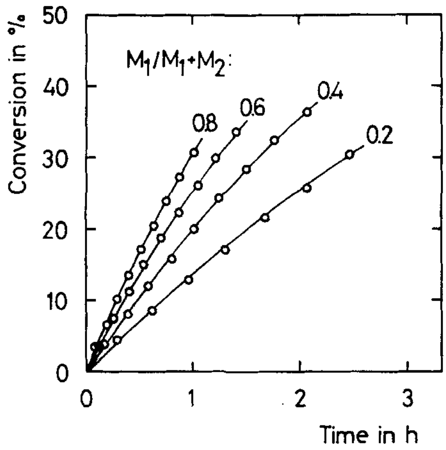


Figure 2. Influence of mole fraction of M_1 in initial monomer mixture f_1 (numerical values at curves) on conversion vs. reaction time curves in copolymerization of 2,4,5-tribromostyrene (M_1) and methyl acrylate (M_2) at 60°C; total monomer concentration [M]=0.5 mol/L, concentration of 2,2'-azobis-isobutyronitrile $[\mathrm{AIBN}]=1\cdot10^{-2}$ mol/L in toluene.

The course of the copolymerization of TBSt for different monomer feed ratios, but at a constant total monomer concentration (0,5 mol/L) in toluene, is represented by the integrated time-conversion curves with MA (Figure 2) and MMA (Figure 3) as comonomers. The familiar pattern of the curves shows an increase of conversion as the mole fraction of TBSt increases in the monomer mixture. Comparison of the examined polymerization systems shows that higher conversions were obtained with MA as a comonomer after the same reaction time, particularly at lower TBSt content in the monomer mixture.

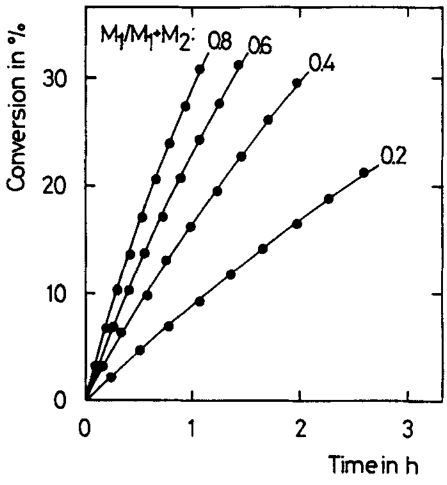


Figure 3. Influence of mole fraction of M_1 in initial monomer mixture f_1 (numerical values at curves) on conversion vs. reaction time curves in copolymerization of 2,4,5-tribromostyrene (M_1) and methyl methacrylate (M_2) at 60°C; total monomer concentration [M]=0.5 mol/L, concentration of 2,2'-azobisisobutyronitrile [AIBN]=$1 \cdot 10^{-2}$ mol/L in toluene.

Copolymer Properties

Weight-average ($\overline{M}_w$) and number-average ($\overline{M}_n$) molecular weight measurements at low conversion (Tables 1 and 2) for both systems were found to lie in the range between $6 \cdot 10^3$ and $60 \cdot 10^3$ and they tend to increase as the mole fraction of TBSt is increased in the monomer mixture. This tendency is probably due to the significantly higher propagation reaction rates at higher TBSt content.

The thermal properties of both types of copolymers were determined by means of thermogravimetry (TGA) and differential thermal analysis (DTA) measurements in a helium atmosphere. The experimental results on the initial thermal stability are expressed as the temperature at which rapid decomposition starts, i. e. 5% weight loss ($T_{5\%}$) is attained. These results, tabulated in Tables 1 and 2, indicate that the thermal stability tends to somewhat increase as the TBSt content in the copolymers increases. Typical TGA curves of copolymers with similar composition for TBSt/MA (53.0 mol% TBSt) and TBSt/MMA (47.0 mol% TBSt) are shown in Figures 4 and 5, respectively. They show that the copolymers start to decompose spontaneously at 20-80°C above the decomposition temperature of poly(methyl-acrylate) or poly(methyl-methacrylate) [12]. Some residue at the end of the fast decomposition region indicates that depolymerization to volatile products

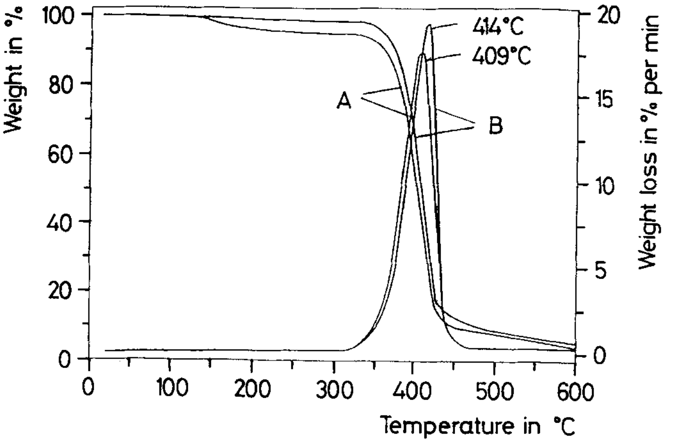


Figure 4. Thermogravimetry and derivative thermogravimetry curves of the copolymer from 2,4,5-tribromostyrene and methyl acrylate in helium; molar ratio: A-0.53/0.47 and B-0.68/0.32, respectively.

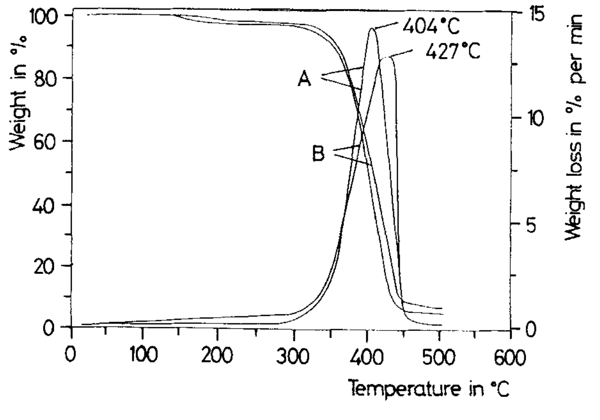


Figure 5. Thermogravimetry and derivative thermogravimetry curves of the copolymer from 2,4,5-tribromostyrene and methyl methacrylate in helium; molar ratio: A-0.32/0.68 and B-0.47/0.53, respectively.

does not go to completion, the usual characteristics of bromine containing polymers [13].

The glass transition temperatures (T_g), determined by differential scanning calorimetry (DSC) measurements over a wide range of copolymer compositions, are shown in Tables 1 and 2. By using the Gordon-Taylor equation [14], a plot of

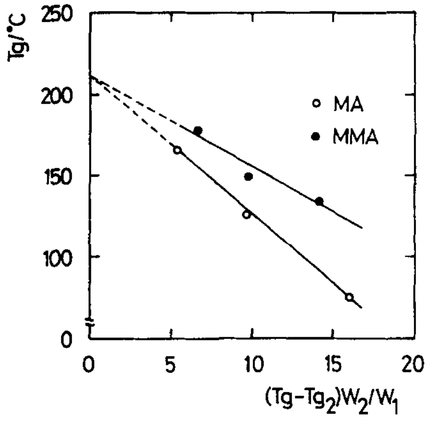


Figure 6. Gordon-Taylor relation of the glass transition temperature T_g vs. composition for a series of copolymers from 2,4,5-tribromostyrene (M_1, weight fraction W_1) with methyl acrylate (MA. M_2, weight fraction W_2) and methyl methacrylate (MMA, M_2, weight fraction W_2) prepared by free-radical copolymerization in toluene, at 60°C with 2,2'-azobisisobutyronitrile as initiator.

T_g against $(T_g\text{-}T_{g2})W_2/W_1$ gives a straight line for both types of copolymers, as presented in Figure 6. Here, T_{g2} marks the glass transition temperature of MA and MMA homopolymers; they are taken to be 6°C and 105°C, respectively [15], and W_1 and W_2 are the weight fractions of TBSt and MA (or MMA), respectively, in the copolymer. The intercept obtained by extrapolating the lines, using the least squares method, when the weight fraction of the comonomers fell to zero, yields the glass transition temperature T_{g1} of 211°C for poly(2,4,5-tribromostyrene). However, a value of 217°C was established experimentaly. These values are far above the 100°C for polystyrene [15] indicating the influence of Br substitution on the glass transition temperature.

CONCLUSIONS

The free radical copolymerization of TBSt with MA or MMA gave copolymers with random order of repeating units and richer in TBSt than in monomer mixtures. The initial reaction rates of both systems depend mainly on TBSt concentration and is in agreement with the copolymerization reactivity ratios found. The conversion of monomer mixture and molecular weight of the obtained copolymers increase as the mol fraction of TBSt is increased.

The resulting copolymers show somewhat higher thermal stability of the corresponding (meth)acrylate homopolymers. However, the glass transition temperature markedly increases with increasing the TBSt content following the Gordon-Taylor equation.

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REFERENCES

[1] H. Horie, H. Shuyama, and T. Oishi, *Polym. J., 25*, 757 (1993).

[2] T. Oishi, H. Horie, and H. Shuyama, *Polym. J., 25,* 781 (1993).

[3] D. Alsheh and G. Marom, *J. Appl. Polym. Sci., 22,* 3177 (1978).

[4] M. Day, T. Suprunchuk, J. D. Cooney, and D. M. Wiles, *J. Appl. Polym. Sci., 33,* 2041 (1987).

[5] C. A. Barson and D. K. Burns, *Eur. Polym. J., 14,* 497 (1978).

[6] D. L. Trumbo and H. J. Harwood, *Polym. Bull., 32,* 207 (1994) .

[7] H. K. Xie and E. Nies, *Makromol. Chem., Makromol. Symp. 58,* 227 (1992).

[8] J. Troitzsh, *Makromol. Chem., Makromol. Symp., 74,* 125 (1993) .

[9] M. Lewin and G. Kirschenbaum, *Recent Advances in Flame Returdancy of Polymeric Materials,* BBC Inc., Norwalk, 1992.

[10] Z. Janovic and Lj. Tomasek, *J. Macromol. Sci.-Pure and Appl. Chem., 33,* 735 (1996).

[11] F. Tüdõs, T. Kelen, T. Földes-Berezsnich, and B. Turcsányi, *J. Macromol. Sci. Chem., A10,* 1513 (1976).

[12] R. T. Conley, Ed., "*Thermal Stability of Polymers*", Vol. 1, M. Dekker, New York, 1977.

[13] K. Pielichowski, A. Puszynski, and J. Pielichowski, *Polymer J., 26* (1994) 822.

[14] M. Gordon and J. S. Taylor, *J. Appl. Chem., 2,* 493 (1952).

[15] A. W. Lee and R. A. Rutherfort, "*The Glass Transition Temperatures of Polymers*", in Polymer Handbook, 2nd Edition, J. Brandrup and E. H. Immergut, Eds., J. Wiley & Sons, New York, 1975, pp. 111-139.

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