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Copolymers of Bromine-Containing Monomers. 7. Copolymers of Styrene With Some Brominated Phenyl Methacrylates

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Styrene was copolymerized with 2,4,6-tribromophenyl methacrylate or pentabromophenyl methacrylate in either aqueous emulsion or dimethyl formamide solutions and the thermal and flammability properties of the resulting polymers were investigated.

The reactivity ratios of the monomers in both media were established. The initial homopolymerization reaction rates established in benzene solution increased in the order styrene > pentabromophenyl methacrylate > 2,4,6-tribromophenyl methacrylate whereas the copolymerization reaction rate have an opposite direction in respect to styrene .The thermal stability of the polymers determined from TGA and DTG measurements, showed that poly(2,4,6-tribromophenyl methacrylate) and its styrene copolymers were thermally stabler and that the copolymers of pentabromophenyl methacrylate with styrene had better flame retardant properties as was demonstrated by limiting oxygen index measurements.

INTRODUCTION

In our earlier communications,[1,2] results of the study of the copolymers of styrene and acrylonitrile and some brominated acrylates were described. It was found that the rates of homopolymerization of 2,3-dibromopropyl acrylate, 2,4,6-tribromophenyl acrylate or pentabromophenyl acrylate and copolymerization with styrene increased with increasing the electronegativity of the substituents and that incorporation of brominated monomers reduced to some extent the thermal properties but improved the flame retardancy of the copolymers obtained.

Some work dealing with homopolymerization of brominated phenyl methacrylates[3] and the copolymerization of these monomers with styrene[4] has been reported. Recently, copolymers of halogenated methacrylic esters with other vinyl monomers have attracted special attention because they can be used for the improvement of flammability characteristics.[5] Most of the end use properties of these copolymers have been described in the patent literature.[6,7]

This paper details the copolymerization reactions of styrene with 2,4,6-tribromophenyl methacrylate and pentabromophenyl methacrylate in aqueous emulsion and in solution and discusses some properties of the copolymers obtained, particularly their thermal and flammability behaviour.

EXPERIMENTAL

Materials

Styrene was washed with 5% aqueous sodium hydroxide solution, dried, and distilled under nitrogen at 10 mm before use. The initiator used in the emulsion experiments was analytical grade potassium persulfate (Merck Chem. Co.) and the emulsifier was purified grade sodium dodecylbenzene sulphonate (Allied Chem. Co.). Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Solvents were purified in the usual manner.

Pentabromophenol and 2,4,6-tribromopehnol (Aldrich Chem. Co.) were reprecipitated from benzene solutions into methanol, m. p. 92—93 °C and 225—226 °C, respectively. Methacryloyl chloride (Aldrich Chem. Co.) was distilled under nitrogen before used.

Measurements

Infrared spectra were recorded on a Perkin-Elmer spectrophotometer Model 147 from films cast from chloroform solutions onto sodium chloride plates. ^{13}C-NMR spectra were recorded on a Varian-CFT 20 spectrometer with complete proton decoupling and ^{1}H-NMR spectra were measured on a 90 MHz Varian EM-90 spectrometer. The measurements were carried out at room temperature on 10% solutions in deuterated chloroform with TMS as internal standard.

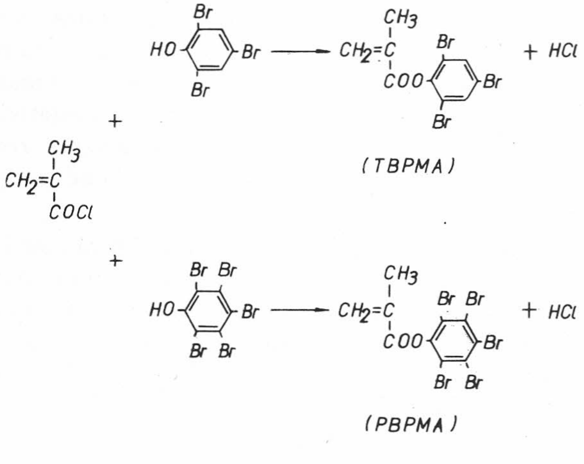
Thermogravimetric analyses (TGA, DTG) were carried out with a Perkin-Elmer TGS-2 and DSC-2 instrument in a nitrogen atmosphere and at a heating rate of 10 °C/min.
The limiting oxygen index measurements were carried out with a Stanton-Redcroft FTA instruments on films cast from methylene chloride solutions (20 wt %) onto glass plates. The films were dried for 24 hours at ambient temperature and then for another 16 hours at 0.1 mm and 26 °C and were finally cut into strips of 80 × 6.5 mm.

Intrinsic viscosities were measured on a Cannon-Fenske capillary viscometer No. 100, in toluene at 30 °C.

Procedures

Brominated monomers

Brominated monomers were prepared by the condensation of methacryloyl chloride with the appropriate brominated phenols according to Schotten-Baumann, following a modified literature procedure[3,4]. The reaction proceeds as follows:



2,4,6-Tribromophenyl methacrylate (TBPMA). Over a period of two hours, solutions of methacryloyl chloride (58 g, 0.55 mole) in 60 mL of dry methylene chloride and of triethanol amine (56 g,0.55 mole) in 60 mL of methylene chloride were added dropwise and simultaneously to a stirred solution of 2,4,6-tribromophenol (166 g, o.5 mole) and hydroquinone (0.2 g) in 400 mL of methylene chloride, cooled in a ice-water bath. Stirring was continued for six hours at room temperature, then the solid was separated by filtration. The solution was washed with water and a sodium dicarbonate solution, dried with sodium sulfate, and finally the solvent was evaporated. The crude product was dissolved in 300 mL of petroleum ether and crystallized by cooling in a refrigerator. Recrystallization from petroleum ether gave 156 g (78%) of white cubic crystals, m. p. 66—67 °C.

Analysis for $C_{10}H_7O_2Br_3$ Calcd.: C, 30.11%; H, 1.77%; Br, 60.10%
Found: C, 30.04%; H, 1.82%; Br, 60.42%

The ^1H NMR spectrum showed a singlet at δ 7.28 ppm (aromatic nucleus) multiple signals at δ 5.37 ppm and 6.30 ppm (methylene group) and signal at 1.88 ppm (methyl group).

The ^{13}C NMR spectrum showed the following signals: $=CH_2$ (δ 134.41 ppm), $=C—$ (δ 128.16 ppm), —COO— (δ 162.98 ppm) and the aromatic ring C—1 (δ 145.79 ppm), *ortho* C—2,6 (δ 118.46 ppm), *metha* C—3.5 (δ 134.66 ppm) and *para* C—4 (δ 119.56 ppm) and the methyl group at δ 18.23 ppm.

Pentabromophenyl methacrylate (PBPMA). For the synthesis of PBPMA the same method as described for TBPMA was used but with toluene as the solvent, and the crude product was recrystallized from ethyl acetate giving white needle crystals in 74% yield, m. p. 242—243 °C.

Analysis for $C_{10}H_5O_2Br_5$ Calcd.: C, 21.57%; H, 0.91%; Br, 71.77%
Found: C, 21.82%; H, 0.90%; Br, 71.98%

The ^1N NMR spectrum showed multiple signals at δ 5.36—6.30 (vinyl group) and singlet at δ 1.88 ppm (methyl group).

The ^{13}C-NMR spectrum for the side chain showed signals for: $=CH_2$ (δ 134.34 ppm), $=C—$ (δ 129.34 ppm), methyl group (δ 18.26 ppm), and the aromatic ring C—1 (δ 147.06 ppm), *ortho* C—2.6 (δ 121.14 ppm), *metha* C—3.5 (δ 128.37 ppm) and *para* C—4 (δ 126.80 ppm).

Polymerization Procedures

Emulsion polymerizations were carried out under a constant stream of nitrogen in a 100 mL, double-jacketed glass reactor equipped with a mechanical stirrer. A mixture of 50 g (2 wt. %) of an aqueous solution of sodium dodecylbenzene sulphonate and 10 g of monomer was placed in the reactor which was thermostatted to 60 °C (± 0.2 °C). The emulsion was purged with nitrogen for 30 minutes before potassium persulfate (0.02 g) was added. The degree of conversion was determined on samples which were withdrawn at regular intervals and precipitated into methanol.

Homopolymerization of brominated monomers in benzene solutions were carried out in 20 mL glass polymerization tubes. Typically 10 mL of the monomer solution (0.354 mol/L) mixed with AIBN (65 mg) was degassed by the three freeze thaw cycles and then sealed at 0.1 mm. The tube was placed in a constant temperature bath at 70 °C for one to five hours and after opening the contents were poured into 50 mL of methanol. The solid was collected by filtration, washed with methanol, and dried at 65 °C and 0.1 mm. The same procedure was used for the copolymerizations with styrene; benzene or dimethyl formamide was used as a solvent and the concentration of monomers were 2.24 mol/L.

RESULTS AND DISCUSSION

Copolymerizations

The free radical copolymerization of styrene (St) with 2,4,6-tribromophenyl methacrylate (TBPMA) or pentabromophenyl methacrylate (PBPMA) were performed in aqueous emulsion, as well as in benzene or dimethyl formamide solutions. Because of the low solubility of PBPMA in St, this reaction was run only in solution. The influence of the molar composition of the initial monomer mixture on the composition of resulting copolymer in both media are shown in Tables I, II and III. In all copolymerizations the reactions were stopped

TABLE I

Copolymerization of 2,4,6-Tribromophenyl Methacrylate (M_1) with Styrene (M_2) in Emulsion at 70 °C

Experiment No.	Monomer feed mol %		Conv. %	Br. %	Copolymer mol. %, exp.	
	TBPMA	St			TBPMA	St
1	10	90	2.4	33.18	24.35	75.65
2	20	80	5.3	39.05	32.63	67.37
3	35	65	4.8	44.27	42.20	57.80
4	50	50	7.9	46.00	46.00	54.00
5	65	35	8.2	48.54	52.30	47.70
6	80	20	2.8	51.44	60.79	39.21

Polymerization conditions: Aqueous Solution (50 g) of sodium benzene-sulfonate (2 wt %), monomers (10 g) and $K_2S_2O_8$ (0.02 g) at 70 °C.

TABLE II

Copolymerization of 2,4,6-Tribromophenyl Methacrylate (M_1) with Styrene (M_2) in DMF at 60 °C

Experiment No.	Monomer feed mol %		Conv. %	Br. %	Copolymer mol. %, exp.	
	TBPMA	St			PBPMA	St
1	10	90	2.5	34.46	26.00	74.00
2	20	80	3.2	42.50	38.70	61.30
3	35	65	3.4	45.59	45.05	54.95
4	50	50	4.0	48.30	51.67	48.33
5	65	35	4.9	50.32	57.40	42.60
6	80	20	4.3	52.60	65.07	34.93

Polymerization conditions: DMF solutions (50 mL) of monomers (0.1 mol) and AIBN (0.24 g) at 60 °C.

TABLE III

Copolymerization of Pentabromophenyl Methacrylate (M_1) with Styrene (M_2) in DMF at 60 °C

Experiment No.	Monomer feed mol %		Conv. %	Br. %	Copolymer mol. %, exp.	
	TBPMA	St			PBPMA	St
1	10	90	2.6	54.77	37.60	62.40
2	20	80	8.8	57.74	43.50	56.50
3	35	65	7.9	60.67	50.50	49.50
4	50	50	7.2	62.12	54.62	45.38
5	65	35	5.6	63.42	58.70	41.30
6	80	20	6.3	65.10	64.50	35.50

Polymerization conditions: DMF Solutions (50 mL) of monomers (0.1 mol) and AIBN (0.24 g) at 60 °C.

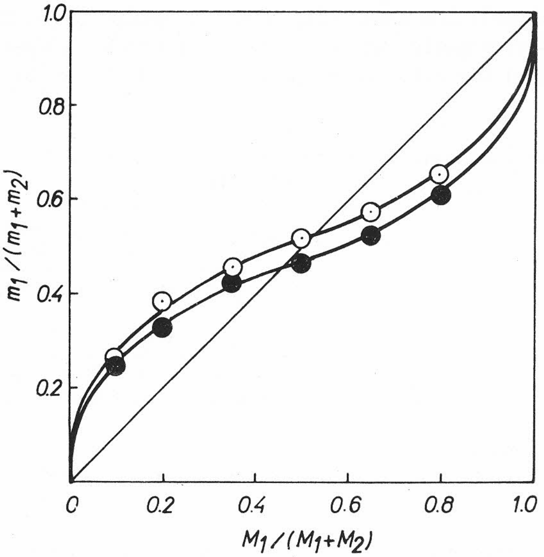


Figure 1. Copolymerization of 2,4,6-tribromophenyl methacrylate (M_1) with styrene at 70 °C in emulsion (●) and at 60 °C in DMF solution (○).

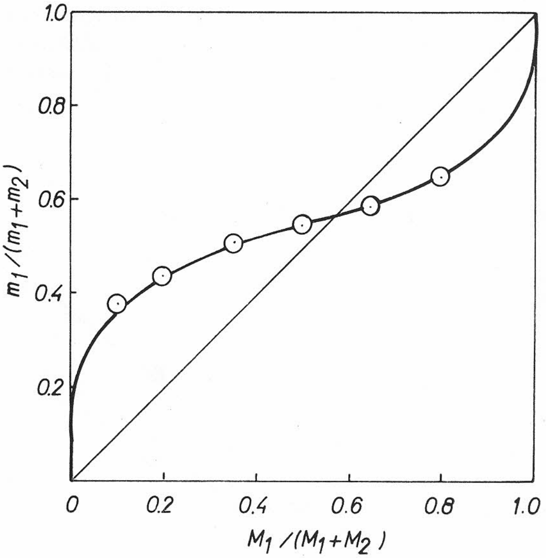


Figure 2. Copolymerization of pentabromophenyl methacrylate (M_1) with styrene at 60 °C in DMF solution (○).

before the copolymerization had reached 10% conversion. The copolymer composition was established by bromine analysis.

The plot of monomer-copolymer mol fraction composition for the brominated monomer (M_1) (Figures 1 and 2) shows a tendency toward ideal copolymerization; a similar observation was found for the brominated acrylic esters.[1]

Using the Kelen-Tüdös mean square relationship[8] and confidence intervals[9] we calculated the reactivity ratios (Table IV) from the experimental data. We related the values of the established reactivity ratios to polar (e) and resonance (Q) effect in the Alfrey-Price scheme. As seen, both parameters increase as the amount of bromine in the monomer increases.

TABLE IV

Copolymerization Parameters for Brominated Methacrylic Monomers (M_1) with Styrene (M_2)

Monomer (M_1)	Solvent	r_1[a]	r_2[a]	Azeotropic Composition	Q_1[b]	e_1[b]
2,4,6-Tribromo-phenyl methacrylate	DMF	0.27 ± 0.05	0.20 ± 0.05	52.3/47.7	1.27	0.91
	Benzene[c]	0.20	0.15	51.5/48.5	1.48	1.07
Pentabromophenyl methacrylate	Aq. Emulsion	0.13 ± 0.06	0.26 ± 0.04	46.0/54.0	0.88	1.04
	DMF	0.26 ± 0.02	0.09 ± 0.02	44.8/55.2	2.35	1.14

[a] Calculated by the Kelen-Tüdos method.[8]
[b] Calculated by assuming that Q = 1.0, e_2 = — 0.8 for Styrene.
[c] Ref. 10.

The tendency to form alternating styrene/phenyl brominated acrylic ester copolymers was also confirmed by the polymerization rates as determined in benzene solution. The amount of copolymer formed at the same feed composition (styrene 95 mol %) and under identical reaction conditions was determined. The results (Figure 3) showed that the initial rate of reaction increased in the

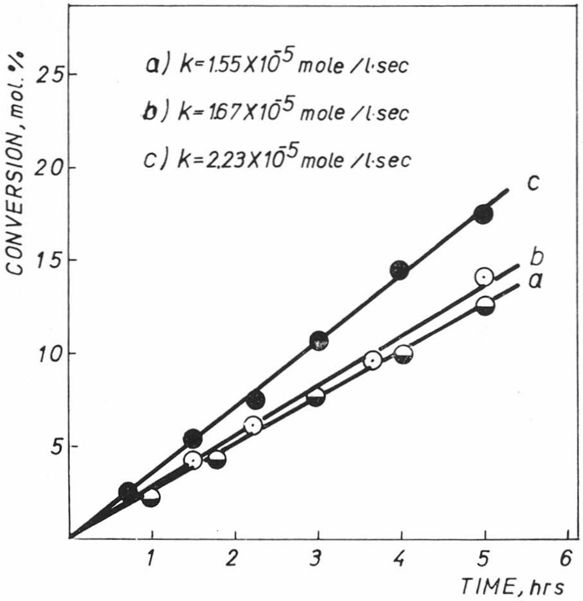


Figure 3. The initial rate of copolymerization of pentabromophenyl methacryate (c) and 2,4,6-tribromophenyl methacrylate (b) with styrene (95 mol %) (a) at 60 °C in benzene with AIBN.

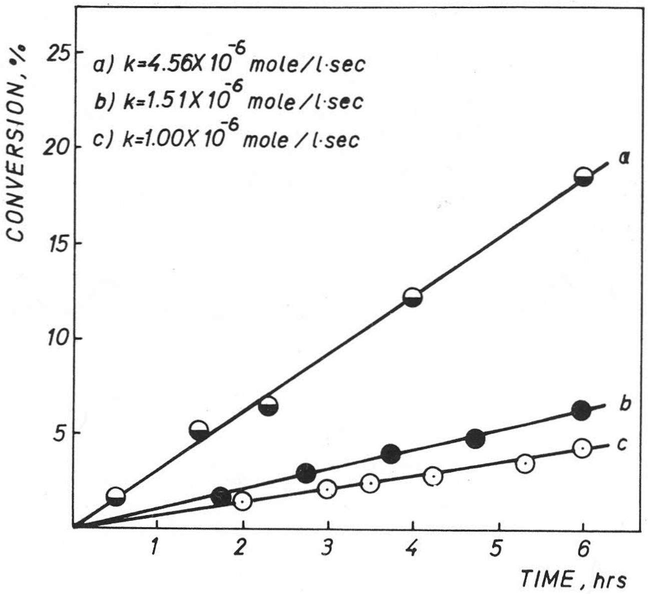


Figure 4. The initial rate of homopolymerization of styrene (a), pentabromophenyl methacrylate (b) 2,4,6-tribromophenyl methacrylate (c) at 70 °C in benzene with AIBN.

order PBPMA $>$ TBPMA $>$ St. Homopolymerization reaction of the monomer followed the opposite trend in respect to styrene (Figure 4). The polymerization rate for styrene is about 3—5 times higher than those for PBPMA and TBPMA, respectively. These results prove that the brominated acrylic monomers are more reactive and polymerize faster than the corresponding methacrylic esters, as was earlier proposed.[10,11]

Copolymer properties

The structure of the copolymers were confirmed by their ^{1}H NMR spectra (Figure 5), which exhibited characteristic chemical shift values for St-TBPMA copolymer (5a) of the methyl protons at $\delta = 0.25$—0.82 ppm, the methylene and methine protons of the polymer backbone chain were at $\delta = 0.91$—2.04 ppm, the phenyl protons of the styrene units, at $\delta = 6.59$ and 7.05 ppm and 3 and 5 protons of the 2,4,6-tribromophenyl group at $\delta = 7.66$ ppm. Similar chemical shift values were found for St-PBPMA copolymer (5b), however, without the protons of the brominated phenyl ring. Solution viscosity measurements of poly(St-co-TBPMA) and poly(St-co-TBPMA), obtained from benzene solution polymerizations, showed only a slight decrease in viscosity when the content of brominated monomer in the copolymers was relatively low (Figure 6). However, when the amount of brominated monomer is high, then significant changes in the intrinsic viscosity of the copolymers, as was exemplified for the copolymers of TBPMA and St (Figure 7), were observed. This is presumably due to chain transfer reactions in growing chain, either from a monomer or from the polymer chain, since this is a general tendency

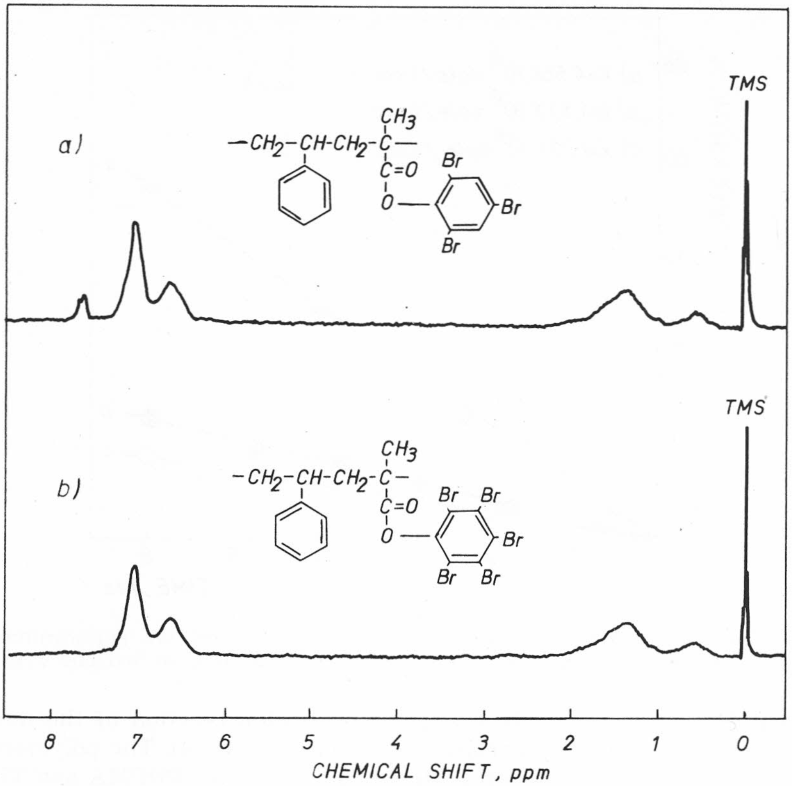


Figure 5. ^{1}H-NMR spectra: a) poly(styrene-co-2,4,6-tribromophenyl methacrylate) and b) poly(styrene-co-pentabromophenyl methacrylate).

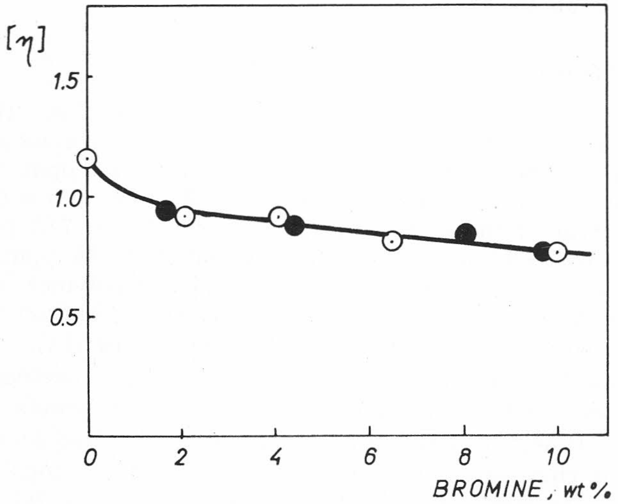


Figure 6. The influence of the copolymer composition of styrene with 2,4,6-tribromophenyl methacrylate (○) and pentabromphenyl methacrylate (●), obtained in bulk on the intrinsic viscosities in toluene at 30 °C.

for bromine containing monomers.[1,2,12] The thermal stabilities of the homopolymers of TBPMA and PBPMA and of their St copolymers were determined TGA and DTG measurement and flammability tests were carried out by limiting oxygen index measurements.

Thermogravimetric decomposition curves of homopolymers (Figure 8) have shown that brominated polymers are less stable in comparison with polystyrene. The better thermal stability of poly-TBPMA is probably due to higher bromine content of the poly-PBPMA which promotes its faster decomposition.

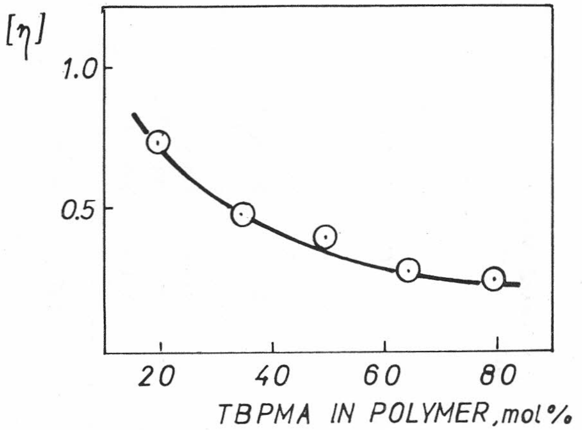


Figure 7. The influence of the composition of styrene and 2,4,6-tribromophenyl methacrylate copolymers, obtained in emulsion at 70 °C, on the intrinsic viscosities in toluene at 30 °C.

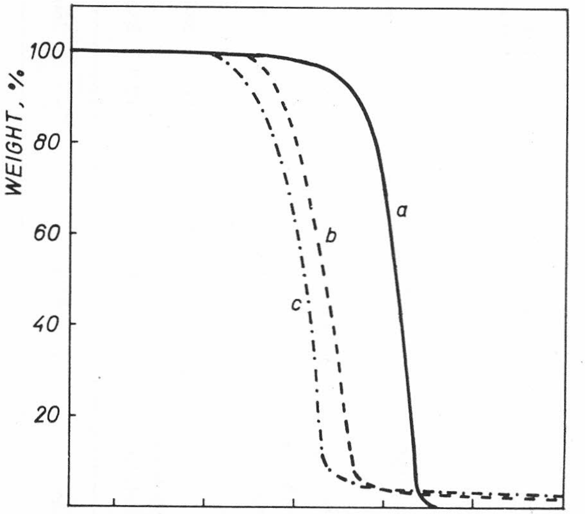


Figure 8. Thermogravimetric analysis of polystyrene (a), poly(2,4,6-tribromophenyl methacrylate (b), and poly(pentabromophenyl methacrylate) (c) in nitrogen.

TABLE V

Thermogravimetric Analysis of Copolymers of Styrene (M_2) with Brominated Monomers (M_1) and Homopolymers of the Latter; Measurements in Nitrogen, 10°/min.

Comonomer (M_1)	M_1/M_2	Br %	A, °C/weight loss %	B, °C (B′, °C)	C, °C/residue, % C′, °C/residue, %	Maximum Degradation Rate Temp., °C
2,4,6-Tribromophenyl methacrylate	45/55	45.6	319/2	363,5	407/4	363,5
	100/0	60.4	262/3.2	333.3	371.5/5.2	350
Pentabromophenyl methacrylate	43.5/56.5	60.7	286.5/1.5	319.5	343/27.3	325
				359	(381.5/11.5)	363
	100/0	72.0	236/4.2	311	339/7.9	324
Polystyrene	0/100	—	360/8.0	413.5	446.5	419

The weight loss of styrene/brominated phenyl methacrylate copolymers with increasing temperature is shown in Figure 9 and Figure 10. The data obtained from the thermograms are summerized in Table V. In contrast with the TGA-curve of poly(St-co-TBPMA) (Figure 9), the thermogravimetric curves for the decomposition of poly(St-co-PBPMA) (Figure 10) have two regions of

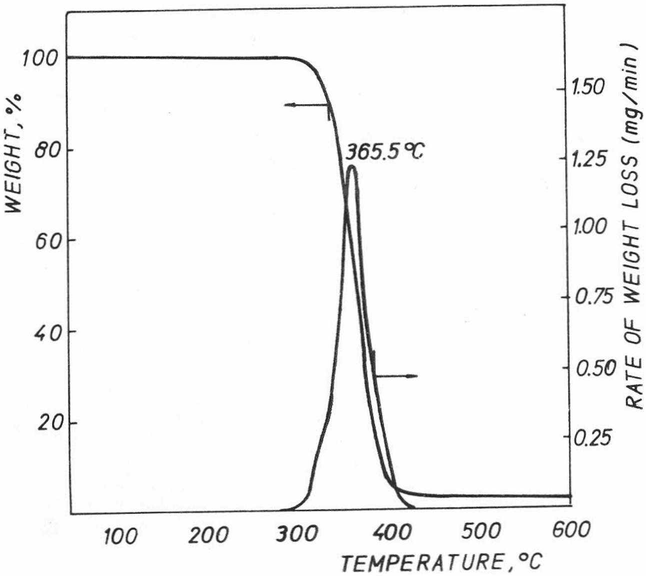


Figure 9. Thermogravimetric analysis of poly(styrene-co-2,4,6-tribromophenyl methacrylate) (molar ratio 55/45) in nitrogen.

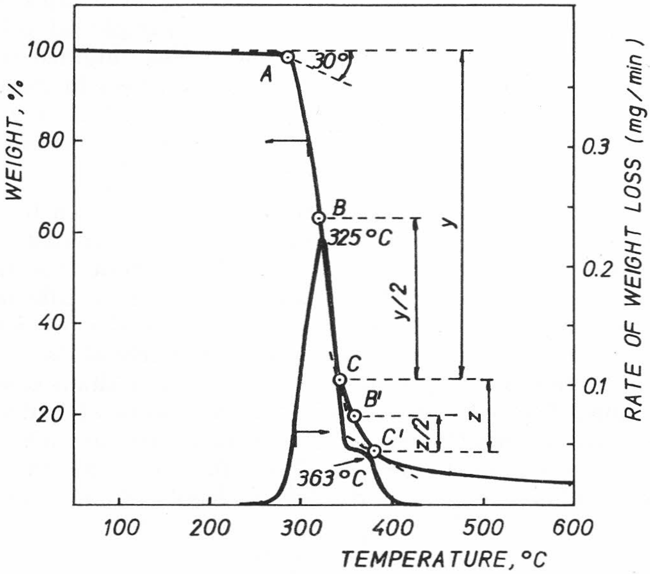


Figure 10. Thermogravimetric analysis of poly(styrene-co-pentabromophenyl methacrylate) (molar ratio 56.5/43.5) in nitrogen.

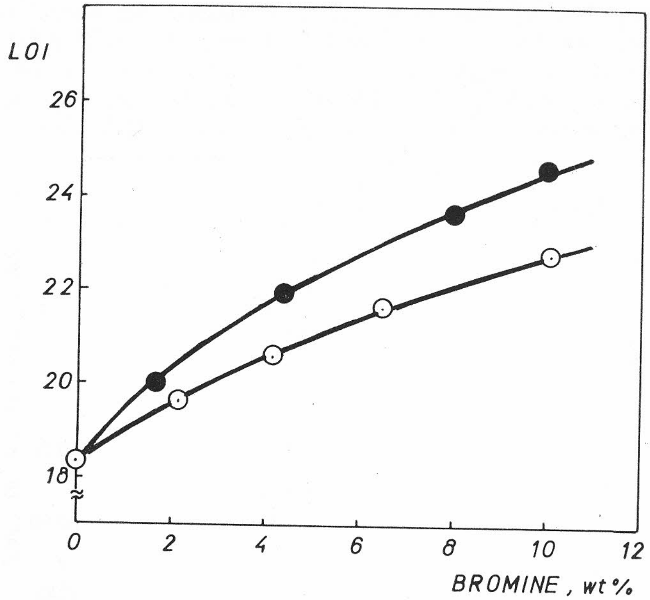


Figure 11. The influence of the content of the brominated monomer (Br wt%) on the limiting oxygen index of poly(styrene-co-2,4,6-tribromophenyl methacrylate) (○) and poly(styrene-co-pentabromophenyl methacrylate (●).

rapid decomposition, separated by the inflexion point C. Point B in Figure 10 marks 50% mass loss of the sample from the onset of heating to temperature C. The temperature reading at the end of the second region of rapid decomposition (at point C′) and for 50% of the mass loss of the sample (at point B′) in the region C to C′ are given in brackets in Table V. The obtained results suggest that both polystyrene and brominated monomer sequences in these copolymers, contribute to their thermal stability characteristics. Also as was found for homopolymers, the St copolymer of TBPMA showed better thermal stability than the corresponding PBPMA copolymer.

The results of the flammability properties, as determined by limiting oxygen index measurements of styrene copolymers with brominated phenyl methacrylate monomers, are shown in Figure 11. It is evident that thermally less stable St-PBPMA, release more HBr, and have a higher LIO in comparison with St-TBPMA copolymers. This finding is in agreement with generally accepted mechanism of flame retardation when the release into the gas phase of HBr and/or Br radical will suppress the free radical chain branching reactions in the flame. This mechanism is based on studies of hydrogen bromide inhibited premixed flames.[13,14] From these results we conclude that TBPMA and PBPMA are efficient flame retardants for St polymers, and compare favourably with other brominated but low molecular weight compounds.[5]

REFERENCES

1. K. Sarić, Z. Janović, and O. Vogl, *J. Macromol. Sci., Chem.* **A-19** (1983) 937.

2. Z. Janović, K. Sarić, and O. Vogl, *J. Macromol. Sci., Chem.* **A-19** (1983) 1137.
3. G. Sumrell, P. G. Campbell, G. E. Ham, and C. H. Schramm, *J. Amer. Chem. Soc.* **81** (1959) 4310.
4. T. Tajima, T. Okita, and T. Otsu, *Nippon Kagaku Kaishi* **4** (1974) 779.
5. R. V. Petrella, *Factors Affecting the Combustion of Polystyrene and Styrene,* from *Flame Retardant Polymeric Materials,* Vol. 2, Eds. M. Lewin, S. M. Atlas, and E. M. Pearce, Plenum Publishing Corp., New York, 1978.
6. H. Kabayashi, T. Kudo, Y. Yanagizava, and K. Hashimoto, *Jap. Pat.* **20**, (1974) 394; *C. A.* **82** (1975) 126010 q.
7. A. H. Weinstein, *U. S. Pat.* **4**, 205, 153; *C. A.* **93** (1980) 187545 s.
8. T. Kelen and F. Tüdos, *J. Macromol. Sci. Chem.* **A9** (1975) 1.
9. T. Kelen, F. Tüdos, and B. Turesanyi, *Polym. Bull.* **2** (1980) 71.
10. T. Otsu, T. Ito, Y. Fuji, and M. Imoto, *Bull. Chem. Soc. Japan,* **41** (1968) 204.
11. R. H. Yocum and E. B. Nyguist, *Functional Monomers, Their Preparation,* Polymerization *and Application,* vol. 1, Marcel Dekker, N. Y. 1973, p. 201.
12. R. C. P. Cubbon and I. D. B. Smith, *Polymer* **10** (1969) 487.
13. C. K. Westbrook, *Comb. Sci. and Tech.* **23** (1980) 191.
14. M. C. Drake and J. W. Hastie, *Combust. Flame* **40** (1981) 201.

SAŽETAK

Kopolimeri na osnovi bromiranih monomera. 7. Kopolimeri stirena i bromiranih fenilmetakrilata

K. Sarić, Z. Janović i O. Vogl

Opisana je reakcija kopolimerizacije stirena s 2,4,6-tribromfenilmetakrilatom, kao i pentabromfenilmetakrilatom, u vodenoj emulziji odnosno otopinama dimetilformamida i benzena, kao i svojstva dobivenih kopolimera, posebno termička stabilnost i svojstva gorivosti.

Određeni su odnosi reaktivnosti monomera, kao i konstante brzine polimerizacije. Redoslijed brzina reakcije homopolimerizacije je u nizu: stiren > pentabromfenilmetakrilat > 2,4,6-tribromfenilmetakrilat; naprotiv, suprotan je redoslijed za reakcije kopolimerizacije sa stirenom. Utvrđeno je da je poli(2,4,6-tribromfenilmetakrilat), kao i kopolimer sa stirenom termički najstabilniji, a kopolimeri stirena i pentabromfenilmetakrilata posjeduju veće vrijednosti graničnog indeksa kisika.