**Journal of Macromolecular Science, Part A**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

# Copolymers of Styrene with Some Brominated Acrylates

K. Saric[a]; Z. Janovic[ab]; O. Vogl[a]
[a] INA-Research Institute, Zagreb, Yugoslavia [b] Polytechnic Institute of New York, Brooklyn, New York

**To cite this Article** Saric, K. , Janovic, Z. and Vogl, O.(1983) 'Copolymers of Styrene with Some Brominated Acrylates', Journal of Macromolecular Science, Part A, 19: 6, 837 — 852

**To link to this Article: DOI:** 10.1080/00222338308060780

**URL:** http://dx.doi.org/10.1080/00222338308060780

J. MACROMOL. SCI.–CHEM., A19(6), pp. 837-852 (1983)

# Copolymers of Styrene with Some Brominated Acrylates

K. SARIĆ and Z. JANOVIĆ*
INA-Research Institute
Zagreb, Yugoslavia

O. VOGL

Polytechnic Institute of New York
Brooklyn, New York 11201

## ABSTRACT

Styrene was copolymerized with 2,3-dibromopropyl acrylate, 2,4,6-tribromophenyl acrylate, or pentabromophenyl acrylate in either aqueous emulsion, dimethylformamide, or benzene solutions with a free radical initiator, and the thermal and flammability properties of the resulting polymers are described. The reactivity ratios of the monomers and the initial reaction rates for homopolymerization and copolymerization reactions in benzene were established. The monomer reactivity ratios were found to depend slightly on the reaction medium. The reaction rates for both homopolymerizations and copolymerizations increased in the order styrene < 2,3-dibromopropyl acrylate < 2,4,6-tribromophenyl acrylate < pentabromoacrylate. The thermal stability of the polymers, determined from TGA and DTG measurements, showed that poly(2,4,6-tribromophenyl acrylate) and its styrene copolymers were the most stable and the copolymers of styrene with 2,3-dibromopropyl acrylate had the best

---

*To whom correspondence should be addressed.

0022-233X/83/1906-0837$3.50/0

flame-retardant properties as was demonstrated by limiting oxygen index measurements.

## INTRODUCTION

Free radical polymerizations and copolymerizations of substituted acrylic esters have been studied extensively [1]. The reactivity of alkyl acrylates and methacrylates depends strongly on the polarity of substituents in the molecule and less on their steric positions [2]. Halogenated acrylic esters show similar reactivities in homo- and copolymerization reactions [3].

The rate of polymerization is generally faster for the acrylates than for the corresponding methacrylates, but electronegative substituents in the $\alpha$-position to the ester group have a retarding influence. Recently, copolymers of halogenated acrylic esters with other vinyl monomers have attracted special attention because they can be used for the improvement of flammability characteristics [4]. Relatively little has been published about polymerization and copolymerization reactions of aromatic bromine-substituted acrylic esters and the properties of these compounds. Some work dealing with homopolymerization of brominated phenylacrylates and methacrylates [5] and the copolymerization of these monomers with styrene [6] or acrylonitrile [7] has been reported. It was shown that the reactivity ratios in these reactions depended upon the solvents used [6]. Most of the end use properties of these copolymers have been described in the patent literature [8, 9].

This paper details the copolymerization characteristics of styrene with 2,3-dibromopropyl acrylate, 2,4,6-tribromophenyl acrylate, or pentabromophenyl acrylate, and discusses some properties of the copolymers obtained, particularly their thermal and flammability behavior.

## EXPERIMENTAL

### Materials

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

Pentabromophenol and 2,4,6-tribromophenol (Aldrich Chemical Co.) were reprecipitated from benzene solutions into methanol, mp 92-93 and 225-226°C, respectively.

2,3-Dibromopropyl acrylate (Great Lakes Chemical Co.) was distilled under nitrogen at 0.3 mm and the middle fraction was collected [bp 93°C, $n_D^{20} = 1.5220$ (Ref. 10, $n_D^{20} = 1.5220$)].

### 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 instrument on films cast from methylene chloride solutions (20 wt%) onto glass plates. The films were dried for 24 h at ambient temperature and then for another 16 h at 0.1 mm and 25°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

Bromophenyl Acrylates (BPhA). 2,4,6-Tribromophenyl acrylate (TBPhA) and pentabromophenyl acrylate (PBPhA) were prepared by the condensation of acryloyl chloride with the appropriate brominated phenols according to Schotten-Baumann, following a modified literature procedure [5, 11].

2,4,6-Tribromophenyl Acrylate (TBPhA). Over a period of 1 h, solutions of acryloyl chloride (30 g, 0.33 mol) in 30 mL of dry methylene chloride and of triethanol amine (33.3 g, 0.3 mol) in 30 mL of methylene chloride were added dropwise and simultaneously to a stirred solution of 2,4,6-tribromophenol (115 g, 0.3 mol) and hydroquinone (0.1 g) in 250 mL of methylene chloride, cooled in an ice-water bath. Stirring was continued for 6 h at room temperature, then the solid was separated by filtration. The solution was washed with water and a sodium dicarbonate solution, then dried with sodium sulfate, and finally the solvent was evaporated. The residual crude product was recrystallized from petroleum ether giving 84 g (72% yield) of white crystals, mp 75.5-76°C.

Analysis: Calculated for $C_9H_5O_2Br_3$: C, 28.09; H, 1.31; Br, 62.29%. Found: C, 28.23; H, 1.15; Br, 62.09%.

The $^1$H-NMR spectrum showed a singlet at δ 7.9 ppm (aromatic nucleus) and multiple signals at δ 6.1-6.9 ppm (vinyl group). The $^{13}$C-NMR spectrum for the side chain showed the following signals: $=CH_2$ (δ 134.25 ppm), =CH– (δ 126.16 ppm), –COO– (δ 161.36 ppm), and for the aromatic ring: C-1 (δ 145.36 ppm), ortho C-2,6 (δ 118,32 ppm), meta C-3, 5 (δ 134.54 ppm), and para C-4 (δ 119.68 ppm).

Pentabromophenyl Acrylate (PBPhA). For the synthesis of PBPhA the same synthetic method as described for TBPhA was used but with toluene as the solvent, and the crude product was recrystallized from ethyl acetate giving white, flat crystals in 76% yield, mp 153°C.

Analysis: Calculated for $C_9H_3O_2Br_5$: C, 19.92; H, 0.56; Br, 73.63%. Found: C, 20.12; H, 0.55; Br, 73.75%.

The $^1$H-NMR spectrum showed multiple signals at δ 6.1-6.9 ppm (vinyl group).

The $^{13}$C-NMR spectrum for the side chain showed signals for: $=CH_2$ (δ 134.89 ppm), =CH– (δ 126.06 ppm), –COO– (δ 161.34 ppm), and for the aromatic ring: C-1 (δ 146.63 ppm), ortho C-2,6 (δ 121.00 ppm), meta C-3,5, (δ 128.35 ppm), and para C-4 (δ 126.89 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 sulfonate and 5 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 min before potassium persulfate (0.01 g) was added. The degree of conversion was determined on samples which were withdrawn at regular intervals and precipitated into methanol.

Homopolymerizations of brominated monomers in benzene or dimethylformamide solutions were carried out in 20 mL glass polymerization tubes. Typically 10 mL of the monomer solution (0.345 mol/L) mixed with AIBN (20 mg) was degassed by three freeze thaw cycles and then sealed at 0.1 mm. The tube was placed in a constant temperature bath at 70°C for 1 to 5 h, 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.

## RESULTS AND DISCUSSION

### Copolymerization Reactions

The free radical copolymerizations of styrene (St) with 2,3-dibromopropyl acrylate (DBPA) or 2,4,6-tribromophenyl acrylate

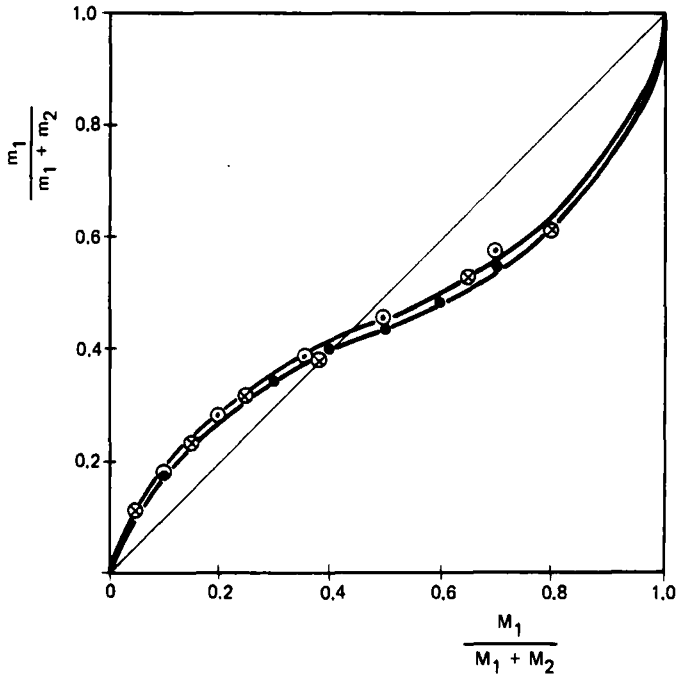

FIG. 1. Copolymerization of 2,3-dibromopropyl acrylate ($M_1$) with styrene at 60°C in emulsion ( ● ), benzene ( ⊗ ), and dimethylformamide ( ⊙ ).

(TBPhA) were performed in aqueous emulsion as well as in benzene or dimethylformamide solutions. Because of the low solubility of pentabromophenyl acrylate (PBPhA) in St, this reaction was run only in solution.

The composition of the copolymers which were obtained at low conversions was determined by bromine analysis. The influence of the molar fraction of brominated monomer ($M_1$) in the initial monomer mixture on the composition of the resulting copolymer is shown in Figs. 1, 2, and 3. In all cases, the plot of monomer-copolymer composition shows a marked tendency toward alternating copolymerization with the azeotropic composition near 50 mol% for TBPhA and about 40 mol% for DBPA.

Using the Kelen-Tüdős mean square relationship [12] and confidence intervals [13], we calculated the reactivity ratios (Table 1) from the experimental data. For the copolymerization of styrene with TBPhA or PBPhA in benzene solution, good agreement was found with reported data [6]. The monomer reactivity ratios depended slightly on the reaction medium, i.e., water versus benzene or DMF.

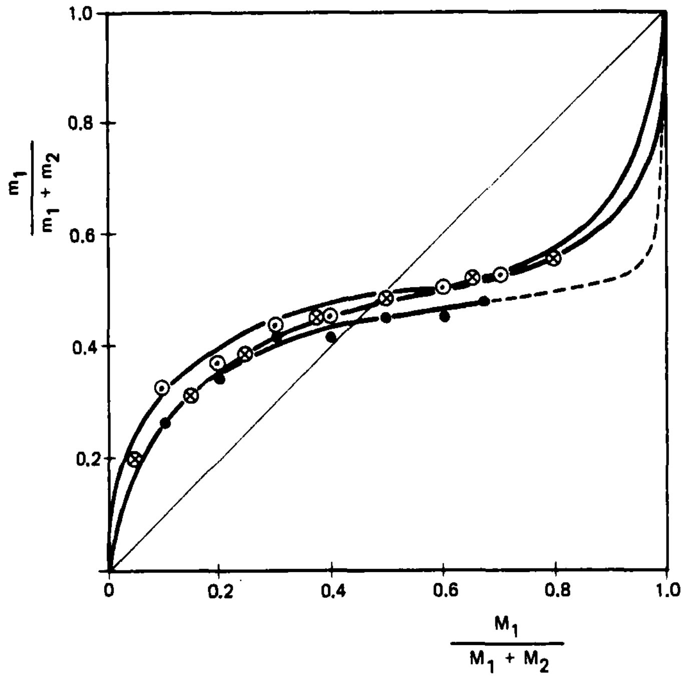

FIG. 2. Copolymerization of 2,4,6-tribromophenyl acrylate ($M_1$) with styrene at 60°C in emulsion ( ● ), benzene ( ⊗ ), and dimethylformamide ( ⊙ ).

The reactivity ratios found were related to the polarization (e) and to the resonance effect (Q) in the Alfrey-Price scheme. As seen, both parameters increase as the amount of bromine in the monomer increases.

The tendency to form alternating styrene/brominated acrylic ester copolymers was also confirmed by the polymerization rates as determined in benzene solution. The amount of copolymer formed from St with the three brominated acrylic esters at the same feed composition (styrene 95 mol%) and under identical reaction conditions was determined. The results (Fig. 4) showed that the initial rate of reaction increased in the order St < DBPA < TBPhA < PBPhA. Homopolymerization reactions of the monomers followed the same trend (Fig. 5). The polymerization rates for the brominated monomers were about 10 times higher than those for styrene. Also, an increase of the polymerization reaction rate was observed with increasing polarity of the monomer. It is important to note that poly(PBPhA) is slightly soluble in benzene, therefore the conversion/time polymerization plot for this monomer is somewhat irregular.

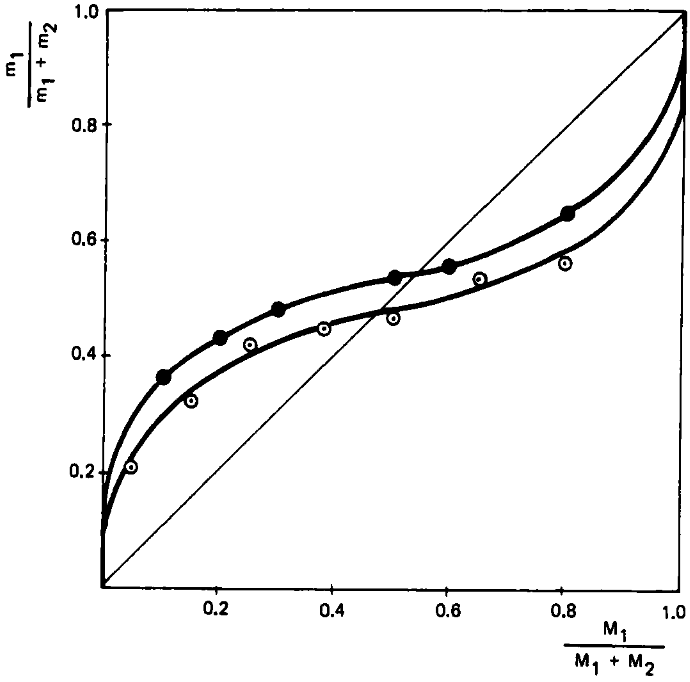

FIG. 3. Copolymerization of pentabromophenyl acrylate ($M_1$) with styrene at 60°C in benzene ( ● ) and dimethylformamide ( ◎ ).

Solution viscosity measurements of poly(St-co-BPhA) and poly(St-co-DBPA), obtained from benzene solution polymerizations, showed only a slight decrease in viscosity if the content of brominated monomer in the copolymer was low (Fig. 6). However, if the content of bromine-monomer in the feed was high, then the solution viscosity was reduced more as demonstrated by the copolymers of DBPA with St (Fig. 7). This is probably due to chain transfer reactions in the growing chain, either from a monomer or from the polymer chain, since this is a general tendency for bromine-containing monomers [14].

## Thermal Stability and Flammability

The thermal stabilities of the homopolymers of the BPhA's, DBPA, and of their copolymers with St were determined by TGA and DTG measurements, and flammability tests were carried out by limiting oxygen index measurements.

TABLE 1. Copolymerization Parameters for Brominated Acrylic Monomers ($M_1$) with Styrene ($M_2$)

| Monomer ($M_1$) | Solvent | $r_1$[a] | $r_2$[a] | Azeotropic composition | $Q_1$ | $e_1$ |
|---|---|---|---|---|---|---|
| 2,3-Dibromopropyl acrylate | DMF | 0.22 ± 0.04 | 0.14 ± 0.02 | 43.1/56.9 | 0.71 | 0.75 |
| | Benzene | 0.16 ± 0.02 | 0.42 ± 0.01 | 40.8/59.1 | 0.64 | 0.84 |
| | Aq emulsion | 0.14 ± 0.03 | 0.43 ± 0.02 | 39.9/60.1 | 0.61 | 0.88 |
| 2,4,6-Tribromophenyl acrylate | DMF | 0.08 ± 0.03 | 0.14 ± 0.02 | 48.3/52.0 | 1.31 | 1.32 |
| | Benzene[b] | 0.10 ± 0.02 | 0.20 ± 0.01 | 47.1/52.9 | 1.03 | 1.18 |
| | Aq emulsion | 0.01 ± 0.03 | 0.21 ± 0.02 | 44.4/55.6 | 0.65 | 1.68 |
| Pentabromophenyl acrylate | DMF | 0.26 ± 0.01 | 0.09 ± 0 | 55.1/44.8 | 0.81 | 1.14 |
| | Benzene[c] | 0.10 ± 0.03 | 0.16 ± 0.01 | 48.3/51.7 | 1.23 | 1.23 |

[a] Calculated by the Kelen-Tüdős method [12].

[b] Ref. 6: $r_1 = 0.10$, $r_2 = 0.20$.

[c] Ref. 6: $r_1 = 0.10$, $r_2 = 0.20$.

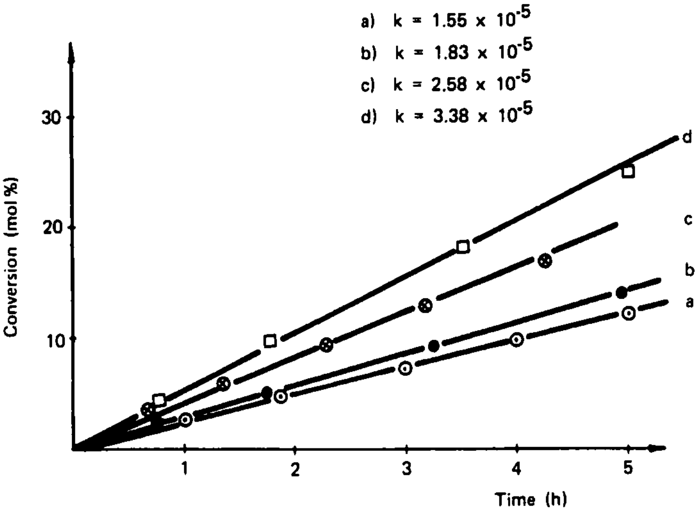

FIG. 4. The initial rate of copolymerization of styrene (95 mol%) (a) with 2,3-dibromopropyl acrylate (b), 2,4,6-tribromophenyl acrylate (c), and pentabromophenyl acrylate (d) at 60°C in benzene with AIBN.

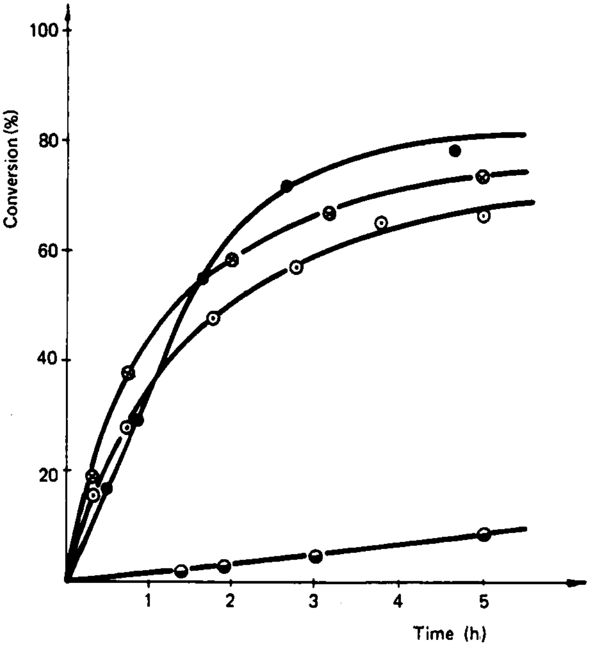

FIG. 5. The rate of homopolymerization of 2,3-dibromopropyl acrylate ( ○ ), 2,4,6-tribromophenyl acrylate ( ⊗ ), pentabromophenyl acrylate ( ● ), and styrene ( ◒ ) at 70°C in benzene with AIBN.

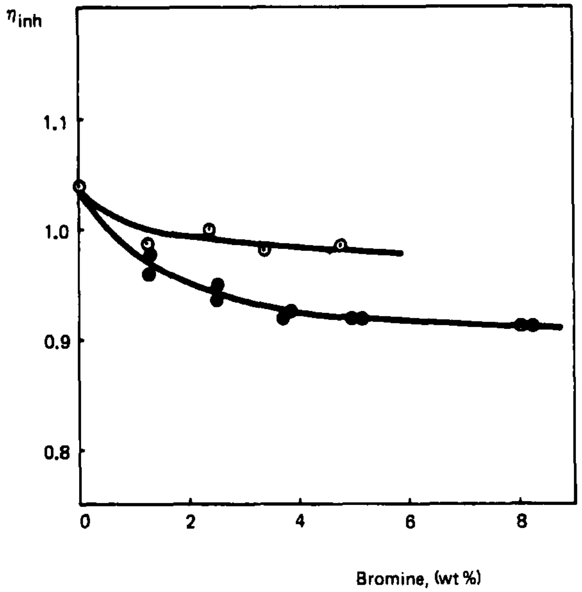

FIG. 6. The influence of the copolymer composition of styrene with 2,3-dibromopropyl acrylate ( ⊚ ), 2,4,6-tribromophenyl acrylate ( ⊗ ), and pentabromophenyl acrylate ( ● ), obtained in benzene, on the inherent viscosities in toluene at 30° C.

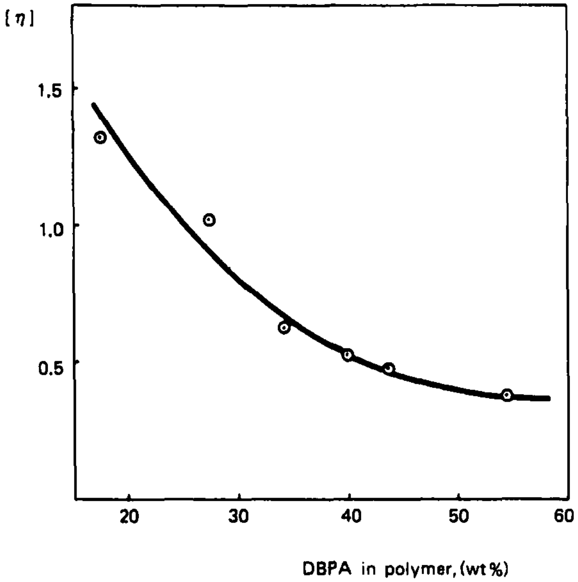

FIG. 7. The influence of the composition of poly(styrene-co-dibromopropyl acrylate), obtained in benzene, on the intrinsic viscosities in toluene at 30° C.

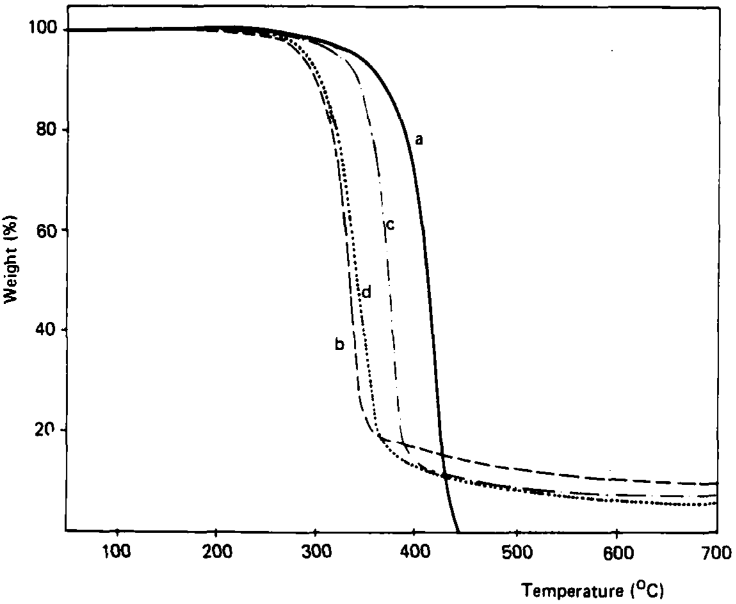

FIG. 8. Thermogravimetric analysis of polystyrene (a), poly(2,3-dibromopropyl acrylate) (b), poly(2,4,6-tribromophenyl acrylate) (c), and poly(pentabromophenyl acrylate) (d) in nitrogen.

Spontaneous decomposition of the homopolymers (Fig. 8) starts in the temperature range 285 to 330°C, i.e., at temperatures which are 20-60°C below the decomposition temperature of polystyrene. Some residue at the end of the fast decomposition region indicated that depolymerization to volatile monomers had not been complete.

The higher stability of poly-TBPhA compared with poly-DBPA is probably due to the stronger C–Br bond in the aromatic compound. However, higher bromine content as in poly-PBPhA promotes faster decomposition. Figure 8 shows the weight loss of styrene/brominated acrylate copolymers with increasing temperature [15], and the data obtained from the thermograms are summarized in Table 2. In contrast to the TGA-curve of poly(St-co-TBPhA) (Fig. 10), the thermogravimetric curves for the decomposition of poly(St-co-DBPA) (Fig. 9) and poly(St-co-PBPhA) (Fig. 11) have two regions of rapid decomposition, separated by the inflection Point C.

Point A in Fig. 9 marks the beginning of the fast decomposition region and Point B marks 50% weight loss of the sample of poly(St-co-DBPA) from the onset of heating to Temperature C. The temperature readings at the end of the second region of rapid decomposition (at Point C') and for 50% of the weight loss of the sample (at Point B') in the Region C to C' are given in parentheses in Table 2. Thermogravimetric curves tracing the decomposition of these copolymers

TABLE 2. Thermogravimetric Analysis of Copolymers of Styrene ($M_2$) with Brominated Monomers ($M_1$) and Homopolymers of the Latter; Measurements in Nitrogen, 10°C/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 (°C) |
|---|---|---|---|---|---|---|
| 2,3-Dibromopropyl acrylate | 31.0/69.0 | 32.0 | 284/4 | 318 | 340/56.2 | 324 |
| | | | | (384) | (430/14) | 384 |
| | 100/0 | 58.8 | 288.5/3.6 | 331 | 354.5/19.2 | 334 |
| 2,4,6-Tribromo-phenyl acrylate | 38.2/61.8 | 43.2 | 319/4.8 | 359 | 408/6.5 | 355 |
| | 100/0.0 | 62.1 | 330/6.7 | 372 | 397/14.0 | 361 |
| Pentabromophenyl acrylate | 42.4/57.6 | 58.5 | 290/3.0 | 310 | 340/31.1 | 300 |
| | | | | (365.5) | (395/12.5) | 371 |
| | 100.0/0.0 | 73.75 | 284/2.6 | 337 | 370/16.8 | 339 |
| Polystyrene | 0/100.0 | - | 360/8.0 | 413.5 | 446.5 | 419 |

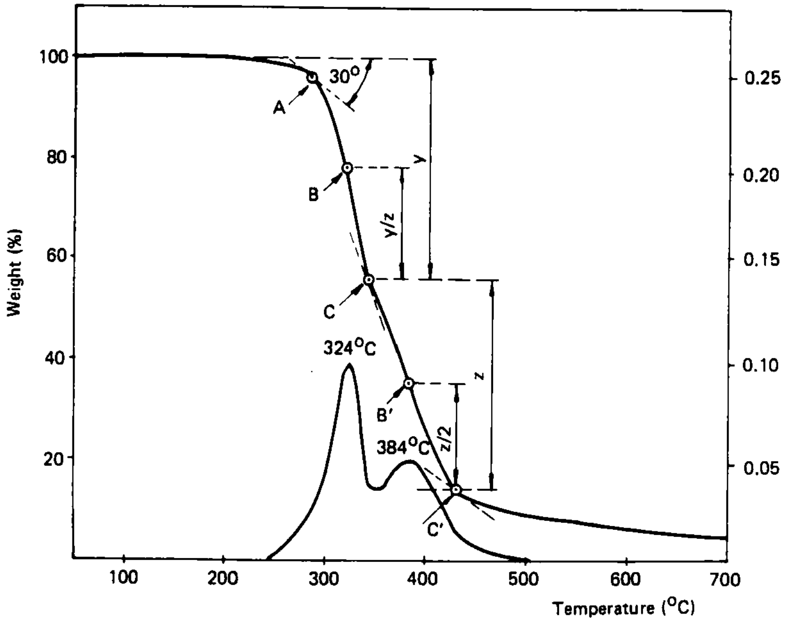

FIG. 9. Thermogravimetric analysis of poly(styrene-co-2,3-dibromopropyl acrylate) (molar ratio 69.0/31.0) in nitrogen.

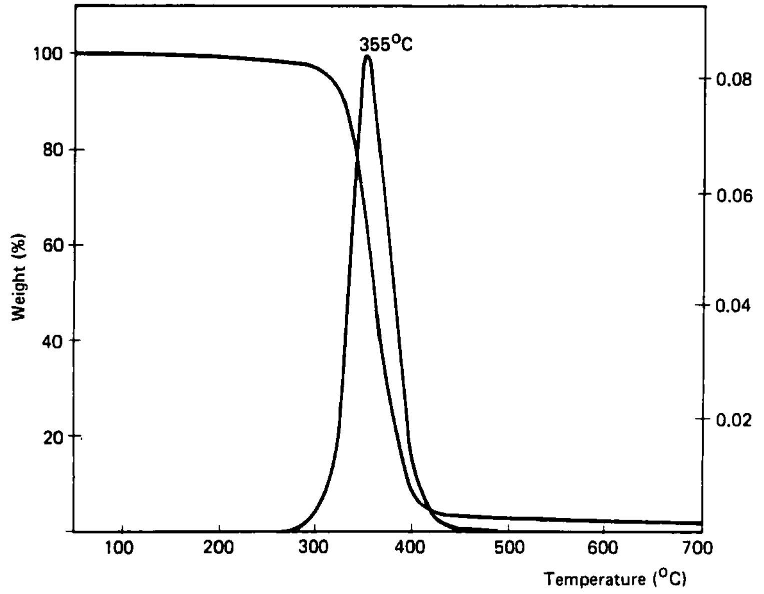

FIG. 10. Thermogravimetric analysis of poly(styrene-co-2,4,6-tribromophenyl acrylate) (molar ratio 61.8/38.2) in nitrogen.

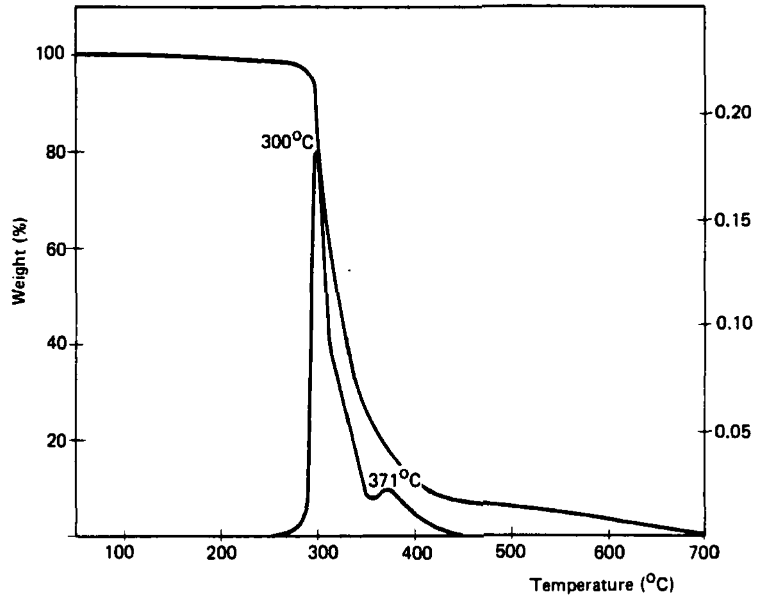

FIG. 11. Thermogravimetric analysis of poly(styrene-co-pentabromophenyl acrylate) (molar ratio 57.6/42.4) in nitrogen.

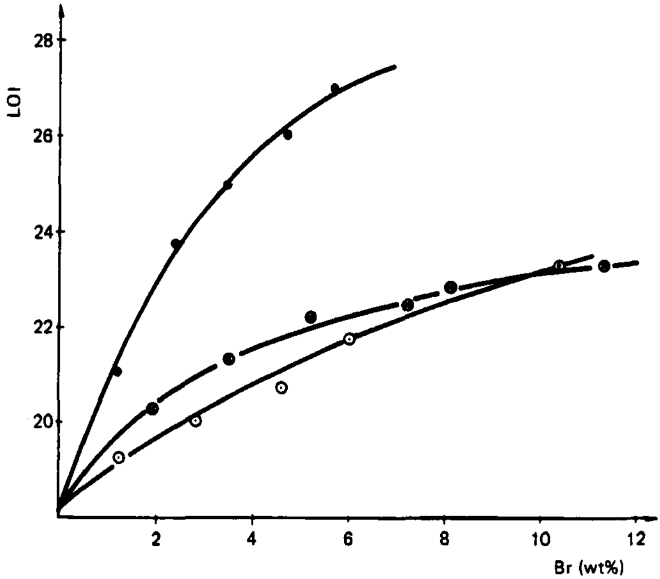

FIG. 12. The influence of the content of the brominated monomer (Br wt%) on the limiting oxygen index of poly(styrene-co-2,3,-dibromopropyl acrylate) ( ● ), poly(styrene-co-2,4,6-tribromophenyl acrylate) ( ⊗ ) and poly(styrene-co-pentabromophenyl acrylate ( ⊙ ).

and the data from Table 2 suggest that both the polystyrene and the brominated monomer sequences contribute to their thermal stability characteristics.

Results of the flammability properties, as determined by limiting oxygen index measurements of styrene copolymers with brominated acrylic monomers, are shown in Fig. 12. There are marked differences in efficiency between poly(St-co-DBPA), a bromo-aliphatic copolymer, and the bromo-aromatic copolymers. This is in agreement with previous reports that the former are thermally less stable than the latter because of differences in the strength of the carbon-bromine bond, and this results in a faster release of hydrogen bromide from the bromo-aliphatic copolymer. Qualitatively similar results have been reported for other aliphatic versus aromatic bromine systems [16]. However, opposite findings have been reported for unsaturated polyester resins [17].

## REFERENCES

[1] L. S. Luskin, in Vinyl and Diene Monomer, Part 1 (E. C. Leonard, ed.), Wiley-Interscience, New York, 1970, Chap. 3.

[2] T. Otsu, T. Ito, and M. Imoto, J. Polymer Sci., A-4, 733 (1966).

[3] C. F. Raley and R. J. Dolinski, in Functional Monomers, Vol. 1 (R. H. Yocum and E. B. Nyquist, eds.), Dekker, New York, 1973, Chap. 2.

[4] V. Stannett, W. K. Walsh, E. Bittencourt, R. Liepins, and J. R. Surles, Appl. Polym. Symp., 31, 201 (1977).

[5] G. Sumrell, P. G. Campbell, G. E. Ham, and C. H. Schramm, J. Am. Chem. Soc., 81, 4310 (1959).

[6] T. Tajima, T. Okita, and T. Otsu, Nippon Kagaku Kaishi, 4, 779 (1974).

[7] A. Miller and I. Szafko, J. Polym. Sci., Polym. Chem. Ed., 15, 1595 (1977).

[8] L. H. Lee, U.S. Patent 3,219,640 (1965).

[9] A. Morimoto, A. Ikeda, Y. Kitagawa, and T. Murata, Japanese Patent 32,173 (1977); Chem. Abstr., 88, 106188z (1978).

[10] C. E. Rehberg, M. B. Dixon, and W. A. Fancette, J. Am. Chem. Soc., 72, 5199 (1950).

[11] H. G. Batz, G. Franzmann, and H. Ringsdorf, Makromol. Chem., 172, 24 (1973).

[12] T. Kelen and T. Tüdős, J. Macromol. Sci.-Chem., A9, 1 (1975).

[13] T. Kelen, F. Tüdős, and B. Turcsányi, Polym. Bull., 2, 71 (1980).

[14] R. C. P. Cubbon and I. D. B. Smith, Polymer, 10, 487 (1969).

[15] F. Hrabak, I. Masarik, K. Bouchal, and M. Slavicek, Eur. Polym. J., 13, 509 (1977).

[16] J. A. Schneider, R. G. Dews, and J. D. Herring, Ind. Eng. Chem., Prod. Res. Dev., 9, 559 (1970).
[17] M. Ravey, Th. Fischler, and M. Kramer, Fire Mater., 2, 34 (1978).

Accepted by editor August 26, 1982
Received for publication September 14, 1982