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*Original Scientific Paper*

# Copolymers of Bromine-Containing Monomers 9. Termopolymerization of Styrene, Acrylonitrile and Pentabromophenyl Methacrylate

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The free radical terpolymerization of styrene, acrylonitrile and pentabromophenyl methacrylate in dimethyl formamide solution was investigated. Polymerizations at low conversion yielded terpolymers that showed good agreement between experimental and theoretical composition data, calculated from the Alfrey-Goldfinger equation. Relationship between the monomer feed and terpolymer compositions are presented on Slocombe's traingular coordinate graphs. By using a computer program the lines of unique composition and binary azeotropic composition were identified. The azeotropic ternary point was determined at a molar ratio for styrene/acrylonitrile/pentabromophenyl methacrylate of 0.28/00.33/0.39, respectively. The experimental results of the terpolymerization agreed well with the theoretical curves over a wide range of monomer composition up to high conversion. The influence of pentabrome phenyl methacrylate on the thermal and flammability characteristic of the terpolymers is described.

## INTRODUCTION

In earlier communications, we reported the terpolymerization of acrylonitrile and styrene with some phenylbrominated acrylic monomers[1,2] and 2,4,6-tribromophenyl methacrylate[3]. It was found that free radical polymerization of the ternary systems followed classical copolymerization theory. In addition, the incorporation of the brominated monomer reduces somewat the thermal stability of the obtained copolymers but improves their flammability characteristic. Pentabromophenyl methacrylate has also been mentioned in the patent literature as an reactive flame retardant for the styrene[4] and butadiene[5] based polymers.

As a continuation of our investigation on copolymers containing vinyl brominated monomers, the present work deals with the kinetic studies of the terpolymerization reaction of styrene, acrylonitrile and pentabromophenyl methacrylate.

Measurements of some properties of the polymers obtained, particularly their thermal and flammability behavior were also undertaken.

## EXPERIMENTAL

The materials, measurements and polymerization procedure used were the same as described in the preceding publications[1,2]. Pentabromophenyl methacrylate was synthetized from methacryloyl chloride and pentabromophenol under the conditions of Schotten-Bauman reaction[6]. Polymerization reactions were carried out in dimethylformamide solutions or in bulk up to high conversion, at 60 °C, using azobisisobutyronitrile as an initiator.

## RESULTS AND DISCUSSION

### *Terpolymerization Reaction*

Terpolymerization reactions of styrene (St), acrylonitrile (AN) and pentabromophenyl methacrylate (PBPMA) monomer mixtures were carried out in dimethylformamide solutions using azobisisobutyronitrile (AIBN) as an initiator. The reactivity ratios for the monomer pairs, presented in Table I.,

TABLE I

*Monomer Reactivity Ratios*[a] *for the Terpolymerization of Styrene* ($M_1$), *Acrylonitrile* ($M_2$) *and Pentabromophenyl Methacrylate* ($M_3$) *in Dimethylformamide Solutions at 60 °C*

| Medium | $r_{12}$ | $r_{21}$ | $r_{13}$ | $r_{31}$ | $r_{23}$ | $r_{32}$ |
|---|---|---|---|---|---|---|
| DMF | $0.30 \pm 0.40$ | $0.16 \pm 0.02$ | $0.09 \pm 0.02$ | $0.26 \pm 0.02$ | $0.28 \pm 0.03$ | $0.12 \pm 0.25$ |

[a] Determined by the method of Kelen and Tudos[6,10].

had been determined previously[6,10]. The relationship between the molar composition of the monomer mixtures and the terpolymers obtained at low conversion are summarized in Table II. The terpolymer composition was determined by elemental analysis for nitrogen and bromine and the calculated values were obtained from Alfrey-Goldfinger terpolymerization equation[7]. Since good agreement between experimental and theoretical data was observed, it is concluded that the free radical polymerization of the ternary system St/AN/PBPMA followed the classical copolymerization theory. This relationship is presented also in the form of triangular plot (Figure 1). according to Slocomb's method[8]. Most of the ternary systems have only two azeotropic copolymers, however, in the investigated monomers three azeotrops, St/AN (0.546/0.454), St/PBPMA (0.475/0.525) and AN/PBPMA (0.45/0.55) mole ratios, respectively, were found. Connecting the point of correspondence, the head of the arrows indicate the initial terpolymer composition and the tail the composition of the monomer feed. The broken lines indicate azeotropic lines drawn between the azeotropic copolymer composition. The arrows tend to be oriented into the external triangular area nearby the righ-hand azeotropic line (St/PBPMA) indicating that polymerization paths into these area will give more homogenous terpolymers.

TABLE II

*Terpolymerization of Styrene (St), Acrylonitrile (AN) and Pentabromophenyl Methacrylate (PBPMA) in DMF at 60 °C*

| Run. No. | Monomer Freed (mol ratio) St | AN | PBPMA | Conversion % | N % | Br % | Terpolymer (mol fract. exp.) St | AN | PBPMA | Terpolymer (mol fract. calc'd)[b] St | AN | PBPMA |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.200 | 0.650 | 0.150 | 6.7 | 3.44 | 50.97 | 29.4 | 46.5 | 24.1 | 28.5 | 48.2 | 23.3 |
| 2 | 0.280 | 0.330 | 0.390 | 9.0 | 1.63 | 60.08 | 27.3 | 31.8 | 40.9 | 28.1 | 33.1 | 38.8 |
| 3 | 0.410 | 0.500 | 0.090 | 4.2 | 3.43 | 43.82 | 41.5 | 40.4 | 18.1 | 41.1 | 40.7 | 18.2 |
| 4 | 0.520 | 0.400 | 0.080 | 8.3 | 3.19 | 43.18 | 44.5 | 37.7 | 17.8 | 45.7 | 36.5 | 17.8 |
| 5 | 0.700 | 0.250 | 0.050 | 7.1 | 2.70 | 40.05 | 52.8 | 31.1 | 16.1 | 54.6 | 29.4 | 16.0 |
| 6 | 0.500 | 0.260 | 0.240 | 4.9 | 1.38 | 55.11 | 42.6 | 24.0 | 33.4 | 40.1 | 26.2 | 33.7 |
| 7 | 0.596 | 0.194 | 0.210 | 9.1 | 1.11 | 55.74 | 44.7 | 20.1 | 35.2 | 44.5 | 21.4 | 34.1 |
| 8 | 0.200 | 0.500 | 0.300 | 4.8 | 2.28 | 58.35 | 24.3 | 40.0 | 35.7 | 24.3 | 41.8 | 33.9 |
| 9 | 0.320 | 0.600 | 0.080 | 7.4 | 4.51 | 40.01 | 38.4 | 47.0 | 14.6 | 38.3 | 45.9 | 15.8 |
| 10 | 0.490 | 0.410 | 0.100 | 7.0 | 3.01 | 45.66 | 42.4 | 37.6 | 20.0 | 43.4 | 36.2 | 20.4 |

[a] Polymerization conditions: DMF solutions (100 mL) of monomers (0.15 moL) and AIBN (0.2 g) at 60 °C.

[b] Calculated from the Alfrey-Goldfinger equation.

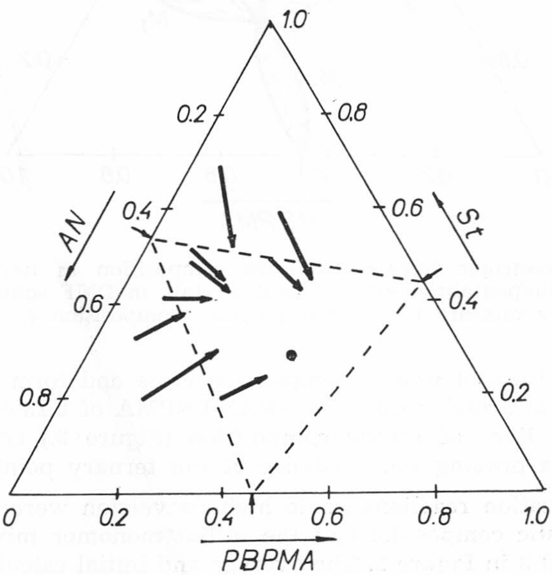


Figure 1. Monomer/terpolymer triangular composition plot for the system styrene/ /acrylonitrile/pentabromophenyl methacrylate in DMF solution at 60 °C.

In order to study the behavior of each monomer during terpolymerization reaction, a computer program to facilitate the ternary monomer — polymer composition calculations based on the Alfrey-Goldfinger equation was used For determination of the azeotropic lines, a graphical method developed by Rios and Guillot[9] was applied. In the case of a unique azeotropy, the amount of one of the three monomers was the same in monomer feed ($M_i$) and in the terpolymer ($m_i$) whereas in the binary azeotropy the ratio of the two monomers was the same in the monomer feed and in the terpolymer ($M_i/M_j = m_i/m_j$). The true or ternary azeotropic composition is defined as the set of monomer fractions $M_i = m_i$ for i = 1, 2, 3; the same in feed and terpolymer.

The azeotropic lines for unique composition for each monomer ($M_1$ = St, $M_2$ = AN, $M_3$ = PBPMA) and the difference between terpolymer composition (dotted lines) and the composition of the monomer mixture (full lines) in the course of the terpolymerization reaction are presented in Figure 2. These

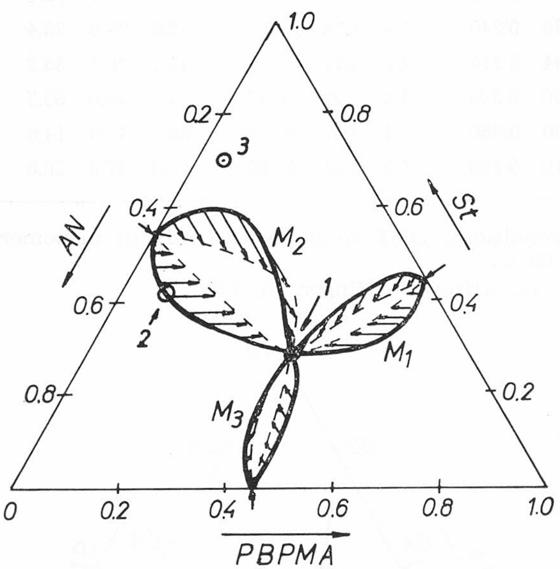


Figure 2. The azeotropic lines of uniform composition in terpolymerizations of styrene/acrylonitrile/pentabromophenyl methacrylate in DMF solution at 60 °C: monomer mixture (———); terpolymer composition (— — —).

three azeotropic lines of unique composition cross and form the true ternary azeotropic point at a molar ratio for St/AN/PBPMA of 0.28/0.33/0.39, respectively. Azeotropic lines of binary composition (Figure 3.) cross at the same composition, thus proving the existence of the ternary point.

Terpolymerization reactions up to high conversion were carried out with three characteristic compositions of the initial monomer mixture, designated as points 1, 2 and 3 in Figure 2. The average and initial calculated composition of the terpolymers, as well as the experimental conversion versus time curves, were established. Within the limits of experimental error, the agreement between the calculated and experimental values was satisfactory. In terpolymerization with monomer mixture of ternary azeotropic composition, the changes in average (Figure 4.) and calculated initial terpolymer composition

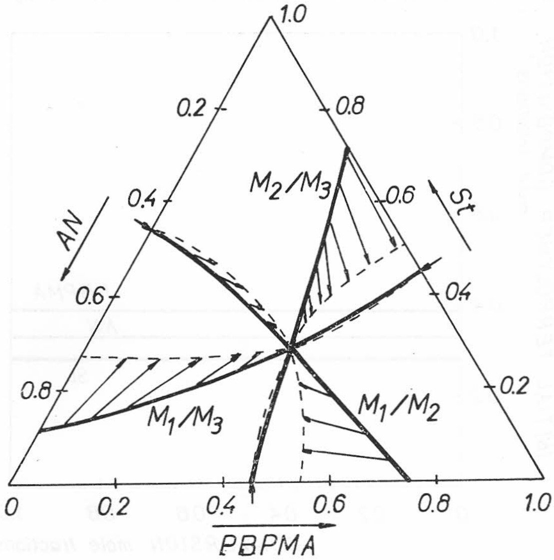


Figure 3. The binary azeotropic lines of uniform composition in terpolymerizations of styrene/acrylonitrile/pentabromophenyl methacrylate in DMF solution at 60 °C: monomer mixture (———); terpolymer composition (— — —).

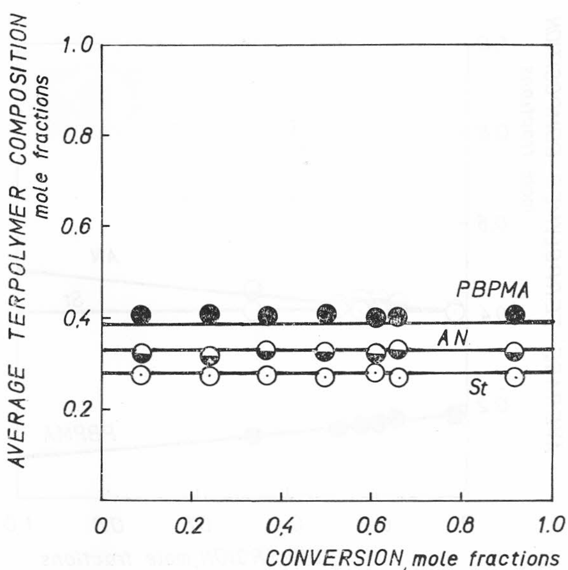


Figure 4. Average terpolymer composition as a function of conversion in terpolymerization of the monomer mixture of styrene/acrylonitrile/pentabromophenyl methacrylate (0.28/0.33/0.39 mol ratio) in DMF solution at 60 °C: experimental points (○), calculated (———).

(Figure 5.), as a function of conversion, were negligible. When the initial monomer composition of St/AN/PBPMA was 0.41/0.50/0.09 which is on the unique azeotropy line to St, then the average calculated and experimental terpolymer composition (Figure 6.) showed constant composition value in

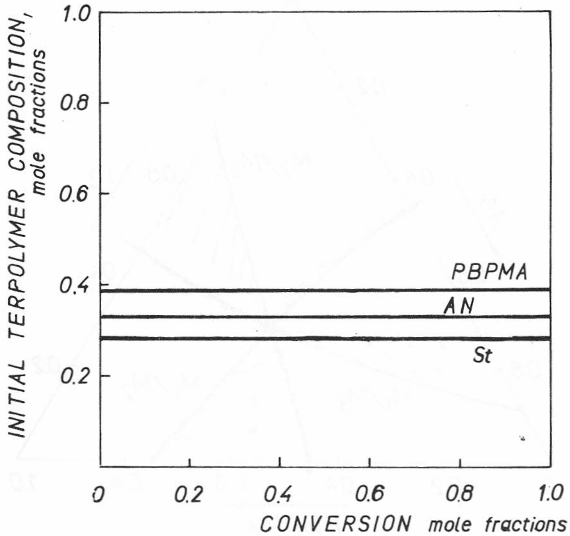


Figure 5. Calculated initial terpolymer composition as a function of conversion in the terpolymerization of styrene/acrylonitrile/pentabromophenyl methacrylate (0.28/0.33/0.39 mol ratio) in DMF solution at 60 °C.

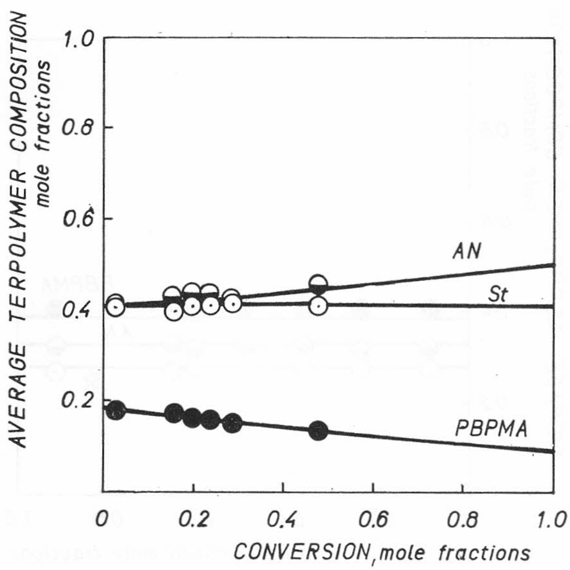


Figure 6. Average terpolymer composition as a function of conversion in terpolymerization of the monomer mixture of styrene/acrylonitrile/pentabromophenyl methacrylate (0.41/0.50/0.09 mol ratio) in DMF solution at 60 °C: experimental points (○); calculated (———).

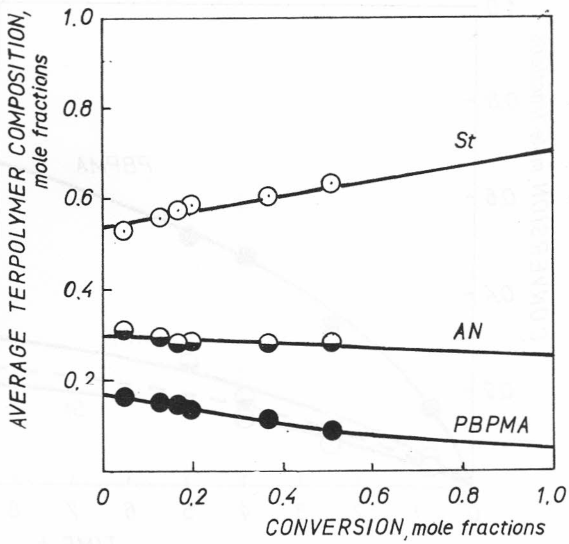


Figure 7. Average terpolymer composition as a function of conversion in terpolymerization of the monomer mixture of styrene/acrylonitrile/pentabromophenyl methacrylate (0.70/0.25/0.05 mol ratio) in DMF solution at 60 °C: experimental points (○); calculated (———).

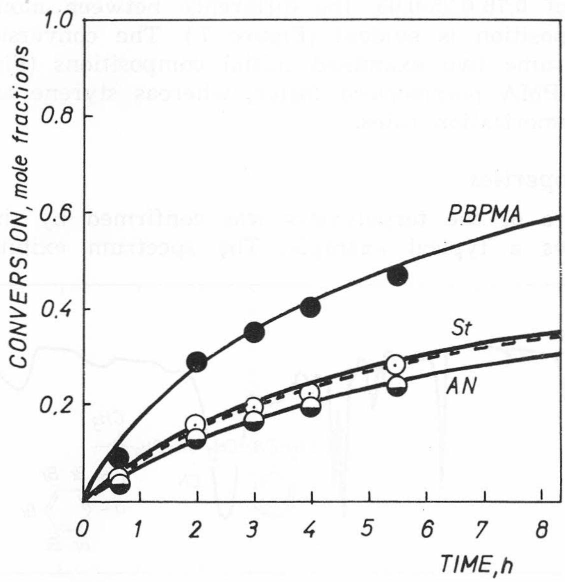


Figure 8: The conversion of monomers in the terpolymerization of styrene (○), acrylonitrile (○), and pentabromophenyl methacrylate (●), 0.70/0.25/0.05 mol ratio, and the overall conversion (– – –) of monomers to terpolymer in DMF solution at 60 °C.

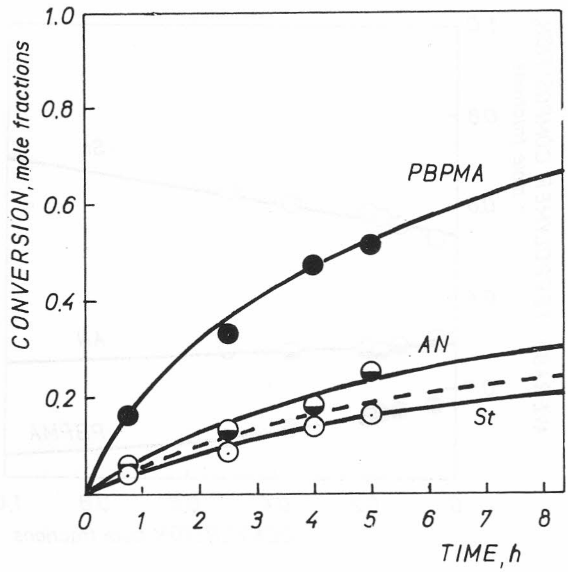


Figure 9: The conversion of monomers in the terpolymerization of styrene (○), acrylonitrile (○), and pentabromophenyl methacrylate (●), 0.41/0.50/0.09 mol ratio, and the overall conversion (———) of monomers to terpolymer in DMF solution at 60 °C.

respect to styrene. In the case when initial monomer composition was St/AN/PBPMA of 0.70/0.25/0.05, the difference between monomer feed and terpolymer composition is evident (Figure 7.). The conversion versus time curves for the same two examined initial compositions (Figure 8. and 9.) showed that PBPMA polymerized faster, whereas styrene and acrylonitrile had similar polymerization rates.

## *Terpolymer Properties*

The structure of the terpolymers was confirmed by their IR spectra. Figure 10. shows a typical example. The spectrum exibits characteristic

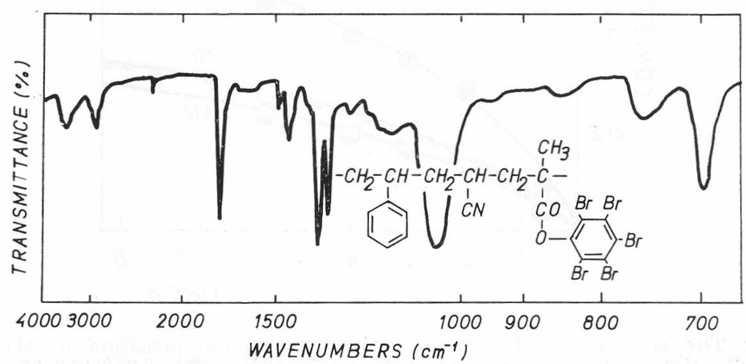


Figure 10. IR spectrum of styrene/acrylonitrile/pentabromophenyl methacrylate terpolymer.

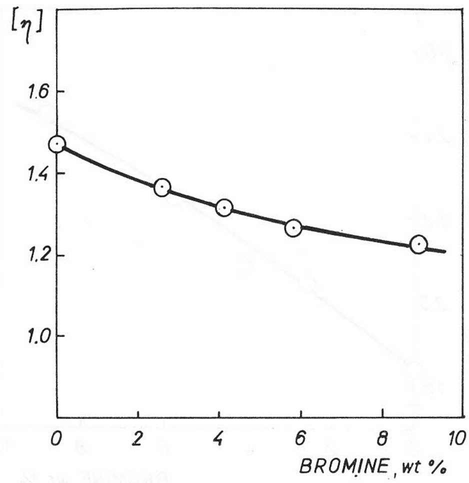


Figure 11. Influence of the amount of pentabromophenyl methacrylate (Br, wt%) [constant styrene and acrylonitrile (0.62/0.38) mol ratio] in terpolymers on the intrinsic viscosities in DMF at 30 °C.

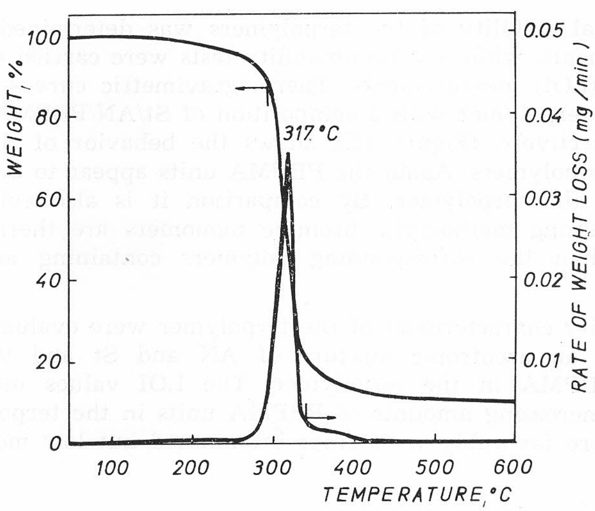


Figure 12. Thermogravimetry and derivate thermogravimetry curves of styrene/acrylonitrile/pentabromophenyl methacrylate terpolymer (0.3/0.3/0.4 mol ratio).

absorption peaks at 2240 $cm^{-1}$ which represents the nitrile band, and absorption at 1760 $cm^{-1}$ showing carbonyl, and at 1602, 1496 and 1455 $cm^{-1}$ in-plane stretching vibration of the phenyl ring and at 695 $cm^{-1}$ out-of-plane phenyl ring deformation.

The intrinsic viscosities of the terpolymers obtained in DMF solutions were rather small but in bulk polymerization they were in the range of about 1.3 dl/g, indicating the high molecular weight of the polymers (Figure 11.).

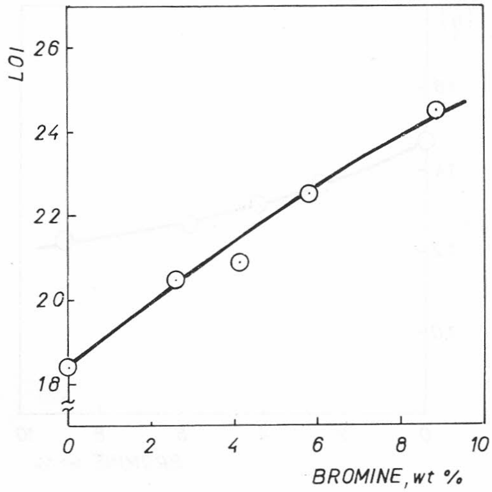


Figure 13. Dependence of the amount of pentabromophenyl methacrylate (Br, wt%) [constant styrene and acrylonitrile (0.62/0.38) mol ratio] on the limiting oxygen index value of terpolymers.

The thermal stability of the terpolymers was determined by TGA and DTG measurements, while the flammability tests were carried out by limiting oxygen index (LOI) measurements. Thermogravimetric curves of the decomposition of the terpolymer with a composition of St/AN/PBPMA of mole ratio 0.3/0.3/0.4, respectively, (Figure 12.), shows the behavior of St/PBPMA[6] and AN/PBPMA[10] copolymers. Again the PBPMA units appear to be the thermally weak links in the terpolymer. By comparison it is also evident that terpolymers containing methacrylic bromine monomers are thermall somewhat more stable than the corresponding polymers containing acrylic bromine monomers.

Flammability characteristics of the terpolymer were evaluated on samples prepared with an azeotropic mixture of AN and St and with increasing amounts of PBPMA in the terpolymer. The LOI values increased almost linearly with increasing amounts of PBPMA units in the terpolymers (Figure 13.) and compare favorably with other brominated but low molecular weight compounds[11].

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## SAŽETAK

**Kopolimeri bromiranih monomera. Terpolimerizacija stirena, akrilonitrila i pentabromfenil-metakrilata**

*Karla Sarić, Zvonimir Janović i Otto Vogl*

Istraživana je terpolimerizacija stirena, akrilonitrila i pentabromfenil-metakrilata slobodnim radikalom u otopini dimetilformamida. Polimerizacije pri niskoj konverziji daju terpolimere koji pokazuju dobro slaganje eksperimentalnih i teorijskih rezultata sastava izračunanih primjenom Alfrey-Goldfinger-ove jednadžbe. Odnos između doziranja monomera i sastava terpolimera prikazan je Slocombeovim dijagramom u obliku istostraničnog trokuta. Linije jednokomponentnog sastava i azeotropnog sastava određene su primjenom računskog programa. Azeotropna trojna točka određena je za molni omjer stiren/akrilonitril/pentabromfenil metakrilat 0,28/0,33/0,39. Eksperimentalni rezultati terpolimerizacije dobro se slažu s teorijskim krivuljama u širokom rasponu sastava monomera do visokih konverzija. Opisan je utjecaj pentabromfenil-metakrilata na termička svojstva i svojstva zapaljivosti terpolimera.