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Copolymers of Bromine-Containing Monomers. 5. Terpolymerization of Acrylonitrile, Styrene, and Pentabromophenyl Acrylate

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ABSTRACT

The terpolymerization of acrylonitrile, styrene, and pentabromophenyl acrylate in dimethylformamide solution was investigated. Experimental terpolymerization data agreed well with calculations using the Alfrey-Goldfinger equation. The relationship between monomer feed and terpolymer compositions are presented on triangular coordinate graphs, and the lines of unique and the lines of binary azeotropic composition were identified. No point of true ternary azeotropic composition was found but a "pseudoazeotropic" region was identified. The experimental results of the terpolymerization agreed well with the theoretical curves over a wide range of monomer composition up to high conversions. The influence of pentabromophenyl acrylate units on the thermal and flammability characteristics of the terpolymers are described.

INTRODUCTION

In our earlier investigations [1, 2] we reported the terpolymerization of acrylonitrile (AN) and styrene (St) with 2,3-dibromopropyl acrylate (DBPA) or with 2,4,6-tribromophenyl acrylate (TBPA). We found that free radical polymerization of the ternary systems followed classical copolymerization theory and that incorporation of the brominated monomers retarded the flammability of the terpolymers.

Pentabromophenyl acrylate (PBPA) has been mentioned as a flame retardant for poly(butylene terephthalate) or polyolefins [3]. Polymers containing bromine monomers have received attention in recent years because they improve flammability characteristics [4]. This improvement is particularly significant in styrene-based polymers [5].

It is the objective of the present study to investigate in detail the terpolymerization of AN and St with PBPA in dimethylformamide (DMF) solution. The kinetics of polymerization of the ternary monomer mixture was also studied and some characteristic properties of the terpolymers, particularly their thermal and flammability behavior, were measured.

EXPERIMENTAL

Materials

Acrylonitrile (AN) was dried over calcium chloride and distilled at atmospheric under nitrogen at 77°C. Styrene (St) was washed with 5% aqueous sodium hydroxide solution, dried over calcium chloride, and distilled under nitrogen at 10 mm immediately before use. Pentabromophenyl acrylate (PBPA) was prepared from acryl chloride and pentabromophenol by the Schotten-Baumann synthesis [6]. Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Solvents were purified in the usual manner.

Measurements

Infrared spectra were recorded by a Perkin-Elmer Model 147 spectrophotometer; the samples were in the form of films cast from chloroform solution onto sodium chloride plates. ¹N-NMR spectra were measured on a 90-MHz Varian EM-360 spectrometer at room temperature on 10% solutions in deuterated acetone with TMS as internal standard.

Thermogravimetric analyses (TGA, DTG) were carried out with Perkin-Elmer TGS-2 and DSC-2 instruments under a stream of nitrogen and at a heating rate of 10°C/min.

Limiting oxygen index (LOI) measurements were carried out with

a Stanton-Redcroft FTA instrument on films cast from dichloromethane solution (20 wt%) onto a glass plate. The films were dried for one day at 20°C and then for 16 h at 25°C and 0.1 mm, and cut into 80 × 6.5 mm samples.

Intrinsic viscosities were determined in a Cannon-Fenske capillary viscometer No. 100 in DMF at 30°C.

Polymerization Procedure

Solution polymerizations were carried out in a 150-mL double-jacketed glass reactor provided with a mechanical stirrer which was connected to a thermostat maintained at 60°C ($\pm 0.2^\circ\text{C}$). A homogeneous solution (100 mL) of the monomer mixture (0.15 mol) in DMF was purged with nitrogen for 1 h and then 3 mL of a solution of AIBN (0.2 g) in DMF was injected. After the polymerization was complete the reaction mixture was poured into methanol and the polymer was isolated by filtration, dissolved in DMF, reprecipitated into methanol, and dried at 60°C and 0.1 mm.

Bulk terpolymerization were carried out up to high conversions in order to prepare terpolymer samples for flammability measurements. The polymerizations were carried out in 20 mL glass polymerizations tubes using 10 g of an azeotropic AN/St mixture (38.5/61.5 mol%) and varying amounts of TBPA. The monomer mixture containing AIBN (0.2 g) was degassed by three freeze-thaw cycles and sealed at 0.1 mm. The tube was then placed in a constant temperature bath at 60°C; after 8 h it was opened, the contents dissolved in DMF, and precipitated into methanol. The solid was collected by filtration, washed with methanol, and dried at 60°C and 0.1 mm.

RESULTS AND DISCUSSION

Terpolymerization Reaction

Free radical terpolymerizations of AN/St/PBPA were carried out in DMF solutions. Reactivity ratios for the monomer pairs presented in Table 1 were determined previously [6-8] and calculated according to the Kelen-Tüdös graphical and mean square relationship [9] and the confidence intervals [10] method. The relationship between the molar composition of polymers obtained in the terpolymerization at low conversion, the calculated values using the Alfrey-Goldfinger [11] equation, and the corresponding composition of the monomer feed mixture are summarized in Table 2. The terpolymer compositions were determined by elemental analysis for nitrogen and bromine.

Small changes in the values of the reactivity parameters of binary copolymerization are known to influence significantly the theoretical values for terpolymer composition [12]. Since good agreement between

TABLE 1. Monomer Reactivity Ratios for the Terpolymerization of Acrylonitrile (M_1), Styrene (M_2), and Pentabromophenyl Acrylate (M_3) in Dimethylformamide Solution at 60°C^a

| r_{12}^8 | r_{21}^8 | r_{13}^7 | r_{31}^7 | r_{23}^6 | r_{32}^6 |
|------------|------------|-----------------|-----------------|-----------------|-----------------|
| 0.16 | 0.30 | 0.87 ± 0.06 | 1.62 ± 8.11 | 0.09 ± 0.02 | 0.26 ± 0.02 |

^aAccording to the Kelen-Tüdös method [9, 10].

experimental and theoretical data was observed, it may be concluded that the free radical polymerization of the ternary system AN/St/PBPA followed classical copolymerization theory.

The relationship between the molar composition in the monomer feed and in the resulting terpolymers is represented in the form of a triangular plot (Fig. 1). Connecting the points of correspondence, the heads of the arrows indicate the initial terpolymer composition and the tails the composition of the monomer feed. It is evident that the arrows point toward a well-defined line which corresponds to the con-

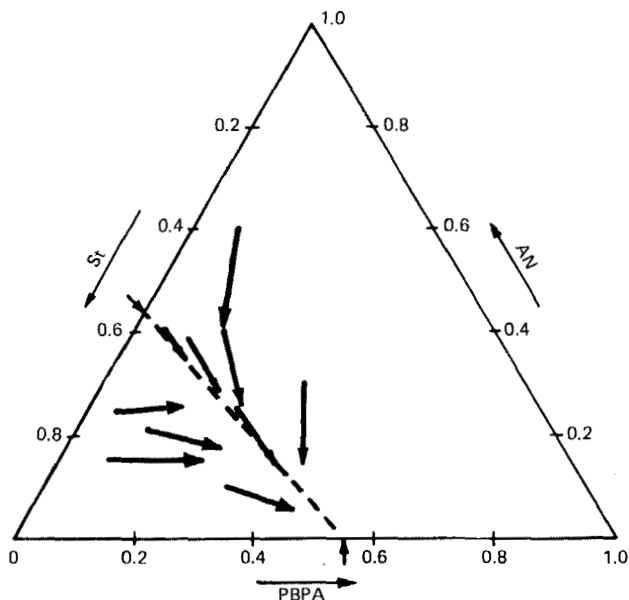


FIG. 1. Monomer/terpolymer triangular composition plot for the system acrylonitrile/styrene/pentabromophenyl acrylate in DMF solution at 60°C .

TABLE 2. Terpolymerization of Acrylonitrile (AN), Styrene (St), and Pentabromophenyl Acrylate (PBPA) in Dimethylformamide (DMF) at 60°C^a

| Run | Monomer feed mole ratio | | | Conversion (%) | N (%) | Br (%) | Terpolymer | | | | | |
|-----|-------------------------|------|------|----------------|-------|--------|-----------------------------|------|------|--|------|------|
| | AN | St | PBPA | | | | Mole fraction, experimental | | | Mole fraction, calculated ^b | | |
| | | | | | | | AN | St | PBPA | AN | St | PBPA |
| 1 | 0.25 | 0.70 | 0.05 | 5.6 | 2.54 | 37.55 | 0.28 | 0.58 | 0.14 | 0.26 | 0.59 | 0.15 |
| 2 | 0.41 | 0.54 | 0.05 | 8.8 | 3.93 | 31.78 | 0.37 | 0.53 | 0.10 | 0.35 | 0.53 | 0.12 |
| 3 | 0.21 | 0.68 | 0.11 | 8.5 | 1.32 | 47.20 | 0.19 | 0.58 | 0.23 | 0.18 | 0.56 | 0.26 |
| 4 | 0.15 | 0.77 | 0.08 | 7.7 | 1.24 | 45.18 | 0.17 | 0.62 | 0.21 | 0.15 | 0.60 | 0.24 |
| 5 | 0.10 | 0.60 | 0.30 | 6.4 | 0.28 | 59.11 | 0.05 | 0.52 | 0.43 | 0.05 | 0.51 | 0.44 |
| 6 | 0.40 | 0.45 | 0.15 | 5.2 | 1.86 | 47.09 | 0.25 | 0.53 | 0.22 | 0.25 | 0.49 | 0.26 |
| 7 | 0.30 | 0.37 | 0.33 | 5.8 | 0.85 | 59.34 | 0.17 | 0.43 | 0.41 | 0.15 | 0.44 | 0.41 |
| 8 | 0.60 | 0.32 | 0.08 | 6.8 | 4.21 | 39.23 | 0.43 | 0.43 | 0.14 | 0.41 | 0.45 | 0.14 |
| 9 | 0.39 | 0.51 | 0.10 | 8.2 | 2.44 | 42.51 | 0.29 | 0.53 | 0.18 | 0.29 | 0.51 | 0.20 |
| 10 | 0.26 | 0.50 | 0.24 | 5.4 | 0.97 | 55.60 | 0.17 | 0.49 | 0.34 | 0.15 | 0.49 | 0.37 |

^aPolymerization conditions: DMF solutions (100 mL) of monomers (0.18 mol) and AIBN (0.2 g) at 60°C.

^bCalculated from the Alfrey-Goldfinger equation.

necting line between binary azeotropic composition of the monomer pairs defined as Slocombe's azeotropic line [13]. The binary azeotropic compositions were AN/St (0.454/0.546) and St/PBPA (0.449/0.551).

The azeotropic line also has some significance with respect to St. In both diagrams the St content was higher in the terpolymer than in the ternary monomer mixture in the region between the azeotropic line at the minimum of St content; for other starting compositions there was a decrease of the St content in the terpolymers. Furthermore, the molar proportion of each monomer in the terpolymer did not vary at random, but depended on the starting monomer composition in the feed.

Slocombe's azeotropic line [13], the connecting line between the binary azeotropic composition of monomer pairs, is approximate. Consideration of partial azeotropy, namely that of a unique or binary or ternary composition, or true azeotropy, allowed the exact location of this boundary. The true or ternary composition is defined [14] as the set of monomer feed fractions $M_i = m_i$ for $i = 1, 2, 3$; where M_i and m_i are the mole fractions of monomer i in the feed and the terpolymer, respectively. In the case of a unique azeotropy, the amount of one of the three monomer was the same in the monomer feed and in the terpolymer ($M_i = m_i$), whereas in the binary azeotropy the ratio of the two monomers was the same in the monomer feed and in the terpolymer ($M_i/M_j = m_i/m_j$).

A computer program to facilitate ternary monomers-terpolymer composition calculations based on the Alfrey-Goldfinger equation [11] by a computer program derived from the Runge-Kutta [15] 4th order integration method, according to Chan and Meyer [16], was used to study the behavior of each monomer during polymerization. A graphic method [17] was applied for the determination of the azeotropic lines. From a practical point of view, it was interesting to determine not only the azeotropic points or azeotropic curves, but also the domains in which the compositional drift is very slight. The arrow plot and the calculations then gave the possibility of defining these domains, which are termed "pseudo-azeotropic" domains.

The azeotropic lines of unique composition for each monomer ($M_1 = \text{AN}$, $M_2 = \text{St}$, $M_3 = \text{PBPA}$), and the difference between terpolymer composition (dotted lines) and the composition of the monomer mixture (full lines) in the terpolymerization reaction, are presented in Fig. 2. The most characteristic azeotropic line is for styrene (M_2) which is located close to Slocombe's azeotropic line with insignificant difference between the composition of the monomer mixtures and the terpolymers. The line for acrylonitrile (M_1) has a similar shape and is located in the region with an AN content lower than 45 mol%. However, the azeotropic line involving polymerization of PBPA has a dif-

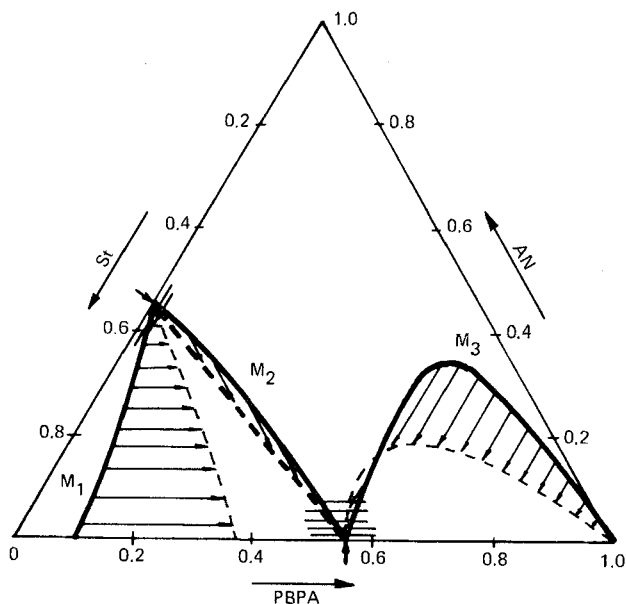


FIG. 2. The azeotropic lines of uniform composition in the terpolymerization of acrylonitrile/styrene/pentabromophenyl acrylate in DMF solutions at 60°C. Monomer mixture (—), terpolymer composition (--).

ferent shape which indicates the greater influence of this monomer on the terpolymerization reaction. The three lines do not intersect; therefore, no true ternary azeotropic point exists, but a "pseudo-azeotropic region," which is hatched in the diagram does exist.

Azeotropic lines of binary composition (Fig. 3) for AN/St (M_1/M_2) and St/PBPA (M_2/M_3) are separated which proves that no ternary azeotropic point exists.

Terpolymerization reactions up to high conversion were carried out with three characteristic different compositions of the initial monomer mixtures. The average and initial, calculated composition of the terpolymers as well as the conversion vs time curves were established. Within the limits of experimental error, the agreement between calculated and experimental values was satisfactory. In terpolymerizations with an initial monomer composition AN/St/PBPA of 0.21/0.68/0.11, the difference between monomer feed composition and contents of monomer units in the terpolymer is evident for both average (Fig. 4) and calculated initial (Fig. 5) terpolymer compositions. The conversion vs time curves for the same initial monomer composition (Fig. 6)

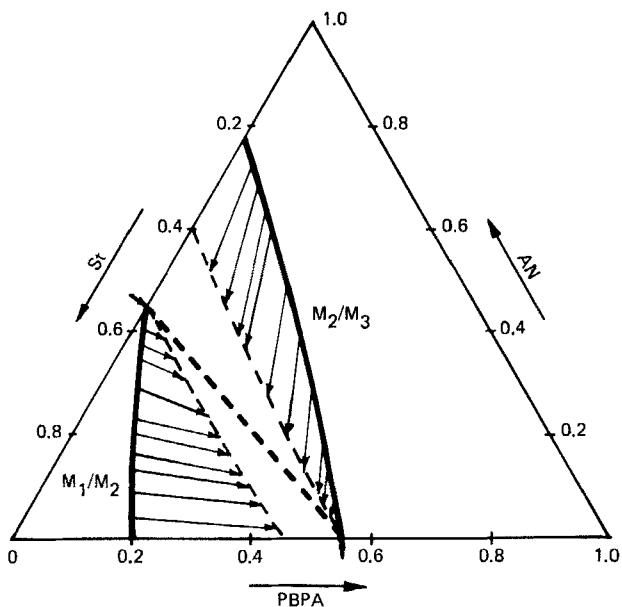


FIG. 3. The binary azeotropic lines of uniform composition in the terpolymerization of acrylonitrile/styrene/pentabromophenyl acrylate in DMS solution at 60°C. Monomer mixture (—), terpolymer composition (--).

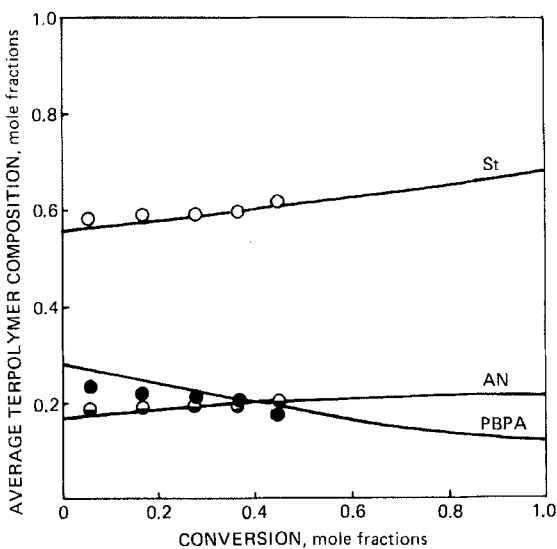


FIG. 4. Average terpolymer composition as a function of conversion in the terpolymerization of monomer mixtures of acrylonitrile/styrene/pentabromophenyl acrylate (0.21/0.68/0.11 mol ratio) in DMF solution at 60°C. Experimental points are shown by the circles, and calculated points by the lines.

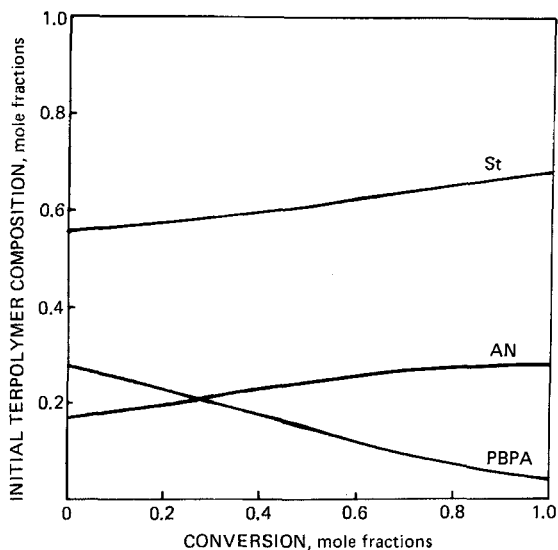


FIG. 5. Calculated initial terpolymer composition as a function of conversion in the terpolymerization of acrylonitrile/styrene/pentabromophenyl acrylate (0.12/0.68/0.11 mol ratio) in a DMF solution at 60°C.

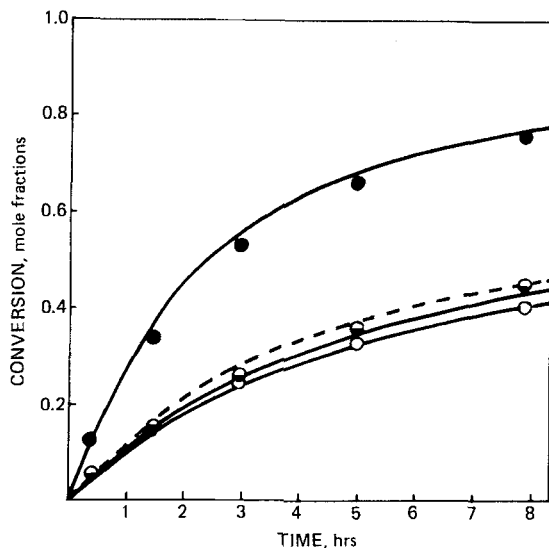


FIG. 6. The conversion of monomers in the terpolymerization of acrylonitrile (●), styrene (○), and pentabromophenyl acrylate (●), 0.21/0.68/0.11 mol ratio, and the overall conversion (--) of monomers to terpolymer in DMF solution at 60°C.

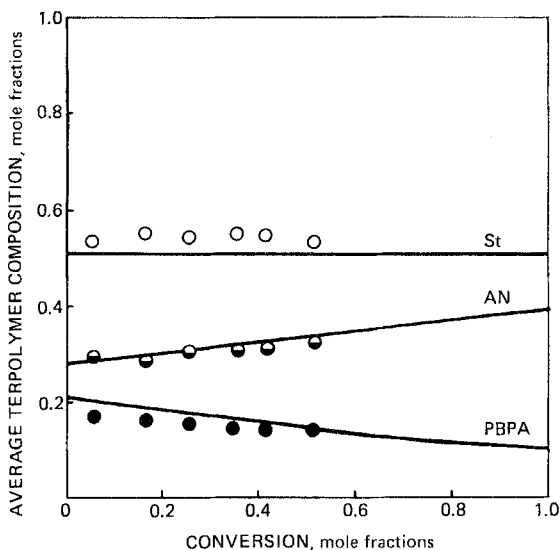


FIG. 7. Average terpolymer composition as a function of conversion in the terpolymerization of the monomer mixtures of acrylonitrile/styrene/pentabromophenyl acrylate (0.39/0.51/0.10 mol ratio) in DMF solution at 60°C. Experimental points are shown by the circles, and calculated points by the lines.

showed that PBPA polymerized much faster, whereas AN and St had similar polymerization rates.

When the initial monomer composition of AN/St/PBPA was 0.39/0.51/0.10, which is on the unique azeotropy line to St, then the average (Fig. 7) and initial (Fig. 8) terpolymer compositions showed constant composition values. The polymerization rates were of the same order (Fig. 6 vs Fig. 9). If the initial monomer mixture was in the pseudo-azeotropic region, (for example, for a AN/St/PBPA composition of 0.41/0.57/0.02 molar ratio, respectively), then the changes in the average (Fig. 10) and initial compositions (Fig. 11) as a function of conversion were rather small.

Terpolymer Properties

The structure of the terpolymers was confirmed by their IR spectra (Fig. 12), which exhibited characteristic 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 the 695 cm^{-1} out-of-plane phenyl ring deformation.

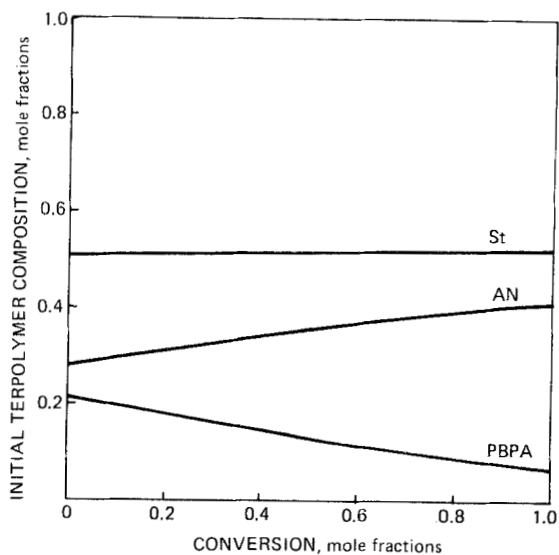


FIG. 8. Calculated initial terpolymer composition as a function of conversion in the terpolymerization of acrylonitrile/styrene/pentabromophenyl acrylate (0.39/0.51/5.10 mol ratio) in DMF at 60°C.

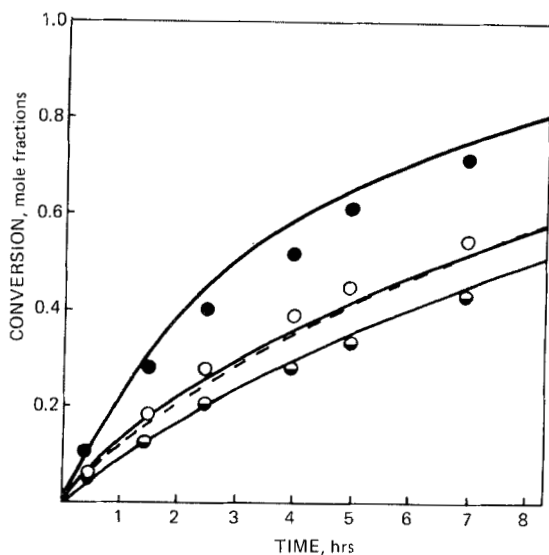


FIG. 9. The conversion of monomers in the terpolymerization of acrylonitrile (●), styrene (○), and pentabromophenyl acrylate (●), 0.39/0.51/0.10 mol ratio, and the overall conversion (--) of monomers to terpolymer in DMF solution at 60°C.

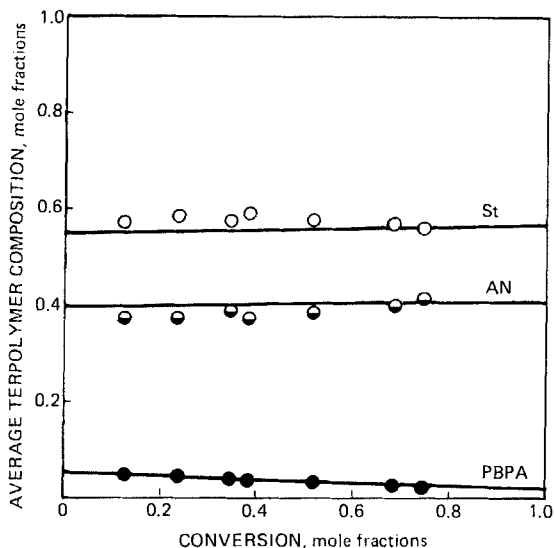


FIG. 10. Average terpolymer composition as a function of conversion in the terpolymerization of the monomer mixtures of acrylonitrile/styrene/pentabromophenyl acrylate (0.41/0.57/0.02 mol ratio) in DMF solution at 60°C. Experimental points are shown by the circles, and calculated points by the lines.

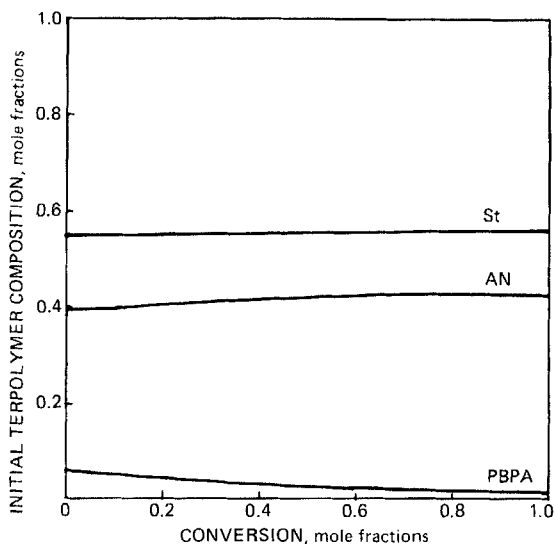


FIG. 11. Calculated initial terpolymer composition as a function of conversion in the terpolymerization of acrylonitrile/styrene/pentabromophenyl acrylate (0.41/0.57/0.02 mol ratio) in DMF solution at 60°C.

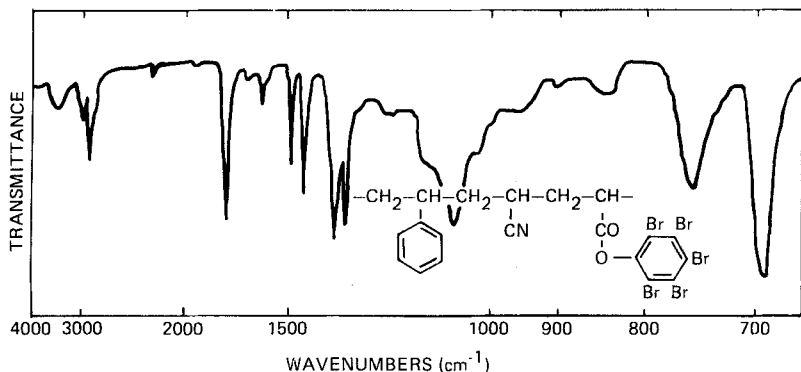


FIG. 12. IR spectrum of acrylonitrile/styrene/pentabromophenyl acrylate terpolymer.

The intrinsic viscosities of the terpolymers obtained in DMF were rather small but in bulk polymerization they were in the range of about 1.5 dL/g, indicating the high molecular weight of the polymers. For example, an St/AN copolymer of azeotropic composition had an intrinsic viscosity of 1.63 dL/g and a terpolymer with 10.2 wt% PBPA, 1.47 dL/g respectively.

The thermal stability of the terpolymers was studied by TGA and DTG measurements (Fig. 13); the flammability characteristics were evaluated by measurements of the limiting oxygen index (LOI) (Fig. 14). The TGA curve shows that the decomposition of the terpolymer AN/St/PBPA with a composition of 0.3/0.5/0.2 mole ratio has two regions of rapid decomposition, clearly separated from each other. These results indicate that the overall thermal stability of the terpolymer depends very much on both the AN/St and the PBPA units of the terpolymer. The thermal behavior of this terpolymer is similar to the thermal degradation behavior of St/PBPA units [6] and AN/PBPA units [7], indicating that the PBPA units appear to be the thermally weak links in the terpolymer.

Flammability characteristics of the terpolymer were evaluated on samples prepared with an azeotropic mixture of AN and St and with increasing amounts (up to 8 wt%) of PBPA in the terpolymer. The LOI values increased with increasing amount of brominated units (PBPA) in the terpolymers. From these results we conclude that the PBPA unit in the terpolymer is an efficient flame retardant unit in AN/St-containing terpolymers; the polymer-bound PBPA units in the terpolymer compare favorably with other brominated but low molecular weight compounds [5].

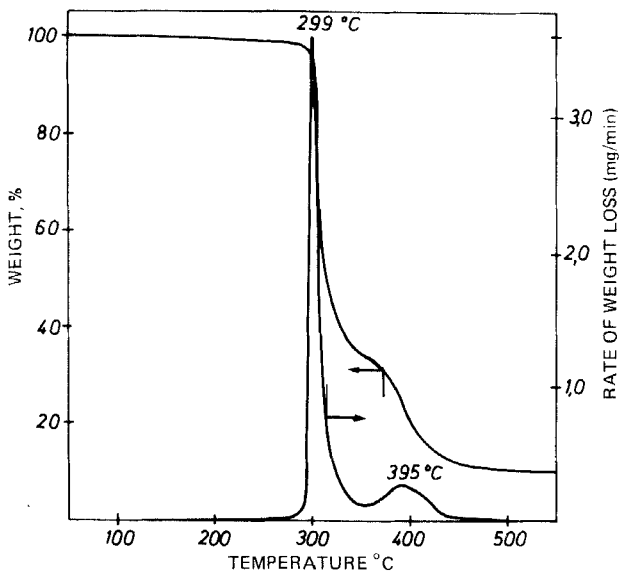


FIG. 13. Thermogravimetry and derivative thermogravimetry curves of acrylonitrile/styrene/pentabromophenyl acrylate terpolymer (0.3/0.5/0.2 mol ratio).

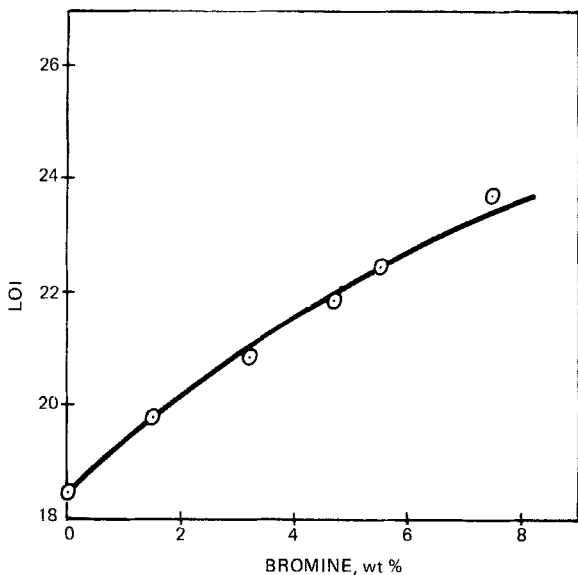


FIG. 14. Dependence of the amount of pentabromophenyl acrylate (Br wt%) [constant acrylonitrile and styrene (0.38/0.62) mol ratio] on the limiting oxygen index value of terpolymers.

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