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Copolymers of Bromine-Containing Monomers. 6. Terpolymerization of Styrene, Acrylonitrile, and 2, 4, 6-Tribromophenyl Methacrylate

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ABSTRACT

2,4,6-Tribromophenyl methacrylate was terpolymerized with styrene and acrylonitrile in aqueous emulsion and dimethylformamide solution. Experimental terpolymerization data agreed well with values calculated from the Alfrey-Goldfinger equation. The relationship between monomer feed and terpolymer compositions is presented on a triangular coordinate graph. The lines of unique composition for each monomer and the lines of binary azeotropic composition for monomer pairs were established for both systems. No true azeotropic composition could be determined, but a "pseudo-azeotropic" region was established. The experimental terpolymerization data agreed well with the theoretical values over a wide range of monomer composition up to high conversions. The influence of 2,4,6-tribromophenyl methacrylate on the thermal stability and flammability behavior of the terpolymers is described.

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INTRODUCTION

We recently reported our results of the terpolymerization of styrene (St), acrylonitrile (AN), and some brominated acrylic monomers [1, 2]. We found that free radical polymerization of the ternary systems followed classical terpolymerization theory. Polymers and copolymers from bromine monomers have received attention in recent years as they decreased flammability as judged by higher limited oxygen index values, particularly in styrene-based polymers [3].

Terpolymers of 2,4,6-tribromophenyl methacrylate (TBPMA) with St and AN or butadiene (bu) have been mentioned only in the patent literature [4, 5].

In this article we report our kinetic studies designed to gain detailed information of the terpolymerization of St with AN and TBPMA in aqueous emulsion and dimethylformamide (DMF) solution. The measurements of some characteristic properties of the terpolymers, particularly their thermal stability and flammability behavior, were also undertaken.

EXPERIMENTAL

Materials

Styrene (St) was washed with 5% aqueous sodium hydroxide solution, dried over calcium chloride, and distilled under nitrogen at 10 mm. Acrylonitrile (AN) was dried over calcium chloride and distilled at atmospheric pressure under nitrogen at 77°C.

2,4,6-Tribromophenyl methacrylate (TBPMA) was prepared from methacryloyl chloride and 2,4,6-tribromophenol by the Schotten-Baumann reaction [6].

The initiator for the aqueous emulsion polymerization was analytical grade potassium persulfate (Merck Chemical Co.); the emulsifier was purified grade sodium dodecylbenzene sulfonate (Allied Chemical Co.). Azobiisobutyronitrile (AIBN) was recrystallized from methanol.

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.

^{1}H-NMR spectra were measured on a 90-MHz Varian EM-390 spectrometer at room temperature on 10% deuterated dimethylsulfoxide solutions with TMS as the internal standard.

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

Limiting oxygen index (LOI) measurements were made with a Stanton-Redcroft FTA instrument on films cast from dichloromethane solution (20 wt%) onto a glass plate. The films were dried for 2 days at 25°C and 0.1 mm, and cut into 80 × 6.5 mm samples.

Viscosity measurements were carried out on a Cannon-Fenske capillary viscometer no. 100 in DMF at 30°C.

Polymerization Procedure

Emulsion polymerizations were carried out as follows: A mixture of 85 mL of an aqueous solution of sodium dodecylbenzene sulfonate (2 wt%) and monomers (15 g) was placed in a 150-mL, double-jacketed glass reactor provided with a mechanical stirrer. The contents of the reactor were heated with stirring to 60°C (± 0.2°C). The emulsion was purged with nitrogen for 1 h before adding potassium persulfate (0.03 g). The degree of conversion was determined on samples withdrawn at regular intervals; the polymer samples were precipitated by pouring the emulsion into methanol. The polymer was isolated, dissolved in DMF, and reprecipitated into methanol.

Solution polymerizations were carried out in the same equipment as that used for emulsion polymerizations. A homogeneous solution (100 mL) of the monomer mixture (0.15 mol) in DMF, at 60°C, was purged with nitrogen for 1 h and then 3 mL of a solution of AIBN (0.2 g) in DMF was added. The terpolymer was precipitated, isolated by filtration, redissolved in DMF, reprecipitated into methanol, and dried at 60°C and 0.1 mm.

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

RESULTS AND DISCUSSION

Terpolymerizations

Terpolymers of St/AN/TBPMA were prepared by free radical polymerization of monomer mixtures in aqueous emulsion or in DMF solution. The reactivity ratios for the monomer pairs had been determined previously [6, 7] and are presented in Table 1. The values of the reactivity ratios depend somewhat on the type of polymerization and also on the polarity of the solvent used for the polymerization.

The relationship between the molar composition of the monomer mixtures and the terpolymers obtained was calculated from the elemental analysis of nitrogen and bromine as well as from the values calculated from the Alfrey-Goldfinger equation [8]. In Table 2 are summarized the data for the emulsion polymerizations and in Table 3 for the solution polymerizations. All polymerization experiments were carried out to low conversions; one can consequently assume that no significant change in the composition of the monomer mixtures occurred. Thus the terpolymer equation can be used. Since good agreement between experimental and theoretical data was observed, it is concluded that the free radical polymerization of the ternary system St/AN/TBPMA follows classical copolymerization theory.

The relationship between the composition of the terpolymers and the monomer feed is depicted by Slocombe's triangle method [9], where the monomer feed and the polymer composition are plotted on a triangular coordinate graph. The graph for emulsion polymerization is shown in Fig. 1 and that for DMF solution in Fig. 2. Connecting the points of correspondence, the arrowhead indicates the initial terpolymer composition and the tail of the arrow indicates the initial monomer feed. One can observe in both cases that the arrows point toward a rather well-defined line which corresponds to the connecting line between the binary azeotropic compositions of the pairs ST/AN and St/TBPMA, the azeotropic line [9]. The binary azeotropic compositions for the emulsion polymerization were St/AN 61.6/38.4 and St/TBPMA 52.6/47.4; for the solution systems St/AN 54.6/45.4 and St/TBPMA 49.0/51.0. The arrows are inclined more in the direction of the azeotropic composition of the pair St/TBPMA and become shorter when located near the azeotropic line, indicating that the compositions of the terpolymers are quite similar to that of the monomer feed.

In order to obtain a clearer understanding of the behavior of each monomer during polymerization, a computer program was utilized to facilitate the calculation of comonomer compositions and terpolymer compositions [10, 11]; a graphic method for the determination of azeotropic lines was used [12]. From the practical point of view, it was useful to determine not only the azeotropic point or the azeotropic curves, but also the domains where the drift of the compositions was only very slight. The arrow plot and the calculations then gave the possibility of defining these domains, which are termed "pseudo-azeotropic" domains (or "near-azeotropic" region [13]). The azeotropic lines of unique composition ($M_j = m_i$) for the three monomers, and the difference between terpolymer composition (dotted lines) and the composition of the monomeric mixture (solid lines) in the terpolymerization (M_1 = St, M_2 = AN, M_3 = TBPMA) are presented in Figs. 3

TABLE 1. Monomer Reactivity Ratio[a] for the Terpolymerization of Styrene (M_1), Acrylonitrile (M_2), and 2,4,6-Tribromophenyl Methacrylate in Emulsion and DMF Solution [6]

Medium	r_{12}	r_{21}	r_{13}	r_{31}	r_{23}	r_{32}
Emulsion	0.44 ± 0.04	0.10 ± 0.02	0.26 ± 0.04	0.13 ± 0.06	0.06 ± 0.03	0.88 ± 0.03
DMF	0.30	0.16	0.20 ± 0.05	0.27 ± 0.05	0.20 ± 0.04	0.98 ± 0.04

[a] Determined by the method of Kelen and Tüdős.

TABLE 2. Terpolymerization of Styrene (St), Acrylonitrile (AN), and 2,4,6-Tribromophenyl Methacrylate (TBPMA) in Emulsion at 70°C[a]

							Terpolymer						
	Monomer feed mol ratio						Mol fraction, experimental			Mol fraction, calculated[b]			
Run no.	St	AN	TBPMA	Conversion (%)	N (%)	Br (%)	St	AN	TBPMA	St	AN	TBPMA	$[\eta]^c$ (dL/g)
1	0.710	0.180	0.110	9.7	1.56	38.82	0.613	0.175	0.212	0.624	0.177	0.199	0.90
2	0.520	0.400	0.080	9.8	3.02	26.98	0.561	0.288	0.151	0.532	0.319	0.149	2.17
3	0.200	0.500	0.300	9.6	1.78	46.07	0.333	0.265	0.402	0.340	0.276	0.384	
4	0.094	0.779	0.127	8.4	3.43	43.57	0.246	0.433	0.321	0.240	0.451	0.309	0.77
5	0.560	0.260	0.180	6.0	1.48	38.39	0.532	0.186	0.282	0.533	0.196	0.271	0.80
6	0.345	0.325	0.330	8.9	1.46	45.34	0.384	0.219	0.397	0.429	0.193	0.378	
7	0.392	0.493	0.115	6.3	3.44	33.71	0.434	0.360	0.206	0.464	0.331	0.205	1.18
8	0.395	0.387	0.218	4.9	1.95	40.09	0.448	0.251	0.301	0.454	0.242	0.304	
9	0.596	0.194	0.210	9.45	0.88	39.22	0.572	0.119	0.309	0.550	0.151	0.299	
10	0.605	0.325	0.070	9.5	3.24	25.35	0.540	0.308	0.152	0.576	0.289	0.135	1.63

[a] Polymerization conditions: Aqueous solution (85 g) of sodium benzenesulfonate (2 wt%), monomers (15 g), and $K_2S_2O_8$ (0.03 g) at 70°C.

[b] Calculated from the Alfrey-Goldfinger equation [8].

[c] In DMF at 30°C.

TABLE 3. Terpolymerization of Styrene (St), Acrylonitrile (AN), and 2,4,6-Tribromophenyl Methacrylate (TBPMA) in DMF at 60°C[a]

							Terpolymer					
	Monomer feed mol ratio						Mol fraction, experimental			Mol fraction, calculated		
Run no.	St	AN	TBPMA	Conversion (%)	N (%)	Br (%)	St	AN	TBPMA	St	AN	TBPMA
1	0.710	0.180	0.110	3.6	1.92	32.68	0.574	0.214	0.212	0.590	0.209	0.201
2	0.520	0.400	0.080	3.2	4.30	26.05	0.483	0.382	0.135	0.511	0.360	0.129
3	0.200	0.500	0.300	7.3	2.27	44.29	0.329	0.314	0.357	0.308	0.335	0.357
4	0.094	0.779	0.127	6.6	4.99	37.94	0.251	0.519	0.230	0.221	0.546	0.233
5	0.560	0.260	0.180	2.9	1.78	37.37	0.513	0.219	0.268	0.511	0.231	0.258
6	0.345	0.325	0.330	4.1	1.42	43.34	0.434	0.203	0.363	0.404	0.227	0.369
7	0.392	0.493	0.115	3.7	3.77	31.81	0.439	0.376	0.185	0.450	0.381	0.169
8	0.395	0.387	0.218	2.8	2.42	39.98	0.407	0.302	0.291	0.436	0.287	0.277
9	0.516	0.245	0.239	5.7	1.44	41.88	0.463	0.199	0.338	0.488	0.203	0.309
10	0.523	0.192	0.285	7.6	1.03	43.20	0.478	0.151	0.371	0.490	0.158	0.352

[a] Polymerization conditions: DMF solutions (100 mL) of monomers (0.19 mol) and AIBN (0.2 g) at 60°C.

[b] Calculated from the Alfrey-Goldfinger equation [8].

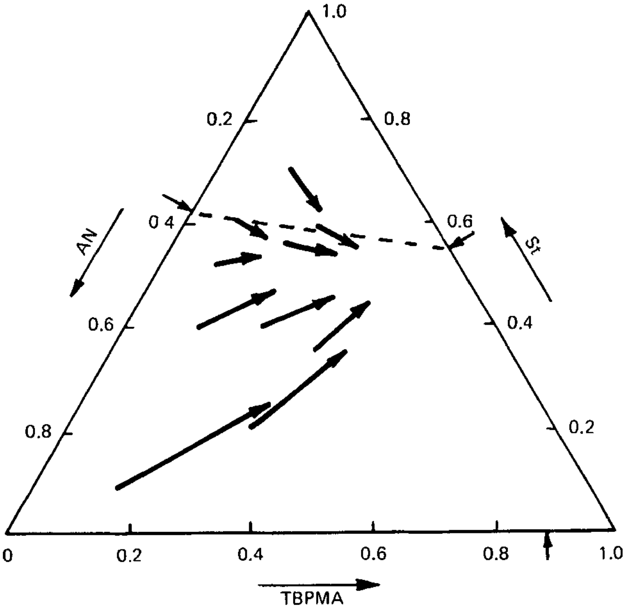

FIG. 1. Monomer/terpolymer triangular composition plot for the system styrene/acrylonitrile/2,4,6-tribromophenyl methacrylate in emulsion at 70°C.

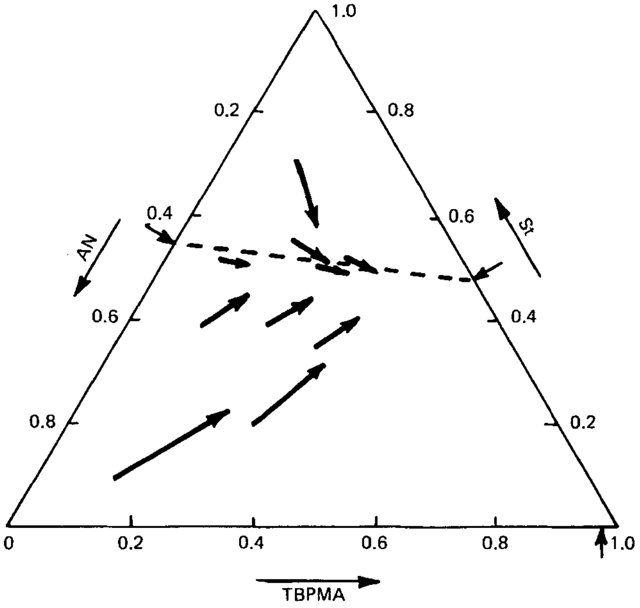

FIG. 2. Monomer/terpolymer triangular composition plot for the system styrene/acrylonitrile/2,4,6-tribromophenyl methacrylate in DMF solution at 60°C.

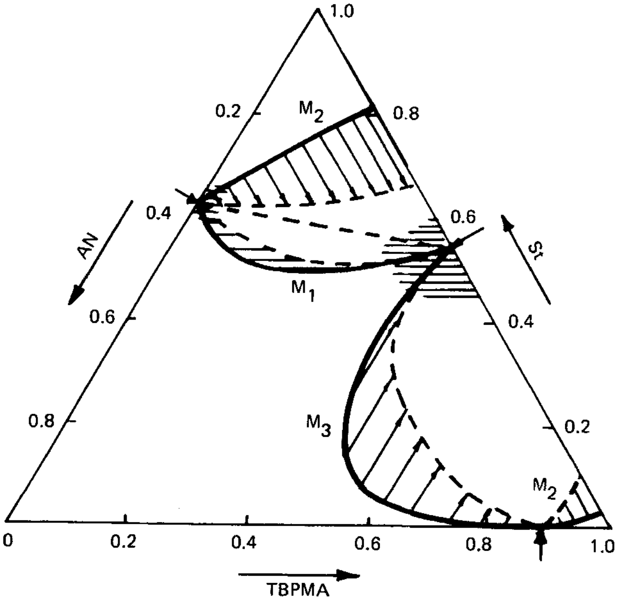

FIG. 3. The azeotropic lines of uniform composition in terpolymerizations of styrene (M_1)-acrylonitrile (M_2)-2,4,6-tribromophenyl methacrylate (M_3) in emulsion at 70°C: Monomer mixture (—), terpolymer composition (--).

and 4. The three lines do not intersect; therefore, no true azeotropic point exists, but "near-azeotropes" could be predicted for the hatched region in the diagram.

Azeotropic lines of binary composition ($M_i/M_j = m_i/m_j$) of St/AN (M_1/M_2) and St/TBPMA (M_1/M_3) for emulsion polymerization and solution polymerization in DMF are presented in Figs. 5 and 6. It is evident that the slopes of these lines depend strongly on the polymerization media, particularly for the M_1/M_3 compositions.

Terpolymerizations up to high conversions were carried out with three different compositions of the initial comonomer mixtures. The average value and the initial values of the terpolymer compositions were calculated. Within experimental error the agreement between calculated values and experimental data of the average composition is satisfactory. In terpolymerization with an initial monomer composition St/An/TBPMA of 0.71/0.18/0.11, there is a difference between the composition of the monomer feed and the number of monomer units in the terpolymer; for emulsion and solution polymerization, calculated

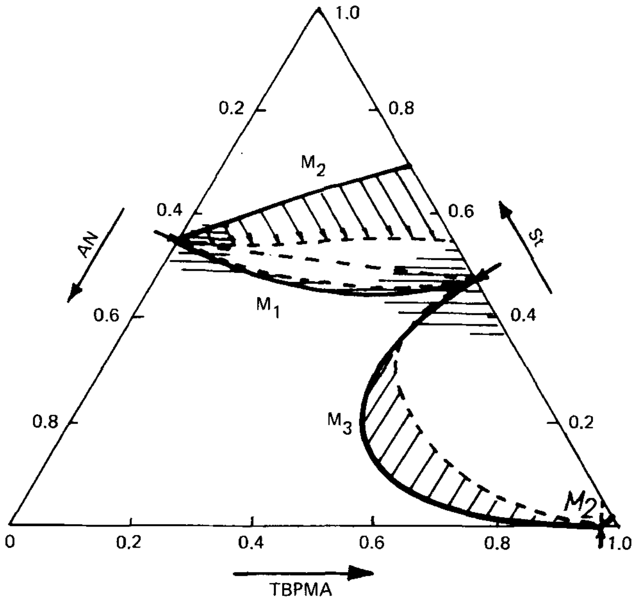

FIG. 4. The azeotropic lines of uniform composition in terpolymerizations of styrene (M_1)-acrylonitrile (M_2)-2,4,6-tribromophenyl methacrylate (M_3) in DMF solution at 60°C: Monomer mixture (—), terpolymer composition (--).

values for the average terpolymer composition (Figs. 7 and 8) and for the initial terpolymer composition (Figs. 9 and 10) were obtained. When the initial total comonomer composition of St/AN/TBPMA in the feed had a molar ratio of 0.61/0.33/0.07, this composition was located on the azeotropic line for emulsion polymerization. For this composition the average (Fig. 11) and initial (Fig. 12) terpolymer composition depended very little on conversion. When the composition of the initial monomer mixture was on the unique azeotropic line with respect to styrene, as is the case for the St/AN/TBPMA 0.51/0.32/0.17 molar ratio for emulsion polymerization (Fig. 13) and for DMF solution polymerization (Fig. 14), the change in the average terpolymer composition for styrene is negligible whereas that for AN and TBPMA is rather substantial.

Terpolymer Properties

The structure of the terpolymers was confirmed by their IR spectra. Figure 15 shows a typical example. The spectrum exhibits character-

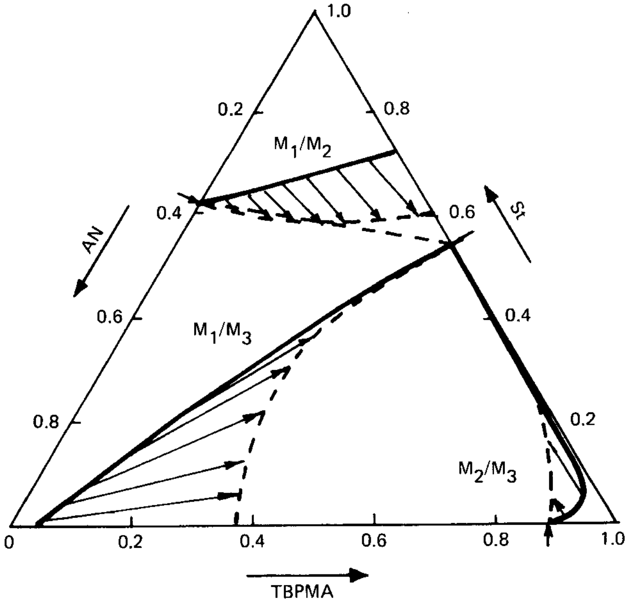

FIG. 5. The binary azeotropic lines of uniform composition in terpolymerizations of styrene (M_1)-acrylonitrile (M_2)-2,4,6-tribromophenyl methacrylate (M_3) in emulsion at 70°C: Monomer mixture (—), terpolymer composition (--).

istic absorption peaks at 2240 cm^{-1} which represent the nitrile band, and an absorption at 1760 cm^{-1} is indicative of the carbonyl group. Characteristic absorption bands are also at 1602 cm^{-1}, 1496 cm^{-1}, and 1455 cm^{-1}, which are the in-plane stretching vibrations of the phenyl ring, and a band at 695 cm^{-1}, the out-of-plane phenyl ring deformation.

The intrinsic viscosities of the terpolymer obtained in emulsion polymerization were in the range of 0.9 to 2.2 dL/g (Table 2), showing that the polymers are of high molecular weight. Comonomer mixtures with higher TBPMA content gave terpolymers with a lower value of the intrinsic viscosity [shown for bulk polymerization (Fig. 16)]. It is well known that bromine-containing monomers [14] or bromine-containing compounds in polymerization mixtures are the cause of chain transfer in radical polymerization. However, chain transfer is observed primarily with aliphatic carbon bromine rather than with aromatic carbon bromine bonds.

The thermal stability of the terpolymers was studied by TGA and DTG measurements (Fig. 17); their flammability characteristics were

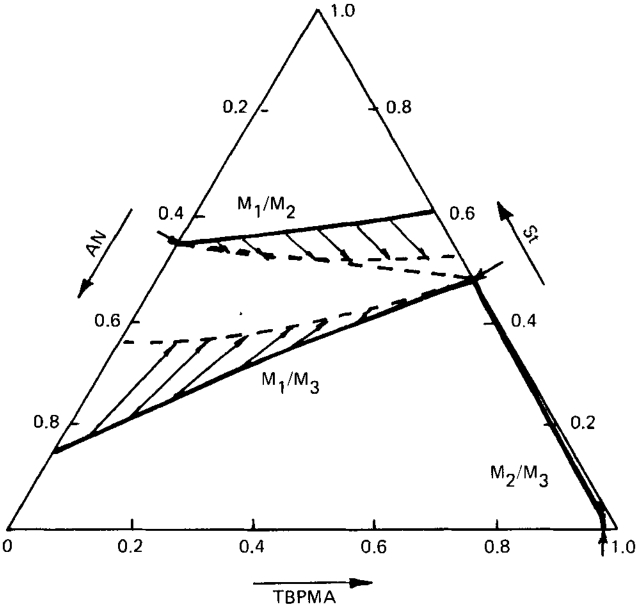

FIG. 6. The binary azeotropic lines of uniform composition in terpolymerizations of styrene (M_1)-acrylonitrile (M_2)-2,4,6-tribromophenyl methacrylate (M_3) in DMF solution at 60°C: Monomer mixture (—), terpolymer composition (--).

evaluated by limiting oxygen index (LOI) measurements (Fig. 18). The TGA curve shows that the decomposition of the terpolymer St/AN/TBPMA with a mol ratio of 0.5/0.3/0.2 has two regions of rapid decomposition. These results demonstrate that the overall thermal stability of the terpolymer depends very much on both the AN/St and the TBPMA units in the terpolymer. The thermal behavior of this terpolymer is similar to the thermal degradation behavior of St/TBPMA and AN/TBPMA copolymers [6], indicating that the TBPMA is the thermally weak link in the terpolymer.

Flammability characteristics of the terpolymer were determined on samples prepared with an azeotropic mixture of AN and St and with increasing amounts (up to 8 wt%) of TBPMA in the terpolymer. The LOI values increased with increasing amounts of brominated units (TBPMA) in the terpolymers. From results shown in Fig. 18, we conclude that TBPMA is an efficient flame retardant for St/AN copolymers; it compares favorably with other brominated compounds of low molecular weight [3] that have been incorporated into St and AN polymers.

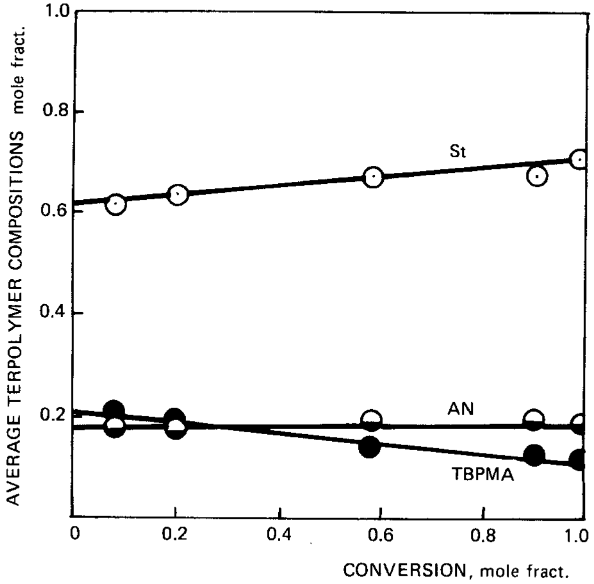

FIG. 7. Average terpolymer composition as a function of conversion in the terpolymerization of the monomer mixtures of styrene/acrylonitrile/2,4,6-tribromophenyl methacrylate (0.71/0.18/0.11 mol ratio) in emulsion at 70°C: Experimental (○), calculated (—).

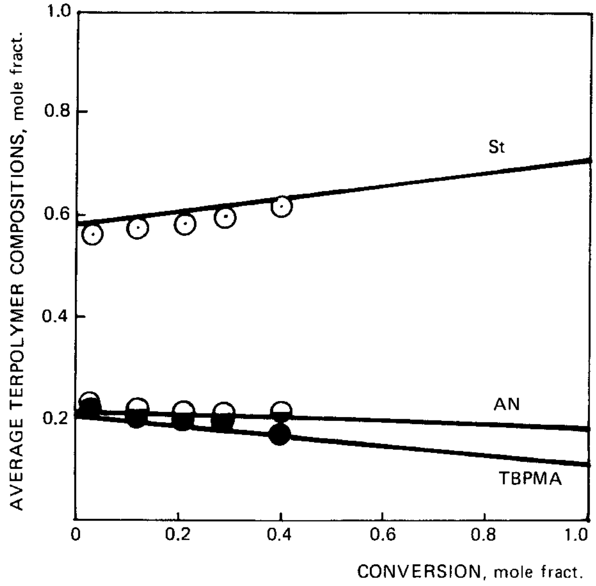

FIG. 8. Average composition as a function of conversion in the terpolymerization of the monomer mixture of styrene/acrylonitrile/2,4,6-tribromophenyl methacrylate (0.71/0.18/0.11) in DMF solution at 60°C: Experimental (○), calculated (—).

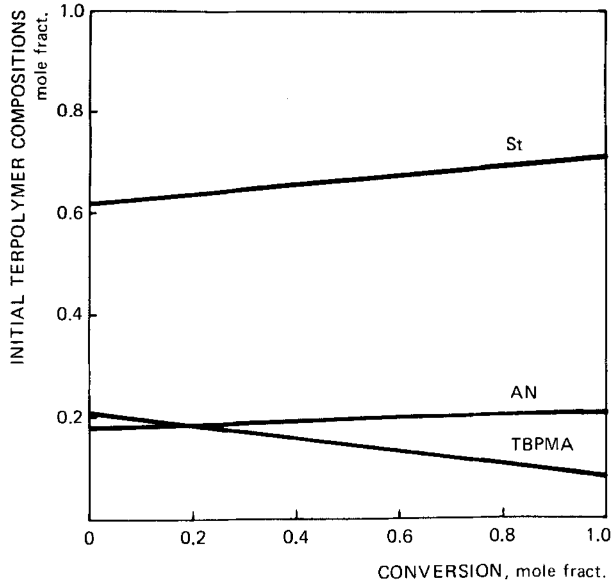

FIG. 9. Calculated initial terpolymer composition as a function of conversion in the terpolymerization of styrene/acrylonitrile/2,4,6-tribromophenyl methacrylate (0.71/0.18/0.11 mol ratio) in emulsion at 60°C.

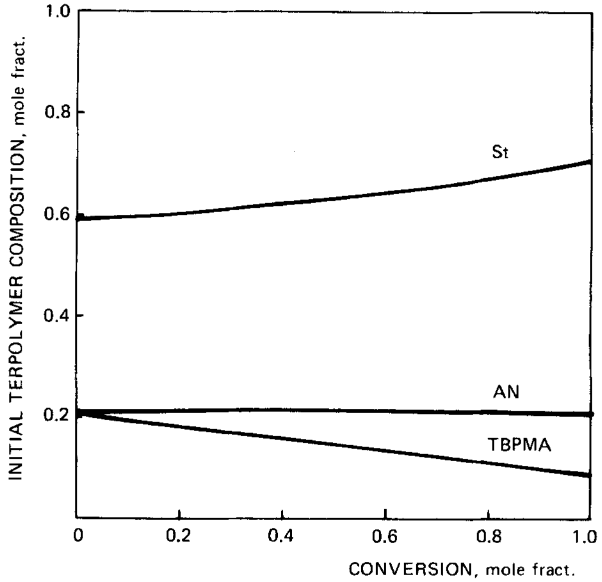

FIG. 10. Calculated initial terpolymer composition as a function of conversion in the terpolymerization of styrene/acrylonitrile/2,4,6-tribromophenyl methacrylate (0.71/0.18/0.11 mol ratio) in DMF solution at 60°C.

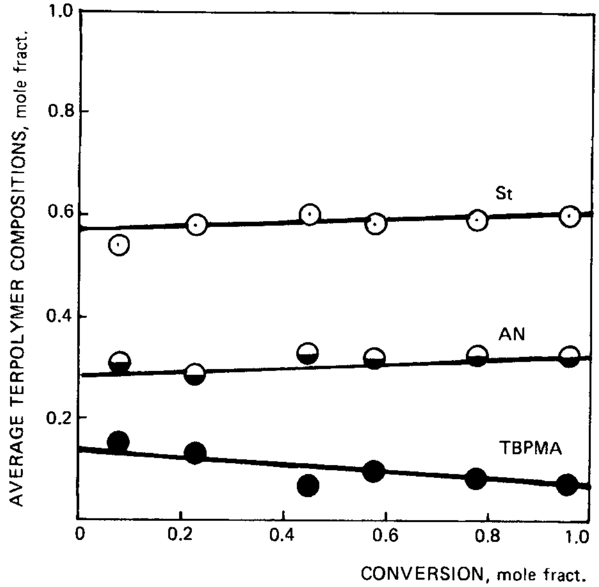

FIG. 11. Average terpolymer composition as a function of conversion in the terpolymerization of monomer mixtures of styrene/acrylonitrile/2,4,6-tribromophenyl methacrylate (0.60/0.335/0.070 mol ratio) in emulsion at 70°C: Experimental (o), calculated (—).

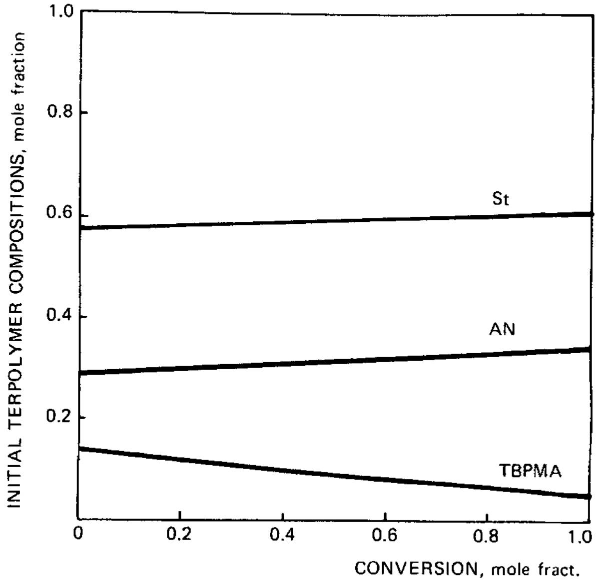

FIG. 12. Calculated initial terpolymer composition as a function of conversion in the terpolymerization of styrene/acrylonitrile/2,4,6-tribromophenyl methacrylate (0.605/0.324/0.070 mol ratio) in emulsion at 70°C.

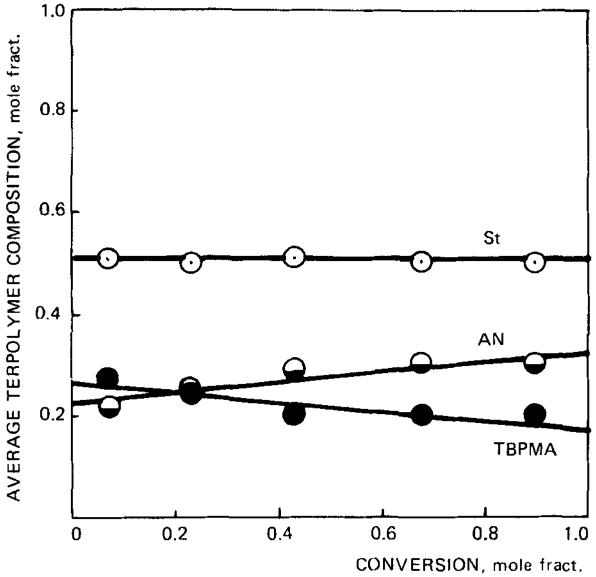

FIG. 13. Average terpolymer composition as a function of conversion in the terpolymerization of monomer mixture of styrene/acrylonitrile/2,4,6-tribromophenyl methacrylate (0.51/0.32/0.17 mol ratio) in emulsion at 70°C: Experimental (○), calculated (—).

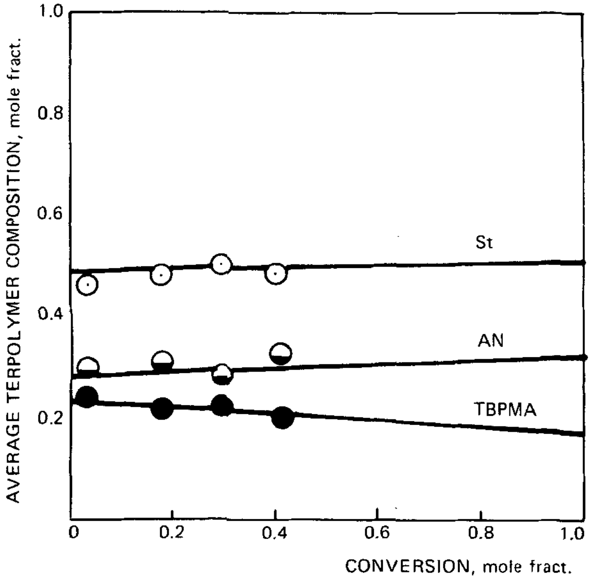

FIG. 14. Average terpolymer composition as a function of conversion in the terpolymerization of monomer mixture of styrene/acrylonitrile/2,4,6-tribromophenyl methacrylate (0.51/0.32/0.17 mol ratio) in DMF solution at 60°C: Experimental (○), calculated (—).

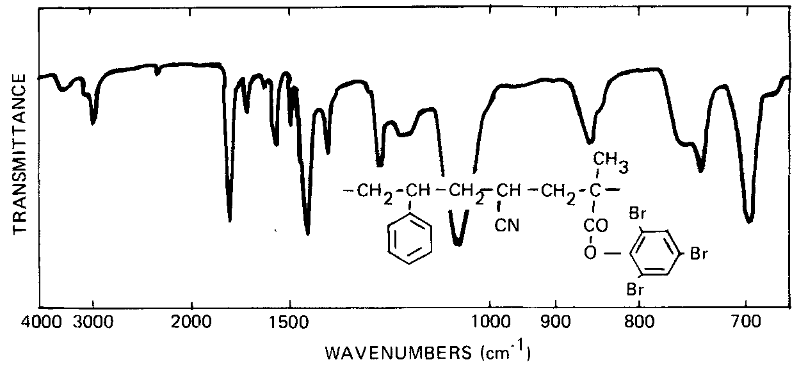

FIG. 15. IR spectrum of a styrene/acrylonitrile/2,4,6-tribromophenyl methacrylate terpolymer.

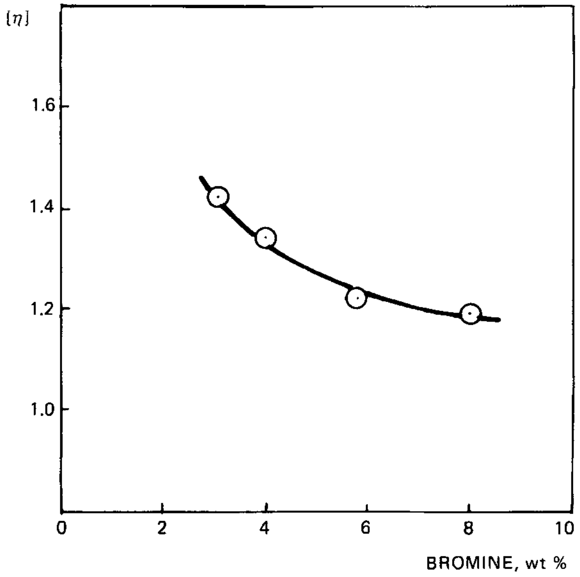

FIG. 16. The influence of the amount of 2,4,6-tribromophenyl methacrylate (Br wt%) [constant styrene and acrylonitrile (0.62/0.38) mol ratio] on the intrinsic viscosities in toluene at 30°C.

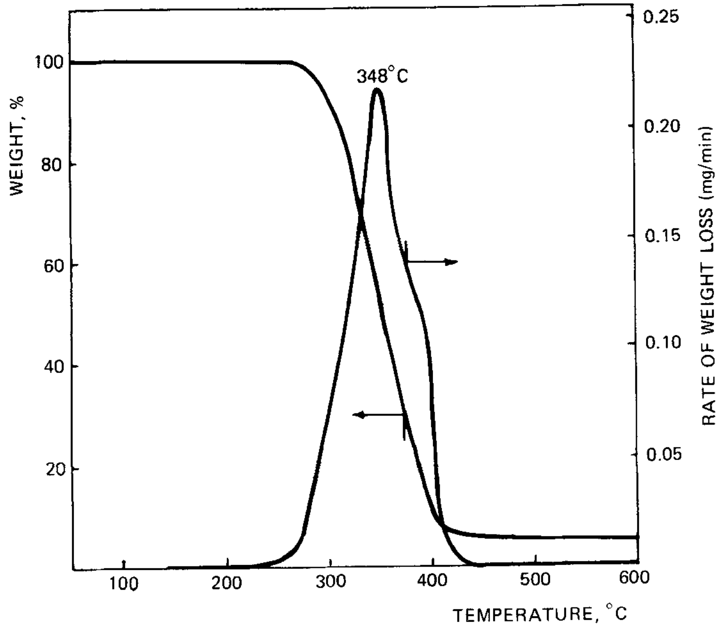

FIG. 17. Thermography and derivative thermogravimetry curves of styrene/acrylonitrile/2,4,6-tribromophenyl methacrylate terpolymer (0.5/0.3/0.2 mol ratio).

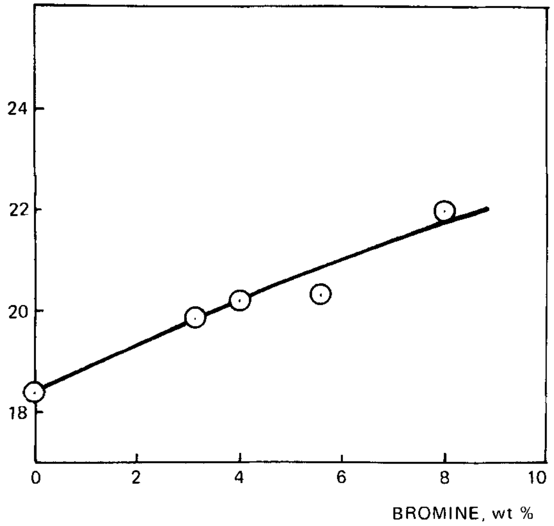

FIG. 18. Dependence of the amount of 2,4,6-tribromophenyl methacrylate (Br wt%) [constant styrene and acrylonitrile (0.62/0.38) mol ratio] on the limiting index value of terpolymers.

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