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Copolymers of Acrylonitrile with Some Brominated Acrylates

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ABSTRACT

Acrylonitrile was copolymerized with 2,3-dibromopropyl acrylate, 2,4,6-tribromophenyl acrylate, or pentabromophenyl acrylate in either aqueous emulsion or dimethylformamide solutions with azobisisobutyronitrile as the free radical initiator. The thermal properties and the flammability characteristics of the resulting polymers were also investigated. The reactivity ratios of the monomers and the initial reaction rates for homopolymerization and copolymerization reactions in dimethylformamide were determined. 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 pentabromophenyl acrylate > 2,4,6-tribromophenyl acrylate > 2,3-dibromopropyl acrylate > acrylonitrile. Thermal stability measurements (determined from TGA and DTG) showed that

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poly(2,4,6-tribromophenyl acrylate) and its acrylonitrile copolymers were the most stable polymers and the copolymers of 2,3-dibromopropyl acrylate with acrylonitrile had the best flame-retardant properties as was demonstrated by limiting oxygen index measurements.

INTRODUCTION

The copolymerization of acrylonitrile (AN) with halogenated acrylic esters and the properties of these copolymers have not been studied extensively. It has, however, been mentioned that the rate of copolymerization decreases with increasing electronegativity of the substituents as well as the molecular weight of the copolymers [1]. The reactivity ratios for various AN-substituted acrylate copolymerization systems have also been determined [2, 3].

Recently, copolymers of brominated acrylic esters with vinyl monomers have attracted renewed attention because they have been shown to have by themselves or impart onto other polymers substantially lower flammability [4, 5]. Most of the end-use properties of these copolymers have been described in the patent literature [6].

In the previous paper [7] we described the copolymerization of styrene with selected brominated acrylates and some properties of these copolymers.

This paper deals with the copolymerization of AN with 2,3-dibromopropyl acrylate (DBPA), 2,4,6-tribromophenyl acrylate (TBPhA), and pentabromophenyl acrylate (PBPhA). Some properties of the copolymers, particularly their thermal stability and flammability behavior, are also subjects of our investigation.

EXPERIMENTAL

Materials

Acrylonitrile (AN) was distilled under nitrogen.

2,3-Dibromopropyl acrylate (Great Lakes Chemical Co.) (DBPA) was distilled under nitrogen at 0.3 mm and the middle fraction was collected: bp 93°C, $n_D^{20} = 1.5220$ (Ref. 7, $n_D^{20} = 1.5220$). 2,4,6-Tribromophenyl acrylate (TBPhA) and pentabromophenyl acrylate (PBPhA) were prepared by a Schotten-Baumann reaction [8] with acryl chloride of 2,4,6-tribromophenol or pentabromophenol.

The initiator used in the emulsion polymerization experiments was analytical grade potassium persulfate (Merck Chemical Co.); the emulsifier was sodium dodecylbenzene sulfonate (purified grade) (Allied Chemical Co.). Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Solvents were purified in the usual manner.

Measurements

Infrared spectra were measured on a Perkin-Elmer Spectrophotometer Model 147 on films cast from dimethylformamide (DMF) solutions onto sodium chloride plates.

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

The limiting oxygen index (LOI) measurements were carried out with a Stanton-Redcroft FTA instrument (Dake Corp.) on films pressed at 170°C and 300 MPa which were ultimately cut into strips of 80 × 6.5 mm.

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

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 10 g of monomer was placed in the reactor which was thermostated to 60°C ($\pm 0.2^\circ\text{C}$). The emulsion was purged with nitrogen for 30 min before potassium persulfate (0.02 g) was added. The degree of conversion to polymer was determined on samples which were withdrawn at regular intervals and precipitated into methanol.

Solution polymerizations in DMF (50 mL solutions) of monomer(s) (0.1 mol) were carried out in the same equipment used for the emulsion polymerization (under nitrogen), with AIBN (0.24 g) as the initiator at 60°C.

RESULTS AND DISCUSSION

Copolymerization Reactions

Free radical copolymerizations of AN with DBPA or TBPhA were carried out in aqueous emulsion as well as in DMF solutions. Because of the low solubility of TBPhA in AN, the emulsion polymerization was not attempted and this copolymerization was only done in solution. The influence of the molar composition of the initial monomer mixture on the composition of the resulting copolymers in both media are shown in Tables 1-5. In all copolymerizations the reactions were stopped before the copolymerization had reached 10% conversion; the copolymer composition was established by bromine analysis.

In all cases the plot of comonomer-copolymer mol fraction composi-

TABLE 1. Copolymerization of 2,3-Dibromopropyl Acrylate (M_1) with Acrylonitrile (M_2) in DMF at 60°C^a

Expt no.	Monomer feed (mol%)		Conversion (%)	Br (%)	Copolymer (mol%, expt)	
	DBPA	AN			DBPA	AN
1	10	90	5.7	22.56	10.8	89.2
2	15	85	8.6	28.84	15.8	84.2
3	30	70	2.7	40.80	30.7	69.3
4	50	50	5.8	49.33	50.5	49.5
5	70	30	8.1	53.13	64.8	35.2
6	80	20	8.8	55.55	77.1	22.9

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

TABLE 2. Copolymerization of 2,3-Dibromopropyl Acrylate (M_1) with Acrylonitrile (M_2) in Emulsion at 60°C^a

Expt no.	Monomer feed (mol%)		Conversion (%)	Br (%)	Copolymer (mol%, expt)	
	DBPA	AN			DBPA	AN
1	10	90	5.4	22.23	10.6	89.4
2	20	80	7.8	33.70	20.8	79.2
3	30	70	5.4	40.48	30.2	69.8
4	40	60	5.6	45.40	40.1	59.9
5	50	50	8.5	48.90	49.2	50.8
6	60	40	7.6	51.75	59.0	41.0
7	70	30	9.0	53.82	68.0	32.0
8	80	20	8.9	55.79	78.5	21.5

^aPolymerization conditions: Aqueous solutions (50 g) of sodium benzene-sulfonate (2 wt%), monomers (10 g), and $K_2S_2O_8$ (0.02 g) at 60°C.

TABLE 3. Copolymerization of 2,4,6-Tribromophenyl Acrylate (M_1) with Acrylonitrile (M_2) in DMF at 60°C^a

Expt no.	Monomer feed (mol%)		Conversion (%)	Br (%)	Copolymer (mol%, expt)	
	TBPA	AN			TBPA	AN
1	10	90	6.5	28.70	10.6	89.4
2	20	80	5.7	40.88	21.0	79.0
3	30	70	3.4	47.33	30.7	69.3
4	40	60	3.1	52.95	44.4	55.6
5	50	50	5.1	56.24	57.0	43.0
6	60	40	5.5	57.16	61.5	38.5
7	70	30	6.0	59.09	73.1	26.9

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

TABLE 4. Copolymerization of 2,4,6-Tribromophenyl Acrylate (M_1) with Acrylonitrile (M_2) in Emulsion at 60°C^a

Expt no.	Monomer feed (mol%)		Conversion (%)	Br (%)	Copolymer (mol%, expt)	
	TBPA	AN			TBPA	AN
1	20	80	6.5	42.76	23.4	76.6
2	30	70	7.0	50.02	36.4	63.6
3	33.75	66.25	6.4	52.08	41.8	58.2
4	40	60	4.3	54.56	50.2	49.8
5	60	40	3.7	56.87	71.6	28.4
6	70	30	4.2	60.02	80.0	20.0

^aPolymerization conditions: Aqueous solutions (50 g) of sodium benzene-sulfonate (2 wt%), monomers (10 g), and $K_2S_2O_8$ (0.02 g) at 60°C.

TABLE 5. Copolymerization of Pentabromophenyl Acrylate (M_1) with Acrylonitrile (M_2) in DMF at 60°C^a

Expt no.	Monomer feed (mol%)		Conversion (%)	Br (%)	Copolymer (mol%, expt)	
	PBPA	AN			PBPA	AN
1	10	90	4.7	42.90	12.0	88.0
2	30	70	3.5	61.52	33.0	67.0
3	40	60	3.3	47.94	52.1	47.9
4	50	50	7.5	69.24	60.0	40.0
5	60	40	3.3	70.72	69.5	30.5
6	80	20	3.9	72.54	85.4	14.6

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

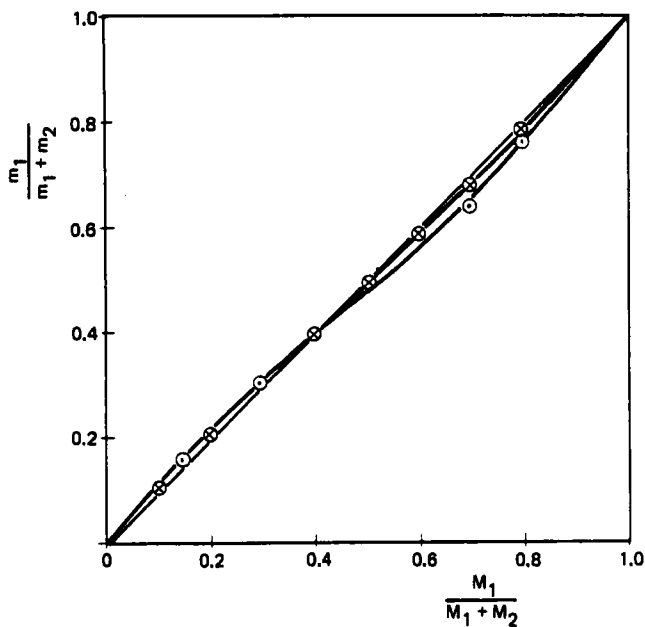


FIG. 1. Copolymerization of 2,3-dibromopropyl acrylate (M_1) with acrylonitrile at 60°C in emulsion (⊙) and dimethylformamide (⊙).

tion for the brominated monomer (M_1) (Figs. 1-3) shows a tendency toward ideal copolymerization; only very small deviations of these compositions from ideal behavior were found.

Using the Kelen-Tüdös mean square relationship [9] and confidence intervals [10], we calculated the reactivity ratios (Table 6) from the experimental data. For the copolymerization of AN with DBPA in DMF solution, good agreement was found with earlier data [3]. We compared the values of our reactivity ratios with those represented in the polar and resonance effects of the Alfrey-Price scheme.

The structure of the three brominated acrylic esters influenced the rate of copolymerization with AN of the same feed composition (AN 95 mol%) when the copolymerization was carried out in DMF solutions. Figure 4 shows that the initial rates are slightly dependent on the type of brominated acrylic monomer. Analysis of the homopolymerization behavior of the monomers used in this work also showed (in DMF solution) that the initial polymerization rate of the brominated acrylic monomers and AN were similar; however, at higher conversion the rates increased and changed in the order PBPhA > TBPhA > DBPA > AN (Fig. 5). The polymerization rates for the brominated acrylic monomers were about five times higher than those for AN.

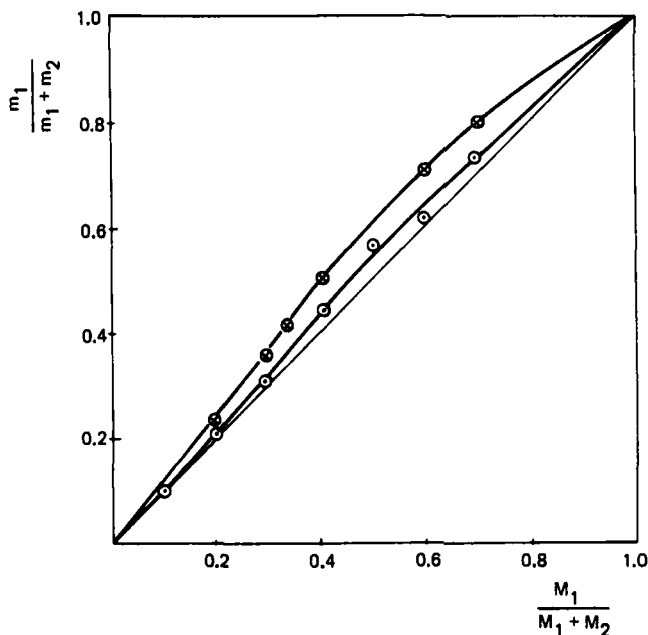


FIG. 2. Copolymerization of 2,4,6-tribromophenyl acrylate (M_1) with acrylonitrile at 60°C in emulsion (\odot) and dimethylformamide (\circ).

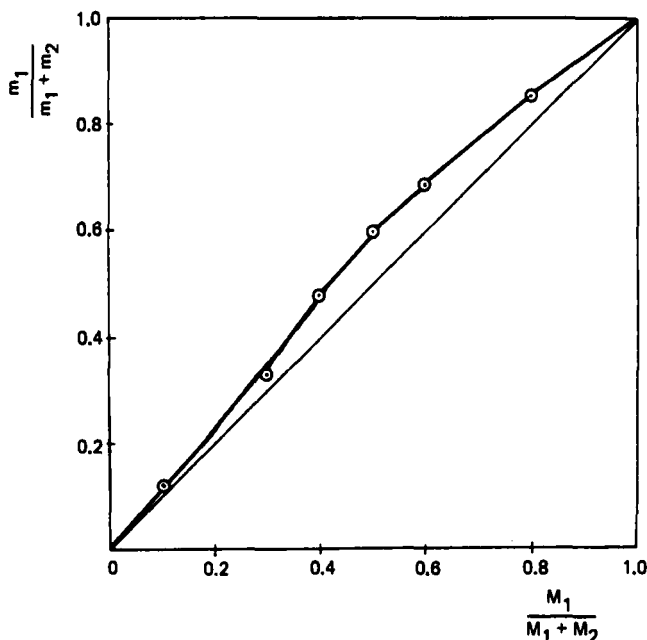


FIG. 3. Copolymerization of pentabromophenyl acrylate (M_1) with acrylonitrile at 60°C in dimethylformamide.

Solution viscosity measurements of the AN-brominated acrylic monomers showed a significant decrease of the intrinsic viscosity of the copolymers when the content of brominated acrylic monomer in the copolymer was increased, as exemplified for the copolymers of TBPhA and AN (Fig. 6). This lower intrinsic viscosity and presumably lower molecular weight is probably caused by chain transfer reactions of the growing chain involving the bromine atoms of the monomer or of the polymer; this is known to be the behavior of radical polymerization involving bromine-containing monomers and polymers [11].

Thermal Stability and Flammability

The thermal stabilities of AN-brominated acrylic ester copolymers were determined by TGA and DTA measurements. Flammability tests were carried out by measurements of the limiting oxygen index (LOI).

The decomposition of homopolymers of brominated acrylic monomers in nitrogen (Fig. 7) showed similar decomposition temperature and behavior for all three homopolymers, but a marked difference was noted for the decomposition of AN. The fact that polyacrylonitrile

TABLE 6. Copolymerization Parameters for Brominated Acrylic Monomers (M_1) with Acrylonitrile (M_2)

Monomer (M_1)	Solvent	r_1^a	r_2^a	Azeotropic composition	Q_1^c	e_1^c
2,3-Dibromopropyl acrylate	DMF ^b	0.75 ± 0.05	0.87 ± 0.01	34.2/65.8	0.32	0.55
	Aq emulsion	0.86 ± 0.02	0.91 ± 0.02	39.1/60.9	0.36	0.70
2,4,6-Tribromophenyl acrylate	DMF	1.25 ± 0.08	0.96 ± 0.04			
	Aq emulsion	2.05 ± 0.09	0.96 ± 0.04			
Pentabromophenyl acrylate	DMF	1.62 ± 0.11	0.87 ± 0.06			

^a Calculated by the Kelen-Tüdös method [9].

^b Reference 3: $r_1 = 0.70$, $r_2 = 0.96$.

^c $Q_2 = 0.6$, $e_2 = 1.2$.

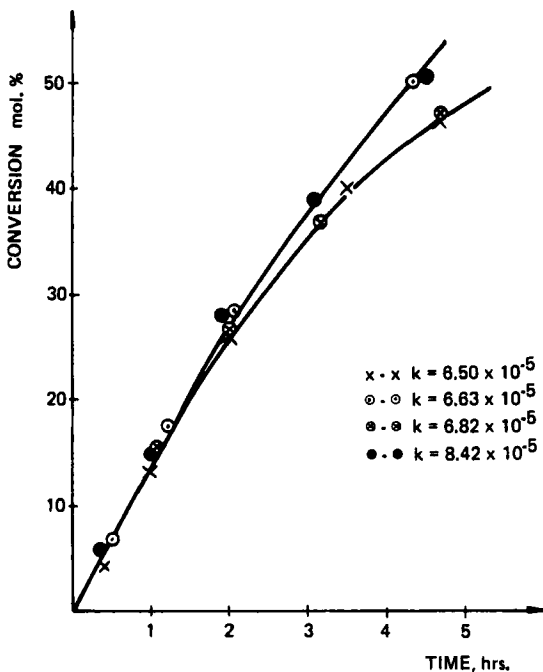


FIG. 4. Initial rate of copolymerization of 2,3-dibromopropyl acrylate (●), 2,4,6-tribromophenyl acrylate (⊙), and pentabromophenyl acrylate (○) with acrylonitrile (95% mol) (x) at 60°C in dimethylformamide with AIBN as the initiator.

leaves a substantial residue under these conditions of pyrolysis is well established [12]. The decomposition behaviors of brominated acrylic polymers have been described in an earlier paper [7].

The weight loss curve of copolymers of AN and brominated acrylates as a function of constantly increasing temperature is presented in Figs. 8-10. The data obtained from the thermal degradation spectrum are summarized in Table 7. Point A in Fig. 8 marks the temperature of the beginning of the fast decomposition region and Point B is the temperature at which 50% of the sample of poly(AN-co-DBPA) had degraded and indicates the weight lost from the onset of heating to temperature C, the leveling out of the curve. The temperature readings at the end of the second region of rapid decomposition (Point C') and for 50% of the weight loss of the sample (Point B') in the region C to C' are given in parentheses (Table 7). Thermogravimetric curves showing the decomposition of these copolymers and the data

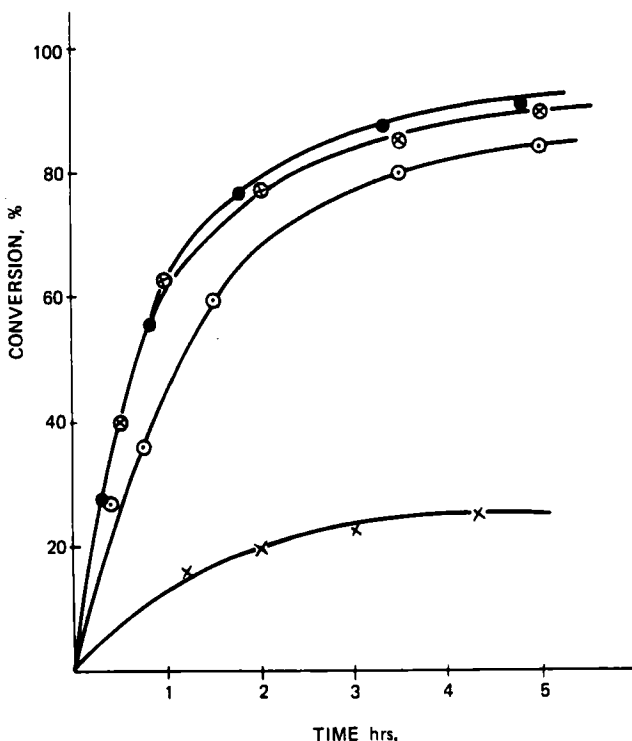


FIG. 5. Rate of homopolymerization of 2,3-dibromopropyl acrylate (●), 2,4,6-tribromophenyl acrylate (⊗), pentabromophenyl acrylate (⊙), and acrylonitrile (×) at 70°C in dimethylformamide with AIBN as the initiator.

from Table 7 suggest that both polyacrylonitrile and the brominated acrylic monomer sequences contribute to the thermal stability of the AN-brominated acrylate copolymers.

The flammability properties of copolymers of AN and brominated acrylic monomers were determined by LOI measurements and are shown in Fig. 11. There are marked differences in the efficiency of radical scavenging in the flame between poly(AN-co-DBPA), a copolymer of AN with a brominated acrylate monomer with an aliphatic carbon-bromine bond, and poly(AN-co-TBPhA), a copolymer of AN with a brominated acrylate monomer with an aromatic carbon-bromine bond. These results are in agreement with previous reports which emphasize that aliphatic carbon-bromine bonds are thermally less stable than aromatic carbon-bromine bonds. The differences in the strength of the carbon-bromine bond, however, result in a faster re-

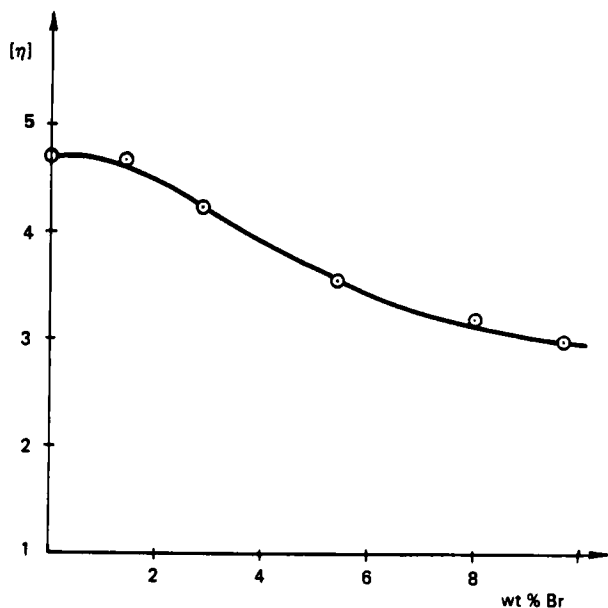


FIG. 6. Influence of the composition of acrylonitrile and 2,4,6-tribromophenyl acrylate copolymer, obtained in emulsion, on the intrinsic viscosities in dimethylformamide at 30°C.

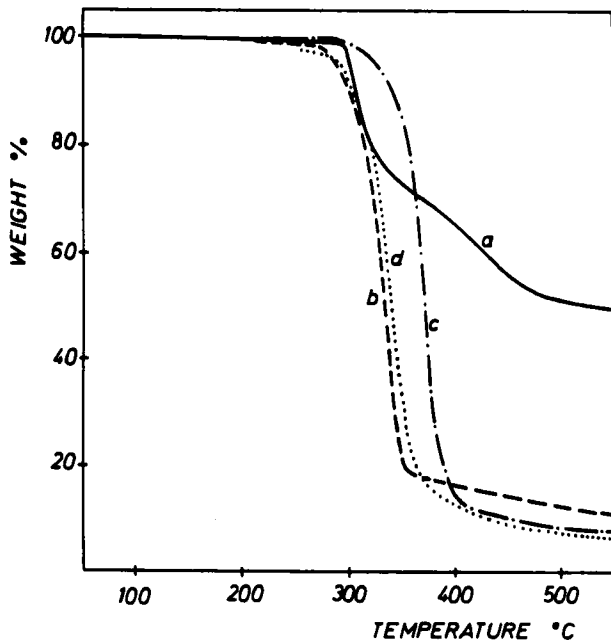


FIG. 7. Thermogravimetric analysis of polyacrylonitrile (a), poly(2,3-dibromopropyl acrylate) (b), poly(2,4,6-tribromophenyl acrylate) (c), and poly(pentabromophenyl acrylate) (d), in nitrogen.

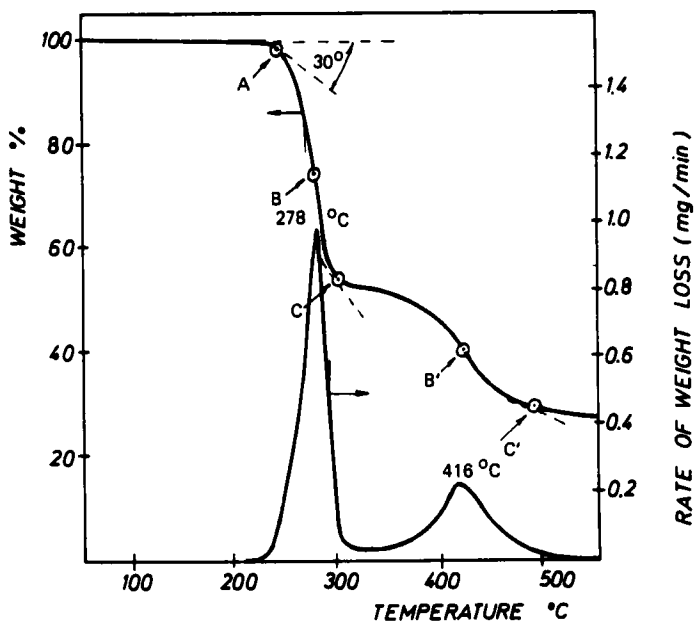


FIG. 8. Thermogravimetric analysis of poly(acrylonitrile-co-2,3-dibromopropyl acrylate) (molar ratio 69.3/30.7) in nitrogen.

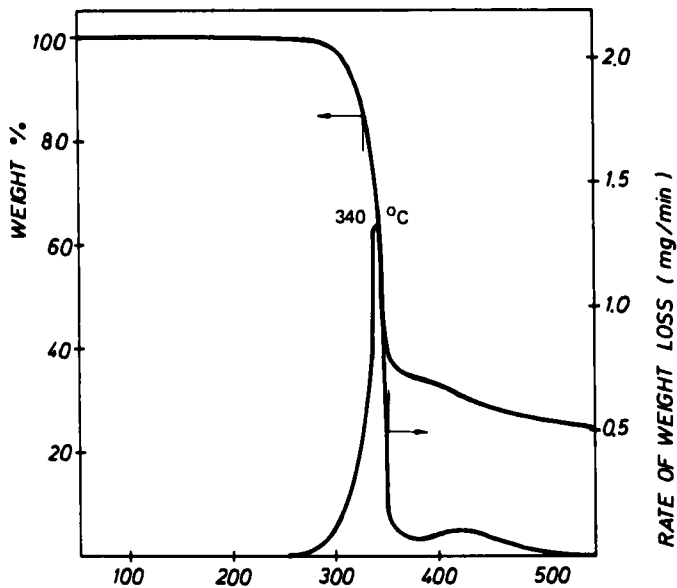


FIG. 9. Thermogravimetric analysis of poly(acrylonitrile-co-2,4,6-tribromophenyl acrylate) (molar ratio 69.3/30.7) in nitrogen

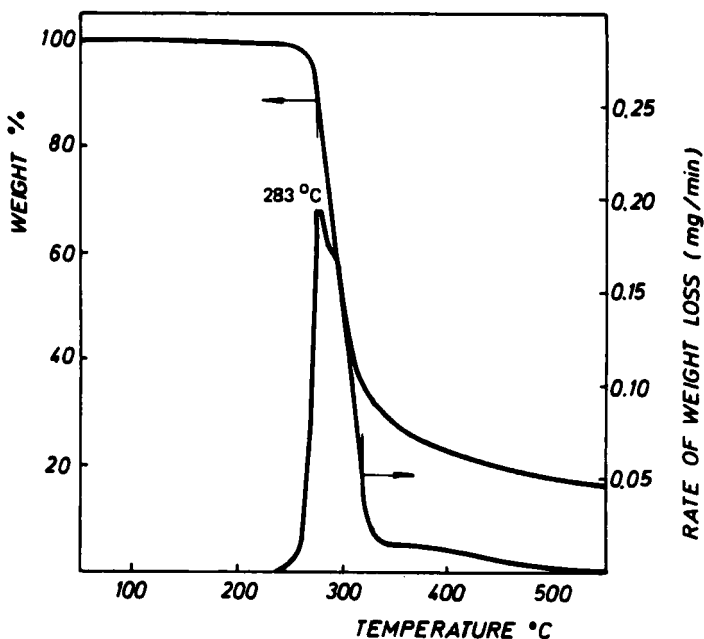


FIG. 10. Thermogravimetric analysis of poly(acrylonitrile-co-pentabromophenyl acrylate) (molar ratio 67.0/33.0) in nitrogen.

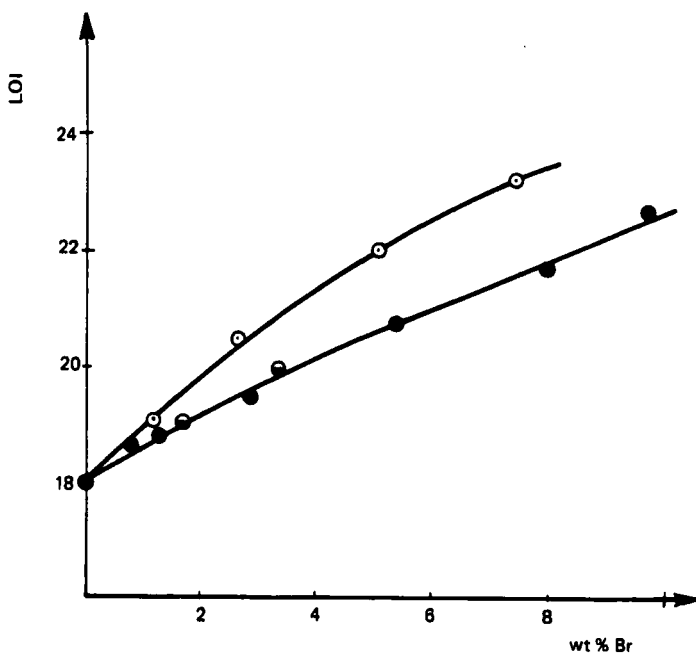


FIG. 11. Influence of the content of brominated monomer (Br wt%) on the limiting oxygen index of poly(acrylonitrile-co-2,3-dibromopropyl acrylate) (\circ), poly(acrylonitrile-co-2,4,6-tribromophenyl acrylate) (\bullet), and poly(acrylonitrile-co-pentabromophenyl acrylate) (\circ).

TABLE 7. Thermogravimetric Analysis of Copolymers of Acrylonitrile (M_2) with Brominated Monomers (M_1) and Homopolymers of the Latter; Measurement in Nitrogen, $10^\circ\text{C}/\text{min}$

Comonomer (M_1)	M_1/M_2	Br (%)	A, $^\circ\text{C}/\text{weight loss } \%$	B, $^\circ\text{C}$ (B', $^\circ\text{C}$)	C, $^\circ\text{C}/\text{residue } \%$ (C', $^\circ\text{C}/\text{residue } \%$)	Maximum degradation rate temp ($^\circ\text{C}$)
2,3-Dibromopropyl acrylate	30.7/69.3	40.8	243/1.7	276 (416)	297/54.3 (474/29.7)	278
	100/0	58.8	288.5/3.6	331	354.5/19.2	416
2,4,6-Tribromophenyl acrylate	30.7/69.3	47.3	301/2.3	340 (420)	356/36.6 (457/28.1)	334
	100/0	62.1	330/6.7	372	397/14.0	340
Pentabromophenyl acrylate	33.0/67.0	33.0	264/2.0	289	332/30.9	420
	100.0/0	73.75	284/2.6	337	370/16.8	361
Polyacrylonitrile	0/100.0	-	297/1.5	310 (415)	336/75.5	284
					500/52.0	339
						305
						430

lease of hydrogen bromide (or bromine radicals in the flame) from the bromoaliphatic copolymer. Qualitatively similar results have been reported for other systems where aliphatic carbon-bromine bonds were compared with aromatic carbon-bromine bonds [13]. The field of coordinating chemical structure, physical state, and morphology with flammability behavior is still in flux. Consequently, some results show an apparent opposite effect; for example, in unsaturated polyester resins [14].

REFERENCES

- [1] M. A. Askarov and S. R. Pinkhasov, Uzb. Khim. Zh., **11**, 25 (1967); Chem. Abstr., **66**, 105288r (1967).
- [2] A. Miller and J. Szafko, J. Polym. Sci., Polym. Chem. Ed., **15**, 1595 (1977).
- [3] J. Ch. Jung and S. I. Woo, Pollimo, **2**, 130 (1978); Chem. Abstr., **90**, 39331s (1979).
- [4] V. Stannett, W. K. Walsh, E. Bittencourt, R. Liepins, and J. R. Surles, Appl. Polym. Symp., **31**, 201 (1977).
- [5] D. W. van Krevelen, Ibid., **31**, 269 (1977).
- [6] W. J. Jackson, Jr., J. R. Caldwell, and E. H. Hill, U.S. Patent 3,143,535 (1964); Chem. Abstr., **61**, 10800h (1964).
- [7] K. Sarić, Z. Janović, and O. Vogl, J. Macromol. Sci.-Chem., **A19**(5), 837 (1983).
- [8] C. E. Rehberg, M. B. Dixon, and W. A. Francette, J. Am. Chem. Soc., **72**, 5199 (1950).
- [9] T. Kelen and F. Tüdös, J. Macromol. Sci.-Chem., **19**, 1 (1975).
- [10] T. Kelen, F. Tüdös, and B. Turesanyi, Polym. Bull., **2**, 71 (1980).
- [11] R. C. P. Cubbon and I. D. B. Smith, Polymer, **10**, 487 (1969).
- [12] N. Grassie and R. McGuchan, Eur. Polym. J., **7**, 1091 (1971).
- [13] J. A. Schneider, R. G. Dews, and J. D. Herring, Ind. Eng. Chem., Prod. Res. Dev., **9**, 559 (1970).
- [14] M. Ravery, Th. Fischler, and M. Kramer, Fire Mater., **2**, 34 (1978).

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