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Copolymers of Bromine-containing Monomers 8. Copolymers of Acrylonitrile with some Brominated Phenyl Methacrylate

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Acrylonitrile was free radical copolymerized with 2,4,6-tribromophenyl methacrylate of pentabromophenyl methacrylate in aqueous emulsion or dimethylformamide solutions. The thermal and flammability characteristics of the resulting polymers were investigated. The reactivity ratios of the monomers and the initial rates for homopolymerization and copolymerization reactions were determined. The monomer reactivity ratios were found to depend slightly on the reaction medium and the reaction rates are in the order acrylonitrile > pentabromophenyl methacrylate > tribromophenyl methacrylate.

Thermal stability determined from TGA and DTG measurements showed that poly(2,4,6-tribromophenyl methacrylate) and its acrylonitrile copolymers were thermally more stable than the poly(pentabromophenyl methacrylate) and its acrylonitrile copolymers, though the latter showed better flame-retardant properties as was demonstrated by limiting oxygen index measurements.

INTRODUCTION

Free radical polymerizations and copolymerizations of substituted acrylic and methacrylic esters have been studied extensively.[1] It was shown that the rate of polymerization is generally faster for the acrylates than for the corresponding methacrylates and that halogenated esters show similar reactivity in homo- and copolymerization reactions.[2] Recently, copolymers of brominated (meth) acrylic esters with other vinyl monomers have attracted special attention because they can be used for the improvement of flammability characteristics.[3] Relatively little has been published about polymerization and copolymerization reactions of aromatic bromine-substituted (meth)acrylic esters and the properties of these compounds.

Copolymerization of acrylonitrile (AN) or styrene with some brominated acrylic monomers and some properties of the obtained copolymers were described in our previous communications.[4,5] In addition, we described the copolymerization of styrene with selected brominated phenyl methacrylates.[6] Some work dealing with polymerization and copolymerization of these monomers has been reported.[7,8] Most of the end use properties of these copolymers have been described in the patent literature.[9]

This paper details the copolymerization reactions of AN with 2,4,6-tribromophenyl methacrylate (TBPMA) and pentabromophenyl methacrylate (PBPMA) in aqueous emulsion or solutions and discusses some properties of the copolymers obtained, particularly their thermal and flammability behaviour.

EXPERIMENTAL

Materials

Acrylonitrile (AN) was distilled under nitrogen just prior to use. 2,4,6-Tribromophenyl methacrylate (TBPMA) and pentabromophenyl methacrylate (PBPMA) were prepared by a Schotten-Bauman reaction with methacryloyl chloride of 2,4,6-tribromophenol or pentabromophenol.[6] The initiator used in the emulsion polymerization experiments was analytical grade potassium persulfate (Merck 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 a film 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 70 °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

Homopolymerizations of brominated monomers in dimethylformamide solutions were carried out in 20 mL glass polymerization tubes. Typically, 10 mL of the monomer solution (0.35 mol/L) mixed with AIBN (65 mg) was degassed by three freeze —thaw cycles and then sealed under a pressure of 0.1 Torr. The tube was placed in a constant temperature bath at 70 °C for one to five hours and after opening the contents were poured into 50 mL of methanol. The solid was collected by filtration, washed with methanol, and dried.

The same procedure was used for the copolymerization of brominated monomer with acrylonitrile.

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 70 °C (±0.2 °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.

RESULTS AND DISCUSSION

Copolymerizations

Free radical copolymerization of AN with TBPMA was carried out in aqueous emulsion as well as in DMF solutions. Because of the low solubility of PBPMA in AN, the emulsion polymerization was not attempted and this copolymerization was only done in solution. The initial rates of copolymerization in DMF of the same feed composition (AN, 95 mol %) were slightly influenced by the structure of brominated phenyl methacrylated as shown in Figure 1. Analysis of the homopolymerization behaviour of the monomers used showed that the initial polymerization rates were in the order AN > > PBPMA > TBPMA (Figure 2.). The polymerization rate for AN is about

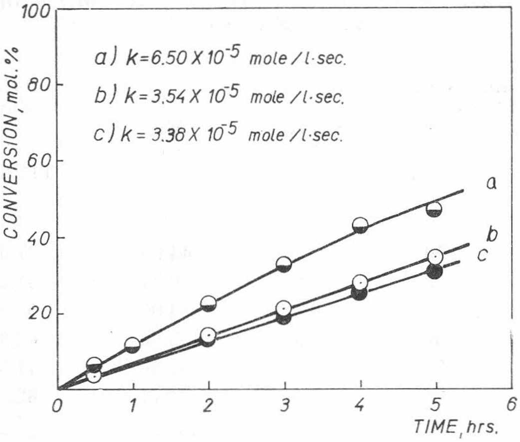

Figure 1. The initial rate of acrylonitrile homopolymerization (a) and copolymerization with 2,4,6-tribromophenyl methacrylate (b) and pentabromophenyl methacrylate (c). Acrylonitrile, 95 mol %, at 60 °C in dimethylformamide with AIBN.

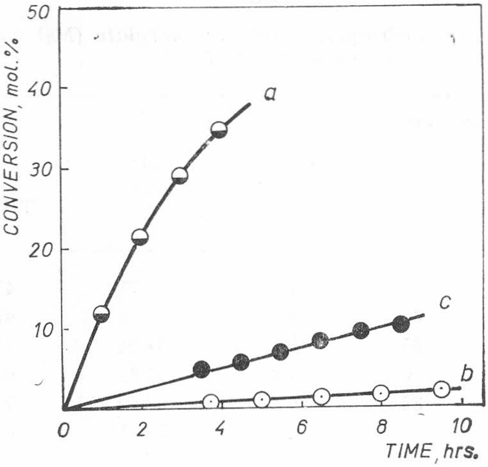

Figure 2. The rate of homopolymerization of acrylonitrile (a), 2,4,6-tribromophenyl methacrylate (b) and pentabromophenyl methacrylate (c) at 70 °C in dimethylformamide with AIBN.

6—8 times higher than those for PBPMA and TBPMA, respectively. These results proved that the brominated phenyl methacrylates were less reactive and polymerized slower than the corresponding acrylic esters, as proposed earlier.[2]

The influence of the molar composition of the initial monomer mixture on the composition of the resulting copolymer is shown in Tables I, II and III. In all copolymerizations, the reactions were stopped before the copolymerization reached 10% conversion; the copolymer composition was established by bromine analysis.

TABLE I

Copolymerization of 2,4,6-Tribromophenyl Methacrylate (M_1) with Acrylonitrile (M_2) in DMF at 60 °C[a]

Experiment No.	Monomer feed mol. %		Conv. %	Br %	Copolymer mol. %, exp.	
	TBPMA	AN			TBPMA	AN
1	10	90	6.2	44.95	27.9	72.1
2	20	80	6.9	50.77	41.2	58.8
3	35	65	6.4	54.08	53.2	46.8
4	50	50	7.9	55.90	62.3	37.7
5	65	35	8.7	57.36	71.5	28.5
6	80	20	3.4	58.74	82.5	17.5

[a] Polymerization conditions: DMF solutions (50 mL) of monomers (0.1 mole) and AIBN (0.24 g) at 60 °C.

TABLE II

Copolymerization of 2,4,6-Tribromophenyl Methacrylate (M_1) with Acrylonitrile (M_2) in Emulsion at 70 °C[a]

Experiment No.	Monomer feed mol. %		Conv. %	Br %	Copolymer mol. %, exp.	
	TBPMA	AN			TBPMA	AN
1	10	90	7.2	50.71	41.1	58.9
2	20	80	9.3	53.18	49.5	50.5
3	35	65	8.1	54.94	57.3	42.7
4	50	50	7.8	56.21	64.1	35.9
5	65	35	6.4	57.40	71.9	28.1
6	80	20	6.9	58.61	81.4	18.6

[a] Polymerization conditions: Aqueous solutions (50 g) of sodium dodecyl benzene sulfonate (2 wt %), monomers (10 g) and $K_2S_2O_8$ (0.04 g) at 70 °C.

TABLE III

Copolymerization of Pentabromophenyl Methacrylate (M_1) with Acrylonitrile (M_2) in DMF at 60 °C[a]

Experiment No.	Monomer feed mol. %		Init. conc. monomer mole/L	Conv. %	Br %	Copolymer mol. %, exp.	
	PBPMA	AN				PBPMA	AN
1	10	90	0.8	5.8	54.08	22.3	77.7
2	20	80	0.8	6.3	60.44	33.3	66.7
3	30	70	0.8	3.2	62.36	38.1	61.9
4	50	50	0.4	8.9	65.24	47.9	52.1
5	65	35	0.3	4.2	65.95	51.0	49.0
6	80	20	0.3	5.6	67.31	57.8	42.2

[a] Polymerization conditions: DMF solution (50 mL) of monomers (0.1 mole) and AIBN (0.24 g) at 60 °C.

The plot of monomer-copolymer mol fraction composition for the TBPMA (M_1) (Figure 3) in both media shows a tendency toward alternating copolymerization, whereas for the PBPMA the azeotropic point (Figure 4) was found. Using the Kelen-Tüdös mean square relationship[10] and confidence intervals[11] we calculated the monomer reactivity ratios (Table IV) from the experimental data. 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 decrease as the amount of bromine in the monomer increases.

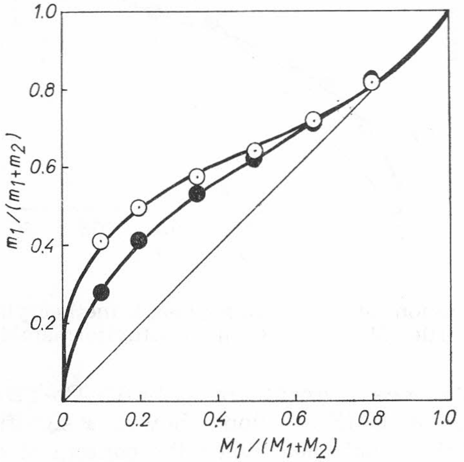

Figure 3. Copolymerization of 2,4,6-tribromophenyl methacrylate (M_1) with acrylonitrile (M_2) in emulsion (○) at 70 °C and in dimethylformamide (●) at 60 °C.

TABLE IV

Copolymerization Parameters for Brominated Methacrylic 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]
2,4,6-Tribromo-phenyl methacrylate[b]	DMF	0.98 ± 0.04	0.20 ± 0.04	0.98/0.02	0.65	—0.08
	Aq. emulsion	0.88 ± 0.03	0.06 ± 0.03	0.89/0.11	1.27	—0.52
Pentabromophenyl methacrylate	DMF	0.12 ± 0.05	0.28 ± 0.03	0.45/0.55	0.24	—0.64

[a] Calculated by the Kelen-Tüdos method.[10]

[b] Ref. 7; $r_1 = 0.74$; $r_2 = 0.19$.

[c] $Q_2 = 0.6$; $e_2 = 1.2$.

Copolymer Properties

The structure of the copolymers was confirmed by their IR spectra (Figure 5), which exibited characteristic absorption peaks at 2240 cm^{-1}, which represents the nitrile band, and absorption at 1760 cm^{-1} showing carbonyl and at 3000—2950 cm^{-1}, which represents —CH_3 group. Two strong peaks at 740 cm^{-1} and 855 cm^{-1} which appear in AN-TBPMA copolymers represent the C—H stretching of the aromatic ring.

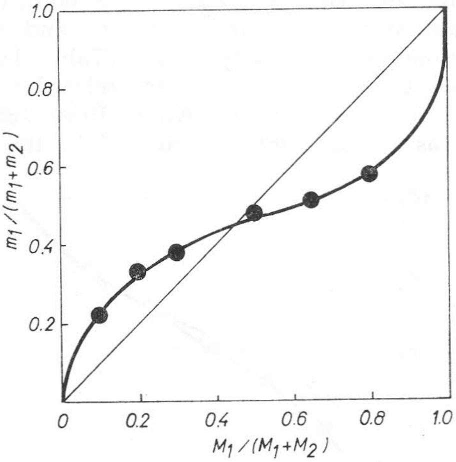

Figure 4. Copolymerization of pentabromophenyl methacrylate (M_1) with acrylonitrile (M_2) at 60 °C in dimethylformamide.

Solution viscosity measurements of poly(AN-Co-TBPMA) and poly(AN--Co-PBPMA) obtained in DMF solutions showed a significant decrease of the intrinsic viscosity of the copolymers when the content of brominated monomer in the copolymer was increased (Figure 6). This lower intrinsic viscosity and presumable lower molecular weight is probably caused by chain transfer

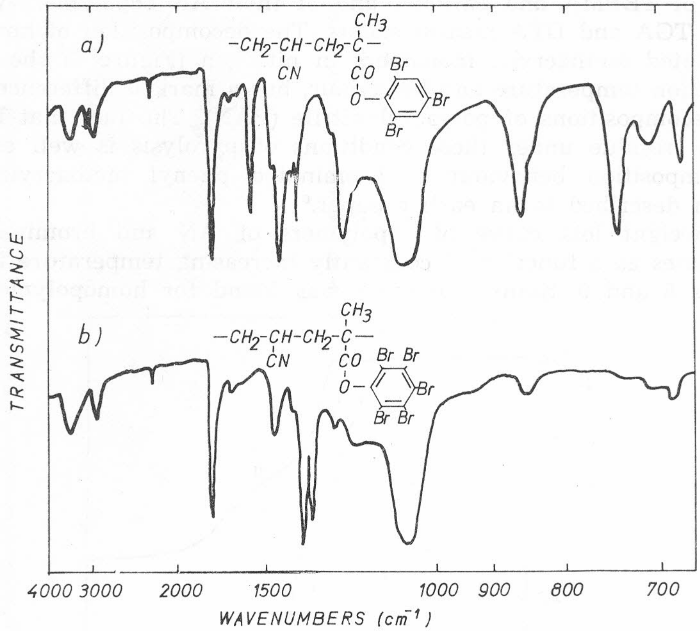

Figure 5. IR spectrum of a) Poly(acrylonitrile-co-2,4,6-tribromophenyl methacrylate), b) Poly(acrylonitrile-co-pentabromophenyl methacrylate).

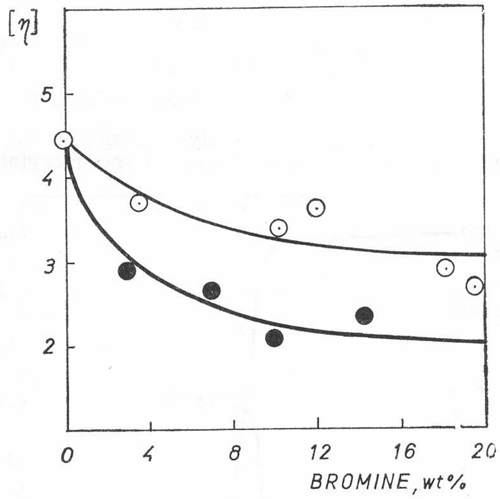

Figure 6. The influence of the content of brominated monomer (Br wt %) in poly-(acrylonitrile-co-2,4,6-tribromophenyl methacrylate (○) and poly(acrylonitrile-co-pentabromophenyl methacrylate) (●) on the intrinsic viscosities in dimethylformamide at 30 °C.

reactions of the growing chain involving the bromine atoms of the monomer or of the polymer, since this is a general tendency of radical polymerization involving bromine-containing monomers.[11,5,6] The thermal stabilities of homopolymers of TBPMA and PBPMA and of their AN copolymers were determined by TGA and DTA measurements. The decomposition of homopolymers of brominated methacrylic monomers in nitrogen (Figure 7) showed similar decomposition temperature and behaviour, but a marked difference was noted for the decompositions of polyacrylonitrile (PAN). The fact that PAN leaves substantial residue under these conditions of pyrolysis is well established.[12] The decomposition behaviour of brominated phenyl methacrylic polymers have been described in an earlier paper.[6]

The weight loss curve of copolymers of AN and brominated phenyl methacrylates as a function of constantly increasing temperature is presented in Figures 8 and 9. Similar to what was found for homopolymers, the AN

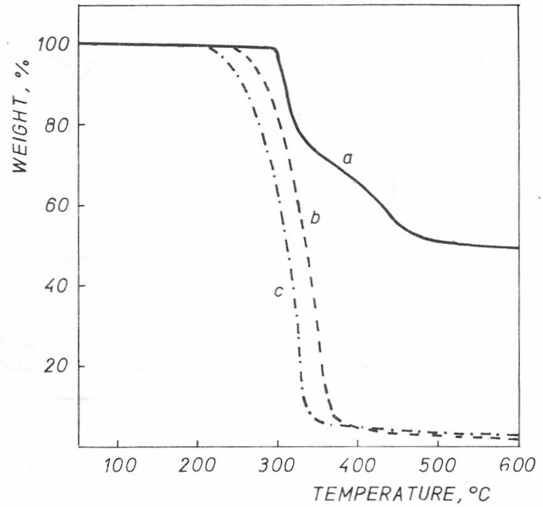

Figure 7. Thermogravimetric analysis of polyacrylonitrile (a), poly(2,4,6-tribromophenyl methacrylate), (b) Poly(pentabromophenyl methacrylate), (c) in nitrogen.

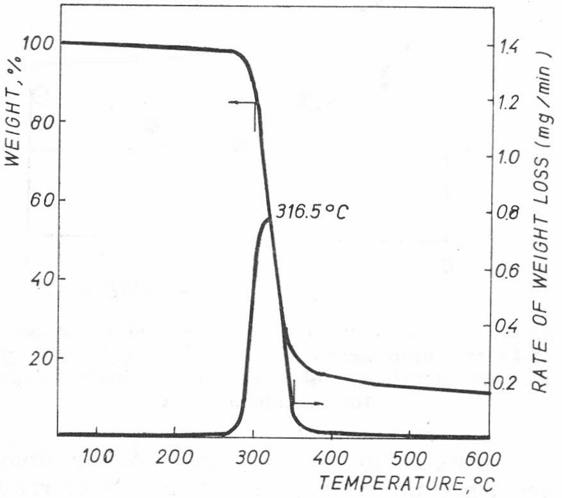

Figure 8. Thermogravimetric analysis of poly(acrylonitrile-co-2,4,6-tribromophenyl methacrylate) (molar ratio 46.8/53.2) in nitrogen.

copolymer of TBPMA showed higher thermal stability than the corresponding PBPMA copolymers. This behaviour is probably due to a higher bromine content of the PBPMA which promotes its faster decomposition. The somewhat higher thermal stability of copolymers in comparison with homopolymers suggests that acrylonitrile monomer sequences contribute to the higher thermal stability of the copolymers. In addition, the copolymers of AN with brominated methacrylic esters are slightly more thermostable than the corresponding one with acrylic esters[4], since the maximum degradation rate temperature is by 30—50 °C higher for the formers.

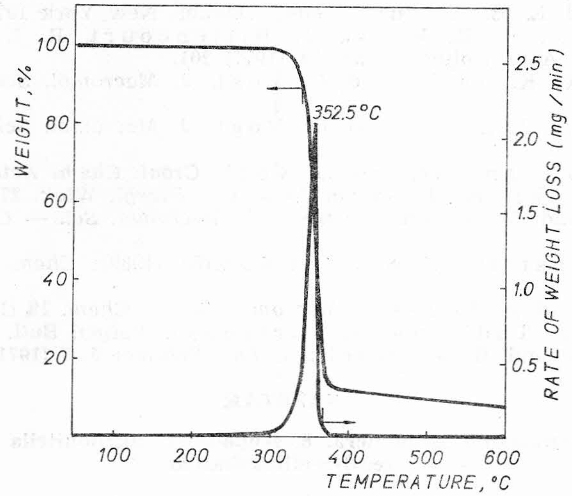

Figure 9. Thermogravimetric analysis of poly(acrylonitrile-co-pentabromophenyl methacrylate) (molar ratio 61.9/38.1) in nitrogen.

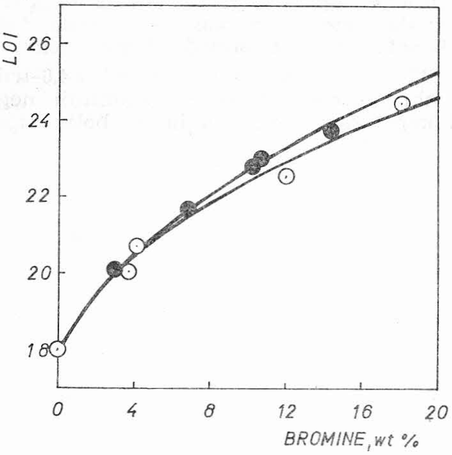

Figure 10. The influence of the content of the brominated monomer (Br wt %) on the limiting oxygen index of poly(acrylonitrile-co-2,4,6-tribromophenyl methacrylate) (○) and poly(acrylonitrile-co-pentabromophenyl methacrylate) (●).

The flammability properties of copolymer of AN and brominated phenyl methacrylates up to 20 wt. % Br contents were determined by measuring of the limiting oxygen index (LOI), and are shown in Figure 10. Only slightly higher values of LOI were found for PBPMA indicating that both brominated monomers are efficient flame retardants for AN polymers.

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SAŽETAK

Kopolimeri bromiranih monomera. 8. Kopolimeri akrilonitrila s bromiranim fenil-metilakrilatom

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Istraživane su termalne značajke i upadljivost polimerâ dobivenih kopolimerizacijom akrilonitrila s 2,4,6-tribromfenil-metakrilatom ili pentbromfenil-metakrilatom. Određeni su omjeri reaktivnosti monomerâ i početne brzine homopolimerizacije i kopolimerizacije. Opaženo je da omjeri reaktivnosti monomerâ donekle ovise o vrsti reakcijskog medija, a reakcijske brzine opadaju u slijedu akrilonitril > pentabromfenil-metakrilat > tribromfenil-metakrilat.

Mjerenja TGA i DTG pokazala su da su poli(2,4,6-tribromfenil-metakrilat) i njegovi kopolimeri s akrilonitrilom termalno stabilniji nego poli(pentabromfenil-metakrilat) i njegovi kopolimeri, koji pak imaju bolju otpornost prema plamenu.