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## Terpolymerization of Butadiene, Acrylonitrile, and Methacrylic Acid

M. B. Jerman<sup>a</sup>; Z. Janović<sup>a</sup>

<sup>a</sup> INA Research and Development Institute, Zagreb, Yugoslavia

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## Terpolymerization of Butadiene, Acrylonitrile, and Methacrylic Acid

M. B. JERMAN and Z. JANOVIĆ

INA

Research and Development Institute  
Zagreb, Yugoslavia

### ABSTRACT

The terpolymerization of butadiene, acrylonitrile, and methacrylic acid in emulsion, using potassium persulfate as initiator and sodium dioctylsulphosuccinate as emulsifier, was investigated. For the binary system butadiene ( $M_1$ ) and methacrylic acid ( $M_2$ ), the following monomer reactivity ratios were determined:  $r_{12} = 0.18 \pm 0.05$  and  $r_{21} = 0.52 \pm 0.09$ . When polymerizations were stopped at low conversions they gave terpolymers which show good agreement between experimental and theoretical copolymerization composition data, calculated from the Alfrey-Goldfinger equation. The relationships between monomer feed and terpolymer compositions are presented on triangular coordinate graphs as proposed by Slocombe. By using a computer program, the lines of unique composition and the lines of binary azeotropic composition were established. No point of true azeotropic composition was found, but a "pseudo-azeotropic" region was recognized. The influence of composition on glass transition temperature and thermal characteristics of the terpolymers is described.

## INTRODUCTION

Carboxylated butadiene polymers are a known class of elastomeric materials with wide usefulness [1]. The carboxylic moieties in the butadiene polymer chain provide additional modifications of physical and chemical properties, particularly in terpolymer systems.

Terpolymerization is a useful method for preparing such polymers. However, attention must be paid to obtaining a homogeneous structure of multicomponent systems.

Only a few studies have been published with data of the ternary polymerization of butadiene (Bu), acrylonitrile (AN), and methacrylic acid (MAA) [2, 3]. Most of the preparations and end-use properties have been claimed in the patent literature [4, 5].

In the present study the terpolymerization of Bu/AN/MAA carried out in emulsion was investigated. The kinetics of the polymerization of the ternary monomer mixture, the identification of the azeotropic composition, and the measurements of some properties of the terpolymers, particularly their thermal behavior, were other objectives of this investigation.

## EXPERIMENTAL

Materials

Butadiene (Hüls Chem. Co.), polymerization grade, was distilled over molecular sieves and condensed at  $-20^{\circ}\text{C}$ . Acrylonitrile was distilled at atmospheric pressure at  $77^{\circ}\text{C}$ . Methacrylic acid (Fluka) was distilled at  $63\text{--}64^{\circ}\text{C}$  (12 mm). Other chemicals were the initiator, analytical grade potassium persulfate (Merck), and the emulsifier, sodium dioctylsulfosuccinate (Aerosol OT, American Cyanamid Co.). They were commercial products.

Measurements

IR spectra were recorded on a Perkin-Elmer Model 137 B spectrophotometer. The samples were in the form of films cast from tetrahydrofuran solution onto sodium chloride plates.

$^1\text{H-NMR}$  spectra were determined on a 90-MHz Varian EM-390 spectrometer. The measurements were carried out in deuterated chloroform or methanol solutions with TMS as internal standard.

Molecular weights of terpolymers were determined by gel permeation chromatography on a Varian-8500 model instrument in tetrahydrofuran solutions.

Thermogravimetric analyses and glass transition temperature measurements were carried out on Perkin-Elmer TGS-2 and DSC-2 in-

struments under a stream of nitrogen and a heating rate of 10 and 20°C/min, respectively.

The copolymer composition was determined by nitrogen estimation by the Dumas method for the acrylonitrile content and by acid titration for the methacrylic acid content. Acid titration was performed in dimethylformamide solution using 0.1 N alcoholic KOH with phenolphthalein as indicator.

### Polymerization Procedure

Emulsion polymerization was carried out in the following way. Distilled water (1.8 parts) was placed in a magnetically stirred Wheaton pressure bottle, purged with nitrogen, and Aerosol OT (0.025 parts) and potassium persulfate (0.03 parts) were added. The reactor was cooled to -20°C and the monomers (1 part) were added. The reactor was placed in a thermostated water bath which was maintained at 50 ± 0.5°C.

All polymerizations were carried out to low conversions. The polymerization was stopped by pouring the reaction mixture into saturated aqueous NaCl. The emulsion was broken, the product was filtered off, and it was washed with water. The polymer was finally dried for 24 h at 60°C and 0.1 mm.

### Esterification

The methyl ester of butadiene-acrylonitrile-methacrylic acid terpolymer was prepared via an acyl chloride intermediate with oxalyl chloride and subsequent esterification with methanol and pyridine [6]. Thus, to a solution of terpolymer (5 g) in dry tetrahydrofuran (200 mL), oxalyl chloride (3 mL) was added. After 6 h of stirring at 45°C a mixture of methanol (5 mL) and pyridine (5 g) was added and stirring was continued for another 6 h. The precipitate was removed by filtration and the polymeric ester was precipitated in methanol, separated, and dried.

## RESULTS AND DISCUSSION

### Terpolymerization

Free radical terpolymerization of Bu/AN/MAA was carried out in aqueous emulsion. Reactivity ratios for the monomer pairs presented in Table 1 had been determined previously [7, 8] except for the binary system Bu-MAA which we estimated experimentally. Calculations were carried out according to the Kelen-Tüdös graphical and mean square relationship [9] and the confidence intervals method [10]. The results

TABLE 1. Monomer Reactivity Ratios for the System Butadiene (1)-Acrylonitrile (2)-Methacrylic Acid (3)

$r_{12} = 0.35 \pm 0.01$	$r_{21} = 0.05 \pm 0.01$	Ref. 7
$r_{23} = 0.128 \pm 0.001$	$r_{32} = 2.40 \pm 0.03$	Ref. 8
$r_{13} = 0.18 \pm 0.05$	$r_{31} = 0.52 \pm 0.09$	This work

TABLE 2. Copolymerization of Butadiene (Bu) and Methacrylic Acid (MAA) in Emulsion at 50°C<sup>a</sup>

Expt	Monomer feed mole fraction		Conversion (wt%)	Copolymer mole fraction		COOH <sup>b</sup> (wt%)
	Bu	MAA		Bu	MAA	
1	0.863	0.137	10.6	0.675	0.325	22.72
2	0.705	0.295	9.9	0.536	0.464	30.34
3	0.518	0.482	4.5	0.435	0.565	37.27
4	0.373	0.627	10.3	0.375	0.625	38.01
5	0.285	0.715	8.0	0.322	0.678	40.31

<sup>a</sup>Polymerization conditions: monomers, 25 g; water, 45 g;  $K_2S_2O_8$ , 0.75 g; Aerosol OT (75%), 0.85 g.

<sup>b</sup>By titration

are illustrated in Table 2 and by Fig. 1. The values obtained for the reactivity ratios,  $r_{12} = 0.18 \pm 0.05$  and  $r_{21} = 0.5 \pm 0.09$ , are in good accordance with the values calculated from Q and e data [3].

The relationship between the molar compositions of the polymer obtained in terpolymerizations carried out to low conversions, the composition values calculated using the Alfrey-Goldfinger [11] equation, and the corresponding compositions of the monomer feed mixtures are summarized in Table 3. The terpolymer compositions were determined by elemental analysis for nitrogen and by acid titration. Small changes in values of the reactivity parameters of binary copolymerizations are known to influence significantly the calculated values for terpolymer composition [12]. The good agreement observed between experimental and theoretical data is an indication of the reliability of the reactivity parameters of the binary copolymers.

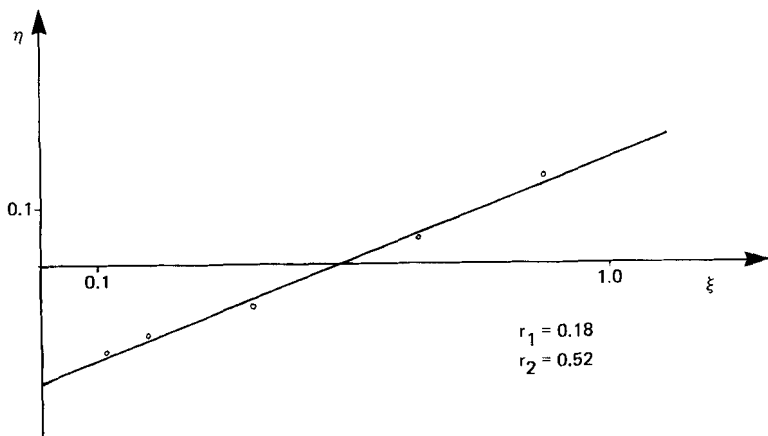


FIG. 1. Kelen-Tüdös plot for determination of monomer reactivity ratios of butadiene-methacrylic acid emulsion polymerization.

Moreover, it can be concluded that the free radical polymerization of the ternary system Bu/AN/MAA follows classical copolymerization theory.

The relationship between the molar compositions in the monomer feed and in the resulting terpolymers is represented in the form of triangular plots as proposed by Slocombe [13] (Fig. 2). Connecting the points of correspondence, with the heads of the arrows indicating the initial terpolymer composition and the tails of the arrows indicating the composition of the monomer feed, one can observe that the arrows point toward a line which corresponds to the connecting line between binary azeotropic compositions of the pairs Bu/AN (59/41) and Bu/MAA (36.9/63.1), designated by Slocombe as the azeotropic line. Further, the arrows become shorter when located near the azeotropic line, indicating that the composition of the terpolymers becomes similar to that of the corresponding monomer feed.

The behavior of each monomer during the polymerization reaction was examined by computing the theoretical copolymerization curves. Monomer and polymer compositions calculated by the Alfrey-Goldfinger equation were computed by the Runge-Kutta 4th order integration procedure according to Chan and Meyer [12] by using a computer program. A graphic method developed by Rios and Guillot [14] for determination of azeotropic lines was used. The unitary azeotropic lines ( $M_1 = m_1$ ) for the three monomers and the difference between terpolymer composition (dashed lines) and the composition of the monomeric mixture (full lines) in the terpolymerization reaction ( $M_1 = \text{Bu}$ ,  $M_2 = \text{AN}$ ,  $M_3 = \text{MAA}$ )

TABLE 3. Terpolymerization of Butadiene (Bu), Acrylonitrile (AN), and Methacrylic Acid (MAA) in Emulsion at 50°C<sup>a</sup>

Expt	Monomer feed mole fraction			Conversion (wt%)	N <sup>b</sup> (wt%)	COOH <sup>c</sup> (wt%)	Terpolymer composition					
	Bu	AN	MAA				Mole fraction, experimental			Mole fraction, calculated <sup>d</sup>		
							Bu	AN	MAA	Bu	AN	MAA
1	0.733	0.132	0.135	2.0	4.01	21.69	0.511	0.182	0.307	0.597	0.131	0.272
2	0.572	0.098	0.330	1.0	2.13	28.89	0.461	0.103	0.436	0.490	0.064	0.446
3	0.548	0.209	0.243	3.0	4.11	20.92	0.520	0.186	0.294	0.501	0.145	0.354
4	0.537	0.328	0.135	5.0	6.30	17.66	0.482	0.277	0.241	0.526	0.252	0.222
5	0.364	0.501	0.135	6.0	5.68	19.81	0.470	0.254	0.276	0.472	0.324	0.204
6	0.218	0.649	0.133	13.0	10.15	15.80	0.350	0.438	0.212	0.413	0.381	0.206
7	0.205	0.313	0.482	6.0	4.35	34.60	0.229	0.222	0.549	0.305	0.149	0.546

<sup>a</sup> Polymerization conditions: monomers, 25 g; water, 45 g; K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, 0.75 g; Aerosol OT (75%), 0.85 g.

<sup>b</sup> By the Dumas method.

<sup>c</sup> By titration.

<sup>d</sup> According to the Alfrey-Goldfinger equation [11].

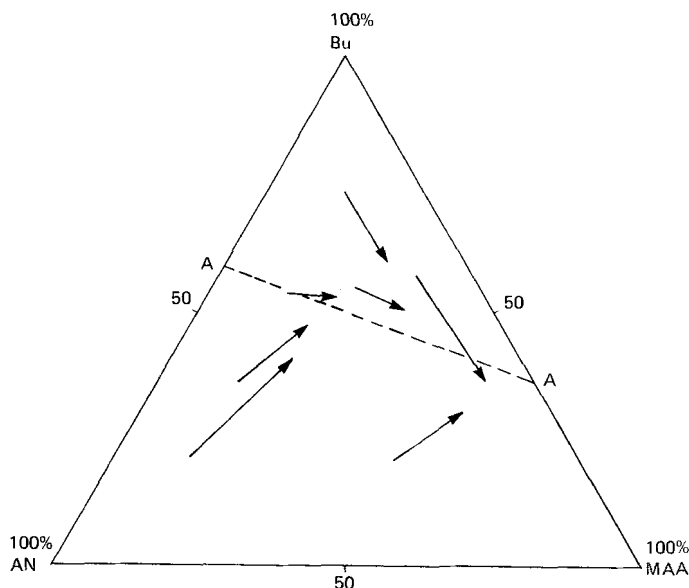


FIG. 2. Monomer-terpolymer triangular composition plot for the system butadiene-acrylonitrile-methacrylic acid in emulsion at 50°C.

in emulsion are presented in Fig. 3. The three lines do not intersect; therefore, no true azeotropic point exists.

Azeotropic lines of binary composition ( $M_1/M_j = m_i/m_j$ ) of Bu/AN ( $M_1/M_2$ ) and Bu/MAA ( $M_1/M_3$ ), presented in Fig. 4, are separate again proving that no ternary azeotropic point exists.

Terpolymerizations up to high conversions were examined with two characteristic different compositions of the initial monomer ( $f$ ) mixture. The average ( $F_x A_v$ ) and instantaneous ( $F$ ) terpolymer compositions were calculated in dependence on conversion. In terpolymerization with an initial monomer composition ( $f$ ) Bu/AN/MAA of 0.218/0.644/0.133 mole ratio (Table 3, Expt 6), the difference between monomer feed composition and the contents of monomer units in the terpolymer (Fig. 5) is evident. When the initial monomer composition of Bu/AN/MAA was 0.537/0.328/0.135 molar ratio (Table 3, Expt 4), which is located on Slocombes azeotropic line and nearby for the unique azeotropic line for butadiene, the dependence of the average and the instantaneous terpolymer composition on conversion is negligible for butadiene but more pronounced for acrylonitrile and methacrylic acid (Fig. 6).



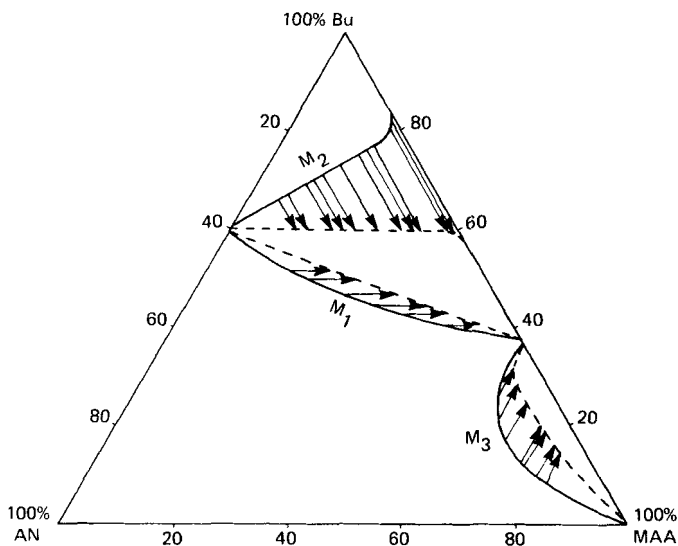


FIG. 3. Unitary azeotropic lines in terpolymerization reaction of butadiene-acrylonitrile-methacrylic acid in emulsion at 50°C; monomer mixture (—), terpolymer composition (--).

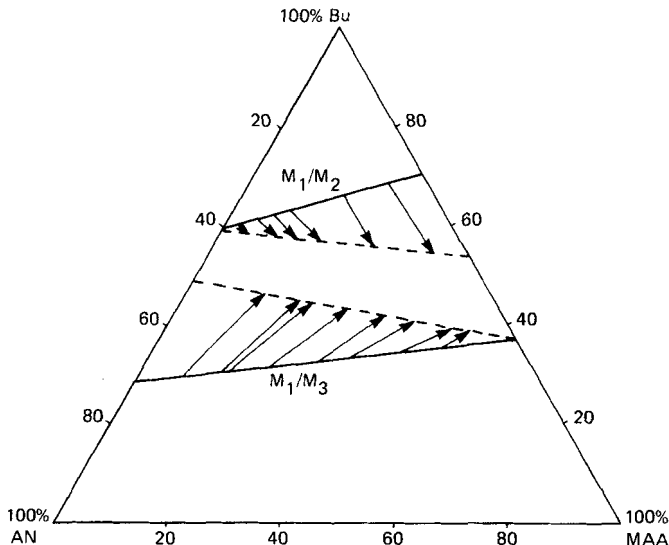


FIG. 4. Binary azeotropic lines in terpolymerization reaction of butadiene-acrylonitrile-methacrylic acid in emulsion at 50°C; monomer mixture (—), terpolymer composition (--).

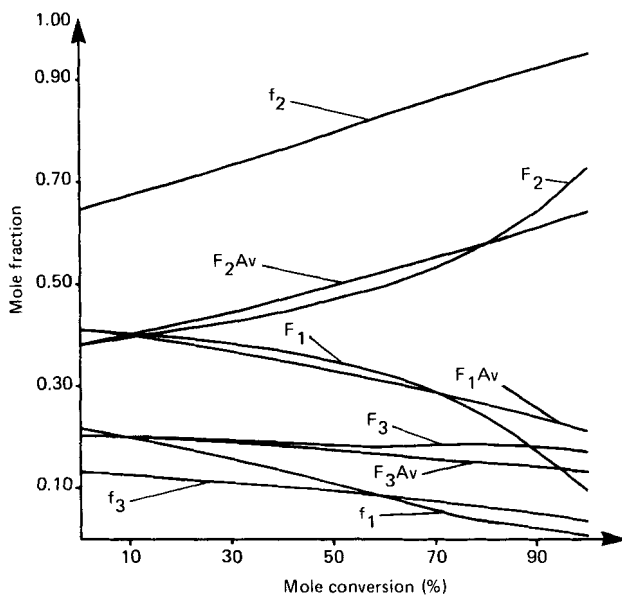


FIG. 5. The variation of monomers ( $f$ ), instantaneous ( $F$ ) and average ( $F_x Av$ ) terpolymer compositions during the terpolymerization reaction of butadiene (1), acrylonitrile (2), and methacrylic acid (3). Monomer mixture feed molar ratio:  $f_1 = 0.218$ ,  $f_2 = 0.649$ ,  $f_3 = 0.133$ .

TABLE 4. Glass Transition Temperatures of Bu/AN/MAA Terpolymers

Sample	Composition (wt%)			$T_g$ ( $^{\circ}C$ )
	Bu	AN	MAA	
1	17.3	16.5	66.2	224
2	31.3	38.5	30.2	209
3	36.7	8.0	55.3	88
4	45.6	14.4	40.0	30
5	48.1	32.4	19.5	19

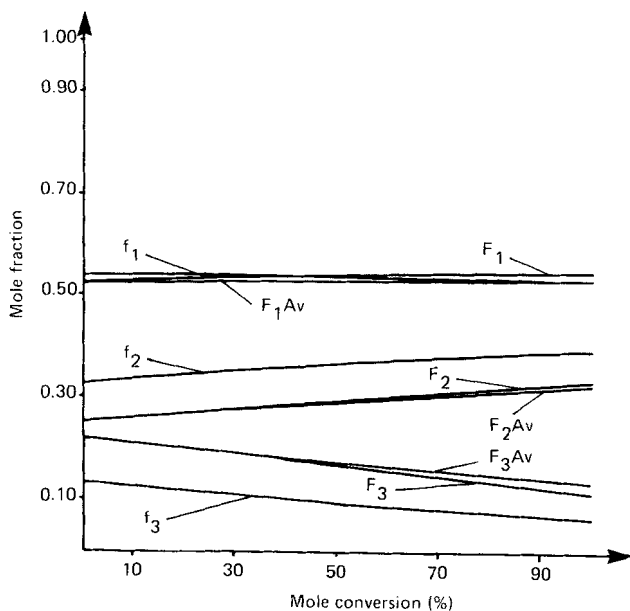


FIG. 6. The variation of monomers ( $f$ ), instantaneous ( $F$ ), and average ( $F_{xAv}$ ) terpolymer compositions during the terpolymerization reaction of butadiene (1), acrylonitrile (2), and methacrylic acid (3). Monomer mixture feed molar ratio:  $f_1 = 0.537$ ,  $f_2 = 0.328$ ,  $f_3 = 0.135$ .

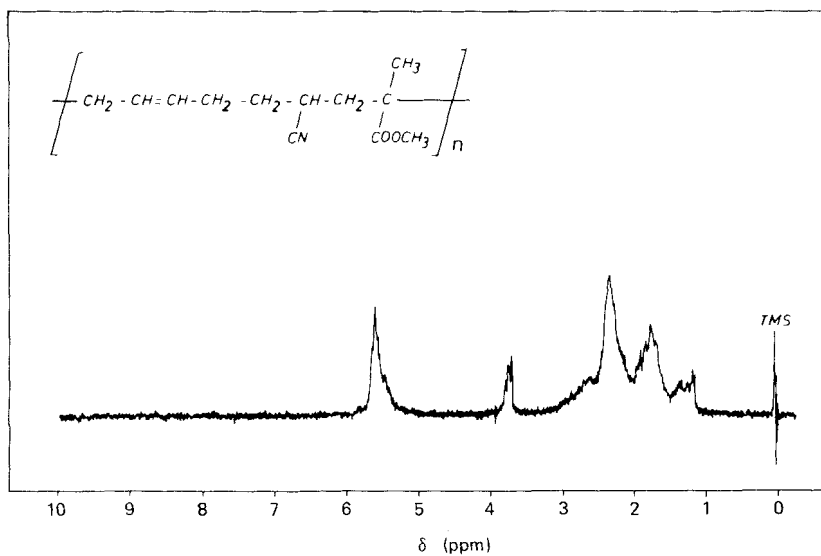


FIG. 7.  $^1\text{H-NMR}$  spectrum of methyl ester of butadiene-acrylonitrile-methacrylic acid terpolymer in  $\text{CDCl}_3$  at room temperature.

### Terpolymer Properties

The structure of terpolymer was confirmed by the  $^1\text{H-NMR}$  spectrum of its more soluble methyl ester (Fig. 7). A characteristic chemical shift value for the methyl protons of methacrylic acid was at  $\delta = 1.1\text{--}1.5$  ppm, for the methine and methylene protons of the polymer backbone chain at  $\delta = 1.3\text{--}3.0$  ppm, for the methyl ester group at  $\delta = 3.8$  ppm, and for the butadiene methine groups at  $\delta = 5.65$  ppm.

Molecular weights estimated by gel permeation chromatographic analyses were for  $\bar{M}_w$  in the range from 20,000 to 25,000 indicating that a high molecular weight polymer was obtained.

The thermal stability and the glass transition temperatures were studied by TGA and DSC measurements. The influence of the composition of terpolymers on the values of  $T_g$  are presented in Table 4.

It is evident that  $T_g$  is highly dependent on the content of butadiene units in the terpolymer.

The TGA curves show that for the terpolymers Bu/AN/MAA with various compositions the rates of decomposition are quite different (Fig. 8). These results indicate that the overall thermal stability of the polymer depends very much on the thermal stability of each contained unit, particularly on the MAA content. The thermal be-

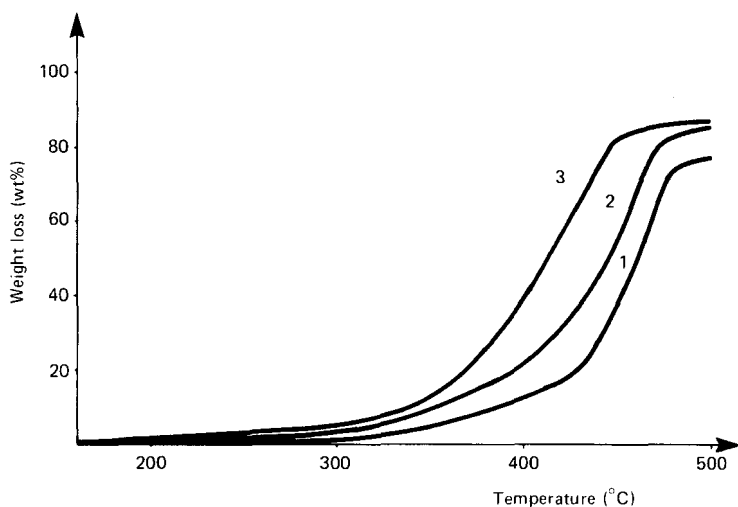


FIG. 8. TGA thermograms of terpolymers of various composition: (1) 48.1% Bu, 32.4% AN, 19.5% MAA; (2) 45.6% Bu, 14.4% AN, 40.0% MAA; (3) 17.3% Bu, 16.5% AN, 66.2% MAA.

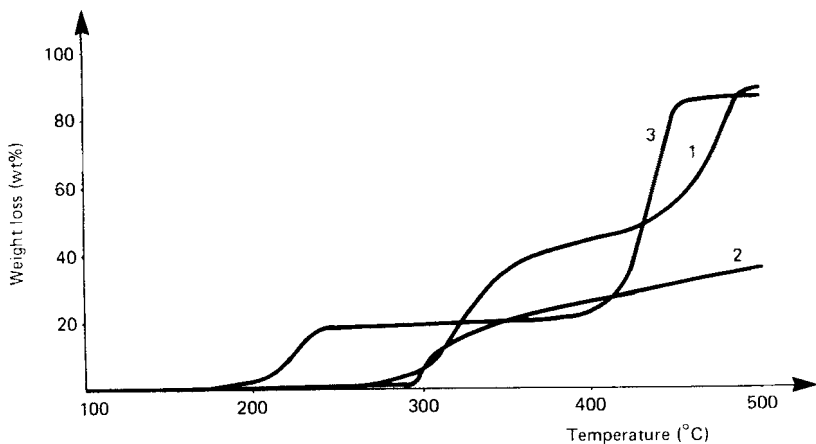


FIG. 9. TGA thermograms of homopolymers: (1) polybutadiene, (2) polyacrylonitrile, (3) polymethacrylic acid.

havior of the terpolymers is similar to the thermal degradation behavior of homopolymers (Fig. 9), indicating that MAA appears to be thermally the weakest link in the terpolymer.

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