

COMPOSITION OF TERNARY COPOLYMERS AND COPOLYMERIZATION CONSTANTS OF BUTYL METHACRYLATE, GLYCYDYL METHACRYLATE AND METHACRYLIC ACID*

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THE previous paper [1] reported the synthesis of ternary thermosetting copolymers of butyl methacrylate (BMA), glycidyl methacrylate (GMA) and methacrylic acid (MA) capable of hardening at increased temperatures.

The purpose of this paper is to study the composition of copolymers obtained in relation to the composition of the initial monomer mixture and determine the copolymerization constant of BMA with GMA, BMA with MA and GMA and MA.

EXPERIMENTAL

Copolymerization of BMA with GMA, BMA with MA and GMA with MA was effected in cyclohexanone solution at 80° by a radical mechanism in the presence of azobisisobutyronitrile. Monomer concentration in the reaction mixture was 30%, and the quantity of initiator 0.2 moles-%.

The purification of initial products and GMA synthesis are described in paper [1].

The monomers, solvent and initiator were placed in ampoules which were cooled to -40° and evacuated three times, nitrogen being subsequently introduced. Then, the ampoules were placed in a thermostat, in which a given temperature was maintained with an accuracy of up to $\pm 0.1^\circ$ and copolymerization was carried out. The degree of monomer conversion did not exceed 10%. The copolymers obtained were purified by re-precipitation with petroleum ether and dried to constant weight *in vacuo*. Copolymer composition was calculated from the carboxyl and glycidic group contents. The content of carboxyl groups was determined by titration of a copolymer batch dissolved in acetone with 0.05 N potassium hydroxide solution with phenolphthalein. Glycidic group content was determined by the King method [2] using acetone as solvent.

DISCUSSION

Copolymerization constants, r_1 and r_2 were calculated from the Fineman and Ross equation [3].

Figure 1 presents the diagrammatic determination of copolymerization constants from the data of Tables 1-3. The straight lines on the diagrams were drawn through the experimental points by the method of least squares. The gradient of the straight line is r_1 and the section cut of on the ordinate is equal to

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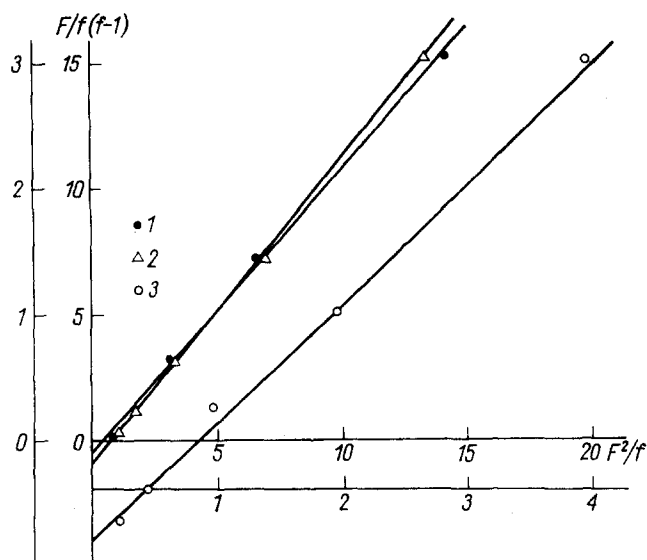


FIG. 1. Determination of constants r_1 and r_2 in copolymerization of GMA with BMA, GMA with MA and BMA with MA: 1—BMA-MA; 2—GMA-MA; 3—GMA-BMA.

TABLE 1. COPOLYMERIZATION OF GMA (M_1) WITH BMA (M_2)

Initial monomer mixture, mole-%		Content of glycidic groups in the copolymer, %	Copolymer composition, mole-%	
M_1	M_2		m_1	m_2
50.00	50.00	19.47	50.65	49.35
66.70	33.30	25.75	67.00	33.00
80.00	20.00	30.75	79.80	20.20
33.30	66.70	13.85	36.00	64.00
20.00	80.00	21.75	21.75	78.25

TABLE 2. COPOLYMERIZATION OF GMA (M_1) WITH MA (M_2)

Initial monomer mixture, mole-%		Content of glycidic groups in the copolymer, %	Acid number of the copolymer, mg KOH/g	Copolymer composition, mole-%	
M_1	M_2			m_1	m_2
50.0	50.0	17.95	176.50	50.75	49.25
66.7	33.3	25.50	106.90	70.63	29.37
80.0	20.0	30.95	65.35	82.80	17.20
88.9	11.1	33.55	34.50	90.10	9.90
94.1	5.9	35.75	19.35	35.00	5.00

TABLE 3. COPOLYMERIZATION OF BMA (M_1) WITH MA (M_2)

Initial monomer mixture, mole-%		Acid number of the copolymer, mg KOH/g	Copolymer composition, mole-%	
M_1	M_2		m_1	m_2
50.0	50.0	224.00	53.80	46.20
66.7	33.3	133.00	70.40	29.60
80.0	20.0	68.35	83.70	16.30
88.9	11.1	38.48	90.55	9.45
94.1	5.9	21.10	94.70	5.30

the negative value of r_2 . For the copolymerization of GMA with MA and BMA with MA the initial monomer ratios were such that reaction took place in a homogeneous medium. The values of the copolymerization constants obtained are shown in Table 4.

As shown in the Tables, in all the cases investigated, GMA is the most reactive and MA the least reactive, monomer. During copolymerization of GMA with MA the product of copolymerization constants, $r_1 \times r_2 = 1$ which characterizes the random arrangement of both types of monomer units in the polymer chain.

In the event of copolymerization of GMA with BMA and BMA with MA, the $r_1 \times r_2 < 1$, i.e. in these systems the monomer units alternate in the polymer chain and the tendency for alternation is stronger for copolymerization of BMA with MA which is obviously due to the varying polarity of these monomers (see Table 5.)

TABLE 4. COPOLYMERIZATION CONSTANTS

Monomers		r_1	r_2	$r_1 \times r_2$	Literature source
M_1	M_2				
GMA	BMA	0.94	0.79	0.74	—
GMA	BMA	0.75	0.69	0.57	[9]
BMA	MA	1.11	0.53	0.59	—
BMA	MA	1.20	0.75	0.90	[4]
GMA	MA	1.18	0.85	1.00	—

TABLE 5. ACTIVITY FACTORS OF BMA, GMA AND MA

Monomer	Q	e	Literature source
GMA	0.80	0.32	—
GMA	0.87	0.38	[7]
GMA	0.78	-0.02	[6]
BMA	0.72	-0.23	[6]
MA	0.55	0.65	—

Of all systems studied, only in copolymerization of GMA with BMA, (r_1 and $r_2 < 1$) was an azeotropic mixture obtained with a BMA content in the initial monomer mixture of 30 moles-% (Fig. 2).

From the copolymerization constants obtained the activity factors, Q and e were determined for GMA and MA by the semi-quantitative system of Alfrey and Price [5]. The Q and e values available for BMA were used in the calculation [6]. The results obtained are shown in Table 5.

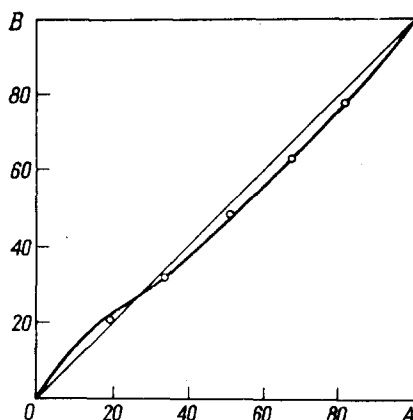


FIG. 2. Dependence of copolymer composition on the composition of the initial monomer mixture during copolymerization of GMA with BMA. *A*—BMA content in the monomer mixture, mole-%; *B*—BMA content in the copolymer, mole-%.

TABLE 6. COMPOSITIONS OF TERNARY COPOLYMERS OF BMA, GMA AND MA

Composition of monomer mixture, mole-%			Content of glycidic groups in the copolymer, %	Acid number of copolymer mg KOH/g	Copolymer composition, mole-%					
					from analytical data			calculated		
BMA	GMA	MA			BMA	GMA	MA	BMA	GMA	MA
33.3	33.3	33.4	15.00	126.0	38.0	33.8	28.2	37.5	35.0	27.5
50.0	25.0	25.0	11.50	90.0	52.3	26.9	20.8	51.3	26.5	20.4
25.0	50.0	25.0	22.10	89.0	28.1	51.1	20.8	27.8	51.5	20.7
25.0	25.0	50.0	12.41	218.0	29.6	25.9	44.5	31.0	26.5	42.5
66.6	16.7	16.7	7.30	61.0	67.5	17.8	14.8	67.5	18.6	13.9
80.0	10.0	10.0	4.40	36.0	80.1	11.0	8.9	79.7	11.7	8.6

The activity factors of GMA, as follows from the table, satisfactorily agree with literature data.

The copolymerization constants were used to estimate the composition of ternary copolymers of BMA, GMA and MA which were synthesized in cyclohexanone at 80° by a radical mechanism, as described in paper [1]. The degree of monomer conversion was less than 20%. The theoretical composition of three-component polymers was calculated by the Alfrey and Goldfinger differential equation [8].

The compositions of some copolymers obtained are shown in Table 6.

The similarity of copolymer compositions calculated from the Alfrey-Goldfinger equation and from chemical analysis data verifies the sufficient accuracy of determining r_1 and r_2 and the applicability of the Alfrey-Goldfinger equation for the case described.

CONCLUSIONS

(1) Copolymerization constants, r_1 and r_2 were determined in copolymerization of GMA with BMA, GMA with MA and BMA with MA.

(2) It was found that GMA is the most reactive and MA the least active monomer in the systems investigated.

(3) In the copolymerization of GMA with BMA an azeotropic mixture, with a content of 30 moles-% of BMA in the initial monomer mixture, is formed.

(4) The activity factors, Q and e were determined for GMA and MA according to the Alfrey and Price system.

(5) The composition of ternary copolymers of BMA, GMA and MA were estimated from the copolymerization constants obtained. Experimental and calculated data showed satisfactory agreement.

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POLYMERIZATION OF ETHYLENE IN THE PRESENCE OF VARIOUS COMPOSITE CATALYSTS BASED ON TiCl_3 *

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SEVERAL regularities have now been elucidated for polymerization in the presence of composite catalysts based on TiCl_3 , however the nature of the active centres of these composite catalytic systems has not so far been clarified.

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