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A. A. BERLIN, G. L. POPOVA, and E. F. ISAEVA

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**Abstract**

**Full Text**

## **Reports of the Academy of Sciences of the USSR**

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**Chemistry**

A. A. BERLIN, G. L. POPOVA, and E. F. ISAEVA

### **ON CONDENSATION TELOMERIZATION AND A NEW TYPE OF UNSATURATED POLYESTERS (POLYESTER ACRYLATES)**

*(Presented by Academician A. V. Topchiev, 25 VI 1958)*

A study of the polymerization of dimethacrylic, allyl methacrylic, and carboxyallyl methacrylic esters of glycols showed that, as the distance between double bonds increases, the rate of polymerization increases <sup>(1-2)</sup>.

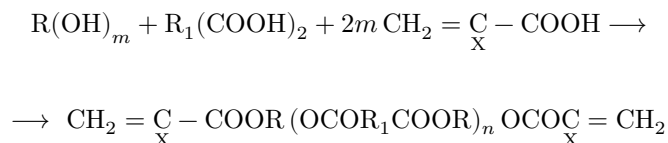
This feature of di- and polyfunctional acrylates distinguishes them from the corresponding simple and complex diesters of allyl and vinyl alcohols.

The possibility of obtaining highly active di- and polyfunctional monomers with a large size of "transverse" groups is of considerable theoretical and practical interest, since in this case it becomes possible: 1) to vary the flexibility of transverse bonds, 2) to regulate contraction in the transition from monomer to three-dimensional polymer, and 3) to obtain heat-resistant polymeric products with a wide range of physicomechanical properties.

For the synthesis of such substances we used the principle of regulating chain growth in the polyesterification of dibasic acids with glycols and glycerol by adding methacrylic (or acrylic) acid. Such a method for obtaining comparatively low-molecular compounds with a specified type of terminal functional groups should be regarded as an example of telomerization proceeding by a condensation mechanism ( "condensation telomerization" ).

The mechanism of reactions of this kind has not yet been studied, although there are indications of the possibility, during polyesterification, of amidolysis processes leading to a decrease in polydispersity and  $M_{av}$  upon the addition of saturated monobasic acids in the polyesterification of dicarboxylic acids with glycols <sup>(3,4)</sup>.

In general form, the process of formation of polyesters with terminal methacrylic (or acrylic) groups, which we have named "polyester acrylates," may be represented by the scheme



The condensation telomerization reaction was carried out in inert solvents (benzene, toluene) with azeotropic removal of the reaction water.

Phosphoric, sulfuric, ethylsulfuric, and *p*-toluenesulfonic acids were tested as catalysts.

The highest rate of the process (8-12 hours) and the highest yields of polyester acrylates (85-95% of theoretical, based on the dibasic acid)

achieved when using 2-3% sulfuric or *p*-toluenesulfonic acid in the presence of 0.5-0.8% hydroquinone.

Under the adopted conditions, the degree of polymerization of the polyester acrylate depends mainly on the ratio of the components and, first of all, on the dosage of methacrylic (or acrylic) acid.

For calculating the degree of polymerization, as a first approximation one may use the simple relation derived for analogous polyesters:

$$n = \frac{2L}{B},$$

where  $L$  is the number of moles of dibasic acid, and  $B$  is the number of moles of monobasic acid.

Accordingly, at the ratio: 1 mole of dibasic acid, 2 moles of glycol, and 2.0 moles of methacrylic acid, the formation of polyester acrylates with  $n = 1$  may be expected. When glycerol is used, a monomeric product should be obtained with 4.0 moles of monobasic acid.

Reducing the amount of methacrylic acid to 0.5-0.1 mole leads to the production of more highly polymeric polyester products ( $n \geq 4$ ). After distillation, washing, and drying, the synthesized polyesters were purified from resin-like impurities with active aluminum oxide.

It was not possible to carry out fractional distillation of the polyester acrylates under a vacuum down to  $10^{-5}$  mm because of their low volatility and very great tendency toward polymerization.

Determination of the average molecular weight by the cryoscopic method, molecular refraction, bromine and ester numbers, elemental analysis, and hydroxyl-group content indicates that the main mass of the synthesi-

### Table 1

### Physicochemical characteristics of polyester acrylates

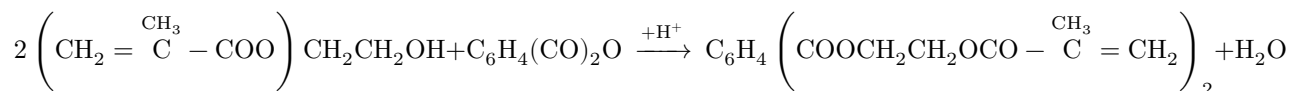
No.	Name of compound (by meanat for- 20°; M <sub>cr</sub> , M <sub>cr</sub> , mola)ps	Viscosity found calc.	$n_D^{20}$	$d_{20}^{20}$ , g/cm <sup>3</sup>	MR, found	MR, calc.	Bromi ber, found	Bromi ber, calc.	Ester ber, found	Ester ber, calc.	Note
1	Dimethacrylate-390 bis-50125 ethylene glycol ph-tha-late	110-310	1.5000	1.180	97.29	96.94	80.0	82	570.0	575.0	No HO groups were found in any of the polyester acrylates
2	Dimethacrylate-478 bis-150125 ethylene glycol ph-tha-late	110-395	1.4930	1.165	119.20	118.64	63.0	64	470.0	486.6	No HO groups were found in any of the polyester acrylates

No.	Name of compound (by meanat formula)	Viscosity for- 20°	$M_{cr}$	$M_{cr}$	$n_D^{20}$	$d_{20}^{20}$	MR	MR	Bromi-ber, found	Bromi-ber, calc.	Ester-ber, found	Ester-ber, calc.	Note
3	Dimethyl-100520 bis-150200 triethylene glycol phthalate	1.489	11.165	140.50	1.466	1.165	140.50	140.46	60.0	56.5	393.0	395.7	Acid numbers of the purified polyester acrylates are close to 0.0
4	Dimethyl-100580 bis-300400 ethylene glycol sebacinate	1.466	1.095	152.30	1.489	1.095	152.30	153.39	50.0	53.1	336.0	372.0	Acid numbers of the purified polyester acrylates are close to 0.0
5	Tetra-300150 bis-50004000 glycerin phthalate	1.489	1.180	143.30	1.489	1.180	143.30	135.47	72.0	122.8	550.0	573.0	

No.	Name of compound (by meanat for- 20°; M <sub>cr</sub> , M <sub>cr</sub> , n <sub>D</sub> <sup>20</sup> )	m <sub>cr</sub> found	m <sub>cr</sub> calc.	n <sub>D</sub> <sup>20</sup>	d <sub>20</sub> <sup>20</sup> , g/cm <sup>3</sup>	MR, found	MR, calc.	Bromi	Bromi	Ester	Ester	Note
								num- ber, found	num- ber, calc.	num- ber, found	num- ber, calc.	
6	Tetraacrylate bis-glycerin se-ba-ci-nate	3000	622	1.4870	1.20	148.0	158.40	60	102.8	535	540	

...products consists of polyesters with  $n$  corresponding to the calculated value (see Table 1).

This conclusion is confirmed by the fact that dimethacrylate-(bis-ethylene glycol)-phthalate, synthesized from the methacrylic ester of ethylene glycol by the reaction:



practically does not differ from the corresponding product synthesized by the method of condensation telomerization at  $\frac{L}{B} = \frac{1}{2}$  (see Table 2).

**Table 2**

**Comparison of the physicochemical constants of dimethacrylate-(bis-ethylene glycol)-phthalate obtained by the one- and two-stage methods**

	Elemental	Elemental	Elemental	Ether num- ber	Bromine num- ber	d <sub>4</sub> <sup>20</sup>	n <sub>D</sub> <sup>20</sup>	M <sub>cp</sub>	MR
	com- position, %	com- position, %	com- position, %						
	C	H	O						
Calculated data	61.53	5.64	32.83	575	82.0	—	—	390	96.64

	Elemental com- posi- tion, %	Elemental com- posi- tion, %	Elemental com- posi- tion, %	Ether num- ber	Bromine num- ber	$d_4^{20}$	$n_D^{20}$	$M_{cp}$	MR
One- stage syn- the- sis method	61.65	5.50	32.85	570	80.0	1.18	1.500	350	97.20
Two- stage syn- the- sis method	—	—	—	572	80.2	1.18	1.500	—	97.20

The polyester acrylates described in the present work are finding ever-increasing application for obtaining various polymeric materials.

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*Note: Figure translations are in progress. See original paper for figures.*

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