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Abstract

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Chemistry

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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 ([1–2]).

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 ([3,4]).

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

$$R(OH)_m + R_1(COOH)_2 + 2m\,CH_2 = \underset{X}{C} - COOH \longrightarrow$$

$$\longrightarrow\; CH_2 = \underset{X}{C} - COOR\,(OCOR_1COOR)_n\,OCO\underset{X}{C} = CH_2$$

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 mean formula)	Viscosity at 20°, cps	M_{cr}, found	M_{cr}, calc.	n_D^{20}	d_{20}^{20}, g/cm^3	MR, found	MR, calc.	Bromine number, found	Bromine number, calc.	Ester number, found	Ester number, calc.	Note
1	Dimethacrylate-bis-ethylene glycol phthalate	4020-50125	350	390	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-bis-ethylene glycol phthalate	100-150125	395	478	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 mean formula)	Viscosity at 20°, cps	M_{cr}, found	M_{cr}, calc.	n_D^{20}	d_{20}^{20}, g/cm^3	MR, found	MR, calc.	Bromine number, found	Bromine number, calc.	Ester number, found	Ester number, calc.	Note
3	Dimethacrylate-bis-triethylene glycol phthalate	100-150	520 200	566	1.4891	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	Dimethacrylate-bis-ethylene glycol sebacinate	100-300	580 4000	602	1.4660	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	Tetramethacrylate-bis-glycerin phthalate	3000-5000	591-4000	586	1.4890	1.180	143.30	135.47	72.0	122.8	550.0	573.0	

No.	Name of compound (by mean formula)	Viscosity at 20°, cps	M_{cr}, found	M_{cr}, calc.	n_D^{20}	d_{20}^{20}, g/cm^3	MR, found	MR, calc.	Bromine number, found	Bromine number, calc.	Ester number, found	Ester number, calc.	Note
6	Tetramethacrylate-bis-glycerin sebacinate	3000–5000	—	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:

$$2\left(CH_2=\overset{CH_3}{C}-COO\right)CH_2CH_2OH + C_6H_4(CO)_2O \xrightarrow{+H^+} C_6H_4\left(COOCH_2CH_2OCO-\overset{CH_3}{C}=CH_2\right)_2 + H_2O$$

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 composition, %	Elemental composition, %	Elemental composition, %	Ether number	Bromine number	d_4^{20}	n_D^{20}	M_{cp}	MR
	C	H	O						
Calculated data	61.53	5.64	32.83	575	82.0	–	–	390	96.64

	Elemental composition, %	Elemental composition, %	Elemental composition, %	Ether number	Bromine number	d_4^{20}	n_D^{20}	M_{cp}	MR
One-stage synthesis method	61.65	5.50	32.85	570	80.0	1.18	1.500	350	97.20
Two-stage synthesis 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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