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## Abstract

## Full Text

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# Carbonium Polymerization of Polyester Acrylates

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At the present time, a new class of unsaturated polyesters with reactive double bonds in the terminal groups, which has been called polyester acrylates, has acquired practical significance (⁀1). The properties of polyester acrylates and of the products of their polymerization under the influence of radical initiators have been described in a number of works ($^{2-}$4). The structure of the double bonds of polyester acrylates makes it possible to assume that these oligomers will be active in carbonium polymerization. The possibility of carbonium polymerization of certain polyester acrylates was shown in (⁀5). It was noted that the formation of a three-dimensional structure of polyester-acrylate polymers in this case proceeds through the stage of formation of a soluble polymer ($\beta$-polymer). A method for obtaining the $\beta$-polymer of polyester acrylates under the action of titanium tetrachloride is described in (⁀6). The formation of $\beta$-polymers by a radical mechanism proceeds with a sufficient yield in the copolymerization of esters of the acrylic series with a tetrafunctional ester in the medium of a precipitant and chain-transfer agent, or else in the medium of an organic solvent under the action of such an initiator as azodinitrile of diisobutyric acid (⁀7). The preparation of $\beta$-polymers from polyester acrylates is of great scientific and practical importance. These polymers possess unsaturation and can be converted into articles of the most varied shapes and types, with subsequent curing into three-dimensional infusible networks.

In the present communication we give some results of an investigation of carbonium polymerization and of the properties of the $\beta$-polymers formed in this process from dimethacrylate (bis-triethylene glycol) phthalate (MGF-9), tetramethacrylate (bis-glycerin) phthalate (TMGF-11), and diethylenglycol phthalate dimethacrylate with a degree of polymerization equal to 2 (MDF-2).

Polymerization was carried out in vacuum at $20 \pm 0.1^{\circ}$, with a catalyst concentration of $\sim 0.4$ mole/liter. The catalyst—titanium tetrachloride—was purified by repeated distillation in vacuum in the cold. Polyester acrylates, previously purified on a column with calcined aluminum oxide, were degassed in vacuum for 1.5-2 hr. The duration of the reaction was 4-6 hr. After the experiment was completed, the ampoule in which the reaction had taken place was opened and acetone was added. The insoluble polymer formed in the reaction was filtered

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off on a Schott crucible, washed repeatedly with methyl alcohol, and dried in vacuum to constant weight. After washing with methanol and drying, the three-dimensional polymer lost its ability to swell. The $\beta$-polymer was precipitated from the filtrate with methyl alcohol. After repeated washing with methanol, the $\beta$-polymer had a faint coloration. Upon repeated precipitation from acetone solution, the $\beta$-polymers of polyester acrylates were white in color. The maximum yield of $\beta$-polymer (up to 40%) was obtained for MDF-2, an oligomer with a large distance between methacrylic groups; the minimum yield (5-8%) was obtained for MGF-11, an oligomer with four methacrylic groups. The $\beta$-polymers of all the polyester acrylates investigated rather rapidly—from several hours to two days—are converted, both in air and in vacuum, into insoluble polymers. To investigate the structure of the synthesized polymers, infrared spectra were taken of the initial oligomers, of $\beta$-polymers in benzene solutions, and of insoluble films obtained by converting $\beta$-polymers in air into three-dimensional polymers (see Figs. 1 and 2). On the basis of the IR-spectral data it may be concluded that both the $\beta$-polymer and the three-dimensional polymer obtained by crosslinking the $\beta$-polymer in air are characterized by considerable unsaturation.

**Fig. 1.** IR spectra of MGF-9 resin (*1*), $\beta$-polymer based on MGF-9 resin (*2*)

The absorption band in the region of 1630 $\text{cm}^{-1}$ may be assigned to the stretching vibrations of the $C = C$ bond of an unconjugated group ([8]). This band is present in methyl methacrylate and absent in its polymer. Consequently, it may serve as an indicator of the degree of unsaturation of the polymer. The presence of an absorption band at 1630 $\text{cm}^{-1}$ in the three-dimensional polymer stored in air for 3 months indicates that the residual double bonds do not react with atmospheric oxygen at room temperature.

**Fig. 2.** IR spectrum of a $\beta$-polymer based on MGF-9 resin cured in air

For the three-dimensional polymers obtained by carbonium polymerization of polyester acrylates, and for $\beta$-polymers that were converted into three-dimensional polymers during storage in vacuum and in air, thermomechanical

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* V. P. Maksimova took part in the experimental work.

Fig. 3. Thermomechanical curves of $\beta$-polymer MGF-9, cured in air (1); catalytic three-dimensional polymer MGF-9 (2); $\beta$-polymer MGF-9, formed at 130° (3)

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curves were recorded on Kargin dynamometric balances. This method makes it possible to study many structural changes occurring in a polymer upon heating or under the action of chemical reagents, caused by the development of chemical reactions ([9,10]).

Figure 3 presents the thermomechanical curves of a $\beta$-polymer MGF-9 specimen molded at 50°, which passed into an insoluble state in air (specimen A), and of a three-dimensional polymer specimen obtained by carbonium polymerization of MGF-9 and molded at 130° (specimen B). As is evident from these curves, in case B, beginning at temperatures of 60–70°, rather large deformations develop, although the specimen was molded at high temperature and the initial polymer before molding had a three-dimensional structure. With a further increase in temperature, obser-

an increase in deformation is observed, which reaches a maximum in the temperature region of 130–140°. A completely analogous course of the curve is observed for sample A. The decrease in deformability in the temperature region above 140° is due to the development of structuring of the polymer. In general, the polymers studied are characterized by a course of the thermomechanical curves analogous to that known for thermosetting polymers (11). When a $\beta$-polymer sample is formed at 130° (Fig. 3, 3), the maximum on the thermomechanical curve is absent, since structuring of the sample occurred during the forming process. As is seen from curve 1 (Fig. 3), above temperatures of 210–220° the deformability of the polymers again increases, which is obviously due to destruction processes. Thus, the results of the thermomechanical study agree with the data of IR analysis on the unsaturation both of soluble polyether acrylate polymers and of three-dimensional polymers obtained by carbonium polymerization.

**Fig. 3.** Thermomechanical curves of $\beta$-polymer MGF-9, cured in air (1); catalytic three-dimensional polymer MGF-9 (2); $\beta$-polymer MGF-9, formed at 130° (3)

The property of $\beta$-polymers of polyether acrylates to transform spontaneously into three-dimensional infusible products was used by us to obtain varnish coatings. Solutions of $\beta$-polymers MGF-9, TMGF-11, and MDF-2 in acetone were applied to glass, metal, and ceramic surfaces. After evaporation of the solvent at room temperature, crosslinking of the polymer occurred in air due to residual double bonds. In this case elastic films were obtained on the surface, resistant to the action of a number of aggressive media (50% sulfuric, nitric, hydrochloric, and hydrofluoric acids at room temperature). To obtain coatings based on polyether acrylates when curing them by a radical mechanism, it is necessary to select oxidation-reduction systems, since atmospheric oxygen in this case is a strong inhibitor. When $\beta$-polymers are used to obtain coatings, curing of the film occurs under the action of atmospheric oxygen and does not require any initiating systems, which is a great advantage of these polymers.

**Table 1**

Properties of fibers based on $\beta$-polymers of polyether acrylates (average values)

| Initial oligomer | Fiber diameter, $\mu$ | Strength, rkm | Elongation at break, % |
|---|---|---|---|
| MDF-2 | 12 | 37 | 80 |
| MGF-9 | 9 | 60 | 28 |
| TMGF-11 | 50 | 3.7 | <10 |

Concentrated solutions of $\beta$-polymers of polyether acrylates in mixed solvents exhibit good spinnability. This made it possible to obtain fibers based on such polymers which, after forming and drawing, crosslink in air, acquiring a three-dimensional structure. The fibers obtained are characterized by the properties given in Table 1.

Thus, as a result of the carbonium polymerization of polyether acrylates, it proved possible by a fundamentally new route to obtain $\beta$-polymers, capa-

capable of spontaneous curing in air, as well as three-dimensional polymers possessing unsaturation and differing substantially in their properties from the three-dimensional polymers obtained by radical polymerization of polyester acrylates.

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