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Abstract

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RADIATION POLYMERIZATION OF POLYESTER ACRYLATES

In the present work the aim was to study the kinetics of the radiation polymerization of polyester acrylates (PEA) and to compare the regularities obtained with the features of three-dimensional thermally initiated polymerization, studied by A. A. Berlin, G. V. Korolev, and others ([1]-[3]). The literature contains no information whatever on the radiation-initiated polymerization of PEA; the available kinetic data on the radiation curing of unsaturated polyesters (PE), which, like PEA, give a three-dimensional structure, are rather semiquantitative, because methods were used that are poorly suited for studying the kinetics of crosslinking (viscometry, dilatometry, etc.) ([4], [5]).

In this work, for the first time we applied a method developed by us for measuring, directly during irradiation, the amount of heat evolved during polymerization. A detailed description of the apparatus is given in ([6]).

The oligomeric PEA MB, MBF-1, and MBF-2 were chosen as objects of study; they are products of the condensation of methacrylic acid, butanediol (MB), and phthalic acid (MBF) with different lengths of the oligomeric chain. As a high-viscosity inert solvent, the saturated analogue of polyester acrylates, IDF-2 (a condensation product of isobutyric acid, diethylene glycol, and phthalic acid), was used ([7]).

Irradiation of the PEA was carried out in a Co^{60} GUT-400 unit (dose rate from 3 to 21 rad/sec) and in an electron accelerator with an energy of 0.6 MeV (dose rate 10^4–10^5 rad/sec) at 20-25° C. Before irradiation, the PEA samples were evacuated to 10^{-3} mm Hg. To study the kinetics of PEA polymerization, a differential thermographic apparatus was used, with a sensitivity of $3 \cdot 10^{-5}$ cal/sec per 1 mm of recorder scale. On the scale of an EPP-09 instrument, the rate curve of heat evolution versus irradiation time was recorded (heat of polymerization, 13.5 kcal per 1 mole of double bonds). The entire area under the curve is equal to the amount of heat evolved during irradiation; after differentiation (the method of transfer to tracing paper and weighing was used), kinetic curves were constructed in coordinates of percent conversion–dose (time). Treatment of the kinetic curves by the method described in the literature ([8]) gave curves of the dependence of the reduced rates (W/M) on the dose rate and the degree

Fig. 1. Kinetic curves of polymerization of MBF-1 in bulk under irradiation with ^{60}Co γ-quanta (dose rate 21 rad/sec): 1—in vacuum; 2—in air

Figure 1: Fig. 1. Kinetic curves of polymerization of MBF-1 in bulk under irradiation with ^{60}Co γ-quanta (dose rate 21 rad/sec): 1—in vacuum; 2—in air

of conversion.

It was established (see Fig. 1) that oxygen is an effective inhibitor of the polymerization process. In addition, for the radiation polymerization of PEA there is strict proportionality between the initial rate of polymerization (W_0/M) and the square root of the dose rate. Both these facts, as well as the considerable aftereffect observed in the polymerization of PEA at room temperature, indicate a radical-chain mechanism of the conversion.

Along with these regularities, common to thermally initiated polymerization of PEA, there are a number of features specific only to radiation polymerization, which can be explained by applying to

to the conditions of three-dimensional polymerization the hypothesis of "hot radicals" (^{9}), which consists in the following.

The formation under conditions of three-dimensional polymerization of PEA of a network polymer and the stabilization of reacting groups (free radicals and double bonds) in the three-dimensional network leads to a sharp decrease in the number of collisions in such systems. Consequently, dissipation of the energy released as a result of acts of growth of polymer chains, or of the energy of radiation or photochemical excitation of individual groups, is hindered if energy exchange takes place mainly through collisions. Therefore, in polymerization systems of three-dimensional structure, the probability of formation of hot radicals must increase sharply. However, since the probability of collisions is small, the probability of realization of hot radicals as reagents possessing increased reactivity is also small. But in three-dimensional polymerization a specific mode of realization of excess energy is possible, a mode inherent only in such reaction systems, in which the reacting groups are so immobile that their reactivity is determined not by true chemical activity, but only by mobility.

Fig. 1. Kinetic curves of polymerization of MBF-1 in bulk under irradiation with ^{60}Co γ-quanta (dose rate 21 rad/sec): **1**—in vacuum; **2**—in air.

These groups are attached to the polymer chains from which the three-dimensional network is constructed, and therefore their mobility depends on the mobility of the chains themselves. Under conditions of hindered energy exchange by collisions, the principal channels for dissipation of excess energy can only be polymer chains. In other words, energy transfer will occur by successive excitation of energy levels along the polymer chain, as a result of which the mobility of those chain segments over which, at a given moment, the excess energy is dissipating will increase.

Fig. 2 and Fig. 3

Figure 2: Fig. 2 and Fig. 3

Table 1

Influence of the initial viscosity of PEA and of their mixtures with IDF-2 on the rate of radiation polymerization (dose rate 21 rad/sec)

No.	Oligomer	Kinematic viscosity at 25° C, cSt	Polymerization rate referred to the current oligomer concentration, min^{-1}: $W_0/M \cdot 10^3$	Polymerization rate referred to the current oligomer concentration, min^{-1}: $W_{5\text{-}10}/M \cdot 10^3$
1	MB	3	4.0	–
2	MBF-1	115	4	–
3	MBF-2	500	4.3	–
4	IDF-2	700	–	–
5	MB + 50% IDF-2	Increase in viscosity ↓	3.5	3.5
6	MB + 60% IDF-2	Increase in viscosity ↓	3.5	6
7	MB + 71% IDF-2	Increase in viscosity ↓	4	7
8	MB + 83% IDF-2	Increase in viscosity ↓	3	8

The independence obtained in our work (see Fig. 2 and Table 1) of the reduced initial reaction rates (W_0/M) of all PEA and their solutions

in IDF-2 on the initial viscosity (from 3 cSt for MB to 500 cSt for MBF-2 and mixtures of PEA with IDF-2) indicates that the increase in chain mobility under radiation-chemical initiation is so great that, in the early stages of polymerization, the rate of the chain-termination reaction ceases to be limited by diffusion, as is the case in chemically initiated polymerization. Hence there is a sharp weakening of the dependence of the initial rate on the viscosity of the reaction medium. Beginning with 5-7% conversion, radiation polymerization passes into the diffusion region, and the observed increase in W/M with increasing viscosity of the initial system is explained, as in the case of chemical initiation,

Fig. 2. Curves of the polymerization rate of PEA (referred to the current concentration of oligomer) at different viscosities of the initial PEA under irradiation with γ-rays of ^{60}Co in vacuum (dose rate 21 rad/sec): 1 –MBF-2; 2 –MB

Fig. 3. Dependence of the polymerization rate of MBF-1 at room temperature on conversion: 1 –thermal initiation (4% CPK); 2 –radiation-chemical initiation (dose rate 21 rad/sec)

by a decrease in the chain-termination rate constant at an unchanged or only slightly changing chain-growth rate constant (W_{5-10}/M in Table 1).

Another and most interesting feature of radiation curing of PEA at room temperature is the high conversion for all the oligomers studied (Fig. 1, 1; for all PEA, 100% conversion was obtained), whereas in the case of chemical initiation high conversions are not reached even at elevated temperatures (1-3). If, in the case of thermal polymerization, at a certain conversion a rigid polymer framework is formed with pendant unreacted double bonds, then the increased energy of the hot radicals, due both to the chain-propagation reaction itself and to the action of radiation, as indicated above, can be transferred to the polymer chain, which "swings" ; its segments become more mobile, as a result of which the possibility exists for further chain growth. Therefore, while at a certain conversion the rate of thermally initiated curing decreases sharply, the rate of radiation curing, on the contrary, increases (see Fig. 3). In this figure, the rate of chemical initiation is greater than the rate of radiation initiation.

The proposed hypothesis also explains the improvement in the physicomechanical properties of polymers obtained by radiation curing. Thus, in the"】【final stopped (finish_reason=stop)】

case, the heat resistance of the radiation-produced PEA, determined from the loss in polymer weight upon heating for 24 hours at 200° (the specimens for studying heat resistance were obtained under the action of electrons with $E = 0.6$ MeV), proved to be several times higher than for chemically cured oligomers. Apparently, the increased energy of individual elements of the three-dimensional structure increases the rate of relaxation of mechanical stresses, i.e., a kind of high-temperature local "annealing" of the entire polymer occurs, relieving the stresses. Owing to this, the physicomechanical properties are improved.

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