INVESTIGATIONS IN THE FIELD OF THE RADIATION-INDUCED SOLID STATE POLYMERIZATION*

VI. GAMMA-RADIATION INITIATED SOLID STATE POLYMERIZATION OF VINYL LAURATE

By

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(Received December 2, 1964)

In connection with the gamma radiation-induced solid phase polymerization of cethyl methacrylate we have developed a hypothesis of the advanced effect of long-chain aliphatic substituents on the solid phase polymerization of vinyl monomers [1]. The polymerization of methyl methacrylate in solid phase advances very slowly [2]. But in a glass-like solid phase, obtained by addition of paraffin oil, a more significant polymerization rate can be observed [3]. Cethyl methacrylate, however, having a long-chain aliphatic substituent, can be easily polymerized in solid phase. As to the vinyl esters, successful studies on solid phase polymerization of vinyl acetate could only recently be made [2]. Its polymerization also takes place slowly, effected only by very high dose rates. Solid phase polymerization of vinyl stearate, initiated by gamma-radiation and accelerated electrons, was investigated [4, 5] and it was stated that the polymerization reaches a maximum near to the melting point, and benzoquinone acts as inhibitor on the reaction.

Investigations of the solid phase polymerization of vinyl laurate promised to be interesting in general from the point of view of the influencing effect of the long-chain aliphatic substituent on the solid phase polymerization of vinyl esters.

Experimental

Our applied methods were the same, as mentioned in our previous paper [1]. According to the method described in the literature [6] vinyl laurate was obtained by the transesterification of vinyl acetate with lauric acid. The purity of the monomer used was 100% which was estimated by means of a gaschromatographic analysis.

Characteristics of the twice distilled vinyl laurate were: boiling point 89 °C/0.4 torr, melting point 3 °C, $n_D^{25} = 1.4387$. When the polymerization ended the polymeric system was solved in benzoquinone-containing gasoline

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* Part V. Makromolekulare Chemie: in press.

at the temperature of radiation in order to prevent further reactions during treatment. The polymer was precipitated from the solution by the addition of methanol at a temperature of about −15 to −20°C. In this way polymer is precipitated in a suitable form for drying.

The kinetics of the liquid phase polymerization was measured by the dilatometric method.

Results and discussion

The kinetics of the gamma-radiation initiated liquid phase polymerization of vinyl laurate at different temperatures is shown on Fig. 1.
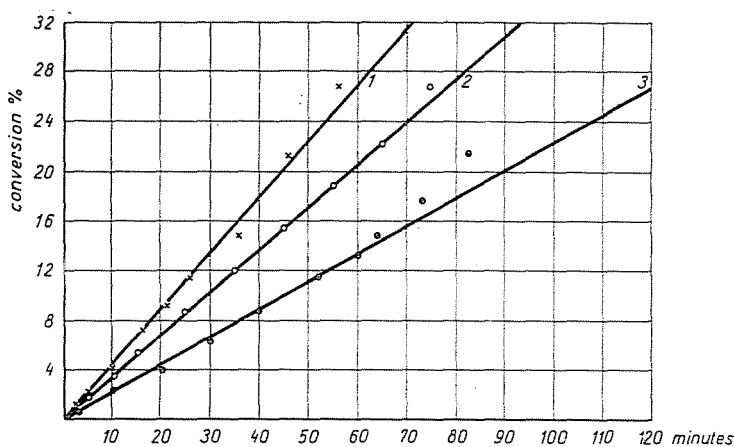

Fig. 1. Kinetics of liquid phase polymerization of vinyl laurate at a dose rate of 46.000 r/h by 30°C (3), 40°C (2) and 50°C (1)

The activation energy of the liquid phase polymerization based on the measurement of the dependence of polymerization rate from temperature could be determined and was found to be 6.65 kcal/mole, which shows good coincidence with that found by other vinyl monomers.

Fig. 2 shows the dependence of the rate in liquid phase radiation initiated polymerization of vinyl laurate in function of the dose rates. The polymerization rate varies with the 0.51 power of the dose rate, the value of which is generally accepted as an evidence of radical mechanism and a bimolecular chain termination reaction. The fact that inhibitors (like benzoquinone, diphenylpicrylhydrazil [DPPH]) inhibit the liquid phase radiation polymerization, gives another proof of the above statement.

Fig. 3 shows the kinetics of solid phase polymerization of vinyl laurate at different temperatures.

Fig. 4 shows the same at 0°C, with varying dose rates. On the basis of the figures it can be established that the kinetics of the solid phase polymerization of vinyl laurate up to 20% conversion has a linear character, above it a re-
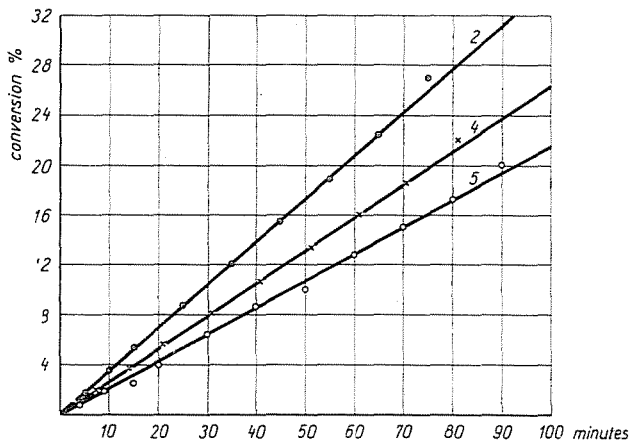

Fig. 2. Kinetics of liquid phase polymerization of vinyl laurate with varied dose rate: 2. — 46.100 r/h., 4. — 28.250 r/h., 5. — 18.040 r/h.
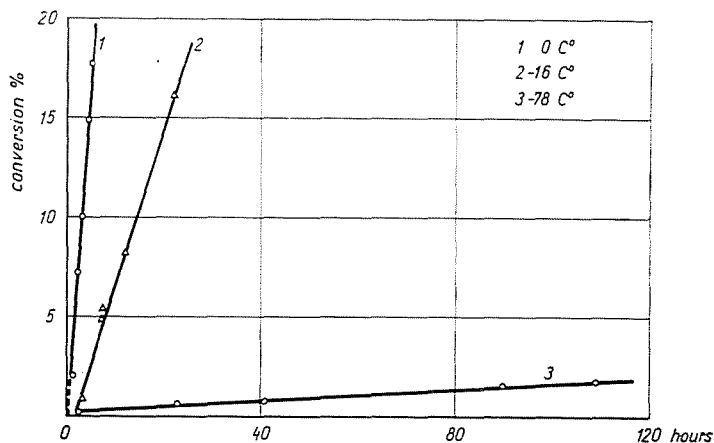

Fig. 3. Kinetics of solid state polymerization of vinyl laurate with a dose rate of 22.050 r/h at 0, —16 and —78°C.

tarding tendency, 0.65 being the exponent of the dependence of solid phase polymerization rate with the dose rate referring to radical polymerization mechanism in the solid phase, too.

The Arrhenius diagram for temperature dependence of polymerization rates is shown on Fig. 5. It can be seen that the rate of solid phase polymerization has its maximum near to the melting point, i. e. the dependence has the

same character as in case of cethyl methacrylate [1] and vinyl stearate [4, 5]. It should to be mentioned that in the applied temperature range with the method of differential thermoanalysis no secondary transition point was observable
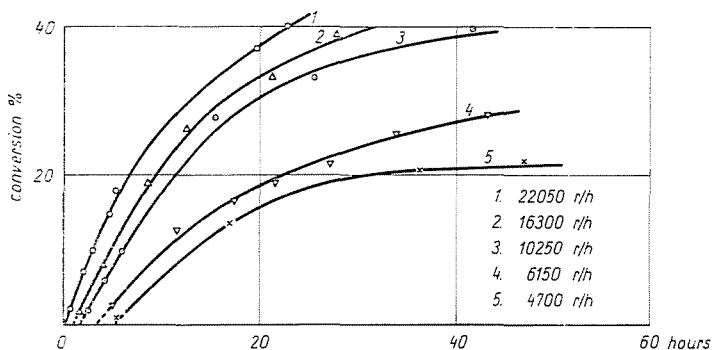

Fig. 4. Kinetics of the solid state polymerization of vinyl laurate at $0°$ C with varied dose rates
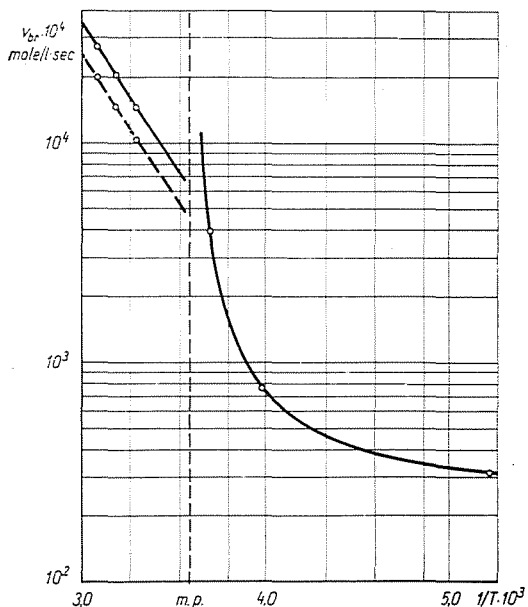

Fig. 5. Dependence of polymerization rate of vinyl laurate on the temperature in liquid phase at a dose rate of 46.000 r/h (below calculated for 22.050 r/h) and in solid state at a dose rate of 22.050 r/h.

in the solid state, therefore, the diversion of the Arrhenius curve cannot be explained by this fact.

The variation of the molecular weight of polymers, obtained by solid phase polymerization of vinyl laurate can be seen in Fig. 6. The molecular

weights grow with advancing conversion, and finally, after reaching a conversion of about 30—40 % some insoluble products are formed. Similarly the molecular weight of the polymers increases in function of the growing dose rates, thus they differ from our previous observations with cethyl methacrylate and vinyl stearate, where the molecular weight of polymers showed no relation
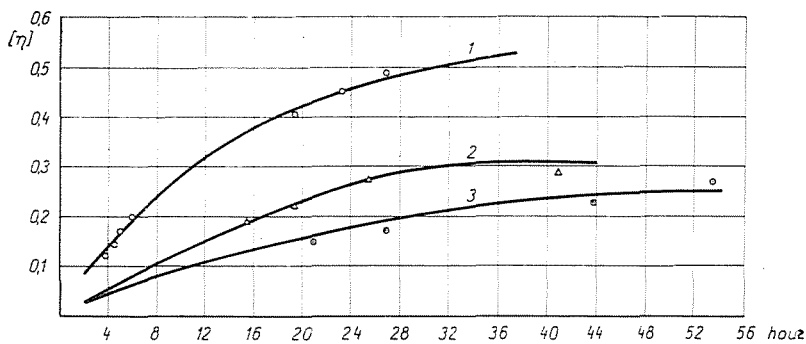
Fig. 6. Variation of molecular weight of polyvinyl laurate obtained in solid state at 0° C in function of conversion and dose rate: 1. — 22.050 r/h., 2. — 10.250 r/h., 3. — 6.150 r/h.
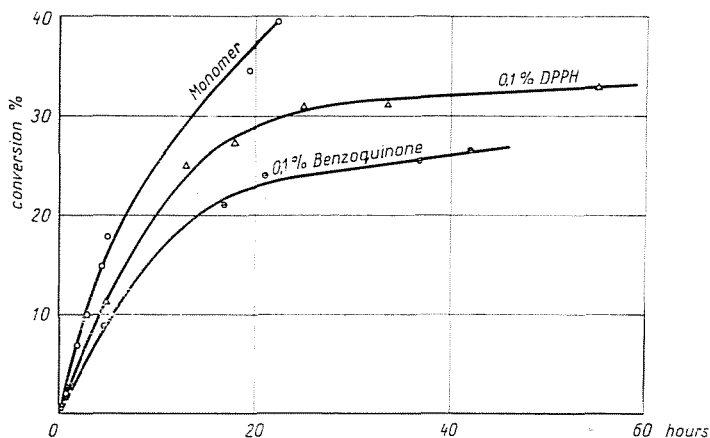
Fig. 7. Kinetics of solid state polymerization of vinyl laurate at 0° C by dose rate of 22.050 r/h. in the presence of 0,1% of diphenylpicrylhydrazile and benzoquinone

to the conversion grade, dose rate or temperature. This difference leads to the conclusion that the molecules of vinyl laurate are more mobile in solid state and at 0° C, than those of other monomers having similar character.

Fig. 7 shows the kinetics of solid phase polymerization of vinyl laurate in the presence of 0,1 % DPPH and benzoquinone resp., whereas Fig. 8 shows the effect of varying concentration of these inhibitors with the conversion achieved during the same radiation period. The inhibitors have a well notice-

able retarding effect on the solid phase polymerization of vinyl laurate. The explanation of this effect can be given in this case as by other monomers having long chain aliphatic substituents with associated position of the molecules, where their polar, resp. apolar parts adjoined. Inhibitors which do not
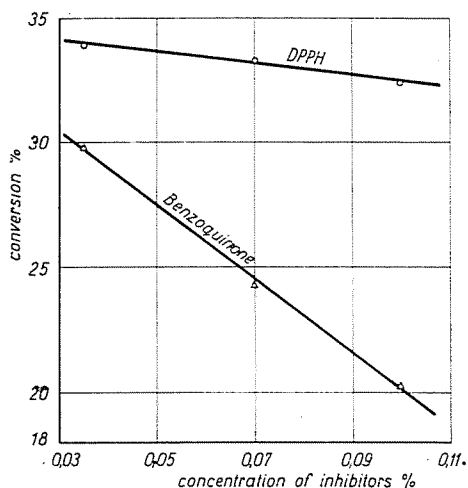

Fig. 8. Dependence of conversion of solid state polymerization of vinyl laurate on the concentration of inhibitors at 0° C, at a total dose of 918.600 r., irradiated with dose rate of 22.050 r/h.
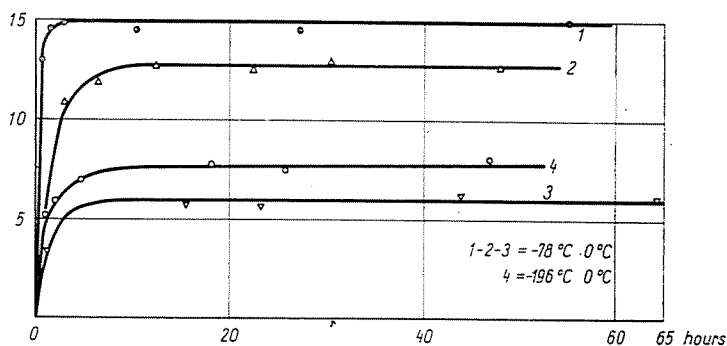

Fig. 9. Kinetics of post-polymerization of vinyl laurate irradiated at —78° C with dose rate of 22.050 r/h. and heated up to 0° C. 1: total dose 695.900 r., 2. 331.825 r., 3. 169.344 r., 4. irradiated at —196° C and then heated up to 0° C. in case of total dose 169.344. r.

dissolve well in pure hydrocarbons, are placed next to the polar end of one molecule by crystallization of the system, so that they give a higher inhibiting effect (they are concentrated around the vinyl groups) compared to those in case of solid phase polymerization of monomers with shorter aliphatic substituents.

The kinetics of post-polymerization of vinyl laurate is shown in Fig. 9. In three cases radiations of different durations were carried out at $-78°$ C, followed by warming up to $0°$ C. In another case radiation was effected at $-196°$ C followed by warming up to $0°$ C. The kinetical curves prove that post-polymerization is very rapid: the greater the total dose of preliminary irradiation, the higher is the degree of conversion that the polymerization can reach. In the case of the same total dose, lower temperature of irradiation results a higher rate and a higher conversion. From these measurements we can conclude that the quenched active centres formed by radiation become rather mobile already at $0°$ C and that they disappear quickly by spontaneous recombination or polymerization followed by chain termination reactions. In the same circumstances irradiation at lower temperature results in a higher number of active centres thus giving an accelerated post-polymerization and greater conversion as result.

Summary

Gamma-radiation initiated solid state polymerization of vinyl laurate is characterized by a maximum rate near the melting point. Inhibitors considerably retard the polymerization. Kinetics of postpolymerization, as well as the variations of molecular weight of polymers formed in solid phase, lead to the conclusion that in the solid state vinyl laurate molecules are more mobile than cethyl methacrylate and vinyl stearate of similar structure at temperatures near to the melting point.

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