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POLYMERIZATION OF VINYL OLEATE IN THE LIQUID-CRYSTALLINE STATE

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In the case of solid-phase polymerization, at certain parameters of the monomer crystal lattice, the formation of stereoregular polymers is possible ([1,2]). The observed rapid polymerization in the solid state is explained by the favorable orientation of the monomer molecules before their incorporation into the growing macromolecule. However, in almost all cases the increase or decrease in the rate of polymerization is caused not only by the indicated orientation of the monomer units in the crystal lattice, but also by the destruction of the latter in the process of "growth" of the polymer chains through the monomer crystal.

In this connection it seemed interesting to us to investigate the polymerization process in a medium in which a certain orientation of the monomeric units would be preserved owing to a relatively weak intermolecular interaction between them. The small energy of intermolecular interaction would make it possible to exclude completely the development of stresses in such a quasicrystalline lattice owing to their rapid relaxation. These conditions will obviously be fulfilled if the monomeric substance is in the liquid-crystalline state ([1,7]).

The choice of a monomer capable of polymerizing in the liquid-crystalline state is associated with a number of difficulties. First, many of them contain azo-, azoxy-, and other reactive and unstable groups. Second, the presence of bulky substituents at the vinyl bond determines a low limiting polymerization temperature, which in most cases will be below the temperature of existence of the mesomorphic state, thereby excluding polymerization itself in the liquid-crystalline state.

It is known that esters of fatty acids possess many properties characteristic of typical liquid crystals; for example, upon cooling their liquid phase passes into a transparent, waxlike mass, which becomes crystalline upon further lowering of the temperature; further, they form among themselves a continuous series of solid solutions without a temperature minimum and, finally, in a certain temperature interval they are optically uniaxial and positive ([3–5]).

A thermographic study of various esters of fatty acids also showed that they exist in two forms, α and β, according to the terminology of Garner and Randall ([5]),

Figure 1 and Figure 2

Figure 1: Figure 1 and Figure 2

the α-form (which, apparently, is identical with the smectic form of a liquid crystal) being the most stable for esters of fatty acids having an even number of carbon atoms (3,6).

In investigating the phase transformations of vinyl oleate it was established that it possesses a liquid-crystalline state in a certain temperature interval. The temperature interval of existence of the liquid crystal was determined thermographically and by visual monitoring of the form of the crystals in a polarizing microscope. The thermogram of vinyl oleate is shown in Fig. 1.

The first peak ($t = -18^\circ$) corresponds to the transition from an isotropic liquid to a liquid-crystalline state. At $t = -45^\circ$, a transition to the crystalline state is observed. As is seen from the thermogram, the thermal effect of the transition to the crystalline state is 5-7 times greater than the thermal effect of the transition from the liquid to the liquid-crystalline state. It should be noted that upon heating, the transition from the crystalline state to the liquid-crystalline state is observed at $t = -32^\circ$, and it should apparently be regarded as the melting temperature of crystalline vinyl oleate. Thus, the general scheme of phase transitions in the case of vinyl oleate is as follows:

Cooling

$$\text{isotropic liquid} \xrightarrow{-18^\circ} \text{liquid crystal} \xrightarrow{-45^\circ} \text{crystal.}$$

Heating

$$\text{isotropic liquid} \xleftarrow{-18^\circ} \text{liquid crystal} \xleftarrow{-32^\circ} \text{crystal.}$$

The broad region of the mesomorphic state of the vinyl ester of oleic acid is explained by the lower melting temperature in comparison with the esters of the corresponding saturated acids and by the presence of polarizing centers—double bonds (7). In addition, the arrangement of terminal methyl groups in the vinyl oleate molecule is the same as in the case of ethyl margarate (3), which also promotes the manifestation of mesomorphism.

The vinyl ester of oleic acid was obtained by the transvinylation reaction in the interaction of oleic acid and

Fig. 1. Thermogram of vinyl oleate (cooling curve).
1 —integral thermocouple,
2 —differential thermocouple

Fig. 2. Dependence of the refractive index of the medium and the polymer yield on the irradiation dose. 1 —polymerization in the liquid state at $t = 0^\circ$; 2 —polymerization in the liquid-crystalline state at $t = -25^\circ$; 3 —polymerization in the solid state at $t = -78^\circ$. Dose rate 218 r/sec

vinyl acetate (^{8}). The refractive index of vinyl oleate $n_D^{30} = 1.4536$, bromine number 103-106, boiling point 166°/1 mm Hg.

Radiation polymerization of the vinyl ester of oleic acid in bulk was carried out in the liquid, liquid-crystalline, and solid states. The presence of a double bond in the substituent accounts for the very slow polymerization of vinyl oleate in comparison with other complex vinyl esters (^{9}).

Radiation polymerization of vinyloleate in the liquid state is characterized by a small activation energy (1.5-2 kcal/mole), and the overall rate of polymer formation decreases as the temperature is lowered. However, when the monomer is in the mesomorphic state ($t = -25°$), the polymerization rate increases substantially (Fig. 2). An increase in the polymerization rate in the liquid-crystalline state was observed at low degrees of conversion (polymer yield 20-25%). The polymerization rate at $t = -25°$ decreases if the initial monomer contains 5-10% polymer obtained by radiation polymerization at $t = 20°$.

In polymerization in the solid state, the initial rate of polymer formation is somewhat lower than the polymerization rate in the liquid-crystalline state, which is apparently associated with the lower mobility of the monomer units in the true crystal.

At degrees of monomer-polymer conversion above 50%, polymerization is complicated by processes of polymer crosslinking, which makes it impossible to construct a complete kinetic curve.

The structure of the polymers formed depends substantially on the phase state of the monomer. In liquid-phase polymerization of vinyloleate, a transparent polymer is formed, representing an isotropic viscous liquid. If, however, polymerization is carried out in the liquid-crystalline or crystalline state, crystalline polymers are formed, resembling fats in appearance.

Figure 3 (see insert to p. 1089) shows X-ray diffraction patterns of polymers: an amorphous polymer obtained by polymerization in the liquid state, and a crystalline polymer obtained by polymerization in the liquid-crystalline and solid states. A partially crosslinked polymer obtained by radiation polymerization in the solid state also possesses some crystallinity. The melting temperature of the crystalline polymers lies in the temperature range 34-40°.

The intrinsic viscosity of all samples of polyvinyloleate, regardless of the polymerization conditions, ranges from 0.08 to 0.1. It is interesting to note that amorphous polyvinyloleate obtained by liquid-phase polymerization is soluble in the monomer. Polyvinyloleate obtained by polymerization in the mesomorphic and solid states separates at room temperature into a distinct crystalline phase that is difficult to separate from the monomer. The crystalline polymer separating from the monomer is soluble in it when heated to a temperature of 28-30°, which is 6-8° below its melting temperature. The amorphous polymer is soluble in the monomer at any temperature. Separation of the crystalline polymer into a separate phase is determined in this case only by its ability to form

Fig. 4. Dependence of the refractive index n_D of polyvinyloleate on temperature: a—crystalline polymer, b—amorphous polymer

Figure 2: Fig. 4. Dependence of the refractive index n_D of polyvinyloleate on temperature: a—crystalline polymer, b—amorphous polymer

crystalline structures in the monomer solution. The lowering of the melting (dissolution) temperature of the polymer present in the monomer is explained by the small content of the latter in the separating polymer particles. The reverse formation of crystalline structures (and, correspondingly, separation of the polymer into a separate phase if it is in monomer solution) at room temperature 20–22° proceeds very slowly, over 2–4 days, and very rapidly at 0°.

Fig. 4. Dependence of the refractive index n_D of polyvinyloleate on temperature: a—crystalline polymer, b—amorphous polymer.

The refractive index of the amorphous polymer is n_D^{30}1.4780, which is considerably higher than the value n_D^{30}1.4749 reported in earlier work. Of interest is the dependence of the refractive index on temperature for the crystalline polymer (Fig. 4). The break in the curve in the region of 34—38° also indicates the presence of a phase transition in the polymer. For the crystalline specimen it would be more correct to consider two values of the refractive index, n_e and n_o, but the difference between them is insignificant. The ability of polyvinyl oleate specimens obtained in the liquid-crystalline and solid states to crystallize is undoubtedly connected with their definite microtacticity. Polyvinyl oleate obtained by polymerization in the liquid-crystalline and solid states probably does not differ in structure, although the lattice energy of the liquid crystal is very small and the molecules of the monomer units possess a certain degree of freedom in the liquid crystal. At present the microtacticity of polyvinyl oleate specimens obtained under different phase states of the monomer is being studied.

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