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Abstract

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On the Mechanism of Carbonium Polymerization of Unsaturated Polyesters

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In connection with the establishment of the possibility of polymerizing certain unsaturated polyesters by a carbonium mechanism under the action of the catalyst $TiCl_4$ (^{1}), and with the production of polymers possessing valuable physicomechanical and chemical properties (^{2}), the study of the mechanism of this process is of great interest. We therefore carried out an investigation of the joint carbonium polymerization of dimethacrylate-bis-triethylene glycol phthalate (MGF-9) with styrene.

The polymerization was carried out in a solution of carefully dried ethyl chloride at a total monomer concentration of ~1.25 mole/l and catalyst concentrations of ~0.003 and 0.015 mole/l at 0°C. The experimental procedure is described in (^{3}). The compositions of the copolymers were determined by IR spectroscopy (^{3}), and the constants of copolymerization were calculated from the approximate composition equation (^{4}). The minimal degrees of conversion (up to 3 wt.%) made it possible to obtain sufficiently accurate results from this equation.

In studying the homopolymerization of MGF-9 under the action of $TiCl_4$, we found that the bromine numbers of the polymers obtained were ~1/2 the bromine number of the starting product. All the calculations given below were made on the assumption that only one double bond of the oligomer molecule participates in the polymerization process. Figure 1 presents curves showing the dependence of copolymer composition on the composition of the initial mixture for $TiCl_4$ concentrations of 0.003 and 0.015 mole/l, respectively. It is evident from the figures that, for both catalyst concentrations, enrichment of the copolymers in the MGF-9 oligomer is observed in comparison with the composition of the initial mixture. Indeed, the copolymerization constants for the two cases have the following values: $r_1 = 0.15$ (styrene); $r_2 = 0.75$ (MGF-9) for the system with the lower $TiCl_4$ concentration, and $r_1 = 0.36$ (styrene) and $r_2 = 0.54$ (MGF-9) for the system with the higher catalyst concentration.

The high reactivity found for dimethacrylate-bis-triethylene glycol phthalate in carbonium polymerization is in itself unexpected, since the structure of the double bond and the nature of the substituents indicate that this oligomer should be less reactive than styrene. Indeed, methyl methacrylate, which has a double

Figure 1

Figure 1: Figure 1

bond of analogous structure, is lower than styrene in the reactivity series (^{5}). Our investigations of the joint polymerization of styrene and methyl methacrylate under the action of $TiCl_4$ showed that, at a monomer concentration of 2.5 mole/l and $TiCl_4$ 0.015 mole/l (monomer ratio 1:1), the copolymer consists predominantly of styrene. At the same concentrations, homopolymerization of methyl methacrylate does not proceed either at 0° or at $-78°$. It follows from this that methyl methacrylate is far less reactive in carbonium polymerization than styrene.

In attempting to explain why different values of the constants r_1 and r_2 were obtained at different catalyst concentrations, we must first of all note the deviation of both composition curves from the theoretical ones.

(Fig. 1 A, curve 3, and B, curve 4), calculated on the basis of the obtained values of r_1 and r_2. Agreement of the theoretical curve with the experimental one for low concentrations of $TiCl_4$ (0.003 mol/l) is observed only at low (up to 30 mol.%) and high (above 80 mol.%) contents of MGF-9 in the initial mixture. The values of the constants r_1 and r_2 were also calculated for the region of greatest deviation from the theoretical curve for the system with a low concentration of $TiCl_4$. In this case the following values of the constants were obtained:

Fig. 1. Dependence of the copolymer composition on the composition of the initial mixture. $TiCl_4$ concentration ≈ 0.003 mol/l (A), and ≈ 0.015 mol/l (B): 1 –experimental curve, 2 –theoretical curve for $r_1 = 0.05$ and $r_2 = 2.45$, 3 –same, $r_1 = 0.15$ and $r_2 = 0.75$, 4 –same, $r_1 = 0.36$ and $r_2 = 0.54$.

$r_1 = 0.05$ and $r_2 = 0.45$. The theoretical curve of copolymer compositions calculated from these constants (see Fig. 1 A, curve 2) agrees well with the experimental points for the region of initial MGF-9 compositions of 30–70%. Using these same values of the constants r_1 and r_2, a theoretical curve was calculated for the second system (with the higher concentration of $TiCl_4$). The curve passes rather close to the point of maximum enrichment of the copolymer with oligomer (Fig. 1 B, curve 2). The ratio of the number of moles of oligomer to the number of moles of $TiCl_4$ (for the system with a low catalyst concentration) is given in Table 1.

Table 1

Experiment No.	Conc. MGF-9, mol/l	Conc. $TiCl_4$	MGF-9 : $TiCl_4$	Content of MGF in initial mixture, mol.%
24	0.131	0.00312	41	11
20	0.294	0.00306	96	24
16	0.493	0.00291	169	40.6
18	0.745	0.00292	255	61.3
17	0.755	0.00291	259	61
19	1.041	0.00320	325	80
21	1.221	0.00300	407	96

From the data of the table it is evident that, in the region of initial concentrations of the oligomer MGF-9 in the reaction mixture of 30–70 mol.%, where there is good agreement with the theoretical curve calculated from the constants $r_1 = 0.05$ and $r_2 = 2.45$, the molar ratio of oligomer to catalyst is sufficiently large (> 100). The initial part of the experimental curve, calculated for the values of the constants $r_1 = 0.15$ and $r_2 = 0.75$, corresponds to a molar ratio of oligomer to catalyst of 40.

For the system with the higher catalyst concentration, the molar ratio of oligomer to catalyst does not exceed 53. It is precisely for this system that anomalous enrichment of the copolymer with styrene is observed.

The results obtained indicate that the reactivity of the oligomer changes depending on the ratio of the amount of oligomer to the amount of catalyst. The change in the constants r_1 and r_2 in our case cannot be explained—

is not a consequence of a change in the microheterogeneity of the system, as was observed in works (^{6}, ^{7}) during the copolymerization of styrene with a bifunctional monomer (a diether) by a radical mechanism. In our systems, crosslinked polymers that precipitate during the reaction are not formed. Consequently, the change in reactivity is due to changes depending on the initial composition of the system. The ability of $TiCl_4$ to form complexes with groups that can serve as electron donors should be taken into account. In a number of studies it has been shown that chlorinated tin is capable of forming complexes with esters (^{8}), and that carbonyl oxygen binds compounds of the Lewis-acid type into complexes (^{9}). In view of the great analogy in structure between $SnCl_4$ and $TiCl_4$, it is reasonable to assume that $TiCl_4$ is capable of forming complexes with oligomer molecules. Chlorinated tin is capable of forming complexes with two ester molecules. On the basis of our data, $TiCl_4$ can form cluster-type complexes, where several catalyst molecules bind a larger number of oligomer molecules. The preferential formation of catalyst complexes with oligomer molecules is confirmed by kinetic data. A small amount of oligomer strongly inhibits the polymerization of styrene. This indicates that the initiation rate decreases owing to the formation, predominantly, of oligomer-catalyst complexes, which are only slightly reactive in carbonium polymerization. Because the cluster complexes oligomer-catalyst are probably sufficiently strong, as a result of growth with one of the molecules of the complex all the other oligomer molecules entering into the complex must also participate in growth. Owing to the influence of steric factors in the growth steps, the carbonium ion of styrene reacts predominantly with an oligomer molecule, which leads to values of the constants $r_1 < 1$. In a system with a low catalyst concentration, in the region of initial oligomer concentrations of 30-70 mole %, the ratio of the amount of oligomer to catalyst is large (see Table 1). This apparently creates favorable conditions for the formation of complexes with a larger number of oligomer molecules than in the second system (with a higher catalyst concentration), as a result of which in the first system a considerable enrichment of the copolymer with oligomer occurs, whereas in the second system it is insignificant. And only in the region of initial oligomer concentrations of about 70%, where the oligomer-catalyst ratio becomes greater than 50, is anomalous enrichment of the copolymer with oligomer observed (Fig. 1B). Not in all cases does the formation of cluster complexes monomer-catalyst lead to an increase in the reactivity of the monomer in carbonium polymerization. A striking example of such a case may be methyl methacrylate, which can also form cluster complexes with the catalyst. This is indicated by an increase in the viscosity of the monomer in the presence of $TiCl_4$ under conditions excluding the course of polymerization by either the carbonium or the radical mechanism. However, the structure of these complexes is probably such that participation of one molecule in the growth step does not entail the necessity for other molecules, included in the cluster complex, to enter into the reaction. Perhaps the reason for this is the presence of only one double bond in the methyl methacrylate molecule. As a consequence, only one definite arrangement of molecules should lead to participation of the entire cluster complex in the growth reaction. In the case of the oligomer, the presence of two double bonds and the large size of the molecule itself increase the range of structures leading to participation of the entire cluster complex in growth steps.

In the region of high oligomer concentrations ($> 80\%$) in both systems, enrichment of the copolymer with styrene is observed in comparison with the composition of the initial mixture. This is probably explained by the fact that the double bonds of the side branches of the macromolecules begin to participate in the growth steps, since their concentration increases sharply. Owing to the influence of steric factors they react predominantly with styrene. This assumption

is confirmed by data on the unsaturation of these copolymers, which is practically absent.

Thus, on the basis of data on the copolymerization of an oligomer with styrene in the presence of $TiCl_4$, it may be concluded that the reactivity of the oligomer in carbonium polymerization depends not only on the structure of the double bond, but also on the entire molecule as a whole. The structure of the oligomer molecule determines the composition and structure of the polar oligomer–catalyst complex. The composition and structure of the polar complex determine the reactivity of the unsaturated polyester in carbonium polymerization. The latter determines the composition and, consequently, essentially the entire complex of physicomechanical properties of the copolymers.

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