CHEMISTRY

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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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SOME FEATURES OF THE CARBONIUM POLYMERIZATION OF THE STYRENE-α-METHYLSTYRENE SYSTEM

The present work is devoted to a study of the joint cationic polymerization of styrene with α-methylstyrene. This system was first studied by us, and the phenomenon of a sharp increase in the rate of polymerization of styrene in the presence of small additions of α-methylstyrene was discovered.

The dependence of the rate of joint polymerization on the composition of the initial mixture was investigated; the compositions and molecular weights of the corresponding polymers were determined. The data obtained were compared with the results obtained in the study of the separate polymerization of these same monomers.

Special attention was paid to the investigation of the kinetics in the region of low concentrations of the more active component—α-methylstyrene. The influence on the acceleration effect observed in this region of a number of factors was studied: temperature, catalyst concentration, total monomer concentration, additions of water and hydrogen chloride. The polymerization was carried out with the catalyst $SnCl_4$ in ethyl chloride solution at 0°. The rate was determined by the dilatometric method. To determine the compositions of the copolymers, the method of infrared spectroscopy was used. The compositions of the copolymers were determined by comparing the spectra of the copolymers with the spectra of mixtures of the separate polymers. The molecular weights of the polymers were determined by the osmotic method.

Fig. 1. Rates of joint polymerization of the styrene–α-methylstyrene system. Concentration of $SnCl_4$, 0.002 mole/l. Total monomer concentration, 2.5 mole/l. Initial molar ratio styrene : α-methylstyrene: exp. 24—0 : 1; exp. 28—1 : 4; exp. 31—1 : 2.5; exp. 23—1 : 1; exp. 30—2.5 : 1; exp. 27—4 : 1; exp. 41—1 : 0.

The kinetic curves obtained for various initial ratios of the monomers, presented in Fig. 1, show that in the concentration range from 0.7 to 1.7 mole/l for α-

methylstyrene (at a total monomer concentration of 2.5 mole/l), the polymerization of styrene with α-methylstyrene proceeds without an induction period, with a gradually decreasing rate.

A comparison of the compositions of the copolymers with the compositions of the initial mixtures is given in Table 1, from which it follows that the copolymers are very strongly enriched in α-methylstyrene, as the more active component.

On the basis of the data on the compositions of the copolymers, using the integral composition equation, the constants of joint polymerization were calculated –

ization: α-0.05 (styrene), $\beta = 2.90$ (α-methylstyrene). As is seen from the data presented, the product of the copolymerization constants in this system is less than unity, which may be due to the action of polar or steric factors ([1,2]). In cationic polymerization, a tendency toward alternation of monomers can occur only as a result of the action of a steric factor. In the present system the rate of interaction of the carbonium ion of α-methylstyrene with its own monomer is lowered because of the presence of two substituents at one of the carbon atoms at the double bond.

Table 1

Experiment no.	Initial molar ratio styrene : α-methylstyrene	Molar ratio in copolymers styrene : α-methylstyrene	Degree of polymerization, %
89	21.5 : 1	5.3 : 1	5.9
16	10.8 : 1	1.77 : 1	2.3
14	4.3 : 1	0.75 : 1	12.9
10	1.1 : 1	0.30 : 1	20.3
1	0.75 : 1	0.20 : 1	9.2
17	0.47 : 1	0.13 : 1	27.3

Table 2

Experiment no.	Initial molar ratio styrene : α-methylstyrene	Molecular weight	Degree of polymerization, %
94	1 : 0	70,000	
67	22.5 : 1	54,900	58.6
63	11.3 : 1	47,000	73.0
89	21.5 : 1	28,200	5.9
27	4.5 : 1	23,800	24.7
23	1.14 : 1	26,400	22.0
31	0.47 : 1	21,400	27.4
28	0.28 : 1	23,500	19.0

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

Experiment no.	Initial molar ratio styrene : α-methylstyrene	Molecular weight	Degree of polymerization, %
54	0 : 1	26,700	50.2

The steric effect is also manifested in the separate polymerization of α-methylstyrene, as is confirmed by the reduced heat effect of its polymerization ([3]).

The molecular weights of the polymers are given in Table 2.

Of greatest interest is the kinetics in the region of small additions of the more active component. The kinetic curves for this region are shown in Fig. 2.

Fig. 2. Rates of joint copolymerization of the styrene—α-methylstyrene system at low concentrations of α-methylstyrene. Concentration of $SnCl_4$ 0.002 mole/l. Total concentration of monomers 2.5 mole/l. Initial molar ratio styrene : α-methylstyrene: exp. 74—4 : 1, exp. 67—21 : 1, exp. 63—13 : 1, exp. 79—20 : 1 (with triple concentration of $SnCl_4 = 0.006$ mole/l), exp. 77—50 : 1 (with triple concentration of $SnCl_4$), exp. 86—20 : 1 (total concentration of monomers reduced by a factor of 1.6)

shown in Fig. 2. Characteristic here is the effect of a strong increase in the rate of polymerization with time, beginning at a certain stage of polymerization characteristic for each given ratio of monomers,

ization. The degree of polymerization corresponding to the onset of acceleration, and the value of the maximum rate, depend on the initial ratio of the monomers. The greatest value of the maximum rate was observed at a component ratio of 10 mol styrene : 1 mol α-methylstyrene*. It was shown that, with increasing catalyst concentration, and also with increasing total monomer concentration, the acceleration of polymerization increases and the degree of polymerization corresponding to the onset of acceleration decreases (Fig. 2). At the same time, the time before the onset of acceleration is inversely proportional to the concentration of catalyst and α-methylstyrene and does not depend on the concentration of styrene, while the maximum rate is proportional to the concentration of α-methylstyrene and to the square of the concentration of styrene.

Fig. 3. Effect of additions of water and HCl on the rate of joint polymerization of the styrene—α-methylstyrene system in the presence of low concentrations of

α-methylstyrene. Concentration of $SnCl_4$, 0.002 mol/l. Total monomer concentration, 2.5 mol/l. Initial molar ratio of styrene : α-methylstyrene: exp. 82—10 : 1 ([HCl] = 0.004 mol/l), exp. 88—10 : 1 ([HCl] = 0.010 mol/l), exp. 95—20 : 1 ([$SnCl_4$] = 0.006 mol/l, [H_2O] = 0.012 mol/l).

Temperature has a strong effect on the observed phenomenon: lowering the temperature greatly decreases the ratio of the maximum rate to the initial rate and increases the induction period.

The observed maximum rates considerably exceed the sum of the rates of separate polymerization of these same monomers at the same initial concentrations.

As can be seen from Table 2, the average degrees of polymerization of the polymers obtained in the presence of acceleration (experiments Nos. 63 and 67) are lower than the average degree of polymerization of polystyrene (experiment No. 94) obtained under the same conditions. At the same time, the maximum rates in the case of acceleration are 26 times (molar concentration ratio of styrene to α-methylstyrene = 10 : 1) and 14 times (molar concentration ratio = 20 : 1) greater than the rate of polymerization of styrene.

From these data it follows that the observed effect of an increase in rate is associated with initiation events.

A sharp influence of additions of water and hydrogen chloride on the acceleration of polymerization also speaks in favor of this assumption. As can be seen from Fig. 3, the acceleration effect is strongly inhibited by additions of water and HCl. Below we shall discuss the possible reasons for the small increase in rate in the presence of high concentrations of HCl.

It is known that molecules of water and HCl readily form complexes with Friedel—Crafts catalysts. By binding the catalyst into a complex, they should thereby change the conditions of initiation and, consequently, also influence all processes associated with initiation events. Therefore their influence on the increase of rate with time in the present case is consistent with the assumption that this increase is due to initiation events. Apparently, in this system there is selective complex formation of α-methylstyrene with $SnCl_4$, which accounts for the high initiation rates in the presence of small additions of this monomer. From the found dependence of the rate on the concentration of the components it follows that formation of the initial active center occurs by interaction of com—

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* In experiments with very great acceleration the polymerization process proceeded nonisothermally. However, owing to the small temperature coefficient of this process, the observed slight increase in temperature had little effect on the reaction rate.

complex catalyst—α-methylstyrene with styrene. Competing complex formation of $SnCl_4$ with H_2O and HCl should remove the rate-increase effect, which is indeed observed experimentally.

Fig. 4

Figure 4: Fig. 4

Another interesting factor observed in the region of low concentrations of α-methylstyrene in the initial mixture is the effect of a partial decrease in the initial rate of polymerization of styrene upon introduction of small additions of α-methylstyrene (Fig. 4).

The effect of inhibition of the polymerization of a less active monomer by small additions of a more active monomer is well known in radical polymerization. It is due to the antibatic relationship between the activities of the monomer and of the corresponding radical. In ionic polymerization, owing to the absence of a method for determining the individual chain-growth constants, such an antibatic relationship could not be established by direct methods.

The effect we have observed, namely the decrease in the initial rate of polymerization of styrene by small additions of α-methylstyrene, is an indirect indication that such an antibatic relationship also occurs here.

As the process proceeds, the polymerization rate, owing to depletion of α-methylstyrene, should increase somewhat, approaching the polymerization rate of pure styrene.

Additions of H_2O and HCl, by eliminating the acceleration effect apparently caused by initiation acts, make it possible to observe acceleration of the process due to an increase in the chain-growth rate as the less active carbonium ions of α-methylstyrene are depleted (see the curve of experiment 82 in Fig. 3, and also Table 2, experiments Nos. 89 and 67).

Fig. 4. Dependence of the initial rates of copolymerization of the styrene–α-methylstyrene system on the initial ratio of the components. $SnCl_4$ concentration 0.002 mol/l. Total monomer concentration 2.5 mol/l

Thus, it has been shown in this work that the reactivity of the α-methylstyrene molecule toward the carbonium ion of styrene is considerably higher than the reactivity of styrene, and that small additions of this more active component cause a sharp increase in the polymerization rate of styrene. The observed effect is apparently of a more general nature and is associated with the sharp difference in the activities of the monomers, since we have shown that in the styrene–isobutylene system, in the region of small additions of the more active component, isobutylene, a sharp increase in the polymerization rate was likewise observed.

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CITED LITERATURE

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