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Abstract

Full Text

CHEMISTRY

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THE EFFECT OF DIMETHYLFORMAMIDE ADDITIONS ON THE COMPOSITION OF COPOLYMERS OF METHACRYLIC ACID WITH METHYL METHACRYLATE AND WITH STYRENE

(Presented by Academician A. V. Kargin, March 24, 1962)

The question of the influence of the medium in which radical copolymerization takes place on the composition of the copolymer and on the relative-activity constants remains insufficiently clear to this day. There is evidence ([1,2]) that the medium does not exert a substantial influence on the composition of the copolymer. We supposed that the most promising way of changing the activities during copolymerization, and consequently the alternation of monomer units in the copolymer, is the introduction into the initial monomer mixture of various additives whose molecules can form complex compounds with molecules of the more reactive monomer.

Fig. 1. Dependence of the viscosity of mixtures of dimethylformamide with MMA *(1)* and with MAA *(2)* on their composition

In the present paper the results are set forth of a study of the influence of additions of dimethylformamide and ethyl alcohol, introduced into the copolymerizing mixtures methacrylic acid (MAA)—methyl methacrylate (MMA) and MAA—styrene, on the composition of the copolymers formed. These monomer pairs were chosen as objects of study because, in their copolymerization, first, a more rapid conversion of MAA takes place ([3,5]), and, second, because the carboxyl group of MAA is capable of forming hydrogen bonds with various polar groups ([5]).

In order to establish the presence of complex formation between MAA molecules and polar additives, we carried out a viscometric study of their mixtures over

the entire composition range.

Experimental Part

The initial monomers were purified by repeated distillation under vacuum. Dimethylformamide and ethyl alcohol were introduced into the monomer mixtures as additives. Viscometric tests were carried out with an Ostwald viscometer at 25°C. The results of the viscometric tests are presented as graphical data in the figure.

Curve 2 in Fig. 1, which shows the change in viscosity with change in composition for mixtures of MAA with dimethylformamide, has a clearly expressed maximum, indicating interaction, apparently due to the forma-

formation of hydrogen bonds between polar groups. The composition of the mixtures is expressed in volume fractions. A similar, although less clearly expressed, maximum was also observed for mixtures of MAA with ethanol. For mixtures of MMA with dimethylformamide no maximum in the change of viscosity was observed (curve 1 in Fig. 1).

In the next series of experiments, the effect of polar additives introduced into the initial monomer mixtures on the composition of copolymers was studied. As already noted, the monomers were purified by vacuum distillation. Benzoyl peroxide was used as the initiator in an amount of 0.5% of the weight of the monomer mixture. Polymerization was carried out at 45° in sealed ampoule dilatometers up to 5% conversion of the monomer.

The copolymer was separated from the monomers by threefold reprecipitation, dried under vacuum, dissolved in an acetone–methanol mixture, and analyzed. The acid number of the copolymer was determined by two methods: by titration in the presence of thymolphthalein and by conductometric titration.

Figure 2 presents data showing the effect of additions of ethyl alcohol (1) and dimethylformamide (2) on the composition of the copolymer formed from the initial equimolar mixture of MAA with MMA. On the ordinate axis are plotted the mole fractions of MAA in the copolymer; on the abscissa axis, the ratio of the number of moles of additive to the mole of MAA. Curves 1 and 2 (Fig. 2) show a decrease in the content of MAA in the copolymers with increasing amounts of ethyl alcohol and dimethylformamide introduced into the initial mixtures of MMA with MAA, the effectiveness of dimethylformamide being considerably higher than that of ethyl alcohol. Similar experiments were carried out in the polymerization of styrene with MAA at different dosages of dimethylformamide. The results of the experiments are illustrated by curve 3, shown in Fig. 2. As in the preceding case, dimethylformamide has a considerable effect on the composition of the copolymer formed, in the direction of decreasing the MAA content.

Fig. 2. Change in the content of MAA in copolymers formed in equimolar mixtures: MMA with MAA with increasing amounts of ethyl alcohol (1) and

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

dimethylformamide (2), and also styrene with MAA with increasing amounts of dimethylformamide (3)

The decrease in the MAA content in the copolymers considered is a consequence of the decrease in the reactivity of MAA in the presence of complex-forming additives. We believe that this decrease in reactivity can be explained by the lower mobility of the complex of the monomer with the additive, and also by steric hindrance in the interaction of this complex with the radical. It is also possible that, upon formation of hydrogen bonds, the effect of the carboxyl group of MAA on the conjugated double bond is reduced. As a result, the unsaturation of this bond and its reactivity decrease; a similar effect is considered in work (5).

Fig. 3. Copolymer composition curves for MMA–MAA, obtained without additives (1) and in the presence of 2 mol of dimethylformamide per 1 mol of MAA (2). m_2, M_2 are the mole fractions of MAA in the copolymer and in the monomer mixture.

It is obvious that the effects considered should be reflected in the character of the copolymer-composition curves when the process proceeds in the presence of additives. Indeed, it follows from Figs. 3 and 4 that the composition curves of the copolymers obtained in the presence of dimethylformamide (curve 2) differ substantially from the composition curves of the copolymers obtained without additives ([1]).

The copolymerization constants r_1 and r_2, calculated from data on the copolymer compositions by the Mayo-Lewis method, are as follows: MMA–MAA system without additives: $r_1 = 0.55 \pm 0.02$, $r_2 = 1.55 \pm 0.06$; MMA–MAA with an addition of dimethylformamide: $r_1 = 0.98 \pm 0.04$, $r_2 = 0.68 \pm 0.05$; styrene–MAA system without additives: $r_1 = 0.2 \pm 0.02$, $r_2 = 0.66 \pm 0.08$; styrene–MAA with an addition of dimethylformamide: $r_1 = 0.53 \pm 0.02$, $r_2 = 0.45 \pm 0.06$.

For both systems r_2 decreases, while r_1 increases.

The results obtained can be explained as follows. Since, in the case of complex formation of MAA molecules, their reactivity, and along with it the rate constants K_{22} and K_{12}, should decrease, $r_1 = K_{11}/K_{12}$ should increase, while $r_2 = K_{22}/K_{21}$ should decrease, because in the first case the denominator decreases, and in the second case the numerator decreases.

The decrease in K_{22} can be detected directly in the homopolymerization of MAA

Fig. 4. Copolymer-composition curves for styrene–MAA obtained without additives (1) and in the presence of 2 moles of dimethylformamide per 1 mole of MAA (2). m_2, M_2—mole fractions of MAA in the copolymer and in the monomer mixture.

Figure 4: Fig. 4. Copolymer-composition curves for styrene–MAA obtained without additives (1) and in the presence of 2 moles of dimethylformamide per 1 mole of MAA (2). m_2, M_2—mole fractions of MAA in the copolymer and in the monomer mixture.

in the presence of dimethylformamide.

Fig. 4. Copolymer-composition curves for styrene–MAA obtained without additives (1) and in the presence of 2 moles of dimethylformamide per 1 mole of MAA (2). m_2, M_2—mole fractions of MAA in the copolymer and in the monomer mixture.

When kinetic studies of the polymerization of MAA in mixtures of benzene with dimethylformamide were carried out, a considerable decrease in the initial rate was found as the dimethylformamide content increased. This question will be covered in a separate communication.

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