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Abstract

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POLYCONDENSATION IN EMULSIONS

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The course of chemical reactions in heterogeneous emulsion systems is often highly specific. Among processes for the synthesis of polymers, the peculiarities of emulsion polymerization are widely known. Thanks to them, polymerization in emulsion systems (droplet and latex variants) has found broad application in industry.

As in the case of polymerization processes, when carrying out polycondensation processes in emulsion systems two cases are possible: 1) the polymer-forming reaction proceeds at the phase boundary; 2) the polymer-forming reaction proceeds in the bulk of one of the phases. The first case occurs in the synthesis of polycondensation polymers by the method of so-called interfacial polycondensation under vigorous stirring (emulsification) of the system, and has been studied fairly well. The second case—the course of the polycondensation reaction in the bulk of one of the phases of an emulsion system, hereinafter called emulsion polycondensation—has not yet been studied.

To carry out emulsion polycondensation, it is necessary, first of all, to create such conditions that both components will be completely in one of the phases. In the case of the polycondensation reaction of diamines and dichloroanhydrides of carboxylic acids, the basic indispensable condition for this must be a sufficiently large value of the distribution coefficient K_1 of the diamine in a two-phase system:

$$K_1 \gg 1 \quad (K_1 = C_{\text{org}}/C_{\text{H}_2\text{O}}).$$

However, the systems usually used for interfacial polycondensation do not provide a sufficiently large value of the diamine distribution coefficient; for a number of interfacial polycondensation systems $K_1 = 0.005 \div 1.0$ ([1]).

Systems ensuring complete transfer of the diamine into the organic phase, and consequently systems suitable for carrying out emulsion polycondensation of diamines with dichloroanhydrides of carboxylic acids (emulsion polyamidation), proved to be emulsions obtained from two miscible liquids with the use of salting-out agents.

We studied certain regularities in the synthesis of the aromatic polyamide—polymetaphenylene isophthalamide—in the emulsion system tetrahydrofuran (THF) —water—soda.

The polymer synthesis was carried out by a procedure analogous to that described in ([2]) and consisting of the following: isophthalic acid dichloroanhydride was dissolved in tetrahydrofuran and, with rapid stirring, added to an aqueous solution of metaphenylenediamine and soda. When the indicated solutions are combined, an emulsion forms, since soda partially salts tetrahydrofuran out of water. The polymer is formed in this emulsion.

It was shown that the conditions for the synthesis of the highest-molecular-weight product are: concentration of isophthalic acid dichloroanhydride in tetrahydrofuran—0.33 mol/l; concentration of metaphenylene-

diamine in water—0.33 mole/liter; concentration of Na_2CO_3 in water—0.66 mole/liter, initial ratio of the organic and aqueous phases 1 : 1, intensive stirring of the system.

Table 1

Comparison of the characteristics of systems in emulsion and interfacial methods of polycondensation

Characteristic	System: emulsion: THF—water	System: interfacial: CCl_4—water
Composition of the two-phase system (ratio of volumes of the organic and aqueous phases)	2.8 : 1	1 : 1
Water content in the organic phase, vol. %	38	0.008*
Amount of diamine transferred into the organic phase, %	96	4
Distribution coefficient of diamine, $K_1 = C_{org}/C_{H_2O}$	8.7	0.04
Distribution coefficient of soda, $K_2 = C_{org}/C_{H_2O}$	0.02	0.000
Surface tension at the interface, dyn/cm	2.0	40.5

Characteristic	System: emulsion: THF–water	System: interfacial: CCl_4–water
Swelling of the polymer in the organic phase, cm^3/g	0.97	0.16
Polymer yield in synthesis relative to theory, %	98	88
Characteristic viscosity in H_2SO_4	1.5–2.0	0.3

* According to data (3), in the absence of soda.

In parallel with the experiments on polymer synthesis, we determined certain characteristics of model emulsion systems, which differed from the real ones only in that they contained no dichloroanhydride. The presence of dichloroanhydride in the organic phase does not substantially affect the characteristics of the two-phase system.

The characteristics of the emulsion system that is optimal for the synthesis of high-molecular-weight polyamide, in comparison with one of the systems of interfacial polycondensation, are given in Table 1.

From the data of Table 1 it is evident that, in the emulsion variant of the synthesis, 96% of the metaphenylenediamine passes into the organic phase, whereas in the interfacial variant–4%. This indicates that the process of polycondensation of the diamine and dichloroanhydride in the tetrahydrofuran–water–soda system proceeds entirely in the organic phase.

To further elucidate the mechanism and the locus of the reaction in the indicated system, the influence of the component ratio on the magnitude of the molecular weight (viscosity) of the polymer was studied. For comparison, an analogous dependence was studied for the polycondensation of the indicated monomers in a dimethylacetamide solution and at the interface of two liquids. The corresponding data are presented in Fig. 1.

From Fig. 1 it is evident that the curve of the dependence of the molecular weight (viscosity) of the polyamide on the component ratio in emulsion polycondensation coincides completely with the analogous dependence for the reaction in a dimethylacetamide solution, is analogous to the theoretical curve for homogeneous cases of polycondensation (4), and does not coincide at all with the same dependence for the interfacial variant of the process. That is, the data of Fig. 1 indicate that polycondensation in the emulsion under consideration proceeds in the same way as in solution. This gives grounds to assume that, in this case, polycondensation indeed takes place entirely within the bulk of the organic phase of the emulsion system.

Table 2

Effect of the distribution coefficients of the diamine and acceptor on the molecular weight of polyamides in the emulsion polycondensation of metaphenylenediamine and isophthaloyl chloride

Name of acceptor	Initial concentration of acceptor, mol/l	Final concentration of component in the organic phase, mol/l	Final concentration of diamine that has passed into the organic phase, %	K_1 (amine)	Final concentration of acceptor in the organic phase, mol/l	Final concentration of acceptor in the aqueous phase, mol/l	K_2 (soda)	Polymer yield, % of theory	$[\eta]$
Na_2CO_3	0.33	0.19	88	9.4	0.060	0.94	0.064	98	1.00
Na_2CO_3	0.66	0.22	96	8.7	0.024	1.18	0.020	98	1.45
NaOH	0.80	0.29	80	3.5	0.027	0.83	0.030	96	0.45
NaOH + NaCl	0.80	0.34	86	6.9	0.001	0.78	0.001	98	1.20
NaOH + NaCl	2.3	0.34	86	6.9	0.001	0.78	0.001	98	1.20

Proceeding from the foregoing, it may be asserted that the process of emulsion polycondensation takes place in the kinetic region, in contrast to interfacial polycondensation, which proceeds in the diffusion region ([5]).

[Fig. 1 and Fig. 2 diagrams visible on page]

Fig. 1. Dependence of the viscosity (molecular weight) of polymetaphenyleneisophthalamide on the ratio of components.
1 —emulsion polycondensation, 2 —polycondensation in dimethylacetamide solution, 3 —polycondensation at the water–CCl_4 interface.

Fig. 2. Scheme of the distribution of component concentrations (ordinate) in different methods of synthesis. The reaction zone is hatched. *A* —diamine in the aqueous phase, *B* —diamine in the organic phase, *C* —acid chloride in the

organic phase, D –soda in the aqueous phase. A', B', C' –the corresponding concentrations at the moment of reaction.

Table 2 gives the results of experiments on the synthesis of polymetaphenyleneisophthalamide in the emulsion system tetrahydrofuran–water in the presence of various acceptors and salting-out agents.

From the data of Table 2 it is seen that, in order to obtain high-molecular-weight polymers in emulsion systems, not only complete transfer is necessary

of diamine into the organic phase, but also the practically complete absence of an HCl acceptor (alkali) in the organic phase.

This achieves separation of the individual stages of the polycondensation process: the principal polymer-forming reaction proceeds in the organic phase of the emulsion system, while neutralization of the by-product HCl that is liberated occurs in the aqueous phase. As a result of such a sharp separation of the zone of the principal reaction and the neutralization zone (alkaline zone), the share of the side reaction–the hydrolysis reaction–in the case of emulsion polycondensation is considerably reduced. This leads to the fact that, in emulsion polycondensation, it becomes possible to obtain high-molecular-weight products in high yields, as is also observed experimentally.

In addition to the distribution coefficient of the diamine, the course of polycondensation and, consequently, the molecular weight of the polymer formed will be greatly influenced by such characteristics of the emulsion system as the composition of the organic phase, the magnitude of the interfacial tension, the degree of dispersion, the swelling of the polymer in the organic phase, and others.

It should be noted that the polycondensation process described by us is undoubtedly emulsion in character. This is confirmed experimentally by the fact that, when experiments are carried out under static conditions or with slight stirring, i.e., under conditions in which emulsions are absent, a polymer with a much lower molecular weight is formed ($[\eta] = 0.36$) than with vigorous emulsification of the system ($[\eta] = 2.0$ at a stirrer speed of 5000 rpm).

Good emulsification of the system during stirring is undoubtedly favored both by the low surface tension at the phase boundary of the emulsion and by the small difference in the specific gravities of these phases.

A schematic comparison of the interfacial and emulsion methods of polycondensation is given in Fig. 2, from which it is seen that, in emulsion polycondensation, the contact of the alkaline zone with the reaction zone (containing acid chloride) is considerably smaller than in the interfacial method of the process.

This also accounts for the fundamental possibility of synthesizing, by the method of emulsion polycondensation, polymers of much higher molecular weight than by the method of interfacial polycondensation.

In conclusion, we note that the system we have investigated is not the only one; emulsion polycondensation may possibly be carried out with the participation

both of other emulsion components and of other reagents.

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