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Abstract

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THE PRODUCTION OF GRAFTED COPOLYMERS OF STYRENE WITH CAPROLACTAM

The production of grafted copolymers of the vinyl type and ϵ-caprolactam is of great interest. The method for obtaining such copolymers may vary.

Flory and Sheffer (^{1}) described the production of polycondensation products of three-dimensional structure during the polymerization of caprolactam in the presence of polybasic acids. On the basis of this method Flory (^{2}) proposed a route for the synthesis of grafted copolymers of acrylic acid. Chapman and Valentine (^{3}) carried out the synthesis of grafted copolymers by conducting the reaction between a copolymer of styrene and methyl methacrylate, on the one hand, and ϵ-caprolactam, on the other. Such a reaction is initiated by water and proceeds at t 220–250°. Korshak and co-workers ($^{4-7}$) carried out the grafting of a number of vinyl monomers onto polycaproamide.

Recently, increasing attention of researchers has been attracted by the method of rapid low-temperature anionic polymerization of ϵ-caprolactam ($^{8-11}$). Wichterle and Gregor (^{12}), in studying the mechanism of the anionic polymerization reaction of caprolactam, showed that polymeric imides obtained as a result of the copolymerization of N-methacryloylcaprolactam (MAC) with styrene catalyze the polymerization of ϵ-caprolactam with the formation of grafted copolymers in toluene solution. Since the possibility of grafting caprolactam onto a copolymer of styrene with MAC had been shown for only one ratio of the latter, 60.9 : 39.1, i.e., for a very high content of the imide component, and also because in that case the reaction medium was toluene, it seemed expedient to us to carry out a series of experiments to clarify certain regularities of this process.

The aim of this investigation was to substantiate the optimal conditions (the amount of catalytic system and the degree of conversion) for copolymers of various composition under conditions of bulk copolymerization. In order to determine the amount of catalytic system necessary and sufficient for obtaining a copolymer with ϵ-caprolactam at a content of from 2 to 50% of the styrene introduced (or the amount of imide groups in the copolymer of styrene with MAC), we obtained copolymers with an imide-component content from 0.9 to

10%.

In view of the fact that the presence of imide groups in a copolymer of styrene with MAC can be determined quantitatively by elemental analysis for nitrogen only when their content is not less than 7.6-10% ($N = 1.0$ and $N = 1.28$) (and this difference lies within the error limits of the method of determination), we used infrared spectroscopy for the evaluation.

The copolymers obtained, as could be assumed on the basis of data from IR spectra, characteristic viscosity, elemental analysis, and thermomechanical curves, are identical products differing only in the number of imide groups in the macromolecule.

Table 1

Calculation of the dependence of the number and molecular weight of grafts on the initiator content

No.	MAC content in the imide copolymer (wt. %)	Amount of MAC (in mol. % relative to ϵ-CL)	Mol. wt. of the imide copolymer	Number of grafts per macromolecule	Mol. wt. of one graft
1	0.9	0.14	50 000	2.5	80 000
2	1.77	0.28	50 000	5	40 000
3	2.62	0.4	50 000	7.5	30 000
4	3.9	0.6	50 000	10	20 000

Thus, in accordance with the proposed Table 1, for example, for a copolymer/ϵ-caprolactam ratio of 20 : 80, we have different amounts of cocatalyst for one and the same copolymer/ϵ-caprolactam ratio.

As is evident from the calculation given in Table 1, it is also possible, by regulating the amount of cocatalyst, to vary the number and molecular weight of the grafts.

Fig. 1. Dependence of the conversion of caprolactam (1) and of the nitrogen content in the copolymer (2) on the amount of catalytic system

Fig. 2. Dependence of the amount of catalytic system on the amount of styrene introduced into the graft copolymer

It is known (^{11}) that the most effective catalytic system for the high-rate low-temperature polymerization of ϵ-caprolactam is the system consisting of the sodium salt of caprolactam and N-acetylcaprolactam, taken in an equimolecular ratio. Therefore the principle of equimolecularity was maintained in the present case as well.

The optimum amount of catalytic system was determined from the conversion of the starting products after extraction with water and was monitored by the method of elemental analysis. In Fig. 1, by way of example, are shown the curves for the conversion of caprolactam (1) and the nitrogen content in the graft copolymer (2), on the basis of which the optimum styrene : MAC ratio is selected for a copolymer/ϵ-caprolactam ratio of 20 : 80. It is evident that in this case the optimum ratio is styrene/MAC = 97.4 : 2.6 (which corresponds to 0.4 molar percent of the catalytic system calculated on ϵ-caprolactam), since increasing the content of the imide component in the copolymer does not increase the conversion, and only lowers the molecular weight of the polyamide graft in the graft copolymer, while decreasing it entails a decrease in conversion.

Using the indicated method for determining the optimum conditions for other copolymer/ϵ-caprolactam ratios, we obtained the following dependence for determining the necessary and sufficient amount of catalytic system (Fig. 2). In this case, the optimum value was taken to be a yield not lower than 94%, for a reaction duration of 1 h at $t = 180^\circ$.

The polystyrene/polyamide ratio was controlled by the nitrogen content, determined by the Kjeldahl method in the graft copolymer after extraction with water.

Thus, taking into account that, under our specific conditions, the optimum for the polymerization of ϵ-caprolactam is the presence of a catalytic system equal to 0.2 mole % relative to ϵ-caprolactam, we were able to establish that, with an increase in the amount of styrene introduced into the graft copolymer, the presence of imide groups in the copolymer of styrene with MAC should increase proportionally to $\mathrm{tg}\,\alpha$.

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