Preparation of poly(propylene—propyl methacrylate) copolymer

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An effective procedure of chemical modification of polypropylene by polar monomer, *i.e.* n-propyl methacrylate, as well as a method for isolation of the formed poly(propylene—propyl methacrylate) copolymer from the polymer mixture containing polypropylene and copolymer on the basis of their different solubility in *o*-xylene at laboratory temperature has been elaborated. In the solution the copolymer is held by the effect of poly(propyl methacrylate) excess in macromolecules. Under given conditions, only that part of copolymer which contains more than 65 mass % of poly(propyl methacrylate) can be isolated.

Разработан эффективный способ химической модификации полипропилена полярным мономером, пропилметакрилатом и метод изоляции образовавшегося сополимера поли(пропилен—пропилметакрилат) из полимерной смеси с полипропиленом на основании их различной растворимости в *о*-ксилоле при комнатной температуре. Сополимер удерживается в растворе при влиянии избытка полипропилметакрилата в макромолекуле. При данных условиях удается изолировать только ту часть сополимера, которая содержит больше, чем 65 вес. % полипропилметакрилата.

The activated chemical modification of oxidized powdered isotactic polypropylene by vinyl monomers in the aqueous emulsion at 30°C [1, 2] gives rise to a polymer bonded to polypropylene (copolymer) and to a smaller amount of free homopolymer. The homopolymer can be separated from the solid phase of polypropylene by means of simple filtration of the emulsion in which it occurs. The powdered material which is found on the filter represents a polymer mixture consisting of the formed copolymer and nonmodified polypropylene because the modification takes place on the surface of the powdered polypropylene. For the isolation of copolymer from the polymer mixture there is no universal method yet. It is due to the fact that this separation strongly depends on the synthesis method and on the nature of the polymers composing the backbone and graft chains. The methods for isolation of block- and graft-copolymers from mixtures after polymerization have been compiled by *Ceresa* [3] and *Ikada* [4].

This paper deals with the isolation of poly(propylene—propyl methacrylate) copolymer from nonmodified polypropylene. The copolymer was prepared by chemical modification of polypropylene by n-propyl methacrylate in emulsion.

Experimental

Materials

Polypropylene (PP) — a powdered isotactic product of Slovnaft, Bratislava, with bulk weight 0.395 kg dm^{-3}, granularity 0.10—0.15 mm, $\bar{M}_w = 3.3 \times 10^5$ g mol^{-1}, and $\bar{M}_w/\bar{M}_n = 4.1$. The nonisotactic portions were removed from polypropylene by extraction with boiling n-heptane. PP used in this study was oxidized in fluidized bed for 60 min with oxygen enriched with ozone (concentration of ozone was 1.2×10^{-5} kg dm^{-3}). The hydroperoxidic groups were removed from the oxidized PP before use by decomposing them in the system KI—glacial acetic acid [5]. The polymer processed in such a way contained 2.2×10^{-2} moles of O_2 kg^{-1} of a more stable type of peroxide [6].

n-Propyl methacrylate (PrMA) was prepared by preesterification of methyl methacrylate with n-propanol under acid conditions. Before use, it was prepolymerized and distilled *in vacuo* in nitrogen atmosphere. The purity of monomer determined by gas chromatography was 99.6 mass %.

Other components of the polymerization system, *i.e.* water, aqueous solutions of triethylenetetramine (TETA), and $FeSO_4 \cdot 7H_2O$ as well as the ionic emulsifier Mersol H ($C_{17}H_{35}SO_3Na$) described earlier [2] were deprived of oxygen by boiling in nitrogen atmosphere.

Nitrogen and oxygen were additionally purified [7] and the solvents used were anal. grade chemicals.

Procedures and equipment

The modification of powdered isotactic polypropylene was described earlier [8]. The polymerization system contained the oxidized powdered PP, monomer, activator of initiator (PP peroxide), the $FeSO_4$—TETA chelate (mole ratio 2:3), and ionic emulsifier Mersol H. The temperature of reaction was 30°C. The reaction product, *i.e.* the solid phase of polypropylene containing the bonded poly(propyl methacrylate), was obtained by filtrating the emulsion on a fritted glass. The homopolymer was isolated from the filtrated emulsion by precipitation with methanol. The result of modification and homopolymerization was expressed as mass fraction (%) of the consumed PrMA with reference to its initial quantity. The composition of the product was expressed as mass fraction (%) of the bonded poly(propyl methacrylate) (PPrMA) in the solid phase. The residues of homopolymer were removed from the surface of the solid powdered product by repeated cold extraction with acetone. The copolymer formed under these conditions as well as nonmodified polypropylene remained insoluble. Thus the subsequent isolation of the pure copolymer was reduced to its separation from a mixture with nonmodified polypropylene.

The infrared spectra of polymers were measured with the instrument UR-20 (Zeiss, Jena) using the KBr technique. The content of PPrMA in the isolated samples of copolymer as well as in the insoluble residue was determined by means of the calibration curve according to the absorbance at $\nu = 1730\ \text{cm}^{-1}$. The calibration curve was plotted according to the absorbance of the $C=O$ groups of mechanical mixtures of PP and homopoly(propyl methacrylate).

The content of oxygen in polymers was determined by means of an elemental analyzer (C. Erba, Milan, Model 1102). It was used for calculating the content of PPrMA in the isolated samples.

Results and discussion

Synthesis of copolymer

It has resulted from preliminary experiments that a more stable type of the peroxide of PP was important for the modification of PP with polar n-propyl methacrylate, like for the modification of PP with styrene [5, 6, 9]. In order that the polymer might contain as little peroxidic residues as possible and the formation of homopolymer during the synthesis might be suppressed to the utmost, the unnecessary hydroperoxidic groups of oxidized PP were removed before polymerization.

It was found earlier [10] that the result of the modification of PP was most affected by two factors, *i.e.* by the concentration of the activator of initiator (chelate $FeSO_4$—TETA) and by that of the emulsifier (Mersol H). The simultaneous influence of these factors on the result of PP modification by n-propyl methacrylate, like for the modification of PP with styrene [5, 6, 9]. In order that the polymer might contain as little peroxidic residues as possible and the given in Table 1. The specification and results of the experiment as well as the theoretically expected results are summarized in Table 2. The result of the mathematical processing of the experimental results is an approximation polynomial which expresses the relationship between the investigated variables and mass fraction (%) of PrMA bonded to PP in 1 h. Its form is

$$Y = 22.58 + 8.05x_1 - 0.92x_2 + 0.06x_1x_2 - 4.30x_1^2 - 1.50x_2^2 \qquad (1)$$

Table 1

Conditions of the planned experiment[a]

x_i	Concentrations mol dm^{-3} 10^{-3}	Factor level −1.414	 −1	 0	 1	 1.414	I_i
x_1	Chelate	0.328	0.918	2.295	3.672	4.262	1.377
x_2	Emulsifier	1.197	2.872	7.180	11.488	13.163	4.308

a) System consisted of 1 g PP, 1 g PrMA, and 5 ml aqueous phase containing dissolved activator and emulsifier. Temperature 30°C, time 1 h.

Table 2

Detailed description of the planned experiment and its results (Y_{exp}). Results expected according to regression (Y_{theor}) expressed as mass fraction (%) of the PrMA bonded to PP in 1 h

n	x_1	x_2	Y_{exp}	Y_{theor}
1	−1	−1	11.6	9.7
2	1	−1	24.8	25.7
3	−1	1	9.8	7.8
4	1	1	23.2	24.0
5	−1.414	0	0.1	2.6
6	1.414	0	26.8	25.4
7	0	−1.414	20.4	20.9
8	0	1.414	17.6	18.3
9	0	0	22.5	22.6
10	0	0	21.5	22.6
11	0	0	23.5	22.6
12	0	0	22.2	22.6
13	0	0	23.2	22.6

The stationary conditions are: $x_{1s}=0.93$ (3.58×10^{-3} mol dm^{-3}), $x_{2s}=-0.29$ (5.94×10^{-3} mol dm^{-3}), $Y_s=26.47\%$.

The error of the determination was ±0.82%. The validity of regression eqn (*1*) was proved on the basis of F test because $4.4=F<F_{crit}^{0.05}=6.09$.

A graphical expression of eqn (*1*) is the contour diagram given in Fig. 1. As evident, the optimum conditions for the modification of PP by n-propyl methacrylate

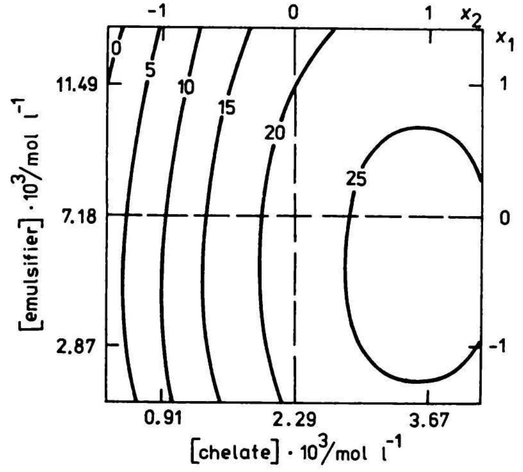

Fig. 1. Contour diagram expressing the influence of concentration of FeSO$_4$—TETA chelate and emulsifier Mersol H on the percentage of PrMA bonded to PP at 30°C in 1 h.

are in the experimental region (x_{1s}, x_{2s}) while maximum 26.5 mass % of the bonded monomer (Y_s) may be obtained in the given time interval. Under these conditions, the time course of PP modification by n-propyl methacrylate and the simultaneous homopolymerization were followed (Fig. 2). The course of polymerization is similar to that of the current emulsion polymerization. Thus a high efficiency of modification (expressed as mass fraction in % of the bonded polymer from the total amount of the formed polymer) was reached. It varied in the range 90.2—93.7%.

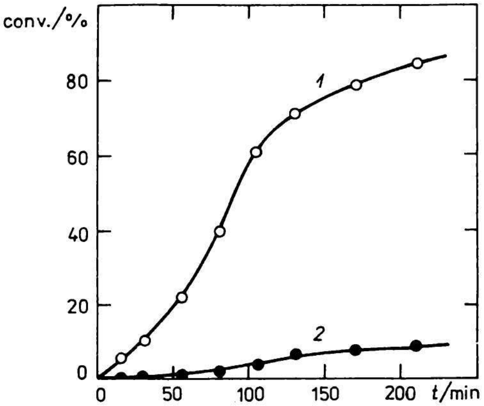

Fig. 2. Influence of time on mass fraction (%) of PrMA polymerized under optimum conditions.
1. Bonded PrMA; *2.* PPrMA homopolymer.

Isolation of copolymer

The isolation of poly(propylene—propyl methacrylate) copolymer (PP—PPrMA) from the mixture with PP after synthesis was made possible, on the one hand, by solubility of both polymers in selected solvents at 120°C (the crystallites of isotactic PP started to melt in pure solvent [13]) and, on the other hand, by solubility of only one of them (copolymer) in a solution cooled to laboratory temperature (by slow cooling of the hot solution nonmodified PP started to separate from the solution and, to a certain extent, entrained a part of copolymer into the insoluble portion). In order to prevent side reactions, we worked in inert atmosphere. As the bonding of PPrMA branches to PP is carried out through an etheric bond [14], it is not assumed that the PPrMA branches could be eliminated from the PP backbone at this temperature.

From the view-point of realization of the separation process, it was convenient to use *o*-xylene and the following procedure of isolation of PP—PPrMA copolymer from its mixture with PP was elaborated: A polymer mixture in *o*-xylene of 10 g dm^{-3} concentration was heated in a glass tube in nitrogen atmosphere for 2 h at 120°C in consequence of which the whole sample was dissolved. The solution was allowed to cool freely to laboratory temperature (the rate of cooling was about 1°C min^{-1}) whereby a portion of polymer was eliminated from solution. It was separated from the copolymer solution by centrifugation at 12000 revolutions in a minute lasting 1 h and subsequent filtration through a fritted glass S_2. The copolymer was precipitated from the filtrate by methanol and dried at laboratory temperature. The insoluble residue was dried at 50°C.

Characterization of the isolated copolymer and insoluble portion

Six samples of the modified PP containing 6.4—42.2 mass % of the bonded PPrMA in the solid phase were prepared by polymerizing during different periods of time under the established optimum conditions (Fig. 1). The samples were subjected to the separation procedure and the quantity of the isolated copolymer as well as of the insoluble residue was determined gravimetrically. The proportion of both polymer substances in the isolated copolymer and in insoluble residue was determined from the content of oxygen found by elemental analysis and by infrared spectroscopy (Fig. 3). The quantitative and qualitative results describing separation of the samples of copolymer are given in Table 3.

From this table it is obvious that the quantity of the isolated copolymer (column I) increases with the quantity of PPrMA bonded to PP (column IX) owing to which the quantity of the insoluble residue decreases (column IV). However, it is remarkable that the content of PP in the isolated copolymer (difference between the values in column I and column II) remains constant after

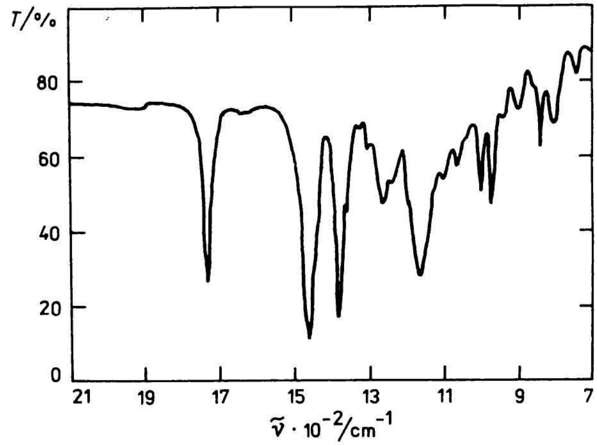

Fig. 3. Infrared spectrum of poly(propylene—propyl methacrylate) copolymer; sample *5* in Table 3.

Table 3

Quantitative and qualitative characterization of separation process. Solvent *o*-xylene, weight of polymer mixture 0.4 g, amount of solvent 40 cm^3

No.	$\tau_{\text{polym.}}$/min	Isolated copolymer m/mg			Insoluble residue m/mg			Total balance of PPrMA m/mg		
		I	*II*	*III*	*IV*	*V*	*VI*	*VII*	*VIII*	*IX*
1	15	11.6	7.7	7.9	388.5	12.7	18.6	20.4	26.5	25.6
2	30	24.8	19.3	19.8	375.3	20.2	22.9	39.5	42.7	40.0
3	45	43.6	37.0	37.9	356.4	19.6	26.0	56.6	63.9	65.2
4	60	62.7	54.7	56.2	337.3	28.3	34.0	83.0	90.2	90.4
5	80	95.7	87.7	89.1	304.3	34.1	40.5	121.8	129.6	131.6
6	100	128.7	120.6	122.1	271.3	41.5	46.6	162.1	168.7	168.8

I — Total isolated copolymer determined gravimetrically; *II, V* — PPrMA determined by infrared analysis; *III, VI* — PPrMA determined by elemental analysis from the content of oxygen; *IV* — total isolated insoluble residue determined gravimetrically; *VII* — sum of columns *II* and *V*; *VIII* — sum of columns *III* and *VI*; *IX* — total bonded PPrMA determined gravimetrically from the weight increase of PP.

60 min of polymerization (samples 4—6). This experimental result is in accordance with the assumed mechanism of the modification of powdered isotactic PP in emulsion involving the existence of long-living radicals [9]. According to this mechanism, the initiation stops proceeding after some time of polymerization and PrMA is bonded only to the polymer radicals generated before in consequence of which the elongation of PPrMA chains bonded to PP occurs.

As for samples *1* and *2*, the quantity of PPrMA analytically found in the insoluble portion was greater than that found in the isolated copolymer (columns V and VI or II and III). It may be due to the fact that the part of copolymer in which the content of PP is so high that it determines its insolubility at laboratory temperature gets into the insoluble portion. That occurs at the beginning of reaction when all potential initiating centres are not in operation yet and the chains of PPrMA are not long enough. Thus it may be assumed that those macromolecules of copolymer in which the ratio of particular polymers reaches a certain limit pass into the solution. Under the given conditions, it was established experimentally [7] that the content of PPrMA in the copolymer was higher than 65 mass %. However, the results given in Table 3 suggest that the content of PPrMA in the insoluble residue increases with the content of PPrMA bonded to PP. This can be caused by physical binding of the soluble copolymer to the insoluble portion which increases with the concentration of copolymer in the solution. It may be also assumed that the copolymer in mixture with nonmodified PP and copolymer containing a low amount of PPrMA constitute a more stable system [15], which could result in the observed distribution of copolymer in the products of the separation process. These facts cannot be affected by certain differences between the quantities of PPrMA determined by different methods though we may infer from balance columns VII and VIII in comparison with the values known from the synthesis (IX) that the elemental analysis shows a better picture of the real content of PPrMA in the products of separation than infrared spectroscopy. The balance of the distribution of PP in the mixture (*e.g.* for the sample *5* in Table 3) enables us to calculate (approximately, by using a similar composition as found for the isolated copolymer and for its portion in the insoluble residue as well) that only 3—4% of the original PP mass participate in the reaction producing PP—PPrMA copolymer.

On the basis of mechanism of "living" polymerization of modification, we may assume that bonded PPrMA is of high-molecular nature with the relative molecular weight of 10^6 (like the homopolymer originating in the same system [16, 17]), which is about ten times more than the molecular weight of PP. Therefore we may duly suppose that the predominance of PPrMA in the copolymer is one of the principal causes that bonded PPrMA fundamentally influences the properties of the whole copolymer in consequence of which it remains in the solution at laboratory temperature. The influence of the presence of isotactic part of the PP molecule expresses itself in repeated dissolution of the isolated copolymer by the fact that the time necessary for its dissolution at laboratory temperature is 4—5 times longer than for the dissolution of poly(propyl methacrylate) homopolymer itself. The presence of peaks in the i.r. spectrum of copolymer at $\nu = 975$ and $1000\ \mathrm{cm}^{-1}$ proves that PP occurs in the crystalline form. It is worth to note that analogous conclusions are also valid for poly(propylene—styrene) copolymer isolated from a mixture with PP [18].

It results from these facts that the product of polymerization represents a complicated system consisting of a mixture of nonmodified PP and PP—PPrMA copolymer formed. In principle, there are two types of copolymer. One of them contains more than 65 mass % of PPrMA and the second one contains less PPrMA, which determines the solubility of copolymer at laboratory temperature.

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