Solution properties of isotactic polypropylene grafted with styrene studied by light scattering and by viscometry

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A copolymer of isotactic polypropylene and polystyrene was synthesized by polypropylene grafting. With the increasing time of polymerization its molecular mass increased. This supports the course of this type of polymerization under existence of long-living radicals. The copolymer was kept in solution at room temperature by high-molecular branches of polystyrene and formed aggregates which can disintegrate at increased temperature.

Графтизацией полипропилена был синтезирован сополимер изотактический полипропилен—полистирол. С повышением времени полимеризации повышался молекулярный вес, что подтверждает течение этого типа полимеризации в присутствии долгоживущих радикалов. Сополимер удерживается в растворе при лабораторной температуре высокомолекулярными ветвями полистирола, причем агрегируется в формы нарущительные при повышенной температуре.

During activated polymerization of vinyl monomer in emulsion at 30 °C in the presence of peroxidized isotactic powdered polypropylene, part of the monomer is bonded to a polymer (graft polymer) and part of it polymerizes freely in emulsion (homopolymer) [1].

In view of the solution properties, the homopolymer of styrene has been studied most thoroughly [2]. It has high relative molecular mass of the order between 10^6 and 10^7 and shows a narrow molecular mass distribution. Both properties of the polymer are caused by the presence of the initiator of polymerization in the heterogeneous phase; the polymerization then proceeds under strongly limited termination (the existence of "long-living radicals") [3]. The branches bonded to the solid phase of polypropylene grow in the same medium as nonbonded; they show therefor similar characteristics [4, 5].

In this paper we study solution properties of isolated copolymer poly(propylene—styrene) by the light-scattering method and by viscometry.

Experimental

Materials

Polypropylene (i-PP) — isotactic, powdered (Slovnaft, Bratislava) has been described earlier [5].

Styrene was deprived of stabilizer by shaking with 10 % aqueous solution of NaOH, washed with water, dried with $CaCl_2$, and twice rectified in a nitrogen atmosphere.

Emulsifier, Mersol H (C₁₇H₃₅SO₃Na) was the product of Leuna Werke (GDR).

Chelate FeSO₄-triethylenetetramine was used in mole ratio 2:3.

Other compounds — p-xylene, 1,2-dichlorobenzene, benzene, methyl alcohol, and acetone were purified by distillation.

Nitrogen was purified on a catalyst composed of 55 % MnO₂, 40 % MgO, and 5 % Cr₂O₃.

Procedures and equipments

Polypropylene was oxidized at room temperature for 1 h with oxygen containing 1.2×10^{-5} kg dm⁻³ of ozone. The hydrogen peroxide content determined iodometrically was 1.5×10^{-2} mol O₂ kg⁻¹, the oxygen content of the more stable type of peroxides was 2.2×10^{-2} mol kg⁻¹ [1].

Polypropylene grafted with styrene was prepared by polymerization in ampoules rotating in a bath at constant temperature of 30 °C [5]. The ampoules were filled in a nitrogen atmosphere with components of the polymerization system in the order: 2.5 g of polypropylene, 8.75 cm³ of water, 3.75 cm³ of styrene. Emulsifier Mersol H (8.8× ×10⁻³ mol dm⁻³), FeSO₄ · 7H₂O (2.4×10⁻³ mol dm⁻³), and triethylenetetramine (3.6× ×10⁻³ mol dm⁻³) were dissolved in the liquid phase (emulsion). The polymerization time was 3 h, 4 h, 4¹/₂ h, 5 h, and 6 h. The solid phase containing copolymer isotactic polypropylene—polystyrene (i-PP—PS) and unchanged i-PP was retained on a sintered glass filter. It was gradually washed with water, benzene, 5 % HCl solution in methanol, and with acetone to remove residues of the polymerization system, homopolymer (PS), and Fe³⁺. It was dried in air to constant mass. From the increase in the mass of i-PP, the conversion of styrene bound to i-PP in % was determined. The homopolymer PS in the filtrate was not evaluated [1].

The copolymer i-PP—PS was isolated from a mixture with i-PP as follows: powdered polymeric material was dissolved at 120 °C in p-xylene (1 g/150 cm³) in the presence of 0.2 % antioxidant 2246 (with respect to polymer). After 2 h dissolution, pure solution was allowed to cool and the undissolved fraction was separated by centrifugation. Since the insoluble sediment still contained part of the copolymer, the procedure was repeated 2—3 times until all copolymer soluble at room temperature was obtained. The copolymer was obtained from solution by precipitation in an excess methanol, retained on a sintered glass filter and vacuum dried to constant mass. The composition of the copolymer (expressed as mass fraction PS x) was determined by differential refractometry in p-xylene from relation

$$\mathbf{v}_{\rm cop} = \mathbf{x}\mathbf{v}_{\rm PS} + (1 - \mathbf{x}) \mathbf{v}_{\rm PP} \tag{1}$$

where v_{cop} , v_{PP} , and v_{PS} are the refractive index increments of the copolymer and its components, where

$$v_{\rm PS} = 0.1062 [6]$$
 and $v_{\rm PP} = -0.0016 [6]$

The light-scattering measurements were done on a Brice—Phoenix, model 2000 photometer using monochromatic nonpolarized light at the wavelength of 546 nm. The measurements were carried out in a cylinder cell, type C-105, using a teflon stop-cock to avoid solvent evaporation. The temperature was kept constant during measurement by an electrically heated jacket of the cells. Dilution of sample solutions was done directly in a cell and the measured data were evaluated by the Zimm method. Freshly distilled p-xylene and 1,2-dichlorobenzene were used as solvents.

Refractive index increments were measured on a visual refractometer (Phoenix Precision Instruments, Philadelphia), model BP-2000-V using the light of the wavelength of 546 nm. The temperature was kept constant during measurement by a thermostat containing silicon oil. The apparatus was calibrated with a KCl solution in distilled water.

Viscometric measurements were carried out in an Ubbelohde suspended-level viscometer adapted according to Seide—Deckert and Berger—Deckert [7], which allowed to prepare solution directly in the apparatus. The diameter of the capillary was chosen so that the kinetic energy and the capillary curvature corrections were negligible. The copolymer concentration in *p*-xylene (0.5—2.5 g cm⁻³) was chosen so that the relative viscosity of solution (at 25 °C) ranged between 1.2 and 2. The measured values were evaluated by the method of least squares using the Huggins relation [8].

Results and discussion

Three groups of isolated i-PP—PS copolymers with different content of the bonded styrene (obtained via polymerizations proceeding for different time) were studied. Table 1 shows the composition of the original solid phase achieved after polymerization and the composition of isolated copolymers of the three groups of samples.

The multiple isolation of the copolymer from the same mixture with i-PP provides a picture of chemical heterogeneity of the sample studied with respect to different solubility of fractions of different composition. Table 2 presents the composition of the copolymers according to the number of isolations from the same polymer mixture. It is seen that only the sample No. 7 shows certain polydispersity in the chemical composition. During isolation I, the high content of PS in the sample prevails the effect of i-PP on the solubility of copolymer and therefore the percentage of the obtained fraction is highest. With the decreasing PS content which keeps the copolymer in solution, the percentage of isolated copolymer is lower than 80 %, the sample is insoluble in p-xylene at room temperature and remains during isolation in the sediment with the unchanged i-PP and forms a fraction of about 25–35 % of the copolymer that cannot be isolated by this method.

Table 1

	Synthesis of copolymer		Isolated copolymer		
Sample	Polymerization time h	Bound ST %	$\frac{v_{cop}}{\text{cm}^3 \text{ g}^{-1}}$	PS in copolymer %	$\frac{M_m}{\text{g mol}^{-1}}$
1	3	19.7	0.0890	84.1	3.08 × 10 ⁶
2		19.9	0.0898	85.0	3.09×10^{6}
3		20.5	0.0902	85.2	3.40×10^{6}
4		20.7	0.0878	82.9	2.78×10^{6}
5	41/2	28.7	0.0968	89.8	1.07×10^{7}
6		29.1	0.0961	90.3	1.44×10^{7}
7	6	38.0	0.1035	97.6	2.20×10^{7}
8		37.1	0.1018	94.5	2.11×10^{7}

Characterization of the studied copolymers*

* Groups of samples 1-4, 5 and 6, and 7 and 8 were prepared parallelly. The values of molecular masses of copolymers, M_m , were measured by light scattering at 25 °C in *p*-xylene.

Table 2

Characterization of the copolymers of the selected samples according to the number of isolations from the same sample*

Sample	Isolation (number)	$\frac{v_{\infty p}}{\mathrm{cm}^3 \mathrm{g}^{-1}}$	PS in copolymer %	Isolated copolymer %
1	I	0.0890	84.1	36.9
	II	0.0887	83.9	22.7
5	I	0.0968	89.8	40.2
	II	0.0971	90.1	24.7
7	I	0.1035	97.6	41.6
	II	0.0986	93.0	26.6
	111	0.0980	92.4	7.5

* Selected samples from Table 1.

Molecular masses of i-PP-PS copolymers

Light scattering at laboratory temperature

The measurements were done in p-xylene. The typical Zimm diagram for the sample No. 7 is illustrated in Fig. 1. The molecular masses of the studied samples

ISOTACTIC POLYPROPYLENE GRAFTED WITH STYRENE

Fig. 1. Zimm diagram of the sample No. 7 (Table 1) in p-xylene at 25 °C..



thus obtained are summarized in Table 1, which shows that their values increase with the polymerization time.

Light scattering at increased temperatures

The measurements of solutions of the i-PP—PS copolymers were done at 110 °C and 140 °C. *p*-Xylene and 1,2-dichlorobenzene were used as solvents (i-PP—PS was not soluble in the latter solvent at room temperature). The values of the light scattering before and after the measurement of samples at increased temperatures for 3 h showed that no significant changes occur in the copolymer as a result of the possible degradation. Figs. 2 and 3 show the typical Zimm plots for the samples No. 7 and No. 5 from Table 1. The values for M_m obtained at increased temperature for the studied copolymers are gathered in Table 3. This table also includes approximate number of aggregated macromolecules calculated from the ratio of relative molecular masses of the samples at 25 °C (Table 1) and at 110 °C and 140 °C, respectively.

The results indicate significant aggregation of macromolecules of the i-PP—PS copolymer in *p*-xylene solution at room temperature. Its reason lies in the insolubility of a part of the macromolecule formed by i-PP under the given conditions; it is kept in solution by high-molecular PS branches. One can expect that it takes place in the form of aggregate (micelle) with the nucleus composed of the i-PP part of the copolymer, the PS part being directed towards the solvating medium. Table 3 also shows that at 110 °C the aggregates start to disintegrate and decay at 140 °C.

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As these results show, the molecular mass of the copolymer increases with the polymerization time; this is in line with the idea of the polymerization mechanism initiated by heterogeneous initiator under the conditions of limited termination (the presence of "long-living radicals") [5]. It is remarkable that with increasing



Fig. 2. Zimm diagram of the sample No. 7 (Table 1) in p-xylene at 110 °C.

Fig. 3. Zimm diagram of the sample No. 5 (Table 1) in 1,2-dichlorobenzene at 140 °C.

T	a	Ы	e	3

Sample	Temperature ℃	Solvent	M _m	N**
1	140	1,2-Dichlorobenzene	6.10 × 10 ⁵	6
2	140		6.20×10^{5}	6
3	110		6.30 × 10 ⁵	5
3	140		5.00×10^{5}	7
4	140		5.52 × 10 ⁵	5
5	140		1.34×10^{6}	8
6	140		1.60×10^{6}	9
7	110	p-Xylene	2.38×10^{6}	9
7	140	1,2-Dichlorobenzene	1.77×10^{6}	12
8	140		2.11×10 ⁶	10

Values of molecular masses of the i-PP—PS copolymers measured by light scattering at increased temperature*

* The numbering of samples as in Table 1.

** N — number of macromolecules in the micelle.

 M_m of the copolymer the number of aggregated macromolecules in micelle increases. This leads to an opinion that also high-molecular PS branches of the copolymer contribute to the process of the association of the studied macromolecules.

Viscometry

Table 4 shows the results of viscometric measurements of the chosen copolymer samples differing in the PS content. The limiting viscosity numbers $[\eta]$ were found to increase with the increasing time of polymerization (Table 1), which was caused by a rise in the dimension of aggregates with the increasing percentage of the bonded PS (Table 2). The relatively high values of the Huggins constants, $k_{\rm H}$, point to the aggregated and branched character of the studied copolymer aggregates in solution.

Table 4

Sample	$\frac{[\eta]}{\mathrm{cm}^3\mathrm{g}^{-1}}$	k _H
1	109.4	0.70
5	173.2	0.64
7	249.6	0.58

Viscometric characterization of the selected samples of copolymer in p-xylene at 25 °C*

* The numbering of samples as in Table 1.

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