

Esterification of polyacrylic acid bonded to polypropylene by alcohol

P. CITOVICKÝ, V. CHRÁSTOVÁ, and J. BENISKA

*Department of Chemical Technology of Plastics and Fibres,
Slovak Technical University, CS-812 37 Bratislava*

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Dedicated to Professor RNDr. J. Gašperík, founder of the Department of Organic Technology and of the Department of Chemical Technology of Plastics and Fibres of the Slovak Technical University on the occasion of the 40th anniversary of their foundation

By means of an experimental design the conditions for the optimal esterification of polyacrylic acid bonded to isotactic powdered polypropylene by *n*-butyl alcohol, catalyzed by *p*-toluenesulfonic acid were chosen. It was not possible to obtain a polymer with more than 50 % of esterified polyacid, which is explained by mutual interaction of carboxyl groups. The apparent rate constant of the esterification of polyacrylic acid by *n*-butyl alcohol $k = 4.8 \times 10^{-6} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ was determined at 120 °C in the presence of 20 mole % of the catalyst according to the acidic groups. This rate constant has a lower value than the rate constant k of the esterification of low-molecular carboxyl acids by alcohols in homogeneous conditions.

Методом планированного эксперимента подбирали условия оптимальной этерификации полиакриловой кислоты, фиксированной на изотактическом порошкообразном полипропилене, с *n*-бутанолом при катализировании *p*-толуолсульфоновой кислотой. Однако, не удалось получить полимер с выходом выше 50 % поликислоты, что объясняется взаимодействием карбоксильных групп. При 120 °C в присутствии 20 моль % катализатора по отношению к кислым группам была определена кажущаяся константа скорости этерификации полиакриловой кислоты с *n*-бутанолом $k = 4,8 \cdot 10^{-6} \text{ дм}^3 \text{ моль}^{-1} \text{ с}^{-1}$, значение которой ниже, чем в случае этерификации низкомолекулярных карбоксильных кислот спиртами в гомогенных условиях.

By the chemical modification of isotactic powdered polypropylene by acrylic acid [1] a polymer with polar carboxyl groups is obtained. These groups lower the typical hydrophobicity on the surface of polypropylene, or they can act as centres of

successive polymeranalogue modifications, which enable to fix on polypropylene compounds with special effects. A typical reaction for the acidic carboxyl groups is their esterification with alcohols in acidic medium. This is well known for low-molecular acids [2], less for polymeric acids. Their esterification was studied, for instance, with the aim of inserting into the polymer functional groups, which would be biologically active, etc. [3—6].

This paper describes the conditions for the esterification of polyacrylic acid bonded to powdered isotactic polypropylene by *n*-butyl alcohol in acidic medium. The characteristic feature of this reaction is the presence of a heterogeneous carrier of the polyacid in the system.

Experimental

Powdered isotactic polypropylene with 9.6 mass % of bonded polyacrylic acid (PP—PAAc) was prepared by chemical modification of low oxidized polypropylene by acrylic acid in emulsion [1, 7]. The used *n*-butyl alcohol (BuOH) and *p*-toluenesulfonic acid (PTS) were of anal. grade purity.

The esterification of acidic groups of PP—PAAc was made in sealed ampoules statically inserted in a tempered bath. From the ampoules with 1.5 g weighed PP—PAAc (containing 2 mmol acidic groups) oxygen was removed by vacuum, whereby the vacuum was interfered by purified nitrogen. The catalyst solution PTS in BuOH (the catalyst concentration was expressed as a mole fraction y (mole %) according to the content of carboxyl groups in the system) was charged in nitrogen atmosphere and finally the volume of the liquid phase was completed to 5.5 ml by BuOH. After the completion of the esterification, the ampoule was cooled and the powdered polymer was captured on a sintered glass filter, where it was washed with acetone, dried in air at laboratory temperature to a constant mass. From the mass increase of the polymer the yield of the esterification was calculated in % of reacted starting polyacrylic acid present in the system.

Results and discussion

The esterification of acidic groups in PP—PAAc was investigated by means of BuOH, which had a sufficiently high relative molecular mass to determine reliably gravimetrically the amount bonded to the solid phase. To make accessible the reaction centres of the polyacid, bonded to powdered carrier, it was necessary to use the liquid phase [7, 8] with its solvation effect on the polyacid. BuOH was suitable for that purpose, which besides this does not dissolve the polypropylene and has a sufficiently high boiling point and it is possible to charge the catalyst PTS dissolved in BuOH.

The informal experiments have shown that for a sufficient penetration of powdered PP—PAAc (1.5 g) by the liquid 5.5 ml of BuOH are necessary. In this

way, approximately a 30-fold excess of moles of alcohol according to the acidic groups in the system is simultaneously formed. The dispersion of water, formed during the reaction, into the alcohol, out of the reach of the reaction centres, contributes also to the shift of the reaction equilibrium in the closed system. The catalyst mole fraction used in homogeneous conditions, which did not exceed 3 mole % [9–12] was insufficient during esterification to reach a substantial formation of ester. The reason for this was evidently the dissipation of the catalyst in the volume of the alcohol outside the reach of the reaction centres of the polymer, which was fixed on the solid phase. It has been shown that the PTS concentration and the reaction temperature (maximum 120 °C, at which temperature the interfering of the original powdered form of PP—PAAc does not yet take place) are the two factors which most influence the ester formation.

The influence of both factors was investigated at the same conditions as in the informal experiments at constant time by means of an experimental design with statistical evaluation [13]. The basic values of the experiment, the formulation of the plan, and the obtained results are in Tables 1 and 2. From Table 2 basic data for

Table 1
Basic values of the experimental design

x_i	Factor	Factor level			I_i
		-1	0	1	
x_1	$\frac{\text{mole fraction PTS}}{\text{mole \% according to } -\text{COOH}}$	4	12	20	8
x_2	$t/^\circ\text{C}$	90	105	120	15

Table 2

Formulation of the experimental design and the results of the fraction (%) of the esterified acidic groups in PP—PAAc during 6 h, obtained experimentally (Y_{exp}) and calculated from the regression eqn (1) (Y_{theor})

i	x_1	x_2	Y_{exp}	Y_{theor}
1	-1	-1	13.9	13.1
2	-1	0	19.0	19.1
3	-1	1	27.5	28.2
4	0	-1	22.4	23.5
5	0	0	31.2	32.1
6	0	1	45.6	43.7
7	1	-1	27.2	26.9
8	1	0	39.0	38.0
9	1	1	50.9	52.1

the regression equation, which expresses the influence of the PTS mole fraction (x_1) and temperature (x_2) on the amount (%) of esterified acidic groups of PP—PAAc (Y) over 6 h, were obtained (the relation of the code values x_i to the values of the PTS concentration or to the reaction temperature is in Table 1)

$$Y = 32.06 + 9.44 x_1 + 10.07 x_2 + 2.53 x_1 x_2 - 3.53 x_1^2 + 1.53 x_2^2 \quad (1)$$

The error of the determination was ± 0.8 mole % of esterified groups. It was determined by means of the F -test, whereby $F_{0.05}^{3.5} = 4.84 < 5.41 = F_{\text{crit}, 0.05}^{3.5}$, that the regression equation (1) is valid in the range of the experimental error. The contour diagram is the graphical expression of the mentioned equation (Fig. 1). The

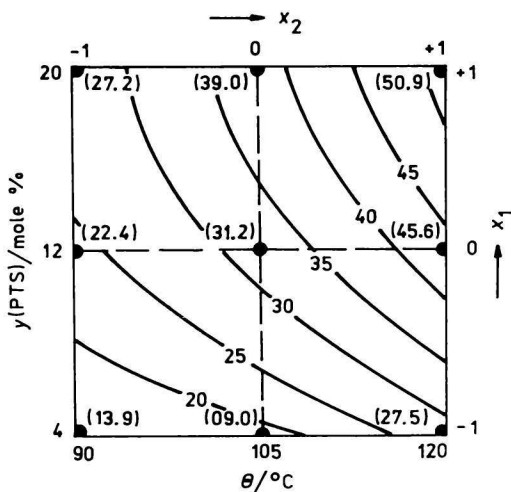


Fig. 1. Contour diagram of the influence of the mole fraction y (mole %) of *p*-toluenesulfonic acid (PTS) in mixture and the reaction temperature θ on the portion (%) of esterified acidic groups in PP—PAAc by *n*-butyl alcohol during 6 h. The numbers at the isolines are theoretical values (%) and those in the brackets are experimentally obtained conversions (%).

numbers at the isolines are the theoretical values of the mole fraction (mole %) of the esterified acidic groups of PP—PAAc during 6 h. The values in brackets are mole fractions (mole %), which were obtained experimentally (Table 2).

From Fig. 1 it is evident that under the given conditions approximately 50 mole % of esterified acidic groups of PP—PAAc were obtained, and this at the highest temperature and the highest PTS content. From the tendency of the reaction temperature it results that its increase over 120 °C is supposed to further positively influence the result of esterification, however, this has not been experimentally proved. By an experiment outside of the experimental area at 135 °C and 20 mole % PTS only 51.8 mole % of esterified polyacid was gained. It is also impossible to substantially influence the reaction by increasing the PTS content, because that is only a change near the isoline for 50 mole %. A similar result, according to the

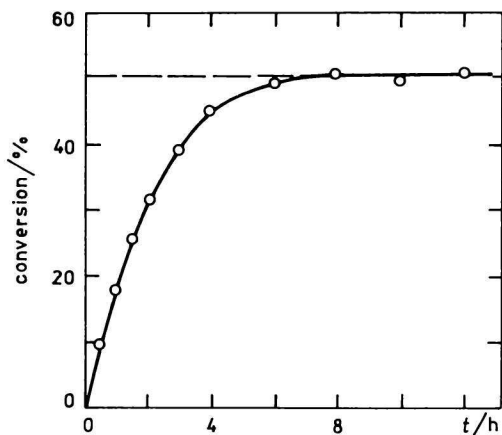
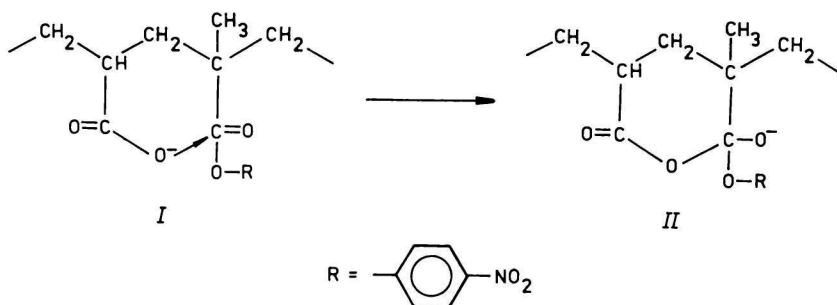


Fig. 2. Influence of time on the conversion (%) of esterified acidic groups in PP—PAAc by *n*-butyl alcohol at 120 °C in the presence of PTS (20 mole %).

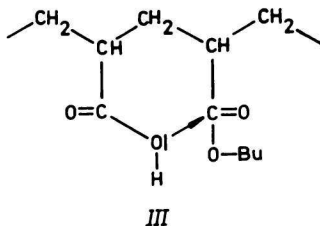
maximum conversion, was obtained also by the study of the time dependence of the reaction (Fig. 2).

One reason for the incomplete esterification of PP—PAAc could be the reversible reaction — the hydrolysis of the ester by the water formed. This presumption was disproved so that experiments with the esterification of a larger amount of PP—PAAc by BuOH were carried out in an open system, where the water could leave at 120 °C, or at 100 °C in the azeotropic mixture with *n*-heptane. During a 12 h reaction we did not succeed to exceed substantially 50 % of esterified polyacid from the original PP—PAAc.

A possible explanation of the maximum reached conversion near 50 % may be in the mutual influencing of the adjacent groups of the polymer, which can increase their reactivity on the one hand [14], or on the other it can cause that part of them do not react at all [15]. For instance, for the copolymer *p*-nitrophenyl methacrylate with acrylic acid it is possible to illustrate this by the following scheme [16, 17] which indicates by what mechanism the alkaline hydrolysis of ester is accelerated in comparison with low-molecular compounds



In the case when $R = H$, structure *I* can illustrate an association of groups in the polyacrylic acid bonded to polypropylene after neutralization of half their amount during its alkalimetric determination [7]. For this weakly dissociated acid, the state of partly esterification of the acidic groups will be illustrated by a similar structure *III*



Then the attempt for the esterification of the second carboxyl group was not successful, because the conditions for the addition of the nucleophilic agent BuOH to the carbon of the carbonyl group were not given [18]. By the hydrolysis of the polyacrylic acid ester the reason for a similar hindering is explained by the influence of the adjacent carboxyl groups and also by steric hindrances in the polymer chain in the surroundings of the reaction centres [19, 20]. The hydrogen of the carboxyl group has the possibility to dissociate in the associate, and the oxygen can act as a nucleophilic agent. The possible formation of a hydrogen bond with the oxygen of the solvent (alcohol) acts against, which can hinder the electrophilic addition to the adjacent group [21]. That is to say that the mentioned facts assume the existence of a suitable microstructure of the polymer chain. But a certain orientation of the acidic groups of PP—PAAc was done before, and that during the formation of their associates [7].

When isobutyl alcohol was used, a lower content (%) of esterified acidic groups of PP—PAAc was obtained as expected. The attempts to bind the stabilizer 2-hydroxy-4-(2-hydroxyethoxy)benzophenone in an *o*-xylene solution were not very successful (9 % reacted groups) and they drew attention to the fact that the steric factors are not the only hindrance for the bonding of such compounds. It may also be the suitable choice of the used solvent, which makes easier a sufficient contact between the low-molecular compound and the reactive group of the polymer.

From the initial steps of the esterification at 120 °C, where a substantial decrease of the content of the acidic groups of the system did not take place yet (up to 2 h, Fig. 2), by means of the dependence for a bimolecular reaction with degeneration of the order, when one component is present in great excess [22]

$$kt = \frac{1}{b} \ln \frac{a}{c} \quad (2)$$

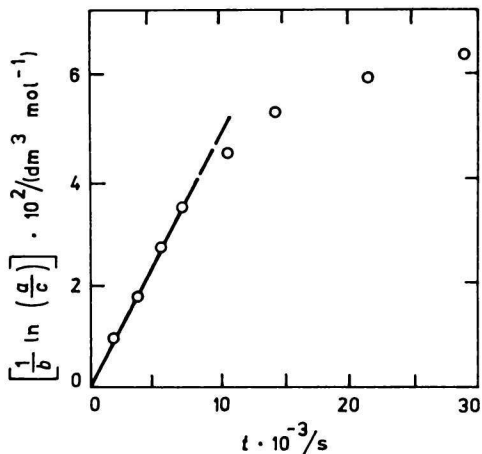


Fig. 3. Graphical illustration of eqn (2) for the determination of the rate constant of the esterification of acidic groups in PP—PAAc by n-butyl alcohol at 120 °C in the presence of PTS (20 mole %).

where k is the rate constant, a and b the initial concentration of the acidic groups or n-butyl alcohol, c their concentration in time t and from the graphical evaluation (Fig. 3), the apparent rate constant of the reaction $k_{120^\circ\text{C}} = 4.8 \times 10^{-6} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ was determined. This value indicates that the esterification of the polyacrylic acid bonded to powdered polypropylene is a much slower reaction in comparison with the reactions of low-molecular acids in a homogeneous phase [2]. This is in consequence of a very low dissociation constant of the polyacrylic acid [7, 23] and of the interaction among the carboxyl groups and this enhances the demand for the conditions of their esterification.

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