

# Oxidized Powdered Polypropylene Initiated Emulsion Copolymerization of Methyl Methacrylate with Acrylonitrile

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Emulsion copolymerization of acrylonitrile (AN) with methyl methacrylate (MMA) initiated by hydroperoxide groups bonded to powdered isotactic polypropylene in the presence of  $\text{Fe}^{2+}$ /EDTA activator and nonionic ethylene oxide-type emulsifier was investigated at 30 °C. As found, AN does almost not undergo polymerization under the given conditions, whereas MMA forms a homopolymer. The AN with MMA copolymerization rate, as well as  $[\eta]$  of the P(AN-co-MMA) copolymer formed, decreases in relation to the increasing concentration of AN in the comonomer mixture. The composition change of P(AN-co-MMA) copolymers was examined in regard to the monomer content in the feed and changes in the copolymer composition with conversion were investigated. Reactivity ratios were estimated from the results of analysis of the P(AN-co-MMA) copolymer; under the given conditions of emulsion polymerization initiated by hydroperoxide groups bonded to a solid polymer carrier, the  $r_{\text{AN}} = 0.09$  and  $r_{\text{MMA}} = 0.86$  values were found.

Emulsion polymerization initiated by oxidized isotactic polypropylene powder in the presence of an amine-type activator was utilized not only for the synthesis of a high-molecular polystyrene [1, 2], but also for the preparation of block copolymers of styrene with methyl methacrylate [3], acrylonitrile [4] or *p*-*tert*-butylstyrene [5]. It was started from the live character of such initiated emulsion polymerization of styrene [1], proceeding by an unchanged rate even after separating the solid powdered initiator from the emulsion immediately at the beginning of the reaction.

In continuation of our preceding results, this paper deals with the emulsion copolymerization of acrylonitrile (AN) with methyl methacrylate (MMA) employing the initiation system consisting of oxidized isotactic polypropylene present in the emulsion during the whole time of polymerization; it formed an independent solid phase. This paper is aimed to ascertain how the initiation mode and the different amount of AN and MMA in the feed influence the copolymerization of these monomers, which are not only more polar, but also more water-soluble than styrene. Also the change of limiting viscosity number  $[\eta]$  with conversion was investigated; the copolymerization reactivity ratios  $r_{\text{AN}}$  and  $r_{\text{MMA}}$  were estimated and the change of composition of the copolymer P(AN-co-MMA) with conversion was studied.

## EXPERIMENTAL

The powdered isotactic polypropylene (PP, Slovnaft, Bratislava) was freed from the atactic

portion by extraction with boiling heptane. The PP hydroperoxides were obtained by oxidation with ozone ( $12 \text{ mg dm}^{-3}$ ) enriched oxygen at room temperature; the hydroperoxide content was determined iodometrically [6]. The activator — disodium salt of ethylenediaminetetraacetic acid (EDTA) and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  were anal. grade and were employed as aqueous ( $c = 4.0 \times 10^{-2} \text{ mol dm}^{-3}$ ) solutions. Emulsifier,  $\text{R}(\text{OC}_2\text{H}_4)_{30}\text{OH}$  (Slovasol 2430, nonionic type, Chemical Works, Nováky) was used as a 0.145 M aqueous solution. All solutions were stored in an inert atmosphere. The monomers — MMA (pure, Chemical Works, Žilina) and AN (pure, Loba Chemie, Austria) were liberated from stabilizers by redistillation in nitrogen atmosphere. All other chemicals were anal. grade.

## Procedures

The polymerization was performed in glass ampoules in which the weighted initiator was deprived of oxygen by repeated evacuation and filling with nitrogen. Components of the polymerization system (activator, emulsifier, water, monomers) were added in an inert atmosphere and their concentration is given in mol per  $\text{dm}^3$  of the emulsion. The polymerization was carried out at constant stirring and 30 °C. The polypropylene powder was separated from the emulsion at the end of polymerization by filtration through the sintered glass filter  $\text{S}_1$ ; residue of the emulsion system was removed from the oxidized PP by successive washing with water

and methanol and its mass was determined after drying. The homopolymer or the copolymer formed in the emulsion was precipitated with methanol by the procedure already reported [1–3]. The conversion was calculated in mass % with respect to the mass of monomers used.

Composition of the polymerization system was as follows: Initiator — oxidized isotactic PP (hydroperoxide content  $1.9 \times 10^{-2}$  mol  $O_2$ /kg PP, 0.4 g); activator ( $c = 1.11 \times 10^{-3}$  mol  $dm^{-3}$ , i.e.  $Fe^{2+}$  (0.5  $cm^3$ ) and EDTA (0.5  $cm^3$ ); emulsifier — Slovasol 2430 ( $c = 7.25 \times 10^{-2}$  mol  $dm^{-3}$ ); monomers — MMA and AN (total volume 6  $cm^3$ , mole fraction of AN in the mixture of comonomers  $x_{AN}$  was 0, 0.13, 0.45, 0.62, and 0.76); water was filled up to 18  $cm^3$  of emulsion in all experiments.

Composition of copolymers was estimated either from the IR spectral analysis of samples in nujol on a spectrophotometer IR-20 (Zeiss, Jena), or from elemental analyses on a CHNO analyzer (Erba, Milan). The reactivity ratios were computed by Kelen—Tüdös or Ezrielev—Brokhina—Roskin methods employing the proper programs.

For viscometric measurements the Ubbelohde dilution viscometer was used. The copolymer P(AN-co-MMA) was dissolved and measured in *N,N*-dimethylformamide at 30 °C. The limiting viscosity number  $[\eta]$  was determined by a double extrapolation of the relations  $(\eta - \eta_0)/\eta_0 c$  or  $[\ln(\eta/\eta_0)]/c = f(c)$  against zero concentration.

## RESULTS AND DISCUSSION

As found, homopolymerization of methyl methacrylate proceeds relatively fast like that of styrene [7] in a heterogeneously initiated system and the dependence of conversion on the reaction time does not show changes even though no decomposition of hydroperoxides is taking place in the system after about 15 min of polymerization [8] (Fig. 1). Acrylonitrile itself does almost not form polymer in a comparable polymerization system, although approximately 1/3 of hydroperoxides present decomposes even in the presence of AN in the first 15 min like in the polymerization of MMA. The inability of AN to polymerize in the system initiated by the oxidized PP powder was also seen on copolymerization of this monomer with MMA. The dependence of comonomers MMA and AN conversion on the reaction time (Fig. 2) shows that the increase in AN mole fraction in the mixture of monomers  $x_{AN}$  results in the decrease of the copolymerization rate. Increase of the AN content in the monomer mixture is also reflected in lowering of the  $[\eta]$  value of copolymers P(AN-co-MMA) at comparable conversions (Fig. 3).

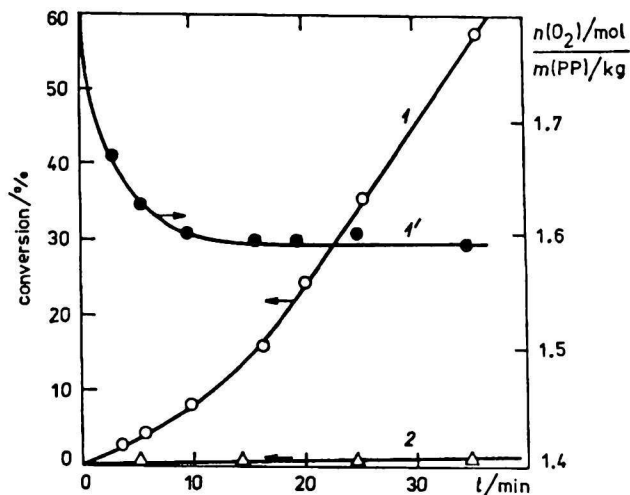


Fig. 1. Dependence of conversion of methyl methacrylate (1), resp. acrylonitrile (2), and residual hydroperoxides content (1') on reaction time at emulsion polymerization initiated by oxidized isotactic polypropylene powder at 30 °C; activator  $FeSO_4$ —EDTA ( $1.11 \times 10^{-3}$  mol  $dm^{-3}$ ), emulsifier Slovasol 2430 ( $7.25 \times 10^{-2}$  mol  $dm^{-3}$ ).

These results can be partially due to the initiating mode of the investigated polymerization and to the place of radical generation from the initiator. As already mentioned [3, 9], formation of primary radicals on the surface of PP in a layer of emulsifier of micelles swelled by the monomer is assumed in the emulsion polymerization of styrene initiated by peroxides of isotactic water-insoluble polypropylene powder. The monomer together with the activator participate actively on the decomposition of peroxides [1, 10]. The polymer radicals after

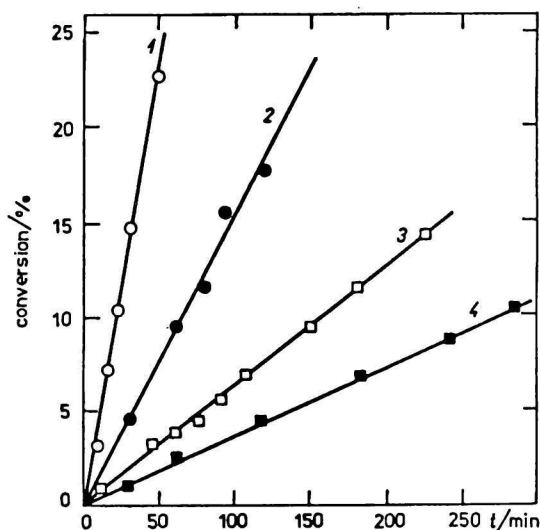
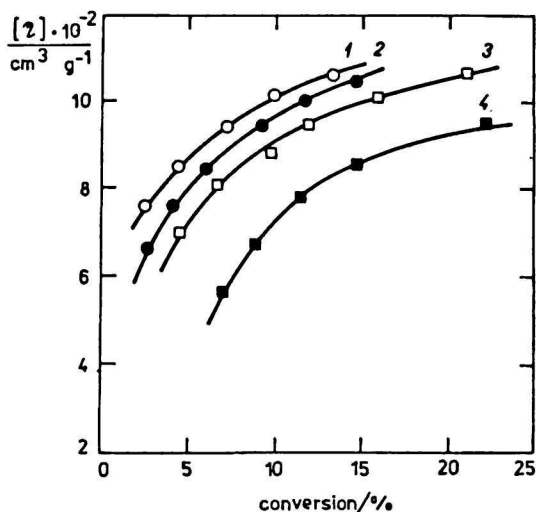


Fig. 2. Conversion curves of polymerization of acrylonitrile with methyl methacrylate in emulsion in the presence of oxidized isotactic PP as initiator at 30 °C and various AN mole fraction in the mixture of monomers;  $x_{AN}$ : 1. 0.13, 2. 0.45, 3. 0.62, 4. 0.76.



**Fig. 3.** Dependence of  $[\eta]$  of copolymers P(AN-co-MMA) (in DMF at 30 °C) on conversion of monomers at emulsion copolymerization initiated by oxidized PP powder with an increasing AN mole fraction in the starting mixture of monomers;  $x_{\text{AN}}$ : 1. 0.13, 2. 0.45, 3. 0.62, 4. 0.76.

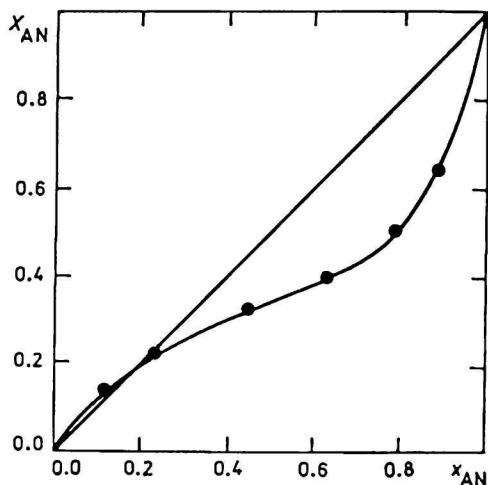
achieving certain length after initiation of polymerization quit the PP surface; the polymer particles are formed, in which polymerization proceeds.

Another situation can emerge with emulsion polymerization of AN, which is more water-soluble (7.5 mass % at 30 °C) than styrene (0.035 mass % at 30 °C), or MMA (1.51 mass % at 30 °C). It is assumed [11, 12] that a great portion of particles is formed in the aqueous phase of this system during a homogeneous nucleation with a common emulsion polymerization of AN initiated by a water-

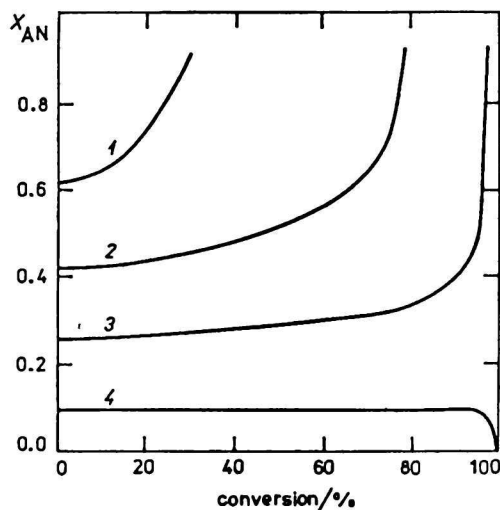
soluble initiator. This process can be influenced negatively in our case, because the initiating centres bound to a solid polypropylene powder can quit its surface relatively with difficulty and therefore do not penetrate the emulsifier layer into the aqueous phase to the monomer to start polymerization. This can represent one of the possibilities causing lowering of the rate of AN emulsion polymerization in the system with the initiator bound to a powdered polymeric carrier.

An important role in polymerization of AN with MMA is also played by the local concentration of both monomers in the reaction site; this is associated — in addition to solubility — with further properties of both comonomers and the polymerization system, too. Moreover, it is known [13] that the  $P_{\text{AN}}$  polymer radical possesses a greater, relative reactivity to MMA than the  $P_{\text{MMA}}$  to AN. These factors influence not only the AN with MMA copolymerization rate, but also the composition of the copolymer being formed.

As illustrated in Fig. 4, the relationship between the AN mole fraction in the copolymer  $X_{\text{AN}}$  and that in the monomer mixture  $x_{\text{AN}}$  shows that the MMA portion prevails in any case in the copolymer P(AN-co-MMA) besides of copolymerization occurring in a composition close to the azeotropic point ( $x_{\text{AN}} = 0.15$ ). This was also evidenced by the values of the measured reactivity ratios ( $r_{\text{AN}} = 0.09$ ,  $r_{\text{MMA}} = 0.86$ ) which are both smaller than one and lower than  $r_{\text{AN}} = 0.15$  and  $r_{\text{MMA}} = 1.65$  reported [14] for copolymerization of AN with MMA proceeding by the radical mechanism.



**Fig. 4.** Plot of the copolymerization of AN with MMA in an emulsion system, containing oxidized PP powder as an initiator, obtained from the predetermined reactivity ratios  $r_{\text{AN}} = 0.09$ ,  $r_{\text{MMA}} = 0.86$ ; temperature 30 °C. ● Experimental values of the AN mole fraction in the copolymer  $X_{\text{AN}}$  were estimated by means of elemental analyses and IR spectroscopy.



**Fig. 5.** Change of the P(AN-co-MMA) copolymer composition with conversion for various composition of the mixture of comonomers; the mole fraction  $x_{\text{AN}}$ : 1. 0.9, 2. 0.6, 3. 0.3, 4. 0.1.

Changes in composition of the P(AN-co-MMA) copolymer with conversion calculated for various starting mole fractions of AN in the mixture of comonomers seen in Fig. 5 reveal that copolymer, the composition of which does not undergo changes with conversion, can be obtained exclusively on polymerization of the monomers mixture in the region close to azeotropic composition; this copolymerization displayed high conversions. Composition of the copolymer considerably influenced by the increasing conversion associates with the rise of AN mole fraction in the mixture of monomers; it is, however, obvious that copolymerization of AN with MMA in mixtures rich in the AN component proceeds only to the low conversions in the applied polymerization system.

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