

Redox polymerization systems for the preparation of grafted polypropylene. II.

Grafting of polypropylene with vinyl or diene monomers in the presence of Fe²⁺ chelates

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The oxidized polypropylene was grafted with vinyl or diene monomers in emulsion at 35°C in the presence of Fe²⁺ chelates. The activation effect of Fe²⁺ chelates on the rate of polymerization is interpreted from the point of redox reactions of coordinated compounds.

In the previous work [1] the suitability of some metal salts in the presence of triethylenetetramine (TET) for the grafting of oxidized isotactic polypropylene with styrene in emulsion at 35°C was studied. The metal salts forming a chelate with TET and being at least in two oxidation degrees (Fe²⁺, Co²⁺, and Mn²⁺ sulfates) were found to be active. Simultaneously the authors pointed to the relation between the activation ability of chelate and redox potential of its central ion and its stability constant.

This work extends the problem of the grafted polypropylene preparation to the investigation of iron(II) sulfate ability to activate grafting with styrene or with other vinyl or diene monomers in the presence of different chelating agents. The obtained results are correlated with stability, formation, and reactivity of iron(II) chelates present in the system.

Experimental

Chemicals

Polypropylene — powdered (Pilot plant, Research Institute of Macromolecular Chemistry, Brno). The isotactic fraction was isolated by extraction with boiling heptane [2].

Styrene (ST) was shaken with 10% sodium hydroxide solution and distilled under nitrogen.

Chloroprene (CP) was shaken with the mixture of CaO—CaCO₃ to remove the acidic residue before twofold distillation in a nitrogen atmosphere.

Acrylonitrile (AN) was twice distilled under nitrogen.

Methyl methacrylate (MMA) and vinyl acetate (VAC) were shaken with the mixture of CaO—CaCO₃ to remove the acidic residues and distilled twice in a nitrogen atmosphere. The monomers were pre-polymerized before second distillation.

Methacrylamide (MAA) was prepared by dehydration and hydrolysis of acetone cyanohydrin and twice recrystallized from acetone.

Iron(II) sulfate, crystalline, anal. grade (Lachema, Brno).

Triethylenetetramine (TET) was synthesized from ethylenediamine and ethylene chloride as described in [3].

Ethylenediamine (ED) was freshly distilled before use.

Ammonium hydrate, 25–27%, anal. grade (Lachema, Brno).

Ethylenediaminetetraacetic acid (EDTA), disodium ethylenediaminetetraacetate (EDTA Na₂) and tetrasodium ethylenediaminetetraacetate (EDTA Na₄), all of anal. grade (Lachema, Brno).

Nitrilotriacetic acid (NTA) anal. grade (Lachema, Brno).

Oxalic acid (Ox) anal. grade (Lachema, Brno).

Salicylic acid (Sal) anal. grade (Lachema, Brno).

Mersol H, emulsifier (Leuna Werke, GDR).

Nitrogen (high purity) was purified both on copper filings at 450°C and on CuCO₃ · Cu(OH)₂ packing at 170°C.

Working procedure

Fluid oxidation of isotactic polypropylene (0.10–0.15 mm particle size) was carried out in an equipment described in [3] with the ozone enriched oxygen for 30 minutes.

The active oxygen content of the oxidized polypropylene was determined by iodometry with KI in glacial acetic acid at room temperature.

Polymerization procedure was the same as described earlier [1]. Water phase (total volume 15 ml) contained the following activation components: iron(II) sulfate (concentration of Fe²⁺ = 1.33 × 10⁻³ mol l⁻¹ of water phase), complexing and some of the chelating agents (concentration according to Table 1), and emulsifier (concentration

Table 1

The effect of complexing or chelating agent in the presence of FeSO₄ on styrene polymerization at 35°C

No.	Reagent	Fe : chelating agent*	Grafted styrene units/3 hrs [%]	Homopolymer/3 hrs [%]
1	—	—	0.7	4.2
2	NH ₃	1 : 6	1.5	27.1
3	ED	1 : 3	12.5	10.9
4	TET	2 : 3	19.3	8.5
5	EDTA	1 : 1	0.8	25.0
6	EDTA Na ₂	1 : 1	0.6	25.9
7	EDTA Na ₄	1 : 1	0.7	26.6
8	NTA	1 : 1	0.7	8.2
9	NTA Na	1 : 1	0.8	9.3
10	NTA Na ₂	1 : 1	1.0	7.2
11	NTA Na ₃	1 : 1	0.6	18.5
12	Ox	1 : 3	0.8	21.8
13	Ox Na	1 : 3	0.9	21.9
14	Ox Na ₂	1 : 3	0.7	25.2
15	Sal	1 : 3	0.8	0.2
16	Sal Na	1 : 3	1.0	13.3

* Fe²⁺ and chelating agent molar ratio.

$19.5 \times 10^{-3} \text{ mol l}^{-1}$). Organic phase consisted of 3 ml of styrene ($2.61 \times 10^{-2} \text{ mol}$); when other monomers were employed they were charged in a constant concentration $2.61 \times 10^{-2} \text{ mol}$. At the same time, the polymerization system contained 0.4 g of the oxidized isotactic polypropylene as a macromolecular initiator (peroxides content was $1.4 \times 10^{-2} \text{ mol O}_2/\text{kg}$ of polypropylene). The polymerization reaction at 35°C was interrupted after 3 hours. The unchanged polypropylene as well as the grafted polypropylene (copolymer) were filtered off on a sintered glass. Homopolymer was separated from the filtered latex by precipitation. Conversion in both cases was expressed in weight % of styrene converted.

Results

1. The effect of complexing and chelating agent in the presence of FeSO_4 on grafting polypropylene with styrene.

The results of polypropylene grafting at 35°C with styrene activated by FeSO_4 in the presence of chosen complexing or chelating agent are summarized in Table 1.

2. Grafting of polypropylene with different types of monomers activated by Fe^{2+} —TET chelate.

The obtained results of polypropylene grafting with several vinyl and one diene monomers in the presence of Fe^{2+} —TET chelate at 35°C are in Table 2. Monomers are listed according to decreasing grafted polymer content formed in the system.

Table 2

The effect of different types of monomers in the presence of Fe^{2+} —TET on polymer formation at 35°C

No.	Monomer	Grafted styrene units/3 hrs [%]	Homopolymer/3 hrs [%]
1	VAC	90.8	8.6
2	CP	72.7	6.5
3	MMA	50.0	4.6
4	ST	19.3	8.5
5	AN	4.1	0.1
6	MAA	0.3	0.5

Discussion

Complexing and chelating agents employed together with iron(II) sulfate as an activator of grafting contained the following donor atoms:

- nitrogen (ammonia, ethylenediamine, and triethylenetetramine),
- nitrogen and oxygen (ethylenediaminetetraacetic acid, nitrilotriacetic acid, and their sodium salts),
- oxygen (oxalic acid, salicylic acid, and their sodium salts).

Molar ratios of Fe^{2+} vs. chelating agent were chosen so that a completely coordinated compound would be formed. Only in the case of nitrilotriacetic acid and its salts two of the coordinated positions of the chelate were hydrated. As the insufficient emulsification of the polymerization system at a lower concentration of emulsifier has been observed

[1] (especially with ethylenediaminetetraacetic acid, nitrilotriacetic acid, and oxalic acid or salicylic acid), in the present experiment higher concentration of the emulsifier was employed.

By the above-mentioned selection coordinated compounds with a broad range of stability constant were obtained. The stability of pure nitrogen coordinated compounds was increasing from the ammoniacal complex through the ethylenediamine chelate to the triethylenetetramine chelate. The ability of the nitrogen coordinated compounds to activate grafting increased proportionally to their stability. At the same time the amount of homopolymer decreased. Beside the stability effect of lower oxidation degree of the chelate central ion these compounds possess another common quality: no or minimum stability of their higher oxidation degree leading to the immediate reduction (high reactivity) [1]. Finally the differences in the activation effects of NH_3 , ED, and TET will depend both on their contribution to the increase of iron redox potential due to coordination and their ability to stabilize temporarily higher oxidation degree of iron till the moment of reduction as a part of the oxidation-reduction reactions series of the system.

Most of the chelating agents containing nitrogen-oxygen or donor atoms form highly stable Fe^{3+} chelates. This is an important difference in comparison with the amine chelates of Fe^{2+} . The mentioned differences resulted in the insufficient ability of these agents to activate significantly the grafting reaction. They decompose only peroxides sites of the oxidized polypropylene which initiate homopolymerization. In this connection we attempted to determine the peroxides content in the grafted polypropylene, but the iodometric analysis failed due to iron adsorbed on the polypropylene surface.

Suitability of the above-mentioned system for the polypropylene grafting was also verified for some vinyl monomers and chloroprene (Table 2). Physical and chemical nature of the monomer used in alkaline polymerization system in the presence of Fe^{2+} -TET chelate should be taken into consideration when evaluating the results of polymerization. First, monomers of acidic nature like acrylic and methacrylic acids would not be suitable as they decompose chelates. Second, strongly polar acrylonitrile

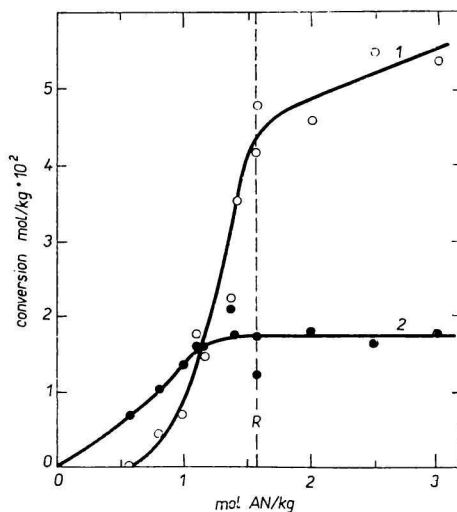


Fig. 1. Yield of polymer (mol kg^{-1} of water phase) as a function of acrylonitrile concentration (mol kg^{-1} of water phase) after 3 hours polymerization at 35°C .
 1. conversion of grafted monomer;
 2. conversion of homopolymer.
 R — the region of acrylonitrile solubility in water at 35°C .

would also react with amine chelate (addition) therefore the result of polymerization will be almost the same as in the case when only iron salt is present. The lowest yield was found with the methacrylamide polymerization which is the only perfectly water soluble from the employed monomers. At the concentration used we did not achieve the saturation of water phase which substantially influenced the rate of polymerization as it was observed in the acrylonitrile polymerization. In this case the yield of polymer strongly increases with the monomer concentration till this is close to its solubility on water (R) at a given temperature (Fig. 1). With the other monomers slightly soluble in water (vinyl acetate, chloroprene, methyl methacrylate, and styrene) the yield of grafted copolymer decreases in mentioned sequence. In the same sequence, perhaps with the exception of chloroprene, generally decreases also the reactivity of their polymer radicals which is in agreement with the fact that the reactivity of growing radicals is a decisive factor effecting the rate of polymerization.

References

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