

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

Grafting of polypropylene with styrene in the presence of triethylenetetramine metal chelates

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The oxidized isotactic polypropylene was grafted with styrene in emulsion at 35°C in the presence of metal chelates of triethylenetetramine. The activation effect of these chelates on the rate of polymerization is interpreted from the viewpoint of redox reactions of the coordinated compounds.

Suitability of the iron(II) sulfate—triethylenetetramine (TET) system for the grafting of oxidized isotactic polypropylene with styrene in emulsion at 35°C has been previously reported [1, 2]. Further study [3] confirmed that Fe^{2+} —TET complex formation conditions the formation of a grafted copolymer, the optimum amount of which will be produced when the reaction is activated with a completely coordinated chelate of the molar ratio $\text{Fe}^{2+} : \text{TET} = 2 : 3$. Under these conditions the amount of grafted polymer substantially depends on both the concentration and the type of emulsifier used. As the highest yields were obtained at a very low concentration of the emulsifier (0.13%), it was assumed that it would act as a detergent in the reaction system. The comparison of the effect of two ionogenic emulsifiers (Mersol H and potassium myristate) showed that higher yields of grafted polymer were obtained with potassium myristate. This fact was attributed to the alkane chain length of the emulsifier [4].

The present study extends the problem of the preparation of grafted polypropylene with styrene to the verification of different metal salts ability to activate the grafting reaction in the presence of triethylenetetramine. The obtained results are correlated with the formation, stability, and reactivity of Me^{n+} —TET 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 [5].

Styrene was shaken with 10% sodium hydroxide solution and vacuum distilled under nitrogen.

Metal salts (Mn^{2+} , Fe^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Cr^{3+} , and Mg^{2+} sulfates, then Cu^+ , Hg^+ , Hg^{2+} , Sb^{3+} , Sn^{2+} , Ti^{4+} , Al^{3+} , Pb^{2+} chlorides, and AgNO_3) were of anal. grade or freshly recrystallized.

Mersol H, emulsifier (Leuna Werke, GDR).

Potassium myristate, emulsifier (Carl Roth Karlsruhe, GFR).

Nitrogen (high purity) was further purified on copper filings at 450°C and on $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$ 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 the preceding paper [1] with the ozone enriched oxygen for 30 minutes.

The active oxygen content in 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]. The components of the polymerization system were charged into the ampoules in the following order: polypropylene, metal salt aqueous solution, triethylenetetramine aqueous solution, emulsifier aqueous solution, water, and styrene. Water phase of the polymerization system (total volume 15 ml) contained the following components of the activation system: metal salt, (concentration $\text{Me}^{n+} = 1.33 \times 10^{-3} \text{ mol l}^{-1}$ of water phase) triethylenetetramine (concentration $1.33\text{--}2.66 \times 10^{-3} \text{ mol l}^{-1}$ according to the type of chelate), and emulsifier (concentration of mersol and potassium myristate [4] $3.9 \times 10^{-3} \text{ mol l}^{-1}$ and $3.7 \times 10^{-3} \text{ mol l}^{-1}$, respectively). Organic phase of the system contained 3 ml of styrene. Simultaneously the polymerization system comprised 0.4 g of the oxidized isotactic polypropylene as a macromolecular initiator (peroxides concentration was $2.4 \times 10^{-2} \text{ mol O}_2/\text{kg}$ 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 consumed.

Results

The effect of different metal salts in the presence of triethylenetetramine on the yield of polymer is shown in Table 1. Metal ions are listed according to their decreasing activity on grafting.

Discussion

The following metal salts employed together with triethylenetetramine as an activator of polypropylene grafting with styrene were chosen:

- a) transition metal salts of lower oxidation degree whose chelates with TET are known and described [7] *e.g.* Mn^{2+} , Fe^{2+} , Co^{2+} , and Ni^{2+} sulfates,
- b) metal salts being only in one oxidation degree (their chelates are known, *i.e.* Zn^{2+} , Cd^{2+} sulfates),
- c) other metal salts as Cu^{2+} , Cr^{3+} , Mg^{2+} , and Fe^{3+} sulfates, Cu^+ , Hg^+ , Hg^{2+} , Ti^{4+} , Sb^{3+} , Pb^{2+} , Sn^{2+} , Al^{3+} chlorides, and AgNO_3 .

Fe^{2+} , Co^{2+} , Mn^{2+} , Ni^{2+} , and Cu^{2+} salts forming chelates were used in molar ratios $\text{Me}^{n+} : \text{TET} = 1 : 1$, $2 : 3$, and $1 : 2$. With the others such a molar ratio was selected as to give a completely coordinated chelate. Metal chelates whose stability constants have not been described in the literature were studied at $2 : 3$ molar ratio. There was

Table 1

The effect of metal ion in the presence of TET on the polymerization of styrene at 35°C

No.	Me ⁿ⁺	Me ⁿ⁺ : TET ^a	Grafted styrene units/3 hrs [%]	Homopolymer/3 hrs [%]
1 ^b	—	—	0.0	2.0
2	Fe ²⁺	1 : 1	39.5	4.7
3		2 : 3	48.2	5.6
4		1 : 2	48.5	5.9
5	Co ²⁺	1 : 1	10.9	6.3
6		2 : 3	10.6	7.3
7		1 : 2	10.8	8.8
8	Mn ²⁺	1 : 1	3.9	1.8
9		2 : 3	5.5	2.1
10		1 : 2	5.9	3.1
11	Hg ⁺	2 : 3	1.4	3.3
12	Sb ³⁺	2 : 3	1.2	4.3
13	Ni ²⁺	1 : 1	0.7	2.1
14		2 : 3	0.8	3.7
15		1 : 2	0.8	4.1
16	Ag ⁺	1 : 1	0.7	1.8
17	Pb ²⁺	2 : 3	0.6	3.7
18	Cu ⁺	1 : 1	0.5	4.9
19	Cu ²⁺	1 : 1	0.4	4.9
20		2 : 3	0.5	8.4
21		1 : 2	0.5	9.2
22	Sn ²⁺	2 : 3	0.2	3.5
23 ^c	Ti ⁴⁺	2 : 3	—	6.5
24	Mg ²⁺	2 : 3	—	5.1
25	Fe ³⁺	2 : 3	—	3.3
26	Cd ²⁺	1 : 1	—	2.2
27	Al ³⁺	2 : 3	—	1.8
28	Zn ²⁺	1 : 1	—	0.5
29	Hg ²⁺	2 : 3	—	0.4
30	Cr ³⁺	2 : 3	—	0.2
31 ^d	Fe ²⁺	2 : 3	85.3	3.9
32 ^d	Co ²⁺	2 : 3	20.3	4.8
33 ^d	Mn ²⁺	2 : 3	8.0	1.6
34 ^d	Ni ²⁺	2 : 3	1.4	2.8
35 ^d	Cu ²⁺	2 : 3	0.4	5.2

a) Metal ion and TET molar ratio.

b) Only TET was added (concentration 1.99×10^{-3} mol l⁻¹).

c) 15% solution of TiCl₄ in HCl was kept in a stock; acid was neutralized with NaOH in the ampoule before TET was added.

d) Instead of mersol potassium myristate was employed.

used low concentration of emulsifier, at which condition grafted polymer was formed predominantly. By changing the type of emulsifier we intended to find out whether the yield of the grafted polymer is not dependent on the type of the Me^{n+} -TET chelate used.

The activation effect of metal ions, their complexes and chelates on the rate of polymerization is interpreted by their influence on the rate of peroxides decomposition. So the estimated activation effect of metal ions in the presence of polyamine type chelating agent is thought to be due to the redox character of the peroxide-chelate reaction [6]. According to that, from the metal salts studied (in the presence of TET), only those being at least in two oxidation degrees and producing stable chelates with triethylenetetramine were found to be active grafting agents (Fe^{2+} , Co^{2+} , Mn^{2+} salts). The fulfilment of only one condition is not sufficient as it could be evident from the results with Cr^{3+} and Fe^{3+} or Zn^{2+} and Cd^{2+} salts used.

The comparison of Fe^{2+} , Co^{2+} , and Ni^{2+} salts showed that their activation effect in the chelate with TET on the rate of polymerization decreases from Fe^{2+} to Ni^{2+} salts (the yield of grafted polymer decreases). Decrease in the redox potential of their transition to higher oxidation degree follows the same course, too. (One might suppose that this sequence will be retained even though the redox potential will change due to chelation.)

The easy oxidation of central ion probably will not be the only important condition of a good activation ability of the chelate. Stability (lability) of the chelate which influences its reactivity may be important too. Unlike moderately stable Fe^{2+} and Co^{2+} chelates less stable Mn^{2+} chelate (though according to the central ion redox potential it would rank between Fe^{2+} and Co^{2+}) could be placed after Co^{2+} as the polymerization results show (Table 2). On the other hand, highly stable Cu^{2+} chelate is a very weak activator too.

An interesting question arises in connection with Cu^{2+} -TET chelate concerning the assumed continuous reduction of higher oxidation metal ion state in redox reaction with peroxide [6] (the recovery of the active chelate state). The rate of such reduction will be influenced probably by the stability of chelate: e.g., unlike the stable Cu^{2+} -TET chelate, Fe^{3+} -TET chelate formed is totally unstable and only immediate central ion reduction to lower oxidation degree prevents it from the hydrolysis. Apparently the

Table 2

Comparison of the chelate stability constant ($\log K_{30^\circ}$) [7]
of the grafted styrene conversion in the presence of this chelate
and redox potential of the solvated ion (E)

Me^{n+}	$Me^{n+} : TET^a$	$\log K_{30^\circ}$	E [V]	Grafted styrene units/3 hrs [%]
Mn^{2+}		8.2	-1.51	5.5
Fe^{2+}	2 : 3	12.1	-0.77	48.2
Co^{2+}		14.6	-1.84	10.6
Ni^{2+}		19.9	-	0.8
Cu^{2+}	1 : 1	20.6	-0.17 ^b	0.5

a) Metal ion and TET molar ratio.

b) For the reaction $Cu^+ \rightarrow Cu^{2+}$.

chelate agent keeps metal ion in an active state for a short time till its next reduction. Thus the lability of the chelate with higher oxidation degree of central ion (and also its reactivity) has shown to be one of the important factors influencing the ability of the studied chelates to activate grafting reaction.

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