

A new initiation redox system for synthesis of grafted copolymers

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Dedicated to Professor Ing. J. Beniska, DrSc., in honour of his 60th birthday

Vinyl and acryl monomers were grafted on the oxidized polymer powder by means of a new initiation redox system. The grafting was carried out in an emulsion system in the presence of hydroperoxidated polymer, Cu(II) salt, and ammonia as complex-forming components and organic or inorganic reducing agent. This initiation system enables to prepare copolymers of vinyl chloride grafted on polyolefins with high effectiveness.

На окисленный полимерный порошок были привиты винильные и акрильные мономеры с помощью новой окислительно-восстановительной иницирующей системы. Прививка проводилась в эмульсионной системе в присутствии гидроперекисного полимера, медной соли и аммиака в качестве комплексообразующих компонентов и органического или неорганического восстанавливающего агента. С помощью этой иницирующей системы можно получать привитые сополимеры винилхлорида с полиолефинами с высокой степенью эффективности.

The main aim of the preparation of grafted copolymers of vinyl chloride on polyolefins is an improvement of physicomechanical and rheological properties of mixtures on the base of poly(vinyl chloride). For the synthesis of such copolymers the transfer reactions on polyolefin are frequently used. The polymerization takes place in block, solution or suspension system and peroxides are used as initiators. Besides the required copolymer, considerable amount of undesirable homopolymer is formed during the polymerization [1]. A macromolecular initiator, *i.e.* hydroperoxidated polymer is used for reducing the formation of homopolymer. *Natta* and his coworkers have found that the grafting prevails over homopolymerization provided polyamines have been added to the ozonized polyolefin [2].

Mikulášová and coworkers [3—5] investigated the polymerization of monomers in the presence of hydroperoxidated polypropylene powder. They have found that the formation of homopolymer may be prevented by using Fe(II) salts in combination with an appropriate complex-forming agent. The authors of papers [3—5] investigated several vinyl and acryl monomers but they did not study vinyl chloride.

This study is concerned with a new efficient initiation redox system for grafting vinyl chloride on hydroperoxidated low-density polyethylene powder which proved to be suited to preparation of other grafted copolymers as well.

Experimental

The following polymers were used for modification: Powdered polyethylene (PE) — Bralen RA 7-20/P3, MFI 0.7 g min^{-1} ; polypropylene (PP) — Tatren TF-411, MFI 0.9 g min^{-1} ; suspension poly(vinyl chloride) (PVC) — Slovinyl S-703 with the *K*-value 70.0.

The following monomers were employed: Vinyl chloride (VC) — rectified; styrene (ST) — distilled in nitrogen atmosphere after removing the stabilizer and drying with CaCl_2 ; methyl methacrylate (MMA) — after distillation and partial polymerization redistilled in inert atmosphere.

Furthermore, we used the sodium salts of alkanesulfonic acids C_{15} (Mersolat H, Bayer) as emulsifier, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, disodium salt of ethylenediaminetetraacetic acid (Chelaton 3), ammonia or ammonium hydroxide (26 mass % aqueous solution), cyclohexanone, benzene, and nitrogen. All the substances as well as the reducing agents in Table 3 and the salts of transition metals in Table 4 were anal. grade chemicals.

Procedures

The polymer powders were oxidized with oxygen containing ozone (12 mg dm^{-3}) in a column in fluid state for 15 min at laboratory temperature. The concentration of hydroperoxides was determined iodometrically [6].

The polymerization was performed in nitrogen atmosphere in rotating cells of stainless steel (volume 300 cm^3 , temperature $(50 \pm 0.1) \text{ }^\circ\text{C}$). The solid phase was filtered off from the product and the conversion of monomer was determined gravimetrically.

10 g of ozonized polyethylene (hydroperoxide content $6 \times 10^{-3} \text{ mol kg}^{-1}$), 100 g of aqueous solution of Mersolate H (0.1mass %), 0.69 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, and 0.93 g of Chelaton 3 (mole ratio $n(\text{Fe}^{2+}) : n(\text{Chelaton 3}) = 1 : 1$) were added into the polymerization cell. After removing oxygen with streaming nitrogen, 20 g of vinyl chloride were added.

The efficiency of grafting was estimated by extraction with a solvent in an apparatus

according to *Morgan and Corelli* [7]. PVC was extracted with cyclohexanone, and polystyrene and PMMA with benzene.

The *K*-value of poly(vinyl chloride) was calculated from the relative viscosity of PVC solution in cyclohexanone according to the Fikentscher's relation [8].

Results and discussion

At first, the known initiation system was used for grafting vinyl chloride on polyethylene [4]. The obtained results are presented in Fig. 1. It results from these data that the conversion of vinyl chloride was relatively high. However, it appeared that only a small part of monomer was bonded to polyethylene. It was disclosed on the basis of further experiments that the above system did not allow to prepare the grafted copolymer of vinyl chloride with more efficiency.

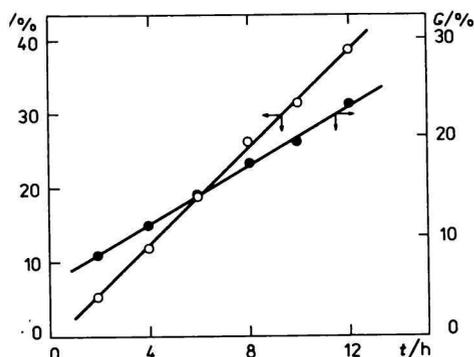


Fig. 1. Dependence of conversion (*C*) and grafting efficiency (*G*) of vinyl chloride on polymerization time using the Fe^{2+} —Chelaton 3 system.

Composition of the reaction mixture: 10 g of ozonized PE, 100 g of aqueous solution of Mersolat H (0.1 mass %), 0.3 g of fructose.

Concentrations of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and NH_3 $3.2 \times 10^{-5} \text{ mol dm}^{-3}$ and 0.3 mol dm^{-3} , respectively.

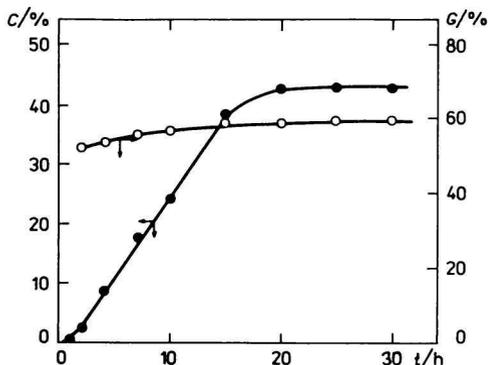


Fig. 2. Dependence of conversion (*C*) and grafting efficiency (*G*) of vinyl chloride on time. Composition of the reaction mixture is the same as in Fig. 1.

In order to use the monomer in the grafting reaction better, we tested a greater number of redox systems. On the basis of experimental results, it has been established that the most efficient initiation system consists of hydroperoxidated polyethylene, Cu(II) salt, and reducing agent in the presence of ammonia or ammonium hydroxide. Mersolat H of 0.1 mass % concentration in

the aqueous phase was used for improving the interaction of polyethylene with the polymerization system.

The influence of concentration of individual components of the system on conversion and efficiency of grafting of vinyl chloride was investigated at constant composition of the polymerization mixture (10 g of hydroperoxidated polyethylene, 20 g of vinyl chloride, 100 g of aqueous solution of Mersolat H of 0.1 mass % concentration, and 0.3 g of ascorbic acid). The influence of ammonia concentration on the grafting process at constant amount of the used $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.0008 g) for the polymerization time of 4 h is presented in Table 1. The results show that a rise in ammonia concentration over 0.1 mol dm^{-3} has only small influence on conversion and efficiency of grafting of vinyl chloride. Moreover, it has been found that NH_3 not only raises the pH value of solution but also forms a complex with Cu(II) ions, with which it supports the course of the redox reaction [9].

The influence of the amount of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ used in the initiation system is described in Table 2. The composition of the reaction mixture was equal to that

Table 1

Influence of the ammonia concentration in the form of ammonium hydroxide on conversion and efficiency of grafting of vinyl chloride

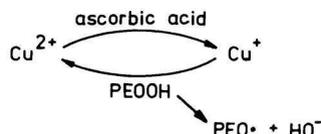
$[\text{NH}_3] \times 10^3 / (\text{mol dm}^{-3})$	0	15	100	300	1500
pH of aqueous phase	7.4	10.8	11.3	11.5	11.8
Conversion of monomer / %	0.1	5.8	19.1	24.2	25.4
Efficiency of grafting / %	—	22.4	65.5	66.0	67.3

Table 2

Influence of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ concentration on conversion and efficiency of grafting of vinyl chloride

$[\text{CuSO}_4 \cdot 5\text{H}_2\text{O}] \times 10^7$ mol dm^{-3}	$[\text{Cu}^{2+}] / [\text{VC}]$ $1 \times 10^{-4} \%$ (ppm)	Conversion of monomer %	Efficiency of grafting %
0	0	8.4	18.5
4	0.1	14.1	20.7
40	1.2	18.1	25.2
200	6.2	32.2	53.8
320	9.9	76.0	68.8
2000	61.8	77.0	67.2
6500	201.1	74.5	66.9

one used in the preceding case, the ammonia concentration was 0.3 mol dm^{-3} and the polymerization time was 20 h. It is obvious that the efficiency of grafting is constant at $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ concentrations exceeding 1×10^{-3} mass % of copper (10 ppm) with respect to vinyl chloride. It has appeared [9] that the proper reducing agent is the Cu^+ ion produced from Cu^{2+} by the effect of ascorbic acid which reacts with the hydroperoxidic groups of polyethylene (PEOOH). As the concentration of the Cu(II) salt in the system is much lower than that of PEOOH, it is evident that the reaction obeys the following scheme



where $\text{PEO} \cdot$ initiates the polymerization of monomer. A more detailed mechanism was presented earlier [9].

It has appeared on the basis of further experiments that a great number of other organic and inorganic reducing agents may be used instead of ascorbic

Table 3

Influence of different reducing agents on conversion and efficiency of grafting of vinyl chloride on powdered polyethylene

Experiment	Reducing agent	NH_3	Time of	Conversion of	Efficiency of
			polymerization	monomer	grafting
			h	%	%
1	Citric acid	/	17	20.8	41.8
2	Dihydroxymaleic acid	—	4	7.8	26.3
3	Dihydroxymaleic acid	/	4	10.2	55.4
4	Dihydroxymaleic acid	/	20	66.4	66.9
5	Glucose	/	20	76.7	70.1
6	Fructose	/	20	74.0	59.7
7	Galactose	/	20	78.5	70.5
8	Diethylenetriamine	/	17	78.8	51.6
9	Diethylenetriamine	—	17	12.1	27.1
10	Triethylenetetramine	/	20	48.2	40.7
11	Hexamethylenetetramine	/	20	18.6	55.7
12	Hydrazine sulfate	/	17	28.1	50.8
13	Benzoin	/	20	25.1	74.7
14	Sodium thiosulfate	/	20	19.7	45.2
15	Sodium iodide	/	20	25.1	61.0
16	Sodium bromide	/	20	10.7	55.2
17	Sodium sulfide	/	20	14.1	55.4

acid (Table 3). In each case, 0.3 g of the reducing component was used while the concentrations of ammonia and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ were 0.3 mol dm^{-3} and $3.2 \times 10^{-5} \text{ mol dm}^{-3}$, respectively. It results from Table 3 that the reducing agents may be divided into a few classes: endiols (ascorbic acid and dihydroxymaleic acid); reducing sugars (glucose, fructose, galactose); polyamines (diethylenetriamine, triethylenetetramine, hexamethylenetetramine); halides (sodium iodide, sodium bromide); other substances.

Table 4

Comparison of efficiency of different salts of the metals with transition valency ($c_M = 3.2 \times 10^{-5} \text{ mol dm}^{-3}$) for grafting vinyl chloride on polyethylene in the presence of constant quantities of NH_3 ($c = 0.3 \text{ mol dm}^{-3}$) and ascorbic acid ($c = 8 \times 10^{-3} \text{ mol dm}^{-3}$)

Compound of the metal with transition valency	Conversion of vinyl chloride	Efficiency of grafting
	%	%
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	16.1	22.6
$\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$	1.9	—
$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	2.7	—
$\text{MnCl}_2 \cdot \text{H}_2\text{O}$	2.5	—
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	76.0	68.0

In order to elucidate the role of the Cu(II) ions in initiation reactions, we investigated the polymerization of vinyl chloride in the presence of different metals with transition valency ($c_M = 3.2 \times 10^{-5} \text{ mol dm}^{-3}$). The time of polymerization was 20 h and the other conditions remained unchanged. Table 4 contains the results obtained from the investigation of the efficiency of different metals with transition valency in the process of grafting. It has appeared that the maximum effect was achieved by the use of Cu(II) salts. It is doubtlessly due to a smaller equilibrium constant of the complex formation of the other metals with the ligands containing nitrogen [10].

For better understanding of the mechanism of initiation, we investigated the time dependence of the polymerization of vinyl chloride (Fig. 2). It has been shown that the developed system allows to obtain a higher efficiency of grafting in comparison with the Fe^{2+} —Chelaton 3 system. This efficiency does not change with time. A certain amount of homopolymer apparently is formed owing to the transfer to the monomer of vinyl chloride.

Mikulášová and coworkers explained the course of polymerization of styrene and methyl methacrylate in the presence of hydroperoxides of propylene by the mechanism of "living polymerization" [11]. In order to elucidate the mechanism of grafting, we investigated the change in K -value of the homopolymer (PVC)

during polymerization. It is obvious from Table 5 that the K -value of PVC did not practically change. These facts make evident that the propagation reaction proceeds in the aqueous phase according to laws of common suspension polymerization though the initiation takes place on the surface of the polyethylene powder.

In further experiments, the proposed redox system was used for grafting different vinyl and acryl monomers on some powdered polymers containing the hydroperoxidic groups (Table 6). The composition of the reaction mixture was similar as stated for the experiments described in Fig. 2. It follows from Table 6 that the highest efficiency of grafting was achieved with methyl methacrylate.

Table 5

Influence of polymerization time on the K -value of copolymer of PVC

Time of polymerization/h	6	9	15	20	30
K -value	67.9	68.1	66.4	68.2	66.7

Table 6

Usage of different hydroperoxidated polymers for grafting vinyl and acryl monomers at constant concentrations of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ($3.2 \times 10^{-5} \text{ mol dm}^{-3}$), NH_3 (0.3 mol dm^{-3}), and ascorbic acid ($8 \times 10^{-3} \text{ mol dm}^{-3}$)

Polymer	Content of hydroperoxides	Monomer	Time of polymerization	Conversion of monomer	Efficiency of grafting
	mol kg^{-1}		h	%	%
PP	16.2	VC	20	69.3	75.7
PE	6.0	ST	17	73.5	59.0
PVC	15.0	MMA	17	94.5	91.9

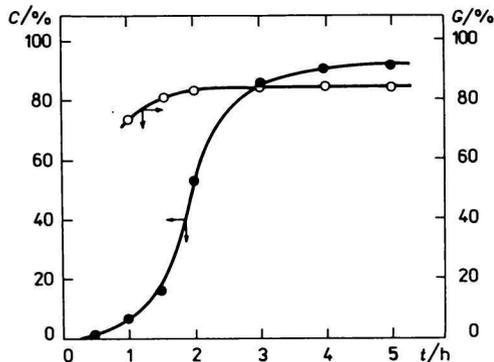


Fig. 3. Dependence of conversion (C) and grafting efficiency (G) of methyl methacrylate for grafting on powdered polyethylene. Composition of the reaction mixture is the same as in Fig. 1.

This fact is also evident in Fig. 3 which represents the efficiency of grafting of methyl methacrylate on powdered polyethylene.

It results from the above-mentioned facts that the developed initiation redox system enables to prepare not only copolymers of vinyl chloride with polyolefins but also other copolymers grafted by the use of different monomers and oxidized polymers.

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