

# Oxidized poly(vinyl chloride) as a heterogeneous initiator of emulsion polymerization

V. CHRÁSTOVÁ, D. MIKULÁŠOVÁ, and P. CITOVIČKÝ

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

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Low-oxidized powdered poly(vinyl chloride) (concentration of hydroperoxidic groups was  $1.9 \times 10^{-2}$  mol  $O_2$   $kg^{-1}$  PVC) was used as a heterogeneous initiator for the synthesis of high-molecular polystyrene or poly(methyl methacrylate) in emulsion. The influence of combination of four types of activator and two types of emulsifier on amount of the arising polymer was investigated.

As for homopolymerization of styrene, the best results were achieved with an activator of the  $FeSO_4$ —Chelaton III type or activator consisting of  $FeSO_4$ —triethylenetetramine in combination with a nonionic emulsifier. The  $FeSO_4$ —triethylenetetramine activator is not suited for homopolymerization of methyl methacrylate in the presence of ionic as well as nonionic emulsifier.

The influence of concentration of emulsifier and initiator on the course of polymerization of styrene was also investigated.

Слабоокисленный порошкообразный поливинилхлорид (концентрация гидроперекисных групп  $1,9 \cdot 10^{-2}$  моль  $O_2$   $кг^{-1}$  ПВХ) был использован в качестве гетерогенного инициатора синтеза высокомолекулярного полистирола или полиметилметакрилата в эмульсии. Исследовано влияние сочетаний четырех типов активатора и двух типов эмульгатора на количество образующегося полимера.

Хотя полимеризация проводилась аналогичным методом как при использовании окисленного изотактического полипропилена, эти два вида гетерогенного инициатора оказывают довольно различное влияние на эмульсионную полимеризацию.

В случае гомополимеризации стирола лучшие результаты были достигнуты с активатором хелатного типа  $FeSO_4$ —Хелатон III или  $FeSO_4$ —триэтиленetetрамин в сочетании с неионогенным эмульгатором; при гомополимеризации метилметакрилата активатор  $FeSO_4$ —триэтилентетрамин не подходит ни в случае ионного, ни неионного эмульгаторов.

При указанной полимеризации стирола было исследовано влияние концентрации эмульгатора и инициатора также на ход полимеризации.

It has been found in preceding studies [1—3] that the hydroperoxide of powdered isotactic polypropylene may be used as a heterogeneous initiator of organic character for emulsion polymerization of vinyl monomers. Provided the components of the polymerization system are conveniently selected, only homopolymer is formed in the emulsion and no bonding of polystyrene to oxidized polypropylene appears [4].

In addition to the aqueous and oily phase the heterogeneous initiator represents further solid phase in the emulsion polymerization system, which brings about certain peculiarities affecting not only the course of polymerization but also the properties of the arising polymer. For example, it was found that the heterogeneously initiated emulsion polymerization of styrene obeys the mechanism of living polymerization and prepared polystyrene has extremely high molecular weight which grows with increasing conversion [5].

Following the preceding results, the possibility of using further type of heterogeneous initiator, *i.e.* oxidized powdered poly(vinyl chloride), for the emulsion polymerization of styrene and methyl methacrylate was investigated in this study.

## Experimental

### Chemicals

Poly(vinyl chloride) (PVC), type S-PVC-V-701, powdered, product of CHZWP, Nováky. It contained 60 mass % of particles with 0.063 mm diameter.

Styrene — shaken with 10 mass % sodium hydroxide solution, dried, two times distilled under reduced pressure in inert atmosphere.

Methyl methacrylate — after the first vacuum distillation prepolymerized and further vacuum distilled in nitrogen atmosphere.

Triethylenetetramine (TETA) — characteristics are given in paper [1]; an aqueous solution of  $6.0 \times 10^{-2}$  mol dm<sup>-3</sup> concentration was used.

Chelaton III (EDTA) — disodium salt of ethylenediaminetetraacetic acid and pentahydrate of iron(II) sulfate, anal. grade chemicals, were used as aqueous solutions of  $4.0 \times 10^{-2}$  mol dm<sup>-3</sup> concentration.

Emulsifiers — anionic Mersol H and nonionic Slovasol 2430 the characteristics of which are given in papers [1, 2] were used as 0.145 M aqueous solutions.

Solvents — toluene and methanol were anal. grade.

Nitrogen — (high purity) was deprived of the rest of oxygen [2] and used as an inert gas.

### Working procedures

The polymerization was performed in ampoules as described earlier [1, 2]. The initiation centres on the powdered poly(vinyl chloride) were generated by fluid oxidation during 30 min at laboratory temperature and atmospheric pressure. Oxygen contained ozone in

12 mg dm<sup>-3</sup> concentration and its rate of flow was 0.18 m<sup>3</sup> min<sup>-1</sup>. The content of active oxygen (peroxidic groups) determined iodometrically with KI in glacial acetic acid was  $1.9 \times 10^{-2}$  mol O<sub>2</sub> kg<sup>-1</sup> PVC.

The following components of the polymerization system were successively dosed in inert atmosphere into the ampoules containing constant quantity of the oxidized PVC (0.4 g) deprived of trace oxygen: activator—triethylenetetramine ( $3.3 \times 10^{-3}$  mol dm<sup>-3</sup>) or FeSO<sub>4</sub>—EDTA in mole ratio 1:1 ( $2.2 \times 10^{-3}$  mol dm<sup>-3</sup>) (other concentration of activator is given in Table 1), emulsifier—anionic Mersol H or nonionic Slovasol 2430 ( $2.4 \times 10^{-2}$ — $8.8 \times 10^{-2}$  mol dm<sup>-3</sup>), and monomer—styrene (1.44 mol dm<sup>-3</sup>) or methyl methacrylate (1.65 mol dm<sup>-3</sup>); concentrations are given in mol dm<sup>-3</sup> of emulsion. The polymerization was carried out at 30°C. When the polymerization was finished, the emulsion was separated from the solid phase by filtration through a sintered glass (S<sub>i</sub>) and precipitated with methanol. The conversion of monomer was expressed in mass % with respect to the initial mass of monomer. The rate of polymerization was expressed in mol dm<sup>-3</sup> s<sup>-1</sup> with respect to the volume of emulsion. When the percentage of the modified poly(vinyl chloride) was estimated, the solid phase on the sintered glass (S<sub>i</sub>) was washed with water and acetone, extracted with benzene at 60°C, and washed again with acetone. The mass percentage of the polymer bonded to poly(vinyl chloride) was calculated with respect to the dosed mass of monomer.

The viscometric measurements serving for characterization of the relative molecular weights of polystyrene and poly(methyl methacrylate) were carried out in a Ubbelohde diluting viscometer in toluene at 25°C. The flow-time of pure solvent was greater than 100 s and for this reason kinetic energy correction was not applied. The limiting viscosity number  $[\eta]$  was determined from the relationship  $(\eta - \eta_0)/\eta_0 c = f(c)$ , where  $\eta$  and  $\eta_0$  are solution and/or solvent flowing times (in s), respectively and  $c$  is the concentration of solution (in g/100 cm<sup>3</sup>). The equations  $[\eta] = 1 \times 10^{-4} \bar{M}_v^{0.72}$  or  $[\eta] = 7.1 \times 10^{-5} \bar{M}_v^{0.73}$  [6] were used for the calculation of the relative molecular weight of polystyrene and poly(methyl methacrylate).

## Results and discussion

The possibility of using oxidized powdered poly(vinyl chloride) as a heterogeneous initiator of emulsion polymerization of styrene and methyl methacrylate was tried in several polymerization systems. Simultaneously, the influence of different combinations of initiator with activators, *i.e.* FeSO<sub>4</sub>, TETA, EDTA, FeSO<sub>4</sub>—TETA, and FeSO<sub>4</sub>—EDTA (in the presence of ionic or nonionic emulsifier), on the yield of produced polymer was investigated. The results of these polymerizations are presented in Table 1. They include the values of the viscometrically determined relative molecular weights of the homopolymers of styrene and methyl methacrylate as well as the amount of polystyrene and poly(methyl methacrylate) bonded to PVC (in polymerizations No. 6 and 12 the composition of system was intentionally chosen to be favourable for the formation of grafted copolymer [7]). Like in the modification of polypropylene, better yields were achieved in the modification of PVC with MMA than with styrene which should be due to chemical

Table 1

Results of the polymerization of styrene and methyl methacrylate initiated by oxidized poly(vinyl chloride) at 30°C

No.	FeSO <sub>4</sub> · 10 <sup>3</sup>	EDTA · 10 <sup>3</sup>	TETA · 10 <sup>3</sup> c/mol dm <sup>-3</sup>	E <sub>1</sub> · 10 <sup>2</sup>	E <sub>2</sub> · 10 <sup>2</sup>	St	Conversion after 2 h			MMA c/mol dm <sup>-3</sup>	Conversion after 2 h		$\bar{M}_{v,r}$ · 10 <sup>-6</sup> PMMA
							%		$\bar{M}_{v,r}$ · 10 <sup>-6</sup> PSt		%		
							Homo- polymer	Grafted PVC			Homo- polymer	Grafted PVC	
1	—	—	—	—	↑	↑	0.0	0.0	—	↑	0.3	0.0	—
2	—	—	3.3	—	↑	↑	4.5	0.0	7.3	↑	0.2	0.0	—
3	2.2	—	—	—	2.4	↑	79.0	21.1	12.9	↑	77.1	4.5	20.0
4	—	2.2	—	—	↓	↑	0.1	0.0	—	↑	0.3	0.0	—
5	2.2	2.2	—	—	↓	1.44	62.1	2.0	12.2	1.65	69.9	2.8	14.8
6	2.2	—	1.6	—	0.8	↓	50.9	4.6	22.5	1.65	43.8	19.6	18.1
7	—	—	—	↑	—	↓	0.0	0.0	—	↓	0.3	0.0	—
8	—	—	3.3	—	—	↓	4.0	0.0	10.5	↓	0.3	0.0	—
9	2.2	—	—	2.4	—	↓	47.0	4.3	18.5	↓	62.8	15.6	19.9
10	—	2.2	—	—	—	↓	0.3	0.0	—	↓	0.2	0.0	—
11	2.2	2.2	—	—	—	↓	43.8	1.2	13.7	↓	73.7	4.2	9.0
12	2.2	—	1.6	0.8	—	↓	2.6	9.6	9.8	↓	0.6	69.1	—

E<sub>1</sub> — Mersol H, E<sub>2</sub> — Slovasol 2430, St — styrene, PSt — polystyrene, MMA — methyl methacrylate, PMMA — poly(methyl methacrylate).

character of the monomer [8]. In contrast to polypropylene, if poly(vinyl chloride) is subjected to grafting, the result may be influenced also by polar character of the chlorine bonded to the polymer chain.

If the oxidized PVC was used as a heterogeneous initiator of homopolymerization, it appeared that, in contrast to the oxidized powdered polypropylene, the polymerization proceeded only in the presence of activator. Anyway, a polymer with high molecular weight was formed. Triethylenetetramine which activates homopolymerization according to preceding experience [1] preserves this property with reference to PVC only in the polymerization of styrene (Table 1). Even in this case, the activation effect of TETA is, however, relatively small in comparison with the effect of the  $\text{FeSO}_4$ —EDTA or  $\text{FeSO}_4$ —TETA chelates (in the presence of nonionic emulsifier) or with the effect of metallic component alone (in the presence of both types of emulsifiers). The advantage of using the one-component activator TETA for the polymerization of styrene consisted in the fact that only homopolymer was formed in a system with ionic as well as nonionic emulsifier and no grafting of poly(vinyl chloride) occurred. In order to influence positively the yield of polystyrene in the presence of the one-component activator TETA, the influence of concentration of both emulsifiers used on the percentage of arising polystyrene was investigated. Though the increasing concentration of emulsifier, to a certain extent, positively influenced the increase in conversion of styrene, as stated in preceding papers [1, 9], it was not possible in this case after 2 h polymerization to obtain a higher conversion than about 25% (Fig. 1).

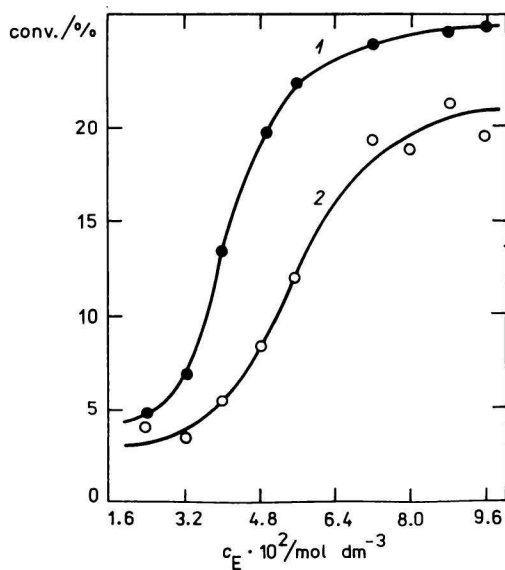


Fig. 1. Dependence of conversion (%) on concentration of Slovasol 2430 (1) and Mersol H (2), for the polymerization of styrene initiated by oxidized PVC ( $1.9 \times 10^{-2} \text{ mol O}_2 \text{ kg}^{-1} \text{ PVC}$ ). Activation by TETA ( $3.3 \times 10^{-3} \text{ mol dm}^{-3}$ ),  $30^\circ\text{C}$ .

On the basis of the values listed in Table 1 it follows that, from the view-point of the yield of polystyrene as well as poly(methyl methacrylate), it is most convenient to use the system containing  $\text{FeSO}_4$ —EDTA type of activator with an ionic and especially nonionic emulsifier. This system produces relatively small amounts of the grafted copolymer (the presented results were obtained after 2 h reaction) which have no significant influence on the kinetics of homopolymerization (polymerization proceeds a few minutes) and may be neglected. The conversion curves for the polymerization of styrene in a system initiated by the oxidized PVC with the  $\text{FeSO}_4$ —EDTA activator in the presence of ionic and nonionic emulsifier are given in Fig. 2. The rates of polymerization achieved with nonionic emulsifier were greater than the rates with Mersol H.

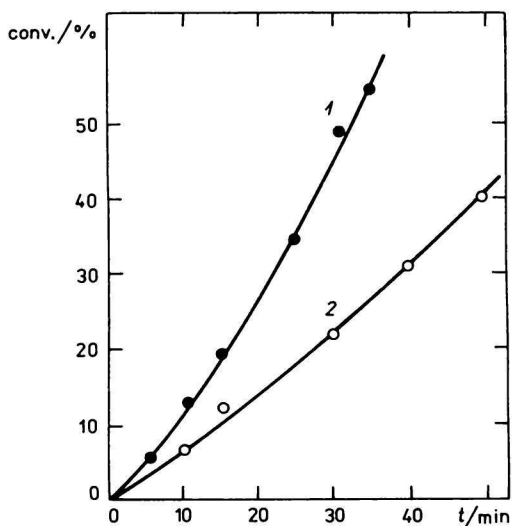
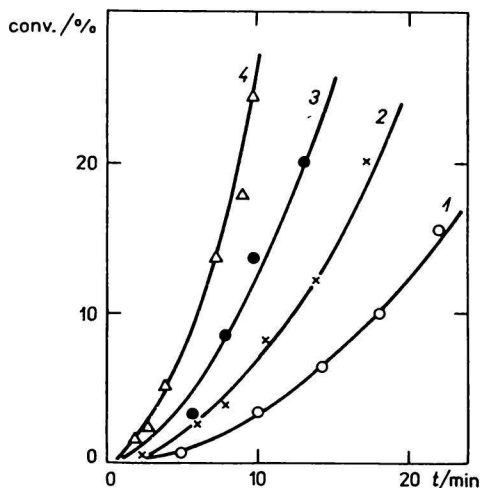


Fig. 2. Dependence of conversion (%) on time, for the polymerization of styrene at 30°C in the system containing oxidized PVC ( $1.9 \times 10^{-2}$  mol  $\text{O}_2$   $\text{kg}^{-1}$  PVC),  $\text{FeSO}_4$ —EDTA (mole ratio 1:1) and two types of emulsifiers ( $4.8 \times 10^{-2}$  mol  $\text{dm}^{-3}$ ).  
1. Slovasol 2430; 2. Mersol H.

Furthermore, we investigated the influence of concentration of the heterogeneous initiator on the rate of styrene polymerization in the presence of the  $\text{FeSO}_4$ —EDTA activator and Slovasol 2430. The concentration of the heterogeneous initiator was changed by altering the weight of the PVC oxidized to a constant degree. The kinetic relationships of styrene polymerization at varying concentration of initiator are represented in Fig. 3. Since the conversion curves were not linear, the rate of polymerization was determined from the relationship between logarithm of the numerical value of conversion (%) and polymerization time according to the procedure described in [3]. The determined reaction order with respect to the concentration of heterogeneous initiator is equal to 0.8. It is somewhat lower than the value 1.05 found for the emulsion polymerization of

Fig. 3. Conversion curves of the polymerization of styrene at 30°C in the system containing  $\text{FeSO}_4$ —EDTA (mole ratio 1:1), Slovasol 2430 ( $4.8 \times 10^{-2} \text{ mol dm}^{-3}$ ), and increasing amounts of oxidized PVC ( $1.9 \times 10^{-2} \text{ mol O}_2 \text{ kg}^{-1} \text{ PVC}$ ) expressed in grams.

1. 0.1 g; 2. 0.2 g; 3. 0.4 g; 4. 0.6 g.



styrene initiated by the oxidized polypropylene with the activator TETA when the concentration of peroxidic groups was changed by varying weight of the heterogeneous initiator [3]. The lower value of the reaction order determined in this work may be, to a certain extent, influenced by the type of the used initiator that was the peroxide of oxidized PVC as well as by the type of the used activator

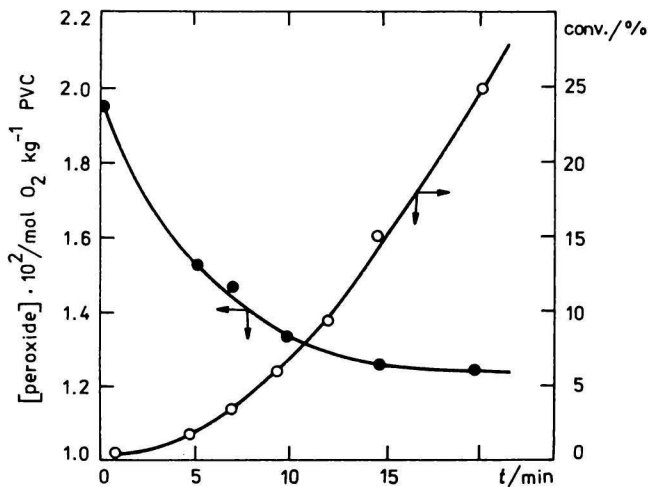


Fig. 4. Content of residual peroxides of PVC and conversion (%) as a function of time for the polymerization of styrene in the system containing oxidized PVC,  $\text{FeSO}_4$ —EDTA (mole ratio 1:1), Slovasol 2430 ( $4.8 \times 10^{-2} \text{ mol dm}^{-3}$ ) at 30°C.

that was the  $\text{FeSO}_4$ —EDTA chelate. It was shown that the decomposition of the peroxide of poly(vinyl chloride) proceeded more rapidly in the presence of  $\text{FeSO}_4$ —EDTA activator (during the first 10 min of polymerization) (Fig. 4) than in the presence of the activator TETA (30 min [3]). It may be assumed that the efficiency of initiation should be very low owing to a fast decomposition of the peroxide bonded to the surface of PVC by the effect of such efficient activator as the  $\text{FeSO}_4$ —EDTA chelate. Thus only few primary radicals can take part in growth reactions. This effect may manifest itself in the course of the investigated polymerization in the region of low conversions, *i.e.* in the first stage when the number of the polymer—monomer particles is not yet stationary.

Besides the powdered oxidized polypropylene and polyethylene [10], the powdered oxidized PVC, as an organic type of heterogeneous initiator, offers further opportunity of using this kind of initiation for radical polymerization. The high-molecular polystyrene or poly(methyl methacrylate) may be prepared in the presence of oxidized poly(vinyl chloride) in the investigated emulsion polymerization system if the specific features of thus initiated polymerization are respected.

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