

Role of polypropylene polyhydroperoxide in the emulsion polymerization of styrene and methyl methacrylate

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The rate of the polymerization of styrene and methyl methacrylate initiated by powdered oxidized polypropylene depends on the concentration of polyhydroperoxide. The exponent 0.5 of this relationship was found for the polymerization of styrene on condition that the content of the solid phase in the system was constant and for the polymerization of methyl methacrylate in the stationary region of conversion curves. If the change in the concentration of polyhydroperoxide was achieved by changing the content of the solid phase in the system, the unit reaction order was found for the polymerization of styrene. This reaction order is equal to the sum of the experimentally determined exponents for the concentrations of triethylenetetramine and polyhydroperoxide.

The stationary course of the polymerization of styrene and the autocatalytic course of the polymerization of methyl methacrylate are attributed to the specific character of the decomposition of polypropylene polyhydroperoxide during polymerization which is one of the causes of long-living radical existence in this type of polymerization.

Скорость полимеризации стирола и ММА инициированной окисленным порошкообразным полипропиленом зависит от концентрации полигидроперекиси. Показатель 0,5 приведенной зависимости установлен при полимеризации стирола при условии, что содержание твердой фазы в системе было постоянное, и при полимеризации ММА в стационарной области кривых конверсии. Когда изменение концентрации полигидроперекиси достигалось изменением содержания твердой фазы в системе, определился при полимеризации стирола единичный порядок реакции, который равняется сумме экспериментально установленных показателей для концентрации триэтилентетрамина и полигидроперекиси.

Стационарный ход полимеризации стирола и автокаталитический ход полимеризации ММА дается в связь со специфическим характером распада полигидроперекиси полипропилена во время полимеризации, который является одной из причин, что при приведенном типе полимеризации существуют долговременные радикалы.

It has been shown [1] that oxidized polypropylene in combination with a suitable activator may be used as an initiator in emulsion polymerization at 35°C. The results obtained at the polymerization of styrene indicate the formation of a polymer with high molecular weight and narrow molecular weight distribution. It has been proved that the rate of styrene polymerization as well as the molecular weight of the polymer formed depends on the concentration of emulsifier and the concentration of triethylenetetramine used as an activator.

The block polymerization initiated at 80°C by other type of macromolecular initiator [2], *i.e.* the polymer peroxides of diacids, prepared by the reaction of dichlorides of dicarboxylic aliphatic acids and sodium peroxide, shows some features in common with the above-mentioned polymerization. However, the causes of similar features (increase in the molecular weight of polymer with conversion, narrow molecular weight distribution) are quite different for both the polymerizations.

As for the multicomponent polymerization system mentioned in [1], attention has been paid mainly to the effect of activator [3] and emulsifier [4] on the course of styrene polymerization. The effect of the hydroperoxide groups of oxidized polypropylene (polyhydroperoxide of polypropylene) on the rate of the homopolymerization initiated by them has remained unexplained. This problem is analyzed in the present paper for two monomers.

Experimental

Chemicals

Polypropylene — powdered, isotactic. Use was made of two kinds of polypropylene of different bulk density (g dm^{-3}): 350 (PP_I) and 108 (PP_{II}). Polypropylene was oxidized by oxygen containing ozone (12 mg dm^{-3}) at laboratory temperature. The content of polypropylene polyhydroperoxide was estimated iodometrically [5].

Methyl methacrylate (MMA) — stabilized — was purified in an inert atmosphere by vacuum distillation, prepolymerization, and further vacuum distillation.

Styrene was purified in the same manner as described earlier [5].

Emulsifiers: Slovasol 2430 — unionic type of the composition $\text{CH}_3(\text{C}_2\text{H}_4\text{O})_{29}\text{C}_2\text{H}_4\text{OH}$; Slovafof 920 — unionic type of the composition $\text{C}_9\text{H}_{19}-\text{C}_6\text{H}_4\text{O}-(\text{C}_2\text{H}_4\text{O})_{19}\text{C}_2\text{H}_4\text{OH}$; Mersol H — ionic type of the composition $\text{CH}_3(\text{CH}_2)_{16}\text{SO}_3\text{Na}$. These substances were used in the form of aqueous solutions. Before polymerization they were boiled in an inert atmosphere for one hour and subsequently they were cooled.

Triethylenetetramine (3,5-diaza-1,8-octanediamine) was synthesized from 1,2-dichloroethane and 1,2-diaminoethane [6]. It was used in the form of aqueous solution.

Water — distilled in glass apparatus — was boiled for one hour before use and then it was cooled in an inert atmosphere.

Nitrogen — used as an inert gas — was deprived of the rest of oxygen by passing through a column (at laboratory temperature) the filling of which consisted of MnO_2 (55%), MgO (40%), and Cr_2O_3 (5%).

The chemicals used for analytical determinations were anal. grade reagents.

Procedure

The ampules of about 20 ml volume were used for the polymerization of monomers. The ampules with weighed oxidized polypropylene were put into separate suction flasks connected in series. They were evacuated to 65 Pa for 2 h. After cancelling the vacuum with nitrogen, they were evacuated again, closed, and allowed to stand for 12 h in vacuum. Afterwards they were evacuated for another 2 h. On balancing the underpressure with nitrogen the components of the polymerization system were dosed into the ampules by means of a system of burettes protected by inert atmosphere. The filled ampule was sealed and after shaking the content it was put into a frame revolving in thermostated water bath. On isolating the polymer formed, polypropylene was filtered off by a sintered glass. The polymer formed was precipitated from emulsion with methanol and after filtration it was dried in vacuum. The conversion was expressed in moles of monomer consumed referred to a litre of emulsion.

At autocatalytic course of the conversion curves the conversion increases with time t exponentially, *i.e.* $\text{conv} = K t^a$. The exponent a was determined from the logarithmic relation $\log(\text{conv}) = f(\log t)$. The instantaneous rate V_p at arbitrary conversion was calculated from the relation obtained by differentiating the original equation, by the use of the determined constant a

$$V_p = \frac{d(\text{conv})}{dt} = a K t^{a-1} = \frac{a(\text{conv})}{t}$$

Results

The conversion curves in Fig. 1 represent the influence of the concentration of polypropylene polyhydroperoxide in the range 3.2×10^{-4} — 16.8×10^{-4} mol dm^{-3} on the rate of the polymerization of styrene in the presence of the unionic emulsifier Slovasol 2430.

Besides, the decomposition of polyhydroperoxide was investigated during polymerization. The dependences obtained express the content of residual polyhydroperoxide as a function of polymerization time and are presented in Fig. 2.

The effect of the concentration of polypropylene polyhydroperoxide on the rate of styrene polymerization was also examined in the presence of the ionic emulsifier Mersol H. The change in the concentration of polyhydroperoxide was achieved either by using a constant weighed amount of polypropylene oxidized to varying degree or by using a varying amount of polypropylene with a constant content of hydroperoxide groups. The rates of styrene polymerization evaluated from the conversion curves are given in Table 1.

The relationship between the rate of styrene polymerization and the concentration of polyhydroperoxide expressed in logarithmic coordinates is presented in Fig. 3. The slopes of

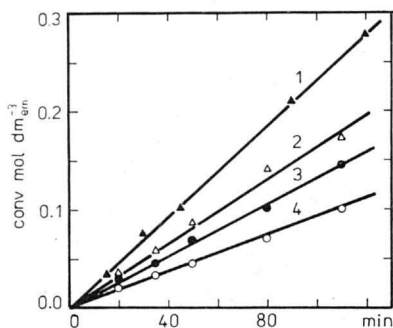


Fig. 1. Conversion curves for the emulsion polymerization of styrene in the presence of Slovasol 2430 ($2.4 \times 10^{-2} \text{ mol dm}_{\text{em}}^{-3}$), triethylenetetramine ($1.68 \times 10^{-3} \text{ mol dm}_{\text{em}}^{-3}$), and polypropylene polyhydroperoxide PP₁ of varying concentration ($\text{mol dm}_{\text{em}}^{-3}$):

1. 11.0×10^{-4} ; 2. 7.0×10^{-4} ; 3. 5.1×10^{-4} ;

4. 3.2×10^{-4} .

Temperature 30°C.

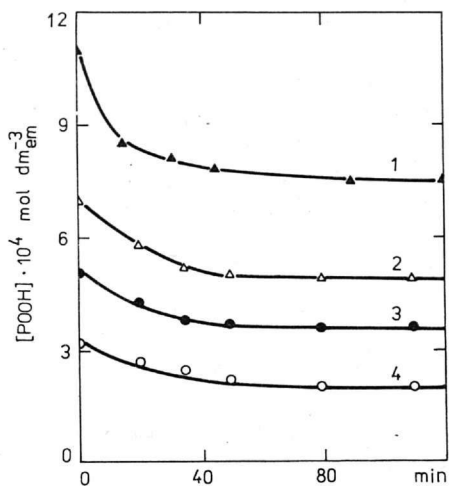


Fig. 2. Concentration of residual polypropylene polyhydroperoxide as a function of time for the polymerization of styrene under conditions stated in Fig. 1.

Table 1

Influence of the concentration of polypropylene polyhydroperoxide [POOH] on the rate of styrene polymerization V_p in the presence of the emulsifier Mersol H ($2.4 \times 10^{-2} \text{ mol dm}_{\text{em}}^{-3}$) and triethylenetetramine [TETA] used as an activator at 35°C

Weighed amount PP _{II} g	[POOH] · 10 ³ mol kg ⁻¹ PP	[POOH] · 10 ⁴ mol dm _{em} ⁻³	[TETA] · 10 ³ mol dm _{em} ⁻³	$V_p \cdot 10^5$ mol dm _{em} ⁻³ s ⁻¹
0.4	5.3	1.18	3.15	1.22
	6.5	1.44		1.46
	8.7	1.93		1.54
	11.5	2.56		1.88
	13.5	3.00		1.96
	18.0	4.00		2.27
0.8	25.2	5.60	4.33	2.99
	6.6	0.37		0.44
		0.73		0.85
		1.10		1.02
		1.47		1.70
		1.83		2.87
2.93	3.30			

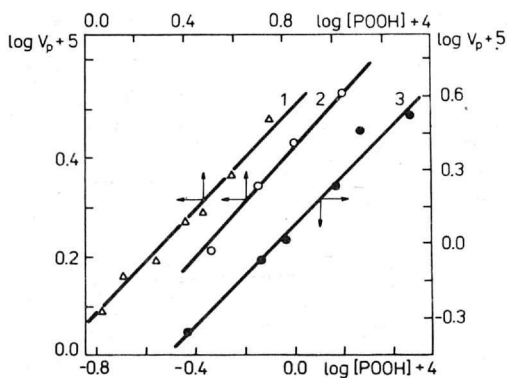


Fig. 3. Logarithmic dependence of the rate of the emulsion polymerization of styrene on the concentration of polypropylene polyhydroperoxide. Polymerization conditions are stated in Fig. 1 (curve 2) and in Table 1 (curve 1 for a constant weighed amount of polypropylene and curve 3 for a varying weighed amount of polypropylene).

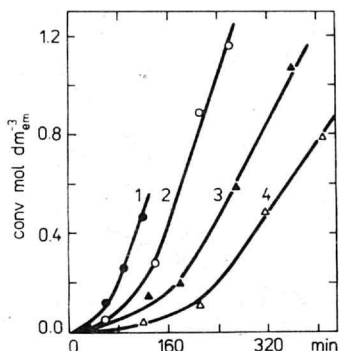


Fig. 4. Conversion curves for the emulsion polymerization of methyl methacrylate in the presence of Slovafo1 920 (4.54×10^{-2} mol $\text{dm}_{\text{em}}^{-3}$), triethylenetetramine (2.02×10^{-3} mol $\text{dm}_{\text{em}}^{-3}$), and polypropylene polyhydroperoxide PP_1 of varying concentration (mol $\text{dm}_{\text{em}}^{-3}$):
1. 12.7×10^{-4} ; 2. 10.0×10^{-4} ; 3. 5.9×10^{-4} ;
4. 4.0×10^{-4} . Temperature 30°C .

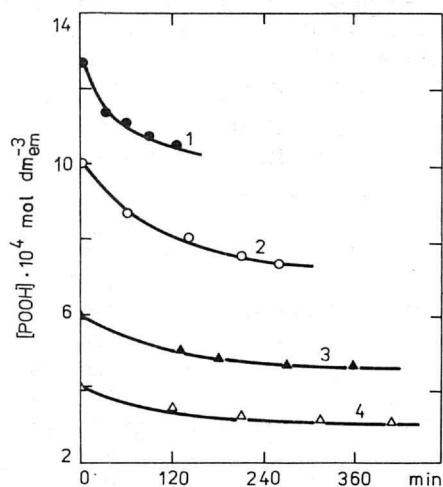


Fig. 5. Concentration of residual polypropylene polyhydroperoxide as a function of time for the emulsion polymerization of methyl methacrylate under conditions stated in Fig. 4.

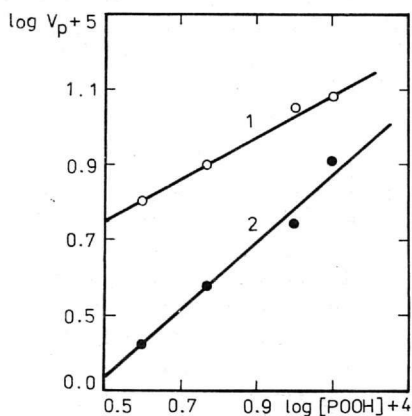


Fig. 6. Logarithmic dependence of the rate of the emulsion polymerization of methyl methacrylate on the concentration of polypropylene polyhydroperoxide for the stationary (curve 1) and non-stationary (curve 2) region of the conversion curves presented in Fig. 4.

straight lines 1 and 2 are identical within the error range (0.52 and 0.54) while the value of the slope of straight line 3 is equal to 1.05.

The polymerization of methyl methacrylate, which is a monomer differing considerably from styrene by its chemical character, initiated by polypropylene polyhydroperoxide showed some peculiarities. The unionic type of emulsifier Slovafo 920 proved to be the most convenient among the investigated ionic and unionic types of emulsifiers. The course of the polymerization of methyl methacrylate initiated by polyhydroperoxide of the polypropylene oxidized to varying degree is presented in Fig. 4. The results of the parallel investigation of the decomposition of polyhydroperoxide during polymerization are given in Fig. 5.

Because of the autocatalytic character of the conversion curves obtained for the polymerization of methyl methacrylate the relationship between the rate of polymerization and the concentration of polyhydroperoxide was evaluated by means of the experimental constant $a = 2.3$ from the instantaneous rate at 10% conversion as well as from the linear sections of conversion curves in the region of higher conversions. This relationship is drawn in logarithmic coordinates in Fig. 6. The slope of the straight line for non-stationary region of the conversion curves is equal to 0.9 and for stationary region to 0.55.

Discussion

The results obtained for the polymerization of styrene and methyl methacrylate initiated by a heterogeneous initiator, *i.e.* oxidized powdered polypropylene, prove the existence of a relation between the rate of these polymerizations and the concentration of polypropylene polyhydroperoxide. The reaction order 0.5 found at a constant content of the solid phase in the polymerization system irrespective of the kind of emulsifier, provided the concentration of triethylenetetramine is higher than the concentration of polyhydroperoxide, is in agreement with the mechanism proposed for the polymerization of styrene [7].

The increase in the concentration of hydroperoxide groups due to increasing portion of the solid phase in the polymerization system, however, results in an increased rate of polymerization much more markedly than it has been observed at a constant content of the solid phase. The unit exponent found in this case indicates that probably owing to increasing adsorption caused by increasing amount of polypropylene, not only the concentration of polyhydroperoxide but also other components of the polymerization system which are important for the initiation taking place on the surface of polypropylene are responsible for the increase in the rate of polymerization provided the concentration of polyhydroperoxide is varied in this manner. From this point of view the concentrations of triethylenetetramine and monomer must be taken into consideration in addition to the concentration of polyhydroperoxide. From the data given in [7] it may be ascertained that the reaction order of the polymerization of styrene with respect to the concentration of

triethylenetetramine is equal to 0.5 if Mersol H is used as an emulsifier. As the rate of the investigated polymerization of styrene does not depend on the concentration of monomer [8] under conditions used, the unit exponent determined may be considered to be equal to the sum of the reaction orders with respect to the concentration of polyhydroperoxide (0.5) and to the concentration of triethylenetetramine (0.5).

The importance of the surface area of polypropylene for the investigated polymerization is also indicated by the fact that polypropylene with different bulk densities gives different rates of polymerization. The effect of this factor in which the specific surface of the polypropylene is, in a certain manner, reflected manifests itself in this study, for instance at lower rates of the polymerization of styrene in the presence of Slovasol 2430 if polypropylene with considerably higher bulk density, *i.e.* smaller specific surface is used. If polypropylene of equal kind is used, the rates of the polymerization of styrene are higher in the presence of unionic emulsifier than in the presence of ionic emulsifier [4].

The course of the decomposition of polypropylene polyhydroperoxide during the polymerization of styrene is interesting from two view-points, *i.e.* as regards the limitation of the decomposition (about 30% of decomposed hydroperoxide groups) and as regards the relatively high velocity with which this limit is reached (about 30 min at 30°C). But the conversion curves confirm that the polymerization proceeds as a stationary process far beyond this limit. It may be stated that the heterogeneous initiator with that character of decomposition, emulsion polymerization system, and relatively low temperature make possible the existence of long-living radicals which has been assumed [1] and proved indirectly by the preparation of block copolymers [9].

The autocatalytic course of conversion curves of the polymerization of methyl methacrylate which is due to increasing concentration of free radicals in the polymerization system, is unusual in emulsion polymerization. However, if the experimental results obtained at the polymerization of methyl methacrylate and styrene are compared, a significant difference not only in the character of conversion curves but also in the course of the decomposition of polypropylene polyhydroperoxide can be ascertained. In the polymerization of methyl methacrylate polyhydroperoxide is decomposed relatively more slowly than in the polymerization of styrene though the extent of its decomposition is not much different in both cases. Owing to this character of the decomposition of polyhydroperoxide the increase in the concentration of free radicals during the polymerization of methyl methacrylate may be explained on the assumption that the low-molecular radicals arising during the initiation of polymerization on the surface of polypropylene are not able to diffuse into latex particles and bring about termination inside them. Therefore, it must be assumed that the cause of the different reaction order with respect to the concentration of polyhydroperoxide in non-stationary and stationary

region does not consist in a different mechanism of termination in these two regions but in specific properties of the heterogeneous polyhydroperoxide which, as proved by e.s.r. measurements [10], prevents the arising low-molecular radicals to diffuse off from the solid surface.

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