MECHANISM AND KINETICS OF GRAFTING OF POLYPROPYLENE BY WATER-SOLUBLE MONOMERS IN EMULSION

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Received November 13th, 1985

Oxidized isotactic polypropylene powder was grafted at 30°C in aqueous emulsions with water-soluble monomers such as acrylic acid and acrylamide. The decomposition of the polypropylene —O—O— groups, initiating the graft polymerization, proceeds due mainly to the effect of the activator used, *viz.* a chelate of iron(II), and is favoured by the monomer and the necessarily present water-insoluble liquid phase. The grafting reaction order with respect to the concentration of the water-soluble monomer is 2 and higher. A mechanism and kinetics are suggested for the polypropylene grafting by these water-soluble monomers, involving the concept of presence of long-living radicals bonded to the solid polypropylene phase.

Previously[1] we described the synthesis of isotactic polypropylene powder grafted by water-soluble monomers (acrylic acid and acrylamide) in aqueous emulsions at 30°C. More recently[2] we examined the effects of the various components of the polymerization system (monomer, iron chelate, emulsifier, and organic liquid phase) on the formation of some of the emerging types of polymer in the system (graft polymer or homopolymer). In the present work, attention is paid to the —O—O— groups of the oxidized polypropylene as the initiator of the grafting by water-soluble monomers. In the kinetic study, some previously established facts associated with the polymerization mechanism in this system are discussed.

EXPERIMENTAL

Chemicals

Isotactic polypropylene powder and Mersol H anionic emulsifier were as described[3]. Iron(II) sulphate heptahydrate and chelating agents, *viz.* disodium ethylenediaminetetraacetic acid and 1,8-diamino-3,6-diazaoctane, were of reagent grade purity. The monomers, *viz.* acrylic acid, acrylamide, styrene, 2-hydroxyethyl methacrylate, propyl methacrylate, ethyl acrylate, and butyl acrylate were purified by double vacuum distillation or recrystallization. Propionamide, propionic acid, solvents, and nitrogen were of reagent grade purity.

Procedures

Isotactic polypropylene powder was fluid oxidized at room temperature with oxygen containing

ozone (12 mg l^{-1}). The polymer samples used contained hydroperoxidic oxygen[3] in amounts of 0·7 or 15 mmol kg^{-1}.

The polymerization was performed at 30°C under nitrogen in rotating glass ampoules[4]. The solid polypropylene phase containing also the grafted polymer was collected on a glass filter, where it was purified and dried[2]. The compositions of the polymerization systems are given in Table I. The concentrations of the water-soluble components of the liquid phase are related to the aqueous emulsion volume (mol l^{-1}), those of the water-insoluble liquid phase are related to the total liquid phase volume (%). The concentration of chelate is identified with that of Fe^{2+}; the chelates were $FeSO_4$–disodium ethylenediaminetetraacetic acid (1 : 1 molar ratio) and $FeSO_4$–1,8-diamino-3,6-diazaoctane (2 : 3 molar ratio). The result of the polypropylene grafting, determined gravimetrically as the sample weight increment, was expressed in per cent values with respect to the initial monomer bonded to the solid polypropylene phase or, for the kinetic measurements, in mol l^{-1} with respect to the emulsion volume. The formation of the homopolymer could be disregarded[2].

The hydroperoxide content of the polypropylene was determined iodometrically with KI at 20°C in glacial acetic acid. In this manner, the residual hydroperoxide was also determined in the polypropylene samples after the graft polymerization, which had been freed from the components of the polymerization system, particularly iron[5].

RESULTS AND DISCUSSION

Attempts to analyze the differently reactive —O—O— groups in the oxidized polypropylene grafted by the polar monomer (hydroperoxide, determinable at 20°C with KI in glacial acetic acid[2,6,7], or peroxide determined with KI in chloroacetic acids at 40° after removing the hydroperoxide from the polymer[5]) were not altogether successful because the grafts interfered with the peroxide determination. Nevertheless, we were able to assess the type of the —O—O— groups from which the grafting-initiating radicals arise. We employed the method[5] based on a comparison of the results of polymerization obtained with the oxidized polypropylene and with

TABLE I

Composition of the polymerization systems with Mersol H as emulsifier and $FeSO_4$–disodium ethylenediaminetetraacetic acid as chelate, $t = 30°C$

System	HOO- group content of polypropylene		Emulsion volume	Concentration of emulsifier	Concentration of chelate	Monomer	$[M]_0$	Water-insoluble solvent
No	g	mmol . . kg^{-1}	ml	mmol l^{-1}	mmol l^{-1}		mol l^{-1}	(%(V/V))
1	0·6	15	10	8·4	3·8	acrylamide	0·7	ethyl acetate (60)
2	0·6	15	10	8·4	3·8	acrylic acid	0·7	benzene (35)
3	1·0	0·7	6	4·8	1·3	acrylamide	2·36—4·52	ethyl acetate (30)
4	1·0	0·7	11	10·6	1·8	acrylic acid	1·27—3·36	hexane (50)

the same polypropylene previously iodometrically freed from hydroperoxide. The results, for the water-soluble monomers, acrylates and methacrylates, and styrene are given in Table II.

Grafting of polypropylene by acrylic acid or acrylamide in the presence of $FeSO_4$ or $FeSO_4$–disodium ethylenediaminetetraacetic acid as the activator of initiator is initiated by the hydroperoxidic groups of the polypropylene (henceforth referred to simply as hydroperoxide); in their absence this process virtually does not occur. The negative effect of removal of hydroperoxide from polypropylene on the conversion is less pronounced if less polar monomers such as acrylates and methacrylates or styrene are used. This indicates that the structure of the monomer affects the decomposing ability of the chelate also with respect to the decomposition of the peroxidic groups of the polypropylene (henceforth referred to as peroxide) associated with the formation of radicals which initiate the grafting reaction.

On the other hand, if the polymerization is conducted in alkaline medium in the presence of $FeSO_4$–1,8-diamino-3,6-diazaoctane as the activator of initiator, the removal of hydroperoxide from the polypropylene prior to its use in the polymerization system has a positive effect on the bonded polymer yield (except for the water-soluble monomer). This effect is particularly marked with the low-polar styrene, in agreement with our previous observations[8]. In this case the initiator of the polypropylene grafting reaction is obviously peroxide. However, from the decrease in the percent of the bonded acrylamide brought about by removal of hydroperoxide from the polypropylene it can be inferred that hydroperoxide also contributes to the initiation, which for strongly polar monomers in combination with the $FeSO_4$–1,8-dia-

TABLE II

Amounts of monomer bonded to polypropylene (%) in 20 min of reaction. Symbols: A oxidized polypropylene, B oxidized polypropylene after reduction, EDT disodium ethylenediaminetetraacetic acid, DAO 1,8-diamino-3,6-diazaoctane

System No[a]	Monomer	$FeSO_4$		$FeSO_4$–EDT		$FeSO_4$–DAO	
		A	B	A	B	A	B
1	acrylamide	1·7	0·1	26·7	0·2	28·3	20·9
2	acrylic acid	5·0	0·0	23·0	0·1	—	—
1[b]	methyl methacrylate	—	—	14·3	9·5	37·8	39·7
1[b]	propyl methacrylate	—	—	4·4	1·7	41·6	44·1
1[b]	ethyl acrylate	—	—	42·7	9·2	85·5	88·0
1[b]	butyl acrylate	—	—	20·3	8·8	78·3	83·2
1[b]	styrene	—	—	0·8	0·4	23·3	34·3

[a] Conforming to Table I; [b] the water-soluble monomer was replaced with another, ethyl acetate was omitted and the volume was brought to 10 ml with water.

mino-3,6-diazaoctane activator has been suggested previously for theoretical reasons[2].

The participation of the water-soluble monomer in the decomposition of the

TABLE III

Effect of components of the polymerization system on the decomposition of hydroperoxidic groups in polypropylene and on the grafting of polypropylene by water-soluble monomers in 20 min. System numbering conforms to Table I, activator: $FeSO_4$–disodium ethylenediaminetetraacetic acid; H_d decomposed hydroperoxide, M_b bonded monomer

System No[a]	Monomer	Solvent	$[H_d]$ %	$[M_b]$ %
1	acrylamide	—	17·8	0
1	acrylamide	ethyl acetate	40·6	26·7
2	acrylamide	butyl alcohol	33·9	16·8
1	acrylamide	benzene	29·3	10·5
1[b]	acrylamide	ethyl acetate	1·8	0·1
1[c]	acrylamide	ethyl acetate	14·1	1·7
1[d]	acrylamide	ethyl acetate	2·4	0·1
1[e]	acrylamide	ethyl acetate	50·2	28·3
1[f]	acrylamide	ethyl acetate	15·4	0·1
1	propionamide	ethyl acetate	17·4	0
1	—	ethyl acetate	10·7	0
2	acrylic acid	—	0	0
2	acrylic acid	benzene	29·8	23·0
2	acrylic acid	hexane	36·9	30·8
2	acrylic acid	ethyl acetate	3·0	1·7
2[b]	acrylic acid	benzene	0	0
2[c]	acrylic acid	benzene	12·8	5·0
2[d]	acrylic acid	benzene	1·6	2·2
2[f]	acrylic acid	benzene	4·7	0
2	propionic acid	benzene	20·6	0
2	—	benzene	13·3	0
2	2-hydroxyethyl methacrylate	benzene	43·0	99·9
2[e]	2-hydroxyethyl methacrylate	benzene	60·0	98·3
2	2-hydroxyethyl methacrylate	ethyl acetate	29·3	68·4
2[e]	2-hydroxyethyl methacrylate	ethyl acetate	44·3	53·7

[a] For systems 1 and 2, 60 and 35% (*V*/*V*) solvents, respectively; [b] free from chelate; [c] $FeSO_4$ free from chelating agent; [d] disodium ethylenediaminetetraacetic acid free from $FeSO_4$; [e] $FeSO_4$–1,8-diamino-3,6-diazaoctane chelate; [f] free from emulsifier.

hydroperoxide was examined by determining the residual hydroperoxide content of sample after the polymerization (Table III). Here, acrylamide appears to be more active than acrylic acid (samples without solvent). The general reactivity of the two monomers is commensurable; they differ particularly in their polarity and in the pH of the emulsion in their presence. The pH of the liquid phase was deliberately left unadjusted to allow the effect of the nature of the monomer used to manifest itself. If the conversions of the bonded monomer are also taken into account, the significance of the various components of the polymerization system in the grafting process can be assessed. In this manner it is possible to account, from the point of view of formation of active centres for grafting, not only for the necessity of presence of the water-soluble liquid phase in the system, but also for the previously established[1] particular suitability of use of polar substances for the grafting by acrylamide (sample with ethyl acetate in system No 1) and of nonpolar substances for acrylic acid (sample with benzene and hexane in system No 2) or 2-hydroxyethyl methacrylate. We chose short reaction times for the grafting (Tables II and III) because, as found previously[1], the change in the polypropylene surface polarity brought about by the bonding of the polar grafts does not affect, up to a certain degree of conversion, the time dependence.

Table III shows that some percents of decomposed hydroperoxide, for samples that were in contact with extracting solvents, are nearly zero. This indicates that the possibility of extraction of polypropylene hydroperoxide with solvents[6] is minimal in the conditions of this polymerization.

It has been found for the polymerization of the sparingly water-soluble acrylonitrile[2] that the concentration of the dissolved fraction has a considerable effect on the grafting rate. For the grafting of the relatively stable polypropylene by water-soluble monomers such as acrylic acid or acrylamide, this fact was found true over wider concentration regions of the monomers (Figs 1 and 2). The shapes of the time dependences of polypropylene grafting by the both monomers are different, as has been reported[1]. This concerns particularly the autocatalytic nature of the acrylamide bonding. While for acrylic acid the conversion curves are nonlinear in the starting region only (Fig. 1), for acrylamide the nonlinearity is characteristic over the whole concentration and time regions (Fig. 2). The time course of hydroperoxide decomposition during the polymerization was also followed (Fig. 3). This decomposition during the polypropylene grafting by acrylic acid virtually ceases in approximately 50 min, similarly as in the case of styrene[9]; in the presence of acrylamide, on the other hand, the decomposition takes place throughout the entire process. This can account for the shape of the conversion curves for the grafting of the relatively stable polypropylene (Fig. 2) if the concept based on the presence of long-living radicals[9] is adopted for this system as well: here the major effect arises from the concentration of macroradicals increasing due to the proceeding decomposition of the initiator, the termination reactions being substantially limited.

The grafting reaction order with respect to the concentration of acrylic acid, calculated from the logarithmic dependence of the grafting rate on the monomer concentration, was 2·01 ± 0·08. This bears out the assumption of restriction of termination reactions, although other reasons for the increased exponent of the monomer concentration are also feasible[10]. The monomer-solvent combinations were chosen such that no induced decomposition of hydroperoxide took place (Table III). With regard to this fact and to the dependences shown in Figs 1 and 2, a kinetic scheme could be set up for the grafting of polypropylene by water-soluble monomers, taking into account the polymerization initiation mechanism suggested previously[2]. The concentration of initiator (hydroperoxide) in time t, $[I]_t$, can be expressed basically *via* the equation for monomolecular decomposition. There are only two differences: (*i*) in addition to the initial concentration of initiator, $[I]_0$, its "stationary" concentration $[I]_s$, *i.e.*, the limiting concentration approached by the initiator during the decomposition, must also be included, and (*ii*) the instantaneous concentration of initiator, $[I]_t$, is a function not only of time but also of the initial concentrations of monomer, $[M]_0$, and activator, $[A]_0$. Thus,

$$[I]_t = ([I]_0 - [I]_s) \exp(-k[M]_0 [A]_0 t) + [I]_s . \qquad (1)$$

If the initiation efficiency is ignored, and the limited termination is taken into account,

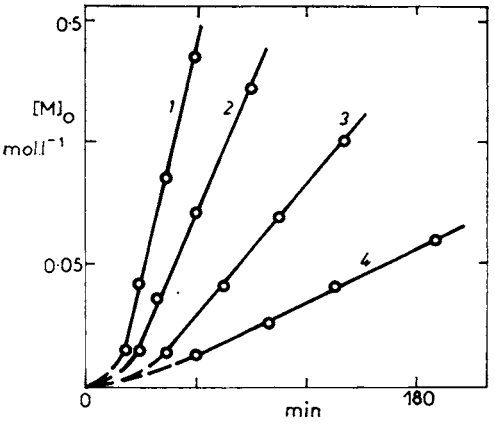

FIG. 1

Time course of grafting of polypropylene by acrylic acid in system No 4 (Table I). M_b bonded monomer (in mol l^{-1}, y - axis). $[M]_0$ (mol l^{-1}): *1* 3·36, *2* 2·42, *3* 1·75, *4* 1·27 (instead 0·5 read 0·15 on y - axis)

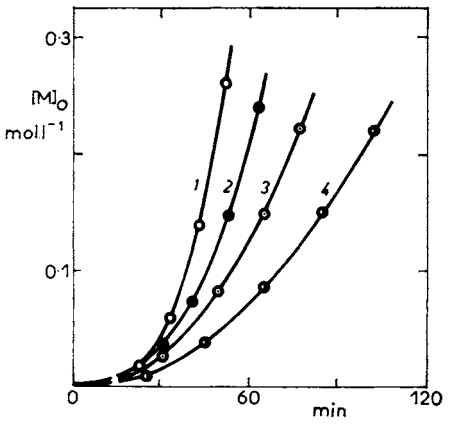

FIG. 2

Time course of grafting of polypropylene by acrylamide in system No 3 (Table I). M_b bonded monomer (in mol l^{-1}, y - axis). $[M]_0$ (mol l^{-1}): *1* 4·52, *2* 3·54, *3* 2·91, *4* 2·36

the difference between the initial initiator concentration and that in time t can be identified with the concentration of radicals in time t, $[P^\bullet]_t$:

$$[I]_0 - [I]_t = \Delta[I]\{1 - \exp(-k[M]_0[A]_0 t)\} = [P^\bullet]_t , \qquad (2)$$

where $\Delta[I] = [I]_0 - [I]_s$.

The polymerization rate in the range of exponential shape of the conversion curve is a function of the instantaneous concentration of macroradicals; hence,

$$v_p = k_p[M]_0[P^\bullet]_t = k_p[M]_0 \Delta[I]\{1 - \exp(-k[M]_0[A]_0 t)\} . \qquad (3)$$

If the exponential term in this equation is expanded into the corresponding series and only the first two terms of this expansion are regarded (which is reasonable), we obtain

$$v_p = kk_p \Delta[I][A]_0 t[M]_0^2 . \qquad (4)$$

At t = const and if $\Delta[I]$ is independent of the concentration of monomer ($[A]_0$ is high and virtually invariable), the grafting rate depends on the concentration of monomer as

$$v_p = k'[M]_0^2 . \qquad (5)$$

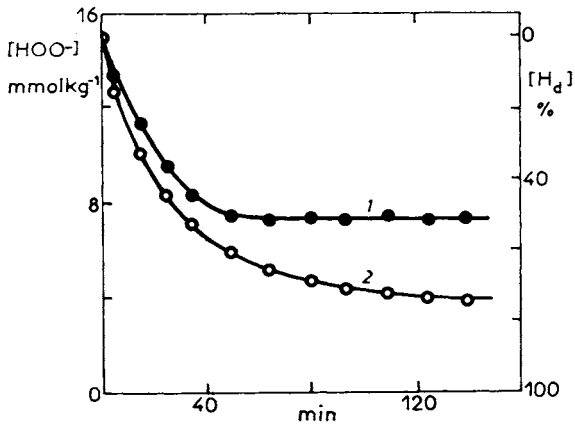

FIG. 3

Course of decomposition of hydroperoxidic groups in polypropylene; H_d decomposed hydroperoxide. *1* acrylic acid, system No 2 (Table I), *2* acrylamide, system No 1

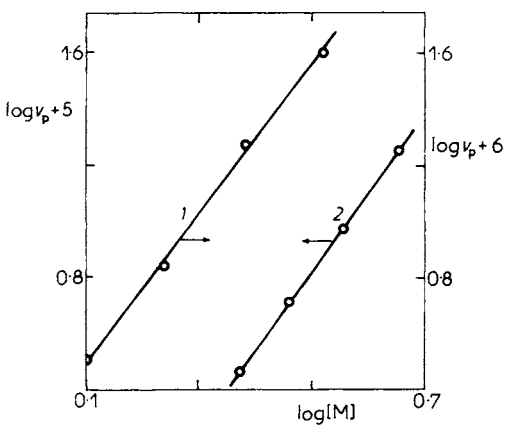

FIG. 4

Dependence of polypropylene grafting rate on the concentration of monomer, evaluated based on Figs 1 and 2. *1* acrylic acid, time 1 350 s, *2* acrylamide, time 2 700 s

It follows from Eqs (*4*) and (*5*) that if the polymerization rate in a constant time is calculated for the polypropylene grafting by acrylamide (by the empirical formula $v_p = a\xi/t$, where ξ is the degree of conversion and a is a factor which is obtained as the slope of the plot of $\ln \xi$ *vs* $\ln t$), the reaction order of the value of 2 with respect to the monomer should be confirmed. Fig. 4, however, indicates a reaction order higher than two, *viz.* 2·9 at $t = 2\,700$ s. This may be due to the fact that $\Delta[I]$, the difference between the initial and stationary concentrations of initiator, is a function of the concentration of monomer rather than a constant as assumed in Eqs (*4*) and (*5*). This is indicated by the experimental results (Table III) which give evidence that the monomer participates in the initiation reaction. This applies not only to the grafting of polypropylene by acrylamide, but also to the starting, nonstationary region for acrylic acid, where the reaction order at 1 350 s was 2·7 (Fig. 4). The grafting reaction rate with respect to the concentration of monomer can be assumed to depend not only on the kind of monomer used but also, to an extent, on the solvent which can affect considerably the physico-chemical parameters of the reactions involved.

The experimental and calculated data are consistent with the hypothesis of the presence of long-living radicals also during the grafting of polypropylene by water-soluble monomers. This is also borne out by the fact that the polymerization of the water-soluble monomer only ceases if there is lack of the monomer for polymerization, if conditions are established for the system to be able to cope with the gradual change in the polarity of the polypropylene surface during the grafting[1].

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Translated by P. Adámek.