

# Accumulation and Desorption of Free Radicals in Emulsion Copolymerization

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## Synopsis

The emulsion copolymerization of styrene with acrylonitrile, seeded on a polybutadiene support and initiated either with potassium persulfate or  $\gamma$ -rays has been studied. The original technique of support activation consists of two steps: the start of the copolymerization in the presence of a small fraction of monomers, followed by the addition of the rest of monomers, which leads to a great increase in the reaction rate. The experimental data provide evidence for a new mechanism that takes into account the desorption—reentry of the free oligoradicals into another particle, their transfer to the polybutadiene support, which results in the accumulation of trapped free radicals. As a consequence of free radicals' accumulation, the overall copolymerization rate increases. The accumulation as well as the desorption processes place this type of copolymerization far from Smith-Ewart theory case II.

## INTRODUCTION

In the field of emulsion polymerization, special interest has been focused on the problems of both the adsorption of free radicals formed in aqueous phase and the desorption of oligoradicals from the polymer particles, which determine the average number of free radicals ( $\bar{n}$ ) existing in a monomer-swollen polymer particle.<sup>1,2</sup> The complexity of these processes is peculiar to the heterogeneous media: each step of the molecular chain formation occurs in a different phase of the reaction system.<sup>3</sup>

The use of seeded emulsion (co)polymerization simplified the study of this question.<sup>4</sup> Thus, the particle number ( $N_t$ ), the surface ( $S$ ), and the degree of coverage with emulsifier are known, making it easier to interpret kinetically the experimental data. The value of  $\bar{n}$  can be easily derived from experiment.<sup>5</sup>

As regards the seeded emulsion (co)polymerization, numerous cases of deviation from Smith-Ewart theory stating  $\bar{n} = 0.5$  (case II) have been reported. Such deviations are discussed in terms of free radical desorption<sup>5</sup> and modifications in the capture efficiency of free radicals formed in the aqueous phase.<sup>6</sup>

A previous article on seeded emulsion copolymerization<sup>7</sup> pointed out the possibility of increasing the reaction rate by performing the copolymerization in two steps: during the first step (activation), a small fraction (5–10%) of the amount of vinylic monomers is added together with the initiator; in the second step, the remaining quantity of monomers is added. During the activation step, the free radicals are trapped in the support which contributes significantly to the increase in the copolymerization rate noted in the second step.

TABLE I  
 Recipes for the Seeded Emulsion Copolymerization of St with AN  
 (Parts by Weight - g). All Recipes Include 70 Parts  
 by Weight Water

Ingredients	Recipe							
	1	2	3	4	5	6	7	8
	Activation							
Polybutadiene	—	4	4	4	8	8	—	5.9
Styrene	—	1.3	—	1	1.1	1.1	—	0.8
Acrylonitrile	—	0.55	—	0.44	0.5	0.5	—	0.38
Initiation	—	KP <sup>a</sup>	$\gamma$ -rays	$\gamma$ -rays	$\gamma$ -rays	$\gamma$ -rays	—	KP <sup>b</sup>
	Copolymerization							
Polybutadiene	4	—	—	—	—	—	5.9	—
Styrene	18.4	18.4	18.4	18.4	15.8	15.8	16.5	16.5
Acrylonitrile	7.9	7.9	7.9	7.9	6.8	6.8	7.1	7.1
T-dodecyl mercapthane	0.11	0.11	0.11	0.11	0.09	—	0.1	0.1
Initiation	KP <sup>a</sup>	—	Posteffect	Posteffect	Posteffect	Posteffect	KP <sup>b</sup>	—

<sup>a</sup>0.07 parts by weight - g.

<sup>b</sup>Variable concentration.

This article deals with an explanation of the activation mechanism which takes into account the free radicals' accumulation into the polymer particle and the processes of free radicals' desorption from particle. These aspects are studied for the case of styrene (St) with acrylonitrile (AN) emulsion copolymerization seeded on a polybutadiene support (PB). To distinguish the two types of copolymerization, the one where initiation occurs in the presence of the whole quantity of monomer is referred to as copolymerization with initiation in aqueous phase; the other one, performed in two steps, is called copolymerization on an activated support. It is noteworthy that, from the point of view of the initiation, neither of these is a pure case, for in each both types of initiation are present to a certain extent.

## EXPERIMENTAL

The copolymerization reactions have been carried out in a reactor equipped with stirrer, reflux condenser, inlet system for the reactants and for the inert gas, as well as with a sampling system. The monomers were freshly distilled and the initiation has been performed with recrystallized potassium persulfate (KP) or  $\gamma$ -rays from a Co<sup>60</sup> source, of an initial activity of 500 Ci (dose rate  $2.7 \times 10^5$  rad/h). The chain transfer agent was tertiary dodecyl mercapthane (tDM).

The seeding support was a PB latex, the particle size of which being  $\bar{d}_1 = 110$  nm. The copolymerization recipes are listed in Table I.

As regards the copolymerization on a  $\gamma$ -ray-activated support, the conversion was determined after the Co<sup>60</sup> source had been removed (posteffect experiment).

The copolymerization has been performed at 70°C and the conversion was gravimetrically measured.

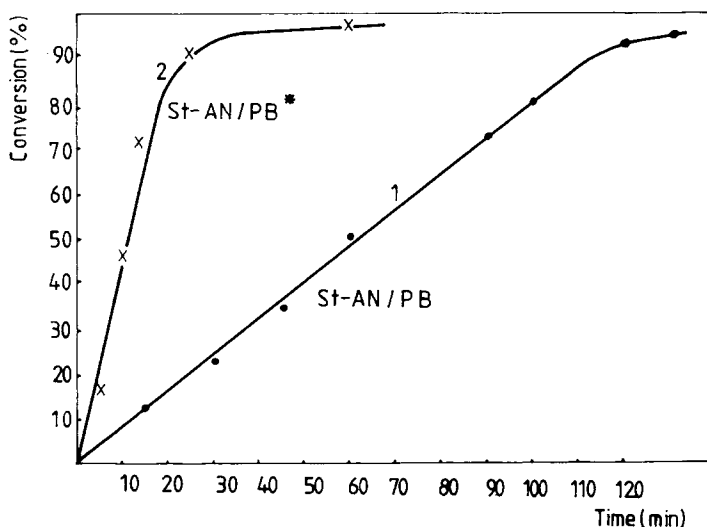


Fig. 1. Seeded emulsion copolymerization of St with AN on a nonactivated PB support (recipe 1, curve 1) and on an activated PB support during 60 min (recipe 2, curve 2).

## RESULTS AND DISCUSSION

The seeded emulsion copolymerization on an activated support, carried out under different experimental conditions, provides the opportunity of accounting for various aspects of the reaction mechanism. The resulting information allows for the derivation of a quantitative equation for both the aqueous-phase initiation copolymerization and the copolymerization on an activated support.

The St-AN copolymerization has been carried out at an azeotropic composition in monomer-swollen polymer particles ( $r_{st} = 0.41$ ,  $r_{an} = 0.038$ ). Since the PB support was used before, the general features of such a reaction were already known.<sup>4,8-12</sup> As has been mentioned, there are some peculiar aspects which distinguish this type of copolymerization from similar ones. At a small concentration of vinyl comonomers and of KP,<sup>7</sup> trapped free radicals are fixed in the tridimensional structure of PB, which, together with those radicals generated continuously in aqueous phase, lead to an increased copolymerization rate over that observed in the absence of activation.

Figure 1 shows the conversion versus time curves for the activated copolymerization (curve 2) and for the common, aqueous phase-initiated copolymerization (curve 1).

In both cases the shape of the curve is characteristic of the seeded emulsion polymerization: the copolymerization rate ( $R_p$ ) reaches its highest value from the very start of the reaction and, up to conversion of more than 80%,  $R_p = ct$ .

If Eq. (1):

$$R_p = k_p M_p \bar{n} N_t \quad (1)$$

(where  $k_p$  is the propagation constant and  $M_p$  is the monomer concentration in the particle) is analyzed from the standpoint of the kinetic model put forward by Nomura et al.,<sup>5</sup> it becomes obvious that, at a constant reaction temperature,  $k_p$  and  $M_p$  remain constant. At an emulsifier concentration

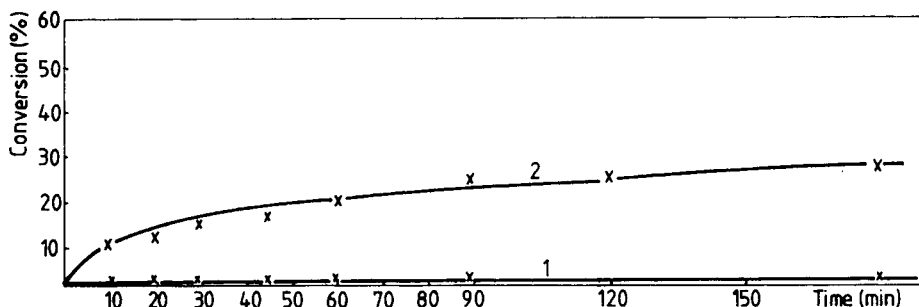


Fig. 2. Posteffect copolymerization of St with AN on an irradiated PB support (recipe 3, curve 1) and on a comonomer-activated support (recipe 4, curve 2).

small enough and a support surface large enough,<sup>8</sup>  $N_i$  remains practically unchanged. Since  $N_i$  and  $S$  are practically invariable, and in aqueous phase, important changes in the monomer and initiator concentrations do not occur, the increase in the copolymerization rate is due to changes in  $\bar{n}$  as a result of an accumulation process related to the trapping.

This conclusion was supported by an attempt to activate the PB support with KP only, with KP and AN,<sup>7</sup> or with  $\gamma$  irradiation (Fig. 2, curve 1). In all those cases the radical species came from the aqueous phase. In none of them did the activation of the support succeed, the necessity of the presence of vinylic monomers showing affinity for PB (Fig. 2, curve 2) being thus proved.

The oligoradicals formed in aqueous phase enter through adsorption into the particles where, in the conditions of a small monomer concentration, the probability of chain transfer to PB is higher. Once the activation is complete, the irradiation is stopped and the contact with the remaining monomers results in a significant copolymerization rate, even though free radicals are no longer being generated in the aqueous phase (Fig. 2, curve 2).

The idea of activation as a consequence of trapped free radicals' accumulation is supported by the fact that it requires some time to become manifest (Fig. 3). After the consumption of the monomers added for activation, an

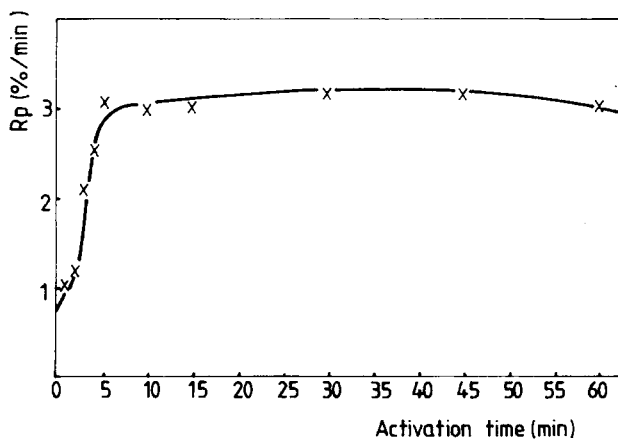
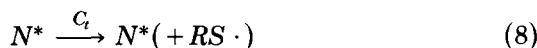


Fig. 3. The influence of the activation time (recipe 2) on the reaction rate during the copolymerization step.

increase in the period of contact with residual KP in the activation step has no effect on the copolymerization rate in the second step.

The transfer to the seeded support is favored not only by a low monomer concentration in the particle, but also by the PB structure. If PB is substituted by a St-AN copolymer, a decrease in the copolymerization rate during the activation experiments is noted.<sup>7</sup>

Experimental conditions discarding any possibility of new particle formation<sup>4</sup> have been chosen to enable the study of the free radical desorption and accumulation. A kinetic scheme accounting for the steps of the seeded emulsion copolymerization (azeotropic composition),<sup>8</sup> as can be deduced from the experimental data, is shown below:



where:  $A$  is the rate constant of the oligoradicals' adsorption from the aqueous phase,  $D$  is the desorption coefficient having here the signification of the rate constant for the oligoradicals' desorption from the polymer particle,  $R_{\dot{i}}$  the oligoradical concentration in aqueous phase,  $C_s$  the rate constant of the chain transfer to the PB support (free radical accumulation),  $C_t$  the rate constant of the chain transfer to *t*-dodecyl mercapthane (tDM),  $N_o$  the number of particles without a free radical,  $N^*$  the number of particles with untrapped free radical,  $N^{\odot}$  the number of particles with trapped free radicals.  $RS\cdot$  stands for the free radical obtained by chain transfer to tDM.

Figure 4 shows the conversion as a function of time at the seeded copolymerization of St with AN after the  $Co^{60}$  source, used to activate the PB seeding support, has been removed. In the absence of KP and of the  $Co^{60}$  source, the free radicals are no longer generated in aqueous phase and the possible desorption of free radicals accumulated into the support during the activation step, can thus be studied.

In the absence of tDM, the posteffect copolymerization proceeds at a high and constant rate (0.65%/min) up to a conversion of about 60%. This conversion limit appears as a consequence of the disappearance of monomer droplets.<sup>13</sup> Beyond this limit, the  $M_p$  of the whole particle starts decreasing. The copolymerization rate also drops. Comparatively, it should be noted, that

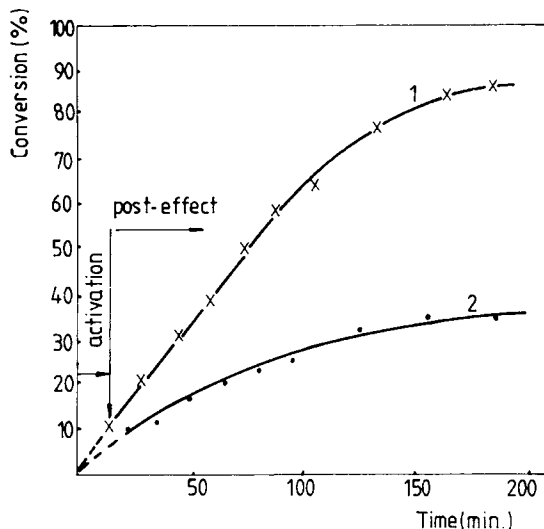


Fig. 4. Posteffect copolymerization of St with AN in the absence of tDM (recipe 5, curve 1) and in the presence of tDM (recipe 6, curve 2).

in the case of the copolymerization with continuous generation of free radicals in the aqueous phase, the rate is constant up to conversions exceeding 80% (Fig. 1). In the latter case, the copolymerization rate keeps constant even after the monomer droplets disappear, for the reaction goes on in a peripheral region of the particle (shell), where  $M = ct$ .

In the presence of tDM, the reaction rate is not constant (see Fig. 4, curve 2) due to the continuous decrease of  $\bar{n}$  as a result of the chain transfer to tDM, followed by desorption. In this case the copolymerization rate remains within the domain corresponding to  $\bar{n} < 0.5$ . The disappearance of trapped free radicals cannot be attributed to the mutual termination of two free radicals coexisting in a particle. The termination takes place after the desorption of free radicals resulted by reinitiation with  $RS\cdot$  (6) and readsorption in  $N^*$  (5). In this way,  $N^*$  decreases, bringing about a decrease of  $\bar{n}$  and, subsequently, of the copolymerization rate (1). Under such circumstances, the copolymerization is of a nonsteady type:  $(dN^*/dt) \neq 0$  and  $(dR_w/dt) \neq 0$ .

The chain transfer to the monomer seems to be nonexistent because, in the absence of tDM, a decrease in  $N^*$  was not noted.

The formation of trapped free radicals in the PB structure during the copolymerization of a small quantity of comonomers is a result of a complex process involving the adsorption of oligoradicals formed in the bulk of the solution, chain transfer, desorption, and readsorption into another particle. This is why the concentration of the oligoradicals formed in aqueous phase (related to the KP concentration) is expected to have a significant effect on the above-mentioned processes. Figure 5 shows the curves of conversion versus time for the St-An copolymerization in the presence of a nonactivated PB support, at initial KP concentrations ranging from  $1.75 \cdot 10^{-3}$  mol/L to  $5.828 \cdot 10^{-3}$  mol/L. The reaction rates increase with the increasing KP concentration.

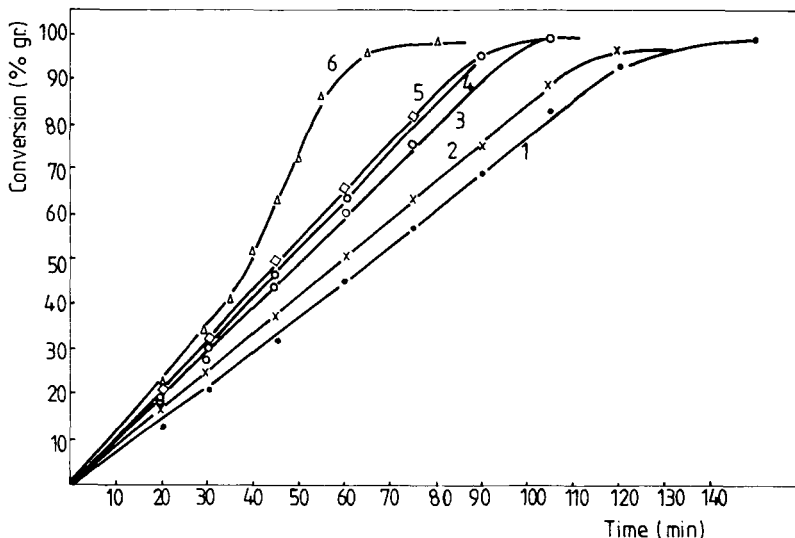


Fig. 5. Seeded emulsion copolymerization of St with An on a nonactivated PB support (recipe 7), at different KP concentrations (mol/L)  $\times 10^3$ : 1-1.75; 2-2.33; 3-3.5; 4-4.08; 5-4.66; 6-5.828.

At every single KP concentration (except the maximum one, Fig. 5, curve 6) the specific trend of seeded emulsion copolymerization is observed, namely the initial rate is the highest and keeps constant for conversions up to 80%. This remark justifies the use of the steady-state conditions for the kinetic analysis:

$$\frac{dN^*}{dt} = AR_w N_o - AR_w N^* - DN^* = 0 \quad (10)$$

$$\frac{dR_w}{dt} = k_i I + DN^* - AR_w N_t = 0 \quad (11)$$

where  $k_i$  is the rate constant of the initiation ( $4 \cdot 10^{-5}$  L/mol.s),  $I$  the KP concentration, and  $N_t = N_o + N^*$  stands for the overall number of particles.

An equation, which is second order in ( $N^*$ ), can be derived from Eqs. (10) and (11):

$$2D(N^*)^2 + 2k_i I(N^*) - k_i I N_t = 0 \quad (12)$$

leading to case II of the Smith-Ewart theory ( $\bar{n} = 0.5$ ) if the desorption coefficient is zero 5.

By means of Eq. (12), Eq. (1) becomes Eq. (13) for  $\bar{n} = N^*/N_t$ :

$$R_p = k_p M_p \left[ -B + \sqrt{B^2 + BN_t/N_A} \right] \quad (13)$$

where  $N_A$  stands for Avogadro's constant and  $B$  is a parameter which includes the desorption coefficient:

$$B = \frac{k_i I}{2D} \quad (14)$$

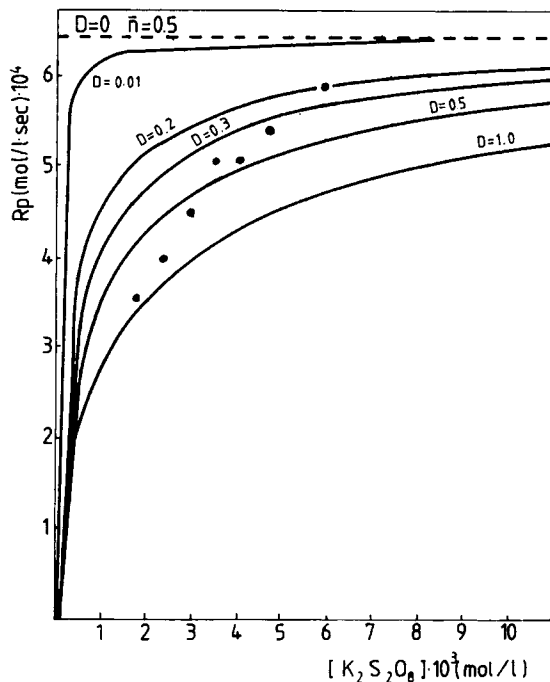


Fig. 6. The dependence of the copolymerization rate on the KP concentration, calculated with Eq. (13) for different desorption coefficients (—). The experimental points (●) represent the  $R_p$  values for the curves in Figure 5.

Relation (13) links together the copolymerization rate of an azeotropic mixture ( $M_p = 6.4$  mol/L and  $k_p = 875$  L/mol.s) to the KP concentration and desorption coefficient.

Figure 6 shows the copolymerization rate calculated from the curves in Figure 5, as a function of the initial KP concentration. It can be seen that the  $R_p$  is strongly dependent on the initiator concentration ( $I$ ), but the curves calculated for different values of the desorption coefficient ( $D$ ), according to Eq. (13), do not follow the experimental points. At small KP concentrations the experimental points are fitted by curves calculated for high desorption coefficient, while at high KP concentrations, the experimental points are fitted by curves calculated for small desorption coefficient. It is as if the desorption decreases with an increase in frequency of entries into the particle of the oligoradicals formed in aqueous phase. The decreased desorption could be due to the accumulation of the trapped free radicals in the PB structure, which, at a high KP concentration, can lead even to an autoacceleration process (curve 6, Fig. 5).

As the trapped free radicals accumulate, a number of particles containing a free radical ( $N^{\circ}$ ) became transformed into particles containing a trapped free radical ( $N^{\circ}$ ). If the steady-state condition is applied:

$$\frac{dN^{\circ}}{dt} = C_s N^* - C_t N^{\circ} = 0 \quad (15)$$



and the increased probability of chain transfer to the support, due to the higher frequency of entry of free oligoradicals into the particle (related to the high KP concentration in aqueous phase) is taken into account, the number of particles with a trapped free radical ( $N^{\circ}$ ) can be defined:

$$N^{\circ} = C_1 I N^* \quad (16)$$

where  $C_1$  is a constant characteristic to the process of trapped free radical accumulation in a PB support and expresses the probability ratios of the chain transfer to the support and to tDM, respectively.

For  $N_t = N_o + N^* + N^{\circ} = N_o + N^*(1 + C_1 I)$  Eq. (13) changes into an equation considering the desorption and the accumulation of free radicals as well:

$$R_p = k_p M_p (1 + C_1 I) \left[ -B + \sqrt{B^2 + \frac{2BN_t}{(C_1 I + 2)N_A}} \right] \quad (17)$$

Equation (17) shows that for  $D = 0$  and  $C_1 = 0$ , i.e., the desorption and accumulation processes are ignored, case II of Smith-Ewart theory applies.

Figure 7 shows the calculated curves of the  $R_p$  dependence on the KP concentration according to Eq. (17). The experimental points are fitted by the curve corresponding to a desorption coefficient  $D = 1.19$  and an accumulation coefficient  $C_1 = 110$ , that have to be regarded as specific constant for the St-AN copolymerization on a nonactivated PB support.

As has been seen, if the desorption and accumulation processes are given a quantitative significance in seeded emulsion copolymerization on an unactivated PB support, it is possible to account for the experimental data. Consid-

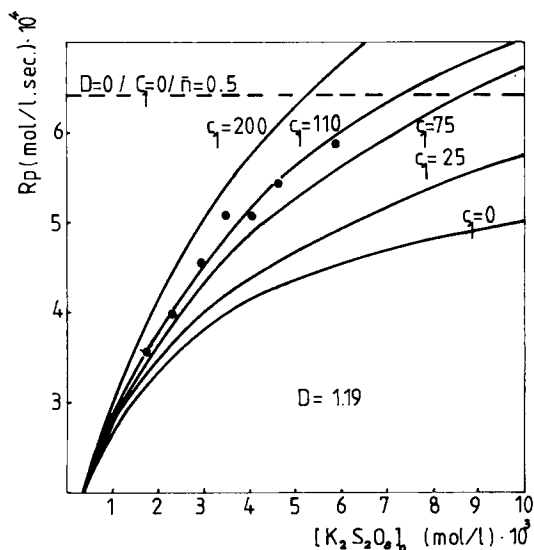


Fig. 7. The dependence of the calculated copolymerization rate on the KP concentration (—) according to Eq. (17), for a desorption coefficient of  $D = 1.19$  and different accumulation coefficients  $C_1$ . (●) Experimental points.

ering an activated support, the desorption and accumulation phenomena take on other dimensions.

The activation takes place in the conditions of specific ratios of aqueous-phase/monomers and monomers/support. During the activation step, characterized by a desorption coefficient  $D_a$ , a strong accumulation (of  $C_2$  coefficient) of trapped free radicals occurs due to the increased probability of chain transfer to the support, which is detrimental to propagation. The activation of the PB support results in the formation of a number of particles containing trapped free radicals ( $N_a^\circ$ ).

The derivation of  $N_a^\circ$  is shown above and depends on the KP concentration used in the activation step:

$$N_a^\circ = C_2 I \left[ -B_a + \sqrt{B_a^2 + \frac{2B_a N_t}{(C_2 I + 2)N_A}} \right] \quad (18)$$

where  $B_a$  is a parameter related to the adsorption-desorption processes of the activation step:

$$B_a = \frac{k_i I}{2D_a} \quad (19)$$

For the seeded emulsion copolymerization of St-AN on an activated support (step 2), the dependence of the conversion versus time curves on the KP concentration found experimentally are shown in Figure 8. Again, it is to be noted that the higher rates were obtained for the activated support at the same KP concentration. The copolymerization rate also increases with the increasing KP concentration.

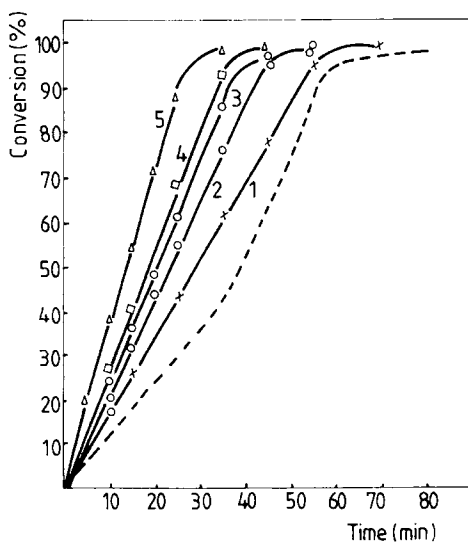


Fig. 8. Emulsion copolymerization of St with AN seeded on an activated PB support (recipe 8) at different KP concentrations (mol/L)  $\times 10^3$ : 1-2.33; 2-3.5; 3-4.08; 4-4.66; 5-5.828. The dotted curve stands for curve number 6 in Figure 5.

An average number of free radicals per particle exceeding 0.5 after the initial activation step, has been calculated from the reaction rates of the curves shown in Figure 8. This implies the existence of some particles with two or more free radicals, the termination ability of which is decreased.

For an overall particle number  $N_t$  comprising particles without a free radical ( $N_o$ ), particle with untrapped free radical ( $N^*$ ), particles with trapped free radical occluded during the activation step ( $N_a^\circ$ ) or occluded during the copolymerization ( $N^\circ$ ), the kinetic equation becomes:

$$R_p = k_p M_p \left\{ (1 + C_1 I) \left[ -B + \sqrt{B^2 + \frac{2BN_t}{(C_1 I + 2)N_A}} \right] + C_2 I \left[ -B_a + \sqrt{B_a^2 + \frac{2B_a N_t}{(C_2 I + 2)N_A}} \right] \right\} \quad (20)$$

The comparison of Eq. (20) with the experimental data (Fig. 9) was performed starting from the simplified hypothesis stating that during the postactivation step, the desorption and accumulation processes have the same characteristics as the seeded copolymerization on a nonactivated PB support ( $D$  and  $C_1$  constants). For  $D = 1.19$  and  $C_1 = 110$ , a computer program has been applied which helped fitting the experimental data in order to determine the  $D_a$  and  $C_2$  values. The simplex algorithm gave as optimal values  $D_a = 5.2$

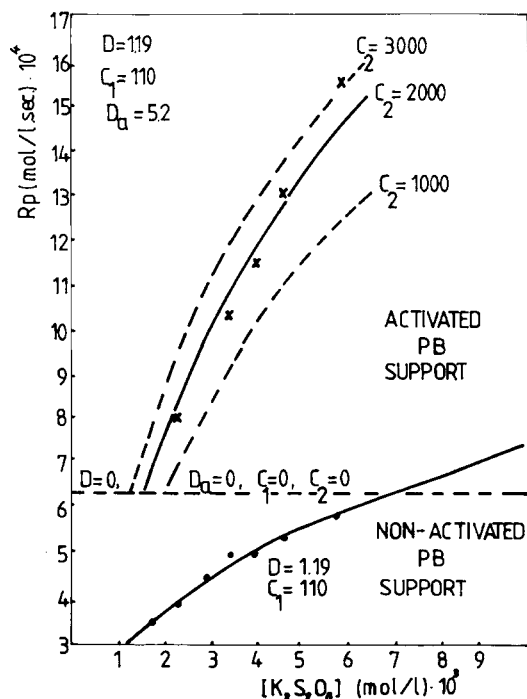


Fig. 9. The emulsion copolymerization rate in the presence of an activated PB support, as a function of the KP concentration (as given in Fig. 8), for different accumulation coefficients ( $C_2$ ). The desorption coefficients were  $D = 1.19$ ,  $D_a = 5.2$  whereas  $C_1 = 110$ .

and  $C_2 = 2000$  (Fig. 9).

A comparison of the desorption and accumulation coefficients for the activation step ( $D_a$  and  $C_2$ ) with those recorded at the copolymerization step ( $D$  and  $C_1$ ), reveals a higher desorption coefficient for the activation step ( $D_a > D$ ), simultaneously with a higher accumulation coefficient ( $C_2 > C_1$ ) noted at the same step. These values are accounted for by the fact that the activation of the support is performed in the presence of a small amount of comonomers that does not reach the saturation limit of the support. This will provide a concentration of comonomers beyond the solubility equilibrium limit in aqueous phase. Under such circumstances, desorption takes place easily and the low monomer concentration in the PB particle increases the probability of chain transfer to the support. It can be concluded that free radical accumulation occurs during the activation step, even if a stronger desorption process takes place at the same time.

### CONCLUSIONS

The emulsion copolymerization of St with AN seeded on a PB support has given evidence for oligoradical desorption, that becomes manifest in the presence of a chain-transfer agent. The oligoradicals formed in aqueous phase or resulting from desorption reenter another particle.

The PB support allows for the accumulation of the trapped free radicals by occlusion. The accumulation is favored by the use of a small concentration of comonomers and of high KP concentration. The emulsion copolymerization on an activated support takes place at high rates.

The kinetic equation deduced from the mechanism dealt with so far, verifies the experimental data only if the free radical desorption and accumulation processes are taken into account. The desorption and accumulation coefficients for the copolymerization initiated in aqueous phase, as well as for the copolymerization on an activated support containing trapped free radicals have been determined.

The desorption and accumulation processes place the emulsion copolymerization of St with AN seeded on a PB support far from case II of Smith-Ewart theory.

The authors wish to thank Mrs. G. Moraru for her contribution in latex preparation.

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Received November 11, 1987

Accepted April 4, 1988