Polymerizations in the presence of seeds: 3. Emulsion polymerization of vinyl acetate in the presence of quartz powder*

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(Received 28 July 1987; revised 4 January 1988; accepted 20 January 1988)

The emulsion polymerization of vinyl acetate in the presence of quartz powder ('Suprasil') was investigated. Ultrasonic velocity measurements showed that the concentration of monomers in the vicinity of the particles is very high compared with the concentration in the bulk dispersion medium. Therefore, polymerization in a surface layer around the particles should be enhanced. Electron micrographs of samples extracted during the first step of the polymerization and the dependence of reaction rate on pH value and initiator concentration can be explained in terms of this surface coating process.

(Keywords: polymer composites; emulsion polymerization; fillers for plastics; quartz powder; poly(vinyl acetate))

INTRODUCTION

Polymerizations in the presence of highly dispersed inorganic materials are increasingly of interest because of the possibility of producing an 'ideal' polymer–filler system. Such systems exhibit bulk properties other than the sum of the properties of the ingredients. Conditions for excess properties to occur are, for instance, the homogeneous distribution of filling material without any aggregates throughout the whole polymeric matrix, and the existence of a polymeric boundary layer on the inorganic particle surface with a defined thickness and structure.

In applying emulsion polymerization techniques to produce filled materials there are several complications:

(1) The quartz powder shows a very strong tendency to form large aggregates in aqueous media.

(2) The formation of polymer particles is possible without there being any inorganic material inside these particles, i.e. a structured boundary layer does not exist.

The aim of this paper is to show experimental evidence of polymerization within the surface layer of quartz powder particles, which results in a homogeneous distribution of these particles in the disperse system.

EXPERIMENTAL

The polymerizations were carried out as batch polymerizations in a 2 l reactor (stirring rate 200 min^{-1}). The ingredients (water, emulsifier, filling material, monomer) were added to the reaction vessel and heated, stirring continuously, until the reaction temperature was reached (60.0±0.1°C if no other temperature is indicated). Then the aqueous solution of the initiator (preheated to the reaction temperature) was added, and polymerization started[1]. The recipe is given in *Table 1*.

The monomer conversion was determined gravimetrically. Hydroquinone was used as inhibitor. The anionic surfactant 'Semisuxol WS' has a number-average molar mass of $\bar{M}_n = 1840$ and a critical micelle concentration of $CMC = 3.6 \times 10^{-3}$ mol l^{-1}. The emulsifier concentration applied in the polymerization runs is smaller than the *CMC*. The quartz powder used was 'Suprasil' (Chemische Fabrik Faehrbruecke, GDR) with an average particle diameter of $\bar{D}_n = 26$ nm. A transmission electron microscope BS 613 (Tesla, CSSR) was used to take the micrographs.

The ultrasound velocity was determined by measuring the pulse travelling time in the system over a constant distance. A computer checked all necessary parameters (temperature, time, pulse travelling time) and calculated the sound velocity. The accuracy of the absolute velocity determination was ± 1.5 m s^{-1}. The equipment is described in detail elsewhere[2].

CALCULATION OF SEED PARTICLE NUMBER

In seeded emulsion polymerizations, the number of seed particles must exceed a minimal value in order to prevent new particle formation and, hence, to promote the seed particle growth.

It is possible to apply a model developed by Schmutzler[3] in order to calculate the minimal seed particle number. This model of homo-emulsion polymerization is based on the experimental finding that primary particles are produced in the aqueous phase by a

Table 1 Polymerization recipe

Ingredient	Amount
Bidistilled water	1250.0 g
Emulsifier 'Semisuxol WS' (Buna, GDR)	2.3 g
Vinyl acetate	120.0 g
$K_2S_2O_8$	Variable

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* Part 2: *Acta Polym.* 1986, **37**, 468

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0032-3861/88/071323-06$03.00

collapse and micellization process of oligomeric chains immediately after the reaction begins. The number of these primary particles N_1 that originate per unit time can be calculated as follows, assuming the polymerization reaction does not take place inside these particles:

$$\left(\frac{\mathrm{d}N_1}{\mathrm{d}t}\right)_0 = \frac{3}{4\pi r_0^3 \rho_T} \frac{\mathrm{d}M}{\mathrm{d}t} \qquad (1)$$

where r_0 and ρ_T are the radius and the density of primary particles, respectively; and $\mathrm{d}M/\mathrm{d}t$ is the monomer conversion per unit time. The diameters of these particles are in the range of 10 nm and therefore they are very unstable because of their low energy barrier (primary coagulation process). Hence, the primary particles can aggregate either with other primary particles[4]:

$$-\left(\frac{\mathrm{d}N_1}{\mathrm{d}t}\right)_1 = 8\pi D_1 r_0 N_1^2 W_{11} = k_{11} N_1^2 \qquad (2)$$

or with aggregates of particles formed previously by aggregation according to (2):

$$-\left(\frac{\mathrm{d}N_1}{\mathrm{d}t}\right)_2 = 4\pi(D_1 + D_2) r N_1 N_2 W_{12} = k_{12} N_1 N_2 \qquad (3)$$

Here D_1 and D_2 are the diffusion coefficients of primary particles and aggregates, respectively; r is the effective radius and W_1 and W_2 are functions of the particle–particle and particle–aggregate interactions. The quantities in (2) and (3) can be calculated using some geometric considerations and the DLVO theory of colloidal interaction (for a detailed discussion of this see ref. 3).

The steady state is characterized by the condition that the number of primary particles formed in the aqueous phase is equal to the number of primary particles lost during aggregation:

$$\left(\frac{\mathrm{d}N_1}{\mathrm{d}t}\right)_0 = \left(\frac{\mathrm{d}N_1}{\mathrm{d}t}\right)_1 + \left(\frac{\mathrm{d}N_1}{\mathrm{d}t}\right)_2 \qquad (4)$$

Where there is a sufficiently high aggregate number, all newly originated primary particles (and, additionally, all newly originated oligomeric chains) aggregate exclusively with these previously formed aggregates:

$$\left(\frac{\mathrm{d}N_1}{\mathrm{d}t}\right)_1 < \left(\frac{\mathrm{d}N_1}{\mathrm{d}t}\right)_2 \qquad (5)$$

An equivalent condition is:

$$N_1(k_{11}/k_{12}) < N_2 \qquad (6)$$

These conditions ((5) and (6)) agree with the experimental result that the particle number remains nearly constant in emulsion polymerization systems after the primary aggregation process has finished. In this case, the aggregates are the seeds of the final latex particles. Substituting (1)–(4) into condition (6), the number of polymer particles is given by:

$$N_2^2 > \frac{3k_{11}}{8\pi k_{12}^2 r_0^3 \rho_T} \frac{\mathrm{d}M}{\mathrm{d}t} \qquad (7)$$

This number of polymer particles is necessary in order to prevent any new particle formation in seeded emulsion polymerizations.

Condition (7) was experimentally verified using polymer seed latexes of poly(vinyl acetate), polystyrene and poly(methyl methacrylate), and the corresponding monomers[3,5,6]. In the case of soapless emulsion polymerization of vinyl acetate, a particle number $N_2 = 2 \times 10^{13}\ \mathrm{cm}^{-3}$ was obtained.

If an inorganic seed material is used, condition (7) can be applied in the same way. In this case, the seed particle radius is a constant, in contrast to the polymeric seed latexes, where the radii can be varied by altering the quantities of the recipe or during the course of the process. The number of seed particles should exceed the value N_2 given by condition (7) in order to prevent separated particle formation. Assuming that a particle number of $2 \times 10^{13}\ \mathrm{cm}^{-3}$ is required, and inserting a particle density of $2.7\ \mathrm{g\ cm}^{-3}$, the appropriate lower limit of seed volume fraction is listed in *Table 2*.

Obviously, the diameters of filler particles must be very much lower than $D \approx 300$ nm in order to obtain polymer-coated particles. In most cases, emulsion polymerization is carried out in the presence of surfactants. Hence the number of particles according to condition (7) is some orders of magnitude greater than the value discussed above, and the filler particle dimension required is reduced to $D \ll 100$ nm. This condition is realized in the systems studied in the experiments of this paper. From this point of view it is obvious that Furusawa *et al.*[7] found no tendency of the encapsulation of bare silica particles (diameter 190 nm) during the soapless emulsion polymerization of styrene.

RESULTS AND DISCUSSION

Influence of filler concentration

The influence of filler content on conversion–time curves is shown in *Figure 1*. It can be seen that the rate of reaction decreases with increasing quantities of quartz powder (*Figure 2*). There are various explanations for this behaviour:

(i) The initiator radicals (as well as the monomer or oligomeric radicals) are able to recombine with fixed radicals on the Suprasil surface.

(ii) The radicals within the aqueous phase can be fixed to the particle surface without recombining, and therefore the diffusion-controlled polymerization reaction is hindered.

(iii) The persulphate can react with impurities in the quartz powder without any polymerization.

In the literature there are some other experimental

Table 2 Lower limit of the seed volume fraction Φ_{min} (in order to prevent a second particle generation) as a function of quartz particle diameter

D (nm)	Φ_{min}
25	1.6×10^{-4}
50	1.3×10^{-3}
100	0.01
150	0.04
200	0.10
250	0.22
300	0.53

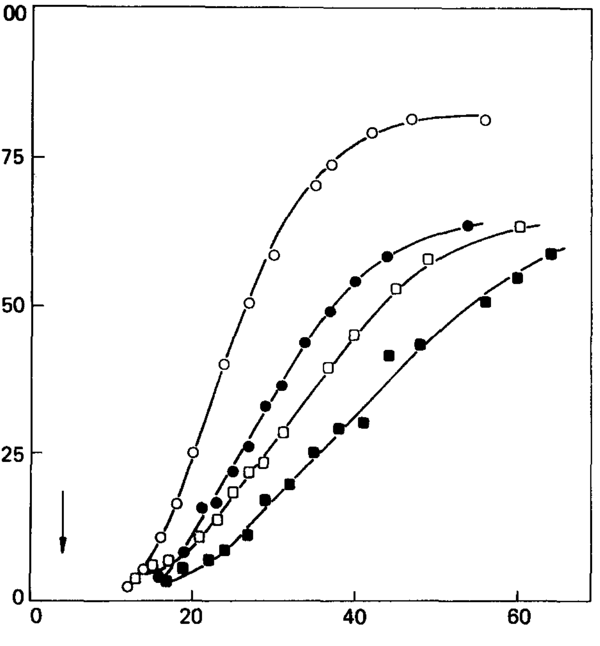

Figure 1 Influence of the amount of filler on conversion in vinyl acetate emulsion polymerization: (○) 0 g Suprasil; (●) 30 g Suprasil; (□) 60 g Suprasil; (■) 90 g Suprasil. The arrow indicates the addition of the initiator (0.75 g $K_2S_2O_8$)

findings: (i) The rate of emulsion polymerization of styrene in the presence of fumed silica (average diameter ≈ 14 nm) is not affected by the amount of silica in the reaction mixture[8]. Nevertheless, the authors of this paper have discussed the fact 'that the silica particles may have acted as "seeds" for further growth of polymer'. This conclusion was drawn from electron micrographs of the latexes polymerized. (ii) Arai *et al.*[9] investigated the emulsion polymerization of methyl methacrylate in the presence of calcium sulphite powder. They observed that the reaction rate immediately above the saturation point of $CaSO_3$ in water is lower than below this saturation point. But with increasing calcium sulphite concentration above the saturation point this rate also increases. In these two papers, just as in our experiments, no unambiguous explanation could be offered until now. (iii) Aslamazova *et al.*[10] observed an increase in the rate of polymerization of butyl methacrylate in the presence of increasing amounts of Aerosil. They discussed a specific interaction of monomers with the silanol groups of the Aerosil and an improved initiator efficiency due to accelerated decomposition of initiator molecules on the quartz powder surface. (iv) Additionally, Ivančev[11] explains the reduced efficiency of the initiator due to the fixing of both radicals of an adsorbed radical pair, with recombination being more probable as a result.

Analysing the experimental results and the data from the literature, it is impossible to distinguish between the individual interpretations. Some further experimental work is required in this field.

Sound velocity during emulsion polymerization

Recently, an ultrasound velocity method was developed for monitoring emulsion polymerization (i.e. the conversion–time relation)[12,13]. In a simplified model, the ultrasound velocity v of a multicomponent aqueous system can be described as follows:

$$v = v_0 + \sum_i \left(\frac{\Delta v}{\Delta c}\right)_i c_i \qquad (8)$$

where v_0 is the sound velocity in water, c_i is the concentration of ingredient i, and $(\Delta v/\Delta c)_i$ is the velocity–concentration coefficient (i.e. the calibration constant of a binary system containing only water and the ingredient i). Higher-order terms will be neglected in (8). Hence, the influence of ingredient i on the sound velocity of ingredient j is also neglected. This assumption does not always necessarily hold true; but the model was well verified for the case of vinyl acetate[12]. In the system investigated, (8) can be written as:

$$v = v_0 + \left(\frac{\Delta v}{\Delta c}\right)_{\mathrm{VAC<S}} c_{\mathrm{VAC<S}} + \left(\frac{\Delta v}{\Delta c}\right)_{\mathrm{VAC>S}} (c_{\mathrm{VAC,tot}} - c_{\mathrm{VAC<S}})$$
$$+ \left(\frac{\Delta v}{\Delta c}\right)_{\mathrm{PVAC}} c_{\mathrm{PVAC}} + \left(\frac{\Delta v}{\Delta c}\right)_{\mathrm{Em}} c_{\mathrm{Em}} + \left(\frac{\Delta v}{\Delta c}\right)_{\mathrm{K_2S_2O_8}} c_{\mathrm{K_2S_2O_8}}$$
$$+ \left(\frac{\Delta v}{\Delta c}\right)_{\mathrm{SiO_2}} c_{\mathrm{SiO_2}} \qquad (9)$$

where the index 'VAC < S' denotes vinyl acetate below its saturation point in water, 'VAC > S' is vinyl acetate above the saturation point, 'VAC,tot' is the total amount of vinyl acetate, and 'PVAC', 'Em' and '$K_2S_2O_8$' are the polymer, the emulsifier and the initiator, respectively.

The contributions of the initiator and of the quartz powder to the sound velocity are negligible in the present system[14]. The coefficient $(\Delta v/\Delta c)_{\mathrm{VAC<S}}$ was determined experimentally in the presence of the emulsifier. The solubility of VAC in the emulsifier solution is nearly constant at 3% by weight (determined by ultrasonic velocity measurements) in the temperature range between 55 and 65°C. The value of $(\Delta v/\Delta c)_{\mathrm{PVAC}}$ can be deduced from *Figure 3a*.

The sum of the total vinyl acetate and poly(vinyl acetate) content is constant during the whole process. Applying (9), it is then possible to calculate the proportion of vinyl acetate dissolved in the water from

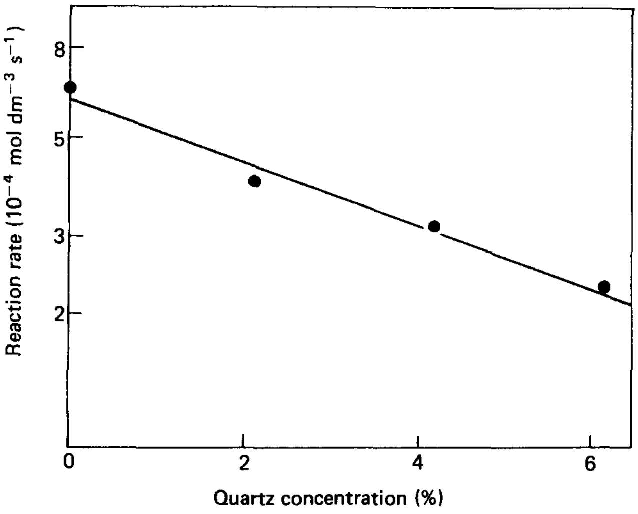

Figure 2 Rate of polymerization as a function of quartz concentration (0.75 g $K_2S_2O_8$)

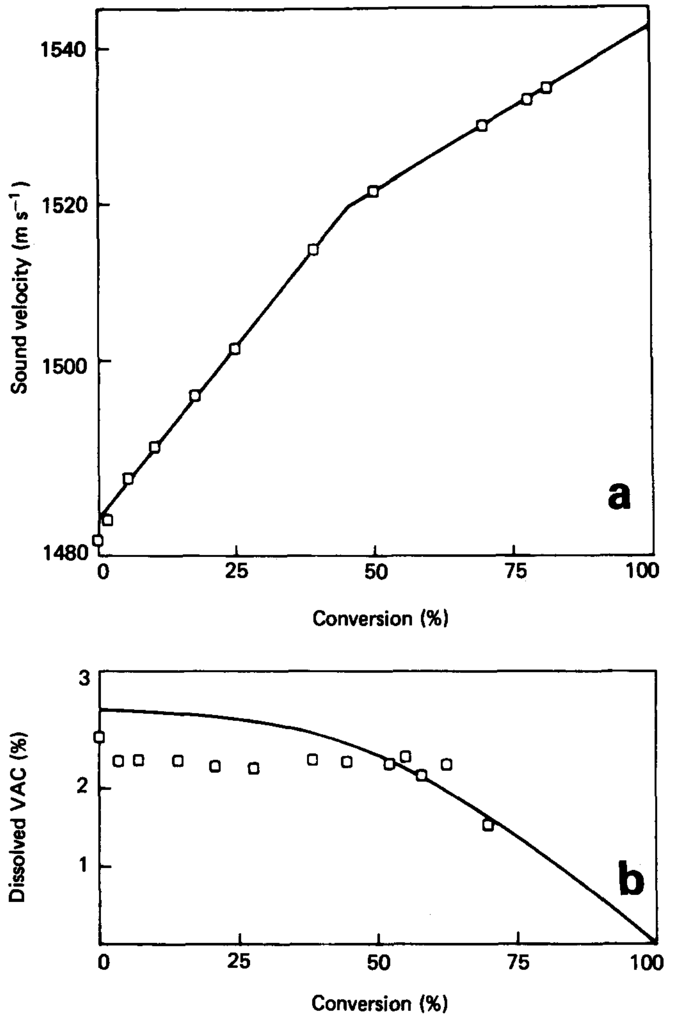

Figure 3 (a) Ultrasonic velocity as a function of conversion (60 g Suprasil; 0.75 g $K_2S_2O_8$): (□) experimental; (———) calculated. (b) Proportion of vinyl acetate dissolved in the water: (□) experimental value in the presence of 60 g quartz; (———) calculated from homo-emulsion polymerization data in the absence of quartz

ultrasonic data as a function of monomer conversion. It can be seen from *Figure 3b* that the proportion of vinyl acetate dissolved in the aqueous medium containing filler particles is smaller than in the case of homo-emulsion polymerization. The missing amount of vinyl acetate must be located within the aggregates of the quartz powder, i.e. in a surface layer around the particles. Therefore, the polymerization in the vicinity of the particles should be enhanced because of the very high monomer concentration in this surface layer region.

Electron microscopy

The conclusion drawn above can be verified by an electron microscopic observation of the polymerization products. The quartz powder exhibits a very strong tendency to form large aggregates in aqueous media (*Figure 4*). This behaviour does not change if aqueous solutions of anionic or non-ionic emulsifiers are added in order to disperse the filler particles. Surprisingly, the quartz powder is dispersed in an ideal manner if emulsion polymerization is carried out in its presence. During the first period of the emulsion polymerization, which is characterized by a drastic decrease of surface tension[15], the aggregates lose their aggregative behaviour (*Figure 5*). The quartz particles appear as single particles, and only a very small number of small-sized aggregates can be observed.

Ivančev *et al.*[16] observed a homogeneous distribution of Aerosil particles during the solution polymerization of styrene. In the case of solution polymerization, a homogeneous distribution arises owing to the polymerization (and the grafting) of the styrene in the vicinity of the particles, and, therefore, owing to the existence of a polymeric surface layer around the particles. The same effect can be discussed in emulsion polymerization systems. Here it is enhanced by the comparatively high monomer concentration in the surface layer of the particles (compared with the limited monomer concentration in the water phase).

Additionally, in emulsion polymerizations the surface-active, low-molecular-weight oligomeric chains produced in the aqueous phase act as detergents during the first period of the reaction. Electron micrographs of samples extracted during the later stages of the reaction show polymer particles only. The quartz particles should be located within these polymer particles.

Therefore, the emulsion polymerization technique is a very effective method for producing 'filled' polymeric materials.

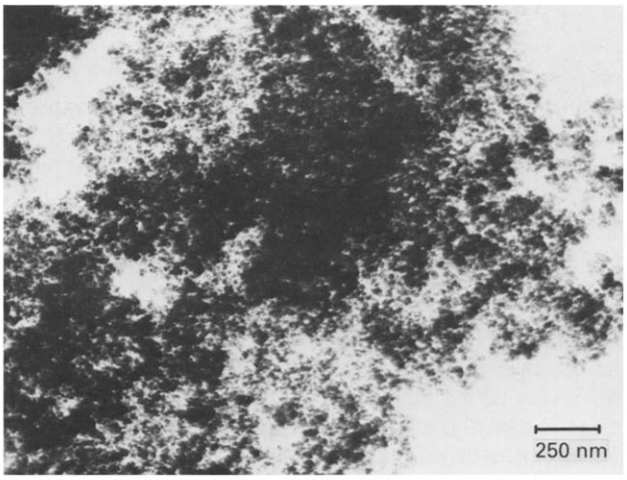

Figure 4 Aggregates of quartz powder in aqueous media

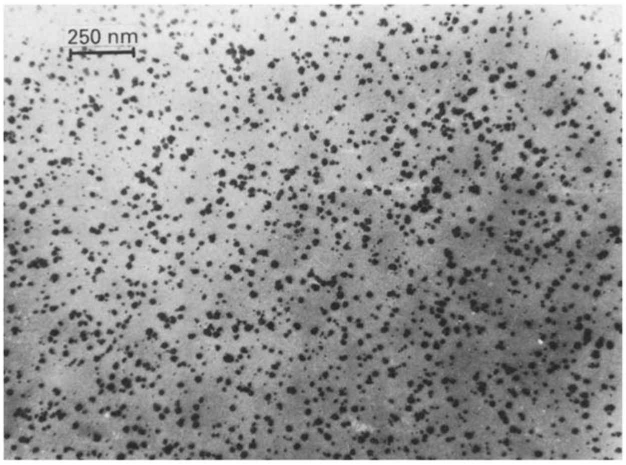

Figure 5 Suprasil particles extracted during the first step of the emulsion polymerization (0.7% PVAC in the aqueous phase)

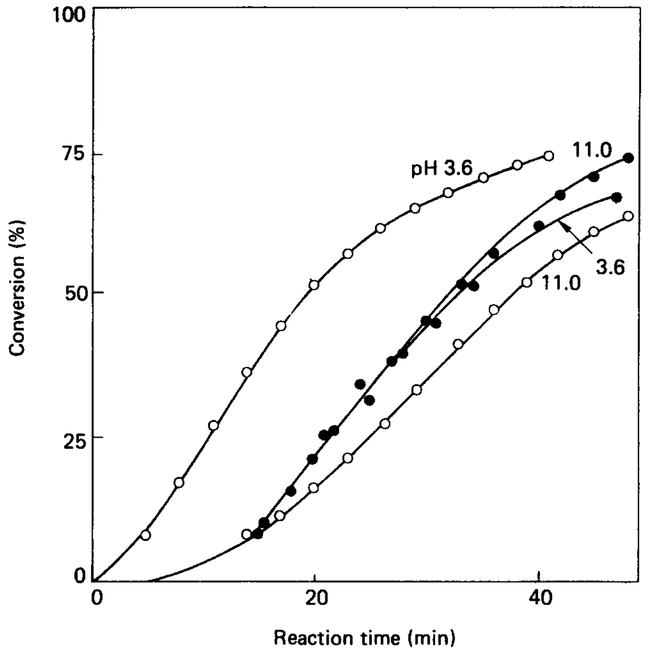

Figure 6 Conversion–time relation as a function of the pH value (pH 3.6 and pH 11.0) of the aqueous phase: (○) 0 g Suprasil; (●) 60 g Suprasil

Influence of the pH value

The influence of the pH value of the aqueous phase on the conversion is shown in *Figure 6*. The homo-emulsion polymerization exhibits the usual behaviour of polymerizations initiated by persulphate. The acid medium catalyses the decomposition of the initiator molecules because H^+ ions are present[17]. Therefore, the polymerization rate in the acid water phase is higher than in a neutral or basic one. Where quartz powder is present, only a very small difference in polymerization rates could be observed. The pH value of the aqueous phase does not exert any perceptible influence on the conversion.

A 'pure' quartz surface (containing only silanol ionic end-groups) shows a strong tendency to adsorb H^+ ions or to react with OH^- ions from the bulk[18]. Therefore, the influence of the pH value should be observed in the presence of quartz. But whereas the pH value of the water was changed, the pH value in the surface layer around the particles, obviously, remained nearly constant, owing to the 'buffering' effect of the monomer adsorbed on the quartz particle surface (see above). Hence, the absence of any influence of the pH value on the reaction rate also indicates that the surface layer of the particles is the main reaction locus, owing to the high monomer concentration in this region and to the radical adsorption onto this layer.

Activation energy and influence of initiator concentration

The Arrhenius plots of reaction rates of the homo- and Suprasil-seeded emulsion polymerization of vinyl acetate are shown in *Figure 7*. The activation energy of polymerization calculated using this plot is $E_A = 113\ \mathrm{kJ\ mol^{-1}}$ in the case of the unseeded reaction and $E_A = 116\ \mathrm{kJ\ mol^{-1}}$ in the case of the Suprasil-seeded reaction. The filling material does not exert any influence on the activation energy. This behaviour is well known from literature in the case of the emulsion polymerization of styrene[11], butyl methacrylate[19] and methyl methacrylate[16] in the presence of seeds.

The dependence of the reaction rate on the initiator concentration is plotted in *Figure 8*. The initiator exponents of the reaction rate are 0.65 for the unseeded and 0.88 for the seeded polymerizations. These two values differ from the micellar Smith–Ewart case II result (0.4), but they do fall within the usual region of initiator exponents of vinyl acetate emulsion polymerization (0.7)[20]. The difference in reaction rates decreases with increasing initiator concentration. This behaviour can be explained as follows. First, the higher the initiator concentration, the higher the number of adsorbed fixed radicals on the particle surface and therefore the lower the retardation of polymerization due to the seed particles (see above). Secondly, with increasing initiator concentrations the proportion of 'usual' emulsion polymerization increases in the aqueous phase and, at very high initiator concentrations, the proportion of 'surface layer' polymerization will be negligible.

Analysing the above results, it is difficult to decide what is the main effect.

SUMMARY

The emulsion polymerization in the presence of a sufficiently high inorganic seed particle number is a useful procedure for coating these particles by the polymer generated during the reaction. A very high concentration of the adsorbed monomer on the particle surfaces, which is indicated by ultrasonic velocity measurements, favours

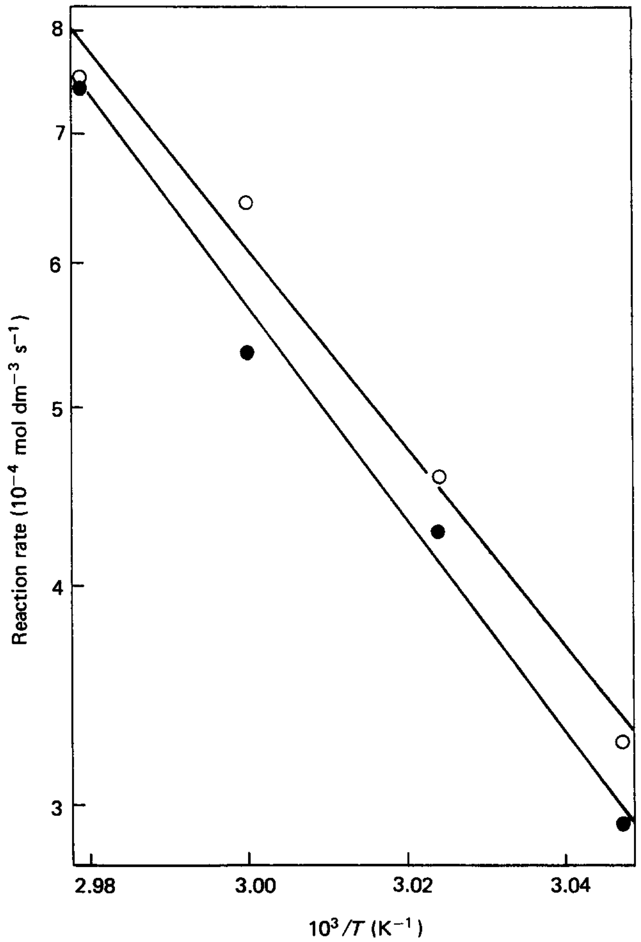

Figure 7 Arrhenius plot of the reaction rate: (○) 0 g Suprasil; (●) 60 g Suprasil

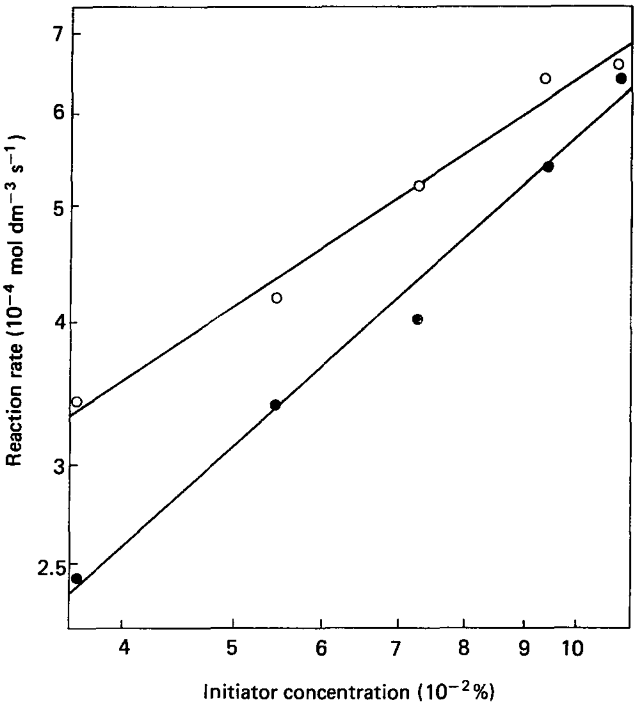

Figure 8 Influences of the initiator concentration on the reaction rate: (○) 0 g Suprasil; (●) 60 g Suprasil

this surface coating process. Electron micrographs of samples extracted during the reaction support this interpretation. The influence of seed particle concentration, pH value, initiator concentration and temperature on the reaction rate was investigated.

The main condition for the formation of polymer-coated inorganic filler particles by using the emulsion polymerization technique is the existence of a sufficiently high seed particle number in the reaction medium. This condition can be fulfilled by using particles with average diameters $\leqslant 100$ nm.

Various experimental findings have been presented to prove that inorganic filler particles are coated by the polymer generated during emulsion polymerization:

(i) The amount of dissolved monomer in the water phase is reduced when quartz powder is present. The missing amount is located on the particle surface.

(ii) Electron micrographs of samples extracted during the first step of the polymerization show a very strong disaggregation of the quartz aggregates. Further polymerizations produce polymer particles that contain the filling material.

(iii) The dependence of the reaction rate on pH value and initiator concentration can be explained in terms of this surface coating process.

ACKNOWLEDGEMENTS

The authors wish to thank their colleagues for helpful discussions. The financial support of the Kombinat VEB Chemische Werke Buna is gratefully acknowledged.

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