

Emulsion Polymerization of Unsaturated Monomers in the Presence of Inorganic Ultrafine Particles

I. CAPEK* and V. JURANIČOVÁ

Polymer Institute, Slovak Academy of Sciences, SK-842 36 Bratislava

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The emulsion polymerization of unsaturated monomers initiated by ammonium peroxodisulfate in the presence of inorganic ultrafine particles (IUP) was studied. The rate of emulsion polymerization of butyl acrylate increased with increasing amount of SiO_2 but decreased in the case of TiO_2 . In the emulsion polymerization of methyl methacrylate the rate of polymerization decreased with increasing amount of both SiO_2 and TiO_2 . In the emulsion polymerization of ethyl acrylate it increased with emulsifier concentration in the presence of both SiO_2 and TiO_2 particles. In the butyl acrylate system the rate of polymerization increased with emulsifier concentration in the presence of SiO_2 but decreased in the presence of TiO_2 .

The addition of IUP was found to increase agglomeration of particles which was much more pronounced with TiO_2 . The rate of polymerization parallels the number of particles. Polymer formed in the presence of SiO_2 or TiO_2 in the butyl acrylate system was found to be insoluble in solvents for poly(butyl acrylate) while that formed in the methyl methacrylate system was insoluble in solvents for poly(methyl methacrylate).

The encapsulation of fine inorganic powder is useful to improve the physical properties of the composite polymer products. The emulsion polymerization is an ideal method for their preparation. The process of emulsifier adsorption is fairly complicated; the behaviour depends on many factors, *e.g.* the nature of the emulsifier and inorganic additive, the temperature, the continuous phase, *etc.* Among these factors, the solvency of the medium liquid can influence the adsorption in two ways [1], by the energetic factor (the difference in energy of interaction between emulsifier and solvent (water, *etc.*) and between emulsifier and polymer molecule) or the relative interaction polymer—solvent and solvent—solvent, which leads to the expectation that adsorption is best from a poor solvent. It was demonstrated that the radical graft polymerization of vinyl monomers introduced polymer chains into the carbon black surface [2]. The radical graft polymerization of vinyl monomers from inorganic ultrafine particles, such as silica, titanium(IV) oxide, and ferrite, by use of azo groups introduced into their surface produced stable polymer-grafted ultrafine particles in organic solvents [3].

Hasegawa *et al.* [4] have reported a new process, which makes possible the encapsulation of submicron-sized fine powders with a polymer film. The uniform encapsulation of a powder by soapless emulsion poly-

merization is attained by the adsorption of sufficient emulsifier molecules for the formation of preferential polymerization loci prior to the polymerization. An ionic emulsifier is more effective than a nonionic one. Pretreatment can be carried out effectively when an electrostatic interaction between powder surface and ionic end group occurs.

The possibility of using metal oxides ZnO , MgO , NiO , CuO , Al_2O_3 , TiO_2 , and PbO_2 as heterogeneous initiators for the radical emulsion polymerization of styrene and methyl methacrylate was discussed by Mikulášová *et al.* [5]. From the studied metal oxides as heterogeneous initiators of polymerization only aluminium oxide and titanium(IV) oxide were not suitable.

The effect of inorganic salts was investigated to clarify the relationship between the character of the micelles and the initiation step of the emulsion polymerization of vinyl monomers [6]. The polymerization was accelerated by adding sodium dithionite (SD) of the concentration less than $0.042 \text{ mol dm}^{-3}$ in the reaction system and was retarded or inhibited at higher concentrations. It was concluded that the interaction between SD and monomer solubilized in the micellar surface plays an important role in the initiation step of the polymerization.

Since the surface of inorganic colloid particles usu-

* The author to whom the correspondence should be addressed.

ally has negative charges on electrical double layer, which contributes to preventing coagulation by electrostatic repulsion among particles, the initiator APS of radical polymerization is expected to induce efficient polymerization of vinyl monomer. Dispersion polymerization of styrene (St) or MMA was reported to give the polymer/SiO₂ composites [7]. It was shown that each particle of these composites is wholly and homogeneously covered with PSt or PMMA. Amounts of attached polymers on silica particles increased with the reaction temperature and time.

In this paper, the emulsion polymerization of butyl acrylate, methyl methacrylate, and ethyl acrylate was carried out with two different types of inorganic ultrafine particles keeping the rate of initiation constant to elucidate the main locus of radical formation and growth events in the heterogeneous polymerization. For this purpose we followed the effect of emulsifier concentration, the type and amount of inorganic powder, and the type of unsaturated monomer on the kinetic, colloidal, and molecular mass parameters of emulsion polymerization.

EXPERIMENTAL

Commercially available butyl acrylate (BA), methyl methacrylate (MMA), ethyl acrylate (EA), ammonium peroxodisulfate (the water-soluble initiator, APS), dibenzoyl peroxide (DBP), and 2,2'-azobis(isobutyronitrile) (AIBN) (Fluka), were purified by usual methods. The emulsifier used was a reagent grade sodium dodecylsulfate (SDS, Fluka). TiO₂, which was supplied by Ishihara Sangyo Co., had an average particle size 20–50 nm. The SiO₂ powder used was "Suprasil" (Chemische Fabrik Fahrbruecke, Germany) with an average particle size 26 nm. The SiO₂ or TiO₂ particles were dispersed in water and polymerized under ultrasonic irradiation. Twice distilled water was used as a polymerization medium (in the emulsion runs).

The batch polymerizations were run at 60°C. In all emulsion runs the recipe comprised 100 g of water, 10 g of monomer, 0.025 g of NaHCO₃, and 0.1 g of APS. Amounts of SDS, initiator, and inorganic powder varied as shown later. Concentrations of monomer, initiator, and particles as well as polymerization rates are related to the aqueous phase. In the bulk (MMA or BA) polymerization the recipe comprised 10 g of monomer and 6 g of porous SiO₂ (with specific surfaces 33 m² g⁻¹). Concentration of initiator was 0.0004 mol dm⁻³ or 0.004 mol dm⁻³, respectively. The polymerization technique and the measurements of particle size and number (a light scattering method) were the same as described earlier [8, 9]. Polymers prepared at various conversions with different additives (TiO₂, SiO₂) were made free of IUP and monomer by extraction with solvents (toluene, acetone) and precipitation into ethanol–water ($\varphi_r = 2/1$). The microscopic rate

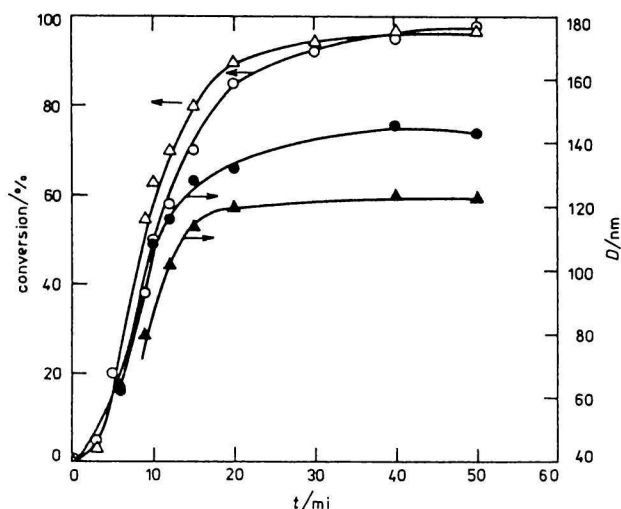


Fig. 1. Variation of monomer conversion and particle size (D) in the emulsion polymerization of BA in the presence and absence of SiO₂ initiated by APS with the reaction time and the BA concentration. $c(\text{SDS}) = 0.01 \text{ mol dm}^{-3}$, $c(\text{APS}) = 0.0044 \text{ mol dm}^{-3}$ ○ and ● without additive, Δ and ▲ with 0.5 g of SiO₂.

of polymerization ($\text{mol dm}^{-3} \text{ s}^{-1}$) is estimated from the conversion–time dependence (dx/dt , where x is the mass fraction of monomer to polymer) and the initial number of moles of monomer present per unit volume of the reaction medium. Conversion of monomer was determined by gravimetric measurements. Limiting viscosity numbers were measured in acetone ($[\eta] = 7.5 \times 10^{-5} M^{0.73}$) or toluene ($[\eta] = 7.1 \times 10^{-5} M^{0.73}$) at 25°C and used to estimate the viscosity-average molecular masses $V_2 \rightarrow ([\eta] = M_v)$ [10, 11].

RESULTS AND DISCUSSION

Rate of Polymerization

The conversion *vs.* time data for the emulsion polymerization of butyl acrylate initiated by ammonium peroxodisulfate in the absence and presence of IUP are shown in Fig. 1. The conversion curves are linear in both systems from 10 to 50 or 60 % conversion and the final conversion close to 100 % is reached. Fig. 2 shows that the reaction rate of the emulsion polymerization of butyl acrylate decreases with increasing concentration of TiO₂ but increases with increasing concentration of SiO₂. The emulsion polymerization of methyl methacrylate, however, decreases with increasing amount of both SiO₂ and TiO₂ (Fig. 3).

Aslamazova *et al.* [12] observed an increase in the rate of polymerization of butyl methacrylate in the presence of SiO₂. They discussed a specific interaction of monomer with the silanol groups of SiO₂ and an increased initiator efficiency due to the accelera-

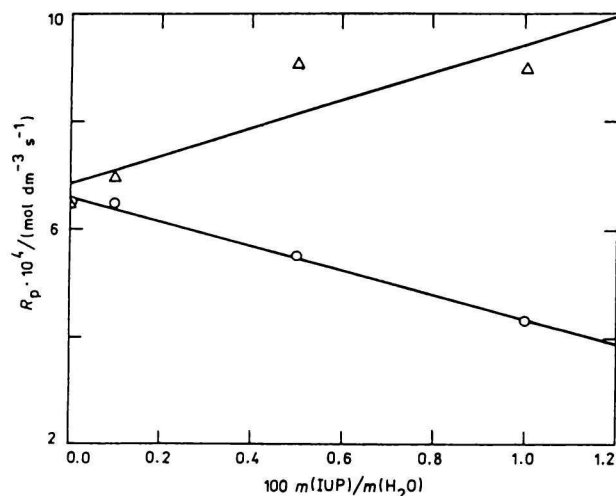


Fig. 2. Variation of the rate of polymerization (R_p) in the emulsion polymerization of BA initiated by APS with the IUP amount. $c(\text{SDS}) = 0.01 \text{ mol dm}^{-3}$, $c(\text{APS}) = 0.0044 \text{ mol dm}^{-3}$ ○ with TiO_2 , Δ with SiO_2 .

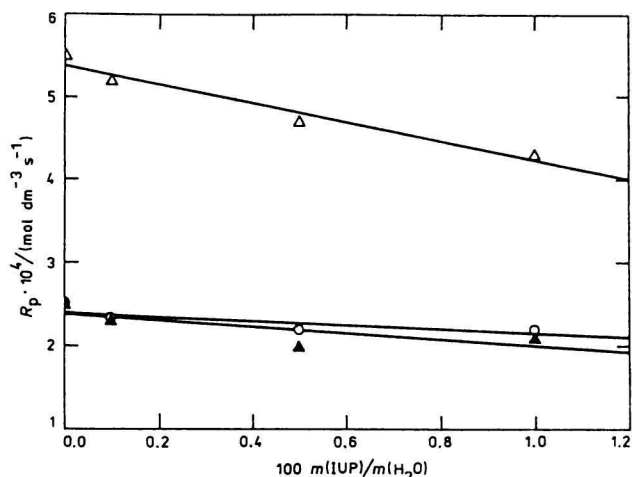


Fig. 3. Variation of the rate of polymerization (R_p) in the emulsion polymerization of MMA initiated by APS with the IUP amount. $c(\text{SDS}) = 0.01 \text{ mol dm}^{-3}$, $c(\text{APS}) = 0.00044 \text{ mol dm}^{-3}$. ○ with TiO_2 , Δ with SiO_2 . $c(\text{SDS}) = 0.01 \text{ mol dm}^{-3}$, $c(\text{APS}) = 0.001 \text{ mol dm}^{-3}$ ▲ with SiO_2 .

tion decomposition of initiator molecules on the SiO_2 particle surface.

The rate of emulsion polymerization of St in the presence of SiO_2 is not affected [13]. Arai *et al.* [14] reported that the emulsion polymerization of MMA is not affected by the calcium sulfite powder at low concentration. But at the increased concentration of CaSO_3 above the saturation point its rate also increases.

Ultrasonic velocity measurements showed that the concentration of monomer in the vicinity of the particles is very high when compared with the concen-

tration in the bulk dispersion system [15]. Therefore, polymerization in a surface layer of the particle should be enhanced.

There are various explanations for this behaviour:

i) The radicals within the aqueous phase can be fixed to the particle surface and therefore the normal termination is hindered (the rate increases).

ii) The peroxodisulfate can react with impurities in the inorganic powder without any polymerization (the rate decreases).

iii) The growing radicals fixed to the particle surface are deactivated by oligomer radicals, which are formed in the aqueous phase.

iv) The stable composite particles favour the increase of both the number of polymer particles and the rate of polymerization.

v) The concentration of monomer in the vicinity of the particles or within the pores of inorganic particles may be higher when compared with the concentration in the continuous phase. Therefore, polymerization in a surface layer of the composite particle should be enhanced.

The effect of emulsifier (SDS) concentration on the rate of polymerization in the presence of IUP is summarized in Figs. 4 (EA) and 5 (BA). In all runs the rate of polymerization increases with increasing $c(\text{SDS})$. The reaction order in dependence on $c(\text{SDS})$ was found to be increased as follows:

0.4 (SiO_2) < 0.5 (TiO_2) < 0.6 (without additive) (the EA system)

0.4 (TiO_2) < 0.5 (no additive) < 0.6 (SiO_2) (the BA system)

These results show that the addition of IUP slightly decreases the reaction order in dependence on

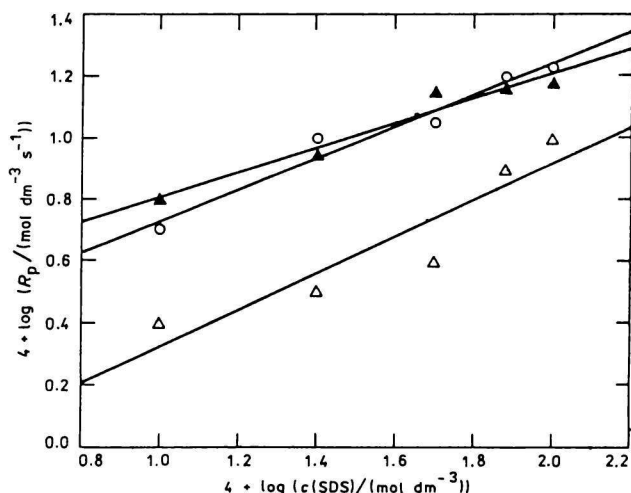


Fig. 4. Variation of the rate of polymerization (R_p) in the emulsion polymerization of EA initiated by APS with the SDS concentration. $c(\text{APS}) = 0.0044 \text{ mol dm}^{-3}$ Δ without additive, ○ with TiO_2 , ▲ with SiO_2 .

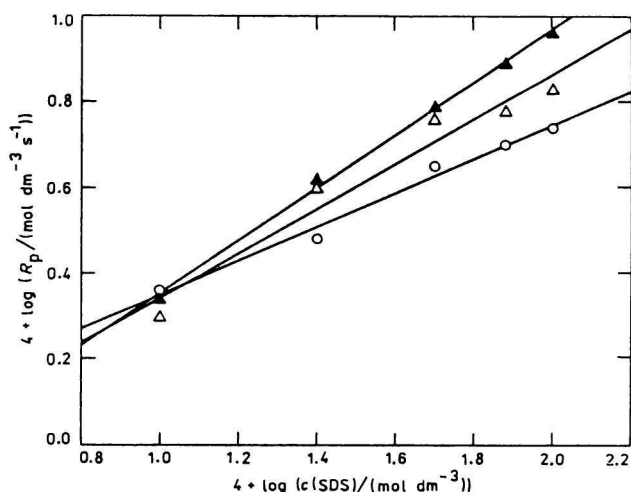


Fig. 5. Variation of the rate of polymerization (R_p) in the emulsion polymerization of BA initiated by APS with the SDS concentration. $c(\text{APS}) = 0.0044 \text{ mol dm}^{-3}$ Δ without additive, \circ with TiO_2 , \blacktriangle with SiO_2 .

the concentration of emulsifier. This may be ascribed to the interaction of IUP with emulsifier which decreases the total free amount of emulsifier. This effect is more pronounced in the TiO_2 systems.

The effect of porous SiO_2 particles on the AIBN, DBP, and APS ($c = 0.004 \text{ mol dm}^{-3}$) initiated (bulk) polymerization of MMA. The rate of polymerization (R_p) and the specific surface (S_{sp}) of modified SiO_2 particles were found to vary with the initiator type and concentration

$R_p / (\text{mol dm}^{-3} \text{ s}^{-1})$: 1.2×10^{-4} (DBP) $< 1.7 \times 10^{-4}$ (AIBN) $< 5.1 \times 10^{-4}$ (APS)

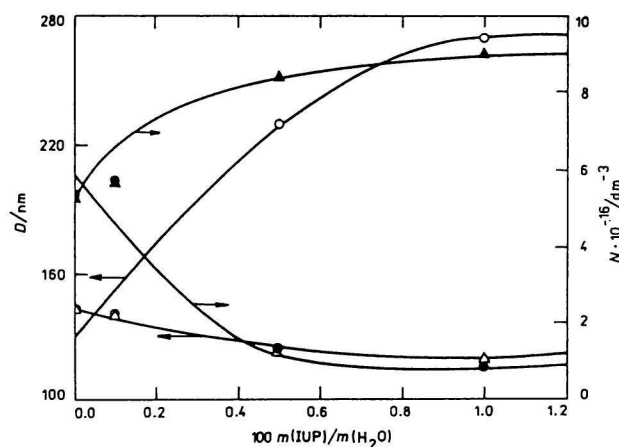


Fig. 6. Variation of the particle diameter (D) and number (N) in the emulsion polymerization of BA initiated by APS with the IUP amount. Δ and \blacktriangle with SiO_2 , \circ and \bullet with TiO_2 .

$S_{sp} / (\text{m}^2 \text{ g}^{-1})$: 16 (AIBN) < 22 (DBP where $c(\text{initiator}) = 0.004 \text{ mol dm}^{-3}$) < 23 (APS)

and

$R_p / (\text{mol dm}^{-3} \text{ s}^{-1})$: 1.0×10^{-4} (DBP) $= 1.0 \times 10^{-4}$ (AIBN) $< 1.1 \times 10^{-4}$ (APS)

$S_{sp} / (\text{m}^2 \text{ g}^{-1})$: 22 (AIBN) > 20 (DBP where $c(\text{initiator}) = 0.0004 \text{ mol dm}^{-3}$) > 16 (APS)

These results indicate that the rate of polymerization is very high and comparable with that in the emulsion systems. On the other hand, the polymerization is independent of the initiator concentration. The acceleration of polymerization can be ascribed to a decreased termination of growing radicals. The immobilization of growing radicals in the pores of SiO_2 particles leads to the increased concentration of growing radicals, decreased macroradical termination, and increased rate of polymerization. The decrease in specific surface caused by polymerization indicates that the polymerization proceeds in the pores of SiO_2 particles. Specific surface of the composite SiO_2 varies from 16 to 23 $\text{m}^2 \text{ g}^{-1}$ while S_{sp} of the pure SiO_2 is 32 $\text{m}^2 \text{ g}^{-1}$. These results indicate that the polymerization of monomer in the pores of IUP contributes to the whole polymerization process.

Colloidal Parameters

Variation of the particle size (diameter, D) in the emulsion polymerization of butyl acrylate with the additive and the reaction time is summarized in Fig. 1. These results indicate that the particle growth is most pronounced at the beginning of polymerization. The addition of SiO_2 favours the formation of smaller and larger number of composite (polymer/IUP) particles. The small particles may result also from the depressed aggregation of primary particles at the beginning of the polymerization.

Variation of the particle size or number of particles with the type and the amount of IUP in the emulsion polymerization of BA is summarized in Fig. 6. These results show that SiO_2 and TiO_2 have an opposite effect on the colloidal particle parameters, *i.e.* SiO_2 favours the formation of smaller particles while TiO_2 more favours agglomeration of existing particles. Results summarized in Figs. 2 and 6 indicate that the number of particles parallels the rate of polymerization. Thus, the rate of polymerization is a function of the particle concentration as suggested in the micellar model [16].

Variation in the particle size and the number of particles in the emulsion polymerization of MMA with the SiO_2 or TiO_2 amount is summarized in Figs. 7 and 8. We can see that the particle size in the run increases with TiO_2 . In other two runs the value of D is nearly constant. The number of particles in the runs was found to decrease with the IUP concentration for both TiO_2 and SiO_2 ($c(\text{APS})$ both runs). In

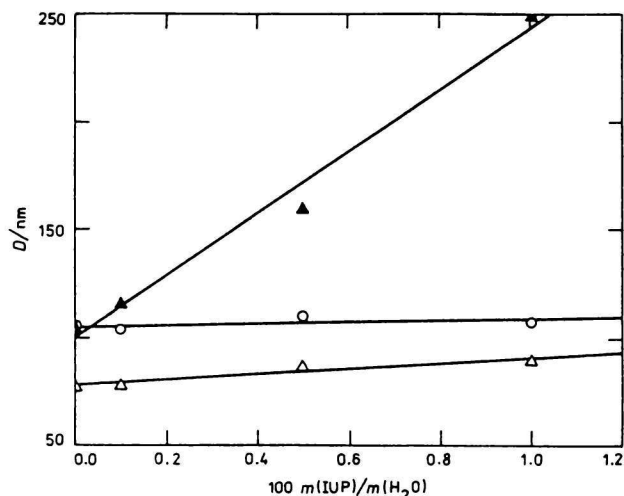


Fig. 7. Variation of the particle diameter (D) in the emulsion polymerization of MMA initiated by APS with the IUP amount. $c(\text{SDS}) = 0.01 \text{ mol dm}^{-3}$, $c(\text{APS}) = 0.00044 \text{ mol dm}^{-3}$ Δ with TiO_2 , \circ with SiO_2 . $c(\text{SDS}) = 0.01 \text{ mol dm}^{-3}$, $c(\text{APS}) = 0.001 \text{ mol dm}^{-3}$ Δ with SiO_2 .

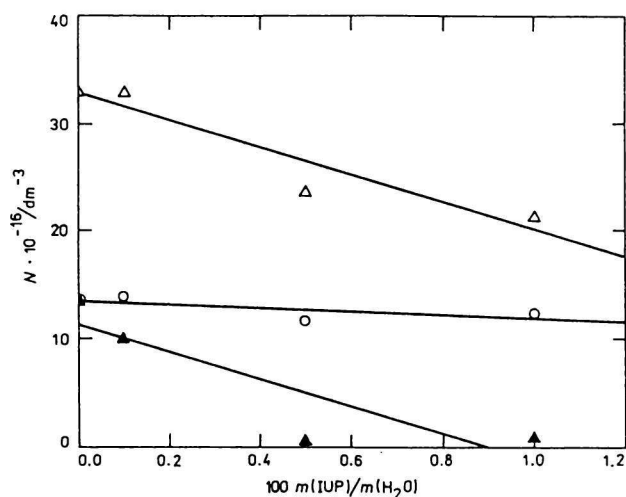


Fig. 8. Variation of the particle number (N) in the emulsion polymerization of MMA initiated by APS with the IUP amount. $c(\text{SDS}) = 0.01 \text{ mol dm}^{-3}$, $c(\text{APS}) = 0.00044 \text{ mol dm}^{-3}$ Δ with TiO_2 , \circ with SiO_2 . $c(\text{SDS}) = 0.01 \text{ mol dm}^{-3}$, $c(\text{APS}) = 0.001 \text{ mol dm}^{-3}$ Δ with SiO_2 .

the runs with a very low APS concentration, the colloidal parameters of dispersion are nearly independent of IUP concentration. The effect of $c(\text{SDS})$ on the colloidal parameters of composite particles in the emulsion polymerization of EA or BA is summarized in Figs. 9–11. The dependences of D or $\log N$ vs. $\log c(\text{SDS})$ are linear in all EA runs. In the systems with SiO_2 or without additive the particle size decreases and the number of particles increases with $c(\text{SDS})$, as expected. In the run with TiO_2 , however, D increases and N decreases with $c(\text{SDS})$. This may be discussed in terms of agglomeration of particles with $c(\text{SDS})$.

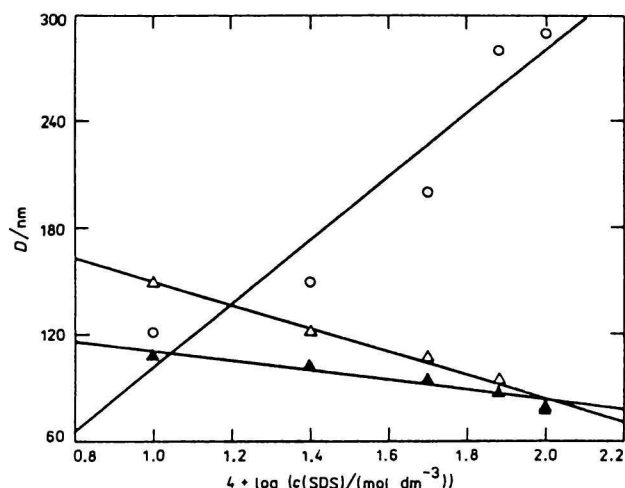


Fig. 9. Variation of the particle diameter (D) in the emulsion polymerization of EA initiated by APS with the SDS concentration. $c(\text{APS}) = 0.0044 \text{ mol dm}^{-3}$ Δ without additive, \circ with TiO_2 , \blacktriangle with SiO_2 .

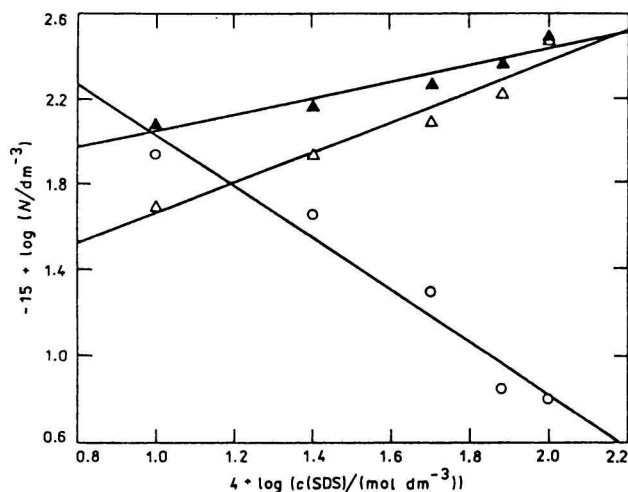


Fig. 10. Variation of the particle number (N) in the emulsion polymerization of EA initiated by APS with the SDS concentration. $c(\text{APS}) = 0.0044 \text{ mol dm}^{-3}$ Δ without additive, \circ with TiO_2 , \blacktriangle with SiO_2 .

According to the emulsion polymerization theory [17], the relation between the number of particles and the emulsifier concentration (c) can be expressed as $N \propto (c)^x$ where $x = 0.6$.

The observed values of x , however, differ from 0.6 and vary with the additive as follows

$-1.2 (\text{TiO}_2) < 0.4 (\text{SiO}_2) < 0.7$ (no additive) (for the EA system)

The value of 0.7 results from the higher hydrophilicity of EA or poly(EA). The decrease in x with IUP is caused by the increased agglomeration which is much more pronounced in runs with TiO_2 .

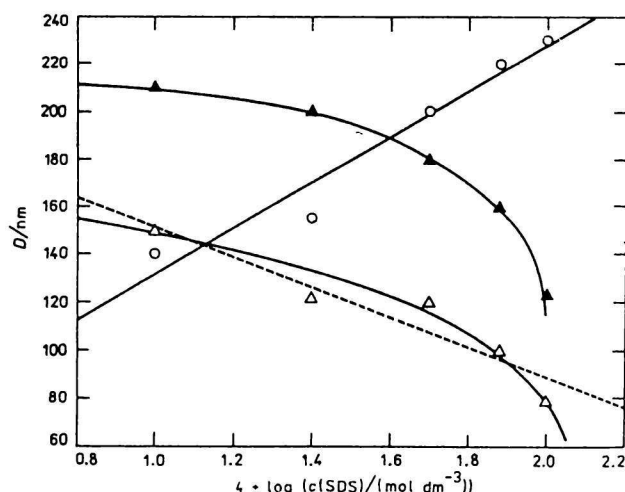


Fig. 11. Variation of the particle diameter (D) in the emulsion polymerization of BA initiated by APS with the SDS concentration. $c(\text{APS}) = 0.0044 \text{ mol dm}^{-3}$. Δ without additive, \circ with TiO_2 , \blacktriangle with SiO_2 .

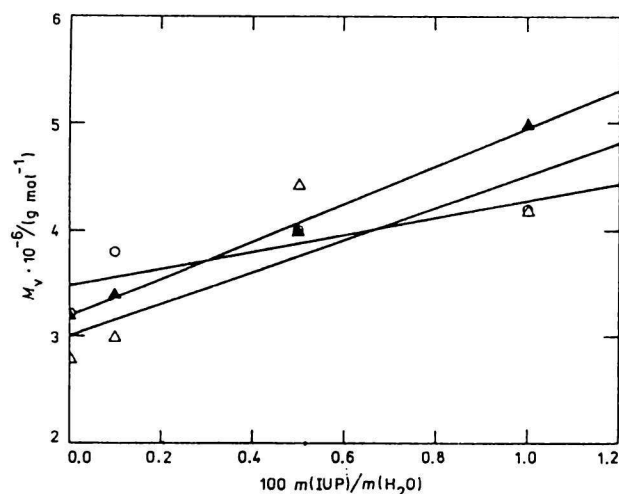


Fig. 12. Variation of the viscosity-average molar mass (M_v) in the microemulsion polymerization of MMA with the IUP amount. $c(\text{SDS}) = 0.01 \text{ mol dm}^{-3}$, $c(\text{APS}) = 0.00044 \text{ mol dm}^{-3}$. Δ with TiO_2 , \circ with SiO_2 . $c(\text{SDS}) = 0.01 \text{ mol dm}^{-3}$, $c(\text{APS}) = 0.001 \text{ mol dm}^{-3}$. \blacktriangle with SiO_2 .

In the BA runs the value of x varied as follows (obtained from the experimental dependences of $\log N$ vs. $\log c(\text{SDS})$)

$$-0.6 (\text{TiO}_2) < 0.6 (\text{SiO}_2) < 0.7 (\text{no additive})$$

These results are similar to those obtained for the emulsion polymerization of EA. Thus, the IUP additive initiates the agglomeration of particles which is more pronounced with TiO_2 .

Coagulum (in mass %) was found to vary with the IUP (0.5 g) type as follows ($c(\text{SDS}) = 0.005 \text{ mol}$

dm^{-3}): $4.8 (\text{TiO}_2) > 0.61 (\text{no additive}) > 0 (\text{SiO}_2)$ (for the BA runs). Thus, the latexes formed in the presence of SiO_2 are the most stable. In the MMA runs the large amounts of coagulum were found.

Surface tension (γ in mN m^{-1}) was found to decrease with increasing $c(\text{SDS})$ (as expected). The decrease was less pronounced in the systems with SiO_2 or TiO_2 . With increasing $c(\text{SDS})$ from $0.001 \text{ mol dm}^{-3}$ to 0.01 mol dm^{-3} surface tension ($\gamma/(\text{mN m}^{-1})$) decreased from 50 to 44 (no additive), 55 to 47 (SiO_2), and 53 to 45 (TiO_2), respectively. These results indicate that inorganic particles bind or adsorb some amount of emulsifier molecules. The effect is more pronounced with SiO_2 particles. Interaction of a IUP particle with emulsifier is expected to form a core/shell aggregate. Moreover, the porous SiO_2 particles may absorb some amount of both monomer and emulsifier. The monomer-saturated shell, thus, should favour the growth events and the formation of larger number of particles as well. This may be a reason why the smaller particles and higher rates are observed with SiO_2 particles. This is not a case with nonporous TiO_2 particles.

Relative Molecular Masses, resp. Molar Masses

It was observed that the poly(butyl acrylate) (PBA) formed in the presence of SiO_2 or TiO_2 is insoluble in solvents for PBA. This behaviour indicates that the crosslinked polymer products were formed. On the contrary, the emulsion polymerization of MMA in the presence of SiO_2 or TiO_2 produces soluble PBA. Fig. 12 shows that the viscosity-average molar mass of the polymer slightly increases with increasing the IUP amount. The polymer/IUP medium, thus, depresses termination of growing radicals.

CONCLUSION

The addition of inorganic SiO_2 ultrafine particles favours the formation of small composite particles, which is attributed to the formation of emulsified SiO_2 particles and to the polymerization in the monomer-swollen shell and the surface pores.

The (nonporous) TiO_2 particles act as a promoter of coagulation which leads to larger particles and/or coagulum. Variation in the rate of polymerization with the type and concentration of IUP is discussed in terms of interaction of IUP with emulsifier or initiator molecules, the increased concentration of monomer in the vicinity of the particle surface layer or in the pores of inorganic particles, and the depression of the termination.

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