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Kinetics of Styrene and Butyl Acrylate Polymerization in Anionic Microemulsions in Presence of Layered Silicates

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The effect was studied of various layered silicates (sodium montmorillonite and different organomodified montmorillonites) on kinetics of styrene (St) and butyl acrylate (BuA) in anionic (sodium dodecyl sulfate) microemulsion polymerization. The dependence of the polymerization rate on the conversion exhibits two rate intervals. The presence of layered silicates affects the conversion and polymerization rate of both St and BuA. The size of polymer particles increases with polarity of Cloisite and the increase is more pronounced in poly(butyl acrylate) particles. The kinetic, colloidal and molecular weight parameters are influence both by the monomer and layered silicate polarities. Different approaches (Ugelstadt, Nomura and Gilbert models) were used for evaluation of polymerization kinetics. The desorption constants (k_{des}) decrease in presence of the studied layered silicates (Cloisite Na, Cloisite 30B, Cloisite 20A). The decreasing values of the desorption constants in the presence of clays; demonstrate a clear effect, which implies the decreasing of the probability of the radical exit from particles in the presence of the layered silicates.
KEY WORDS: Microemulsion Polymerization / Layered Silicates / Kinetics / Nanolatexes / Nanocomposites /

The synthesis of nanoclay composites from dispersed systems exhibit an increased interest in the last years. The main reasons include the encapsulation of layered silicates, nanolayer stabilization, *in situ* polymerization of the monomers in intergalleries of the layered silicates and the possibility of obtaining hybrid particles and nanoparticles.[1–5] Even through the numerous reports about emulsion, miniemulsion and suspension polymerization of different monomers in presence of layered silicate can be found in the literature, the kinetics data are rather rare.[1,6,7]

Some other papers[8,9] deal with the bulk polymerization of selected monomers, for example methyl methacrylate in presence of montmorillonite (MMT). It was found that an optimal ratio of MMT/initiator (benzoyl peroxide) promotes an increase in the polymerization rate of methyl methacrylate.[8] Presence of an organomodified montmorillonite also increases the polymerization rate of styrene in bulk polymerization.[9] In the case of emulsion polymerization of styrene the reaction rate is enhanced by the presence of sodium montmorillonite, however the study handles only one level of inorganic filler.[10]

In the miniemulsion polymerization of styrene in presence of laponite the silicate layers can be on the surface of the particle but also inside the emulsion-latex particle depending on the initiator nature.[7] In suspension polymerization of styrene in presence of different organophilic montmorillonites silicates are likely also inside the particle.[11] For suspension polymerization of methyl methacrylate in presence of organophilic montmorillonite the clay layers are situated both inside and on the surface of the latex particles.[12] In this case, the kinetics of the monomer polymerization is much influenced by the presence of clay. Van Herk *et al.* reported the presence of clays

inside the latex particle by using a coupling systems based on titanium or silica precursors.[13]

Concerning the layered silicates–initiator interactions the overall view of the process must take into account at least some aspects: the modification of polarity brought by the clay presence in the dispersion media;[14] the possibility of adsorption on the clay surface of the persulfate counterion[15,16] or the interaction of the sulfate ion on acid bridges of the middle crystal of the aluminosilicate structure.[14]

In previous studies[17,18] we have reported the dependence of clay mineral swelling capacities on the different monomers polarity. For sodium montmorillonite swelling capacity was found to be more than 100 wt. % for acrylic monomers. Another important argument related to monomer-clay interaction is related by the expansion of d_{001} (interlayer distance of (001) reflection plane) specific to clay galleries when the montmorillonite is dispersed in the monomer phase.[12] In perspective clays d_{001} is very much affected by the presence of different organic solvents.[19,20] The Cloisite Na+ has a basal spacing of 11.7 Å; the quaternary commercial organoclays Cloisite 20A and 30B have d-spacing of 24.2 and 18.5 Å in that order.[21] The solubility parameters depend on dispersion and polar interactions, as well as on hydrogen bonding related to the solvent. The most important parameter however is considered the dispersion which is determinant for clay exfoliation.

We have already reported the kinetics data on emulsion polymerization of vinyl acetate with different stabilizing systems (anionic, nonionic and protective colloids).[22–26] In the studied systems usually the presence of montmorillonite enhances both the conversion and the polymerization rate of

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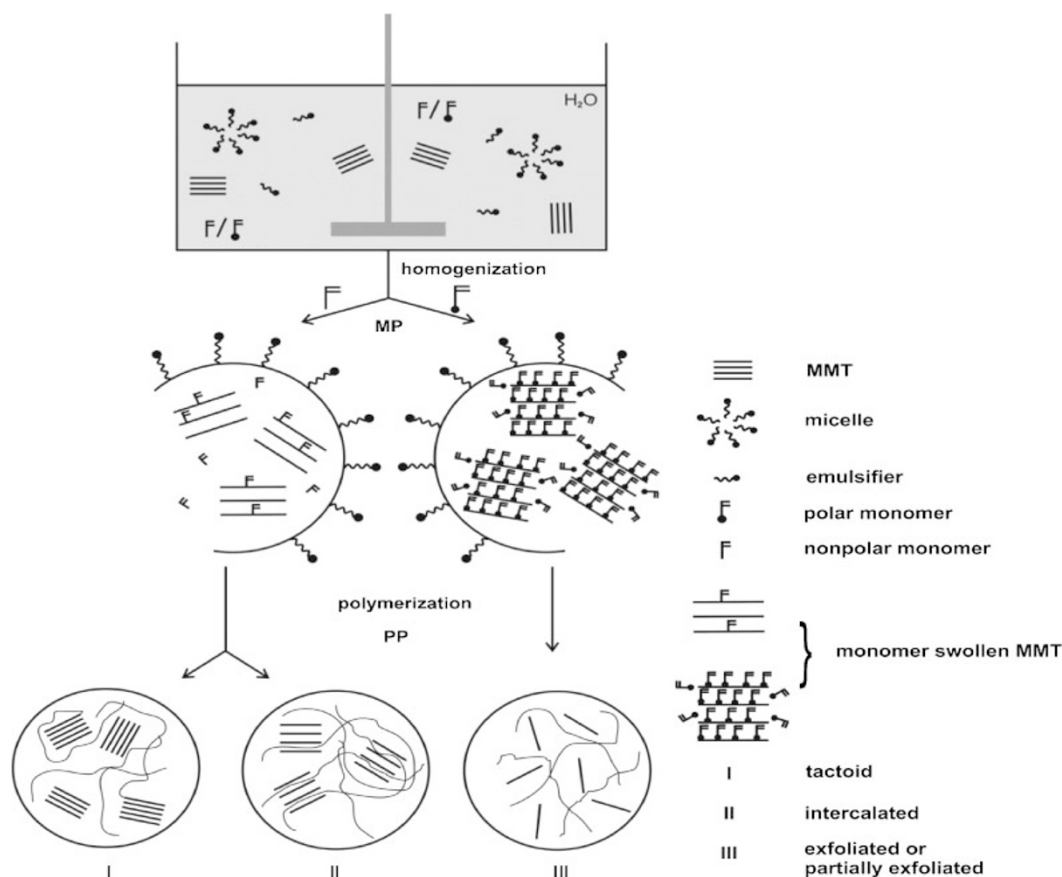
Scheme 1. The mechanistic routes of polymer-montmorillonite nanocomposites formation in the mini- or microemulsion polymerizations of polar and nonpolar monomers.

the monomer. However in some cases for high concentration of layered silicate related to monomer (over 12.5 wt. %) a small decrease of the process intensity can be observed.

Involving the microemulsion polymerization of acrylic monomers we reported some contributions regarding the kinetic behavior.[27–31] In previous papers we have studied also the conditions of obtaining polymer-clay stable latexes, with controlled dimension of the particles and polymer-clay nanocomposites through microemulsion polymerization.[32,33] In specific conditions hybrid nanolatexes are achieved.

To analyze the dispersion states and the basal spacing expansion of natural montmorillonite in organic liquids, Choi *et al.* have used the Hansen solubility parameters.[34] The hydrogen bonding components (δ_h) and the polar components (δ_p) of liquids are the primary parameters for the dispersion states and for the basal spacing expansion. The degree of expansion by monomers reflects the structure of polymer-MMT nanocomposites: large basal spacing produces exfoliated structures and small basal spacing produces interacted structures. The correlation between the basal spacing expansion and the structure of polymer-MMT nanocomposites is reasonable because the polymerization rate depends on the monomer concentration. Both δ_h and δ_p involve dipole-dipole interactions, monomer dipole moments are associated with the basal spacing expansion that is related to the structure of polymer-

MMT nanocomposites. Furthermore, because monomers with high dipole moment values enlarge the basal spacing, the monomer dipole moments are a useful tool for predicting the structure of the polymer-MMT nanocomposites prepared *via in situ* polymerization methods. The basal spacing expansion depends on polar components (δ_p) and hydrogen-bonding components (δ_h) of organic liquids. Liquids with high δ_h values showed expansion in the order of methyl alcohol > ethyl alcohol > 2-propyl alcohol > n-hexane > toluene > benzene, and monomers with high δ_p values exhibited expansion in the order of n-butyl acrylate > acrylonitrile > methyl methacrylate > styrene. Because dipole-dipole interactions involved both δ_h and δ_p, liquid dipole moments were adopted to explain the expansion of MMT in polymer-MMT nanocomposites. Monomers with high dipole moments showed large basal spacings before polymerization and produced exfoliated polymer-MMT nanocomposites, whereas those with low dipole moments showed smaller basal spacings and produced intercalated polymer-MMT nanocomposites (Scheme 1). Intercalation implies the insertion of one or several polymer chains in the galleries of the original layer tactoids, which leads to some longitudinal expansion of the galleries. Exfoliation (delamination) implies complete breakage of original layer stacking order and homogeneous dispersion of layers in the polymer.[35]

In this paper we study the influence of selected layered silicates, montmorillonite type (Cloisite Na, Cloisite 30B, and Cloisite 20A) with different polarity on the kinetic, colloidal and molecular weight parameters of microemulsion polymerizations of nonpolar styrene or polar butyl acrylate. The intercalation of the polar and nonpolar monomer and their polymer in Na^+-montmorillonite, provides compact three-dimensional nanocomposites with interesting functional properties. Monomer is located in two domains within the particle: the clay interlayer spaces and the polymer phase. A polar BuA is expected to show larger basal spacing before polymerization and produce intercalated or partially exfoliated polymer-MMT nanocomposites, whereas unpolar St should show smaller basal spacing and produce partially intercalated polymer-MMT nanocomposites (Scheme 1). The restricted penetration of monomer into the interlayer space is expected to slow the overall rate of polymerization. This can be also related to the more complex fate of radicals formed by the chain transfer events within the clay interlayer spaces. The polymerization mechanism of nanocomposite formation is discussed in terms of variations of the maximum polymerization rate ($R_{p,max}$), particle dimensions (d_p), number of polymer particles (N_p), average number of radicals per particle ($\bar{n}$), desorption rate constants (k_{des}) of radicals from particles and viscosity average molecular weight (M_v) with the reaction conditions and the type of monomer and clay.

EXPERIMENTAL

Materials

Styrene (St) and butyl acrylate (BuA), commercial products were purified by rectification, before use. Sodium dodecyl sulfate (SDS) was provided by Sigma-Aldrich and ammonium persulfate (APS) was purchased from Loba Feinchemie. Both were used without further purification. Twice-distilled water was used as dispersion medium. Layered silicates were provided by Southern Clay Products Inc. and used as received. The used layered silicates montmorillonite type were used in different forms: sodium form (Cloisite®Na (Cl Na); 92 meg/100 g), organomodified with different quaternary ammonium salts (methyl, tallow, bis-2-hydroxyethyl)-(Cloisite® 30B (Cl 30B); 90 meg/100 g), (dimethyl, dihydrogenated tallow)-(Cloisite® 20A (Cl 20A); 95 meg/100 g).

Procedures

Batch microemulsion polymerizations were carried out at 65 °C. The polymerization mixture consisted of 1.74 g monomer, 3.86 g SDS, 19.32 g water, 0.07 g APS (for St polymerizations) or 0.007 g APS (for BuA polymerizations). Water was removed by evaporation at 105 °C for 4 h. First the water surfactant mixture was prepared and then the inorganic partner (Cloisite − 0.239 g) was added under sonication. The mixture was sonicated for more than 30 min (depending on Cloisite type) until the Cloisite was well dispersed in the water system. The monomer was added under mechanical stirring to the previous mixture. The initiator was used as a water solution to achieve its better distribution in the dispersion system. All the components were kept under nitrogen atmosphere. Before starting the polymerizations all the mixtures were bubbled with nitrogen gas to remove oxygen. The polymerization started when the systems were brought to 65 °C (polymerization temperature).

The kinetics of polymerization was followed by the dilatometry. A glass dilatometer (volume 12 mL) equipped with a glass capillary (0.983 mm) was used. The microemulsion was directly introduced in the dilatometer using a syringe. The dilatometer was placed in a constant temperature bath and the volume change of the polymerizing system, which is quantitatively related to the percent conversion, was followed with time. The lowering of the liquid level was detected at different polymerization times by means of a cathetometer (KM-8, Russia). The polymerization kinetics was followed by recording the variation of the height of the liquid in the capillary as a function of time. Temperature at the dilatometer wall was monitored using a thermocouple with an accuracy of 0.1 °C. The results for the polymerization kinetics were expressed as a percentage conversion of the monomer to the polymer. After a present time, the content of the dilatometer was poured into large amount of ethanol and the product was isolated by filtration and then dried to a constant weight.

### Polymer and Latex Characterization

The average particle sizes were determined by the light scattering method using Particle Sizer Model BI-90, Brookhaven Instruments Corp. Limiting viscosity numbers [η] of poly(butyl acrylates) and poly(styrenes) were determined with Ubbelohde viscometer either in acetone (butyl acrylate) or in toluene (styrene) at 25 °C.

RESULTS AND DISCUSSION

Dilatometry is a very tempting method to achieve large number of experimental data for polymerization processes which some times is rather hard to obtain by gravimetry. However the reproducibility of these kinds of measurements is not every time easy to achieve. The main advantage of involving dilatometry in this study of polymerization processes remains the possibility to obtain the information without interfere the process. The bulk polymerization of styrene in presence of LS was studied before.[9] The microemulsions were found to be thermodynamically stable. Under these conditions dilatometry may be a required method to study kinetics of polymerization.

Variation of monomer conversion in the microemulsion polymerization of St with the reaction time for various types of Cloisite is summarized in Figure 1.

The curves are concave downward and the polymerization is found to be relatively fast. The data indicate that the conversion of *ca.* 80% is reached in *ca.* 15 min. In all cases the colloidal stable polymer latexes were formed. The presence of the different layered silicates influences the polymerization
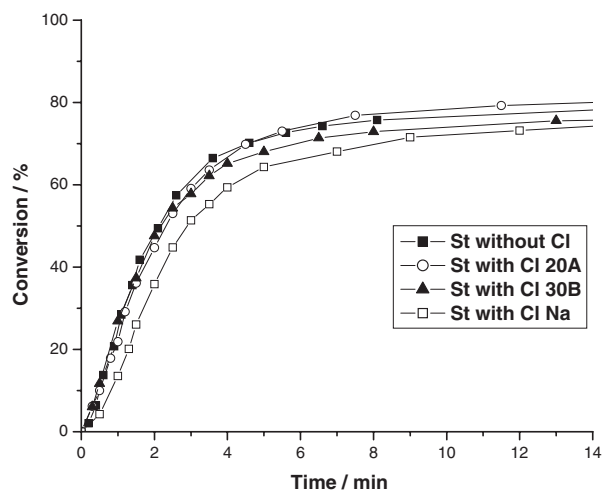
Figure 1. Variation of monomer conversion with the reaction time and presence of Cloisite in the microemulsion polymerization of St. Recipe: 1.74 g styrene, 19.32 g water, 3.86 g SDS, 0.07 g APS, 0.239 g Cloisite.
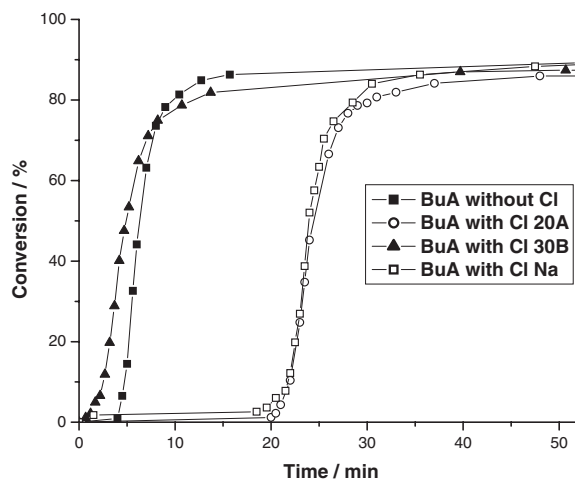
Figure 2. Variation of monomer conversion with the reaction time and presence of Cloisite in the microemulsion polymerization of BuA. Recipe: 1.74 g BuA, 19.32 g water, 3.86 g SDS, 0.007 g APS, 0.239 g Cloisite.

process of the monomers in the microemulsion systems. It is evident from the conversion plots the influence of the layered silicates nature on the polymerization process depends on the polarity ratio between monomer and the inorganic partner. For example in the case of St as the difference of Cloisite polarity decreases the final conversion is higher. The systems ClNa-St showed a lower conversion than the sample without inorganic filler. This behavior could be explained by the higher polarity of ClNa. Cloisite 30B has polar ethanol end groups of organic modifiers but 20A has only saturated alkyl groups. Presumably the organic modifier of 30B organoclay is more polar than that of 20A organoclay.

In the case of BuA (Figure 2), the inhibition period in two samples with Cloisite is observed. The conversion of monomer begins to increase later (since *ca.* 20 min.) and the final conversion is reached in about 45 min. As Figure 2 shows, the highest conversion is reached for the system with ClNa (in contrast to polymerization of St). This can be attributed to more polar character of monomer (BuA in comparison with St).

These observations involving the difference of polarity can be related also by the swelling capacity with St and BuA of layered silicates with different hydrophobic character previously reported.[6,18,22,24,25] For example the swelling capacity of ClNa with St exceeds 100 wt.% while by using Cl 20A (less polar than ClNa) the swelling capacity can exceed 300 wt.%.

By considering the two aspects showed above one can take into account that as the polarity differences between monomer and the inorganic filler decrease the polymerization reaches higher conversions.

The final conversion of the St decreases in presence of different kinds of clays, however for the BuA an opposite tendency is observed. For the maximum reaction rates of St in presence of clays, the calculated values evidence small difference related to the system without inorganic filler, but in the case of BuA a decreasing tendency is more obvious.

Besides, the polymerization reaches the limiting conversion *ca.* at 80–90%. The limiting conversion can't be ascribed to the consumption of initiator because the half time of APS is much above 50 h at 60 °C.[36] The low T_g for PBuA disfavors the glassy state approach. The appearance of the limiting conversion can be discussed in terms of the low monomer concentration at the reaction loci and the low radical entry efficiency. The low concentration of monomer at the reaction loci results from the main location of monomer in the dead monomer/polymer particles and/or the mixed (monomer/emulsifier) micelles. The depressed transfer of monomer from the monomer/polymer particles and/or mixed micelles through the aqueous phase to the reaction loci strongly depresses the rate of polymerization. The depressed flux of monomer through the aqueous phase disfavors the formation of surface active oligomeric radicals which enter the dead monomer/polymer particles. The synergistic effect of BuA which acts as a co-emulsifier, increases with SDS concentration.[37,38] Under the present reaction condition, the co-emulsifier properties of BuA are nearly comparable with those of 1-pentanol.[37] This can enhance the monomer concentration in inactive mixed micelles. The penetration of monomer into the interfacial zone increases the total surface area or the number of mixed micelles. If the monomer concentration in micelles is much below a certain critical level then the entry of radical may not initiate the polymerization. These micelles thus can strongly compete with the polymer particles in capturing radicals and the formation of polymer.

Variation of the polymerization rates of styrene with conversion in presence of Cloisite are demonstrated in Figure 3. It can be described by a curve with two rate intervals.

The rate of polymerization (R_p) first increases up to a maximum ($R_{p,max}$) and then decreases to the final conversion. The initial increase in the polymerization rate can be attributed to the robust particle nucleation and to the monomer saturation condition. The maximum polymerization rate lies in the
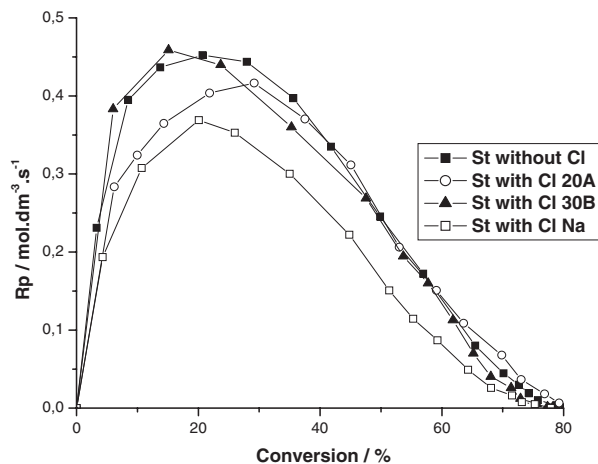
Figure 3. Dependence of the polymerization rate (R_p) on conversion in the microemulsion polymerization of St. Recipe: 1.74 g St, 19.32 g water, 3.86 g SDS, 0.07 g APS, 0.239 g Cloisite.
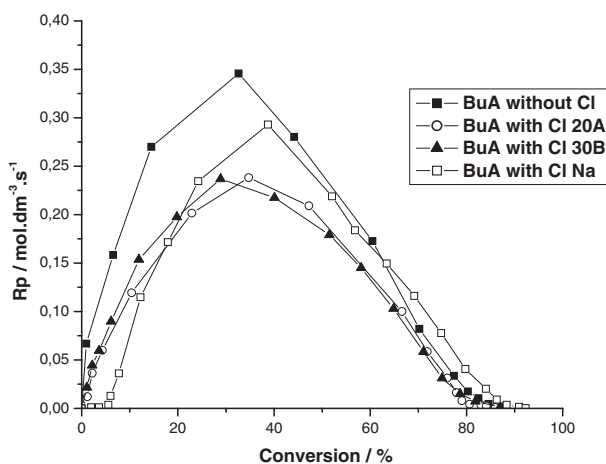
Figure 4. Dependence of the polymerization rate (R_p) on conversion in the microemulsion polymerization of BuA. Recipe: 1.74 g BuA, 19.32 g water, 3.86 g SDS, 0.007 g APS, 0.239 g Cloisite.

conversion range 15 to 30%. The values of $R_{p,max}$ vary from 369×10^{-3} mol·dm^{-3}·s^{-1} (St with ClNa), over 426×10^{-3} mol·dm^{-3}·s^{-1} (St with Cl 20A) to 465×10^{-3} mol·dm^{-3}·s^{-1} (St with Cl 30B).

Variation of the polymerization rates with conversion and type of Cloisite in polymerization of BuA are illustrated in Figure 4. Under the present reaction conditions (the high SDS concentration), the penetration of BuA into the interfacial layer is increased due to which the number of monomer/swollen micelles is increased. At high SDS concentration, the dissociation degree of SDS and the dielectric constant of water decreased while the counterion binding of SDS in the aqueous phase increased.[39] This is accompanied with increased amount of BuA in the interfacial layer and in the aqueous phase. The similar behavior but in the lower extend might appear with above mentioned styrene polymerization. Both increase the aqueous phase polymerization and the flux of monomer from monomer droplets to the reaction loci.

Table I. Variation of kinetic and colloidal parameters with the Cloisite type in the emulsion polymerization of BuA

Cloisite	Con.$_f$ (%)	$R_{p,max} \times 10^3$ (mol·dm^{-3}·s^{-1})	d_p (nm)	$N_p \times 10^{-19}$ (dm^3)	$\bar{n}$ (particle)
—	87	346	33	0.418	0.927
Cl 20A	86	238	45	0.161	1.658
Cl 30B	87	237	55	0.089	2.955
Cl Na	92	293	94	0.019	17.324

The positions of the maximum polymerization rates are located at the conversion of *ca.* 35%, which is later than in polymerization of styrene. Figure 4 also shows that the curves are broader and the values of maximum rate of polymerization are lower than in system with St. The highest $R_{p,max}$ (346×10^{-3} mol·dm^{-3}·s^{-1}) was observed in system without Cloisite.

In Table I, kinetic and colloidal parameters of BuA and their variation with the type of Cloisite are collected. As can be seen, diameters of the latex particles (d_p) increased in presence of layered silicates. This is also related to the silicate polarity. As the polarity of the inorganic partner increases, the average diameters of the latex particles increase or the colloidal stability of polymer particles decreases. The surface area of emulsifier increases with Cloisite. This behavior could be related also to the polarity by a higher hydration level. Table I also shows that N_p, which is the number of final polymer particles per unit volume of the continuous phase, decreases with the increasing polarity of Cloisite.

The polymerization rate decreases by the addition of Cloisite. This is related to the decrease of the monomer concentration at the reaction loci, the number of polymer particles, and the average number of radicals per particle ($\bar{n}$). Monomer is located in two domains within the particle: the clay interlayer spaces and the polymer phase. The restricted penetration of monomer into the Cloisite clusters probably slows the rate of polymerization. The increased contribution of polymerization within the interlayer domains decreases the overall rate of polymerization. Polar BuA is expected to easily penetrate the interlayer spaces than unpolar St. The pre-adsorbed monomers attract reactants to the interlayer spaces during the polymerization. The more monomers in the basal spacing the faster the polymerization rate within the Cloisite cluster.

The $\bar{n}$ was estimated from the polymerization rates divided by the number of particles and the appropriate constants. The values of $\bar{n}$ depend on the mechanistic events such as the decomposition rate of initiator, the entry of oligomeric radicals into the particles, the nature of the reaction loci, the chain transfer to monomer, the desorption of radicals from particles, etc. As Table I show, the number of radicals in the particles increases with the polarity of Cloisite, and we can see that the values are relative high even for the pure BuA. We have earlier reported that $\bar{n}$ lies well below 0.5 for the small PBuA particles with diameter around and below 50 nm.[40,41] In the present paper $\bar{n}$ is *ca.* 0.9 for the weight ratio BuA/SDS (9.0/20) = 0.45. When the weight ratio BuA/SDS is increased to 0.5 and 1.0 $\bar{n}$ decreased to 0.6–0.3 and below 0.1. The reactions proceeded in all runs *ca.* under the same reaction conditions.

Table II. Variations of kinetic and colloidal parameters with the Cloisite type in the emulsion polymerization of St

| Cloisite	Con.$_f$ (%)	$R_{p,max} \times 10^3$ (mol·dm^{-3}·s^{-1})	d_p (nm)	$N_p \times 10^{-19}$ (dm^3)	$\bar{n} \times 10^5$ (particle)
—	81	452	26	0.795	2.90
Cl 20A	83	426	29	0.585	3.71
Cl 30B	78	465	34	0.340	6.98
Cl Na	78	369	38	0.243	7.74

The comparison of the $\bar{n}$ values as a function of BuA/SDS weight ratio leads to the conclusion that $\bar{n}$ is inversely proportional to the BuA/SDS weight ratio. At high SDS and low BuA concentrations, the penetration of BuA and/or its radical is increased due to which the number of radicals increases.

Table II shows that the estimated kinetic parameters for polymerization of St are similar to those obtained for the polymerization of BuA, but the variations are somewhat less distinct. With increasing polarity of Cloisite, the values of d_p and $\bar{n}$ increased, but the values of N_p decreased.

The comparison of the diameters of the PSt and PBuA latex particles (d_p) are illustrated in Figure 5. The size of polymer particles was found to increase with the polarity and the increase is more pronounced in poly(butyl acrylate) particles.

Formation of larger particles is accompanied with the higher accumulation of radicals in the larger particles and with the decreased desorption of monomeric radicals from particles.

Figure 6 shows that the number of polymer particles decreased with the addition of Cloisite, which can indicate poor particle nucleation. The particle size and number vary with the area of emulsifier molecules (stability, see above) and the particle nucleation mode. The homogeneous nucleation is operative with polar BuA monomer even in the microemulsion systems.[42] The micellar nucleation dominates in the micro-emulsion polymerization of St and early in the microemulsion polymerization of BuA. When the microdroplets vanish from
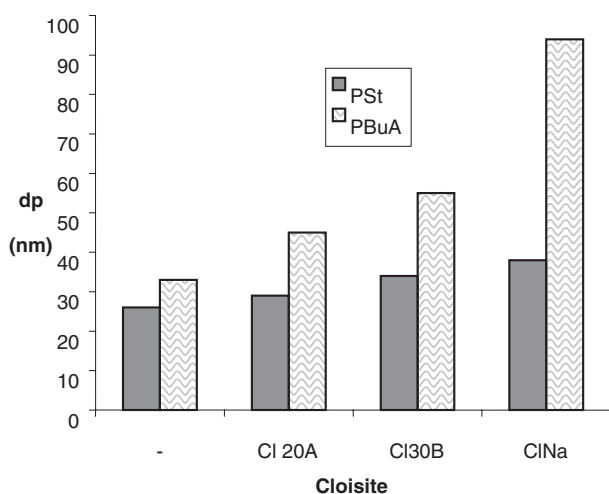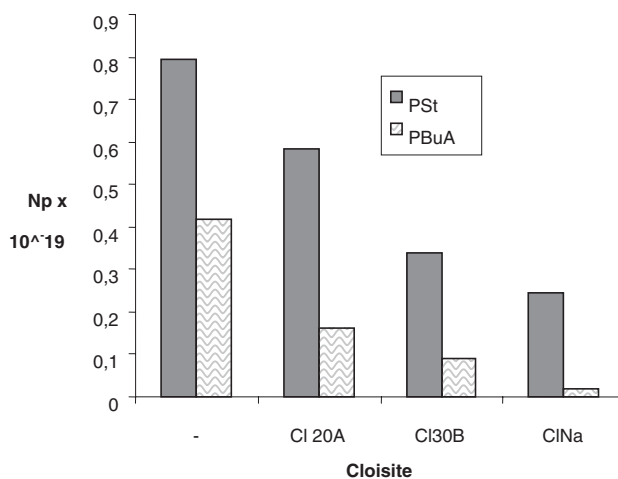
Figure 6. Variation of the number of final polymer particles per unit volume with the type of Cloisite.

the polymerization system, homogeneous nucleation takes over and the longer chain oligomeric radicals form in the aqueous phase and then adsorb emulsifier to become the loci for further polymerization. Cloisite is expected to partition between the monomer microdroplets and water. Monomers and initiator (radicals) easily penetrate the interlayer spaces through the aqueous phase. The high concentration of emulsifier and Cloisite favours the interactions between radicals, amphiphiles and Cloisite which can increase the hydrophobic nature and colloidal stability of the intermediate clusters. The former can enhance the flux of monomer into the reaction loci. The heterocoagulation of unstable latex particles or intermediate cluters can increase the particle size which seems to be more pronounced in the BuA systems.

The numbers of radicals per particle ($\bar{n}$) of polystyrene are well below 0.5 (Figure 7), which indicates extensive desorption of monomeric radicals from polymer particles. The values of $\bar{n}$ slightly increase with increasing polarity and particle size. Figure 7 also indicates that the $\bar{n}$ values are by *ca.* 3–4 orders in magnitude larger for BuA in comparison to St. The accumulation of surface active BuA monomeric radicals in the interfacial layer is supposed to be one of the possible reasons for this difference.

The specific desorption rate constants k'_{des} (cm^2·s^{-1}) and k_{des} (s^{-1}) were calculated with three models (Ugelstadt/O'Tool model, Nomura model and Gilbert model).[43,44] The details of these calculations are given in our previous paper.[45] The specific desorption rate constant k_{des} (s^{-1}) is related to k'_{des} (cm^2·s^{-1}) by the following equations:[43]

$$k_{des} a_p / v_p = k'_{des} / [(\pi/6)^{2/3} d^2_p] \tag{1}$$

The exit rate constants (calculated by all proposed models Ugelstadt, Nomura, Gilbert) are shown in Tables III and IV.

For both BuA and St, desorption constants (k_{des}) decrease with addition of Cloisite. The chain transfer to monomer and desorption of monomeric radicals from the polymer particle decreases the concentration of radicals in the polymer

Figure 5. Variation of the diameter of the PS and PBuA latex particles with the type of Cloisite.
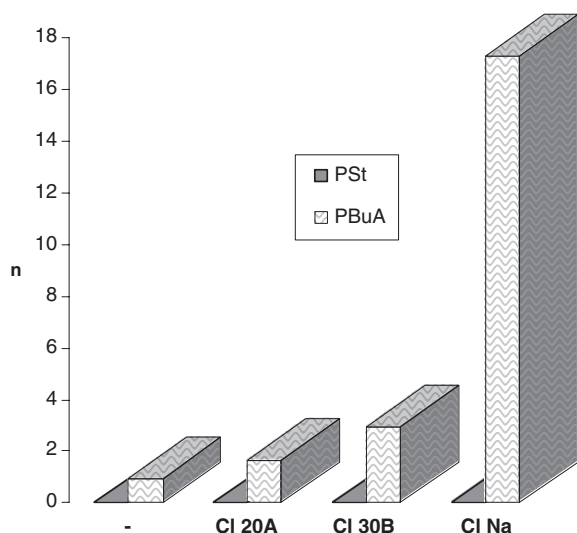
Figure 7. Variation of the average number of radicals in a particle of the PSt and PBuA with the type of Cloisite.

Table III. Variation of desorption rate coefficients with Cloisite type in the emulsion polymerization of butyl acrylate

Cloisite	k_{des} (s^{-1})	
	Nomura	Gilbert
—	15.545	0.966
Cl 20A	8.359	0.568
Cl 30B	5.596	0.394
Cl Na	1.916	0.142

Table IV. Variation of desorption rate coefficients with Cloisite type in the emulsion polymerization of styrene

Cloisite	k_{des} (s^{-1})		
	Ugelstadt	Nomura	Gilbert
—	0.685	0.168	0.115
Cl 20A	0.564	0.135	0.092
Cl 30B	0.274	0.098	0.067
Cl Na	0.312	0.078	0.054

particles.[46] But in presence of layered silicates the number of radicals in the polymer particles strongly increases and on the other hand, desorption of monomeric radicals decreases. These data are showing that layered silicates are acting as a barrier for radical's desorptions. The penetration of monomer into the interlayer space and its polymerization can lead to the immobilization of growing radicals. This can be attributed also to the change of polymer chain conformation by the intercalation of polymer chains.[47] The depressed reactivity of intercalated polymer radicals is accompanied by depressed rates of both addition and chain transfer events. In the former case the overall rate of polymerization slows down. In the latter one the concentration of monomer radicals is lower. Furthermore, the monomer radicals are supposed to be intercalated and therefore their desorption rate from polymer particles is depressed.

The viscosity-average molecular weights (M_v) were calculated from the limiting viscosity numbers (intrinsic viscosities) [η] at 25 °C using the Mark-Houwink equation:

Table V. Variations of molecular weight parameters with the Cloisite type in the emulsion polymerization of butyl acrylate

Cloisite	$[\eta]$ (cm$^3 \cdot$g^{-1})	M_v ×10^{-5}
—	0.8158	7.072
Cl 20A	0.4488	3.528
Cl 30B	0.4546	3.770
Cl Na	0.8260	4.385

Table VI. Variations of molecular weight parameters with the Cloisite type in the emulsion polymerization of styrene

Cloisite	$[\eta]$ (cm$^3 \cdot$g^{-1})	M_v ×10^{-5}
—	0.0208	4.115
Cl 20A	0.1873	0.148
Cl 30B	0.3643	0.230
Cl Na	0.2211	1.843

$$[\eta] = K \cdot M_v^a \qquad (2)$$

where K and a are Mark-Houwink constants dependent on the type of polymer, solvent, and the temperature of the viscosity determinations. In the present work the values of K and a, for PBuA as a polymer and acetone as a solvent, are 0.685×10^{-4} and 0.75, and for PSt in toluene are 1.34×10^{-4} and 0.71, respectively.[36]

The measured values of limiting viscosity numbers [η] and viscosity-average molecular weights (M_v) of polybutylacrylate and polystyrene are listed in Tables V and VI.

The viscosity-average molecular weights in samples without Cloisite are found to be relatively high, and they are decreasing in presence of Cloisite. The decrease in M_v with increasing radical concentration disfavors the classical bimolecular termination. This can result in the favor of primary radical termination. Three months aging of polymer (PBuA and PSt)/ clay dispersions at room temperature led to the formation of crosslinked polymer/clay nanocomposites. This can be discussed in terms of intercalation and exfoliation of Cloisite by polymer chains and their reactions with clay. The presence of the Fe^{3+}, Mn^{2+} ions in the Cloisite and initiator APS can form redox system, which continuously generate radicals even at a room temperature within the clay and polymer chains. The combination of these radicals forms crosslinked polymer net or the percolating network of MMT nanoparticles in the polymer matrix.

The above observed kinetic behavior could be related with previously observed data for emulsion polymerization of vinyl monomers in presence of layered silicates.[10,17,22–25] For emulsion polymerization there is a certain ratio monomer/ nanoclay (1: 0.125 wt.) until the polymerization rates are increased in the presence of layered silicate. Over this ratio the reaction rates are decreased. Taking into account that the ratio used for these experiments was 1: 0.138 wt. monomers to nanoclay, the decreasing reaction rates could be explained by the large amount of layers which can induce a physical barrier effect for the radical propagation process. This behavior must

be observed in relation with the desorption constants (for all calculated models) which suggest a smaller probability of the radicals exit in the presence of the layered silicates.

CONCLUSIONS

The influence of various layered silicates, montmorillonite type with different polarity, on the styrene and butyl acrylate emulsion polymerizations was investigated. For comparison, the corresponding polymerizations in the absence of layered silicates were also carried out.

The experimental data showed that the polymerization mechanism of nanocomposite formation is influenced by the polarity differences between partners. The kinetic, colloidal and also the molecular weight parameters of microemulsion polymerization of styrene and butylacrylate are directly proportional to the clay polarity. The decreasing values of the desorption constants calculated by all used models (Ugelstadt, Nomura, Gilbert) in the presence of clays, showed a clear effect induced by the presence of the inorganic layers, which implies the decreasing probability of the radical exit in the presence of the layered silicates. The depressed reactivity of intercalated polymer radicals is accompanied by depressed rates of both addition and chain transfer events.

The viscosity-average molecular weights are decreasing in presence of Cloisite. The decrease in M_v with increasing radical concentration disfavors the classical bimolecular termination. This can result in the favor of primary radical termination.

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