INFLUENCE OF GLASS TRANSITION TEMPERATURE ON LATEX PARTICLE MORPHOLOGY

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SUMMARY: The effect of the combination of second stage reaction temperature and seed polymer glass transition temperature (T_g) on particle morphology was studied by using a polar seed polymer and a non-polar second stage polymer. Copolymers having different ratios of MMA and MA, and thus different T_g's, were made as seed polymers. The seed copolymers had T_g's in the 52-98 °C range and were used in reactions with styrene as the second stage monomer. The styrene was fed over 3.3 hours to the reactor, which was controlled at temperatures between 50 and 70 °C.

The equilibrium morphology for these systems was inverted core-shell but it is clear from these studies that it is relatively easy to keep the non-polar second stage polymer from penetrating the seed particle when the reaction temperature is less than about 15 °C above the seed polymer T_g for slow monomer feed rates. The second stage polystyrene was found to penetrate the seed particle to different extents as the reaction temperature was increased while keeping the same radical flux to the particles.

Introduction

The control of latex particle morphology has become an increasingly important subject since the latex particle morphology has a dramatic effect upon the physical properties of composite latices. Models have been developed to make predictions of latex particle morphology but the models have until now been restricted to equilibrium conditions[1)]. In this work non-equilibrium conditions are considered.

Since the diffusion rate of polymeric radicals is dependent on the viscosity within the particles, such mobility changes with the T_g of the seed polymer and the concentration of the

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second stage monomer in the particles. On the one hand, if the rate of diffusion of polymeric radicals within the particle is much higher than the reaction rate, the thermodynamic equilibrium morphology should be the result (in the present system that is an inverted core-shell). On the other hand, if the diffusion is restricted due to high particle viscosity, reaction will occur faster than the diffusion and kinetically controlled, or non-equilibrium structures will result.

The goal of the present work was to determine the seed particle T_g where the morphology for composite latex particles prepared from a polar seed latex and a non-polar second stage polymer changes from being kinetically controlled to thermodynamically controlled. This was done by investigating the influence of the difference between the reaction temperature, T_R, and the T_g of the polar seed polymer (PMMA/PMA copolymer) on the particle morphology. Both the T_g of the seed polymer and the T_R were varied. Earlier experiments and computations have shown that the T_g of the seed polymer, the monomer feed rate, and the T_R during the second stage collectively influence the final composite particle morphology[2-4)].

Methods

Methyl methacrylate (Aldrich), methyl acrylate (Acros) and styrene (Aldrich) were purified from inhibitors by passing the monomers through a column with aluminum oxide active base (Fisher). The cleaned monomers were stored at -10 °C before use. Boiled, deionized water was used and all other chemicals were of analytical grade and used as supplied.

Seed latices were prepared by a surfactant free emulsion polymerization process performed at 80°C in a one liter glass reactor with a water-heating jacket. Potassium persulfate (KPS) was used as initiator and sodium bicarbonate ($NaHCO_3$) was used as a buffer. The reactor was under nitrogen blanket throughout the reactions. The solids contents of the seed latices were initially set to 7%. The initiator concentration used was $3.2*10^{-3}$ mol/l water.

The second stage polymerizations were run in a 250-ml glass reactor with a heating water bath. The reaction temperature was varied between 50 and 70°C and the ratio of styrene to seed polymer was 1:1. The monomer feed rate was 0.3 times the particle volume/hr (giving a feed time of 3.3 hours) with an initial radical flux of $4*10^{13}$ radicals/(m^2*s), where the area refers to the total particle surface.

During both the seed and second stage polymerizations, samples were withdrawn from the reactor throughout the reaction for gravimetric analysis. The particle sizes were determined by quasi-elastic light scattering (QELS) with a Coulter®, Nano-sizer™.

The glass transition temperatures of the seed latices were determined by DSC analysis. The instrument was a Perkin Elmer DSC-4 and the samples were analyzed in a temperature range between 20°C and 150°C. The heating rate was 10°C/minute.

The molar ratios of PMMA/PMA in the resultant copolymer seed latices were determined with ^{1}H-NMR, Bruker AM 360 run at 360 MHz and ambient temperature.

The morphologies of the second stage latices were examined with an Hitachi H600 transmission electron microscope. In the TEM micrographs, the polystyrene (PS) phase appears dark and the PMA/PMMA as the bright phase and all samples were viewed as microtomed slices.

Results and discussion

The results from the DSC and NMR analyses as well as from the particle size analysis of the seed polymers can be seen in Table 1.

Table 1. Experimental data for the seed latices.

Seed	Particle diameter	T_g (DSC)	NMR analysis PMMA/PMA	T_g^a
	nm	°C	wt %	°C
1	330	98	81/19	93
2	320	88	77/23	88
3	390	77	68/32	78
4	380	52	43/57	52

$^{a)}$ T_g calculated with the Fox equation by using the NMR composition data

Semi-batch reactions with second stage monomer fed over 3.3 hours were carried out for each of the latices. The particle morphologies were observed from TEM micrographs of microtomed sections of the particles. For seed #1 with a T_g=98 °C, a distinctive core-shell (CS) morphology was observed where the core was completely free of the second stage polymer, as shown in Fig. 1. Notice that even with such a sharp boundary between the phases that the shell appears to be somewhat non-uniform in the structure. This feature is characteristic of all of the composite latex particles produced in this study.

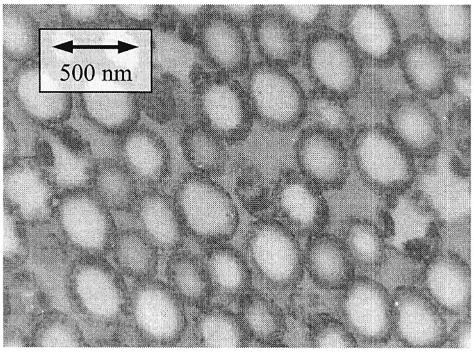

Fig. 1 TEM micrograph for second stage reaction with seed #1 (T_g=98 °C) at T_R=70 °C.

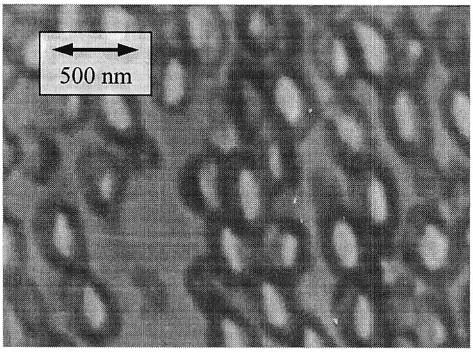

Fig. 2 TEM micrograph for second stage reaction with seed #2 (T_g=88 °C) at T_R=60 °C.

Fig. 2 shows a similar result for seed #2 (T_g=88 °C) at T_R=60 °C, yielding the same (T_R-T_g) of -28 °C as the conditions of Fig. 1. Continuing with morphology comparisons at similar (T_R-T_g)'s, we display the TEM results for seeds #3 (Fig. 3) and #4 (Fig. 4) at T_R's of 70 and 50 °C, respectively. These conditions yield (T_R-T_g) values of -7 and -2 °C, and produce very similar CS morphologies. Again the shell phase is distinctively separated from the core and is, in these experiments, even more composed of discontinuous sections of polystyrene.

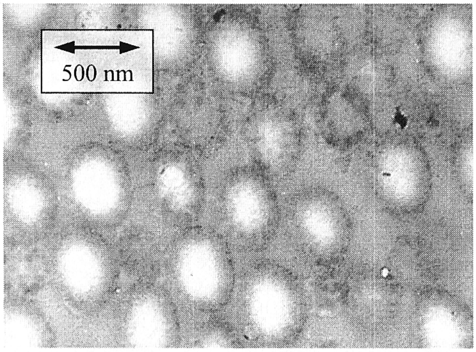

Fig. 3 TEM micrograph for second stage reaction with seed #3 (T_g=77 °C) at T_R=70 °C.

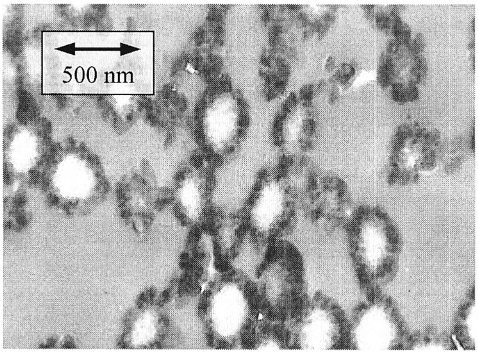

Fig. 4 TEM micrograph for second stage reaction with seed #4 (T_g=52 °C) at T_R=50 °C.

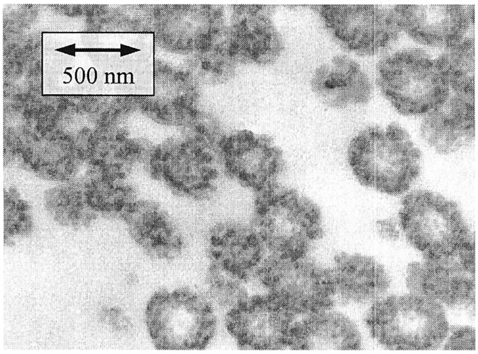

Fig. 5 TEM micrograph for second stage reaction with seed #4 (T_g=52 °C) at T_R=70 °C.

With an interest in obtaining results for conditions which produced a positive value of (T_R-T_g), we performed a similar experiment for seed #4 as described above, but this time at T_R=70

°C. At this (T_R-T_g)= +18 °C the particle morphology is a mixture of micro domains within the core and a very discontinuous shell, as shown in Fig. 5. The presence of micro domains in the core indicate that the polystyrene radicals were allowed to penetrate the seed particle during the reaction and produce phase separated polymer at various places within the particle.

Conclusions

The results presented in this short study demonstrate how it is possible to produce very similar non-equilibrium morphologies at variety of different conditions. When the reaction temperature is below the seed polymer T_g and the second stage monomer is fed slowly, there is no tendency for the polymer radicals to penetrate far into the seed particle. Under these conditions very distinctive CS particles are formed, with the shells composed of non-uniformly structured second stage polymer. Conversely, when the reaction temperature is higher than the seed polymer Tg by about 15 °C, polymer radicals can penetrate the seed particle to produce an occluded morphology.

Acknowledgments

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