

## Size Shrinkage of Methacrylate-based Terpolymer Latexes Synthesized by Free Radical Polymerization: Kinetics and Influence of Main Reaction Parameters

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**ABSTRACT:** Monodisperse PMMA-based terpolymer particles were synthesized by surfactant-free free radical emulsion polymerization. Particles with a wide and controllable range of size and polymer content were prepared by varying monomer amount, reaction temperature and initiator concentration. A kinetic study of the evolution of the terpolymer colloid composition and morphology reveals a mechanism of fast homogeneous nucleation. Copolymerization of the three monomers yields particles whose composition changes continuously during the reaction, which impacts polymer properties. Temperature and monomer amount are key parameters, particularly in the nucleation and growth stages of the reaction. A linear relationship between the particle size and reaction temperature is observed. This is attributed to the fact that the concentration of small, nucleated primary particles with high surface area, initiated at higher temperatures, is too large for efficient stabilization and hence they are more prone to aggregation. The linear relationship between the volume of the colloids and the ratio of main monomer to water in the reaction batch is due to the growth of the particles that continues while there is MMA available. The initiator concentration is not significant in terms of size and concentration of methacrylate-based colloids since primary particles are formed very early during polymerization and they are not dependent on the number of growing chains. The resulting “tailor-made” latexes are promising for a number of unique biotechnological and IC manufacturing applications.

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The bottom-up assembly of nanoscale functional architectures in solution is a goal shared by researchers in many fields.<sup>1</sup> Expected benefits include greater control over material properties and innovative technologies.<sup>2</sup> In this context, polymer spheres with controlled size, shape, composition, surface morphology, and structure have received widespread attention owing to their potential applications in different areas spanning from biomedical and pharmaceutical<sup>3</sup> to integrated circuit manufacturing.<sup>4,5</sup> In particular, particle size contributes significantly to material properties, such as the specific surface area.<sup>6</sup> The latter has a significant impact on the colloidal behavior of polymer spheres largely dependent on the surface charge density and functionalization.<sup>7</sup>

An attractive colloidal synthesis method, which we have employed, is offered by free radical emulsion polymerization in the absence of an emulsifier, due to the flexibility offered in terms of final polymer composition and tunable reaction parameters. Furthermore, the synthesis method of free radical emulsion polymerization has been shown to be a suitable tech-

nique to provide monodisperse spherical particles in the size range from tens to hundreds of nanometers, which is difficult to achieve by other single-step techniques.<sup>8</sup> The key step in this process consists of the precipitation of growing macroradicals within the continuous medium. Precipitation takes place when the macroradicals reach a certain critical chain length depending upon the solvency of the continuous phase.<sup>6</sup> Basic requirements for the generation of monodisperse particles by this process include a short particle formation stage since the actual particle number density appears to be determined in the first stage of the reaction. Furthermore, the particle growth stage has to be free from both the formation of new nuclei and the coalescence of existing ones.

However, once the polymer particles are formed, the initiator and the monomers can be expected to partition between the water and the polymer phase and the amount in each phase is determined by the choice of reaction conditions. The ultimate particle size and distribution are also a function of the extent of coalescence during or after the particle formation stage. In

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the case of monodisperse particles, however, coalescence between large particles is negligible and therefore a narrow size distribution is retained.

In determining the final particle dimensions there are many factors involved. The initial medium solvency is relevant in this respect, since particle formation is restricted to the early stages of the reaction. The solvent of choice for our reaction is water that presents many advantages over organic solvents being relatively inexpensive and environmentally friendly. Furthermore, water assists in the transfer of heat of polymerization, reducing the risk of uncontrolled autoacceleration of the reaction, typical of many vinyl monomers such as acrylates,<sup>9</sup> due to a decrease in the translational diffusion of the growing macromolecules when the viscosity of the reacting fluid is high and the random coils entangle with each other. Furthermore, in the case of emulsion polymerization, aqueous media allows tight control over the size of the colloids by changing significant reaction parameters for size ranges in the order of hundreds of nanometers.

As emulsion polymerization is highly sensitive to even small changes in the numerous reaction parameters involved, its control can become complex especially when dealing with terpolymerizations due to the different reactivity ratios of the reacting monomers. The type and concentration of the monomers, the initiator concentration, the ionic strength of the continuous medium, and the polymerization temperature strongly affect the polymerization rate, the final particle size, and the average molecular weight of the latexes. In particular, from an evaluation of the kinetics and the mechanism of the polymerization reaction, the role of the initiator deserves to be highlighted. Fragments originating from initiator dissociation and incorporated onto the particle surface influence colloidal properties such as stability.

In this paper we report a combined study of PMMA-based terpolymer colloids with free radical emulsion polymerization. We investigate the effect of some of the above-mentioned parameters on the particle size, size distribution, shape, and morphology within the context of the suggested mechanism of the surfactant-free emulsion polymerization for a complex ternary system such as methyl methacrylate, methoxypolyethylene glycol methacrylate, and 4-vinylpyridine. To our knowledge, this system has not previously been investigated to this extent.

The initiator APDH, and all comonomers, except methyl methacrylate, are soluble in water at the reaction temperature of 343 K while the final terpolymer is insoluble in water. The combination of the three monomers is essential to the particle size shrinkage. In the absence of surfactant, the first nuclei formed may not be sufficiently stable leading to coagulation

thus increasing the size and the size polydispersity of the particles. However, amphiphilic macromonomers, such as the methoxypolyethylene glycol methacrylate used here, exhibit the typical properties of conventional surfactants but also have an unsaturated reactive polymerizable group, which allows their incorporation into the surface layer of the polymer particles by copolymerization. The final effect is an effective steric stabilization of the colloids. The 4-vinylpyridine is also bound on the particle surface contributing, together with the presence of amino groups from the aza-initiator, to the electrostatic stabilization of the colloids.

## EXPERIMENTAL

### Materials

Methyl methacrylate (99% purity, Aldrich), methoxypolyethylene glycol metacrylate (average molecular weight 454, Aldrich), 4-vinylpyridine (95% purity, Aldrich), 2,2'-azobis (2-methylpropionamidine) dihydrochloride (97%, Sigma-Aldrich), 4-vinylpyridine (95% purity, Aldrich), were used as received without further purification. The effect of the inhibitor on the particle size was found to be negligible.

### Preparation of Polymer Particles

*Emulsifier-free Emulsion Polymerization Process.* Poly(methylmethacrylate) (PMMA)-based spheres were synthesized by an emulsifier-free emulsion radical polymerization, using a modification of the procedure described by K. Nishimoto *et al.*<sup>10</sup> Detailed polymerization conditions and characterization of the products are summarized in Table I. A typical polymerization procedure (which we refer to as our standard recipe), was as follows: 50 mL of methyl methacrylate (MMA), 3 mL of methoxypolyethylene glycol methacrylate (MPEGMA), 0.45 g of the aza-type polymerization initiator 2,2'-azobis(2-methylpropionamidine) dihydrochloride (pre-dissolved in 50 mL of water) (APDH), and 200 mL of ion-exchanged water (DIW) were charged in a 1 dm<sup>3</sup> round-bottomed three-necked flask. In order to prevent aggregation of the particles, 3 mL of a third comonomer 4-vinylpyridine (4-ViPy) was added to the system. This solution was heated to 343 K while stirring at 600 rpm. Before the process was initiated, *i.e.*, monomer is added, to eliminate the effects of oxygen, the solution was purged with nitrogen for 15 min and the reaction was carried out under nitrogen gas atmosphere for an estimated optimum time of 6 h, until the conversion exceeded 90%, as determined thermogravimetrically. Finally, the system was quenched in a cold-water bath to discontinue the reaction. In order to monitor the change in PMMA particle size during the reaction in

**Table I.** Emulsifier-free emulsion polymerization conditions and characterization results for PMMA latexes

EMULSIFIER-FREE EMULSION POLYMERIZATION					
Polymerization conditions <sup>a</sup>		SEM		DLS	
Fixed conditions	Variable	Size (nm)	Std. Dev. (nm)	Size (nm)	Std. Dev. (nm)
[Initiator] <sub>0</sub> = 5.8 mmol/L	4	342,4	16,5	650,7	11,4
	8,25	352,8	52	498,3	13
	12,5	293	13,2	443,5	12,9
	25	366,9	15,1	571,6	12
	50	505,4	18	628,6	12,9
Monomer = 12.5 mL	60	—	—	898,6	8,7
	65	275,4	14,7	—	—
	70	293	13,2	443,5	12,1
	80	350,2	18,5	549,4	11,7
Monomer = 12.5 mL T <sub>reaction</sub> = 70 °C Variable: [Initiator] <sub>0</sub> mmol/L	0,19	276,1	11,8	678,2	12,5
	0,4	—	—	—	—
	0,5	320,6	76,9	—	—
	0,7	230,8	15,5	368,9	11,5
	1,4	285,5	10	580,7	11,4
	3,6	295,5	28,6	514,9	11,8
	5,8	293	13,2	443,5	12,1

<sup>a</sup>MPEGMA and 4-ViPy were always maintained at 3 mL, and the initiator concentrations are based on the total volume of the liquid phase (306 mL).

our kinetic study, 10 mL samples were withdrawn every 6–7 min and immersed in a cold-water bath to inhibit the polymerization. The initiator was added as soon the temperature in the bath reached (333 ± 2) K. This time was taken as time zero for our kinetic study.

**Post-synthesis Treatment.** The dispersions resulting from the synthesis presented above were centrifuged at 5,000 rpm for 45 min, the supernatant solutions discarded, and the particles re-suspended in DIW using ultrasonic treatment (1 h). This process was repeated 3 times. To compare two different post-synthesis treatments, 10 mL of the polymer colloidal suspension was dialyzed for two days against DIW. The dialysis was changed every 12 h. The two treatments gave PMMA particles with comparable surface charge ( $\zeta$  potential) versus pH and ionic strength and showed similar Fourier Transform Infrared (FT-IR) characteristics.

**Measurement of the Percentage Yield of Latex.** The percentage yield of polymer as latex was determined at the end of each reaction. After dialysis or a washing/centrifuge cycle, the total quantity of latex was weighted. A small sample was taken, approximately 3 mL, and placed in a vial, which was then weighed, and dried in an oven at 353 K for 10 h and reweighed to constant weight. The yield was calculated as the percentage of monomer converted to latex. Typically latex yields of at least 90% were obtained.

### Characterization of Polymeric Particles

**Conversion.** The monomer conversion was measured by thermogravimetry. 5 mL of suspension was centrifuged, the supernatant decanted and then dried in an oven at 353 K and weighted. The conversion was approximated according to the following equation:

$$\text{conversion \%} = \frac{W_{ds}}{[W_{mo}/(W_{wa} + W_{mo})] \times W_{sa}} \times 100$$

where  $W_{ds}$ ,  $W_{mo}$ ,  $W_{wa}$ , and  $W_{sa}$  are the weights of the dried polymer latex, fresh monomer, water, and latex colloidal solution sample, respectively. The result was obtained as an average value of two measurements.

**Particle Size and Size Distribution.** The particle size and size distribution were measured by Dynamic Light Scattering (DLS) using a Nicomp particle sizer (model 370, PSS, Santa Barbara, CA) at fixed scattering angles of 90° and 60°. To fit the experimental data, an Inverse Laplace Transform (Nicomp) algorithm was applied. Samples were diluted with DIW to a concentration of 0.1 wt % of PMMA. The number-( $D_n$ ), volume-( $D_v$ ), and area-( $D_a$ ) average diameters were calculated. The polydispersity in this case is expressed as  $D_v/D_n$ .<sup>11</sup>  $D_v$  equals to weight-average diameter,  $D_w$ , when polymer particles are assumed to have identical density regardless of their particle sizes.<sup>12</sup>

Scanning Electron Microscopy (SEM) (Philips XL-30 FEG) studies on the dried particles were carried out in order to evaluate the size, shape, and morphology

of the polymer particles. For some of the PMMA latexes it was necessary to use a relatively low electron beam voltage of 3 eV with a spot size of 2 due to exposure-induced sample damage. Average particle diameters were determined by counting 100 particles in SEM images. The number, weight average diameter of the particles  $d_n$ ,  $d_w$  can be calculated by the following equation:

$$d_n = \sum n_i d_i / \sum n_i, \quad d_w = \sum n_i d_i^4 / \sum n_i d_i^3,$$

where  $n_i$  is the intensity of the size distribution.

The uniformity of the particles was calculated by the equation:  $U = d_w/d_n$ . The diameter of non-spherical particles, such as in case of a fast reaction temperature ramp, was not given due to their anomalous morphologies.

**Particle Surface Charge Density.** Particle surface charge density was estimated by zeta ( $\zeta$ ) potential measurements that were performed on a Nicomp 380/ZLS by Electrophoretic Light Scattering (ELS) at 298 K, at a scattering angle of 14.8°, and with  $\lambda$  (HeNe laser) = 632.8 nm. Solutions of colloidal particles from the kinetic study, diluted with DIW to a concentration of 0.2 wt % of PMMA, were measured after post-synthesis treatment.

**Molecular Weight.** Molecular weight and molecular weight distribution were measured by Gel Permeation Chromatography (GPC) on a Shimadzu appara-

tus (UV and RI detection) operating at room temperature at 1 mL/min with a PLgel D column (Polymer Laboratories) in chloroform. Linear polystyrene standards were used for calibration.

**Terpolymer Composition.** The relative reactivities between the terpolymers were qualitatively estimated by proton NMR analysis on the kinetic samples after post-synthesis treatment and solvent evaporation under vacuum conditions.  $^1\text{H}$  NMR spectra were recorded on a Bruker Avance 300 apparatus operating at 300 MHz at room temperature using polymer samples dissolved in  $\text{CDCl}_3$ . The peaks were attributed to the hydrogen atoms of the terpolymer. The integrals related to the alpha-methyl protons of MMA, which show triad peaks syndiotactic (rr), heterotactic (mr), and isotactic (mm) in the range  $\delta = 0.66\text{--}1.21$  ppm, together with the integrals related to the protons of the  $\text{OCH}_3$  group of MPEGMA ( $\delta = 3.38$  ppm), and to the two protons in alpha with respect to the N atom in the pyridine ring ( $\delta = 8.44$  ppm), were used for the calculations to determine the amount of each comonomer incorporated into the precipitated terpolymer at each sampling time. If  $x$ ,  $y$  and  $z$  represent the number of protons considered for the 4-ViPy, MMA, and MPEGMA and the respective integrals are  $m$ ,  $n$  and  $o$ , then we derive the following equations to obtain the percentage of each comonomer that was incorporated into the terpolymer:

$$2x = m$$

$$3y = n$$

$$3z = o$$

$$\% \text{ViPy} = \frac{x}{(x + y + z)} 100$$

$$\% \text{MMA} = \frac{y}{(x + y + z)} 100$$

$$\% \text{MPEGMA} = \frac{z}{(x + y + z)} 100$$

**Chemical Composition and Surface Functional Groups.** To investigate the colloid chemical composition and main functionalities, the particles were mixed thoroughly with KBr (IR grade), in order to have a final PMMA concentration of 0.01 wt %, and FT-IR spectra were taken with a FT-IR spectrophotometer Mattson Galaxy 7001.

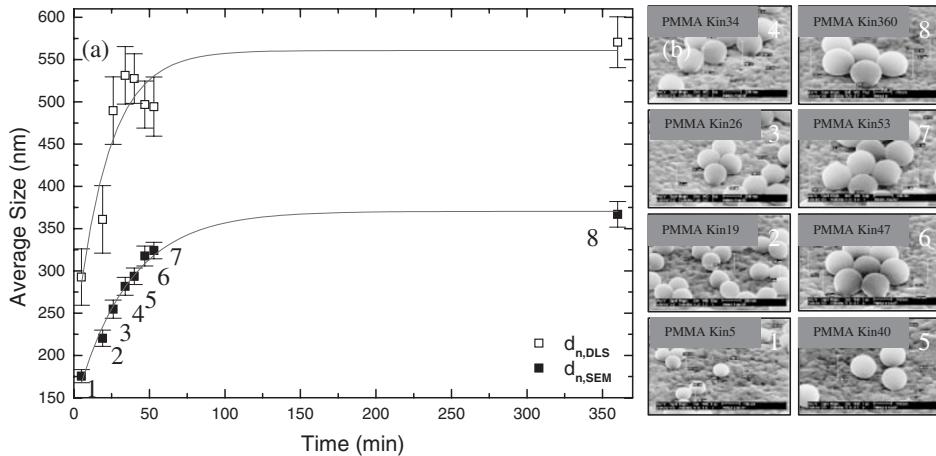
## RESULTS AND DISCUSSION

### Kinetics Study

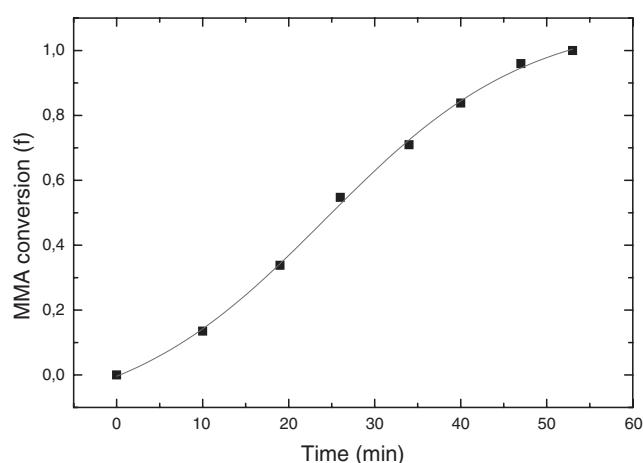
The aim of the kinetics study presented in this section is to investigate the shrinking of the size of the particles by choosing different reaction times, and to gain insight into the reaction kinetics and mechanism. During polymerization, small amounts of reaction mixture were withdrawn to measure monomer-to-polymer conversion, particle size, and particle size distribution. The particle diameter and size distribution, main parameters of the resulting surfactant-free

emulsion polymerization product, were measured by two independent methods: DLS and SEM. The sampling times, from the start of the reaction, were 5, 19, 26, 34, 40, 47, and 53 min with time zero corresponding to the time when the temperature in the reaction vessel reaches 333 K, the initiator is added to the comonomers, and starts to dissociate. The final temperature of 343 K is reached within the first sampling period.

From Figure 1, showing the size and shape evolution of PMMA, it is evident that the reaction kinetics are very fast and the particles have already reached their final size after 45 min of reaction. Estimated typical ranges for the activation energies of the individual processes in free radical polymerization are: initiator dissociation  $110 < E_d < 160$  kJ/mol, propagation  $15 < E_p < 40$  kJ/mol, termination  $2 < E_t < 20$  kJ/mol, chain transfer  $40 < E_{tr} < 80$  kJ/mol.<sup>13,14</sup> For this reason, we can safely assume that the reaction rate-determining step is the initiator dissociation and that,



**Figure 1.** (a) Dependence of the PMMA particle DLS ( $d_{n,DLS}$ ) and SEM ( $d_{n,SEM}$ ) diameter on the reaction time (first order exponential decay fitting); (b) SEM images of the PMMA particles corresponding to the points in (a).



**Figure 2.** MMA conversion versus reaction time in PMMA radical emulsifier-free emulsion polymerization.

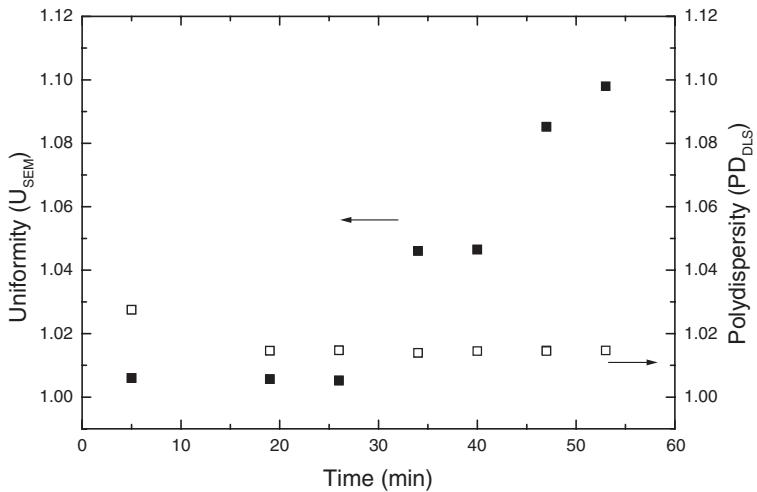
under the current experimental conditions, the formation of radicals by homolytic scission of the aza-initiator is very fast due to the fact that APDH has a short half-time life ( $t_{1/2}$ ) corresponding to  $0,693/k_d$ , where  $k_d = 3 \times 10^{-5} \text{ s}^{-1}$  is the dissociation constant. The fragment originating from the initiator homolysis is very reactive in forming a stabilized radical-monomer and radical-polymer. The reaction of a primary free radical with a first monomer is indeed reported in the literature to occur very rapidly, essentially in the diffusion-limited regime.<sup>15</sup>

The conversion of MMA was obtained from the weight of PMMA contained in the reaction mixture according to the method already presented in the Experimental Section. Figure 2 presents monomer conversion as a function of reaction time. Complete conversion was achieved after the first hour of reaction and is greater than 90%, which indicates good reaction performance for the investigated system and confirms the fast kinetics.

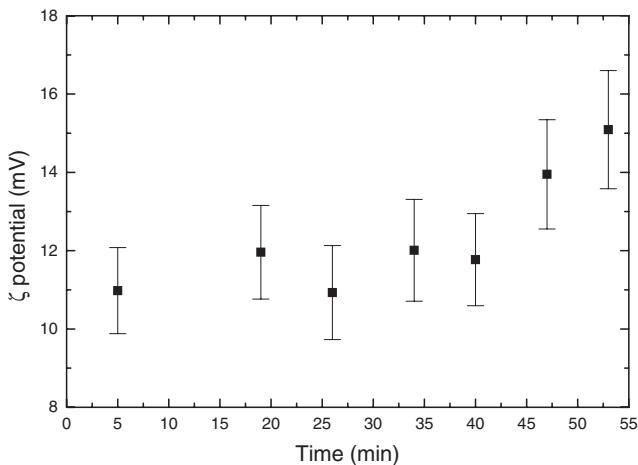
Good correlation was found for SEM and DLS determined particle diameter trends. The diameters measured by DLS are larger than those determined by SEM since the former technique determines the diameter of solvent-swollen particles, whereas the latter measures particles in the dry state.<sup>16</sup> At the end of the polymerization, the particle diameter is *ca.* 350 nm as determined by SEM, while the DLS determined diameter is *ca.* 550 nm, implying *ca.* 57% swelling of the particles with water. This swelling is acceptable considering the presence in the terpolymer of hydrophilic groups such as 4-ViPy and MPEGMA. The error bars for the DLS measurements are  $\pm 12$  nm. In fact, the average standard deviation for the size measured by DLS (angle 90°) was *ca.* 12% (23% for the two samples taken after 5 min and 19 min of reaction), while for the size measured by SEM the average standard deviation was *ca.* 3% (4% for the two samples taken after 5 min and 19 min of reaction).

In Figure 3, particle uniformity from SEM data and size polydispersity from DLS size measurements are plotted against the time of reaction. As expected, the particles are monodisperse in size at the end of the reaction. Coincident with a slight decrease in polydispersity, we observe enhanced uniformity. The swelling of the particles results in low polydispersity. Given that the polydispersity values are relatively constant throughout the polymerization, the major impact on the DLS measurements can be attributed to the swelling effect, whose analysis is beyond the scope of the present work.

One common technique used to determine the effect of various parameters (*e.g.*, salt, polymer, pH, reaction mechanism and kinetics) on the surface charge properties of the colloids is microelectrophoresis from which the  $\zeta$  potential can be calculated using electrophoretic mobility data.<sup>17</sup> The use of systems such as, in our case, the comonomer 4-ViPy with the water-



**Figure 3.** Uniformity (calculated from SEM data) and polydispersity (calculated from DLS data) versus reaction time.



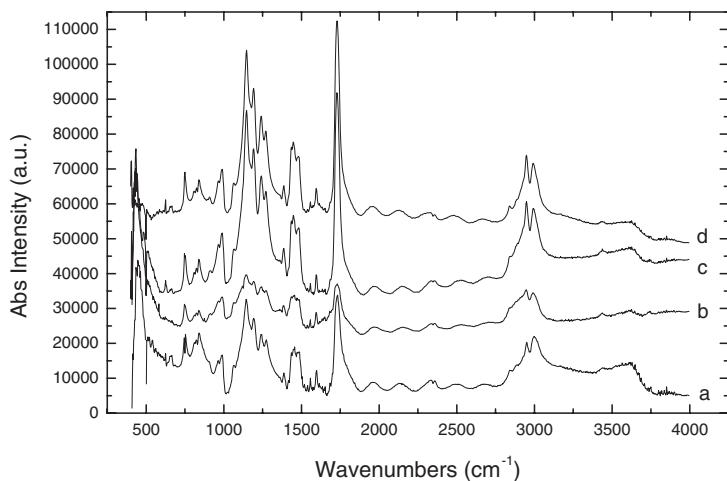
**Figure 4.** Evolution of the  $\zeta$  potential (measured by ELS) at the colloid surface versus reaction time.

soluble cationic initiator APDH, results in the production of uniform latexes with positive surface charges.  $\zeta$  potential measurements were used to characterize the surface charge and study its dependence on different parameters. Figure 4 shows the  $\zeta$  potential of the PMMA colloidal particles versus reaction time. The increase in surface charge density, assumed to be proportional to the measured  $\zeta$  potential, can be explained by the fact that, depending upon the increase in the average size, the specific surface area of the particles increases, which involves an increase in the surface charge from the cationic initiator. Conductometric titration studies confirmed that, in our case the amino functionality originates from both the dissociation of the initiator and, to a lesser extent, from the cationic 4-ViPy comonomer.<sup>18</sup> The surface groups stabilize the particles against agglomeration and impart a positive charge to the colloid surface for pH values lower than the  $pK_a$ , thus providing electrostatic repulsion forces between the particles in solution.<sup>19</sup>

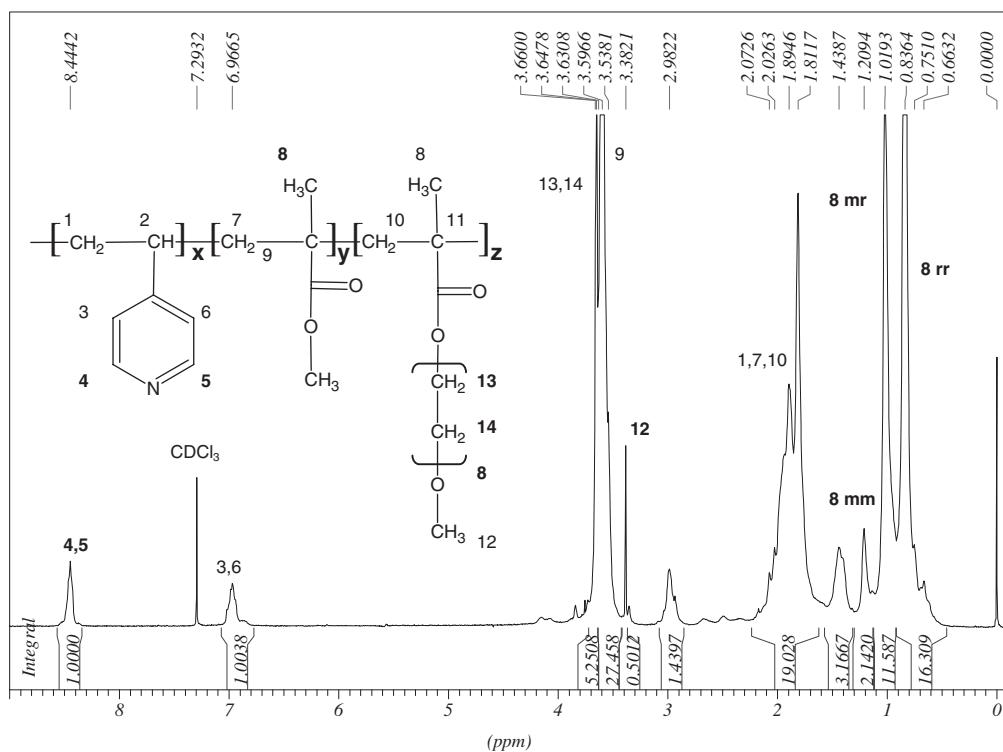
We used FT-IR to investigate the surface groups and structure of the latexes. The following characteristic peaks were observed in the FT-IR spectra in Figure 5 upon completion of the terpolymer synthesis (wavenumber in  $\text{cm}^{-1}$ ): 3453 (w) primary amine (NH stretching), 2992-2954 (m) alkyl group (CH stretching), 1738,74 (s) methacrylate carbonyl group (CO stretching), 1650-1580, primary amine (NH bending), 2830 (shoulder, w)  $\text{OCH}_3$  stretching, 1453  $\text{CH}_2$  groups ( $\text{CH}_2$  scissor vibration), double-peak at 1240 and 1270, acetate group (COC stretching), 975-840 (m-w) main C-C chain (CC stretching), 760-625 (m) CH bonds (CH out of plane deformation). Interestingly, spectra a, b, and c, corresponding to sampling times of 5, 19, and 26 min from the time zero, respectively, show that in this case, while the peak positions remain constant, the spectral lineshapes are broader and the relative intensities are lower at incomplete reaction times.

Under these conditions, the physical-chemical and mechanical properties of the material can be influenced by the presence of unreacted monomer inside the micelle-like structure self-assembled in aqueous solution, where the more polar and hydrophilic parts of the copolymer, such as the 4-ViPy and the MPEGMA, are oriented towards the polar water molecules, while the more hydrophobic alkyl PMMA sequence is directed towards the inside. In support of this explanation, during SEM analysis with a beam voltage of 5 keV, the PMMA particles sampled at shorter times were observed to show a greater tendency to suffer electron beam-induced damage.

Copolymerization of two or more vinyl monomers ordinarily yields polymers whose composition differs from that of the starting monomer mixture.<sup>20</sup> For a three-monomer system, a mathematical treatment has been developed and analytically integrated in order to



**Figure 5.** FT-IR spectra of PMMA-based terpolymer nanoparticles at different sampling times from the start of the polymerization: after a) 5, b) 19, c) 26, and d) 360 min of reaction.



**Figure 6.**  $^1\text{H}$  NMR spectra of the PMMA-based terpolymer particles after 47 min of reaction.

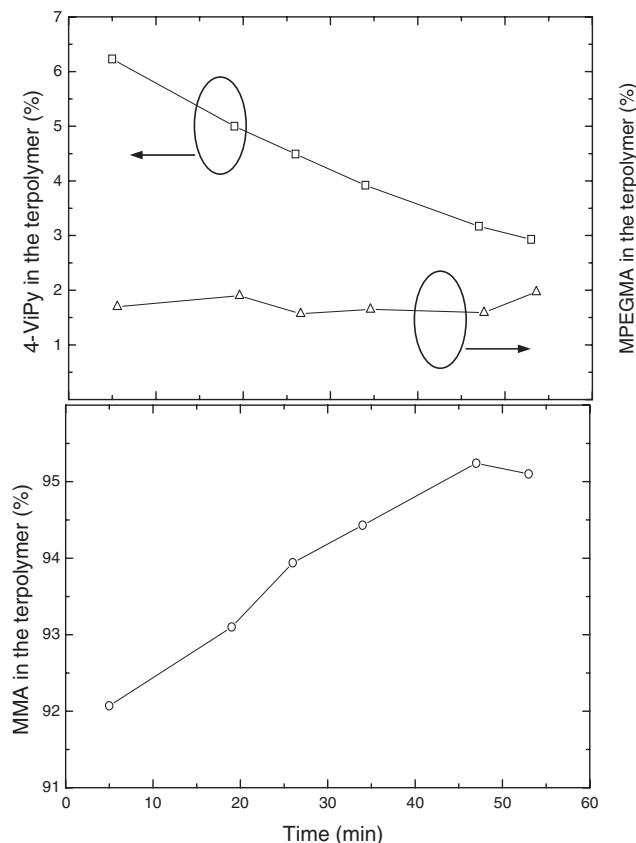
predict the composition of the initially formed terpolymer from the initial feed composition.<sup>21</sup> The treatment of a three-component system requires reactivity ratios determined from the individual two-component systems. The reactivity ratios measure the reactivity of an active centre towards the addition of a homopolymer during the addition of a heteropolymer.<sup>22</sup> Copolymerization can readily occur between monomers of similar reactivities and only with difficulty between monomers of differing reactivities.<sup>23</sup> As a consequence, a batch polymerization can yield a wide spectrum of polymer compositions and thus physical properties. To obtain a polymer with a con-

stant composition, it is necessary to continuously re-adjust the composition of the system during the reaction to avoid obtaining a heterogeneous material that forms a biphasic structure in the solid state.

In order to determine the relative amount of each termonomer incorporated in the terpolymer versus the reaction time, proton nuclear magnetic resonance,  $^1\text{H}$  NMR, was performed on each sample after dissolution in  $\text{CDCl}_3$ . A representative  $^1\text{H}$  NMR spectrum together with the chemical formula of the terpolymer and the peak assignation to the respective H atoms, are presented in Figure 6. The main features of the spectrum related to the PMMA are the peaks corre-

sponding to the methyl ester group ( $\text{COOCH}_3$ ) at  $\delta = 3.60\text{--}3.63$  ppm, the methylene backbone ( $\text{CH}_2$ ) at  $\delta = 1.81\text{--}2.08$  ppm, and the alpha-methyl protons ( $\text{CH}_3$ ) of both MMA and MPEGMA at  $\delta = 0.84\text{--}1.21$  ppm. On the basis of the alpha-methyl protons, which show triad peaks syndiotactic (rr), heterotactic (mr), and isotactic (mm) respectively at  $\delta = 0.84$ , 1.02, and 1.21, it is possible to investigate the tacticity of the PMMA in the terpolymer for each reaction time. Independent of the reaction time, the PMMA in the terpolymer was richer in syndiotactic content (52–55% rr) in comparison with commercial PMMA (48% rr).<sup>24</sup> The presence of the comonomers MPEGMA and 4-ViPy, having different hydrophobicity, could affect the conformation and tacticity of the polymer chains. The main features of the spectrum related to the 4-ViPy are the peaks corresponding to the aromatic hydrogen atoms in alpha position to the heteroatom (H 4 and 5) at  $\delta = 8.44$  ppm, the other two aromatic hydrogen atoms (H 3 and 6) at  $\delta = 6.97$  ppm, and the backbone CH and  $\text{CH}_2$  groups at  $\delta = 1.81\text{--}2.07$  ppm. Finally, the peak at  $\delta = 3.38$  ppm is assigned to the hydrogens of the  $\text{OCH}_3$  group of the MPEGMA side chain and the peaks related to the hydrogens of the MPEGMA backbone overlap with the PMMA ester peaks.<sup>8</sup> The  $\text{CH}_2$  groups of the PEG chain are found at 3.66 ppm. The methyne protons of the 4-ViPy residue are buried at around 1.6 ppm. The signal at 2.8–3.1 ppm could be tentatively attributed to moisture interacting with 4-ViPy or oligoethylene glycol residues. The composition of the terpolymer was determined by comparing the integrals of the methyl and methylene peaks, according to the formulas reported in the Experimental Section. It is evident from Figure 7 that throughout the entire range of monomer conversion, the composition is not the same for the copolymers produced at the beginning of the reaction and at the end of the reaction. In other words, the copolymer composition is not independent of conversion.

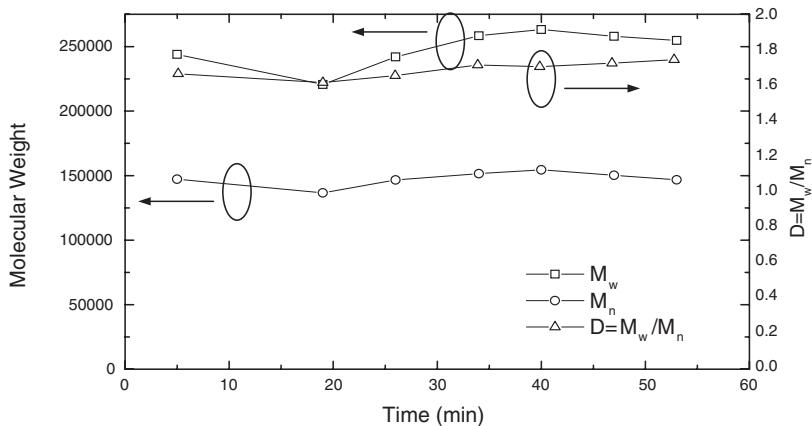
At the beginning of the copolymerization the monomer composition is the same as that charged into the reactor. Since 4-ViPy has the highest reactivity ( $Q = 1$ ), it reacts more rapidly than MMA ( $Q = 0.74$ ) and MPEGMA ( $Q = 0.42$  for methyl acrylate) and the amount of 4-ViPy in the solution decreases more with respect to the other comonomers, until it reaches almost zero before the end of the reaction. At the end of the reaction, the copolymers that are produced contain mostly MPEGMA, besides MMA, because 4-ViPy has already fully reacted. In general, the instantaneous terpolymer composition can vary considerably during a batch polymerization and give rise to a spectrum of polymer properties. Complications such as different partition coefficients for the monomers



**Figure 7.** Evolution of the percentage 4-ViPy, MPEGMA and MMA in the terpolymer versus time of reaction, as determined from the  $^1\text{H}$  NMR spectra.

and the initiator between the aqueous and reacting phase, should also be taken into account for a more quantitative analysis.

The molecular weight of the terpolymer for different reaction times was monitored by GPC in  $\text{CHCl}_3$ . From a plot of molecular weight versus time shown in Figure 8, it can be seen that as the reaction proceeds, the molecular weight of the particles shows a slight increase for reaction times between 20 and 40 min, and then levels off. This increase is probably an artefact of the particle isolation procedure at low conversions. In general, we can say that the molecular weight is almost constant throughout the reaction from the time when measurements were started. The data collected with the RI detector show the same trend. The average values of the weight average molecular weight ( $M_w$ ) and the number average molecular weight ( $M_n$ ) are around 250,000 and 150,000, respectively.  $M_n$  is the simple average of total mass of the chains divided by the number of chains, while  $M_w$  is a summation of the square of the molecular weights divided by a summation of the molecular weights of all the molecules present. The basis for  $M_w$  is that the larger molecules contribute more to the properties of the polymer. The ratio  $M_w/M_n$ ,



**Figure 8.** Evolution of the molecular weight and molecular weight distribution of the terpolymer as a function of time of reaction (UV detector).

which is a measure of the distribution of different length polymer chains, was always less than 1.7, implying a well-controlled polymerization process.<sup>25</sup>

#### Reaction Mechanism

According to Zhang *et al.*, in emulsifier-free emulsion terpolymerization, particles are formed in several steps.<sup>26</sup> At the outset, in the batch-feeding mode, there is a homogeneous solution of the initiator and the three monomers. MPEGMA and 4-ViPy act as stabilizers due to the effect of the steric hindrance and high hydrophilicity in the diluent. Polymerization starts and oligomeric chains appear in solution that grow by free radical propagation until, at some critical chain length, they achieve a high degree of ‘supersaturation’ and form the new polymer phase by collapse of the chains upon themselves, thus forming primary particles (homogeneous nucleation).<sup>27</sup>

From our SEM analysis it seems that mature particles are formed at a very early stage, related to the fact that the homocoagulation step of the precursors spans a very short time. The rate of particle formation in the initial stage is thus equal to the effective rate of radical generation that is strictly dependent on the initiator efficiency. Soluble oligomers subsequently formed will then have a choice of forming more new particles by this process, or being captured by pre-existing particles. Three limiting cases may be considered: a) when primary particles are stable enough so that no flocculation takes place; b) when primary particles are colloidally unstable; c) seeded polymerizations. Due to the presence of the positive charge, arising from both the fragmentation of the aza-initiator and due to the high reactivity of 4-ViPy from the first stage of the reaction, we can safely assume that the early latex particles formed by coagulation are stable under our experimental conditions. The operating nucleation mechanism is thus considered to be homo-

genous nucleation until the precursor particle reaches a critical size having high surface charge density and stability. The combination of the three comonomers is essential to the particle size shrinkage. The two comonomers 4-ViPy and MPEGMA contributes to the stabilization of the precursor particles in two different ways: the former by electrostatics, the latter by steric hindrance.

When monomer was supplied in a batch mode, the 4-ViPy polymerized preferentially because its solubility in aqueous phase is higher (the solubility is 2.9 g 4-ViPy in 100 g water at 293 K and 0.16 g MMA in 100 g water at 293 K). Following the nucleation period, preferential aggregation of the smaller particles in the propagation step leads to a uniform particle size with a narrower size distribution compared with the initial particles. The smallest particles disappear first in the polymerization because of their larger radius of curvature and higher surface energy. The coexistence and competition between homogeneous nucleation, coagulation, propagation, and aggregation results in size polydispersity in the first stage, while the competition between propagation and aggregation results in a gradual increase in size monodispersity in the latter stage. A reaction mechanism, involving homogeneous nucleation, is most consistent with our experimental findings.

#### Particle Size Control

Particle size control is a function of several thermodynamic and kinetic factors, including monomer-polymer solubility, reactant composition, and in particular MMA content and initiator concentration, temperature, and solvent medium among others.<sup>28</sup> Our experiments demonstrate that it is possible to synthesize monodisperse PMMA-based terpolymer particles, in the absence of added surfactants, using a cationic initiator and a cationic comonomer. The particle diam-

ters cover a range from *ca.* 230 nm to *ca.* 500 nm, measured by SEM. From the sizes measured by DLS it was possible to quote percentages of swelling of the polymer in aqueous medium spanning in the range from 42% to 90%. Under the conditions specified in the experimental section, the preparations were found to be reproducible. Stirring was an important variable, together with the rate of temperature rise. An increase in polydispersity was observed in the absence of adequate stirring, as confirmed by other authors.<sup>29</sup>

In our experiments we did not investigate the influence of ionic strength on the colloid size. We assume a low ion concentration for reactions in deionized water at neutral pH values, with  $5 \times 10^{-2}$  estimated as the safe upper limit of ionic strength in order to keep the system below the critical coagulation concentration at the temperature of the reaction.<sup>30</sup>

#### Influence of Monomer Concentration

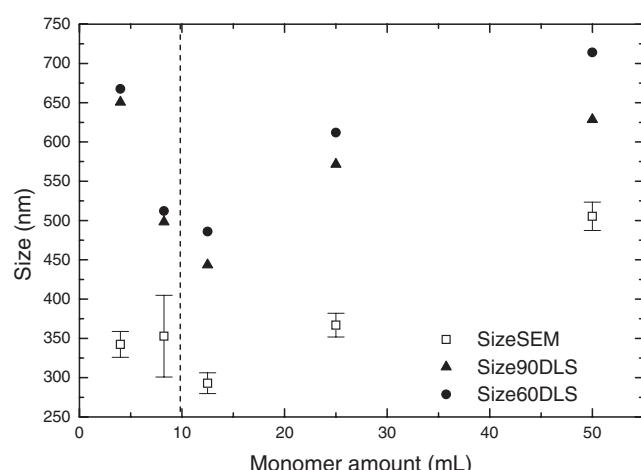
In the first group of experiments in Table I, aimed at understanding the effects of the amount of MMA in the feed, we changed the quantity of the main monomer, MMA, between 4 and 50 mL. The amounts of the other components, water, MPEGMA, 4-ViPy, and APDH were 125 mL, 1.5 mL, 1.5 mL, and 5.8 mmol/L, respectively. These reactions were conducted at 343 K, under a nitrogen atmosphere for a polymerization period of 6 h. As seen in Figure 9, the average size increases with increasing amount of MMA in the feed and the particle size distribution is narrow. This is expected, given that MMA is the main monomer in the terpolymer used in excess with respect to the other comonomers. To test the effect of changing the ratio between MMA and the other

comonomers, we used the same polymerization recipe in terms of temperature, solvent and main monomer amount, but doubled the quantity of MPEGMA and 4-ViPy, *i.e.*, x and y, respectively. The size as characterized by SEM was 309.7 nm ( $\pm 13.4$  nm), very close to the value of 293 nm ( $\pm 13.2$  nm) obtained with the standard recipe.

Different comonomers, with different hydrophilicities, will provide different reactivities and hydrophilic properties, leading to different polymerization behaviors in the aqueous phase and therefore in the final composition and size of the particles.

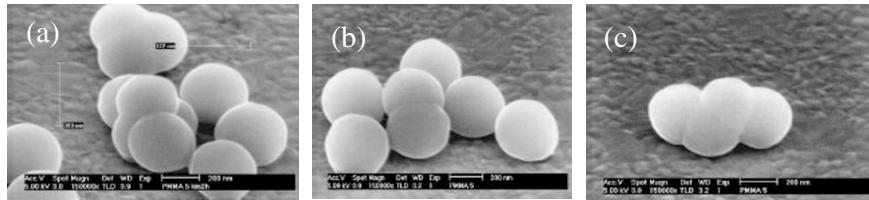
Our experimental results are in agreement with the model presented in the previous section in which primary particles are formed very early during the polymerization process. MMA is used in excess in the synthesis (compared to other monomers), and therefore forms a separate phase, referred to as "monomer storage droplets," in the reaction medium. After the nucleation step, monomer molecules diffuse from these droplets into the growing polymer phase stabilized by MPEGMA oligomers, cationic comonomer 4-ViPy (at the outer/uppermost layer of the particles), and the cationic initiator (attached to the ends of the growing terpolymer chains). This process continues until all the monomer is consumed. Therefore, if there is more monomer in storage, the particles are large, as was observed in our case.<sup>31</sup> There is a linear relationship between the volume of the colloids and the ratio of main monomer to water in the reaction batch. This is explained by the fact that the diameter of the colloids increases in a cubic root relationship with the ratio of monomer to water from 293 to 505 nm.

The equation of the curve was found to be, for experiments at 343 K,  $\log [\text{diameter}] = 0.333 \log [\text{MMA}] + 2.285$ . These results are in good agreement with those reported by Egen and Zentel for pure MMA.<sup>30</sup> The authors claim that the concentration of the primary particles depends on the hydrophobicity of the monomers and can be varied by the addition of salt. Hence, the relationship between the composition of the reaction batch and the size of the colloids differs from monomer to monomer. This relationship can, however, be described for all systems by the same linear trend with the same slope (master curve) shifted by a constant parameter that depends on the particular monomers. This is consistent with the suggested homogeneous nucleation mechanism. However, if not enough MMA is present in the reaction feed, the morphology and shape of the particles are affected in terms of molecular mass, shape and size. This could explain the outliers and the higher standard deviations on the size measurement at a MMA concentration below an estimated lower limit of 6 mL. Furthermore, monodisperse colloids larger than *ca.*



**Figure 9.** Dependence of particle size of the terpolymer latexes on polymerization conditions: added MMA amount.

\*The average standard deviations for the size measured by DLS at angles of 60° and 90° were 16% and 12%, respectively.

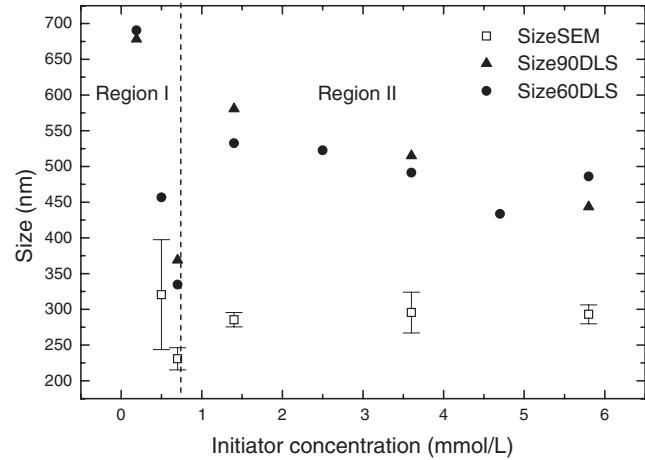


**Figure 10.** Effect of the fast temperature ramp on the particle shape and size distribution after (a) 120 and (b)–(c) 360 min from the beginning of the reaction.

500 nm cannot be made, at least for MMA, because the dispersion becomes unstable for the high volume content of monomer necessary for the synthesis.<sup>30</sup>

#### Influence of Temperature

An independent set of experiments was carried out to assess the effect of temperature in which the monomer concentration, ionic strength, and initiator concentration were kept constant. The temperature value was varied in the range 333–353 K, the lower limit being the dissociation temperature of the initiator (330 K). At 333 K, the polymerization rate slowed down resulting in a strong decrease in the yield of the reaction to 16%. From this set of experiments, it is evident that the reaction temperature affects the polymerization rate and the final particle size and shape. In fact, temperature influences both the thermodynamic factors such as reactivity as well as the kinetics of initiator decomposition, which in turn determines the rate of polymerization and particle nucleation. Surprisingly, increasing the temperature gives rise to larger colloids. The latex diameters measured by SEM are 275, 293, and 350 nm ( $\pm 15$  nm) for temperatures of 338, 343, and 353 K, respectively. The latex diameters measured by DLS at 60° show the same trend, *i.e.*, 403, 486, and 522 nm ( $\pm 17\%$ ), respectively. This behavior is in contrast with the findings reported for polystyrene latexes.<sup>32</sup> In the work of Goodwin *et al.*, the final polystyrene particle diameter decreased as the temperature of the reaction was raised within the range 328–358 K. A possible explanation for the behavior observed in our study is that the concentration of small particles with increasing surface, being initiated at higher temperatures, is too large for an efficient stabilization and the particles are more prone to aggregation. The temperature plays a major role in the first phase of the reaction, during nucleation. Furthermore, as shown in Figure 10, if the temperature ramp is too fast, the shape of the particles is strongly influenced, resulting in polynucleation within the same particle or the collapse of several nucleating spheres into one structure. It was also found, in agreement with other authors,<sup>31</sup> that the cationic latexes undergo coagulation upon prolonged heating at high temperatures. This is confirmed by



**Figure 11.** Dependence of the particle size of the terpolymer latexes on polymerization conditions: APDH concentration in the initial suspension.

\*The average standard deviations for the size measured by DLS at angles of 60° and 90° were 17% and 12%, respectively.

the observation that the yield at 353 K was lower than at 343 K.

#### Influence of Initiator Concentration

The results obtained at 343 K for the variation of final particle diameter as a function of the concentration of initiator used at constant ionic strength and monomer concentration are given in Figure 11. The interpretation of the effect of the initiator is not straightforward. Upon inspection of the data, we can distinguish two regions: the first one for initiator concentrations below 0.7 mmol/L, and the second for concentrations above this value. Based on SEM analysis showing irregular shaped particles for low initiator concentrations, we can conclude that the concentration of APDH must be maintained sufficiently high to provide effective initiation at the temperature of the reaction. In fact, when less initiator is used, the resulting particles exhibit a large polydispersity and the rate of polymerization is slower. Hence, the plot of the size versus the initiator concentration is restricted to the second region corresponding to initiator concentrations above 0.7 mmol/L. Over this range, the preparation did not appear to be sensitive to the initial concentration of APDH, in contrast with the results reported for poly-

styrene.<sup>31</sup> This is in agreement with the insignificant effect of the initiator concentration on the size and concentration of methacrylate-based colloids, observed by Egen and Zentel.<sup>30</sup> We can extend their model to our case, in which very early during polymerization, primary particles are formed independent of the number of growing chains (initiator). This is not in agreement with the data presented elsewhere<sup>33</sup> for the same initiator in the polymerization of a polystyrene-based terpolymer, showing an increase in the polymer particle size with the initiator concentration. The latter phenomenon was explained by the fact that as the number of free radicals increases more oligomer radicals are formed, which in turn results in a decrease in the nucleation rate and in larger particles.<sup>33</sup> Furthermore, upon increasing the concentration of the cationic initiator, an enhanced colloid stabilization effect is expected due to the higher number of decomposed fragments incorporated onto the particle surface or attached to the ends of the growing terpolymer chains.

## CONCLUSIONS

Here we have reported a single-step process for the formation of highly monodisperse terpolymer lattices, covering a wide range of particle diameters in the absence of surfactants. Using MMA as the main monomer, combined with MPEGMA and 4-ViPy as co-monomers, it is possible, by suitable choice of monomer concentration, reaction temperature, and initiator concentration, to obtain monodisperse PMMA-based latexes at concentrations of the order of 10% w/v with particle diameters ranging from 200 nm to 500 nm.

A kinetics study during the terpolymerization reaction reveals a mechanism of fast homogeneous nucleation during the first minutes of the reaction. Copolymerization of the three monomers yields particles whose composition changes continuously during the polymerization. Close to the end of the reaction, the copolymers that are produced contain mostly MPEGMA and MMA. 4-ViPy has already fully reacted because of its intrinsically higher reactivity and solubility. The instantaneous terpolymer composition can vary considerably during a batch polymerization and give rise to a spectrum of polymer properties.

This extensive study provides a solid foundation for the development and application of latexes with various sizes, surface physical-chemical properties and mechanical properties.

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