Synthesis of Bimodal PVC Latexes by Emulsion Polymerization: An Experimental and Modeling Study

*Hugo M. Vale, Timothy F. McKenna**

Summary: The onset and extent of secondary particle formation in the seeded emulsion polymerization of vinyl chloride were investigated by performing a series of seeded polymerizations at different concentrations of seed latex and surfactant. It was found that, in general, both the onset and the extent of secondary particle formation are determined not only by the rate of homogeneous nucleation, but also by the rates of particle coagulation. A comparison of methods to compute the evolution of the particle size distribution in vinyl chloride emulsion polymerization was also carried out. For growth processes, the widely-used pseudo-bulk model gives correct answers. For processes involving particle formation, on the other hand, this model cannot be used because it neglects, among others, the effects of nucleation and coagulation on the radical number distribution. To surmount this problem, we propose to use the zero-one-two model, for which the full population balance equations are given here.

Keywords: emulsion polymerization; modeling; particle size distribution; poly(vinyl chloride) (PVC)

1. Introduction

Bimodal PVC latexes, used in the manufacture of low viscosity plastisols, can be synthesized by seeded emulsion polymerization.[1] Basically, the process consists of two separate polymerization stages: (i) synthesis of the seed by classical emulsion polymerization; (ii) simultaneous growth of the seed and formation of a second population of smaller particles by seeded emulsion polymerization. Qualitatively, the mechanisms that govern the evolution of the particle size distribution (PSD) during the second stage are well understood.[2] From a quantitative point of view, however, the situation is much less favorable. This problem is common to the generality of the processes of synthesis of bimodal latexes,[3] and basically has to do with a lack of quantitative knowledge of some key phenomena of emulsion polymerization (secondary particle formation, colloidal stability, etc.).

Few experimental works related the process in question have appeared in the open literature. Gatta et al.[4] investigated secondary particle formation (SPF) in the seeded emulsion polymerization of vinyl chloride (VCM). They found that a limited amount of emulsifier was not enough to prevent SPF; to obtain a monodisperse final latex, the number of seed particles per unit volume of water also had to be above a certain critical value. Their results show that the minimum number of particles decreases with increasing seed diameter, and are consistent with an interpretation (not done by the authors) in terms of a minimum value for the product $(N\bar{d})_{\mathrm{seed}}$, the critical value of which would be 6.8×10^8 m/L. Similar experiments were performed by Tauer & Petruschke,[5] who found that SPF could be prevented if $(N\bar{d})_{\mathrm{seed}} > 3.7 \times 10^9$ m/L, for surfactant concentrations in the range $3.7 < [S] < 22$ mM. For $[S] > 22$ mM, SPF

CNRS-LCPP/ESCPE-Lyon, BP 2077, 43 Bd du 11 Novembre 1918, 69616 Villeurbanne Cedex, France
E-mail: mckenna@cpe.fr

was again observed independently of high values of $(N\overline{d})_{\text{seed}}$. These two studies seem to corroborate each other, as both relate the onset of SPF to a minimum value of the product $(N\overline{d})_{\text{seed}}$. However, very distinct values are presented for this parameter. Regarding the extent of SPF and its relation to the operating conditions (which would be the most valuable information), no experimental data or explanations are reported in the literature.

The number of models proposed to describe the evolution of PSD in VCM emulsion polymerization is also limited. Min & Gostin,[6] pioneers in the use of population balance models, are the only ones who specifically considered the synthesis of bimodal PVC latexes. Nevertheless, these authors neglected homogeneous nucleation and thus assumed that new particles would only be formed in presence of micelles, which is in disagreement with the experimental findings cited above.[4,5] Another model was developed by Forcolin et al.,[7,8] but the authors only performed numerical simulations to assess the influence of the concentrations of emulsifier and buffer, and agitation rate on latex stability and PSD. More recently, Kiparissides et al.[9] proposed a model to evaluate the effect of oxygen concentration on the kinetics and PSD of VCM emulsion polymerization. Nevertheless, the surface charge density of the particles (which plays a primordial role in determining colloidal stability) was determined by an empirical expression that gives values two orders of magnitude smaller than those found experimentally.[10] Despite such incoherence, the model could successfully explain the effect of the oxygen concentration on the evolution of conversion and particle size.

The above paragraphs show that further experimental and modeling work is required if we are to improve our quantitative understanding of the evolution of PSD during the synthesis of bimodal PVC latexes. In particular, additional experimental data is needed on SPF, to quantify the effects of the concentrations of seed particles and surfactant upon the number of new particles formed. One of the purposes of this paper is to report preliminary results on this subject. Some innovative contributions do the modeling of PSD will be presented as well.

2. Experimental

Vinyl chloride monomer, without inhibitor, was supplied by CIRES, with a purity of 99.99% as indicated by gas chromatography. Ammonium persulfate (ACS) was used as the initiator. Sodium dodecyl sulfate (99%) was used as the surfactant. Deionized water was used throughout the work.

All polymerizations were carried at $50.0 \pm 0.5\,^{\circ}\text{C}$ in a 1.5-L jacketed stainless steel reactor. The initial charge – composed of surfactant, water, and seed latex (in seeded experiments) – was first added to the reactor. Residual oxygen was then removed by purging with nitrogen, followed by 30 min of vacuum. After that, the desired amount of VCM was charged and the reactor contents heated to the polymerization temperature. In the seeded experiments, the system was allowed to equilibrate for 1.5 h at the reaction temperature. The polymerization was started by introducing the initiator, dissolved in 25 mL of water, via nitrogen pressure. All batches contained 1125 g of water, 100 g of monomer, and 0.25 g of initiator.

The seed latex was prepared by washing a latex (previously synthesized in ab initio polymerization; $\overline{d} = 80$ nm) with a mixture of anionic and cationic ion-exchange resins (Dowex MR-3, Aldrich).

Monomer conversion was determined by conventional gravimetric analysis and average particle size was measured by dynamic light scattering (Malvern Zetasizer 1000HS). In seeded polymerizations, the extent of secondary particle formation was determined by examining the final latex by TEM and counting the number of small (new) and big (seed) particles.[11]

3. Results and Discussion

A series of polymerizations (ab inito and seeded) were performed to analyze the effect of the number of seed particles per unit volume of aqueous phase (N_{seed}) at constant values of the initial concentration of free surfactant in the aqueous phase ($[S]_{w,0}$), and vice-versa. To compute $[S]_{w,0}$, the amount of surfactant adsorbed on the surface of the seed particles was estimated by means of the corresponding adsorption isotherm.[12] In all experiments, $[S]_{w,0}$ was kept below the estimated CMC of the surfactant. The experimentally-measured CMC of SDS in presence of initiator ($[\mathrm{APS}] = 1.0$ mM) is 8 mM at 50 °C; the presence of VCM may modify this value, but such effect could not be quantified.

The results of the seeded polymerizations, expressed in terms of the ratio of new to seed particles, are summarized in Figure 1. It is worth noting that the difference between the diameters of new and seed particles was always large enough to permit a clear identification of both populations.

Multiplying the ratio of new to seed particles by N_{seed}, we can compute the number of new particles formed per unit volume of aqueous phase, N_{new}. This quantity can then be plotted together with the number of particles formed in absence of seed (i.e., in ab initio polymerizations), as shown in Figure 2.

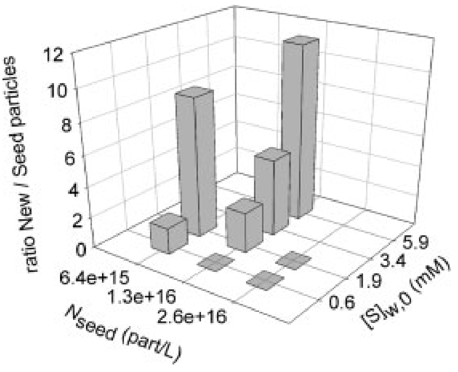

Figure 1.
Ratio of new to seed particles as a function of seed concentration and initial concentration of free surfactant in the aqueous phase. The diameter of the seed is 80 nm.

A lot can be learned from the analysis of Figure 2. The first obvious thing is that, as noticed by previous authors,[4,5] micelles are not necessary in order to form secondary particles. This was already expected given the significant role of homogeneous nucleation in VCM emulsion polymerization.[13]

The second observation is that, for a given concentration of seed particles (e.g., $N_{\mathrm{seed}} = 1.3 \times 10^{16}$ part/L), the number of new particles formed increases with surfactant concentration. This is an evidence that coagulation plays a role in secondary particle formation. Indeed, because N_{seed} is constant, the rate of production of precursor particles via homogeneous nucleation is also constant. Therefore, a variation of N_{new} can only be due to the effect of the surfactant upon the rates of coagulation of the precursor particles with themselves or with the seed particles.

Figure 2 also shows that increasing N_{seed} while keeping $[S]_{w,0}$ fixed leads to a decrease of the extent of secondary particle formation. This can be explained in terms of two effects: (i) increasing N_{seed} decreases the rate of production of precursor particles because more aqueous-phase radicals will preferentially enter seed particles; (ii) increasing N_{seed} augments the rate of coagulation between precursor and seed particles.

In sum, the data show that in general, both the onset and the extent of SPF are determined not only by the rate of homogenous nucleation, but also by the rates of homo- and/or heterocoagulation. Obviously, SPF can be completely prevented (in the absence of micelles) by a value of N_{seed} sufficiently large to capture most aqueous-phase radicals and reduce homogeneous nucleation to a negligible level. This appears to correspond to the condition determined by Tauer & Petruschke.[5] But SPF can also be avoided for lower values of N_{seed}, as long as the rate of coagulation of the precursor particles (favored at low surfactant concentrations) compensates for the rate of formation of precursor particles.

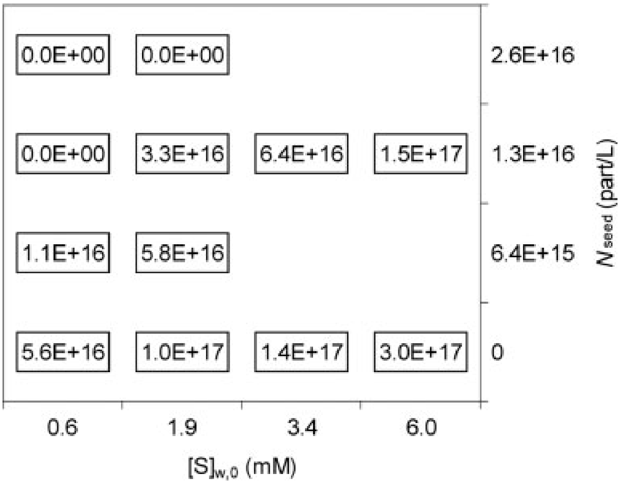

Figure 2.
Plot of the number of new particles formed as a function of seed concentration and initial concentration of free surfactant in the aqueous phase.

This is probably what we see in Figure 2 for $N_{\text{seed}} = 1.3 \times 10^{16}$ part/L and $[\text{S}]_{\text{w},0} = 0.6$ mM.

Additional experiments with seeds of different diameters are in course to find out if the effects of N_{seed} and seed diameter can be interpreted in terms of a single parameter.

4. Modeling of the PSD

Before we can aspire to build a sound model for the process addressed here, we need to have a better understanding of crucial phenomena like SPF (Section 3) and particle coagulation,[14,15] among others. But there also some questions to be resolved from a more theoretical point of view, namely with respect to the modeling of the PSD, as will be discussed below.

4.1 The Pseudo-Bulk and Zero-One Models

Two approaches are currently in use to describe the evolution of PSD in emulsion polymerization: the pseudo-bulk model and the zero-one model.[14] Both are simplifications of an infinite set of population balance equations (PBEs) that take into account the particle size as well as the number of radicals per particle.[16]

The zero-one model is valid for systems where termination in the particles is so fast as not to be rate-determining (thus, particles can have either zero or one radical). Because of this restriction, the zero-one model is only applicable to small particles. Employing the method of Casey et al.,[17] we can conclude that in the case of vinyl chloride this approach would only be valid for particles of swollen diameter below 10 nm. Clearly, this condition is too severe for any practical application.

The pseudo-bulk (PB) model is based on a single PBE that only accounts for particle size; all particles of the same size are assumed to have the same number of radicals. This approach is by large the most employed in the polymer reaction engineering field and has been utilized in all models of VCM emulsion polymerization developed so far.[6–9] Nevertheless, the PB model is not without its limitations. In fact, in this approach, the average number of radicals per particle ($\overline{n}$) is computed by an approximate expression[18,19] that neglects the effects of nucleation, coagulation, growth, and dynamics. Although this simplification works well in certain conditions, it is not valid in general. In particular, it can lead to severe errors when simulating particle formation processes, since the contribution of the effects neglected can then be significant. Examples of cases where the PB model works well and fails will be given in the following section.

To surmount the difficulties encountered with the zero-one and PB models, we need to find an alternative that allows for the fact that intraparticle termination is not instantaneous and that correctly accounts for particle size as well as number of radicals per particle. The simplest option is the zero-one-two model, described next.

4.2 The Zero-One-Two Model

In a zero-one-two (0-1-2) system,[20–22] the entry of a radical into a particle containing *two* radicals is assumed to result in pseudo-instantaneous termination. This simplification is valid when $\overline{n}$ is low, but termination is rate-determining. The 0-1-2 model is thus well suited for VCM emulsion polymerization, seeing that $\overline{n}$ is usually in the range 0.001–0.1 and the zero-one model is not applicable. In fact, the 0-1-2 approach has been used with success by Ugelstad et al.[23] to describe the kinetics of this system.

On the basis the 0-1-2 model, the full set of PBEs for a perfectly-mixed batch reactor reads

$$\begin{aligned}
\frac{\partial}{\partial t}\begin{bmatrix} f_0 \\ f_1 \\ f_2 \end{bmatrix} &= -\frac{\partial}{\partial v}\begin{bmatrix} 0 \\ Kf_1 \\ 2Kf_2 \end{bmatrix} + \begin{bmatrix} -\rho & k_{\mathrm{des}} & 2c \\ \rho & -\rho - k_{\mathrm{des}} & \rho + 2k_{\mathrm{des}} \\ 0 & \rho & -\rho - 2k_{\mathrm{des}} - 2c \end{bmatrix}\begin{bmatrix} f_0 \\ f_1 \\ f_2 \end{bmatrix} \\
&+ \begin{bmatrix} 1/2\int_{v_{\mathrm{nuc}}}^{v-v_{\mathrm{nuc}}} \beta(v-v',v')[f_0(v-v')f_0(v') + f_2(v'-v')f_2(v')]dv' - f_0(v)\int_{v_{\mathrm{nuc}}}^{\infty} \beta(v,v')f(v')dv' \\ \int_{v_{\mathrm{nuc}}}^{v-v_{\mathrm{nuc}}} \beta(v-v',v')[f_0(v-v')f_1(v') + f_1(v-v')f_2(v')]dv' - f_1(v)\int_{v_{\mathrm{nuc}}}^{\infty} \beta(v,v')f(v')dv' \\ \int_{v_{\mathrm{nuc}}}^{v-v_{\mathrm{nuc}}} \beta(v-v',v')f_0(v-v')f_2(v')dv' + 1/2\int_{v_{\mathrm{nuc}}}^{v-v_{\mathrm{nuc}}} \beta(v-v',v')f_1(v-v')f_1(v')dv' - f_2(v)\int_{v_{\mathrm{nuc}}}^{\infty} \beta(v,v')f(v')dv' \end{bmatrix} \\
&+ \begin{bmatrix} 0 \\ \delta(v - v_{\mathrm{nuc}})R_{\mathrm{nuc}} \\ 0 \end{bmatrix}
\end{aligned} \tag{1}$$

where f_n $(v,\ t)$ is the number density function for particles having n radicals, v is the unswollen volume of a particle, K is the rate coefficient of volume growth, ρ is the total entry frequency of radicals into particles, k_{des} is the desorption frequency, c is the pseudo-first-order rate coefficient for termination, β is the coagulation rate coefficient, R_{nuc} is the rate of particle nucleation, and v_{nuc} is the unswollen volume of the nucleated particles. The overall distribution is given by $f(v,t) = \sum_n f_n(v,t)$. It is worth noting that: (i) in the limit $c \to \infty$, we recover the zero-one equations; (ii) by summing up along the columns, Eq. (1) reduces to the PB model with $\overline{n} = (f_1 + 2f_2)/f$.

To the best of our knowledge, Eq. (1) has not previously been used to describe the evolution of PSD in emulsion polymerization (nor for VCM, nor for any other system). The numerical solution of Eq. (1) can be carried out by means of a recently developed method.[24]

In Figure 3, we present a comparison of the results obtained with the PB and 0-1-2 models for the growth of PVC seed. As we can see, the final PSDs are identical. This shows two things. On one hand, it indicates that the hypotheses of the PB model are valid for growth processes and, on the other hand, it demonstrates that the 0-1-2 model is applicable to vinyl chloride emulsion polymerization.

Figure 4 shows what happens when the same two models are used to simulate a process involving particle formation. The results are now very distinct. These differences are expectable given the assumptions made in the PB model with respect to the calculation of $\overline{n}$. Indeed, in particle formation processes, one can anticipate the contributions of particle nucleation and coagulation to be important for the small particles.

Because the 0-1-2 model is much harder to solve than the PB model (the number of PBEs and coagulation terms is much

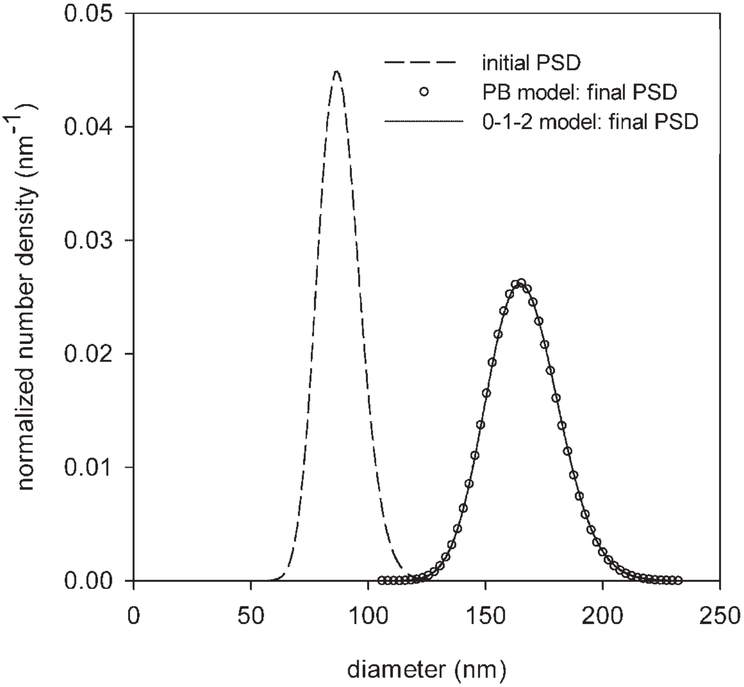

Figure 3.
Growth of a PVC seed. Comparison of the PSDs computed with the PB and 0-1-2 models.

higher), a simpler alternative would desirable. One possibility, currently under evaluation, is to use the 0-1-2 model for the small particles and the PB model for the remaining particles. A similar hybrid approach (zero-one plus PB) has been proposed by Coen et al.[25] to model the emulsion polymerization of butyl acrylate.

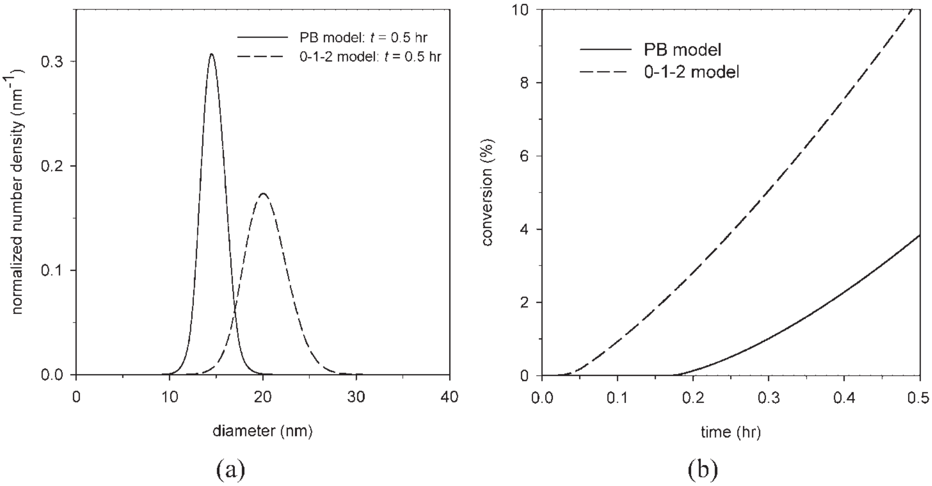

Figure 4.
Ab initio synthesis of a PVC latex. Comparison of the results obtained with the PB and 0-1-2 models: (a) final PSD; (b) evolution of monomer conversion.

5. Conclusions

In this work, we have experimentally investigated the onset and extent of secondary particle formation in the seeded emulsion polymerization of vinyl chloride. To this purpose, a series of seeded polymerizations at different concentrations of seed latex and surfactant were conducted. It was found that, in general, both the onset and the extent of secondary particle formation are determined not only by the rate of homogenous nucleation, but also by the rates of homo- and/or heterocoagulation.

A comparison of methods to compute the evolution of the PSD in vinyl chloride emulsion polymerization was also carried out. The zero-one model is of no practical utility because of the severe restriction imposed on the particle size. The widely-used PB model can be used to simulate growth processes, but not processes involving particle formation, because it neglects, among others, the effects of nucleation and coagulation on the radical number distribution. For more accurate description of the PSD, namely if the process involves particle formation, the 0-1-2 model can and should be applied.

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[1] M.J. Bunten, in: *Encyclopedia of Polymer Science and Engineering*, H.F. Mark, Ed., Wiley, New York, **1985**; vol. 17, p. 329.
[2] T. Lys, PhD Thesis, Université Claude Bernard Lyon I, **2004**.
[3] S. Boutti, PhD Thesis, Université Claude Bernard Lyon I, Lyon, **2003**.
[4] G. Gatta, G. Beneta, G. Talamini, G. Vianello, *Adv. Chem. Ser.* **1969**, *91*, 158.
[5] K. Tauer, M. Petruschke, *Acta Polym.* **1986**, *37*, 313.
[6] K. W. Min, H.I. Gostin, *Ind. Eng. Chem. Prod. Res. Dev.* **1979**, *18*, 272.
[7] S. Forcolin, A. M. Marconi, A. Ghielmi, A. Butté, G. Storti, M. Morbidelli, *Plastics, Rubber and Composites* **1999**, *28*, 109.
[8] S. Melis, A. Ghielmi, G. Storti, M. Morbidelli, *Entropie* **1998**, *212/213*, 65.
[9] C. Kiparissides, D. S. Achilias, C. E. Frantzikinakis, *Ind. Eng. Chem. Res.* **2002**, *41*, 3097.
[10] J. Neelsen, W. Jaeger, G. Reinisch, K.-H. Goebel, *Acta Polym.* **1982**, *33*, 185.
[11] B. R. Morrison, R. G. Gilbert, *Macromol. Symp.* **1995**, *92*, 13.
[12] H. M. Vale, T. F. McKenna, *Colloids Surf. A: Physicochem. Eng. Aspects* **2005**, *268*, 68.
[13] J. Ugelstad, P. C. Mork, A. Berge, in: *Emulsion Polymerization and Emulsion Polymers*, P. A. Lovell, M. S. El-Aasser, (Eds.), John Wiley & Sons, Chichester, **1997**, p. 589.
[14] H. M. Vale, T. F. McKenna, *Prog. Polym. Sci.* **2005**, *30*, 1019.
[15] M. Fortuny, C. Graillat, T. F. McKenna, *Ind. Eng. Chem. Res.* **2004**, *43*, 7210.
[16] K. W. Min, W. H. Ray, *J. Macromol. Sci., Revs. Macromol. Chem.* **1974**, *C11*, 177.
[17] B. S. Casey, B. R. Morrison, I.A. Maxwell, R. G. Gilbert, D.H. Napper, *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 605.
[18] J. T. O'Toole, *J. Appl. Polym. Sci.* **1965**, *9*, 1291.
[19] E. Saldívar, P. Dafniotis, W. H. Ray, *J. Macromol. Sci., Revs. Macromol. Chem. Phys.* **1998**, *C38*, 207.
[20] G. Lichti, R. G. Gilbert, D. H. Napper, *J. Polym. Sci., Part A: Polym. Chem.* **1980**, *18*, 1297.
[21] P. A. Clay, R. G. Gilbert, *Macromolecules* **1995**, *28*, 552.
[22] S. W. Prescott, M. J. Ballard, R. G. Gilbert, *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 1076.
[23] J. Ugelstad, P. C. Mork, P. Dahl, P. Rangnes, *J. Polym. Sci., Part C* **1969**, *27*, 49.
[24] H. M. Vale, T. F. McKenna, *Ind. Eng. Chem. Res.* **2006**, submitted.
[25] E. M. Coen, S. Peach, B. R. Morrison, R. G. Gilbert, *Polymer* **2004**, *45*, 3595.