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Effect of Monomer Feed Rate on Chain Transfer to Polymer in Semibatch Emulsion Polymerization of Vinyl Acetate Studied by NMR Spectroscopy

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ABSTRACT: The effect of growth-stage monomer feed rate on the extent of chain transfer to polymer in semibatch emulsion homopolymerizations of vinyl acetate has been studied by using ^{13}C NMR spectroscopy to quantify the mol % branches in the poly(vinyl acetate) formed. Three 37.5% final solids content emulsion homopolymerizations of vinyl acetate were carried out at 70 °C using identical seed stages, but different monomer feed rates of 0.35, 1.39, and 2.08% min^{-1} in the growth stages. The polymerizations performed using the feed rate of 0.35% min^{-1} proceeded under monomer-starved conditions throughout, and the mol % branches increased steadily with overall conversion. Use of the higher feed rates led to lower instantaneous conversions from the end of the seed stage (17% overall conversion) to about 40% overall conversion, from which point onward the polymerizations proceeded under monomer-starved conditions. During the period of reduced instantaneous conversion, the frequency of chain transfer to polymer was lower, and the cumulative mol % branches reduced. However, as the polymerization progressed further and high instantaneous conversions were recovered, the mol % branches increased steadily. Thus, the lower values of mol % branches for the final samples of poly(vinyl acetate) from the reactions run at the two higher monomer feed rates result directly from the lower frequency of chain transfer to polymer in the period of monomer flooding that followed the start of the monomer feeds. The variation of conversion and mol % branches for two polymerizations carried out under the same conditions but to different final solids contents (37.5 and 50%) were virtually identical and confirm that the variation of instantaneous conversion with overall conversion is the principal factor controlling the mol % branches.

Introduction

Although the occurrence of chain transfer to polymer in emulsion polymerization of vinyl acetate is well established and important in terms of polymer properties, most of the evidence for branching in poly(vinyl acetate) has been indirect.[1,2] However, in a previous publication,[3] we reported on the use of ^{13}C NMR resonances to quantify the mol % branches in poly(vinyl acetate) prepared by free-radical bulk and emulsion polymerization. The ^{13}C NMR spectra were fully interpreted in terms of structural features arising from (i) normal and inverted repeat unit placements, (ii) chain transfer to polymer, and (iii), in the case of emulsion polymerization, hydrolysis of acetate side groups. The spectra showed that although chain transfer to polymer proceeds via both the backbone tertiary C−H and the methyl side group (see Scheme 1), abstraction of methyl side group hydrogen atoms is by far the dominant reaction. The branch point CH_2 carbons (labeled α and β in Scheme 1), however, give resonances that overlap with those from CH_2 carbons in, and adjacent to, inverted repeat units, preventing their use in quantification of the level of branching. Nevertheless, the well-resolved signal at $\delta_C \approx 61$ due to the end group ultimate CH_2 carbon (labeled U in Scheme 1) can be used to determine the mol % branches in poly(vinyl acetate), because one end group of this type is formed for each chain transfer to polymer event and other reactions that could contribute to the number of these end groups are not significant.[3]

Scheme 1. Mechanisms of Chain Transfer to Polymer in Free-Radical Homopolymerization of Vinyl Acetate

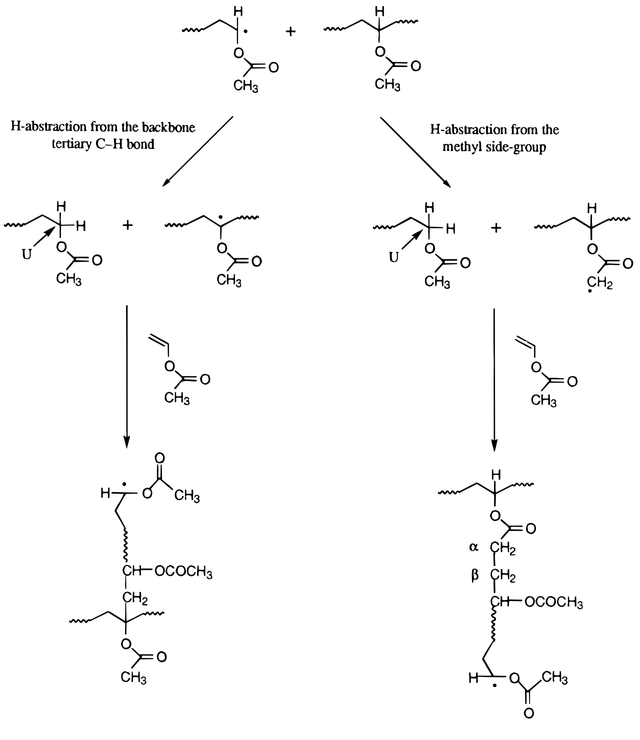

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Table 1. Emulsion Polymerization Formulation (~2 dm^3 Scale)

formulation component	seed stage (mass/g)	growth stage (mass/g)
vinyl acetate	135.0	675.0
deionized water	1215.0	135.0
aerosol OT-75	9.30	24.83
sodium bicarbonate	0.90	
ammonium persulfate	1.00	3.00

Besides establishing ^{13}C NMR methods for measurement of branching levels in poly(vinyl acetate), the previous studies[3] examined the effects of polymerization process, conversion, and polymerization temperature on the extent of branching. In the present paper, we report ^{13}C NMR investigations of the effects of monomer feed rate on the extent of chain transfer to polymer in semibatch emulsion homopolymerization of vinyl acetate. Such effects are often distinguished in relation to *monomer-starved* and *monomer-flooded* conditions, terms that often are loosely defined. The most satisfactory means of specifying the monomer-starved condition is to state that the monomer concentration in the particles must be below its equilibrium value for the temperature and pressure of polymerization. However, as in the work reported here, most researchers do not measure the equilibrium monomer concentration in the particles or the monomer concentration in the particles as a function of conversion, so the most common means of defining monomer-starved conditions is in terms of the instantaneous monomer conversion. This inevitably leads to ambiguities in defining the demarcation between monomer-starved and monomer-flooded conditions. In the present paper, the demarcation does not need to be defined because the crossover from monomer-starved to monomer-flooded conditions will produce a smooth change (not a step change) in the extent of branching. Thus, the terms are used here simply to indicate periods in the polymerizations when the mole fraction of monomer in the latex particles is either very low or high, respectively.

Experimental Section

Purification of Reagents. Vinyl acetate (Aldrich, >99%) was washed three times with dilute sodium hydroxide solution to remove the phenolic inhibitor, followed by washing thoroughly with water before drying over anhydrous calcium chloride. Tetrahydrofuran (Prolabo, 99%) (THF) was dried by heating under reflux over anhydrous calcium chloride for 1 h and then distilled under nitrogen at atmospheric pressure. Water was deionized by passage through a series of Milli-RO6 (Millipore) ion exchange columns. Ammonium persulfate (BDH, 99.5%), sodium bicarbonate (BDH, 99.0%), Aerosol OT-75 (Cytec), and hydroquinone (Aldrich, 99%) were used as supplied.

Emulsion Polymerizations. Table 1 gives the formulation used for the emulsion polymerizations, which were performed under a flowing nitrogen atmosphere at 70 °C on scales of approximately 2 dm^3 in flanged reaction vessels. The seed-stage water (less 45 g), Aerosol OT-75, and sodium bicarbonate were weighed into the reaction vessel, which then was equipped with a nitrogen inlet, condenser, and mechanical stirrer before being placed in a water bath thermostated to ±1 °C. A steady flow of nitrogen was established while the surfactant/buffer solution attained the bath temperature, after which the seed-stage vinyl acetate was added. When the temperature had stabilized, a solution of the seed-stage ammonium persulfate in water (40 g) was added and washed into the reaction vessel with a further quantity of water (5 g). The seed-stage reaction was allowed to proceed for 60 min before beginning the growth stage, in which a solution of the growth-stage Aerosol OT-75 in the growth-stage vinyl acetate was metered into the reaction vessel at a controlled rate using a Watson-Marlow 505S peristaltic pump. Three reactions were carried out using different growth-stage feed rates, which were (i) 2.9 g min^{-1}, (ii) 11.7 g min^{-1}, and (iii) 17.5 g min^{-1}. In each case, three further quantities of ammonium persulfate (1.00 g) in water (40 g) were added and washed in with water (5 g) at the following times from the beginning of the seed stage: (i) 60, 120, and 180 min for the 2.9 g min^{-1} feed rate, (ii) 60, 75, and 90 min for the 11.7 g min^{-1} feed rate, and (iii) 60, 70, and 80 min for the 17.5 g min^{-1} feed rate. On completion of the growth-stage addition, a further 60 min reaction time was allowed for completion of the polymerization before cooling the latex to room temperature and passing it through a 53 μm sieve.

For each polymerization, aliquots (ca. 10 cm^3) were removed at the end of the seed stage and at intervals thereafter. To quench the reaction, each aliquot was transferred directly to a sample bottle which was placed in an ice/water bath and contained a preweighed quantity (ca. 0.3 g) of a 1% aqueous hydroquinone solution. The aliquots were used to monitor the conversion and the level of branching. Conversions were determined from duplicate measurements of solids content using a mass-balance approach to account for previously removed aliquots and nonpolymeric solids. Samples for analysis by NMR spectroscopy were prepared as follows: (i) dialysis of the latex (contained in Visking tubing) against an approximately 1000× excess of deionized water for a minimum of 10 days with at least one change of water each day, (ii) freeze−thaw cycling of the dialyzed latex until complete coagulation resulted, (iii) decanting of the supernatant from the coagulated polymer before washing with deionized water and drying to constant weight at 60 °C under vacuum, and (iv) transfer of the dried polymer to the NMR tube.

NMR Spectroscopy. ^{13}C NMR spectra were recorded at 23 ± 1 °C using a Varian Associates Unity 500 spectrometer operating at 125.8 MHz. Samples of poly(vinyl acetate) were dissolved in $CDCl_3$ to give solutions of concentration ca. 100 mg cm^{-3}. Chemical shifts were referenced to the solvent peak at 77 ppm. To maximize the signal-to-noise ratio in a given time, all spectra were run with continuous ^1H decoupling using a pulse interval of 0.5 s and a pulse flip angle of 70°. Under these rapid pulse conditions, the relative intensities do not necessarily reflect the relative abundance of each type of carbon because of differential relaxation times and nuclear Overhauser enhancements (NOE). In particular, the intensities of primary and quaternary carbons are underestimated relative to CH and CH_2 carbons. To ensure quantitative accuracy of data calculated from the spectra, the data were corrected using a factor determined previously[3] from fast pulse spectra (run under the same conditions as used in the present work) and NOE-suppressed spectra.

Results and Discussion

NMR Determination of mol % Branches in Poly(vinyl acetate). The resonances observed in the ^{13}C NMR spectra of the samples of poly(vinyl acetate) from the emulsion polymerizations were identical to those already reported and assigned,[3] and so spectra are not included here. As previously established, the mol % of branched repeat units in poly(vinyl acetate) was calculated from the fast pulse spectra run in $CDCl_3$ using the following equation:[3]

$$\text{mol \% branches} = \frac{100 \times 0.8 \times I_{60-62}}{0.5 \times [I_{24-74} - (0.2 \times I_{60-62})]} \quad (1)$$

where I_{60-62} is the end group ultimate CH_2 integral ($60 \le \delta_C \le 62$), I_{24-74} is the total backbone carbon integral

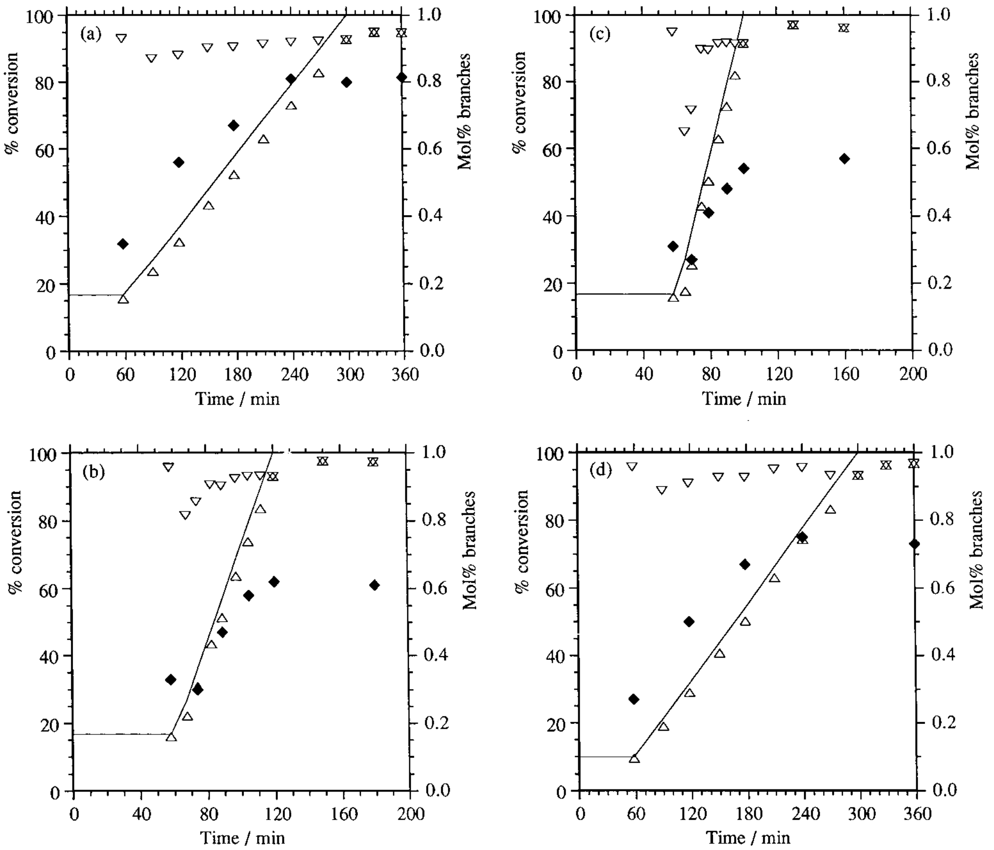

Figure 1. Variation of instantaneous conversion (▽), overall conversion (△), and mol % branches (◆) with reaction time for a series of emulsion homopolymerizations of vinyl acetate carried out at 70 °C. The solid lines show the monomer feed profiles. (a)–(c) are 37.5% final solids reactions in which the growth-stage monomer feed rates were 0.35, 1.39, and 2.08% $\min^{-1}$, respectively. For comparison, (d) shows data from a previous 50% final solids reaction[3] carried out at 70 °C with a monomer feed rate of 0.38% $\min^{-1}$ using the same procedure as for the 37.5% final solids reactions.

($24 \leq \delta_C \leq 74$), and the factor of 0.8 corrects for differences in longitudinal relaxation times and NOE.

Results from Emulsion Polymerization of Vinyl Acetate. Our previous work on chain transfer to polymer in vinyl acetate emulsion polymerization was carried out using a formulation that gave latexes with a 50% final solids content and employed a growth-stage monomer feed rate that was low enough to achieve monomer-starved conditions.[3] The aim of the present studies was to investigate the effect of increasing the growth-stage monomer feed rate on the extent of chain transfer to polymer and the level of branching in the poly(vinyl acetate) produced. Initial experiments carried out with the previously used 50% solids formulation showed, however, that excessive coagulum was formed at high growth-stage monomer feed rates, rendering the results inaccurate. The formation of coagulum at high feed rates was reduced to tolerable levels (<1%) very simply by reducing the amount of monomer/surfactant mixture used in the growth stage, such that the final solids content was 37.5%; the seed stage and the ratio of Aerosol OT to vinyl acetate used in the growth stage were the same as for the previous emulsion polymerizations, as were the quantities of initiator and buffer. Thus, in all respects except the final solids content, the procedures/formulation used for the emulsion polymerizations described here were identical to those reported previously.[3] The lower final solids content enabled much higher growth-stage monomer feed rates to be accessed and had the further benefit that the effect of final solids content could be assessed by comparison of the results with those from the previous study.

Parts a–c of Figure 1 are plots of conversion and mol % branches versus time for the three 37.5% final solids emulsion polymerizations of vinyl acetate. The instantaneous conversion is the percentage conversion of the monomer added up to that point in time (including the monomer used in the seed stage), whereas the overall conversion is the percentage conversion of the total amount of monomer in the formulation. The normalized growth-stage monomer feed rates (given in % $\min^{-1}$) were calculated as the ratio of the monomer mass feed rate to the total mass of monomer in the formulation. For each polymerization, at the end of the seed stage the conversion is in the range 93–96% and the level of branching in the poly(vinyl acetate) is 0.31 ± 0.01 mol %. Given that the seed stages were identical in formulation and procedure, these results show the good reproducibility of this stage of the emulsion polymerizations. Increasing the growth-stage monomer feed rate leads to a reduction in the instantaneous conversion that becomes more significant as the feed rate is increased and clearly has its greatest effect in the period immediately after starting the feed. The effect of growth-stage monomer feed rate on mol % branches is more clearly evident in Figure 2, which shows the variation of mol % branches with overall conversion for each of the emulsion polymerizations. Before interpreting the mol % branches data in relation to the conversion data, the factors controlling chain transfer to polymer need to be considered.

The mole fraction of branched repeat units in polymer formed at a particular instant in time is equal to the probability that a propagating chain radical undergoes

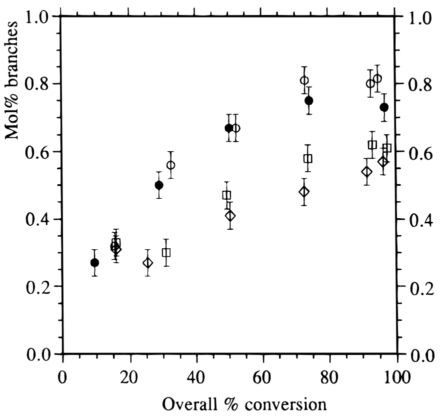

Figure 2. Variation of the mol % branches with overall conversion for the 37.5% final solids emulsion homopolymerizations of vinyl acetate carried out at 70 °C using growth-stage monomer feed rates of 0.35 (○), 1.39 (□), and 2.08% min^{-1} (◇). Data from a previous 50% final solids reaction[3] carried out at 70 °C with a monomer feed rate of 0.38% min^{-1} using the same procedure as for the 37.5% final solids reactions are shown for comparison (●).

chain transfer to polymer rather than propagation. On this basis, the mol % branches is given by

$$\text{mol \% branches} = 100 \times \left[\frac{\left(\frac{k_{\text{trP}}}{k_{\text{p}}}\right)\frac{[\text{P}]}{[\text{M}]}}{\left\{\left(\frac{k_{\text{trP}}}{k_{\text{p}}}\right)\frac{[\text{P}]}{[\text{M}]}\right\} + 1} \right] \quad (2)$$

where k_{trP} and k_{p} are the rate coefficients for chain transfer to a polymer repeat unit and for propagation, respectively, and [P] and [M] are the concentrations of polymer repeat units and monomer, respectively. Thus, the two factors that control the extent of chain transfer to polymer and branching are the rate coefficient ratio $k_{\text{trP}}/k_{\text{p}}$ and the concentration ratio [P]/[M].

In the present studies, $k_{\text{trP}}/k_{\text{p}}$ can be assumed to be constant because all the polymerizations were carried out at the same temperature (70 °C). Hence, the extent of chain transfer to polymer will have been controlled by [P]/[M], which in emulsion polymerizations needs to be considered in terms of the concentrations within the particles (i.e., $[\text{P}]_{\text{p}}$ and $[\text{M}]_{\text{p}}$) because they are the principal loci for propagation and chain transfer to polymer. The ratio $[\text{P}]_{\text{p}}/[\text{M}]_{\text{p}}$ is controlled by the instantaneous conversion and the partitioning of monomer and is particularly sensitive to these quantities when the instantaneous conversion is high.[4] Although quantitative correlation of the mol % branches data with the instantaneous conversion data using an integrated form of eq 2 is possible, such analysis is not justified because of the difficulty in accurately accounting for partitioning of vinyl acetate (which has high water solubility) and the errors involved in calculating $[\text{P}]_{\text{p}}/[\text{M}]_{\text{p}}$ from high values of instantaneous conversion determined gravimetrically.

As can be seen from Figure 1a–c, the effect of increasing the growth-stage monomer feed rate is to reduce the instantaneous conversion in the period following the start of monomer feeding. After passing through a minimum, the instantaneous conversion steadily recovers to values above 90%, and the polymerization then proceeds under highly monomer-starved conditions with, more importantly, high values of $[\text{P}]_{\text{p}}/[\text{M}]_{\text{p}}$. For all the polymerizations, the variation of instantaneous conversion with overall conversion is similar beyond about 40% overall conversion, showing that the effects of monomer feed rate must result primarily from the period in which the overall conversion increases from 17% (i.e., the end of the seed stage) to 40%. The reduction in the instantaneous conversion during this period becomes more pronounced as the monomer feed rate increases, which naturally leads to larger reductions in the ratio $[\text{P}]_{\text{p}}/[\text{M}]_{\text{p}}$ and hence in the level of branching. Figure 1a shows that at the lowest monomer feed rate of 0.35% min^{-1} the reduction in the instantaneous conversion is quite small (the minimum value is 87%), and the polymerization can be considered to have proceeded essentially under monomer-starved conditions throughout the growth stage. For this reaction, the mol % branches increases steadily, but at a reducing rate, as the overall conversion increases (see Figure 2), consistent with previous observations of similar vinyl acetate emulsion homopolymerizations.[3] However, the polymerizations employing monomer feed rates of 1.39 and 2.08% min^{-1} show reductions in the instantaneous conversion to observed minimum values of 81% and 65%, respectively (see Figure 1b,c). The consequence is that significantly lower values of $[\text{P}]_{\text{p}}/[\text{M}]_{\text{p}}$ exist over the 17–40% overall conversion interval and result in a reduced frequency of chain transfer to polymer during this period. The effect can be seen in the mol % branches data, which are lower for the samples removed during this period than for the samples removed at the end of the seed stages. The effect is more significant than it may appear because the mol % branches is a cumulative quantity and includes branches present in the poly(vinyl acetate) formed earlier in the reaction (i.e., in the seed stage). The subsequent samples were removed at times corresponding to overall conversions above 40% (i.e., when the instantaneous conversion had recovered to values ≥90%), and so the mol % branches steadily increases in accord with normal observations on monomer-starved polymerizations. Thus, the lower values of mol % branches for the final samples of poly(vinyl acetate) from the reactions run at the two higher monomer feed rates result directly from the lower frequency of chain transfer to polymer in the period of monomer flooding that follows the start of the monomer feeds.

Figure 1d shows data from the previously reported vinyl acetate emulsion polymerization[3] on which the present work was based. This polymerization was carried out at 70 °C using a growth-stage monomer feed rate of 0.38% min^{-1} but with a final solids content of 50%. Hence, the results may be compared with those shown in Figure 1a (i.e., for the 37.5% solids polymerization carried out at the same temperature and using essentially the same monomer feed rate); the comparison shows that changing the final latex solids content had no significant effect on the variation of instantaneous conversion with reaction time and, consequently, no major effect on the variation of mol % branches with overall conversion (see Figure 2). Given that the instantaneous conversions are high (i.e., there are relatively small total amounts of unreacted vinyl acetate) and that vinyl acetate has a relatively high solubility in water, the slightly lower values of mol % branches for the 50% solids polymerization may be a consequence of the smaller proportion of aqueous phase, since at any particular overall conversion this would result in a higher value of $[M]_p$ than for the 37.5% solids polymerization.

Conclusions

The results from this study show that, in accord with simple predictions from eq 2, the variation of instantaneous conversion with overall conversion is the principal factor controlling the mol % branches in poly(vinyl acetate) produced by emulsion polymerization. Increasing the growth-stage monomer feed rate has its greatest effect in the period immediately after starting the feed, since it can lead to a period of significantly reduced instantaneous conversion during which the frequency of chain transfer to polymer is reduced. The lower values of mol % branches in poly(vinyl acetate) produced by the emulsion polymerizations run at the higher monomer feed rates, therefore, resulted directly from the lower frequency of chain transfer to polymer in the period of monomer flooding that follows the start of the monomer feed.

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References and Notes

(1) Daniels, W. In *Encyclopedia of Polymer Science and Engineering*; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; Wiley-Interscience, John Wiley & Sons: New York, 1989; Vol. 17, p 393.

(2) Vandezande, G. A.; Smith, O. W.; Bassett, D. R. In *Emulsion Polymerization and Emulsion Polymers*; Lovell, P. A., El-Aasser, M. S., Eds.; John Wiley & Sons: Chichester, 1997; Chapter 16, p 563.

(3) Britton, D.; Heatley, F.; Lovell, P. A. *Macromolecules* **1998,** *31*, 2828.

(4) Lovell, P. A. In *Emulsion Polymerization and Emulsion Polymers*; Lovell, P. A., El-Aasser, M. S., Eds.; John Wiley & Sons: Chichester, United Kingdom, 1997; Chapter 7, p 239.

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