Chain Transfer to Polymer in Emulsion Copolymerizations

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SUMMARY: Chain transfer to polymer in emulsion copolymerizations of (i) vinyl acetate (VAc) with n-butyl acrylate (BA) and (ii) BA/acrylic acid with (a) methyl methacrylate (MMA) and (b) styrene (S) has been studied using ^{13}C NMR spectroscopy to quantify the level of branching in the copolymers produced. The results reveal synergistic effects in which the inclusion of a small amount of comonomer leads to disproportionate changes in the level of branching. The data from the VAc/BA copolymerizations show that radicals with VAc end units abstract hydrogen atoms from BA repeat units more frequently than from VAc repeat units and that radicals with VAc end units are more effective in abstracting hydrogen atoms from BA repeat units than are radicals with BA end units. These effects lead to higher levels of branching in VAc/BA copolymers than results from the corresponding homopolymerizations and are a consequence of the efficacy of hydrogen abstraction at BA backbone tertiary C–H bonds by the highly-reactive VAc-ended chain radicals. In contrast, the effect of introducing MMA or S to an acrylate polymerization is to disproportionately reduce the level of branching, with S being more effective than MMA in moderating chain transfer to polymer. These effects arise because propagating radicals with MMA or S end-groups have longer lifetimes compared to those with acrylate end groups and have a very much lower tendency to abstract hydrogen atoms from acrylate repeat units.

Introduction

Chain transfer to polymer in free-radical polymerization leads to the formation of branched polymers and has significant consequences for polymer rheological and mechanical properties. Although this has been studied thoroughly for preparation of low density polyethylene by free-radical polymerization of ethylene[1-3)], until our work during the past decade, chain transfer to polymer in free-radical polymerizations of other monomers had received far less attention. ^{13}C NMR spectroscopy is the principal analytical tool employed in our studies. The structural features arising from chain transfer to polymer have been

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identified through the presence of distinctive resonances that enabled the chemistry of chain transfer to polymer to be elucidated and the extent of chain transfer to polymer to be to quantified. In particular, we have reported studies of chain transfer to polymer in bulk, solution and emulsion free-radical homopolymerizations of vinyl acetate (VAc)[4,5)] and n-butyl acrylate (BA)[6-9)]. This work established unequivocally that chain transfer to polymer in free-radical homopolymerizations of VAc proceeds principally via hydrogen abstraction from the methyl side-group with only a minor contribution from hydrogen abstraction at backbone tertiary C–H bonds (Scheme 1a) and that chain transfer to polymer occurs more extensively in free-radical polymerizations of BA, proceeding via abstraction of hydrogen atoms from backbone tertiary C–H bonds (Scheme 1b).

More recently, our attention has turned to the important topic of chain transfer to polymer in free-radical copolymerizations, in particular emulsion copolymerizations. These studies are framed around the NMR methods we have established for quantifying the extent of chain transfer to polymer in free-radical homopolymerizations of VAc and BA. This paper reports results from studies aimed at determining the effects of comonomers on the nature and extent of chain transfer to polymer for emulsion copolymerizations in which the principal monomer is BA or VAc.

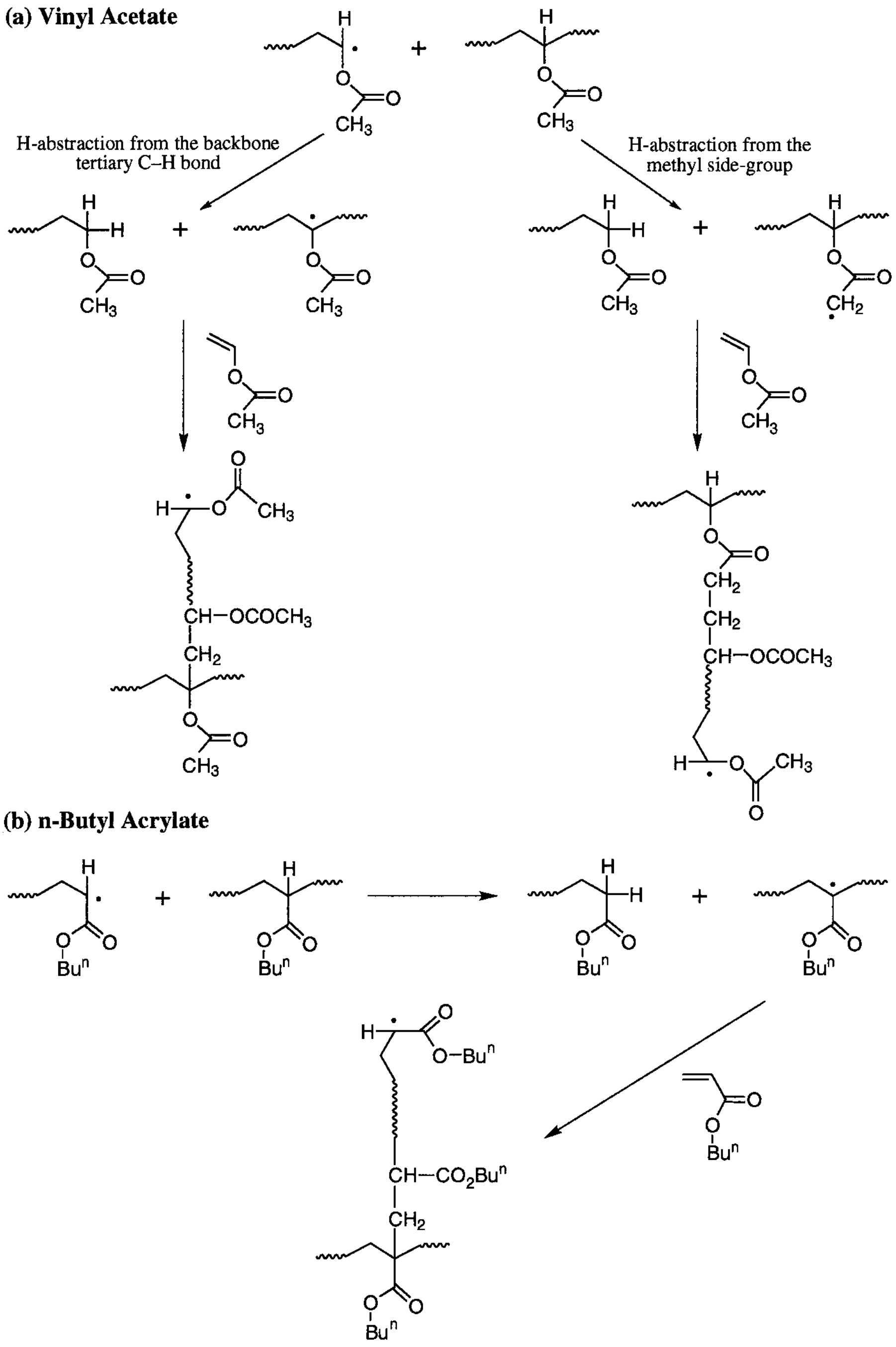
Experimental

Emulsion Copolymerization

The emulsion copolymerizations were carried out using previously reported semi-batch processes that employ sequential seed and growth stages. The VAc/BA reactions were performed at 70 °C using a formulation comprising ammonium persulfate as initiator, Aerosol OT as surfactant and sodium bicarbonate as buffer, with 16.7 wt% of the total monomer mixture used in the seed stage and a 37.5 wt% final latex solids content[5)]. Emulsion copolymerizations of BA with acrylic acid (AA) and (i) methyl methacrylate (MMA) or (ii) styrene (S) were carried out at 75 °C using a formulation and procedure designed for preparation of pressure-sensitive adhesives[10)] in which the level of AA was fixed at 5 mol% of the total monomer mixture, the only difference being that the chain transfer agent was not included. For these reactions, potassium persulfate was used as initiator and Aerosol MA as surfactant, with 5.0 wt% of the total monomer mixture used in the seed stage and a 50.0 wt% final latex solids content.

Analytical Procedures

Samples were taken at regular intervals during the course of each emulsion copolymerization. In order to quench the reaction, each aliquot was transferred directly to a sample bottle which



Scheme 1. Mechanisms of branching via chain transfer to polymer in free-radical homopolymerizations of (a) vinyl acetate and (b) n-butyl acrylate.

was placed in an ice/water bath and contained a pre-weighed quantity of a 1 % aqueous hydroquinone solution. The aliquots were used to monitor the conversion and the degree of branching. Conversions were determined from duplicate measurements of solids content using a mass-balance approach to account for previously removed aliquots and non-polymeric 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 de-ionized water for a minimum of 7 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 de-ionized water and drying under vacuum to constant weight at 60 °C (VAc/BA copolymers) or 30 °C (BA/AA/MMA and BA/AA/S copolymers), and (iv) transfer of the dried polymer to the NMR tube.

^{13}C NMR spectra were recorded at 23±1 °C using a Varian Associates Unity 500 spectrometer operating at 125.8 MHz. Samples of the copolymers 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. In order to maximise the signal-to-noise ratio in a given time, spectra were normally run with continuous ^1H decoupling using a pulse interval of 0.5 s and a pulse flip angle of 70° (VAc/BA copolymers) or 45° (BA/AA/MMA and BA/AA/S copolymers). Under these rapid pulse conditions, the relative intensities may 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. In order to check the quantitative accuracy of these fast pulse spectra, some samples were analysed again with NOE suppression by inverse gated decoupling11) and with a pulse interval of 10.5 s to allow complete recovery of all carbons. Additionally, the DEPT technique12) was used to determine the multiplicity of the peaks, *i.e.* whether a carbon was primary, secondary, tertiary or quaternary.

Results and Discussion

VAc/BA Emulsion Copolymerizations

All the reactions proceeded under monomer-starved conditions during the growth stage and had similar conversion-time profiles. Representative conversion data are shown in Figure 1. Thus the ratio of polymer to monomer concentration in the latex particles was high during each of the copolymerizations, conditions that promote chain transfer to polymer, i.e., branching. Since there were no significant differences in the conversion-time data, differences between the levels of branching in the copolymers can be ascribed to the changes in the composition of the VAc/BA comonomer mixture.

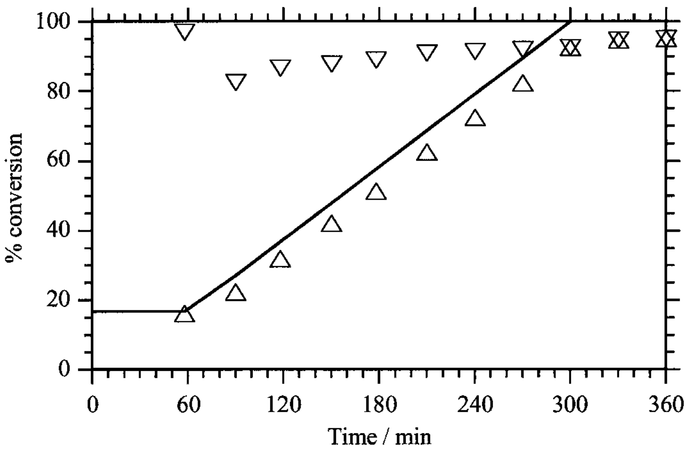


Figure 1. Representative plot of instantaneous conversion (▼) and overall conversion (▲) for VAc/BA emulsion copolymerizations (the data are from the copolymerization comprising 40 wt% BA).

The ^{13}C NMR spectra of the copolymers show features that are common to those in the spectra of both poly(vinyl acetate) and poly(n-butyl acrylate) [4,6-8], including those arising from chain transfer to polymer. In this respect, the most significant resonances are those at:

(i) $\delta_C \approx 61$, which is due to $CH_2\underline{C}H_2OCOCH_3$ end groups arising from hydrogen-abstractions by polymeric radicals with VAc end units (see ref.[4]). This was used to calculate the percentage of VAc repeat units that are at chain ends ($\%V_{ends}/V$), which quantifies the frequency of chain transfer to polymer involving VAc-ended radicals.

(ii) $\delta_C \approx 44\text{-}48$, which is due to quaternary carbons (C_q) in branched BA repeat units with different numbers of adjacent vinyl acetate repeat units. This was used to calculate the percentage of BA repeat units that are branched ($\%B_{Cq}/B$).

The $\%V_{ends}/V$ and $\%B_{Cq}/B$ data shown in Figure 2 are for the final copolymers from VAc/BA emulsion copolymerizations carried out using mixtures of VAc and BA comprising 0, 5, 10, 15, 20, 40, 60, 80 and 100 wt% BA and are corrected for the effects of differences in longitudinal relaxation times and NOE. Taking into account experimental error, the data show nominally linear variations of $\%V_{ends}/V$ and $\%B_{Cq}/B$ with comonomer composition in which $\%V_{ends}/V$ increases and $\%B_{Cq}/B$ decreases as mol% BA increases. These linear dependencies can be predicted theoretically[13] and the observations show that there is synergism in chain transfer to polymer for VAc/BA copolymerization. Inclusion of only small amounts of either monomer leads to disproportionate increases in the level of branching

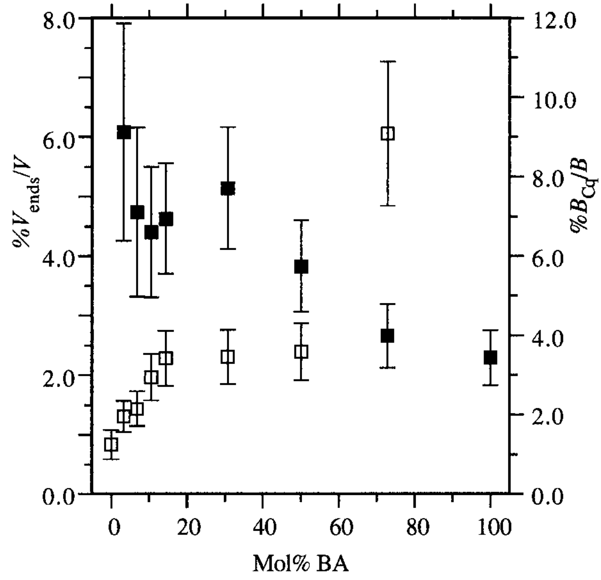
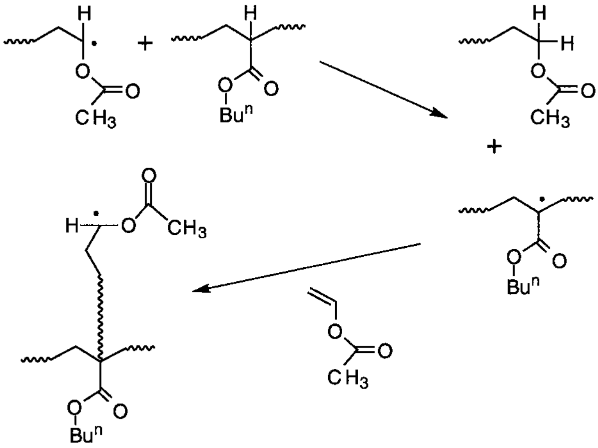


Figure 2. Variation of $\%V_{ends}/V$ (□) and $\%B_{Cq}/B$ (■) with mol% BA for the final copolymers from monomer-starved VAc/BA semi-batch emulsion copolymerizations.

compared to the equivalent homopolymerization. This may be quantified by further analysis of the data[13)] which indicates that radicals with VAc end units abstract hydrogen atoms from BA repeat units about 7-8x more rapidly than from VAc repeat units and that radicals with VAc end units are about 3-4x as effective in abstracting hydrogen atoms from BA repeat units than are radicals with BA end units. These observations are a consequence of the efficacy of hydrogen abstraction at BA backbone tertiary C–H bonds by the highly-reactive VAc-ended chain radicals (Scheme 2). This additional mechanism of chain transfer to polymer in the VAc/BA emulsion copolymerizations, therefore, has very significant effects on the level of branching, the effects being most prominent at low levels of either monomer.

In summary, by copolymerizing VAc with relatively small amounts of BA (which is a common commercial practice), the relatively high susceptibility of acrylic tertiary C–H bonds to abstraction leads to significant increases in the total level of branching in the VAc-based copolymers produced. Additionally, from the perspective of acrylic polymers, the presence of VAc leads to a much higher level of acrylic branch points than would occur in an all-acrylate polymerization.



Scheme 2. Mechanism of branching in VAc/BA copolymerizations involving abstraction of hydrogen atoms from backbone tertiary C–H bonds in BA repeat units by propagating radicals with VAc radical ends.

BA/AA/MMA and BA/AA/S Emulsion Copolymerizations

Our studies of emulsion copolymerizations of BA with MMA/AA and with S/AA have been less extensive and only preliminary results are reported here. The ^{13}C NMR spectra of the copolymers showed the normal repeat unit resonances of the homopolymers plus additional resonances arising from different repeat units sequences and from chain transfer to polymer at tertiary C–H bonds in BA repeat units. The $33 < \delta_C < 42$ region contained resonances for the CH_2 and CH carbons adjacent to the C_q branch point carbon, but also from various repeat unit sequences; hence this region could not be used to quantify branching. Instead the C_q branch point carbon resonance at $\delta_C \approx 48$ and the end-group $CH_2\underline{C}H_2(COOBu)$ resonance at $\delta_C \approx 31$ were used to calculate mol% branches with respect to the acrylic (BA+AA) repeat units. Since the latter gave more accurate results, only data calculated from the end-group CH_2 resonance are presented in Table 1. Final copolymers from similar BA/AA emulsion copolymerizations have about 3 mol% branches (e.g., see the data for BA emulsion homopolymerization in Figure 2). Thus, in contrast to the effect of VAc, the effect of introducing MMA or S is to disproportionately reduce the level of branching. Quite clearly, S is much more effective than MMA in moderating chain transfer to polymer in acrylate polymerizations.

The results can be interpreted in terms of the reactivity of propagating radicals with MMA or S end units compared to those with BA or AA end units. The MMA and S radicals have

Table 1. Mol% branches with respect to the total acrylic (BA+AA) repeat units for the final copolymers from BA/AA/MMA and BA/AA/S emulsion copolymerizations.

Comonomer Composition (mol%)				Mol% Branches
BA	AA	MMA	S	
90	5	5	–	2.5
85	5	10	–	1.8
90	5	–	5	0.9
85	5	–	10	0.4

much lower reactivity and longer lifetimes than BA and AA radicals, and have a very much lower tendency to abstract hydrogen atoms from acrylic repeat units. This combination of effects leads to the reduction in chain transfer to polymer and branching. The difference between the effects of MMA and S are in part a consequence of the instantaneous conversions being lower for the emulsion copolymerizations containing S (as can be seen from the conversion data presented in Figure 3), which gives rise to a lower time-averaged ratio of polymer to monomer concentration. However, the differences between the conversion curves for the copolymerizations using 5 mol% MAA and 5 mol% S are not sufficient to explain the large difference in mol% branches (2.5 *vs.* 0.9 mol%, respectively). Clearly, propagating radicals with S end units have less propensity for abstracting hydrogen atoms from acrylic repeat units than those with MMA end units.

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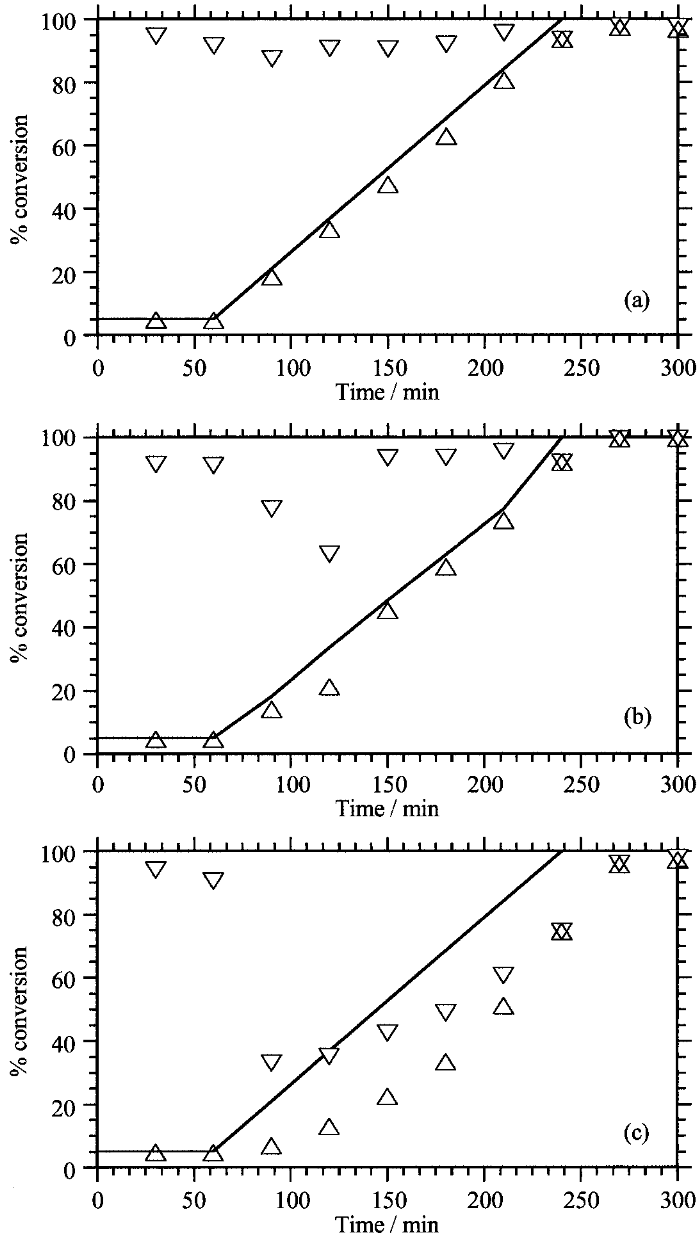

Figure 3. Plots of instantaneous conversion (▼) and overall conversion (▲) for acrylate-based emulsion copolymerizations: (a) BA90/AA5/MMA5; (b) BA90/AA5/S5 and (c) BA85/AA5/S10. The solid lines show the monomer feed profiles.

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