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Chain Transfer to Polymer in Emulsion Polymerization

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SUMMARY: Chain transfer to polymer in emulsion polymerizations of acrylate monomers and vinyl acetate has been studied using ^{13}C NMR spectroscopy to elucidate the chemistry by which chain transfer occurs and to quantify the mol% branches resulting from the reaction. In emulsion polymerizations of n-butyl acrylate, ethyl acrylate and methyl acrylate, chain transfer to polymer proceeds via abstraction of hydrogen atoms from backbone tertiary C–H bonds and typically gives rise to 2-4 mol% branches in the polymers obtained at complete conversion, the level of branching increasing with reaction temperature. For these acrylates, there is no evidence for a significant difference between the extent of chain transfer to polymer. In emulsion polymerizations of vinyl acetate, chain transfer to polymer proceeds mainly via H-abstraction from methyl side-groups, though there is a small contribution from abstraction at backbone tertiary C–H bonds. The levels of branching that result are substantially lower than in acrylate emulsion polymerizations, typically being in the range 0.6-0.8 mol% in the polymers obtained at complete conversion. The level of branching increases with temperature and as the degree of monomer starving (and hence instantaneous conversion) increases. Emulsion copolymerization of vinyl acetate with a small amount (5-20 wt%) of n-butyl acrylate gives rise to a significant increase in the level of branching (to values around 1.3-1.6 mol%), which results predominantly from H-abstraction of backbone tertiary C–H bonds in n-butyl acrylate repeat units by propagating radicals with vinyl acetate end units.

Introduction

Chain transfer to polymer is an important process in free-radical polymerizations of olefinic monomers because it leads to formation of branched polymers with significant consequences for rheological and mechanical properties. The effects of chain transfer to polymer have been most thoroughly studied and documented for free-radical polymerization of ethylene, as used

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in the preparation of low density polyethylene[1-3]. Although chain transfer to polymer is known to occur in free-radical polymerizations of many other monomers, they have received far less attention. In view of this, over the past several years we have investigated chain transfer to polymer in free-radical bulk, solution and emulsion polymerizations using ^{13}C NMR spectroscopy as the principal analytical tool. Unique resonances from the structural features arising from chain transfer to polymer can be identified and used first to elucidate the chemistry of chain transfer to polymer, and then to quantify the extent of chain transfer to polymer. The aims of the research reported here were to determine unambiguously the chemistry of chain transfer to polymer in polymerizations of (i) acrylate monomers and (ii) vinyl acetate, and to correlate the extent of branching to emulsion polymerization conditions. In this paper, an overview of our observations is presented, based around both new and previously published results.

Simple Theory

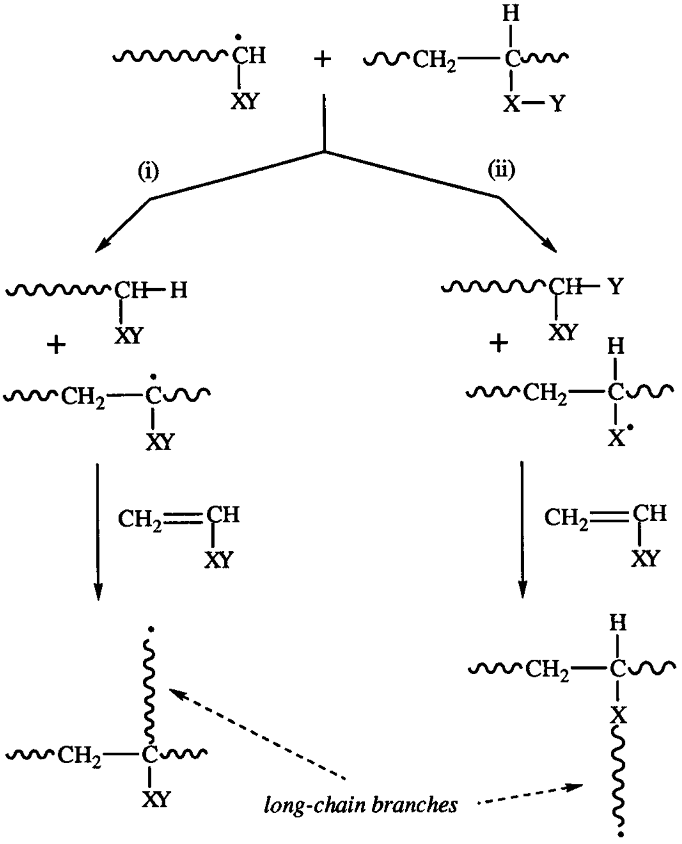
Chain transfer to polymer may proceed both intermolecularly and intramolecularly. However, under the usual conditions of monomer starving in emulsion polymerizations[4], the high instantaneous conversions (*i.e.*, high concentrations of polymer in the latex particles) dictate that intermolecular chain transfer to polymer should be dominant.

There are generally two possibilities for chain transfer, involving abstraction of backbone and side-group atoms, respectively, as depicted in general terms in Scheme 1. Assuming that one process is dominant, as is normally the case in homopolymerizations, the mole fraction of branched repeat units in the polymer formed over a small interval of conversion is equal to the probability, P_{trP}, that a propagating chain radical undergoes chain transfer to polymer rather than propagation, which is given by

$$P_{\mathrm{trP}} = \frac{k_{\mathrm{trP}}[\mathrm{P}]}{k_{\mathrm{trP}}[\mathrm{P}] + k_{\mathrm{p}}[\mathrm{M}]} \qquad (1)$$

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. This equation can be rearranged to the more instructive form shown below

$$P_{\mathrm{trP}} = \frac{\left(\dfrac{k_{\mathrm{trP}}}{k_{\mathrm{p}}}\right)\dfrac{[\mathrm{P}]}{[\mathrm{M}]}}{\left\{\left(\dfrac{k_{\mathrm{trP}}}{k_{\mathrm{p}}}\right)\dfrac{[\mathrm{P}]}{[\mathrm{M}]}\right\} + 1} \qquad (2)$$

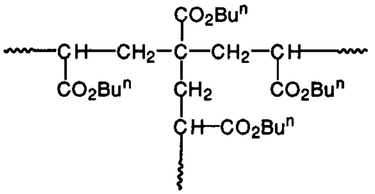


Scheme 1: General reaction scheme for intermolecular chain transfer to polymer via abstraction of (i) a hydrogen atom from a tertiary backbone C–H bond and (ii) an atom (Y; usually hydrogen) from a side group (X–Y; *e.g.* $OCOCH_2$–H for vinyl acetate).

Equation (2) shows quite clearly that there are two factors of importance in determining the extent of chain transfer to polymer: (i) the rate coefficient ratio k_{trP}/k_p and (ii) the concentration ratio [P]/[M]. Since chain transfer to polymer can be expected to have a higher activation energy than propagation, k_{trP}/k_p (and hence P_{trP}) should increase with temperature. At a fixed temperature, however, the extent of chain transfer to polymer is controlled by [P]/[M]. Recent studies$^{5)}$ of n-butyl acrylate solution polymerization have shown very clearly that [P]/[M] must always be considered as the local value, *i.e.*, in the vicinity of the propagating radical. In the case of emulsion polymerization, therefore, [P]/[M] needs to be considered as the value within the latex particles.

Emulsion Polymerization of Acrylates

Most of our work on acrylates has concerned copolymerizations of n-butyl acrylate with other (meth)acrylate monomers. Our early work[6-8)] on emulsion copolymerization of n-butyl acrylate with methyl methacrylate and acrylic acid revealed that, in addition to the normal resonances arising from the comonomer repeat units, the ^{13}C NMR spectra of the acrylic copolymers showed distinct CH, CH_2 and C_q resonances at δ_C 40.4 – 41.1, 38.4 and 49.1, respectively (with C_6D_6 as the NMR solvent). When the spectra were recorded under quantitative conditions (*i.e.*, with long intervals between pulses and suppression of the Nuclear Overhauser effect), the relative intensities of these resonances were 3:3:1, in accord with those required for the CH, CH_2 and C_q carbon atoms in the branch point (shown as structure (I) below) resulting from abstraction of a hydrogen atom at a backbone tertiary C–H bond.



(I)

These additional CH, CH_2 and C_q resonances appear consistently in the ^{13}C NMR spectra of polymers derived from acrylate monomers and show unambiguously that chain transfer to polymer occurs via route (i) of Scheme 1. The results from this earlier work[6-8)] showed that the mol% branches increased with conversion and with reaction temperature, and that there were significant changes in molar mass distribution as a consequence of chain transfer to polymer. The results also showed that the level of branching is moderated by the inclusion of methyl methacrylate as a comonomer, an observation that is thought to arise because methyl methacrylate gives rise to polymeric radicals with end-units of lower reactivity and, of course, to repeat units that do not have tertiary hydrogens for abstraction.

More recently, we have carried out separate monomer-starved semi-batch emulsion homopolymerizations of n-butyl acrylate, ethyl acrylate and methyl acrylate at 75 °C using the same formulation and reaction conditions. The level of branching in the polymers was determined using the same strategy for polymer work-up and analysis as published previously[6-8)], except that the ^{13}C NMR spectra were recorded (at 125 MHz) using a more powerful instrument and the mol% branches were calculated from the ratio of the total integral for the branch point CH and CH_2 carbons to the total integral for backbone carbons, including those in the branch points. This method of calculation was shown to give accurate quantitative data, even for spectra recorded under fast pulse conditions[5)]. The spectra of the polymers obtained at 100% conversion are shown in Figure 1. In each case the characteristic

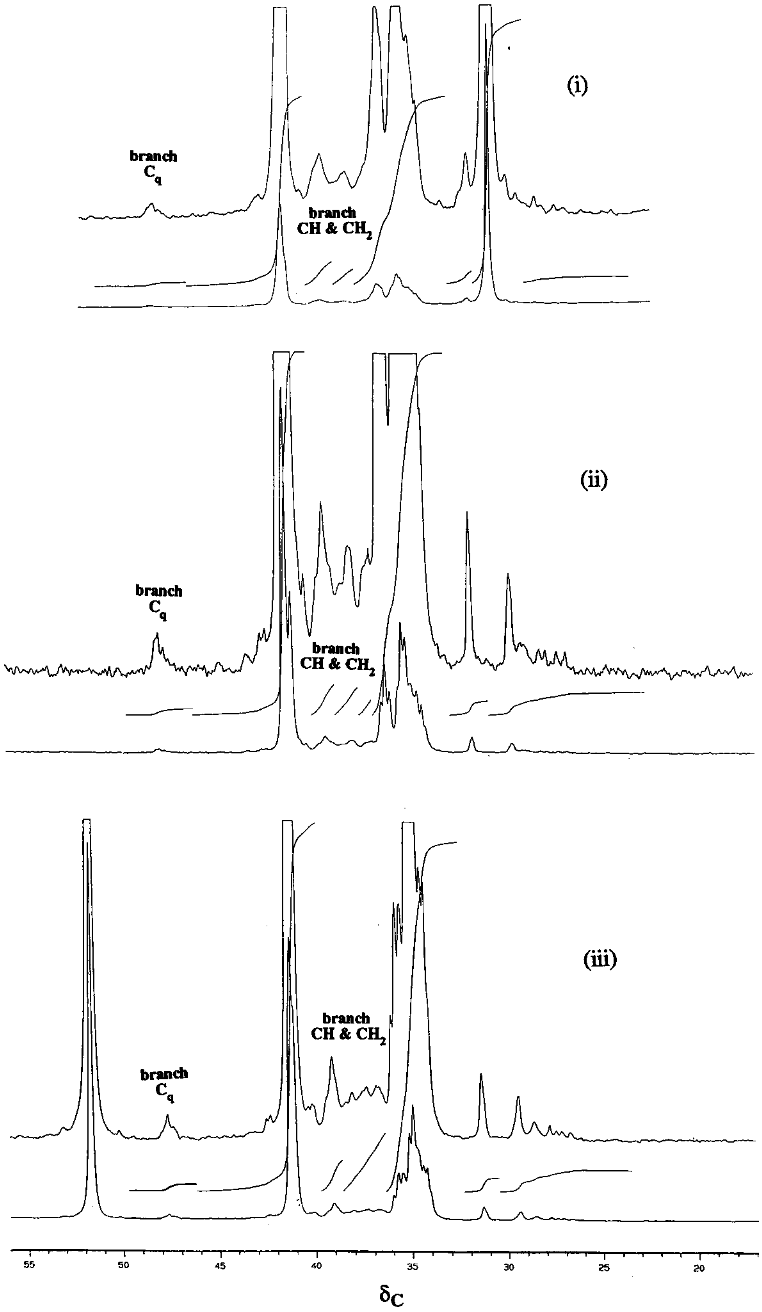


Figure 1: ^{13}C NMR spectra (recorded in $CDCl_3$) of polymers prepared by emulsion homopolymerization of acrylate monomers at 75 °C: (i) poly(n-butyl acrylate), (ii) poly(ethyl acrylate) and (iii) poly(methyl acrylate).

branch-point CH, CH_2 and C_q resonances are present, though at slightly lower chemical shifts than previously observed due to the change in NMR solvent from C_6D_6 to $CDCl_3$. The mol% branches data obtained from the spectra shown in Figure 3 are: 3.0 mol% for n-butyl acrylate, 2.4 mol% for ethyl acrylate and 3.0 mol% for methyl acrylate. The differences between the values are close to the uncertainties arising from experimental error (*ca.* ± 0.3 mol%) and so cannot be considered significant. The indication from the results is, therefore, that these three acrylate monomers do not behave significantly differently from each other in terms of chain transfer to polymer in emulsion polymerization.

Emulsion Polymerization of Vinyl Acetate

Evidence for chain transfer to polymer in emulsion polymerization of vinyl acetate is mainly to be found in observations of the reduction in degree of polymerization when poly(vinyl acetate) (PVAc) is hydrolyzed to produce poly(vinyl alcohol)[9,10). Such observations clearly show that chain transfer to polymer proceeds via H-abstraction from the methyl side-group, *i.e.*, via route (ii) of Scheme 1. Recently, we have begun to investigate chain transfer to polymer in emulsion polymerizations of vinyl acetate using ^{13}C NMR spectroscopy, the first results from these studies having just been published[11). These initial studies concerned semi-batch emulsion polymerizations carried out under monomer-starved conditions at 50% final latex solids content using sodium dioctylsulfosuccinate (Aerosol OT) as the sole colloid stabilizer. Figure 2 shows the ^{13}C NMR spectrum of a sample of poly(vinyl acetate) obtained at complete conversion from an emulsion polymerization run at 70 °C. The spectrum is complex but can be fully interpreted in terms of structural features arising from (i) normal and inverted repeat unit placements, (ii) chain transfer to polymer and (iii) hydrolysis of acetate side-groups (see Table 1)[11). Although there is evidence for chain transfer to polymer via H-abstraction from both backbone tertiary C–H bonds and methyl side-groups, the results show clearly that the latter make the dominant contribution. Since it is possible to rationalize[11) that the $CH_2\underline{C}H_2OCOCH_3$ end group resonance (at $\delta_C \approx 61$) arises exclusively from chain transfer to polymer events, then the number of such end groups and the number of branch points must be equal. Thus the mol% branches has been calculated by taking the ratio of the integral for this end group signal to half the sum of the integral for all backbone carbons, including those in branch points.

As for the acrylate polymerizations, the total mol% branches was found to increase steadily with overall conversion, in this case from about 0.2 mol% at the completion of the seed stage, to about 0.8 mol% at the end of the reaction for polymerizations carried out at 70 °C. Similarly, reducing the temperature of emulsion polymerization from 70 to 60 °C led to a decrease in the mol% branches; for the final polymers, the level of branches was about 0.8 mol% for the reaction performed at 70 °C and about 0.6 mol% when it was carried out at 60 °C (compare polymerizations (i) and (ii) in Figure 3). However, in all cases, the level of branching is much lower than in the acrylate polymers.

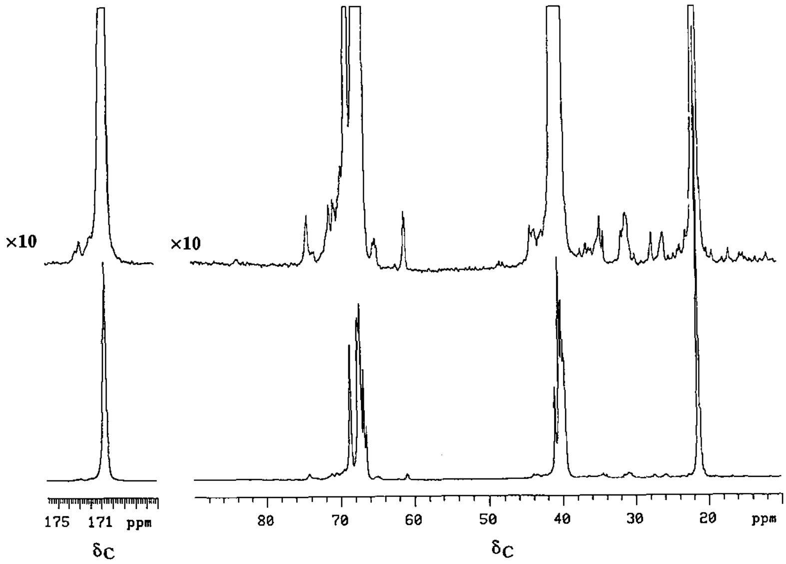


Figure 2: ^{13}C NMR spectrum (recorded in C_6D_6) of poly(vinyl acetate) prepared by emulsion polymerization at 70 °C. Assignments of the peaks are given in Table 1.

Table 1: Assignment of resonances in the ^{13}C NMR spectrum of poly(vinyl acetate) recorded in C_6D_6, as shown in Figure 2. For a more detailed assignment see ref.[11]).

Chemical shift, δ_C [a]	Assignment
21.2	Acetate CH_3
25.5 – 37.5	Inverted addition CH_2 + CH_2 carbons in side-group branches + $\underline{C}H_2CH_2OCOCH_3$ in end groups resulting from H-abstraction
39.0 – 41.5	Main-chain CH_2
41.5 – 44.0	CH_2 carbons adjacent to a main-chain branch + $CH(OH)\underline{C}H_2CH(OAc)$ in hydrolyzed units
47.5 – 48.0	$CH(OH)\underline{C}H_2CH(OH)$ in hydrolyzed units
61.0	$CH_2\underline{C}H_2OCOCH_3$ in end groups resulting from H-abstraction
64.5 – 65.5	CH adjacent to main-chain branch + $\underline{C}H(OH)$ in hydrolyzed units
65.5 – 70.0	Main-chain CH
70.0 – 74.0	Inverted addition CH
83.8	C_q carbon in a main-chain branch
170.0 – 171.5	Main-chain C=O

[a] Values of δ_C were 0.3–0.7 lower for spectra in $CDCl_3$

More recently, we have investigated the effect of monomer feed rate on the mol% branches. A series of emulsion homopolymerizations of vinyl acetate were carried out at 70 °C using the same formulation and procedure as in the earlier work[11)], except that the amount of monomer and surfactant were reduced (in proportion) to give a final latex solids content of 37.5%. The variations of mol% branches with overall % conversion for these, and the earlier emulsion polymerizations, are shown in Figure 3. Comparison of polymerizations (i) and (iii) (both run at 70 °C with essentially the same monomer feed rate) shows that changing the final latex solids content had no significant effect on the mol% branches. The more important point to make, however, is that the variations of instantaneous and overall % conversion with reaction time for polymerizations (i) and (iii) were similar. Thus the observations are in accord with Equation (2) because the similar variations of instantaneous % conversion with reaction time give rise to similar variations of the [P]/[M] ratio with reaction time. The effect of monomer feed rate on the mol% branches is substantial, as can be seen from the data for polymerizations (iii), (iv) and (v). Again this is consistent with Equation (2) because as the monomer feed rate increases, the instantaneous % conversion reduces, leading to lower [P]/[M] ratios in the latex particles and, hence, to lower levels of chain transfer to polymer.

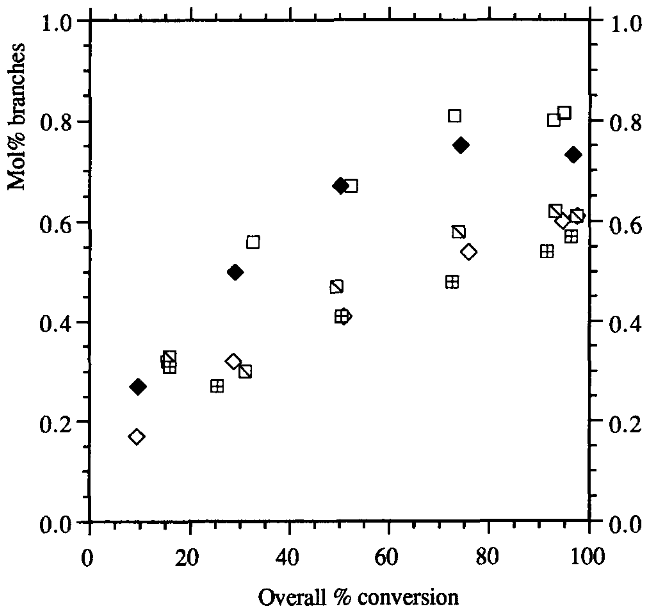


Figure 3: Variation of mol% branches with overall % conversion for monomer-fed semi-batch emulsion polymerizations of vinyl acetate (carried out at 70 °C except where indicated): (i) ◆, 0.38 % min^{-1} monomer feed rate, 50% final latex solids content; (ii) ◇, 0.38 % min^{-1}, 50% (60 °C); (iii) □, 0.35 % min^{-1}, 37.5%; (iv) ▧, 1.39 % min^{-1}, 37.5%; (v) ⊞, 2.08% min^{-1}, 37.5%. The monomer feed rates refer to the percentage of total monomer.

Emulsion Copolymerization of Vinyl Acetate with n-Butyl Acrylate

Having established the chemistry of chain transfer to polymer in acrylate and vinyl acetate homopolymerizations, we have just begun to investigate emulsion copolymerizations of vinyl acetate with n-butyl acrylate. The initial results from our first studies of these systems are presented here. The emulsion polymerizations were carried using procedures and conditions identical to those of reaction (iii) in Figure 3, the only difference being the use of mixtures of vinyl acetate and n-butyl acrylate (5, 10, 15 and 20 wt% n-butyl acrylate) in place of vinyl acetate. A spectrum of the final copolymer from the polymerization carried out using 15 wt% n-butyl acrylate is shown in Figure 4.

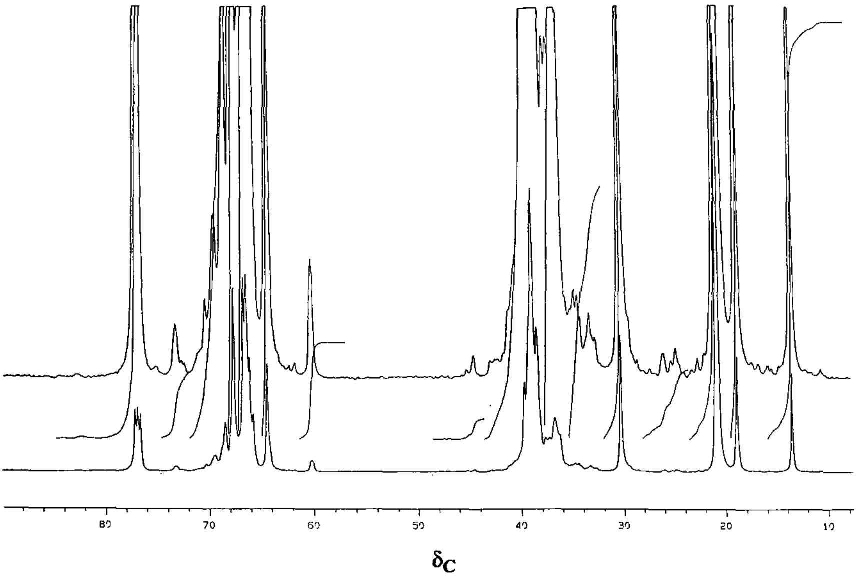
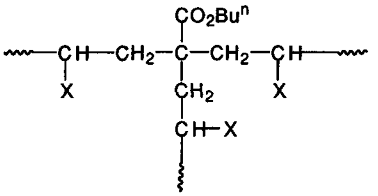


Figure 4: ^{13}C NMR spectrum (recorded in $CDCl_3$) of the final polymer from emulsion copolymerization of vinyl acetate (85 wt%) and n-butyl acrylate (15 wt%) at 70 °C.

As would be expected, the spectrum has features that are common to those in the spectra of both poly(vinyl acetate) and poly(n-butyl acrylate) (see refs.[6-8,11]) and Table 1 above). With respect to chain transfer to polymer, 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 H-abstractions by polymeric radicals with vinyl acetate end units (see ref.[11]) and Table 1 above), and (ii) at $\delta_C \approx 44$, which is due to quaternary carbons in branched n-butyl acrylate repeat units with adjacent vinyl acetate repeat units, *i.e.*, to branch structures of type (II) shown below in which at least two of the substituent groups X are from vinyl acetate.



(II)

Initial analyses of the spectra of the final polymers from the copolymerizations shows that the mol% branches determined using the $\delta_C \approx 61$ signal is increased from about 0.8 mol% for the corresponding vinyl acetate emulsion homopolymerization (see polymerization (iii) in Figure 3), to about 1.3 mol% for the 5 and 10 wt% n-butyl acrylate copolymerizations, and to about 1.6 mol% for the 15 and 20 wt% n-butyl acrylate copolymerizations. The mol% branches resulting from H-abstraction at n-butyl acrylate repeat units was determined from the signal at $\delta_C \approx 44$ and found to be in the approximate range 0.3-0.5 mol%. These observations lead to the interpretation that the increase in mol% branches arises from H-abstraction at backbone tertiary C–H bonds in n-butyl acrylate repeat units, predominantly by polymeric radicals with vinyl acetate end units. The high proportion of vinyl acetate in the monomer mixtures, together with the use of monomer-starved conditions, gives rise to a high probability that the quaternary branch points will have three adjacent vinyl acetate repeat units.

In summary, therefore, by copolymerizing vinyl acetate with relatively small amounts of n-butyl acrylate (which is common practice in commercial vinyl acetate emulsion polymerizations), the relatively high susceptibility of acrylic tertiary C–H bonds to H-abstraction chain transfer reactions leads to substantial increases in the total level of branching in the polymers produced.

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