Chain Transfer to Polymer in Free-Radical Bulk and Emulsion Polymerization of Vinyl Acetate Studied by NMR Spectroscopy

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ABSTRACT: Chain transfer to polymer in free-radical bulk and emulsion polymerization of vinyl acetate has been studied using ^{13}C NMR spectroscopy. The poly(vinyl acetate) (PVAc) spectra have been 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. Although evidence was obtained for chain transfer to polymer via H-abstraction from both backbone tertiary C−H bonds and methyl side groups, the latter make the dominant contribution. The spectral assignments facilitated calculation of the mole percent branches and the mole percent of inverted repeat units in the PVAc samples produced, the latter quantity taking values of 1.44 ± 0.24 mol % independent of conversion in the emulsion polymerizations. The absence of an initiator effect in the bulk polymerizations shows that the propagating PVAc chain radicals are the principal hydrogen atom abstractors. In both bulk and emulsion polymerization, the mole percent branches increased steadily with overall conversion. However, because the emulsion polymerizations proceed almost exclusively within the latex particles and at high instantaneous conversions, the levels of branching in the PVAc produced (final levels = 0.61−0.75 mol %) were much higher than in the PVAc produced by bulk polymerization (final levels = 0.13−0.23 mol %). Increasing the temperature of emulsion polymerization from 60 to 70 °C led to an increase in the mole percent branches but had no measurable effect on the mole percent of inverted repeat units.

Introduction

The effects of branching on the rheological and mechanical properties of polymers are significant and well established, particularly in the case of low-density polyethylene, for which the branches result as a consequence of both inter- and intramolecular chain transfer to polymer during its preparation by free-radical polymerization of ethylene at high temperature and pressure.[1−3] More recently,[4−7] using NMR spectroscopy, we have established that chain transfer to polymer occurs extensively in free-radical homopolymerizations and copolymerizations of *n*-butyl acrylate and that it involves abstraction of hydrogen atoms from backbone tertiary C−H bonds. In the present paper we present results from a study of chain transfer to polymer in free-radical homopolymerization of vinyl acetate. Although this reaction is well established,[8,9] the evidence for chain transfer to polymer is indirect, deriving principally from the reduction in degree of polymerization when poly(vinyl acetate) is hydrolyzed to produce poly(vinyl alcohol).[8,10,11] This observation indicates that chain transfer to polymer proceeds via H-abstraction from the methyl side group, i.e., as shown on the right-hand side of Scheme 1. Although the alternative process shown on the left-hand side of Scheme 1, involving H-abstraction from backbone tertiary C−H bonds, yields a tertiary radical compared to the primary radical generated by abstraction from the methyl group, the latter radical is stabilized by resonance with the C═O group. When considered together with the 3:1 ratio of methyl to methine hydrogen atoms, the methyl side group can reasonably be expected to be the principal source of chain transfer to polymer. However, to date, there has been no detailed study of the extent to which the two processes contribute.

The objectives of the studies reported herein were to examine the fine structure of poly(vinyl acetate) using NMR spectroscopy, looking for unique resonances from structural features arising from the chain transfer processes shown in Scheme 1 and to use these unique resonances to quantify the extent of chain transfer to polymer in bulk and emulsion homopolymerizations of vinyl acetate.

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. For the bulk polymerizations, which were carried out on a small scale, the inhibitor-free monomer was distilled under nitrogen at reduced pressure before use. 2,2′-Azobis(2-cyanopropane) (BDH, 97%) (AZBN) and benzoyl peroxide (BDH, ca. 75%, supplied wet) (BPO) were purified by recrystallization from toluene and dried over silica gel under vacuum overnight. 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. Cyclohexane (Aldrich, 99%) was dried over sodium wire. 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.

Bulk Polymerizations. Solutions of initiator in monomer (5−10 g) were transferred to Carius (thick-walled glass) tubes

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

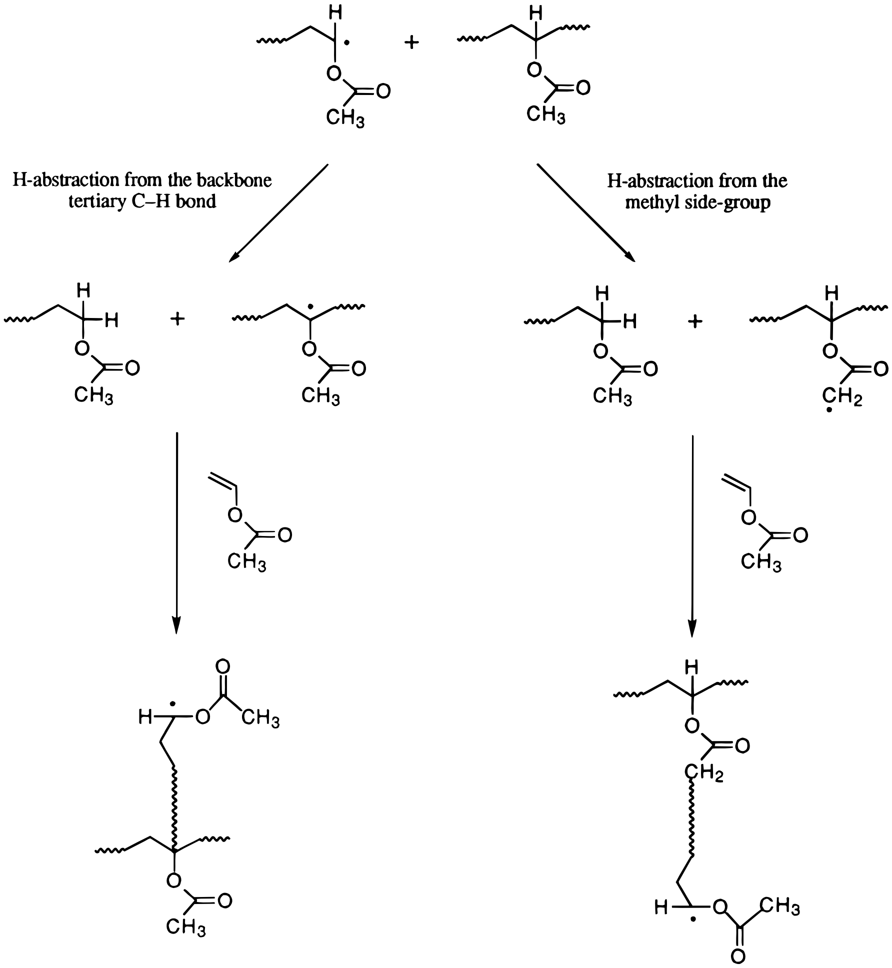


Table 1. Emulsion Polymerization Formulation (~3 dm^3 Scale)

formulation component	seed stage (mass/g)	growth stage (mass/g)
vinyl acetate	135.0	1215.0
deionized water	1215.0	135.0
Aerosol OT-75	9.35	45.65
sodium bicarbonate	0.90	
ammonium persulfate	1.00	3.00

and degassed by several cycles of the following sequence of operations: (i) freezing in liquid nitrogen, (ii) application of high vacuum, (iii) sealing from the vacuum pump, and (iv) thawing. Finally, the Carius tubes were permanently sealed under vacuum using a blowtorch. Polymerizations were performed at 70 °C using initiator (AZBN or BPO) at a concentration of 0.5 wt % (to monomer) by immersing the corresponding sealed Carius tube in a water bath thermostated to ±1 °C for a period of 14 h, which gave rise to very high conversions. Polymerizations also were carried out at 70 °C using AZBN at a concentration of 0.01 wt % (to monomer) over a range of reaction times corresponding to conversions in the range 10−90%.

For each polymerization, the Carius tube was cooled in liquid nitrogen after the designated reaction time and opened. The product was dissolved in THF (ca. 300 cm^3), to which hydroquinone (ca. 0.1 g) had been added as an inhibitor. The polymer was recovered from this solution by precipitation into cyclohexane at room temperature, followed by washing with cyclohexane and then drying under vacuum at 60 °C to constant weight.

Emulsion Polymerizations. Table 1 gives the formulation used for the emulsion polymerizations, which were performed under a flowing nitrogen atmosphere at 60 or 70 °C on scales of approximately 3 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 over a period of 240 min using a Watson-Marlow 505S peristaltic pump. At 60, 120, and 180 min from the beginning of the seed stage, further quantities of ammonium persulfate (1.00 g) in water (40 g) were added and washed in with water (5 g). On completion of the growth stage, 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. The masses of coagulum on the reaction vessel, stirrer, and sieve were determined after drying each of these components in an oven at 60 °C.

For each polymerization, aliquots (ca. 10 cm^3) were removed at the end of the seed stage and at 30 min intervals thereafter. To quench the reaction, each aliquot was transferred directly to a sample bottle that 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 degree of branching. Conversions were determined from duplicate measurements of solids content

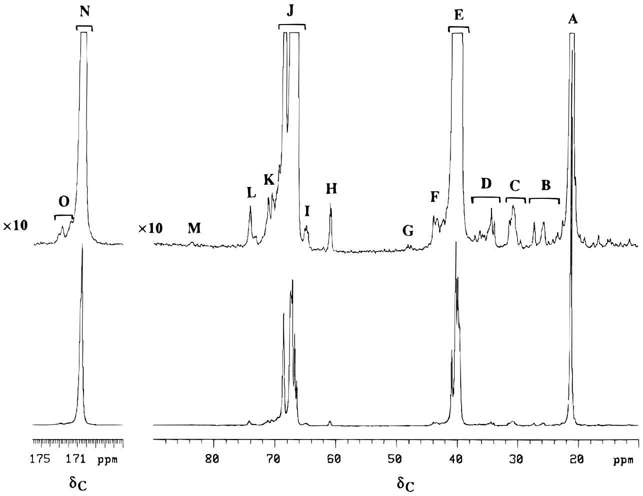


Figure 1. ^{13}C NMR spectrum of poly(vinyl acetate) recorded using C_6D_6 as solvent. The spectrum was obtained using fast pulses and is of the polymer obtained after 360 min in the emulsion polymerization carried out at 70 °C. Other than the resonance from the solvent, no peaks were evident in the range $90 < \delta_C < 165$, even on 20× expansion of the spectrum; hence, this region of δ_C is not shown. The assignments of the labeled peaks are given in Table 2.

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 $CDCl_3$ or C_6D_6 to give solutions of concentration ca. 100 mg cm^{-3}. Chemical shifts were referenced to the solvent peak at 77.0 ppm ($CDCl_3$) or 128.4 ppm (C_6D_6). To maximize the signal-to-noise ratio in a given time, ^{13}C spectra were normally 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 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. To check the quantitative accuracy of these fast pulse spectra, some samples were analyzed again with NOE suppression by inverse gated decoupling[12] and with a pulse interval of 10.5 s to allow complete recovery of all carbons. Additionally, the DEPT technique[13] was used to determine the multiplicity of the peaks, i.e. whether a carbon was primary, secondary, tertiary, or quaternary. ^{13}C longitudinal relaxation times (T_1) were measured using the inversion−recovery technique.[14]

Results and Discussion

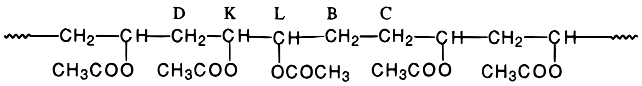
NMR Spectra. Figure 1 shows the complete ^{13}C spectrum of the final sample (360 min) from the emulsion polymerization carried out at 70 °C. (This particular spectrum is shown because it contains the most information in terms of the number of resonances and their intensity.) Assignments of the peaks are given in Table 2, and those peaks of significance are discussed in detail below.

Table 2. Assignments of the ^{13}C NMR Spectrum of Poly(vinyl acetate) in C_6D_6 (See Figure 1)

peak	chemical shift/ppm [a]	assignment
A	21.2	acetate CH_3
B	25.5−27.5	inverted addition CH_2
C	29.5−32.0	inverted addition CH_2 + side-chain branch β-CH_2[b]
D	33.5−37.5	inverted addition CH_2 + penultimate CH_2[b] + side-chain branch α-CH_2[b]
E	39.0−41.5	main-chain CH_2
F	41.5−44.0	CH_2 adjacent to main-chain branch[b] + CH(OH)*C*H_2CH(OAc)[b]
G	47.5−48.0	CH(OH)*C*H_2CH(OH)[b]
H	61.0	ultimate CH_2[b]
I	64.5−65.5	CH adjacent to main-chain branch[b] + CH(OH)[b]
J	65.5−70.0	main-chain CH
K	70.0−72.0	inverted addition CH
L	74.0	inverted addition CH
M	83.8	branch C_q[b]
N	170.0−171.5	main-chain C=O
O	171.5−173.5	unassigned C=O

[a] Chemical shifts were 0.3−0.7 ppm lower for spectra in $CDCl_3$. [b] See the text for discussion of these assignments.

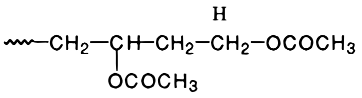
In addition to intense peaks A, E, J, and N assigned to carbons in head-to-tail units produced by the normal propagation mode, a number of smaller peaks are observed. From previous studies of poly(vinyl acetate) and poly(vinyl alcohol),[15,16] the small peaks B, C, and D (CH_2) and K and L (CH) are associated with sequences containing inverted repeat units, as indicated below:



$$\sim CH_2-\overset{D}{CH_2}... $$

Using substituent increment parameters,[17] the following chemical shifts are predicted for these carbons: B, 27 ppm; C, 31 ppm; D, 36 ppm; K, 76 ppm; L, 80 ppm. Thus the assignment of the CH_2 carbons B−D is in good agreement with the predicted chemical shifts. The predictions of the chemical shifts for the CH carbons K and L are somewhat high, especially compared to the predicted chemical shift of 67 ppm for a regular head-to-tail CH carbon; nevertheless, the predictions are useful in placing the CH resonances in the correct order of appearance in the spectrum.

For the present study of chain transfer, the most significant peak is H, shown by DEPT spectra to be a CH_2 carbon. From its chemical shift, this peak undoubtedly arises from a CH_2O group. Its T_1 value of 0.50 s is 3-fold greater than that of the main-chain CH_2 carbons (T_1 = 0.17 s), indicating considerably greater mobility. Therefore, this peak is assigned to the ultimate CH_2 carbon in the end group formed when a propagating chain undergoes chain transfer by H-abstraction, i.e., to the structure:



$$\sim CH_2-\underset{OCOCH_3}{CH}-CH_2-\overset{H}{CH_2}-OCOCH_3 \qquad \text{(I)}$$

The chemical shift predicted for the ultimate CH_2 using chemical shift increments[17] is 62 ppm, which is fully consistent with this assignment. The penultimate CH_2 in this end group is predicted to appear at 34 ppm, a region obscured by more intense CH_2 peaks from

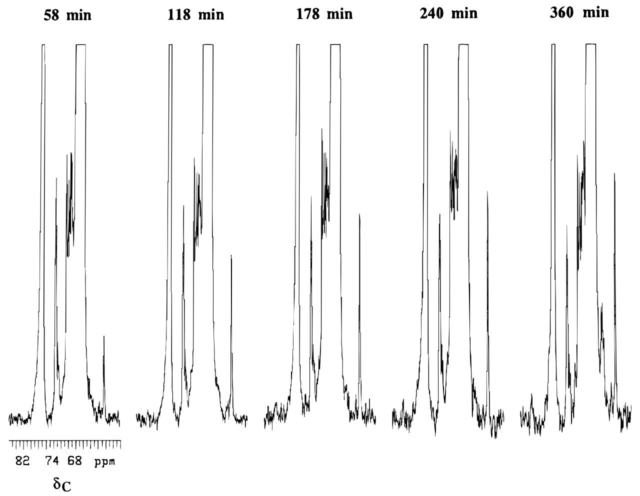


Figure 2. ^{13}C NMR spectra in the range $56 < \delta_C < 86$ of the poly(vinyl acetate) samples removed after 58, 118, 178, 240, and 360 min in the emulsion polymerization carried out at 70 °C. The peak at $\delta_C \approx 77$ is due to the solvent ($CDCl_3$).

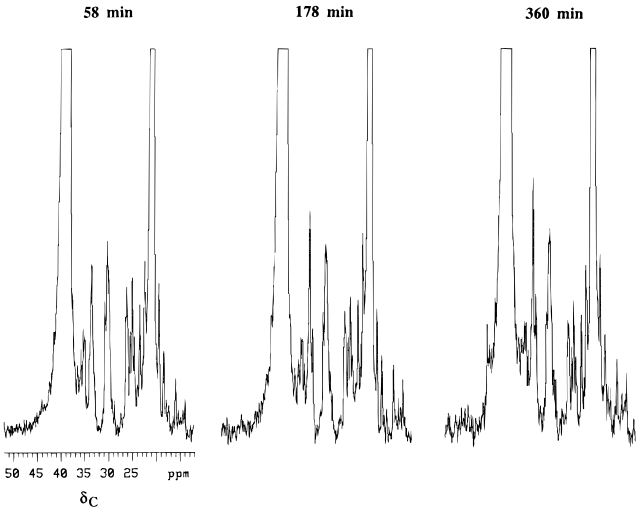
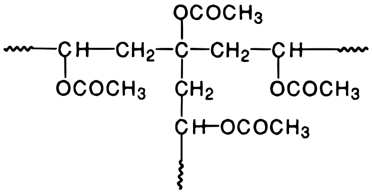


Figure 3. ^{13}C NMR spectra in the range $12 < \delta_C < 52$ of the poly(vinyl acetate) samples removed after 58, 178, and 360 min in the emulsion polymerization carried out at 70 °C.

inverted repeat units. However, the peak from this carbon can be identified using the observation that the extent of chain transfer increases with conversion of monomer, whereas the extent of inverted addition does not. This is demonstrated clearly by Figures 2 and 3. Figure 2 shows spectra of the 56−86 ppm region for samples removed at different times during the emulsion polymerization performed at 70 °C, the main-chain peak having been normalized to the same height in each spectrum. (Note that these spectra were run using the more convenient solvent $CDCl_3$, as no peaks were found in the $CDCl_3$ solvent region of ca. 77 ppm in spectra recorded in C_6D_6; chemical shifts were found to be 0.3−0.7 ppm lower in $CDCl_3$ compared to C_6D_6.) There is a clear increase in the intensity of the distinctive end-group CH_2O peak H with time, whereas the inverted addition peaks K and L remain essentially constant. Figure 3 shows similar spectra for the 12−52 ppm region. Again, most of the minor peaks assigned to inverted units remain essentially constant, but there is a small yet clear increase in intensity with time of the part of peak D at ca. 34 ppm, which we attribute to the underlying penultimate CH_2 carbon in the end group of structure I.

While there is no doubt that end-group structure I exists, the assumption so far has been that it arises exclusively from chain transfer to polymer. The other processes that could generate end groups of structure I are (a) termination by disproportionation and (b) chain transfer to species other than polymer. Termination by disproportionation would give rise not only to end groups of structure I but also to an equivalent number of 1,2-disubstituted olefinic end groups that would not be expected to copolymerize easily with vinyl acetate for reasons of steric hindrance and lack of substantial C═C bond polarity differences (cf. reactivity ratios for copolymerizations of 1,2-disubstituted olefins with α-substituted olefins in which all substituents are the same[18]). Thus, if disproportionation is significant, unsaturated end groups should remain, and be detectable, in the final polymer. The fact that the poly(vinyl acetate) spectra show no resonances in the olefinic region (100−150 ppm), even at high expansions, indicates that termination by disproportionation is negligible in comparison to chain transfer processes. Besides chain transfer to polymer, the only other processes to consider are chain transfer to monomer and surfactant. On the basis of molar mass measurements, Lee and Mallinson[19] concluded that chain transfer to Aerosol OT occurs in emulsion polymerization of vinyl acetate. Assuming that chain transfer to Aerosol OT took place in the work reported here and that the Aerosol OT product radicals (most likely alkyl radicals) initiated polymerization, which is not unreasonable, then chemically bonded Aerosol OT residues should be present in the poly(vinyl acetate). The samples analyzed by NMR had been exhaustively dialyzed against water, which should have removed all of the free Aerosol OT and most (if not all) of the physically adsorbed Aerosol OT. Any Aerosol OT resonances in the NMR spectra of the poly(vinyl acetate) could, therefore, be assigned to residues arising from chain transfer to Aerosol OT. There are weak peaks in the region below 20 ppm that correspond to peaks present in the spectrum of Aerosol OT, but the total intensity of these peaks is only a very small fraction of the intensity of end-group peak H. Thus chain transfer to Aerosol OT may have taken place but makes a negligible contribution to formation of end groups of structure I. Chain transfer to monomer has long been accepted as a process that occurs in vinyl acetate polymerizations. This was thought to occur exclusively via abstraction of a hydrogen atom from the methyl group until Litt and Chang[20] published (controversial) evidence from polymerizations of deuterated vinyl acetates that chain transfer was dominated by abstraction of the vinylic α-hydrogen atom (which, following reinitiation, would give rise to chains with 1,1-disubstituted olefinic end groups). Recent NMR studies by Starnes, Chung, and Benedikt[21] were aimed at resolving this issue and have provided no significant evidence in support of the hypothesis of Litt and Chang. On the contrary, their results from studies of deuterated vinyl acetates provide strong evidence that chain transfer to monomer proceeds predominantly via the (more plausible) H-abstraction from the methyl group. Therefore, considering this to be the more important reaction, the poly(vinyl acetate) chains resulting from propagation or bimolecular termination (coupling) of the product radical would have vinyl ester end groups. As stated above, in our work, olefinic peaks are absent in the spectra of the poly(vinyl acetate) samples. Hence, if chain transfer to vinyl acetate did occur, then the vinyl ester end groups resulting from the product radical must have subsequently copolymerized with vinyl acetate; this would yield a branch point that is indistinguishable from one produced by the corresponding chain transfer to polymer event (i.e., abstraction of a hydrogen atom from the methyl side group of a poly(vinyl acetate) repeat unit). In our work, therefore, the end-group peak H can be used unambiguously to determine the mole percent of branch points in poly(vinyl acetate).

The peaks F (CH_2), G (CH_2), I (CH), and M (C_q) are now considered together. These peaks were observed most clearly in the spectra of samples removed from the emulsion polymerization performed at 70 °C and are most prominent for the final (360 min) sample (see Figures 2 and 3). Although the intensities of these peaks relative to the total intensity increases systematically with polymerization temperature and conversion, their intensity relative to each other is constant as far as their low intensity and overlap with the wings of adjacent intense peaks permits an estimation. This pattern of a weak C_q peak to the high-frequency side of the main-chain CH, a small CH peak at 2−3 ppm to the low-frequency side of the main-chain CH, and a small CH_2 peak at 2−3 ppm to the high-frequency side of the main-chain CH_2 is identical to that observed in spectra of poly(*n*-butyl acrylate) prepared by free-radical polymerization[4−7] and may reasonably be attributed to the same origin, i.e., a branch point formed by chain transfer to polymer involving abstraction of a backbone tertiary hydrogen atom (as shown on the left-hand side of Scheme 1):

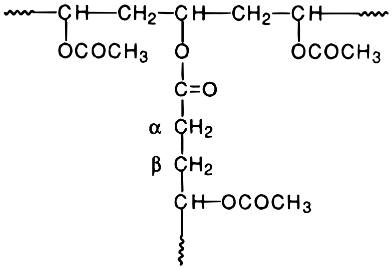


(II)

Peak F is assigned to the CH_2 carbons adjacent to the branch point and peak I is assigned to the CH carbons nearest to the branch. For this structure, the relative intensities of the C_q, CH, and CH_2 peaks should be 1:3:3. However, because the spectra were recorded using rapid pulsing, which discriminates strongly against slowly relaxing quaternary carbons, the intensity of the branch C_q peak is attenuated relative to those of the CH and CH_2 peaks.

Although the C_q peak M may be considered diagnostic for a branch point of structure II, partial hydrolysis of acetate side groups during emulsion polymerization provides an alternative explanation of peaks F and I, as well as an interpretation of peak G. Hydrolysis will lead to CH(OH) peaks in the CHO region, and CH(OH)-CH_2CH(OAc) and CH(OH)CH_2CH(OH) diad peaks in the CH_2 region. The studies of partially hydrolyzed poly(vinyl acetate) reported by Amiya[16] show that the CH_2 carbons in CH(OH)CH_2CH(OAc) and CH(OH)CH_2-CH(OH) diads lie ca. 3 and 6 ppm, respectively, to the high-frequency side of the CH_2 carbon in a CH(OAc)CH_2-CH(OAc) diad, consistent with the chemical shifts observed for peaks F and G. In a spectrum of partially hydrolyzed poly(vinyl acetate) recorded in this work (though not illustrated here), the CH(OH) carbon appeared ca. 3 ppm to the low-frequency side of the CH(OAc) carbon, consistent with peak I. The absence of peak G in the poly(vinyl acetate) from bulk polymerizations and the growth of peaks F, G, and I with polymerization time during the emulsion polymerizations is consistent with the occurrence of hydrolysis on exposure to water. Further studies are planned in order to fully resolve these assignments.

If chain transfer to the backbone CH carbons was the only chain transfer process, then, neglecting differential relaxation, the intensity of peak H would be one-third of those of peaks F and I. The fact that the intensity of H is significantly greater than one-third that of either F or I shows quite conclusively that other chain transfer processes are operative. The most probable processes are chain transfer to methyl groups in both monomer and polymer. As discussed above, the absence of olefinic peaks in the NMR spectra shows that if chain transfer to monomer occurs, it must be followed by copolymerization of the resulting vinyl ester end group with vinyl acetate, which leads to the same branch structure as chain transfer to polymer at the methyl side group (i.e., the process shown on the right-hand side of Scheme 1). This branch structure is shown below and contains two distinct CH_2 environments (labeled α and β) at the beginning of the secondary chain,



The predicted[17] chemical shifts for α and β are 33 and 30 ppm, respectively, values that are significantly different from those of the main-chain CH_2 carbons. Unfortunately, they fall in a region occupied by several CH_2 resonances arising from inverted repeat units. Given the higher incidence of inverted addition relative to chain transfer and the additional complication of splitting due to tacticity effects, unlike the penultimate CH_2 of the end group from chain transfer, the two CH_2 branch resonances are not so easily identified. Nevertheless, tentative assignments for these carbons are possible on the basis of the integrals for the peaks. The integral of C is greater than that of B by an amount approximately equal to the integral of H, an observation that leads us to the inference that the peaks labeled C include the peak from carbon β. Similarly, since the penultimate end-group CH_2 is assigned to D and the integral of D is greater than that of B by an amount approximately twice the integral of H, we conclude that the peak for carbon α forms part of the group of peaks labeled D.

The mole percent of branched repeat units in poly(vinyl acetate), referred to simply as the "mole percent branches" from here onward, was first calculated using the ratio of the integral of peak H to half the total backbone carbon integral. Three emulsion polymerization samples (60 °C, 178 min; 70 °C, 58 and 118 min) were examined using both (a) NOE suppression with full relaxation and (b) fast pulse conditions. For these samples, the mole percent branches data from conditions (a) were systematically lower by a factor of 0.8 ±

0.1 than those from conditions (b). Consideration of the T_1 values alone would suggest that the mole percent branches data from fast pulses should be less than those from slow pulses. The fact that the opposite is observed shows that the ultimate end-group CH_2 carbon has a significantly larger NOE than the main-chain carbons. All mole percent branches data presented in the following discussion were calculated from fast pulse spectra run in $CDCl_3$ using a correction factor of 0.8 for the integral of peak H to account for the differences in T_1 and NOE, i.e., using the equation

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

where I_{60-62} and I_{24-74} are the integrals for the $60 \leq \delta_C \leq 62$ and $24 \leq \delta_C \leq 74$ regions, respectively.

Bulk Polymerizations. The bulk polymerizations of vinyl acetate were performed in part to obtain clean samples of poly(vinyl acetate) free from impurities to assist with the assignment of peaks in the NMR spectra but also for comparison with the emulsion polymerizations. The first bulk polymerizations were carried out to essentially complete monomer conversion using both AZBN and BPO as initiators at the relatively high level of 0.5 wt % to vinyl acetate with the objective of evaluating contributions from the initiator; these polymerizations gave poly(vinyl acetate) with 0.21 and 0.23 mol % branches, respectively. The difference between the levels of branching is within the error of measurement, showing that propagating poly(vinyl acetate) chain radicals are the principal hydrogen atom abstractors. This observation is consistent with recently published work[22,23] on the free-radical grafting polymerization of styrene, methyl methacrylate, and benzyl acrylate onto *cis*-1,4-polybutadiene, for which primary radicals from the initiator were only found to contribute significantly to hydrogen atom abstraction from *cis*-1,4-polybutadiene when the polymeric radicals were of relatively low reactivity, such as the polystyrene chain radical. With reactive polymeric radicals, such as poly(benzyl acrylate) chain radicals, there was no effect of initiator. Given that poly(vinyl acetate) chain radicals are not stabilized by resonance and are of very high reactivity, the absence of an initiator effect is, therefore, expected.

Before considering the variation of mole percent branches with conversion, some fundamental principles that govern the extent of chain transfer to polymer will be outlined. The mole fraction of branched repeat units in 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

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

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

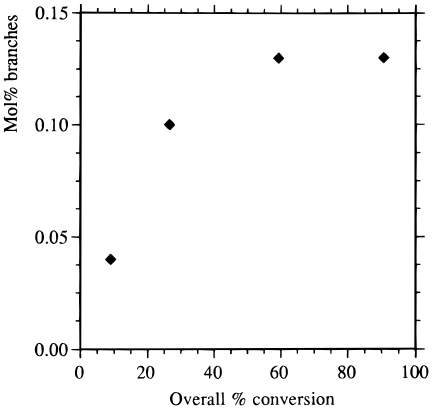


Figure 4. Variation of the mole percent branches with percent conversion for the bulk polymerization of vinyl acetate carried out at 70 °C using 0.01% (w/w) AZBN as initiator.

$$P_{\mathrm{trP}} = \frac{\left(\frac{k_{\mathrm{trP}}}{k_{\mathrm{p}}}\right)\frac{[\mathrm{P}]}{[\mathrm{M}]}}{\left\{\left(\frac{k_{\mathrm{trP}}}{k_{\mathrm{p}}}\right)\frac{[\mathrm{P}]}{[\mathrm{M}]}\right\} + 1} \qquad (3)$$

which clearly reveals that the two factors of importance in determining the extent of chain transfer to polymer are (i) the rate coefficient ratio $k_{\mathrm{trP}}/k_{\mathrm{p}}$ and (ii) the concentration ratio [P]/[M]. Since chain transfer to polymer can be expected to have a much higher activation energy than propagation, $k_{\mathrm{trP}}/k_{\mathrm{p}}$ (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]. For a homogeneous polymerization, [P]/[M] must increase with conversion of monomer to polymer and give rise to a progressive increase in P_{trP}. If [P] and [M] are taken as averages over the complete reaction volume, the variation of [P]/[M] with conversion is given by

$$\frac{[\mathrm{P}]}{[\mathrm{M}]} = \left(\frac{1}{1-c}\right) - 1 \qquad (4)$$

in which c is the fractional conversion of monomer to polymer. Thus, eqs 3 and 4 combine to predict that the mole percent branches should increase monotonically with increasing conversion. Figure 4 shows the variation of mole percent branches with conversion for the bulk polymerization performed at 70 °C using AZBN at the lower concentration of 0.01 wt % to vinyl acetate. Although, as expected, the mole percent branches increases with conversion, in contrast to the prediction presented above, the rate of increase diminishes with conversion. This suggests that diffusion processes (i.e., translational diffusion and/or reaction diffusion) may limit the reaction as the monomer concentration decreases and the viscosity of the reaction medium increases. Quantitative analysis of the effect, however, is not justified given the significant uncertainties in the data at such low levels of mole percent branches.

Emulsion Polymerizations. Although emulsion polymerizations of vinyl acetate are most commonly carried out in the presence of “protective colloids”, such as poly(vinyl alcohol) or hydroxyethylcellulose, they were excluded from the formulation used in the present work to reduce the complexity of the NMR spectra. The

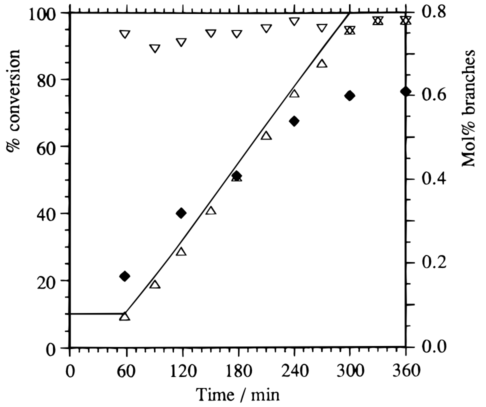


Figure 5. Variation of (i) instantaneous percent conversion (▽), (ii) overall percent conversion (△), and (iii) mole percent branches (◆) with reaction time for the emulsion polymerization of vinyl acetate carried out at 60 °C. The solid line shows the monomer feed profile.

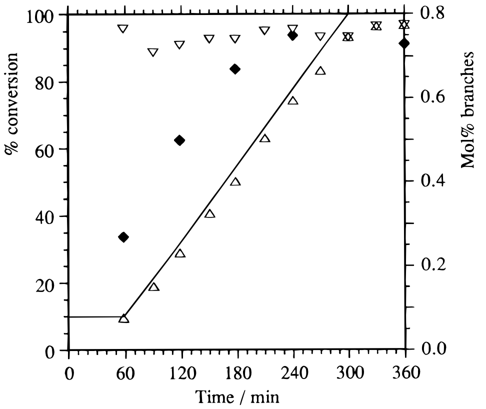


Figure 6. Variation of (i) instantaneous percent conversion (▽), (ii) overall percent conversion (△), and (iii) mole percent branches (◆) with reaction time for the emulsion polymerization of vinyl acetate carried out at 70 °C. The solid line shows the monomer feed profile.

formulation employed was based on that reported by El-Aasser et al.[24] for emulsion copolymerization of vinyl acetate with *n*-butyl acrylate and was developed further with the aim of achieving a commercially realistic solids content of 50% (compared to the 33% solids content of the original work). Preliminary experiments showed that the 1:1 (w/w) mixture of Aerosol OT and Aerosol MA surfactants used by El-Aasser et al.[24] was unsatisfactory for vinyl acetate homopolymerization at 50% solids content, very high levels of coagulum being formed. In view of this, several emulsion polymerizations were carried out using mixtures comprising different weight ratios of these surfactants, leading to the observation that the use of Aerosol OT alone gave the lowest level of coagulum (0.8%), which was acceptable although higher than desired.

Figures 5 and 6 show plots of conversion and mole percent branches as a function of reaction time for emulsion polymerizations carried out at 60 and 70 °C, respectively. There are three obvious conclusions concerning the mole percent branches. First, the levels of branching are significantly higher than observed in the bulk polymerizations of vinyl acetate. Second, the level of branching increases steadily with percent conversion. Third, the level of branching is higher at 70 °C. The last two observations are more clearly evident from inspection of Figure 7, which shows the variation of mole percent branches with overall percent conversion for both emulsion polymerizations.

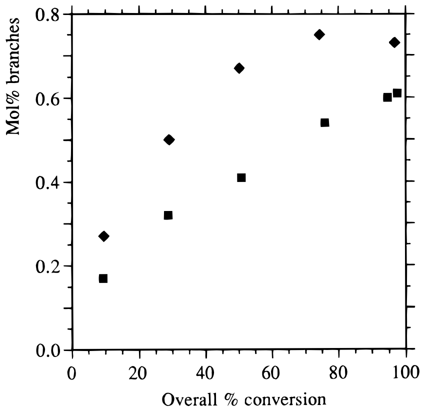


Figure 7. Variation of the mole percent branches with overall percent conversion for the emulsion polymerizations of vinyl acetate carried out at 60 °C (■) and 70 °C (◆).

Even when performed at the lower temperature of 60 °C, emulsion polymerization gave rise to a higher level of branching than the bulk polymerizations run at 70 °C, showing that the concentration ratio [P]/[M] was the dominant factor in determining the mole percent branches. Recent studies[7] of *n*-butyl acrylate solution polymerization have shown that [P]/[M] must always be considered in terms of *local* concentrations in the vicinity of the propagating chain radical. In view of this, the locus of polymerization must be considered in order to explain the higher levels of branching resulting from the emulsion polymerizations. Based on the *n*-butyl acrylate results,[7] except for the initial 10−20% conversion, the bulk polymerizations of vinyl acetate may be considered to have a homogeneous distribution of polymer repeat units and monomer throughout the reaction mixture; i.e., [P]/[M] should depend only on the overall conversion in accordance with eq 4. In the emulsion polymerizations, however, polymerization proceeds almost exclusively within the latex particles, in which case the polymer repeat unit and monomer concentrations of interest are those within the particles, i.e., $[P]_p$ and $[M]_p$, respectively. Because the emulsion polymerizations proceeded under monomer-starved conditions with high instantaneous conversions, the concentration ratio $[P]_p/[M]_p$ was high at all times during these reactions. (On the basis of the instantaneous conversion data, $[P]_p/[M]_p$ has values around 10−20 for most of the reaction in both emulsion polymerizations.) In comparison to the bulk polymerizations, therefore, the time-averaged local value of [P]/[M] was much higher in the emulsion polymerizations. Only when the bulk polymerizations attained high conversions (around 90−95%) would the concentration ratio [P]/[M] achieve values similar to those existing for most of the time during the emulsion polymerizations. Clearly then, from eq 3, the much higher local values of [P]/[M] in the emulsion polymerizations give rise to the higher values of mole percent branches.

The two emulsion polymerizations will now be considered in comparison with each other and with previous studies of *n*-butyl acrylate emulsion copolymerizations.

In comparison of the two emulsion polymerizations at 60 and 70 °C, inspection of Figures 5 and 6 reveals that the instantaneous conversion versus reaction time curves are very similar. Hence, these polymerizations have similar variations of $[P]_p/[M]_p$ with overall conversion. The higher level of branching at 70 °C must, therefore, be a consequence of the increased value of k_{trP}/k_p at the higher reaction temperature.

The trend for the mole percent branches to increase (though at a reducing rate) with increasing overall percent conversion is similar to that reported here for bulk polymerization of vinyl acetate and to observations[4−7] on solution and emulsion polymerizations of *n*-butyl acrylate. As can be seen from Figures 5 and 6, there is a steady increase in the instantaneous conversion from the beginning of the monomer feed stage onward, which, due to its effect on $[P]_p/[M]_p$, clearly must lead to an increase in the level of branching. Thus the general trend is readily explained, with the reducing rate of increase in mole percent branches again presumed to be a consequence of diffusion effects. However, in view of the difficulty in accurately accounting for partitioning of vinyl acetate (which has high water solubility) and the errors involved in calculating $[P]_p/[M]_p$ from (high values of) instantaneous conversion determined gravimetrically, quantitative correlation of the mole percent branches data with the instantaneous conversion data has not been attempted.

In comparison with previously published[4−6] data for *n*-butyl acrylate emulsion copolymerizations, the levels of branching are much lower (by factors of 3−6) in the vinyl acetate emulsion polymerizations. Given that the instantaneous conversions were similar in the *n*-butyl acrylate emulsion copolymerizations, these results indicate that the rate coefficient ratio k_{trP}/k_p is smaller for free-radical polymerization of vinyl acetate than for *n*-butyl acrylate. If the Arrhenius frequency factors for the two systems were similar, these observations would imply that the difference between the activation energies for chain transfer to polymer and for propagation is greater for vinyl acetate than for *n*-butyl acrylate. There is, however, no good reason to assume that the ratio of the frequency factors for chain transfer to polymer and for propagation would be same for these two systems. Although theoretical calculations of frequency factors and activation energies for propagation and simple chain transfer events are now being made,[25−27] calculations on more complex reactions, such as chain transfer to polymer, have not yet been attempted. Experimental measurements of k_p by pulsed-laser polymerization[28] have revealed (through comparison of data for *n*-butyl methacrylate and *n*-butyl acrylate) important effects of α-methyl substituents, the inferences being that they lead to (a) hindered rotations in the transition state, which reduce the magnitude of the propagation frequency factor, and (b) increases in the activation energy for propagation, both effects causing reductions in k_p. In the absence of such relevant information for both chain transfer to polymer and propagation, however, the results reported here cannot be interpreted in detail. Nevertheless, differences between the relative stabilities of the radicals involved can be discussed and may be of influence in the transition states. The radical produced by H-abstraction from an *n*-butyl acrylate repeat unit is both tertiary and stabilized by resonance with a C=O group and of much higher stability than a propagating poly(*n*-butyl acrylate) radical, which, although similarly stabilized by resonance with a C=O group, is secondary and far less sterically hindered. For vinyl acetate, chain transfer to polymer proceeds predominantly via H-abstraction from the methyl side group, which produces a primary radical that is less sterically hindered than a propagating poly(vinyl acetate) radical, though it is stabilized by resonance with the acetate C=O group; the stabilities of these radicals should not, therefore, be so markedly different as for their equivalents in *n*-butyl acrylate polymerization. Hence, in terms of radical stabilities, chain transfer to polymer in *n*-butyl acrylate polymerization should be energetically more favorable than in vinyl acetate polymerization.

Conclusions

^{13}C NMR spectra of poly(vinyl acetate) produced by free-radical bulk and emulsion polymerization have been 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. Although the spectra showed the occurrence of both possible modes of chain transfer to polymer (i.e., via the backbone tertiary C−H and the methyl side group), abstraction of methyl side-group hydrogen atoms is clearly the predominant reaction. Unfortunately, the unique CH_2 carbons in branch points that result from the latter reaction give resonances that overlap with those from CH_2 carbons in, and adjacent to, inverted repeat units. However, the number of ultimate CH_2 carbons (i.e., end groups), the signal from which was observed in an otherwise clear region of the spectrum at $\delta_C \approx 61$, was shown by a process of elimination to be equal to the number of branch points. Thus, the integral for the ultimate CH_2 carbon resonance was used to calculate the mole percent branches in poly(vinyl acetate).

Changing the initiator from AZBN to BPO had no effect on the extent of branching in bulk polymerizations. This observation leads us to infer that propagating poly(vinyl acetate) chain radicals are the principal hydrogen atom abstractors, which is entirely reasonable in view of their very high reactivity.

Due to the high instantaneous conversions and the compartmentalization of the reaction into monomer-swollen latex particles, the levels of branching in the poly(vinyl acetate) produced by the emulsion polymerizations were much higher than those for the (homogeneous) bulk polymerizations. Increasing the temperature of the emulsion polymerization from 60 to 70 °C led to an increase in the level of branching that can be interpreted in terms of an increase in the rate coefficient ratio k_{trP}/k_p. Additionally, in both bulk and emulsion polymerization, the mole percent branches increased steadily with overall conversion as a consequence of increases in the concentration ratio [P]/[M], though not in quantitative accordance with the predictions of eqs 3 and 4, most probably due to neglect of diffusion effects in the equations. Hence, although analysis of the mole percent branches data to determine k_{trP}/k_p is possible if [P]/[M] is known, a series of values would be obtained for different levels of conversion. Given that the error in the measurement of branching level is significant (estimated to be about ±20%), further experiments in which other errors are minimized (in particular those associated with knowledge of [P]/[M]) would be necessary to justify such determinations of k_{trP}/k_p for use in modeling work.

Overlap of CH_2 carbon resonances arising from inverted repeat units, branch points, and end groups

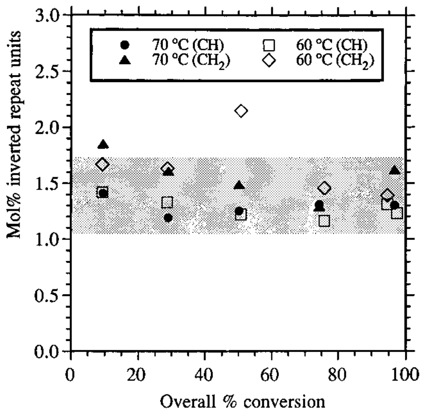


Figure 8. Variation of the mole percent inverted repeat units in poly(vinyl acetate) with overall percent conversion for the emulsion polymerizations carried out at 60 and 70 °C. The mole percent inverted repeat units was calculated (i) from the integral for peak L (CH) and (ii) from the integral for peak C (CH_2) corrected for the contribution from side-group branch CH_2 (β) carbons by subtracting from it the integral for peak H. The equations used were for (i) $(100I_{71.5-74.5})/\{0.5[I_{24-74} - (0.2I_{60-62})]\}$ and (ii) $\{100[I_{28-32} - (0.8I_{60-62})]\}/\{0.5[I_{24-74} - (0.2I_{60-62})]\}$, where $I_{71.5-74.5}$, I_{24-74}, I_{60-62}, and I_{28-32} are respectively the integrals for the ranges of chemical shift indicated by the subscripts. (Note that the spectra used were run in $CDCl_3$ using fast pulse conditions and that these equations take into account the difference in T_1 and NOE for peak H.) The shaded area in the plot represents a ±20% error about the mean value of 1.44 mole percent.

complicates absolute assignment of individual peaks in the 22−37 ppm region of the spectra. Nevertheless, the level of inverted repeat units can be calculated on the basis of the assignments discussed earlier and given in Table 2. The data obtained from two separate calculations of the mole percent of inverted repeat units for the emulsion polymerizations are plotted in Figure 8 and have a mean value of 1.44 mol % (with a standard deviation of 0.24 mol %), which is in good agreement with literature values[29,30] of 1.15 mol % (polymerization at 25 °C), 1.26−1.33 mol % (50 °C), 1.52−1.59 mol % (80 °C), and 1.86 mol % (110 °C) determined from measurements of molar mass after hydrolysis and selective chain scission at 1,2-diol linkages. (Data calculated from fast pulse spectra were in good agreement with those from spectra obtained with NOE suppression and full relaxation, an observation that is expected because the integrals used are dominated by resonances from main-chain CH and CH_2 carbons, which should have similar values of T_1 and NOE.) A further important feature of the data is that, within the experimental error for these calculations (estimated to be ±20% of the mean value), the effects of conversion and of a 10 °C change in temperature on the level of inverted repeat units are negligible. In contrast, the same changes in conversion and temperature had significant effects on the extent of chain transfer to polymer (Figure 7), an observation which suggests that it will be possible to unambiguously assign all the resonances in the 22−37 ppm region by analyzing poly(vinyl acetate) samples produced by bulk polymerizations carried out over a wide range of temperature, in particular much higher temperatures than so far employed.

The principal aim of the work described in this paper was to establish unique ^{13}C NMR resonances that can be used to quantify the mole percent branches in poly(vinyl acetate). This has been achieved and has led to important conclusions concerning the mode and extent of chain transfer to polymer in free-radical polymerizations of vinyl acetate. The work has laid the foundation for further studies of the effects of polymerization process variables on the mole percent branches (including effects of comonomers) and for studies of correlations between changes in molar mass distribution and the extent of chain transfer to polymer, all of which have great commercial relevance. Additionally, similar studies of the chemistry by which protective colloids become grafted to poly(vinyl acetate) during emulsion polymerization are possible and will be assisted by the complete interpretation of the ^{13}C NMR spectrum of poly(vinyl acetate) expected to result from the further work on bulk polymerization described above.

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