

# Chain Transfer to Polymer in Free-Radical Solution Polymerization of *n*-Butyl Acrylate Studied by NMR Spectroscopy

Nasir M. Ahmad,<sup>†</sup> Frank Heatley,<sup>‡</sup> and Peter A. Lovell<sup>\*,†</sup>

Polymer Science and Technology Group, Manchester Materials Science Centre, University of Manchester and UMIST, Grosvenor Street, Manchester M1 7HS, United Kingdom, and Department of Chemistry, University of Manchester, Manchester M13 9PL, United Kingdom

Received August 26, 1997; Revised Manuscript Received January 21, 1998

**ABSTRACT:** The effects of the initial monomer concentration,  $[M]_0$ , and percent conversion on the extent of chain transfer to polymer in free-radical solution polymerization of *n*-butyl acrylate has been studied. The polymerizations were carried out in cyclohexane at 70 °C using 0.1% (w/w) 2,2'-azobis(2-cyanopropane) as initiator and the mole percent branched repeat units (mole percent branches) in the poly(*n*-butyl acrylate) was determined from unique resonances of branch-point carbons in the  $^{13}\text{C}$  NMR spectra. At  $[M]_0 > 10\%$  (w/w) the mole percent branches is independent of  $[M]_0$  and increases from 0.8 to  $\sim 2.2\%$  as conversion increases from 35 to  $\sim 95\%$ . However, for more dilute solutions, with  $[M]_0 \leq 10\%$  (w/w), the mole percent branches increases as  $[M]_0$  decreases and is higher than at equivalent conversions for the more concentrated solution polymerizations; e.g., at  $\sim 25\%$  conversion the mole percent branches increases from 2.7% for  $[M]_0 = 10\%$  (w/w) to 5.9% for  $[M]_0 = 3\%$  (w/w). These observations are explained in terms of the ratio of the concentrations of polymer repeat units and monomer in the vicinity of the propagating chain end. In more concentrated solutions, intermolecular chain transfer to polymer dominates because, at all except the lowest percent conversions, the overall polymer repeat unit concentration is sufficient for overlap of individual polymer coils. However, in the dilute solutions the overall polymer repeat unit concentration is too low for overlap of individual polymer coils and intramolecular chain transfer to polymer dominates. Under these conditions, the local polymer repeat unit concentration within the isolated propagating chains is defined by the chain statistics and so is approximately constant, whereas the monomer is distributed uniformly throughout the solution. Thus, for dilute solutions, as  $[M]_0$  decreases, the probability of chain transfer to polymer (and hence the mole percent branches) increases.

## Introduction

Chain transfer to polymer during free-radical polymerization can lead to the formation of highly branched polymers with significant consequences for properties. This is well-established in the case of low-density polyethylene, which is produced by free-radical polymerization at high temperatures and pressures.<sup>1–3</sup> More recently, using NMR spectroscopy, we have established<sup>4–6</sup> that chain transfer to polymer occurs extensively in emulsion copolymerizations of *n*-butyl acrylate with methyl methacrylate and acrylic acid and involves abstraction of hydrogen atoms from backbone tertiary C–H bonds, as shown in Scheme 1. Despite the additional resonances arising from the comonomer repeat units, the branch point shown as structure I in Scheme 1 could be detected unambiguously: in addition to the normal repeat unit resonances, spectra recorded in  $\text{C}_6\text{D}_6$  solution showed distinct CH,  $\text{CH}_2$ , and  $\text{C}_q$  resonances at  $\delta_{\text{C}}$  40.4–41.1, 38.4, and 49.1, respectively, that were shown to have the relative intensities of 3:3:1 required for the branch point when spectra were recorded under quantitative conditions (i.e., with long intervals between pulses and suppression of NOE). The highly branched nature of *n*-butyl acrylate based polymers prepared by emulsion polymerization had not previously been recognized and the significance of the results for many commercial acrylic polymers prompted us to pursue more detailed studies.

The principal objectives of the present studies were to establish the extent of chain transfer to polymer in solution polymerizations (i.e., at lower concentrations of monomer and polymer) and to investigate contributions from intramolecular reactions in more dilute systems. Since the chemical structure of the resulting branch point is the same for both intermolecular and intramolecular chain transfer to polymer, NMR spectroscopy cannot distinguish between these two events. Nevertheless, by carrying out solution polymerizations at a wide range of initial monomer concentrations the probabilities of intermolecular and intramolecular chain transfer to polymer can be varied in a controlled way, thereby facilitating distinction between the relative contributions of these two processes. In this respect, a further consideration for all the solution polymerizations is the monomer conversion, because at very low conversions the overall polymer concentration is low and intermolecular chain transfer to polymer is of low probability.

The analytical work was simplified by studying homopolymerizations of *n*-butyl acrylate. Cyclohexane was chosen as the diluent because it is a reasonable solvent for poly(*n*-butyl acrylate) and has a low transfer constant,  $C_{\text{trS}}$  (e.g., for free-radical homopolymerizations of ethyl acrylate and styrene at 60 °C, reported values of  $C_{\text{trS}}$  are  $(4.8–6.1) \times 10^{-5}$  and  $(0.24–0.63) \times 10^{-5}$ , respectively<sup>7</sup>). A low value for  $C_{\text{trS}}$  was important, because this minimized potential complications arising from chain transfer to solvent.

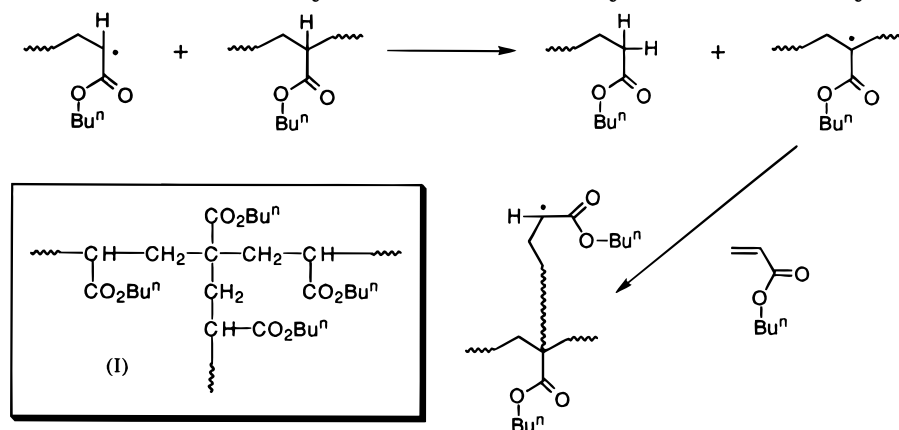
## Experimental Section

**Polymerizations.** *n*-Butyl acrylate (Aldrich, 99%) was washed three times with dilute sodium hydroxide solution to

\* To whom correspondence should be addressed.

<sup>†</sup> Polymer Science and Technology Group.

<sup>‡</sup> Department of Chemistry.

**Scheme 1. Chain Transfer to Polymer in Free-Radical Polymerization of *n*-Butyl Acrylate<sup>a</sup>**

<sup>a</sup> The inset shows in more detail the unique element of structure at the branch point that has been fully characterized<sup>4-6</sup> by <sup>13</sup>C NMR spectroscopy.

remove the phenolic inhibitor, followed by washing thoroughly with water before drying over anhydrous calcium chloride. The inhibitor-free monomer was distilled under nitrogen at reduced pressure, the fraction collected having a purity  $\geq 99.7\%$ , as determined by gas chromatography. Cyclohexane (BDH, 99%) was dried over sodium wire and then distilled under nitrogen at atmospheric pressure; analysis by gas chromatography showed the purity to be  $\geq 99.8\%$ . 2,2'-Azobis(2-cyanopropane) (BDH, 97%) (AZBN) was recrystallized from toluene and dried under vacuum in a desiccator.

Solution polymerizations were performed at 70 °C. To obtain sufficient polymer for analysis by NMR spectroscopy, reactions at initial *n*-butyl acrylate concentrations  $\leq 10\%$  (w/w) were performed on a 1 kg scale, whereas 500 g scale reactions were adequate for concentrations  $>10\%$  (w/w). All of the *n*-butyl acrylate and all except 40 g of the cyclohexane solvent were added to a flanged reaction vessel, which was then equipped with a mechanical stirrer, nitrogen inlet, and a series of two double-surface condensers through which chilled water was passed. After establishing a nitrogen atmosphere and ensuring that the contents of the flask had reached reaction temperature, a solution of the AZBN dissolved in cyclohexane (20 g) was added and washed into the flask with a further quantity of cyclohexane (20 g). In all polymerizations, the initiator concentration was 0.1% (w/w). After further flushing with nitrogen, the system was sealed by closing the open end of the topmost condenser with a balloon. For some polymerizations, aliquots were removed by pipet at predetermined intervals and immediately quenched by cooling in an ice-water bath. At the end of the designated reaction time, the polymerization mixture was similarly rapidly quenched.

For each quenched polymerization mixture, the percent conversion of *n*-butyl acrylate was determined by gas chromatography using a Perkin-Elmer AutoSystem Gas Chromatograph fitted with a 25 m DMS-coated capillary column and a flame ionization detector. Helium flowing at 30 cm<sup>3</sup> min<sup>-1</sup> was used as the carrier gas with the following temperature program: 50 °C for 10 min, followed by heating at 10 °C min<sup>-1</sup> to 150 °C, which was held for a further 5 min. A known quantity of *n*-butyl acetate (Fisons,  $\geq 98\%$ ) was added to the quenched polymerization mixture as an internal standard to facilitate determination of the amount of unreacted *n*-butyl acrylate, from which the percent conversion was calculated. Calibration with solutions of *n*-butyl acrylate and *n*-butyl acetate showed the ratio of their detector response factors to be independent of their concentrations in the ranges of interest. The percent conversion data shown in Table 2 are mean values determined from triplicate analysis of one or two samples from each polymerization mixture.

**NMR Spectroscopy.** Samples for NMR spectroscopy were isolated from the quenched polymerization mixtures through solvent removal by rotary film evaporation at a maximum temperature of 30–35 °C under high vacuum. (Analysis of

**Table 1. Assignments of the <sup>13</sup>C NMR Spectrum of Poly(*n*-butyl acrylate) in CDCl<sub>3</sub> (See Figure 1)**

peak	chemical shift/ppm	assignment
A	25.0	AZBN CH <sub>3</sub>
B	26.8	initiator CH <sub>3</sub> in polymer
C	27.5–30.0	end-group –CH <sub>2</sub> CH <sub>2</sub> COOBu
D	30.5	2-CH <sub>2</sub> in <i>n</i> -butyl side group
E	31.6	end-group –CH <sub>2</sub> CH <sub>2</sub> COOBu
F	33.7–37.4	main-chain CH <sub>2</sub>
G	37.4–38.6	CH <sub>2</sub> adjacent to branch
H	38.6–39.9	CH adjacent to branch
I	40.2	unknown
J	40.7–42.2	main-chain CH
K	42.4	unknown
L	47.2–48.4	branch C <sub>q</sub>

[M]<sub>0</sub> = 3% samples isolated (i) in this way after storage in a refrigerator for 5 months and (ii) by solvent evaporation at 20 °C under vacuum in a vacuum oven gave results identical within experimental error to those isolated shortly after the polymerization in the way described, indicating that further reaction did not occur during the isolation procedure.) In each case, the poly(*n*-butyl acrylate) sample thus obtained was dissolved in CDCl<sub>3</sub> to give a solution of concentration  $\sim 100$  mg cm<sup>-3</sup>. <sup>13</sup>C NMR spectra were recorded at room temperature using a Varian Associates Unity 500 spectrometer operating at 125.8 MHz. Chemical shifts were referenced to the solvent resonance, which was taken to lie at  $\delta_C = 77.0$  ppm. To maximize the signal-to-noise ratio in a given time, <sup>13</sup>C spectra were normally run with continuous proton decoupling using a pulse interval of 0.5 s and a flip angle of 45°. Under these 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<sub>2</sub> carbons. To check the quantitative accuracy of these fast pulse spectra, some samples were analyzed again with NOE suppression by gated decoupling and with a pulse interval of 10.5 s to allow complete recovery of all carbons. Additionally, the DEPT technique<sup>8</sup> was used to determine the multiplicity of the peaks, i.e., whether that carbon was primary, secondary, tertiary, or quaternary.

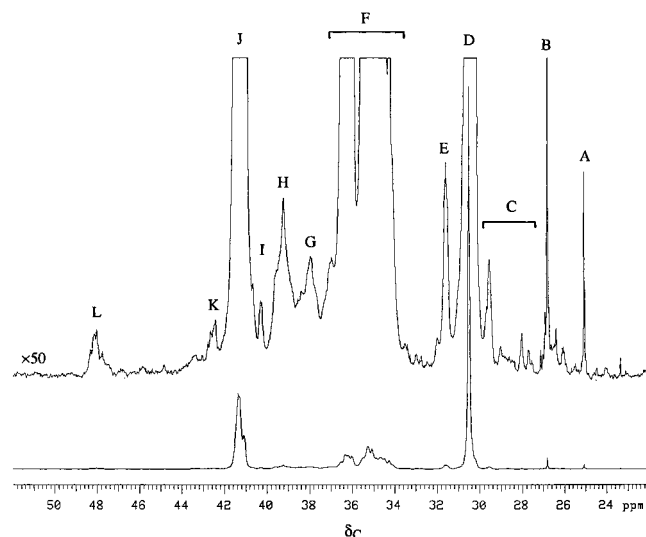
## Results and Discussion

**NMR Spectra.** Figure 1 shows that part of the <sup>13</sup>C NMR spectrum relevant to this work. The form of the spectrum is essentially identical to that of the poly(*n*-butyl acrylate) peaks assigned in previously published spectra of poly[(*n*-butyl acrylate)-*co*-(methyl methacrylate)-*co*-(acrylic acid)] prepared by emulsion copolymerization,<sup>4-6</sup> though the resolution is rather better

**Table 2. Mole Percent Branches in Poly(*n*-butyl acrylate) Prepared by Free-Radical Solution Polymerization of *n*-Butyl Acrylate in Cyclohexane at 70 °C<sup>a</sup>**

reacn <sup>b</sup> code	[M] <sub>0</sub> <sup>c</sup>		reacn time/ min	%	mol % branches <sup>d</sup>	
	% (w/w)	mol kg <sup>-1</sup>			% conversion	$C_q^e$ CH + CH <sub>2</sub> <sup>f</sup>
50BA	50	3.90	420	98	1.6 (2.1)	1.9 (2.2)
40BA	40	3.12	420	97	1.4	2.1
30BA-1	30	2.34	360	95	1.4	2.3
20BA-1	20	1.56	30	35	0.8	1.6
			60	49	1.1	1.8
			120	63	1.2	2.0
			360	82	1.5 (2.9)	2.5 (2.6)
20BA-2	20	1.56	30	38	1.0	1.7
10BA-1	10	0.78	10	7	1.4	2.3
			30	28	1.6	2.7
			360	88	2.3 (4.9)	3.9 (4.4)
			360	88	2.7	3.8
10BA-2	10	0.78	10	7	1.5	2.5
			30	23	1.7	2.7
			360	88	2.7	3.8
			360	88	2.7	3.8
7BA	7	0.55	30	7	1.9	3.3
			180	27	2.1	3.5
			360	27	2.1	3.5
5BA	5	0.39	30	9	2.8	4.2
			120	26	3.0	4.5
			360	26	3.0	4.5
3BA	3	0.23	60	8	3.8	5.3
			360	25	3.4	5.9

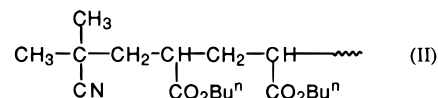
<sup>a</sup> For each polymerization, 2,2'-azobis(2-cyanopropane) was used as initiator at a concentration of 0.1 % (w/w) ( $=6.1 \times 10^{-3}$  mol kg<sup>-1</sup>). <sup>b</sup> The first digits indicate [M]<sub>0</sub> as a % (w/w) and, where separate runs of the same reaction were performed, the number after the hyphen indicates the run number. <sup>c</sup> [M]<sub>0</sub> is the initial concentration of *n*-butyl acrylate. <sup>d</sup> Determined from <sup>13</sup>C NMR spectra recorded under fast pulse conditions with the exception of data given in parentheses, which were from spectra recorded with a 10.5 s pulse interval and NOE suppression. <sup>e</sup> Mole percent branches determined from the ratio of the branch C<sub>q</sub> integral to half the total integral for backbone carbon atoms. <sup>f</sup> Mole percent branches determined from the ratio of one-third of the sum of the branch CH and CH<sub>2</sub> integrals to the total integral for backbone carbon atoms.



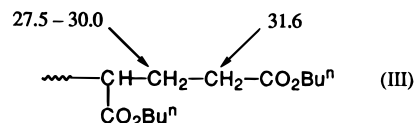
**Figure 1.** Representative <sup>13</sup>C NMR spectrum of poly(*n*-butyl acrylate) recorded using CDCl<sub>3</sub> as solvent. The spectrum was recorded using fast pulses and is of the sample obtained after 360 min reaction for [M]<sub>0</sub> = 20% (w/w). The assignments of the labeled peaks are given in Table 1.

because of the use of a higher resonance frequency. The chemical shifts of peaks in Figure 1 are ca. 1 ppm lower than the corresponding peaks reported previously,<sup>4-6</sup> a variation due to the use of CDCl<sub>3</sub> as NMR solvent in this work instead of C<sub>6</sub>D<sub>6</sub>. Table 1 summarizes the peak assignments.

In addition to the branch-point peaks assigned previously at 37.4–38.6 ppm (branch CH<sub>2</sub>), 38.6–39.9 ppm (branch CH), and 47.2–48.4 ppm (branch C<sub>q</sub>), several other small peaks were observed more clearly, i.e. sharp peaks at 25.0 and 26.8 ppm (CH<sub>3</sub>) and broader peaks at 27.5–30.0 and 31.6 ppm (CH<sub>2</sub>) and 40.2 and 42.4 ppm (CH). The CH<sub>3</sub> peak at 25.0 ppm was assigned to unreacted AZBN initiator from a comparison with the spectrum of AZBN and because its intensity decreases with polymerization time. The remaining CH<sub>3</sub> at 26.8 ppm increases in intensity with reaction time and was therefore assigned to AZBN fragments incorporated in the polymer chain at the initiation site:



The CH<sub>2</sub> peaks at 27.5–30.0 and 31.6 ppm are assigned to the end-group resulting from chain transfer to polymer (see Scheme 1) as follows:



The basis of this assignment is 2-fold. First, the chemical shifts were consistent with values of 27.0 and 33.5 ppm predicted using a chemical shift substituent increment scheme for alkanes;<sup>9</sup> second, the intensity of the well-defined peak at 31.6 ppm was consistently one-third of that of the branch CH or CH<sub>2</sub> peaks. The origin of the CH peaks at 40.2 and 42.4 ppm is still under investigation.

The mole percent of branched repeat units in the poly(*n*-butyl acrylate) samples was determined by referencing the branch C<sub>q</sub> and branch CH + CH<sub>2</sub> integrals to the total integral for backbone carbons and is referred to as the “mole percent branches” from here onward. The extent of chain transfer to polymer correlates directly with the mole percent branches, and these terms are used interchangeably in the following discussion.

**Variation of mole percent Branches with the Initial *n*-Butyl Acrylate Concentration and percent Conversion.** Table 2 presents the results from the series of solution polymerizations of *n*-butyl acrylate carried out in cyclohexane as solvent. As can be seen from the repeat runs, the reproducibility of the results is excellent. However, for rapid pulse spectra, the mole percent branches data determined from the branch C<sub>q</sub> resonance are significantly lower than those determined from the branch CH + CH<sub>2</sub> resonances. This is expected because the total backbone carbon integral was used in the denominator for the calculations and comes predominantly from CH and CH<sub>2</sub> carbons, which relax more rapidly than carbons with no attached hydrogens. When spectra were recorded under conditions that suppressed the NOE and allowed complete relaxation of all carbon nuclei between pulses, the mole percent branches obtained from the branch C<sub>q</sub> and CH + CH<sub>2</sub> resonances were identical within experimental error. The mole percent branches obtained from branch CH + CH<sub>2</sub> resonances increased only slightly under these conditions, showing that, by comparison of the intensities of like carbons in fast pulse spectra, the relative

intensities reflect reasonably accurately the relative abundance of the corresponding type of carbon. Thus, for fast pulse spectra, the mole percent branches data determined from the branch CH + CH<sub>2</sub> resonances are more reliable in absolute terms than those from the branch C<sub>q</sub> resonance. Nevertheless, both sets of data demonstrate the same relative trends that are the focus of this paper.

Two trends are evident from inspection of the data in Table 2: (i) the extent of chain transfer to polymer increases with percent conversion, and (ii) at a given percent conversion, the extent of chain transfer to polymer increases as the initial monomer concentration, [M]<sub>0</sub>, decreases.

To interpret the results, the probability,  $P_{trP}$ , that a propagating chain undergoes chain transfer to polymer rather than propagation needs to be considered. This quantity is given by

$$P_{trP} = \frac{k_{trP}[P]}{k_{trP}[P] + k_p[M]} \quad (1)$$

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 more instructively be written in the form

$$P_{trP} = \frac{\left(\frac{k_{trP}}{k_p}\right) \frac{[P]}{[M]}}{\left\{\left(\frac{k_{trP}}{k_p}\right) \frac{[P]}{[M]}\right\} + 1} \quad (2)$$

Thus the two factors of importance in determining the extent of chain transfer to polymer are the rate coefficient ratio  $k_{trP}/k_p$  and the concentration ratio [P]/[M]. For polymerization of a specific monomer at a fixed temperature, as in the present work,  $k_{trP}/k_p$  is a constant and the extent of chain transfer to polymer is controlled by [P]/[M].

Clearly, for any homogeneous polymerization, [P]/[M] must increase with conversion of monomer to polymer and give rise to a progressive increase in the probability of chain transfer to polymer and, therefore, in the mole percent branches. If [P] and [M] are taken as averages over the complete reaction volume, the variation of [P]/[M] with conversion is independent of [M]<sub>0</sub> and is given by

$$\frac{[P]}{[M]} = \left(\frac{1}{1-c}\right) - 1 \quad (3)$$

in which  $c$  is the fractional conversion of monomer to polymer. This relationship may be substituted into eq 2 to facilitate quantitative prediction of the increase in the mole percent branches with conversion, provided that  $k_{trP}/k_p$  is known. Alternatively, eq 3 can be used to facilitate integration with respect to conversion, thereby permitting evaluation of  $k_{trP}/k_p$ . However, although the observed increases in mole percent branches with conversion are qualitatively consistent with the predictions of eqs 2 and 3, the rate of increase in mole percent branches diminishes with increasing conversion, contrary to the predictions of this simple theory. In view of this, quantitative analysis of the experimental data using eqs 2 and 3 cannot be justified. Since the

chemical processes considered in deriving the equations are unquestionably correct, the simple theory presented is inadequate for fully describing the variation of mole percent branches with conversion. Diffusion limitations to chain transfer to polymer provide the most probable reason for the diminishing rate of increase in mole percent branches with increasing conversion, transport processes and reaction diffusion being the most likely sources of diffusion control. Under conditions of high dilution by solvent, the most likely limiting effect is reaction diffusion.

The increase in mole percent branches (i.e., in the extent of chain transfer to polymer) as [M]<sub>0</sub> decreases also is in conflict with the predictions of the simple theory, implicit in which is the expectation that  $P_{trP}$  should be independent of [M]<sub>0</sub>. This observation is of great significance in relation to one of the principal aims of this work, namely the investigation of intramolecular chain transfer to polymer. The reason for the apparent anomaly becomes evident when it is recognized that chain transfer can occur only in the vicinity of an actively propagating chain end. While this is an obvious statement, it is particularly significant because it highlights the need to consider the *local concentrations in the vicinity of the propagating chain* and not the overall concentrations. This makes no difference to the concentrations of reaction components that are uniformly distributed throughout the reaction volume but has very important consequences when considering the concentration of polymer chain repeat units, as is emphasized in the ensuing discussion. The rationale used in explaining the experimental observations bears close analogy with the failure of the mean field approximation in Flory–Huggins theory at concentrations below which the polymer coils are isolated from each other.<sup>10</sup>

Intramolecular chain transfer to polymer becomes more probable as [M]<sub>0</sub> decreases because [M]<sub>0</sub> defines the upper limit for the overall concentration of polymer repeat units. The critical concentration,  $c^*$ , at which polymer coils just begin to overlap in solution may be estimated as the mass concentration of polymer within a single coil, which is given by  $M/N_A V$  where  $M$  is the molar mass of the polymer,  $N_A$  is the Avogadro constant, and  $V$  is the volume occupied by the polymer coil. If the coil is considered to be a sphere,

$$V = (4\pi/3)(\alpha \langle r^2 \rangle^{1/2})^3 \approx 4\alpha^3 \langle r^2 \rangle^{3/2} \quad (4)$$

where  $\langle r^2 \rangle^{1/2}$  is the root-mean-square end-to-end distance and  $\alpha$  is the expansion parameter. Since  $\langle r^2 \rangle^{1/2} = (C_\infty n l^2)^{1/2}$ , where  $C_\infty$  is the characteristic ratio,  $n (=2M/M_0)$  is the number of bonds in the chain,  $M_0$  is the repeat unit molar mass, and  $l$  is the length of a chain bond, then

$$V \approx 11.3(\alpha l)^3 (C_\infty M/M_0)^{3/2} \quad (5)$$

and  $c^*$  is given by

$$c^* = \frac{0.88}{N_A M^{1/2}} \left( \frac{M_0}{\alpha^2 l^2 C_\infty} \right)^{3/2} \quad (6)$$

Using this equation with typical values for  $\alpha$  ( $\approx 1.25$ ),<sup>11</sup>  $l$  ( $\approx 0.154$  nm), and  $C_\infty$  ( $\approx 8$ ),<sup>11</sup> and with  $M_0 = 128$  g mol<sup>-1</sup>, the value of  $c^*$  can be estimated for any given value of  $M$ : for  $M = 10^3$  g mol<sup>-1</sup>,  $c^*$  is 41 g dL<sup>-1</sup>; for  $M$

$= 10^4 \text{ g mol}^{-1}$ ,  $c^*$  is  $13 \text{ g dL}^{-1}$ ; and for  $M = 10^5 \text{ g mol}^{-1}$ ,  $c^*$  is  $4 \text{ g dL}^{-1}$ . (Note that  $c^*$  values in  $\text{g dL}^{-1}$  may be compared with  $[M]_0$  values quoted as % (w/w) in Table 2.) Hence, for reactions run at  $[M]_0$  below 10% (w/v), for which  $M$  is expected to be low, the contribution from intermolecular chain transfer to polymer is expected to be small relative to that from the intramolecular reaction. This naturally leads to the conclusion that intramolecular chain transfer to polymer is the principal source of branches in polymers produced by dilute solution polymerization. Under these circumstances, the need to consider the concentration ratio  $[P]/[M]$  in terms of local concentrations in the vicinity of the propagating chain becomes paramount. For all dilute solution polymerizations, the local value of  $[P]$  is defined by the chain statistics and hence is approximately the same and, except for the effect of  $[M]$  on kinetic chain length, will also be independent of percent conversion. However, the monomer is uniformly distributed throughout the solution and so the local concentration of monomer in the vicinity of the propagating chain decreases (i.e., the local value of the ratio  $[P]/[M]$  increases) as  $[M]_0$  decreases and as conversion increases. Thus, under conditions where the overall polymer concentration is limited to values at which individual polymer coils do not overlap, the local value of  $[P]$  may be considered approximately constant throughout the polymerization and chain transfer to polymer proceeds exclusively via intramolecular reaction, which becomes more probable as  $[M]_0$  decreases. This explains why the polymerizations performed at *n*-butyl acrylate concentrations <10% (w/w) yield poly(*n*-butyl acrylate) with relatively high mole percent branches, even at low percent conversions, and also why, for these dilute solution polymerizations, the mole percent branches increases as  $[M]_0$  decreases. Under these conditions the increase in mole percent branches with conversion is a consequence solely of the reduction in  $[M]$  because the local  $[P]$  is approximately constant throughout the polymerizations.

In the initial stages of polymerizations performed at higher values of  $[M]_0$ , chain transfer to polymer is also dominated by the intramolecular reaction and polymer molecules with high mole percent branches may be formed, just as in the dilute solution polymerizations. As the conversion increases, however, the overall polymer repeat unit concentration soon exceeds  $c^*$ . Therefore, when such polymerizations are taken to moderate or high conversions, the polymer formed early in the polymerization constitutes only a small proportion of the total polymer formed and the intermolecular reaction makes the dominant contribution to the mole percent branches in the final polymer. Under these circumstances, for the reasons discussed above, the extent of chain transfer to polymer should be approximately independent of  $[M]_0$  and controlled by the percent conversion. For the data presented in Table 2, this is evident in the results for  $[M]_0 \geq 20\%$  (w/w).

For a given percent conversion of monomer to polymer, as  $[M]_0$  decreases there is a gradual change from intermolecular to intramolecular chain transfer to polymer as the principal process that determines the mole percent branches. Ultimately, when  $[M]_0$  is below  $c^*$  for the polymer being formed, only the intramolecular reaction is possible at any conversion. Comparison of the data for the 10BA polymerization with the data for the 30BA, 40BA, and 50BA polymerizations indicates

that the intramolecular reaction makes a substantial contribution to chain transfer to polymer in the 10BA polymerizations, even at higher conversions. This implies that for the polymerizations at  $[M]_0 \leq 10\%$  (w/w),  $[M]_0$  is below  $c^*$ , which is entirely reasonable given the estimates of  $c^*$  calculated earlier and the low molar masses expected for the polymers formed by dilute solution polymerization.

## Conclusions

In the more concentrated solution polymerizations, with  $[M]_0 > 10\%$  (w/w), the mole percent branches increases with percent conversion but is independent of  $[M]_0$  because, for all except the lowest percent conversions, the overall polymer repeat unit concentration is sufficient for overlap of individual polymer coils and intermolecular chain transfer to polymer dominates. However, for more dilute solutions, with  $[M]_0 \leq 10\%$  (w/w), the mole percent branches increases as  $[M]_0$  decreases and is higher than at equivalent conversions for the more concentrated solution polymerizations. These differences arise because the overall polymer repeat unit concentration is too low for overlap of individual polymer coils in the dilute solutions and intramolecular chain transfer to polymer dominates. Under these conditions, the local polymer repeat unit concentration within the isolated propagating chains must be considered. This is defined by the chain statistics and is approximately constant, whereas the monomer is distributed uniformly throughout the solution. Thus, for dilute solutions, as  $[M]_0$  decreases, the local value of  $[P]/[M]$  increases and the probability of chain transfer to polymer (and hence the mole percent branches) increases. The results, therefore, highlight the significance of intramolecular chain transfer to polymer and emphasize the need to consider local concentrations in the vicinity of the propagating chain.

Intermolecular chain transfer to polymer leads to the formation of long-chain branches, whereas the intramolecular reaction may result in branches of any length, depending on where along the polymer chain the backbiting H-abstraction occurs. Since both types of chain transfer to polymer give rise to changes in skeletal structure that can have significant consequences for polymer properties,<sup>1,2</sup> the levels of branching determined in the present study show that the effects of both reactions should be taken into account when preparing acrylate-based polymers. This clearly is of importance for commercial acrylic polymers but also has significance for more academic work. For example, the determination of rate coefficients for propagation and chain transfer to monomer using pulse laser polymerization (PLP)<sup>12–17</sup> requires accurate measurement of the molar mass distribution of the polymer formed, which often is done by gel permeation chromatography (GPC) using a differential refractometer as the detector with the assumption that the polymer chains are linear. The results presented herein show that such an assumption may not be satisfactory in the case of *n*-butyl acrylate, at least when the monomer is polymerized at normal temperatures. Propagation rate coefficients determined using the PLP–GPC combination have recently been reported for *n*-butyl acrylate,<sup>18,19</sup> 2-ethylhexyl acrylate,<sup>19</sup> and dodecyl acrylate.<sup>19</sup> Although in each case the measurements were carried out using GPC with a differential refractometer for detection, the PLP experiments were performed at low temperatures ( $-65 \rightarrow -7$

$^{\circ}\text{C}^{18}$  and  $5 \rightarrow 30\ ^{\circ}\text{C}^{19}$ ), which will have greatly reduced the extent of chain transfer to polymer and, therefore, minimized the effects of branching. Additionally, the use of low conversion bulk polymerization for most PLP studies further reduces the contribution from chain transfer to polymer. Nevertheless, it is only sensible that contributions from chain transfer to polymer should be considered when seeking to determine accurate rate coefficients for acrylate monomers by the PLP-GPC method.

The results presented in this paper are by no means complete. Besides similar studies of other acrylate monomers and studies of the effects of solvency conditions, investigations of changes in molar mass averages and molar mass distribution with  $[\text{M}]_0$  and percent conversion are necessary. The number-average molar mass should be unaffected by chain transfer to polymer for systems where cross-linking does not occur (because the number of polymer molecules is unaffected). However, whereas the molar mass distribution should be considerably broadened and the higher-order molar mass averages (e.g., weight-average and  $z$ -average) should increase for intermolecular chain transfer to polymer, these properties should be unaffected by the intramolecular reaction because it affects only the skeletal structure. An additional factor that requires consideration is that of cross-linking, since cross-links will be formed directly if propagating branches terminate by coupling. Although there was no evidence of gel fractions in the solution polymerizations reported here, we have observed substantial gel fractions in the polymers produced in preliminary studies of both bulk and emulsion homopolymerizations of *n*-butyl acrylate taken to high conversions. These observations also will be the subject of future work.

**Acknowledgment.** The authors thank ICI Acrylics for supporting this work. N.M.A. thanks the Government of Pakistan for a scholarship.

## References and Notes

- (1) Doak, K. 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, 1986; Vol. 6, p 386.
- (2) Small, P. A. *Adv. Polym. Sci.* **1977**, *18*, 1.
- (3) Scholte, T. G. In *Developments in Polymer Characterisation*; Dawkins, J. V., Ed.; Applied Science: London, 1983; Vol. 4, Chapter 1, p 1.
- (4) Lovell, P. A.; Shah, T. H.; Heatley, F. *Polym. Commun.* **1991**, *32*, 98.
- (5) Lovell, P. A.; Shah, T. H.; Heatley, F. *Polym. Mater. Sci. Eng.* **1991**, *64*, 278.
- (6) Lovell, P. A.; Shah, T. H.; Heatley, F. In *Polymer Latexes: Preparation, Characterisation and Applications*; Daniels, E. S., Sudol, E. D., El-Aasser, M. S., Eds.; ACS Symposium Series, Vol. 492; American Chemical Society: Washington, DC, 1992; Chapter 12, p 188.
- (7) Young, L. J. In *Polymer Handbook*, 2nd ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley-Interscience: New York, 1975; Section II, p 57.
- (8) Doddrell, D. M.; Pegg, D. T.; Bendall, M. R. *J. Magn. Reson.* **1982**, *48*, 323.
- (9) Breitmaier, E.; Voelter, W. *Carbon-13 NMR Spectroscopy*, 3rd ed.; VCH Publishers: Weinheim, Germany, 1987; p 315.
- (10) Young, R. J.; Lovell, P. A. *Introduction to Polymers*, 2nd ed.; Chapman and Hall: London, 1991.
- (11) Morawetz, H. *Macromolecules in Solution*, 2nd ed.; High Polymers, Vol. XXI; Mark, H., Marvel, C. S., Melville, H. W., Eds.; John Wiley & Sons: New York, 1975; Chapter III.
- (12) Olaj, O. F.; Bitai, I. *Angew. Makromol. Chem.* **1987**, *155*, 177.
- (13) Davis, T. P.; O'Driscoll, K. F.; Piton, M. C.; Winnik, M. A. *Macromolecules* **1989**, *22*, 2785.
- (14) Buback, M.; Gilbert, R. G.; Russell, G. T.; Hill, D. J. T.; Moad, G.; O'Driscoll, K. F.; Shen, J.; Winnik, M. A. *J. Polym. Sci., Polym. Chem.* **1992**, *30*, 851.
- (15) Buback, M.; Gilbert, R. G.; Hutchinson, R. A.; Klumperman, B.; Kuchta, F.-D.; Manders, B. G.; O'Driscoll, K. F.; Russell, G. T.; Schweer, J. *Macromol. Chem. Phys.* **1995**, *196*, 3267.
- (16) Gilbert, R. G. *Pure Appl. Chem.* **1996**, *68*, 1492.
- (17) Coote, M. L.; Zammitt, M. D.; Davis, T. P. *Trends Polym. Sci.* **1996**, *4*, 189.
- (18) Lyons, R. A.; Hutovic, J.; Piton, M. C.; Christie, D. I.; Clay, P. A.; Manders, B. G.; Kable, S. H.; Gilbert, R. G. *Macromolecules* **1996**, *29*, 1918.
- (19) Beuermann, S.; Paquet, D. A.; McMinin, J. H.; Hutchinson, R. A. *Macromolecules* **1996**, *29*, 4206.

MA971283R