Chain Transfer to Polymer in Free-Radical Solution Polymerization of 2-Ethylhexyl Acrylate Studied by NMR Spectroscopy

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ABSTRACT: The effects of initial monomer concentration, $[M]_o$, and percent conversion on the extent of chain transfer to polymer in the free-radical solution polymerization of 2-ethylhexyl acrylate (EHA) have been studied. The polymerizations of EHA were carried out in cyclohexane at 70 °C using 2,2′-azobis(2-cyanopropane) at 0.1 wt % relative to monomer as the initiator. ^{13}C NMR spectra of PEHA show that branching resulted from hydrogen abstraction at backbone C−H bonds, with no evidence for chain transfer in the side group. The branching levels were determined from unique resonances of branch-point carbons and ranged from 3 to 8 mol %, increasing as the conversion increased and as $[M]_o$ decreased. The trends for variation of branching level with $[M]_o$ and conversion are comparable to those for solution and bulk homopolymerizations of other acrylate monomers and vinyl acetate, although the branching levels for PEHA are much higher than those for poly(*n*-butyl acrylate) prepared under the same conditions.

Introduction

Chain transfer to polymer during free-radical polymerization can lead to highly branched polymers, with significant consequences for their rheological and mechanical properties. This fact is well-established in the case of low-density polyethylene produced by free-radical polymerization at high temperatures and pressures.[1−3]

As part of a research program into correlations of polymerization process conditions and properties for water-borne adhesives prepared by emulsion polymerization, we established by NMR spectroscopy that chain transfer to polymer occurs extensively in monomer-starved semi-continuous emulsion copolymerizations of *n*-butyl acrylate (BA) with methyl methacrylate and acrylic acid.[4,5] Subsequent studies showed that this observation is more general and that chain transfer to polymer is extensive in solution polymerizations of methyl,[6] ethyl,[6] and *n*-butyl[6,7] acrylates (MA, EA, and BA, respectively) and in bulk and emulsion polymerization of vinyl acetate.[8,9] As shown by ^{13}C NMR spectroscopy, chain transfer in the free-radical polymerization of acrylates involves abstraction of hydrogen atoms from backbone tertiary C−H bonds[4−7] (Scheme 1). The extent of chain transfer to polymer increases as conversion increases and, in the case of solution polymerization, as the initial monomer concentration decreases below a critical value.[7] The significance of these high levels of branching in BA-based polymers prompted further studies of acrylate free-radical polymerization. The closely related monomer 2-ethylhexyl acrylate (EHA) is in general use as a component in many water-borne adhesives. As well as backbone tertiary C−H bonds, EHA also contains a tertiary C−H bond in the side group that can be considered a potential site for chain transfer to polymer. This paper reports a study of chain transfer to polymer in the free-radical solution homopolymerization of EHA using high-resolution ^{13}C NMR spectroscopy to determine the site(s) of branching in the poly(2-ethylhexyl acrylate) (PEHA) formed and to quantify the extent of chain transfer for comparison with PBA prepared under similar conditions. Cyclohexane was chosen as the solvent because it is a solvent for both polymers and has a low transfer constant for chain transfer to solvent.[10]

Experimental Section

Purification of Reagents. EHA (Aldrich, 98%) and BA (Aldrich, >99%) were washed three times with dilute sodium hydroxide solution to remove the phenolic inhibitor and then thoroughly washed with distilled water before being dried over anhydrous calcium chloride. Each inhibitor-free monomer was purified further by distillation at reduced pressure under a nitrogen atmosphere. Cyclohexane (BDH) was distilled as described previously.[7] 2,2′-Azobis(2-cyanopropane) (AZBN) of reagent grade was purified by recrystallization from toluene and dried over silica gel under vacuum in a desiccator. Reagent grades of hydroquinone (HQ; Aldrich, >99%), toluene, and methanol were used as received.

Solution Polymerizations of EHA and BA. A series of solution homopolymerizations of EHA and BA was carried out using a procedure described previously.[7] Because of the need to generate sufficient polymer for NMR analysis, the scale of the polymerizations was increased as the dilution of the monomer increased. The exact quantities used for each of the polymerizations are given in Table 1. Unpublished work[11] on BA solution polymerization has shown that the AZBN concentration does not affect the extent of chain transfer to polymer, and so, for each reaction, AZBN was used at a concentration of 0.1 wt % relative to monomer. The experimental procedure was as follows. First, all of the monomer and all except a small amount (~20 g) of the cyclohexane were added to a reaction flask under a nitrogen atmosphere with stirring using a hot water bath as the heat source. After thermal equilibrium had been established at 70 °C, the AZBN was added as a solution in the remaining cyclohexane (~20 g). The polymerization was then run for the time required to achieve the target conversion.

For some polymerizations, samples were removed at intervals and immediately quenched by adding a small amount of

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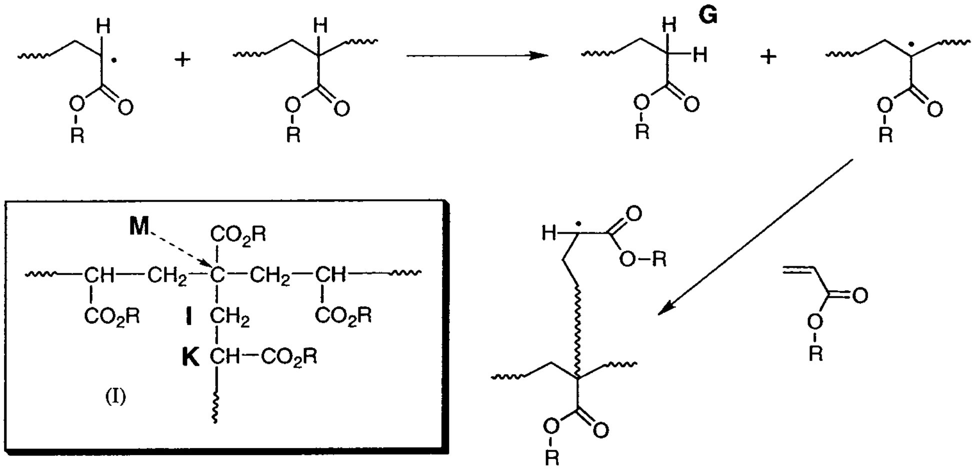
Scheme 1. Chain Transfer to Polymer by Abstraction of the Backbone Tertiary Hydrogen in the Free-Radical Polymerization of 2-Ethylhexyl Acrylate[a]



[a] R = 2-ethylhexyl.

Table 1. Formulations for Free-Radical Solution Homopolymerizations of 2-Ethylhexyl Acrylate (EHA) and *n*-Butyl Acrylate (BA)

reaction code	mass of reaction component (g)				monomer concentration	
	EHA	BA	AZBN	C_6H_6	% (w/w)	mol kg^{-1}
0.23EHA	43.17	–	0.043	956.93	4.3	0.23
0.78EHA	71.93	–	0.072	428.7	14.3	0.78
2.3EHA	43.14	–	0.043	56.86	43.0	2.3
0.78BA	–	100	0.100	899.9	10.0	0.78

HQ (~0.01 g of HQ per 10 g of sample) and placing the sample in an ice–water bath. For each sample, the percentage monomer conversion was determined by gas chromatography using a Perkin-Elmer AutoSystem instrument fitted with a 25-m DMS-coated capillary column and a flame ionization detector. The helium carrier gas pressure was 5.0 psi, which gave a flow rate of 35 cm^3 min^{-1}. A known quantity of *tert*-butyl acetate (Fisons, >98%), approximately equal to the mass of unreacted monomer expected in the sample, was added to the mixture as an internal standard before injection of 1 μL of the resulting solution onto the column. The components in the mixture were separated using the following heating program: a constant temperature of 50 °C was held for 5 min, followed by heating at 20 °C min^{-1} to 180 °C and then holding the temperature constant for 10 min. The injection port and detector were held at temperatures of 200 and 250 °C, respectively. Calibration was achieved using a series of standard solutions of EHA and *tert*-butyl acetate in cyclohexane with concentrations covering the range seen in the samples from the polymerizations. The mean masses of unreacted monomer determined from triplicate analyses of each sample were used to calculate the percentage conversions.

NMR Spectroscopy. Samples for NMR spectroscopy were isolated from the quenched polymerization samples through removal of solvent and residual monomer by rotary film evaporation at a maximum temperature of 55 °C under high vacuum. One sample from a polymerization at 14.3 wt % EHA was isolated by removal of volatiles using vacuum distillation at 50–60 °C and high vacuum provided by a two-stage rotary vacuum pump. This relatively high temperature was necessary because of the high boiling point of EHA (224 °C at 1 atm). Hence, for comparison, some PEHA samples were precipitated from the quenched polymerization mixtures by addition of the solution to a large excess of methanol, residual solvent then being removed by rotary film evaporation at a maximum temperature of 30 °C. Analysis of the branching levels for samples isolated by rotary film evaporation gave results identical within experimental error to those isolated by precipitation, indicating that further reaction did not occur as a consequence of the isolation procedure.

Polymer samples were dissolved in $CDCl_3$ to give a solution of concentration ~100 mg cm^{-3} for NMR spectroscopy. ^{13}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 at δ_c = 77.0 ppm. To maximize the signal-to-noise ratio in a given time, ^{13}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 (NOEs). In particular, the intensities of primary and quaternary carbons are underestimated relative to those of 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 and with a pulse interval of 10.5 s to allow for complete recovery of all carbons. Additionally, the distortionless enhancement by polarization transfer (DEPT) technique[12] was used to determine the multiplicity of the peaks, i.e., whether that carbon was primary, secondary, tertiary, or quaternary.

Results and Discussion

Figure 1 shows the part of the ^{13}C NMR spectrum of PEHA relevant to this work. The form of the spectrum is essentially identical to that of previously published spectra of poly(*n*-butyl acrylate) (PBA) produced by solution polymerization[7] and of spectra[6] of poly(methyl acrylate) (PMA) and poly(ethyl acrylate) (PEA) produced by emulsion polymerization. Table 2 summarizes the peak assignments for the complete spectrum as determined by comparison with the spectra of other acrylic polymers described previously,[4–7] the carbon multiplicity obtained using DEPT spectra, and a comparison of the experimental chemical shifts with those calculated using empirical substituent additivity parameters.[13] The carbon atom labeling scheme is shown in the diagram accompanying Table 2 and in Scheme 1. As for other poly(acrylates),[4–7] a clear quaternary carbon resonance arising from chain transfer by abstraction of a backbone tertiary C–H hydrogen (Scheme 1) was observed at ca. 48 ppm, confirming that chain transfer by this mechanism also occurs in PEHA. The existence of a backbone tertiary radical as well as a terminal secondary radical in the free-radical polymerization of cyclohexyl acrylate in benzene has recently been demonstrated using ESR.[14]

In PMA, PEA, and PBA, peaks from the backbone CH and CH_2 carbons adjacent to the branch were clearly

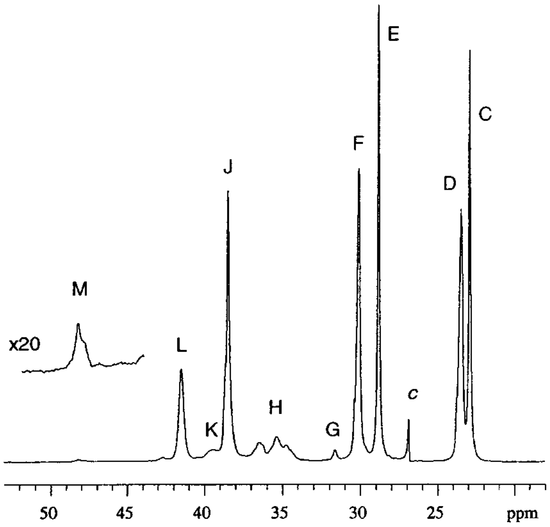
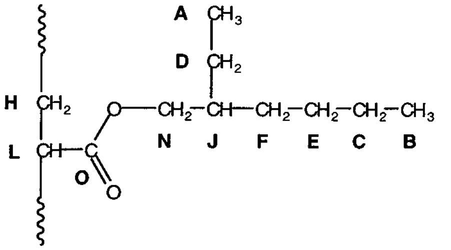


Figure 1. Representative ^{13}C NMR spectrum showing the 18−52 ppm region for PEHA prepared by free-radical solution polymerization (sample: 0.78EHA after 480 min). The NMR solvent was $CDCl_3$, and the spectrum was recorded using fast pulses. The peak labeled *c* is from residual cyclohexane.

Table 2. Assignment of the ^{13}C NMR Spectrum of Poly(2-ethylhexyl acrylate) in $CDCl_3$

peak[a]	chemical shift (ppm)
A	10.7
B	14.0
C	23.0
D	23.5
E	28.9
F	30.1
G	31.7
H	33.5−37.3
I	37.5−38.7
J	38.5
K	39.3
L	41.5
M	47.2−48.4
N	66.9
O	174.3

[a] The labels A−O are defined in Scheme 1 and in the structure given below.



visible in the range of 31−38 ppm, but in PEHA, these peaks are obscured by the peak from the CH carbon in the side chain at 38.5 ppm. The branch CH peak was partially visible as a low-intensity peak at 39.5 ppm, but the branch CH_2 peak was completely hidden in the normal spectrum. However the latter was revealed in the CH_2 subspectrum obtained from DEPT spectra, as shown in Figure 2. The origin of the small peak at ca. 43 ppm is not certain; however, it was shown by DEPT to be due to a CH carbon, which, from its intensity, might be the backbone CH closest to the chain end (i.e., $\underline{C}H(COOR)CH_2CH_2COOR$).

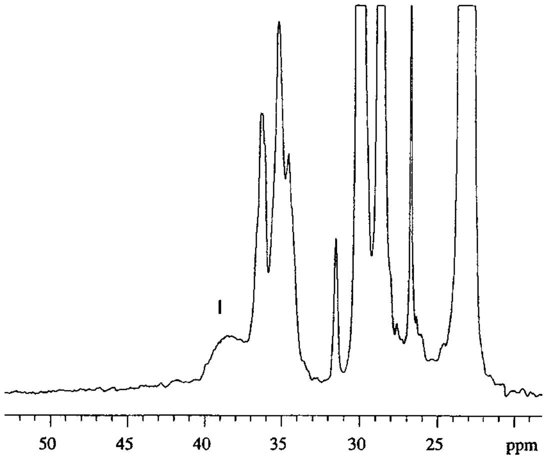
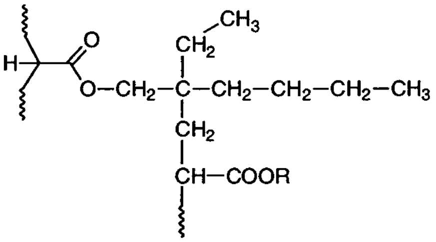


Figure 2. CH_2 subspectrum of the sample in Figure 1 obtained from DEPT spectra.

Noting the greater susceptibility to abstraction of tertiary compared to secondary or primary CH hydrogen atoms, there is the possibility in PEHA of chain transfer by abstraction of the tertiary hydrogen in the ester side group to give the branch structure shown below.



It would reasonably be expected that replacement of the side-group CH hydrogen atom by a PEHA chain would shift the substituted carbon atom by approximately the same amount as the shift of the backbone CH carbon, i.e., by ca. 6 ppm to low frequency to ca. 45 ppm. The spectrum in Figure 1 shows no evidence of such a peak, nor was it observed in any other spectrum. This leads to the conclusion that chain transfer occurred predominantly by abstraction of the backbone tertiary CH hydrogen atom. It is not unreasonable to expect the backbone tertiary C−H bond to be more susceptible to abstraction because, unlike abstraction at the side-group CH, the product radical has additional stabilization via resonance with the carbonyl group.

Each chain transfer to polymer event gives rise to one terminal saturated end group of the structure $-CH_2CH_2COOR$, as shown in Scheme 1. The CH_2 peaks at 31.2−31.9 ppm were assigned to the terminal $-CH_2\underline{C}H_2COOR$ carbon in this end group, as for PBA.[7] If chain transfer to polymer is extensive, as is the case for acrylates, the number of branches and the number of chain ends in the polymer produced will be essentially equal, i.e., the mole percent of CH_2 end groups provides another measure of the mole percent of branches.

The extent of chain transfer to polymer correlates directly with the mole percent of branches, data for which are given in Table 3 for the polymers from each of the solution polymerizations of EHA and BA. The data were calculated from the NMR spectra using the integrals for the branch C_q, branch CH, and end-group CH_2 resonances. As discussed previously,[6] for rapid-pulse spectra, the longer relaxation time of quaternary carbons causes the mole percent of branches data determined from the branch C_q resonance to be significantly lower than those determined from the branch CH

Table 3. Mole Percentage Branches in Poly(2-ethylhexyl acrylate) and Poly(*n*-butyl acrylate) Prepared by Free-Radical Solution Polymerization in Cyclohexane at 70 °C

reaction code[a]		$[M]_o$ [b]		reaction time (min)	% conversion	mol % of branches[c]			
		% (w/w)	mol kg^{-1}			C_q [d]	C_q(corr)[e]	br-$\underline{\mathrm{C}}$H[f]	end $\underline{\mathrm{C}}\mathrm{H}_2$ [g]
2.3EHA	precip	43.0	2.3	840	97	1.6 (3.2)	3.3	3.4 (3.4)	5.1 (5.1)
0.78EHA	rfe	14.3	0.78	50	8	1.9	3.9	3.4	5.1
	vacuum	14.3	0.78	100	26	2.3	4.7	4.6	5.1
	precip	14.3	0.78	480	77	2.7 (6.8)	5.6	5.5 (5.7)	7.0 (6.3)
0.23EHA	rfe	4.3	0.23	150	5	3.8	7.8	6.2	11.4
	rfe	4.3	0.23	480	23	4.6	9.5	7.7	12.1
	precip	4.3	0.23	480	23	5.0 (8.3)	10.3	7.8 (7.8)	11.6 (14.8)
0.78BA	rfe	10.0	0.78	120	3	1.1 (2.6)	–	2.5 (2.6)	–
	rfe	10.0	0.78	255	28	1.7	–	2.8	–
	precip	10.0	0.78	600	61	2.2 (4.3)	–	3.5 (3.6)	–

[a] Polymer isolation methods are denoted by: rfe, rotary film evaporation; vacuum, vacuum distillation; precip, methanol precipitation. [b] $[M]_0$ is the initial monomer concentration. [c] Determined from ^{13}C NMR spectra recorded under fast-pulse conditions with the exception of data given in parentheses, which were from slow-pulse spectra recorded using a 10.5-s pulse interval with NOE suppression; estimated uncertainty is ±10% of the mole percent of branches value. [d] Mole percent of branches determined from the ratio of the branch C_q integral to one-half of the total integral for backbone carbon atoms. [e] Mole percent of branches calculated from the fast-pulse C_q data using a correction factor (see Discussion). [f] Mole percent of branches determined for PEHA from the ratio of one-third of the branch CH integrals to one-half of the total integral for backbone carbon atoms and for PBA from the ratio of the sum of the branch CH and CH_2 integrals to the total integral for backbone carbon atoms. [g] Mole percent of branches determined from the ratio of the end-group CH_2 integral to one-half of the total integral for backbone carbon atoms.

and end-group CH_2 resonances. Under quantitative conditions, however, the percent of branches data determined from the branch C_q resonance should be more reliable than those from the branch CH and end-group CH_2 resonances because the C_q resonance does not overlap with other resonances and can be integrated with greatest accuracy. As can be seen from Table 3, for spectra run under quantitative conditions (data given in parentheses), the mole percent of branches data from the branch C_q and branch CH resonances data are in reasonably good agreement, whereas the end-group CH_2 resonance gives values that are higher because of the difficulty of separating this peak from the adjacent, much stronger, side-group CH_2 resonance (F). Thus, the end-group CH_2 resonance does not provide an accurate measure of the mole percent of branches. In contrast, the close agreement between the quantitative branch C_q and branch CH data, and between the branch CH data from fast-pulse and quantitative spectra, suggests that, under fast-pulse conditions, the branch CH resonance gives an accurate measure of the mole percent of branches. By multiplying the fast-pulse branch C_q values by the mean value (2.06) of the ratio of the quantitative and fast-pulse branch C_q data, all of the fast-pulse branch C_q data have been corrected for the effects of rapid pulsing and NOE; the corrected data are shown as C_q(corr) in Table 3 and, in support of the above inference, can be seen to be in good agreement with the fast-pulse branch CH data. Thus, although each set of data shows the same trends, the C_q(corr) and branch CH data are the most reliable and will be the focus of the discussion.

Solution polymerizations of BA were carried out to verify the consistency with our previous work and to facilitate direct comparison with the data from the EHA solution polymerizations. Hence, the mole percent of branches data calculated for the PBA samples also are included in Table 3. As for PEHA, and in accord with previous work,[4–7] the branch C_q data from quantitative spectra are approximately twice those obtained under fast-pulse conditions, whereas the branch CH plus branch CH_2 resonances give mole percent of branches data from fast-pulse and quantitative spectra that are identical within experimental error (±10% of the mole percent of branches value) and in good agreement with the branch C_q data from quantitative spectra. Furthermore, the PBA mole percent of branches data are identical, within experimental error, to those reported previously[6] for PBA prepared under the same conditions as in the present studies, showing that the results are reproducible and confirming that the EHA data reported here can be compared with the full set of data reported previously for solution polymerizations of BA.[6]

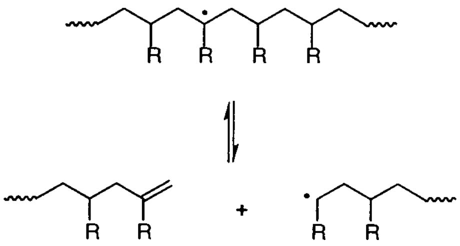
Three trends are evident from inspection of the data for the EHA and BA solution polymerizations: (i) the extent of chain transfer to polymer increases with conversion; (ii) for a given conversion in the EHA polymerizations, the extent of chain transfer to polymer increases as the initial monomer concentration, $[M]_o$, decreases; and (iii) the extent of chain transfer to PEHA is higher than that to PBA at the same $[M]_o$ and conversion.

The first two observations are in accord with, and reinforce, those reported previously[7] for solution free-radical polymerizations of BA. The first observation is also consistent with the reported increase in the proportion of backbone tertiary radical with conversion detected in the polymerization of cyclohexyl acrylate in benzene monitored by ESR.[14] The first observation can be explained in terms of the increase in the ratio of polymer repeat unit to monomer concentration, [P]/[M], as the conversion increases.[4–9] The second observation can be explained[7] in terms of the isolation of polymer molecules in dilute solutions, which causes the *local* polymer repeat unit concentration in the vicinity of the actively propagating chain end to be higher than the overall polymer repeat unit concentration. Because the monomer is distributed uniformly throughout the solution, the *local* value of [P]/[M] is higher when chains become isolated and, as a consequence, chain transfer to polymer is more extensive.

The third observation is new and the most significant of those from the studies presented here. Judging from previous comparative studies of chain transfer to polymer in emulsion homopolymerizations of BA, EA, and MA, which showed no measurable differences in the level of branching in the polymers produced, the 2-ethylhexyl group was only expected to have an influence through contributions from chain transfer in the side group. The contrary observation in the present work is reinforced by comparison of the EHA data from this work with the much wider range of previously published data[7] for branching in BA solution polymerizations that were carried out using conditions identical to those reported in this work. As stated earlier, there is the possibly for chain transfer at the tertiary C−H bond in the 2-ethylhexyl group, but there was no evidence for hydrogen abstraction at this site, and the much higher level of branching in PEHA compared to PBA is entirely due to a greater extent of chain transfer at the tertiary backbone C−H bond. The extent of chain transfer to polymer increases with increases in the ratio of the chain transfer and propagation rate coefficients, k_{trP}/k_P, and in [P]/[M]. Because the values of [P]/[M] are similar for the comparable EHA and BA polymerizations, changes in k_{trP}/k_P must account for the observed differences in the extent of chain transfer to polymer. Values of k_P for both BA[15,16] and EHA[16] have been measured by pulsed-laser polymerization (performed at lower temperatures to minimize contributions from chain transfer); the experiments with EHA were less extensive but were sufficient to show that EHA and BA have very similar values of k_P, with EHA having a slightly higher value than BA at any given temperature. Because differences in k_P cannot be the reason for the differences in the extent of chain transfer to polymer, attention must focus on k_{trP}. One factor that could have an effect on k_{trP} is the size of the 2-ethylhexyl group compared to the *n*-butyl group. This would not be expected to greatly affect the activation energy for chain transfer, but it might lead to changes in the accessibility of the backbone tertiary C−H bond, causing a change in the Arrhenius preexponential factor. For this to be a realistic explanation of the observations, the 2-ethylhexyl group would have to cause the preexponential factor to increase, which implies that the backbone tertiary C−H bond must be more accessible in PEHA than in the other acrylate polymers. PEHA has a lower density (0.903 g cm^{-3})[17] than PBA (1.07 ± 0.06 g cm^{-3}),[18] indicating a greater free volume in PEHA, which could result in a higher Arrhenius preexponential factor. The effects of interactions with the cyclohexane solvent molecules will also be important. Clearly, more substantial evidence is needed to support the hypothesis that differences in Arrhenius preexponential factors can explain the differences between chain transfer to polymer in polymerizations of EHA and the other acrylates. One possible approach would be to model the local conformations of the series of acrylate polymers, as this should afford greater insight into the differences in accessibility of the tertiary backbone C−H bonds. Such studies, however, were not possible within the time constraints of the present work.

Chiefari et al.[19] have recently described the synthesis of acrylate macromonomers by a mechanism involving β-scission of the radical resulting from chain transfer to the backbone tertiary CH carbon (Scheme 2). This scission produces a terminal unsaturated group. However, no unsaturated carbons were observed in the spectra of the polymers prepared in this work. If this scission does occur, the resulting unsaturated group subsequently polymerizes either (i) by recombination with the chain-end radical resulting from the scission, followed by growth of a branch chain (Scheme 1), or (ii) by reaction with another propagating chain. Process i simply delays the growth of the branch chain, whereas process ii results in the same branch point structure as shown in Scheme 1 and is, therefore, experimentally indistinguishable from the Scheme 1 reaction sequence.

Scheme 2. Formation of Macromonomers by β-Scission Following Chain Transfer to Polymer in Solution Polymerizations of Acrylates[19] [a]



[a] R = CO_2R', e.g., R′ = 2-ethylhexyl or butyl.

Chiefari et al.[19] also concluded that, at lower monomer concentrations, chain transfer to polymer occurs predominantly by “backbiting” via a six-membered cyclic intermediate resulting in a four-carbon branch chain of two monomer units, rather than by a remote intramolecular mechanism or an intermolecular mechanism leading to long branches of macromolecular dimensions. Chemical shift prediction software[20] indicates that there are small differences between the chemical shifts of the characteristic branch carbons for four-carbon branches and long branches, as well as between the chemical shifts of the terminal CH_2R carbon at the end of a four-carbon branch and that at the end of a long chain. However, compared to the absolute accuracy of the predictions, the differences are too small to be used as a reliable indicator of the branch length.

In conclusion, therefore, the results show quite clearly that chain transfer to polymer in free-radical polymerizations of EHA proceeds via hydrogen abstraction at the backbone tertiary C−H bond, with no measurable contribution from chain transfer in the 2-ethylhexyl side group, and that chain transfer to polymer is more extensive than for equivalent free-radical polymerizations of BA. A possible interpretation of the latter observation is that the larger side group causes an increase in the Arrhenius preexponential factor for chain transfer at the backbone tertiary C−H bond, although this tentative inference is yet to be substantiated.

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