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## Chain Transfer to Monomer and Polymer in the Radical Polymerization of Vinyl Neo-decanoate

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**Abstract:** Molecular weight distributions of poly(vinyl *neo*-decanoate) produced by the bulk polymerization of the monomer to low conversions were investigated to obtain values of the rate constants for the chain transfer to monomer ( $C_M$ ). The value of  $C_M$  of  $7.5 (\pm 0.6) \times 10^{-4}$  was obtained from a logarithmic plot of the number distribution at 5, 25, and 50 °C, which suggests that the activation energy for chain transfer is on the order of 20-25 kJ mol<sup>-1</sup>. These plots were linear between the number and weight-average degrees of polymerization, but not over the whole molecular weight range for which a significant signal was observed in the gel permeation chromatography (GPC) trace. Modeling suggests that the deviations observed at high molecular weights can be explained by branching of the chains through chain transfer to the polymer, with a branching density as low as  $10^{-5}$ , without affecting the slope at low values of the number of monomer unit,  $N$ . This deviation from the expected distribution of linear chains was used to estimate the branching densities at low conversion.

**Keywords:** chain transfer to monomer, chain transfer to polymer, vinyl neo-decanoate, size exclusion chromatography, free-radical polymerisation.

### Introduction

An important reaction in free-radical polymerization of vinyl monomers is chain transfer of radical activity to monomer rather than addition to the propagating chain. The ratio of the rates of these two reactions determines the maximum number average degree of polymerization that can be

obtained for linear chains. This degree of polymerization is equal to the inverse of the chain transfer constant  $C_M$ , which is the ratio of the second-order-rate coefficient for chain transfer to monomer ( $k_{tr,M}$ ) to that for propagation ( $k_p$ ).

The only literature data available for  $k_{tr,M}$  or  $C_M$  for vinyl *neo*-decanoate are values of  $C_M$  for a series of vinyl esters including vinyl decanoate ( $C_M = 4.5 \times 10^3$ ).<sup>1</sup> The data is not reliable, as the average degrees of polymerizations were not extrapolated to zero initiator concentration or rate of polymerization, as is the case with the commonly used Mayo method. Furthermore, the average degree of polymerization was calculated assuming the same relationship between viscosity and average degree of polymerization as for vinyl

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acetate. The authors reported experiments to validate this but it is highly unlikely considering the difference in Mark-Houwink constants in every solvent that have been reported.<sup>2</sup> A value of  $C_M = 4.5 \times 10^3$  for vinyl decanoate was reported by the authors. No mention was made as to whether the linear or a branched ester of vinyl decanoate was used, despite some indication that the difference in values between the isomers was considerable.

In the Mayo method average molecular weights are usually measured at different rates of polymerization, due to differing initiator concentrations. The data is then extrapolated to a zero rate of polymerization, where the radical concentration is too low for bi-molecular termination of growth to be significant. Clay and Gilbert suggested use of the chain length distribution (CLD) method, making use of the whole molecular weight distribution rather than average molecular weights to determine  $C_M$ .<sup>3</sup> As with the Mayo method, polymer formed at low conversion and low initiator concentrations could be used to find  $C_M$  under conditions such that transfer to polymer or adventitious chain transfer agent are negligible. Clay and Gilbert demonstrated that the instantaneous number distribution  $P(N)$  under these conditions would be given by

$$\lim_{N \rightarrow \infty, [I] \rightarrow 0} P(N) \propto \exp(-C_M N) \quad (1)$$

The cumulative distribution  $\bar{P}(N)$  will be equal to  $P(N)$  as  $C_M$  is independent of conversion, and the slope of a logarithmic plot of  $P(N)$  as a function of  $N$  equal to  $C_M$ . As termination was not negligible at low  $N$  for most experimental conditions they recommended that the slope at high  $N$ , where a linear plot could be obtained, should be used to calculate  $C_M$ . G. Moad and C. Moad later established that there is a large error in  $P(N)$  at high  $N$  due to the very low weight fraction of chains,<sup>4</sup> and suggested that the slope between the number average molecular weight ( $M_n$ ) and the weight average molecular weight ( $M_w$ ) would give a more reliable estimate. The plot in this range was less susceptible to errors in base line correction of the original molecular weight distribution (MWD) obtained by size-exclusion chromatography. Davis, Heuts and Russell have reviewed the Mayo and CLD methods and demonstrated that they are essentially identical, with equally reliable results obtained using the CLD method and the slope determined at the peak molecular weight value ( $M_p$ ) and the Mayo method based on  $M_w/2$ .<sup>5</sup>

The applicability of the CLD method for measuring  $C_M$  for polymerization of vinyl *neo*-decanoate is investigated in this paper. The effects of chain transfer to polymer on the CLD are also discussed and a model for the effect of chain transfer on chain length distributions is developed.

## Experimental

Phenolic inhibitors were removed from a commercial

sample of vinyl *neo*-decanoate (Shell Chemicals Australia) by passing the monomer through a short column of basic alumina ( $Al_2O_3$ ). The monomer was then partially polymerized at 100°C under an atmosphere of nitrogen with 2, 2'-azo-bis-isobutyronitrile (AIBN, Sigma Aldrich, recrystallized from ethanol) added to a final concentration of 10 mg L<sup>-1</sup> to initiate polymerization. Polymerization was stopped by opening the mixture to atmospheric oxygen when solution viscosity had noticeably increased (9% conversion). A portion of the remaining monomer was then distilled under reduced pressure, discarding the first 5% of distillate.

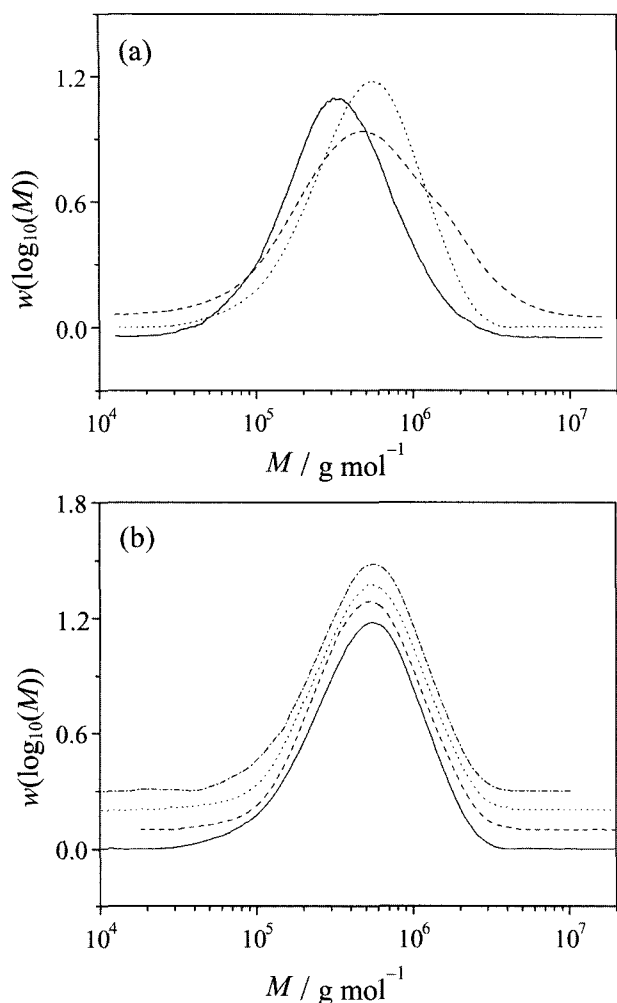
Irgacure 651 (2,2-Dimethoxy-2-phenylacetophenone, Mercury Enterprises, used as supplied) was dissolved in the purified monomer and placed in silica-glass cells of about 5 mm diameter to a depth of 3-5 mm. Oxygen was purged from the mixture by evacuating gas from the cells and refilling the cells with ultra-pure argon gas (BOC Gases) three times. The cells were then placed in a brass cell holder that was kept at a constant temperature by re-circulating water through it from a water bath. A mercury vapour UV light source was used to illuminate the cells, with a glass filter placed between the cell and source to absorb light of wavelengths below 308 nm. This both reduced the intensity of light at frequencies which the initiator adsorbs most intensely and reduced the possibility of polymer decomposition. A 1% solution of *tert*-dibutyl phenol in THF was used to inhibit polymerization after illumination. Illumination times were from 10 min to 4 hr at 5, 25 and 50°C. Samples that were of low enough viscosity to flow after polymerization were kept for analysis.

Polymer was precipitated from solution by addition to an excess of acetone and conversion measured gravimetrically. There should not be a large difference in solubility over the molecular weight range of interest (greater than 10<sup>4</sup> g mol<sup>-1</sup>) so the recovery procedure is not expected to affect the results. Dried polymer was then dissolved in THF (4 mg mL<sup>-1</sup>) for determination of MWD using SEC for the determination of  $k_p$ .<sup>6</sup> Polystyrene standards from Waters and Polymer Laboratories were used for calibration of the instrument (3 × 10<sup>3</sup>–10<sup>7</sup> g mol<sup>-1</sup>). The Mark-Houwink-Sakurada constants used were  $K = 11.0 \times 10^{-5}$  dL g<sup>-1</sup> and  $a = 0.725$  for poly(styrene),<sup>7</sup> and  $K = 7.26 \times 10^{-5}$  dL g<sup>-1</sup> and  $a = 0.716$  for poly(vinyl *neo*-decanoate).<sup>6</sup>

## Results

SEC gives MWD as the cumulative-weight distribution as a function of  $\log_{10}M$ , or the derivative which is given the lower-case symbol  $w(\log_{10}M)$ . Three examples of MWD of polymer produced at low conversions are shown in Figure 1(a).

This figure shows typical plots at varying monomer conversion ( $x$ ) for polymerization of vinyl *neo*-decanoate at 50°C. The low  $M$  polymer produced up to 1% conversion



**Figure 1.** MWD of polymer at (a) (—) 1%, (...) 8.8%, and (---) 50% conversion, offset by 0.05, 0 and 0.05 respectively. (b) (—) 1.8%, (---) 2.9%, (...) 6.2%, and (-·-) 8.8% conversion,  $[I]=1.5 \text{ mmol dm}^{-3}$ , offset by 0 to 0.3.  $T=50^\circ\text{C}$ .

shows a greater slope which may be attributable to chain transfer to an impurity remaining in the monomer. As MWD of polymer for conversions in the range  $2\% < x < 16\%$  (Figure 1(b)) are close to identical, this impurity appears to be completely consumed early in the reaction. MWD of polymer up to intermediate conversions show a broadening of the distribution with little change in  $M_n$ . Experimental conditions and average molecular weights are shown in Table I for all experiments.

Variations in  $M_n$  with initiator concentration and conversion can be seen, but no consistent pattern is clear.  $M_n$  values can be highly dependent on the starting point of the integration and on the baseline, especially for broad distributions, and can be skewed by relatively small amounts of low molecular weight polymer generated by chain transfer to adventitious species. The chain length distribution  $P(M)$  was calculated from the SEC MWD according to the well-known relation-

**Table I.** Average Molecular Weights,  $\Lambda$ , and  $\lambda$  for Low Conversion Experiments Carried out at  $50^\circ\text{C}$

$[I] / \text{mM}$	$x (\%)$	$\bar{M}_n / 10^3 \text{ g mol}^{-1}$	$\bar{M}_w / 10^3 \text{ g mol}^{-1}$	$\Lambda / 10^{-4}$	$\lambda / 10^{-5}$
1.5	1.8	330	650	7.1	$6.1 \pm 0.8$
1.5	2.9	326	655	6.9	$6.3 \pm 0.7$
1.5	6.2	365	670	7.4	$7.6 \pm 0.5$
1.5	7.4	452	753	7.3	$6.7 \pm 0.7$
1.5	8.8	327	713	7.2	$6.7 \pm 0.8$
2	1	240	480	12.9	-
2	1	230	460	10.9	-
2	6	290	570	8.7	$7.2 \pm 0.9$
2	6	300	760	8.3	$7.0 \pm 1.0$
2	12	320	660	7.9	$8.6 \pm 0.5$
2	12	300	780	8.1	$9.8 \pm 1.0$
2	16	310	1800	6.9	$11.9 \pm 1.1$
5	6.4	360	690	6.5	$8.0 \pm 0.6$
5	11	340	930	6.7	$6.7 \pm 0.7$
10	2.4	307	590	7.9	$7.1 \pm 0.5$
10	3.5	350	603	7.8	$6.4 \pm 0.8$
10	9	300	980	7.2	$6.8 \pm 1.0$

ship of Shortt<sup>8</sup>

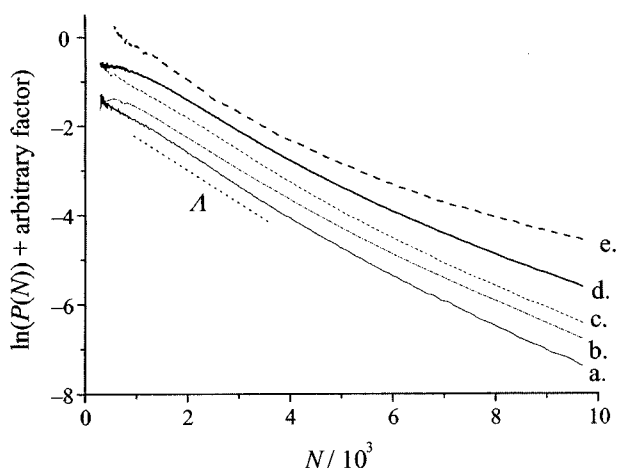
$$\bar{P}(N)M_0 = \bar{P}(M) \frac{w(\log_{10}M)}{M^2} \log_{10}e \quad (2)$$

Distributions were then divided by an arbitrary factor to simplify comparison of the slopes of the logarithmic plots. Typical plots of  $\ln \bar{P}(N)$  as a function of  $N$  are shown in Figure 2 for all initiator concentrations.

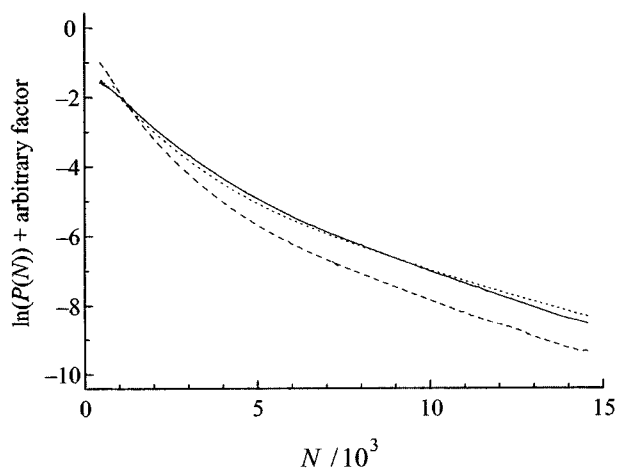
All plots where conversion was between 2 and 15% have a linear region between  $N=1,000$  and  $N=3,000$ , within the range between  $M_n$  and  $M_w$  (Table I), and a negative gradient ( $\Lambda$ ) of  $(7.5 \pm 0.6) \times 10^{-4}$ .

There is less than a 10% variation in the values of slopes in this region even with a greater than five-fold increase in initiator concentration, suggesting that little bimolecular termination is occurring for chains in this range (see Table I). It can be seen in Figure 2 that there is a decrease in the magnitude of the gradient at larger  $N$  in all plots. This deviation from the expected linear plot is small for experiments up to 2-7% conversion but increases at higher conversion. Similar results have been obtained for butyl acrylate<sup>9</sup> and butyl methacrylate.<sup>10</sup>

Logarithmic plots of  $\bar{P}(N)$  from polymer formed up to intermediate conversions at  $50^\circ\text{C}$  and  $5^\circ\text{C}$  are shown in Figure 3.



**Figure 2.** Examples of  $\ln P(N)$  plots. (a) (—) 5 mM initiator and 6.4% conversion; (b) (---) 10 mM, 2.4%; (c) (-·-) 1.5 mM, 2.9%; (d) (—) 2 mM, 12%; (e) (···) 5 mM, 11%. (A) (···) shows  $7.7 \times 10^{-4}$  in range between the number and weight average DP for lower conversions.  $T=50^\circ\text{C}$ .



**Figure 3.** Examples of  $\ln P(N)$  plots for intermediate conversions. (—) and (···) 35%, (---) 50% conversion.  $T=50^\circ\text{C}$ .

The corresponding MWD are broader than those of polymer formed up to lower conversions and this appears as a larger negative gradient in the  $\ln \bar{P}(N)$  plot at low  $N$  and shallower slope at higher. This is most likely due to chain transfer to polymer being a significant mechanism for cessation of chain growth at these higher weight fractions of polymer, with the radical produced continuing to propagate to higher  $N$ .

## Discussion

The much lower molecular weights of chains for  $x=1\%$  in Figure 1 suggest that chain transfer to an impurity was significant for  $x < 1\%$ . This impurity appears to have been con-

sumed rapidly so that chain transfer to it is not significant at higher conversions. A small amount of oxygen in the headspace of the cell is one possibility. Diffusion into the mixture could limit the rate of reaction of oxygen with propagating radicals so that polymerization is retarded rather than inhibited, as has been observed in emulsion polymerization of styrene.<sup>11</sup> This is a minor reaction which has little effect at higher conversions.

The upwards curvature at high  $N$  could be explicable in two ways:

(1) Chain transfer to a second impurity which is consumed over time could lead to a decrease in the magnitude of the slopes of instantaneous distributions with conversion, which would be expected to be more prominent at the high  $N$  side of the cumulative distribution.

(2) Another explanation for the deviation at high  $N$  may be the effect of chain transfer to polymer. While chain transfer to polymer may not have been a significant mechanism for cessation of chain growth, it could nevertheless lead to a significant increase in the number of larger chains, especially at higher conversions. A logarithmic plot of the distribution would show little change in the relative number of short chains, but a significant change in the relative number of long chains so that non-linearity is only observed at larger  $N$ .

Modeling of the expected distributions, taking into consideration these two possibilities, was carried out to see if results for either model could fit the observed distributions.

If the curvature is due to chain transfer to polymer, then the values of  $A$  for  $x$  between 2 and 15% will correspond to  $C_M$ . In this work, a value of  $7.5 \pm 0.6 \times 10^{-4}$  was found for  $C_M$  at  $50^\circ\text{C}$ , while De Bruyn *et al.* found  $C_M=1.5 \times 10^{-4}$  for vinyl acetate using the  $\ln \bar{P}(N)$  method.<sup>12</sup> Busselli *et al.* found that  $C_M$  was  $4.55 \times 10^{-3}$  at  $50^\circ\text{C}$ ,<sup>1</sup> three times greater than  $C_M=1.5 \times 10^{-3}$  determined for vinyl acetate in the same work, and six times greater than the  $C_M$  measured in this work. Other values for chain transfer to vinyl acetate reported vary over a range from  $2.5 \times 10^{-5}$  to  $2 \times 10^{-3}$  at  $50^\circ\text{C}$ .<sup>2</sup> This large disparity in the results is probably due either to the presence of impurities, errors in determination of average molecular weights, or very polydisperse chain length distributions reducing the accuracy of the Mayo method. Taking  $k_p=5,200 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at  $50^\circ\text{C}$ <sup>6</sup> gives  $k_{tr,M}=3.9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for vinyl *neo*-decanoate. This is four times greater than  $k_{tr,M}=1.0 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  calculated for vinyl acetate using  $k_p=6,800 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ <sup>7</sup> and  $C_M=1.5 \times 10^{-4}$ .

The measured  $C_M$  is specific for the commercial mixture of the many possible isomers of the monomer used in these experiments. Variations with isomer composition were not investigated as the composition of commercial examples is thought to be similar, as is indicated by the glass transition temperatures of the homopolymer that are consistently between  $-10$  and  $0^\circ\text{C}$ .<sup>13-15</sup> There will almost certainly be a significant difference in  $C_M$  values for mixtures containing more of the highly branched isomers. Experiments in the

gas phase have shown that the activation energy can be expected to be about 9 kJ mol<sup>-1</sup> less for abstraction of a 2° hydrogen atom from an alkyl chain by a primary alkyl radical than abstraction of a 1° hydrogen atom, while any 3° hydrogen atoms would be even more labile.<sup>16</sup> The activation energy for chain transfer to monomer in polymerization of vinyl acetate was found to be 38.8 kJ mol<sup>-1</sup>,<sup>17</sup> considerably more than  $E_a = 22$  kJ mol<sup>-1</sup> for propagation of vinyl *neo*-decanoate.<sup>6</sup> If the environment from which protons are abstracted is similar in vinyl *neo*-decanoate and vinyl acetate, such a large difference in activation energies should lead to large differences in values of  $C_M$  with temperature. Instead, approximately the same  $C_M$  was found at 5 °C ( $7.5 \times 10^{-4}$ ) and 25 °C ( $8.0 \times 10^{-4}$ ), suggesting an  $E_a$  for chain transfer to monomer of the same magnitude as the  $E_a$  for propagation, approximately 20-25 kJ mol<sup>-1</sup>.<sup>16</sup> Other activation energies for chain transfer to monomer previously calculated are 46.1 kJ mol<sup>-1</sup> for methyl methacrylate (abstraction from 1° H),<sup>18</sup> 32.6 kJ mol<sup>-1</sup> for butyl acrylate<sup>9</sup> (abstraction from 2° H)<sup>9</sup> and 33 kJ mol<sup>-1</sup> for butyl methacrylate (probably abstraction from 2° H).<sup>10</sup> The lower activation energy for  $k_{r,M}$  for vinyl *neo*-decanoate determined relative to vinyl acetate is consistent with abstraction primarily from 2° and 3° positions in the vinyl *neo*-decanoate side chain, as the activation energy for abstraction of a 2° H can be 9 kJ mol<sup>-1</sup> less than a 1° H.<sup>16</sup>

**Chain Transfer to Impurities.** The monomer used in these experiments was purified by polymerization in bulk to 9% conversion before distillation, then purged with an inert gas. This was not sufficient for complete removal of impurities that would retard polymerization, as is evident in Figure 2 where  $x = 1\%$ . Whether impurities behaving as chain transfer agents had an effect on the  $\bar{P}(N)$  at higher conversions is not clear, but the rate coefficient for such a reaction would have to be comparable to  $k_p$  for it not to be almost completely consumed before 1% of the monomer is consumed. If equal to  $k_p$  then the rate of fractional conversion would be equal to that of the monomer and there would be no change in the distribution with conversion, while a lower coefficient would lead to an increase in the amount of impurity relative to the amount of monomer.

It is relatively simple to calculate  $\bar{P}(N)$  when chain transfer to an impurity Z is the dominant mechanism for cessation of chain growth. Negating other terms except transfer to Z from the expression for the instantaneous distribution derived by Clay *et al.* for bulk polymerization<sup>19</sup> gives

$$\frac{\partial \bar{P}(N, t)}{\partial t} = 2k_z[Z][R \cdot] \exp\left(-\frac{k_z[Z]}{k_p[M]}N\right) \quad (3)$$

Where degradative chain transfer to Z occurs and radical concentration is sufficiently low that bimolecular termination involving propagating radicals  $R \cdot$  is negligible, each initiator fragment eventually consumes a molecule of Z, and

$$\frac{d[Z]}{dt} \approx -2k_d[I] \quad (4)$$

Where  $k_d$  is the rate constant for dissociation of the initiator. As values of  $k_d$  for a photoinitiator will be dependent on the wavelength and intensity of the light used to illuminate the cell, the degree to which it is absorbed by solvent, the quantum efficiency of the photo-dissociation reaction, and the geometry of the cell, the notation  $k_d(h\nu)$  will be used. This empirical quantity should remain constant across all experimental conditions used in this work but it is not possible to estimate it *a priori* for Irgacure 651. If the radical concentration is sufficiently low that loss of propagating radicals is primarily by chain transfer to Z, then

$$[R \cdot] \approx \frac{2k_d(h\nu)[I]}{k_z[Z]} \quad (5)$$

If the initial concentration of Z is given the symbol  $[Z]_0$ , then eqs. (3) through (5) can be combined to obtain the instantaneous distribution

$$\frac{\partial \bar{P}(N, t)}{\partial t} \approx 2k_d(h\nu)[I] \exp\left(-\frac{k_z[Z]_0 - 2k_d(h\nu)[I]t}{k_p[M]}N\right) \quad (6)$$

The pre-exponential term in eq. (6) is the rate of formation of new chains. From the difference in the slopes at low and high  $N$  at 5% conversion, it can be estimated that  $k_z \sim 10k_p$  is required to obtain a similar distribution. However, eq. (6) will hold for any value where cessation of chain growth through retardation occurs on a much faster time scale than dissociation of initiator ( $2k_d(h\nu)[I] \ll 7 \times 10^{-4}k_p[M]$ ).

Where each radical produced consumes an impurity,  $t_z$  can be defined as

$$t_z \approx \frac{(1-z)[Z]_0}{2k_d(h\nu)[I]} \quad (7)$$

where  $t_z$  is the time taken to reduce  $[Z]$  to  $(1-z)[Z]_0$ , and  $z$  is the fractional conversion of Z. When  $k_z > 10k_p$ , then  $x < 0.05$  for  $z < 0.5$ , and the approximation that  $[M] \approx [M]_0$  can be made, so that integration of eq. (6) from  $t = 0$  to  $t_z$  gives

$$\bar{P}(N, t) = \frac{[M]_0([M]_0 + C_z([Z]_0 - 2k_d(h\nu)[I]t)N)}{C_z^2 N^2} \frac{\exp\left(\frac{C_z}{[M]_0}(2k_d(h\nu)[I]t_z - [Z]_0)N\right)}{C_z^2 N^2} - \frac{[M]_0([M]_0 + C_z[Z]_0 N) \exp\left(\frac{C_z[Z]_0}{[M]_0}N\right)}{C_z^2 N^2} \quad (8)$$

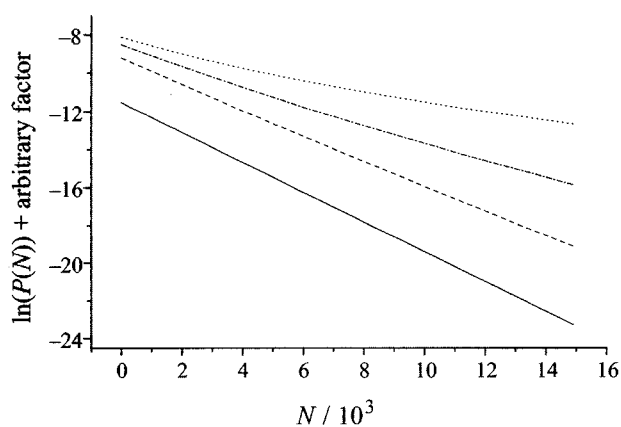
where  $C_z = k_z k_p^{-1}$ .

Predicted values of  $\bar{P}(N)$  (divided by an arbitrary constant in order to offset the data for clarity) are shown as logarithmic plots in Figure 4 for  $z=0, 0.25, 0.5$  and  $0.75$ , where  $2k_d[I]$  is estimated as  $10^{-6} \text{ s}^{-1}$  on the basis of the typical rates seen for vinyl neo-decanoate polymerization.

There is a large change in the slope at low  $N$  as  $z$  increases in the  $\ln \bar{P}(N)$  plot, as well as at high  $N$ , unlike that observed experimentally (Figure 2). A similar plot was obtained for models where  $C_M$  was not negligible and chain transfer to the impurity did not retard polymerization. Thus it is unlikely that the curvature seen at high  $N$  is due to chain transfer to an impurity.

**Long-chain Branching.** The second explanation for the deviation from the expected linear plot is that chain transfer to monomer was the dominant mechanism for cessation of chain growth, but effects of long chain branching became significant at high  $N$  with an increase in conversion. In modeling number distributions for polymerizations of styrene and methyl methacrylate, Clay and Gilbert<sup>3</sup> assumed that the frequency of intermolecular chain transfer to polymer is negligible. While it is probably correct to assume that only a very small fraction of chains will branch at low conversions, the resulting side chains will have a similar mass distribution as the primary chains. Thus while the fraction of chains that branch at a particular molecular weight might be insignificant, especially at low  $N$ , the number of chains corresponding to the length of the branched chains could increase by a significant factor relative to the number of linear chains of that length where the number of linear chains is low, *i.e.* high  $N$ . Chain transfer to polymer will be most significant where the propagating radical is most reactive and vinyl group most stable, and so needs to be considered for vinyl esters.

Chain transfer to polymer must be much less frequent than transfer to monomer for the latter to be the dominant mechanism and equation 1 to be approximately correct at low  $N$ . That is, the fraction of monomer units of polymer chains that are tri-functional branch points ( $\lambda$ ) must be



**Figure 4.** Effect of chain transfer agent on  $\ln \bar{P}(N)$ . (—)  $z=0$ , (---)  $0.25$ , (-·-)  $0.5$ , (···)  $0.75$ .

much less than  $C_M$ .

A number of methods have been used to calculate chain length distributions (CLD) of polymer chains where long chain branching is significant. Methods for solving time-dependent population equations of living and dead polymer chains using the method of moments were reported by a number of workers,<sup>20-23</sup> and a Monte-Carlo approach was shown to be useful for cases where rate coefficients vary with conversion and  $k_t$  is chain length dependent.<sup>24-26</sup> Both methods are complicated by the need to take into consideration more than a single mechanism for cessation of chain growth and the changing concentration of reactants. Two simpler methods that give an approximate CLD for cases where chain transfer to monomer is the dominant mechanism for cessation of chain growth, and low conversions, are presented here in order to determine whether the deviation from equation 1 at high  $N$  can be attributed to branching when  $\lambda < C_M$ .

A number of approximations can be made to calculate an estimated CLD for comparison with experimental data in the limit of low conversion and initiator concentration. These are:

(1) That chain transfer to monomer is the only significant mechanism of cessation of chain growth (so that the original CLD of linear chains and that of new branches are approximately given by eq. (1)).

(2). While intramolecular chain transfer to polymer probably occurs, this will only shift the position of the radical center to a different section of the same chain and so will not be considered. The term 'branching density' ( $\lambda$ ) will be used in this work for the fraction of monomer units that are tri-functional branch points resulting from intermolecular chain transfer only.

(3) Each monomer unit of a linear polymer chain has an equal chance of branching.

(4) Only branching of the monomer units of the original linear chain (primary chain) is considered in order to simplify the derivation of an expression for  $\bar{P}(N)$ . Chain transfer to monomer units of branches will be negligible for cases where  $\lambda^{-1}$  is less than the maximum  $N$  being considered so this simplification should not lead to a large error.

The probability,  $P_{branch}$ , that the total number of monomer units in  $i$  branches is equal to  $N' = N_1 + N_2 + \dots + N_i$ , where  $N_i$  is the length of the  $i^{\text{th}}$  branch, is the probability of each branch propagating to a particular fraction of the total length given by eq. (1), multiplied by the number of combinations.

$$P_{branch}(N', i) = \frac{N'!}{(N-i+1)!} C_M \exp(-C_M N_1) \cdot C_M \exp(-C_M N_2) \dots C_M \exp(-C_M N_i)$$

$$P_{branch}(N', i) = \frac{N'!}{(N-i+1)!} C_M^i \exp(-C_M N') \quad (9)$$

If each monomer unit has an equal probability of being a tri-functional branch point, the probability of a chain of length  $N-N'$  having  $i$  branches ( $b_{Ni}$ ) is related to the branching frequency  $\lambda$  according to

$$b_{Nj} = \frac{((N-N')\lambda)^i}{i!} \exp(-\lambda(N-N')) \quad (10)$$

The probability of a chain of length  $N$  not branching is

$$\left(1 - \sum_{i=1} b_{Nj}\right) = \exp(-\lambda N) \quad (11)$$

Combining the probability of primary chains having grown to a length of  $N-N'$  from eq. (1), the probability of the combined lengths of  $i$  branches being  $N'$  given by eq. (9), and the fraction of primary chains that have  $i$  branches given by eq. (10) gives the fraction of chains of length  $N$  with a primary chain of length  $N-N'$  and  $i$  branches,  $P'(N, N', i)$ .

$$P'(N, N', i) = C_M^{i+1} \frac{N'!}{(N'-i-1)!} \exp(C_M N) \frac{((N-N')\lambda)^i}{i!} \exp(-\lambda(N-N')) \quad (12)$$

Combining all possible ways of obtaining a chain of length  $N$  gives

$$P(N) = C_M \exp(-C_M N) \left( \exp(-\lambda N) + \sum_{i=1}^{N-1} \int_0^{N-i} C_M^i \frac{(N')!}{(N'-i-1)!} \frac{((N-N')\lambda)^i}{i!} \exp(-\lambda(N-N')) dN' \right) \quad (13)$$

There is only a small probability of more than 2 branches per chain when  $\lambda \ll N^1$ , so a large error will not be introduced if only  $i=1$  or 2 are considered.

$$P(N) = C_M \exp(-C_M N) \left[ \exp(-\lambda N) + \int_0^N C_M \lambda (N-N') (1 + 0.5 C_M \lambda (N-N')) \exp(-\lambda(N-N')) dN' \right] \\ = C_M \exp(-C_M N) (\exp(-\lambda N) + \alpha_1 C_M \lambda^{-1} + \alpha_2 C_M^2 \lambda^{-2}) \quad (14)$$

where  $\alpha_1 = (1 - (1 + \lambda N) \exp(-\lambda N))$  and  $\alpha_2 = ((\lambda N - 3) + (3 + 2\lambda N + 0.5\lambda^2 N^2) \exp(-\lambda N))$ .

Figure 5 shows a plot of the expected  $\ln \bar{P}(N)$  for  $N < 10^4$  and  $10^{-5} < \lambda < 8 \times 10^{-5}$  given by eq. (14).

In all cases, the deviation from the linear relation is visible when  $N > 2C_M^{-1}$  (5200) even where  $\lambda = 10^{-5}$ , which is less than 1 branch point for every 10 chains of  $N = 10^4$ .

**Simulations.** A number of simplifications were made in

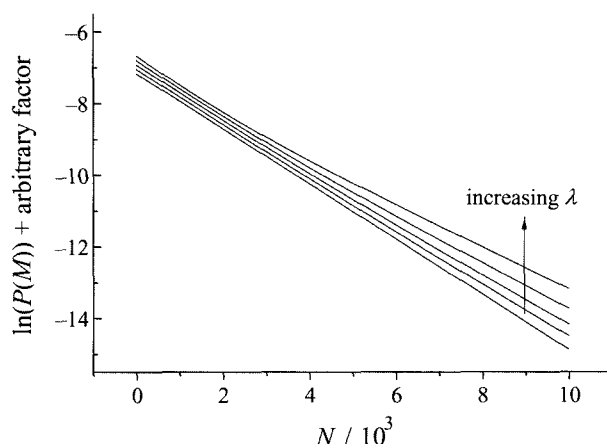


Figure 5. CLD predicted by eq. (17) where  $C_M = 7.5 \times 10^{-4}$ ,  $\lambda = 0, 1, 2, 4, 8 \times 10^{-5}$ .

order to derive a simple expression for the expected number distribution. In order to examine the accuracy of eq. (14), a computer simulation of the effects of randomly joining chains starting with the expected distribution for linear chains was performed. In the simulation, two chains were chosen for each branch step. The probability of the branch being of a certain length  $N'$  was proportional to the number distribution, while the probability of the primary chain being of length  $N''$  was proportional to the weight distribution  $w(N)$ . This is equivalent to chain growth having originated from a branch point rather than an initiator fragment for a small fraction of chains. The distribution was calculated as follows:

(1) Start with the expected distribution for A linear chains given by eq. (1). The absolute distribution of monomer units,  $Aw(N)$ , is given by:

$$Aw(N) = AC_M N \exp(-C_M N) \quad (15)$$

where A is chosen so that the number of chains at the highest  $N$  used in the calculation is  $> 100$ . Only integer values of  $N$ , where  $1 \leq N \leq 10^4$ , and  $P(N)$  were used in this calculation.

(2) For every branching event two chains were chosen. The change in the number distribution was assumed to be negligible for the purposes of choosing  $N'$  so that

$$N' = \frac{-\ln\left(\frac{a}{C_M}\right)}{C_M} \quad (16)$$

where  $a$  is a random number between 0 and 1, and  $N'$  was rounded up to the nearest integer.

(3) Two more random numbers were chosen,  $c$  and  $N''$ , where  $0 < c < 1$  and  $0 < N'' < 10^4$ . Values of  $N''$  were rounded up to the nearest integer. If  $c > w(N'')$ , step 3 was repeated. If  $c \leq w(N'')$ , then the calculation proceeded to step 4.

(4) A single chain was subtracted from the number of chains at  $N=N'$  and 1 added to the number of chains at  $N=N'+N''$  so that after the  $j^{\text{th}}$  branching event

$$w(N')_j = w(N')_{j-1} - N' \quad (17)$$

$$w(N'+N'')_j = w(N'+N'')_{j-1} = \frac{N'+N''}{A''} \quad (18)$$

The process was repeated for  $j$  branching events so that  $\lambda$  is given by

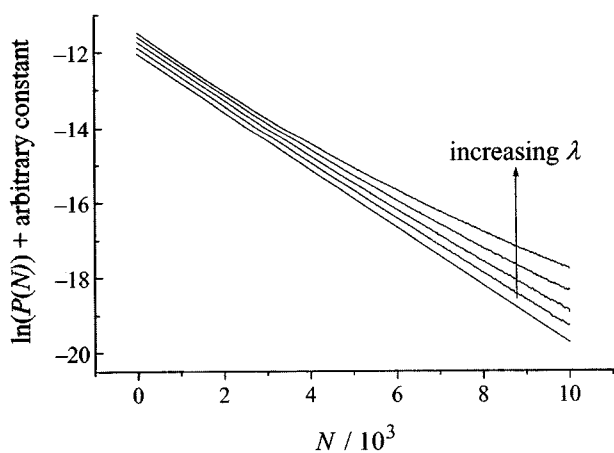
$$\lambda = \frac{j}{\int_1^{\infty} A C_M N \exp(-C_M N) dN' + j C_M^2} \quad (19)$$

A QBasic program to calculate the CLD using this method was written and distributions calculated for  $C_M = 7.5 \times 10^{-4}$  and  $10^{-5} \leq \lambda \leq 8 \times 10^{-4}$ . The results of these calculations are shown in Figure 6 as a plot of  $\ln P(N)$  as a function of  $N$ .

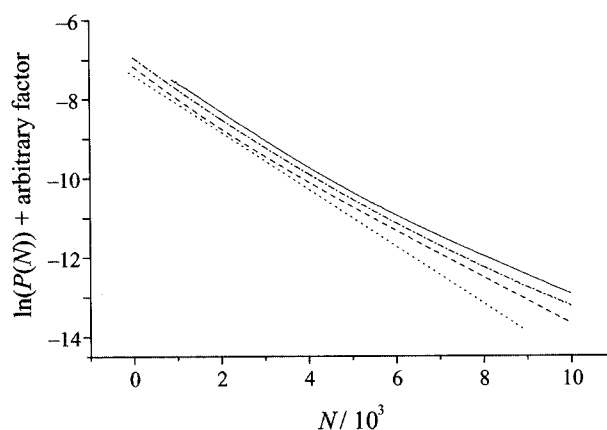
The results are qualitatively the same as those predicted by eq. (14). Where  $N < 2C_M^{-1}$  the slope is  $-C_M$  but above this value there is a significant decrease in the magnitude of the slope, showing that a small amount of branching can have a large effect at large  $N$ . The deviation is slightly more pronounced at high  $N$  for  $\lambda = 8 \times 10^{-5}$  than predicted by eq. (14).

A comparison of the measured  $\ln \bar{P}(N)$  the predicted values from eq. (14) and the simulation where  $\lambda = 8 \times 10^{-5}$  is shown in Figure 7.

The distribution predicted by the simulation and eq. (14) is qualitatively very close to the distribution found by SEC. However, this assumes that such a small amount of branching will have essentially no effect on the hydrodynamic volume and hence the MWD observed by SEC. The validity of this assumption is examined below under the heading 'Intrinsic



**Figure 6.** CLD predicted by randomly joining chains where  $C_M = 7.5 \times 10^4$ ,  $\lambda = 0, 1, 2, 4, 8 \times 10^5$ .



**Figure 7.** Comparison of predicted CLD for  $\lambda = 8 \times 10^{-5}$  and CLD at  $x = 8.8\%$ . (···) linear chains, (---) eq. (17), (-·-) simulation, (·) experimental.

viscosity of branched chains'.

As  $\lambda \ll 7.5 \times 10^{-4}$ , cessation of chain growth due to transfer to polymer could be insignificant and the branching density still large enough to cause the deviation observed.

**Branching Densities.** Eq. (13) may be simplified in order to estimate branching densities from the difference between expected distributions for linear chains and the measured distributions, by making further approximations appropriate for low values of  $\lambda$ . The probability of there being more than one branch on a chain of length  $N-N'$  is  $1 - \exp[-\lambda(N-N')]$ , so the distribution of a single branch may be substituted for the distribution of combined lengths of multiple branches. Eq. (14) is then reduced to

$$P(N) \approx C_M \exp(-\lambda N) \left( \exp(-\lambda N) + C_M \int_1^{N-1} 1 - \exp(-\lambda(N-N')) dN' \right) \quad (20)$$

For large  $N$  eq. (20) is integrated from 0 to  $N$ , and where  $\lambda(N-N') \ll 1$  the approximation that  $\exp(-\lambda(N-N')) \approx 1 - \lambda(N-N')$  can be used to obtain the approximation

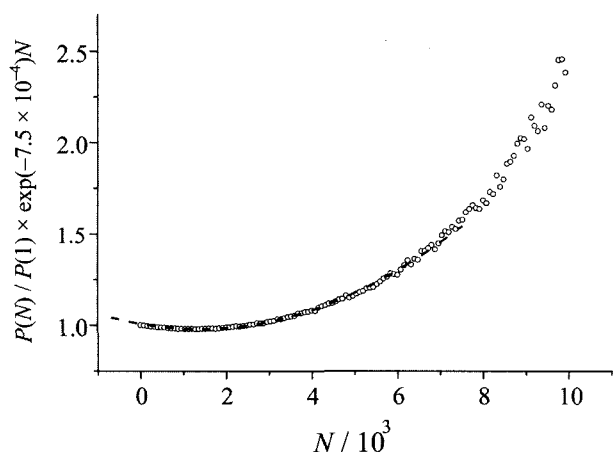
$$1 - \lambda N + 0.5 C_M \lambda N^2 \approx \frac{P(N)}{C_M \exp(-C_M N)} \quad (21)$$

Where distributions are not normalized, the pre-exponential term  $C_M$  can be replaced with  $P(1)$  or  $P(N)$  at some suitably low value of  $N$ .

Second order polynomials  $(1 - yN + zN^2)$  were fitted to the ratio of the simulated distributions to the expected distribution of linear chains for a number of values of  $\lambda$ . An example of a typical plot is shown in Figure 8.

Values of the parameters obtained are shown in Table II. Reasonably accurate values of  $\lambda$  were obtained for the simulated distributions from both  $y$  and  $z$  where  $\lambda \leq 4 \times 10^{-5}$ , and poorer estimates were obtained for larger  $\lambda$ .





**Figure 8.** Polynomial fit to ratio of  $P(N)$  from a simulation where  $\lambda = 4 \times 10^{-5}$ , to that for linear chains.

**Table II. Values of Parameters for Second-order Polynomial Fit to Simulated Data**

$\lambda / 10^{-5}$	$y / 10^{-5}$	$2z / (7.7 \times 10^{-9})$
8	6.9	6.55
4	4.12	3.91
2	1.90	2.02
1	0.88	0.99

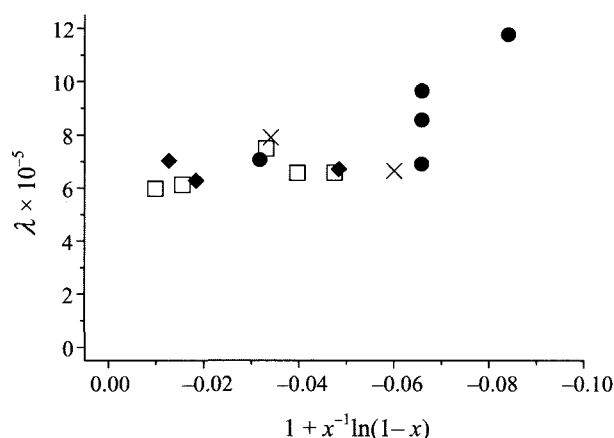
One difference between the simulated data and experimental data is the lack of reliable values for  $N < 500$  in the latter. This will undoubtedly lead to a greater error in estimates of  $\lambda$ . Estimates of  $\lambda$  for all experiments carried out to low conversions using this method are shown in Table I. From differential rate equations for intermolecular chain transfer and conversion of monomer, the following expression for the branching density as a function of  $k_{tr,p}$  and fractional conversion  $x$ , can be derived:<sup>27</sup>

$$\lambda = -C_p \left( 1 + \frac{1}{x} \ln(1-x) \right) \quad (22)$$

Values of  $\lambda$  are plotted as a function of  $1 + x^{-1} \ln(1-x)$  in Figure 9.

The data is not consistent with eq. (22), as a line of best fit does not pass through the intercept and the branching frequency appears to be independent of  $x$  at low conversions. It should be noted that eq. (22) is only valid for intermolecular transfer to polymer. A contribution of intramolecular transfer to polymer, especially at low conversion is not unlikely and might explain differences between this equation and experiment.<sup>28</sup>

Other possible reasons for this result are insufficient accuracy in determining number distributions, or weight fraction of polymer in the immediate environment of the propagating radical is greater than the overall conversion in



**Figure 9.** Values of  $\lambda$  determined from  $P(N)$  as a function of conversion. ( $\square$ )  $[I] = 1.5$ , ( $\bullet$ ) 2, ( $\times$ ) 5, ( $\blacklozenge$ ) 10 mM.  $T = 50^\circ\text{C}$ .

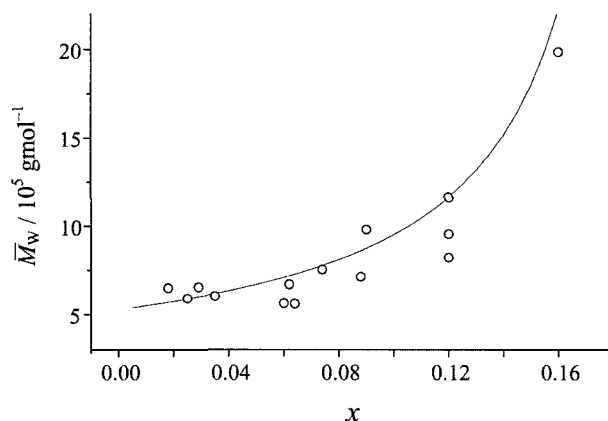
the unstirred reaction. If it is the latter, then the localized weight fraction of polymer would have been about 0.05 through the early stages of the reactions.

Neglecting terms for termination,  $C_p$  may also be obtained from a plot of  $\bar{M}_w$  as a function of conversion using the relation.<sup>29</sup>

$$\bar{M}_w = \frac{2M_0}{C_M - \frac{C_p x}{1-x}} \quad (23)$$

A plot of  $\bar{M}_w$  against fractional conversion is shown in Figure 10, along with the expected trend given by eq. (23) where  $C_M = 7.5 \times 10^{-4}$  and  $C_p = 3 \times 10^{-3}$ . This value of  $C_p$  is 20 times that found for polymerization of vinyl acetate at  $60^\circ$  ( $1.5 \times 10^{-4}$ )<sup>29</sup> but only four times greater than the  $C_M$  for vinyl *neo*-decanoate. This was possibly an overestimate of  $C_p$  as the lowest weight fractions of polymer were not experimentally accessible.

**Intrinsic Viscosity of Branched Chains.** To attribute any



**Figure 10.** Weight-average molecular weights as a function of conversion.  $T = 50^\circ\text{C}$ .

deviations from the expected number distribution to branching, it would be desirable to be able to show that the polymer chains were branched and to estimate  $\lambda$  from an independent experiment.  $^{13}\text{C}$  nuclear magnetic resonance spectroscopy has been used to investigate branching in poly(vinyl acetate)<sup>30</sup> and poly(butyl acrylate).<sup>28</sup> Unfortunately, this method can not be used to determine the amount of branching occurring in samples of poly(vinyl *neo*-decanoate) as the alkyl moieties of the monomer contain multiple peaks overlapping with the expected positions of novel 2° and 3° carbons arising from chain branching. Another method is to use the change in MWD after hydrolysis of acid groups, as has been used to determine the extent of branching in poly(vinyl acetate),<sup>31</sup> but this method is not suitable for a similar measure of the branching density in poly(vinyl *neo*-decanoate) as the decanoate groups hinder complete hydrolysis of the esters.

Differences in intrinsic viscosities of branched and linear polymers can be used as a measure of the amount of branching, although this does not give the branching density directly. A plot of  $\log_{10} [\eta]$  against  $\log_{10} M$  would not be linear if there is a significant difference in intrinsic viscosity of a branched chain ( $[\eta]_b$ ) and that of a linear chain ( $[\eta]_l$ ). As  $[\eta]_b < [\eta]_l$ , the gradient will decrease with increasing  $M$ . The Mark-Houwink plot for poly(vinyl *neo*-decanoate) (Figure 11), is linear up to  $10^6 \text{ g mol}^{-1}$  with a slight increase in the slope at larger  $M$ , most likely due to uncertainties in measuring the low concentration of polymer at these molecular weights.

The branching density therefore is not large enough for a significant deviation in the plot to be measurable using this method. Whether a value of the ratio of the average radii of gyration of branched polymers to linear polymers ( $g$ ) required for the deviation seen in  $\ln \bar{P}(N)$  plots is not large enough to show deviations in Mark-Houwink-Sakurada plots can be determined from a theoretical estimate of  $g$ . For monodisperse polymers with statistically distributed branch numbers, where the average number of branches per chain of length  $N$  is  $\lambda N$ ,  $g$  is given by<sup>32</sup>

$$g = \left( \left( 1 + \frac{\lambda N}{7} \right)^{1/2} + \frac{3\lambda N}{9\pi} \right)^{-1/2} \quad (24)$$

The relationship between  $g$  and the ratio of intrinsic viscosities is

$$g^\varepsilon = \frac{[\eta]_b}{[\eta]_l} \quad (25)$$

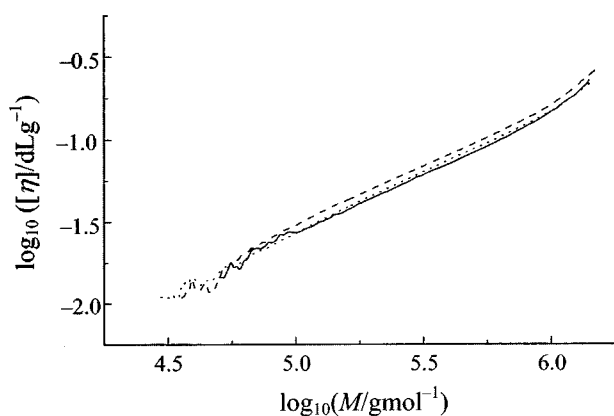
where values of  $\varepsilon$  are determined experimentally for each combination of polymer and solvent. No values for poly(vinyl *neo*-decanoate) have been reported for the reasons already discussed, but  $\varepsilon$  is typically between 0.5 and 1 for other polymers so it is expected that  $\varepsilon$  for poly(vinyl *neo*-decanoate) will be within this range.

Using eq. (24) for the ratio of radii of gyration of branched and linear chains of equal molecular weight, it was found that  $g = 0.91$  for chains where  $\lambda = 10^{-4}$  and  $N = 10^4$  ( $M = 2 \times 10^6 \text{ g mol}^{-1}$ ). For  $\varepsilon = 1$ , the difference in  $\log_{10} [\eta]$  of linear and branched chains is 0.04, about 3% of the total change in  $\log_{10} [\eta]$  over the molecular weight range for which  $[\eta]$  was measured. If  $\varepsilon = 0.5$ , then the difference will only be 1.5% of the total change. Distortions towards apparent lower MW of such a magnitude will be trivial in comparison to the observed enhancement of high MW chains.

## Conclusions

MWD from bulk polymerization of vinyl *neo*-decanoate at low conversion and initiator concentrations were obtained by SEC. The corresponding plots of  $\ln \bar{P}(N)$  as a function of  $N$  were linear between the number and weight average degrees of polymerization, for conversions greater than 1.9% and less than 16%. The rate constant for chain transfer to monomer ( $C_M$ ) did not vary with initiator concentration or conversions and was found to be  $\sim 7.5 \times 10^{-4}$  at 5, 25 and 50°.

Predicted CLD of polymer where chain transfer to an impurity was dominant did not accurately predict the observed linearity at low  $N$  of the  $\ln \bar{P}(N)$  plot for conversions above 1%. Models where chain transfer to monomer was the dominant mechanism for cessation of chain growth, but chain transfer to polymer could generate additional chains of high  $N$ , were consistent with the experimentally observed  $\ln \bar{P}(N)$  plots. The branching density required to cause an observable deviation from a linear plot was low enough for chain transfer to polymer not to be a significant mechanism for cessation of chain growth (*i.e.*,  $\lambda < C_M$ ). This suggests that the slope at low  $N$  did correspond to  $C_M = (7.5 \pm 0.6) \times 10^{-4}$ , five times greater than the most reliable estimate for vinyl acetate at 50°. When combined with literature reports on the propagation rate coefficient of vinyl *neo*-decanoate, this value suggests an  $E_a$  for chain transfer of approximately 20–25  $\text{kJ mol}^{-1}$ , consistent with H abstraction



**Figure 11.** Intrinsic viscosity of poly(vinyl *neo*-decanoate) solutions in THF.<sup>6</sup>

primarily from methine carbons.

A method of measuring branching densities using the difference between measured distributions and that expected where branching is negligible was identified. This method gave good approximate estimates for simulated data and reasonable estimates for experimental data. The branching densities estimated for vinyl *neo*-decanoate, did not follow the expected relationship with conversion, possibly due to the weight fraction of polymer in the immediate environment of the polymerizing chain being greater than overall conversion, as would be expected below the critical overlap concentration. Further application of the treatment developed here to other systems where long-chain branching may be significant is planned to test the model.

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