Computer Optimization of Molecular Mass Distribution in Low Molecular Mass Acrylic Polymers

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A computer model describing the polymerization of acrylic monomers has been developed. The model simulates high conversion polymerization of acrylic monomers in the presence of two types of thiol type chain transfer agents to give low molecular mass acrylates. The model is based on integration of the Mayo equation during the course of the polymerization and keeps into account the relative reagents concentration variations, the changes of the kinetic constant values during polymerization, and the presence of chain transfer agents. The results forecasted by the model have been verified in practice by carrying on a series of polymerization reactions in the conditions above described. A good agreement with the model prediction was obtained.

Keywords: Computer modeling; radical polymerization; acrylates; chain transfer agent

INTRODUCTION

The control of average molecular masses and their distribution has been an important and widely investigated issue in polymer chemistry for many years [1 – 4].

Recently, computer techniques for ready calculation based on mathematical polymerization models [5 – 8], as well as modern analytical techniques such as Gel Permeation Chromatography [9 – 10], a technique that allows the determination of a polymer molecular mass distribution, have promoted new important developments.

A very interesting approach is based on the investigation of the dependence of average molecular mass values, and their distribution, on kinetic parameters, as well as on the improved determination of the kinetic parameters values through studies of molecular masses values distribution obtained by G. P. C. [5].

Therefore, the purpose of this work is to develop a computer polymerization model based on classic polymerization theory that can determine how different reaction parameters may influence the molecular mass distribution during the synthesis of low molecular mass acrylic polymers. These polymers are prepared by batch solution polymerization in the presence of chain transfer agents, without further reactants addition while the polymerization is running.

Indeed, this issue is of relevance for the industrial production of low molecular weight acrylic resins used in several applications, including adhesives and high solids paints.

As the industrial approach involves, for obvious reasons, high monomer conversion, the aim of this work is to test if the well known and relatively simple Mayo polymerization model, known to be accurate at low conversion, can also be reliably used, with some modification, to predict the final polymer molecular mass distribution when the polymerization is carried out to high conversion in the presence of chain transfer agents.

BACKGROUND

The Mayo Eq. [11, 12]] can be used to forecast the degree of polymerization achieved during radical polymerization:

$$
1/\overline{DP} = 1/\overline{DP}_0 + (k_{tr}[T]/k_p[M]) + (kt_{rm}/k_p) + (k_{trs}[S]/k_p[M]) \\
+ (k_{tri}[I]/k_p[M]) + k_{trp}[P]/k_p[M])
\tag{1}
$$

where:

$$
\overline{DP}_0 = (k_p/2k_{td} + k_{tc})(2k_t/2fk_d)^{1/2} ([M]/[I]^{1/2})
\tag{2}
$$

In the above equations, $\overline{DP}_0$ is the average degree of polymerization in absence of chain transfer reactions, $\overline{DP}$ the average degree of

polymerization in the presence of chain transfer reactions to the chain transfer agent, the monomer, the solvent, the initiator, and the polymer, respectively. The kinetic constant k_d represent the thermal decomposition rate of the polymerization initiator, k_p the polymer propagation constant, k_{tr}'s the chain transfer constant to the various chemicals present in the reaction medium (monomer, solvent, initiator, and polymer), k_{td} the termination by disproportioning constant, and k_{tc} termination by coupling of two propagating chains. The term f represent the efficiency factor of the initiator.

As reported in the literature, Eq. (1) is valid only at low conversion (< 10%); at higher conversion, it should be integrated to keep into account the variation of reagents concentration, the decrease in the total volume of reaction, and the changes in the kinetic constant values (especially k_t) that occur during the process of polymerization.

The values of the rate constant are often quoted in the literature [13], but those are usually accurate only at low conversion. As the conversion increase so does the viscosity of the solution and the rate constant may become polymer concentration dependent, as a consequence of the limited diffusion of macromolecules in the reaction medium [8].

A way to obtain a narrow molecular weight distribution within the constraints of batch polymerization and without multiple additions of reactants, may be to carefully select optimal initial concentration of reactants. These should be selected so as to allow the instantaneous DP to vary as little as possible during most of the polymerization process.

To reduce the need for costly and time consuming experimental runs, a computer model based on accepted polymerization models may be employed that calculates the instantaneous $\overline{DP}$ and keeps track on how this varies during the proceeding of the polymerization. Therefore, a computer model based on the integration of the Mayo Eq. (1) with time, and that keeps into account the varying reactants concentrations and kinetic constants with conversion may be employed for this task. Furthermore, by fitting theoretical results generated by the model with experimental data collected from some polymerization runs, may allow to optimize both the initial values of the kinetic constants and their time dependence.

THEORETICAL POLYMERIZATION MODEL

Based on well established theories on radical polymerization [3, 4, 7, 8, 15], a theoretical polymerization model was developed. The task of the model is to calculate conversion to polymer, and both instantaneous and cumulative $\overline{DP}$'s as a function of time, while keeping into account instantaneous reactant concentrations and the variation of the kinetic constants values.

The model used is based on what reported in the literature for similar systems and it has been modified to take into account not only the presence of relatively large amounts of chain transfer agents, but also the limited viscosity increase and volume shrinkage due to the formation of low average molecular mass polymers. At a second stage, the model was further modified to fit experimental results.

According to Eqs. (1) and (2), and neglecting the contributions of k_{trm}, k_{trs}, k_{tri}, and k_{trp}, because of the large initial concentrations of chain transfer agent, the inverse of the instantaneous average $\overline{DP}$ may be written as follows, with T indicating the chain transfer agent:

$$1/\overline{DP}_{inst} = \frac{(1+\delta)\,(2fk_d[I])^{1/2}(2k_t)^{1/2}}{2(1+\delta)\,k_p[M]} + \frac{k_{tr}[T]}{k_p[M]} \qquad (3)$$

where $\delta = k_{t,d}/k_{t,c}$: as the influence of the two termination constants on $\overline{DP}$ is negligible as under the conditions of this work, practically all polymerizing chains terminate by transfer, Eq. (3) may be simplified as follows:

$$1/\overline{DP}_{inst} = \frac{(2fk_dk_t)^{1/2}([I])^{1/2} + k_{tr}[T]}{k_p[M]} \qquad (4)$$

According to literature [14], instantaneous reagents concentration may be calculated by integration of the following differential equation system:

$$-1/V\,dN_i/dt = k_d\,N_i/V \qquad (5)$$

$$dCm = \frac{k_p\,(2fk_d[n_i]^0)^{1/2}}{k_t\,V_{(in)}} * \frac{(1-Cm)\,\exp\,(-k_d\,t/2)}{(1+E\,Cm)^{1/2}} \qquad (6)$$

$$dCt/dt = \frac{k_{tr}(2fk_d\{N_i\}^0)^{1/2}}{k_t V_{(in)}} * \frac{(1 - Cm)\exp(-k_d t/2)}{(1 - E cm)^{1/2}} \quad (7)$$

which describe the variation of initiator, monomer and chain transfer agent concentration as they are used up and the solution volume shrinks during the course of the polymerization.

The changes in the solution volume are kept into account by the following equations:

$$Ni = [I] V \quad (8)$$

$$V = V^0 (1 - E Cm) \quad (9)$$

$$E = \frac{V_{(fin)} - V_{(in)}}{V_{(in)}} \quad (10)$$

$$Cm = \frac{N_M^0 - N_M}{N_M^0} \quad (11)$$

$$Ct = \frac{N_T^0 - N_T}{N_T^0} \quad (12)$$

In regard to the changes in the values of the kinetic constant, k_d was taken constant with the conversion. On the other hand, the termination constant k_t is well known to vary with the conversion of monomer into polymer. Literature reports several model for the change of this constant [8]. Equations (13) to (16) describe the model used in the present study.

$$k_t = k_t^0 + k_t^{min} \qquad \text{for } 0 < C < .1 \quad (13)$$

Equation (13) describes the behavior of k_t during the initial stages of polymerization, in the dilute regimen, where the mobility of the macromolecules is not yet limited by the increasing viscosity of the solution; in this equation, k_t^{min} represents the presence in solution of very short radical chains which have high mobility even in viscous solution [15], while k_t^0 represents a general termination constant

derived from polymerization studies at low conversion and is found in literature [13].

At higher concentrations, in the semidiluted regimen, where the mobility of the macromolecules is mainly translational, k_t is supposed to be slightly decreased by the increasing viscosity of the solution [8], as described in (14):

$$K_t = k_t^{\text{trans}} = k_t^{0*} K' (1 - K_2 C) + k_t^{\text{min}} \quad \text{for } .1 < C < C^{**} \quad (14)$$

where

$$C^{**} = K_c / \overline{(DP)}^{1/2} \quad (15)$$

represents the transition to the semidiluted/entangled regimen.

In the above equations, K' is a proportionality constant for translationally controlled polymerization, K_2 is a coefficient in concentration dependence for translationally controlled termination, and K_c is the critical constant for the onset of reptation [8].

Of the above constants, K_c is the most critical, since it marks the transition to a substantially different polymerization regimen, where the increased viscosity of the solution forces the macromolecules to move only in a snake-like type of motion, thus considerably decreasing their rate of diffusion. This constant is vital to ensure an accurate modeling of the polymerization system at higher conversion; however an accurate value of this constant can only be determined by following a test polymerization and determining experimentally the onset of gelation. In some system where the polymer concentration is low or/ and its $\overline{DP}$ limited, gelation may never occur.

In solutions where termination is controlled by reptation, k_t may be expressed as follows:

$$k_t = k_t^{**(\text{trans})} * \frac{\overline{DP}^{**/2} C^{**1.75}}{\overline{DP}^{/2} C^{1.75}} + k_t^{(\text{min})} \quad \text{for} \quad C^{**} < C \quad (16)$$

where $\overline{DP}'$ is the instantaneous degree of polymerization of the polymeric radicals, $k_t^{**(\text{Trans})}$ is $k_t^{(\text{trans})}$ at $C = C^{**}$, and $\overline{DP}^{**'}$ is the average degree of polymerization of growing radicals at $C = C^{**}$.

The values of k_{tr} and k_p were supposed to decrease with the conversion and were assumed to be the geometric mean between their initial value and the value of k'' obtained by substituting k_{tr}^0 or k_p^0 to k_t^0

in Eqs. (13), (14) and (16):

$$k_{tr}, k_p = (k_{tr}, k_p * k'')^{1/2} \qquad (17)$$

Equation (17) takes into account that the mobility of macromolecular chains is diminished by the increased viscosity of the solution, while that of the monomer or transfer agent molecules is not.

The value of the efficiency factor f was supposed to vary from .7 to .5, as an inverse function of the increased viscosity of the solution that may enhance the "cage effect" and increase the amount that is wasted by side reactions.

Chain transfer agent concentration was assumed to decrease by 5% respect to the value given by Eq. (17), as the polymerization proceeds, to take into account side reactions which may waste part of it.

As Eq. (3) shows, $1/DP_{inst}$ is a function of the sum of $([I])^{1/2}$ and $[T]$ at every time. Thus, $1/\overline{DP}_{tot}$ will be the sum of many $1/\overline{DP}_{inst}$, each determined by the relative instantaneous values of $[I]$, $[T]$, and $[M]$, and in principle, the different evolution of $\overline{DP}_{inst}$ during the course of a polymerization may lead to different $\overline{DP}$ values, although reagent concentrations were chosen to give the same $\overline{DP}$ at low conversion. Furthermore, even molecular mass distribution may differ.

Therefore, being $\overline{DP}_{tot}$ the conversion weighted average of many instantaneous $\overline{DP}$, the polymerization course where the differences between $\overline{DP}_{inst}$ and $\overline{DP}_{tot}$ are minimal should give the lowest overall molecular mass dispersion.

EXPERIMENTAL

Ethylacrylate was washed twice with NaOH 5% to remove polymerization inhibitor, then twice NaHCO$_3$, and, finally, twice with distilled H$_2$O; after drying over MgSO$_4$, it was distilled under vacuum and used under a nitrogen atmosphere.

The initiator, 2-2'-azobisisobutyrronitrile (AIBN), was recrystallized twice from methanol. The chain transfer agents used, n-dodecanethiol and t-dodecanethiol, were used as received after gas chromatographic verification of their purity. Benzene was refluxed and distilled over Na-K alloy under nitrogen atmosphere.

TABLE I   Values of Kinetic constants used in the present study

Kinetic Constant	Value	Units
k_d	1.16 E − 5	sec^{-1}
f^θ	.7	
k_p	2100	liters moles^{-1} sec^{-1}
k_t^0	3.0 E + 7	liters moles^{-1} sec^{-1}
$k_{t(min)}$	2.0 E + 4	liters moles^{-1} sec^{-1}
k_{trs}/k_p	.24 E − 4	
k_{trm}/k_p	.305 E − 4	
k_{tr} (n-dodecanethiol)	3600	liters moles^{-1} sec^{-1}
k_{tr} (t-dodecanethiol)	1060	liters moles^{-1} sec^{-1}
K_c	2.9	
$K^\cdot$	1.45	
K_2	2.0	ml/g

Polymerization experiments were performed using benzene as solvent and into sealed glass vials. The polymerization mixture was carefully prepared under nitrogen and it was degassed twice by freezing and thawing under nitrogen. Polymerization reactions were run at constant temperature of 60°C in a thermostated water bath.

Polymers were precipitated into hexane, then redissolved in chloroform and vacuum dried.

GPC analyses were performed in tetrahydrofuran on a Water Associates Liquid chromatograph Model 120. Separation was performed by three Micro Styragel columns with Exclusion limit of 450,000(poly(styrene) equivalent). Data obtained were reduced through a third order calibration curve obtained running a series of narrow molecular mass poly(styrene) standards. Therefore, all molecular mass values are expressed in poly(stryrene) equivalents and values of molecular mass obtained may be affected by a certain error in respect to absolute values. This choice should not affect the conclusion of the present study.

RESULTS

Polymerizations of ethyl acrylate were run with either n-dodecane thiol or t-dodecane thiol as chain transfer agents; lower average molecular mass values were obtained with the former chain transfer agent which, as it could be expected, is more active because of the lower steric hindrance of its active SH group (Tabs. II and III).

TABLE II   Reagents concentrations and molecular mass values for poly(ethyl acrylate) prepared using *n*-dodecanethiol as a chain transfer agent

[M] mol/L	[I] mol/L	[T] mol/L	Mn	Mw	Mz	Mw/Mn	Mz/Mw	Run
2.6	0.04	0.49	5700	12800	25450	2.2	2.0	D2SHA
2.6	.012	.048	6700	13300	24550	2.0	1.8	D2SHB
2.6	.019	.047	5300	11700	21650	2.2	1.9	D2SHC
5.2	.008	.105	6300	15200	32250	2.4	2.2	D4SHC
5.2	.024	.098	6500	14700	30550	2.3	2.1	D4SHB
5.2	.040	.097	5400	13300	27400	2.5	2.1	D4SHC

TABLE III   Reagents concentrations and molecular mass values for poly(ethyl acrylate) prepared using *t*-dodecanethiol as a chain transfer agent

[M] mol/L	[I] mol/L	[T] mol/L	Mn	Mw	Mz	Mw/Mn	Mz/Mw	Run
2.6	.0040	.049	6600	17440	3100	2.6	1.8	D2THA
2.6	.012	.048	7200	16770	29150	2.3	1.7	D2THB
2.6	.019	.047	6550	17300	31750	2.6	1.8	D2THC
5.2	.008	.105	6000	16700	31900	2.8	1.9	D4THC
5.2	.024	.098	6600	15900	29400	2.4	1.8	D4THB
5.2	.040	.097	6650	16240	29450	2.4	1.9	D4THC

The molecular mass distribution of polymers prepared with *n*-dodecanethiol appears to be more symmetric and less disperse than that of polymers prepared with the other initiator which are skewed on the low molecular mass side (Figs. 1 and 2).

Molecular mass dispersion increases with the monomer initial concentration with either chain transfer agent used.

In any case, molecular mass distribution curves shows a minimum of dispersion for certain initiator concentration/chain transfer concentration ratios.

To fine tune the polymerization model to experimental results, a polymerization of ethyl acrylate was performed extracting samples at different times, quenching them and analyzing them to determine conversion and average molecular mass value (Tab. IV).

DISCUSSION

Initially, a polymerization of Ethyl acrylate was run and followed with time to adjust the polymerization model and to optimize the kinetic constants values. As shown in Figure 1, it has been possible to achieve
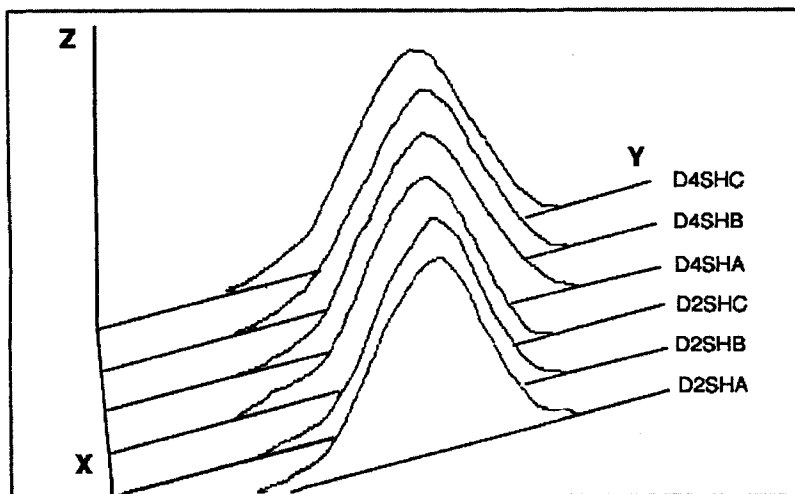
FIGURE 1   Molecular Mass Distribution Curves of poly(ethyl acrylate) obtained with *n*-dodecanethiol as a chain transfer agent. X: Runs; $Y = \text{Log MM}$; $Z = $ relative abundance. See Table II for run identification.
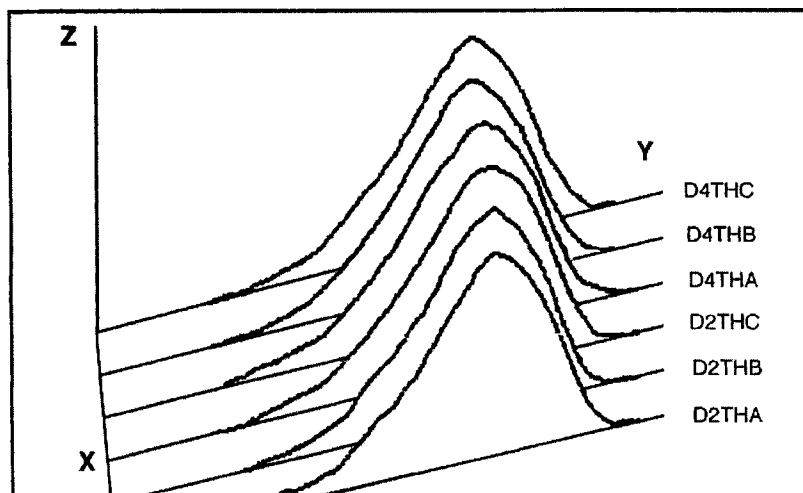

FIGURE 2   Molecular Mass Distribution Curves of poly(ethyl acrylate) obtained with *t*-dodecanethiol as a chain transfer agent. X: Runs; $Y = \text{Log } MM$; $Z = $ relative abundance. See Table III for run identification.

TABLE IV   Conversion and average molecular mass values of poly(ethyl acrylate) during polymerization in the presence of n-dodecanethiol. $[M] = 5.2\,\text{mol/L}$, $[I] = .024\,\text{mol/L}$, $[T] = .098\,\text{mol/L}$

Time	Conversion %	Mn	Mw	Mz	Mw/Mn	Mz/Mw
30'	32	3500	5800	9500	1.7	1.6
60'	52	4000	6700	11700	1.8	1.7
120'	74	4630	8600	15200	1.9	1.8
240'	> 95	6400	13600	27400	2.1	2.0

a significant fit between the conversion values calculated by the model and the experimental values.

The optimized polymerization model has then been used to simulate a large number of polymerization reactions run with different initial concentrations of the reagents, but all aimed to produce a polymer of similar average molecular mass values. In fact, the model forecasted a reduced variance of $\overline{DP}_{inst}$ as a function of conversion for intermediate concentrations of initiator ($[I] = .6\%$ of $[M]$) with both initiators. To verify the results obtained from the computer model, polymerization reactions were run using the reagent concentrations that would lead to the lowest molecular mass distribution, as well as additional ones on either side that would lead to a broader distribution that desired.

The flow chart of the computer program is present in the Appendix.

Results obtained are shown in Tables II and III and confirm the model forecasts.

Examination of the reagents concentrations evolution during polymerization show as the ratios $[I]/[M]$ and $[T]/[M]$ change to a lesser extent as convertion increases in the case of $[I] = .6\%$ $[M]$ than the others.

Regarding monomer initial concentration, model forecasts and experimental data agree that a higher monomer initial concentration lead to a broader molecular mass distribution for constant $[I]/[M]$ and $[T]/[M]$ ratios. The reason for this behavior can be attributed to the higher increase of the reaction medium viscosity in the more concentrated solution, which will change the values of the viscosity constant over a wider range and may give rise to the "gel effect" at lower conversion.

The effect of the different type of chain transfer agent it is shown on the shapes of the molecular mass distribution curves. Polymers

prepared with *t*-dodecanethiol show a molecular mass distribution curve that is quite skewed toward the low mass side while polymers prepared with *n*-dodecanethiol show the opposite (Figs. 1 and 2).

As reported in Table I, the two chain transfer agents have different values of their chain transfer constants, caused by different steric hindrance of the carbon atom supporting the thiol group; these constants are respectively lower and higher than the monomer propagation constants.

As shown by the polymerization model (Fig. 3), *n*-dodecane thiol, with its relatively high value of $k_{tr}(k_{tr} > k_p)$, is very effective in controlling the average $\overline{DP}$ at low conversion, but is quickly used up and is no longer able to control $\overline{DP}_{inst}$ at high conversion. Therefore, thanks also to decreased k_t, macromolecular chains can grow to a larger $\overline{DP}$, thus broadening the overall molecular mass distribution on the high side.

On the other hand, *t*-dodecanethiol, which has a relatively low k_{tr} value $(k_{tr} < k_p)$, is used up at a lesser rate and its concentration will decrease less than the monomer concentration as the polymerization proceeds. Therefore, it will prevent the polymer formed from reaching a high $\overline{DP}$ especially at high conversion (Fig. 4) and thus skewing the molecular mass distribution toward the low side.
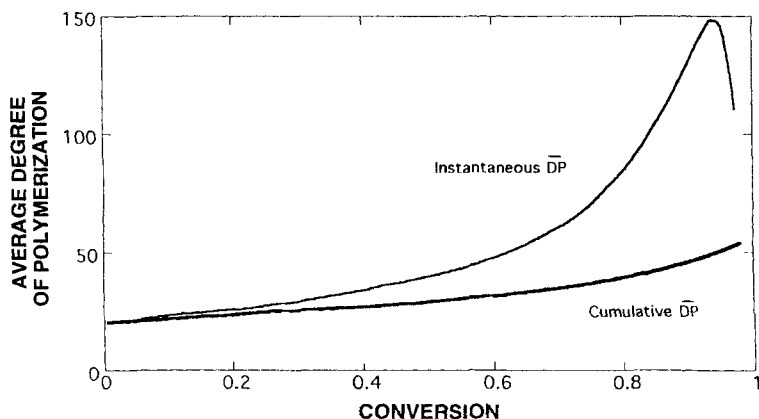

FIGURE 3 $\overline{DP}_{inst}$ (bottom) and $\overline{DP}_{avg}$ (top) as functions of conversion in poly(ethyl acrylate prepared in the presence of *n*-dodecanethiol as a chain transfer agent. ($[M] = 5.2\,mol/L$; $[I] = .024\,mol/L$; $[T] = .0985\,mol/L$).
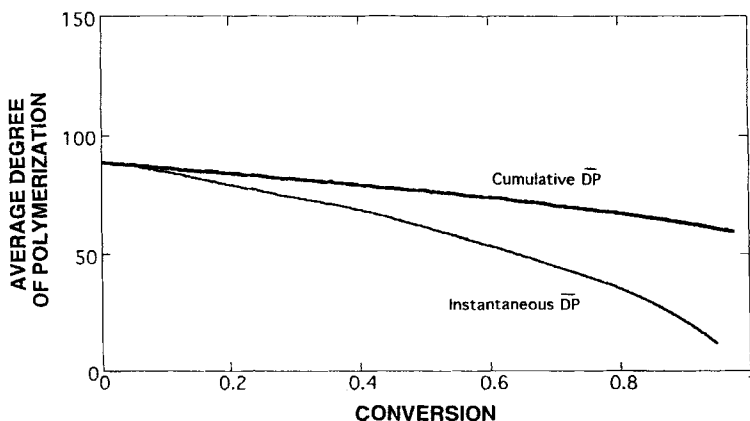
FIGURE 4 $\overline{DP}_{inst}$ (bottom) and $\overline{DP}_{avg}$ (top) as functions of conversion in poly(ethyl acrylate prepared in the presence of t-dodecanethiol as a chain transfer agent. ([M] = 5.2 mol/L; [I] = .024 mol/L; [T] = .0985 mol/L).

CONCLUSION

This study demonstrates how computer modeling techniques, coupled with a sound understanding of the polymerization kinetic, can be helpful in forecasting and optimizing the molecular mass distribution curve of polymers synthesized by radical polymerization.

The well known Mayo equation can furnish acceptable results during most of the course of polymerization if not only reagent concentration, but also kinetic constants variation during polymerization are kept into account. The above can be accomplished through the use of computer modeling and by a process of optimization based on the feeding back of experimental results to improve on the initial estimates of polymerization parameters.

This feed back technique can also help to determine the critical stages during polymerization where the solution behavior of the macromolecules changes as a consequence of viscosity increases (Fig. 5).

This study also evaluates how different chain transfer agents affect the molecular mass distribution depending on their different mechanisms of chain growth control. This results underline the importance of carefully choosing the chain transfer agent depending on the monomer being polymerized and the type of molecular mass distribution desired. The molecular mass distribution can be further controlled by choosing
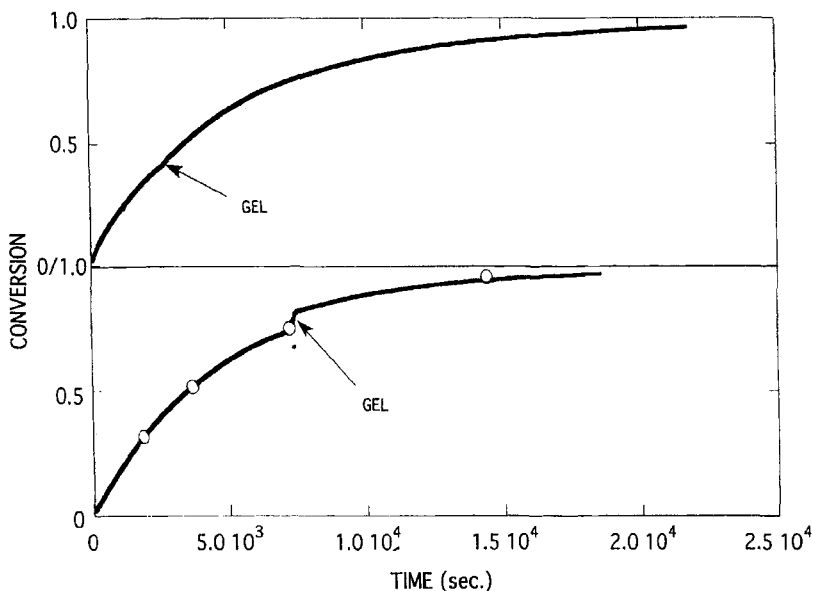
FIGURE 5 Conversion as a function of time of poly(ethylacrylate) prepared in the presence of *n*-dodecanethiol (bottom) and *t*-dodecane thiol (top). ($[M] = 5.2\,mol/L$; $[I] = .024\,mol/L$; $[T] = .0985\,mol/L$).

appropriated reagents concentrations. Again, an optimized computer modeling of the polymerization will be of help by greatly reducing the number of experimental trials necessary to achieve the desired results.

References

[1] Peebles, L. H. Jr. (1971). "Molecular Weight Distribution in Polymers', *Interscience Publ.*, New York.

[2] Gloor, W. E. (1975). *J. Appl. Plym. Sci.*, **19**, 273–79.

[3] Cardenas, J. N. and O'Driscoll, K. F. (1976). *J. Polym. Sci., Polym. Chem.* Ed., **11**, 883–97.

[4] O'Driscoll, K. F. and Mahabadi, H. K. (1976). *J. Polym. Sci., Polym Chem. Ed.*, **13**, 1063–70.

[5] Braks, J. G. and Huang, R. Y. M. (1975). *J. Polym. Sci., Polym. Phys. Ed.*, **13**, 1063–70.

[6] Wu, G. Z. A., Denton, L. A. and Laurence, R. L. (1982). *Polym. Engn. Sci.*, **22**, 1–8.

[7] Mahadabi, H. K. and O'Driscoll, K. F. (1977). *Macromolecules*, **10**, 55.

[8] Tulig, T. S. and Tirrel, M. (1981). *Macromolecules*, **14**, 1501–11.

[9] Moore, J. C. (1964). *J. Polym. Sci.*, **A2**, 835.

[10] Busnel, J. P. (1982). *Polymer*, **23**, 137–41.

[11] Gregg, R. A. and Mayo, F. R. (1947). *Discussion Faraday Soc.*, **2**, 328.
[12] Gee, G. and Melville, H. M. (1944). *Trans. Farday Soc.*, **40**, 240.
[13] Brandrup, J. and Immergut, E. H. (1989). "Polymer Handbook", Wiley, New York.
[14] Ciardelli, F., Farina, M., Giusti, P. and Cesca, S. (1983). "Macromolecole: Scienza e Tecnologia", Pacini Ed. Pisa, **1**, 292.
[15] O'Driscoll, K. F. (1981). *Pure and Appl. Chem.*, **53**, 617–26.

APPENDIX: Flow Chart of The Computer Program Used to Optimize Polymer Molecular Mass Distribution.