

# Solvent Effects in Butyl Acrylate and Vinyl Acetate Homopolymerizations in Toluene

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**ABSTRACT:** A series of butyl acrylate (BA) and vinyl acetate (VAc) homopolymerizations in toluene was conducted to investigate the effect of solvent at different solvent and chain transfer agent (CTA) concentrations. Because the experimental determination of the individual propagation and termination rate constants for these systems is challenging, experimental observations were limited to the lumped rate constant ( $k_p/k_t^{0.5}$ ). Differences in the lumped rate constant, at different solvent and CTA concentrations, were assumed to be attributed to the effect of solvent on the termination rate constant. Our hypothesis was that the termination rate constant  $k_t$  was affected by the presence of solvent. At higher solvent concentrations, chain transfer to solvent occurs more frequently and leads to the formation of shorter chains, which move more easily and are able to

terminate more quickly compared to longer chains. Thus,  $k_t$  will increase, leading to a decrease in the lumped rate constant. The experimental results confirmed the presence of a solvent effect on the lumped rate constant. This effect was more pronounced in the case of VAc compared to BA solution homopolymerizations. Under the investigated conditions, increased CTA concentrations did not substantially affect the rate of BA homopolymerizations, whereas a slight synergistic effect between the CTA and solvent at higher CTA and solvent concentrations was apparent for VAc homopolymerizations. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 871–876, 2004

**Key words:** radical polymerization; kinetics (polym.); modeling; solvent effect; lumped rate constant

## INTRODUCTION

Although stricter environmental regulations and consumer awareness play a major role in the development of new environmentally friendly technologies for polymer production, solution polymerization remains an important technology. It enables the production of polymers with superior properties compared to other technologies, despite its shortcomings. Therefore, there is considerable interest on the effect of various solvents on the kinetics of free-radical polymerization of commercially important monomers such as methyl methacrylate (MMA), butyl acrylate (BA), vinyl acetate (VAc), and styrene (St). According to the classical free-radical polymerization approach, the overall rate of polymerization ( $R_p$ ) is represented using the following equation:

$$R_p = k_p \left( \frac{2fk_d}{k_t} \right)^{1/2} [M][I]^{1/2}$$

where  $k_p$  is the propagation rate constant;  $k_t$  is the termination rate constant;  $k_d$  is the initiator decompo-

sition rate constant;  $f$  is initiator efficiency; and  $[M]$  and  $[I]$  are the monomer and initiator concentrations, respectively. In the presence of solvent, for some monomer–solvent systems, a strong dependency of  $R_p$  on monomer concentration was observed.<sup>1–7</sup> One can speculate that all rate constants as well as initiator efficiency can be affected by the presence of the solvent. The effect of solvent on  $f$  and  $k_d$  depends on the solvent–monomer system. Fernandez-Garcia et al.<sup>1</sup> found that for the BA–benzene system with AIBN initiator at 50°C, the  $2fk_d$  factor increased with monomer concentration up to  $[M] > 3$  mol/L, beyond which it became constant.

Solvent effects on the propagation and termination rate constants have generated considerably more interest. Coote et al.<sup>2</sup> reviewed the main mechanisms by which solvent can affect the kinetics of solution polymerization such as by polarity effects, the formation of radical–solvent complexes or monomer–solvent complexes, and the bootstrap effect. In almost all cases, the reactivity of the propagating radicals was assumed to be affected by the presence of the solvent. Neither of the proposed mechanisms is generally valid for *all* monomers. For example, the decrease in the polymerization rate with the increased initial concentration of aromatic solvents can be explained by the formation of monomer–solvent and radical–solvent complexes. Othman et al.<sup>7</sup> pointed out that the above-mentioned theories can explain the

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observed differences in the polymerization rates between different types of solvents, but in general fail to explain the decrease in polymerization rate in the same solvent at low reaction mixture viscosities. For example, the effect of ethyl acetate on VAc polymerization cannot be explained using this approach.<sup>3,4</sup> Strong retardation effects were also observed for VAc homopolymerizations in toluene.<sup>5</sup> Jovanovic and Dubé<sup>5</sup> and McKenna et al.<sup>6</sup> observed a retardation effect at different initial monomer concentrations in BA homopolymerizations in toluene.

Further complications in the investigation of solvent effects arise from the fact that most experiments enable the investigation of the influence of solvent on the lumped rate constant ( $k_p/k_t^{0.5}$ ) rather than on the individual rate constants. Even when pulsed-laser polymerization combined with size-exclusion chromatography (PLP-SEC) is used, the experimental determination of individual propagation and termination rate constants for some monomers is challenging, regardless if performed in bulk or solution.<sup>8,9</sup> Beuermann and Buback<sup>8</sup> summarized the reasons for the experimental difficulties in obtaining the propagation constant for acrylates above 30°C using PLP-SEC as (1) chain transfer to monomer combined with a high propagation rate coefficient, (2) chain transfer to polymer, and (3) difficulties in the determination of absolute molecular weights when branching is present. Despite these difficulties, most studies conducted using PLP-SEC have shown that there is a small solvent effect on  $k_p$  for most acrylate monomers. For example, in an investigation on a series of solvents (acetonitrile, toluene, benzene, dimethylformamide, cyclohexene, bromobenzene, methyl isobutyrate, etc.) for St and MMA homo- and copolymerizations, Olaj et al.<sup>10</sup> found no pronounced effects on  $k_p$ . On the other hand, Zammit et al.<sup>11</sup> found a strong increase of  $k_p$  with increased solvent concentrations for benzyl alcohol–St and benzyl alcohol–MMA polymerizations.

The investigation of  $k_t$  independently of  $k_p$  has proven to be even more challenging. In the classical free-radical polymerization approach, both constants are assumed to be independent of chain length (i.e., radical reactivity does not depend on the length of the chain). At first, the chain-length-dependent termination rate constant was incorporated into modeling free-radical polymerizations.<sup>12–15</sup> This improved the modeling of existing experimental data. Use of techniques such as SP-PLP (i.e., single-pulse–pulsed-laser polymerization) enables the determination of  $k_t$  independently of  $k_p$ , although the majority of the experiments have been performed using supercritical CO<sub>2</sub> as a solvent.<sup>8</sup> On the other hand, Vanna et al.<sup>16</sup> showed that reversible addition/fragmentation chain-transfer (RAFT) free-radical polymerization could be an easy and accessible method for an independent determination of chain-length dependency of  $k_t$ .

In a previous series of experiments, we examined the effect of toluene on the lumped rate constant of BA and VAc homopolymerizations.<sup>5</sup> As previously mentioned, we assumed that the effect of solvent was more pronounced on the termination rate constant and the modeling was conducted using that hypothesis. In the work presented here, the effects of solvent in combination with chain-transfer agent (CTA) were investigated. The objective was to test the following hypothesis. If, in the presence of solvent, more chain-transfer reactions are occurring, then the concentration of shorter chains, which terminate more quickly compared to longer ones, is higher. In addition, if more CTA is present in the reaction mixture, the concentration of shorter chains will be even higher and, thus, the termination rate constant will further increase, leading to a decrease in the lumped rate constant. In this work, changes in the lumped rate constant were investigated at different solvent and CTA concentrations. BA and VAc homopolymerizations were performed at three different solvent and three different CTA concentrations to test this hypothesis. A modeling approach was used to separate the propagation and termination rate constants, assuming that the effects were mostly attributable to the chain-length dependency of  $k_t$ , as suggested by some authors.<sup>12–15</sup> Only the termination rate constant in the model was adjusted, and the experimental data were modeled using a JAVA-based simulator<sup>17</sup> that incorporates mathematical modeling described by Gao and Penlidis<sup>18</sup> and Dubé et al.<sup>19</sup>

## EXPERIMENTAL

Inhibitor was removed from BA (Aldrich, Milwaukee, WI) and VAc (Aldrich) according to previously described procedures.<sup>5</sup> The initiator, 2,2'-azo(bis)isobutyronitrile (AIBN; PolyScience Inc., Niles, IL) was recrystallized three times in absolute methanol before use. All other reagents such as toluene (ACP Chemicals, Toronto, Canada), ethanol (ACP Chemicals), tetrahydrofuran (THF), sodium hydroxide (ACP Chemicals), calcium chloride (ACP Chemicals), and *n*-dodecyl mercaptan (Acros Organics, Morris Plains, NJ), the CTA, were used as received.

Polymerizations were carried out in glass ampoules (17 cm length, 0.8 cm outer diameter) in a water bath at 60°C. Oxygen was removed from the reaction mixture in three consecutive freeze–thaw cycles under high vacuum. After sealing, the ampoules were weighed and submerged in the water bath. At appropriate time intervals, ampoules were removed from the bath and the reaction was quenched using an ice bath. The contents of each ampoule were poured into a preweighed crystallization dish and a 10-fold excess of ethanol was added. After evaporation of the solvents, the polymer was dried in a vacuum oven at

TABLE I  
Experimental Conditions

Monomer	Monomer/toluene (wt %)	CTA (mol L <sup>-1</sup> )	Initiator (mol L <sup>-1</sup> )
Vinyl acetate	70/30	0, 0.02, 0.06	0.105
	50/50	0, 0.02, <sup>a</sup> 0.06	0.105
	20/80	0, 0.02, <sup>a</sup> 0.06	0.105
Butyl acrylate	70/30	0, 0.02, 0.06	0.002
	50/50	0, 0.02, <sup>a</sup> 0.06	0.002
	20/80	0, 0.02, <sup>a</sup> 0.06	0.002

<sup>a</sup> Previously published results.<sup>5</sup>

30°C to a constant weight. The experimental conditions used are outlined in Table I.

Conversion was determined using gravimetry and was based on total polymer. A Waters Associates (Milford, MA) gel permeation chromatograph equipped with a Waters 410 refractive index detector was used for the determination of the cumulative number- and weight-average molecular weights. Three Waters Ultrastaygel packed columns (10<sup>3</sup>, 10<sup>4</sup>, 10<sup>6</sup> Å) were installed in series. Filtered THF was used as eluent at a flow rate of 0.3 mL/min. Polystyrene (SHODEX, Showa Denko, Tokyo, Japan) standards with molecular weights between 1.3 × 10<sup>3</sup> and 3.15 × 10<sup>6</sup> g/mol were used for calibration. Standards and samples were prepared in THF 0.2% w/v and filtered before injection through 0.45-μm filters to remove any gel, if present. Millennium 32 software (Waters) was used for the data acquisition.

## RESULTS AND DISCUSSION

Between the two investigated monomers, VAc was considerably more affected by the presence of toluene as solvent. This is consistent with previously published results for the same system.<sup>5</sup> In Figures 1 through 3, conversion versus time data are shown for

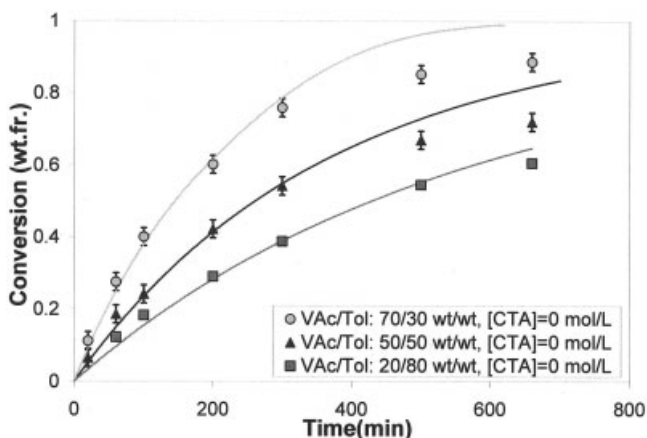


Figure 1 VAc homopolymerization in toluene: conversion versus time at 0 mol/L CTA.

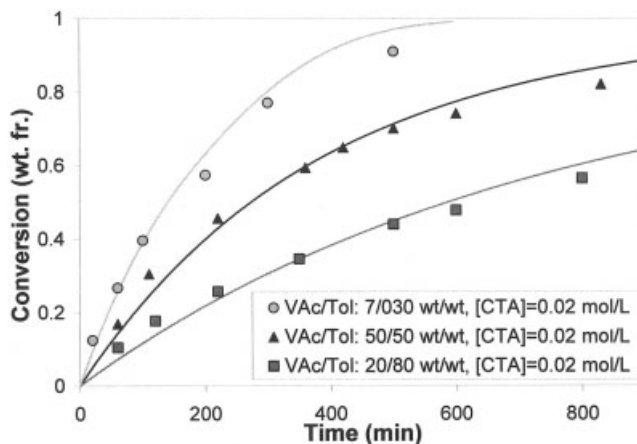


Figure 2 VAc homopolymerization in toluene: conversion versus time at 0.02 mol/L CTA.

three different concentrations of solvent at three different CTA concentrations. A significant difference in the rate of polymerization for all CTA concentrations was observed. In all cases, the lowest rate of polymerization was observed for a VAc/toluene ratio of 20/80 wt %, whereas the highest was observed for a ratio of 70/30 wt %. The observed differences among the polymerization rates cannot be explained by the effect of dilution alone. Thus, the solvent must be a major factor contributing to this behavior.

In Figures 1 through 3, model predictions are presented as solid lines. In almost all cases the model was able to predict the rate of polymerization within the range of experimental error. Successful modeling of the VAc/toluene system was possible only when the effect of solvent was incorporated into the existing model. The effect of solvent on  $R_p$  was assumed to originate in the chain-length dependency of  $k_t$ . As previously discussed, there is a possibility that either  $k_p$  or both  $k_p$  and  $k_t$  were affected by the presence of

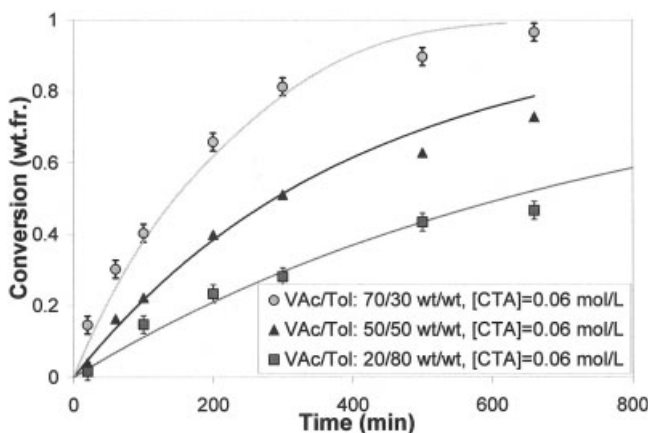
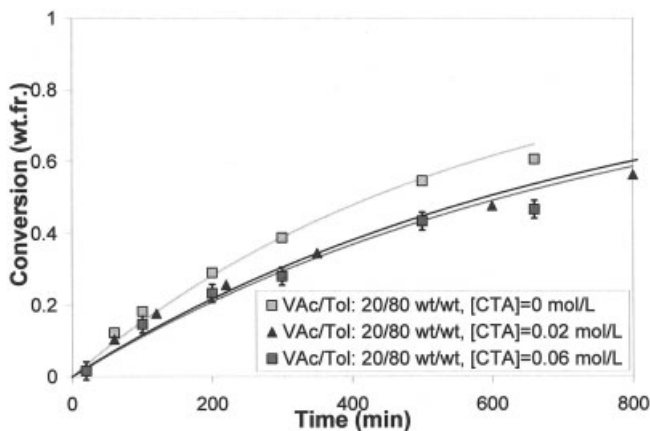


Figure 3 VAc homopolymerization in toluene: conversion versus time at 0.06 mol/L CTA.



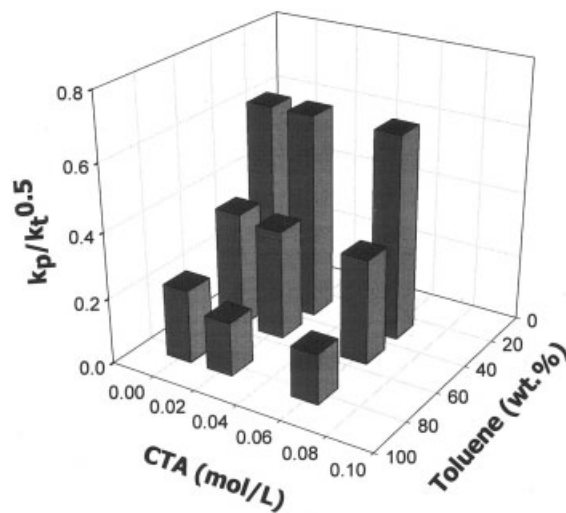
**Figure 4** VAc homopolymerization in toluene (20/80 wt %): conversion versus time at different CTA concentrations.

solvent. However, in this work, the assumption was that only  $k_t$  was affected. With the increasing solvent concentration, it is possible that more chain transfers to solvent reactions are occurring. This would lead to the generation of shorter, more mobile chains, which could terminate faster than longer ones. This would lead to an increase in  $k_t$  with solvent concentration and, thus, to a decrease in  $R_p$  (Figs. 1–3). All ranges of solvents and CTA concentrations investigated in this work were successfully modeled using this approach. The chain-transfer constants to CTA ( $C_{fCTA}$ ) and solvent ( $C_{fS}$ ) used in the model were  $C_{fCTA} = 3.48 \times 10^{-4}$  and  $C_{fS} = 20 \times 10^{-4}$ , respectively.

Is it possible that the presence of CTA, in addition to the presence of solvent, may affect the rate of polymerization? Traditionally, it is believed that the presence of CTA affects only the development of the molecular weight and not the rate of polymerization. If the  $k_t$  chain-length dependency is valid, however, some effects on  $R_p$  are also possible. The experimental design used here enabled us to investigate this hypothesis. In Figure 4, conversion versus time data for three different CTA concentrations at 80 wt % toluene are presented.

The differences in the polymerization rate at 0.06 mol/L indicate that there is a slight effect of CTA on  $R_p$ . At 50 wt % toluene only a slight difference was observed at 0.06 mol/L CTA, whereas at 30 wt % no differences were found among the three CTA concentrations. One can speculate that there is a combination of CTA and solvent concentrations at which their effects on  $R_p$  become synergistic. In the light of the effect on  $k_t$ , this might indicate that at this point, the concentration of short chains originating from the chain transfer to CTA and solvent reactions are becoming so high that the effect of CTA is expressed not only on the molecular weight distribution but also on  $R_p$ .

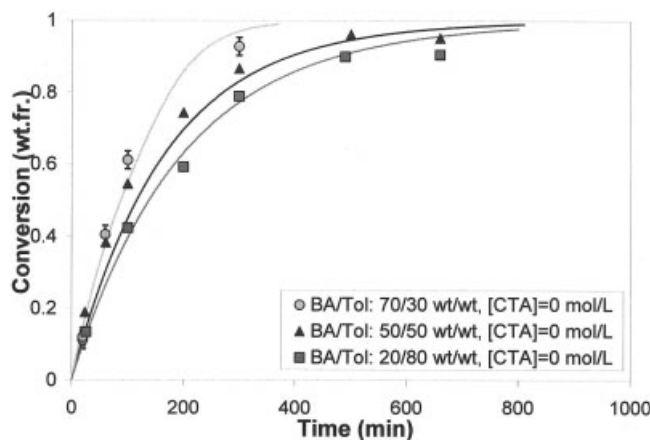
A change in the lumped rate constant in the investigated experimental region (Fig. 5) was obtained using the model. It can be seen that a decrease in the



**Figure 5** VAc homopolymerization in toluene: changes in the lumped constant.

lumped rate constant occurs as the solvent concentration increases. On the other hand, a decrease in the lumped rate constant with an increase in CTA concentration at a particular solvent concentration occurs only at higher solvent concentrations (>50 wt %).

The rates of BA homopolymerizations in toluene were less affected by the presence of toluene compared to those of VAc homopolymerizations. The results at three different CTA concentrations are presented in Figures 6 through 8. Although the same retardation effect was observed as in the VAc homopolymerizations, the effect was far less pronounced in these reactions. As expected, the  $R_p$  at 80 wt % toluene was the slowest among the three investigated solvent concentrations at any CTA level. Again, modeling the reactions was possible when the solvent effects were incorporated into the model, in the form of a change in  $k_t$  with solvent concentration.



**Figure 6** BA homopolymerization in toluene: conversion versus time at 0 mol/L CTA.

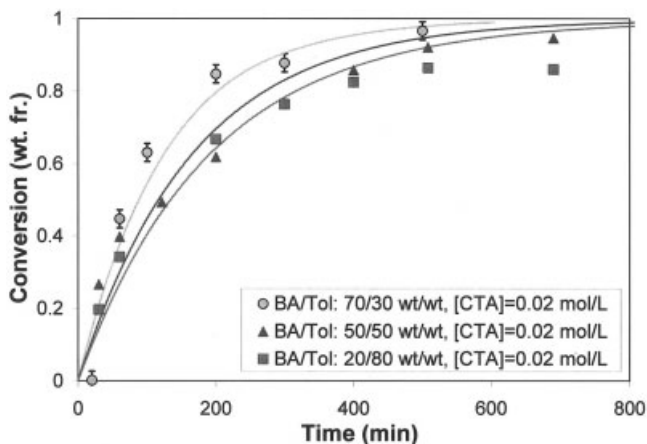


Figure 7 BA homopolymerization in toluene: conversion versus time at 0.02 mol/L CTA.

In Figure 9, the  $R_p$  at 80 wt % toluene and different CTA concentrations was compared. For the VAc homopolymerizations,  $R_p$  was reduced at 0.06 mol/L CTA and 80 wt % toluene, leading us to suspect that there is synergism between the effect of CTA and solvent at this particular CTA and toluene concentration. In the case of BA homopolymerizations, such effects were not observed. This is possibly attributable to the fact that BA was only slightly affected by the presence of solvent when compared to VAc. Similarly, no changes in  $R_p$  were observed at 30 and 50 wt % toluene.

The changes in the lumped rate constant in the investigated experimental space are presented in Figure 10. No differences among different CTA concentrations at any solvent concentration investigated were observed. Only a slight decrease in the lumped rate constant was observed with an increase in solvent concentration at a particular CTA concentration.

The development of the cumulative weight-average molecular weights for VAc homopolymerizations in toluene at 0.06 mol/L CTA is shown in Figure 11. As

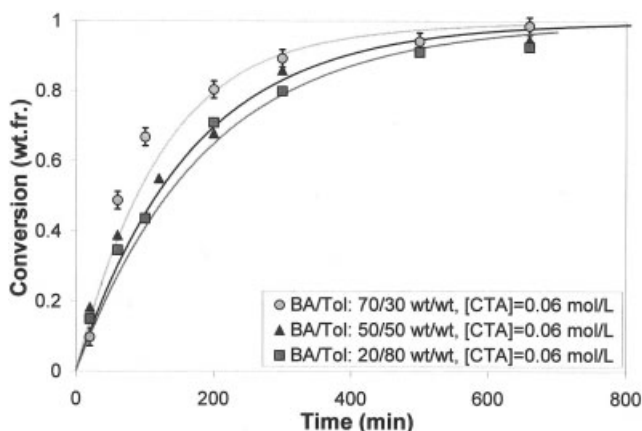


Figure 8 BA homopolymerization in toluene: conversion versus time at 0.06 mol/L CTA.

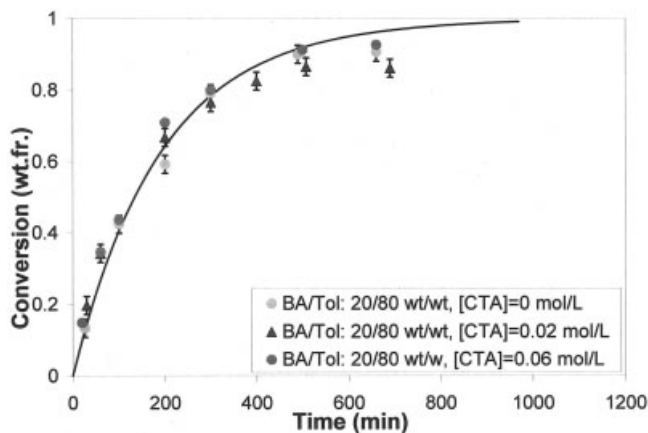


Figure 9 BA homopolymerization in toluene (20/80 wt %): conversion versus time at different CTA concentrations.

expected, the cumulative weight-average molecular weights decreased with increasing solvent concentration. The same trend was observed for other CTA concentrations. This is an additional confirmation of suspected chain transfer to solvent and CTA reactions. Modeling of molecular weight development was performed using the same JAVA-based model. Once the values of  $k_t$  were found to fit the gravimetric data, no other changes were introduced to model the molecular weight development. The agreement between the experimental data and the model predictions is satisfactory.

Molecular weight development in BA homopolymerizations shows a similar trend to those in VAc homopolymerizations. In Figure 12, the  $M_w$  development is shown for different solvent concentrations at 0 mol/L CTA. Similar results were obtained for other CTA concentrations. As expected, with an increased CTA concentration, the cumulative  $M_w$  decreased. At all CTA concentrations, the lowest molecular weights were obtained at 80 wt % toluene. Similar to the mod-

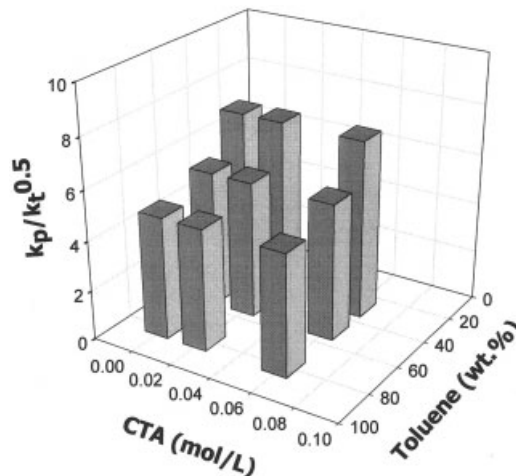


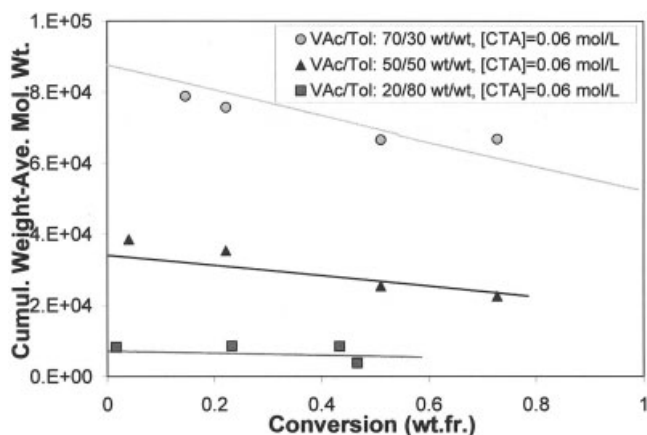
Figure 10 BA homopolymerization in toluene: changes in the lumped constant.

eling of VAc polymerizations, modeling of BA was successful. The observed trends confirm that chain transfer to solvent and CTA reactions were occurring during the polymerization.

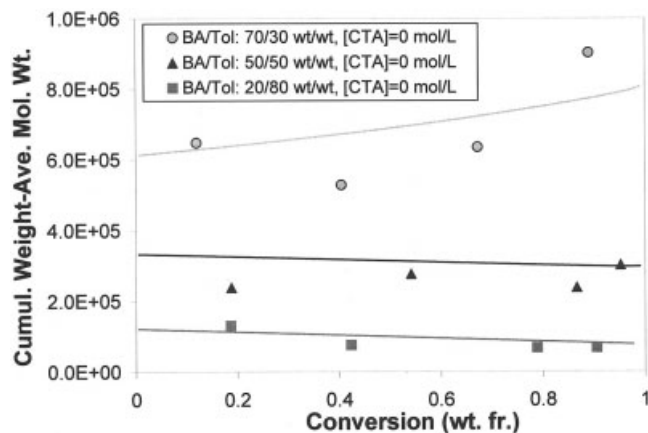
## CONCLUSIONS

An experimental space was investigated to verify the effect of solvent in solution homopolymerizations of BA and VAc in toluene. In addition, *n*-dodecyl mercaptan was used to control the molecular weight. The objective was not only to check for the individual influences of solvent and CTA but also to check for any synergistic effects of the two in the investigated region. For BA and VAc homopolymerizations, the presence of toluene influenced the  $R_p$ . The effect of solvent was more pronounced for VAc. Increasing solvent concentrations from 30 to 80 wt %, with all other factors kept constant, reduced the  $R_p$  by a factor of about 2 for all VAc homopolymerizations, whereas only a slight reduction in  $R_p$  was observed for the BA homopolymerizations. In addition, changing the CTA concentration did not affect the lumped constants to a greater extent in BA homopolymerizations while there was a possible synergistic effect of CTA and solvent in the case of VAc homopolymerizations at high toluene (80 wt %) and CTA (0.06 mol/L) concentrations.

Although it is possible that both terms in the lumped rate constant are affected by the presence of solvent, we demonstrated that it is possible to effectively model these systems when solely the effect on  $k_t$  is considered. In all cases, model predictions for conversion and molecular weight development showed good agreement with experimental data when only the change in  $k_t$  with solvent concentration was incorporated into the model. In this case, we used a hypothetical chain-length dependency of  $k_t$  and an assumption that the generation of large amounts of shorter



**Figure 11** VAc homopolymerizations in toluene: molecular weight development.



**Figure 12** BA homopolymerizations in toluene: molecular weight development.

chains attributed to chain transfer to solvent, and in some cases to CTA, reactions can affect  $k_t$  and thus the lumped constant and  $R_p$ .

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