Mapping Chain Length and Conversion Dependent Termination Rate Coefficients in Methyl Acrylate Free Radical Polymerization

Alexander Theis, Thomas P. Davis, Martina H. Stenzel, and Christopher Barner-Kowollik*

Centre for Advanced Macromolecular Design, School of Chemical Engineering and Industrial Chemistry, The University of New South Wales, Sydney, NSW 2052, Australia

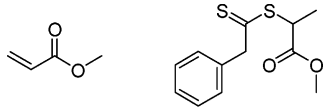
Received June 27, 2005
Revised Manuscript Received September 16, 2005

Introduction

Obtaining reliable data for the termination rate coefficient, k_t, in free radical polymerization has been an ongoing research theme over the last 50 years, and to date, a variety of methods have been developed to probe this parameter as a function of both the monomer to polymer conversion and the chain length of the propagating radicals. The complexities involved in obtaining reliable termination rate coefficient data as well as a critical evaluation of the most prominent methods for its determination have recently been reviewed.[1]

A relatively simple experimental approach to map out the termination rate coefficient as a function of the chain lengths of the terminating radicals by using the RAFT polymerization process was recently devised by our group.[2] We termed this approach the RAFT chain length dependent termination technique (RAFT-CLD-T). Under ideal circumstances, the RAFT methodology allows for a direct correlation of the macromolecular chain length, i, with the monomer to polymer conversion. In contrast to many other types of living radical polymerization, which are based on the persistent radical effect, the propagating radical concentration in RAFT mediated polymerizations is—in the case of chain length independent rate coefficients—not reduced. Thus, with a relatively simple set of kinetic equations, time dependent rate of polymerization data recorded during a RAFT polymerization can be analyzed to yield the termination rate coefficient as a function of the chain lengths of the terminating radicals, when the rate coefficient for initiator decomposition and its efficiencies (k_d and f) as well as the propagation rate coefficient, k_p, are known.[2] Initially, the novel methodology was successfully applied to map out chain length dependent termination rate coefficients in styrene bulk polymerizations.[2,3] Recently, we demonstrated that the RAFT-CLD-T method could also be adapted to methyl acrylate (MA),[4] dodecyl acrylate (DA),[5] butyl acrylate (BA),[6] and methyl methacrylate (MMA)[7] polymerization. Because of special issues in acrylate radical polymerization, i.e., a large propagation rate coefficient[8] and in the case of MA and BA a strong dependence of the (average) termination rate coefficient, $\langle k_t \rangle$, on the monomer to polymer conversion, several modifications have been made to the original method. In addition, an optimized RAFT agent, methoxycarbonylethyl phenyldithioacetate (MCEPDA, see Scheme 1) was designed to minimize interfering effects caused by slow fragmentation or reinitiation.[4]

Scheme 1. Monomer Methyl Acrylate (MA) and the Reversible Addition Fragmentation Chain Transfer (RAFT) Agent Employed in the Current Study (MCEPDA)



When extending the method to dodecyl acrylate (DA) radical polymerization an extended monomer conversion range up to 50% can be covered to determine the chain length dependency of the termination reaction, because the k_t of DA is almost independent of monomer conversion within this interval. However, with the extension of the conversion interval, nonidealities in the polymerization behavior must be considered.[5] A strong deviation from ideal polymerization kinetics for acrylates is caused by chain transfer reactions. Predominantly, intramolecular chain transfer via backbiting leads to less reactive midchain radicals, which induce slower overall propagation rates.[9,10] In contrast to the propagation rate, the rate of backbiting reactions is independent of the actual monomer concentration. Consequently, the apparent monomer reaction order becomes larger than unity.[11] PREDICI simulations using recently estimated kinetic data for the rate coefficients of the backbiting sequence have shown that monomer reaction orders of 1.6−1.9 could easily be obtained, if intramolecular transfer is considered.[5]

In the context of the RAFT process, it was previously demonstrated via PREDICI simulations that the experimentally obtained apparent monomer reaction orders in conventional free radical polymerization are a good approximation for the apparent monomer reaction order in a RAFT mediated polymerization.[5] It thus seems justified to employ the monomer reaction order determined under conventional radical polymerization conditions to the RAFT process under analogous conditions.[5]

Up to now the data evaluation in all RAFT-CLD-T experiments was restricted to conversion regimes where k_t does not vary with conversion. Such a restriction had to be implemented because the primary database of the RAFT-CLD-T method (i.e., time dependent rates of polymerization, R_p) is sensitive to both changes in k_t caused by either chain length *or* conversion dependence. Thus, data obtained in high conversions regimes—although collected—were discarded.

In the present article, we demonstrate that through a three-dimensional analysis of the termination rate coefficient data as a function of both chain length *and* conversion, one can obtain a detailed picture of k_t as a function of these variables. As a monomer, methyl acrylate (MA) was selected, which shows a relatively strong dependence of k_t on conversion. The kinetic parameters required for mapping the termination rate coefficient as a function of the terminating radical chain are available from the literature and are collated in Table 1.

We will demonstrate that the current analysis is in good agreement with reported data on the conversion

* Corresponding author. E-mail: camd@unsw.edu.au.

10.1021/ma051370g CCC: $30.25
Published on Web 11/01/2005

Table 1. Set of Kinetic Data for Methyl Acrylate (MA) Radical Polymerization Using AIBN as Initiator

$c_M{}^0$ (mol L^{-1})	k_p (L mol^{-1} s^{-1})	k_d (s^{-1})	initial f	ΔH (kJ mol^{-1})
9.7[8]	47400[8]	1.1×10^{-4} [12]	0.7[4]	−78[15]

dependence of k_t in high molecular weight regimes (as deduced via single-pulse pulsed-laser-polymerization experiments).[13,14] In addition, the analysis presented in here allows for a complete decoupling of the chain length dependence from monomer to polymer conversion, giving access to the chain length dependence of k_t at any given monomer to polymer conversion up to 80%.

Experimental Section

Materials. Methyl acrylate (99%, Aldrich, M = 86.06 g mol^{-1}) was freed from the inhibitor by percolating over a column of activated basic alumina. 2,2′-azobis(isobutyronitrile) (AIBN, DuPont) was recrystallized twice from ethanol prior to usage. Methyl propionate (99%, Aldrich) was used as received. Methoxy carbonylethyl phenyldithioacetate (MCEP-DA) was synthesized as described earlier.[4]

Polymerizations (DSC). Solutions of methyl acrylate (MA) with AIBN and methyl propionate for the determination of the monomer reaction order or RAFT agent for the CLD-T measurements were thoroughly deoxygenized via four subsequent freeze−pump−thaw cycles and handled inside a glovebox or glovebag filled with dry nitrogen gas. The individual species concentrations can be found in the figure captions describing the associated experiments. Exactly weighed amounts of sample (50−70 mg) were loaded to aluminum pans that were sealed with aluminum lids. The polymerization heat was determined isothermally at 80 °C via measuring the heat flow vs an empty sample pan in a differential scanning calorimeter (Perkin-Elmer DSC 7 with a TAC 7/DX thermal analysis instrument controller). The DSC instrument was calibrated with a standard indium sample of known mass, melting point temperature and known associated enthalpy change. The rate of polymerization, R_p, was calculated using literature values for the heat of polymerization of butyl acrylate (BA, $\Delta H = -78$ kJ mol-1),[15] which should be very similar to the heat of polymerization for MA. The heat of polymerization for MA bulk polymerizations was also independently determined via DSC and determination of the final conversion by SEC ($\Delta H = -78$ kJ mol^{-1}), confirming that the heats of polymerization of BA and MA are identical.

Results and Discussion

In the previous report on the chain length dependent termination rate coefficient in methyl acrylate (MA) bulk free radical polymerization via the RAFT method,[4] the data evaluation was limited to a medium conversion range of up to 40%. In dodecyl acrylate (DA) polymerization, a refinement of our method was introduced, in which the presence of midchain radicals was considered by employing *virtual* higher monomer reaction orders, ω, than unity for the data evaluation procedure (see eq 1).[5]

$$\langle k_t \rangle(t) = \frac{2fk_d[I]_0 e^{-k_d t} - \dfrac{d\left(\dfrac{R_p(t)}{k_p^*([M]_0 - \int_0^t R_p(t)\,dt)^\omega}\right)}{dt}}{2\left(\dfrac{R_p(t)}{k_p^*([M]_0 - \int_0^t R_p(t)\,dt)^\omega}\right)^2} \quad (1)$$

The same evaluation procedure can also be applied to MA polymerizations. Previously, an experimental monomer reaction order for MA of 1.5 was determined at 50 °C in two independent publications.[16] For performing RAFT-CLD-T experiments, higher temperatures are preferred, because the equilibrium constant in the RAFT equilibrium is lowered with increased temperature, which shortens the time to reach steady state radical concentrations in the RAFT system. In addition, the polymerization rate increases resulting in an excellent signal-to-noise ratio in the calorimetric rate measurements. To ensure the validity of the previously determined monomer reaction order[16] at 80 °C, we experimentally determined its value under conditions similar to the conditions used for the RAFT-CLD-T experiments.

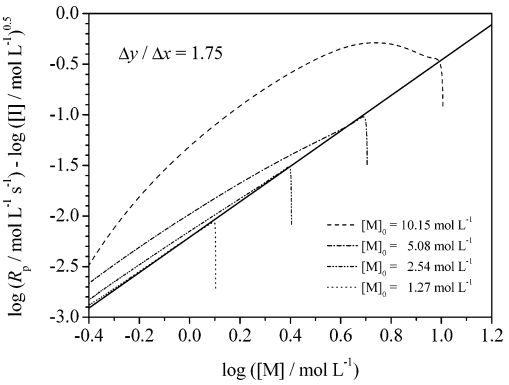


Figure 1. Determination of the monomer reaction order, ω, in methyl acrylate (MA) free radical polymerizations at 80 °C. The plot depicts the evolution of $\log(R_p(t)) - \log [I]^{0.5}$ over the entire conversion range for the bulk and solution polymerizations (with methyl propionate as solvent). The associated initial monomer concentrations are given within the figure. The AIBN concentration was 3.0×10^{-3} mol L^{-1} in each case. The full line was constructed by fitting the initial part of the plots (see text for details) for all concentrations. The slope for the fit represents the reaction order.

For this purpose, calorimetric measurements of the heat of polymerization at 80 °C, using AIBN as initiator and methyl propionate as solvent (which is electronically and sterically very similar to methyl acrylate) were carried out. Since we are mapping the rate of polymerization, R_p, as a function of time up to high conversions, the entire $R_p(t)$ trace of a bulk and three diluted samples can be employed to deduce the reaction order. The advantage of this procedure is that the influence of the polymer concentration on the rate of polymerization can also be determined. However, it must be considered in the calculations that the initiator concentration decreases with increasing reaction time. It was previously shown that the monomer reaction order, ω, can be obtained via eq 2, whereby c is the proportionally constant.[5]

$$\log(R_p) - \log [I]^{0.5} - \log(c) = \omega \log [M] \quad (2)$$

The rate of polymerization can also be used to calculate the actual (current) monomer concentration via eq 3.

$$[M] = [M]_0 - \int_0^t R_p(t)\,dt \quad (3)$$

Since the absolute value of c in eq 2 is insignificant for the slope, ω, the only parameters required with high accuracy are ΔH and k_d (see Table 1). Figure 1 depicts an analysis of the $R_p(t)$ data via eq 2 at 80 °C.

Inspection of Figure 1 indicates that for all monomer concentrations a rapid increase of the rate is observed until the steady state is attained (right-hand side of each curve). After reaching steady state conditions, the rate in the bulk sample increases due to a strong and very early Trommsdorff effect until it subsequently decreases with decreasing monomer concentration. In the diluted samples, the rate decreases immediately after reaching steady-state conditions. The full line, which was constructed by fitting the zero conversion values of all curves, was used to deduce the monomer reaction order via its slope ($\omega = 1.75$).[17] Since the full line represents the rate of polymerization without polymer content, the deviations in all samples to higher rates are a result of the gel effect, depending on the polymer content of each sample.

Although the conversion, X, functionality of the effective propagation rate coefficient can be corrected by considering a higher monomer reaction order, some uncertainty remains regarding the absolute value of k_p, which was extrapolated from PLP data at lower temperatures, where only limited amounts of less reactive midchain radicals are formed.[18] Due to the occurrence of midchain radicals at higher temperatures, the effective propagation rate at 80 °C is somewhat lower and the termination rate may be overestimated in absolute value.

Since the monomer concentration in bulk at low conversions—at which k_p has been originally determined—is different from unity, the propagation rate coefficient, k_p, must be adjusted for the higher monomer reaction order to yield the same initial polymerization rate as under the conditions of a monomer reaction order of unity. The altered propagation rate coefficient, k_p^*, can be calculated via eq 4.[5]

$$k_p^* = k_p[M]_0^{1-\omega} \tag{4}$$

With the literature derived k_p value of 47 400 L mol^{-1} s^{-1},[8] a value of $k_p^* = 8330$ L$^{1.75}$ mol$^{-1.75}$ s^{-1} is returned. The additional kinetic data required for the evaluation of the chain length and conversion dependent termination rate coefficient via eq 1 are listed in Table 1. The experimental methodology is similar to that reported in ref 4, with the present analysis using the same data set (including four different RAFT agent concentrations) up to 80% conversion and eq 1 for the data evaluation.

For a separation of the effects caused by the conversion and chain length dependence, the time dependent k_t data calculated via eq 1 were plotted vs the conversion and chain length axis (calibrated by the experimentally determined M_n vs conversion functions reported in ref 4) in a three-dimensional plot (Figure 2).

The four lines in Figure 2 correspond to the different RAFT agent concentrations (see caption to Figure 2 for the individual reagent concentrations). The data were fitted to a surface graph, using TableCurve 3D as fitting software. As expected from theory, the projection of the data to extremely short chain lengths leads to an almost conversion independent behavior, indicating the validity of the extrapolated projections in the short chain length−high conversion region. The obtained surface function involves several calculation steps and can be found in form of a text file giving the BASIC program in the Supporting Information. The function input parameters are the conversion and the logarithmic chain length, where the conversion range can be between 0.1 and 0.8 and the logarithmic chain length between 0.5 and 3. Thus, specific values for $k_t(X, i)$ can be calculated.

Table 2. α Values (in the Equation $k_t^{i,i} = k_t^0\, i^{-\alpha}$) Obtained for Different Conversions (see Figure 3)

conversion (%)	α
10	0.37
20	0.36
30	0.39
40	0.47
50	0.55
60	0.63
70	0.71
80	0.80

For a more detailed analysis of the result, slash graphs over the conversion range for different chain lengths (Figure 3) and over the chain lengths for different conversions (Figure 4) were prepared.

Figure 3 clearly indicates that the absolute level of k_t and the length of the plateau area with a constant termination rate coefficient decreases with increasing chain length. When comparing the result with conversion dependent termination rate coefficients obtained from nonstationary SP−PLP experiments,[14] it should be noted that the $k_t(X)$ functionality is influenced by the initiator efficiency, which was assumed to decrease linearly with conversion. Such an assumption seems to be justified, since linear or quasi-linear functionalities have been previously reported (see for example ref 19). Since the functionality of f is linear in the enumerator in eq 1, any possible minor deviation from the proposed conversion dependency of f would be directly proportional to k_t, however inducing only limited changes in $\log(k_t)$. In contrast to the data presented here, the SP−PLP determined k_t values are averaged over several chain lengths (i up to 5000) and thus represent an average of k_t at all covered chain lengths. The dotted line in Figure 3, representing the conversion dependence of k_t for $i = 1000$, is in good agreement with the earlier reported conversion dependence (average) of k_t obtained from SP−PLP experiments (which show an initial plateau region of constant k_t up to 15% monomer to polymer conversion at 40 °C and 1000 bar).[14] For shorter chain length, the conversion dependence of k_t is far less pronounced with an increasing plateau area. Such an observation is consistent with a lesser increase in system viscosity and thus a later on-set of a marked decrease in the termination rate coefficient.

It is also gratifying to note that for 20% conversion, Figure 4 returns the same chain length dependence as published before without consideration of midchain radicals.[4] At higher conversions, the decrease of k_t with increasing chain lengths becomes more pronounced and the end of the plateau section, where the conversion dependence becomes effective ($\log(i) = 0.7-1.2$), is visible. This region may be attributed to the limit at which intermolecular entanglements become possible. Since the chain length dependence in general is linear with some sporadic deviations, the graphs were fitted via the frequently used expression $k_t^{i,i} = k_t^0\, i^{-\alpha}$.[20] The α values are increasing with conversion (see Table 2) giving identical values for 30% conversion and similar conversion dependent trends as in the same system previously studied by Buback et al.,[13] thus further underpinning the notion that α is a function of monomer to polymer conversion. Recently there has been a lively discussion within the scientific community on whether

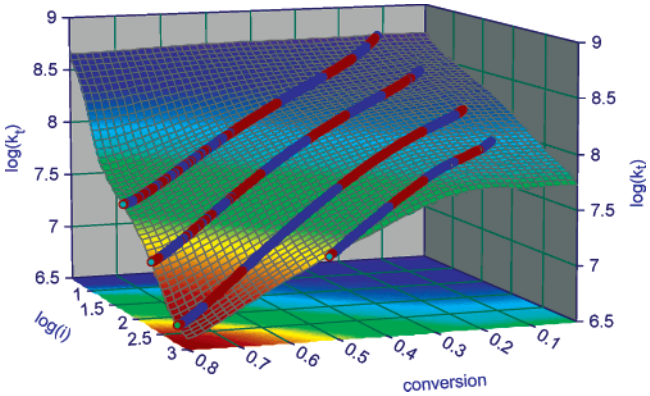


Figure 2. 3-Dimensional plot of the termination rate coefficient for methyl acrylate (MA) radical polymerization at 80 °C, employing four initial RAFT agent concentrations (4.37×10^{-3}, 1.27×10^{-2}, 3.68×10^{-2} and 1.07×10^{-1} mol L^{-1}). The AIBN concentration was close to 3.0×10^{-3} mol L^{-1}. The k_t values are plotted vs monomer conversion and chain length and are fitted to a surface plot using TableCurve 3D software. The correlation of the fit is excellent ($r^2 > 0.9999992$) with the red and blue parts of the experimental data indicating very minor under- and overestimates of the fitted surface. The units for the termination rate coefficient are L mol^{-1} s^{-1}.

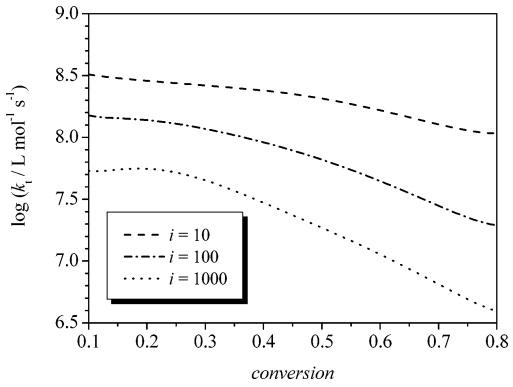


Figure 3. Extracted k_t vs conversion data from Figure 2 for three different chain lengths.

the propagation rate coefficient, k_p, is equally beset by a chain length dependence.[21] A potential chain length dependence of k_p may alter the outcome of the above analysis procedures for small chain lengths.[22] Many techniques (including SP−PLP and RAFT-SP−PLP) are affected by CLD k_p data to some extent. While there is some agreement that k_p is in all likelihood chain length dependent, there is significant disagreement to what extent. Most studies regarding the chain length have been carried out for styrene and methyl methacrylate (MMA), with no report on acrylates. The most significant decrease of k_p with chain length should occur at small i (i.e., when going from 1 to 5 units). However, this most critical region ($i < 3$) is omitted in our three-dimensional analysis and also in the data given in Figure 4. In addition, every conceivable chain length dependency of k_p can be evaluated with our present data with relative ease, resulting in modified $k_t^{i,i}$ functions in the oligomeric region.

Conclusions

The RAFT-CLD-T method has been demonstrated to be capable of mapping termination rate coefficients as both a function of the chain length of the terminating radicals as well as the overall monomer conversion in methyl acrylate free radical polymerizations. MA free

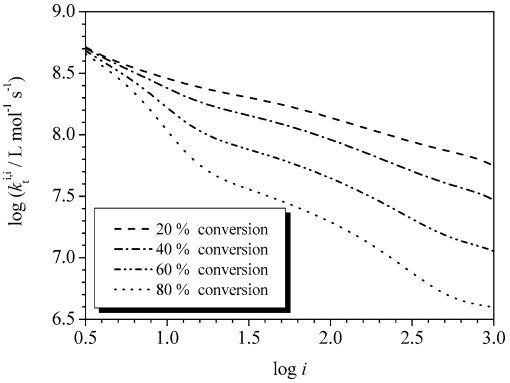


Figure 4. Extracted k_t vs chain length data from Figure 2 for four different conversions.

radical polymerization displays nonidealities due to the presence of less reactive midchain radicals, which lead to a monomer reaction order, ω, exceeding unity ($\omega = 1.75$). The obtained chain length and conversion dependent k_t data, $k_t(X, i)$, can be represented on a three-dimensional surface graph, which subsequently allows for the preparation of slash plots depicting the termination rate coefficient as a function of conversion at various (fixed) chain lengths as well as the chain lengths dependency at a various (fixed) monomer to polymer conversion. The data demonstrate that α (in the frequently used expression $k_t^{i,i} = k_t^0\, i^{-\alpha}$) is dependent on conversion, increasing from 0.36 to 0.80 when going to 80% monomer to polymer conversion. Similarly, the conversion dependence of k_t becomes more pronounced in situations where the terminating radical chain length is large.

Acknowledgment. We are grateful for financial support from the Australian Research Council (ARC) in the form of a Discovery Grant (to C.B.-K. and M.H.S.). T.P.D. acknowledges an Australian Professorial Fellowship (ARC). We thank Dr. Leonie Barner and Mr. Istvan Jacenyik for their excellent management of CAMD.

Supporting Information Available: Text giving the 3D surface in the form of the BASIC program code. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Barner-Kowollik, C.; Buback, M.; Egerov, M.; Fukuda, T.; Goto, A.; Olaj, O. F.; Russell, G. T.; Vana, P.; Yamada, B.; Zetterlund. P. B. *Prog. Polym. Sci.* **2005**, *30*, 605−643.
(2) Vana, P.; Davis, T. P.; Barner-Kowollik, C. *Macromol. Rapid Commun.* **2002**, *23*, 952−956.
(3) Feldermann, A.; Stenzel, M. H.; Davis, T. P.; Vana, P.; Barner-Kowollik, C. *Macromolecules* **2004**, *37*, 2404−2410.
(4) Theis, A.; Feldermann, A.; Charton, N.; Stenzel, M. H.; Davis, T. P.; Barner-Kowollik, C. *Macromolecules* **2005**, *38*, 2595−2605.
(5) Theis, A.; Feldermann, A.; Charton, N.; Davis, T. P.; Stenzel, M. H.; Barner-Kowollik, C. *Polymer* **2005**, *46*, 6797−6809.
(6) Junkers, T.; Theis, A.; Buback, M.; Davis, T. P.; Stenzel, M. H.; Vana, P.; Barner-Kowollik, C. *Macromolecules* **2005**, *38*, 9497−9508.
(7) Johnston-Hall, G.; Theis, A.; Monteiro, M.; Davis, T. P.; Stenzel, M. H.; Barner−Kowollik, C. *Macromol. Chem. Phys.* **2005**, *206*, 2047−2053.
(8) Buback, M.; Kurz, C. H.; Schmaltz, C. *Macromol. Chem. Phys.* **1998**, *199*, 1721−1727.
(9) Busch, M.; Müller, M. *Macromol. Symp.* **2004**, *206*, 399−418.
(10) Plessis, C.; Arzamendi, G.; Alberdi, J. M.; van Herk, A.; Leiza, J. R.; Asua, J. M. *Macromol. Rapid Commun.* **2003**, *24*, 173−177.

(11) Nikitin, A. N.; Hutchinson, R. A. *Macromolecules* **2005**, *38*, 1581−1590.
(12) The initiator decomposition rate coefficient, k_d, of AIBN was determined via on-line UV/VIS spectrometry in ethyl acetate following the protocol described in: Charton, N.; Feldermann, A.; Theis, A.; Davis, T. P.; Stenzel, M. H.; Barner-Kowollik, C. *J. Polym. Sci. Polym Chem.* **2004**, *42*, 5170−5179.
(13) Buback, M.; Egorov, M.; Feldermann, A. *Macromolecules* **2004**, *37*, 1768−1776.
(14) Kowollik, C. Ph.D. Thesis, University of Göttingen, 1999; ISBN 3-89712-705-9.
(15) Madorsky, S. L.; Hart, V. E.; Strauss, S. *J. Res. Natl. Bur. Stand. (U.S.)* **1956**, *56*, 343−349.
(16) (a) Rätzsch, M.; Zschach, I. *Plaste Kautsch.* **1968**, *15*, 12−14. (b) Czajlik, I.; Földes-Berezsnich, T.; Tüdõs, F.; Vértes, E. *Eur. Polym. J.* **1981**, *17*, 131−135.
(17) It should be noted that a certain contribution to the observed reaction order can come from chain length dependent termination itself (see: Russell, G. T. *Macromol. Theory Simul.* **1995**, *4*, 519−548); however, it is extremely likely that the large deviations from unity observed for acrylates are essentially attributable to the presence of midchain radicals in the polymerizing mixture.
(18) Buback, M.; Kurz, C. H.; Schmaltz, C. *Macromol. Chem. Phys.* **1998**, *199*, 1721−1727.
(19) Buback, M.; Huckstein, B.; Kuchta, F.-D.; Russell, G. T.; Schmidt, E. *Macromol. Chem. Phys.* **1994**, *195*, 2117−2140.
(20) Barner-Kowollik, C.; Vana, P., Davis, T. P. In *Handbook of Radical Polymerization*; Matyjaszewski, K., Davis, T. P., Eds.; Wiley and Sons Inc.: New York, 2002; p 209 and literature cited therein.
(21) (a) Willemse; R. X. E.; Staal, B. B. P.; van Herk, A. M.; Pierik, S. C. J.; Klumperman, B. *Macromolecules* **2003**, *36*, 9797−9803. (b) Olaj, O. F.; Vana, P.; Zoder, M.; Kornherr, A.; Zifferer, G. *Macromol. Rapid Commun.* **2000**, *21*, 913−920. (c) Olaj, O. F.; Vana, P.; Zoder, M. *Macromolecules* **2002**, *35*, 1208−1214. (d) Zetterlund, P. B.; Busfield, W. K.; Jenkins, I. D. *Macromolecules* **2002**, *35*, 7232−7237.
(22) Smith, G. B.; Russell, G. T.; Yin, M.; Heuts, J. P. A. *Eur. Polym. J.* **2005**, *41*, 225−230.

MA051370G