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Free Radical Polymerization of Acrylonitrile: Mass Spectrometric Identification of the Nitroxide-Trapped Oligomers Formed in and Estimated Rate Constants for Each of the First Eight Propagation Steps

Per B. Zetterlund, W. Ken Busfield,* and Ian D. Jenkins

School of Science, Griffith University, Nathan, Brisbane, Queensland 4111, Australia

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ABSTRACT: The first 10 addition products in the free radical polymerization of acrylonitrile initiated by AIBN have been trapped and identified; the resulting yields have allowed individual values of the first eight propagation rate constants to be estimated. These are the first realistic experimentally based estimates of a reasonable sequence of early propagation rate constants in any free radical polymerization. In this experiment, the concentration of the nitroxide trapping agent was maintained at a level sufficiently high to prevent the formation of high polymer, yet low enough to allow a competitive monomer addition to form the lower members of the propagation series before being trapped to form the oligomeric addition products. These oligomers were identified and quantified by electrospray ionization mass spectrometry operated in the selected ion recording mode in series with HPLC−UV. The results have allowed the first eight individual propagation rate constants, k_{A_n} ($n = 1-8$), to be estimated:

$$\mathrm{RA}_{n-1}\bullet + \mathrm{A} \xrightarrow{k_{A_n}} \mathrm{RA}_n\bullet$$

The values of k_{A_n} at 75 °C decrease from 5.4×10^3 L mol^{-1} s^{-1} with $n = 1$ to a minimum of 2.1×10^3 L mol^{-1} s^{-1} with $n = 3$ before leveling off with a constant value of 4.8×10^3 L mol^{-1} s^{-1} at $n > 5$.

Introduction

The nitroxide free radical trapping technique is now an established method of both identifying initiation pathways in free radical polymerization[1−9] and measuring relative rate constants for the initiation steps in copolymerization.[10−15] Initially, the method was restricted to systems involving C radical intermediates, but more recently, it has also been shown to give useful information in systems involving S and P radicals.[16−18]

The method relies on the fact that certain nitroxides, although perfectly stable in air under normal temperature conditions, react at close to diffusion-controlled rates with C, S, or P free radicals to form alkoxyamine adducts, which are generally stable. Separation, identification, and quantification of the adducts formed in a free radical reaction performed in the presence of excess nitroxide then identify the reaction pathways prior to the point of trapping. Recently, we have developed a syringe-pump technique for maintaining a low concentration of nitroxide trap during the course of a reaction, thereby effectively slowing the trapping process. Thus, competition for reaction of free radicals with species other than nitroxide, such as monomer molecules, is facilitated prior to eventual trapping. We have previously shown how this method has allowed the chemistry of second- and third-generation radicals formed in propagation processes to be investigated.[8,9]

In this paper, we report that careful optimization of the rate of addition of the nitroxide trap 1,1,3,3-tetramethylisoindolin-*N*-oxyl, TMIO, has enabled the trapping and subsequent identification by electrospray ionization mass spectrometry, ESI-MS, of up to the 11th generation of C radicals for the reaction of cyanoisopropyl radicals with acrylonitrile. The nitroxide trap concentration must be maintained as close to the level below which polymerization occurs (easily observed in this system as polyacrylonitrile precipitates in its monomer) as possible. Quantification of the first nine oligomers has allowed the estimation of individual rate constants for each of the first eight propagation steps. If the trap concentration is constant and known for the duration of the experiment, the rate constants for the addition of monomer units to the growing radical species can be calculated relative to the trapping rate constant. If the trap concentration is not constant, only the ratios of successive values can be obtained using this approach (i.e., $k_{A_n}/k_{A_{n+1}}$). In this work, it has not been possible to maintain the trap concentration sufficiently constant to use the first method; therefore, the second has been applied. The values are dependent, however, on knowledge of the rate constants for radical trapping.

It is generally assumed that the propagation rate constant is independent of chain length when modeling linear free radical polymerization, although evidence in the literature suggests that for shorter chains (less than 20 monomer units) there might be a dependence.[14,15] This paper presents the first realistic estimates of individual rate constants for the early propagation steps in a free radical polymerization.

Experimental Section

Materials. The aminoxyl radical trap, 1,1,3,3-tetramethylisoindolin-*N*-oxyl (TMIO), was prepared as described previously.[19] Acrylonitrile (Aldrich) was purified by distillation and stored under argon in a freezer. The initiator α,α′-azobis(isobutyronitrile) (AIBN) was purified by recrystallization from ethanol and dried under vacuum.

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* To whom correspondence should be addressed.

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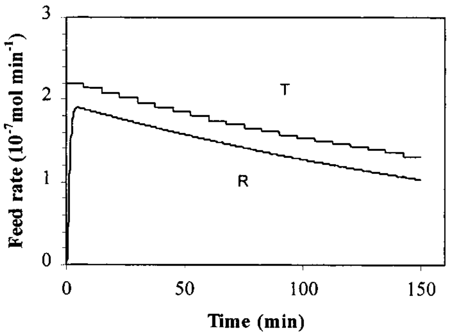

Figure 1. Feed rate of trap and rate of generation of propagation-effective free radicals from the decomposition of AIBN at 75 °C based on $f = 0.6$, corresponding to the most successful experiment with regards to a high yield of oligomers.

Procedure. In a typical experiment, solutions of TMIO and AIBN in neat acrylonitrile were degassed on a high vacuum line with at least three freeze−thaw cycles. Approximately 1 mL of a solution of TMIO in acrylonitrile (approximately 0.027 M) was injected into 3 mL of a solution of AIBN in acrylonitrile (approximately 0.013 M) over 150 min at 75 °C under argon with the aid of a syringe pump (see below for injection rate details). After being cooled, the monomer was evaporated, and the remaining precipitate was dissolved in approximately 1 mL of methanol.

The products were separated and identified with HPLC/ESI-MS using a reverse-phase HPLC column employing methanol/water as eluent (Waters, Radial Pak, C18 analytical column, UV detector set at 270 nm). The ESI-MS was a single-quadrupole VG platform 2 spectrometer with MassLynx version 3.1. All ESI-MS data were acquired in positive ion mode with a cone voltage of 30 V and a source temperature of 90 °C. Elution was in 80:20 methanol:water at a flow rate of 0.6 mL/min with effluent splitting in a T-junction supplying approximately 10 μL/min flow to the ESI-MS source. Sodium acetate (0.024 mM) was added to the solvent to enhance the electrospray ion current.

Nitroxide Trap Feed Rate. The syringe feed rate program for the addition of TMIO to the polymerizing system was designed with the objectives of maintaining a low and relatively constant level of trap concentration throughout the reaction. The level needed to be sufficiently low to maximize the production of trapped oligomers and yet high enough to prevent the formation of high polymer, which is easily observed in the acrylonitrile system by precipitation. Thus, the difference between the rate of addition of trap and the rate of generation of free radicals by the thermal decomposition of AIBN needed to be kept approximately constant throughout the experiment. The rate of generation of radicals from AIBN was computed from the rate constant for thermal decomposition of the initiator,[20] k_d, incorporating the temperature as a function of time to account for the initial temperature increase from ambient to the operating temperature (75 °C). This temperature rise as a function of time was measured in a blank experiment, and the data were fitted with an empirical function to be used in the model. The initiator efficiency f was assumed to be independent of time (i.e., of monomer conversion); a reasonable assumption because the viscosity of the medium remains unchanged (the reactions were carried out in a large excess of monomer). The success of the experiment depends on the delicate balance between the rate of addition of trap and the rate of generation of free radicals. Fine tuning was achieved by multiplying the feed function with a constant until the highest yield of trapped oligomers was obtained.

The trap feed rates for the most successful experiment, with regard to the yields of oligomers, calculated from eqs 1 and 2, where [I] and [R•] are the concentrations of initiator and cyanoisopropyl radicals, respectively, and the calculated rates of generation of free radicals from the decomposition of AIBN at 75 °C are shown in Figure 1.

$$\mathrm{d[I]}/\mathrm{d}t = -k_\mathrm{d}\mathrm{[I]} \tag{1}$$

$$\mathrm{d[R\bullet]}/\mathrm{d}t = 2fk_\mathrm{d}\mathrm{[I]} \tag{2}$$

Computer Simulations. Numerical modeling and parameter optimization procedures were performed using the commercially available software package VisSim Professional (version 2.0j, Visual Solutions Incorporated). Numerical integration was carried out employing the Backward Euler integration algorithm. Simulations were implemented on a standard PC.

Kinetic Analysis. The mechanism for the reaction of initiator (I) with monomer (A) in the presence of trap (T) is outlined below. where R• is the cyanoisopropyl radical.

$$\mathrm{R\bullet + T \rightarrow RT} \qquad k_{\mathrm{T}_0} \tag{4}$$

$$\mathrm{R\bullet + A \rightarrow RA\bullet} \qquad k_{\mathrm{A}_1} \tag{5}$$

$$[\mathrm{R\bullet \rightarrow other\ products}]$$

$$\mathrm{RA\bullet + T \rightarrow RAT} \qquad k_{\mathrm{T}_1} \tag{6}$$

$$\mathrm{RA\bullet + A \rightarrow RA_2\bullet} \qquad k_{\mathrm{A}_2} \tag{7}$$

$$\mathrm{RA}_n\bullet + \mathrm{T} \rightarrow \mathrm{RA}_n\mathrm{T} \qquad k_{\mathrm{T}_n} \tag{6}$$

$$\mathrm{RA}_n\bullet + \mathrm{A} \rightarrow \mathrm{RA}_{n+1}\bullet \qquad k_{\mathrm{A}_{n+1}} \tag{7}$$

By assuming that the reactions are first-order with respect to each reactant, the following kinetic equations can be derived: With the addition of a solution of T in A from the

$$\mathrm{d[R\bullet]}/\mathrm{d}t = 2fk_\mathrm{d}\mathrm{[I]} - k_{\mathrm{T}_0}\mathrm{[R\bullet][T]} - k_{\mathrm{A}_1}\mathrm{[R\bullet][A]} \tag{8}$$

$$\mathrm{d[RA}_n\mathrm{T]}/\mathrm{d}t = k_{\mathrm{T}_n}[\mathrm{RA}_n\bullet]\mathrm{[T]} \tag{9}$$

$$\mathrm{d[RA}_n\bullet]/\mathrm{d}t = k_{\mathrm{A}_n}[\mathrm{RA}_{n-1}\bullet]\mathrm{[A]} - k_{\mathrm{A}_{n+1}}[\mathrm{RA}_n\bullet]\mathrm{[A]} - k_{\mathrm{T}_n}[\mathrm{RA}_n\bullet]\mathrm{[T]} \tag{10}$$

$$\mathrm{d[T]}/\mathrm{d}t = (\mathrm{d}n/\mathrm{d}t)_{\mathrm{add}}/V(t) - \mathrm{[T]}\Sigma(k_{\mathrm{T}_n}[\mathrm{RA}_n\bullet]) \tag{11}$$

syringe pump, all concentrations need to be corrected for the continuous change in volume, and a term had to be added to the differential equation of [T]. Here, $V(t)$ is the volume as a function of time, and $(\mathrm{d}n/\mathrm{d}t)_{\mathrm{add}}$ is the number of moles of T added to the reaction vessel per unit of time.

Consideration of the kinetics of the competing reactions with $\mathrm{RA}_n\bullet$ by monomer and trap leads to the exact eq 12a, where parentheses denote product yields. If the concentrations of monomer and trap remain constant for the duration of the experiment, then the simplified eq 12b is valid.

$$\frac{k_{\mathrm{A}_n}}{k_{\mathrm{T}_{n-1}}} = \frac{\sum_{i=n}^{\infty}(\mathrm{RA}_i\mathrm{T})}{(\mathrm{RA}_{n-1}\mathrm{T})} \times \frac{\int \mathrm{[T]}[\mathrm{RA}_{n-1}\bullet]\mathrm{d}t}{\int \mathrm{[A]}[\mathrm{RA}_{n-1}\bullet]\mathrm{d}t} \tag{12a}$$

$$\approx \frac{\mathrm{[T]}\sum_{i=n}^{\infty}(\mathrm{RA}_i\mathrm{T})}{\mathrm{[A]}(\mathrm{RA}_{n-1}\mathrm{T})} \tag{12b}$$

Thus, if the monomer and trap concentrations are constant and if the k_{T_n}'s are known, each value of k_{A_n} can be calculated from the yields of $\mathrm{RA}_n\mathrm{T}$ and the sum of the yields of all of the higher oligomers. Although [A] can be assumed constant, because it is always in large excess, [T] could not be maintained constant throughout any experiment. HPLC/UV analysis showed that [T] increased with time throughout an experiment. Kinetic simulations performed by numerical integration of eqs 1 and 8−11 indicated that not taking this into account could cause a significant error in the estimated rate constants using eq 12b.

Ratios of successive propagation rate constants can be determined from eq 13b, which was derived by dividing versions of eq 12b for successive propagation steps. In this case, the dependence on variations in [T] is significantly reduced, because the absolute validity of eq 13b requires only that the radical concentrations remain proportional to each other throughout the experiment.

$$\frac{(\mathrm{RA}_n\mathrm{T})\sum_{i=n}^{\infty}(\mathrm{RA}_i\mathrm{T})}{(\mathrm{RA}_{n-1}\mathrm{T})\sum_{i=n+1}^{\infty}(\mathrm{RA}_i\mathrm{T})} = \frac{k_{\mathrm{A}_n}k_{\mathrm{T}_n}\int[\mathrm{RA}_{n-1}\bullet]\,\mathrm{d}t\int[\mathrm{RA}_n\bullet][\mathrm{T}]\,\mathrm{d}t}{k_{\mathrm{A}_{n+1}}k_{\mathrm{T}_{n-1}}\int[\mathrm{RA}_{n-1}\bullet][\mathrm{T}]\,\mathrm{d}t\int[\mathrm{RA}_n\bullet]\,\mathrm{d}t} \qquad (13a)$$

$$\approx \frac{k_{\mathrm{A}_n}k_{\mathrm{T}_n}}{k_{\mathrm{A}_{n+1}}k_{\mathrm{T}_{n-1}}} \qquad (13b)$$

Thus, in this work, $k_{\mathrm{A}_1}/k_{\mathrm{T}_0}$, was estimated from computer simulations of radical, trap, and RT concentrations as a function of time and comparison with the measured yield of RT. The calculation of radical concentration requires knowledge of both k_d and the initiator efficiency, *f*. The latter was derived by comparing the total yield of trapped oligomers, ($\mathrm{RA}_n\mathrm{T}$), with the loss of initiator in the experiment. The value was found to be 0.69, which is in good agreement with literature values for AIBN.[21] As a further check on self-consistency, the simulations allowed the derivation of the final trap concentration, $[\mathrm{T}] = 2.85 \times 10^{-4}$ M. This compares very favorably with the value measured by HPLC/UV of $[\mathrm{T}] = 2.89 \times 10^{-4}$ M. Values of $k_{\mathrm{A}_n}/k_{\mathrm{T}_{n-1}}$ for $n > 1$ were subsequently calculated from k_{A_1} using eq 13b.

Results and Discussion

HPLC/ESI-MS Separation and Quantification. Satisfactory separation of the lower alkoxyamines, RT, RAT, $\mathrm{RA}_2\mathrm{T}$, and $\mathrm{RA}_3\mathrm{T}$, was readily achieved by reverse-phase HPLC with a C18 analytical column (methanol/water), and the products were identified by ESI-MS. The higher oligomeric alkoxyamines, $\mathrm{RA}_n\mathrm{T}$, $n > 3$, on the other hand, exhibited extensive overlapping due to the presence of the diastereomers causing complex and relatively broad elution profiles. The compound $\mathrm{RA}_n\mathrm{T}$ has 2^n stereoisomers, if head-to-tail addition only is assumed. The combination of the low abundance with broad and overlapping elution profiles of the higher oligomers ($n > 3$) means that quantification by HPLC coupled with UV detection lacks precision.

Selected ion recording (SIR) chromatography (i.e., the monitoring of certain *m*/*z* ranges) in the positive ion mode proved to be an effective method of not only detecting the $\mathrm{RA}_n\mathrm{T}$ oligomers but also examining the HPLC elution profiles of individual oligomers. The IC detection limit was improved when the oligomers were separated to some extent by HPLC (methanol/water) as opposed to using injections straight into the ESI-MS unit. For each $\mathrm{RA}_n\mathrm{T}$ species, three different molecular ions were detected: $[(\mathrm{RA}_n\mathrm{T})\mathrm{H}]^+$, $[(\mathrm{RA}_n\mathrm{T})\mathrm{Na}]^+$, and $[(2\mathrm{RA}_n\mathrm{T})\mathrm{Na}]^+$, with $[(\mathrm{RA}_n\mathrm{T})\mathrm{H}]^+$ being by far the most abundant. The detection limit was even further improved by adding sodium acetate to the methanol (0.024 mM), thereby concentrating the IC for each oligomer into one adduct only ($[(\mathrm{RA}_n\mathrm{T})\mathrm{Na}]^+$) and increasing the ionization efficiency (i.e., the signal-to-noise ratio of the ion current is increased). Ion currents of the molecular ions $[(\mathrm{RA}_n\mathrm{T})\mathrm{Na}]^+$ for $3 \leq n \leq 10$ are displayed in Figures 2 and 3. The species RT, RAT, and $\mathrm{RA}_2\mathrm{T}$ have been shown to exhibit molar responses for the ion current different than those for the higher oligomers. The concentrations decrease significantly with increasing *n*, thus making it difficult to directly compare elution profiles of $\mathrm{RA}_n\mathrm{T}$'s.

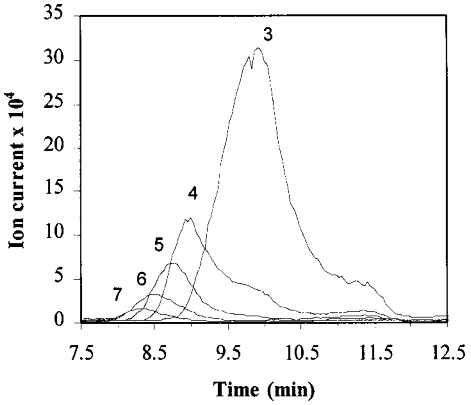

Figure 2. SIR ion current chromatograms of the molecular ions $[(\mathrm{RA}_n\mathrm{T})\mathrm{Na}]^+$, $3 \leq n \leq 7$.

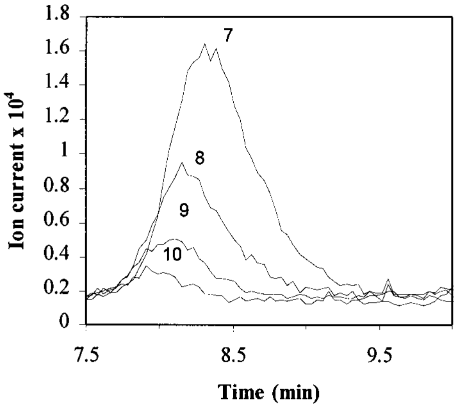

Figure 3. SIR ion current chromatograms of the molecular ions $[(\mathrm{RA}_n\mathrm{T})\mathrm{Na}]^+$, $7 \leq n \leq 10$.

In light of the problems associated with HPLC−UV, quantification of this particular system from the ESI-MS ion current was investigated. It is generally recognized that great caution is warranted when using ESI-MS quantitatively.[22−25] It has been reported, however, that it is possible to extract quantitative information in some cases when the species are sufficiently “similar” chemically and physically (e.g., determination of narrow polymer molecular weight distributions).[26] The reliability of the ESI-MS method to quantify this particular series of oligomers has been thoroughly investigated, and the detailed results will be published elsewhere.[27] Briefly, this was done by comparing the total UV with the ion current response for the system RT + A at 110 °C (i.e., the integral of the ion current). At this temperature, the alkoxyamine dissociates sufficiently to allow the addition of monomer (this is referred to as nitroxide-mediated “living” free radical polymerization), and an oligomeric mixture of $\mathrm{RA}_n\mathrm{T}$ is generated. The UV response for the sum of the species $\mathrm{RA}_{3-12}\mathrm{T}$ was proportional to that of the ion current (operated in the

Table 1. Yield of Oligomers and the Estimated Rate Constants for the Addition of the *n*th Unit of A in the Propagation Step

n	$[RA_nT]$ (mol L^{-1})	$(RA_nT)/(RA_{n+1}T)$	$k_{A_n} \times 10^{-3}$ (L mol^{-1} s^{-1})
0	3.73×10^{-3}	2.14	
1	1.74×10^{-3}	4.62	5.39
2	3.77×10^{-4}	6.13	2.43
3	6.15×10^{-5}	3.68	2.10
4	1.67×10^{-5}	2.89	3.77
5	5.78×10^{-6}	2.93	4.80
6	1.97×10^{-6}	2.82	4.76
7	6.99×10^{-7}	2.99	4.86
8	2.34×10^{-7}	2.86	4.60
9	8.18×10^{-8}		

selected ion recording mode under the conditions described below and with the assumption that T is the only UV chromophore) as the reaction progressed, i.e., as the distribution of RA_nT species changed. This indicated a true molar response for these species under these particular experimental and instrumental conditions. However, it should be borne in mind here that the method used to check the validity of the quantitative use of the ESI-MS data is by nature more sensitive to the species that are more abundant in the RA_nT distribution. The abundance of the higher oligomers was considerably lower than say $RA_{3-5}T$, and thus, any changes in molar response for species with higher n would be more difficult to detect. The oligomeric mixture could thus be quantified by use of UV data for RA_nT ($0 \le n \le 3$) and ion current data for RA_nT ($3 \le n \le 12$). Absolute values of the concentrations were obtained by employing the concentration of T in all its forms as an internal standard, as the amount of T added was known (Table 1). The ion current-based concentrations were computed from the average of six measurements, giving a 95% confidence interval as the average value ±15% (this refers to the reproducibility only of the ion current data). In addition to the products RA_nT, other side products that have been observed and identified previously were obtained[7] in the following percentage yields: ROAT 0.2, RO_2AT 0.4, HAT 2.9, HOAT 0.3 (R = cyanoisopropyl, A = $-CH_2CH(CN)-$, and T = trap; formulas are based on parent peaks in the MS only, and therefore precise structures are uncertain). The mechanism of formation of HAT is uncertain.[9] Separate experiments were carried out to ensure that no significant amount of HAT was formed from RT or RAT, thereby influencing the ratios of RA_nT's which would otherwise be governed by k_{A_n}'s and k_{T_n}'s only. RT and RAT were heated at 75 °C in acrylonitrile for 150 min, resulting in negligible amounts of HAT (less than 2%, i.e., negligible in the context of the small amounts of RT and RAT involved in experiments with A).

Estimation of Rate Constants. It was assumed that the rate of trapping was the same for all species in the system, and k_T was set equal to 10^9 L mol^{-1} s^{-1}.[28] All rate constants estimated from the model will thus be based on this assumed value of k_T (the estimated k_{A_n}'s are proportional to k_T; i.e., a 10% increase in the value of k_T used will result in a 10% increase in all k_{A_n}'s). Examination of data published by Bowry and Ingold[29] indicate that the difference in the rate of trapping between R• and RA_n• is unlikely to be greater than 20% as the methyl group of the cyanoisopropyl radical is "replaced" by a hydrogen atom of acrylonitrile. In the calculations, it was assumed that $RA_{10}T$ and $RA_{11}T$ were present in the same ratios as RA_8T/RA_9T (i.e., $(RA_9T)/(RA_{10}T) = (RA_{10}T)/(RA_{11}T) = 2.9$) to avoid inaccuracies in the summation terms of eq 13b. The estimated values of k_{A_n} are shown in Table 1. The value of k_{A_1}, the rate constant for the addition of A to cyanoisopropyl radicals is greater than all succeeding rate constants for the addition of A to terminal acrylonitrile radical end groups. This is consistent with the fact that the cyanoisopropyl radical is more nucleophilic than the species RA_n• toward the electron-deficient acrylonitrile monomer due to the presence of the electron-donating methyl group. The most interesting and, perhaps, surprising result from this work is the quite significant variation in propagation rate constants in the range $n = 2-5$. The values exhibit a distinct minimum at $n = 3$ before increasing and leveling off to a constant value in the range $n = 5-8$. As the chain length of the radical species increases, one would expect k_{A_n} to asymptotically approach the value of the global propagation rate constant for high polymer, k_p. The values of $k_{A_{5-8}}$ are approximately constant, suggesting that for $n \ge 5$ the value of k_p for high polymer is 4.8×10^3 L mol^{-1} s^{-1}. Unfortunately, no accurate data is available for the polymerization of acrylonitrile;[30] the data in the literature are unacceptably scattered. However, the rate constants for the addition of cyanoisopropyl radicals to a wide range of monomers have been measured by Heberger and Fischer:[31] the value for reaction with acrylonitrile at 42 °C is 2.02×10^3 L mol^{-1} s^{-1}. This is in good agreement with the value determined in this work, when activation energies are taken into account ($k_{A_1} = 5.39 \times 10^3$ L mol^{-1} s^{-1} at 75 °C). PLP data is available for the polymerization of methacrylonitrile by Shipp et al.[32] According to the Arrhenius parameters, k_p (methacrylonitrile) at 75 °C is 94 L mol^{-1} s^{-1}. This is considerably lower than the value obtained here for $k_{A_{5-8}}$ (4.8×10^3 L mol^{-1} s^{-1}). It is known, however, that acrylonitrile propagates approximately 3 orders of magnitude faster than methacrylonitrile at 25 °C.[33]

Some limited information on early kinetic data for the free radical polymerization of other monomers is available. Moad et al.[14] employed the nitroxide trapping technique with an excess of nitroxide to study the reactions of Ph• and $PhCO_2$• generated by benzoyl peroxide (BPO) with methyl acrylate (MA). By use of the same definitions as in this work, the ratios of successive propagation rate constants at 60 °C in bulk MA for the initiating radical Ph• were found to be $k_{MA_1}:k_{MA_2}:k_{MA_3} = 1357:1.07:1$. Deady et al.[15] carried out a modeling study of the pulsed laser photolysis (PLP) process and found that experimentally obtained molecular weight distributions (MWD) of styrene in benzene initiated by 2,2′-azobis(methyl isobutyrate) could best be explained by invoking a chain-length dependence of k_p such that $k_{S_1}:k_{S_2}:k_{S_3}:k_p = 109:14.6:3.3:1$, i.e., a much larger variation than that observed for acrylonitrile in this work. It was recognized, however, that this "improvement" in MWD, in terms of the position of the point of inflection on the MWD plot, was within experimental error.

Conclusions

It has been shown that careful optimization of the nitroxide trapping technique associated with the identification and quantification of trapped oligomers by HPLC/ESI-MS can give valuable kinetic information for the early propagation steps in the free radical polymerization of acrylonitrile initiated by AIBN. The first eight propagation rate constants have been estimated, and the results show that k_{A_n} at 75 °C decreases from $n = 1-3$ ($k_{A_1}:k_{A_2}:k_{A_3} = 2.6:1.2:1$), increases from $n = 3-5$ ($k_{A_3}:k_{A_4}:k_{A_5} = 1:1.8:2.3$), and remains approximately constant for $n > 5$, with a value of $k_{A_n} = 4.8 \times 10^3$ L mol^{-1} s^{-1}.

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