Macromolecules **2002,** *35,* 7232−7237

Free Radical Polymerization of Styrene: Mass Spectrometric Identification of the First 15 Nitroxide-Trapped Oligomers and Estimated Propagation Rate Coefficients

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Received March 4, 2002; Revised Manuscript Received June 10, 2002

ABSTRACT: The first 15 addition products in the free radical polymerization of styrene initiated by AIBN have been trapped using a nitroxide trapping technique. In this experiment, the concentration of trap is maintained at a level sufficiently high to prevent the formation of high polymer yet low enough to allow competitive monomer addition to form the lower members of the propagation series before being trapped to form the oligomeric addition products. These oligomers have been identified and quantified by electrospray ionization mass spectrometry (ESI−MS) in series with HPLC−UV. The observation of single chromatographic peaks for each oligomer indicates that the rate of formation of branched products is negligible. The results have allowed the first 14 individual propagation rate coefficients, k_{S_n} ($n = 1-14$), to be estimated based on the assumption that the successive trapping rate coefficients are constant. $RS_n^\bullet + S \xrightarrow{k_{S_n}} RS_{n+1}^\bullet$. The results show that at 75 °C k_{S_n} increases significantly from $n = 1$ to $n = 3$ and then stays constant to $n = 7$. The value of k_{S_n} for $n = 3-7$ is $6.5 \pm 2 \times 10^4$ M^{-1} s^{-1}. In the range $n = 7-14$, the value decreases steadily by a factor of about 2. The value at $n = 14$ is significantly higher than the IUPAC recommended value for high polymer of 565 M^{-1} s^{-1} at 75 °C. The rate coefficient for the addition of cyanoisopropyl radicals to styrene ($n = 0$) is $1.0 \pm 0.4 \times 10^4$ M^{-1} s^{-1} at 75 °C.

Introduction

The nitroxide free radical trapping technique is now an established method of identifying initiation pathways in free radical polymerization[1−13] and of measuring relative rate coefficients for the initiation steps in copolymerization.[14−18] Initially the method was restricted to systems involving carbon radical intermediates, but more recently, it has also given useful information in systems involving sulfur and phosphorus radicals.[5,19,20] 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 carbon-centered 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 down 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 used this method to investigate the chemistry of up to the 10th generation radicals formed in propagation processes.[9,10,21]

Propagation rate coefficients in free radical polymerization reactions have traditionally been assumed to be independent of chain length. There is, however, an increasing body of experimental evidence indicating that the first few propagation steps exhibit a dependence on chain length[18,21−24] and that there is a long-range chain dependence due possibly to a change in local monomer concentration associated with coil formation.[25] In this paper, we report that careful optimization of the rate of addition of the nitroxide trap 1,1,3,3-tetramethylisoindolin-*N*-oxyl has enabled the trapping and subsequent identification by electrospray ionization mass spectrometry (ESI−MS) of up to the 15th generation of carbon-centered radicals in the reaction of cyanoisopropyl radicals with styrene. The nitroxide trap concentration must be maintained as close as possible to the level below which polymerization occurs. Quantification of the first 15 oligomers has allowed estimation of individual rate coefficients for each of the first 14 propagation steps relative to the trapping rate coefficients.

Experimental Section

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

Computer Simulations. Numerical modeling and parameter optimization procedures were performed on a standard PC 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.

The mechanism for the reaction of initiator radicals ($R^\bullet$) with monomer (S) in the presence of trap (T) used in the simulations is outlined as follows:

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10.1021/ma020325v CCC: $22.00

$$\mathrm{I} \xrightarrow{k_\mathrm{d}} 2\mathrm{R}^\bullet \tag{1}$$

$$\mathrm{R}^\bullet + T \xrightarrow{k_{\mathrm{T}_0}} \mathrm{RT} \tag{2}$$

$$\mathrm{R}^\bullet + \mathrm{S} \xrightarrow{k_{\mathrm{S}_0}} \mathrm{RS}^\bullet \tag{3}$$

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

$$\mathrm{RS}^\bullet + \mathrm{T} \xrightarrow{k_{\mathrm{T}_1}} \mathrm{RST} \tag{4}$$

$$\mathrm{RS}^\bullet + \mathrm{S} \xrightarrow{k_{\mathrm{S}_1}} \mathrm{RS}_2^\bullet \tag{5}$$

$$\mathrm{RS}_n^\bullet + T \xrightarrow{k_{\mathrm{T}_n}} \mathrm{RS}_n\mathrm{T} \tag{6}$$

$$\mathrm{RS}_n^\bullet + \mathrm{S} \xrightarrow{k_{\mathrm{S}_n}} \mathrm{RS}_{n+1}^\bullet \tag{7}$$

Procedure. A successful experiment is one where the trap concentration is low enough to allow formation of oligomeric products while still sufficiently high to prevent polymerization. To achieve these experimental conditions, trap solution was added to the reaction vessel throughout the reaction using a computer-controlled syringe pump (the feed rate program was written in BASIC). The feed rate program consisted of two regions: an early region (the first 78 s), where a high feed rate was used to establish the desired trap concentration, and the remaining region, where the feed rate was set equal to the rate of generation of free radicals from the thermal decomposition of the initiator. The experiment was designed with the aid of computer modeling and simulations of the entire system by numerical integration of eqs 8−12, taking into account the initial temperature increase from ambient to the operating temperature (75 °C). A literature value was used for the rate coefficient for thermal decomposition (k_d) of AIBN at 75 °C,[26] and the trapping rate coefficient k_{T_0} was set equal to 10^9 M^{-1} s^{-1}.[27−31] The temperature as a function of time in the initial stage of the experiment was measured in a blank experiment, and the data were fitted with an empirical function to be used in the model. The value obtained for the initiator efficiency in our previous study using AIBN and acrylonitrile at 75 °C, $f = 0.69$, was employed in the simulations.[21] The value of f was assumed to be independent of time (i.e., of monomer conversion; a reasonable assumption since the viscosity of the medium remains relatively unchanged as the reactions were carried out in a large excess of monomer to low conversions; see Table 1). In the simulations aimed at optimizing the trap solution feed rate, the term in eq 9 describing the addition of S to R$^\bullet$ was excluded since it was here assumed that all k_{T_n}'s were equal. In other words, the predicted trap concentration would not be affected by the extent of oligomer formation. This assumption does not influence the conclusions of this work; it was merely used in the part of the work concerned with optimization of the experimental conditions. The same can be said for the use of f obtained with acrylonitrile. The target trap concentrations ([T] (planned)) displayed in Table 1 are the trap concentrations predicted by the model. According to the model predictions, the trap concentrations remain close to constant throughout each experiment.

Solutions of T and AIBN in neat S were degassed on a high vacuum line with at least three freeze−thaw cycles. 1.0 mL of a solution of T in S (experiment 1, 0.048 M; experiment 2, 0.057 M; experiment 3, 0.014 M) was gradually injected into 3.0 mL of a solution of AIBN in S (experiment 1, 0.023 M; experiment 2, 0.032 M; experiment 3, 0.011 M) at 75 °C under argon with the aid of the computer-controlled syringe pump. The reaction times (experiment 1, 154 min; experiment 2, 123 min; experiment 3, 75 min) were not predetermined, but simply the time taken for the syringe to dispense all trap solution at the precalculated rate based on the concentrations of T (in the syringe) and AIBN (in the reaction vessel). When the syringe was almost empty, the reaction vessel was cooled rapidly in liquid nitrogen, the monomer was evaporated, and the remaining precipitate was dissolved in approximately 1 mL of acetonitrile/chloroform.

Table 1. Data for Successful Experiments (Temperature: 75 °C)

	molar extinction coeff (M^{-1} cm^{-1})	expt 1	expt 2	expt 3
initial [AIBN] (M)		0.023	0.032	0.011
initial [T] (M)		0.048	0.057	0.014
[T] (planned) (mM)		1.33	1.60	0.52
[T] (final, measd) (mM)		0.254	0.551	0.203
time (min)		154	123	75
monomer convn (%)		0.091	0.026	0.0068
f (calcd)		0.72	0.70	0.67
yield RS$_n$T relative to RT				
$n = 0$	713	100	100	100
$n = 1$	1106	14.16	12.69	21.2
$n = 2$	1499	2.32	1.26	1.32
$n = 3$	1616	1.41	0.42	0.95
$n = 4$	1648	1.20	0.28	0.57
$n = 5$	1731	1.28	0.24	0.43
$n = 6$	1669	1.07	0.14	0.28
$n = 7$	1680	1.00	0.10	0.20
$n = 8$	1648	1.04	0.09	0.15
$n = 9$	1765	1.04	0.06	0.09
$n = 10$	1881	0.89		
$n = 11$		0.92		
$n = 12$		0.91		
$n = 13$		0.77		
$n = 14$		0.68		
$n = 15$		0.55		

Product Analysis. The products were separated and identified with HPLC/ESI−MS using a reverse phase HPLC column at room temperature employing acetonitrile/water as eluent (Waters, Radial Pak, C18 analytical column, pore size 5 μm, UV detector set at 270 nm). The ESI−MS was a single quadrupole VG platform 2 spectrometer with MassLynx Version 3.1 software. All ESI−MS data were acquired in positive ion mode with a cone voltage 30 V, a source temperature 90 °C, a flow rate of 0.6−1 mL/min and with effluent splitting supplying approximately 10 μL/min flow to the ESI−MS source. Selected ion recording (SIR) chromatography (monitoring of certain m/z ranges) was employed as a means of quantification in some cases (see Results and Discussion). The SIR experiments were carried out using methanol/water as 90% of the eluent, the remaining 10% of the eluent being a 2.22×10^{-4} M solution of sodium acetate in 50:50 methanol/acetonitrile. It has been shown previously[21] that this technique enhances the sensitivity by monitoring the molecular ions $[(\mathrm{RS}_n\mathrm{T})\mathrm{Na}]^+$.

Absolute product concentrations were calculated based on the amount of trap added, treating the total absorbance of all products containing T as an internal standard. The UV extinction coefficients employed in the product quantifications were estimated as follows. It has been shown recently that there is a chain length dependence of the chromophoric contribution of phenyl groups in styrene oligomers.[32] We have estimated the contribution of each phenyl group for each chain length at 271 nm from the UV spectrum of each oligomer given in ref 32. If we assume that the contribution of the end group, T, is independent of chain length, the extinction coefficient of each oligomer has been estimated by the additivity rule. The contribution for T was the same as that used in our previous work and was equal to that measured for RT (713 M^{-1} cm^{-1}). The contributions for each phenyl group on the chain with $n = 10$ was assumed to be equal to that in the oligomer with $n = 9$ (the highest oligomer examined in ref 32). Estimated molar extinction coefficients at 270 nm are shown in Table 1.

Results and Discussion

In the reaction of cyanoisopropyl radicals with styrene in the presence of the nitroxide trap, the number of

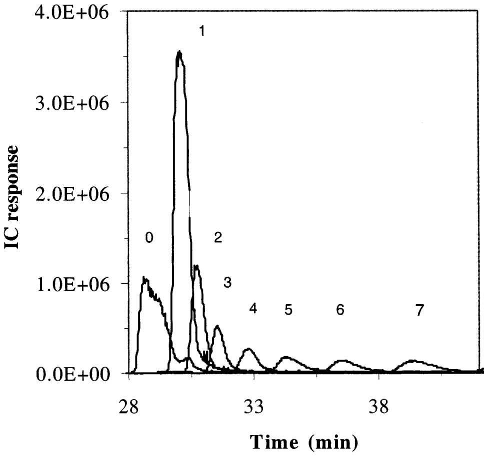

Figure 1. HPLC−SIR ion current (IC) chromatograms of the molecular ions $[(RS_nT)Na]^+$ for $n = 0{-}7$ produced in experiment 1. Initial concentrations: reaction vessel 0.023 M AIBN in styrene; syringe pump 0.048 M nitroxide in styrene; temperature 75 °C; reaction time 154 min.

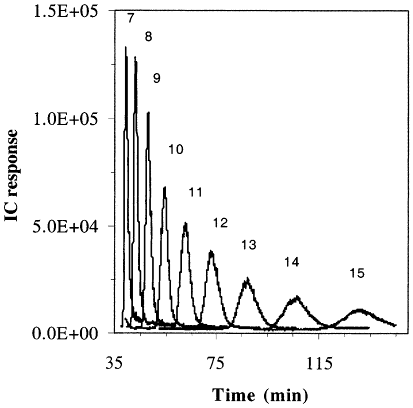

Figure 2. HPLC−SIR ion current (IC) chromatograms of the molecular ions $[(RS_nT)Na]^+$ for $n = 7{-}15$ produced in experiment 1. For details, see Figure 1 caption.

trapped oligomers that can be separated, observed, and identified by HPLC/ESI−MS depends critically on maintaining the optimum concentration of nitroxide in the system throughout the reaction. As explained in the Experimental Section, this was planned and executed by computer simulation of the radical production, which was then used to design the computer control of the syringe addition of nitroxide. The computer simulation, however, requires several uncertain constants and is based on an idealized mechanism and is not guaranteed to give optimum success at the first attempt. Its main use turned out to be the optimization of the process. Proof of the method lies in the observation of the trapped oligomers. Our most successful experiment (experiment 1) yielded the observation of 15 trapped oligomers. The ESI−MS ion currents (IC) as a function of HPLC elution time are shown in Figures 1 and 2. The peaks, obtained by SIR, are all single peaks for each oligomeric mass (RS_nT) indicating that linear isomers elute together and suggesting the absence of any branched isomers.

Some minor products with an overall yield of less than 1% of the total products were observed. These were the oxygenated species ROST, which has been observed previously in a similar experiment,[9] unidentified product(s) (denoted A in Figure 3) appearing in the UV but not the IC trace, and an unidentified species of *m*/*z* 398 (denoted B in Figure 3; this product may have the structure HSST, but this is unconfirmed). The yields of the unidentified species were calculated from UV-data assuming the extinction coefficients were equal to that of the nitroxide. There were no peaks observed in the IC trace corresponding to termination products formed by combination or disproportionation reactions of oligomer radicals. Natural termination processes are therefore negigible in this system as would be expected since the trap concentration is orders of magnitude greater than the concentrations of oligomeric radicals.

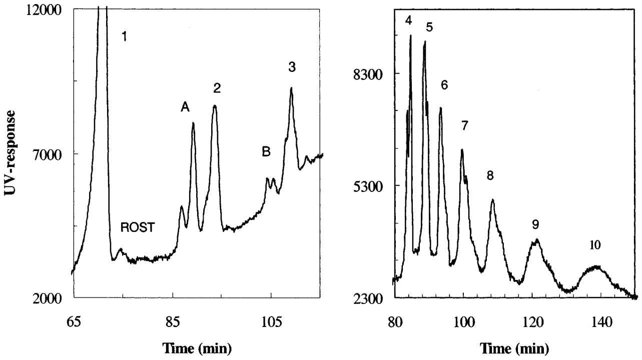

Figure 3. HPLC−UV chromatograms of the products from experiment 1, displaying peaks corresponding to RS_nT for $n = 1{-}10$, ROST, and side products A and B (see text). For details of experiment 1, see Figure 1 caption.

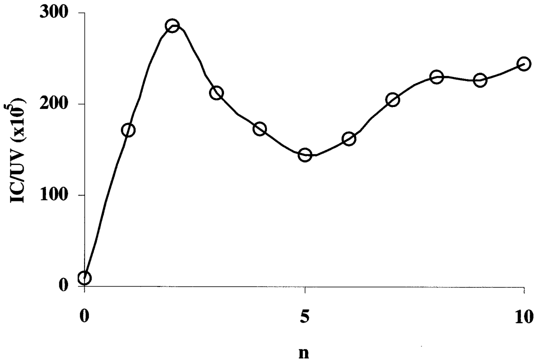

Figure 4. Ratio of the SIR ion current (IC) response (i.e., integral with respect to time) of the molecular ions $[(RS_nT)Na]^+$ to the corresponding concentrations obtained from the UV data as a function of *n* for experiment 1. For details, see Figure 1 caption.

It is well-known that caution is warranted when attempting to use ESI−MS quantitatively.[33−37] It does however appear that, in some cases, it is possible to use the data.[21,37] The IC sensitivities of the trapped oligomers produced in this work were found to vary along the series and, in particular, from experiment to experiment. Without pure samples, normal calibration methods were unavailable. It was therefore not practicable to use IC's to calculate relative concentrations for the whole series of trapped oligomers as was done in the case of acrylonitrile.[21] The clean separation of the oligomers by HPLC (see Figure 3), however, meant that quantification from the UV absorption scan was possible. The UV response was less sensitive than the IC response in experiment 1, resulting in data for only the first 10 oligomers by UV analysis. A graph of the IC response divided by the oligomer concentration from the UV data, shown in Figure 4, indicates that in this experiment, the IC response approaches a constant linear trend in sensitivity with oligomer concentration for the higher oligomers. This has allowed an estimation of the concentrations of oligomers $n = 11-15$ from the IC responses in the case of experiment 1. The results for experiment 1, together with the results for the next two most successful experiments, in terms of the number of trapped oligomers observed (nine in each case), are shown in Table 1. The maximum number of oligomers observed in other experiments performed was five, indicating less than optimum conditions.

The following kinetic analysis is based on the mechanism given in the computer simulation section, assuming that the reactions are first order with respect to each reactant.

$$d[I]/dt = -k_d[I] \tag{8}$$

$$d[R^\bullet]/dt = 2fk_d[I] - k_{T_0}[R^\bullet][T] - k_{S_0}[R^\bullet][S] \tag{9}$$

$$d[RS_nT]/dt = k_{T_n}[RS_n^\bullet][T] \tag{10}$$

$$d[RS_{n+1}^\bullet]/dt = k_{S_n}[RS_n^\bullet][S] - k_{S_{n+1}}[RS_{n+1}^\bullet][S] - k_{T_{n+1}}[RS_{n+1}^\bullet][T] \tag{11}$$

$$d[T]/dt = (dn/dt)_{add}/V(t) - [T]\Sigma(k_{T_n}[RS_n^\bullet]) \tag{12}$$

All concentrations are corrected for the continuous change in volume, caused by the action of the syringe pump, by addition of a term to the differential equation of [T] (eq 12). Here V(t) is the volume as a function of time, and $(dn/dt)_{add}$ is the number of moles of T added to the reaction vessel per unit time.

If [T] and [S] are constant, the ratios of rate constants k_{S_n}/k_{T_n} referring to the successive propagation steps are given by eq 13 (parentheses denote product yields).[21]

$$\frac{k_{S_n}}{k_{T_n}} = \frac{[T]\sum_{i=n+1}^{\infty}(RS_iT)}{[S](RS_nT)} \tag{13}$$

An alternative approach is to consider the summation of product yields for any pair of trapped oligomers, RS$_n$T and RS$_m$T. This yields eq 14, which is independent of the values of [S] and [T]. Extensive computer simulations by numerical integration of eqs 8−12 using different feed rates, yielding both constant and nonconstant [T], for successive pairs of oligomers ($m = n + 1$) have established that eq 14 is much less sensitive than eq 13 to the requirement of the constancy of [T].[21] The error introduced in the rate constant ratio given by eq 13 was estimated by computer simulations to be approximately 15% for a feed rate that yields a value of [T] that changes gradually over the course of the reaction to reach a 25% deviation from the initial value at the end of the reaction.

$$\frac{(RS_nT)\sum_{i=m+1}^{\infty}(RS_iT)}{(RS_mT)\sum_{i=n+1}^{\infty}(RS_iT)} = \frac{k_{S_m}k_{T_n}\int[RS_m^\bullet]\,dt\int[RS_n^\bullet][T]\,dt}{k_{S_n}k_{T_m}\int[RS_m^\bullet][T]\,dt\int[RS_n^\bullet]\,dt} = \frac{k_{S_m}k_{T_n}}{k_{S_n}k_{T_m}} \tag{14}$$

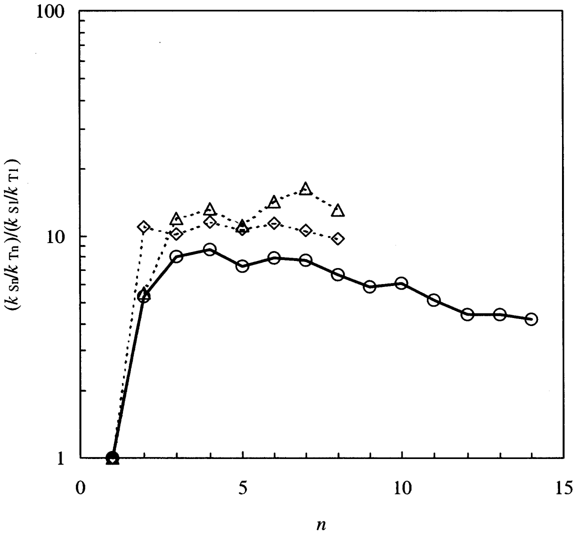

Figure 5. Ratio of the successive propagation rate coefficients to the corresponding trapping rate coefficients (k_{S_n}/k_{T_n}) as a function of chain length n relative to the ratio for the first member of the series (k_{S_1}/k_{T_1}): (○) experiment 1; (△) experiment 2; (◇) experiment 3. For experimental details, see Table 1.

Thus, if the trapping rate coefficients or the ratio of any pair of trapping rate coefficients (k_{T_n}/k_{T_m}) are known, k_{S_n}/k_{S_m} can be calculated from the oligomer yields without any knowledge of [T], and the expression holds for any reasonably constant [T]. With this method (eq 14), individual propagation rate coefficients can only be calculated if one value is known from some independent method. The oligomer yields appear as ratios in eqs 13 and 14, and it follows that any systematic errors in the concentrations will partially cancel. The rate constant ratios will be the most affected by the yields of the products present in the highest concentration for each calculation (i.e., a specific value of n).

The calculation of rate coefficient ratios from eqs 13 and 14 requires the summation of all oligomer concentrations above a certain value of n. For this purpose, we assumed that the concentration of the higher oligomers ($n > 15$ for experiment 1, $n > 9$ for experiments 2 and 3), which were present in such low amounts that they could not be experimentally quantified, were present in decreasing concentrations. These were calculated on the basis that the concentration ratios were the same as the average for the last four measured oligomers. Values of $(k_{S_n}/k_{T_n})/(k_{S_1}/k_{T_1})$, calculated from the product concentrations using eq 14, for the three most successful experiments are shown as a function of n in Figure 5. The ratios k_{S_n}/k_{T_n} increase by a factor of 10 ± 2 from $n = 1$ to 3 and then remain, within experimental error, constant up to $n = 8$. In experiment 1, the value decreases steadily by a factor of about 2 from $n = 8-14$ indicating a trend that may continue with higher oligomers. These rate coefficient ratios are concerned with reactions 6 and 7, a radical−radical reaction and a radical−monomer reaction. Clearly the former reaction is much closer to the limit of diffusion control than is the latter, and reaction 7 is much more likely to be influenced by steric, polar, or other chemical factors. This means that the observed changes in k_{S_n}/k_{T_n} with chain length are likely to be dominated by a change in k_{S_n}. Chain length independence of nitroxide trapping rate coefficients has not been confirmed. Skene et al.[38] reported that the trapping rate coefficients for

1-phenylethyl and 1,3-diphenyl-1-propyl with 2,2,5,5-tetramethylpiperidin-1-oxyl (TEMPO) are 1.2×10^8 and 4.7×10^7 M^{-1} s^{-1}, respectively. This supports the notion that k_{T_n} may indeed decrease with increasing n, indicating that the increase in k_{S_n} from $n = 1$ to 3 may in fact be less than the factor of 10 mentioned above.

Information relating to chain-length dependence of propagation rate coefficients is relatively scarce in the literature. In our previous paper dealing with acrylonitrile initiated by AIBN,[21] we found a small decrease in k_{M_n} (where M denotes monomer) from $n = 1$ to 2 followed by an increase to $n = 4$ $((k_{S_n}/k_{T_n})/(k_{S_1}/k_{T_1}) = 0.86$, 1.54, 1.95 for $n = 2$, 3, and 4, respectively; note that k_{S_n} was defined differently in that work). We however recognize that this trend may be influenced by a chain-length dependence of k_{T_n}. Moad et al.[18] studied the free-radical polymerization of methyl acrylate initiated by benzoyl peroxide by use of the nitroxide trapping technique, and reported that k_{M_1}:k_{M_2} = 1.07:1 and 2.64:1 for the primary radicals $Ph^\bullet$ and $PhCO_2^\bullet$, respectively (based on k_{T_n} being independent of n), and an order of magnitude greater than k_p. Gridnev and Ittel[22] employed a cobalt-catalyzed chain transfer process to obtain information about the rate coefficients for the addition of monomer and dimer radicals to monomer for methacrylonitrile (MAN) and methyl methacrylate (MMA). The monomer radical of MMA (H-MMA$^\bullet$) had a rate coefficient approximately four times greater than that of the dimer radical, both significantly higher than the reported k_p value for MMA (a factor of almost 20 for the monomer radical). The monomer radical H-MAN$^\bullet$ was reported to add to MAN approximately 6 times faster than polymeric radicals. Deady et al.[23] modeled a pulsed laser polymerization (PLP) process of styrene initiated by 2,2′-azobis(methyl isobutyrate) and reported that the molecular weight distributions obtained were consistent with a significant chain length dependence $k_{S_1} > k_{S_2} > k_{S_3} > k_p$. Olaj et al.[25] reported that the values of k_p obtained from pulsed laser polymerization for several systems exhibited a slight but nonetheless significant increase with higher laser frequencies, suggesting that shorter chains propagate faster over at least the first one hundred propagation steps. This is in good agreement with our observed decrease in k_{S_n}/k_{T_n} for values of n greater than about 8. In our recent report on the initial stages in the nitroxide-mediated polymerization of styrene using cumyl-TEISO (1,1,3,3-tetraethylisoindoline-2-oxyl) as the alkoxyamine initiator,[39] we monitored the concentrations of oligomeric adducts Cu−St$_n$−TEISO at 60 °C in bulk styrene as a function of time using HPLC−UV for $n = 1-5$. Since nitroxide trapping is irreversible at this temperature, the oligomer yields allow the calculation of $(k_{S_2}/k_{T_2})/(k_{S_1}/k_{T_1}) = 1.7$ and $(k_{S_3}/k_{T_3})/(k_{S_1}/k_{T_1}) = 1.6$ by use of eq 14. These values are somewhat lower than the values obtained in this study, but if one assumes that the values of k_{T_n} remain constant, $k_{S_1} < k_{S_2}$ in both studies. The initiating radical here is a cumyl radical, and the nitroxide is TEISO.

In principle, the absolute values of k_{S_n}/k_{T_n} can be obtained via eq 13. Unfortunately, the trap concentration as a function of time is not known with accuracy (although the final concentration is known). For example, there is significant variation between the target concentration used in the simulation and the final measured concentration in each successful experiment (Table 1). Values of k_{S_n}/k_{T_n} calculated with the final measured [T] are given in Table 2. The trends of these values with n for each experiment are, of course, the same as those of the relative values calculated from eq 14 and shown in Figure 5. The rate coefficient for the trapping of alkyl radicals by T is almost in the diffusion-controlled region and close to 10^9 M^{-1} s^{-1}.[27−31] However, attached aromatic groups have a small stabilization effect and cause a reduction of a factor of 3−6. For example, the rate coefficient for the trapping of methyl benzyl and dimethyl benzyl radicals by T have been reported to have values of 3.0×10^8 and 1.7×10^8 M^{-1} s^{-1}, respectively.[31] Taking 2×10^8 M^{-1} s^{-1} as the value for the trapping of styryl radicals and assuming no chain length dependence, the estimated rate coefficients for the first 14 propagation steps in the free radical polymerization of styrene at 75 °C are shown in Table 2. These values are significantly greater than k_p (high polymer) for the free radical polymerization of styrene, which has been measured by the IUPAC recommended PLP technique.[40] The value at 75 °C is 565 M^{-1} s^{-1}. This suggests that values of k_{S_n} for oligomers up to at least $n = 14$ have not reached the mean high polymer value and indicates that the long-range chain length dependence of k_p suggested by Olaj et al. may be valid.[25]

Table 2. Rate Coefficients Calculated from Eq 13 Assuming that the Final [T] Is the Average throughout Each Experiment[a]

	expt 1		expt 2		expt 3	
n	$k_Sn/k_Tn \times 10^5$	$k_Sn \times 10^{-4}$ (L mol^{-1} s^{-1})	$k_Sn/k_Tn \times 10^5$	$k_Sn \times 10^{-4}$ (L mol^{-1} s^{-1})	$k_Sn/k_Tn \times 10^5$	$k_Sn \times 10^{-4}$ (L mol^{-1} s^{-1})
1	4.08	0.82	1.51	0.30	0.50	0.10
2	21.7	4.3	8.3	1.66	5.6	1.11
3	32.6	6.5	18.2	3.6	5.2	1.04
4	35.1	7.0	20.0	4.0	5.8	1.16
5	29.8	6.0	16.6	3.3	5.4	1.08
6	32.4	6.5	21.5	4.3	5.7	1.14
7	34.7	6.9	24.5	4.9	5.4	1.08
8	27.1	5.4	19.9	4.0	4.9	0.98
9	23.9	4.8				
10	24.8	5.0				
11	20.8	4.2				
12	17.9	3.6				
13	17.9	3.6				
14	17.1	3.4				

[a] For experimental details, see Table 1.

The data also allows the calculation of the ratio k_{S_0}/k_{T_0} from eq 13 and the final measured value of [T]. Taking k_{T_0} as typical for the reaction of alkyl radicals with T (10^9 M^{-1} s^{-1}), these values give $k_{S_0} = 10.3 \times 10^3$, 10.7×10^3, and 6.4×10^3 M^{-1} s^{-1} for experiments 1, 2, and 3, respectively. These are reasonably consistent with the value of 5.93×10^3 M^{-1} s^{-1} at 75 °C for the same reaction calculated from the data of Fischer et al.[41] Their measurements were made in toluene solution, but the value should not differ greatly from that in bulk monomer, as used in this work. Our results suggest that styrene adds to cyanoisopropyl radicals somewhat slower than to oligomeric styryl radicals (see Table 2). There are steric grounds for expecting k_{S_0} to be less than k_{S_n} ($n > 0$). The former involves the addition of styrene to a tertiary carbon radical in comparison with a secondary carbon radical in the latter case.

Conclusions

Careful optimization of the nitroxide trapping technique in connection with identification and quantification employing HPLC-ESI/MS can give valuable kinetic information for the early propagation steps in the free radical polymerization of styrene initiated by AIBN. The first 14 propagation rate coefficients, k_{S_n}, have been estimated based on the assumption that the trapping rate coefficients, k_{T_n}, are independent of n. The results show that k_{S_n} increases by a factor of about 10 from $n = 1-3$ to a value of $k_{S_n} = 6 \pm 2 \times 10^4$ M^{-1} s^{-1}, which remains constant to $n = 8$ and then falls steadily to $3 \pm 2 \times 10^4$ M^{-1} s^{-1} at $n = 14$.

Acknowledgment. Expert advice on extinction coefficients from Professor Ken Ghiggino and financial assistance from the Australian Research Council are gratefully acknowledged.

References and Notes

(1) Bottle, S.; Busfield, W. K.; Jenkins, I. D.; Thang, S. H.; Rizzardo, E.; Solomon, D. H. *Eur. Polym. J.* **1989**, *25*, 671.
(2) Busfield, W. K.; Jenkins, I. D.; Thang, S. H. *Tetrahedron Lett.* **1985**, *26*, 5081.
(3) Busfield, W. K.; Jenkins, I. D.; Thang, S. H.; Rizzardo, E.; Solomon, D. H. *Eur. Polym. J.* **1993**, *29*, 397.
(4) Rizzardo, E.; Serelis, A. K.; Solomon, D. H. *Aust. J. Chem.* **1982**, *35*, 2013.
(5) Busfield, W. K.; Heiland, K.; Jenkins, I. D. *Tetrahedron Lett.* **1995**, *36*, 1109.
(6) Nakamura, T.; Busfield, W. K.; Jenkins, I. D.; Rizzardo, E.; Thang, S. H.; Suyama, S. *J. Org. Chem.* **1997**, *62*, 5578.
(7) Busfield, W. K.; Jenkins, I. D.; Rizzardo, E.; Solomon, D. H.; Thang, S. H. *J. Chem. Soc., Perkin Trans.* **1991**, *1*, 1351.
(8) Busfield, W. K.; Jenkins, I. D.; Le, P. V. *Polum. Bull. (Berlin)* **1996**, *36*, 435.
(9) Busfield, W. K.; Jenkins, I. D.; Le, P. V. *Polym. Bull. (Berlin)* **1997**, *38*, 149.
(10) Busfield, W. K.; Jenkins, I. D.; Le, P. V. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 2169.
(11) Moad, G.; Rizzardo, E.; Solomon, D. H. *J. Macromol. Sci.—Chem.* **1982**, *A17*, 51.
(12) Moad, G.; Rizzardo, E.; Solomon, D. H. *Aust. J. Chem.* **1983**, *36*, 1573.
(13) Moad, G.; Rizzardo, E.; Solomon, D. H. *Macromolecules* **1982**, *15*, 909.
(14) Busfield, W. K.; Jenkins, I. D.; Monteiro, M. J. *Polymer* **1997**, *38*, 165.
(15) Busfield, W. K.; Jenkins, I. D.; Monteiro, M. J. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 263.
(16) Busfield, W. K.; Jenkins, I. D.; Monteiro, M. J. *Aust. J. Chem.* **1997**, *50*, 1.
(17) Busfield, W. K.; Grice, I. D.; Jenkins, I. D. *Polym. Int.* **1992**, *29*, 119.
(18) Moad, G.; Rizzardo, E.; Solomon, D. H.; Beckwith, A. L. J. *Polym. Bull. (Berlin)* **1992**, *29*, 647.
(19) Busfield, W. K.; Heiland, K.; Jenkins, I. D. *Tetrahedron Lett.* **1994**, *35*, 1109.
(20) Busfield, W. K.; Grice, I. D.; Jenkins, I. D. *Aust. J. Chem.* **1995**, *48*, 625.
(21) Zetterlund, P. B.; Busfield, W. K.; Jenkins, I. D. *Macromolecules* **1999**, *32*, 8041.
(22) Gridnev, A. A.; Ittel, S. D. *Macromolecules* **1996**, *29*, 5864.
(23) Deady, M.; Mau, A. W. H.; Moad, G.; Spurling, T. H. *Makromol. Chem.* **1993**, *194*, 1691.
(24) Huang, M. D.; Monteiro, M. J.; Gilbert, R. G. *Macromolecules* **1998**, *31*, 5175.
(25) Olaj, O. F.; Vana, P.; Zoder, M.; Kornherr, A.; Zifferer, G. *Macromol. Rapid Commun.* **2000**, *21*, 913.
(26) Dixon, K. W. Decomposition Rates of Organic Free Radical initiators. In *Polymer Handbook*; 4th ed.; Brandrup, J., Immergut, E. H., Grulke, E. A., Eds.; Wiley: New York, 1999; p II/12.
(27) Sobek, J.; Martschke, R.; Fischer, H. *J. Am. Chem. Soc.* **2001**, *123*, 2849.
(28) Beckwith, A. L. J.; Bowry, V. W.; Ingold, K. U. *J. Am. Chem. Soc.* **1992**, *114*, 4983.
(29) Beckwith, A. L. J.; Bowry, V. W.; Moad, G. *J. Org. Chem.* **1988**, *53*, 1632.
(30) Chateauneuf, J.; Lusztyk, J.; Ingold, K. U. *J. Org. Chem.* **1988**, *53*, 1629.
(31) Bowry, V. W.; Ingold, K. U. *J. Am. Chem. Soc.* **1992**, *114*, 4992.
(32) Gridnev, A. A.; Cotts, P. M.; Roe, C.; Barth, H. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 1099.
(33) Saf, R.; Mirtl, C.; Hummel, K. *Acta Polym.* **1997**, *48*, 513.
(34) Hunt, S. M. Ph.D. Thesis, University of Wollongong, 1996.
(35) Hunt, S. M.; Sheil, M. M.; Belov, M.; Derrick, P. J. *Anal. Chem.* **1998**, *70*, 1812.
(36) Barton, Z.; Kemp, T. J.; Buzy, A.; Jennings, K. R. *Polymer* **1997**, *38*, 1957.
(37) McEwen, C. N.; Simonsick, W. J.; Larsen, B. S.; Ute, K.; Hatada, K. *J. Am. Soc. Mass. Spectrom.* **1995**, *6*, 906.
(38) Skene, W. G.; Scaiano, J. C.; Yap, G. P. A. *Macromolecules* **2000**, *33*, 3536.
(39) Cresidio, S. P.; Aldabbagh, F.; Busfield, W. K.; Jenkins, I. D.; Thang, S. H.; Zayas-Holdsworth, C.; Zetterlund, P. B. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 1232.
(40) Buback, M.; Gilbert, R. G.; Hutchinson, R. A.; Klumperman, B.; Kuchta, F.-D.; Manders, B. G.; O'Driscoll, K. F.; Russell, G. T.; Schweer, J. *Macromol. Chem. Phys.* **1995**, *196*, 3267.
(41) Heberger, K.; Fischer, H. *Int. J. Chem. Kinet.* **1993**, *25*, 249.

MA020325V