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Chain Length Dependent Polymer End−End Reaction Rate Constants in the Reaction of Polystyryllithium with a Styrene-Terminated Fluorescent-Labeled Polystyrene

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ABSTRACT: Gel permeation chromatography with fluorescence detection has been employed to measure polymer−polymer chain end reaction rate constants. In this study, polystyryllithium (PSLi **1**) of varying chain lengths (degree of polymerization N varying between ∼31 and 246) has been reacted with a styrene-terminated polystyrene **4** (degree of polymerization $M \sim 22$) which is labeled with the fluorescence probe pyrene. This study, which was performed in a good solvent (benzene) at the dilute/semidilute threshold and extending into the semidilute regime, reveals a concentration dependence on **1** of this reaction that is close to first order (0.9 ± 0.1). Interestingly, the reaction rate constant at fixed concentration of polystyryllithium ($c = 0.3$ g/mL) increases with increasing chain length, from 3.6 M^{-1} min^{-1} at $N = 31$ to 10.3 M^{-1} min^{-1} at $N = 246$. Possible reasons for this unexpected rate increase with chain length are discussed in the context of aggregation and supramolecular effects.

Introduction

Measurement of polymer end−end reaction rates has been of interest to both experimental[1−10] and theoretical polymer scientists.[11−20] Fundamental theories have been developed to predict the effect of chain length on reaction rates.[9,17,18,20,21] Several difficulties in measuring polymer reaction rates have hindered experimental studies; e.g., synthesis of suitable monodisperse end-labeled samples and low sensitivity of analytical techniques for the detection of polymer end groups have presented experimental difficulties. The current study uses fluorescent-labeled monodisperse polymers (pd < 1.1) generated by anionic polymer synthesis as a method to overcome sensitivity and polydispersity issues.[22] Although some approaches using fluorescence quenching[23,24] and phosphorescence quenching[5−7] have been employed in the measurement of polymer end−end reaction rates, these methods are limited by the fluorescence and phosphorescence lifetimes of the probes. In the case of activation-controlled reactions,[12,14] the reaction rates occur on time scales which are slower than the luminescence lifetimes of most probes. To address this problem for our system, we developed a GPC-based method that resolves reactant and product based on molecular weight employing fluorescence detection in the analysis of the disappearance of starting material and the formation of the end-to-end coupling product.[22]

Polymer end−end reactions can be divided into two classes: diffusion-controlled (e.g., radical reactions, photophysical processes)[5,7,14,17,18,20,25,26] and activation-controlled reactions (e.g., condensation reactions).[3,9,27] The current study focuses on the activation-controlled reaction of polystyryllithium $\mathbf{1_N}$ [PS_NLi] (N = degree of polymerization) with a second polystyrene molecule **4** which is selectively labeled with one pyrene fluorophore and contains a reactive styrene functionality at the chain end (see Scheme 1). These experiments are performed at 30 °C in benzene, which is a good solvent for polystyrene.

Gel permeation chromatography (GPC) with fluorescence detection is employed to monitor the end−end reaction shown in Scheme 2.[8,22,28] Previous studies of the kinetics of activation-controlled polymer end−end reactions observed either loss of starting material[2] or product formation[3] but were unable to simultaneously measure both. The current study is able to simultaneously monitor both starting material disappearance and product growth using the pyrene probe's excellent fluorescence properties. The pyrene probe **4** allows for measurement of pseudo-first-order rate constants for polymer end−end reactions with high sensitivity. Furthermore, chain length dependent bimolecular rate constants can be extracted from these observed rate constants.

Aggregation effects in solution[29−35] are known to be important to both the structure and propagation kinetics of PSLi and related polybutadienyllithium. In benzene solution, under dilute and semidilute conditions, PSLi has been proposed to possess a dimeric structure.[34,36,37] The manner in which aggregation affects reactivity is not completely understood, and discrepancies exist in the literature as to the kinetic order of PSLi in propagation kinetics which is cited as varying between 0.48 and 0.87 depending on the study.[30] Furthermore, small-angle neutron scattering studies (SANS) have yielded evidence of aggregation of PSLi dimers into larger micellar structures,[30] although the existence of these larger structures is not universally accepted.[32]

The current study addresses the issue of chain length dependence of polymer end−end reaction rates in the reaction of monodisperse polystyryllithium of varying degrees of polymerization with a second monodisperse polystyrene **4** ($M_N = 2300$; $N \approx 22$) which is fluores-

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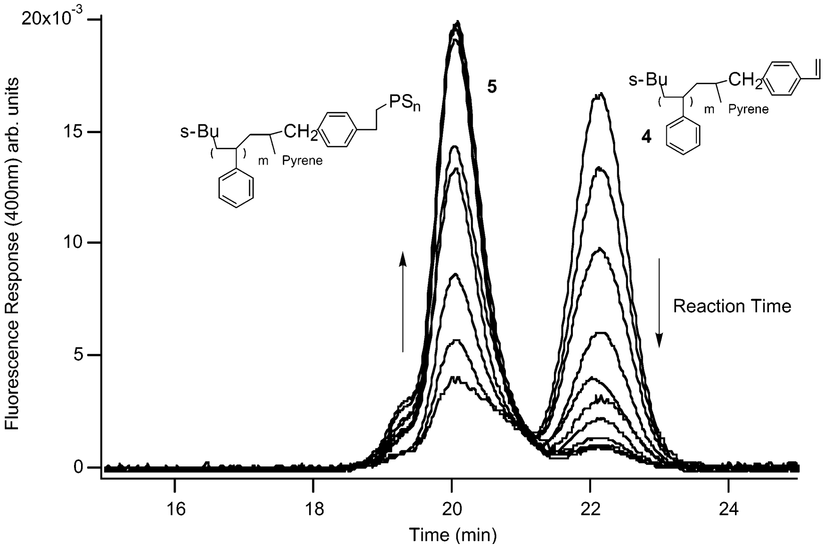
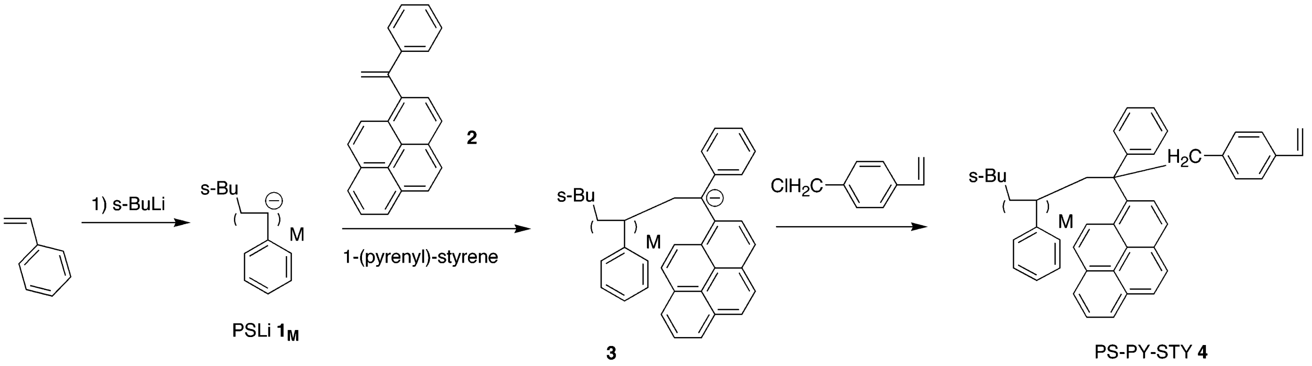
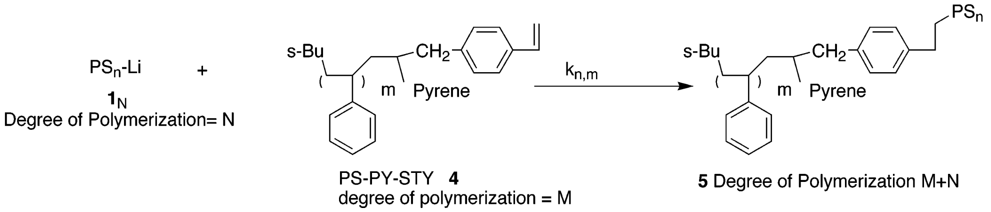


Figure 1. GPC traces with fluorescence detection (excitation at 330 nm, observation at 400 nm) at several reaction times. Peak for starting material **4** decreases with reaction time, and peak for product **5** increases with reaction time. Reaction conditions: benzene, 30 °C.

Scheme 1. Synthesis of Styrene End-Labeled−Pyrene-Labeled Polystyrene 4



Scheme 2. Scheme for Polymer End−End Reaction between PSLi 1_N and 4



cently labeled with a single pyrene unit and contains a terminal reactive styrene moiety. The study is performed in benzene at constant concentration *c* by weight of polystyryllithium ($c = 0.3$ g/mL) which is calculated to be in the dilute regime for chains below 4.6K and in the semidilute regime for chains longer than 4.6K.[38,39] The dependence of the rate on PSLi under our reaction conditions is experimentally measured to be close to unity (0.9 ± 0.1). The chain length dependence study surprisingly reveals an increase in the bimolecular reaction rate constant with increasing molecular weight. The increase in reaction rate appears to track with the overlap parameter c/c^* (see Figure 4).[14] Here the overlap threshold[40] c^* is defined by the relationship $c^* \approx Nm_0/(4/3\pi R_G{}^3)$. The quantity m_0 is the mass of one monomer unit, and R_G is the radius of gyration.[39] This result is discussed in the context of the complex supramolecular environment present in the polystryllithium/benzene system.

Experimental Section

Materials. Styrene (Aldrich) was dried over calcium hydride, distilled onto dibutylmagnesium, and then distilled under reduced pressure fresh prior to use. Benzene was dried over calcium hydride, distilled over polystyryllithium, and distilled fresh prior to use. THF was dried over potassium hydride. 4-(Chloromethyl)styrene was purchased from Aldrich and used as received. 1-(Pyrenyl)styrene (**2**) was synthesized using a modified literature procedure.[41]

Instrumentation. Gel permeation chromatography was performed on a Polymer Labs GPC with a GTI/Spectrovision FD-500 fluorescence detector. 2 PL mixgel 5m C and 1 PL gel 5m 100A columns were used in series, and calibration was performed with polystyrene standards.

Synthesis of 4. 0.91 mmol of *sec*-butyllithium was added to a solution of 2 mL of styrene in 5 mL of dry, degassed benzene under argon. The reaction mixture was aged for 2 h at room temperature. 2 mL of dry THF was added. 1.1 mL (0.13 mmol) of the resultant solution of polystyryllithium was added to a flask containing 38 mg (0.12 mmol) of 1-(pyrenyl)-

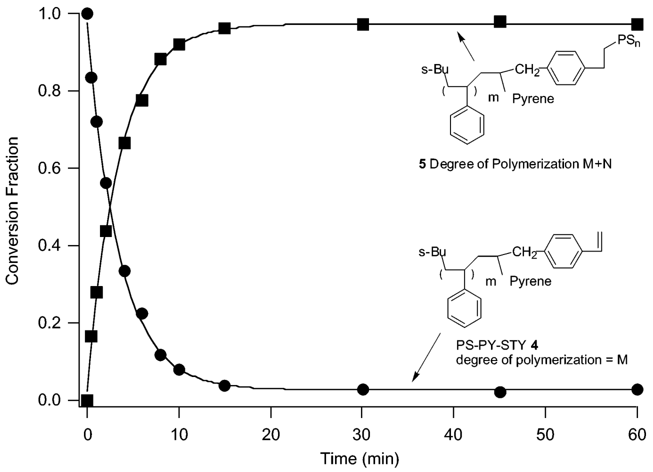


Figure 2. Representative kinetic trace and first-order exponential fit for decrease of starting material **4** and growth of product **5** as measured from area of peaks in Figure 1 (M_N for PS$_N$Li ($\mathbf{1_N}$) = 4500 ± 100 amu, M_N for **5** ($M + N$) = 6900 ± 200).

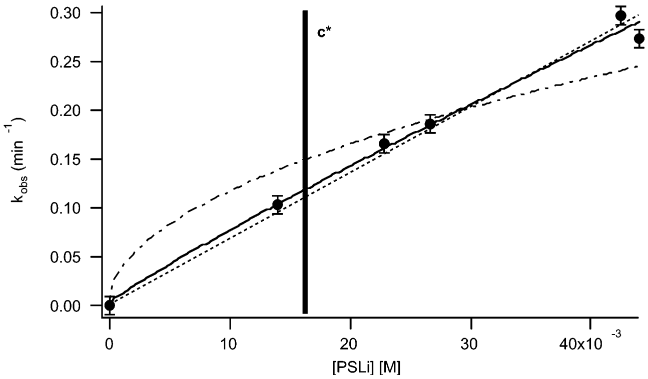


Figure 3. Dependence of observed rate constant k_{obs} on concentration of polystyryllithium (M_N of PSLi ≈ 10K). Data shown with estimated error ± 0.01 min^{-1} and fit to $^1/_2$ order (dashed line), 1 order (dotted line), and 0.91 order (solid line). The value 0.91 was found to fit the data best. The bold vertical line indicates c^*, the transition between dilute and semidilute regimes.[40]

styrene (**2**), which resulted in a deep blue solution of anion **3** (see Scheme 1). After 10 min, an excess (0.26 mL) of 4-(chloromethyl)styrene was added. The solution immediately decolorized. The resulting polymer (**4**) was reprecipitated several times with methanol and then dried under vacuum. The structure was confirmed by ^{1}H and ^{13}C NMR, UV–vis, and fluorescence spectroscopy. The degree of labeling was determined by GPC to be greater than 95%. The molecular weight, M_N, was measured by GPC to be 2300 ± 100 amu.

Measurement of the Rate of Reaction of $\mathbf{1_N}$ with 4. Polystyryllithium $\mathbf{1_N}$ is generated by reaction of an appropriate amount of *sec*-butyllithium with 5.85 mL (50 mmol) of styrene in 10 mL of dry degassed benzene. The GPC molecular weight (M_N) of resultant polystyryllithium is used to confirm the concentration of *sec*-butyllithium added. After reaction is complete (~2 h), this solution is maintained at constant temperature of 30 ± 0.2 °C using an IKA ETS-D4 temperature controller. In a separate flask, **4** (5 mg, 2.2×10^{-3}mmol) is dissolved in a small amount of dry degassed benzene and added to the solution of $\mathbf{1_N}$ in benzene. The addition time is marked with a stopwatch, and aliquots are removed subsequently and quenched onto methanol. A small degree of coupling reaction (few percent) is observed due to the formation of free radical chains ends resulting from oxidation of anionic chains, since the methanol employed is not rigorously degassed (see shoulder in Figure 1 for product peak **4**).[42] However, this is not expected to affect the kinetic analysis. The samples thus generated are dissolved in THF and filtered through a short plug of silica gel to remove lithium salts prior to injection into the GPC (see Figure 1).

Results

The goal of our study was to measure the rate of polymer end–end reactions as a function of chain length using gel permeation chromatography (GPC) with fluorescence detection.[8,22] The experimental requirement was a system in which chain length could be varied systematically and where starting material **4** and the end-to-end coupling product **5** could both be observed through fluorescence. The reaction of polystyryllithium (degree of polymerization *N*) with a macromolecular fluorescent-labeled styrene **4** was chosen for the following reasons. Polystyryllithium can be synthesized at various controlled degrees of polymerization with low polydispersity using anionic polymerization. Reaction of $\mathbf{1_N}$ with fluorescently labeled **4** is clean and yields

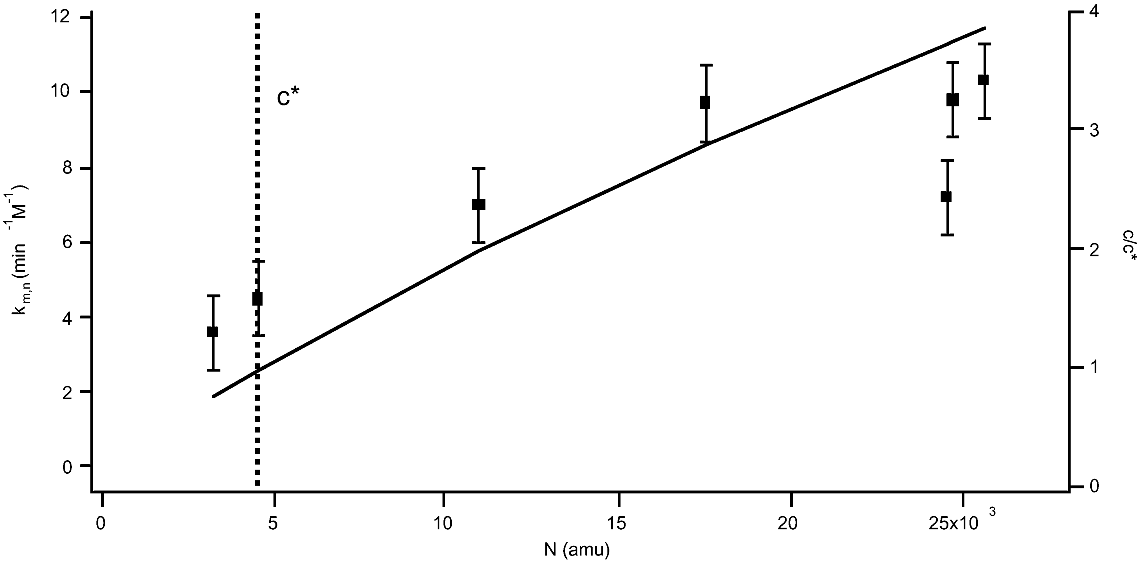


Figure 4. Chain length dependence of bimolecular polymer end–end reaction rate constant $k_{M,N}$ (plotted with estimated error ± 1 M^{-1} min^{-1}). M_N of **4** = 2300 ± 100, $M = 22$. M_N of PSLi ($\mathbf{1_N}$) varied from 4K to 25K ($N = 40-240$). Solid curved line indicates c/c^* as a function of *N* for polystyrene.[38,39] Dotted line indicates transition between dilute and semidilute regimes.

Table 1. Polystyryllithium Samples Used in Chain Length Study (See Figure 4)

M_N (g/mol)	degree of polymerization	[PSLi] (mM)	k_{obs} (min^{-1})	$k_{M,N}$ ($M^{-1}\,min^{-1}$)
3300 ± 200	31 ± 2	87 ± 8	0.31 ± 0.01	3.6 ± 1
4500 ± 100	44 ± 1	63 ± 3	0.29 ± 0.01	4.5 ± 1
11000 ± 300	105 ± 3	27 ± 1	0.19 ± 0.01	7.0 ± 1
17600 ± 600	169 ± 5	18 ± 1	0.17 ± 0.01	9.7 ± 1
24500 ± 3000	236 ± 28	13 ± 2	0.091 ± 0.01	7.2 ± 2
24700 ± 1200	238 ± 12	12 ± 1	0.12 ± 0.01	9.8 ± 1
25600 ± 800	246 ± 8	12 ± 1	0.13 ± 0.01	10.3 ± 1

only one product **5** after quenching with methanol (see Scheme 2). Both **4** and **5** can be resolved by GPC as a function of molecular weight and observed by fluorescence detection (excitation at 330 nm, emission at 400 nm) in a regime in which there is negligible background signal from polystyrene.

Fluorescently labeled **4** is accessible through the synthesis illustrated in Scheme 1 ($M_N = 2300$, degree of polymerization $N = 22$).[41,43] The pyrene moiety was chosen for its excellent stability and UV−vis and emission properties which are at considerably longer wavelength than polystyrene, allowing the selective excitation and detection of the probe versus the entire molecule. The pyrene probe was incorporated using the 1-(pyrenyl)styrene in order to minimize disruption of the polystyrene chain by the probe molecule. The reactive styrene end group was incorporated to allow for reaction of **4** with polystyryllithium.[43] Thus, the polarity of the probe molecule **4** is hydrocarbon-like, which minimizes the possibility of a phase separation that might occur due to specific polar end groups.[44,45]

The reaction illustrated in Scheme 2 was employed for measurement of rate constants for the end-to-end polymer coupling. Polystyryllithium $\mathbf{1_N}$ of varying degree of polymerization N was synthesized in benzene using *sec*-butyllithium as an initiator (see Table 1); the resulting polystyryllithium solution was heated to 30 °C, and kinetics were measured at this temperature. A solution of **4** dissolved in a small amount of benzene was added to the polystyryllithium solution. Aliquots were withdrawn periodically and quenched into methanol. The resulting samples were injected into the GPC to produce a time series of GPC traces (representative examples are shown in Figure 1). The fluorescence of the pyrene is observed in the starting material **4** and product **5**, but the polystyryllithium is effectively nonemissive under these detection conditions (excitation at 330 nm and observation at 400 nm). For this reason we are able to operate under pseudo-first-order kinetic conditions with a 50−100-fold excess of polystyryllithium as compared to **4** without any significant interference in the GPC fluorescence analysis from the polystyryllithium. The fluorescence of the pyrene label is observed to have similar quantum yields of fluorescence in starting material **4** and product **5** as measured by steady-state fluorescence spectroscopy. Thus, the area integration of peaks **4** and **5** in Figure 1 are proportional to the concentrations of starting material and product in the reaction. These areas are used to calculate the fraction conversion as a function of time (see Figure 2). The conversion data for the starting material and product are fit with exponential curves (see Figure 2).

To isolate chain length effects, we sought to operate at constant weight fraction of polystyrene. Thus, all measurements were performed at 0.3 g/mL weight fraction polystyrene. At this constant weight fraction, the overlap parameter c/c^* varies with chain length as $c/c^* \propto M_N^{0.785}$, where we use the relationship $R_G \propto M_N^{0.595}$ which has been determined from data for polystyrene in benzene.[39,40] (The value for m_0 is 104.15 g/mol; the proportionality constant relating c/c^* and M_N is 1.33×10^{-3} using the values from ref 39 and the appropriate unit conversions.) Using these values, the overlap parameter c/c^* which measures the degree to which the chains are interpenetrating varies from 0.8 to 3.9 for chain lengths of $\mathbf{1_N}$ varying from $N = 31$ to 246. Therefore, the weight fraction of polystyryllithium employed in this study corresponds to the semidilute regime ($c/c^* > 1$) for chain lengths greater than 4.6K.[38,39]

However, as we varied the chain length, we would also be varying the concentration of polystyryllithium, and for this reason it was important to assess the dependence of the rate constant on polystyryllithium concentration. To confirm the polystyryllithium concentration dependence (which has been reported of the order of 0.5 in polystyrene propagation[34,37,46] as well as varying between 0.48 and 0.87[30]), we measured the dependence of k_{obs} on polystyryllithium [PSLi] at a constant molecular weight ($M_N = 10K$; $N \approx 100$). The plot of k_{obs} vs [PSLi] was fit to a power dependence, and the best fit was found to be 0.91 ± 0.1 (see Figure 3). Although there is much discussion in the literature regarding aggregation state and reaction mechanism, under our experimental conditions we observe a roughly linear dependence of k_{obs} vs [PSLi] which is consistent with the following rate equation:

$$k_{obs} = k_{M,N}[\mathrm{PSLi}]^{0.9\pm0.1}$$

We use this experimentally determined relationship to calculate the bimolecular rate constant of reaction $k_{M,N}$ as a function of chain length at constant volume fraction polystyrene. (To simplify units, the approximation of a first-order dependence in [PSLi] is made in calculating $k_{M,N}$ from k_{obs}.) These results are presented in Figure 4. It is interesting to note that the bimolecular rate constant $k_{M,N}$ increases as the degree of polymerization increases from $N = 31$ to 246 ($M_N = 3.3K-25.6K$) from $3.6 M^{-1} min^{-1}$ to $10.3\ M^{-1}\ min^{-1} \pm 1\ M^{-1}\ min^{-1}$. Error bars in Figure 4 are based on uncertainties in concentration of [PSLi] and in k_{obs}. The overlap parameter c/c^* is presented in Figure 4.[38,39] The dashed line indicates the transition between dilute and semidilute which occurs for polystyrene at this concentration in benzene at approximately 4.6K. The aggregation of PSLi may result in higher effective chain lengths which may shift the entire c/c^* curve to lower molecular weights.[37,46]

Discussion

Previous studies have employed the use of GPC with fluorescence detection to explore coupling processes in high-temperature melt processing[8,28] and at the thin film interface.[22] Current work extends the GPC−fluorescence detection methodology to measure bimolecular rate constants directly for polymer−polymer reactions in solution. The high sensitivity of fluorescence detection[22] allows for convenient measurement of kinetics under pseudo-first-order conditions. Furthermore, it allows measurement of reaction rates under more concentrated conditions than were previously reported.[2]

The most interesting result of the current study is the observation that the bimolecular rate constant $k_{M,N}$ increases with chain length at constant weight fraction (c) of polystyrene (see Table 1 and Figure 4). The underlying reasons for this effect could be due to changes in the entropy associated with bringing the reactive species together in the appropriate configuration (resulting in differences in the Arrhenius A factor) or changes in the activation energy E_A for product formation once the reactive species are together. Since the chain length increases occur far away from the reactive end groups, it is not expected that increasing the chain length should strongly affect the energetics of bond formation in the addition reaction of $\mathbf{1_N}$ and **4**. A more likely possibility is that the increased chain lengths would affect the entropic term (the Arrhenius A factor). On the basis of our experimental results, the A factor would be expected to increase with increasing chain length. In this regard there are three possible hypotheses which are considered. In the first possibility, the transition between dilute and semidilute regimes would result in a possible reduction of excluded-volume screening.[14,27] In this hypothesis, under semidilute conditions, the interpenetration of polymer chains would make it easier for reactive ends to meet, whereas under dilute conditions, the repulsive interactions between polymer chains would be expected to hinder end group interactions. A second possibility is a change in the supramolecular structure of $\mathbf{1_N}$ with increasing chain length.[30,47−49] In this hypothesis, as N increases, the aggregation number of micelles of $\mathbf{1_N}$ is expected to decrease due to increased excluded-volume repulsive interactions of the polystyryl chains.[48,49] There is a possibility that, from these smaller micelles, $\mathbf{1_N}$ is more reactive.[49] A third possible hypothesis is that the equilibrium between dimeric PSLi and monomeric PSLi is chain length dependent. Thus, as chain length N increases, excluded-volume repulsion of polystyryllithium chains would drive the equilibrium toward monomeric PSLi.[33] Each of these hypotheses is considered (vide infra).

A previous study by Mita et al. of activation controlled anionic polymer reactions has been performed with polystyrylpotassium reacting in an S_N2 reaction with a primary alkyl chloride in benzene with a small amount (5%) of tetrahydrofuran (THF).[2] Under dilute conditions ($c = 0.005-0.035$ g/mL), no chain length dependence was observed for degrees of polymerization 50−394. A similar study under dilute conditions of chain length dependence in the reaction of an amine-terminated poly(ethylene oxide) with a chloro-1,5-naphthalenyldisulfonyl-ended poly(ethylene oxide) also revealed no chain length dependence for degree of polymerizations ranging from 24 to 20 800.[3] The current study is performed in benzene with no solvent additives (such as THF) present and at the transition between dilute and semidilute regimes. Instead of a lack of chain length dependence, we observed an increase in the rate constant with increasing chain length which appears to be correlated to the overlap parameter over the range of chain lengths studied (see Figure 4).

The Mita group study was performed under dilute conditions; in our study, the chains begin to interact as the chain length exceeds 4.6K (the onset of the semidilute range[40] at this constant weight fraction PSLi) and interact more strongly as the overlap parameter c/c^* increases. The possibility has been discussed theoretically, that on transition between the dilute to the semidilute regime, by increasing c at fixed N, the interpolymeric rate constants for activation controlled systems will increase.[14] The effect is interpreted as resulting from a screening of excluded-volume effects which occurs once the polymer chains begin to interpenetrate. Experimental support for this effect is seen by Black and Worsfold,[27] who report the activation-controlled esterification of a benzoyl chloride-terminated polystyrene with a phenol-terminated polystyrene; for a given chain length, increasing the concentration above c^* increases the bimolecular reaction rate by roughly a factor of 2.

However, there are two essential points to stress. (1) If one assumes that pure bimolecular reaction kinetics are occurring (i.e., reactions are dominated by encounters between pairs of chains outside aggregates), then at fixed c theory predicts generally that $k_{M,N}$ decreases as N increases and levels off to a constant when the chain lengths involved M and N are both long enough that c/c^* is much larger than unity.[14] The theory and experiments of refs 14 and 27, respectively, found increasing $k_{M,N}$ when $M = N$ increases at fixed c, a distinct path in parameter space. (2) For the present reactions, **4** of length M is always shorter than $\mathbf{1_N}$ with $2 < N/M < 10$, and theory predicts domination of the kinetics by the small chain M.[15] Thus, one would anticipate only a very weak dependence on N. Taking (1) and (2) together, this suggests that aggregation effects probably underlie the increase of $k_{M,N}$ with increasing N. However, we do not exclude the possibility that relatively simple bimolecular excluded-volume screening effects may play a role.

The underlying reason for an increase in rate as a function of N could be due to differences in the aggregation state of $\mathbf{1_N}$ as a function of N. In the Mita study,[2] a small amount of tetrahydrofuran was present, which is purported to reduce aggregation through coordination to potassium cations. In our study, no additives were present. The solution was predominantly benzene, with only a small amount of cyclohexane/hexane solution from the *sec*-butyllithium initiator. Therefore, in our system, we expect the polystyryllithium chains to be aggregated as dimers, as has been reported previously in the literature.[30,36] The effect of chain length on secondary aggregation of polybutadienyllithium has been noted. A recent SANS study[49] reports that the size of the supramolecular micellar aggregates decreases with increasing length of polybutadienyllithium chains. Furthermore, it has been postulated that the smaller micellar aggregates exhibit higher reactivity, and this result has been suggested[49] as an explanation for the increased reactivity of long chain polybutadienyllithium over shorter chains.[33]

Similar supramolecular aggregates of PSLi have been observed,[29,30] and polybutadienyllithium chain length effects[33] may be applicable to understanding chain length dependence in PSLi polymer reactions. If the PSLi case is analogous to polybutadienyllithium, the increase in chain length would be expected to decrease the size of micellar aggregates. These smaller micellar aggregates have been proposed to exhibit enhanced reactivity.[49] In this model the supramolecular structure of the dimeric aggregates would be chain length dependent, and the reactivity would be dependent on this supramolecular structure. The overall effect would be greater reaction rates with longer chain length.

A third possible explanation[33] would be that, as polystyryllithium chain length increases, the dissociation constant of the dimer also increases, favoring deaggregation to monomer. In this hypothesis, the monomeric PSLi is considered to be the only reactive species; thus, deaggregation is essential to reactivity. This hypothesis has been challenged on the basis of evidence for dimeric reactivity[50] and also thermodynamic arguments.[49]

Conclusion

GPC-based measurement of kinetics using fluorescence detection is demonstrated to be a powerful method to extract bimolecular rate constants of polymer end−end reactions. This method is applied to the problem of measuring the chain length dependence of polymer end−end reaction rates in the reaction of PSLi with a styrene-terminated fluorescently labeled polymer. The results of the current study indicate a nearly first-order dependence of the polymer reaction rate on [PSLi]. The results indicate that the reaction is faster for longer chains than for shorter chains as has been seen previously in the case of polybutadienyllithium.[33] The origin of this effect could be due to increasing overlap parameter c/c^* which leads to screening of excluded-volume interactions,[14] chain length dependent supramolecular effects on micellar size,[49] and/or chain length dependent changes in dimer−monomer equilibrium constant.[33] Further studies will attempt to unravel which of these hypotheses is responsible for this interesting chain length effect.

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