Studying a Slow Polymerization: A Kinetic Investigation of the Living Anionic Polymerization of P═C Bonds

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ABSTRACT: The *n*-butyllithium-initiated living anionic polymerization of MesP═CPh_2 (Mes = 2,4,6-trimethylphenyl) was studied at a variety of temperatures (T = 296.3, 301.8, 307.4, 313.0, 318.6, and 324.2 K) with a fixed monomer-to-initiator ratio (50:1). The consumption of monomer and formation of polymer ^{n}Bu[MesP−CPh_2]$_n$Li was monitored by ^{31}P NMR spectroscopy, and the conversion data obtained were analyzed using first-order kinetics. Up to 50% conversion, the plot of ln $[M]_0/[M]$ vs time was linear, and apparent propagation rate constants (k_p) were extracted (k_p = 21−150 L mol^{-1} h^{-1}, T = 296−324 K). These rate constants were used to construct an Arrhenius plot, and the apparent activation energy for the propagation of P═C bonds was estimated (E_a = 14.0 ± 0.9 kcal mol^{-1}).

Introduction

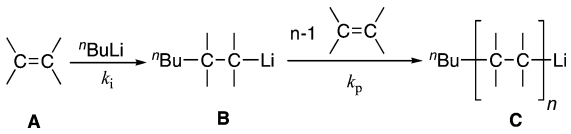
Living polymerization techniques are indispensable tools for the preparation of macromolecules with controlled architectures.[1−4] The discovery of living anionic olefin polymerization a half century ago[5,6] led to a burgeoning field of research and has enabled the construction of complex macromolecules (block copolymers, star polymers, hyperbranched polymers, comb polymers).[1] Detailed kinetic investigations of C═C bond polymerizations, particularly with styrene, allowed for the determination of activation parameters for propagation.[7,8] The effects of solvent, counterion, and temperature on the rates of propagation of styrenic monomers have formed the basis for the textbook models of the mechanism of living anionic polymerization.[9−16]

The living anionic polymerization of alkenes proceeds via a two-step mechanism.[17] The initiation step involves addition of a nucleophilic species, such as *n*-butyllithium, to the C═C bond of monomer **A** forming the propagating species **B** (Scheme 1). Compound **B**, which resembles *n*-butyllithium in terms of its nucleophilicity, then repeatedly adds to the C═C bond of another monomer **A** forming polymer **C**. In the absence of monomer, living polymer **C** will rest indefinitely but can be terminated by controlled addition of an electrophile (i.e., H^+). When the rate of initiation is much faster than the rate of propagation, the rate equation can be expressed as shown below (eq I). Typically, this equation is followed when the polymerization experiment is conducted in polar solvents. The rate constant of propagation is represented by k_p, [living ends] stands for the concentration of the propagating polymer species that remains constant throughout the polymerization, and [M] represents the concentration of monomer **A**.

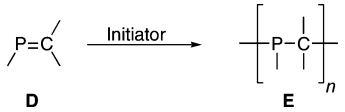
$$\frac{-\mathrm{d}[\mathrm{M}]}{\mathrm{d}t} = k_p[\text{living ends}][\mathrm{M}] \qquad \text{(I)}$$

The development of synthetic routes to main-chain phosphorus polymers is a vibrant area of research due to the potential applications of phosphorus materials as sensors, catalyst supports, ceramic precursors, and biomedical materials.[18−28] One of the key challenges in this field lies in finding suitable synthetic routes to incorporate phosphorus atoms into the macromolecular main chain. Addition polymerization, the most important synthetic route to commodity organic polymers, has received very limited use with heteroatom-containing multiple bonds. In molecular phosphorus chemistry, there has been considerable interest in establishing parallels between the chemistry of P═C bonds and C═C bonds. Common organic reactions such as Diels−Alder, η^2-metal complexation, hydrogenation, and 1,2-addition reactions have been applied to P═C bonds in phosphaalkenes.[29] Recently, the phosphorus−carbon analogy has been expanded to polymer chemistry when the first examples of phosphorus copies of poly(*p*-phenylenevinylene) were reported by our group and the group of Protasiewicz.[23,26−28]

Scheme 1. General Reaction Pathway for the Living Anionic Polymerization of Alkenes



Scheme 2. Addition Polymerization of a Phosphaalkene To Obtain Poly(methylenephosphine)



Another area of considerable interest to our research group is the extension of addition polymerization to P═C bonds. In this regard, we have successfully polymerized phosphaalkenes **D** using radical and anionic methods of initiation to afford poly(methylenephosphine) **E**, a new functional phosphine polymer (Scheme 2).[30,31] Our initial polymerization studies employed high temperatures (150 °C) and long reaction times (24 h) and were performed in the bulk. Such conditions resulted in low yields and the formation of unwanted side products. Importantly, further studies led to the anionic oligomerization of P═C bonds at ambient temperature and in tetrahydrofuran (THF) solution.[32] These results suggested that the polymerization of phosphaalkenes did not necessarily require high (150 °C) temperatures. Most recently, we discovered the ambient temperature living anionic polymerization of MesP═CPh_2 and prepared homopolymers and block copolymers with controlled molecular weights.[33]

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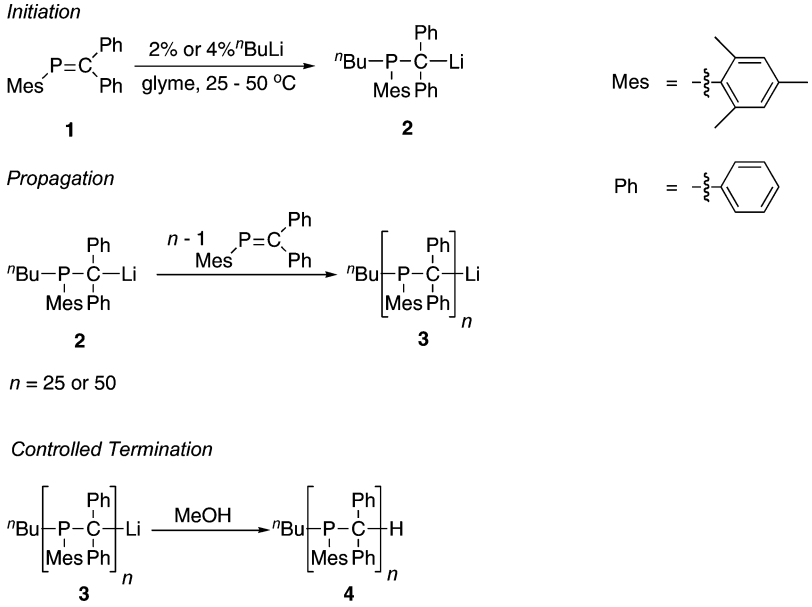
Scheme 3. Proposed Initiation, Propagation, and Termination Steps in the Living Anionic Polymerization of Phosphaalkene 1 Using *n*-Butyllithium as Initiator



We propose that both the initiation and propagation steps in the anionic polymerization of P═C bonds involve nucleophilic addition of a lithium carbanion (i.e., ^{n}BuLi or **2**) to the P═C bond in a regioselective fashion (Scheme 3).[32,33] This postulate is supported by molecular model studies where addition of MeLi to compound **1** affords Mes(Me)P−$CHPh_2$ after quenching with H^+.[34] These observations agree with the calculated polarity of the P═C bond in normally polarized phosphaalkenes ($P_{\delta+}$···$C_{\delta-}$).[35] Morover, the active growing species (i.e., **2** and **3**) are doubly benzylic carbanions which offer substantial π-stabilization by electronic delocalization into the phenyl substituents and the phosphorus atom.

In this paper, we report the first kinetic studies of the living anionic polymerization of P═C bonds. Propagation rate constants are estimated by following the consumption of [**1**] and formation of **3** using ^{31}P NMR data collected over a 9 h period. Kinetic experiments were conducted at several temperatures to elucidate the activation energy for anionic propagation (E_a = 14.0 ± 0.9 kcal mol^{-1}).

Results and Discussion

To study the kinetics of the living anionic polymerization of C═C bonds, specialized capillary tube stop flow techniques are normally employed to measure rates of these rapid reactions.[2]

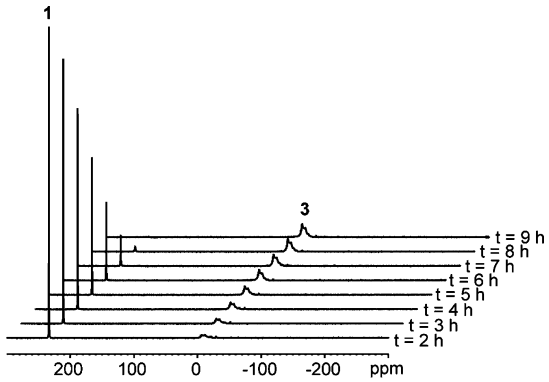


Figure 1. Selected ^{31}P NMR spectra (glyme; 296.3 K) of the ^{n}BuLi-initiated polymerization mixture showing the conversion of **1** to **3** over time ([M]:[I] = 50:1). $[M]_0$ = 0.394 mol L^{-1}.

Table 1. Determination of k_p at Different Temperatures

entry	[M]:[I][a]	temp (K)	k_p[b] (L mol^{-1} h^{-1})	M_n calcd[c] (g mol^{-1})	M_n obsd[d] (g mol^{-1})	PDI
1	50:1	296.3	21.0 ± 2.5	15 900	13 500	1.07
2	50:1	301.8	32.7 ± 3.9	15 900	15 100	1.02
3	50:1	307.4	41.8 ± 4.9	15 900	13 800	1.05
4	50:1	313.0	70.7 ± 8.9	15 900	14 400	1.09
5	50:1	318.6	125 ± 15	15 900	12 300	1.07
6	50:1	324.2	150 ± 17	15 900	13 600	1.05
7	50:2	296.3	16.5 ± 2.1	8 000	8 800	1.09

[a] [MesP═CPh_2]:[^{n}BuLi]. [b] Rate constant of propagation. [c] Calculated using the monomer-to-initiator ratio. [d] Absolute molecular weights were determined using triple-detection GPC.

In contrast to olefin polymerizations, which have half-lives of seconds to minutes, the half-life of phosphaalkene **1** in anionic polymerization reactions is several hours. Consequently, the anionic polymerization of **1** can be conveniently monitored using ^{31}P NMR spectroscopy.

All kinetic experiments performed during the present study were conducted as follows: (i) the monomer **1** was dissolved in glyme in an inert atmosphere; (ii) ^{n}BuLi was added to this solution, and an immediate color change from yellow to red was observed upon initiation (50:1 monomer-to-initiator ratio); and (iii) the reaction mixture was transferred to an NMR tube, and ^{31}P NMR spectra were recorded at 15 min intervals. The relaxation delay and tip angle were set to ensure that the integration of the ^{31}P NMR spectra were reliable (d_1 = 2 s and 30° tip angle).[36] Representative ^{31}P NMR spectra from the ^{n}BuLi polymerization of **1** at 296.3 K are shown in Figure 1. In each spectrum, the signals assigned to the monomer **1** (233 ppm) and the growing polymer **3** (−10 ppm) were integrated separately, and using the known initial concentration of **1**, the percent conversion was calculated. Under otherwise identical conditions, NMR experiments were performed at 296.3, 301.8, 307.4, 313.0, 318.6, and 324.2 K. Upon completion of the polymerization, as determined by ^{31}P NMR spectroscopy, the polymer **3** was quenched with methanol (0.1 mL), precipitated with hexanes (2 × 40 mL), and analyzed by triple-detection GPC. The molecular weights, which are listed in Table 1, were used to confirm that the polymer chain length correlated properly with the initiator concentration. Each experiment was repeated at least twice to ensure reproducibility. Although there was some

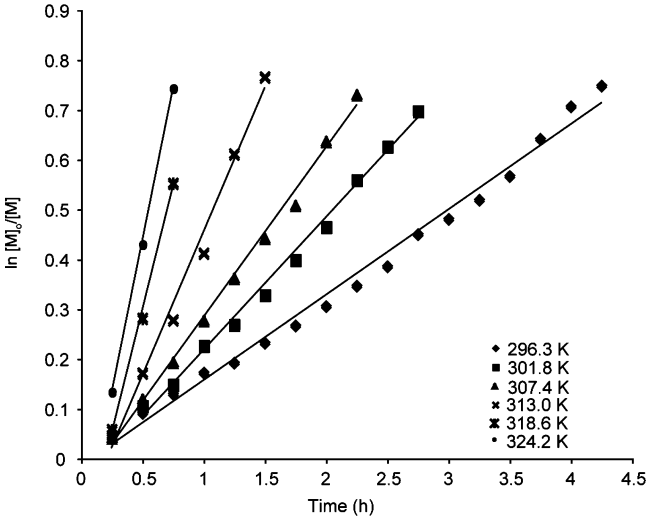


Figure 2. Graph showing ln $[M]_0/[M]$ vs time (h) up to ~50% conversion for the polymerization of **1** with 2% ^{n}BuLi at ~5 K temperature intervals between 296 and 324 K. These plots of ln $[M]_0/[M]$ vs time (h) were fitted to a linear least-squares function to determine rate constants illustrated in Table 1.

variation in the observed molecular weights, the apparent propagation rate constants determined were reproducible at each temperature.

The living polymerization of C═C bonds follows pseudo-first-order reaction kinetics (eq I) with [living ends] remaining constant throughout the polymerization and [M] decreasing over time.[17] Therefore, if the living anionic polymerization of **1** is analogous to that of C═C bonds, a plot of ln $[M]_0/[M]$ vs time should be linear. At all temperatures, the propagation data collected are linear up to ca. 50% conversion (Figure 2). The apparent rate constant of propagation (k_p) was determined by least-squares fitting the data at each temperature, and the results are given in Table 1. Remarkably, the k_p for **1** ($k_p = 21.0 \pm 2.5$ L mol^{-1} h^{-1} at 296.3 K) is several orders of magnitude smaller than that observed for the sodium naphthalide-initiated polymerization of styrene in THF at room temperature ($k_p = 1.4 \times 10^6 - 2.2 \times 10^6$ L mol^{-1} h^{-1}).[9] Since MesCH═CPh$_2$ has not been polymerized, the closest steric comparison for **1** that we have come across is vinylmesitylene. Importantly, the rate constant for polymerization of H$_2$C═CHMes in THF initiated using sodium naphthalide ($k_p = 1.2 \times 10^3$ L mol^{-1} h^{-1}) is several orders of magnitude slower than styrene[11,37] which is attributed to larger steric constraints imposed by a mesityl group as compared to a phenyl group.

The rate constant data were used to prepare an Arrhenius plot from which the apparent activation energy (E_a) of the polymerization was extracted (Figure 3). The E_a for the anionic polymerization of **1** in glyme was calculated to be 14.0 ± 0.9 kcal mol^{-1}, and the preexponential factor ($A = 4.4 \times 10^{11}$ M^{-1} h^{-1}) was also obtained. Interestingly, this activation barrier is much larger than the E_a measured for styrene polymerization in THF with Na^+ counterion ($E_a = 5.9$ kcal mol^{-1}).[7,38] For comparison, bulky substituted olefins have higher activation barriers and, therefore, slower polymerization rates. For example, the sterically hindered monomer α-methylstyrene ($E_a = 7.2$ kcal mol^{-1}) has a higher activation energy than styrene.[8] The high activation barrier in the anionic polymerization of **1** is almost certainly a consequence of the high degree of steric bulk surrounding the P═C bond and, in addition, the propagating polymer species **3** is highly resonance stabilized, lowering its nucleophilicity.

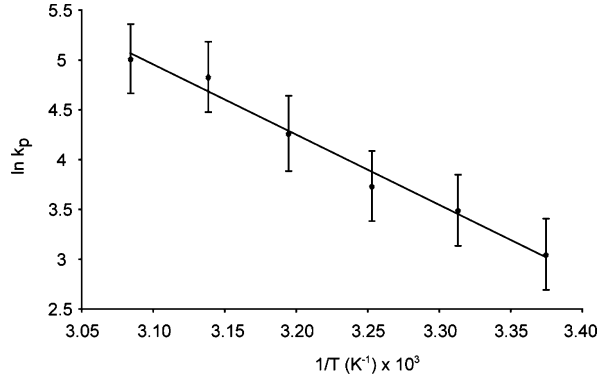


Figure 3. Arrhenius plot for the BuLi-initiated polymerization of **1**. The ln k_p (k_p = apparent propagation rate constant) vs $1/T$ (K^{-1}) data were fit to a linear function. The linear least-squares function ($y = -7051.5x + 26.811$) had an R^2 value of 0.9841. An activation energy (E_a) of 14.0 ± 0.9 kcal mol^{-1} was estimated for the polymerization of **1**. Error bars are reported with 95% confidence.

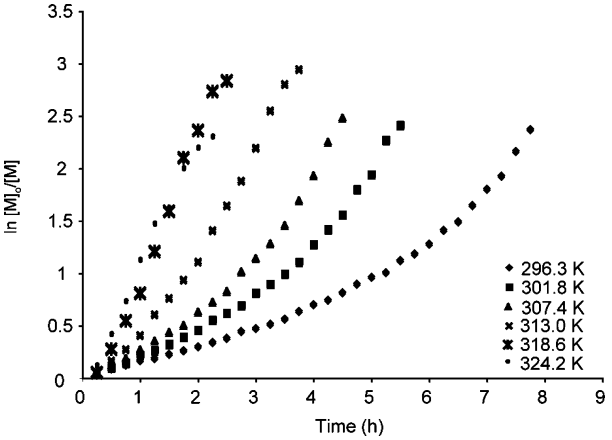


Figure 4. Plot of ln $[M]_0/[M]$ vs time (h) up to ~90% conversion for the polymerization of **1** with 2% ^{n}BuLi at ca. 5 K temperature intervals between 296 and 324 K.

Although rate constant data may be extracted, the plots of ln $[M_0]/[M]$ vs time in the anionic polymerization of **1** only exhibit pseudo-first-order kinetics up to ca. 50% conversion. Thereafter, a deviation from linearity is observed (Figure 4). For comparison, the anionic polymerization of styrene and α-methylstyrene exhibit linear behavior up to 90% conversion.[13,15] Although for styrene the conversion rate decreases as the monomer is consumed, the rate of propagation actually *increases* above 50% conversion for **1**. Interestingly, at higher polymerization temperatures the expected behavior is observed, and the rate of propagation for **1** slows above 50% conversion. Particularly striking is the experiment conducted at 324.2 K, which appears almost linear up to ~80% conversion. To our knowledge, an increase in rate at high conversion has not been observed for the living anionic polymerization of C═C bonds and suggests a more complex mechanism for the P═C system.[39] We speculate that this difference may be a consequence of the phosphine moieties in growing polymer **3** binding Li^+ which leads to autocatalytic behavior and increased propagation rates at late stages in the polymerization (i.e., as phosphine concentrations increase). Detailed studies testing this postulate will be described at a later time.

In the polymerization of olefins, the observed or apparent rate constant k_p in polar solvents is actually composed of two different rate constants (eq II).[17] Because of solvation phenomena, the rate equation must be rewritten in terms of the free-ion rate constant (k_p^{free}) and the ion-pair rate constant ($k_p^{ion-pair}$).[40]

Both rate constants are expected to contribute to the rate of propagation for unsaturated bonds; however, this contribution is not equal, especially in polar solvents. Consequently, increasing the number of ions in solution (i.e., increasing [living ends]) will affect the ion-pair−free-ion equilibrium (i.e., [free-ion chain ends] and [ion-pair chain ends]) and alter the apparent rate of propagation k_p. A preliminary experiment was conducted to test whether this applies to the polymerization of **1** in glyme. Under otherwise identical conditions, the anionic polymerization of **1** was conducted with double the concentration of ^{n}BuLi ([M]:[I] = 50:2) than that used in all other experiments (Table 1, entry 7). If only eq I applied, the reaction rate should be identical for both experiments. However, consistent with eq II, polymerization with a higher concentration of living ends results in a lower propagation rate ($k_p = 16.5 \pm 2.1$ L mol^{-1} h^{-1}) as compared to the experiment with 2% initiator ($k_p = 21.0 \pm 2.5$ L mol^{-1} h^{-1}) at 296.3 K. Future work will focus on determining k_p^{free} and $k_p^{ion-pair}$ by conducting polymerizations with excess counterion (Li^+).

$$-\frac{d[M]}{dt} = k_p^{free}[\text{free-ion chain ends}][M] + k_p^{ion-pair}[\text{ion-pair chain ends}][M] \quad \text{(II)}$$

Summary. In closing, kinetic investigations of the *n*-butyllithium-initiated living anionic polymerization of MesP═CPh_2 are reported. Rate constants over a 25 K range were obtained and used to determine an activation energy for the anionic polymerization of MesP═CPh_2 (14.0 ± 0.9 kcal mol^{-1}). This activation energy is significantly higher than that of styrene (5.9 kcal mol^{-1}) and α-methylstyrene (7.2 kcal mol^{-1}). This large activation energy is most likely a product of the bulky substituents (Mes and Ph) surrounding the P═C bond and the doubly stabilized carbanion formed during polymer propagation. Future work will focus on P═C monomers with different substituents and developing alternative methods to determine k_p^{free} and $k_p^{ion-pair}$.

Experimental Section

General Procedures. All manipulations of air and/or water sensitive compounds were performed under prepurified nitrogen (Praxair, 99.998%) using standard high-vacuum or Schlenk techniques or in an Innovative Technology Inc. glovebox. ^{31}P NMR (121.5 MHz) spectra were recorded at room temperature on a Bruker Avance 300 MHz spectrometer. Chemical shifts are reported relative to 85% H_3PO_4 as an external standard $\delta = 0.0$ for ^{31}P. The relaxation time (t_1) for **1** is 1.33 s. To ensure accurate integrations, a relaxation delay of 2 s with a 30° tip angle was employed for all ^{31}P NMR experiments. Temperature was calibrated for NMR experiments using standard Bruker samples: 4% MeOH in MeOH-d_4 for the 194−283 K range and 80% ethylene glycol in DMSO-d_6 for the 300−400 K range. Molecular weights were estimated by triple detection gel permeation chromatography (GPC-LLS) using a Waters liquid chromatograph equipped with a Waters 515 HPLC pump, Waters 717 plus autosampler, Waters Styragel columns (4.6 × 300 mm) HR5E (2000−4 000 000), HR4 (5000−500 000), and HR2 (500−20 000), Waters 2410 differential refractometer ($\lambda = 940$ nm, 40 °C), Wyatt tristar miniDAWN (laser light scattering detector operating at $\lambda = 690$ nm), and a Wyatt ViscoStar viscometer. A flow rate of 0.5 mL min^{-1} was used, and samples were dissolved in THF (ca. 2 mg mL^{-1}). The refractive index increment of poly(methylenephosphine) **4** ($dn/dc = 0.223$ mL g^{-1}) was determined by plotting the refractive index vs concentration for six solutions of **4** in THF (1−6 mg mL^{-1}). Aqueous NaCl was used to calibrate the Waters 410 differential refractometer.

Materials. Hexanes was dried by passing through activated alumina columns. 1,2-Dimethoxyethane (glyme) was distilled from sodium/benzophenone and was degassed under vacuum at −196 °C prior to use. MeOH was degassed by passing nitrogen through the solvent for 1 h prior to use. ^{n}BuLi (1.6 M in hexane) was purchased from Aldrich and was titrated with *N*-benzylbenzamide prior to use.[41] MesP═CPh_2 was prepared according to literature procedures.[42]

Purification of MesP═CPh_2 (1). Crude **1** was transferred to a short path distillation apparatus and was heated under vacuum with an oil bath (190 °C, 0.01 mmHg). The yellow liquid distilled between 150 and 160 °C, and the distillate was recrystallized from hexanes. The crystalline solid was ground up into a fine powder using a mortar and pestle and was subsequently dried in vacuo for 12 h at 60 °C. ^{1}H NMR was used to confirm purity.

Anionic Polymerization of MesP═CPh_2 for Kinetic Studies. A solution of ^{n}BuLi (12 μL, 1.37 M, 0.016 mmol) in hexanes was added to a stirred solution of **1** (0.250 g, 0.790 mmol) in glyme (2 mL) in the glovebox. Immediately after mixing, an aliquot was removed from the reaction mixture and was transferred to an NMR tube. The sample was loaded into the spectrometer ($T = 296.3$ K), and ^{31}P NMR spectra were recorded every 15 min (72 scans) until the reaction was complete. At completion, the living polymer was terminated by the addition of one drop of degassed MeOH, and the polymer was isolated by precipitation into hexanes (2 × 40 mL) under N_2. The purified polymer was dried in vacuo (4 h at 100 °C). GPC (absolute): $M_n = 13\,500$ g mol^{-1}, PDI = 1.07. Experiments were repeated at least two times at each temperature to ensure reproducibility.

General Procedure for Processing ^{31}P NMR Spectra. The raw NMR data, obtained as described above, were processed using line broadening settings of (LB = 10), and a baseline correction was applied. The sharp signal for **1** ($\delta = 233$) and the broad signal for **2** ($\delta = -10$) were integrated using approximate ranges between 250 and 210 ppm and between 30 and −75 ppm, respectively. The relative integrations, after phasing, were used to determine the percent conversion of monomer to polymer and, consequently, the average concentration of monomer [M] during the acquisition of each spectrum. In each case, the first NMR experiment was started 13.5 min after initiation. Since the acquisition time for 72 scans requires 3 min, the time (t) for the first data point is 15 min (0.25 h). The delay time between NMR experiments was 12 min, which results in data points at $t = 30$, 45, 60 min, etc. The data are tabulated in the Supporting Information.

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Supporting Information Available: Tables of ln $[M]_0/[M]$ vs time at each temperature; figure showing the inversion recovery in the measurement of relaxation time (t_1) for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(36) The relaxation time (t_1) of the phosphorus atom in the MesP═CPh_2 monomer was measured prior to conducting this kinetic analysis to ensure adequate delay time for complete relaxation between data acquisition (t_1 = 1.33 s). This ensures that integrations are reliable. Relaxation times (t_1) for polymer **3** is not a concern as macromolecules relax much faster on the NMR time scale than molecular compounds.
(37) The rate constant ($k_p = 3.3 \times 10^3$ L mol^{-1} h^{-1}**)** for vinyl mesitylene has been reported. See: Bhattacharyya, D. N.; Smid, J.; Szwarc, M. *J. Polym. Sci., Part A* **1965**, *3*, 3099−3106.
(38) The activation energy reported was determined for free polystyryl anions in THF. Solvent has a significant effect on the activation energy as it alters the free-ion to ion-pair equilibrium discussed in the text. For example, in a solvent such as dioxane, the polymerization of styrene proceeds with a much lower rate constant ($k_p \sim 4$ L mol^{-1} s^{-1}) and has a higher activation energy (E_a = 9 kcal mol^{-1}). This slower rate is likely due to lower concentration of free ions than in a polar solvent such as THF. Szwarc, M. *Carbanions, Living Polymers, and Electron Transfer Processes;* Interscience: New York, 1968.
(39) Two small singlet resonances are observed upon careful examination of the ^{31}P NMR spectra of the ^{n}BuLi-initiated polymerization of **1** in glyme (−29 and −102 ppm). These signals account for ≪1% of the total phosphorus, however, and are observed in all polymerization experiments (it was not observed at 50 °C). The signal at −29 ppm may be due to the phosphorus atom next to the propagating carbanion in **3.** For comparison, anion model Mes(^{n}Bu)P−CPH_2Li resonates at −31.1 ppm in THF. See ref 34. The signal at −102 ppm is, as yet, unassigned. Further studies are underway to assign these signals.
(40) A variety of ion pairs may be present in polar solvents including contact and solvent-separated ion pairs. For simplicity, the contributions of each of these species is approximated as $k_p^{ion-pair}$ in eq II. For a thorough discussion, see: Swarc, M. *Adv. Polym. Sci.* **1983**, *49*, 1−177.
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