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Photodimers of 9-Haloanthracenes as Initiators in Atom Transfer Radical Polymerization: Effect of the Bridgehead Halogen

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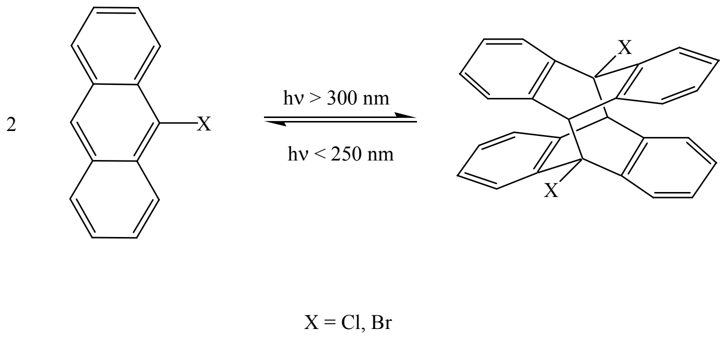
Summary

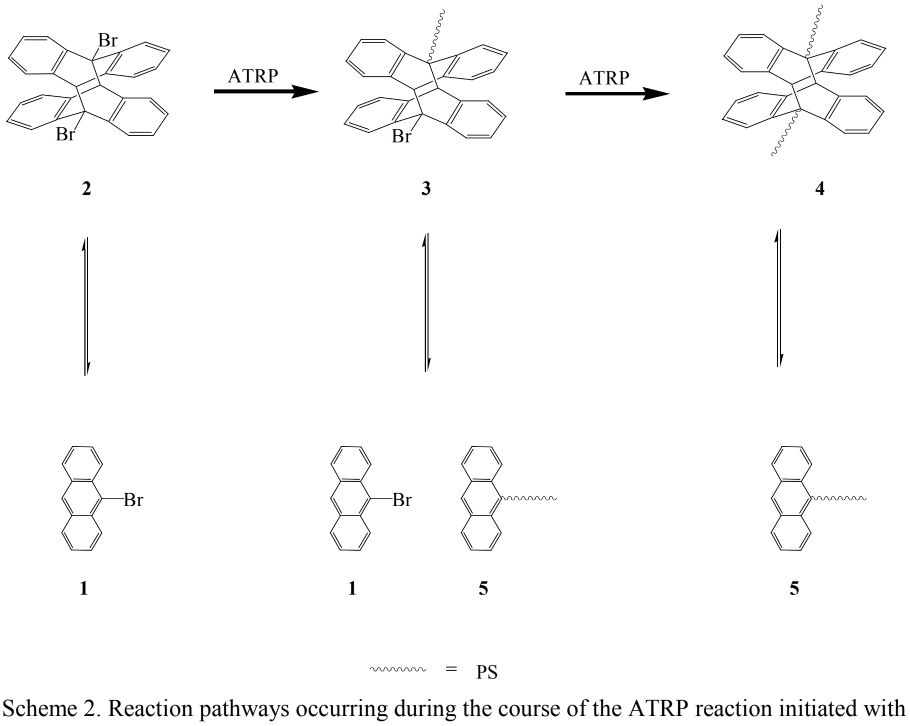
Photodimers of 9-chloroanthracene, formed by a [4+4] cycloaddition reaction of 9-chloroanthracene, were used as initiators in the atom transfer radical polymerization of styrene and compared to results previously obtained using photodimers of 9-bromoanthracene as the initiator. Heat-induced cleavage of the photodimer coupled with slow initiation from the bridgehead radical have been used to account for the lack of control in the systems, and thus changing the halogen on the initiating photodimer could support or refute this model. Reactions performed using analogous procedures produced polymers with number average molecular weight (M_n) values significantly higher in the case of 9-chloroanthracene photodimer-initiated systems, with similar polydispersity index (PDI) values observed in trials catalyzed with CuCl or CuBr. Polymer products showed absorbance bands indicative of regenerated anthracene in all cases, consistent with heat-induced cleavage of the photodimer during the course of the polymerization. Kinetic plots demonstrated that the polymerizations initiated with photodimers of 9-chloroanthracene showed maximum M_n values were obtained after approximately 10% monomer conversion, with a decline in M_n as a function of monomer conversion after this point. The data support slower initiation in the case of 9-chloroanthracene photodimers, followed by heat-induced cleavage throughout the polymerization system.

Introduction

Atom transfer radical polymerization (ATRP) of styrenic monomers typically requires an alkyl halide with a halogen atom located at the benzylic position or α to an ester group to afford a resonance stabilized initiating radical [1-7]. We have recently reported that converting the aryl bromide on 9-bromoanthracene into an alkyl bromide via a [4 + 4] cycloaddition reaction (**Scheme 1**) generates sites able to initiate styrene in ATRP reactions[8]. The pathways found to be occurring throughout the course of the ATRP reaction are summarized in **Scheme 2**. Although adjacent to aromatic groups, the initiating bridgehead radical is held orthogonal to the phenyl groups and thus unable to gain appreciable resonance stabilization, lowering k_{act}/k_{deact} (where k_{act} is the rate constant for activation of the alkyl halide, and k_{deact} is the rate constant for deactivation of the initiating radical) and creating a system where R_i (rate of initiation) is substantially lower than R_p (rate of propagation) due to the extremely low concentration of the initiating radical. As outlined in **Scheme 2**, heat-induced cleavage of the photodimer over the course of the reaction, regenerating the anthracene species (*2* → *1* and *3* → *1* + *5*), was speculated to occur during the polymerization. Thermolysis of the initiating photodimer ocurring prior to initiation reformed 9-bromoanthracene (*2* → *1*), which is inactive as an ATRP initiator due to its inability to undergo homolytic C-Br cleavage under ATRP reaction conditions. Although the end result of the polymerization was anthracene-labeled polymers (*5*), these competing side reactions did not allow for the controlled/“living” characteristics of ATRP.



Scheme 1. Reversible photodimerization of 9-haloanthracenes.



Scheme 2. Reaction pathways occurring during the course of the ATRP reaction initiated with 9-bromoanthracene photodimers.

The ability of 9-bromoanthracene to form photodimers is not unique among substituted anthracenes[9-12]. For example, 9-chloroanthracene is known to photodimerize[13] under similar conditions and is commercially available. While the photodimerization of 9-bromoanthracene has been reported to proceed with side reactions, such as C-Br cleavage[10], no such complications have been reported with 9-chloroanthracene. The increased strength of C(sp^3)-Cl bonds compared to analogous C-Br bonds may also suppress heat-induced cleavage of the photodimer prior to initiation, leaving a larger number of initiating sites intact. Additionally, alkyl chlorides are well known as initiators in ATRP reactions and have lead to many controlled/"living" systems[14-17].

In this paper, a comparison between photodimers of 9-chloro- and 9-bromoanthracene as initiators in ATRP reactions is presented, along with a mechanistic account of the differences in the systems.

Experimental

Materials

9-Bromoanthracene (94%, Aldrich) and 9-chloroanthracene (96%, Aldrich) were recrystallized from ethanol and stored in the dark at room temperature. Styrene (99%, Acros), N,N,N',N",N"-pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich), and anisole (99.7%, Aldrich) were distilled from calcium hydride under reduced pressure and stored in sealed glass ampoules at -15°C. CuBr (98%, Aldrich) and CuCl (99.995+%, Aldrich) were used as received and stored in a desiccator at room temperature. Tetrahydrofuran (THF) was distilled from sodium/benzophenone prior to use, while benzene was passed through a Grubbs-type purification column[18] before use.

Typical photodimerization of 9-bromoanthracene and 9-chloroanthracene (Synthesis of 9,9'-dibromodianthracene and 9,9'-dichlorodianthracene): 2.0 g (7.78 mmoles) of 9-bromoanthracene was dissolved in 65 mL of benzene. The flask was equipped with a condensing column and drying tube, and irradiated with longwave UV light (Blak-Ray; Model B100 AP, λ = 365 nm). The photodimerization was monitored using UV-Vis spectroscopy and was considered complete when the absorption peaks due to anthracene (between 350 – 400 nm, max at 370 nm) completely disappeared (~ 48 hours). The volatiles were removed under vacuum and the residue was washed with cold benzene to afford 9,9'-dibromodianthracene as a yellowish-white solid. The photodimerization of 9-chloroanthracene was carried out in an analogous manner, affording 9,9'-dichlorodianthracene as a white solid. The photodimers were characterized by UV-Vis spectroscopy, ^{1}H NMR, and melting point. 9,9'-Dibromodianthracene: Mp = 200-202°C. ^{1}H NMR ($CDCl_3$): δ (ppm) 7.77 (d, 8H, *J = 8.52*), 6.95 (m, 8H), 5.33 (s, 2H). 9,9'-Dichlorodianthracene: Mp = 210-212; ^{1}H NMR ($CDCl_3$): δ (ppm) 7.58 (d, 4H, J = 7.5), 6.91 (m 12 H), 4.92 (s, 2H).

Typical ATRP procedure using the photodimer of 9-bromoanthracene as the initiator. ($[M]_0$:$[I]_0$ = 50:1; $[Cu(I)]_0$:$[I]_0$ = 2.5:1; $[Cu]_0$ ~ $[PMDETA]_0$): The molar equivalents were determined by monomer to initiating-sites ratio ([I] = [C-X]), while keeping the monomer volume constant (~2.0 mL) and ratio of Cu(I)X (X = Br, Cl) to PMDETA at 1 or as indicated. The 9-bromoanthracene photodimer initiator (89.5 mg, 0.174 mmoles) and CuBr (124.8 mg, 0.870 mmoles) were placed in a two-necked round bottom flask, followed by sealing one with a rubber septa and the other with a Teflon stop cock. The reaction chamber was placed on a Schlenk line and filled with nitrogen gas, after which sequential additions of 2.0 ml styrene (17.4 mmoles) and 2.1 ml THF (~50% by volume) were introduced into the flask via argon purged syringes. The contents were subjected to three freeze-pump-thaw cycles, and the reaction chamber was sealed, removed from the line, and placed in an oil bath preheated to 80°C. The contents of the reaction flask were allowed time to reach the temperature of the oil bath, and finally PMDETA (0.182 mL, 0.870 mmoles) was added through an argon-flushed syringe to start the reaction. The vessel was removed from the oil bath after 48 hours (or as indicated) and the contents were dissolved in THF. The polymeric product was precipitated in cold methanol and dried in a vacuum oven (~ 45°C) prior to characterization. Polymerizations using photodimers of 9-chloroanthrance were performed in an identical manner. On trials where monomer consumption was monitored, the total volume was brought up to ~17 mL by increasing the amount of styrene to 5.5 mL and basing ratios of the remaining reactants on this. Approximately equal volumes of styrene, THF, and anisole (an internal standard for determining monomer conversion using GC) were used.

Characterization

The polymers were characterized on a Waters Gel Permeation Chromatography (GPC) system (consisting of a Waters 1515 isocratic pump, a Waters 717 auto sampler, two Pl-gel 5 mm Mixed C columns (Polymer Labs), a Waters 2487 dual wavelength detector and a Waters 2414 RI detector) that was connected to a PC running Waters Breeze software. A 10 point calibration using polystyrene standards (Polymer Laboratories, Mp range: 5.0×10^2 - 3.05×10^6 Daltons) was used to obtain molecular weights and polydispersities based on the RI traces. Concurrently, the UV detector was set at 370 nm to visualize the distribution of anthracene in the product. The mobile phase was THF (Burdick and Jackson). A Hewlett Packard HP 6890 GC with HP Chemstation software with 1 µl injections in THF solvent was used to determine percent monomer conversion, using anisole as the internal standard in the polymerization. NMR spectra were obtained on a Bruker 300 MHz FT-NMR at room temperature. A Gentech TU-1901 double-beam UV-Vis Spectrophotometer with THF as the solvent was used to obtain UV-Vis spectra.

Results

Previous work in our lab has demonstrated that photodimers of 9-bromoanthracene (9-BA) can act as initiators in the ATRP of styrene, yet the system lacked control due to side reactions such as thermolysis of the photodimer and slow initiation from the bridgehead radical (**Scheme 2**). Furthermore, performing trials in either the presence or absence of incidental laboratory light (to prevent inadvertent photochemistry of the anthracenes) did not impact the polymerization. It was also demonstrated that aryl halides themselves were unable to initiate the polymerization, as expected, ruling out complications that would result if the thermolyzed dimer (i.e., 9-BA itself) was competing with the photodimer for initiation.

This lack of control motivated us to study polymerizations using photodimers of 9-chloroanthracene (9-CA) as initiators under a variety of reaction conditions and compare these results to analogous 9-BA-initiated trials. Representative results are given in **Table 1**. When run under similar conditions (using Cu(I)Cl as the catalyst), polymers formed using photodimers of 9-CA as the initiator resulted in polymers with

Table 1. Results obtained in the ATRP of styrene using photodimers of 9-bromoanthracene or 9-chloroanthracene as initiators.[a]

Run	I[b]	CuX X =	$[M]_0/[I]_0$[c]	$V_{solvent}/V_{total}$[d]	Time (h)	M_n[e] (Daltons)	PDI (M_w/M_n)	Source[f]
1	CA	Cl	50	0.5	48	104800	1.70	t.w
2	CA	Cl	50	Bulk	72	148000	1.50	t.w
3	BA	Cl	50	Bulk	48	26100	1.75	8
4	BA	Cl	50	0.5	48	18700	1.82	8
5[g]	CA	Cl	50	0.5	48	36200	1.51	t.w
6[g]	CA	Cl	50	0.6	48	66600	1.70	t.w
7[g]	BA	Cl	50	0.5	48	23100	1.55	8
8[g]	BA	Cl	50	0.5	48	31600	1.63	8
9[i]	CA	Br	25	0.4	72	43250	1.98	t.w
10[i]	CA	Br	25	0.4	72	51700	1.85	t.w
11[i]	BA	Br	25	0.4	~100	16600	1.60	t.w
12	BA	Br	50	0.7	72	18200	1.61	8

[a] Reactions were run at 80°C with PMDETA as the ligand, Cu(I)X as the catalyst with $[Cu(I)X]_0:[PMDETA]_0:[C\text{-}X]_0 = 2.5:2.5:1$, unless otherwise indicated

[b] Initiator: BA = 9-bromoanthracene photodimer; CA = 9-chloroanthracene photodimer

[c] Ratio of the initial concentration of monomer to initiating sites (C-Br or C-Cl)

[d] Initial concentration of solvent to the total concentration of the reaction mixture. Solvent is THF in all cases

[e] Compared to the RI trace of linear polystyrene standards on a calibrated GPC

[f] t.w. = this work; 8 = previously reported in reference [8]

[g] $[Cu(I)X]_0:[PMDETA]_0:[C\text{-}X]_0 = 1:1:1$

[i] $[Cu(I)X]_0:[PMDETA]_0:[C\text{-}X]_0 = 1:2:2$

similar polydispersity index (PDI) values, but with number average molecular weight (M_n) values significantly higher than reactions initiated with photodimers of 9-BA (**Table 1**, *runs 1-4*). Altering the initial ratios of catalyst, ligand, and initiator impacted both systems in an analogous manner (**Table 1**, *runs 5-8*), with the 9-CA photodimers giving rise to polymers with M_n values 2-4 times higher and similar PDI values compared to similar trials with 9-BA photodimers. Switching the catalyst to Cu(I)Br again generated polymers with M_n values significantly higher when initiated with 9-CA photodimers, but in these cases also showed dramatic effects on PDI values, with lower PDI values occurring in cases using 9-BA photodimers as initiators.

A typical GPC chromatogram of polymer formed using 9-CA photodimers as the initiator is shown is **Figure 1**. The UV-Vis detector was set at 370 nm to allow for visualization of the anthracene in the polymeric products, and its coincidence with the RI trace indicated the polymers formed contained the anthracene chromophore (**Scheme 2**, *5*) rather than the centrally or terminally bound photodimer (*3* or *4*) which does not absorb at this long wavelength. UV-vis spectrometry in conjunction with Beer’s law revealed the polymers contained near-quantitative labeling with anthracene,[19] identical to our findings with polymers formed using 9-BA photodimers as initiators[8].

Propagating polymers initiated with each photodimer were monitored over the course of the reactions, with M_n values and PDI values plotted as a function of monomer conversion. As shown in **Figure 2a (♦)**, polymers formed from 9-CA photodimers demonstrate a sharp initial increase in the M_n values at low monomer conversions

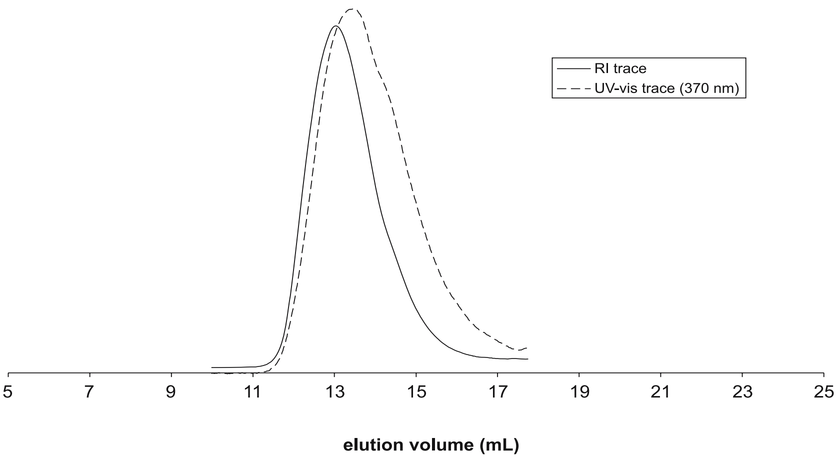


Figure 1. GPC traces of anthracene-labeled polystyrene obtained by ATRP using photodimers of 9-chloroanthracene as the initiator. (Table 1, *run 10*). Solid line: RI trace; dashed line: UV trace (370 nm).

(< 10%), followed by a gradual *decrease* of the M_n of propagating polymers as monomer was continued to be consumed. An analogous plot of a system initiated with 9-BA photodimers shows dramatic differences, with M_n values beginning to slowly plateau and level off near 40% monomer conversion and PDI values (□) steadily increasing over the course of the reaction (**Figure 2b, ♦**). **Figure 3** presents kinetic plots of each system, displaying $\ln([M]_0/[M]_t)$, where $[M]_0$ is the initial concentration of monomer and $[M]_t$ is the concentration of monomer at time *t*, as a function of reaction time, which display first order dependence on monomer concentration for polymerizations initiated with either photodimer.

Discussion

The curved plot of M_n vs. monomer conversion in the case of the 9-BA system (**Figure 2b**) has been previously attributed to slow initiation, where $R_i < R_p$; consistent with a low concentration of the bridgehead radical. A linear correlation between M_n and conversion would be indicative of a controlled radical polymerization, where $R_i \sim R_p$ and all polymer chains are initiated nearly simultaneously. In the cases where photodimers of 9-CA were used as initiators, the pronounced decrease in M_n after ~ 10% monomer conversion may suggest that polymers in the early stages are formed with a centrally bound photodimer (**Scheme 2**, *4*), which cleave during the reaction to form *5* and thus causing the overall M_n to decrease. If this were the case, early GPC traces of the polymerization should show no absorbance at 370 nm, as the anthracene would be in its dimeric form and not visible at this wavelength. Later GPC traces would contain the thermolyzed photodimer, resulting in anthracene-labeled polystyrene that would possess a GPC-UV trace when the detector is set at 370 nm. The increase in the rate of polymerization (**Figure 3**) at later stages (after ~13% monomer conversion) suggests that new initiating sites may be formed during the course of the reaction. The possibility of regenerating photodimers, which could then initiate a chain, from cleaved 9-CA species is a possible explanation for the change in slope observed.

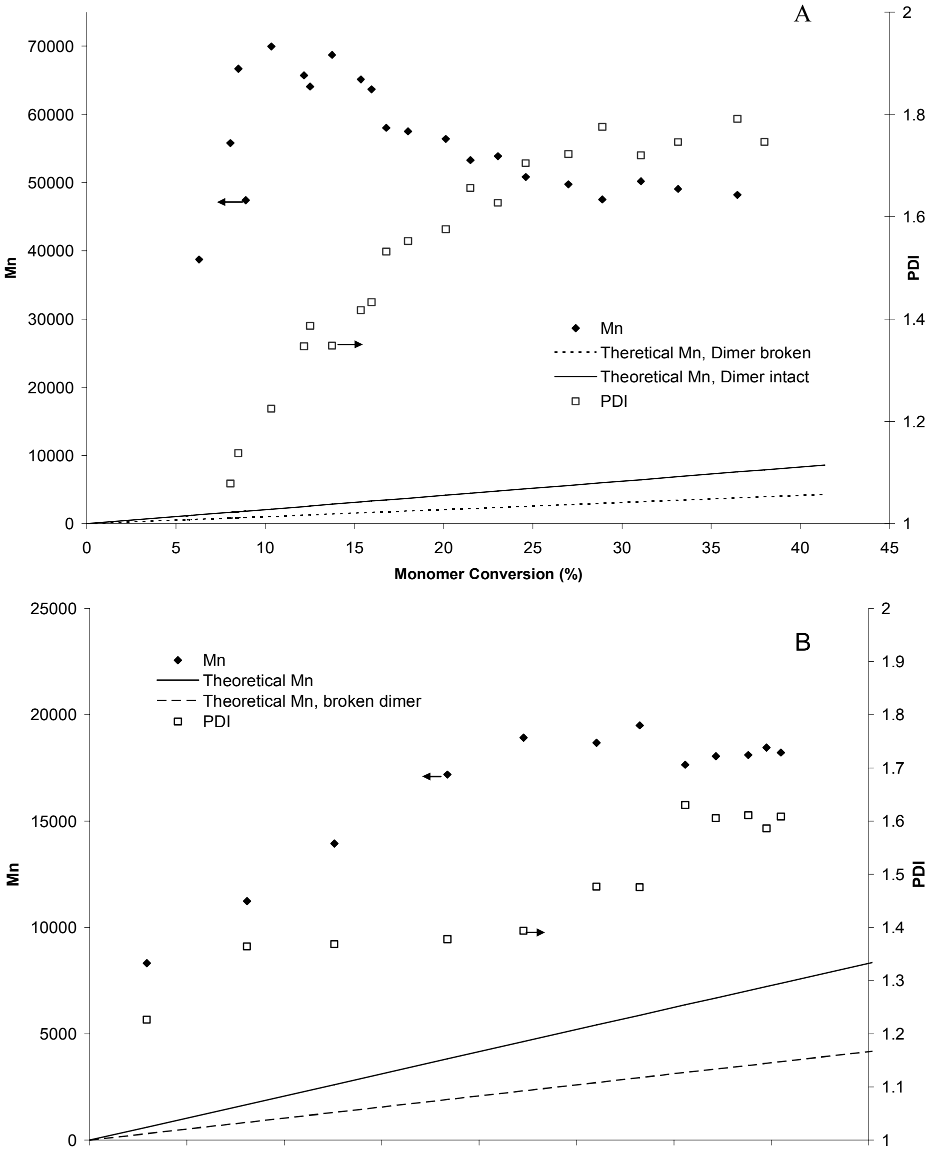


Figure 2. Number average molecular weight (M_n) and PDI (M_w/M_n) vs. % monomer conversion for the ATRP of styrene using photodimers of 9-chloroanthracene (a, **Table 1**, *run 9*) or 9-bromoanthracene (b, **Table 1**, *run 12,* previously published in reference [8]) as the initiator. Calculated M_n values as a function of % monomer conversion are plotted for polymers containing the centrally bound anthracene photodimer (solid line, **Scheme 2**, *4*, or end-labeled polymers (**Scheme 2**, *5*).

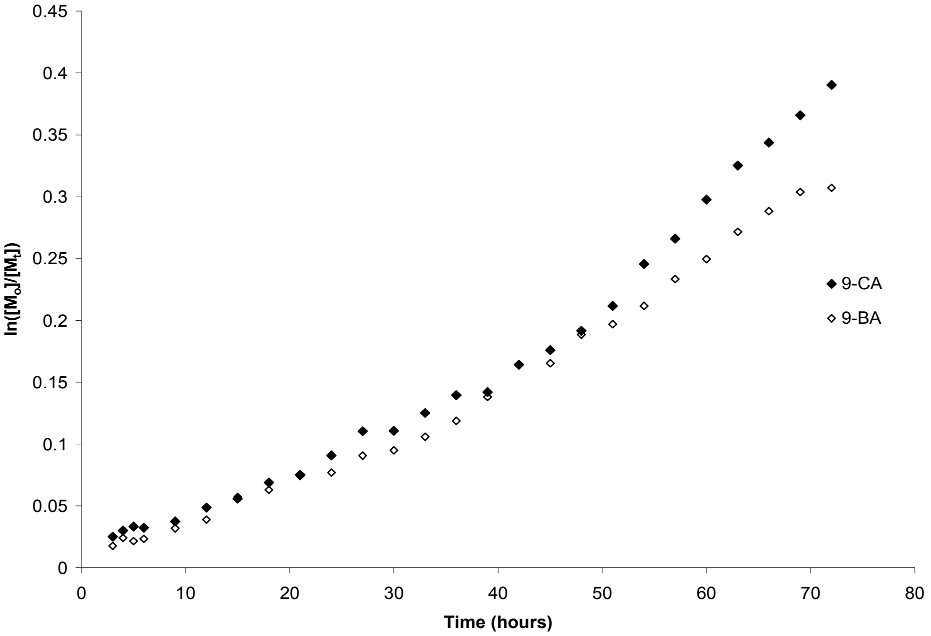
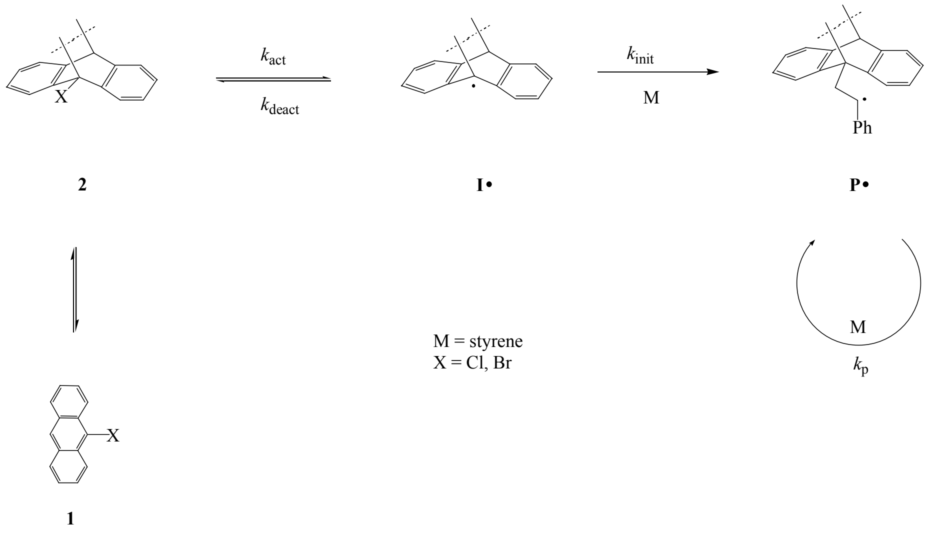


Figure 3. First order kinetic plots for the ATRP of styrene using photodimers of 9-bromoanthracene or 9-chloroanthracene as the initiator. (**Table 1**, *runs 9* and *11*, respectively)



Scheme 3. Mechanistic fate of C-X initiating sites on the photodimer of 9-haloanthracene in the ATRP of styrene.

As shown in **Figure 4**, even the earliest GPC-UV traces show the presence of anthracene-labeled polymers (t = 5 h). The low molecular weight tails on both the GPC-RI and GPC-UV traces, with increased tailing with both time and conversion, suggest that the decreasing M_n values and broadening PDI values are more likely because the initiation is extremely slow in comparison to propagation (decreased R_i/R_p ratio) in the case of 9-CA photodimers. The initiation and propagation resulting from activation of a C-X bond is presented in **Scheme 3,** which shows a single initiating site for clarity. In the case of 9-CA (X = Cl) photodimers, the increased C-Cl bond strength further suppresses the formation of the initiating radical (I·), lowering R_i compared to systems employing 9-BA photodimers (X = Br).[20]

Once initiated, the polymerization will propagate with a rate constant (k_p) independent of the nature of the anthracene moiety (cleaved or intact) because both will propagate via a polystyryl radical (P·), which will have a higher k_{act}/k_{deact} ratio owing to the stability of this resonance stabilized radical compared to the bridgehead species. Furthermore, the increased stability of the 9-chloroanthracene photodimer allows for

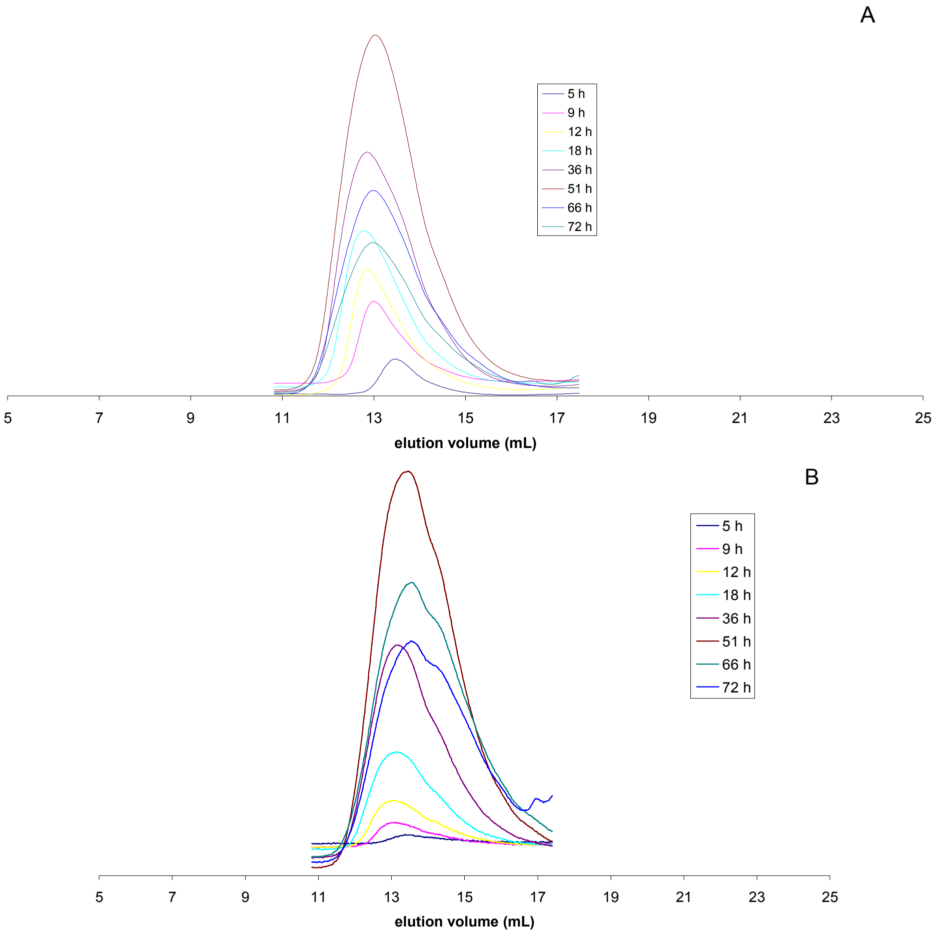


Figure 4. GPC traces of polystyrene initiated with photodimers of 9-chloroanthracene in as a function of time (**Table 1**, *run 9*). RI traces (a) and UV (370 nm) traces (b).

the continual formation of initiating radical, rather than cleavage prior to initiation (**Scheme 1**, *2* → *1*), presumably playing a role in the dramatic differences in M_n as a function of conversion for the two photodimers. The plots of M_n as a function of monomer conversion for 9-CA photodimers suggest the reaction proceeds much like a conventional free radical polymerization, with chains initiating and propagating very quickly compared to initiation despite the conditions being those of typical ATRP. The inability of the bridgehead C-Cl to equilibrate with the active, initiating radical (**Scheme 3**, *2* → *1·*) apparently prevents photodimers of 9-CA to act as initiators in controlled radical polymerizations relying on this equilibrium.

Conclusion

Photodimers of 9-CA and 9-BA were used as initiators in the ATRP of styrene, both giving rise to anthracene-labeled polystyrene due to thermolysis of the photodimers during the course of the reaction. The progress of monitored reactions showed dramatic differences between the two initiators, with a decrease in M_n observed in the propagating polymers after ~10% monomer conversion in the case of 9-CA, while trials using 9-BA photodimers showed a gradual in increase and slow leveling of M_n values near 40% conversion. Differences were attributed to the decreased k_{act}/k_{deact} ratio in the case of 9-CA photodimers, along with suppression of cleavage of the 9-CA photodimers prior to initiation, allowing for the continual generation of initiating sites over the course of the reaction.

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