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## Substituent Effects in Iniferter PhotoPolymerization. Can Bond Homolysis Be Enhanced by Electronics?

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Abstract: Photoinduced-RAFT polymerization is a technique of increasing interest due to the combination of control over polymerization that RAFT processes afford with the mild reaction conditions and spatial and temporal control of photochemical processes. Iniferter RAFT polymerization is an interesting subclass of photoinduced-RAFT that eliminates the need for an added photocatalyst, as the RAFT agent is directly excited by the photon source. Iniferter RAFT is a photochemical process leading to carbon-sulfur bond homolysis. In this work we find a surprising effect of substituents on the dithiobenzoate moiety of the chain transfer agent (CTA). Donating groups dramatically accelerate the iniferter process, while withdrawing groups retard the reaction substantially. This is interpreted though electrochemistry, since homolysis of the carbon sulfur bond is associated with a formal oxidation of the thiocarbonylthio groups and reduction of the carbon to a radical. Through this study, the unique efficiency of 2-cyano-2-propyl 4-methoxydithiobenzoate (CPMODB) as an iniferter was uncovered, as this polymerization was found to progress at a drastically enhanced rate, even when compared to similar Ir(ppy)3 photocatalyzed polymerization using an unsubstituted dithiobenzoate RAFT agent.

Introduction

The need to efficiently synthesize polymers with precise control over molecular weight and architecture has driven the exploration into various controlled polymerization techniques, with reversible deactivation radical polymerization (RDRP) techniques gaining significant attention[1]. Methods such as atom-transfer radical polymerization (ATRP)[1,2], reversible addition–fragmentation chain transfer polymerization (RAFT)[3], and nitroxide mediated polymerization (NMP)[4] to name a few gathered significant attentions because of this. As a part of this development, various external stimuli have been implemented in regards to RDRP techniques[5–9]. Photochemical initiation is one of the more attractive initiation methods, as it brings the added benefits of mild reaction conditions, often at ambient temperatures, as well as spatial and temporal control over the polymerization[10,11]. Some photoinitiated systems have also been shown to display enhanced tolerance to oxygen[12,13]. Among these photo-initiated techniques, photo-induced electron/energy transfer, reversible addition–fragmentation chain transfer polymerization PET-RAFT is of particular interest for a number of reasons. PET-RAFT is a polymerization technique that is efficient, tolerant to a wide range of chemical functionality, it is often oxygen tolerant, and due to many different types of catalysts being available can be activated by a large range of light wavelengths from UV to visible [5–7].
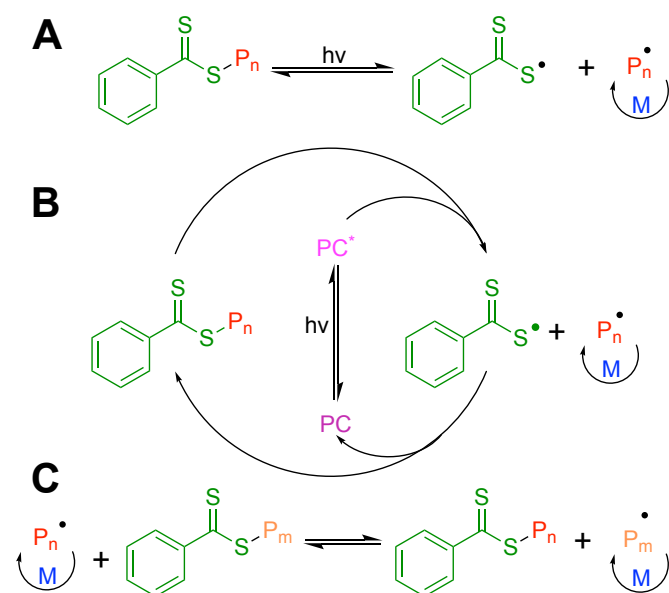
Scheme 1: A) Radical generation in photoiniferter polymerization B) Radical generation in PET-RAFT polymerization following an energy transfer pathway. C) RAFT degenerative exchange which occurs for photoinifter and PET-RAFT reactions. Dithiobenzoate chain transfer agent are shown, where Z is –OCH₃, -CH₃, -H, -OCF₃, or – CN, P_n and P_m are propagating polymer chains and M is monomer.

Typical PET-RAFT polymerization uses a photo-catalyst, such as a transition metal photo-catalyst[14] or an organic molecule[15–17].

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However, the inherent absorptivity of the thiocarbonyl based chain transfer agents utilized in RAFT can be directly excited to initiate the RAFT process in what is termed an iniferter process[18,19,20,21,22] as outlined in (Scheme 1).

First investigated by Otsu[21,22], the iniferter process has been gaining an increased amount of attention in recent years, due to its relation with RAFT polymerization[23–25]. While iniferter RAFT has seen increased attention, the reactions can be slow compared to other catalyzed photochemical processes[11]. In this work, we first set out to systematically study the photoiniferter RAFT mechanism through a Hammett type study by varying substituents on the dithiobenzoate moiety of the chain transfer agent (CTA). This study showed that the more electron donating the para substituent on the transfer agent, the faster the polymerization progressed. Although there are no formal charges in the photoiniferter process, the data suggest that the effects of electronics and partial charges cannot be neglected. This result indicates that a partial positive charge is being built up in the transition state towards bond homolysis, suggesting a formal oxidation of the thiocarbonylthio group. This is consistent with the fact that the carbon-sulfur bond homolysis in the photoiniferter processes, is a formal oxidation of the thiocarbonylthio group and a reduction of the associated carbon. This formal oxidation of sulfur is promoted by donating groups on the Z-group of the CTA, and while the formal oxidation is inhibited by withdrawing groups on the Z-group of the CTA.

In addition, the unique efficiency of 2-cyano-2-propyl 4-methoxydithiobenzoate (CPMODB) in photiniferter processes became apparent. Using CPMODB as an iniferter resulted in polymerization rates that were comparable to transition metal photocatalyzed RAFT processes while also maintaining RAFT control over the molecular weight. The efficiency of the photoiniferter processes using CPMODB would eliminate the need for the added catalyst, enabling rapid and controlled polymerization to occur under mild and catalyst free conditions.

Table 1: Summary of RAFT CTAs studied, the Z group, associated Hammett constant, the redox potential against the standard hydrogen electrode (SHE), The calculated extinction coefficient at 440 nm, and the peak wavelength of absorbance

CTA	Z Group	σ Constant[26]	E_{red}/V (vs SHE)	ε_{440} (M^1cm^{-1})	Peak Wavelength (nm)
CPMODB	-OCH$_3$	-0.27	-1.22	20	510
CPMDB	-CH$_3$	-0.17	-1.14	17	514
CPDB	-H	0	-1.13	14	514
CPTFMODB	-OCF$_3$	0.35	-0.961	15	516
CPCDB	-CN	0.66	-0.848	13	523

Results and Discussion

First a scope of suitable CTAs was established. Using a dithiobenzoate as a common core, a series of five CTAs were obtained consisting of para substituents that encompass a wide range of Hammett sigma constants: 2-cyano-2-propyl 4-methoxydithiobenzoate (CPMODB); 2-cyano-2-propyl 4-methyldithiobenzoate (CPMDB); 2-cyano-2-propyl dithiobenzoate (CPDB); 2-cyano-2-propyl 4-trifluoromethoxydithiobenzoate

(CPTFMODB); and 2-cyano-2-propyl 4-cyanodithiobenzoate (CPCDB) (Table 1).
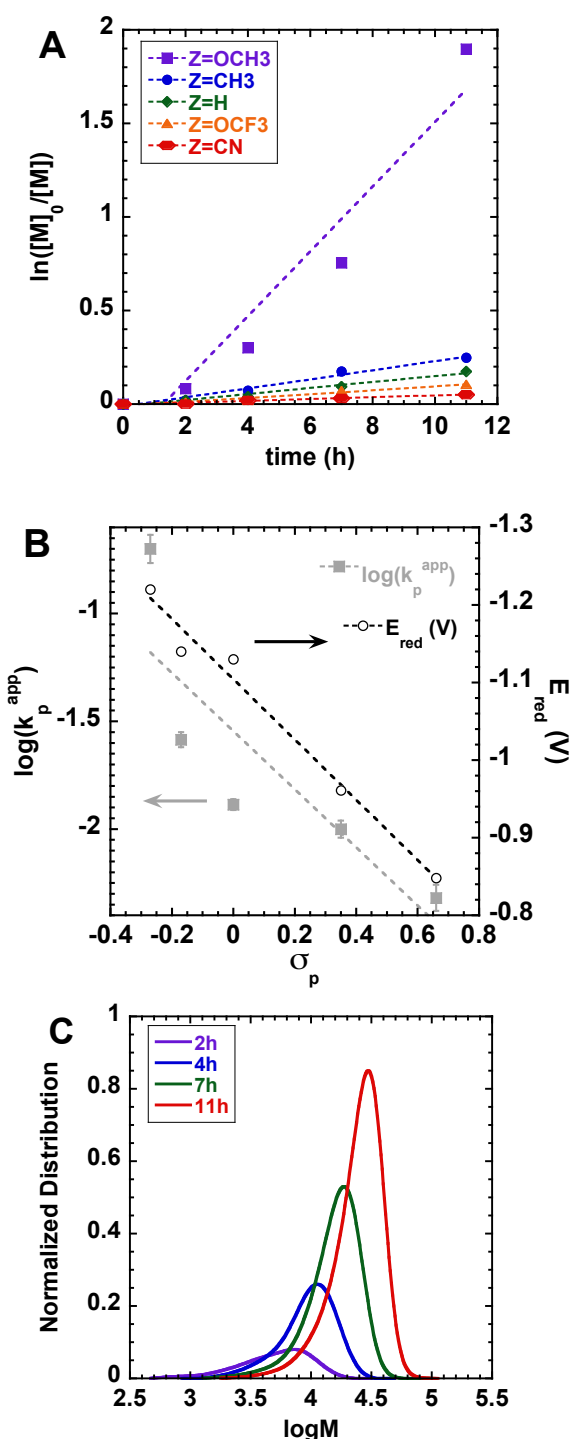

Figure 1: A: Kinetic data for photopolymerization of MMA using various Z groups under blue light irradiation MMA:CTA= 200:1 under blue light (emission peak at 440 ± 20 nm and intensity of 11.6 ± 0.3 mW/cm^2). B: Hammett plot of log($k_p{}^{app}$) fit between 0 and 7h against Hammett σp parameters as well as reduction potential (E_{red}, plotted on a reverse axis) of each CTA. C: Evolution of SEC molecular weight distributions for MMA:CPMODB= 200:1

The UV-Vis spectra of each CTA were measured with limited variability in the spectrum (Figure S1). From the data, excitation coefficients were calculated (Table 1). This data shows that each of CTA have a relatively similar absorbance, with a peak wavelength

between 510-523 nm. The excitation coefficients were all found to be relatively similar as well, although CPTFMODB had a somewhat smaller extinction coefficient. Cyclic voltammetry was performed on these transfer agents. As shown in Figure S2 and Table 1. CTAs with a stronger withdrawing group require a less negative potential for the reduction. This suggests that oxidation of the dithiobenzoate group is promoted when a reasonably strong donating group, such as methoxy, is attached to the Z group.

Table 2: Outcomes of polymerization under blue light (emission peak at 440 ± 20 nm and intensity of 11.6 ± 0.3 mW/cm$_2$) after 11h of irradiation.

Z	Conv.	k_p^{app} (h^{-1})	M_n theory	M_n	M_w/M_n
OCH$_3$	0.85	0.20±0.03	17251	21000	1.28
CH$_3$	0.22	0.025±0.002	6435	7700	1.24
H	0.16	0.017±0.001	3421	5200	1.35
OCF$_3$	0.10	0.011±0.001	2305	4200	1.31
CN	0.05	0.005±0.0007	1246	1800	1.26

With characterization of the transfer agents complete, model methyl methacrylate (MMA) polymerization reactions were conducted with 200:1 mixture of MMA to CTA in 50% DMSO by weight under blue light irradiation (emission peak at 440 ± 20 nm and intensity of 11.6 ± 0.3 mW/cm^2). This blue light irradiation was chosen as a result of the UV-Vis characterization (Figure S1) and based on previous studies of similar dithiobenzoate RAFT polymerization under various ranges visible light wavelengths[19]. The rates of these polymerization reactions were monitored by taking samples at various time points and using NMR to determine monomer conversion and size exclusion chromatography (SEC) to determine the molecular weight (Table 1). All of the transfer agents yielded polymers with low dispersity and acceptable agreement between the experimentally measured number average molecular weights and the theoretical ones, indicating that each RAFT CTA was capable of giving well defined polymers. From this data, a clear trend can be observed. The more electron donating the para substituent on the transfer agent, the quicker the reaction progressed, with CPMODB far outpacing the others, reaching 85% monomer conversion in 11 hours. Although there is some deviation from linearity in the photoiniferter reaction with CPMODB, this is most notable at high conversion where the error of NMR amplifies uncertainties in the semilogarithmic plot. This rate is even more interesting when compared to the Ir(ppy)$_3$ photocatalyzed MMA polymerization using the more commonly used CPDB, which reached 70% conversion in the same amount of time (MMA:CPDB:Ir(ppy)$_3$ 200:1: 0.0002 in 50% DMSO by weight). CPMODB seems to yield a significantly faster polymerization rate while continuing to maintain RAFT control. This exciting finding indicates that CPMODB could be an attractive transfer agent as it removes the need for any added photocatalyst or initiator without sacrificing the speed that is usually associated with those processes which involve a catalyst. The slope of the kinetic semilogarithmic plot was used to determine an apparent rate constant (k_{app}). Using these apparent rates and known sigma constant values for the para substituents on the raft transfer agents, a Hammett plot was constructed (Figure 1). Here we see a clear relationship between the log(k_{app}) with the corresponding sigma Hammett parameter for each RAFT agent. The slope calculated from the Hammett plot was -1.2 with log(k_{app}) plotted against the Hammett sigma parameter (Figure 1). From the negative slope observed on the Hammett plot, we can conclude that there is the formation of a positive charge, or

loss of negative charge, in this reaction. This is consistent with the mechanism where after the excitation of the CTA, the bond cleavage involves the dithiobenzoate portion undergoing formal oxidation, liberating the reduced polymer based propagating radical.
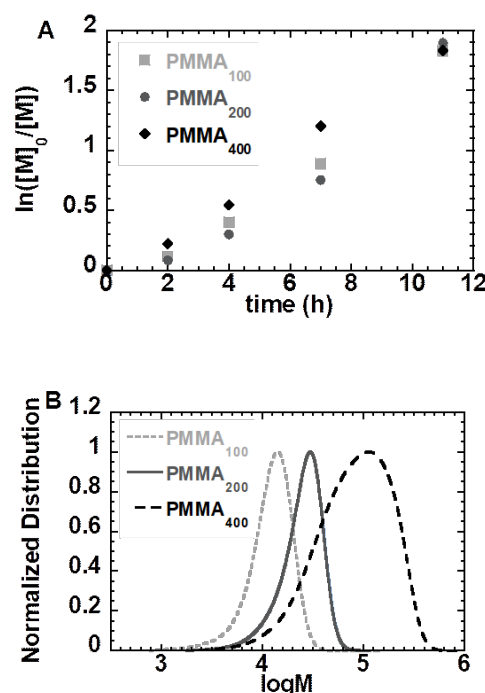

Figure 2: Kinetic and molecular weight data for MMA polymerization using various concentrations of CPMODB as CTA under blue light irradiation light (emission peak at 440 ± 20 nm and intensity of 11.6 ± 0.3 mW/cm^2)

Due to the interesting kinetic results, the CPMODB system was explored further. First, the MMA polymerization was done at varying monomer to CTA ratios, looking at 100:1, 200:1, and 400:1 MMA:CPMODB in 50% DMSO by weight irradiated under blue light (Figure 2 and Table S2). The 100:1, 200:1, and 400:1 ratio trials all progressed at comparable rates, with 200:1 reaching 85% monomer conversion and the 100:1 and 400:1 reaching 84% conversion in 11h. This data suggests that the rate is being limited by the photon source, since altering the concentration of the chromophore, the transfer agent, does not change the rate. The 100:1 and 200:1 trials seemed to be well controlled, with low dispersity values of 1.31 and 1.28 respectively. The 400:1 monomer to CTA ratio trial had problems with control, with a high dispersity for a RAFT polymerization of 2.04 and a higher than expected Mn. This could be due to poorer end group fidelity at the longer chain lengths.

In order to further explore the livingness of the photoiniferter polymerization using CPMODB, a 50 MMA unit macroCTA was synthesized and chain extended with hydroxyl ethyl methacrylate (HEMA) monomer (Figure 3). The extension was performed using 200:1 ratio of macro CTA to HEMA monomer in 50% DMSO by weight under blue light irradiation. From Figure 3 there is clear evidence of a clean extension with the HEMA monomer, showing that the iniferter CPMODB polymerization is a "living" process, as well as compatible with other methacrylic monomers. While there does appear to be low and high MW shoulders after the chain extension, with a Mw/Mn of 1.66, the extension was relatively well controlled.
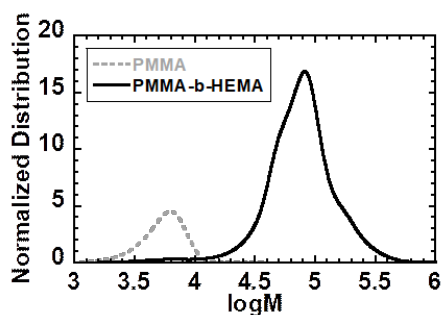
Figure 3: HEMA chain extension of PMMA using 1:200 PMMA macro CTA to HEMA monomer in 50 wt% DMSO by weight excited under blue light for 10h reaching >95% monomer conversion (Mn 55373 g/mol Mw/Mn 1.66). Macro CTA was synthesized using 50:1 MMA:CPMODB in 50 wt% DMSO stirring under blue light for 48h reaching 85% monomer conversion (Mn 4909 g/mol Mw/Mn 1.18).

Conclusion

In this work, we reported a systematic Hammett type study of the photoiniferter RAFT process. From this study, we can see a clear relationship between the rate of the iniferter RAFT process and the electronics of the transfer agent used. This study lends evidence to the mechanism involving a formation of positive charge on the dithiobenzoate, indicating the participating sulfur is undergoing a formal oxidation during the bond cleavage. During this study, we also uncovered the enhanced rate of reaction of the methoxy substituted CPMODB transfer agent in iniferter RAFT polymerization and demonstrated the "livingness" of the polymerization through the synthesis of a MMA HEMA co-block polymer. The rate of polymerization is even more interesting when compared to similar Ir(ppy)3 photocatalyzed systems using the more common CPDB. The CPMODB photoiniferter polymerization rate is significantly more efficient that other dithiobenzoate derivatives, while also maintaining RAFT control. The efficiency of the photoiniferter processes would eliminate a need for the added catalyst, enabling rapid and controlled polymerization to occur under mild and catalyst free conditions.

Conflicts of Interest

There authors declare no conflicts.

Acknowledgements

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