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Tuning Molecular Weight Distributions of Vinylketone-based Polymers using RAFT Photopolymerization and UV Photodegradation

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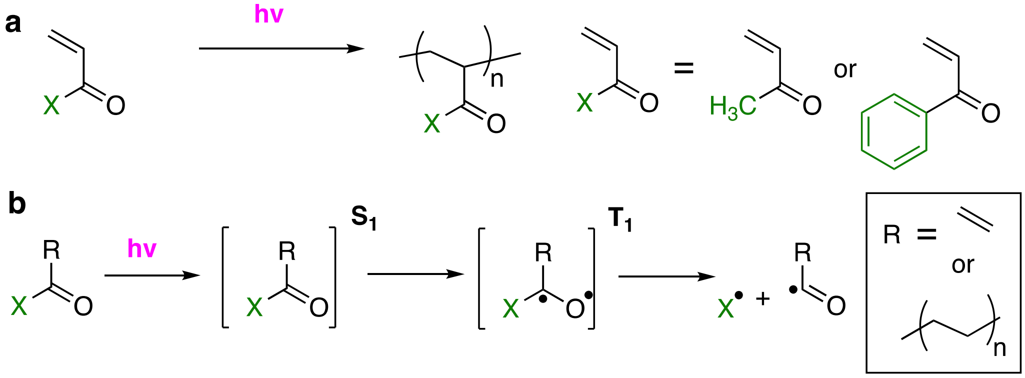
Abstract

The choice of chain transfer agent in Reversible Addition/Fragmentation Chain Transfer (RAFT) polymerization has proven to be instrumental in modulating the dispersity of a certain poly Phenyl Vinyl Ketone (PVK). The monomer, PVK, which can self-initiate when exposed to blue light, was used to synthesize homopolymers, block copolymer by extending with a different monomer and gradient polymers. Regardless of the polymer architecture or degree of polymerization, a consistent trend in polymer dispersity was quantified, with higher loadings of less active chain transfer xanthate leading to higher dispersities. Dispersity could be further modulated by utilizing photodegradation of vinyl ketone polymers under UV irradiation.

Introduction

Vinyl ketone monomers have fascinating properties, arising from the photochemistry of the ketone group.[1–4] The presence of the ketone in the monomer and polymer enables efficient photochemistry through the Norrish type processes possible for carbonyl groups.[5] The UV induced photodegradation of vinyl ketone monomers based on Norrish Type-II processes has been known for decades,[6–8] although recently the Norrish Type-I processes of vinyl ketone monomers and their polymers have been identified.[8,9] In particular, recent work[9,10] has shown that the intrinsic Norrish chemistry of vinyl ketones can facilitate efficient and controlled photopolymerization under blue light, as shown in Scheme 1. Photodegradation has the potential to address several key challenges such as mitigating the challenges of polymers in land pollution, be useful in biomedical applications such as targeted release,[11] or to facilitate photolithography.[12]

The ability to photodegrade vinyl ketone polymers without metal additives under long wavelength UV irradiation is a unique feature of these macromolecules.[13] Importantly, when irradiated by visible light, the generated vinyl ketone polymers showed negligible photodegradation, while irradiation under UV lead to substantial decreases in molecular weight over time.[10,14] However, the ability to tune and control the molecular weight distributions of the generated polymers is an emerging area, with opportunities for applications towards complex monomers, such as vinyl ketones.



Scheme 1: Photoinduced radical generation from vinyl ketone monomers and polymers. a) A schematic of photoinduced vinylketone photopolymerization. b) Proposed mechanism of radical generation by a Norrish Type-I process where S_1 and T_1 are the first excited singlet and triplet states, respectively.

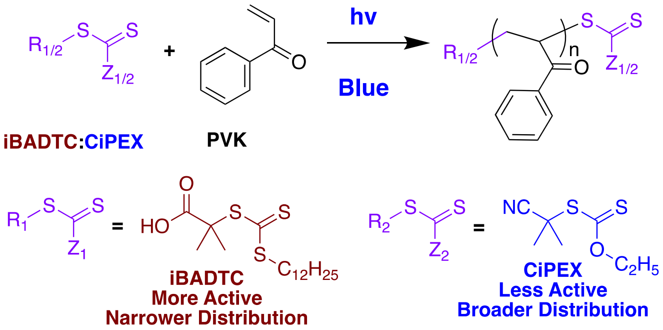
In the past two decades, reversible deactivation radical polymerization (RDRP) methods have emerged as powerful tools to generate polymers with predefined molecular weights and complex architectures from a diverse range of functional monomers.[15–19] In particular, reversible addition-fragmentation chain transfer (RAFT) polymerization and atom-transfer radical polymerization (ATRP) have emerged as two of the most commonly used RDRP methods.[17,20–22] In the earliest developments of RAFT and ATRP, substantial effort was placed on generating predictable molecular weight polymers, and often polymers with narrow molecular weight distributions.[23,24] Both RAFT and ATRP have been used to generate such polymers. However, in the past few years, research efforts have focused on ways to tailor molecular weight distributions (MWDs).[15,25,26] This is because the dispersity of the polymer can for instance impact the self-assembly of block copolymers[27–33] which could facilitate lithographic applications. To enable these applications, it is important to develop new synthetic approaches to polymers with tailored

MWDs. There are several strategies deployed to control the dispersity of polymers. One avenue uses engineering type approaches, where reagents such as new initiating sites are fed into the reaction mixture over the course of the polymerization,[34,35] modulation of chemical streams and residence times by flow chemistry, [25,26,36] or polymers are blended after polymerization.[37] The feeding of components approach modulates the average chain length and shape of the MWD by preprogrammed initiator addition profiles, which requires detailed characterization of the polymerization rates to achieve targeted MWD.[38] Blending pre-synthesized polymers gives distributions which are the weighted average of the constituent polymer MWDs, with shapes that are remnants of their original distributions.[37] The second approach tunes the MWD by modulating the intrinsic polymerization chemistry, by taking advantage of the chemical property that polymer chains are reversibly activated and deactivated in RDRP processes and other related reactions.[17,39,40] By changing the mean number of monomers added per activation/deactivation cycle, the MWD can be tuned efficiently. In the case of ATRP, changing the catalyst loading can dramatically impact the molecular weight distribution and dispersity, with lower catalyst loadings decreasing deactivation rates and enabling broader distributions. In RAFT, the thiocarbonylthio group that deactivates the radical is stoichiometric to the polymer due to the structure of the RAFT chain transfer agents (CTAs), implying that relative deactivation rates cannot be decreased. However, by combining CTAs with different reactivities, polymer MWD and dispersity can be modulated by changing the transient radical lifetime.[40–42] Lower activity CTAs increase the time between chain activation to a radical and its subsequent deactivation, thus increasing the number of monomers added per activation and thereby broadening the MWD.[40–42]

However, to the best of our knowledge, there is no systematic exploration of how vinylketone polymer molecular weight distributions can be systematically tailored. In this manuscript, the photopolymerization of phenylvinylketone (PVK) and methylvinylketone (MVK) are explored in detail, targeting tailored MWDs and dispersity. The dispersity is tuned using a mixture of two CTAs, one a trithiocarbonate, which in prior work has been shown to give poly(PVK) (PPVK) with narrow molecular weight distributions,[9] and a xanthate-based CTA, which has a lower chain transfer constant and gives broader MWDs for more active monomers.[43] Adapting this approach to various polymerization systems enables the synthesis of vinyl ketone polymers with tunable molecular weight, dispersity, as well as, complex block copolymers that retain control over the dispersity, and even gradient polymers. Finally, the photodegradability of PPVK under ultraviolet (UV) radiation was used to further modulate the molecular weight and dispersity of the resulting polymers. Therefore, this work shows the possibility of modulating vinyl ketone polymer distributions, enabling many potential applications such as degradable materials and photolithography arising from the unique photochemistry of both the monomer and the polymer.

Result and Discussion

To explore the possibility of using the intrinsic photochemistry of vinylketone monomers to make polymers with tunable dispersity, mixtures of CTAs were used. As shown in earlier work,[9,10] the CTA 2-[(dodecylthio)thioxomethylthio]isobutyric acid (iBADTC), shown in Scheme 2, is capable of giving polymers of vinyl ketone monomers with narrow molecular weight distributions. Therefore, iBADTC is a higher activity CTA in this system. From the early development of RAFT by Rizzardo, Moad and Thang, and the recent work of Anastasaki and coworkers suggest that CTAs with low transfer constants, such as dithiocarbamates or xanthates for more active monomers, give polymers with higher dispersity.[15,44] Therefore, to synthesize high dispersity polymers, a xanthate-based CTA with a cyanoisopropyl leaving group was selected, or cyanoisopropylethyl xanthate (CiPEX),) as shown in Scheme 2. The excellent leaving group of cyano-isopropyl should facilitate chain initiation from the lower activity CiPEX CTA in the RAFT pre-equilibrium. The polymerization of phenylvinylketone (PVK) using mixed iBADTC:CiPEX CTAs is shown in Scheme 2. In all polymerizations, blue light was chosen as it was found in earlier work to give superior polymerization rates.[10]



Scheme 2: Photopolymerization of PVK using mixed CTAs of iBADTC as a more active CTA, thus giving narrower distributions, and CiPEX as a less active CTA, thus giving larger dispersity.

Initially, PVK was polymerized under blue light of 450 ± 10 nm with an intensity of 7.9 ± 0.4 mW/cm^2 with ratios of iBADTC:CIPEX ranging from 1:0 to 0:1 (Table S1 and S2), in all cases targeting a total degree of polymerization of 50 PVK units. The emission spectrum of the blue LED system is given in Figure S1, and the UV-Visible absorbance spectra of all components is given in Figure 1. As seen in Figure 2a, the photopolymerization of PVK under these conditions was rapid reaching over 80% conversion in 2 h for all conditions. There was no systematic trend in the rate of reaction with the ratio of iBADTC:CiPEX, consistent with the radicals originating from the Norrish type chemistry of PVK, rather than the iniferter process of the CTA. To confirm this, a reaction was run with no CTA, and compared to reactions with CTA. As seen in Figure S2, the steady state rates of all polymerizations were similar, suggesting that the radicals originate from the Norrish chemistry of the PVK monomer.

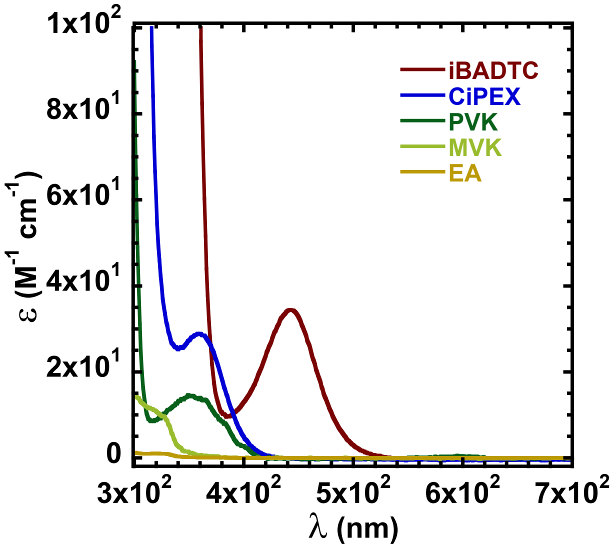


Figure 1: UV-Visible spectra of PVK, MVK, EA, iBADTC and CiPEX.

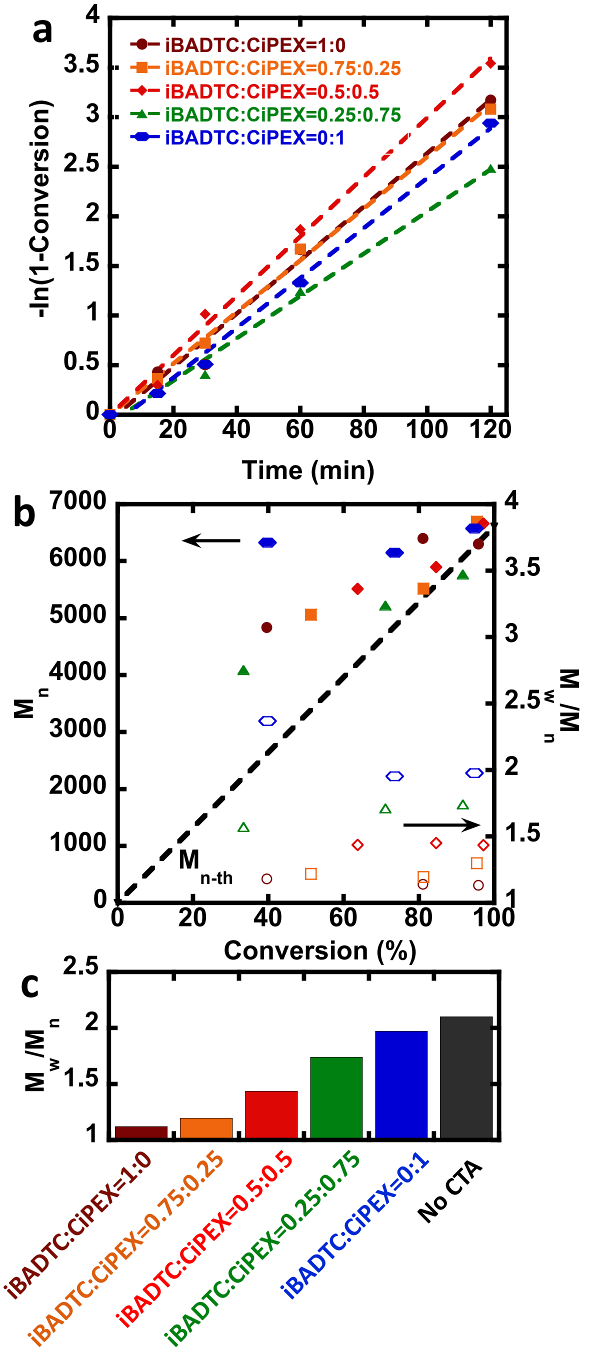


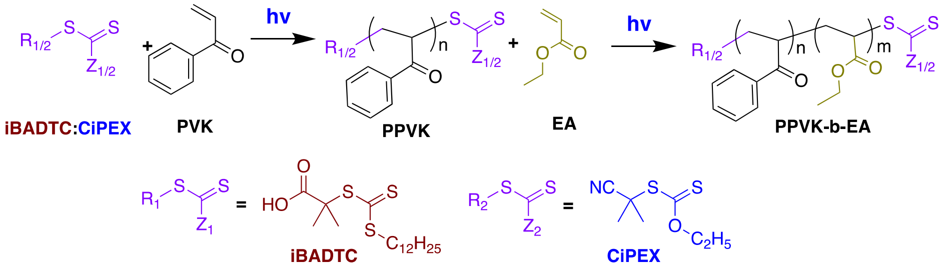
Figure 2. Photopolymerization of PVK under blue light (450 ± 10 nm, 7.9 ± 0.4 mW/cm^2) under conditions [PVK]: [CTA]=50:1, with 33 vol% monomer. Ratios of iBADTC:CiPEX CTAs were varied between 1:0 and 0:1 in 0.25 increments. a) semilogarithmic kinetic plot for each ratio of iBADTC:CiPEX. b) Evolution of M_n (solid points) and M_w/M_n (hollow points) with conversion for each ratio of iBADTC:CiPEX. c) M_w/M_n for the 2h time point compared for each ratio of iBADTC:CiPEX, as well as with no CTA.

As seen in Figure 2b, all polymerizations had good agreement with the theoretical M_n (the filled symbols), especially at high conversion. It would appear that the systems had slightly elevated M_n compared to the theoretical one at lower conversions, especially with more of the less active CiPEX CTA. This is consistent with the slower conversion of CiPEX small molecule CTA to macroCTA, compared to the more active iBADTC as seen in Figure S3. Additionally, as seen in Figure 2b and 2c, the dispersity increased with the fraction of the CiPEX CTA, as anticipated. These results show that a simple system using only blue light can be used to make polymers of PVK with tunable dispersity.

Similarly, Figure S4 shows that the same trends can be observed using a higher ratio of monomer to CTA, where 100 PVK units per 1 CTA molecule was used, although the ratio of the more active iBADTC and less active CiPEX can be used to tune the dispersity. The same photochemical reaction conditions and concentrations were used for the polymerization of PVK at targeted chain length of 100 and chain length of 50, except the concentration of CTAs were halved for the longer chain length. Figure S4a confirms rapid and efficient polymerization of PVK under these conditions, with Figure S4b showing good agreement of measured M_n/M_w with the theoretical M_n. As anticipated, higher ratios of CiPEX to iBADTC did not lead to systematic changes in the polymerization rate, as seen in Table S5. However, in these systems the polymerization with more CTA, targeting DP 50, gave slightly faster polymerization rates. Discrepancies between polymerization rates may be caused by trace amounts of oxygen. Similarly, to the systems targeting a chain length of 50, the polymerizations targeting a chain length of 100 showed a monotonic increase in dispersity with higher ratios of the less active CiPEX CTA. It is important to note that conditions using 100% of the less active CiPEX CTA, produced similar results to conventional radical polymerization of PVK under the same conditions when targeting DP 50 (Figure 2c) and when targeting a chain length of 100 (Figure S4c). However, using CiPEX gives control over the molecular weight with both systems being close to theory at high conversion. In contrast with no CTA, the molecular weight was over 100,000.

In addition to polymerization of PVK, which is an aromatic vinyl ketone, methylvinylketone (MVK) an aliphatic derivative was also explored. As seen in Table S3, the polymerization of MVK showed similar results to PVK, except that the polymerization was substantially slower. MVK photopolymerization required 24h to reach 70-80% conversion, while

PVK reached 80-90% conversion in 2h. This difference is most likely due to the aromatic ring in PVK stabilizing the radicals generated in the Norrish chemistry of the vinyl ketones, thereby leading to a higher rate of radical formation in PVK compared to MVK. As seen in Figure S6 the MWD of PMVK showed monotonic broadening with increasing fraction of CiPEX. This is qualitatively the same as for PPVK as seen in Figure S5. Therefore, the ability to tune the molecular weight distribution and dispersity is possible for both aliphatic and aromatic vinyl ketone monomers.



Scheme 3: Synthesis of block copolymers with polymerization of PVK, followed by chain extension with EA using mixtures of iBADTC and CiPEX CTAs. Both PVK and EA polymerizations were performed under blue light.

In addition to homopolymers of vinylketone monomers, complex structures are also of interest. As shown in earlier work, RAFT synthesized PPVK with narrow MWDs can be successfully chain extended with acrylate monomers.[14] This block copolymer synthesis is shown in Scheme 3. PPVK macroCTAs with tunable dispersity were prepared with targeted chain length of 50 units, following the same photopolymerization conditions as used in Figure 2, except that the polymerizations were run for 3h to ensure essentially full conversion of PVK. In each case, the conversion of PVK was over 95%. The broadening of the molecular weight distribution with higher CiPEX ratios is shown in Figure S7. Although earlier analysis showed that CiPEX is converted to macroCTA more slowly than iBADTC, the NMR data in Figure S3 suggest that at high conversion of PVK monomer, essentially all CiPEX is converted to macroCTA. This indicates that true block copolymers can be made by this approach. Subsequently, the PPVK macroCTA was chain extended with ethyl acrylate. In all cases, the conversion of EA was over 85%, with monomodal MWDs as indicated in Figure S8. Additionally, Figure 3 shows clean shifts of all molecular weight distributions upon chain extension, indicating high livingness of the chains and formation of the block copolymer of PPVK-b-EA. The highly efficient chain extension and formation of a block copolymer is notable due to the high dispersity for many of the PPVK macroCTAs, showing that chain end functionality and dispersity can effectively be decoupled. The efficient block copolymer formation indicates that trithiocarbonate/xanthate chain end functionality must be higher, even for a polymer that has a dispersity close to 2.0, similar to other literature reports.[40]

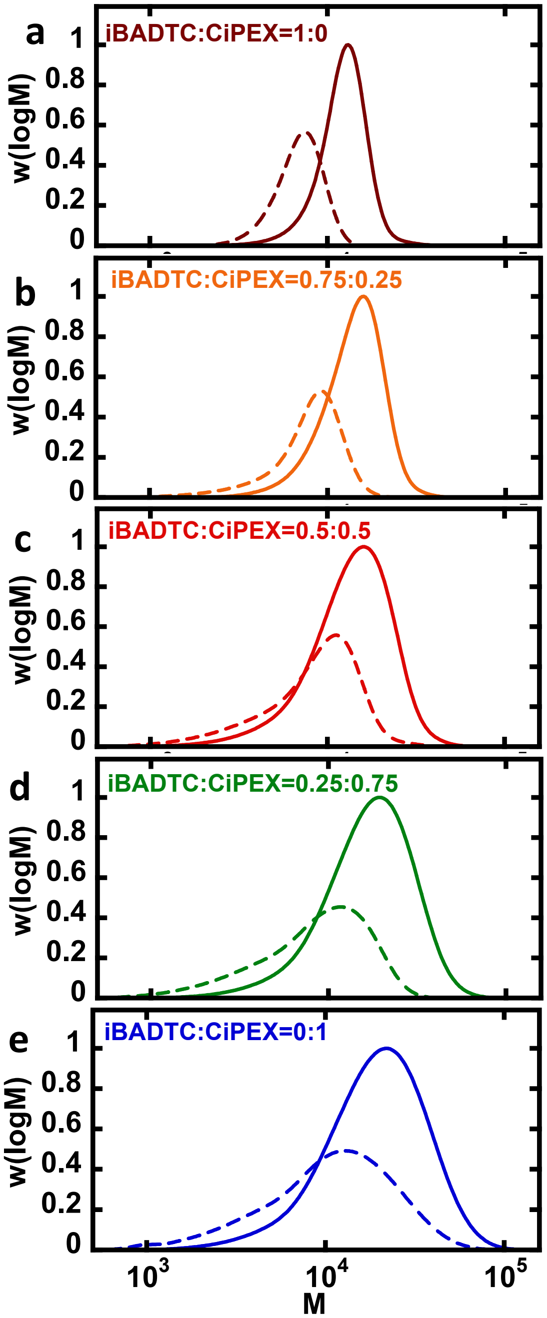


Figure 3: MWD of PPVK (dashed curves) and PPVK-b-EA (solid curves), normalized by M_n, such that the PPVK-b-EA is normalized to a peak height of 1, and the peak height of the PPVK is given by $M_{n\text{-PPVK}}/M_{n\text{-PPVK-b-EA}}$. Distinct ratios of iBADTC:CiPEX CTAs were used with: a) iBADTC:CiPEX=1:0; b) iBADTC:CiPEX=0.75:0.25; c) iBADTC:CiPEX=0.5:0.5; d)

iBADTC:CiPEX=0.25:0.75; e) iBADTC:CiPEX=0:1. Photopolymerization of PPVK performed under the conditions: [PVK]:[CTA]=50:1 with 33 vol% monomer under blue light (450 ± 10 nm, 7.9 ± 0.4 mW/cm^2) for 3h. Chain extension performed under the conditions: [EA]:[PPVK-CTA]=50:1 with 47 vol% monomer under blue light (450 ± 10 nm, 7.9 ± 0.4 mW/cm^2) for 24h.

As indicated in Figure 4, higher fractions of CiPEX gave higher dispersity values of both the PPVK homopolymer and the PPVK-b-EA complex polymer. However, the results are not uniform, with the range of dispersities achievable in the PPVK homopolymer being substantially higher than the range of dispersities in the PPVK-b-EA chains. At high iBADTC loadings, both PPVK and PPVK-b-EA polymers had narrow MWDs and M_w/M_n values near 1.0, for instance, M_w/M_n was 1.10 for PPVK and M_w/M_n was 1.11 for PPVK-b-EA. However, with higher CiPEX loading, the dispersity decreased dramatically in the chain extension (Figure 4). For instance, with a ratio of iBADTC:CiPEX=0:1 the PPVK had a M_w/M_n value of 1.95, while PPVK-b-EA had a M_w/M_n value of 1.56. This decrease in M_w/M_n values upon chain extension is consistent with the idea that during the chain extension the majority living chains all have an opportunity to extend with newly added monomers. Addition of the same number to shorter PPVK chains lead to a relative narrowing of the MWD since the relative difference between shorter and longer chains is reduced, and shorter chains are able to 'catch up' to their longer counterparts. Nevertheless, even with the reduction in the range of dispersity in the block copolymers, a wide range of dispersities are still possible, ranging from ~1.1 to ~1.6.

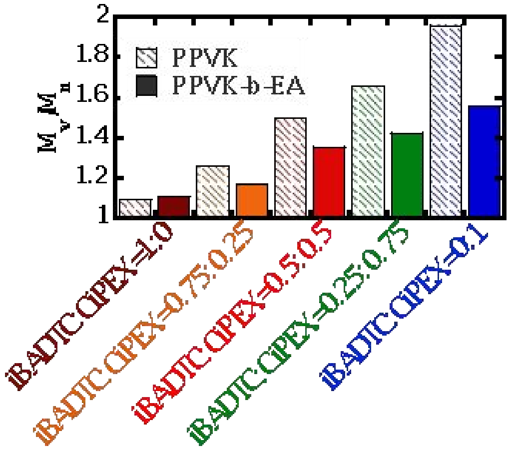
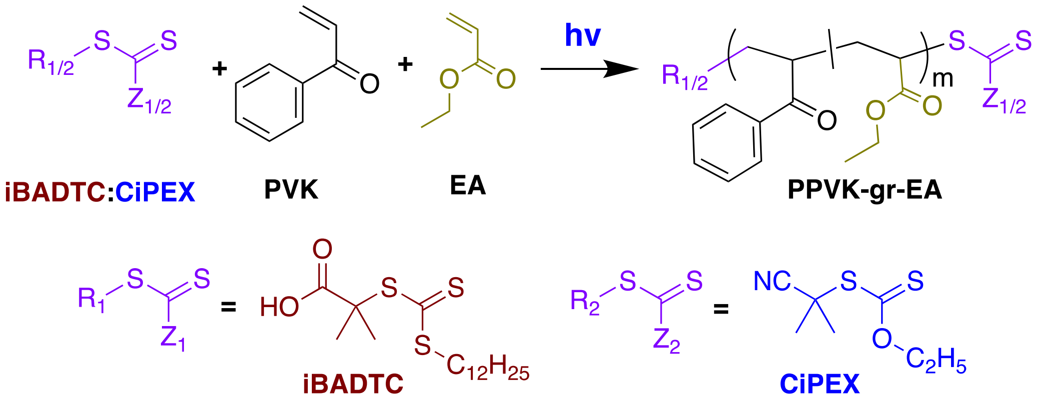


Figure 4: M_w/M_n values of PPVK (dashed) and PPVK-b-EA polymers. Photopolymerization of PPVK performed under the conditions: [PVK]: [CTA]=50:1 with 33 vol% monomer under blue light (450 ± 10 nm, 7.9 ± 0.4 mW/cm^2) for 3h. Chain extension performed under the conditions: [EA]: [PPVK-CTA]=50:1 with 47 vol% monomer under blue light (450 ± 10 nm, 7.9 ± 0.4 mW/cm^2) for 24h.

In addition to the sequential copolymerization under blue light of PVK, followed by EA, to give block copolymers, direct and simultaneous copolymerization of PVK and EA were explored. In particular, both PVK and EA are secondary carbonyl stabilized radicals in their propagating form, therefore, their relative reactivity towards radical polymerization could conceivably be similar. It is important to note that the benzene ring in PVK is not conjugated with the radical through canonical resonance structures. Copolymerization of PVK with EA with distinct ratios of iBADTC:CiPEX was used to generate copolymers with control over molecular weight and dispersity. In all cases, polymerization was performed targeting 50 units of PVK and 50 units of EA, and this copolymerization is displayed in Scheme 4.



Scheme 4: Synthesis of copolymers of PVK and EA using mixtures of iBADTC and CiPEX CTAs, where polymerizations were performed under blue light.

As seen in Figure 5a, PVK is incorporated into the polymer predominantly in the early phase of the reaction, with EA incorporated later in the reaction. This is confirmed when determining the cumulative composition of the polymer as a function of time, which is shown in Figure 5b. The data in Figure 5b indicate that early in the reaction the vast majority of the polymer is comprised of PVK, while later in the reaction, the composition approaches the target of 50% PVK and 50% EA by mole. This implies that the synthesized polymers will have almost exclusively PPVK near the polymer's α-terminus, while the polymers will be almost exclusively PEA near the ω-terminus. In the middle of the polymer, a mixture of PVK and EA will be incorporated, although with almost a block-like structure. Importantly, the conversion data of Figure S9 indicates that although the less active CiPEX CTA is transformed to macroCTA slower than what would be the case for a highly active CTA like iBADTC, CiPEX is consumed faster than PVK, which is itself consumed faster than EA. This data supports the gradient like structure for most polymer, with a PVK rich region near the α-terminus and a EA rich region near the ω-terminus. Figure 5c shows that well defined polymers are formed, with dispersity increasing with the ratio of CiPEX, consistent with the other systems. The range of dispersity is ~1.1 with all iBADTC and ~1.6 with all CiPEX. A summary of the outcomes of the PPVK-gr-EA polymerization are given in Table S4.

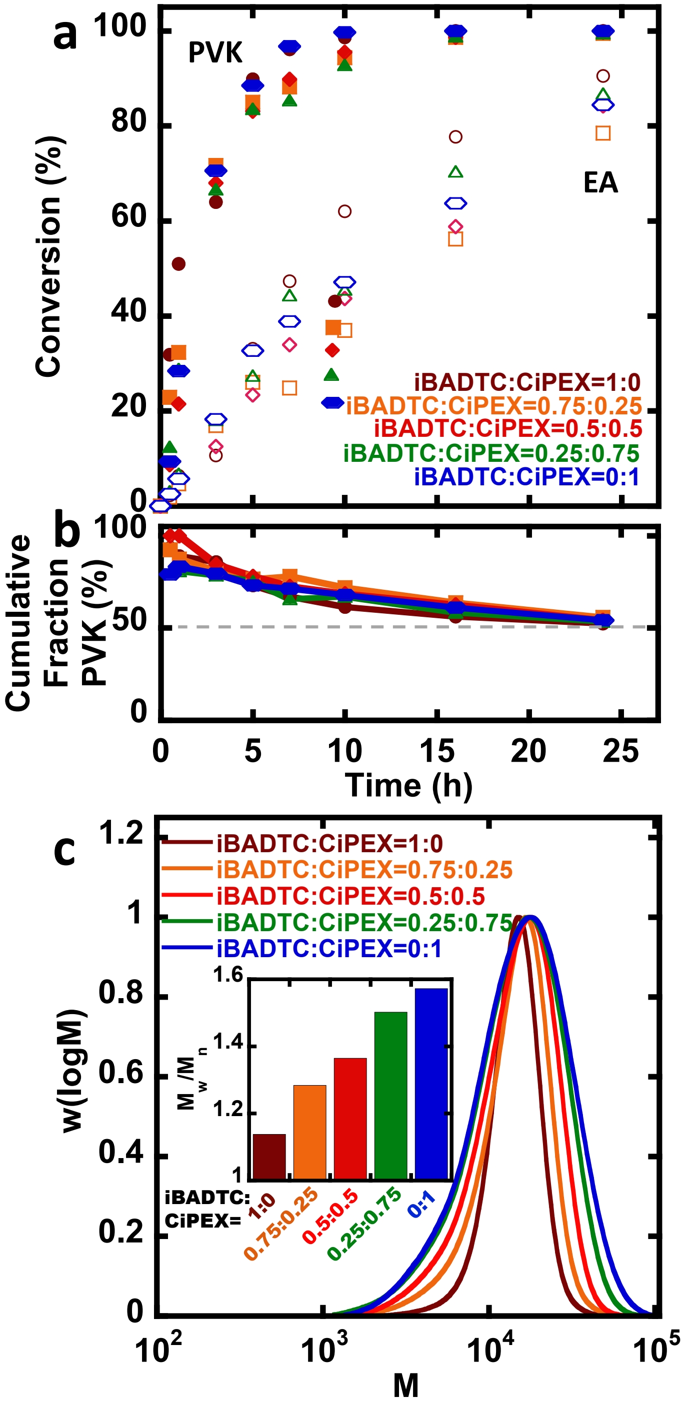
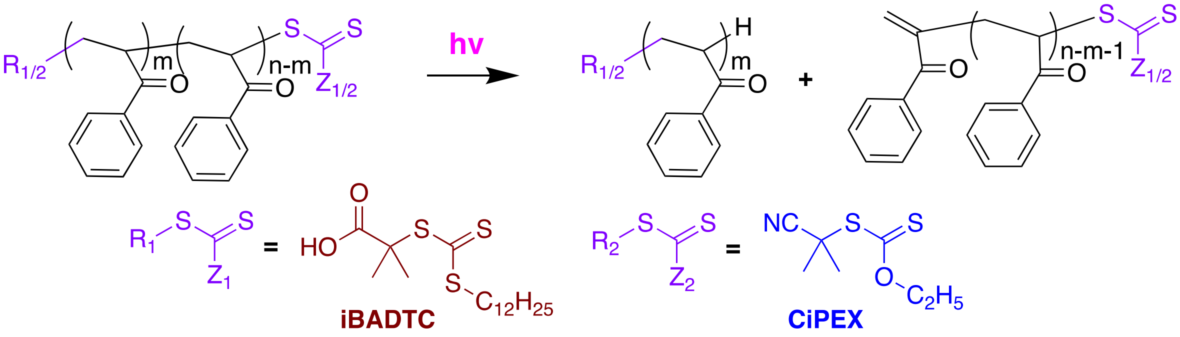


Figure 5: a) Kinetics of PVK (solid points) and EA (hollow points), b) composition, and c) molecular weight distributions of PVK and EA copolymerizations irradiated by blue light (450 ± 10 nm, 7.9 ± 0.4 mW/cm^2) under conditions [PVK]: [EA]: [CTA]=50:50:1 with 33 vol% monomer. Different ratios of iBADTC:CiPEX CTAs were used. Inset shows M_w/M_n for the polymerization of PVK and EA after 24hr of blue light irradiation.

Finally, a unique feature of vinylketone monomers is that they can be photodegraded under relatively long wavelength UV radiation. In the process of photodegradation, random scission of chains will occur, which will lead to both a decrease in polymer molecular weight, but also an increase in chain dispersity, especially for relatively uniform chains. Therefore, photodegradation of PVK was explored as an alternative approach to modulate the dispersity of the synthesized polymers. This approach to modulating the polymer's MWD after synthesis has the ability to either change or modulate the MWD towards a new lower molecular weight, if the polymerization overshot a particular molecular weight. Alternatively, the light induced photodegradation could introduce spatiotemporal control over the MWD. I.e. the same parent chains could be modulated to new MWDs on only certain regions or at certain times. This could be particularly useful in patterning type applications.

It is important to note that upon chain scission, the polymers are expected to have hydrogen terminated and vinyl terminated end-groups, consistent with the Norrish Type-II process established for vinyl ketone photodeagradation.[45–50] This photodegradation process is shown in Scheme 5. Initially PPVK was synthesized under blue light giving polymers with a mean chain length near 50 units. Three polymers were synthesized, one with low dispersity ($M_w/M_n = 1.11$) using only iBADTC, one with moderate dispersity synthesized using equal parts iBADTC and CiPEX ($M_w/M_n = 1.49$), and one with high dispersity synthesized using only CiPEX ($M_w/M_n = 1.99$).



Scheme 5: Photodegradation of PPVK under UV irradiation.

As seen in Figure 6, photodegradation of the PPVK materials was performed under UV irradiation at 310 ± 20 nm with an intensity of 23.2 ± 0.5 mW/cm^2. Figure 6 shows a decrease in molecular weight upon UV irradiation. Commensurate with the decrease in molecular weight was a substantial increase in dispersity for the system synthesized using only iBADTC rising from ~1.1 to ~1.5 after 5h of 310 nm irradiation, and moderate increase in dispersity for the system synthesized with equal parts iBADTC and CiPEX rising from ~1.5 to ~1.9 after 5h of 310 nm irradiation. However, in the system synthesized with only CiPEX, the dispersity remained near 2.0, even as the chain length decreased upon irradiation with 310 nm light. This indicates that UV irradiation after synthesis of vinyl ketone polymers is a further method for modulating the dispersity of the chains, with the greatest impact on dispersity occurring for polymers with narrow molecular weight distributions.

This work primarily focused on tuning polymer dispersity through vinylketone photopolymerization and photodegradation. Dispersity is a critical aspect of the polymer's MWD, governing its relative breadth, future work can focus on expanding this approach to tune higher order moments of the MWD such as skewness or kurtosis, which impact the shape of the distributon.[36]

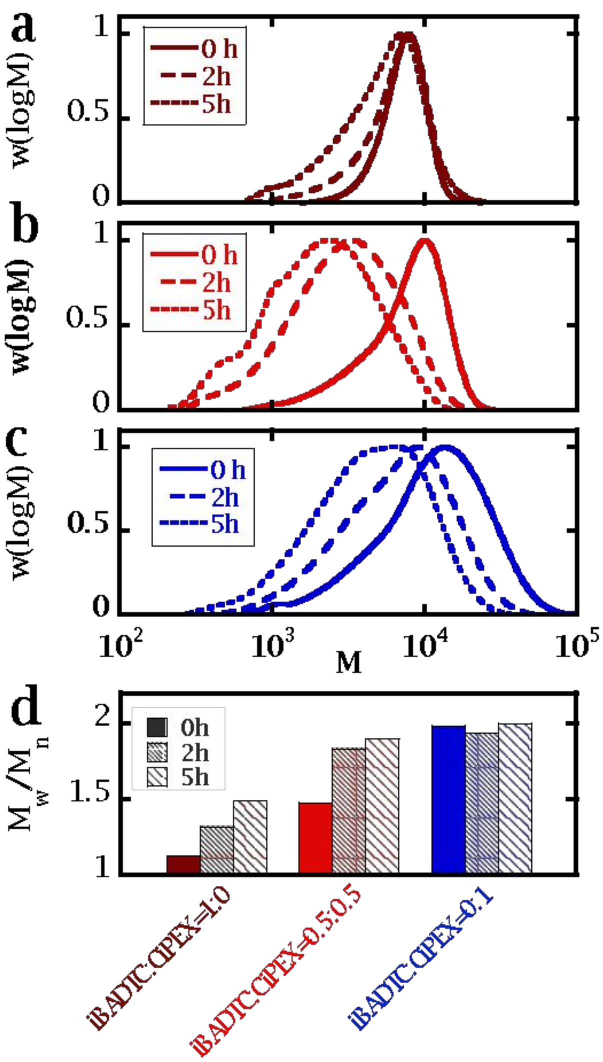


Figure 6: Photodegradation of PPVK polymers with initial chain length near 50 units under UV irradiation (310 ± 20 nm, 23.2 ± 0.5 mW/cm^2). a) Polymers synthesized with iBADTC:CiPEX = 1:0, b) polymers synthesized with iBADTC:CiPEX = 0.5:0.5, and c) polymers synthesized with iBADTC:CiPEX = 0:1. d) Evolution of M_w/M_n with irradiation time for each studied ratio of iBADTC:CiPEX.

Conclusions

The intrinsic photochemistry of vinyl ketone monomers was used to drive synthesis of complex polymers with control over the macromolecular mean chain length and dispersity. The intrinsic photochemistry of vinyl ketones enables efficient photopolymerization, typically reaching high conversion in 2h under blue light. Using a combination of a high activity trithiocarbonate CTA, with a low activity xanthate CTA, vinyl ketone polymers could be synthesized with dispersities in the range of ~1.1-2.0, while maintaining control over the mean chain length. Additionally, the chains were living as evidenced by efficient chain extension in all cases with a second monomer, ethyl acrylate. The unique reactivity of vinyl ketones and acrylates also facilitated the synthesis of polymers with a strong gradient structure, with preferential incorporation of the PVK monomer over EA during initial polymerization. This opens the door to tailoring complex gradient and block-like polymers with tunable dispersity. Finally, photodegradation of the poly (vinyl ketone) enables further modification of the molecular weight distribution, both decreasing average chain length, but also increasing the dispersity, especially for polymers with narrow molecular weight distributions.

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