Redefining the Limits: Atom transfer radical polymerization of vinyl ketone monomers under light.

M. A. Sachini N. Weerasinghe,[a] Lucca Trachsel,[b] Grzegorz Przesławski,[b] Julian Sobieski,[b] Parker Anthony McBeth,[a] Michelle C. Mancini,[a] Roshan Lama,[a] Tochukwu Nwoko,[a] Matthew Paeth,[a] Krzysztof Matyjaszewski,[b] Dominik Konkolewicz [a*]

[a] Department of Chemistry and Biochemistry, Miami University, 651 E High St, Oxford, 45056, OH, USA

[b] Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, PA, 15213, United States

*Correspondence: d.konkolewicz@miamiOH.edu

Abstract

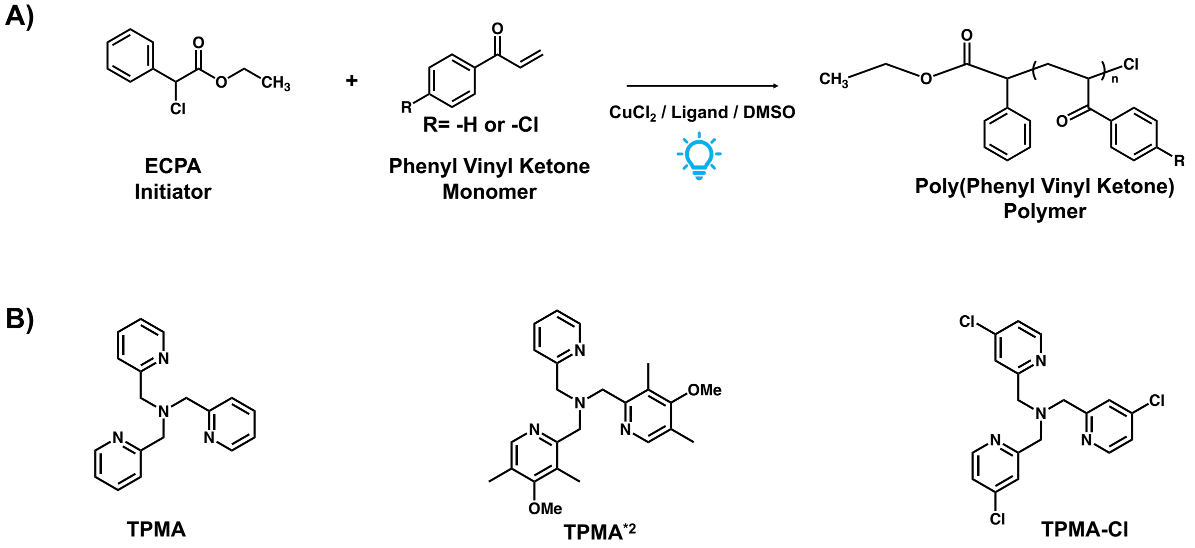
Vinyl ketone polymers, including poly(phenyl vinyl ketone) and poly(*p*-chlorophenyl vinyl ketone) were successfully synthesized under light using atom transfer radical polymerization (ATRP). This marks the first successful attempt at ATRP of vinyl ketones. The polymerization kinetics revealed chain growth and maintained livingness, as further evidenced by successful chain extension using ethyl acrylate. The efficient main-chain cleavability of the polymers was confirmed under UV light. While the attainment of low dispersity remains an enduring challenge, this work offers promising potential for future success.

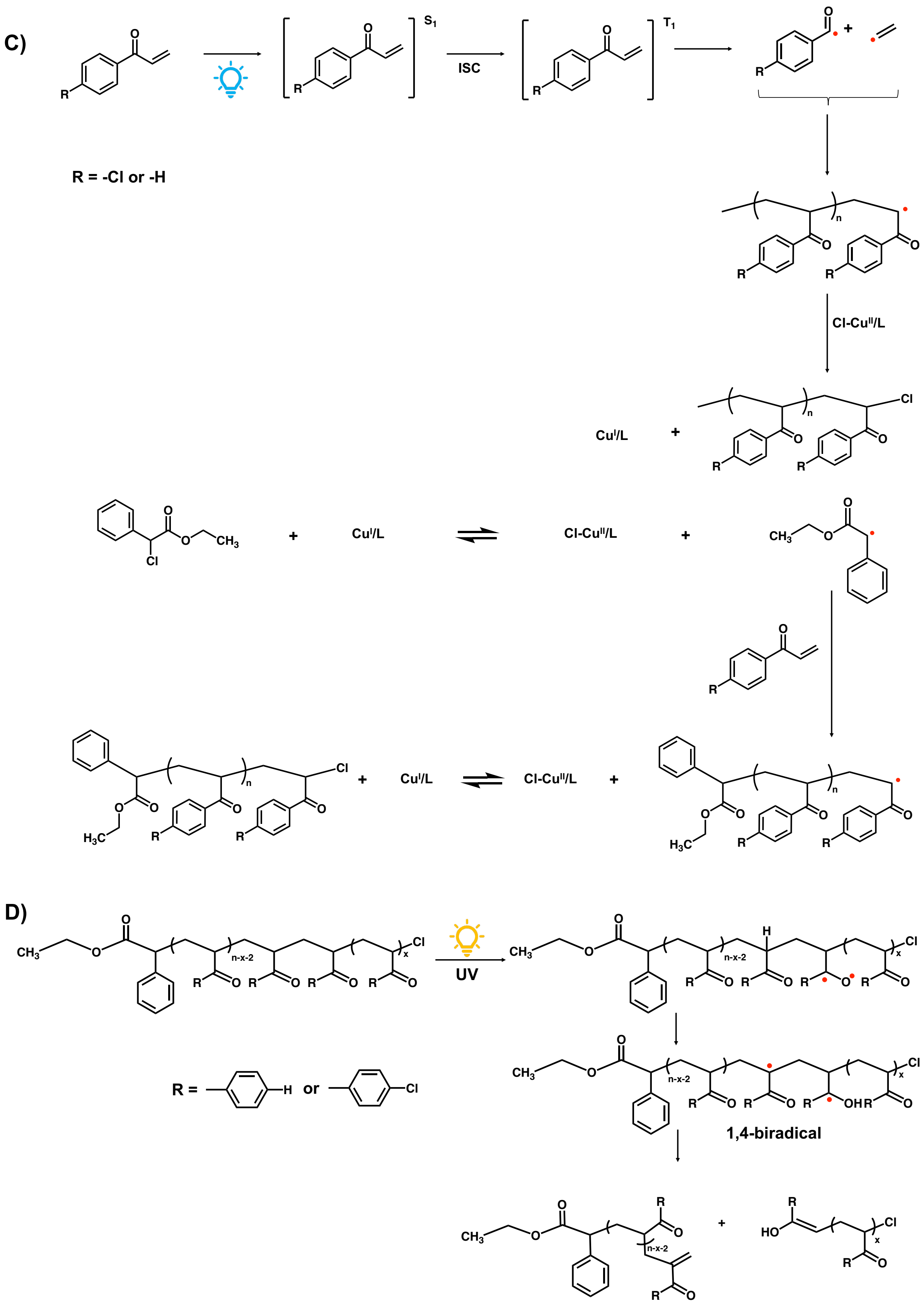
Vinyl ketone monomers and their polymers have garnered considerable interest over the past few years due to their intriguing properties under light.[1–3] Through the Norrish type I pathway, vinyl ketone monomers undergo well-controlled polymerization via self-initiated radical generation under visible light.[4,5] Vinyl ketone polymers also undergo efficient main-chain cleavage upon UV irradiation through the Norrish type II pathway.[2,6] Notably, the facile main-chain degradability of vinyl ketone polymers is a highly valuable feature that is substantially more challenging in many commodity polymers.[6]

The synthesis of well-controlled polymers is highly desirable since the properties of polymer materials are generally structure-dependent.[7,8] Radical polymerization of methyl vinyl ketone (MVK) monomers was reported in 1938 by Levesque and Marvel.[9] Since then, several approaches have been taken to synthesize vinyl ketone polymers, including conventional radical polymerization,[10,11] anionic polymerization,[10,12,13] and reversible deactivation radical polymerization (RDRP) techniques.[5,14–18] Compared to other techniques, reversible deactivation radical polymerization (RDRP) techniques control the number-average molecular weight (M_n) and dispersity (M_w/M_n) through reversible deactivation and activation of a radical chain end, resulting in polymers with tunable molecular weight distributions (MWDs), living end groups, and the ability to form polymers with complex architectures.[19] Among RDRP techniques, reversible addition-fragmentation chain transfer (RAFT) polymerization has been shown to enable control in vinyl ketone polymerization. In 2007, Wooley and coworkers synthesized well-defined homo and block polymers of MVK and phenyl vinyl ketone (PVK) under thermal RAFT polymerization conditions, resulting in homopolymers with $M_w/M_n \leq 1.20$.[14] Later in 2017, Konkolewicz and coworkers identified that PVK can undergo self-initiated RAFT polymerization under 440 nm visible light, while undergoing photodegradation under UV irradiation.[5] Concurrently, Hawker and coworkers synthesized a series of vinyl ketone polymers, including ethyl, methyl, and phenyl vinyl ketones, under visible light-mediated conditions in the presence of Eosin Y, an organic photocatalyst.[15] In this photoinduced energy/electron transfer reversible addition fragmentation chain transfer (PET-RAFT) polymerization, well-controlled vinyl ketone polymers were obtained, overcoming the problem associated with traditional thermal RAFT polymerization. Subsequently, Konkolewicz and coworkers showed that the self-initiated polymerization of PVK occurred with rates that were similar to PET-RAFT using Ir(ppy)$_3$ as the photocatalyst and even faster than PET-RAFT using ZnTPP as the photocatalyst.[4] Additionally, controlled nitroxide-mediated polymerization (NMP) of MVK and PVK was reported, including the ability to chain extend the vinyl ketone polymers with other monomers such as styrene.[17]

However, despite the successes of RAFT and NMP in the control of various vinyl ketones, atom transfer radical polymerization (ATRP)[20,21], another versatile RDRP method, has not yet been reported in the literature. In 2006, Baskaran and coworkers attempted to polymerize MVK, however, the polymerizations were unsuccessful after screening catalyst concentrations, temperature, and the type of initiator, ligand, and solvent.[22] The inability of MVK to undergo polymerization was proposed to occur due to the unfavorable coordination of MVK monomer with CuBr/ligand catalyst, forming an extended coordination complex.[22] Since then, no studies on the ATRP of vinyl ketones have been reported. This study further explores the polymerization kinetics of PVK and its derivatives under photo-ATRP conditions, as well as the livingness and photodegradation of phenyl vinyl ketone polymers produced by ATRP. This work shows the first successful ATRP of vinyl ketone polymers with living characteristics and photodegradable properties, overcoming the previously stated impossibility of ATRP synthesis of vinyl ketone polymers.

Photo-ATRP kinetics of PVK monomers with -H and -Cl substituents at the para positions of the aromatic ring were explored in the presence of three different tris(2-pyridylmethyl)amine (TPMA) ligands, including unsubstituted TPMA, 1-(4-methoxy-3,5-dimethylpyridin-2-yl)-*N*-((4-methoxy-3,5-dimethylpyridin-2-yl)methyl)-*N*-(pyridin-2-ylmethyl)methanamine (TPMA^{*2}), and tris(4-chloro-2-pyridylmethyl)amine (TPMA-Cl). TPMA-based ligands bind strongly to Cu and provide an efficient ATRP activation/deactivation process. Moreover, TPMA can be easily modified with electron-donating groups (EDGs) and electron-withdrawing groups (EWGs), thereby altering the ligand's electronic properties. TPMA^{*2} and TPMA-Cl are TPMA derivatives bearing 4-OMe (methoxy-EDG) and 4-Cl (chloro-EWG) substituents on the pyridine ring, respectively.[23–26] The choice of ECPA initiator can be rationalized by the fact that the stronger C-Cl bond provides a more stable dormant chain end, thereby reducing side reactions and improving control when polymerizing highly reactive vinyl ketone monomers. In contrast, systems employing weaker C-Br bonds generally exhibit poorer control. In addition to that, a polymerization reaction was performed in DMSO, considering its ability to stabilize both Cu complex and vinyl ketone monomers, improving the solubility of all reactants. The general photo-ATRP reaction is illustrated in Scheme 1A, whereas the structures of substituted TPMA ligands used in this study are shown in Scheme 1B. Polymerization kinetics were performed in the presence of ethyl α-chlorophenylacetate (ECPA) initiator, copper(II) chloride ($CuCl_2$/Ligand) deactivators (100 and 300 ppm), anhydrous dimethyl sulfoxide (DMSO) solvent at room temperature, under deoxygenated conditions, and blue light irradiation (λ_{max}=450±10 nm and intensity=12.7±0.6 mW/cm^2).[27] The proposed photo-ATRP mechanism is illustrated in Scheme 1C. Upon blue light irradiation, phenyl vinyl ketone monomers generate radicals via a proposed Norrish type I pathway, in which the vinyl ketone monomer is excited to the singlet (S_1) state, subsequently undergoes intersystem crossing (ISC) to the triplet state (T_1), followed by radical generation. These radicals add monomer and participate in the ATRP dynamic equilibrium. Therefore, phenyl vinyl ketone monomers can be polymerized via photo-ATRP using typical ATRP catalysts, eliminating the need for expensive external photocatalysts. The polymerization processes were proposed to follow an initiator for continuous activator regeneration (ICAR) ATRP approach,[28] where parts per million Cu catalyst were used and the Cu^{I} activators were continuously regenerated by the radical generation from the Norrish type I pathway.





Scheme 1: A) Reaction scheme of ATRP reaction of PVK monomers under blue light irradiation. B) Structures of substituted TPMA ligands used in the study. C) Proposed photo-

ATRP mechanism of vinyl ketone monomers under blue light. D) Proposed Norrish type II mechanism of a vinyl ketone polymer under UV light, illustrating backbone cleavability.

As seen in Figures 1A and B, the polymerization of both PVK and PVK-Cl was slower with higher Cu loading. This could be due to higher Cu concentrations leading to more Cu^{I}-based catalytic radical termination.[29,30] Figures 1A and 1B indicate that PVK and PVK-Cl polymerization were faster in the presence of $TPMA^{*2}$ compared to TPMA. In particular, the conversion of the system with PVK monomer, TPMA ligand, and [Cu]=300 ppm was $\leq 3\%$ even after 7 hours. $TPMA^{*2}$ ligand is more active than the unsubstituted TPMA, due to the donating methoxy and methyl groups, which stabilize Cu^{II}, increasing the ATRP equilibrium constants. This suggests that lower concentrations of Cu^{I} are needed for activation of the end groups, which would reduce the impact of catalytic radical termination.[30] Table S1 also investigated the impact of the electron-withdrawing Cl substituent on TPMA, which generally led to slower polymerization and poorly controlled polymers, presumably due to insufficient Cu^{II} deactivators in solution at ATRP equilibrium. Comparing PVK and PVK-Cl monomers, PVK-Cl monomer with the electron-withdrawing Cl substituent resulted in higher monomer conversion and relatively broader MWDs. The higher monomer conversion could be due to the ability of the -Cl group to stabilize the propagating radical by lowering the energy of the singly occupied molecular orbital (SOMO). Attempts to polymerize PVK with a -OMe substituent led to poorly controlled polymers.

Figures 1C and 1D show the evolution of M_n and M_w/M_n with conversion. In all cases, the polymers had relatively high dispersity, in the range of 1.5-2.0. However, the M_n increased with conversion, consistent with a living-like polymerization, albeit with relatively broad MWDs. Interestingly, systems using 300 ppm of Cu catalyst had lower dispersity values but also had M_n substantially lower than predicted. In contrast, 100 ppm reactions had M_n closer to $M_{n\text{-}th}$, ($M_{n\text{-}th}=M_{\text{Monomer}}\times([\text{Monomer}]_o/[\text{ECPA}]_o)\times$Monomer Conversion, where M_{Monomer} is the molecular weight of the monomer, $[\text{Monomer}]_o$ is the initial concentration of the monomer, and $[\text{ECPA}]_o$ is the initial concentration of the initiator), although the dispersity was higher. Generally, ATRP reactions generated polymers with lower dispersity with higher catalyst loading, due to higher deactivator concentrations. The lower M_n in the presence of higher catalyst loading suggests either the formation of new chains or transfer reactions catalyzed by higher ratios of Cu complexes to ATRP initiators. Despite the high dispersity, these represent the first successful ATRP reactions of vinyl ketone-based monomers.

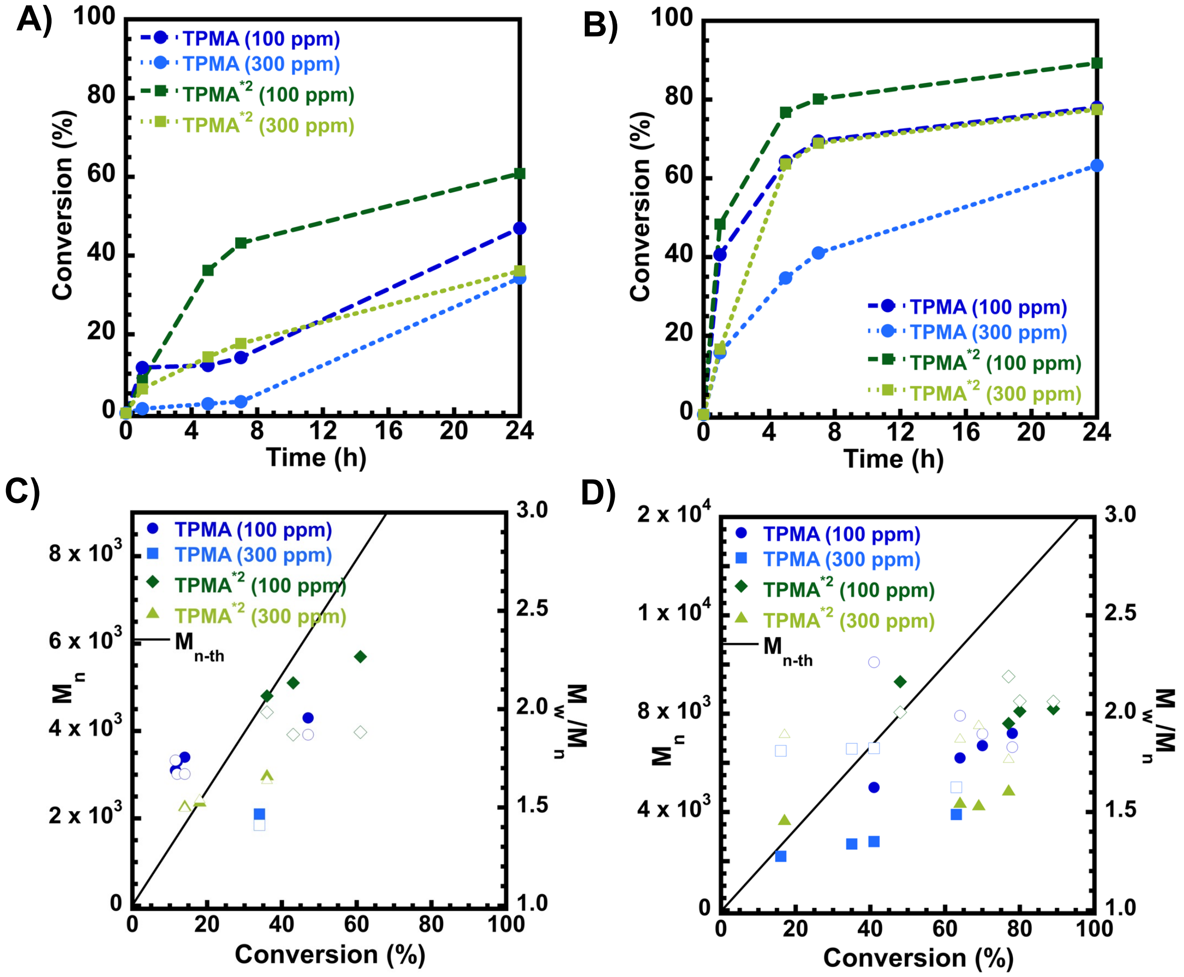


Figure 1: A) Polymerization kinetics of PVK monomer. B) Polymerization kinetics of PVK-Cl monomer. C) Evolution of M_n and M_w/M_n with the conversion% in the PVK monomer system. D) Evolution of M_n and M_w/M_n with the conversion% in the PVK-Cl monomer system. Reaction conditions: in the presence of a mole ratio of monomer:$CuCl_2$:ligand:ECPA=100: 0.0X:0.0X:1 (For 100 ppm 0.0X=0.01 and 300 ppm 0.0X=0.03) and the mass ratio of monomer:DMSO (anhydrous)=1:0.75. The reaction was performed under deoxygenated conditions, at room temperature, and with blue light irradiation (λ_{max}=450±10 nm and intensity=12.7±0.6 mW/cm^2).

Figure 2 demonstrates the impact of catalyst loading on the control of polymerization. PVK-Cl was polymerized in the presence of [Cu]=100 ppm, targeting a degree of polymerization (DP) of 100, and [Cu]=400 ppm targeting DP=25. This was chosen to maintain the same ratio of ATRP end group to Cu catalyst. Figure 2 shows that indeed the MWD shifted to lower values with the lower targeted degree of polymerization.

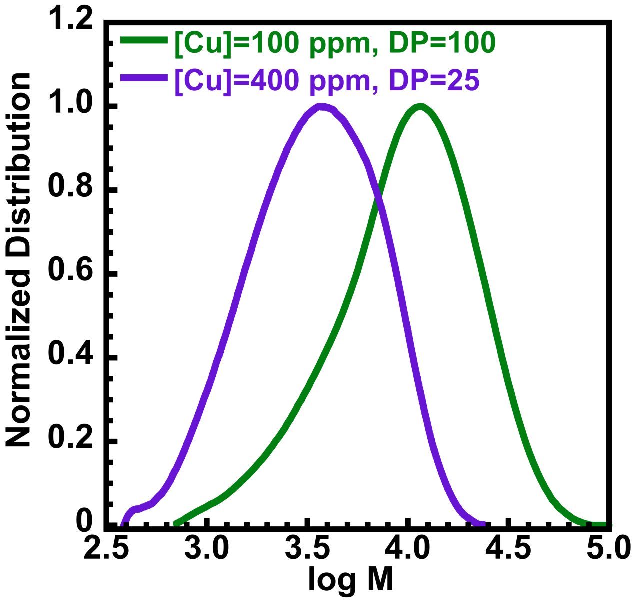


Figure 2: Effect of catalyst loading on polymerization of PVK-Cl monomer. Polymerizations were conducted with [Cu]=100 ppm and [Cu]=400 ppm, targeting DP=100 and DP=25, respectively. Reaction conditions: in the presence of a mole ratio of monomer:$CuCl_2$:ligand:ECPA=100:0.0X:0.0X:1 (For DP=100 and 100 ppm 0.0X=0.01 and DP=25 and 400 ppm 0.0X=0.01) and the mass ratio of monomer:DMSO (anhydrous)=1:0.75. The reactions were performed under deoxygenated conditions, at room temperature, and with blue light irradiation. (λ_{max}=450±10 nm and intensity=12.7±0.6 mW/cm^2).

To verify the living nature of the photo-ATRP synthesized PVK-based polymers, chain extension reactions were performed. Photo-ATRP polymerization of PVK-Cl monomer resulted in poly(PVK-Cl) macroinitiator with 60% monomer conversion, M_n=4500, and M_w/M_n=1.65. After isolation of poly(PVK-Cl) macroinitiator, it was extended with ethyl acrylate (EA) following ARGET ATRP conditions in the presence of $CuCl_2$, Me_6Tren, and ascorbic acid at 70 °C.[31] A successful chain extension reaction resulted in poly(PVK-Cl)-*b*-poly(EA) polymer with 89% monomer conversion, M_n=37500, and M_w/M_n=2.26, as seen in Figure 3. Beyond the primary characterization of the extended block by size exclusion chromatography, a diffusion ordered spectroscopy NMR experiment was conducted. Figure S1C clearly shows the same diffusion coefficient for the whole poly(PVK-Cl)-*b*-poly(EA) polymer, indicating the movement of a single entity in the solution and a successful chain extension. In addition to determining the livingness of vinyl ketone polymers made by ATRP following a chain extension reaction, as seen in Figure S3A, 2-chloro-2-phenylacetate functionalized monomethyl ether poly(ethylene glycol) macroinitiator (M_n=3360 and M_w/M_n=1.05) was chain extended with PVK monomer in the presence of TPMA, $CuCl_2$, under deoxygenated conditions with blue light irradiation (λ_{max}=450±10 nm and intensity=50 mW/cm^2). A successful chain extension reaction yielded a narrow molecular-weight poly(ethylene glycol)-*b*-poly(PVK) polymer with >98% monomer conversion, M_n=43,300, and M_w/M_n=1.11, as illustrated in Figure S2B.

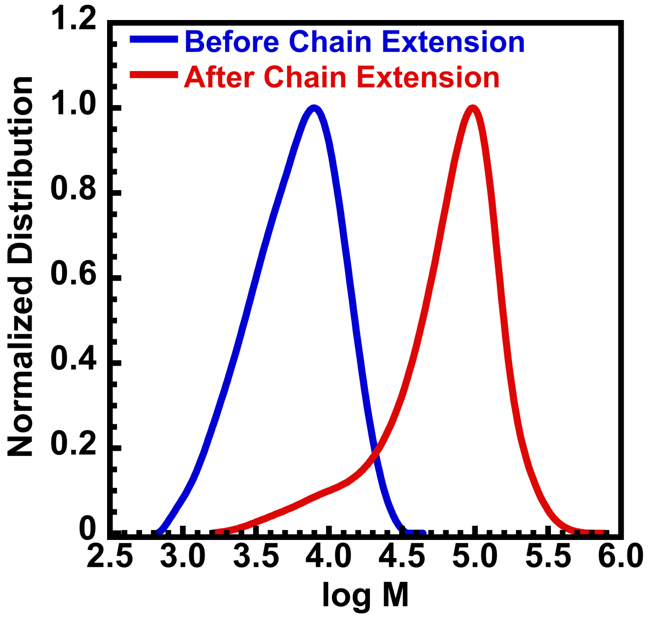


Figure 3: Chain extension reaction of poly(PVK-Cl) macroinitiator with EA to obtain poly(PVK-Cl)-*b*-poly(EA). Reaction conditions: (synthesis of poly(PVK-Cl) macroinitiator) in the presence of a molar ratio of PVK-Cl:$CuCl_2$:TPMA:ECPA=100:0.03:0.03:1 and the mass ratio of monomer:DMSO (anhydrous)=1:0.75, at room temperature, and with blue light irradiation (λ_{max}=450±10 nm and intensity=12.7±0.6 mW/cm^2). Reaction conditions: (chain extension reaction) in the presence of a mole ratio of EA:$CuCl_2$:Me_6Tren:poly(PVK-Cl) macroinitiator:ascorbic acid=400:0.4:2.4:1:0.2 and the mass ratio of monomer:DMSO=1:2, under deoxygenated conditions and at 70 °C.

Finally, the photodegradability of the poly(PVK) and poly(PVK-Cl) was confirmed. Scheme 1D illustrates the Norrish type II mechanism. The carbonyl group in vinyl ketone polymer undergoes photoexcitation to the singlet excited state (S_1) upon UV irradiation. This is followed by intersystem crossing (ISC) to a higher energy triplet state (T_n), which then relaxes to the lowest triplet state (T_1) via internal conversion (IC). 1,4-Biradical is formed after γ–H abstraction, which then undergoes elimination. This produces two fragments, with one fragment with an alkene and the other having a ketone functional group.[2,6] The continuation of this process leads to backbone cleavage of the polymer. Both poly(PVK) and poly(PVK-Cl) polymers were subjected to UV light-induced degradation (λ_{max}=350 nm and intensity=2.5± 0.13 mW/cm^2) for different exposure times. Figures 4A and 4B illustrate the changes in MWD, clearly demonstrating a shift toward lower molecular weight over time. After 24 hours under UV light, the initial M_n=9400 (M_w/M_n=2.18) of the poly(PVK) polymer decreased to M_n=2200

(M_w/M_n=1.44), while the initial M_n=9000 (M_w/M_n=1.94) of the poly(PVK-Cl) polymer dropped to M_n=2300 (M_w/M_n=1.38) (Table S6). Therefore, these results demonstrate the efficient main-chain cleavability/photodegradability of vinyl ketone polymers prepared under ATRP conditions.

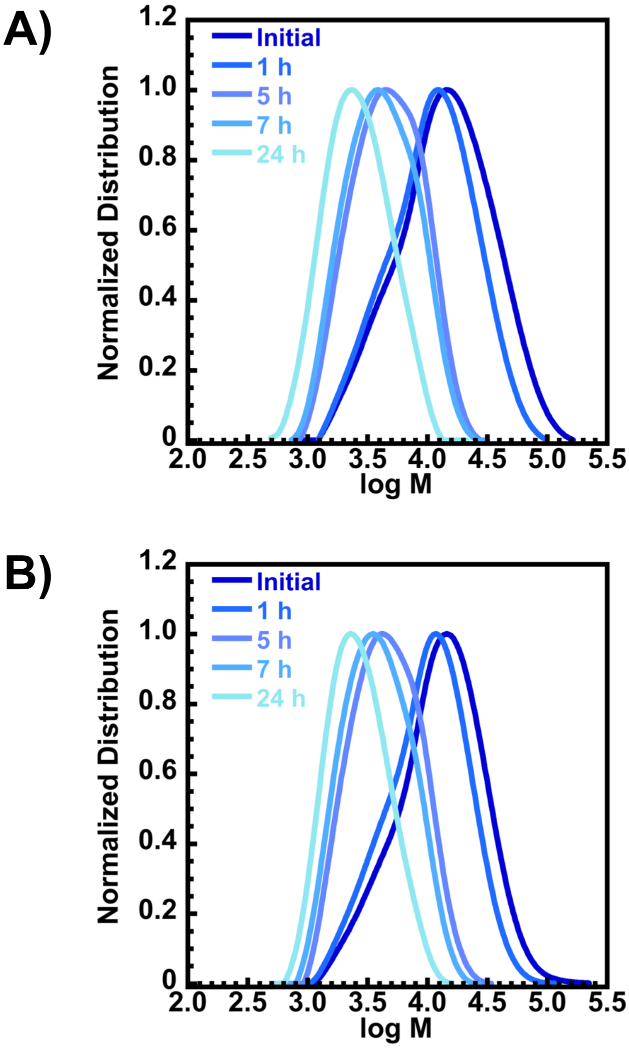


Figure 4: Evolution of MWDs with the degradation time (1, 5, 7, and 24 h). A) Poly(PVK). B) Poly(PVK-Cl). Conditions: Under UV light irradiation (λ_{max}=350 nm and intensity=2.5±0.13 mW/cm^2) and at room temperature.

In summary, two different vinyl ketone polymers were synthesized following ATRP. The chain growth and livingness of polymers were confirmed through polymerization kinetics and a subsequent chain extension experiment. This is the first successful attempt at the polymerization of vinyl ketones under ATRP conditions. With the highly efficient and strongly binding TPMA-based ligands, acceptable control over the reaction was achieved, although narrow molecular weight distributions remain an ongoing challenge. Additionally, efficient photodegradability of poly(PVK) and poly(PVK-Cl) under UV light was demonstrated for the polymer synthesized by ATRP. This work expands the ATRP monomer scope to vinyl ketones and provides access to new living, degradable polymer materials.

Conflicts of Interest

The authors declare no competing interests.

Acknowledgements

This work was supported by the National Science Foundation under award number CHE-2203727 for reaction development and optimization, CHE 2401112 for validation, chain extension, and livingness, CHE-2304670 for DOSY NMR. We would like to acknowledge Dr. Anne Carroll for the assistance in NMR at Miami University and Dr Kate Bradford for project discussions.

Author Contributions

M.A.S.N.W., L.T., G.P., J.S., P.A.M., M.C.M, R.L., T.N., M.P. K.M., D.K. were involved in methodology. M.A.S.N.W., L.T., G.P., J.S., P.A.M., M.C.M, R.L., were involved in formal analysis. M.A.S.N.W. wrote the first Draft. M.A.S.N.W., L.T., K.M., and D.K. were involved in conceptualization and validation. All authors were involved in editing the manuscript.

References

(1) De Alwis Watuthanthrige, N.; Reeves, J. A.; Dolan, M. T.; Valloppilly, S.; Zanjani, M. B.; Ye, Z.; Konkolewicz, D. Wavelength-Controlled Synthesis and Degradation of Thermoplastic Elastomers Based on Intrinsically Photoresponsive Phenyl Vinyl Ketone. *Macromolecules* **2020**, *53* (13), 5199–5207.

(2) Pal, D.; Konar, D.; Sumerlin, B. S. Poly (Vinyl Ketones): New Directions in Photodegradable Polymers. *Macromol Rapid Commun* **2023**, *44* (15), 2300126.

(3) Nadgorny, M.; Collins, J.; Xiao, Z.; Scales, P. J.; Connal, L. A. 3D-Printing of Dynamic Self-Healing Cryogels with Tuneable Properties. *Polym Chem* **2018**, *9* (13), 1684–1692. https://doi.org/10.1039/c7py01945a.

(4) Reeves, J. A.; De Alwis Watuthanthrige, N.; Boyer, C.; Konkolewicz, D. Intrinsic and Catalyzed Photochemistry of Phenylvinylketone for Wavelength-Sensitive Controlled Polymerization. *ChemPhotoChem* **2019**, *3* (11), 1171–1179.

(5) Reeves, J. A.; Allegrezza, M. L.; Konkolewicz, D. Rise and Fall: Poly (Phenyl Vinyl Ketone) Photopolymerization and Photodegradation under Visible and UV Radiation. *Macromol Rapid Commun* **2017**, *38* (13), 1600623.

(6) Weerasinghe, M. A. S. N.; McBeth, P. A.; Mancini, M. C.; Raji, I. O.; Needham, P. M.; Yehl, K.; Oestreicher, Z.; Konkolewicz, D. Controlling Photodegradation in Vinyl Ketone Polymers. *Chemical Engineering Journal* **2024**, 149307.

(7) Matyjaszewski, K.; Xia, J. Atom Transfer Radical Polymerization. *Chem Rev* **2001**, *101* (9), 2921–2990.

(8) Perrier, S. 50th Anniversary Perspective: RAFT Polymerization□ A User Guide. *Macromolecules* **2017**, *50* (19), 7433–7447.

(9) Marvel, C. S.; Levesque, C. L. The Structure of Vinyl Polymers: The Polymer from Methyl Vinyl Ketone. *J Am Chem Soc* **1938**, *60* (2), 280–284.

(10) Thomas, P. R.; Tyler, G. J.; Edwards, T. E.; Radcliffe, A. T.; Cubbon, R. C. P. The Anionic Polymerization of Some Alkyl Vinyl Ketones. *Polymer (Guildf)* **1964**, *5*, 525–531.

(11) Lyons, A. R. Polymerization of Vinyl Ketones. *Journal of Polymer Science: Macromolecular Reviews* **1972**, *6* (1), 251–293.

(12) Kinoshita, A.; Namariyama, Y. Syntheses of Photocrosslinkable Polymer from Modified Poly (Methyl Vinyl Ketone). *J Appl Polym Sci* **1983**, *28* (3), 1255–1261.

(13) Lyons, A. R.; Catterall, E. The Organo-Metal Initiated Polymerization of Vinyl Ketones—I: The Nbutyllithium Initiated Polymerization of Methyl Isopropenyl Ketone. *Eur Polym J* **1971**, *7* (7), 839–848.

(14) Cheng, C.; Sun, G.; Khoshdel, E.; Wooley, K. L. Well-Defined Vinyl Ketone-Based Polymers by Reversible Addition− Fragmentation Chain Transfer Polymerization. *J Am Chem Soc* **2007**, *129* (33), 10086–10087.

(15) Lee, I.-H.; Discekici, E. H.; Anastasaki, A.; de Alaniz, J. R.; Hawker, C. J. Controlled Radical Polymerization of Vinyl Ketones Using Visible Light. *Polym Chem* **2017**, *8* (21), 3351–3356.

(16) Zhao, Y.; Liu, X.; Liu, Y.; Wu, Z.; Zhao, X.; Fu, X. When CMRP Met Alkyl Vinyl Ketone: Visible Light Induced Living Radical Polymerization (LRP) of Ethyl Vinyl Ketone (EVK). *Chemical Communications* **2016**, *52* (81), 12092–12095.

(17) Hepperle, J. A. M.; Luftmann, H.; Studer, A. Controlled Nitroxide-mediated Radical Polymerization of Methyl and Phenyl Vinyl Ketone. *J Polym Sci A Polym Chem* **2012**, *50* (11), 2150–2160.

(18) Uehara, K.; Wagner, C. B.; Vogler, T.; Luftmann, H.; Studer, A. Poly (Vinyl Ketone) s by Controlled Boron Group Transfer Polymerization (BGTP). *Angewandte Chemie International Edition* **2010**, *49* (17), 3073–3076.

(19) Corrigan, N.; Jung, K.; Moad, G.; Hawker, C. J.; Matyjaszewski, K.; Boyer, C. Reversible-Deactivation Radical Polymerization (Controlled/Living Radical Polymerization): From Discovery to Materials Design and Applications. *Prog Polym Sci* **2020**, *111*, 101311.

(20) Matyjaszewski, K. Dual Catalysis in Atom Transfer Radical Polymerization. *NSF Award Number 2401112. Directorate for Mathematical and Physical Sciences* **2024**, *24* (2401112), 1112.

(21) Sobieski, J.; Gorczyński, A.; Jazani, A. M.; Yilmaz, G.; Matyjaszewski, K. Better Together: Photoredox/Copper Dual Catalysis in Atom Transfer Radical Polymerization. *Angewandte Chemie International Edition* **2025**, *64* (2), e202415785.

(22) Mittal, A.; Sivaram, S.; Baskaran, D. Unfavorable Coordination of Copper with Methyl Vinyl Ketone in Atom Transfer Radical Polymerization. *Macromolecules* **2006**, *39* (16), 5555–5558.

(23) Kaur, A.; Ribelli, T. G.; Schröder, K.; Matyjaszewski, K.; Pintauer, T. Properties and ATRP Activity of Copper Complexes with Substituted Tris (2-Pyridylmethyl) Amine-Based Ligands. *Inorg Chem* **2015**, *54* (4), 1474–1486.

(24) Enciso, A. E.; Lorandi, F.; Mehmood, A.; Fantin, M.; Szczepaniak, G.; Janesko, B. G.; Matyjaszewski, K. P-Substituted Tris (2-pyridylmethyl) Amines as Ligands for Highly Active ATRP Catalysts: Facile Synthesis and Characterization. *Angewandte Chemie* **2020**, *132* (35), 15020–15030.

(25) Ribelli, T. G.; Lorandi, F.; Fantin, M.; Matyjaszewski, K. Atom Transfer Radical Polymerization: Billion Times More Active Catalysts and New Initiation Systems. *Macromol Rapid Commun* **2019**, *40* (1), 1800616.

(26) Lorandi, F.; Fantin, M.; Jafari, H.; Gorczynski, A.; Szczepaniak, G.; Dadashi-Silab, S.; Isse, A. A.; Matyjaszewski, K. Reactivity Prediction of Cu-Catalyzed Halogen Atom Transfer Reactions Using Data-Driven Techniques. *J Am Chem Soc* **2023**, *145* (39), 21587–21599.

(27) Parnitzke, B.; Nwoko, T.; Bradford, K. G. E.; Watuthanthrige, N. D. A.; Yehl, K.; Boyer, C.; Konkolewicz, D. Photons and Photocatalysts as Limiting Reagents for PET-RAFT Photopolymerization. *Chemical Engineering Journal* **2023**, *456*, 141007.

(28) Matyjaszewski, K.; Jakubowski, W.; Min, K.; Tang, W.; Huang, J.; Braunecker, W. A.; Tsarevsky, N. V. Diminishing Catalyst Concentration in Atom Transfer Radical Polymerization with Reducing Agents. *Proceedings of the National Academy of Sciences* **2006**, *103* (42), 15309–15314. https://doi.org/10.1073/pnas.0602675103.

(29) Schröder, K.; Konkolewicz, D.; Poli, R.; Matyjaszewski, K. Formation and Possible Reactions of Organometallic Intermediates with Active Copper (I) Catalysts in ATRP. *Organometallics* **2012**, *31* (22), 7994–7999.

(30) Fantin, M.; Lorandi, F.; Ribelli, T. G.; Szczepaniak, G.; Enciso, A. E.; Fliedel, C.; Thevenin, L.; Isse, A. A.; Poli, R.; Matyjaszewski, K. Impact of Organometallic Intermediates on Copper-Catalyzed Atom Transfer Radical Polymerization. *Macromolecules* **2019**, *52* (11), 4079–4090.

(31) Bradford, K. G. E.; Gilbert, R. D.; Weerasinghe, M. A. S. N.; Harrisson, S.; Konkolewicz, D. Spontaneous Gradients by ATRP and RAFT: Interchangeable Polymerization Methods? *Macromolecules* **2023**, *56* (21), 8784–8795.

Table of Contents Use Only