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Letter

Fast, oxygen-tolerant RAFT polymerization of hydrogels

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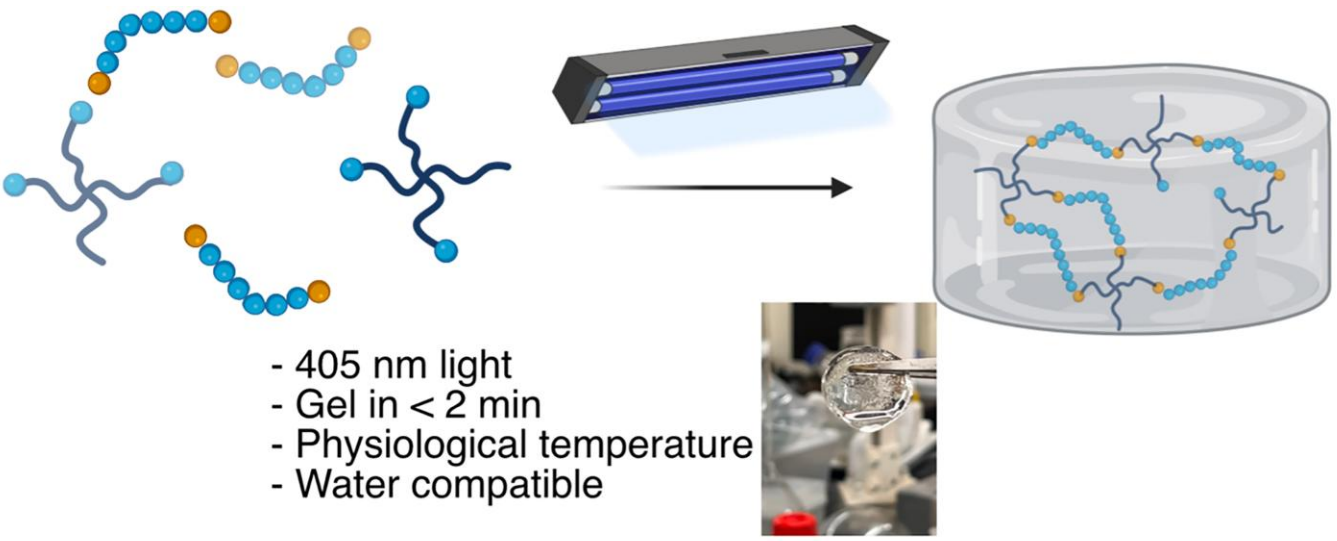
Abstract

Synthetic hydrogels are an attractive platform for cell culture, as they are water-rich, and they can often be used to encapsulate cells within a 3D matrix under the right chemical conditions. Many hydrogels form via free-radical polymerization in the presence of initiating species under ultraviolet (UV) light. The combination of free radicals and UV light during polymerization can lead to decreased viability and cellular stress. Here, we demonstrate a photoiniferter strategy to polymerize hydrogel networks without exogenous initiators and UV light. We demonstrate the formation of soft hydrogels with xanthate functional polymers by using visible light. Importantly, polymerization proceeds equally well under nitrogen and under ambient conditions with a range of monomers. We suggest this process as a way to diversify monomer choice for synthetic hydrogel development in the absence of UV light and free-radical initiators.

Keywords: photoiniferter, RAFT, xanthate.

Graphical Abstract



Hydrogels made from synthetic polymer precursors span a wide range of applications, from injectable redox-based hydrogels[1] to antifouling coatings[2] to cell culture environments[3,4] and tissue engineering.[5] Hydrogels are highly useful networks for cell culture applications due to their affinity for water, their stability under physiological conditions, and the 3D matrix structure that surrounds cells.[6,7] Most commonly, hydrogels are formed by cross-linking polymer chains into a network via the free-radical polymerization of vinyl functional monomers, initiated by redox or ultraviolet-sensitive species. Limitations of this standard approach include toxic byproducts[8–10] and high-energy light,[11] both of which can be damaging to embedded cells. Michael-addition reactions of multifunctional polymers are a popular alternative to free-radical-initiated network formation, though tuning the kinetics of Michael-addition reactions can be difficult within the strict confines of physiological conditions.[12] We sought to find an alternative solution to this issue by using in situ reversible addition-fragmentation chain transfer (RAFT) polymerization. RAFT polymerizations are

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traditionally highly oxygen-sensitive and polymerize slowly, so they are rarely used for cell applications.[13] The goal of our paper was to explore whether specialized RAFT polymerizations could be effectively tuned to create soft hydrogels quickly and under oxygen-tolerant conditions.

RAFT polymerizations offer several advantages over free-radical polymerizations. RAFT polymerizations use far lower radical concentrations than typical free-radical polymerizations, potentially reducing the oxidative stress on cells. Owing to their reversibility, they can be started and stopped at will, enabling the synthesis of complex structures and sequences through careful reaction design. Additionally, polymers with RAFT end groups are nontoxic to cells.[14] A final benefit of RAFT-cross-linked hydrogels is their ability to produce highly homogeneous[15] cross-linked networks with chain-end functionality, enabling the preparation of living hydrogels that can be modified after fabrication.[16,17]

A key limitation in the use of RAFT for biocompatible hydrogel fabrication is its high sensitivity to oxygen.[18,19] Oxygen is a well-known radical scavenger, but molecular oxygen is required for viable cell culture. Several techniques have been developed to impart oxygen tolerance to RAFT polymerizations, such as employing alkyl amine electron donors or photoredox catalysts.[20] Alternatively, the oxygen can be overwhelmed with excess radicals from the initiating species. Here, we have taken inspiration from this last concept by exploiting the high radical flux produced by xanthates in photoiniferter (PI)-RAFT polymerization to rapidly consume environmental oxygen during the polymerization, followed by rapid reoxygenation by diffusion to maintain cell viability.[21]

The PI concept was recently described by Otsu[22] and it uses molecules that can simultaneously act as **ini**tiator, trans**fer** agent, and **ter**minator. This means that no exogenous initiators are needed, which simplifies the reaction setup and reduces concerns of byproduct cytotoxicity. Given that xanthates enable polymerization and cross-linking in air[23] and that trithiocarbonate disulfides can mediate PI-RAFT and produce telechelic polymers,[24,25] we hypothesized that xanthate disulfides would provide a facile way to produce telechelic polymers, similarly to trithiocarbonate disulfides, and produce gels rapidly in open air, similarly to traditional xanthates. To do this, we employed a bisxanthate proposed by Zhang et al.[26] and translated it to an aqueous system to support future cell applications.

Our goal was to develop a new approach to synthesize polymers and hydrogels rapidly, without toxic radicals and side products, in the presence of oxygen and water. If successful, this would represent a fundamentally new strategy to form polymers and hydrogels in the presence of living cells. To accomplish this, we employed xanthate-mediated PI-RAFT polymerizations because of their fast kinetics.[27–29] Inspired by recent work on bis(trithiocarbonates)[24,25] and xanthates, we selected a xanthogen disulfide [bis(xan)] as the PI.

The polymerization reactions of bis(xan) follow a traditional RAFT mechanism. Light of 405 nm puts bis(xan) into an excited state in which it can rapidly fragment through β-scission into 2 thiyl radicals. These radicals can then react with vinyl monomers through a single unit monomer insertion pathway (Supplementary Scheme S1)[24] or react with and consume molecular oxygen to form hydroperoxyl side products. The addition of a monomer into bis(xan) changes its chemistry, resulting in better initiating radicals upon excitation and fragmentation relative to thiyl radicals. When the xanthates are again excited by light, a secondary carbon radical is formed that propagates rapidly. From there, the growing polymer enters RAFT equilibrium.

We assessed the compatibility of bis(xan) to create polymers with a suite of acrylic monomers (Supplementary Table S1) under a nitrogen atmosphere in dioxane. The water-insoluble monomers tested were alkyl esters, including methyl acrylate (MA), ethyl acrylate (EA), *n*-butyl acrylate (nBA), and isodecyl acrylate (iDA). The water-soluble monomers tested included acrylates [and hydroxyethyl acrylate (HEA)] and acrylamides [acrylamide (AAm), *N*,*N*-dimethylacrylamide (DMAA), and *N*-isopropylacrylamide (NIPAAm)].

All polymerizations except AAm yielded a viscous liquid after 30 min. For the alkyl esters, smaller pendent alkyl groups corresponded to better-controlled polymerizations than their larger counterparts (pEA, pnBA, piDA, Supplementary Table S1). The largest pendent alkyl-group polymer, piDA, had a large dispersity ($Đ > 2$). For the acrylamides, only monomers with substituted amides polymerized. AAm did not polymerize, whereas pDMAA and pNIPAm formed readily, with pDMAA showing lower dispersity than did pNIPAAm (Supplementary Fig. S3). The amide protons are likely responsible for the large dispersity and failed polymerizations due to aminolysis reactions of bis(xan).[30] Regardless, the polymers that did form represent wide-range pendent functionality, demonstrating the broad utility and applicability of bis(xan).

To determine the air tolerance and suitability for cell encapsulation of these polymerizations, the same monomers were polymerized with bis(xan), this time without nitrogen purging to remove air. Mirroring the nitrogen condition, all polymerizations except AAm yielded a viscous liquid after 30 min. Further, similar molecular weights and dispersity were observed when polymerizations were conducted in air and nitrogen (Supplementary Table S1).

To further investigate the influence of air on these reactions, we analyzed the polymerization kinetics. Ideally, polymerizations would approach full conversion within 10 min to be useful for encapsulating cells. To this end, MA polymerization under air or nitrogen was monitored via nuclear magnetic resonance (NMR). Polymerizations were conducted in air or under nitrogen with 405-nm light at 38°C with spectra collected at 0, 1, 5, and 10 min (Fig. 1a). Polymerization under nitrogen or air displayed nearly identical kinetics, each reaching 97% conversion within 10 min. The polymerization is remarkably fast compared with those of prior publications using 365-nm light.[26] Future studies could control for the solution volume as well as the effect of added oxygen.

A brief study was then conducted to determine the impact of heat on the polymerization reactions by using MA monomers. We compared reactions at 38°C and 60°C in air (Supplementary Table S2). In comparison with pMA synthesized at 38°C, pMA synthesized at 60°C was more narrowly dispersed. This was most likely due to the change in the RAFT equilibrium at elevated temperatures.[31] Although not useful for cell applications, temperature could be another useful handle for controlling this polymerization.

To further characterize the air tolerance, we conducted an analysis on the degree of polymerization (DP) via gel permeation chromatography (GPC) due to end-group signals overlapping with polymer signals for some samples. Polymerizations of MA in air and nitrogen with a targeted DP of 25 were conducted by using a monomer:bis(xan) ratio of 25:1. The resultant polymers yielded DP values of 32 and 35 monomers per chain for air

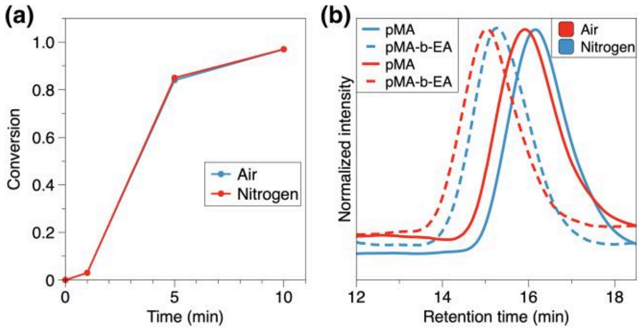

Fig. 1. Bis(xanthates) mediate ultra-fast polymerizations of acrylates and produce living polymers. a) Conversion over time of xanthate-mediated PI polymerization of 50 wt% MA under air and nitrogen atmosphere and b) GPC chromatogram showing degree of polymerization of pMA and pMA-b-EA synthesized in air and under nitrogen.

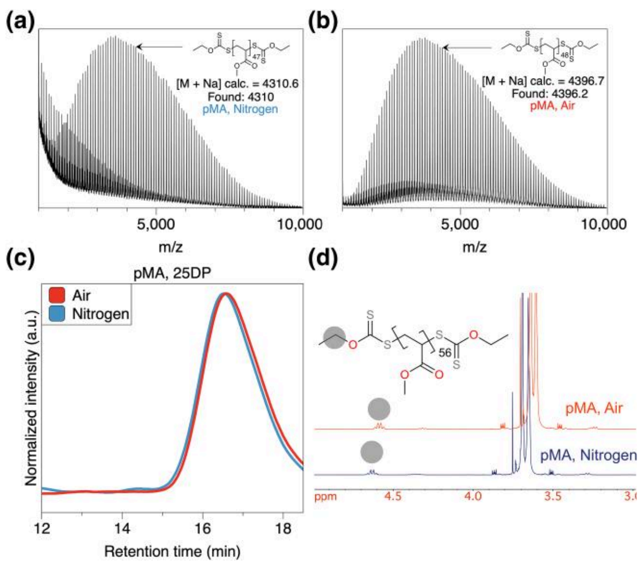

Fig. 2. Structural characterization of pMA synthesized with bis(xanthates) in air and nitrogen. a) MALDI-ToF spectra of pMA synthesized in nitrogen (Mn = 4,300 g/mol), b) MALDI-ToF spectra of pMA synthesized in air (Mn = 4,400 g/mol), c) GPC (DMF) chromatogram of pMA polymers with a targeted DP of 25, and d) ^{1}H NMR spectra showing characteristic xanthate peaks.

and nitrogen, respectively (Fig. 1b and Supplementary Table S3). We then attempted to re-initiate polymerization by redissolving the pMA polymers and adding EA (1 eq. EA relative to MA). Successful chain extension was demonstrated for both samples via the shift to earlier elution times (Fig. 1b). Interestingly, the final DP measured by using GPC was nearly twice as high as the targeted DP both in air and under nitrogen. This behavior is consistent both with prior reports studying bis(-trithiocarbonates)[24] and with a "polymerizing through" mechanism in which some xanthates react with and consume oxygen. Despite the higher-than-predicted DP, we were able to produce living polymers capable of further reaction in open air and under nitrogen.

To confirm the telechelic nature of polymers resulting from synthesis via bis(xan), we analyzed the structure of pMA via matrix-assisted laser desorption/ionization time-of-flight (MALDI-ToF), GPC, and NMR (Fig. 2). For these reactions, pMA was synthesized at a target DP of 25 [25:1 MA:bis(xan)],

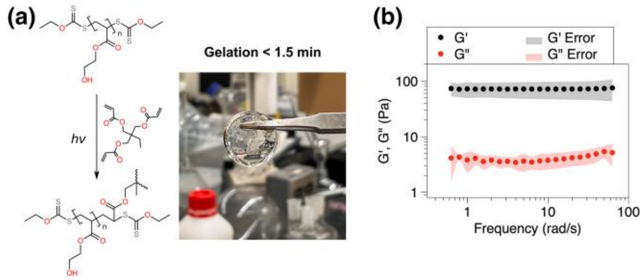

Fig. 3. Xanthate-functionalized polymers rapidly form cross-linked gels in pure water. a) Schematic of pHEA cross-linking in the presence of trimethylolpropane triacrylate and the resultant gel and b) storage and loss moduli of pHEA gels ($n = 3$).

either in air or under nitrogen, and characterized by using MALDI-ToF (Fig. 2a and b). MALDI-ToF showed that pMA polymerized through a photoiniferter approach with bis(xan) is well controlled, with polymerizations performed in air and under nitrogen having a dispersity of 1.11 (Supplementary Figs S1 and S2). The MALDI-ToF spectra also showed the air- and nitrogen-synthesized polymers to have very similar molecular weights (Mn = 4,600 g/mol in nitrogen, Mn = 4,800 in air). Additionally, MALDI-ToF analysis detected the sodiated forms of both polymers, consistently with pMA bearing the α and ω functionality expected in the telechelic polymer (Supplementary Scheme S1).

GPC confirmed that the polymers had nearly identical molecular weights and dispersity values (Fig. 2c). ^{1}H-NMR results revealed CH_3–CH_2–O peaks that were characteristic of chain-end *O*-ethyl xanthates attached to pMA synthesized in air and under nitrogen (Fig. 2d). Further, these results unambiguously showed end-group fidelity via a downward shift in the xanthate functional groups in pMA relative to their ppm in the bis(xan) precursor (4.6 ppm in Fig. 2d, 4.7 ppm in Supplementary Fig. S4).

We then set about testing their utility in forming hydrogels. The goal for hydrogel fabrication is to enable a hydrogel system to be useful for tissue engineering, namely cell culture. Hydrogels for cell culture should reach the critical gel point within 10 min without agitation so that cells do not settle to the bottom of the solution. Gelation cannot be too fast, as proper mixing must occur to limit heterogeneity.[12] We hypothesized that a fast gelation rate could be attained in water with one of the water-soluble polymers synthesized via bis(xan).

To test gelation rate, pHEA was selected as a model hydrophilic polymer. First, HEA was polymerized in water via bis(xan). After 10 min of 405-nm-light irradiation, the trifunctional vinyl cross-linker trimethylolpropane triacrylate was added at 1 wt% of the solution. The sample was again irradiated and, within 1.5 min, a cross-linked gel had formed (Supplementary Video S1). Following the successful fabrication of gels in water, several gels were prepared by using the same protocol and left to swell in phosphate-buffered saline for 48 h. The resultant gels were colorless and optically transparent (Fig. 3a). To determine the properties of the resultant hydrogels, the modulus was then characterized by using parallel-plate rheology. The G′ and G″ values of the gels were determined, resulting in a G′ of 72 ± 24 Pa and G″ of 4.5 ± 0.9 Pa at 1 Hz (Fig. 3b). G′ and G″ were observed to be frequency-independent, indicating that the samples had reached the critical gel point defined by the Winter–

Chambon criterion.[32] The small standard deviation of these modulus values indicates that the hydrogel formed had consistent network properties. Therefore, by using bis(xan), we were able to rapidly fabricate soft hydrogels in water with consistent modulus values. Future studies could further explore the physical properties of gels prepared with bis(xan), including their gel fraction and swelling ratios.

In this study, we demonstrated bis(xan)-mediated PI polymerizations to be very fast and not impacted by the presence of oxygen. The polymers produced could be chain extended with additional monomers. Finally, hydrogels were fabricated by using pre-synthesized polymer and a trifunctional cross-linker in ∼1.5 min. This approach provides a facile route to quick hydrogel fabrication by using light in the visible spectrum at physiological temperature without radical initiators and their decomposition products. Overall, our approach enables an optimal combination of rapid polymerization/gelation kinetics and water and air tolerance while producing well-defined telechelic polymers with minimal components. These properties make this system suitable for preparing custom water-soluble acrylic and acrylamide polymers used to form hydrogels to culture cells via cross-linking.

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Supplementary data

Supplementary material is available at *Chemistry Letters* online.

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Conflicts of interest statement. None declared.

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