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COMMUNICATION TO THE EDITOR

Photoirradiated Atom Transfer Radical Polymerization with an Alkyl Dithiocarbamate at Ambient Temperature

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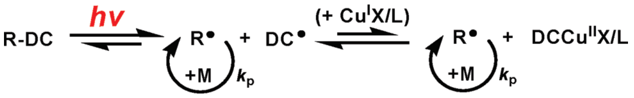
Introduction. Iniferter polymerization using a dithiocarbamate (DC) under thermal or UV irradiation conditions is one of the earliest controlled radical polymerization (CRP) techniques, reported by Otsu and co-workers in 1982 as a method for preparing well-defined polymers.[1] It has been demonstrated that this technique can be used to prepare various macromolecular structures such as block copolymers,[2] graft copolymers,[3] and star and hyperbranched polymers.[4] However, the structures and compositions of the polymers were relatively poorly controlled, with broad molecular weight distribution (MWD), due to the inefficient chain transfer reaction of the DC. Significant improvements in iniferter polymerization were made recently in the presence of copper catalyst and various alkyl DCs, as reported by the authors' group[5] and others,[6] producing polymers with controlled molecular weight (MW), narrow MWD, and high initiation efficiency. The intrinsic limitation of the slow chain transfer reaction in iniferter polymerization was overcome by significant enhancement of activation and deactivation by copper catalyst.[5]

Several CRP techniques invented later, such as nitroxide-mediated polymerization (NMP),[7] atom transfer radical polymerization (ATRP),[8] and reversible addition−fragmentation chain transfer (RAFT) polymerization,[9] allow the synthesis of well-defined (co)polymers with predictable MW, narrower MWD, a wider range of functionalities, a higher degree of chain end-functionality, and controllable macromolecular architecture. All CRP systems rely on a dynamic equilibrium between propagating radicals and dormant chains via a reversible deactivation mechanism.[10] Generally, ATRP requires alkyl (pseudo)halide as an initiator and a transition metal/ligand complex as a catalyst; RAFT polymerization requires a conventional initiator such as AIBN and a RAFT agent as a chain transfer agent (CTA). Recently, the authors' group presented synergetic effects on the concurrent ATRP and RAFT polymerization in the presence of a copper complex and RAFT agent.[5,11] This concurrent technique provides several advantages over either ATRP or RAFT polymerization: (1) new chain generation is eliminated by the direct activation of a CTA by the copper complex;[11a] (2) hence, preparation of purer block copolymer and very high molecular weight (co)polymers are possible;[11a,b] (3) control of the polymerization is maintained by a fast chain transfer reaction between propagating radicals and CTAs;[11a−d] (4) thus, the required minimum concentration of deactivator, Cu(II), to produce well-defined polymer is below ppm levels, while retaining a narrow MWD;[11b] and (5) even a catalyst complex with inefficient ligands for ATRP provides well-controlled polymerization.[11d]

Scheme 1. Simplified General Mechanism for ATRP with Dithiocarbamate under UV Irradiation



Development of active and versatile initiating systems in CRP is still one of the vigorously studied subjects from scientific and industrial viewpoints.[12] Various methods to activate dormant species such as thermal, photochemical, or chemical stimuli have been developed. Among them, CRP triggered by photochemical stimuli has attracted a great deal of attention due to the easy control of the polymerization, fast polymerization rate, and the realization of ambient temperature polymerization even with heat-sensitive or thermo-degradable monomers at room temperature or below.[13] As stated above, the iniferter technique actively adopted the advantages of photochemical initiation because of the presence of a DC moiety that is photocleavable by UV irradiation. For a RAFT system, γ-ray,[14] plasma,[15] and UV−vis[13c−h] irradiation have been applied to activate or initiate polymerization. UV irradiation has been used for NMP using nitroxide with a chromophore moiety to facilitate cleavage of the carbon−oxygen bond.[16] Among these activation methods, UV irradiation without externally added photoinitiator is an easy and effective method for well-controlled polymerization.[13c−h] Externally added photoinitiators continuously generate growing chains with different chain lengths, which will broaden the MWD and contaminate polymers without living chain-end functionality. ATRP with an alkyl halide has not yet efficiently used UV irradiation as an activation method due to the absence of a photocleavable moiety, although there is one report on ATRP of methyl methacrylate (MMA) with 2,2-dichloroacetophenone initiator under visible light irradiation.[17] It was proposed that the photoexcitation of a copper complex increased the equilibrium constant (K_{eq}) in ATRP, based on the observed polymerization kinetics. We reexamined this system and found the values of k_{act} with a ratio of ethyl 2-bromoisobutyrate/CuBr/*N*,*N*,*N*′,*N*″,*N*‴,*N*‴-hexamethyltriethylenetetramine (HMTETA)/2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) = 20/20/20/100 mM at 22 °C under UV and without UV irradiation were 0.10 and 0.092 $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$, respectively, an insignificant difference. As far as we know, there is no report on the combination of iniferter polymerization and ATRP under UV irradiation at ambient temperature, while there are several reports on the combination of ATRP and a photoinduced radical polymerization to synthesize block copolymers.[18]

In this Communication, we take advantages of both iniferter polymerization and ATRP. Iniferter polymerization uses a photocleavable DC moiety, which will be activated by UV irradiation; ATRP contains a copper complex that facilitates deactivation of propagating radicals rather than activation of initiator, particularly, at low temperature, as in the current system (Scheme 1). Therefore, inefficient chain transfer reactions in iniferter polymerization were overcome by the fast deactivation of radicals by the copper complex, which produced well-defined polymers with predictable MW and narrow MWD. Polymerization was

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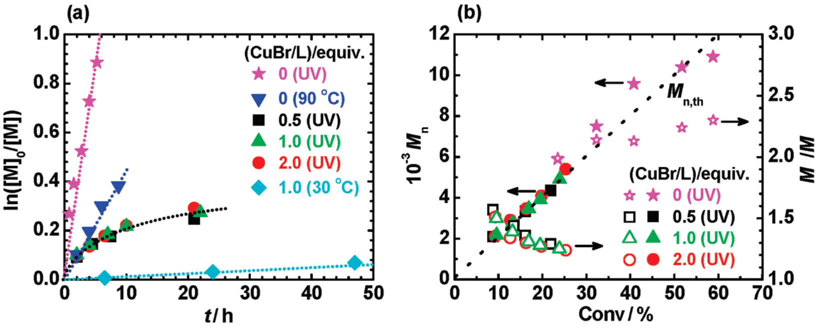

Figure 1. (a) Kinetic plot of monomer conversion vs time and (b) dependence of M_n (filled symbols) and M_w/M_n (open symbols) vs percent conversion for the MMA polymerization. All polymerizations were performed in 50% (v/v) anisole at 30 °C, unless otherwise mentioned: MMA/EMADC (with or without CuBr/L, as shown in the figure) = 200/1 (0/0−2/2) at given temperatures; L = HMTETA.

successful at room temperature without an externally added photoinitiator.

Results and Discussion. ATRP of MMA with 2-(*N*,*N*-diethyldithiocarbamyl)isobutyric acid ethyl ester (EMADC) and a copper complex was performed under UV irradiation. Before investigating UV-irradiated ATRP of MMA, several control experiments were carried out. All of the results of control experiments are described in Table S1 of the Supporting Information. Iniferter polymerization with a ratio of MMA/EMADC = 200/1 in 50% (v/v) anisole at 30 °C without UV irradiation resulted in no polymer, even after 71 h reaction (entries S1a−S1c). On the other hand, the same polymerization with the same ratio at 90 °C resulted in relatively high conversion (~32%) after 8.75 h, reaction providing a number-average MW (M_n) > 300 000 at all observed conversions, and the ratio of number- and weight-average MW (M_w/M_n) was > 2, which demonstrates poorly controlled polymerization (entries S2a−S2d). This is due to the slow generation of radicals by heating and the low chain transfer constant of EMADC. ATRP of MMA with a ratio of MMA/EMADC/CuBr/HMTETA = 200/1/1/1 in 50% (v/v) anisole at 90 °C without UV irradiation provided poorly controlled polymers that had higher M_n compared to $M_{n,th}$ and a relatively high M_w/M_n, as shown in entries S3a−S3d and in a previous report,[5a] since activation of EMADC by the copper catalyst is not fast enough to control the polymerization. As can be seen in entries S4a−S4e, iniferter polymerization of MMA with a ratio of MMA/EMADC = 200/1 in 50% (v/v) anisole at 30 °C under UV irradiation (230−400 nm using a UV filter) resulted in relatively fast polymerization showing ~60% conversion after 5.25 h polymerization. The M_w/M_n values were, however, always higher than 2, as in conventional iniferter polymerizations.[1] ATRP of MMA at 30 °C with a ratio of MMA/EMADC/CuBr/HMTETA = 200/1/1/1 in 50% (v/v) anisole without UV irradiation proceeded very slowly, resulting in 6.6% conversion after 47 h reaction due to slow activation of the DC initiator by the copper catalyst. As can be seen in entries S5a−S5c, the values of M_n are much higher than $M_{n,th}$ and M_w/M_n was higher than 1.5. This is because the amount of deactivators that were formed by radical−radical coupling was insufficient due to slow activation.

Photoinduced ATRP of MMA at 30 °C under UV irradiation (230−400 nm using a UV filter) with a ratio of MMA/EMADC/CuBr/HMTETA = 200/1/1/1 in 50% (v/v) anisole offered a well-controlled polymerization, as shown in entries S6a−S6e (Table S1) and Figure 1. Figure 1a compares rates of polymerization (R_p) under various polymerization conditions. R_p was highest with UV irradiation in the absence of a copper complex but lowest with the copper complex without UV irradiation, while the value of R_p was between those for the reactions with UV-irradiated ATRP. Similar R_p was observed for UV-induced ATRP with 0.5, 1, and 2 equiv of copper complex compared to initiator since the contribution on activation of initiator by the copper complex is minor in this system compared to that by UV irradiation. The slower polymerization at increasing time might be due to the accumulation of deactivator, Cu(II), or decomposition of activator, Cu(I), as polymerization proceeds. Well-controlled M_n that is almost identical to $M_{n,th}$ with low M_w/M_n were observed in UV-irradiated ATRP, as shown in Figure 1b. This is due to the dramatic increase of k_{act} under UV irradiation (~65-fold), compared to that without UV irradiation, and fast deactivation of propagating chains by the deactivator, as will be detailed later. The values of M_w/M_n were below 1.3 at around 20% conversion, while those of iniferter polymerization under UV irradiation at the same temperature were above 2. R_p of UV-induced ATRP was much higher, as compared to the ATRP at 30 °C without UV irradiation.

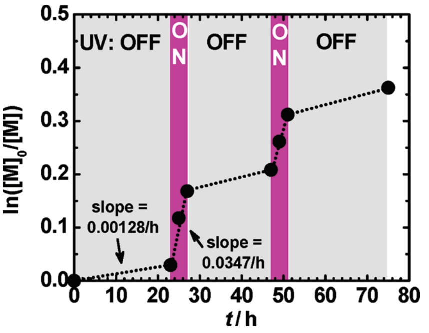

Figure 2. Effect of UV irradiation during the ATRP of MMA with EMADC in 50% (v/v) anisole at 30 °C: MMA/EMADC/CuBr/HMTETA = 200/1/1/1.

To study the effect of UV irradiation on the ATRP with the DC initiator system, the irradiation was turned on and off intermittently during the MMA polymerization. Figure 2 shows ln([M]$_0$/[M]) vs time for MMA polymerization at 30 °C under UV irradiation with a ratio of MMA/EMADC/CuBr/HMTETA = 200/1/1/1 in 50% (v/v) anisole. The polymerization proceeded very slowly due to the slow activation of the dormant species by copper catalyst at 30 °C without UV irradiation ($R_p^{app} = 1.28 \times 10^{-3}\ h^{-1}$ for the first slope in Figure 2), while the polymerization proceeded more than 25-fold faster upon UV irradiation ($R_p^{app} = 3.47 \times 10^{-2}\ h^{-1}$ for the second slope in Figure 2). After 75 h polymerization (8 h under UV irradiation and 67 h without UV irradiation), PMMA with M_n = 5950 and M_w/M_n = 1.40 was obtained at 30.5% conversion. ATRP of MMA with DC is thus photoswitchable, where the reaction barely proceeds without UV

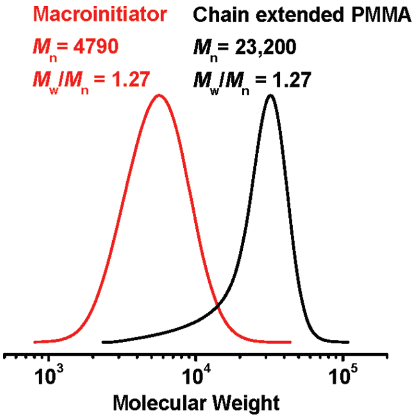

Figure 3. Molecular weight distribution of PMMA-DC macroinitiator before (left side) and after chain extension with MMA (right side). Experimental conditions for chain extension with MMA: MMA/PMMA-DC/CuBr/HMTETA = 1000/1/1/1 in 50% (v/v) anisole under UV irradiation at 30 °C (PMMA-DC: M_n = 4790; M_w/M_n = 1.27).

irradiation but can restart under UV irradiation while keeping the controlled M_n and low M_w/M_n. This is due to the fact that, although carbon-centered radicals are generated extremely slowly without UV irradiation, upon UV irradiation DC initiators rapidly generate carbon-centered radicals that induce radical propagation and are deactivated by Cu(II) species. The measured values of k_{act} with a ratio of EMADC/CuBr/HMTETA/TEMPO = 5/5/5/25 mM at 22 °C under UV and without UV irradiation were 0.50 and 0.0075 M^{-1} s^{-1}, respectively, which is a large difference.

To confirm the retention of the DC group at the chain end and demonstrate the living character of the polymerization, chain extension of MMA from the PMMA-DC macroinitiator (M_n = 4790, M_w/M_n = 1.27) was conducted. Chain extension was carried out at 30 °C under UV irradiation with a ratio of MMA/PMMA-DC/CuBr/HMTETA = 1000/1/1/1 in 50% (v/v) anisole. After 6 h polymerization, a chain-extended PMMA (M_n = 23 200 and M_w/M_n = 1.27) with little tailing in the low-MW region was obtained at 17.7% conversion (Figure 3). Peak deconvolution indicated around 5% dead chains in the PMMA-DC macroinitiator, demonstrating the DC groups at the PMMA chain ends were quite well maintained, which allowed clean chain extension with MMA, while retaining a low M_w/M_n value.

Conclusions. Well-controlled polymerization of MMA was achieved using a copper catalyst and DC initiator under UV irradiation at ambient temperature. The living and controlled characters of this polymerization were confirmed by both the linear evolution of M_n with conversion, low M_w/M_n, and successful chain extension of resulting macroinitiator. The polymerization was photocontrollable; i.e., polymerization proceeded mainly under UV irradiation while maintaining controlled M_n and low M_w/M_n throughout the procedures. The current technique may find use in a variety of practical applications where thermally unstable monomers are used and suitable for micropatterning.

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Supporting Information Available: Experimental procedures, analytical methods, detailed results of control experiments, and comparison of k_{act} under UV and without UV irradiation. This material is available free of charge via the Internet at http://pubs.acs.org.

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