Ambient Temperature RAFT Polymerization of Acrylic Acid Initiated with Ultraviolet Radiation in Aqueous Solution

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Received February 5, 2007
Revised Manuscript Received March 14, 2007

Introduction. Recently, reversible addition−fragmentation chain transfer (RAFT) polymerization has gained considerable attention for the synthesis of polymers with both low polydispersity and functionalizable end groups.[1−6] With the exception of the RAFT technique, the polymerization of acrylic acid (AA) is difficult to perform directly in a controlled fashion without recourse to protective group chemistry.[7] The RAFT technique employs thiocarbonylthio compounds in order to mediate the polymerization via a reversible chain transfer process leading to an equilibrium under which all the propagating chains grow proportionally with conversion. Very recently, Millard et al.[8] have reported the polymerization of acrylic acid and *N*-isoproylacrylamide under γ-irradiation via RAFT in aqueous media. However, there are certain practical limitations of employing γ-irradiation for commercial applications compared to ultraviolet (UV) radiation. For instance, handling and setting up of UV lamps is facile, safer and cheaper than using γ-irradiation (e.g., from a ^{60}Co source). UV radiation is already used extensively in industry for several purposes, e.g., cross-linking and photopolymerizations. This report deals with employing UV radiation (365 nm) as the source of initiation instead of a thermal azo-initiator in the presence of the RAFT agent, S,S-bis(α,α′-dimethyl-α″-acetic acid) trithiocarbonate (TRITT, in literature this RAFT agent is also abbreviated as BDMAT) for the polymerization of AA in water at room temperature. To our best knowledge this the first report detailing the UV-initiated RAFT polymerization at room temperature in water of AA using the RAFT technique. An added advantage of this polymerization is that it occurs in an environmentally friendly solvent like water and—importantly—at ambient temperatures, thus making it a highly valuable tool for the use of the RAFT process in bioconjugate chemistry which requires low temperatures ($T < 37$ °C) to avoid protein/biomolecule denaturation. Previously, our group reported the UV-initiated (365 nm) RAFT polymerization of styrene and methyl methacrylate (MMA)[9] in bulk. These polymerizations were performed without the addition of photoinitiators. Lu et al.[10,11] reported the RAFT agent-mediated polymerization of methyl acrylate (MA) under long-wave ultraviolet radiation in combination with a photoinitiator (acylphoshine oxide). Cai and co-workers also investigated the effect of the radiation wave range on RAFT agent mediated polymerization of MA, *n*-butyl acrylate, and MMA using either trithiocarbonates or dithioesters and photoinitiator.[10] They found that UV-initiated RAFT polymerization is best performed at long wavelengths.[11]

Experimental Section. Materials. All chemicals and solvents were purchased from Sigma-Aldrich, Acros, and Fluka in purities of >99% and were used as received unless otherwise mentioned. AA was distilled under vacuum and used immediately. The synthesis of the RAFT agent TRITT has been described elsewhere.[12,13]

Polymerization. The monomer, AA, was dissolved with TRITT in pure water. The monomer concentrations and the monomer/chain transfer agent (CTA) ratios are given in Tables 1 and 2. No photoinitiator was added. After dissolution, the stock solution was divided and transferred into glass sample vials, containing close to 5 mL of solution. The vials were sealed using rubber septa and degassed by percolating with nitrogen for 20 min each. The samples were subsequently placed in an incubator equipped with a UV lamp ($\lambda_{\max} = 365$ nm) at room temperature. The energy of the UV lamp is 0.015 W (measured by an OPHIR laser power meter (model AN/2)). It has recently been demonstrated that trithiocarbonate RAFT agents are much more stable under UV irradiation at 351 nm than dithioester-type RAFT agents.[14] Lu et al. reported that the absorbance of trithiocarbonates is remarkably lower (yet still significant) than that of dithioesters in the wavelength range between 365 and 405 nm.[11] Yet, initiating radicals are likely formed by the UV-induced release of the (radical) R-group of the employed trithiocarbonate.

The samples were removed periodically to investigate the reaction kinetics. Monomer to polymer conversions were evaluated using ^{1}H NMR spectroscopy. The polymer samples were purified from water via freeze-drying for 2 days. The dried poly(acrylic acid) (PAA) samples were subsequently analyzed via a *N*,*N*-dimethylacetamide (DMAc) gel permeation chromatography (GPC) and the apparent number-average molecular weights, M_n, the full molecular weight distributions as well as the polydispersities, M_w/M_n, were obtained relative to polystyrene standards.

Characterization. ^{1}H NMR spectra were recorded on a Bruker spectrometer (300 MHz) in D_2O. GPC was performed in DMAc (0.03% w/v LiBr, 0.05% butylated hydroxyl toluene stabilizer) at 50 °C (flow rate: 0.85 mL min^{-1}) using a Shimadzu modular system comprising a DGU-12A solvent degasser, an LC-10 AT pump, a CTO-10A column oven, and a RID-10A refractive index detector. The system was equipped with a Phenomenex 5.0 μm bead-size guard column (50×7.8 mm^2) followed by four Phenomenex 5.0 μm bead-size (300×7.8 mm^2) columns (10^5, 10^4, 10^3, and 500 Å). Calibration was performed with low polydispersity polystyrene standards ranging from 500 to 10^6 g mol^{-1}. The incubator from Ratek, OM11, was equipped with an UV lamp (365 nm) from Ultra Violet Product (UVP).

Results and Discussion. Polymerization of Acrylic Acid in Aqueous Solution under Ultraviolet Radiation via RAFT at Ambient Temperature. Acrylic acid was polymerized in the presence of a trithiocarbonate CTA, TRITT, at different ratios of monomer to CTA. The polymerization was performed without the addition of a photoinitiator. Initiation is likely to proceed by the TRITT derived R-group radicals. Table 1 and Figure 1 summarizes the polymerization of AA at room temperature in water at [AA]/[CTA] = 600. As can be seen

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10.1021/ma0703094 CCC: $37.00

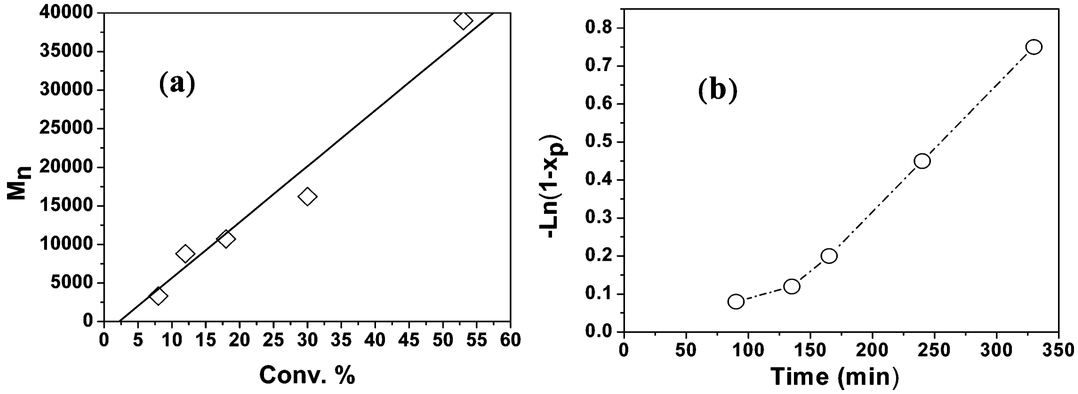

Figure 1. (a) Number-average molecular weight, M_n, vs conversion and (b) Pseudo-first-order conversion vs time plot for the RAFT polymerization of AA ($[AA]_0 = 1.5$ mol L^{-1}) in water at a ratio of $[AA]/[TRITT] = 600$ at room temperature, initiated via UV radiation (365 nm).

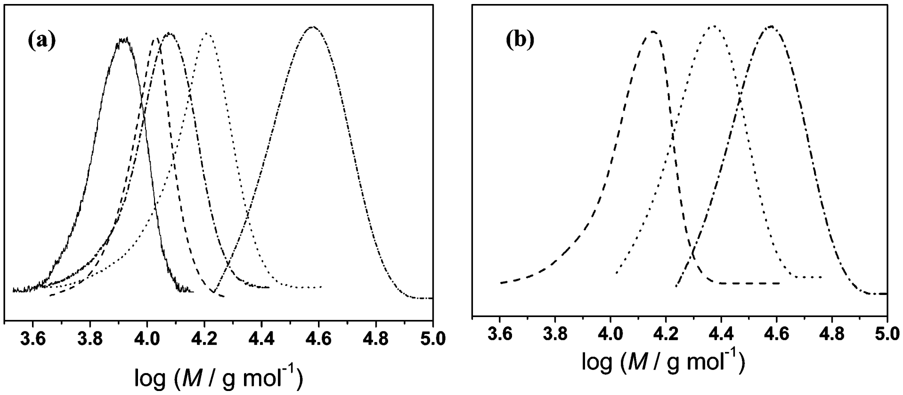

Figure 2. (a) Evolution of molecular weight distribution of poly(acrylic acid) with time: $[AA]_0 = 1.5$ mol L^{-1}, $T = 25$ °C, $[AA]/[TRITT] = 600$, UV-irradiation = 365 nm, in water, time = (—) 90 min, (--) 135 min, (-•-) 165 min, (•••) 240 min, and (-••) 330 min. (b) Dependence of the molecular weight distribution of poly(acrylic acid) on the ratio monomer/CTA using S,S-bis(α,α′-dimethyl α″-acetic acid) trithiocarbonate (TRITT) as CTA. $[AA]_0 = 1.5$ mol L^{-1}, $T = 25$ °C, UV-irradiation = 365 nm, in water, $[M]_0/[TRITT]_0$ = (—) 400, (•••) 800, and (-•-) 1000.

Table 1. Reversible Addition Fragmentation Chain Transfer Homopolymerization of Acrylic Acid by Ultraviolet Initiation (365 nm) at Room Temperature in Water[a]

time (min)	convn[b] (%)	$M_{n,GPC}$[c] (g mol^{-1})	PDI	$M_{n,theor}$[d] (g mol^{-1})
90	8	3000	1.04	3500
135	12	8800	1.05	5200
165	18	10 700	1.06	7800
240	36	16 200	1.11	15 500
330	53	39 000	1.08	23 000

[a] RAFT polymerization initiated by ultraviolet radiation at $[AA]/[TRITT] = 600$, $[AA]_0 = 1.5$ mol L^{-1}. [b] Monomer conversion determined by ^1H NMR. [c] Number-average molecular weight determined by GPC using DMAc as eluent with PS standards. [d] Theoretical number-average molecular weight as calculated from the monomer conversion.

Table 2. Influence of the Monomer/Chain Transfer Agent Ratio in the Reversible Addition Fragmentation Chain Transfer Polymerization of Acrylic Acid in Water during Ultraviolet Initiation (365 nm) at Room Temperature with *S,S*-Bis(α,α′-dimethyl-α″-acetic acid) Trithiocarbonate as RAFT Agent, Reaction Time = 3 h and $[AA]_0 = 1.5$ mol L^{-1}

$[M]_0/[CTA]_0$	convn[a] (%)	$M_{n,GPC}$[b] (g mol^{-1})	PDI	$M_{n,theor}$[c] (g mol^{-1})
400	22	12 900	1.10	6300
800	25	23 000	1.07	14 400
1000	33	34 000	1.08	23 700

[a] Monomer conversion determined by ^1H NMR. [b] Number-average molecular weight determined by GPC using DMAc as eluent with PS standards. [c] Theoretical number-average molecular weight as calculated from the monomer conversion.

from Table 1, the apparent number-average molecular weights, M_n, obtained using polystyrene standards are almost comparable to the theoretical M_n values of PAA. The polydispersity indices (PDI) of the resulting polymers are extremely narrow, i.e., PDI ≤ 1.10, indicating a well-controlled polymerization process via the RAFT process. The difference between the theoretical and the experimental molecular weights can be assigned to the calibration of the GPC on the basis of polystyrene equivalents. As can be seen from Figure 1a, with $[AA]/[CTA] = 600$, there is a linear dependence of the molecular weight with conversion indicating the controlled fashion of the process. Figure 1b, depicts the first-order time−conversion plot which indicates an induction period at the beginning which is often observed in the RAFT process. After the induction period, the first-order plot is linear. Such induction periods have been observed in certain cases[15] although they are not generally anticipated when employing trithiocarbonates.[16] These results indicate that the radical concentration is approximately constant over the duration of the polymerization. As no photoinitiator was employed, the induction period may be caused by the slow UV-induced release of (initiating) R-group radicals from the TRITT RAFT agent; alternatively—and given the aqueous environment, somewhat more likely—the presence of some residual oxygen may have contributed to the initial quenching of UV generated radicals. It might be possible to suppress the induction period by the addition of a photoinitiator.[11]

As can be seen from Figure 2a, the GPC traces are unimodal and narrow at all conversions and the PDI remains below 1.1 which again demonstrates the very well-controlled behavior of the polymerization under the mentioned reaction conditions. TRITT is a symmetrical trithiocarbonate which has already been used for thermal polymerizations via RAFT for acrylates, methacrylates, and styrenics.[12,17−19] The present report explicitly demonstrates that, under ultraviolet radiation initiation, TRITT can be used to initiate and control the polymerization of AA in order to obtain well-defined linear PAA at room temperature.

The influence of the monomer/CTA ratio was also studied. Table 2 and Figure 2b summarize the results. As can be seen from Table 2, high molecular weight and well-defined PAA was obtained by increasing the monomer/CTA ratio. The PDI still remains very low and the GPC traces are also unimodal, indicating the controlled behavior of the RAFT process initiated via ultraviolet radiation.

Quinn et al.[9] reported the living polymerization of styrene and methyl methacrylate with 1-phenylethyl phenyldithioacetate (1-PEPDTA) initiated by ultraviolet radiation without the addition of photoinitiator. However, they showed that at the longer times around 48 h, the molecular weight distributions (and thus the PDI) became broader, indicating a loss of control at higher conversions. In the present report, almost 50% conversion was reached using TRITT in 5.5 h in a controlled fashion which is faster and more efficient compared to the polymerization of styrene or MMA under ultraviolet radiation, where no control was observed after 30% of conversion. The characteristic yellow color of the polymer was retained after 5.5 h indicating that the chromophoric trithiocarbonate moiety is still retained and is not decomposed under the reaction conditions.

Conclusions. We present the facile synthesis of PAA using the RAFT process initiated via ultraviolet radiation in aqueous solution at ambient temperature. The chain transfer agent TRITT was used to control the polymerization effectively at conversions as high as 50% without losing the control at ambient temperature in water which is an intriguing way to obtain well-definfed PAA. The UV-initiated RAFT polymerization using trithiocarbonates is thus an ideal tool for the generation of polymer-protein conjugates as well as the facile grafting (including the grafting of biological molecules) onto solid linear surfaces as well as micro- and nanoparticles.

Acknowledgment. The authors are grateful to the Australian Research Council (ARC) Linkage Grant Scheme and the University of New South Wales for financial support. L.B. acknowledges receipt of a UNSW Gold Star Award. C.B.-K. acknowledges receipt of an Australian Professorial Fellowship and T.P.D. receipt of a Federation Fellowship (both ARC). Mr. Istvan Jacenyik is acknowledged for the excellent management of CAMD.

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MA0703094