Well-controlled reversible addition–fragmentation chain transfer radical polymerisation under ultraviolet radiation at ambient temperature†

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Controlled reversible addition–fragmentation chain transfer radical polymerisation of methyl acrylate was carried out under long-wave ($\lambda \geqslant 365$ nm) ultraviolet radiation using an acylphosphine oxide as a photoinitiator at ambient temperature; the polymerisation shows a "living" character at high conversions of polymerisation and leads to well-defined polymers with narrow polydispersities ($M_w/M_n < 1.1$).

Since its discovery in 1998,[1] Reversible Addition Fragmentation chain Transfer (RAFT) polymerisation has become a highly versatile technique for the controlled/"living" radical polymerisation of a wide range of monomers under various conditions.[1–2] The RAFT radical polymerisation is carried out using a thiocarbonylthio compound as a Chain Transfer Agent (CTA), which mediates the growing chain radicals *via* an equilibrium of radical intermediates.[1–2] From both academic and industrial standpoints, it is clearly desirable to develop a RAFT process under mild conditions. Rizzardo *et al.*[3] and McCormick's group[4] have respectively reported the RAFT polymerisation using conventional radical initiators at ambient temperature by adjusting the structure of the CTA. The RAFT polymerisation under γ-radiation has also been reported recently.[5] Of particular relevance to this communication is Quinn *et al.*'s recent paper[6] on the RAFT polymerisation of styrene and methyl methacrylate under UV radiation using a CTA as the source of primary radicals at 42 °C, which was well controlled at low conversions (below 30%). However, the polymerisation was clearly less controlled at relatively high conversions (over 30%) due to the photolysis of CTA residues under UV radiation.

In this communication, we describe a novel strategy for well-controlled RAFT polymerisation under UV radiation at ambient temperature, even at high conversions (over 85%), *via* the combination of employment of a suitable photoinitiator and a suitable wavelength range of UV radiation. S-dodecyl-S′-(α,α′-dimethyl-α″-acetic acid) trithiocarbonate (DDMAT)[7] and cumyl dithiobenzoate (CDB)[8] were synthesized as candidate CTAs. A high-pressure mercury vapor lamp, with peak emissions at 254 nm, 302 nm, 313 nm, 365 nm and 405 nm and the emission at 365 nm being maximum, was used as a UV radiation source.

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† Electronic supplementary information (ESI) available: UV–vis spectroscopy for CTAs and photoinitiator, photolysis of CTAs and RAFT polymerisation protocol and self-block chain extension. See DOI: 10.1039/b512057h

In order to suppress the photolysis of CTA residues and facilitate the initiation of polymerisation, a suitable UV wavelength range is necessary to achieve a controlled/"living" RAFT polymerisation under UV radiation. UV–vis spectroscopy studies indicate that CDB shows undesirable strong absorption at 365 nm, while DDMAT shows much weak absorption at 365 nm but strong absorption in the shorter wavelength range (see ESI Figure S1). Moreover, the photolysis experimental results suggest that, under full-wave UV radiation emitted by the high-pressure mercury vapor lamp, both CTAs are photolyzed, and CDB is photolyzed much faster than DDMAT (see Fig. 1 and ESI Figure S2), which is consistent with what is reported in the literature.[6] This indicates that DDMAT is more stable than CDB under full-wave UV radiation. Thus DDMAT was selected for further RAFT polymerisation.

As shown in Fig. 1, once the short-wave ($\lambda \leqslant 313$ nm) UV radiation is cut off using soda glass, the photolysis of DDMAT is remarkably suppressed. This is crucial for this particular "living" RAFT polymerisation, otherwise photolysis of CTA residues unavoidably leads to deactivation of RAFT polymerisation. In the RAFT polymerisation described below, soda glass was used to cut off the short-wave ($\lambda \leqslant 313$ nm) UV radiation, *i.e.*, only long-wave UV radiation was selected for "living" RAFT polymerisation.

Based on our experiments, the long-wave UV radiation cannot homolytically cleave the CTA to initiate polymerisation in the time scale investigated ($t \leqslant 6$ h). Thus a photoinitiator is necessary to generate primary free radicals. For this purpose, a suitable photoinitiator must have strong absorption in such a wavelength
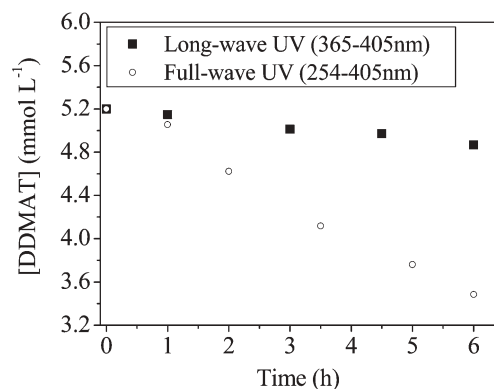

Fig. 1 Photolysis of DDMAT under long-wave and full-wave UV radiation at 30 °C monitored by UV–vis spectrophotometry. Conditions: I = 300 μW/cm², [DDMAT]$_0$ = 5.2 mmol L^{-1} in methyl acrylate/benzene (3 : 1, v/v).

range that the absorption of CTA is negligible. Acylphosphine oxides are highly efficient photoinitiators. They photolyze rapidly to form benzoyl and phosphonyl radicals under UV radiation.[9–11] Among them, (2,4,6-trimethylbenzoyl)diphenylphosphine oxide (TPO) is commercially available. Its α-cleavable rate constant (k_α)[9] is over 10^9 s^{-1} and the addition rate constant of the phosphonyl radical is very large ($k_{add} = 1.79 \times 10^7$ [M^{-1} s^{-1}])[12]. Moreover, its strong absorption at 365 nm and 405 nm matches the UV radiation selected for DDMAT, at which DDMAT has sufficiently less absorption (see ESI Figure S1). Thus TPO is an excellent photoinitiator for the RAFT polymerisation under long-wave UV radiation.

Methyl acrylate (MA) in benzene was polymerized in a septa capped round-bottomed flask in a thermostatic water bath at 30 °C under UV radiation at intensity of 300 μW/cm^2 using TPO as a photoinitiator and DDMAT as a CTA (the detailed polymerisation protocol is described in the ESI). Only slight retardation of polymerisation was observed. The polymerisation shows typical pseudo first order kinetics with respect to MA monomer up to the conversion over 75% (see ESI Figure S3).

Remarkable "living" characters were observed for the RAFT polymerisation under these conditions (see Fig. 2): the number-average molecular weight increases linearly with the conversion of polymerisation as well as quite low polydispersities at high conversions (conversion = 88%, M_n = 11 500, M_w/M_n = 1.09).

The "living" character of this RAFT polymerisation was further confirmed by the quantitative self-block chain-extension: a poly(methyl acrylate)-based (PMA-based) macro-CTA was synthesized via RAFT polymerisation at conversion of 84%. This macro-CTA was chain-extended with addition of MA monomer, benzene and TPO under long-wave UV radiation at ambient temperature (the detailed synthesis protocol is described in the ESI). Nearly quantitative blocking efficiency was confirmed by a clear GPC trace evolution from the PMA-based macro-CTA (M_n = 10 100, M_w/M_n = 1.06) to the chain-extended self-block PMA (M_n = 21 000, M_w/M_n = 1.17; see Fig. 3). A shoulder at high molecular weight is observed (see Fig. 3) from the GPC trace of this chain-extended self-block PMA, presumably due to recombination of polymer radicals. Further investigation is under way to clarify this phenomenon.

It is interesting to note that our preliminary experimental results show that the RAFT polymerisation was well controlled under
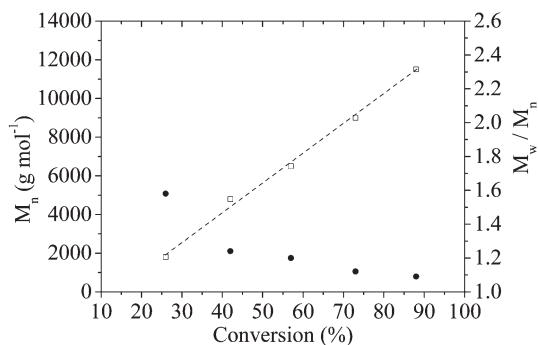

Fig. 2 Evolution of molecular weight (□) and polydispersity index (●) with conversion for the polymerisation of MA under long-wave UV radiation. Conditions: I = 300 μW/cm^2, [MA]$_0$ = 8.1 mol L^{-1}, in benzene using DDMAT as a CTA and TPO as a photoinitiator at 30 °C.
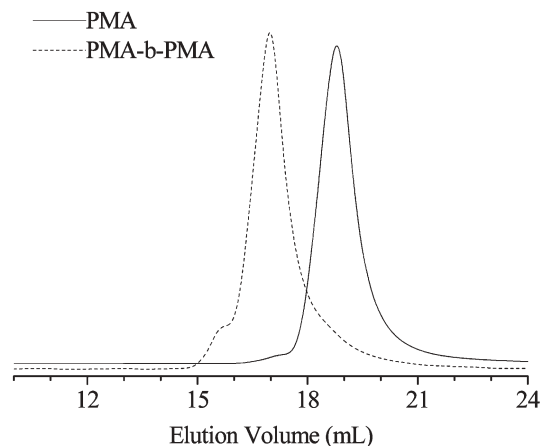

Fig. 3 GPC traces for the PMA-based macro-CTA (M_n = 10 100, M_w/M_n = 1.06) and the corresponding "self-block copolymer" (M_n = 21 000, M_w/M_n = 1.17).

sunlight instead of the radiation of a high-pressure mercury vapor lamp, without changing any condition as above-mentioned for the RAFT polymerisation. Further studies on RAFT polymerisation under sunlight are in progress.

In summary, the well-controlled RAFT polymerisation of MA was achieved even at high conversions using TPO as a photoinitiator and DDMAT as a CTA under long-wave UV radiation at ambient temperature. The "living" character of this polymerisation was confirmed by both the linear tendency of molecular weight evolution with conversion and a self-blocking experiment. Our preliminary results suggest that this novel strategy can also be applied for the controlled polymerisation of methacrylates and styrenic monomers once a suitable CTA and/or radiation source is selected; this work is in progress but beyond the scope of this communication. Moreover, this method shows potential application in the polymerisation of thermo-unstable monomers and monomers containing thermo-denaturalizable biomolecular moieties.

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