PAPER

Ketoprofen as a photoinitiator for anionic polymerization†

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A new photoinitiating system for anionic polymerization of acrylates based on the efficient photodecarboxylation of Ketoprofen (**1**) and the related derivatives **3** and **4** that generate the corresponding carbanion intermediates is presented. Carbanion intermediates are confirmed by deuterium incorporation in the trapped Michael adducts and by spectroscopic detection using laser flash photolysis (LFP). This novel anionic initiating system features excitation in the near UV and visible regions, potential characteristics of photocontrolled living polymerization, and metal-free photoinitiators generated from photoexcitation, different from typical anionic polymerization where the polymerizations are initiated by heat and strong base containing alkali metals.
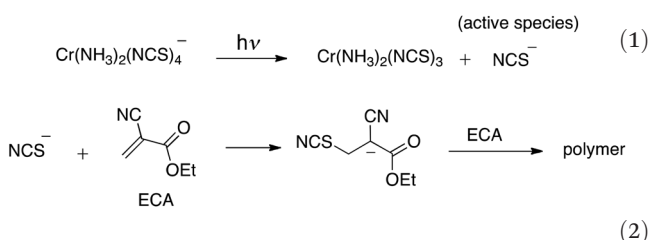
Introduction

Photopolymerization has become an important tool for industrial applications in biomaterials, surface coatings, optical recording, stereolithography, and nanocomposites.[1] Better than the traditional initiation by heat, photoinitiating systems offer milder reaction, temporal and spatial control, cost efficiency and energy-saving conditions that typically involve three different initiating species: free radicals, cations, and in a few cases, anions. The most widely used process is still free radical polymerization, but this can suffer from poor control of molecular weight and dispersity, as well as difficulties in preparing well-defined polymers. To overcome these drawbacks, much effort has been devoted to the development of new photoinitiating systems such as living and step-growth polymerizations.[2] Although the development of radical and cationic photopolymerizations has been in an advanced stage, very few successes have been reported on photoinitiated anionic sources.

Kutal *et al.* reported the first anionic photopolymerzation of a cyanoacrylate by using an isothiocyanate (NCS⁻) as initiating species generated from ligand exchange of the Cr-complex upon irradiation eqn (1) and (2).[3] Subsequent investigations on anionic photoinitiating systems involve employing organometallic complexes (*e.g.* metallocenes and transition metal complex)[4] or generation of Lewis bases (*e.g.* pyridine).[5] As far as we are aware, there are no literature reports of metal-free and carbanion-induced anionic photoinitiating species. It occurred to us that a suitably selected carbanion possessing (i) high quantum yields for generation upon photolysis (ii) relatively long lifetime for initiating polymerization and (iii) absorption of light near the visible region feasible for ease of use and potential biological applications, could fill this void. In this work, we report a novel anionic photoinitiating system based on the Ketoprofen (KP, **1**) chromophore that is capable of photoinitiating anionic polymerization of a variety of acrylates and related compounds.

Our design is based on the photodecarboxylation of Ketoprofen **1**, a well-known nonsteroidal anti-inflammatory drug (NSAID) that has been extensively studied due to its phototoxicity and exceptional photochemical and photophysical properties.[6] The fascinating phenomenon of KP involves an efficient photodecarboxylation ($\Phi = 0.75$) to give carbanion **2a** with a remarkable lifetime range from *ca.* 250 ns in water to minutes under rigorously dry conditions such as NaH/THF.[7] Scaiano and co-workers have expanded its use towards the development of the ketoprofenate photocage[8] and have further replaced the benzophenone (BP) chromophore with xanthone **3** ($\Phi = 0.67$) for better UVA absorption properties ($\lambda_{max} = 340$ nm).[9] Carbanion **2** and its derivatives have been shown to undergo intramolecular S_N2 reaction, aldol condensation and photo-Grignard type (or intermolecular S_N2) reaction in encap-

$$Cr(NH_3)_2(NCS)_4^- \xrightarrow{h\nu} Cr(NH_3)_2(NCS)_3 + NCS^- \quad \text{(active species)} \quad (1)$$

$$NCS^- + \text{ECA} \longrightarrow \text{NCS} \cdots \text{OEt} \xrightarrow{\text{ECA}} \text{polymer} \quad (2)$$

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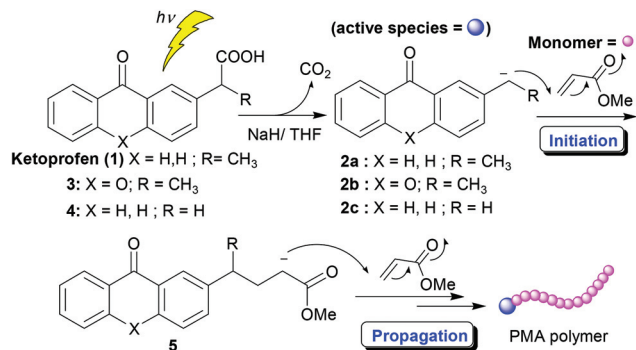
Scheme 1 The concept for anionic photopolymerization of methyl acrylate (MA) by KP-type initiators.

sulated zeolites.[10] These results suggest the possibility that photogenerated **2** could also undergo Michael addition to acrylates (Scheme 1) and potentially initiate anionic photopolymerization (*i.e.* **2a–c** to **5**).

The KP derivatives **1**, **3** and **4** undergo photodecarboxylation with high quantum yields ($\Phi = 0.66–0.75$) in aqueous solution (pH > 7) to give their respective carbanion intermediates, which play a crucial role in our photoinitiating system. The carboxylate forms of the acids are required for photodecarboxylation; in other words, a basic environment is needed. 3-Xanthoneacetic acid (**3**), readily prepared according to the literature procedure,[9a] was selected to test the viability of a modified BP chromophore with longer absorption wavelength to minimize the potential absorption interference of undesired byproducts and polymers. Derivative **4**, previously studied in our group,[11] was selected to test for the versatility of the KP-type molecules for polymerization and to compare with the polymerizing ability of a primary *vs.* secondary carbanion. To the best of our knowledge, this study concerning the development of innovative anionic photoinitiators with photosensitivity in the near UV and visible regions is unique and different from the current methods for photoinitiated polymerization.

Results and discussion

Product studies

Under typical reaction conditions, photolysis of photoinitiator **1** in a solution of anhydrous NaH/THF (10^{-3} M, 350 nm, 16 lamps, Ar-purged; with an excess of NaH) for 30 min generates a reactive carbanion **2** that rapidly attacks the carbon–carbon double bond of the electrophilic monomer (*i.e.* 1,4-Michael addition) to yield the resonance-stabilized carbanion **5** (Scheme 1). Polymerization proceeds *via* the repetitive addition of MA units to the growing anionic chain, eventually yielding BP-endcapped poly(methyl acrylate) (PMA) as a rubbery solid product after workup and filtration. The structure of the polymer was characterized by ^{1}H, ^{13}C-NMR, MALDI-MS, and GPC analyses. The number-average molecular weight (M_n) of

**Table 1** Photopolymerization[b] of MA in various conditions

PI[a]	[PI] (M)	Base[c]/solvent	[MA] (M)	Time (min)	Conv.[d] (%)
1	0.8×10^{-3}	NaH/THF	8×10^{-2}	5	32
1	0.8×10^{-3}	NaH/THF	8×10^{-2}	30	48
1	0.8×10^{-3}	0.25% v/v NaOH$_{(aq)}$/CH$_3$CN	4×10^{-2}	5	7
1	0.8×10^{-3}	0.25% v/v NaOH$_{(aq)}$/CH$_3$CN	8×10^{-2}	5	13
1	0.8×10^{-3}	0.5% v/v NaOH$_{(aq)}$/CH$_3$CN	8×10^{-2}	5	Trace
1[e]	1.8×10^{-2}	—[f]	1.1×10^1	10	48
4	0.8×10^{-3}	NaH[c]/THF	8×10^{-2}	30	65
4[e]	1.8×10^{-2}	—[f]	1.1×10^1	10	95
3	0.8×10^{-3}	NaH/THF	8×10^{-2}	30	15

[a] PI: photoinitiator; MA: methyl acrylate monomer. [b] Photolyses were carried out at $\lambda = 350$ nm under argon purge. [c] Excess amount of NaH (10 equiv.) and 0.1 M NaOH$_{(aq)}$ were used as the base. [d] Conversions (%) were calculated gravimetrically. [e] In their sodium carboxylate salt forms. [f] No solvent was involved but the mixture of PI sodium salts and monomer.

PMA ranges from 1001 to 16 910 with a polydispersity index (M_w/M_n or PDI) under 1.4 and close to unity varying according to the conditions. The results of photopolymerization of PMA employing **1**, **3** and **4** as photoinitiators under various conditions are compiled in Table 1.

In control experiments under conditions such as in the dark or in the absence of a photoinitiator, no detectable polymers were formed, indicating that MA polymerization requires light and an active anionic species. Photoinitiation of 3-ethylbenzophenone (**6**), the major protonation product of **2a**, can be discounted since no polymerization was found by replacing the KP initiator with the isolated pure photoproduct **6** under the same reaction conditions. As summarized in Table 1, the higher concentration ratio of monomer-to-initiator leads to higher PMA conversion. A longer irradiation time results in more photodecarboxylation of PIs (*i.e.* more active anionic species formed) that enhances the polymerization. NaH/THF provides the best reaction solvent environment for photopolymerization, which is in accordance with the reported long lifetimes (~minutes) of the carbanion in rigorously dry THF.[7] Proton source from water, under conditions of NaOH$_{(aq)}$/CH$_3$CN, inhibits the polymerizing process by scavenging the photogenerated initiating species or reactive anionic centres of propagating polymer chains, which results in poor yield. This inhibition of polymerization by protonation was evidenced by deuterium incorporation in the isolated products shown in Scheme 2 and Fig. 2, which is consistent with a photopolymerization pathway that is *via* an anionic mechanism.

With regard to polymerizing ability among the three PIs, we observed that **4** > KP (**1**) ≫ **3**, which indicates that primary carbanion reacts faster than a secondary one, consistent with the protonation rate constant (k_H^+) studies by Cosa and coworkers that show steric hindrance plays the key role in controlling the carbanion reactivity.[12] As for **3**, much lower conversion was observed, presumably due to a much shorter-lived
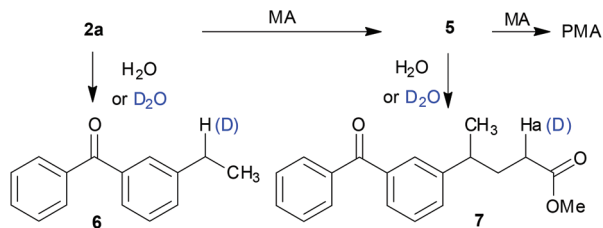
Scheme 2 Mechanistic evidence for proton trapped anionic active species.

xanthone carbanion (τ < 20 ns in 0.1 M KOH/CH$_3$CN) as reported[9a] previously by LFP detection. It is obvious that kinetically competitive protonation *vs.* nucleophilic attack (*i.e.* Michael addition) mainly depends on the selected solvent system where less proton sources would lead to better polymerization. Therefore, a solvent-free system has been investigated by preparing rigorously dried sodium carboxylate salts of **1** and **4** as photoinitiators directly dissolved in the MA solution without the need of a solvent. Upon photolysis (10 min) the resulting mixture polymerized, transitioning to a viscous gel and then into a rubbery solid with a significant amount of entrapped gas bubbles (carbon dioxide) as shown in Fig. 1(b) (also see the ESI†). The CO$_2$ bubble formation visually identifies the photodecarboxylation properties of KP and its derivatives. This system gave rise to very efficient and quantitative polymerization with M_n = 16 910 and M_w/M_n = 1.05 for **1**; whereas M_n = 7919 and M_w/M_n = 1.13 for **4**. It is worth noting that in this solvent-free system, **4** is twice as efficient as **1** in terms of polymerizing ability, besides, the monodispersed polymer chain (PDI ~ 1) strongly corroborates a polymerization mechanism *via* an anionic process.

The fact that carbanion **2** suffers from the drawback of the termination step by protonation in the propagating process of polymerization seems crucial to find a suitable solvent environment not only to prolong the carbanion lifetime but also to exclude the proton sources involved for potential applications in "living" anionic photopolymerization. Vigorously dried THF with an excess amount of NaH provides the best solvent environment for anionic initiation of KP. As shown in Fig. 1(a), irradiation of **1** in NaH/dried THF solution for 5 min resulted in obvious yellow colour, indicating the formation of long-lived benzyl carbanion.[7] The addition of monomer MA led to rapid decolouration, accounting for the reaction between active yellow anionic species with MA, followed by polymer chain propagation of PMA. Preliminary polymerization studies towards other monomers, namely Michael acceptors or electrophilic acrylates (*e.g.* methyl methacrylate and acrylonitrile) and epoxides (*e.g.* styrene oxide) for ring-opening anionic polymerization were examined under the same conditions which successfully yielded the respective polymers. Although further details remain to be explored, it is clear that KP is a potential photoinitiator for many related polymeric systems *via* an anionic mechanism.

To provide direct evidence for the proposed anionic mechanism, we have trapped the Michael adduct intermediate **5** by water (or D$_2$O). Photolysis of **1** in deoxygenated 0.25% NaOD$_{(aq)}$/CH$_3$CN (0.1 M NaOD/D$_2$O) yielded deuterated **6** as the anticipated major product, along with deuterated **7** and PMA (Scheme 2). Deuterated **7** was characterized by ^{1}H-NMR spectra and MS analysis, clearly showing 41% deuterium at δ 2.24 ppm assigned to be α-hydrogen (H$_a$) adjacent to the carboxylate (Fig. 2). Deuterium incorporation in one of the α-hydrogen atoms of the methyl ester group in **7** indicates that the requisite carbanion intermediate **5** receives a deuterium atom from the aqueous solvent and that **7** is not formed *via* hydrogen abstraction from a radical intermediate since D$_2$O is an extremely poor deuterium radical donor but an excellent D$^+$ source.

Laser flash photolysis (LFP)

To gain better insights into the mechanisms of this novel anionic photoinitiating system, LFP studies were conducted to understand more detailed photochemical and physical properties of carbanion **2a** reacting with the selected monomer
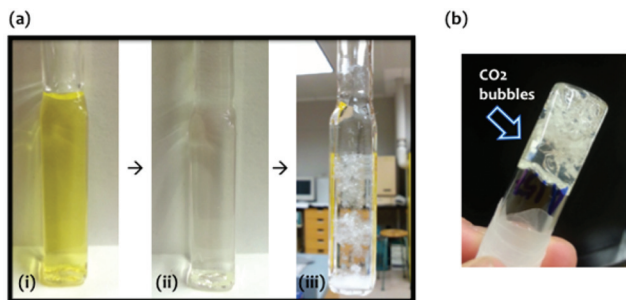

Fig. 1 (a) Photographic images showing formation of long-lived benzyl carbanion **2a** and the polymerization process: (i) after photolysis of **1** in NaH/THF (10^{-3} M, 350 nm, Ar-purged) for 5 min; (ii) addition of MA quenches the yellow colour for 1 min; (iii) formation of PMA (5 min after addition of MA). (b) Representative image of gas bubble formation in PMA after photolysis of KP carboxylate salt in MA for 10 min.
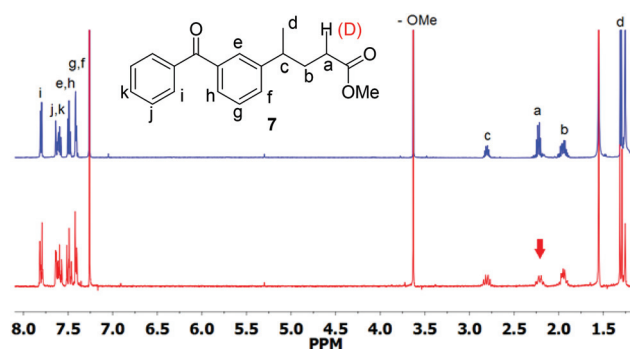

Fig. 2 ^{1}H NMR (500 MHz, CDCl$_3$) spectra of purified **7** from irradiation in NaOH(aq)/CH$_3$CN (top) and NaOD(aq)/CH$_3$CN (bottom), showing the decrease of integrated area (41% deuterium) of the peak at 2.24 ppm assigned to Ha adjacent to carboxylate.

MA. Carbanion **2a** in several solvent conditions has been extensively investigated and characterized spectroscopically by LFP,[6b–d,13] (*e.g.* in water **2a** absorbs at *ca.* 600 nm with a lifetime of 250 ns). LFP of a nitrogen-saturated flowing solution of **2a** (λ_{ex} = 355 nm) in 0.25% v/v NaOH$_{(aq)}$/CH$_3$CN gave rise to transient spectra that were similar to those reported (broad absorption bands at 330, 530, and 600 nm). The band at 530 nm with a lifetime of 5 μs was readily quenched by oxygen with k = 2.1 × 10^7 s^{-1} (τ = 46 ns), suggesting that it is the triplet excited state. The approximate quenching rate constant k_q of 2.4 × 10^9 L mol^{-1} s^{-1} was estimated based on the known oxygen concentration in aerated CH$_3$CN. The decay at 600 nm was fitted to a single exponential with a lifetime *ca.* 622 ns. Based on literature precedent,[6b,c,12] we assign the band at 600 nm as the benzyl carbanion **2a**. Efficient quenching of carbanion **2a** was observed upon addition of monomer MA, and by varying the concentration of MA (Fig. 3(a)), we were able to produce a Stern–Volmer quenching plot (Fig. 3(b)). The quenching plot shows a linear correlation and the slope indicates a bimolecular quenching rate constant k_q of 1.20 × 10^{10} L mol^{-1} s^{-1}. This could further evidence that our novel photopolymerization of MA is *via* an anionic initiating system, where carbanion **2a** serving as an initiating species generated from photodecarboxylation of KP is readily quenched by MA.

We also used another monomer methyl methacrylate (MMA) to quench the carbanion **2a**. The addition of increasing amounts of MMA allowed us to produce a quenching plot, whose slope gave a bimolecular quenching rate constant of 1.24 × 10^{11} L mol^{-1} s^{-1} (also see the ESI†). It is worth noting that the quenching rate constant k_q by MMA is one-order magnitude faster than MA. However, under our experimental conditions for observing photoinitiated anionic polymerization, the triplet excited state at about 530 nm was also observed since the efficiency for carbanion formation is relatively low (but sufficient to result in significant polymerization since the carbanion needs to act only as an anionic initiator). We therefore cannot rule out that added methyl acrylate (MA) may also quench the triplet excited state *via* some undetermined mechanism.
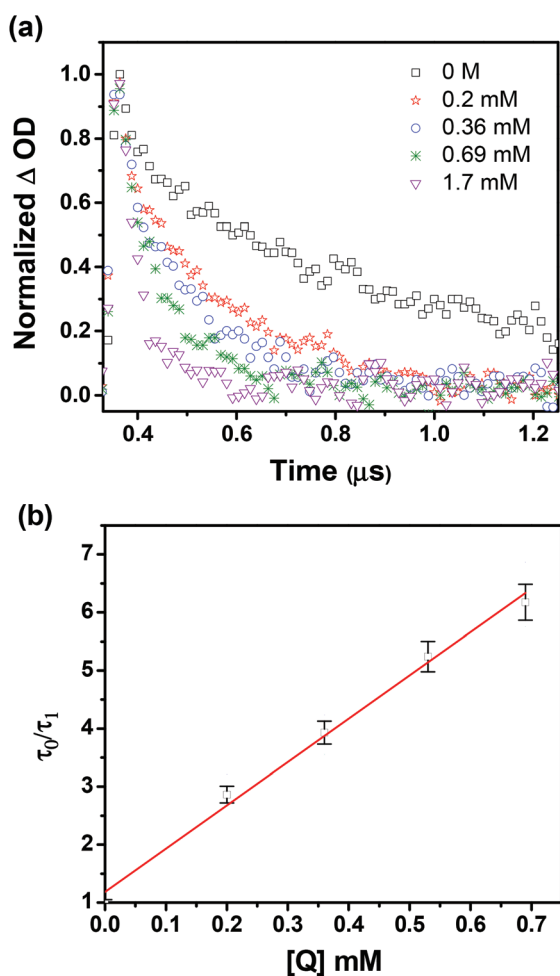
Conclusion

In summary, we have demonstrated for the first time that KP and its derivatives are useful photoinitiators for anionic photopolymerization of acrylate and related monomers. Deuterium incorporation and successfully trapped Michael adducts, LFP, and quenching studies all are evidence that the photopolymerization is the result of an anionic mechanism. Furthermore, photogenerated long-lived carbanion derived from Ketoprofen under vigorously dry and basic conditions or a solvent-free system gave rise to high conversion of polymerization. These results represent a promising new strategy in the area of anionic photopolymerization as it provides several advantages over conventional means, *e.g.* better control of molecular weight and dispersity of polymers and milder reaction conditions without the use of very strong bases such as methyl lithium, and photoexcitation using wavelengths near the visible region, and without the use of heavy metals or organometallic complexes. New avenues and practical applications are anticipated for this potential "living" photoinitiating method.

Fig. 3 (a) Normalized transient decays for **2a** in deoxygenated NaOH$_{(aq)}$/CH$_3$CN without and after addition of 0.2, 0.36, 0.69 and 1.7 mM MA after 355 nm excitation monitored at 600 nm. The decay signals were acquired by single shot measurements three times. (b) Stern–Volmer plot: quenching rate constant of each decay as a function of quencher (methyl acrylate) concentration [Q]. The data represent the average of three experiments.

Experimental

General

All NMR spectra were recorded on Bruker AC300 (300 MHz) and Avance 500 (500 MHz) instruments. EI MS spectra were recorded using a double focusing mass spectrometer (Kratos MS50) coupled with a MASPEC data system. Accuracy mass analysis and MALDI MS were carried out at the UVIC Genome BC Proteomics Centre. A mg mL^{-1} solution of the analyte was

diluted by a factor of 10–100 and injected by liquid infusion at ~300–500 nL min^{-1} by using a syringe pump through a nano ESI source. MALDI MS was recorded on a Voyager DE STR MALDI-TOF (Voyager) mass spectrometer using an α-cyano-4-hydroxycinnamic acid (CHCA) or a *trans*-2-[3-(4-*tert*-butyl-phenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) matrix. All photo-irradiation experiments were performed in a Rayonet photochemical reactor equipped with 16 lamps of 350 nm and a cooling fan system. Pyrex tubes were all dried and used as photolysis vessels (tubes sealed with a rubber septum). During irradiation, solutions were purged with a stream of argon. Preparative TLC was carried out on silica gel GF uniplates (20 cm × 20 cm) and purchased from Analtech. CDCl$_3$ and D$_2$O were purchased from Cambridge Isotope laboratory. Compounds were characterized by ^{1}H and ^{13}C NMR, and mass spectroscopy techniques. The disappearance of the starting materials and appearance of the products were monitored by NMR and TLC plates. The resulting polymers were characterized by NMR, MALDI-MS, and gel permeation chromatography (GPC) analyses.

Materials

All chemicals were purchased from Aldrich. All monomers were stirred over CaH$_2$ for 24 h and distilled under vacuum prior to use. Styrene oxide was used without further purification. Acetonitrile and THF for photolysis were HPLC grade. Other solvents (ACS grade) were used for synthesis as received. THF was freshly distilled following reflux over sodium/benzophenone.

Syntheses of photoinitiators 1, 3 and 4

Ketoprofen (**1**) was purchased from Aldrich and used as received. 3-Xanthoneacetic acid (**3**) was readily prepared by Ullmann coupling of (4-hydroxyphenyl)-acetic acid and *o*-iodo-benzoic acid, followed by acid-catalyzed ring closure with an overall yield of 30% according to the literature procedures.[14] Compound **4** was also prepared following the procedures described in the literature previously published in our group.[11b] The structures of the photoinitiators **3** and **4** were confirmed by spectral analysis of ^{1}H-NMR and ^{13}C-NMR, which are in good agreement with those reported.

3-Xanthoneacetic acid (3).[9c] An off-white solid. m.p. 221–223 °C (Lit. 223 °C). ^{1}H NMR (300 MHz, DMSO-d$_6$) δ 12.5 (s, br, 1 H, –COOH), 8.20 (dd, *J* = 7.9, 1.6 Hz, 1 H), 8.09 (d, *J* = 2.0 Hz, 1 H), 7.88 (td, *J* = 7.8, 1.7 Hz, 1 H), 7.77 (dd, *J* = 8.5, 2.3, 1 H), 7.67 (d, *J* = 8.3 Hz, 1 H), 7.63 (d, *J* = 8.5 Hz, 1 H), 7.48 (td, *J* = 7.6, 1.1 Hz, 1 H), 3.78 (s, 2 H); ^{13}C NMR (75 MHz; DMSO-d$_6$) δ 176.3, 172.9, 155.8, 154.8, 137.3, 136.0, 131.8, 126.7, 126.4, 124.7, 121.4, 121.1, 118.6, 118.4, 40.2.

3-Benzoylphenylacetic acid (4).[11b] An off-white crystal. m.p. 97–98 °C (Lit. 96–98 °C). ^{1}H NMR (300 MHz, CDCl$_3$) δ 12.5 (s, br, –COOH), 7.65–7.81 (m, 4H), 7.55–7.61 (m, 1 H), 7.41–7.54 (m, 4 H), 3.71 (s, 2 H); ^{13}C NMR (75 MHz; CDCl$_3$) δ 196.6, 176.7, 138.1, 137.6, 133.7, 133.6, 132.7, 131.2, 130.3, 129.4, 128.8, 128.5, 40.8.

Preparation for the salt forms of the photoinitiators 1 and 4

A solution of 500 mg of Ketoprofen **1** (or **4**) in CH$_3$CN was titrated with 0.1 M NaOH(aq) solution until the pH ≈ 7–8. The solvent was evaporated in a warm water bath (≤50 °C) and the residue was washed with methanol several times to remove the additional water and dried *in vacuo*. The carboxylate salts of **1** and **4** as white powders were then prepared and were ready to use.

General procedures for photopolymerization

Method A. To a solution of 10 mg (0.039 mmol) of **1** in 50 mL of anhydrous THF was added an excess amount of dry NaH (95%, 0.40 mmol), followed by purging with argon for 20 min prior to irradiation. The mixture solution in a Pyrex tube sealed with a rubber septum was then irradiated at 350 nm for 5 min under an argon atmosphere. The obvious color change from transparent to yellow indicates the formation of carbanion. Subsequently, 3.5 mL (3.9 mmol) of freshly distilled methyl acrylate (MA) or selected monomer was injected using a syringe, and polymerization was performed at room temperature for 15 min until the yellow colour disappeared, indicating the depletion of carbanion. The reaction was then terminated by addition of acidified methanol. THF was evaporated and the residue was precipitated into methanol and dried *in vacuo* to give poly(methyl acrylate) (PMA) as a transparent plastic gel (yield: 48%; M_n = 4260 g mol^{-1} and M_w/M_n = 1.13 determined by GPC). Polymerization conversions were calculated gravimetrically. All the other polymerizations using different solvents and concentrations were performed under identical experimental conditions unless otherwise stated. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.8–7.3 (BP aromatic head), 3.62 (methyl ester tail), 3.52 (PMA–OCH$_3$), 2.17 (br, PMA backbone), 1.85–1.71, 1.55 (PMA backbone), 1.43–1.29, 1.13 (PMA), 0.82 (d, *J* = 6.7 Hz, –CH$_3$); ^{13}C NMR (75 MHz; CDCl$_3$) δ 175.7 (BP C=O), 174.8 (PMA, C=O), 173.0 (C=O, ester tail end), 144.5, 131.1, 67.8, 67.6, 51.6 (–OCH$_3$), 41.2, 41.1, 40.8, 35.9, 34.8–34.1 (br), 22.6, 14.1.

Method B (solvent-free conditions). To a vial of 10 mg of Ketoprofen sodium salt was added 3.5 mL of freshly purified methyl acrylate (MA), followed by purging with argon for 20 minutes prior to irradiation. The mixture solution in a Pyrex vial sealed with a cap and Parafilm was then irradiated at 350 nm (16 lamps) for 10 minutes. The resulting polymer was washed with methanol and dried *in vacuo* to give a PMA polymer with 95% conversion yield (M_n = 16 910 g mol^{-1} and M_w/M_n = 1.05). The polymer had rubbery and elastic properties consistent with linear long-chained ones.

Control experiments were performed for all three photoinitiators **1**, **3** and **4**, respectively, in the dark, in the absence of photoinitiators and under various solvent conditions. Without the addition of MA, photolyses (350 nm, 16 lamps, 5 min) of **1**, **3** and **4** in 0.25% v/v NaOH$_{(aq)}$/CH$_3$CN all undergo photodecarboxylation to its corresponding carbanions **2a–c**, followed by protonation to give products, **6**, 2-methyl-xanthen-9-one, and 3-methylbenzophenone in quantitative conversions as

reported.[9a,11b,12] The structures of the resulting photoproducts were confirmed by spectral analysis of ^{1}H-NMR, which are in good agreement with those reported.

3-Ethylphenyl(phenyl)methanone (6).[12] ^{1}H-NMR (300 MHz, CDCl$_3$) δ 7.76–7.72 (m, 2 H), 7.59 (m, 1 H), 7.55–7.48 (m, 2 H), 7.44–7.29 (m, 4 H), 2.65 (q, J = 7.6 Hz, 2 H, –CH$_2$–), 1.20 (t, J = 7.6 Hz, 3 H, –CH$_3$); The structure of **6** was confirmed by ^{1}H-NMR and in good agreement with the reported one.

2-Methyl-xanthen-9-one.[9a] ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.33 (dd, J = 8.0, 1.6 Hz, 1 H), 8.11 (d, J = 1.6 Hz, 1 H), 7.70 (ddd, J = 7.6, 7.8, 1.6 Hz, 1 H), 7.53 (dd, J = 8.4, 2.4 Hz, 1 H), 7.47 (dd, J = 8.4, 0.7 Hz, 1 H), 7.40–7.33 (m, 2 H), 2.45 (s, 3 H, –CH$_3$).

3-Methylbenzophenone.[11b] ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.82–7.78 (m, 2 H), 7.63–7.56 (m, 3 H), 7.51–7.45 (m, 2 H), 7.41–7.33 (m, 2 H), 2.35 (s, 3 H, –CH$_3$).

Procedure for trapping the Michael adduct 7

To a solution of 10 mg (0.039 mmol) of **1** in 50 mL of 0.25% v/v NaOH(aq)/CH$_3$CN (0.1 M NaOH(aq) solution was used) was added 10 equiv. of freshly purified MA (0.35 mL, 0.39 mmol), followed by purging with argon gas for 20 min prior to irradiation. The mixture solution in a Pyrex tube was then irradiated at 350 nm for 5 min under an argon atmosphere. The mixture was washed with 1% HCl and then extracted with 50 mL CH$_2$Cl$_2$. The organic layer was dried over MgSO$_4$ and concentrated *in vacuo*. The remaining crude residue was purified by preparative TLC plate (35% ethyl acetate/*n*-hexanes as the eluent) to give rise to **6** as a major product in a relative yield of 83% and trapped Michael adduct **7** as a minor in a relative yield of 11% as determined by ^{1}H-NMR. Deuterium incorporation experiment was carried out under the same reaction conditions but using 0.1 M NaOD/D$_2$O aqueous solution instead to give rise to a mixture of deuterated **6** and **7**, and PMA, where **7**-D was purified by using a preparative TLC plate as shown in Fig. 2.

Methyl 4-(3-benzoylphenyl)pentanoate (7). ^{1}H-NMR (500 MHz, CDCl$_3$) δ 7.78 (d, J = 8.4 Hz, 2 H), 7.62 (s, 1 H), 7.61–7.56 (m, 2 H), 7.47 (t, J = 8.4 Hz, 2 H), 7.40–7.38 (m, 2 H), 3.61 (s, 3 H, OMe), 2.73 (sextet, 1 H), 2.24 (m, 2 H), 1.85 (m, 2 H), 1.28 (d, J = 6.9 Hz, 3 H, Me); ^{13}C NMR (125 MHz; CDCl$_3$) δ 196.9 (C=O), 174.0 (methyl ester C=O), 146.3, 145.1, 137.8, 137.7, 134.3, 132.0, 130.3, 130.1, 128.6, 128.3, 51.5 (OMe), 39.3, 33.2, 32.5, 21.9 (Me); IR (CHCl$_3$, cm^{-1}) 3115, 3110, 2998, 2967, 1746 (C=O), 1643 (C=C), 1475, 1407, 1210, 855; MS (EI) m/z 319 [M + Na]$^+$; HRMS, calcd for C$_{20}$H$_{14}$ONa: 319.1310; Found 319.1305.

Gel permeation chromatography (GPC) analyses

GPC measurements were performed using a Viscotek model 302 liquid chromatography system equipped with refractive index (RI), low-angle light scattering (LALS, θ = 7°), right-angle light scattering (RALS, θ = 90°), and UV detectors. THF was used as the eluent at a flow rate of 1 mL min^{-1}, and the column temperature was set at 35 °C. All polymer solutions were filtered through membrane filters with a nominal pore size of 0.45 μm before injection into the GPC column. The data were collected and analyzed on a Dell Dimension 2300 computer with appropriate GPC software from Viscotek. Two ViscoGEL HR high-resolution columns (styrene-divinylbenzene columns) in series were used: G3000 HR 60 k and GMHHR-MMixed Bed 4 M columns. The molecule weight distribution for the PMA polymer was determined from GPC data using an algorithm from Viscotek, which relies on LALS detection from a 670 nm diode laser source.

Laser flash photolysis (LFP)

Ketoprofen samples at concentration ranging from 0.2 to 2 mM were prepared in neat CH$_3$CN in either the presence or absence of a base. The base concentration used was always at least 10 fold higher than that of KP to ensure complete dissociation of the acid. 0.1 M sodium hydroxide aqueous solution was used. The laser flash photolysis systems were conducted using a Nd:YAG laser with a pulse width of 10 ns and excitation wavelength of 355 nm. All the transient spectra and kinetics were recorded by employing a flow system with a quartz cell with a 2 mL capacity. Samples were purged with nitrogen or oxygen for 30 min prior to measurements. The quenching rate constants were obtained with static cells (0.7 cm). The optical density at 355 nm was 0.18.

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