Organotellurium-Mediated Controlled/Living Radical Polymerization Initiated by Direct C−Te Bond Photolysis

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Controlled/living radical polymerization (LRP) has been revolutionizing the synthesis of structurally well-defined polymeric materials.[1] LRP relies on the reversible generation of a reactive carbon-centered radical from an inactive dormant species, and thermal and chemical stimuli have been predominantly used to activate it.[2] In contrast, LRP triggered by photo stimuli has attracted a great deal of attention because of the potential application to photoinduced fabrication of nanoarchitectures by using, for example, photolithography. The conditions should also be suitable for the production of biomaterials[3] because the polymerization can be conducted at ambient temperatures without any catalysts.

There have been several reports on reversible addition fragmentation chain transfer (RAFT) polymerization under UV−vis radiation in the absence[4] or presence[5] of a photoinitiator. However, the uses of RAFT are limited due to decomposition of the dormant species under irradiation. RAFT under γ-ray[6] and plasma[7] radiations have also been reported. However, the need for special radiation sources makes these methods synthetically unattractive. In addition, since the radicals generated from the monomers act as initiators, control of the α-polymer end structure is difficult.[8]

We have previously reported a ditelluride-mediated photopolymerization of styrene in the presence of an organotellurium chain-transfer reagent, in which a tellanyl radical is photochemically generated from a ditelluride compound and activates the dormant species.[9] However, the polymerization is sluggish, and the method could not be applied to acrylates due to the difficulty in activating the polyacrylate dormant species. As we have already reported the reversible generation of carbon-centered radicals from organotellurium compounds by UV−vis irradiation,[10] we envisioned that this condition would be applicable to LRP. We report here the photoinduced organotellurium-mediated LRP (TERP)[11] by direct photolysis of the C−Te bond of the dormant species (Scheme 1). Highly efficient activation of the dormant species occurred upon irradiation with low intensity UV and visible light, including sunlight. Polyacrylates having various polar functional groups with low to high molecular weights, and low polydispersity indices (PDIs) were synthesized. To the best of our knowledge, this is the first successful example of LRP which is triggered by direct photolysis of a dormant species.

Organotellurium transfer reagent **1**,[11c] which absorbs at a λ_{max} of 351 nm ($\epsilon = 260$ M^{-1} cm^{-1}), was selected for this study (Figure 1). The absorption was assigned as an $n(Te)−\sigma^*(C−Te)$ transition by using time-dependent DFT calculations.

Photoinduced TERP of *n*-butyl acrylate (BA, 100 equiv) was carried out in the presence of **1** in a Pyrex tube by irradiation with a 500 W high-pressure mercury lamp. The temperature of the reaction mixture became 50−55 °C due to irradiation. Monomer

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Scheme 1. Photoinduced Reaction of **1** with a Vinyl Monomer and TEMPO[a,b]
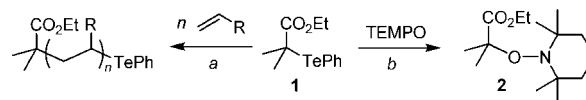
[a] See Table 1 and main text for reaction conditions. [b] *hν* (500 W high-pressure Hg lamp, >470 nm cutoff filter), C$_6$D$_6$, rt, 10 min, 96%.
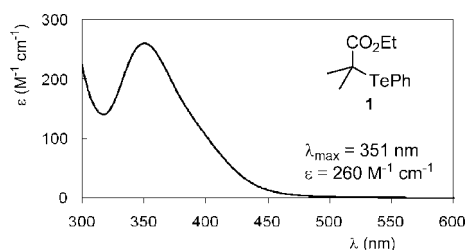

Figure 1. UV−vis spectrum of **1** in benzene.

conversion reached a maximum of 93% after 2 h. However, the number average molecule weight (M_n) of the resulting poly(butyl acrylate) (PBA) was ~25% smaller than the theoretical M_n, and the PDI was considerably large (1.87) (Table 1, run 1). Formation of diphenylditelluride (12%) and deposition of tellurium metal powder were also observed in the reaction mixture, indicating the loss of the phenyltellanyl polymer end group. We attributed the decomposition to the intensity of the light. Therefore, we irradiated the reaction mixture through a short-wavelength cutoff filter (>470 nm), and we obtained a highly controlled PBA with M_n close to the theoretical value and a low PDI (run 2). Ditelluride and tellurium metal did not form. A >580 nm cutoff filter was also effective (run 3). High molecular weight PBAs ($M_n = 100\,000−220\,000$) with low PDIs (<1.20) were obtained by changing the BA/**1** ratio (runs 4 and 5).

The effects of the light source were examined next. The use of a 1% neutral density (ND) filter was also effective (run 6), indicating that the effect of the cutoff filter is not the wavelength but the intensity of the light. Weak intensity light sources, such as a black light (100 W) and even sunlight, effectively promoted LRP (runs 7 and 8). On the other hand, the polymerization did not proceed in the dark at all under otherwise identical conditions (run 9). Polymerization stopped when the light was turned off, due to the recombination of polymer end radicals with phenyltellanyl radical or the occurrence of a termination reaction involving polymer end radicals.[12] However, the polymerization restarted upon turning on the light, and well-controlled PBA with a M_n of 12 400 and a PDI of 1.10 in 96% monomer conversion was obtained even after three cycles of turning the light off and on (see Supporting Information). The results clearly showed that the tellurium ω-end group was

Table 1. Photoinduced Polymerization in the Presence of **1**[a]

run	monomer[b]	filter[c]	conv (%)[d]	M_n (theor)	M_n (exptl)[e]	PDI[e]
1	BA	none	93	11 900	9000	1.87
2	BA	>470 nm	98	12 500	13 000	1.09
3	BA	>580 nm	95	12 100	12 600	1.11
4	BA[f]	>470 nm	90	119 000	120 800	1.13
5	BA[f]	>470 nm	90	230 400	223 000	1.18
6	BA	1% ND[g]	95	12 200	12 800	1.12
7	BA	BL[h]	82	10 500	11 000	1.15
8	BA	sunlight[i]	88	11 300	11 000	1.18
9	BA	dark	0	--	--	--
10	BA	dark[j]	89	11 400	10 300	1.14
11[k]	BA	>470 nm	86	11 000	10 500	1.16
12	HEA	>470 nm	95	11 000	11 600[d]	1.23
13	AA[l]	>550 nm	90	7560	7000[m]	1.34[l]
14	NIPAM[n]	>550 nm	92	10 400	11 800	1.15
15	NVP	>580 nm	93	10 300	9200	1.12
16	NVC[o]	>640 nm	96	18 500	21 200	1.11
17	NVI	>580 nm	90	8200	9000	1.14

[a] A solution of **1** and monomer (100 equiv) in a Pyrex tube under a nitrogen atmosphere was irradiated with a 500 W high-pressure Hg lamp through a filter for 2 h. The temperature of the reaction mixture became 50−55 °C due to the irradiation. [b] See text for monomer abbreviation. [c] Short-wavelength cutoff filter was used. [d] Determined by ^{1}H NMR. [e] Determined by gel permeation chromatography calibrated against poly(methyl methacrylate) standards. [f] Polymerization was carried out with 1000 and 2000 equiv of the monomer for 3 and 5 h for runs 4 and 5, respectively. [g] Neutral density (ND) filter (1%) was used instead of short-wavelength cutoff filter. [h] Black light (BL, 100 W) was used. [i] The reaction was carried out in sunlight at noon for 2 h. [j] The reaction was carried out in the dark at 100 °C for 24 h. [k] Polymerization was carried out at 0 °C for 4 h. [l] THF was used as a solvent. [m] Determined after converting carboxylic acid to methyl ester. [n] The reaction was carried out in a 1:4 DMF/water mixture at 20 °C. [o] DMF was used as a solvent.

preserved during the polymerization and that the amount of dead polymers was negligible.

The synthetic scope of the photopolymerization was examined. Although a high temperature and a long reaction time (100 °C, 24 h) were required to reach a high monomer conversion under thermal conditions (run 10),[13] the polymerization proceeded smoothly at even 0 °C by irradiation (run 11). The results clearly demonstrate the high efficiency of the photochemical conditions.

Various acrylates and acrylamides with polar functional groups, such as free hydroxyl, carboxylic acid, and amide groups, could be used under the polymerization conditions. Thus, polymerization of 2-hydroxylethyl acrylate (HEA), acrylic acid (AA), and *N*-isopropyl acrylamide (NIPAM) gave the corresponding polymers with controlled M_n's and low PDIs in all cases (runs 12−14). Not only conjugated monomers, such as acrylates, but also nonconjugated monomers were successfully polymerized by photoirradiation. For example, *N*-vinylpyrrolidone (NVP),[14] *N*-vinylcarbazole (NVC), and *N*-vinylimidazole (NVI) were polymerized under photoirradiation (runs 15−17).

Effective generation of a carbon-centered radical from **1** was ascertained by using a control experiment. When a 1:1 mixture of **1** and TEMPO in C_6D_6 was irradiated with a 500 W Hg lamp through a >470 nm cutoff filter for 10 min, TEMPO adduct **2** and diphenylditelluride formed in nearly a quantitative yield (Scheme 1). Adduct **2** formed due to the coupling of the carbon-centered

radical generated from **1** with TEMPO, and phenyltellanyl radicals dimerized to form diphenylditelluride

A plausible mechanism for the polymerization is shown in Scheme 2. Organotellurium dormant species **3** undergoes dissociation−combination (DC) mediated polymerization upon irradiation. However, a degenerative transfer (DT) mechanism may compete against the DC mechanism since the DT mechanism is the predominant mechanism under thermal conditions.[15] Further mechanistic and synthetic studies are currently underway.

Scheme 2. Plausible Polymerization Mechanism under Irradiation (P and P′ Denote Polymer Species)
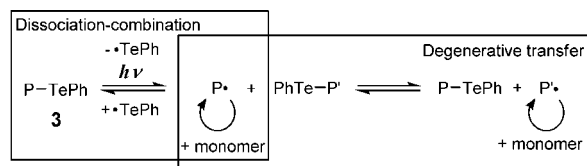
Supporting Information Available: Calculated structure of **1**, typical experimental procedures, and spectra of **2**. This information is available free of charge via the Internet at http://pubs.acs.org/.

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