Practical Protocols for Organotellurium-Mediated Living Radical Polymerization by in Situ Generated Initiators from AIBN and Ditellurides

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Living radical polymerization (LRP) has become an increasingly important tool for the synthesis of nanostructural macromolecules with defined structures possessing a variety of functional groups since radical species are compatible with many polar functional groups that do not tolerate ionic and metal-catalyzed polymerization conditions.[1] LRP relies on the controlled and reversible generation of active polymer-end radicals from dormant species, and a variety of new methods have recently been developed for the precise control of this process.[2] Among these methods, organotellurium-mediated living radical polymerization (TERP) has unique versatility, molecular weight control, functional group compatibility, and ease of polymer-end transformations.[3] However, a drawback of TERP may be the sensitivity of initiators toward oxygen, and thus the initiators must be stored under an inert atmosphere and manipulated using standard syringe techniques. Therefore, the development of a new initiating system using shelf stable reagents is highly desirable. Because ditellurides are excellent radical capturing reagents,[4] we anticipated that radicals generated from diazo compounds would react with ditellurides to form organotellurium compounds, which could be used directly as initiators for TERP. We report here one such binary system for TERP starting from shelf stable reagents, namely azoisobutyronitrile (AIBN) and ditellurides (Scheme 1). While the effect of diphenyl ditelluride on the molecular weight control in the AIBN-initiated polymerization of styrene has been reported,[5] there is no direct experimental evidence for the involvement of organotellurium compounds during the polymerization process. This work, however, clearly reveals the crucial role of the carbon−tellurium bond both in the initiators and in the dormant polymer species for the precise control of the polymerization process.[6]

Scheme 1

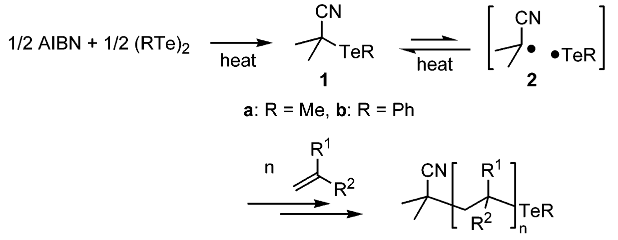
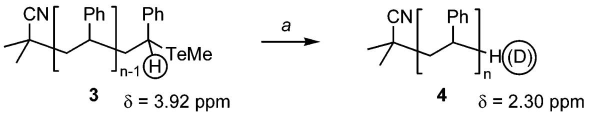


Table 1. Polymerization of Vinyl Monomers with AIBN and Ditellurides

run	method[a]	monomer	R	condns (°C/h)	yield (%)	M_n [b]	PDI[b]
1	A	St	Me	100/15	98	9400	1.15
2	A	BA	Me	100/24	69	8300	1.12
3	A	MMA	Me	80/13	74	8600	1.37
4[c]	A	MMA	Me	80/13	81	8300	1.12
5	B	St	Me	90/36	54	11700	1.20
6	B	St	Ph	80/56	55	19000	1.20
7	B	BA	Me	100/48	>3	2900	1.06
8	B	BA	Ph	100/24	25	4600	1.07
9	B	MMA	Me	80/13	95	28800	1.14
10	B	MMA	Ph	80/4	96	50100	1.22
11	C	St	Me	90/32	88	9200	1.38
12	C	St	Ph	90/45	93	6900	1.48
13	C	BA	Me	100/24	38	3400	1.10
14[d]	C	BA	Me	100/24	89	7800	1.24
15	C	BA	Ph	100/24	88	7200	1.18
16[e]	C	MMA	Me	80/0.5	100	13100	1.55

[a] A: Purified **1a** was used as an initiator (**1**:monomer = 1:100). B: The initiator was prepared in situ by heating a solution of AIBN and ditelluride in α,α,α-trifluoromethylbenzene at 80 °C for 3 h (AIBN:ditelluride:monomer = 1:1:100). C: AIBN, ditelluride and monomer (1:1:100) was heated as indicated. [b] Calibrated by gel permeation chromatography using polystyrene standards for polystyrene samples or polyMMA standards for polyMMA and polyBA samples. [c] Dimethyl ditelluride (1 equiv) was added. [d] 0.7 equiv of dimethyl ditelluride was used. [e] 10 equiv of dimethyl ditelluride were used.

Scheme 2



[a] AIBN (0.1 equiv), $Bu_3SnH(D)$ (3 equiv), $C_6H_5CF_3$, 80 °C, 1 h; 89% and 96% yields for **4** and **4**-d_1, respectively.

Before attempting the binary initiating system, we first examined the polymerization of styrene (St), butyl acrylate (BA), and methyl methacrylate (MMA) using purified **1a** (R = Me), which was prepared from 2-bromo-2-methylpropionitrile and methyltellanyllithium (Table 1, entries 1−4, method A). The desired polymers formed with the predicted molecular weight and low polydispersity in high yields in all cases. While the previous initiators required the addition of dimethyl ditelluride for the precise control of the polymerization of MMA,[3b] **1a** afforded polyMMA with an acceptable level of polydispersity without ditelluride (PDI = 1.37, entry 2). The addition of 1 equiv of dimethyl ditelluride further controlled the polymerization of MMA (PDI = 1.12, entry 3). The existence of the methyltellanyl end group in polySt **3** was confirmed by the characteristic benzylic proton signal at 3.9 ppm in the ^{1}H NMR spectrum of a sample prepared from **1a** and 30 equiv of styrene (Scheme 2). In addition, reduction of **3** by either tributyltin hydride or deuteride afforded **4** or **4**-d_1, respectively.[7] Selective incorporation of the deuterium atom in the polymer was ascertained by MALDI−TOF mass spectroscopy by an increase of one mass number in the ions seen for **4**-d_1 compared to those for **4** (Figure 1). The mass spectroscopy analyses also revealed the formation of the well-defined polySt (PDI = 1.04). The ^{2}H NMR spectrum of **4**-d_1 further supported the selec-

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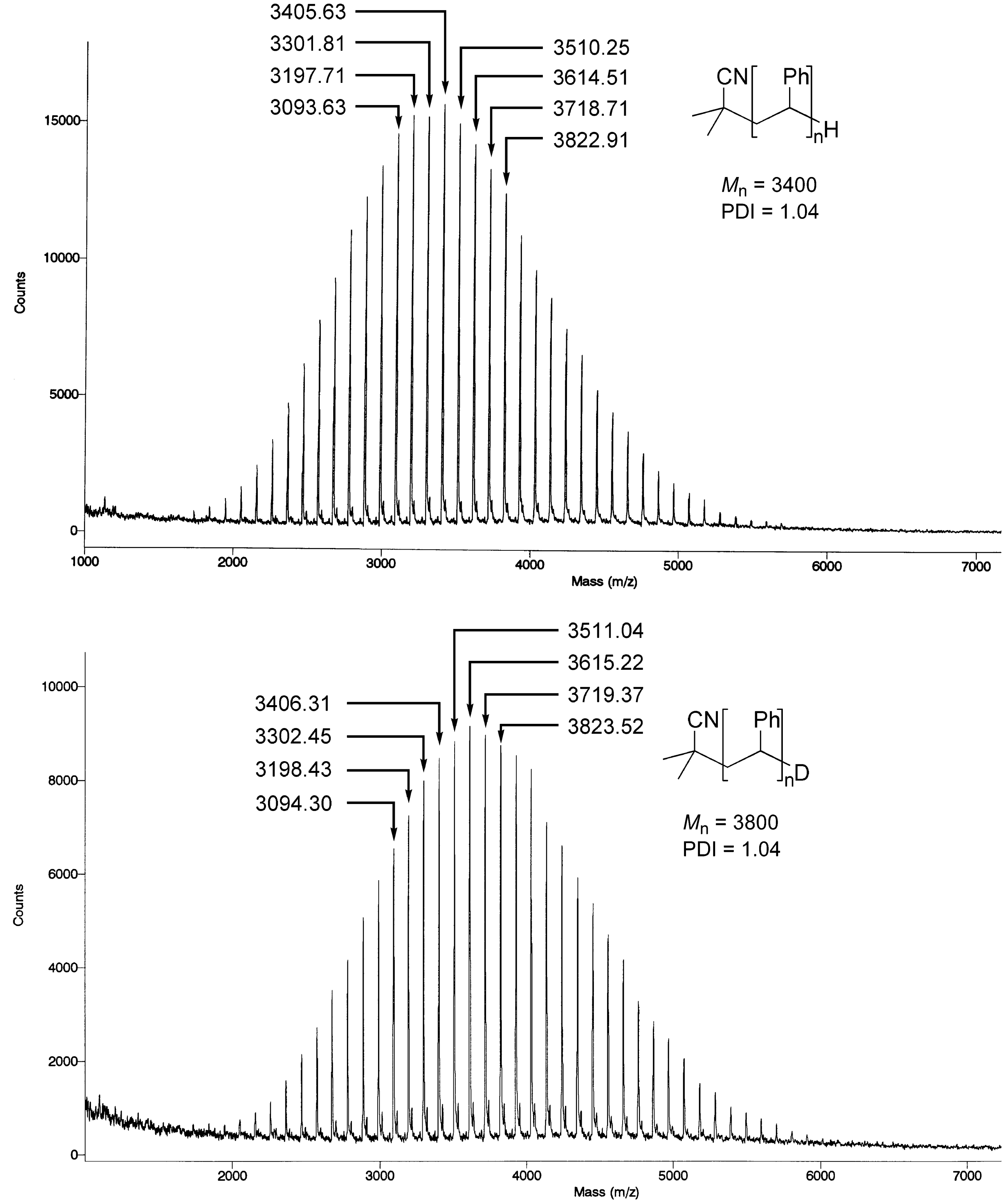

Figure 1. MALDI−TOF MS spectra of **4** (top) and **4**-d_1 (bottom) obtained by method A. The molecular ions were observed as silver ion adducts [$m/z = (M + \mathrm{Ag})^+$]. Molecular weight ($M_n$) and polydispersity (PDI) were directly obtained by MS spectra.

tive incorporation of deuterium at the benzylic position (δ = 2.30 ppm, broad singlet). The same labeling experiments with polyBA and polyMMA also revealed the existence of the methyltellanyl group at the polymer end (see Supporting Information). The desired polymers formed with very narrow molecular weight distributions (PDI = 1.06 for polyBA and PDI = 1.11 for polyMMA). These results clearly indicate that **1a** also possesses excellent or even superior versatility compared with the previously reported initiators[3] in terms of versatility and molecular weight controllability.

We next examined the binary system using in situ generated initiators (method B). Thus, initiator **1a** was prepared by heating an equimolar amount of AIBN (0.20 mmol) and dimethyl ditelluride (0.20 mmol) in C_6D_6 (0.8 mL) at 80 °C for 3 h. The ^{1}H NMR of the crude mixture indicated the formation of **1a** (0.07 mmol, 17% yield based on the tellurium atom) and 2,2,3,3-tetramethylsuccinonitrile (0.14 mmol, 69% yield), a dimer of the AIBN-derived radical, together with the recovered dimethyl ditelluride (0.18 mmol, 90%). The rather low coupling efficiency of the AIBN-derived radical with dimethyl ditelluride is not surprising because ca. 40% of the radical generated from AIBN dimerizes in solvent cages before diffusing to bulk solutions.[8] The phenyltellanyl-substituted **1b** could also be prepared in 8% yield by using commercially available diphenyl ditelluride instead of dimethyl ditelluride. The **1**/ditelluride ratio varied upon changing the starting AIBN/ditelluride ratio, but no conditions were found where all the ditelluride was converted to **1** (see Supporting Information).

The in situ generated **1** also initiated polymerization of St, BA, and MMA, but the efficiency and controllability varied depending on the vinyl monomers (Table 1, entries 5−10). Phenyltellanyl-substituted initiator **1b** generally promoted the polymerization much faster than **1a**, while the controllability of the molecular weight distribution was slightly less efficient with **1b** than with **1a**. Because **1b** has a lower bond dissociation energy than **1a** (105 and 120 kJ/mol by density functional theory calculations, respectively[9]), the observed trend is due to the faster radical generation from the phenyltellanyl-substituted initiator or dormant species than from the methyltellanyl-substituted ones. PolyMMA with the anticipated molecular weight and low polydispersity (PDI < 1.26) was successfully obtained, indicating that polymerization is initiated exclusively by **1** (entries 9 and 10).[10] Because the reaction mixture contained the unreacted ditelluride, further addition of the ditelluride was unnecessary. As the remaining ditelluride also shifts the equilibrium constant to the dormant organotellurium species from the polymer-end radicals, the rate of the polymerization using method B was considerably slower compared to that using method A, especially in the polySt and polyBA syntheses.[11] Styrene was slowly polymerized upon prolonged heating at 80−90 °C with low polydispersity (PDI = 1.20) (entries 5 and 6), while polymerization of BA was not complete within a period of time for practical use (entries 7 and 8).

Polymerization by heating a mixture of AIBN, ditelluride, and vinyl monomer (method C) was especially effective for the controlled polymerization of BA (entries 13−15). The results could be attributed to the decrease of ditelluride in the reaction mixture due to the decrease of homocoupling of the AIBN-derived radical, which now reacted preferentially with BA followed by the ditelluride to form dormant species. The polymerization was almost completed within 24 h at 100 °C by changing the AIBN/ditelluride ratio (entry 14) or by using diphenyl ditelluride (entry 15), and the desired polyBA formed with low polydispersity (PDI < 1.24). PolySt with low polydispersity was also formed by method C when the polymerization was carried out below 90 °C with the combination of dimethyl ditelluride (entry 11),[12] whereas polymerization using diphenyl ditelluride or a higher temperature resulted in the formation of polySt of high polydispersity (PDI > 1.4). Polymerization of MMA could not be controlled even in the presence of an excess of ditelluride (entry 16). As the polymerization proceeded very rapidly with the formation of high-molecular-weight polyMMA, the result must be attributed to the preferential occurrence of the conventional AIBN-initiated free radical polymerization.

The existence of an organotellanyl end group in the polySt and polyBA prepared by method C was also confirmed directly by ^{1}H NMR spectroscopy and by MALDI TOF MS and ^{2}H NMR spectra after treatment of the polymer with tributyltin hydride or deuteride (see Supporting Information). While the ^{1}H NMR spectra were very similar to those prepared by method A, MALDI TOF MS analysis revealed the existence of a series of new peaks. The newly observed peaks also increased one mass number upon the deuterium-labeling experiment. Therefore, these peaks were also derived from dormant species possessing organotellanyl end groups; however, the origin of the new peaks is unclear at the present time.

In summary, we have developed a new initiating system for TERP using shelf stable diazo compounds and ditellurides. The obtained polymer possesses an organotellanyl end group, which would be useful for polymer-end manipulations and for block copolymer synthesis.[3] Since methods B and C do not require purification and handling of air-sensitive organotellurium compounds, these new methods are especially suitable for the practical use of TERP.[13] Method C is the most convenient and is useful for the polymerization of styrene and acrylate derivatives because of the simplicity of the reaction procedure with a high level of controllability of the resulting polymers, while method B should be useful for the controlled polymerization of methacrylate derivatives. Method A using purified initiators, however, is certainly the choice to obtain the living polymers with the highest level of controllability for both molecular weight and polydispersity.

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Supporting Information Available: Experimental section. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) B3LYP density functionals with LANL2DZ basis set for the tellurium atom and 6-31G(d) basis set for the rest were used. The obtained energies resulted from the sum of Hartree−Fock and zero-point vibrational energies of **1** and the corresponding radicals.

(10) The predicted M_ns are 28 400 and 58 200 based on 17% and 8% formation of **1a** and **1b**, respectively.

(11) Addition of dimethyl ditelluride in the polymerization of BA using purified **1a** dramatically slowed down the polymer formation.

(12) The reaction temperature was critical in controlling the polymerization in method C, and polySt of low polydispersity (PDI $<$ 1.4) was obtained below 90 °C.

(13) The toxicity of organotellurium compounds is not clear. They should be handled with care. See: Chasteen, T. G.; Bentley, R. *Chem. Rev.* **2003**, *103*, 1.

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