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Organotellurium Compounds as Novel Initiators for Controlled/Living Radical Polymerizations. Synthesis of Functionalized Polystyrenes and End-Group Modifications

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The synthesis of functionalized macromolecules with defined structures by controlled “living” radical polymerization is becoming increasingly important since radicals are compatible with a wide variety of polar functional groups, which do not lend themselves to ionic and metal-catalyzed polymerization conditions.[1,2] Various initiating systems have been developed for nitroxide-mediated polymerization (NMP),[3] atom transfer radical polymerization (ATRP),[4] and reversible addition−fragmentation chain transfer (RAFT).[5] However, the invention of a new system presents an excellent opportunity to control, with greater precision, molecular structure and to functionalize polymer end-groups.[6]

We have already reported that organotellurium compounds undergo reversible carbon−tellurium bond cleavage upon thermolysis and photolysis,[7] and that the resulting carbon-centered radicals can react with a variety of radical acceptors.[8,9] Since NMP also relies on reversible generation of carbon-centered radicals and persistent nitroxyl radicals at the polymer end, we decided to investigate the use of organotellurium compounds as unimolecular radical initiators for living radical polymerization. The advantages of organotellurium compounds over nitroxides, as we foresaw them, e.g., more facile synthesis of tailor-made initiators and ease of polymer end-group modifications, would be highly useful in the syntheses and synthetic transformations of these compounds.[10] We report here several new organotellurium-based initiators for controlled/living radical polymerization of styrene derivatives that allows accurate molecular weight control with defined end-groups, which can be transformed into a variety of end-group modified polystyrenes.

Previous reports on the NMP indicate that the efficiency of the initiators is closely related to their bond dissociation energies (BDEs).[11] Therefore, we first calculated the BDEs of the organotellurium compounds **1**−**5**.[12] DFT calculations indicated that the BDEs of **1** and **3** are 112−123 kJ/mol, the values of which are very similar to those of the corresponding TEMPO analogue (119 kJ/mol).

Bulk polymerization of styrene (X = H) was carried out at 105 °C for 16−18 h, and the results are shown in Table 1 (entries 1−8). The polymer-end mimetic initiator **1a** (R = Me) initiated the polymerization efficiently, and afforded polystyrene with the predicted molecular weight and low polydispersity ($M_n = 9200$, PD = 1.17) in 96% yield (Table 1, entry 1). The initiator **1b** also promoted polymerization, but the control of the molecular weight was less efficient. Benzyl telluride **2** also initiated polymerization with acceptable polydispersity. The result is in sharp contrast to the NMP polymerization, in which benzyl derivatives are far less efficient than the 1-phenylethyl derivatives (cf. **1a** vs **2**).[2e] The ester **3** also initiated polymerization efficiently with low polydispersity.

Scheme 1

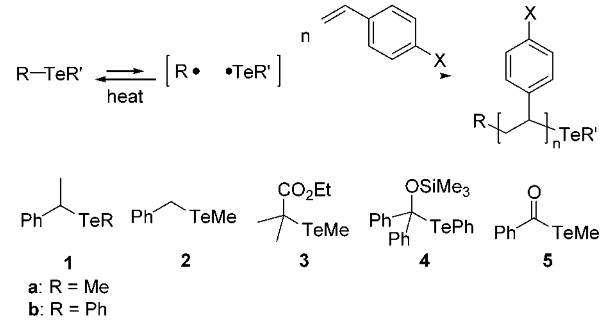

Table 1. Effects of Initiators for Polymerization of Styrene[a]

entry	X	initiator	conversion (%)	M_n[b]	PD[b]	BDE (kJ/mol)[c]
1	H	**1a**	96	9 200	1.17	123
2	H	**1b**	91	15 900	1.45	112
3	H	**2**	89	9 000	1.46	142
4	H	**3**	79	9 000	1.15	114
5	H	**4**	76	50 700	1.80	25
6	H	**5**	83	25 400	1.58	182
7[d]	H	**1a**	78	35 700	1.21	
8[e]	H	**1a**	84	62 600	1.30	
9	Cl	**1a**	88[f]	8 800	1.41	
10	OMe	**1a**	94[g]	10 900	1.17	

[a] Bulk polymerization was carried out with 100 equiv of styrene at 105 °C for 16−18 h under a nitrogen atmosphere. [b] Molecular weight (M_n) and polydispersity (PD) were calibrated by size exclusion chromatography using polystyrene standards for samples after single precipitation from MeOH. [c] Bond dissociation energy of the initiator obtained by B3LYP DFT calculations with the LANL2DZ basis set for tellurium atom and the 6-31G(d) basis set for the rest. [d] The reaction was carried with 500 equiv of styrene. [e] The reaction was carried out with 1000 equiv of styrene. [f] The reaction was carried out at 100 °C for 17 h. [g] The reaction was carried out at 100 °C for 36 h.

The ability to initiate polymerization of **4** and **5**, which possess the lowest and highest BDEs among the organotellurium compounds examined, was found to be unsatisfactory. These results may suggest that both the BDEs and the reactivity of the initiating radicals toward styrene are important factors in controlling the polymerization process. It is also worth mentioning that, while the first-generation initiators for NMP required high temperature and long reaction times, e.g., 130 °C for 72 h, initiators **1a** and **3** promoted polymerization under much milder conditions. Molecular weight increased linearly with the increase of styrene, and the products were obtained with low polydispersity (entries 7 and 8).

Because polymerization proceeds under neutral conditions, styrenes possessing a variety of functional groups, such as chlorine and methoxy groups, could also be polymerized with use of **1a** as

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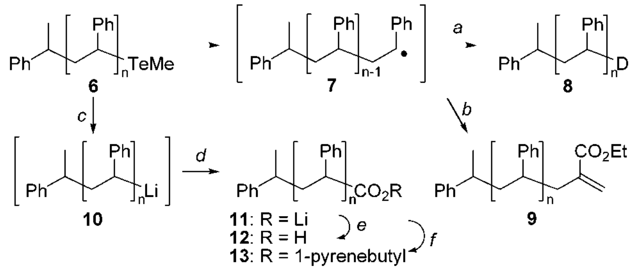
Scheme 2 [a]



[a] AIBN (0.1 equiv), Bu_3SnD (3 equiv), $C_6H_5CF_3$, 80 °C, 4 h. [b] AIBN (0.1 equiv), ethyl tributylstannylmethylacrylate (4 equiv), $C_6H_5CF_3$, 80 °C, 6 h. [c] BuLi (1.5 equiv), THF, −72 °C, 3 min. [d] CO_2 (excess). [e] Aqueous HCl (excess). [f] 2,4,6-$Cl_3C_6H_2COCl$ (2 equiv), Et_3N (2 equiv), THF, room temperature, 1.5 h, then 1-pyrenebutanol (4 equiv), DMAP (4 equiv), CH_2Cl_2, room temperature, 3 h.

the initiator (entries 9 and 10). It is worth noting that *p*-methoxy-substituted styrene, which is a poor monomer for ATRP,[13] was successfully polymerized by this method.

The "living" nature of the current polymerization was ascertained by several control experiments. First, the molecular weight (M_n) increased linearly with an increase in the amount of styrene used (see above). Second, the molecular weight also increased linearly with an increase of the conversion of styrene (see Supporting Information). Third, a block copolymer was formed by the treatment of a starting polystyrene block prepared from **1a** and 100 equiv of styrene with 4-methoxystyrene (100 equiv) ($M_n = 18000$, PD $= 1.19$). Finally, the high level of fidelity of the end-group was confirmed by labeling experiments.[14] Thus, treatment of the polymer block **6** prepared from **1a** and 100 equiv of styrene with tributyltin deuteride afforded **8** quantitatively through the radical intermediate **7**.[9a] The ^2H NMR of **8** clearly revealed >93% incorporation of deuterium at the benzylic position.

The virtue of the current method is the ease of the end-group transformations.[15] Thus, trapping of the radical intermediate **7** with ethyl tributylstannylmethylacrylate afforded the enoate-functionalized polymer **9** with 61% end-group functionalization. Furthermore, the end-group of **6** could be transformed by ionic reactions through tellurium−lithium transmetalation. Therefore, treatment of **6** with butyllithium followed by trapping of the resulting lithium species **10** with carbon dioxide gave lithium carboxylate **11**, which was treated with aqueous HCl to give carboxylic acid **12**.[16] The esterification of **11** with pyrenebutanol afforded **12**, UV spectra of which revealed 86% incorporation of the carboxylate residue to the polymer end. The functional groups in **11** and **12** would afford good foundations for the further end-group modifications.

Detailed mechanisms of the current polymerization are not clear at the present time. One possible explanation is that tellurium radicals have sufficient lifetime to act as persistent radicals.[17] Because tellurium radicals are less stable than nitroxyl radicals and usually form ditellurides,[18] an alternative mechanism in which ditellurides serve as the capping reagent for the reactive polymer ends to give the dormant species is also plausible. In this case, the high reactivity of ditellurides toward carbon-centered radicals must be responsible for the high control of the polymerization process.[19] Degenerative chain-transfer of the reactive polymer end and the dormant tellurium species may also occur. Further synthetic and mechanistic studies are in progress, and will be reported in due course.

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Supporting Information Available: Preparations and spectroscopic data of initiators, kinetics plots of monomer conversion, and determination of polymer end-groups (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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