Highly Versatile Organostibine Mediators for Living Radical Polymerization

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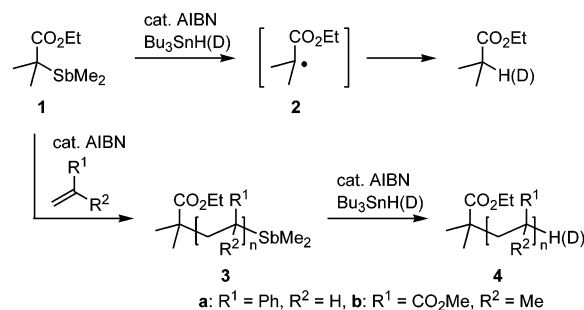Received August 30, 2004; E-mail: yamago@sci.osaka-cu.ac.jp

Free radical polymerization (RP) is one of the most valuable industrial processes for producing organic materials in the world.[1] This is due to its versatility for polymerizing a variety of vinyl monomers having polar functional groups, which do not lend themselves to ionic and metal-catalyzed polymerization conditions, under mild conditions. The major drawback of RP is, however, the low controllability of macromolecular structure, and the polymers obtained are of broad molecular weight distribution.

Living radical polymerization (LRP) has been developed recently to overcome this problem.[2] The nitroxide-mediated radical polymerization (NMP),[3] the atom transfer radical polymerization (ATRP),[4] and the reversible addition−fragmentation chain transfer radical polymerization (RAFT)[5] are the three representative methods for conducting LRP, and we have recently reported the organotellurium-mediated LRP (TERP) as the fourth method.[6−8] Although these methods provide well-defined macromolecules with monodisperse and narrow molecular weight distribution, their industrial applications have been quite limited due to several deficiencies. First, the monomers successfully polymerized are limited to a certain class of conjugated monomers,[3−7] and applications to unconjugated monomers have been extremely limited.[9] Second, the polymerization often requires high temperature and long reaction time to achieve high conversion.[3,5,6] Third, removal of catalyst(s) and additive(s) from the polymers require laborious processes.[4] Fourth, physiological activities of the promoters are not well-known.[6,7] In this respect, a new LRP method, which would be applicable to mass production of living polymers, is still sought.

We report here that trivalent organostibines serve as excellent mediators for LRP. The organostibine-mediated living radical polymerization (SBRP) proceeded under mild conditions to reach high conversion to give well-defined polymers with narrow molecular weight distributions. A notable feature is that the SBRP can control the polymerization of both conjugated and unconjugated monomers. Furthermore, while the generation of ethyl radical from triethylstibine was demonstrated by an electron spin resonance spectroscopic study,[10] the synthetic use of organostibines as the source of carbon-centered radicals has not been reported.[11] Therefore, this is the first example of the synthetic use of organostibines in this manner.

We initially examined the radical-mediated reduction of trialkyl-stibine **1** with Bu₃SnH as a proof-of-principle experiment for the generation of carbon-centered radicals from organostibines (Scheme 1). We found that **1** was quantitatively reduced to ethyl 2-methylpropionate in the presence of azo-bis-isobutyronitrile (AIBN) and

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Scheme 1

Bu₃SnH at 80 °C. When Bu₃SnD was employed, the corresponding deuterated product was formed. In addition, the reduction did not proceed in the presence of a radical inhibitor such as TEMPO. All these results support the efficient generation of radical **2** by the reaction of the tributyltin radical with **1**.

We next examined the styrene polymerization reaction. After heating **1** and styrene (100 equiv) at 100 °C for 48 h, polystyrene with a predicted molecular weight ($M_n = 7700$) and a low polydispersity index (PDI = 1.16) was obtained in good yield (Table 1, run 1). The rate of the polymerization reaction increased considerably with the addition of AIBN (0.1−1.0 equiv) and provided well-controlled polystyrene with respect to molecular weight and PDI (run 2). The molecular weight of polystyrene was shown to increase linearly when the quantity of styrene used was increased. The desired high-molecular-weight polystyrenes with narrow molecular weight distributions were obtained in all cases (runs 3−6).[12] The molecular weight also increased linearly with the conversion of styrene (data are not shown). This linear evolution of molecular weight and the observed low polydispersity index strongly supports the living character of the current polymerization.

The existence of the organostibine polymer end was confirmed by several control experiments. The presence of the dimethylstibino group in polystyrene **3a** (R¹ = Ph, R² = H) was suggested by the characteristic benzylic proton signal at 2.7 ppm in the ¹H NMR spectrum. Reduction of **3a** with Bu₃SnD afforded deuterated polystyrene **4a**. Both the MALDI-TOF mass spectroscopy (see Supporting Information) and the ²H NMR spectroscopy ($\delta = 2.30$ ppm, broad singlet) of **4a** clearly reveal the chain-end structure of the polymer, which possesses an ethyl methylpropionate moiety at the α-end and the deuterium atom at the ω-end.

The most notable feature of the organostibine mediator was that it could control the polymerization of both conjugated and unconjugated vinyl monomers. Thus, organostibine **1** promoted the controlled polymerization of various conjugated monomers (runs 7−11) such as *n*-butyl acrylate (BA), methyl methacrylate (MMA),

Table 1. Living Radical Polymerization Using **1** at 60 °C[a]

run	monomer[b] (equiv)	AIBN (equiv)	conditions (°C/h)	yield (%)	M_n[c]	PDI[c]
1	St (100)	0	100/48	82	7700	1.14
2	St (100)	0.5	60/19	99	8700	1.17
3	St (200)	0.5	60/24	99	15 800	1.22
4	St (500)	0.5	60/36	76	25 200	1.20
5	St (700)	0.5	60/36	76	41 200	1.16
6	St (1000)	0.5	60/36	65	49 400	1.23
7	BA (100)	0.3	60/1	96	12 400	1.13
8	MMA (100)	0.3	60/4	100	11 000	1.24
9[d]	NIPAM (100)	0.1	60/12	99	13 400	1.06
10[d]	NIPAM (200)	0.3	60/12	99	26 700	1.09
11[d]	AN (100)	0.1	60/18	81	15 000	1.05
12	VP (100)	0.5	60/0.5	99	10 800	1.14
13	VP (300)	0.5	60/0.8	95	28 600	1.18
14	VP (500)	0.5	60/1	92	42 100	1.22
15	VA (25)	0.1	60/5	92	2800	1.26

[a] Mixture of **1**, AIBN, and monomer was heated under a nitrogen atmosphere. [b] St, styrene; BA, *n*-butyl acrylate; MMA, methyl methacrylate; NIPAM, *N*-isopropyl acrylamide; AN, acrylonitrile; VP, 1-vinyl-2-pyrrolidinone; VA, vinyl acetate. [c] Number-average molecular weight (M_n) and polydispersity index (PDI) were obtained by size exclusion chromatography calibrated by polySt standards for runs 1−6 and polyMMA standards for others. [d] Reaction was carried out in DMF.

N-isopropyl acrylamide (NIPAM), and acrylonitrile (AN) and also unconjugated monomers (runs 12−15) such as 1-vinyl-2-pyrrolidinone (VP) and vinyl acetate (VA).[13] In all cases, we observed virtually complete conversion of monomers within 1−18 h at 60 °C. The molecular weight of polyVP increased linearly when the amount of VP used was increased, and the desired polymers with low PDIs were obtained in all cases (runs 12−14), suggesting that the polymerization proceeded in a living manner.

The current methodology is also compatible with a variety of polar functional groups. Consequently, the polymerization of NIPAM, AN, and VP proceeded in a highly controlled manner and gave the desired polymers in excellent yields (runs 9−14).

A block copolymer of conjugated and unconjugated monomers could be synthesized by using the living polymer end of macroinitiators **3a** and **3b**. Thus, **3a** (M_n = 4400, PDI = 1.05) or **3b** (M_n = 4700, PDI = 1.27) were treated with VP (100 equiv) in the presence of AIBN (0.25 equiv) in DMF at 60 °C for 8 h to afford poly(St-*block*-VP) (M_n = 27400, PDI = 1.05) and poly(MMA-*block*-VP) (M_n = 20500, PDI = 1.31) in 87 and 99% yields, respectively. In both cases, the macroinitiators were completely converted to the corresponding block copolymers (see Supporting Information). These are the first examples of the successful block copolymerization of stepwisely added conjugated and unconjugated monomers. Such block copolymers would be of great importance as functional organic materials with new or improved properties.[14]

Kinetic experiments using the same protocol as described previously[7,15] suggested that the SBRP proceeds by similar mechanism to the TERP, namely, the degenerative transfer mechanism. The rate constant of the degenerative transfer k_{ex} for the dimethylstibino group transfer in the styrene polymerization was obtained as 1.1×10^4 M^{-1} s^{-1}, which is ca. 2 times higher than the value of the methyltellanyl group transfer in the TERP. Since a higher rate constant of degenerative transfer leads to a lower polydispersity index,[16] the SBRP is, in principle, better than the TERP in terms of the molecular weight controllability. Indeed, the organostibine could control the polymerization of MMA (run 8), whereas the structurally related organotellurium compound failed to achieve control and required the addition of ditelluride.[6b] The observed higher controllability in the SBRP over the TERP is consistent with the kinetic studies.[17]

In summary, we have demonstrated that organostibines serve as excellent mediators for the highly controlled living radical polymerization of conjugated and unconjugated vinyl monomers. The versatility, the mild conditions, and the high efficiency of the SBRP would be highly attractive for the mass production of living polymers. Organostibines show higher reactivity toward the group-transfer reaction than organotelluriums do, and the result suggests that the former are better precursors for carbon-centered radicals than the latter. Therefore, the current work would also shed new light on the synthetic applications of organostibines in radical-mediated organic synthesis,[18] which has so far been unexplored.[19]

Supporting Information Available: Preparation of **1**, typical experimental procedures, and kinetic experiments (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Experimental M_ns were slightly lower than the theoretical ones presumably because carbon-centered radicals derived from AIBN also generated the polymerization. We thank a referee for reminding us of this point.

(13) PDI increased as the molecular weight of polyVA increased due to the occurrence of head-to-head addition. See ref 9b.

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(17) Theoretical calculations of model compounds also suggest that organostibines show higher reactivity toward the group-transfer reaction than organotelluriums. The activation energies for the degenerative transfer of methyl radical with trimethylstibine and dimethyltelluride were calculated to be 3.1 and 7.9 kJ/mol, respectively, at the B3LYP/6-31G*+LANL2DZ-(d,p)(Sb, Te) level of theory.

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(19) Toxicity of organostibine compounds is not yet clear. They should be handled with care.

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