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Optimization of Organotellurium Transfer Agents for Highly Controlled Living Radical Polymerization

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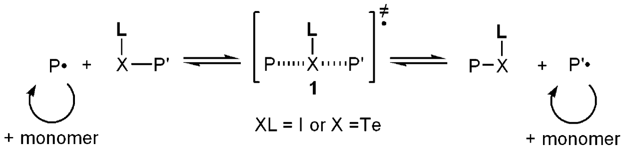
Living radical polymerization (LRP) has been recognized as one of the most efficient methods for the controlled synthesis of macromolecules possessing a variety of polar functional groups with defined monomer sequences and architechtures.[1] Stable free radical polymerization,[2] atom transfer radical polymerization,[3] and degenerative transfer polymerization including reversible addition−fragmentation chain transfer radical polymerization and catalytic chain transfer polymerization[4] are the three representative processes for conducting LRP. Organoiodine-mediated radical polymerization (IRP)[5] is operationally simple and effective in polymerization of several vinyl monomer, though the level of control in molecular weight and its distribution is usually modest. We recently developed organotellurium-mediated living radical polymerization (TERP),[6−9] which shows high versatility in polymerizing a variety of monomers and gives living polymers with molecular weights predicated from the monomer/transfer agent ratio and with narrow molecular weight distributions.

Mechanistic studies revealed that both IRP and TERP proceed mainly via a degenerative transfer mechanism, in which the polymer end radical P undergoes an iodine atom transfer (XL = I) or tellanyl group transfer (X = Te) reaction, respectively, with the corresponding dormant species P′XL to generate new radical P′ and dormant species PXL (Scheme 1).[6,10] The difference between organoiodine and tellurium is, however, the rate of the iodine atom and tellanyl group transfer reactions; the rate constant, k_{ex}, of the methyltellanyl group transfer reaction is ca. 5 times faster than that of the iodine atom transfer reaction. The results are consistent with theoretical predictions that the faster exchange reaction leads to a lower polydispersity index (PDI = M_w/M_n) for the resulting polymer.[11] The results are also consistent with the previous reports showing the reactivity of phenyltellanyl group transfer reaction higher than the iodine atom transfer reaction toward vinyl radicals,[12,13] though an inverse reactivity was reported toward alkyl radicals.[14]

Since the organotellanyl group transfer reaction proceeds through transition state **1** (Scheme 1, X = Te), the untransferable substituent L would affect the rate of the group transfer reaction and, thus, the PDI control. Despite this, to the best of our knowledge, there is no report on the effect of the L group on the group transfer reactions. We have used exclusively methyl-substituted organotellurium transfer agents (L = Me) due to their ease of preparation and purification. Here we report the first study on the effect of substituent L in organotellanyl group transfer reactions, which should lead to the generation of new, highly efficient transfer agents for TERP. An alternative method for increasing the PDI control would be the use of heteroatom compounds other than tellurium. Indeed, we have recently reported that organostibines[15−17] and organobismuthines[18] also serve as efficient transfer agents in living radical polymerization. However, these heteroatom compounds are less stable than organotellurium compounds toward oxygen and require more careful handling. Therefore, the development of efficient organotellurium transfer agents is highly desirable.

Scheme 1. Degenerative Transfer (Atom or Group Transfer) Mechanism of Organoiodine-Mediated Radical Polymerization (IRP) and Organotellurium-Mediated Living Radical Polymerization (TERP)



Phenyltellanyl- (**2a**), *p*-methoxyphenyltellanyl- (**2b**), *p*-trifluoromethylphenyltellanyl- (**2c**), 2-furyltellanyl- (**2d**), and *n*-butyltellanyl- (**2e**) substituted organotellurium transfer agents were prepared by a method similar to that used for the synthesis of methyltellanyl derivative **2f**.[7] The efficiencies of transfer agents **2a**−**2f** were examined in the bulk polymerization of styrene (100 equiv). High monomer conversion was observed in all cases after heating at 100 °C for 24 h. Polystyrenes with number-average molecular weights (M_ns) predetermined from the styrene/**2** ratio ($M_n \approx 10\,000$) and low PDIs (<1.25) were obtained in all cases (Table 1, runs 1−6). Transfer agents **2a**−**2c** showed higher PDI controls (PDI < 1.10) than conventional transfer agent **2f** (runs 1−3 vs 6), but **2d** and **2e** showed slightly lower control than **2f** (runs 4 and 5). While organostibine **2g**[15] and organobismuthine **2h**[18] exhibit better PDI control than **2f** (runs 7 and 8), it is worth noting that **2a**−**2c** shows higher PDI controls than **2g** and similar level of controls to **2h**.

We also examined the bulk polymerization of styrene in the presence of azobis(isobutyronitrile) (AIBN) (1.0 equiv) at 60 °C (runs 9−14). The polymerization reached to a high monomer conversion after heating at 60 °C, and polystyrenes with low PDIs were obtained in all cases (PDI = 1.17−1.33). Although the level of PDI control was slightly lower than that without AIBN, it is still acceptable. The lower control in the presence of AIBN can be attributed to an increase in the formation of dead polymers originated from the radical species derived from the azo-initiator upon its consumption.[11] Not only styrene but also *n*-butyl acrylate (100 equiv) was successfully polymerized under the controlled manner by **2a** in the presence of AIBN at 60 °C (87% conversion, M_n = 13 000, PDI = 1.18).

The effects of the substituent L on the group transfer reaction were quantitatively analyzed through kinetic experiments. Polystyrene macrotransfer agents **3a**−**3e** (M_n = 3000−3800, PDIs = 1.06−1.24) were prepared from **2a**−**2e** and styrene and were subjected to polymerization with a large excess of styrene (2.1−3.3 mM) and with different concentrations of AIBN at 60 °C. The time dependent consumption of the macrotransfer agent and the formation of the chain-elongated polymer were analyzed by a gel permeation chromatography (GPC) method previously developed (see Supporting Information).[19] The second-order rate constant k_{ex} for the group transfer reaction and the first-order rate constant k_d for thermal C−TeL bond

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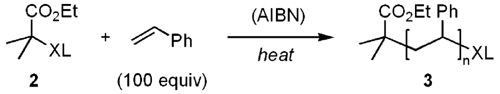
Table 1. Effects of Heteroatom and Substituent of Transfer Agent 2 in Polymerization of Styrene with and without Azobis(isobutyronitrile) (AIBN)



a: XL = TePh, **b**: XL = TeC_6H_5OMe-*p*, **c**: XL = $TeC_6H_5CF_3$-*p*,
d: XL = Te-2-furyl, **e**: XL = TeBu-*n*, **f**: XL = TeMe,
g: XL = $SbMe_2$, **h**: XL = $BiMe_2$

run	transfer agent (XL)	AIBN (equiv)	convn (%)[b]	M_n(theor)[c]	M_n(expt)[d]	PDI[d]
1	**2a** (TePh)	0	99	10 300	12 200	1.08
2	**2b** (TeC_6H_5OMe-*p*)	0	90	9400	11 400	1.09
3	**2c** ($TeC_6H_5CF_3$-*p*)	0	81	8400	9100	1.06
4	**2d** (Te-2-furyl)	0	88	9200	7800	1.23
5	**2e** (TeBu-*n*)	0	99	10 300	11 100	1.25
6	**2f** (TeMe)	0	98	10 200	12 000	1.12
7[e]	**2g** ($SbMe_2$)	0	82	8500	7700	1.14
8[f]	**2h** ($BiMe_2$)	0	96	10 000	10 500	1.07
9	**2a** (TePh)	1.0	100	10 400	9500	1.24
10	**2b** (TeC_6H_5OMe-*p*)	1.0	100	10 400	12 100	1.17
11	**2c** ($TeC_6H_5CF_3$-*p*)	1.0	99	10 300	10 600	1.16
12	**2d** (Te-2-furyl)	1.0	99	10 300	10 800	1.24
13	**2e** (TeBu-*n*)	1.0	100	10 400	10 300	1.33
14	**2f** (TeMe)	1.0	100	10 400	9700	1.22
15[e]	**2g** ($SbMe_2$)	0.5	99	10 300	8700	1.17
16[f]	**2h** ($BiMe_2$)	0.2	100	10 400	10 500	1.09

[a] Bulk polymerization was carried out at 100 °C (for 24 h for runs 1−6, for 48 h for run 7, and for 3 h for run 8) and 60 °C (for 11 h for runs 9−14, for 19 h for run 15, and for 18 h for run 16). [b] Monomer conversion was determined by ^1H NMR. [c] The theoretical number-average molecular weight (M_n) was obtained as the product of monomer/**2** ratio and monomer conversion. [d] The experimental M_n and polydispersity index (PDI) were obtained by size exclusion chromatography calibrated by polystyrene standards. [e] The values were taken from ref 15. [f] The values were taken from ref 18.

Table 2. Kinetic Parameters for the Activation of Polystyrene Heteroatom Transfer Agents 3 (PSt−XL) in Styrene Polymerization at 60 °C[a]

run	XL	k_{ex} ($\times 10^3$ M^{-1} s^{-1})	C_{ex}	k_d ($\times 10^{-5}$ s^{-1})
1	TePh	9.6	28	1.0
2	TeC_6H_5OMe-*p*	12	35	4.4
3	$TeC_6H_5CF_3$-*p*	15	44	0.5
4	TeBu-*n*	3.5	10	1.2
5[b]	TeMe	5.8	17	1.2 [15][c]
6[d]	$SbMe_2$	11	32	∼0
7[e]	$BiMe_2$	18	53	[30][c]
8[f]	I	1.2	3.5	∼0

[a] The XL denotes the heteroatom and its untransferable substituent. The k_d, k_{ex}, and k_p are the rate constants of thermal dissociation of the C−X bond, degenerative transfer reaction, and propagation reaction, respectively, and C_{ex} is the exchange constant ($=k_{ex}/k_p$), where the k_p value of styrene polymerization (340 M^{-1} s^{-1} at 60 °C) was taken from ref 20. [b] The values were taken from ref 6. [c] Data obtained at 100 °C. [d] The values were taken from ref 16. [e] The values were taken from ref 18. [f] The values were taken from ref 10.

dissociation were successfully obtained for each transfer agent (Table 2), except for the 2-furyltellanyl derivative, where sufficient baseline separation by GPC could not be obtained. The exchange constant C_{ex} (k_{ex}/k_p), where k_p is the propagation constant of styrene polymerization (340 M^{-1} s^{-1} at 60 °C),[20] was also calculated. The rate constant k_{ex} for the phenyltellanyl, *p*-methoxyphenyltellanyl, and *p*-trifluoromethylphenyltellanyl group transfer reactions were determined to be $9.6 - 15 \times 10^3$ M^{-1} s^{-1}, the values of which are 1.6−2.6 times faster than that of the methyltellanyl group transfer reaction (runs 1−3 vs 5). As the faster group transfer reaction leads to higher PDI control, the kinetic data are consistent with the observed higher PDI control using **2a**−**2c** possessing aryl substituents than that using methyltellanyl derivative **2f**.[21] Butyltellanyl group undergoes slightly slower transfer reaction than methyltellanyl group (run 4 vs 5), and the results are also consistent with the polymerization results. The faster aryltellanyl group transfer reactions can be explained by considering the stabilizing effect of the aryl group on the transition state by delocalizing the spin density on the tellurium atom. Both electron withdrawing and donating groups at the para position on the phenyl group slightly enhance the group transfer reactions (run 2 and 3 vs 1), suggesting that the transition state possesses weak ambiphilic character. Despite of significant effect of L on the PDI control, its effect on the transition state and its structure would be rather small because the difference of k_{ex} value is within three times. Therefore, the organotellanyl group transfer reaction should take place nearly a concerted manner without formation of any meaningful intermediate in all cases.[8,22]

We recently reported that dimethylbismuthanyl group transfer reaction is among the fastest group transfer reactions so far reported followed by dimethylstibanyl group transfer reaction (runs 6 and 7). However, the current results reveal that the aryltellanyl group transfer reactions takes place similar rate to the dimethylbismuthanyl and dimethylstibanyl ones. All of the results clearly indicate that both heteroatom and untransferable substituents affect the group transfer reactions and, thus, the control over the molecular weight distribution in living radical polymerization. The rate of phenyltellanyl group transfer reaction is 8 times faster than that of the iodine atom transfer reaction (run 1 vs 8), and the results are virtually identical to the previous report involving a vinyl radical.[12] Therefore, the current work also confirms the higher reactivity of the organotellanyl group than that of the iodine atom toward carbon-centered radicals.

The rate constants k_d for the thermal dissociation in the polystyrene dormant species were very small in all cases ($k_d < 5 \times 10^{-5}$ s^{-1} at 60 °C), but the results clearly revealed that organotellurium compounds also serve as radical initiators by C−Te bond homolysis.[23] The results are in sharp contrast to organostibine and iodine transfer agents, which do not show apparent bond homolysis (runs 6 and 8). Since the addition of an azo-initiator causes the formation of dead polymers upon its consumption and decrease the PDI control,[11] efficient thermal generation contributes considerably to the precise control of polymerization reactions.

In summary, we have shown that the untransferable substituent L on the tellurium atom considerably influences the group transfer reaction and leads to an increase in the control over the molecular weight distribution in TERP. A significant high-level of control was observed using organotellurium transfer agents possessing aryl group as the untransferable substituent L. Combining this fact with high functional group compatibility and versatility of TERP, we believe that the new transfer agents will find various synthetic applications for the precision synthesis of varieties of functional polymeric materials.

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Supporting Information Available: Text giving preparation of **2a**−**2e**, typical experimental procedures, and kinetic analyses, a scheme showing the activation process of the polymerization, and figures showing GPC chromatograms, plots of concentrations vs *t*, and NMR spectra, and a table of exprerimental conditions. This material is available free of charge via the Internet at http://pubs.acs.org.

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(23) The k_d value is less accurate than the k_{ex} value because the former is more sensitive to the experimental error. Furthermore, as the k_d values obtained this study were very small, we do not think that detailed comparison of the substituent effects on the k_d is significant.

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