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Kinetic Study on Role of Ditelluride in Organotellurium-Mediated Living Radical Polymerization (TERP)

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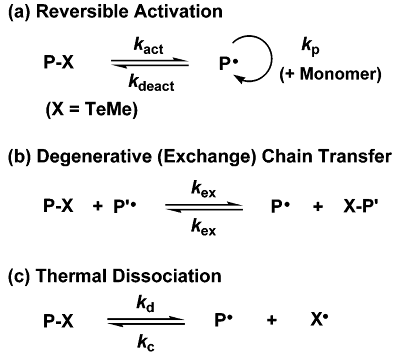
ABSTRACT: The role of dimethyl ditelluride $(MeTe)_2$ for the organotellurium-mediated living radical polymerizations (TERPs) of styrene (St) and methyl methacrylate (MMA) was kinetically studied. For both St and MMA, there was a rapid reversible activation−deactivation process mediated by $(MeTe)_2$, i.e., $P{-}TeMe + MeTe^{\bullet} \rightleftarrows P^{\bullet} + (MeTe)_2$: $(MeTe)_2$ worked as an efficient deactivator of the propagating radical $P^{\bullet}$, and the radical $MeTe^{\bullet}$ worked as a highly reactive activator of the dormant species P−TeMe. This rapid reversible process accounted for the dramatic improvement of the polydispersity controllability with the addition of even a small amount of $(MeTe)_2$ for these polymerizations.

Introduction

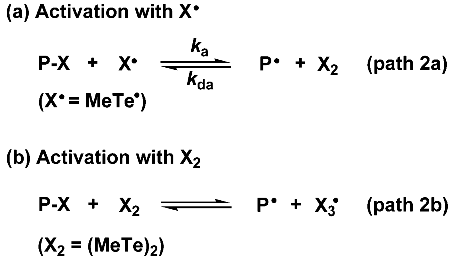
The past decade has witnessed the rapid development of living radical polymerization (LRP) as a useful tool for synthesizing well-defined, low-polydispersity polymers.[1−14] Mechanistically, LRP is based on the reversible activation−deactivation processes (Scheme 1a). The dormant species P−X is activated by thermal, photochemical, and/or chemical stimuli to produce the propagating radical $P^{\bullet}$. In the presence of monomer M, $P^{\bullet}$ will undergo propagation until it is deactivated back to P−X. If a living chain experiences the activation−deactivation cycles frequently enough over a period of polymerization, all living chains will have a nearly equal chance to grow, yielding low-polydispersity polymers (the "living" chain denotes the sum of the dormant and propagating radical chains). Thus, a sufficiently large pseudo-first-order activation rate constant k_{act} (Scheme 1a) is a requisite to obtain low-polydispersity polymers in a reasonable period of time.[4,5]

Organotellurium-mediated LRP (TERP) is a new class of LRP characterized by good polydispersity controllability, high monomer versatility, good tolerance to functional groups, and easiness of block copolymer synthesis and polymer-end transformation.[6−14] We previously studied the activation processes for the TERPs of several monomers including styrene (St), methyl methacrylate (MMA), and methyl acrylate (MA),[10,13] for which the activation mainly occurred by degenerative (exchange) chain transfer (Scheme 1b) with a small contribution of thermal dissociation (Scheme 1c). The exchange constants C_{ex} $(= k_{ex}/k_p)$ for St and MA were large enough to yield low-polydispersity polymers, while that for MMA was too small to yield low-polydispersity polymers, where k_{ex} and k_p are the rate constants of exchange (Scheme 1b) and propagation, respectively. (For the MMA system, due to the small k_{ex}, both rates of activation and deactivation are low.) Yamago et al.[7,10] synthesized poly(methyl methacrylate)s (PMMAs) with low-polydispersities ($M_w/M_n \sim$ 1.15) by the addition of a small amount of dimethyl ditelluride $(MeTe)_2$, without which M_w/M_n exceeded 1.35, where M_n and M_w are the number- and weight-average molecular weights, respectively. This suggests that k_{act} increases in the presence of $(MeTe)_2$. Ditellurides have been known as efficient trapping agents of carbon-centered radicals,[15,16] suggesting that $(MeTe)_2$ may be a good deactivator X_2 (Scheme 2a) in TERP. The role of ditellurides as a deactivator was qualitatively confirmed by the formation of the dormant species P−X by heating a mixture of conventional radical initiator (azo initiator), monomer, and $(MeTe)_2$.[8] In this work, we determined the activation and deactivation rate constants relevant to $(MeTe)_2$ for St and MMA and clarified the role of $(MeTe)_2$ in improving polydispersity controllability.

Scheme 1. Reversible Activation Processes (X = TeMe)



Scheme 2. Possible Activation Mechanisms with $(MeTe)_2$



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Experimental Section

Materials. St (99%, Nacalai Tesque, Japan) and MMA (99%, Nacalai) were purified by fractional distillation. 2,2′-Azobis(isobutyronitrile) (AIBN; 98%, Nacalai) was purified by recrystallization from methanol. Methyl 1-phenylethyl telluride (PE-TeMe) and $(MeTe)_2$ were prepared as described previously.[6,7] 2,2,6,6-Tetramethylpiperidinyl-1-oxy (TEMPO; 99%, Aldrich) and all other reagents were commercially obtained and used as received.

Measurements. The gel permeation chromatography (GPC) analysis was made on a Shodex GPC-101 liquid chromatograph (Tokyo, Japan) equipped with two Shodex KF-804L polystyrene (PSt) mixed gel columns (300 × 8.0 mm; bead size = 7 μm; pore size = 20−200 Å). Tetrahydrofuran (THF) was used as eluent with a flow rate of 0.8 mL/min (40 °C). Sample detection and quantification were made with a Shodex differential refractometer RI-101 calibrated with known concentrations of polymers in THF. The column system was calibrated with standard polystyrenes (PSts) and PMMAs. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a JEOL (Japan Electron Optics Laboratory, Tokyo) JNM-AL400 (400 MHz) at ambient temperature with flip angle 45°, spectral width 7936.5 Hz, acquisition time 4.129 s, and pulse delay 10.0 s. The UV−vis absorption spectra were recorded on a Shimadzu UV-3600 (Kyoto, Japan) with a quartz cell with an optical path length of 1 cm. The sample concentration was 1.0 mM, for which spectroscopic grade benzene was used as a solvent.

Polymer−Methyl Tellurides. A PSt−TeMe (M_n = 3000 and M_w/M_n = 1.17) and a PMMA−TeMe (M_n = 2500 and M_w/M_n = 1.07) were prepared as described previously.[13] The chain extension test[17] showed that, for both cases, the polymer contained 3% of potentially inactive species without a TeMe moiety at the chain end, for which the experimental data shown below have been corrected.

Determination of Deactivation Rate Constants. A mixture of a monomer (1 mL), AIBN (1.0 mM), and $(MeTe)_2$ (0−3.0 mM) in a Schlenk flask was heated at 60 °C for 10 min under an argon atmosphere, diluted by THF, and analyzed by GPC.

Determination of Activation Rate Constants. The above-described polymer−methyl tellurides were used as probe adducts (P_0−Xs). A mixture of a monomer (3 mL), a P_0−X (5.0 mM), $(MeTe)_2$ (0−3.0 mM), and AIBN (1 mM) in a Schlenk flask was heated at 60 °C under an argon atmosphere. After a prescribed time *t*, an aliquot (0.1 mL) of the solution was taken out by a syringe, quenched to room temperature, diluted by THF to a known concentration, and analyzed by GPC.

Light Irradiation Experiment. A mixture of deuterated toluene (toluene-d_8; 0.8 mL), PE-TeMe (20 mM), TEMPO (20 mM), and $(MeTe)_2$ (20 mM) in an NMR tube (with the diameter of 5 mm) was irradiated by visible light (at a wavelength λ of 470 nm) at room temperature under an argon atmosphere with a 300 W xenon lamp (MAX-301, Asahi Spectra, Japan) with an optical band-pass filter (FX0470, Asahi Spectra, λ = 470 ± 10 nm). The distance between the sample and the light source was 11.5 cm. The intensity of the light was 70% of the full power. The sample was analyzed by ^{1}H NMR.

Results and Discussion

Deactivation. We determined the deactivation rate constant k_{da} (Scheme 2a) for $(MeTe)_2$ by the Mayo method.[18] The Mayo method has been used to determine the deactivation rate constants for copper-catalyzed atom transfer radical polymerizations[19] and dithioester-mediated LRPs.[20] A solution of MMA or St with a fixed amount of AIBN (1 mM) and various amounts of $(MeTe)_2$ (0.5−3 mM for MMA and 0.03−0.27 mM for St) was heated at 60 °C for 10 min. The alkyl (free) radical produced by the decomposition of AIBN will add to the monomer until it is deactivated by X_2 to form P−X and $X^\bullet$ ($MeTe^\bullet$) (Scheme 2a) or by $X^\bullet$ to form P−X. The $X^\bullet$ can combine not only with $P^\bullet$ but also with $X^\bullet$ with the probabilities *f* and 1 − *f*, respectively. Consequently, one X_2 molecule deactivates (1 + *f*) molecules of $P^\bullet$. The *f* will decrease with $[X^\bullet]$ (hence $[X_2]$), ranging from 1 to 0. We here assume a constant *f* for the examined range of $[X_2]_0$. Then, if the activation of the formed P−X is negligible, as in the present case with a short polymerization time (10 min), the number-average degree of polymerization x_n of the product polymer is given by eq 1, in which R_t and R_{tr} are the rates of termination (self-termination of $P^\bullet$) and conventional chain transfer (e.g., transfer to monomer), respectively.

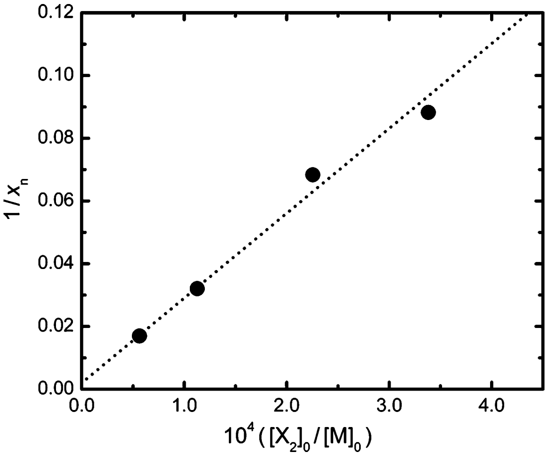

Figure 1. Plot of $1/x_n$ vs $[X_2]_0/[M]_0$ for the methyl methacrylate (MMA)/$(MeTe)_2$/azobis(isobutyronitrile) (AIBN) system (60 °C): $[(MeTe)_2]_0$ = 0.5−3.0 mM; $[AIBN]_0$ = 1.0 mM. The x_n is the number-average degree of polymerization, X_2 is $(MeTe)_2$, and M is monomer (MMA).

$$x_n = \frac{k_p[M][P^\bullet]}{R_t + R_{tr} + (1+f)k_{da}[X_2][P^\bullet]} \tag{1}$$

When R_t and R_{tr} are negligibly small compared with $(1 + f)k_{da}[X_2][P^\bullet]$ for a sufficiently high $[X_2]$, eq 1 will take the form shown in eq 2.

$$\frac{1}{x_n} = \frac{(1+f)k_{da}}{k_p}\frac{[X_2]}{[M]} \tag{2}$$

For the present experiments, the decays of $[X_2]$ and [M] for 10 min were so small (<10% and <0.1% decays, respectively) that x_n may be assumed to be constant during the polymerization and that the $[X_2]$ and [M] in eq 2 may be approximated to be those at $t = 0$, $[X_2]_0$ and $[M]_0$, respectively. Figure 1 shows the plot of $1/x_n$ vs $[X_2]_0/[M]_0$ for MMA. The plot was approximately linear with the intercept close to zero (in this scale of the ordinate axis), suggesting the validity of eq 2 in the studied condition. The slope of the straight line gave $(1 + f)k_{da}/k_p = 290$. Since $f = 0−1$, we had k_{da}/k_p = 145−290. This value is large enough for $(MeTe)_2$ to be an efficient deactivator: even with a small $[X_2]$ of 10 mM, the relative rate of propagation (k_p[M]) to the deactivation ($k_{da}[X_2]$) is only about 5 (for $[M]_0$ = 10 M in bulk and f = 0.5). With the known k_p (830 M^{-1} s^{-1}),[21] k_{da} was calculated to be 1.2×10^5−2.4×10^5 M^{-1} s^{-1}. Figure 2 shows the Mayo plot for St. The $1/x_n$ was approximately proportional to $[X_2]_0/[M]_0$, yielding k_{da}/k_p = 1000−2000. With the known k_p (340 M^{-1} s^{-1}),[22] we had k_{da} = 3.4×10^5−6.8×10^5 M^{-1} s^{-1}. Thus, $(MeTe)_2$ is an efficient deactivator for both St and MMA polymerizations. The k_{da}/k_p and k_{da} values for St are slightly larger than those for MMA (about 7 and 3 times, respectively), meaning that $(MeTe)_2$ is more reactive with $PSt^\bullet$

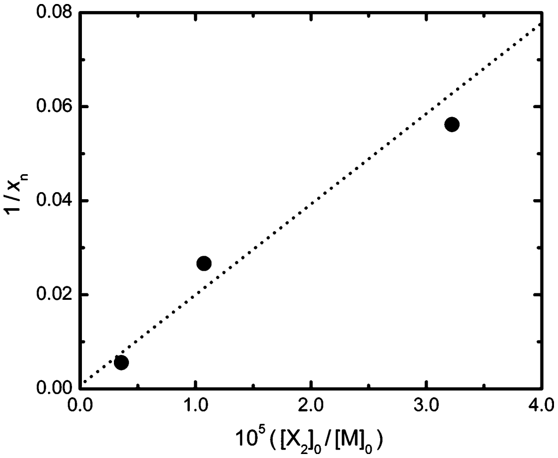

Figure 2. Plot of $1/x_n$ vs $[X_2]_0/[M]_0$ for the styrene (St)/$(\mathrm{MeTe})_2$/azobis(isobutyronitrile) (AIBN) system (60 °C): $[(\mathrm{MeTe})_2]_0 = 0.03{-}0.27$ mM; $[\mathrm{AIBN}]_0 = 1.0$ mM. The x_n is the number-average degree of polymerization, X_2 is $(\mathrm{MeTe})_2$, and M is monomer (MMA).

than PMMA$^•$. There has been a k_{da} value reported for ditelluride: the k_{da} of 5-hexenyl radical with diphenyl ditelluride $(\mathrm{PhTe})_2$ was 4.8×10^7 $\mathrm{M^{-1}\ s^{-1}}$.[15] This value is much larger than those obtained in this work. As the reactivity of carbon-centered radicals highly depends on their substituents, such as in the addition reaction,[23] the observed difference in k_{da} must be attributed to the nature of the alkyl radicals and also the substituents on the Te atom (Me vs Ph).

Activation. We then determined k_{act} in the presence of $(\mathrm{MeTe})_2$ by the GPC peak resolution method.[4,5,24] A solution of MMA with a fixed amount of PMMA−TeMe ($M_n = 2500$, $M_w/M_n = 1.07$) as a probe $P_0{-}X$ (5 mM), a fixed amount of AIBN (1 mM), and various amounts of $(\mathrm{MeTe})_2$ (0−3 mM) was heated at 60 °C. Similarly, a St solution of PSt−TeMe ($M_n = 3000$, $M_w/M_n = 1.17$) (5 mM), AIBN (1 mM), and $(\mathrm{MeTe})_2$ (0−0.27 mM) was heated at 60 °C. When a $P_0{-}X$ is activated to $P_0^•$, the $P_0^•$ will propagate until it is deactivated to give a new adduct $P_1{-}X$. (The subscripts 0 and 1 denote the numbers of activation.) Since $P_0{-}X$ and $P_1{-}X$ are generally different in chain length and its distribution, they may be distinguishable by GPC. By following $[P_0{-}X]$, k_{act} can be determined from eq 3, in which I_0 and I are the concentrations of $P_0{-}X$ at times zero and t, respectively.

$$\ln(I_0/I) = k_{act}t \tag{3}$$

With the low $[P_0{-}X]_0$ value of 5 mM in this work, a large number of monomer units were added to $P_0^•$ during an activation−deactivation cycle,[4,5,25] which allowed accurate GPC peak resolution, i.e., accurate estimation of I (Supporting Information). Figure 3a shows the plot of $\ln(I_0/I)$ vs t for MMA. The plot gave a linear line passing through the origin, in all examined cases, from the slope of which we obtained k_{act}. Importantly, as Figure 3a shows, k_{act} increased with an increase of $[X_2]_0$.

The activation for this system possibly occurs via degenerative chain transfer (Scheme 1b), thermal dissociation (Scheme 1c), and the activation due to $(\mathrm{MeTe})_2$. If these processes coexist, k_{act} will take the form shown in eq 4

$$k_{act} = k_{ex}[P^•] + k_d + k^{app}[X_2] \tag{4}$$

in which k_d (Scheme 1c) is the thermal dissociation rate constant and k^{app} is the apparent second-order activation rate constant due to X_2. (The possible activation processes due to X_2 are given in Scheme 2 and will be discussed later.)

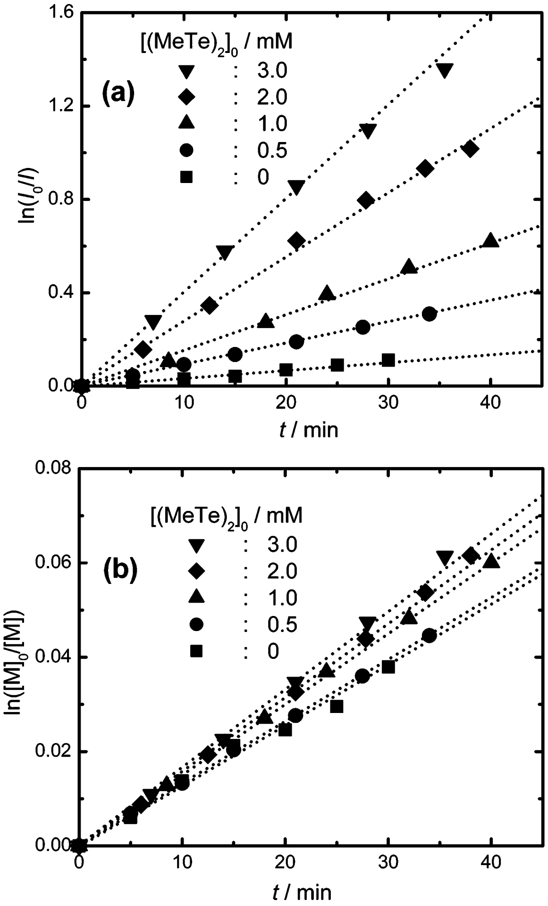

Figure 3. Plots of (a) $\ln(I_0/I)$ and (b) $\ln([M]_0/[M])$ vs t for the methyl methacrylate (MMA)/poly(methyl methacrylate)−TeMe ($P_0{-}X$)/azobis(isobutyronitrile) (AIBN)/$(\mathrm{MeTe})_2$ system (60 °C): $[P_0{-}X]_0 = 5.0$ mM; $[\mathrm{AIBN}]_0 = 1.0$ mM; $[(\mathrm{MeTe})_2]_0$ as indicated in the figure. The I is $[P_0{-}X]$, and M is monomer (MMA).

Figure 3b shows the plot of $\ln([M]_0/[M])$ vs t for MMA (for the same system as shown in Figure 3a). The plot was linear, and the slope of the line, which corresponds to $k_p[P^•]$, was approximately the same for all cases. (The $[P^•]$ slightly increased with $[X_2]_0$ for an unclear reason, but the increase was minor in any case.) This means that the $k_{ex}[P^•]$ term in eq 4 was almost the same for all examined values of $[X_2]_0$. Figure 4 shows the plot of k_{act} vs $[X_2]_0$. The k_{act} linearly increased with an increase of $[X_2]_0$. The intercept of the straight line represents $k_{ex}[P^•] + k_d$ (approximately invariable for the present experiments (see above)), and the slope of the line represents k^{app} to be 0.2 $\mathrm{M^{-1}\ s^{-1}}$. Figure 5 shows the plot of k_{act} vs $[X_2]_0$ for St. The k_{act} linearly increased with an increase of $[X_2]_0$, as in the MMA system, and $[P^•]$ (data not shown) was also almost the same for all examined $[X_2]_0$. From the slope of the straight line in Figure 5, we obtained $k^{app} = 8.8$ $\mathrm{M^{-1}\ s^{-1}}$. The k^{app} value for St is about 45 times larger than that for MMA.

Two possible mechanisms for the activation of P−X due to X_2 are (1) the reaction of P−X with $X^•$, which is formed from X_2 by the deactivation of $P^•$ (Scheme 2a), and (2) the direct reaction with X_2 to form $P^•$ and $X_3^•$ (Scheme 2b). To examine the latter possibility, we heated a toluene-d_8 solution of PE-TeMe (methyl 1-phenylethyl telluride, a low-mass model of PSt-TeMe) (20 mM), $(\mathrm{MeTe})_2$ (20 mM), and TEMPO (20 mM) at 60 °C. If PE−TeMe is activated, the produced $\mathrm{PE}^•$ will predominantly be trapped with TEMPO to form PE−TEMPO

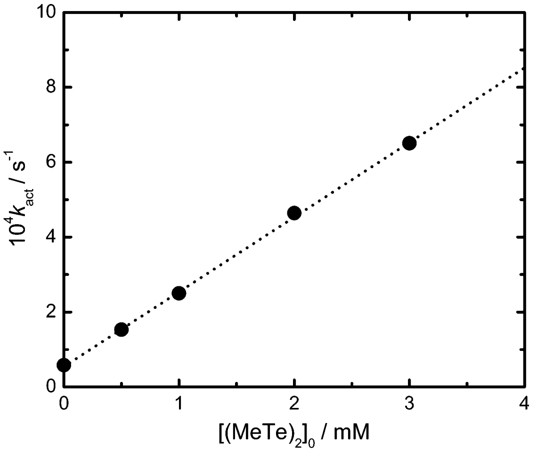

Figure 4. Plot of k_{act} vs $[(MeTe)_2]_0$ for the methyl methacrylate (MMA) system in Figure 3. The k_{act} is the pseudo-first-order activation rate constant (Scheme 1a).

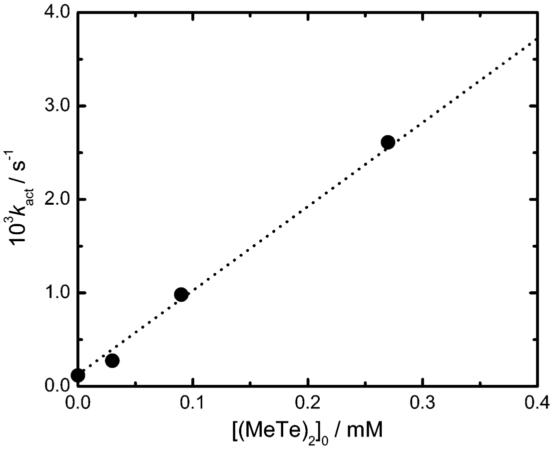

Figure 5. Plot of k_{act} vs $[(MeTe)_2]_0$ for the styrene (St)/polystyrene−TeMe (P_0−X)/ azobis(isobutyronitrile) (AIBN)/$(MeTe)_2$ system (60 °C): $[P_0\text{−}X]_0 = 5.0$ mM; $[AIBN]_0 = 1.0$ mM; $[(MeTe)_2] = 0\text{−}0.27$ mM. The k_{act} is the pseudo-first-order activation rate constant (Scheme 1a).

rather than deactivated by $(MeTe)_2$ to form PE−TeMe again, since the rate constant of the former reaction (2.4×10^8 M^{-1} s^{-1})[26] is much larger than that of the latter one ($(3.3\text{−}6.6) \times 10^5$ M^{-1} s^{-1} (for PSt$^\bullet$) (see above)). This is a so-called nitroxide-trapping experiment.[27−29] No formation of PE−TEMPO was observed by ^{1}H NMR analysis after the heat treatment for 10 h. This result clearly ruled out the occurrence of path 2b (Scheme 2b).

We then examined path 2a (Scheme 2a) by carrying out the same experiment under visible light irradiation producing X$^\bullet$ by the photolysis of X_2[30] at room temperature. Figure 6 shows the UV−vis absorption spectra of $(MeTe)_2$ (solid line) and PE−TeMe (broken line). The absorption band appeared at <600 nm for $(MeTe)_2$ and at <450 nm for PE−TeMe. To avoid the direct photolysis of PE−TeMe, the irradiation experiment was made at $\lambda = 470$ nm. Figure 7 shows the ^{1}H NMR spectra before and after irradiation (10 and 20 min). As time elapsed, the intensity of the signal at 4.2 ppm for the methine proton (**a**) of PE−TeMe decreased, while that of the signal at 4.8 ppm for the methine proton (**a′**) of PE−TEMPO increased. The reaction extent calculated from the intensities of the two signals was 24 and 48% for 10 and 20 min, respectively. This result clearly shows that PE−TeMe is activated by MeTe$^\bullet$ (path 2a). In the actual polymerization under thermal conditions, the deactivation of P$^\bullet$ with $(MeTe)_2$ provides MeTe$^\bullet$, which serves as an activator

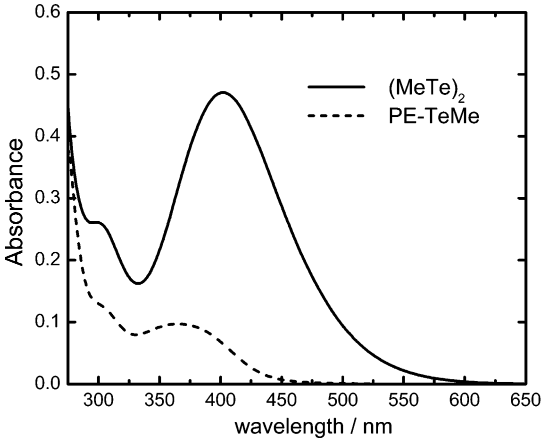

Figure 6. UV−vis spectra of $(MeTe)_2$ (solid line) and methyl 1-phenylethyl telluride (PE−TeMe) (broken line) in benzene (room temperature): $[(MeTe)_2] = [PE\text{−}TeMe] = 1.0$ mM.

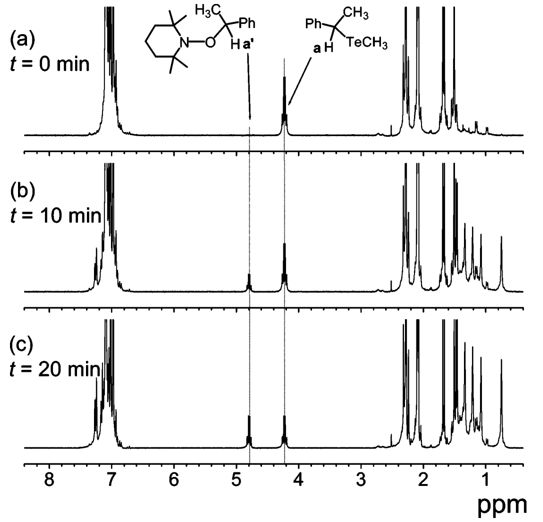

Figure 7. ^{1}H NMR spectra for the mixture of methyl 1-phenylethyl telluride (PE−TeMe), $(MeTe)_2$, and 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) in toluene-d_8 under visible light irradiation at $\lambda = 470$ nm (room temperature): $[PE\text{-}TeMe]_0 = [(MeTe)_2]_0 = [TEMPO]_0 = 20$ mM.

of P−X. Thus, the $k^{app}[X_2]$ term in eq 4 is identical to $k_a[X^\bullet]$, where k_a is defined in Scheme 2a. The observed difference in k^{app} for St and MMA systems is hence ascribed to the differences in k_a and/or $[X^\bullet]/[X_2]$.

This is the first experimental evidence for the occurrence of the homolytic substitution reaction of tellurium-centered radicals with organotellurium compounds to generate carbon-centered radicals, though this type of reaction has been proposed in some literature.[26,31] While chalcogen radicals are believed to be inert to this type of reaction,[28,31] our results clearly demonstrate their high reactivities. Despite the observed high reactivity toward the homolytic substitution reaction, the tellurium-centered radicals show low reactivity toward addition reactions to alkynes and alkenes.[30] Thus, the X$^\bullet$ generated from X_2 does not initiate polymerization. If it occurs, the observed high controllability would not be realized. These seemingly conflicting reactivities of tellurium-centered radicals play crucial roles for the polydispersity control in TERP in the presence of ditellurides.

It is important to note that, as Figures 4 and 5 show, k_{act} (a pseudo-first-order activation rate constant (Scheme 1a)) increased by an order of magnitude by the addition of 10^{-2} and 10^{-3} M $(MeTe)_2$ for the MMA and St polymerizations,

Table 1. Polymerization of Styrene (St) Including Methyl 1-phenylethyl Telluride (PE−TeMe) (40 mM) and Azobis(isobutyronitrile) (AIBN) (20 mM) with and without $(MeTe)_2$ at 60 °C for 8 h

$[(MeTe)_2]$/mM	conversion/%	M_n	M_w/M_n
1.0	27	5900	1.18
0	27	5600	1.48

respectively, in the examined conditions. This explains why low-polydispersity PMMAs are obtainable even with a small amount of $(MeTe)_2$, as previously reported,[7,10] and also suggests that such an improvement of polydispersity control should be attained for St, too, which has not been examined before. The improvement for the St polymerization will be observed particularly at low conversions, since low polydispersities are achievable at high conversions even without $(MeTe)_2$. (A sufficiently large number of activation−deactivation cycles are attained at a high conversion even without $(MeTe)_2$ due to degenerative chain transfer (Scheme 1b).) To confirm this, we carried out a St polymerization including PE−TeMe (40 mM) and AIBN (20 mM) with and without a catalytic amount (1 mM) of $(MeTe)_2$ at 60 °C for 8 h. A low-polydispersity PSt with $M_n = 5900$ and $M_w/M_n = 1.18$ (conversion = 27%) was obtained with $(MeTe)_2$, while a PSt with $M_n = 5600$ and $M_w/M_n = 1.48$ (conversion = 27%) was formed without it (Table 1). Thus, $(MeTe)_2$ has an expected effect for St polymerization, too.

Another interesting implication of this work is possible development of a photoinduced TERP using the photolytic formation of $X^\bullet$ from X_2 and the subsequent activation. This is currently examined in our laboratory.

Conclusions

$(MeTe)_2$ worked as an efficient deactivator to produce $MeTe^\bullet$, and $MeTe^\bullet$ worked as a highly reactive activator, resulting in a dramatic increase of k_{act} with an increase of $[(MeTe)_2]$, for both St and MMA polymerizations (Scheme 2a). This accounts for the significant improvement of the polydispersity controllability with even a small amount of $(MeTe)_2$ for these polymerizations. Both k_{da} (Scheme 2a) and k^{app} (apparent activation rate constant with $(MeTe)_2$ defined in eq 4) were larger for St than MMA. The work of a ditelluride as a deactivator and that of a tellurium-centered radical as an activator would also appear for other tellurides with different substituents (other than Me used in this work).

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Supporting Information Available: GPC chromatograms for the determination of k_{act}. This material is available free of charge via the Internet at http://pubs.acs.org.

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