

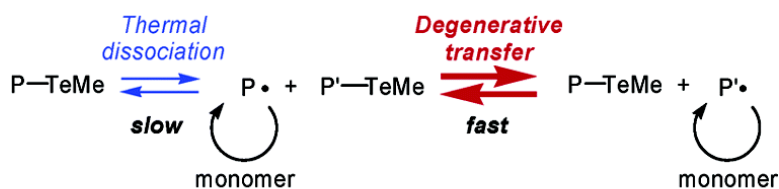
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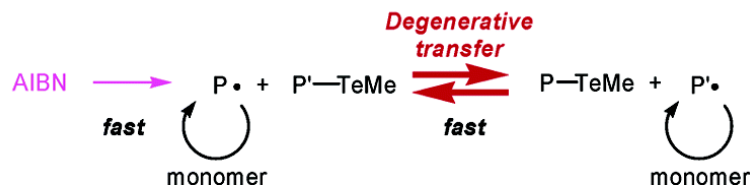
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TERP at high temperature without conventional radical initiator.



TERP at low temperature with conventional radical initiator.



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Mechanism-Based Invention of High-Speed Living Radical Polymerization Using Organotellurium Compounds and Azo-Initiators

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Living radical polymerization (LRP) is now recognized as a powerful method to synthesize nanostructural macromolecules with defined structures possessing various functional groups which are not compatible with ionic or metal-catalyzed polymerization conditions.^{1,2} Organotellurium-mediated living radical polymerization (TERP) is a new class of LRP, which exhibits unique features in terms of versatility, molecular weight controllability, functional group compatibility, and ease of polymer-end transformations.³ Despite its synthetic potential, the largest disadvantage of this method is the unusually long time required for completion of the polymerization (13–24 h), even at relatively high temperatures (80–100 °C). The reaction conditions would be unacceptable for monomers that undergo unwanted side reactions at high temperatures and thus would also be unsuitable from an industrial point of view. Therefore, development of a new TERP system, which promotes the polymerization under much milder conditions, is highly desirable.

LRP relies on the reversible generation of active carbon-centered radical species (P^{*}) from the dormant species (P–X) as in Scheme 1a.¹ Two activation mechanisms are possible for TERP (X = TeMe), namely the thermal dissociation (TD, Scheme 1b) and the degenerative chain transfer (DT, Scheme 1c) mechanisms. We have proposed that TERP mainly proceeds via the TD mechanism based on the observation of reversible carbon–tellurium bond cleavage on thermolysis⁴ and on the similarity of bond dissociation energies of the methyltellanyl initiators (X = TeMe) and 2,2,6,6-tetramethyl-1-piperinyloxy (X = TEMPO) derivatives with the same P moiety.^{2a,3a} During the course of our kinetic studies to elucidate the mechanism of TERP, we found that the TERP predominantly proceeds by DT rather than TD. We first report here the kinetic studies of TERP. We also report a new and extremely mild system for TERP based on the mechanistic studies; polymerization of styrene, acrylate, and methacrylate derivatives can now be completed within 2–11 h at 40–60 °C and gives the desired polymers with the expected molecular weight and narrow molecular weight distributions.

The rate constant k_{act} for the generation of active radical species from the dormant species can be expressed as $k_{act} = k_d + k_{ex}[P^*]$, where k_d and k_{ex} are the first- and second-order rate constants for the TD and DT processes, respectively. Thus, the measurement of k_{act} as a function of $[P^*]$ unambiguously determines the contributions of the TD and DT processes. The rate constant k_{act} of the polystyrene macroinitiator **1** ($M_n = 3000$, PDI = 1.17) was obtained in the polymerization of styrene with **1** (5.4 mM) at 60 and 100 °C in the

Scheme 1

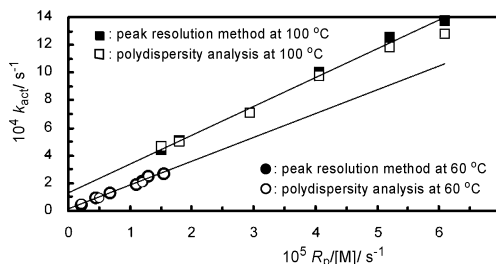
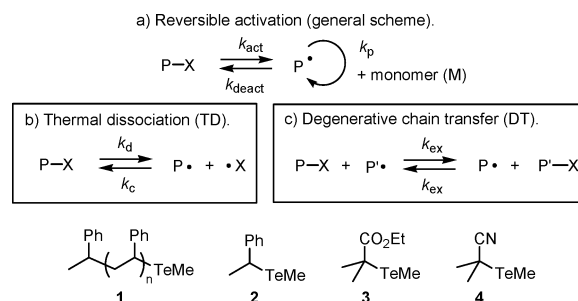


Figure 1. Plot of k_{act} vs $R_p/[M]$ for **1** in the styrene polymerization at 60 °C (circles) and 100 °C (squares): $[1]_0 = 5.4$ mM; $[AIBN]_0 = 0$ –26 mM (60 °C); $[VR-110]_0 = 0$ –100 mM (100 °C). The k_{act} was determined by the GPC peak resolution method (● and ■) and the polydispersity analysis method (○ and □).⁷ See also Supporting Information.

presence of 2,2'-azobisisobutyronitrile (AIBN: 0–26 mM at 60 °C) or 2,2'-azobis(2,4,4-trimethylpentane) (VR-110: 0–100 mM at 100 °C) as a radical source by observing the consumption of **1** by gel permeation chromatography, as described previously (peak resolution method).⁵ We also determined $[P^*]$ by measuring the polymerization rate $R_p (= k_p[M][P^*])$ as a function of the added azo-initiator concentration, where the propagation rate constant k_p was taken from the literature⁶ and $[M]$ is the monomer concentration.

Correlation of k_{act} and $R_p/[M]$ reveals that the k_{act} linearly increases with an increase of R_p at both 60 and 100 °C (Figure 1, solid circles and squares). Thus, we could obtain $k_d = 1.2 \times 10^{-5}$ and $1.4 \times 10^{-4} s^{-1}$ by the extrapolation to $[P^*] = 0$, and $k_{ex} = 5.7 \times 10^3$ and $2.4 \times 10^4 M^{-1} s^{-1}$ from the slope of the line, which corresponds to the exchange constant $C_{ex} (= k_{ex}/k_p) = 17$ and 20 at 60 and 100 °C, respectively. The k_{act} obtained by the polydispersity analysis⁷ (empty circles and squares) was almost identical to the one obtained by the peak resolution method. The results clearly suggest that TERP proceeds via both the TD and DT mechanisms. *This is the first example quantitatively demonstrating that a certain LRP proceeds via two competing pathways.*

The k_d value of TERP is very similar to that of the nitroxide-mediated LRP (NMP) ($k_d = 1.3 \times 10^{-4} s^{-1}$ at 100 °C for X = TEMPO),⁵ and the results are consistent with the similarity of bond

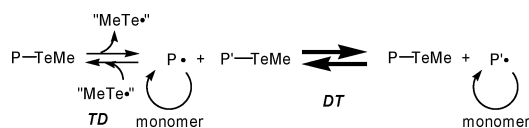
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Scheme 2

Table 1. Polymerization with **4** in the Presence of AIBN

entry	monomer ^a	method ^b	conditions (°C/h)	yield (%)	M_n^c	PDI ^e
1	St	A	60/11	94	11300	1.17
2	St	A ^d	60/11	82	4300	1.11
3	St	A ^e	40/23	82	7400	1.21
4	St	B	100/16	96	9200	1.17
5	BA	A	60/4	99	15900	1.19
6	BA	B	100/24	89	10300	1.13
7	MMA	A	60/2	93	11000	1.36
8 ^f	MMA	A	60/2	98	9600	1.15
9 ^f	MMA	B	80/13	92	9700	1.18
10 ^g	NIPAM	A	60/3	99	30600	1.09
11 ^g	AN	A	60/6	99	37800	1.16
12 ^f	HEMA	A	60/2	99	22300	1.18

^a St: styrene, BA: *n*-butyl acrylate, MMA: methyl methacrylate, NIPAM: *N*-isopropyl acrylamide, AN: acrylonitrile, HEMA: 2-hydroxyethyl methacrylate. ^b A: A mixture of **4** (1 equiv), AIBN (1 equiv) and monomer (100 equiv) was heated. B: A mixture of **4** (1 equiv) and monomer (100 equiv) was heated. ^c Number-average molecular weight (M_n) and polydispersity index (PDI) were obtained by size exclusion chromatography calibrated by polySt standards for entries 1–4 and 11 and polyMMA standards for others. ^d Two equivalents of **4** was used. ^e V-70 was used instead of AIBN. ^f Dimethyl ditelluride (1 equiv) was added. ^g Reaction was carried out in DMF.

dissociation energies of structurally related organotellurium and nitroxyl compounds. These similarities suggest that the thermally generated radicals from organotellurium compounds initiate the polymerization in the previously reported conditions (80–100 °C). The exchange constant C_{ex} is ca. 5 times higher than that for the iodide-mediated LRP ($C_{ex} = 3.6$ for $X = I$)⁸ and ca. 10 times lower than that for the dithioester derivatives ($C_{ex} = 180$ for $X = SCSMe$).⁹ The results are also consistent with the fact that TERP is more controllable than the iodide-mediated LRP^{2d} but slightly less controllable than the dithioester-mediated LRP, the so-called RAFT process.^{2c}

From these results, we propose the mechanism of TERP as depicted in Scheme 2; the TD of the organotellurium compounds generates the corresponding carbon-centered radicals, which predominantly undergo the DT-mediated polymerization. Recent theoretical calculations suggest that the activation energy of the DT process of organotellurium compounds is much lower than the TD process.^{4b,10} Therefore, the high temperature required for the previous conditions must be due to the slow TD process to generate the active radical species from the dormant organotellurium compounds.

The above conclusion opens the very intriguing possibility that the polymerization would proceed under much milder conditions if one could supply radical species under mild conditions. Indeed, the bulk polymerization of styrene (100 equiv) with the organotellurium initiators **2–4** in the presence of AIBN (1 equiv) was complete within 11 h at 60 °C to give polystyrene with low polydispersity (PDI = 1.17), while the previous conditions required 16 h at 100 °C for completion (Table 1, entry 1 vs 4). The polymerization proceeded even at 40 °C by employing 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70) instead of AIBN (entry 3). The addition of AIBN was found to be remarkably effective for the polymerization of butyl acrylate (BA); the polymerization was complete within 4 h at 60 °C, while the previous conditions required 24 h at 100 °C (entry 5 vs 6). Methyl methacrylate (MMA) also polymerized within 2 h at 60 °C (entries 7–9). These results suggest that the TERP of BA and MMA also proceeds predominantly by the DT mechanism at this temperature. While the rate

enhancement of the LRP in NMP and atom transfer radical polymerization by the addition of radical initiators has been reported,¹¹ this is the first example showing such dramatic rate enhancement while maintaining a high level of molecular weight controllability.

Several features of the new TERP protocol are worth mentioning. First, the addition of a proper amount of AIBN significantly enhances R_p in all cases but does not cause a significant formation of the dead polymer. Therefore, the methyltellanyl group was retained almost completely at the polymer end. Second, the molecular weight of the obtained polymer was controlled by the organotellurium-initiator/monomer ratio (entries 1 and 2). Third, poly(methyl methacrylate) with low polydispersity was obtained by the addition of dimethyl ditelluride (entry 8).^{3b} Finally, this method also possesses broad versatility, and monomers with polar functional groups, such as NIPAM, AN, and HEMA, could also be polymerized in a highly controlled manner (entries 10–12). The versatility and mild reaction conditions of this new method would be suitable for the mass production of structurally defined macromolecules.¹²

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Supporting Information Available: Typical experimental procedures (PDF). This material is available free of charge via the Internet at <http://www.pubs.acs.org>.

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