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Photoinduced Switching from Living Radical Polymerization to a Radical Coupling Reaction Mediated by Organotellurium Compounds

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S Supporting Information

ABSTRACT: An efficient and simple method for the synthesis of symmetric macromolecules by photoinduced switching from radical polymerization to a radical coupling reaction is reported. Structurally well-defined telechelic polyisoprenes and ABA-triblock copolymers were prepared by successive organotellurium-mediated living radical polymerization (TERP) under thermal conditions, followed by a polymer-end radical coupling reaction under photoirradiation.

Modulation of the reaction pathway using external stimuli has been a significant challenge in organic and polymer syntheses, because such methods would considerably expand the structural diversity of products from a limited number of precursors. Although a variety of chemical stimuli have been used for this purpose, physical stimuli, such as thermal and photochemical stimuli, like those used in the pericyclic reactions,[1] are attractive due to their "green" character.

We have already reported that organotellurium-mediated living radical polymerization (TERP) possesses several synthetic advantages over other living radical polymerization (LRP) methods,[2] such as high monomer versatility, high compatibility toward functional groups and solvents,[3] and ease of the living-end transformation for the synthesis of block copolymers[4] and end-functionalized polymers.[5] In addition, we have reported that TERP can be initiated by thermal,[2c,4a] chemical,[6] and photochemical stimuli.[3d] While expanding the synthetic applicability of TERP to dienes, we found that the reaction pathway can be selectively switched from LRP to a radical-coupling reaction (RC) by using photostimuli. Furthermore, this method made it possible to synthesize telechelic polymers and symmetrical ABA-triblock copolymers with controlled macromolecular structures (Scheme 1).

It has been reported that the reaction course can be changed from LRP to RC by adding an excess amount of Cu(0) to polystyrene prepared via Cu(I) catalyzed atom transfer radical polymerization[7] and by adding dienes to polyacrylonitrile, poly(vinyl acetate), and poly(*N*-vinyl pyrrolidone) prepared via cobalt-mediated radical polymerization.[8] However, to the best of our knowledge, there is no report on the selective switching of the reaction course without chemical stimuli.

Scheme 1. Sequential LRP-RC, and Its Application to the Synthesis of ABA-Triblock Copolymers

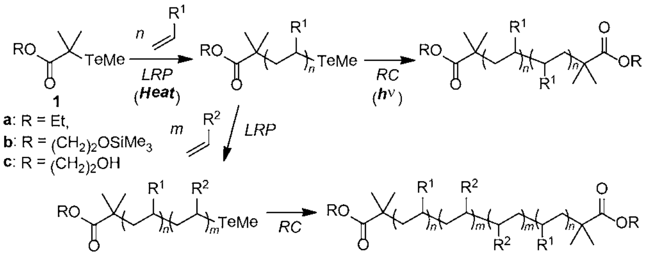

Table 1. Organotellurium-Mediated LRP of Ip[a]

run	Ip (equiv)	$(TeMe)_2$ (equiv)	time (h)	conv (%)[b]	$M_{n(GPC)}$[c] ($M_{n(NMR)}$)	M_w/M_n[c]
1	100	0	24	35	4700 (2500)	1.15
2	100	1	14	25	3500 (1700)	1.10
3	300	1	12	12	6100 (2700)	1.10
4	1000	1	8	8	11500 (5800)	1.12
5	2000	1	8	9	19900 (12100)	1.14
6[d]	100	0	24	44	9300 (3100)	1.43

[a]A mixture of **1a** (1 equiv) and isoprene was heated at 120 °C. [b]Determined from ^{1}H NMR spectroscopy. [c]Determined from GPC calibrated against PSt standards. M_n determined from ^{1}H NMR spectroscopy is shown in parentheses. [d]Polymerization was carried out in the presence of 1-[(1-cyano-1-methylethyl)azo]formamide (1 equiv).

We first examined TERP of isoprene (Ip, 100 equiv) in the presence of organotellurium chain transfer agent (CTA) **1a** (R = Et) under thermal conditions. The monomer conversion reached 35% after heating at 120 °C for 36 h, and polyisoprene (PIp) **2a** with a narrow molecular weight distribution (MWD, M_w/M_n = 1.15, where M_w and M_n refer to weight and number average molecular weights, respectively) was obtained (Table 1, run 1). The $M_{n(GPC)}$ obtained from gel permeation chromatography (GPC) by using polystyrene (PSt) standards was considerably different from the value calculated by ^{1}H NMR [$M_{n(NMR)}$] due to the lack of appropriate standards, but the $M_{n(GPC)}$ is used for the following discussions. ^{1}H NMR spectral analysis showed that the polymer main chain mainly contained (1,4) isomeric units (90%) together with (1,2) and (3,4) units (5% each) (Chart 1).[9] The isomeric ratio is identical to that for

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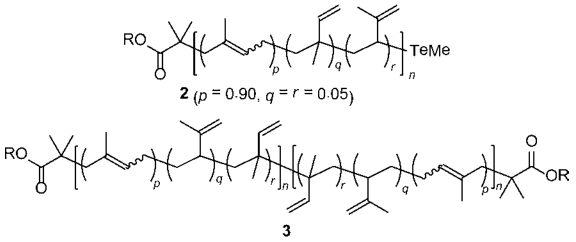
Chart 1. Structure of PIp 2 and Dimer 3



2 (p = 0.90, q = r = 0.05)

3

PIp prepared by using free radical polymerization and other LRP methods,[10] and the results are consistent with the involvement of free radicals in the carbon−carbon bond formation step. Although the polymerization exhibited high MWD control at low monomer conversions, MWD became broad as the monomer conversion increased due to the formation of high molecular weight polymers probably from RC of polymer-end radicals (see Figure S7 in Supporting Information, SI). Therefore, the polymerization was stopped at low monomer conversions in the following experiments.[10a]

The addition of dimethyl ditelluride (1.0 equiv) considerably enhanced the rate of monomer conversion and MWD control (run 2, Figure S8 in SI). The results are consistent with our previous reports on the role of the ditelluride in the polymerizations of styrene and methacrylate.[4a,11,12] Structurally well-controlled PIps with high molecular weights and narrow MWDs ($M_n \approx 19900$, $M_w/M_n < 1.14$) were obtained by increasing the Ip/**1a** ratio (runs 3−5). Although addition of an azo-initiator, 1-[(1-cyano-1-methylethyl)azo]formamide, increased the rate of polymerization,[6] MWD control decreased (run 6). This is because azo-initiator-derived radicals generated significant amounts of PIps which lead to the formation of large amounts of dead polymers.[13]

The RC of **2a** was examined next. After thermal polymerization of Ip (100 equiv), as shown above, crude **2a** (M_n = 1800, M_w/M_n = 1.15, 9% monomer conversion) was irradiated with a 500 W Hg lamp through a >390 nm cutoff filter at room temperature for 1 h.[14] **2a** completely disappeared, and coupling product **3a**, which had an M_n (3500) nearly double that of **2a** and a narrow MWD (1.13), was obtained (Table 2, run 1). The methyltellanyl group was quantitatively recovered as dimethyl ditelluride. The dimeric structure was further confirmed by using matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS), which showed a series of molecular ion peaks corresponding to **3a** (Figure 1). The efficiency of RC (x_c) was determined to be 0.97 using a GPC peak resolution method.[7a,15] On the other hand, RC under thermal conditions at high temperatures was sluggish and did not go to completion even after heating at 140 °C for 24 h (Table 2, run 2, and Figure S12 in SI). Since the dimer forms via a coupling reaction involving polymer-end radicals, the low x_c under thermal conditions is due to the low efficiency of the generation of polymer-end radicals from **2a** and also the potential side reaction at high temperature.

Table 2. Radical Coupling Reaction of PIps[a]

	PIp-TeMe			Product		
run	$M_{n(GPC)}$[b]	M_w/M_n[b]	time (h)	$M_{n(GPC)}$[b]	M_w/M_n[b]	x_c[c]
1	1800	1.15	1	3500	1.13	0.97
2[d]	3000	1.09	24	4100	1.26	0.51
3	3000	1.09	2	5900	1.10	0.95
4	9700	1.09	1	17200	1.11	0.87

[a] A 500 W high-pressure Hg lamp was irradiated through a >390 nm cutoff filter. [b] Determined from GPC calibrated against PSt standards. [c] Coupling efficiency (x_c) calculated by a GPC peak resolution method.[7a,15] [d] The reaction was carried out in the dark at 140 °C in benzene.

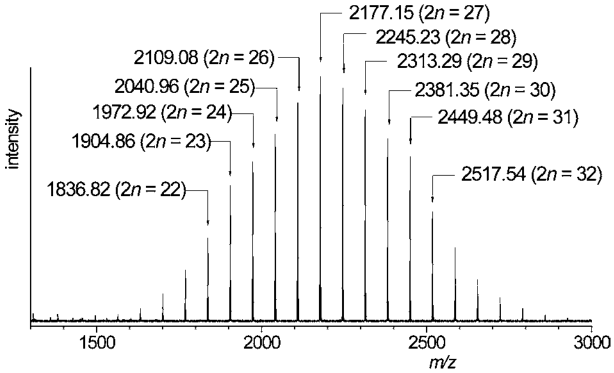


Figure 1. MALDI-TOF MS spectrum of **3a** (Table 2, run 1). The molecular ions were observed as silver ion adducts [$m/z = (M + \mathrm{Ag})^+$].

Selective RC proceeded for higher molecular weight PIps. The corresponding dimers were selectively obtained with a high x_c (0.87−0.95) (Table 2, runs 3 and 4). Since the propagation rate of Ip polymerization was slow at room temperature,[16] dimerization selectively occurs without chain elongation. The results clearly show that selective switching from LRP to RC occurred upon photoirradiation.

Hydroxyl-telechelic PIp **3c** was prepared from either CTA **1b** or **1c** having trimethylsiloxy or hydroxyl groups, respectively. Polymerization of Ip (200 equiv) in the presence of **1b** gave α-trimethylsiloxy PIp **2b** (M_n = 2300, M_w/M_n = 1.11 after 8% monomer conv.), which was converted to **3b** (M_n = 4400, M_w/M_n = 1.12) with high coupling efficiency (x_c = 0.93) by photoirradiation. The silyl group was removed by tetrabutyl ammonium fluoride to give **3c** (M_n = 4200, M_w/M_n = 1.12). Alternatively, **1c** prepared from **1b** could be directly used for the polymerization of Ip to give α-hydroxyl PIp **2c** (M_n = 3200, M_w/M_n = 1.09, 14% monomer conv.), which afforded **3c** (M_n = 6400, M_w/M_n = 1.10) in an excellent coupling efficiency (x_c = 0.96) by photoirradiation.

Symmetric ABA triblock copolymers were synthesized from organotellurium macroCTAs. For example, poly(methyl methacrylate) (PMMA)-TeMe (M_n = 4300, M_w/M_n = 1.16), prepared from **1a** and methyl methacrylate (MMA), was treated with Ip (300 equiv) in the presence of dimethyl ditelluride at 120 °C for 10 h, affording the structurally well-controlled block copolymer PMMA-*b*-PIp-TeMe (M_n = 7000, M_w/M_n = 1.11, 10% monomer conv.). Irradiation of the copolymer afforded symmetric triblock copolymer PMMA-*b*-PIp-*b*-PMMA with a nearly double M_n (12800) and a narrow MWD (1.11) with x_c = 0.92 (Table 3, run 1, Figure 2). The same triblock copolymers with high molecular weight (M_n = 22100 and 28900) were successfully synthesized in a controlled manner (Table 3, runs 2 and 3). Structurally well-defined PSt-*b*-PIp-*b*-PSt (M_n = 17000, M_w/M_n = 1.18) was also synthesized from PSt-TeMe (M_n = 5900, M_w/M_n = 1.15) by using sequential TERP of Ip and RC (Table 3, run 4). Since various di- and triblock copolymers have already been prepared by using TERP,[3e,4a,c,d] such copolymers would be transformed to

Table 3. Synthesis of ABA Triblock Copolymers from Organotellurium MacroCTAs

	MacroCTA			Ip polymerization[a]			AB diblock copolymer		RC[b]	ABA triblock copolymer	
run	structure	$M_{n(GPC)}$[c]	M_w/M_n[c]	equiv	time (h)	conv (%)[d]	$M_{n(GPC)}$[c]	M_w/M_n[c]	x_c[e]	$M_{n(GPC)}$[c]	M_w/M_n[c]
1[f]	PMMA-TeMe	4300	1.16	300	10	10	7000	1.11	0.92	12800	1.11
2[f,g]	PMMA-TeMe	9100	1.18	400	8	7	12300	1.15	0.90	22100	1.13
3[f,g]	PMMA-TeMe	13700	1.16	400	8	6	16600	1.18	0.88	28900	1.15
4	PSt-TeMe	5900	1.15	500	10	8	9700	1.12	0.86	17000	1.18

[a] A mixture of macroCTA (1 equiv), $(TeMe)_2$ (1 equiv), and Ip was heated at 120 °C. [b] The polymerization mixture was irradiated with a 500 W high-pressure Hg lamp through a >390 nm cutoff filter at 20 °C. [c] Determined from GPC calibrated against PMMA or PSt standards. [d] Determined from ^{1}H NMR spectroscopy. [e] Determined from GPC using a peak resolution method.[7a] [f] 1,4-Dioxane was used as a solvent. [g] The polymerization of isoprene was carried out without $(TeMe)_2$.

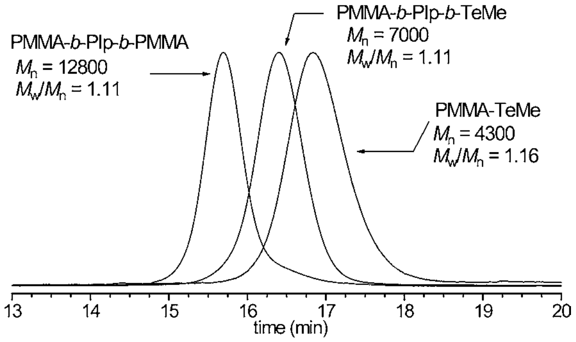


Figure 2. GPC profiles of block copolymerization and RC for the preparation of PMMA-PIp-PMMA (Table 3, run 1). The polymers were analyzed without purification.

the corresponding symmetrical multiblock copolymers under the current conditions.

In summary, Ip was polymerized in a controlled manner by TERP under thermal conditions. Since conjugated dienes are one of the challenging monomers in LRP,[10,17,18] TERP provides a new synthetic route to polydienes with controlled structures. Furthermore, selective switching from LRP to RC upon photoirradiation occurred with high coupling efficiency, and this method provides structurally well controlled telechelic PIps and symmetrical ABA-triblock copolymers. Considering the high versatility of TERP for the synthesis of homo and block copolymers, we believe that the current method would be useful for providing varieties of structurally well controlled new polymers for advanced macromolecular engineering.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthesis of **1b** and **1c**, polymerization and RC reaction procedures, GPC profiles, and NMR spectra of PIp and new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(12) Since dimethyl ditelluride possesses a similar bond dissociation energy to **1**, dimethyl ditelluride would thermally generate a

methyltellanyl radical under the reaction conditions. By reacting the tellanyl radical with **1** or the dormant species generating the initiating radicals, the rate of polymerization was increased.

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(14) Direct irradiation without a cutoff filter led to the formation of a black precipitate, probably the tellurium element, which decreased the irradiation efficiency (see Figure S11 in SI).

(15) For the determination of the coupling efficiency of RC, the equation $x_c = (1 - M_{n(\mathrm{precursor})}/M_{n(\mathrm{Product})})/2$ is often used. However due to the difference of the structure of polyisoprene and polystyrene standards, the GPC peak resolution method should be more reliable. For details about the equation, see ref 7a.

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