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Radical Polymerization Initiated by Electron Transfer Driven C−Si Bond Dissociation

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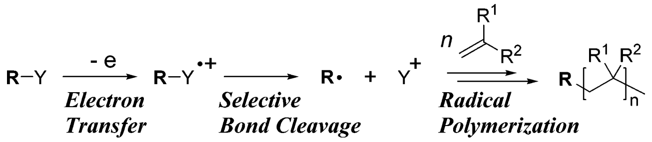
ABSTRACT: New binary systems consisting of benzylsilane(stannanes) and aminium salts initiate radical polymerization. Polymerization of vinyl monomers such as methyl methacrylate and butyl acrylate proceeded under mild conditions to afford the corresponding polymers in moderate to excellent yields. Polymerization of styrene resulted in the formation of oligomers. In contrast, the aminium salts inhibit or retard the radical polymerization of such vinyl monomers. The mechanism may involve initial single electron transfer from a benzylsilane(stannanes) to an aminium salt followed by C−Si bond cleavage to give a benzyl radical, which initiates radical polymerization.

Introduction

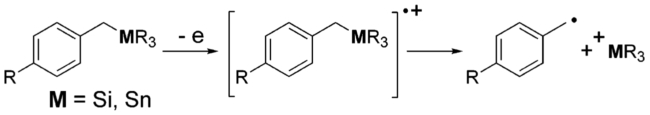
Electron transfer reactions are one of the most fundamental processes in chemistry and biology, and are widely utilized in synthetic organic chemistry.[1] The removal of one electron from neutral organic molecules (R−Y) generates the corresponding radical cation species ($R{-}Y^{\bullet+}$) (Scheme 1). The resulting radical cations are usually unstable transient species which often undergo fragmentation reactions to give neutral organic radicals ($R^{\bullet}$) and cations (Y^{+}). The reactivity patterns of radical cations have been studied for a great number of radical cation reactions[2] which are generated by chemical,[3] electrochemical,[4,5] and photochemical[6] one-electron oxidation reactions. Therefore, the modes of bond cleavage in radical cations are well predictable,[7] and radical cations ($R{-}Y^{\bullet+}$) can be used as precursors of organic radicals ($R^{\bullet}$). Thus, we envisaged a new radical initiating system by employing radical cations as precursors of radicals (Scheme 1).

Scheme 1. Radical Initiating System by Employing Radical Cation

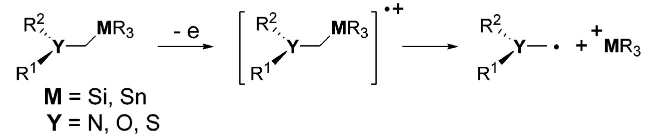


Scheme 2. Substrates toward Single Electron Transfer

(a) (π + σ) system



(b) (n + σ) system



The redox potentials of substrates must be controlled for achieving the selective oxidation. Thus, the precursors of radical cations (R−Y) should have lower oxidation potentials than other substrates in the polymerization system. The concept of electroauxiliary has been developed in our group recently.[4] An electroauxiliary lowers the oxidation potential of the substrate molecule to facilitate the electron transfer. For example, introduction of a trimethylsilyl group ($-SiMe_3$) as an electroauxiliary on the benzylic carbon lowers the oxidation potential significantly (Scheme 2a). The silyl group also facilitates electron transfer from a heteroatom. The interaction of a C−Si σ orbital with a neighboring nonbonding orbital of a heteroatom raises the HOMO level to facilitate the electron transfer (Scheme 2b). The resulting radical cation is also stabilized by interaction with the C−Si σ orbital. Another important feature of the silyl group is the selective cleavage of the C−Si bond in the radical cation. For example, the oxidative electron-transfer reactions of benzylsilanes[8−11] and allylsilanes[8] lead to facile cleavage of the C−Si bond. In the case of enol silyl ethers,[12] selective O−Si bond cleavage takes place upon oxidation. Similar oxidative bond cleavage reactions were also reported for analogous germanium[13] and tin[10,14] compounds. Mechanistic and theoretical studies have clarified the detailed mode of C−Si bond cleavage in radical cations which fragment to the corresponding carbon-centered radicals and formal silyl cations. The fragmentation seems to be assisted by nucleophilic attack on silicon.[11]

Free radical polymerization is very important for the synthesis of macromolecules. Available methods for initiation of conventional free radical polymerization are often based on the thermal homolytic cleavage of covalent bonds such as in the thermal decompositions of azo-compounds or peroxides. Photoinduced bond cleavage reactions are also used for initiation of free radical polymerization.[15] However, photochemical initiation systems require the continuous irradiation during polymerization, and sometimes this process compete with the direct photochemical initiation. On the basis of the discussion described above, we envisaged a new initiating system using electron-transfer driven C−Si bond cleavage. In the literature, there are only a few reports on the initiation of radical polymerization by photoinduced C−Si bond cleavage.[16] In this paper, we report a new method for the generation of radicals for polymerization utilizing chemically induced electron-transfer processes followed by facile C−Si bond cleavage.

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Scheme 3

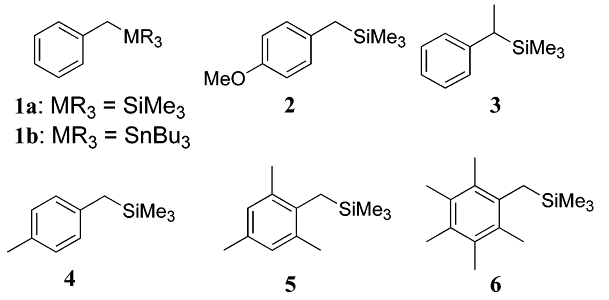


Table 1. Oxidation Potentials of Benzylsilanes and Benzylstannanes

substrates	**1a**	**1b**	**2**	**3**	**4**	**5**	**6**
E_{ox} (V)[a]	1.68	1.25	1.37	1.63	1.55	1.48	1.36

[a] Oxidation potentials (peak potentials) (V vs SCE) were determined in 0.3 M MeCN solution of $Bu_4N(C_6F_5)_4$ at room temperature using Osteryoung square wave voltammetry.

Scheme 4. Preparation of Triarylaminium Salts

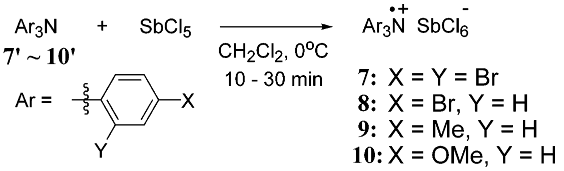


Table 2. Oxidation Potentials of Triarylamines

substrates	**7′**	**8′**	**9′**	**10′**
E_{ox} (V)[a]	1.68	1.22	0.85	0.65

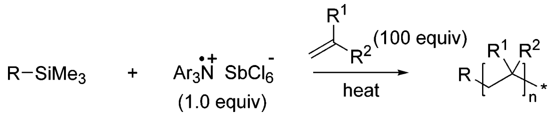
[a] Oxidation potentials (peak potentials) (V vs. SCE) were determined in 0.3 M MeCN solution of $Bu_4N(C_6F_5)_4$ at room temperature using Osteryoung square wave voltammetry.

Results and Discussion

Preparation of Substrates. We selected benzylsilanes and -stannanes as precursors of free radical polymerization initiators. Benzylsilanes and -stannanes were synthesized from the corresponding organomagnesium reagents and trimethylsilyl chloride or tributylstannyl chloride, respectively (Scheme 3). The oxidation potentials of the thus-obtained compounds were determined by Osteryoung square wave voltammetry[17] (Table 1). The introduction of electron donating groups such as methoxy and methyl groups on the phenyl ring of benzyltrimethylsilanes clearly reduced the oxidation potential significantly. Switching from silicon to tin also leads to a remarkable decrease of the oxidation potential, and benzyltributylstannane (**1b**) possess the lowest oxidation potential (1.25 V) among the precursors examined.

Organic oxidants seemed to be suitable for the oxidation of benzylsilanes and -stannanes to initiate the polymerization in homogeneous solution. Triarylaminium salts are known to be persistent radical cations,[18] and serve as effective organic single electron-transfer reagents. Advantages of triarylaminium salts involve easy fine-tuning of oxidizing ability by selecting appropriate subsitituents on the aryl rings. Thus, we synthesized several substituted triarylamines and oxidized them using antimony pentachloride in CH_2Cl_2 to obtain the corresponding triarylaminium hexachloroantimonates (Scheme 4). The oxidation potentials of triarylamines (**7′**−**10′**) serve as good indicators of the oxidizing ability of the corresponding triarylaminium salts (Table 2). For example, tris(2,4-dibromophenyl)aminium hexachloroantimonate (**7**) is a strong oxidizing agent, whereas tris(*p*-bromophenyl)aminium hexachloroantimonate (**8**) is a mild oxidant. The introduction of an electron-donating group such as methyl (**9**) and methoxy (**10**) groups significantly reduces the oxidizing ability.

Scheme 5. Radical Polymerization of Vinyl Monomers Using the Binary System



Polymerization of Vinyl Monomers. We examined the radical polymerization of styrene (St), methyl methacrylate (MMA), and butyl acrylate (BA) by treating benzylsilane with aminium salt in the presence of monomer (Scheme 5). The results are summarized in Table 3.

Polymerization of MMA did not occur by heating a mixture of the monomer and aminium salt **8** in the absence of benzylsilane at 100 °C for 45 h, indicating that **8** does not serve as an initiator for the polymerization (entry 1). MMA did not polymerize even by the treatment with benzylsilane **1a** and aminium salt **8** at 80−100 °C for 24 h (entry 2). BA did not polymerize under similar conditions, either (entry 3). The monomers were recovered unchanged. However, the use of **2**, which has lower oxidation potential (1.37 V) than **1a** was found to be effective for polymerization. When benzylsilane **2** and aminium salt **8** were used, polymerization of MMA proceeded smoothly to afford poly(MMA) in moderate yield at 100 °C (entry 4), although the polymerization did not occur efficiently at 80 °C (entry 5). These results indicate the importance of the oxidation potentials of benzylsilanes.

The polymerization was facilitated when acetonitrile was used as a solvent (entries 6 and 7). This is probably because nucleophilic attack of the solvent assisted the C−Si bond cleavage after the initial single electron transfer.[11]

Aminium salt **7**, which has stronger oxidizing ability than **8**, was also effective. Polymerization proceeded smoothly to give poly(MMA) in good yield (entry 8). It is important to note that the monomer was not oxidized under the reaction condition, although aminium salt **7** is considerably strong oxidant. Another important observation is that the polymerization did not proceed when equal amount of **8** (1.0 equiv based on the benzylsilane) was used (entry 9). The use of an excess amount of benzylsilane is necessary in order to conduct the polymerization. Polymerization of BA also proceeded under the similar conditions, and gave the poly(BA) in moderate yields (entries 10 and 11).

For the polymerization of styrene, the use of benzylsilane derivatives **2**−**6** with aminium salt **8** afforded poly(St) in moderate yield in all cases (entries 12−17). However, the molecular weights of polymers were smaller, probably because polymer-end styryl radicals are very susceptive to oxidation under the oxidative condition and such process leads to termination.

Next, we examined the use of aminium salts **9** and **10** in order to conduct the polymerization under much milder oxidative conditions (Table 4). Polymerization of MMA did not proceed when benzylsilane **2** and **6** were used with aminium salt **9** (entries 1 and 2). Benzylstannane **1b**, however, initiated the polymerization effectively. Polymerization of MMA proceeded smoothly even when the amount of benzylstannane **1b** was smaller than that of the aminium salt **9**. (entries 3−5). This is in contrast to the case of the binary system consisting of **2** and **8**. Furthermore, polymerization proceeded even at 40 °C to give the polymer in moderate yield (entry 6).

Polymerization of BA also proceeded under similar reaction conditions to give poly(BA) in good yield (entry 7). The results can be ascribed to the lower oxidation potential of **1b** (E_{ox} =

Table 3. Radical Polymerization of Vinyl Monomers Using Binary System Based on 7 and 8

entry	monomer[a] (equiv)	benzylsilane (equiv)	aminium salt	solvent	condin. (°C/h)	yield (%)	M_n/PDI[b]
1	MMA	none	**8**	none	100/45	0	
2	MMA	**1a** (1.0)	**8**	none	80/24	0	
3	BA	**1a** (1.0)	**8**	none	80−100/24	0	
4	MMA	**2** (3.8)	**8**	none	100/19	65	143800/4.23
5	MMA	**2** (1.9)	**8**	none	80/47	7	
6	MMA	**2** (1.9)	**8**	MeCN	80/2	38	96400/3.54
7	MMA	**2** (2.0)	**8**	MeCN	80/17	99	95200/3.76
8	MMA	**2** (2.0)	**7**	MeCN	80/16	87	54800/4.82
9	MMA	**2** (1.0)	**8**	MeCN	80/25	0	
10	BA	**2** (2.0)	**8**	MeCN	80/7	57	59700/2.39
11	BA	**2** (2.0)	**7**	MeCN	80/25	22	18000/1.92
12	St	**2** (3.8)	**8**	none	100/24	41	13500/1.68
13	St	**2** (1.0)	**8**	MeCN	60/42	25	2800/1.39
14	St	**3** (1.0)	**8**	MeCN	60/24	36	3800/1.61
15	St	**4** (1.0)	**8**	MeCN	60/29	35	4200/1.62
16	St	**5** (1.0)	**8**	MeCN	60/29	38	4100/1.53
17	St	**6** (1.0)	**8**	MeCN	60/32	32	3700/1.51

[a] MMA: methyl methacrylate. BA: butyl acrylate. St: styrene. [b] Number-average molecular weight (M_n) and polydispersity index (PDI) were determined by size exclusion chromatography calibrated using poly(MMA) and poly(St) standard samples.

Table 4. Radical Polymerization of Vinyl Monomers Using Binary System Based on 9 and 10

entry	monomer[a] (equiv)	benzylsilane (equiv)	aminium salt	solvent	condition (°C/h)	yield (%)	M_n/PDI[b]
1	MMA	**2** (2.0)	**9**	none	60−80/46	0	
2	MMA	**6** (2.0)	**9**	none	80/53	0	
3	MMA	**1b** (0.6)	**9**	none	80/24	>99	78200/2.95
4	MMA	**1b** (1.0)	**9**	none	60/19	51	125900/2.68
5	MMA	**1b** (0.2)	**9**	MeCN	60/24	62	143800/4.51
6	MMA	**1b** (1.0)	**9**	MeCN	40/48	39	136800/3.63
7	BA	**1b** (1.0)	**9**	MeCN	60/25	69	35200/2.42
8	MMA	**1b** (1.0)	**10**	MeCN	60/24	0	

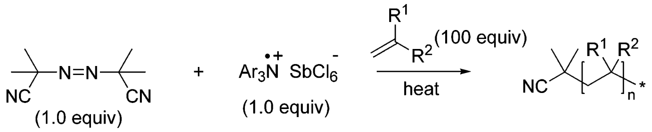
[a] MMA: methyl methacrylate. BA: butyl acrylate. St: styrene. [b] Number-average molecular weight (M_n) and polydispersity index (PDI) were determined by size exclusion chromatography calibrated using poly(MMA) standard samples.

Table 5. AIBN-Initiated Radical Polymerization in the Presence of Aminium Salts

entry	monomer[a]	aminium salt	condition (°C/h)	yield (%)	M_n/PDI [b]
1	MMA	**7**	60/24	4	
2	MMA	**8**	60/24	0	
3	MMA	**9**	60/24	44	7600/2.27
4	MMA	**10**	60/24	0	
5	BA	**8**	60/48	0	
6	BA	**9**	60/21	86	44600/2.71
7	BA	**10**	60/24	0	
8	St	**8**	60/24	90	76700/2.57
9	St	**9**	60/24	83	46700/3.15
10	St	**10**	60/24	34	24700/1.86

[a] MMA: methyl methacrylate. BA: butyl acrylate. St: styrene. [b] Number-average molecular weight (M_n) and polydispersity index (PDI) were determined by size exclusion chromatography calibrated using poly(MMA) and poly(St) standard samples.

Scheme 6. AIBN-Initiated Radical Polymerization in the Presence of an Aminium Salt



1.25 V) compared with the analogous benzylsilane derivatives. However, aminium salt **10**, which is the weakest oxidant among the aminium salts we examined, was inefficient even when **1b** was used (entry 8).

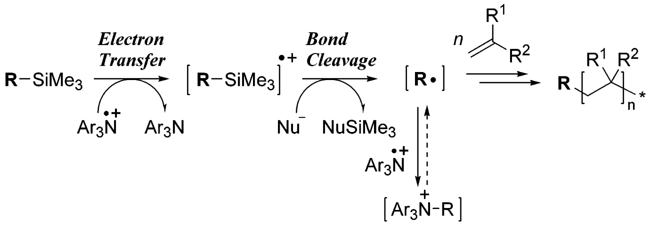
The results described above demonstrate that the binary systems consisting of a benzylsilane(stannane) and a triarylaminium salt serve as effective initiators of radical polymerization, if we choose an appropriate combination.

Effect of Aminium Salts on AIBN-Initiated Radical Polymerization. To obtain deeper understanding about the role of aminium salts, we next examined azobis(isobutyronitrile) (AIBN) initiated radical polymerizations in the presence of aminium salts (Table 5).

Surprisingly, aminium salt **7** inhibited the bulk polymerization of MMA completely (entry 1). Aminium salts **8** and **10** also inhibited the polymerization completely (entries 2 and 4). However, when aminium salt **9** was used, polymerization did occur but very slowly, and gave the poly(MMA) in low to moderate yield (entry 3). For the polymerization of BA, a similar inhibiting effect was observed when aminium salts **8** and **10** were used (entries 5 and 7), although aminium salt **9** did not inhibit the polymerization completely; polymerization proceeded very slowly to give the polymer in high yield (entry 6). For the polymerization of styrene, the inhibiting effect was not observed in all cases, and poly(St) was formed in all cases (entries 8−10).

Proposed Mechanism for the Binary System. The mechanism of the polymerization initiated by the present binary system still remains ambiguous in several points, but the following discussion seems to be reasonable. We confirmed by a control experiment (Table 3, entry 1) that the aminium salt did not initiate polymerization.[19] The importance of the redox potential of benzylsilanes(stannanes) and that of the aminium salt indicates that initiation involves single electron-transfer reaction between these two components. We have also demonstrated that aminium salts serve as efficient inhibitors for radical polymerization of MMA and BA. On the basis of these observations, we propose the mechanism shown in Scheme 7. The initiation reaction begins with single electron transfer from benzylsilane(stannane) to triarylaminium salt to generate the corresponding radical cation. The selective C−Si (C−Sn) bond cleavage of the radical cation gives benzyl radical, which seems to be assisted by nucleophilic attack on Si (or Sn) by the solvent.

Scheme 7. Proposed Mechanism of the Binary Initiating System



The radical thus generated initiates the polymerization. The radical may also be trapped by residual aminium salt to form ammonium salt.[20] Therefore, the polymerization was retarded in the presence of an aminium salt in some cases. However, in other cases the process seems to be reversible because it has been reported that benzylphenyldimethylammonium salts initiated radical polymerization under thermal or photochemical condition.[21] Further studies are needed to elucidate the detailed mechanism.

Summary

New binary initiating systems for radical polymerization of vinyl monomers have been developed using benzylsilanes and aminium salts. The combination of a benzylsilane and an aminium salt having appropriate redox potentials is crucial to the success of the polymerization. Usually benzylsilanes with lower oxidation potentials serve as better initiators. Benzylstannane−aminium salts systems have also found to be effective, permitting the polymerization under milder reaction conditions. A mechanism involving the initial single electron transfer from benzylsilanes(stannane) to aminium salts to generate a benzyl radical has been proposed. The potential applications of the present binary systems in radical/ionic crossover reactions are under investigation.[22]

Experimental Section

General Data. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were measured on a Varian MERCURYplus-400 spectrometer. ^{1}H NMR spectra were recorded using $CDCl_3$ as a solvent and are reported in parts per million (δ) from internal tetramethylsilane (TMS) or residual solvent peak. ^{13}C NMR spectra were recorded in $CDCl_3$ and reported in parts per million using $CDCl_3$ ($\delta = 77.0$ ppm) as an internal standard. Analytical gel permeation chromatography (GPC) was performed on a Shimadzu CLASS-LC10/M10A equipped with a Shodex GPC K-804L and a Shodex GPC K-805L column at 40 °C with $CHCl_3$ as eluent with flow rate of 1.0 mL/min. The number-average molecular weight (M_n) and polydispersity indexes (PDI) of poly(St), poly(MMA), and poly(BA) were determined by the analytical GPC calibrated at 40 °C in $CHCl_3$ with RI detector using standard polystyrene samples for poly(St), or standard poly(methyl methacrylate) samples for poly(MMA) and poly(BA).

Voltammetry. Electrochemical measurements were carried out using Bioanalytical System BAS 100B. Oxidation potentials were measured in 0.3 M MeCN solution of $Bu_4N(C_6F_5)_4$ at room temperature by Osteryoung square wave voltammetry[17] using a glassy carbon as a working electrode, a platinum wire as a counter electrode, and an SCE reference electrode.

Materials. Butyl acrylate (BA) (Wako Pure Chemical Industries), methyl methacrylate (MMA) (Wako Pure Chemical Industries), and styrene (St) (Kanto Chemical Co) were washed with 1 N NaOH, washed with water several times to neutralize the solution, and distilled over CaH_2. 2,2-Azobis(isobutylonitrile) (AIBN, 98% purity) (Wako Pure Chemical Industries) and benzyltrimethylsilane (98% purity) (Lancaster) were purchased and used without further purification. Benzylsilane derivatives **2**−**6**,[23,24] benzyltributylstannane,[24] and triarylamine derivatives[25,26] were synthesized according to the literature and purified by distillation or recrystallizataion.

Preparation of Aminium Salts. Tris(2,4-dibromophenyl)aminium hexachloroantimonate (**7**),[25,27] tris(*p*-bromophenyl)aminium hexachloroantimonate (**8**),[27] tris(*p*-methylphenyl)aminium hexachloroantimonate (**9**),[27] and tris(*p*-methoxyphenyl)aminium hexachloroantimonate (**10**)[27] were prepared from the corresponding amines and pentachloroantimony according to the literature procedure. A typical procedure is as follows: Pentachloroantimony (4 mL, 9.44 g, 31.6 mmol) was slowly added to a CH_2Cl_2 solution (50 mL) of (*p*-methylphenyl)amine (14.37 g, 20 mmol) at 0 °C under argon atmosphere over 3 min. The reaction mixture was stirred at room temperature for 20 min. Hexane (anhydrous) (100 mL) was added to this solution. The dark blue-green aminium salt precipitated quickly, and was collected by filtration. The aminium salt powder thus-obtained was washed with hexane several times and dried under vacuum at room temperature to give **8** as dark blue-green powder in >99% yield (28.99 g).

Experimental Procedure for the Polymerization of Methyl Methacrylate Initiated by Benzylsilane and Triarylaminium Salt. Typical Procudure (Table 3, Entry 7). A MeCN solution (0.5 mL) of tris(*p*-bromophenyl)aminium hexachloroantimonate (**8**) (81.6 mg, 0.10 mmol), **2** (38.9 mg, 0.20 mmol) and methyl methacrylate (1.001 g, 10.0 mmol) was stirred at 80 °C for 17 h under argon atmosphere. The reaction mixture was dissolved in $CHCl_3$ (5 mL), and poured into vigorously stirred hexane (200 mL). The precipitated polymer was collected by filtration, and was dried under vacuum at room temperature to obtain the poly(MMA) in 99% yield (0.999 g). Analytical GPC calibrated by poly(MMA) standards indicated that the polymer formed with $M_n = 95\,200$ and PDI = 3.76.

Experimental Procedure for the AIBN-Initiated Polymerization of Methyl Methacrylate in the Presence of Triarylaminium Salt. Typical Procedure (Table 5, Entry 3). A solution of tris(*p*-methylphenyl)aminium hexachloroantimonate (**9**) (62.2 mg, 0.10 mmol), AIBN (16.4 mg, 0.10 mmol), and methyl methacrylate (1.001 g, 10.0 mmol) was stirred at 60 °C for 24 h under argon atmosphere. The reaction mixture was dissolved in $CHCl_3$ (5 mL), and poured into vigorously stirred hexane (200 mL). The precipitated polymer was collected by filtration, and was dried under vacuum at room temperature to obtain the poly(MMA) in 44% yield (0.443 g). Analytical GPC calibrated by poly(MMA) standards indicated that the polymer formed with $M_n = 7600$ and PDI = 2.27.

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