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Living Anionic Polymerization of Styrenes Containing Adamantyl Skeletons

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Abstract  Anionic polymerizations of a series of para-substituted styrene derivatives containing adamantyl groups, 4-(1-adamantyl)styrene (1), 3-(4-vinylphenyl)-1,1’-biadamantane (2), 4-(1-adamantyl)-α-methylstyrene (3), 4-(1-adamantyloxy)styrene (4), 1-adamantyl 4-vinylbenzoate (5), and N-(1-adamantyl)-N-(4-vinylbenzylidene)amine (6), were carried out in THF at −78 °C. The polymerizations of 1-6 quantitatively proceeded to afford the well-defined polymers possessing the predicted molecular weights and the narrow molecular weight distributions ($M_w/M_n = 1.03-1.10$). The stability of the propagating chain ends was confirmed by the sequential copolymerizations of 1-6 with various monomers. The resulting poly(1), poly(2), poly(3), poly(4), poly(5), and poly(6) showed remarkably high glass transition temperatures at 234, 232, 273, 184, 227, and 254 °C, respectively, indicating the drastic substituent effect of adamantyl groups.

1. Introduction.
It is well known that the thermal property is very important to design the novel functional polymeric materials. The incorporations of bulky and rigid alicyclic substituents in the main chain or in the side chain are usually very effective to increase the glass transition temperature ($T_g$) of various parent polymers [1,2]. In particular, introduction of a bulky adamantane ring gives the high $T_g$ and excellent thermal stabilities to the parent polymers. In fact, a number of polymers containing adamantyl skeletons in the main chains and in the side chains have been synthesized via the stepwise [3-7], and chain polymerizations [8-15]. As an example of main chain type polymer, we have synthesized a poly(1,3-adamantane) via the ring-opening polymerization of highly strained [3.3.1]propellane derivatives, 1,3-dehydroadamantanes [16]. Furthermore, 1,3-dehydroadamantane undergoes the spontaneous copolymerization with electron-deficient monomers such as acrylonitrile and methyl acrylate in the absence of initiator to form the alternating copolymers containing adamantyl skeleton in the main chain [17].

We have succeeded in the living anionic polymerizations of alkyl methacrylates, 1-adamantyl methacrylates and 3-methacryloyloxy-1,1’-biadamantane, to afford the well-defined polymers exhibiting markedly high $T_g$ values [18]. The resulting polymers possessed the predicted molecular weights based on the molar ratios between monomers and initiators and the narrow molecular weight distributions. In addition, they exhibited remarkably high $T_g$ values and enhanced thermal stabilities derived from the adamantyl groups in each monomer unit. Very recently, we have successfully
shown that the anionic polymerization of 2-(1-adamantyl)-1,3-butadiene quantitatively proceeds to afford the well-defined homopolymers and block copolymers carrying the adamantyl group in the side chain [19]. It is well known that styrenes and α-methylstyrenes are also the representative monomers capable of the living anionic polymerization as well as methacrylates and 1,3-dienes.

In this study, we newly designed and anionically polymerized six para-substituted styrene derivatives, 4-(1-adamantyl)styrene (1) [20], 3-(4-vinylphenyl)-1,1'-biadamantane (2) [20], 4-(1-adamantyl)-α-methylstyrene (3), 4-(1-adamantyloxy)styrene (4), 1-adamantyl 4-vinylbenzoate (5), and N-(1-adamantyl)-N-(4-vinylbenzylidene)amine (6), in order to prove the substituent effects of rigid and bulky adamantyl groups on thermal properties of the resulting polystyrenes. In addition, since the monomers possessed the electron-donating group, 4, or the electron-withdrawing groups, 5 and 6, the effect of linkage between adamantyl skeleton and the polymer framework on the polymerizability can be clarified as well as the substituent effect on the thermal property.

![Chart 1. Monomers Containing Adamantyl Groups.](image)

2. Results and Discussion.


Novel monomers, 1 and 3, were synthesized from 1-adamantyl bromide as illustrated in Scheme 1. In the case of 2, 3-bromo-1,1'-biadamantane was the starting compound. In these cases, the bulky adamantyl groups were directly connected to the styrene or α-methylstyrene framework. The phenyl ring was introduced on the adamantane ring by the coupling reaction of 1-adamantyl bromide and phenylmagnesium bromide in methylene chloride.

![Scheme 1. Synthesis of 1-3.](image)
Ether type monomer 4 was synthesized as shown in Scheme 2. The adamantyl ether was prepared by the coupling reaction of 1-adamantyl bromide and a phenol derivative, 4-hydroxybenzaldehyde. The resulting benzaldehyde was converted into the corresponding styrene via the Wittig reaction.

**Scheme 2. Synthesis of 4.**

Scheme 3 shows the synthetic routes of ester 5 and imine 6. In these cases, the Grignard reagent prepared from 4-chlorostyrene was converted into either 4-vinylbenzoic acid or 4-vinylbenzaldehyde. The ester 5 was prepared by the reaction of acid chloride and lithium salt of 1-adamantanol. The condensation between 4-formylstyrone and 1-aminoadamantan e gave the imine monomer possessing the C=N linkage.

**Scheme 3. Synthesis of 5 and 6.**

2.2. Anionic Polymerization.

At first, the anionic polymerization of 1 was carried out in THF at –78 °C as shown in Table 1. The initiators included sec-butyllithium (s-BuLi), cumylpotassium, potassium naphthalenide, and oligo(s-methylstyril)dipotassium [20]. During the course of the polymerization, the polymerization system showed a characteristic red color. The coloration disappeared instantaneously by quenching with a small amount of degassed methanol. The complete consumption of monomer was always achieved within 8 h regardless of the counterion of the initiator, and the yield of polymer was quantitative in each case after the termination. The \(^1\)H and \(^13\)C NMR analysis revealed that the vinyl polymerization of 1 proceeded smoothly. In all cases, SEC curves of the resulting poly(1)s were unimodal, and the \(M_n/M_w\) values were always within 1.13, indicating the narrow molecular weight distributions. Furthermore, reasonable agreements were observed between the \(M_n\) values obtained by RALLS-SEC and the predicted ones based on the feed molar ratios between 1 and initiator. The stability of the propagating carbanion derived from 1 was confirmed by the quantitative initiation
efficiency in the postpolymerization. These results clearly show that the polymerization of 1 quantitatively proceeds in a controlled fashion to afford a polymer with well-defined chain structure under the condition employed here. The monomer possessing the bulky biadamantane side chain 2 and α-methylstyrene derivative 3 also underwent the anionic polymerizations to give the tailored polymers quantitatively in THF at –78 °C as shown in Table 1.

Next, we have examined the polymerization of adamantyl ether 4. The polymerization of 4 occurred with either s-BuLi or potassium naphthalenide in THF at –78 °C without difficulty, and the resulting poly(4) possessed tailored $M_n$ and narrow molecular weight distribution. On the other hand, no polymeric product of 4 was produced with diphenylmethyl lithium in THF at –78 °C after 2 h. The bulky and low nucleophilic carbanion, diphenylmethyl lithium, could not initiate the polymerization of 4 at all, since the electron density of vinyl group in the para-substituted styrene was increased by the electron-donating property of the adamantylxoy group. This means the low anionic polymerizability of 4 compared with that of styrene due to the substituent effect. By contrast, even the low nucleophilic diphenylmethyl anions can initiate the anionic polymerization of adamantlyls ester 5 and adamantyl imine 6. In these cases, the anionic polymerizability of 5 and 6 was higher than that of styrene, since the electron density of the vinyl groups was significantly reduced by the electron-withdrawing nature of COOAd and CH=N-Ad groups.

Table 1. Anionic Polymerization of 1-6 in THF.

<table>
<thead>
<tr>
<th>monomer</th>
<th>initiator</th>
<th>temp. °C</th>
<th>time h</th>
<th>yield %</th>
<th>$M_n \times 10^3$</th>
<th>$M_n/M_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>s-BuLi</td>
<td>–78</td>
<td>5 min</td>
<td>100</td>
<td>11</td>
<td>16</td>
</tr>
<tr>
<td>2</td>
<td>s-BuLi</td>
<td>–78</td>
<td>1</td>
<td>100</td>
<td>26</td>
<td>26</td>
</tr>
<tr>
<td>3</td>
<td>s-BuLi</td>
<td>–78</td>
<td>8</td>
<td>100</td>
<td>54</td>
<td>57</td>
</tr>
<tr>
<td>4</td>
<td>Cumyl-K</td>
<td>–78</td>
<td>3</td>
<td>100</td>
<td>8.4</td>
<td>11</td>
</tr>
<tr>
<td>5</td>
<td>K-Naph</td>
<td>–78</td>
<td>3</td>
<td>100</td>
<td>10</td>
<td>14</td>
</tr>
<tr>
<td>6</td>
<td>K-Naph/α-MeSt</td>
<td>–78</td>
<td>3</td>
<td>100</td>
<td>12</td>
<td>14</td>
</tr>
<tr>
<td>1</td>
<td>s-BuLi</td>
<td>–78</td>
<td>16</td>
<td>100</td>
<td>13</td>
<td>11</td>
</tr>
<tr>
<td>2</td>
<td>K-Naph</td>
<td>–78</td>
<td>16</td>
<td>100</td>
<td>6.7</td>
<td>7.2</td>
</tr>
<tr>
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<td>4</td>
<td>100</td>
<td>11</td>
<td>13</td>
</tr>
<tr>
<td>4</td>
<td>K-Naph</td>
<td>–78</td>
<td>6</td>
<td>100</td>
<td>7.1</td>
<td>7.1</td>
</tr>
<tr>
<td>5</td>
<td>s-BuLi</td>
<td>–78</td>
<td>2</td>
<td>100</td>
<td>15</td>
<td>20</td>
</tr>
<tr>
<td>4</td>
<td>Ph₂CHLi</td>
<td>–78</td>
<td>2</td>
<td>0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>K-Naph</td>
<td>–78</td>
<td>2</td>
<td>100</td>
<td>9.0</td>
<td>10</td>
</tr>
<tr>
<td>6</td>
<td>Ph₂CHLi</td>
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<td>4</td>
<td>40</td>
<td>3.7</td>
<td>24</td>
</tr>
<tr>
<td>6</td>
<td>Ph₂CHK</td>
<td>–95</td>
<td>4</td>
<td>100</td>
<td>9.3</td>
<td>14</td>
</tr>
<tr>
<td>6</td>
<td>s-BuLi/α-MeSt</td>
<td>–78</td>
<td>24</td>
<td>100</td>
<td>16</td>
<td>32</td>
</tr>
<tr>
<td>6</td>
<td>Ph₂CH</td>
<td>–78</td>
<td>1</td>
<td>100</td>
<td>20</td>
<td>23</td>
</tr>
<tr>
<td>6</td>
<td>K-Naph/α-MeSt</td>
<td>–78</td>
<td>1</td>
<td>100</td>
<td>29</td>
<td>25</td>
</tr>
</tbody>
</table>

* By RALLS-SEC.

b By SEC using polystyrene standards.

The living nature of the polymerization systems of 1-6 allows us to synthesize the block copolymers via the sequential copolymerization with various comonomers such as styrene, α-methylstyrene, and isoprene. For example, a novel ABA triblock copolymer of 1 (A monomer) and isoprene (B monomer) was anionically obtained with s-BuLi in cyclohexane at 50 °C via the three stage copolymerization as shown in Scheme 4. The 1,4-polyisoprene segment in the triblock copolymer was quantitatively hydrogenated with para-toluene sulfonohydrazide in xylene at 120 °C to give a triblock copolymer, poly(1)-b-poly(ethylene-alt-propylene)-b-poly(1). These well-defined
ABA triblock copolymers before and after hydrogenation possessed outer hard A segments and soft middle B segment and showed \( T_g \)s at \(-60 \) and \( 220 \) °C. The higher \( T_g \) was corresponding to the poly(1) terminal segments as shown later. The analysis of mechanical property also indicates the potential of the block copolymer as a novel thermoplastic elastomer showing very high service temperature [21].

![Scheme 4. Synthesis of New Thermoplastic Elastomers.](image)

2.3. Thermal Properties of Polymers.

Thermal stability of the resulting polymers was first investigated by thermogravimetric analysis (TGA) under nitrogen. The polystyrenes, poly(1), poly(2), poly(4), poly(5), and poly(6), were stable until \( 340 \) °C, and poly(3), poly(\( \alpha \)-methylstyrene) derivative, started to decompose around \( 290 \) °C on heating. The initial decomposition temperatures of polymers carrying adamantyl groups were slightly higher than the corresponding non-substituted polymers such as polystyrene and poly(\( \alpha \)-methylstyrene).

Next, the \( T_g \) values of a series of polymers were analyzed by differential scanning calorimetry (DSC). The \( T_g \)s of poly(1), poly(2), and poly(3) were observed at 234, 232, and 274 °C, respectively. These are 110-130 °C higher than the \( T_g \) value of parent polystyrene (\( T_g \approx 100 \) °C) or poly(\( \alpha \)-methylstyrene) (\( T_g \approx 165 \) °C). In each case, no melting behavior was observed before the thermal degradation. The \( T_g \) value of poly(\( \alpha \)-methylstyrene) derivative, poly(3), was apparently higher than that of poly(1), the polystyrene counterpart. On the other hand, the number of adamantyl group did not affect the \( T_g \) value by comparing poly(1) and poly(2). Figure 1 shows a relationship between \( T_g \) and molecular weight of poly(1), poly(4), poly(5), and poly(6). Apparently, the \( T_g \) values increased with the molecular weight in each case and became almost constant at the high molecular weight region similar to the case of polystyrene. The \( T_g \) values of high molecular weight samples for poly(1), poly(4), poly(5), and poly(6) reached 234, 184, 227, and 254 °C, respectively. The linkages between adamantyl skeleton and the polystyrene backbone played a very important role to determine the \( T_g \)s of polymers as well as the main chain structure.

3. Conclusion.

Herein, the novel polymers having predicted \( M_w \)s and narrow molecular weight distributions are synthesized by the living anionic polymerization of a series of novel styrene monomers possessing the
adamantyl skeletons. The incorporation of bulky and stiff adamantyl and 1,1’-biadamantyl moieties unequivocally induces the decreasing of chain mobility to result in the drastic $T_g$ enhancement of a series of novel 4-substituted polystyrenes.

![Figure 1. Relationship between $T_g$ and $M_n$ of Polymers.](image)