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## Polymerization of Hydroxy-Containing Diazoacetates: Synthesis of Hydroxy-Containing "Poly(substituted methylene)s" by Palladium-Mediated Polymerization and Poly(ester-ether)s by Polycondensation through O-H Insertion Reaction

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**Supporting Information** 



**ABSTRACT:** Two types of polymerization of hydroxy-containing diazoacetates are described. The polymerization of hydroxycontaining diazoacetates using palladium complexes proceeded successfully under chain-growth mechanism even without a protecting group to give C–C main chain polymers bearing a hydroxy-containing ester substituent on each carbon of the backbone. The resulting polymers had a slightly branched structure due to chain transfer reaction with the hydroxy groups, while the polymers obtained by polymerization of silyl-protected diazoacetates and subsequent deprotection had a completely linear structure. The hydroxy-containing polymers with an appropriate hydrophilic/hydrophobic balance showed a lower critical solution temperature-type phase separation in an aqueous medium. On the other hand, the polymerization of hydroxy-containing diazoacetates using  $InCl_3$  as a catalyst proceeded under step-growth mechanism to give oligomers having a distinct repeating unit (ester-ether), where a new ether bond was generated through O–H insertion reaction of diazocarbonyl groups into hydroxy groups.

### ■ INTRODUCTION

Recently, polymerization of alkyl diazoacetates has received attention as a useful method for preparing C–C main chain polymers bearing an ester substituent on each carbon of the backbone.<sup>1,2</sup> The resulting polymers, "poly(substituted methylene)s", are expected to have unique properties due to the structural characteristics of dense packing of the substituents around the polymer chain compared to vinyl polymer analogues, i.e., poly(acrylate)s and poly(methacrylate)-s. For example, we have recently reported palladium-mediated polymerization of pyrenylmethyl diazoacetate and demonstrated that the efficiency of intrachain eximer formation of the resulting poly(methacrylate)s is much higher than that of the corresponding pyrene-containing poly(methacrylate)s.<sup>3</sup> The palladium-based initiating systems are effective for polymerization of alkyl diazoacetates bearing

various ester groups, affording poly(alkoxycarbonylmethylene)s with a variety of side chain ester groups.<sup>4</sup> However, the substituents were limited to hydrophobic groups for the polymerization of diazocarbonyl compounds so far. The availability of hydrophilic groups including hydroxy group would allow us to prepare a new type of hydrophilic polymeric material.

Polymers based on 2-hydroxyethyl methacrylate (HEMA) or related hydroxy-containing monomers have been widely used in the biomedical field such as contact lenses, owing to their biocompatibility and lack of toxicity.<sup>5</sup> Most of the polymers of HEMA reported before the late 1990s were synthesized via free

 Received:
 April 15, 2014

 Revised:
 June 12, 2014

 Published:
 June 26, 2014

Scheme 1. Synthesis of Hydroxy-Containing Poly(substituted methylene)s by Polymerization of Silyl Protected Monomers S2– S6 and Subsequent Deprotection (i–iii) and Direct Polymerization of Hydroxy-Containing Monomers H2–H6 without Using a Protecting Group (iv)



entry	monomer	initiating system	[monomer]/[Pd]	yield (%) <sup>b</sup>	$M_{\rm n}^{\ c}$	$M_{ m w}/{M_{ m n}}^c$	$T_{g}^{d}$ (°C)
1	<b>S2</b>	$(\eta^3$ -C <sub>3</sub> H <sub>5</sub> )PdCl	50	40	6500	1.53	30
2	<b>S2</b>	$(\eta^3$ -C <sub>3</sub> H <sub>5</sub> )PdCl/NaBPh <sub>4</sub> <sup>e</sup>	50	73	7500	1.31	n.d.
3	<b>S</b> 3	$(\eta^3$ -C <sub>3</sub> H <sub>5</sub> )PdCl	50	53	7700	1.29	-25
4	<b>S4</b>	$(\eta^3$ -C <sub>3</sub> H <sub>5</sub> )PdCl	50	58	6400	1.28	-36
5	<b>S5</b>	$(\eta^3$ -C <sub>3</sub> H <sub>5</sub> )PdCl	50	50	8100	1.30	n.d.
6	<b>S6</b>	$(\eta^3$ -C <sub>3</sub> H <sub>5</sub> )PdCl	50	50	8700	1.26	n.d.
7	<b>S2</b>	$(\eta^3$ -C <sub>3</sub> H <sub>5</sub> )PdCl	200	57	10300	1.67	n.d.
8	<b>S</b> 4	(NHC)Pd/NaBPh4 <sup>e</sup>	200	11	48700	1.94	n.d.
$a[{(\eta^3-C_3H_5)}]$	$PdCl_{2} = 2.2$	–2.6 mM, in THF at –20 $^{\circ}$ C	for 13 h. <sup>b</sup> After purifi	cation with prepa	rative GPC. <sup>c</sup> ]	Determined by	GPC (PMMA

standards). <sup>*d*</sup>Determined by DSC for the polymers obtained after deprotection. <sup>*e*</sup>[NaBPh<sub>4</sub>]/[Pd] = 1.2.

radical polymerization which produces ill-defined polymers because living anionic polymerization of HEMA without a protecting group is not possible due to the labile proton in the hydroxy group. However, the development of living/controlled radical polymerization techniques over the past two decades has enabled the preparation of well-defined poly(HEMA)s with various architectures by direct polymerization; thus, the scope of application of poly(HEMA)s and related hydroxy-containing polymers has been widened.<sup>6–8</sup>

Herein, we will report the synthesis of hydroxy-containing poly(substituted methylene)s by Pd-initiated polymerization of silyl-protected diazoacetates and subsequent deprotection of the obtained polymers as well as direct polymerization of hydroxy-containing diazoacetates without a protecting group. The resulting polymers, which can be regarded as analogues of poly(HEMA) or poly(2-hydroxyethyl acrylate) [poly(HEA)], are expected to show unique properties such as high hydrophilicity and superior thermal and mechanical property due to denser packing of the hydroxy groups around the polymer chain.<sup>9</sup>

Furthermore, we will describe results of the attempts to polymerize the same monomers via a different mechanism based on versatile reactivities of diazocarbonyl compounds with various functional groups,<sup>10</sup> more specifically, step-growth polymerization of hydroxy-containing diazoacetates as an ABtype monomer through O–H insertion reaction. This type of polymerization would offer poly(ester–ether)s, whose structure is completely different from the polymers obtained using palladium complexes mentioned above. It will be noteworthy if the hydroxy-containing diazoacetates actually have the ability to afford two totally different types of polymers depending on the reaction conditions (so-called "dual reactivity as a monomer").

#### RESULTS AND DISCUSSION

Synthesis of Hydroxy-Containing Poly(substituted methylene)s: Polymerization of Silyl-Protected Monomers and Subsequent Deprotection (Scheme 1, i–iii). First, we carried out polymerization of silyl-protected monomers with differing spacer lengths using  $(\eta^3$ -C<sub>3</sub>H<sub>5</sub>)PdClbased initiating systems, which were recently reported to polymerize alkyl diazoacetates in a high initiating efficiency.<sup>11</sup> The polymerization results are summarized in Table 1. The polymerization of S2 with a feed ratio of [S2]/[Pd] = 50/1using  $(\eta^3$ -C<sub>3</sub>H<sub>5</sub>)PdCl was conducted in THF at -20 °C for 13 h, giving a polymer with  $M_{\rm p} = 6500$  and  $M_{\rm w}/M_{\rm p} = 1.53$  in 40% yield after purification with preparative recycling GPC to remove lower molecular weight oligomers (entry 1). The addition of NaBPh4 as a cocatalyst resulted in increase of polymer yield (entry 2). However, a small amount of polyTHF was formed along with the polymerization of S2. This results suggest that some cationic species capable of polymerizing THF are present in this system, as is the case with the polymerization of ethyl diazoacetate (EDA) using  $(\eta^3-C_3H_5)$ -PdCl/borate systems.<sup>11</sup> To avoid the concomitant formation of polyTHF, the following polymerization was conducted with  $(\eta^3$ -C<sub>3</sub>H<sub>5</sub>)PdCl alone. The polymerization proceeded irrespective of the spacer lengths, producing polymers with GPCestimated  $M_{\rm n}$ s of 6400–8700 in 50–58% yields (entries 3–6). In entry 7, the polymerization of S2 was performed with a feed ratio of [S2]/[Pd] = 200 to give a polymer with a higher  $M_n$ . However, the increment was not proportionate to the monomer feed ratio, suggesting chain transfer occurs during the polymerization. Furthermore, we carried out the polymerization using  $(NHC)Pd/NaBPh_4$  initiating system (NHC = Nheterocyclic carbene),<sup>12</sup> which can afford high-molecularweight polymers  $(M_n > 20000)$  from alkyl diazoacetates, yielding a polymer with approximately  $M_{\rm n}$  = 50 000 but in a low yield (entry 8).

The obtained polymers were deprotected by tetrabutylammonium fluoride in THF to produce hydroxy-containing polymers. Figures 1A and B show <sup>1</sup>H NMR spectra of the products obtained from **S4** before and after deprotection, recorded in CDCl<sub>3</sub> and DMSO- $d_6$ , respectively. Quantitative deprotection was confirmed by the disappearance of the signals

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**Figure 1.** <sup>1</sup>H NMR spectra of the products obtained by (A) polymerization of **S4** (Table 1, entry 4) recorded in  $CDCl_3$ , (B) polymerization of **S4** (Table 1, entry 4) and subsequent deprotection recorded in DMSO- $d_6$ , and (C) direct polymerization of **H4** (Table 2, entry 3) recorded in DMSO- $d_6$ .

corresponding to the *tert*-butyldimethylsilyl group (f and g) as well as the appearance of the signal assignable to the hydroxy group (h') in the spectrum obtained after deprotection reaction. A series of hydroxy-containing polymers with differing spacer lengths were prepared in a similar manner, and the polymer structures were confirmed by <sup>1</sup>H NMR as well (Figures S1–S4).

The glass transition temperature  $(T_g)$  of the resulting hydroxy-containing polymers was measured by differential scanning calorimetry (Table 1 and Figure S5). The  $T_g$  for poly**S2**' (Table 1, entry 1) was 30 °C, and the  $T_g$ s decreased with increasing the methylene spacer length.

Another interest is water solubility of the resulting polymers. Some polymeric compounds having a large number of hydroxy groups are insoluble in water despite the building blocks are hydrophilic themselves, as represented by cellulose. The reason comes from the fact that crystalline structures are formed via inter- and intramolecular hydrogen bonds, which should be enhanced by denser packing of the hydroxy groups. Likewise, poly(hydroxymethylene) obtained by polymerization of vinylene carbonate followed by hydrolysis has been reported to be insoluble in water,<sup>13</sup> while poly(vinyl alcohol) is water-soluble. Then, water solubility of hydroxy-containing poly(substituted methylene)s obtained from S2–S6 was examined, revealing that polyS2'–polyS4' were readily soluble in water whereas polyS6' was insoluble. Interestingly, an aqueous solution of polyS5' with a spacer length in-between exhibited a solubility transition depending on the temperature.

It is known that some hydroxy-containing homopolymers and copolymers with an appropriate hydrophilic/hydrophobic balance show a lower critical solution temperature (LCST)-type phase separation in water.<sup>14–18</sup> Aoshima and co-workers

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have systematically synthesized a series of poly(hydroxyalkyl vinyl ethers) by living cationic polymerization of silyl-protected vinyl ethers with different spacer lengths and subsequent deprotection and revealed that poly(4-hydroxybutyl vinyl ether) undergoes an LCST-type phase separation in water.<sup>15a</sup> In other instances, poly(HEMA) with degrees of polymerization between 20 and 35 was found to show temperature-responsive behavior, with cloud points ranging from 28 to 39 °C for 0.5 wt % aqueous solutions.<sup>16a</sup> Also, poly(2-hydroxypropyl acrylate) [poly(HPA)] was reported to exhibit an LCST of 16 °C at a concentration of 10 wt %.<sup>14</sup> Considering that these (meth)acrylate polymers and polyS4' are all isomers with each other having the same chemical formula per a repeating unit ( $C_6H_{10}O_3$ ), polyS4' should show thermosensitive behavior (Chart 1). In fact, polyS4' was soluble in water

Chart 1. Chemical Structures of Poly(HEMA), Poly(HPA), and PolyS4'



but underwent no transition upon heating at least up to 90 °C. Alternatively, polyS5' with a longer spacer, which makes the repeating unit more hydrophobic with a chemical formula of  $C_7H_{12}O_3$ , showed an LCST-type phase separation in an aqueous medium. These results suggest that hydrophilicity of polyS5' is enhanced by denser packing of the hydroxy groups, reaching a comparative level with poly(HEMA) and poly-(HPA). On the other hand, the opposite situation was observed in thermoresponsive polymers bearing N-isopropylamide side chains reported by Hashidzume and co-workers,<sup>19</sup> where polymers with the extra alkylamide side chains prepared by copolymerization of N-isopropylacrylamide with N,N'-diisopropylfumaramide had a lower phase separation temperature (less hydrophilicity) compared to N-isopropylacrylamide homopolymer. They explained that the steric hindrance caused by the extra side chains destabilizes the hydrated state of Nisopropylamide units, resulting in a lower phase separation temperature.

Figure 2 shows the temperature dependence of the transmittance of polyS5' in water. A 0.5 wt % solution of polyS5' with  $M_n = 13700$  (determined before deprotection) turned opaque at around 20 °C with increasing temperature, and the cloudy solution became clear without significant hysteresis when the temperature decreased. The cloud point increased with decreasing  $M_n$  of the polymers [about 25 °C for polyS5' with  $M_n = 8100$  (entry 5 in Table 1, determined before deprotection)], indicating that cloud point can be controlled by changing  $M_n$ . For shorter chain polymers, however, the terminal structure has been recognized as an important factor that governs thermosensitive behavior.<sup>20,21</sup> MALDI-TOF-MS analysis of the polymers obtained from S5 before deprotection indicated that a major component in polyS5' has Cl- and  $-CH_2CH_2CH_2CH_2OH$  at  $\alpha$ - and  $\omega$ -chain ends, respectively (Figure S6).<sup>22</sup> Also, it is known that the phase separation



**Figure 2.** Temperature dependence of the transmittance for 0.5 wt % aqueous solutions of polyS5' (circle:  $M_n = 8100$ ,  $M_w/M_n = 1.30$ ; triangle:  $M_n = 13700$ ,  $M_w/M_n = 1.66$ ; determined before deprotection) during a heating (solid line) and cooling (broken line) cycle.

behavior depends on the tacticity of the polymers;<sup>23,24</sup> the broadness of the main chain CH signals (*a* and *a'*, in Figure 1 and Figures S1–S4) suggests that the products obtained by polymerization of **S2–S6** using  $(\eta^3-C_3H_5)PdC1$  are atactic polymers.<sup>11</sup>

Synthesis of Hydroxy-Containing Poly(substituted methylene)s: Direct Polymerization of Hydroxy-Containing Monomers (Scheme 1, iv). Recently, de Bruin et al.<sup>25</sup> and our group<sup>11</sup> have reported that Rh- and Pd-initiated polymerization of alkyl diazoacetates proceeds to give polymers even in the presence of alcohols and H<sub>2</sub>O. Thus, we attempted direct polymerization of hydroxy-containing monomers without a protecting group to avoid time-consuming protectiondeprotection processes. The polymerization of H2-H6 was carried out under a similar condition as for the silyl-protected monomers. After the polymerization was initiated, N<sub>2</sub> release was observed and the reaction mixtures turned heterogeneous, suggesting the formation of hydroxy-containing polymers that show low solubility toward THF. After 13 h, the reaction mixtures were quenched with a HCl/methanol mixture and purified by dialysis to remove the initiator-derived residues and low-molecular-weight oligomers. The polymer structure was confirmed by NMR analysis. Figure 1C shows the <sup>1</sup>H NMR spectrum of polyH4' recorded in DMSO- $d_6$ . The spectrum was almost identical to that of polyS4' (Figure 1B), which was obtained by the protection-deprotection method. To estimate the molecular weight by GPC analysis, the obtained products were treated with tert-butyldimethylsilyl chloride and pyridine to afford silyl-protected polymers with quantitative protection confirmed by <sup>1</sup>H NMR (Figure S7). The  $M_{\rm n}$  and  $M_{\rm w}/M_{\rm n}$  values of the resulting polymers are summarized in Table 2. Interestingly, the direct polymerization of H2-H6 with a feed ratio of [H2-H6]/[Pd] = 50/1 produced polymers with  $M_{\rm n} {\rm s}$  = 7400–9100, which are comparable to those of the polymers obtained from the aforementioned silyl-protected monomers. However, the shape of GPC curve was somewhat different. Figures 3A,B show the GPC curves of the products obtained by the polymerization of S4 and H4 for 13 h, respectively (polyH4' was transformed into the silyl-protected polymer). The molecular weight of the highest peak top  $(M_p)$ in the GPC curve for the polymer obtained with H4 ( $M_p$  = 7900) was slightly lower than that of the polymer obtained with S4 ( $M_p$  = 8900). In addition, small peaks appeared in the higher

Table 2. Direct Polymerization of H2-H6<sup>a</sup>

entry	monomer	[monomer]/[Pd]	yield <sup><math>b</math></sup> (%)	$M_n^c$	$M_{\rm w}/M_{\rm n}^{\ c}$
1	H2	50	29	7400	1.17
2	H3	50	25	7800	1.59
3	H4	50	29	8100	1.29
4	H4	200	11	13700	2.31
5	H5	50	35	9100	1.40
6	H6	50	32	8800	1.47

 ${}^{a}[\{(\eta^{3}-C_{3}H_{5})PdCl\}_{2}] = 3.9-4.6 mM, in THF at -20 °C for 13 h. {}^{b}After purification by dialysis (MWCO = 1000) against distilled water or methanol. CDetermined by GPC (PMMA standards) of the products obtained after purification by dialysis (MWCO = 1000) against distilled water or methanol and treatment of$ *tert*-butyldimethylsilyl chloride.



Figure 3. GPC curves of the products obtained by (A) polymerization of S4 (entry 4 in Table 1), (B) polymerization of H4 for 13 h and treatment with *tert*-butyldimethylsilyl chloride (entry 3 in Table 2), and (C) polymerization of H4 for 7 days and treatment with *tert*-butyldimethylsilyl chloride.

molecular weight region of the GPC curve as shoulders for the direct polymerization, and the intensity of the shoulder peaks increased with time (Figure 3C; polymerization for 7 days), while this kind of peak shift was not observed for the polymerization of the silyl-protected monomers. This is attributed to chain transfer of propagating chain with the hydroxy groups on the side chains. The plausible mechanistic details will be described below.

In the previous work, we have reported that polymerization of EDA using  $(\eta^3 - C_3 H_5)$ PdCl in the presence of alcohols or  $H_2O$  (ROH) with a feed ratio of [Pd]/[ROH]/[EDA] = 1/20/30 proceeds to give polymers with RO- and H- groups at their  $\alpha$ - and  $\omega$ -chain ends, respectively, as a major product.<sup>11</sup> Based on this result of the chain-end structure analysis, we have proposed the mechanism described in Scheme 2A, where Pd-OR was generated as a major initiating species during the period for initiator preparation to yield polymers, and a part of the RO-initiated polymers could also be formed by chain transfer of propagating chains with ROH followed by initiation with the resulting Pd-OR species. Herein, we carried out polymerization in the presence of an equimolar amount of an alcohol with a monomer as a model reaction for the polymerization of hydroxy-containing monomers. The polymerization of EDA in the presence of *n*-butanol was conducted with a feed ratio equivalent to the H2-H6 polymerization condition with respect to the [OH]/[diazo] ratio ([Pd]/[nbutanol]/[EDA] = 1/50/50), giving a polymer with  $M_p = 2500$ in 51% yield. The  $M_n$  was not so low compared to that of the polymers obtained in the absence of an alcohol  $(M_{\rm p} = 4300,$ yield = 49%) despite the system contains an excess of nbutanol, indicating that neither termination via protonolysis nor the frequent chain transfer did operate in this system. In the MALDI-TOF-MS spectrum of the polymer, we observed a main set of signals assignable to the polymer with  $n-C_4H_9O$ and H at  $\alpha$ - and  $\omega$ -chain ends, respectively (Figure S8).

Accordingly, we can propose a mechanism for the direct polymerization of hydroxy-containing diazoacetates, as shown

Scheme 2. Proposed Mechanism for (A) Polymerization of EDA in the Presence of Alcohols and (B) Direct Polymerization of H2–H6



in Scheme 2B. First,  $Pd-O(CH_2)_rOCOCHN_2$  (HX-Pd) should be generated as a major initiating species in the early stage of the reaction. Then, the polymerization was initiated from the species to yield the polymer (polyHX'-Pd), which is likely the main product in the direct polymerization of H2-H6.<sup>26</sup> In addition, HX-Pd could also be formed in the course of polymerization by chain transfer of propagating chains with the hydroxy groups on the side chains of the unreacted monomers accompanied by the generation of H-terminated polymer (polyHX'-H). The resulting two polymers (polyHX'-Pd and polyHX'-H) can act as a macromonomer because they have a diazo group as a potential propagation site at their  $\alpha$ -chain end. Homopolymerization of the macromonomers or copolymerization with the unreacted monomer should result in polymers with a branched structure (path A). In addition, the chain transfer should occur with the hydroxy groups on the side chains of the polymers but probably with less frequency due to steric hindrance, while this reaction can also produce polymers with a branched structure through "grafting-from" elongation (path B). These scenarios will explain the appearance of high- $M_{\rm n}$  shoulders in GPC curves after standing for a long period shown in Figure 3. The degree of branching could be controlled by modifying the initiating system and polymerization conditions, as is the case with self-condensing vinyl polymerization of inimers.<sup>2'</sup>

Polycondensation of Hydroxy-Containing Diazoacetates through O-H Insertion Reaction. The aforementioned results revealed that the direct polymerization of hydroxy-containing diazoacetates using  $(\eta^3$ -C<sub>3</sub>H<sub>5</sub>)PdCl can produce hydroxy-containing poly(substituted methylene)s, although a part of hydroxy groups are involved in chain transfer reaction to give polymers with a slightly branched structure. On the other hand, it is known that some transition metals or Lewis acids catalyze O-H insertion reaction of diazocarbonyl compounds with alcohols to provide a new C-O bond,<sup>28</sup> suggesting that H2-H6 can be polymerized by using the insertion in a step-growth manner. Actually, we have recently succeeded in polycondensation of bis(diazocarbonyl) compounds with aromatic diols or dicarboxylic acids via O-H insertion reaction.<sup>29</sup> Herein, we attempted step-growth polymerization of hydroxy-containing diazoacetates as an ABtype monomer through O-H insertion reaction (Scheme 3 and

Scheme 3. Polycondensation of H2–H6 through O–H Insertion Reaction

$$n \underset{O}{\overset{H}{\xrightarrow{}}} O (CH_2)_{x} O H \longrightarrow \begin{pmatrix} CH_2 - C - O (CH_2)_{x} O \\ O \\ O \end{pmatrix}_{n}$$

Table S1). When  $Rh_2(OAc)_4$ , which is one of the most common catalysts for O–H insertion, was used for the polycondensation of H4, an oligomer with  $M_n = 750$  was obtained. In the <sup>1</sup>H NMR spectrum of the product (Figure 4A), the undesirable peaks derived from C==C forming coupling of diazocarbonyl groups,<sup>30</sup> which is occasionally encountered as an unwanted side reaction of diazocarbonyl decomposition, were observed. To suppress the side reaction, we examined the polycondensation using other catalysts including recently reported InCl<sub>3</sub> that can effectively catalyze O–H insertion of EDA into various alcohols.<sup>31</sup> The polycondensation of H4 was conducted using InCl<sub>3</sub> as a catalyst, yielding an oligomer again  $(M_n = 540, M_w/M_n = 1.97, yield = 64\%)$ , but the signals corresponding to C==C forming coupling became negligible in the <sup>1</sup>H NMR spectrum (Figure 4B). In addition, a set of signals assignable to the expected repeating unit that should be generated via O-H insertion reaction was observed, and no other significant peaks were present. The obtained products were insoluble into water, while the products obtained by palladium-mediated polymerization of the same monomer were readily soluble in water. Accordingly, it was demonstrated that two types of products with different structures and property can be obtained from a single monomer by changing initiating systems.

#### CONCLUSIONS

We have demonstrated that two types of polymerization are available from a single monomer depending on initiating systems, namely, chain-growth and step-growth polymerization of hydroxy-containing diazoacetates. The polymerization of hydroxy-containing diazoacetates using palladium complexes and subsequent deprotection produced hydroxy-containing poly(substituted methylene)s, which can be regarded as analogues of poly(HEMA) or poly(HEA) but possess denser packing of the hydroxy groups around the polymer chain. It was found that polyS5' shows an LCST-type phase separation in an aqueous medium at around room temperature. In addition, the direct polymerization of hydroxy-containing diazoacetates without a protecting group successfully proceeded to give polymers, although the polymers had a slightly branched structure due to chain transfer reaction with hydroxy groups. To our knowledge, this is the first example of the syntheses of hydrophilic poly(substituted methylene)s from diazoacetates. It should be noted here that the hydroxy-containing diazoacetates can be successfully polymerized despite the polymer chain-end has a nucleophilic Pd-C growing species. Furthermore, we have found that polymerization of hydroxy-containing diazoacetates using InCl<sub>3</sub> as a catalyst proceeded under step-growth mechanism to give oligomers with a distinct repeating unit (ester-ether), where a new ether bond was generated through O-H insertion reaction of diazocarbonyl groups into hydroxy groups. Combination of chain- and step-growth polymerization using both initiating systems would afford a new type of branched polymers. The further investigation is under way in our laboratory.

#### EXPERIMENTAL SECTION

**Materials.** Tetrahydrofuran (THF) was dried over Na/K alloy and distilled before use. CH<sub>2</sub>Cl<sub>2</sub> was dried over CaH<sub>2</sub> and used without further purification.  $[(\eta^3-C_3H_5)PdCl]_2$  (Aldrich, 98%), 1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene(1,4-naphthoquinone)-palladium(0) dimer [(NHC)Pd, Aldrich], Rh<sub>2</sub>(OAc)<sub>4</sub> (AZmax, 99%), NaBPh<sub>4</sub> (Kanto Chemical, >99.5%), *tetr*-butyldimethylsilyl chloride (TCI, >98.0%), tetrabutylammonium fluoride solution (TCI; 1 mol/L in THF), and InCl<sub>3</sub> (Alfa Aesar, 99.99%) were used as received. Ethyl diazoacetate (EDA; 2.5 M solution in CH<sub>2</sub>Cl<sub>2</sub>) was prepared according to the literature.<sup>32</sup> Caution! Extra care must be taken for preparation and handling of the diazoacetates because of their potential explosiveness.

Synthesis of Hydroxy-Containing Diazoacetates (H2–H6). H2–H6 were prepared according to the similar procedure reported by Fukuyama and co-workers.<sup>33</sup> As an example, the synthesis of H2 is as follows. Ethylene glycol (2.0 mL, 36 mmol) and NaHCO<sub>3</sub> (1.0 g, 12 mmol) were dissolved in acetonitrile (30 mL), and bromoacetyl bromide (0.52 mL, 6.0 mmol) was added slowly at 0 °C. After stirring 10 min at the temperature, the reaction was quenched with water. The solution was extracted with CH<sub>2</sub>Cl<sub>2</sub>, and the organic phase was washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated, and



Figure 4. <sup>1</sup>H NMR spectra of the products obtained by polycondensation of H4 using (A) Rh<sub>2</sub>(OAc)<sub>4</sub> and (B) InCl<sub>3</sub>, recorded in CDCl<sub>3</sub>.

the residue was used in the next reaction without purification. The residue obtained and *N*,*N'*-ditosylhydrazine (4.1 g, 12 mmol) were dissolved in THF (30 mL) and cooled to 0 °C. 1,8-Diazabicyclo-[5,4,0]undec-7-ene (4.5 mL, 30 mmol) was added dropwise and stirred at the temperature for 10 min. After the quenching of the reaction by the addition of saturated NaHCO<sub>3</sub> solution, this was extracted with diethyl ether. The organic phase was washed with brine, dried over MgSO<sub>4</sub>, and evaporated to give the crude product. Purification of the crude was performed with recycling GPC to give H2 (0.12 g, 15% in two steps) as a pale yellow oil.

**H2.** Yield: 15%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz), δ (ppm): 4.81 (s, 1H,  $-CH=N_2$ ), 4.31 (t, J = 4.4 Hz, 2H,  $-CO_2CH_2-$ ), 3.84 (t, J = 4.4 Hz, 2H,  $-CH_2OH$ ). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz), δ (ppm): 167.4 ( $-CO_2-$ ), 66.5 ( $-CO_2CH_2-$ ), 61.1 ( $-CH_2OH$ ), 46.4 ( $-CH=N_2$ ). Anal. Calcd for C<sub>4</sub>H<sub>6</sub>N<sub>2</sub>O<sub>3</sub>: C, 36.92; H, 4.65; N, 21.54. Found: C, 37.20; H, 5.60; N, 19.11.

H3. Yield: 22%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz), δ (ppm): 4.81 (s, 1H,  $-CH=N_2$ ), 4.31 (t, J = 6.8 Hz, 2H,  $-CO_2CH_2-$ ), 3.68 (t, J = 6.0 Hz, 2H,  $-CH_2OH$ ), 1.88 (m, 2H,  $-CH_2CH_2CH_2-$ ). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz), δ (ppm): 167.4 ( $-CO_2-$ ), 61.8 ( $-CO_2CH_2-$ ), 58.8 ( $-CH_2OH$ ), 46.2 ( $-CH=N_2$ ), 31.9 ( $-CH_2CH_2CH_2-$ ). Anal. Calcd for C<sub>5</sub>H<sub>8</sub>N<sub>2</sub>O<sub>3</sub>: C, 41.66; H, 5.59; N, 19.44. Found: C, 40.92; H, 6.14; N, 17.76.

H4. Yield: 45%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz), δ (ppm): 4.80 (s, 1H,  $-CH=N_2$ ), 4.19 (t, J = 6.4 Hz, 2H,  $-CO_2CH_2-$ ), 3.64 (t, J = 6.0 Hz, 2H,  $-CH_2OH$ ), 1.74 (m, 2H,  $-CO_2CH_2CH_2-$ ), 1.61 (m, 2H,  $-CH_2CH_2OH$ ). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz), δ (ppm): 167.1 ( $-CO_2-$ ), 64.7 ( $-CO_2CH_2-$ ), 62.0 ( $-CH_2OH$ ), 46.1 ( $-CH=N_2$ ), 28.9 ( $-CO_2CH_2CH_2-$ ), 25.3 ( $-CH_2CH_2OH$ ). Anal. Calcd for  $C_6H_{10}N_2O_3$ : C, 45.56; H, 6.37; N, 17.72. Found: C, 45.11; H, 6.97; N, 16.85.

H5. Yield: 53%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz), δ (ppm): 4.82 (s, 1H,  $-CH=N_2$ ), 4.16 (t, J = 6.8 Hz, 2H,  $-CO_2CH_2-$ ), 3.60 (t, J = 6.4 Hz, 2H,  $-CH_2OH$ ), 1.68 (m, 2H,  $-CO_2CH_2CH_2-$ ), 1.58 (m, 2H,  $-CH_2CH_2OH$ ), 1.43 (m, 2H,  $-CH_2CH_2CH_2CH_2-$ ). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz), δ (ppm): 167.0 ( $-CO_2-$ ), 64.7 ( $-CO_2CH_2-$ ), 62.1 ( $-CH_2OH$ ), 46.0 ( $-CH=N_2$ ), 32.0 ( $-CO_2CH_2CH_2-$ ), 28.4 ( $-CH_2CH_2OH$ ), 22.0 ( $-CH_2CH_2CH_2CH_2-$ ). Anal. Calcd for  $C_7H_{12}N_2O_3$ : C, 48.82; H, 7.02; N, 16.27. Found: C, 48.57; H, 7.48; N, 15.93.

**H6.** Yield: 28%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz),  $\delta$  (ppm): 4.78 (s, 1H, -CH=N<sub>2</sub>), 4.16 (t, *J* = 6.4 Hz, 2H, -CO<sub>2</sub>CH<sub>2</sub>-), 3.62 (t, *J* = 6.4 Hz, 2H, -CO<sub>2</sub>CH<sub>2</sub>-), 1.57 (m, 2H, Hz, 2H, -CH<sub>2</sub>OH), 1.66 (m, 2H, -CO<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 1.57 (m, 2H, -CH<sub>2</sub>OH), 1.57 (m, 2H), -CH<sub>2</sub>OH), -C

Synthesis of Silyl-Protected Diazoacetates (S2–S6). S2–S6 were prepared by the reaction between the corresponding hydroxycontaining diazoacetates (H2–H6) and *tert*-butyldimethylsilyl chloride. As an example, the synthesis of S2 is as follows. H2 (95 mg, 0.73 mmol) and imidazole (0.15 g, 2.2 mmol) were dissolved in dry THF (6 mL). Into the mixture, a THF (6 mL) solution of *tert*butyldimethylsilyl chloride (0.17 g, 1.1 mmol) was added dropwise and stirred at the temperature for 90 min. The reaction mixture was quenched by adding water. The resulting solution was extracted with CHCl<sub>3</sub>, and the combined organic layer was washed with water, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. Purification of the crude was performed with recycling GPC to give S2 (0.10 g, 56%) as a pale yellow oil.

**S2.** Yield: 56%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz), δ (ppm): 4.73 (s, 1H,  $-CH=N_2$ ), 4.18 (t, J = 4.8 Hz, 2H,  $-CO_2CH_2-$ ), 3.76 (t, J = 4.8 Hz, 2H,  $-CH_2OSi[CH_3]_2C[CH_3]_3$ ), 0.85 (s, 9H,  $-OSi[CH_3]_2C[CH_3]_3$ ), 0.03 (s, 6H,  $-OSi[CH_3]_2C[CH_3]_3$ ). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz), δ (ppm): 166.7 ( $-CO_2-$ ), 66.1 ( $-CO_2CH_2-$ ), 61.5 ( $-CH_2OSi[CH_3]_2C[CH_3]_3$ ), 46.1 ( $-CH=N_2$ ), 25.9 ( $-OSi[CH_3]_2C[CH_3]_3$ ), 18.4 ( $-OSi[CH_3]_2C[CH_3]_3$ ), -5.3 ( $-OSi[CH_3]_2C[CH_3]_3$ ). Anal. Calcd for C<sub>10</sub>H<sub>20</sub>N<sub>2</sub>O<sub>3</sub>Si: C, 49.15; H, 8.25; N, 11.46. Found: C, 49.41; H, 7.97; N, 11.20.

**S3.** Yield: 68%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz), δ (ppm): 4.71 (s, 1H,  $-CH=N_2$ ), 4.24 (t, J = 6.0 Hz, 2H,  $-CO_2CH_2-$ ), 3.65 (t, J = 6.0 Hz, 2H,  $-CH_2OSi[CH_3]_2C[CH_3]_3$ ), 1.57 (m, 2H,  $-CH_2CH_2CH_2-$ ), 0.87 (s, 9H,  $-OSi[CH_3]_2C[CH_3]_3$ ), 0.03 (s, 6H,  $-OSi[CH_3]_2C[CH_3]_3$ ). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz), δ (ppm): 166.8 ( $-CO_2-$ ), 62.0 ( $-CO_2CH_2-$ ), 59.4 ( $-CH_2OSi[CH_3]_2C[CH_3]_3$ ), 46.1 ( $-CH=N_2$ ), 32.1 ( $-CH_2CH_2CH_2-$ ), 26.0 ( $-OSi[CH_3]_2C[CH_3]_3$ ), 18.4 ( $-OSi[CH_3]_2C[CH_3]_3$ ), -5.3 ( $-OSi[CH_3]_2C[CH_3]_3$ ). Anal. Calcd for C<sub>11</sub>H<sub>22</sub>N<sub>2</sub>O<sub>3</sub>Si: C, 51.13; H, 8.58; N, 10.84. Found: C, 51.11; H, 8.73; N, 9.68.

**S4.** Yield: 79%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz),  $\delta$  (ppm): 4.72 (s, 1H, -CH=N<sub>2</sub>), 4.17 (t, *J* = 6.4 Hz, 2H, -CO<sub>2</sub>CH<sub>2</sub>-), 3.63 (t, *J* = 6.0 Hz, 2H, -CH<sub>2</sub>OSi[CH<sub>3</sub>]<sub>2</sub>C[CH<sub>3</sub>]<sub>3</sub>), 1.71 (m, 2H, -CO<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 1.57 (m, 2H, -CH<sub>2</sub>CH<sub>2</sub>OSi[CH<sub>3</sub>]<sub>2</sub>C[CH<sub>3</sub>]<sub>3</sub>), 0.89 (s, 9H, -OSi[CH<sub>3</sub>]<sub>2</sub>C

 $\begin{array}{l} [CH_3]_3), 0.05 \; (s, 6H, -OSi[CH_3]_2C[CH_3]_3). \ ^{13}C \; NMR \; (CDCl_3, 100 \\ MHz), \; \delta \; \; (ppm): \; 166.8 \; (-CO_2-), \; 64.9 \; (-CO_2CH_2-), \; 62.6 \\ (-CH_2OSi[CH_3]_2C[CH_3]_3), \; 46.1 \; (-CH=N_2), \; 29.2 \; (-CO_2-CH_2CH_2-), \; 26.0 \; (-OSi[CH_3]_2C[CH_3]_3), \; 25.6 \; (-CH_2CH_2OSi[CH_3]_2C[CH_3]_3), \; 18.4 \; (-OSi[CH_3]_2C[CH_3]_3), \; -5.3 \; (-OSi[CH_3]_2-C[CH_3]_3), \; Anal. \; Calcd \; for \; C_{12}H_{24}N_2O_3Si: \; C, \; 52.91; \; H, \; 8.88; \; N, \; 10.29. \\ Found: \; C, \; 52.88; \; H, \; 9.51; \; N, \; 10.26. \end{array}$ 

**S5.** Yield: 68%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz), δ (ppm): 4.71 (s, 1H,  $-CH=N_2$ ), 4.13 (t, J = 6.4 Hz, 2H,  $-CO_2CH_2-$ ), 3.59 (t, J = 6.0 Hz, 2H,  $-CH_2OSi[CH_3]_2C[CH_3]_3$ ), 1.64 (m, 2H,  $-CO_2CH_2CH_2-$ ), 1.52 (m, 2H,  $-CH_2CH_2OSi[CH_3]_2C[CH_3]_3$ ), 1.38 (m, 4H,  $-CH_2CH_2-CH_2CH_2CH_2-$ ), 0.87 (s, 9H,  $-OSi[CH_3]_2C[CH_3]_3$ ), 0.02 (s, 6H,  $-OSi[CH_3]_2C[CH_3]_3$ ). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz), δ (ppm): 166.9 ( $-CO_2-$ ), 65.0 ( $-CO_2CH_2-$ ), 63.0 ( $-CH_2OSi[CH_3]_2C-[CH_3]_3$ ), 46.1 ( $-CH=N_2$ ), 32.5 ( $-CO_2CH_2CH_2-$ ), 28.8 ( $-CH_2-CH_2OSi[CH_3]_2C[CH_3]_3$ ), 26.1 ( $-OSi[CH_3]_2C[CH_3]_3$ ), 22.4 ( $-CH_2-CH_2CH_2CH_2CH_2-$ ), 18.4 ( $-OSi[CH_3]_2C[CH_3]_3$ ), 25.2 ( $-OSi[CH_3]_3$ ), -5.2 ( $-OSi[CH_3]_2C-[CH_3]_3$ ). Anal. Calcd for  $C_{13}H_{26}N_2O_3Si: C, 54.51;$  H, 9.15; N, 9.78. Found: C, 55.25; H, 9.55; N, 9.31.

**S6.** Yield: 63%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz),  $\delta$  (ppm): 4.71 (s, 1H,  $-CH=N_2$ ), 4.14 (t, J = 6.8 Hz, 2H,  $-CO_2CH_2-$ ), 3.58 (t, J = 6.4 Hz, 2H,  $-CH_2OSi[CH_3]_2C[CH_3]_3$ ), 1.63 (m, 2H,  $-CO_2CH_2CH_2-$ ), 1.50 (m, 2H,  $-CH_2CH_2CSi[CH_3]_2C[CH_3]_3$ ), 1.35 (m, 4H,  $-CH_2CH_2CH_2CH_2CH_2CH_2-$ ), 0.88 (s, 9H,  $-OSi[CH_3]_2C[CH_3]_3$ ), 0.03 (s, 6H,  $-OSi[CH_3]_2C[CH_3]_3$ ). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz),  $\delta$  (ppm): 166.9 ( $-CO_2-$ ), 65.1 ( $-CO_2CH_2-$ ), 63.2 ( $-CH_2OSi[CH_3]_2C[CH_3]_3$ ), 46.1 ( $-CH=N_2$ ), 32.8 ( $-CO_2CH_2CH_2-$ ), 29.0 ( $-CH_2-CH_2OSi[CH_3]_2C[CH_3]_3$ ), 26.1 ( $-OSi[CH_3]_2C[CH_3]_3$ ), 25.8 ( $-CH_2-CH_2CH_2CH_2CH_2CH_2CH_2-$ ), 18.5 ( $-OSi[CH_3]_2C[CH_3]_3$ ), -5.2 ( $-OSi[CH_3]_2C[CH_3]_3$ ). Anal. Calcd for C<sub>14</sub>H<sub>28</sub>N<sub>2</sub>O<sub>3</sub>Si: C, 55.96; H, 9.39; N, 9.33. Found: C, 55.97; H, 9.71; N, 9.09.

Polymerization Procedure. As a representative example, the procedure for the polymerization of S2 (run 1 in Table 1) is described as follows. Under a nitrogen atmosphere, a THF (0.50 mL) solution of  $[(\eta^3-C_3H_5)PdCl]_2$  (1.5 mg, 4.1 × 10<sup>-3</sup> mmol) was placed in a Schlenk tube and was cooled to -20 °C. The polymerization was started by the addition of a THF (0.50 mL) solution of S2 (0.10 g, 0.41 mmol) by using a syringe, and the reaction mixture was stirred at -20 °C for 13 h. After the volatiles were removed under reduced pressure at -20 °C, 10 mL of 1 N HCl/methanol, 10 mL of 1 N HCl aqueous solution, and 20 mL of CHCl3 were added to the residue. The resulting solution was then extracted with CHCl<sub>3</sub>, and the combined organic layer was washed with 1 N HCl aqueous solution and water, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. Purification with preparative recycling GPC gave polyS2' (33 mg, 40%). For the purification of polyH2'-polyH6', dialysis of polymers was done against water (polyH2'-polyH4') or methanol (polyH5' and polyH6'), using cellulose acetate dialysis tubing [cutoff molecular weight (MWCO) = 1000 g/mol].

**Deprotection Procedure.** The following is a typical deprotection procedure. A portion of the product obtained by polymerization of S2 (70 mg) was dissolved in THF (2 mL), and tetrabutylammonium fluoride solution (0.96 mL, 1.0 M in THF) was added dropwise at room temperature under stirring. After 1 h, 1 N HCl aqueous solution (2 mL) was added dropwise, and the mixture was stirred for 24 h. The solution was transferred into a dialysis bag [cellulose acetate, MWCO = 1000 g/mol)] and dialyzed against water (polyS2'-polyS4') or methanol (polyS5' and polyS6').

**Protection Procedure.** The following is a typical protection procedure. A portion of polyH2' (20 mg) was dissolved in pyridine (0.5 mL), and an acetonitrile (2 mL) solution of *tert*-butyldimethylsilyl chloride (0.32 g) was added at room temperature under stirring. After 24 h, the reaction mixture was quenched by adding water. The resulting solution was extracted with CHCl<sub>3</sub>, and the combined organic layer was washed with water, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure.

**Measurements.** The number-average molecular weight  $(M_n)$  and polydispersity ratio [weight-average molecular weight/number-average molecular weight  $(M_w/M_n)$ ] were measured by means of gel

permeation chromatography (GPC) on a Jasco-ChromNAV system equipped with a differential refractometer detector using THF as eluent at a flow rate of 1.0 mL/min at 40 °C, calibrated with six poly(MMA) standards (Shodex M-75;  $M_{\rm p} = 2400-212\ 000, M_{\rm w}/M_{\rm p} <$ 1.1) and dibutyl sebacate (molecular weight = 314.5). The columns used for the GPC analyses was a combination of Styragel HR4 and HR2 (Waters; exclusion limit molecular weight = 600K and 20K for polystyrene, respectively; column size =  $300 \text{ mm} \times 7.8 \text{ mm}$  i.d.; average particle size = 5  $\mu$ m). Purification by preparative recycling GPC was performed on a JAI LC-918R equipped with a combination of columns of a JAIGEL-3H and a JAIGEL-2H (Japan Analytical Industry; exclusion limit molecular weight = 70K and 5K for polystyrene, respectively; column size =  $600 \text{ mm} \times 20 \text{ mm}$  i.d.) using  $\text{CHCl}_3$  as eluent at a flow rate of 3.8 mL/min at room temperature. <sup>1</sup>H (400 MHz) and <sup>13</sup>C (100 MHz) NMR spectra were recorded on a Bruker Avance 400 spectrometer at room temperature (monomers) or at 50 °C (polymers). The glass transition temperature  $(T_g)$  of the polymer was determined by differential scanning calorimetry (DSC; EXSTAR DSC 6000, Seiko Instruments) in the range from -100 to 150 °C. The heating and cooling rates were 20  $^{\circ}$ C/min. The  $T_{\sigma}$  of the polymers was defined as the temperature of the midpoint of a heat capacity change on the second heating scan. MALDI-TOF-MS analyses were performed on a PerSeptive Biosystems Voyager RP (reflector mode) using dithranol as a matrix and sodium trifluoroacetate as an ion source. Elemental analyses were performed on a YANAKO CHN Corder MT-5.

#### ASSOCIATED CONTENT

#### Supporting Information

<sup>1</sup>H NMR spectra, MALDI-TOF-MS spectra, DSC thermograms, and table for polycondensation of hydroxy-containing diazoacetates. 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.

#### ACKNOWLEDGMENTS

This research was supported by JSPS KAKENHI Grants 22550113 and 26104525 and Adaptable and Seamless Technology Transfer Program through target-driven R&D (A-STEP) from the Japan Science and Technology Agency (JST). The authors thank Venture Business Laboratory in Ehime University for its assistance in NMR and MALDI-TOF-MS measurements and Integrated Center for Science (INCS) in Ehime University for its assistance in elemental analysis.

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