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Synthesis of dendronized polymers through Pd-initiated C1 polymerization of diazoacetates with different generation ester-type dendron groups†

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A series of diazoacetates with an ester-type dendron unit of 1st to 3rd generation as an ester substituent were newly prepared and their Pd-initiated polymerization was conducted to afford dendronized C1 polymers with the SEC-estimated number-average molecular weight ($M_{n,SEC}$) of up to 16 700 and a relatively narrow molecular weight distribution ($Đ$ = 1.12–1.37). The glass transition temperature (T_g) of these dendronized polymers increased with the increasing generation of the dendron unit, where the degree of increase (ΔT_g) was much larger than that observed with their vinyl polymer counterparts (polymethacrylates with the same dendron substituents). The diazoacetate with the 3rd generation dendron unit was successfully copolymerized with benzyl diazoacetate to afford a copolymer, whose dendron-derived units were converted to those with multiple hydroxy groups *via* deprotection of acetonide-protecting groups at the peripheral positions.

Introduction

Transition-metal initiated polymerization of diazoacetate is one of the representative examples of C1 polymerization, where the backbone of carbon–carbon (C–C) main chain polymers is constructed from "*one carbon unit*".[1–8] All the main chain carbon atoms of the polymers obtained by the C1 polymerization of diazoacetate have an alkoxycarbonyl group (ester) as a substituent, which is the most striking characteristic of the polymers, in comparison to their vinyl polymer counterpart, poly(alkyl acrylate), whose alkoxycarbonyl substituents are located on every other carbon atom on the main chain. The structural feature of C1 polymers is expected to bring about enhanced physical properties or functionalities because of the dense packing of the ester substituents around the polymer main chain, and we and other research groups have indeed observed enhanced properties in some C1 polymers in comparison to their vinyl polymer counterparts with the same ester substituents.[9–28]

As initiators for the polymerization, some Rh and Pd complexes have been reported to be effective, yielding high number-average molecular weight (M_n) polymers in good yield. Our group has been focusing on the development of Pd-based initiating systems for the diazoacetate polymerization, reporting some effective systems such as (NHC)Pd(nq)/$NaBPh_4$ (NHC = *N*-heterocyclic carbene, nq = naphthoquinone),[29] π-allylPdCl/$NaBPh_4$,[30,31] and $(nq)_2Pd/NaBPh_4$.[32] Although these initiating systems can afford high M_n polymers in good yield, it is difficult to control M_n of the product, and the controlled polymerization of diazoacetate with Pd-based initiating systems is one of our current important objectives. (Some Pd-based initiators have been reported to be effective for the controlled polymerization of diazoacetate by other research groups.[33–35])

Meanwhile, in the course of our research, we have found and reported that, when the monomer has a sterically bulky ester substituent such as cyclotriphosphazene[13,36] and benzyl ether-type dendrons,[26] the π-allylPdCl/$NaBPh_4$-initiated polymerization of such diazoacetates proceeds in a controlled manner to give polymers with a narrow molecular weight distribution (MWD). In particular, for the latter monomer, we have revealed that the use of the dendron unit with a higher generation leads to a narrower MWD of the C1 polymer products.[26] In addition, we introduced protected carboxyl groups at the peripheral positions of the benzyl ether-type dendron unit of the monomer, and after its polymerization followed by deprotection we observed enhanced acidity of the resulting C1 polymer in comparison to its vinyl polymer counterpart.

Herein, we attempted to introduce ester-type dendron units[37–40] in place of the above-described benzyl ether-type dendron units as an ester substituent of the monomers.

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Whereas the ester-type dendron has been utilized for preparation of dendronized polymers *via* ring-opening metathesis polymerization (ROMP) and radical polymerization so far,[41–45] the results obtained here will be the first example of a dendronized C1 polymer with an ester-type dendron. In addition, because the C1 polymer with a benzyl-ether type dendron described above is the only example of a dendronized C1 polymer, this attempt to prepare new diazoacetates with dendron units and to investigate their polymerization behavior should be worthwhile for extending the scope of dendronized polymers[46–51] as well as developing the promising chemistry of C1 polymerization. Diazoacetate with an ester-type dendron substituent with a higher generation is expected to undergo controlled polymerization in a similar manner to that with a benzyl ether-type dendron[26] because of the steric bulkiness of the substituent as well. In addition, because the acetonide-protecting groups at the peripheral positions of the dendron unit can be removed to liberate multiple hydroxy groups, the incorporation of the ester-type dendron unit *via* copolymerization with other diazoacetates can be an effective general method for introducing highly hydrophilic substituents into the C1 polymer backbone. We report the synthesis of new diazoacetates with a series of ester-type dendron substituents and their polymerization behavior with π-allylPdCl/NaBPh$_4$ as an initiator. In addition, copolymerization of a dendron-containing monomer with other less bulky diazoacetates and deprotection of the acetonide-protecting group to yield C1 copolymers with multiple hydroxy groups are described.

Results and discussion

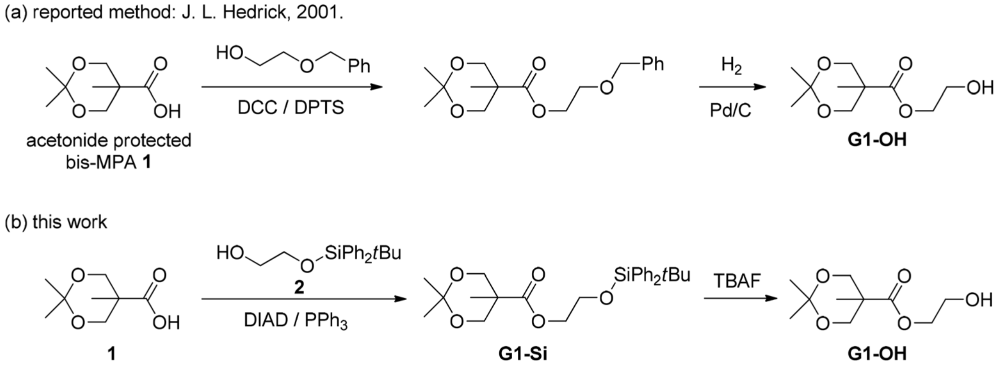
Monomer syntheses

For the synthesis of ester-type dendron-containing diazoacetates required for this study, we should prepare ester-type dendrons having a hydroxy group at their core, which will be transformed to a diazoacetyl group with the standard diazoacetylation using bromoacetyl bromide and *N*,*N*′-ditosylhydrazine.[52] In addition, for efficient progress of C1 polymerization of the sterically bulky diazoacetates, we considered that the presence of a CH$_2$CH$_2$ linker between the dendron and diazoacetyl group would be suitable. The syntheses of the desired precursor compounds meeting these conditions, **G1-OH** in Scheme 1 and its G2,3-derivatives **G2-OH** and **G3-OH** in Scheme 2, have been reported by Hedrick and coworkers,[39] who used esterification of acetonide-protected bis-MPA **1** [bis-MPA: 2,2-bis(hydroxymethyl) propionic acid] with 2-benzyloxyethanol, followed by deprotection with hydrogenation with Pd/C for the introduction of a 2-hydroxyethyl group as shown in Scheme 1(a) for the synthesis of **G1-OH** as a representative example. However, in order to avoid the use of hydrogenation for benzyl-ether deprotection, we attempted to use partially silyl-protected ethylene glycol **2** for the introduction of the linker unit. The non-protected hydroxy group in **2** was used for the esterification of **1** to yield **G1-Si**, followed by TBAF-mediated deprotection of a silyl-group to afford **G1-OH** as shown in Scheme 1(b).

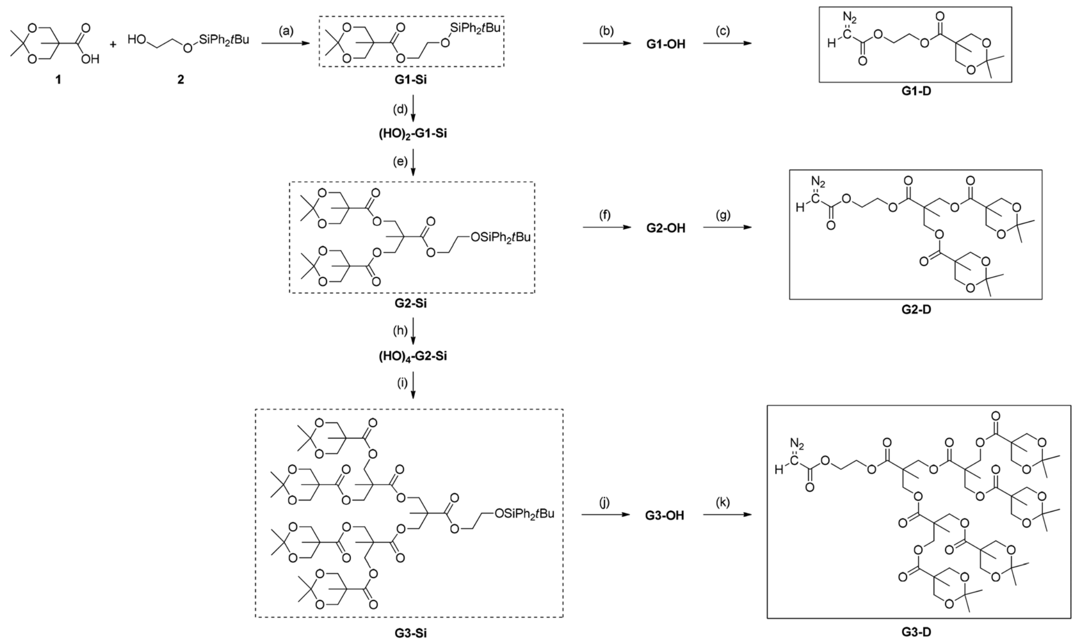
Then, as shown in Scheme 2, the 1st generation diazoacetate monomer **G1-D** was successfully prepared by diazoacetylation of the precursor alcohol **G1-OH** with the standard procedure reported by Fukuyama and coworkers.[52] In addition, as summarized in Scheme 2, starting from **G1-Si**, the systematic divergent syntheses of **G2-D** and **G3-D** were also realized by repeating (1) the acetonide-deprotection with CuCl$_2$·2H$_2$O, (2) esterification of the hydroxy groups with **1**, (3) silyl deprotection, and (4) diazoacetylation. Experimental procedures and characterization data for the isolated new compounds are described in the ESI.†

Homopolymerization of diazoacetates with an ester-type dendron G(1–3)-D

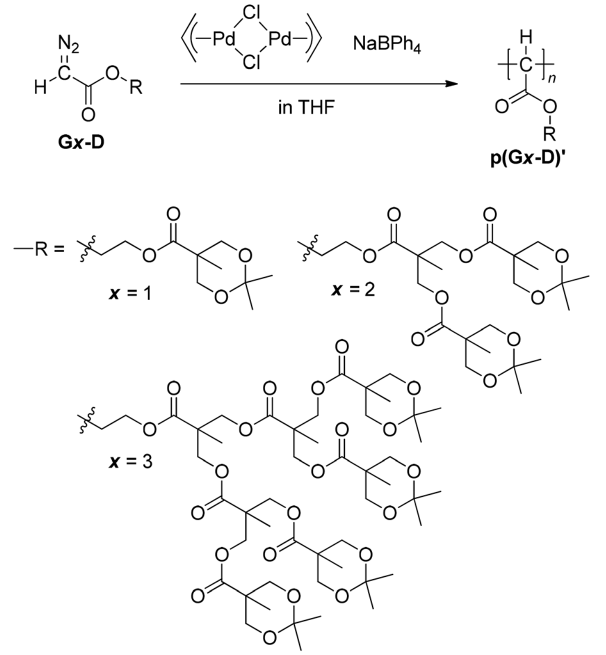
Following the results of the polymerization of diazoacetates containing a benzyl ether-type dendron in our previous publication,[26] we tried to polymerize diazoacetates with a series of ester-type dendrons, **G(1–3)-D**, using π-allylPdCl/NaBPh$_4$ as an initiator (Scheme 3 and Table 1). As shown in runs 1 and 2, when polymerization of **G1-D** with a feed ratio of [**G1-D**]/[Pd] = 50 was conducted at room temperature and −20 °C, the results at −20 °C were better with respect to M_n and polymer yield. Then, at −20 °C, the polymerization was conducted with increasing feed ratios of 100 and 200 (runs 3 and 4), resulting



Scheme 1 Methods for preparation of hydroxyethyl ester of acetonide protected bis-MPA.



Scheme 2 Synthetic routes for diazoacetates with an ester-type dendron **G(1–3)-D**. Reagents and conditions: (a) diisopropyl azodicarboxylate (DIAD), PPh_3, THF, RT, 12 h (88%); (b) tetrabutylammonium fluoride (TBAF), THF, RT, 3 min (71%); (c) bromoacetyl bromide, pyridine, THF, 0 °C, 3 h; *N*,*N*′-ditosylhydrazine, 1,8-diazabicyclo[5.4.0]-7-undecene (DBU), THF, 0 °C, 3 h (66%); (d) $CuCl_2 \cdot 2H_2O$, −10 to 0 °C, 20 h (81%); (e) **1**, DIAD, PPh_3, THF, RT, 46 h (72%); (f) TBAF, THF, RT, 15 h (66%); (g) bromoacetyl bromide, pyridine, THF, 0 °C, 5 h; *N*,*N*′-ditosylhydrazine, DBU, THF, 0 °C, 5 h (64%); (h) $CuCl_2 \cdot 2H_2O$, −10 to 0 °C, 20 h (70%); (i) **1**, DIAD, PPh_3, THF, 50 °C, 72 h (63%); (j) TBAF, THF, RT, 30 min (77%); (k) bromoacetyl bromide, pyridine, THF, 0 °C, 7 h; *N*,*N*′-ditosylhydrazine, DBU, THF, 0 °C, 7 h (55%).



Scheme 3 Homopolymerization of diazoacetates with an ester-type dendron **G(1–3)-D**.

in the gradual increase of M_n with the feed ratio of up to $M_{n,SEC}$ = 16 700, with a moderate polymer yield of 61% and 64%. A further increase of the feed ratio to [**G1-D**]/[Pd] = 300 did not lead to a higher M_n, but lower polymer yield (run 5). MWDs of products in runs 1–5 in the range of $Đ$ = 1.29–1.37 were relatively narrow for products obtained with this initiator.

As for the polymerization of **G2-D**, the results of polymerization at −20 °C are again better than those at room temperature (runs 6 and 7), and with the increase of the [**G2-D**]/[Pd] feed ratio to 100 and 200 at −20 °C (runs 8 and 9), the $M_{n,SEC}$ increased up to 14 200. Compared to the results of **G1-D**, MWDs of **p(G2-D)**s obtained at −20 °C were narrower in the range of $Đ$ = 1.14–1.31; these low $Đ$ values cannot be considered as higher controllability of **G2-D** than that of **G1-D** but indicated the same level of controllability, on the basis of the comparison with the data reported for their vinyl polymer counterparts as discussed later in this paper. Meanwhile, the polymer yield became slightly lower (42–50%), suggesting that the sterically larger ester substituent in **G2-D** brought about lower reactivity because of its steric demand during the polymerization. Fig. 1 shows ^1H NMR spectra of **G2-D** and **p(G2-D)′** of a sample obtained in run 6, where we can observe broad signals in the spectrum of **p(G2-D)′** corresponding to each signal in the spectrum of the monomer except for the signal for the H on the diazo-bearing carbon atom, which was converted to a main chain C*H* exhibiting a broad signal at 3.0–3.8 ppm in the spectrum of **p(G2-D)′**.

In contrast to **G1-D** and **G2-D** affording polymers in moderate yield (*ca.* 50%), the polymerization of **G3-D** with a [**G3-D**]/[Pd] feed ratio of 50 afforded a polymer in a low yield of 30% (run 10), suggesting that the ester substituent of **G3-D** is too bulky for the

Table 1 Homopolymerization of diazoacetates with an ester-type dendron **G(1–3)-D**[a]

Run	Monomer (M)	Temp.	[M]/[Pd]	Yield[b] (%)	M_n[c]	$Đ$[c]	$M_{n,MALS}$[d]	$Đ_{MALS}$[d]	T_g[e] (°C)
1	**G1-D**	RT	50	48	4900	1.29			
2	**G1-D**	−20 °C	50	56	6500	1.29	10 900 (DP = 42, IE = 0.66)	1.34	5
3	**G1-D**	−20 °C	100	61	10 900	1.32			
4	**G1-D**	−20 °C	200	64	16 700	1.37			
5	**G1-D**	−20 °C	300	51	13 800	1.30			
6	**G2-D**	RT	50	35	4200	1.12			
7	**G2-D**	−20 °C	50	49	8700	1.19	12 700 (DP = 24, IE = 1.0)	1.21	10
8	**G2-D**	−20 °C	100	50	10 300	1.14			
9	**G2-D**	−20 °C	200	42	14 200	1.31			
10	**G3-D**	−20 °C	50	30	7000	1.16			39

[a] In THF for 15 h, [monomer] = *ca.* 0.1 M, $[NaBPh_4]/[Pd]$ = *ca.* 1.2. [b] Determined by gravimetry after purification with preparative SEC. [c] Determined by SEC calibrated using PMMA standards. [d] $M_{n,MALS}$ values were determined by SEC-MALS. The average degree of polymerization (DP) values were calculated from $M_{n,MALS}$. Apparent initiator efficiency (IE) values were calculated from $M_{n,MALS}$ and polymer yield. [e] Determined by DSC measurements.

polymerization to proceed effectively. Also, the narrow MWD of the **p(G3-D)′** ($Đ$ = 1.16) suggests that the polymerization of **G3-D** would proceed with the same level of controllability as those of **G1-D** and **G2-D** as well (see discussion below).

SEC-MALS measurements were carried out for the samples in runs 2 and 7 in Table 1. As reported in our previous publication for C1 polymers obtained from diazoacetates, the $M_{n,MALS}$ values were 1.5–1.7 times higher than those estimated by standard PMMA-calibrated SEC. In addition, on the basis of the $M_{n,MALS}$ and polymer yield, the apparent initiator efficiency ([Pd acting as an initiator]/[Pd employed]) was calculated for these samples and is listed in Table 1. These data indicate that while 66% of π-allylPdCl employed for the polymerization of **G1-D** acted as an initiator, the Pd complex almost quantitatively participated in the initiation in the case of polymerization of **G2-D**. These results suggest more efficient initiation of **G2-D** with bulkier ester substituents than **G1-D**.

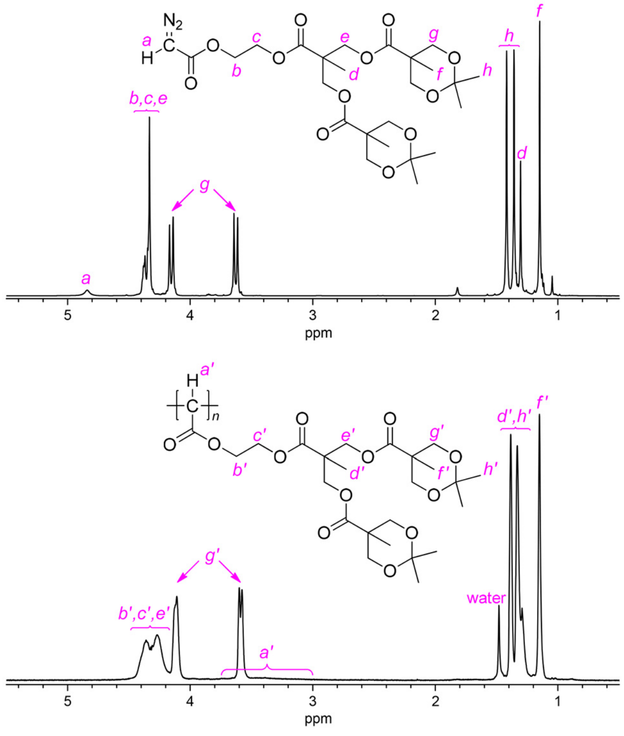


Fig. 1 ^1H NMR spectra of **G2-D** (upper) and **p(G2-D)′** (lower) recorded in $CDCl_3$.

Fortunately for us, A. Hult and coworkers reported the preparation and physical properties of polymethacrylates with the same ester-type dendron as ours with 1st to 4th generation *via* atom transfer radical polymerization (ATRP).[41,42] Coincidentally, as shown in Chart 1, the oxyethylene spacer unit between the dendron and the main chain of the polymethacrylates is exactly the same as ours, making the comparison here more relevant. In their report, they prepared polymethacrylate with a 1st generation dendron *via* ATRP and polymers with higher generations *via* divergent transformation (post-polymerization modification) therefrom. Importantly to us, the SEC-determined $Đ$ value gradually decreased with the increase of the dendron generation, from 1.24 to 1.11 (Chart 1), even though the polymethacrylate backbone is identical for these dendronized polymers. These results indicated that probably because of the higher rigidity and bulkiness of the polymer chain with the increase of the dendron generation, the SEC-determined $Đ$ value became lower. Accordingly, the results of the apparent narrower MWD with the increase of dendron generation in the C1 polymerization of **G(1–3)-D** cannot be considered as improved controllability of the polymerization as well. However, these results at least indicate that the relatively high controllability for **p(G1-D)′** is retained for **p(G2-D)′** and **p(G3-D)′**.

Fig. 2 shows the charts of DSC measurements of **p[G(1–3)-D]′** samples obtained in runs 2, 7, and 10. It is clearly demonstrated that the glass transition temperature (T_g) increased with the increase of the dendron generation, indicating that the increased side chain bulkiness would restrict the main chain mobility. In particular, the higher T_g (39 °C) of **p(G3-D)′** despite its lower M_n indicates that the steric demand caused by the ester-type dendron G3 unit led to severe restriction for the main chain mobility.

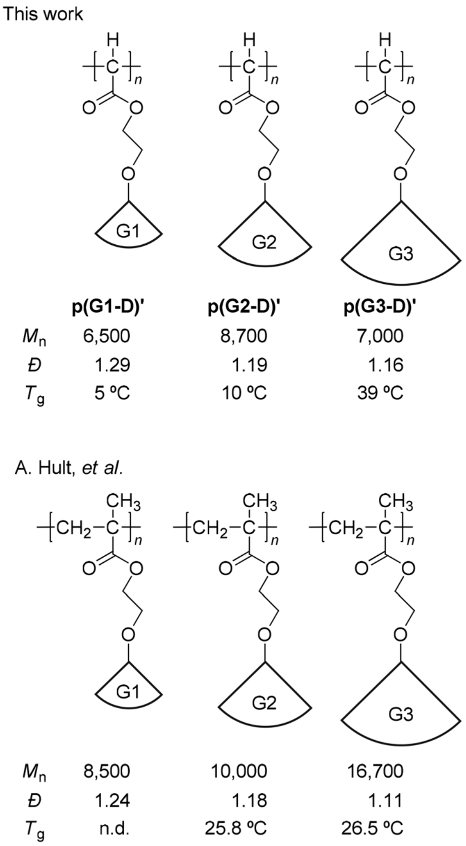


Chart 1 Comparison of M_n, $Đ$, and T_g values between **p[G(1–3)-D]′** and the corresponding polymethacrylates.

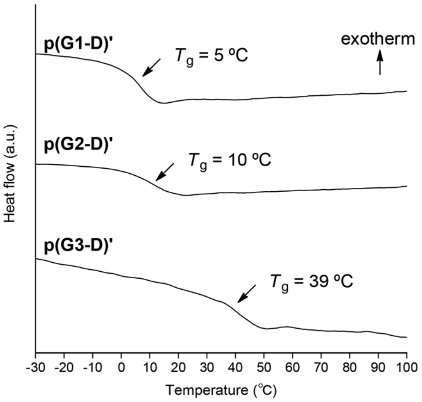


Fig. 2 DSC thermograms of **p[G(1–3)-D]′** samples (second heating, heat rate = 10 °C min^{-1}).

With respect to the observed T_gs, the results reported by A. Hult and coworkers[41,42] are again quite helpful for us to conduct reasonable comparison of the C1 polymers with their vinyl polymer counterparts. They reported that the T_g increase was 0.7 °C with the dendron generation increase from G2 to G3 as listed in Chart 1. In contrast, the T_gs of our polymers increased from 10 to 39 °C, whose ΔT_g is a much larger value of 29 °C. These results clearly demonstrate that because of the denser packing of the ester-type dendron in our dendronized C1 polymers without any CH_2 unit in the main chain, the restriction of the main chain mobility caused by the generation increase from G2 to G3 is enhanced to a much greater extent compared to their vinyl polymer counterparts.

Copolymerization of G3-D with benzyl diazoacetate (BDA)

Although homopolymerization of **G3-D** did not proceed effectively (run 10, Table 1), we can expect that the monomer with the bulky ester substituent can be used as a comonomer with other diazoacetates with a non-sterically demanding ester substituent. Considering facile determination of the copolymer composition using signal intensities in the ^{1}H NMR spectra of the resulting copolymers, we chose benzyl diazoacetate (BDA) as a less bulky comonomer for the copolymerization with **G3-D** and the results are summarized in Table 2. The copolymerization with a feed ratio of [**G3-D**]/[BDA] = 1 : 5 ([monomers]/[Pd] = 100 : 1) resulted in the formation of a copolymer with $M_{n,SEC}$ = 12 900 and a composition of [**G3-D′**]/[BDA′] = 1 : 5.4 (run 1 in Table 2), which was determined from the signal intensity ratio in the ^{1}H NMR spectrum of the copolymer; in the spectrum of Fig. 3(a), the composition was calculated by using the intensity of OCH_2 of BDA′ at 4.3–5.1 ppm and that of all Hs of **G3-D′** except for Me–Hs and main chain CH of BDA′ at 2.7–4.3 ppm. Whereas the composition of the product in the above example was close to the monomer feed ratio, when the relative feed ratio of **G3-D** was increased to [**G3-D**]/[**BDA**] = 1 : 2 in run 2, the composition of the product was [**G3-D′**]/[BDA′] = 1 : 4.2, whose **G3-D′** composition was much lower than that in the feed ratio, suggesting that the bulkiness of **G3-D** restricts its efficient incorporation into the product in the copolymerization with a relatively high **G3-D** content in the feed ratio. The $M_{n,MALS}$ of the copolymer sample obtained in run 2 was 27 600, which was again much higher than that estimated by SEC $M_{n,SEC}$ (= 13 000) with calibration using standard PMMAs.

Run 3 in Table 2 shows the results of homopolymerization of BDA under the same conditions as those in runs 1 and 2. Although the comparison is not straightforward because the molecular weight of **G3-D** is much higher than that of BDA, it is at least confirmed that the use of **G3-D** as a comonomer did not prevent the progress of the polymerization of BDA.

Next, we attempted to remove the acetonide-protecting groups of the copolymer sample obtained in run 1 in Table 2 with aqueous HCl-treatment in THF. As shown in Fig. 3(b), disappearance of the Me–H signals derived from the acetonide group after the HCl-treatment was clearly observed in comparison to the precursor polymer in Fig. 3(a). Although the presence of many hydrophilic hydroxy groups at the peripheral positions of the dendron unit could change the polymer solubility,[53,54] the product after the deprotection was still soluble in organic solvents such as $CHCl_3$, probably because of the relatively low content of the **G3-D** unit in the copolymer. These results indicate that the copolymerization of **G3-D** with other diazoacetates can be an effective method for introducing the highly hydrophilic repeating unit in the C1 polymer after the deprotection.

Table 2 Copolymerization of **G3-D** with BDA[a]

Run	Feed ratio ([**G3-D**]/[BDA])	Yield[b] (%)	Composition[c] ([**G3-D′**]/[BDA′])	M_n[d]	$Đ$[d]	$M_{n,MALS}$[e]	$Đ_{MALS}$[e]	T_g[f] (°C)
1	1 : 5	52	1 : 5.4	12 900	1.44			
2	1 : 2	41	1 : 4.2	13 000	1.42	27 600	1.23	16
3	0 : 1	67		11 000	1.48	18 400	1.33	26

[a] In THF for 15 h; [$NaBPh_4$]/[Pd] = *ca.* 1.2. [b] Determined by gravimetry after purification with preparative SEC. [c] Determined by ^1H NMR measurements. [d] Determined by SEC calibrated using PMMA standards. [e] Determined by SEC-MALS. [f] Determined by DSC measurements.

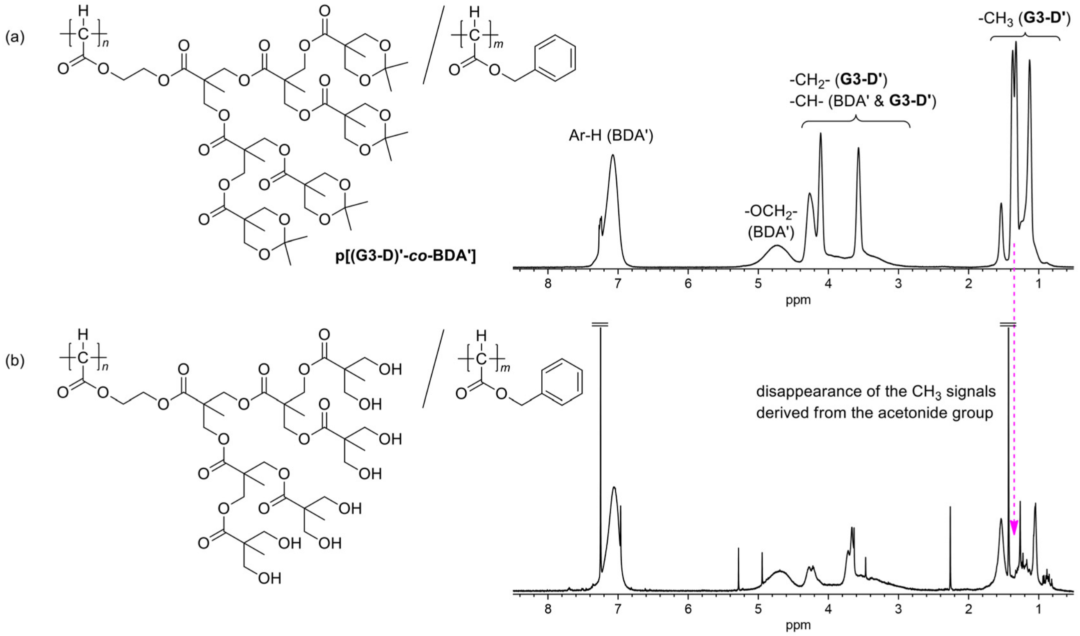


Fig. 3 ^1H NMR spectra of (a) **p[(G3-D)′-*co*-BDA′]** (run 1 in Table 2) and (b) its deprotected product.

Conclusions

We have demonstrated that Pd-initiated polymerization of diazoacetates with a series of ester-type dendrons, **G(1–3)-D**, proceeded to afford a new type of dendronized C1 polymer, **p[G(1–3)-D]′**. Although MWDs of **p(G2-D)′** and **p(G3-D)′** with higher generation dendrons were narrower than that of **p(G1—D)′**, these results did not indicate that steric bulkiness of the ester substituent led to higher controllability of the polymerization, but showed that the polymerization of **G(1–3)-D** proceeded with a similar level of controllability, on the basis of the comparison with the reported data of their vinyl polymer counterparts. T_gs of the dendronized polymers clearly increased with the increase of the dendron generation, indicating that the steric demand of the ester substituent restricts the mobility of the polymer main chain. In particular, the degree of T_g increase (ΔT_g) is much larger than that observed in the reported data of their vinyl polymer counterparts, clearly demonstrating the much higher level of rigidity of the C1 polymer main chain because of the denser packing of the substituents along the main chain. Copolymerization of **G3-D** with BDA proceeded to afford copolymers, and their acetonide-protecting groups were successfully removed with HCl treatment, demonstrating that the use of **G(1–3)-D** as a comonomer with other diazoacetates is an effective method for incorporating multiple hydroxy groups in the C1 polymer backbone. These results indicate that the new dendron-containing diazoacetates can be utilized for developing new functional C1 polymers, which is now underway in our laboratory.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

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