Synthesis of Structurally Controlled, Highly Branched Polymethacrylates) by Radical Polymerization Through the Design of a Monomer Having Hierarchical Reactivity

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ABSTRACT: The controlled synthesis of highly branched (HB) poly(methyl methacrylate) (PMMA) with a molecular weight of up to $88 \times 10^3$ g/mol and low dispersity ($D < 2.0$) was achieved by the radical copolymerization of vinyltelluride, H$_2$C=CHTePh (4cD), and MMA in the presence of the organotellurium chain transfer agent 6cI at 30 °C. Control of the branching structure was suggested by the Mark-Houwink-Kuhn-Sakurada plots corresponding to samples in solution and trapped ion mobility spectroscopy-time of flight mass spectrometry in the gas phase. The mechanism of 4cD for the structural control of HB-PMMA synthesis comes from the hierarchical reactivity of the C-Te bond of 4cD, which serves as the branching point only after 4cD reacts and is incorporated into the polymer chain. In contrast, copolymerization using previously reported vinyltellurides 4aA (H$_2$C=C(Me)TeMe) and 4aB (H$_2$C=C(Me)-CH=CHTeMe) could not control the branching structure due to the β-carbon fragmentation reaction from the intermediate radicals generated from 4aA and 4aB. The theoretical calculations suggest that the suppression of the undesired fragmentation reaction when using 4cD is due to the acceleration of the desired propagation reaction forming a branched structure instead of decelerating the fragmentation reaction. Due to the versatility of radical polymerization, methacrylates with bulky substituents, such as t-butyl methacrylate, and polar functional groups, such as N,N-dimethylmethacrylate (DMAEM), were also used as monomers to afford structurally controlled corresponding HB polymers. These studies clearly open a new possibility for the use of HB polymers in macromolecular engineering.

Introduction

Highly branched polymers (HBPs) have attracted significant attention because of their characteristic topology and physical properties, such as a lower hydrodynamic volume, lower intrinsic viscosity, lower glass transition temperature, and larger number of terminal groups than the corresponding linear polymers.\(^{1,4}\) Therefore, HBPs are promising for various applications, such as lubricants, coatings, catalysts, and drug and gene delivery.\(^{5-10}\) Control of the three-dimensional (3D) structure of HBPs, i.e., molecular weight, dispersity, number of branching points, branching density, and chain-end functionalities, would significantly improve and modify polymer properties and contribute to the design and synthesis of new polymer materials.\(^{10}\) However, the development of a practical and effective method to synthesize structurally well-controlled HBPs has been a significant challenge.

Although dendrimers and dendrons are the most 3D-structurally controlled HBPs, the requirement of multistep synthesis limits their practical applications.\(^{11-13}\) In contrast, hyperbranched polymers, which are HBPs with uncontrolled 3D structures, are easily synthesized in one step by 1) condensation polymerization of AB$_n$ monomers or A$_n$ and B$_m$ monomers, in which A and B refer to two functional groups that react with each other and n represents the number of B groups,\(^{14-15}\) and 2) self-condensing vinyl (co)polymerization (SCV(C)P) or self-condensing ring-opening polymerization using the AB* monomer, in which A and B* refer to alkene and initiating groups, respectively.\(^{16-20}\) Some control over the 3D structure was achieved by using special polymerization conditions, such as emulsion polymerization\(^{21}\) or the slow addition technique,\(^{22}\) and no general method has been realized so far.

Recently, two groups independently reported the controlled polymerization of HBPs via condensation polymerization using well-designed AB$_n$ monomers. Yokozawa et al. reported aromatic AB$_2$ monomer 1, in which the reactivity of the B group was enhanced after 1 was incorporated into a polymer (Scheme 1a).\(^{23-24}\) Gao et al. reported the “click” polymerization of AB$_2$ monomer 2 with alkyne and azide groups in the presence of a ligand-free Cu catalyst, and catalyst transfer enabled control (Scheme 1b).\(^{25-26}\) However, the lack of structural versatility in monomers significantly limits their utilization in materials science.

In contrast, we have recently reported a new one-step method to synthesize dendritic HBP 3 by radical polymerization (Scheme 1c).\(^{27-28}\) The method relies on the copolymerization of vinyl monomer 4 with substituent X, which potentially acts as an initiating group. However, the X group of 4 does not initiate the polymerization alone because of the difficulty in generating unstable vinyl radical species. In contrast, it becomes active and serves as a branching point after 4 has reacted as a monomer forming dormant species 7, which can generate a stable alkyl radical. Stepwise C-X bond activation through intermediate 8 gives 3. This unique hierarchical reactivity of the vinyl and X groups is in sharp contrast to the AB* monomers in self-condensing vinyl polymerization, in which A and B* groups react independently.
The concept was initially verified by using vinyl telluride 4aA (X = TeMe, R’ = H, R = Me) in a one-step copolymerization with acrylates (R’ = CO2R, R’ = H) and acrylamides (R’ = CONRR’, R4 = H) as monomer 5 under organotellurium-mediated radical polymerization (TERP) using chain transfer agent 6aI (X = TeMe, E” = CO2Et).27, 29-30 Structurally controlled HB polycrylates and polycrylamides with dendritic generation up to the 7th generation were synthesized by changing the 4/6 ratio (Scheme 1d). Furthermore, the method was extended to the synthesis of HB polystyrene (R1 = Ph, R4 = H) using 4aB (X = TeMe, R1 = H, R2 = C(CH3)=CH2) as a comonomer.28

Our method uses radical polymerization, which is characterized by its high versatility in monomer species and can be extended to other important monomer classes, such as methacrylate derivatives (R’ = CO2R, R’ = H). However, extension of the use of 4aA and 4aB to methacrylates has been unsuccessful thus far (see below). Therefore, understanding the reaction mechanism of the copolymerization and generating a new design of vinyl comonomer 4 are essential to expand the generality of this method. Here, we report the controlled synthesis of HB-poly(methyl methacrylate) (PMMA, R3 = CO2Me, R4 = H) under TERP based on the design of new comonomer 4cD (X = TePh, R1, R2 = H) based on the analyses of side reactions.

Very recently, Zhong and coworkers reported the synthesis of HB poly(butyl acrylate) and polystyrene by using the same concept under copper-catalyzed atom transfer radical polymerization (ATRP) using vinyl bromide 4bC (X = Br, R1 = CO2Bu, R4 = H) as a comonomer and 6b (X = Br) as an initiator.31 Despite the achievement, the method required the slow addition of 4bC to realize statistical copolymerization and could synthesize rather low-molecular-weight polymers. More importantly, the method was only applicable to acrylate and styrene. Therefore, this is the first example of the synthesis of structurally controlled HB poly(methacrylates).

Results and Discussion

The synthesis of an HB PMMA of the 4th dendritic generation was attempted by the copolymerization of MMA and 4aA or 4aB, which were used for the synthesis of HB-polyacrylates or polystyrenes, respectively, in the presence of organotellurium chain transfer agent 6aI (X = TeMe, E” = CO2Et). For example, a mixture of 6aI, 4aA, and MMA in a 1/15/500 ratio was heated at 60 °C in the presence of AIBN (0.20 equiv.) as a radical initiator and dimethyl ditelluride (1.0 equiv.) (Table 1, run 1).32 Monitoring the polymerization by 1H NMR showed a nearly equal consumption ratio of 4aA and MMA, indicating the occurrence of statistical copolymerization (Figure 1a). However, despite the steady consumption of both monomers, the number average molecular weight determined by size exclusion chromatography (Mn(MALLS) = 7 × 103) was nearly constant throughout the polymerization (Figure 1b), and the dispersity was rather high (D = 1.7). As HBPs have smaller hydrodynamic volumes than linear polymers, the Mn(MALLS) of HBPs are usually underestimated from their theoretical values (Mn(Theo) = 42.1 × 103) here was too large. The results suggest the occurrence of undesired side reaction(s). The polymerization in the absence of ditelluride also shows almost identical results, giving similar Mn(MALLS) (∼7.9 × 103) and dispersity (D = 1.87) throughout the polymerization, suggesting that the effect of ditelluride was negligible (run 2).

The same copolymerization was next examined using 4aB as the vinyl telluride monomer at 90 °C without an azo initiator (run 3). The statistical copolymerization occurred smoothly judging from the monomer conversion, though the consumption of MMA over 4aB took place much faster than that using 4aA (see Supporting Info). The time course of Mn(MALLS) exhibited results similar to those obtained using 4aA, and the Mn(MALLS) (13.4 × 103) and Mn determined by multangle laser light scattering (Mn(MALS) = 19.1 × 103 after 79% MMA conversion were significantly smaller than Mn(Theo) (40.7 × 103).

To clarify the origin of the unexpected results, the structure of the polymer products was analyzed for the PMMA samples synthesized by mixing 6aI/4aA/MMA in the ratio of 1/3/50 and reduced the polymer-end tellanyl group by PhSH (Table 1, run 4).33 Matrix-assisted laser desorption ionization-time of flight (MALDI-TOF) mass spectrometry indicated that the signals of linear PMMA 9d (X = H) were most prominent (Figure 1c). This is mainly because the 6aI/4aA ratio was low, so the
also formed by a side reaction, as discussed below. Three prom-
determined from MALLS and


copolymerization of MMA and


two linear polymers


(The formation of 10, 11, and 12 is explained by the β-carbon

terminal alkene group in 10d and 11d was sup-
ported by the 1H NMR analyses by observing two characteristic


correlation between $M_w$ and $D$ vs MMA conversion for Table 1, run 1. MALDI TOF mass spectra of the product polymers prepared in Table 1 c) run 3 and d) run 4. e) Structures of molecules formed in the copolymerization of MMA and 4aA or 4aB in the presence of 6aI.

copolymerization of 4aA and MMA was insufficient, but 9 was also formed by a side reaction, as discussed below. Three prominent molecular ion peaks corresponding to the desired HB PMMA 3dA ($X = H, R' = CH_2, R_1, R_2 = Me, R_3 = CO_2Me$) and two linear polymers 10d and 11d having polymer-end group structures different from that of 4aA were also observed. The existence of the terminal alkene group in 10d and 11d was supported by the 1H NMR analyses by observing two characteristic exomethylene hydrogens at 4.6 and 4.8 ppm (see Supporting Info). Molecular ion peaks corresponding to linear polymer 12d ($X = H$) and an uncharacterized polymer were also observed as minor peaks. The ratio among 3A, 9d, 10d, 11d, and 12d was determined to be 22.45:11:16:6 assuming the equal ionization ability of each polymer.

The formation of 10, 11, and 12 is explained by the β-carbon fragmentation of mid-chain radical 13 formed from intermediate 8aA (Scheme 2a). Scission occurred in two directions: at the α-end (path a) to give radical 14 and olefin 10 and at the ω-end (path b) to give olefin 11 and radical 15. Radicals 14 and 15 eventually formed dormant species 9 and 12, respectively. The mechanism suggests that fragmentation occurred exclusively at the polymer main chain originating from 4aA, and the amount of β-carbon fragmentation (β-ratio) against the consumed 4aA was estimated to be 34% from the amount of 10 and 11 determined from 1H NMR.

Table 1. Synthesis of HB-PMMA 3bD by copolymerization of 6, 4, and MMA

| run | Reagents (ratio) | Azo | Temp. (°C) | Time (h) | Conv. (%) | Conv. MMA (%) | $M_w$(theo) $(× 10^3)$ | $M_w$(SEC) $(× 10^3)$ | $M_w$(MALLS) $(× 10^3)$ | $D$ |
|-----|-----------------|-----|------------|----------|-----------|---------------|----------------------|--------------------|----------------------|-----|
| 1   | 6aI/TeMe) 4aA/MMA (1/5/500) | AIBN | 60 | 12 | 64 | 83 | 42.0 | 7.4 | n.d. | 1.74 |
| 2   | 6aI/4aA/MMA (1/15/500) | AIBN | 60 | 12 | 57 | 84 | 42.4 | 7.9 | n.d. | 1.87 |
| 3   | 6aI TeMe) 4aA/MMA (1/1/500) | - | 90 | 8 | >99 | 79 | 40.6 | 13.4 | 19.1 | 2.11 |
| 4   | 6aI/TeMe) 4aA/MMA (1/1/50) | AIBN | 60 | 6 | 52 | 79 | 4.1 | 4.3 | n.d. | 1.24 |
| 5   | 6aI/TeMe) 4aA/MMA (1/1/50) | - | 90 | 8 | >99 | 72 | 3.9 | 6.0 | n.d. | 1.37 |
| 6   | 6cI/4cD/MMA (1/15/500) | V70 | 30 | 30 | 24 | 62 | 81 | 40.9 | 29.2 | 42.0 | 1.73 |
| 7   | 6cI/4cD/MMA (1/1/500) | V70 | 30 | 11 | 57 | 76 | 3.9 | 4.8 | n.d. | 1.64 |
| 8   | 6cI/4cD/MMA (1/15/500) | AIBN | 60 | 24 | 69 | 82 | 41.4 | 15.6 | 32.5 | 1.68 |
| 9   | 6cI/4cD/MMA (1/30/500) | V70 | 30 | 48 | 51 | 72 | 36.5 | 31.5 | 42.5 | 1.58 |
| 10  | 6cI/4cD/MMA (1/60/500) | V70 | 30 | 96 | 43 | 60 | 30.8 | 24.4 | 36.8 | 1.59 |
| 11  | 6cI/4cD/MMA (1/1/250) | V70 | 30 | 48 | 62 | 75 | 19.1 | 19.2 | 22.5 | 1.58 |
| 12  | 6cI/4cD/MMA (1/1/1000) | V70 | 30 | 50 | 80 | 88 | 88.5 | 68.6 | 87.5 | 1.91 |
| 13  | 6cI/4cD/DMAMA (1/1/500) | V70 | 30 | 36 | 73 | 87 | 62.2 | 37.5 | 50.8 | 1.81 |
| 14  | 6cI/4cD/DMAMA (1/1/500) | V70 | 30 | 36 | 79 | 85 | 67.2 | 14.5 | n.d. | 1.63 |
| 15  | 6cI/4cD/DMAMA (1/1/500) | V70 | 30 | 24 | 69 | 87 | 44.0 | 37.3 | 46.8 | 1.91 |

- Determined by 1H NMR. - Determined by SEC calibrated against PMMA standards. *Calculated from $M_w$(MALLS)/$D$, where $M_w$(MALLS) was determined from MALLS and $D$ was determined from SEC. - Not determined. **tert-butyl methacrylate was used as a comonomer. /α-(Dime-thylamino)ethyl methacrylate was used as a comonomer.
The same structural analysis of polymer products was carried out using 4aB (run 5). MALDI-TOF mass analyses of the polymer sample indicate the formation of fragmented PMMAs 17d, 18d, and 12d in addition to linear PMMA 9d and the desired HB-PMMA 3dB (Figure 1d, 1e). Linear PMMs 9 and 12 must be derived from fragmented radicals 14 and 15, respectively. The formation of 3dB, 9d, 17d, and 18d were in the ratio of 46:25:15:14 assuming the same ionization efficiency. Therefore, failure of the controlled synthesis of HB-PMMA using 4aA and 4aB originated from the same fragmentation reaction from radical intermediate 13 and 16, respectively, derived from vinyltelluride 4 (Scheme 2b).

The observed fragmentation would be explained by considering thermodynamic and kinetic effects. Among the radicals involved in fragmentation, i.e., 13, 14, 15, and 16, the most stable radical is allylic radical 16, followed by ester-substituted tertiary radicals 14 and 15, and tertiary alkyl radical 13 is the least stable. Therefore, the thermodynamics cannot explain the observed fragmentation reaction. The other possibility would be kinetic effects; for example, steric repulsion between the methyl group derived from MMA would facilitate fragmentation.

To clarify this possibility, monomer 4cD, which lacks the methyl group, was synthesized. Due to the low boiling point of 4aD, which possesses a methyltellanyl group, 4cD, which possesses a phenyltellanyl group, was used. The reactivity of methyltellanyl and phenyltellanyl groups in TERP is very similar. Copolymerization was conducted by mixing thyltellanyl and phenyltellanyl groups in TERP is very similar.

Supporting Info). The effect of temperature was briefly examined. The lack of results strongly support the formation of structurally controlled polymers with different 3D structures was examined next. The copolymerization by mixing 6cI/4cD/MMA in a ratio of 1/15/500 at 60 °C using AIBN as a radical initiator. The copolymerization also proceeded smoothly, reaching MMA and 4cD conversions of 82% and 69%, respectively, and yielding polymers with M_{SEC} = 15.6 × 10^3 and M_{MALLS} = 32.4 × 10^3 (run 8). However, the structural control slightly decreased judging from the difference between M_{MALLS} and M_{theo} (41.4 × 10^3) and rather broad dispersity (D = 2.7). In addition, the NMR analyses revealed the presence of 3% olefinic protons, most likely derived from the β-carbon fragmentation reaction (Supporting Info). Therefore, low temperature is a better condition for increasing the structural control in HB-PMMA synthesis.

Figure 2. a) Time evolution of the consumption of 4cD (red empty squares) and MMA (black dots) by 1H NMR analysis, b) correlation between the MMA conversion vs M, and D and c) time evolution of the SEC traces from 4 to 24 h for Table 1, run 6. d) MALDI TOF mass spectrum of polymer mixture prepared according to Table 1, run 7.

The generality of the method for synthesizing HB-PMMA 3Ds with different 3D structures was examined next. The control of branching numbers was achieved by changing the 4cD/6cI ratio to 30 and 60 while keeping the MMA/6cI ratio at 500 (runs 9 and 10). Both 4cD and MMA reached high conversion (>60%) in both cases, and 3Ds with controlled 3D structures having similar M_{MALLS} and M_{theo} Values with low dispersity (D < 2.0) were obtained. Judging from the amount of 4cD and its conversion, 3D of the 4th and 5th dendritic generations were formed in runs 9 and 10, respectively. Molecular weight control could also be successfully carried out by changing the MMA/6cI ratio from 250 to 1000 while maintaining the 4cD/6cI ratio as 15 (runs 11 and 12). After high conversion of MMA (>70%) and 62 and 80% conversion of M, and 3Ds with controlled 3D structures having similar M_{MALLS} and M_{theo} Values with low dispersity (D < 2.0) were obtained. Judging from the amount of 4cD and its conversion, 3D of the 4th and 5th dendritic generations were formed in runs 9 and 10, respectively. Molecular weight control could also be successfully carried out by changing the MMA/6cI ratio from 250 to 1000 while maintaining the 4cD/6cI ratio as 15 (runs 11 and 12). After high conversion of MMA (>70%) and 62 and 80% conversion of 4cD, the resulting high-molecular-weight HB-PMMAs of the 3rd dendritic generation were synthesized. The similarity of M_{MALLS} and M_{theo} and low dispersity (D < 2.0) indicate successful structural control.

The Mark-Haukwin-Khun-Sakurada (MHKS) plot of 3D samples prepared in runs 6 and 9-12 was obtained by SEC-MALLS viscometer measurements (Figure 3). The exponent coefficient of the MHKS equation (a = 0.55–0.35) obtained from the slope is significantly lower than that of linear PMMA.
The scope of monomer versatility was examined next by using tert-butyl methacrylate (tBMA) and 2-(dimethylamino)ethyl methacrylate (DMAEM) instead of MMA by mixing 6c, 4cD, and the monomer in a ratio of 1/15/500 (runs 13 and 14). Statistical copolymerization took place despite the bulky and polar functional groups present, tBMA and DMAEM, respectively, and monomer conversion was high (>80%) in both cases. For the HB-PDMAEM sample, the controlled branched structure was suggested by the $M_{n}(MALLS)$ being close to the $M_{n(\text{theo})}$ and low dispersity ($D < 1.81$), while $M_{n(\text{SEC})}$ was significantly smaller than $M_{n(\text{theo})}$. While MALLS could not be measured for the HB-PDMAEM sample due to the lack of appropriate solvent for the measurement, the significantly smaller $M_{n(\text{SEC})}$ than $M_{n(\text{theo})}$ and the low dispersity ($D < 1.63$) strongly support the successful synthesis of structurally controlled HB-PDMAEM.

The degree of branching (DB) was next examined. In HB-PDMAEM 3c, polymerized 4cD has three local structures (Figure 5a): a doubly activated structure with H1, a singly activated structure with H2 and dormant end group X2, and an unbranched structure with H3 and two dormant end groups X1 and X3 (Figure 5a). The DB can be defined as follows:

$$DB = \frac{(H^f + H^o)(H^f + H^2 + H^o)}{in which $H^f$, $H^o$, and $H^2$ denote the number of H1, H2, and H3 in 3c, respectively. 3c also has three different dormant end groups, $X_1$ corresponding to the PMMA end, $X_2$, and $X_3 (X_3')$, the numbers of which [X1, X2, and X3 (X3')] have the following relations with H1, H2, and H3:

$$H^f = X_1 + X_1 - 1$$

$$H^o = X_2$$

$$H^2 = X_3 (= X_3')$$

Therefore, the above equation for determining DB can be rewritten as follows:

$$DB = (X_1^2 + 2X_2 - 1)(X_1^2 + X_2 + 2X_3 - 1)$$

The effect of the branching structure on the molecular volume of 3dD in the gas phase was also clarified by trapped ion mobility spectroscopy (TIMS)-TOF MS measurements, in which the ionized polymer molecule is propelled through a TIMS tunnel by a gas flow. A 2D plot (heat map) of the m/z ratio versus the inverse of the ion mobility ($1/K_0$ [V·s·cm⁻²]) of 3dD (X = H) with 1-3 branching units m derived from 4cD and n = 19-22 MMA units synthesized in run 7 is shown in Figure 4. A series of intense bright spots corresponding to the doubly charged molecular ion mass of 3dD with different m and n values were observed. Each molecular ion having the same m and n is connected by lines to estimate the effect of the branching structure on the ion mobility, which reveals that the mobility of ionized 3dD increases with increasing branching number m. The results also indicate that the collision cross-section of 3dD systematically increases with increasing m, which further supports the successful synthesis of structurally controlled HB-PMMA under the current conditions.

The intrinsic viscosity ($[\eta]$) of all HB-PMMA is smaller than that of linear PMMA having the same molecular weight and is systematically decreased with decreasing branching number (MMA/4cD ratio). All these results strongly support the successful synthesis of structurally well-controlled HB-PMMA.

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\[ \eta = 0.71 \]
The contributions of the $X_1$, $X_2$, and $X_3$ groups were determined by deuterium labeling experiments using deuterium labled CTA 6cII ($X = \text{TePh}, E^* = \text{CO:CD})$ and selective and stepwise reduction of the dormant ends by PhSD and BuSnD. Thus, HB-PMMA was synthesized by mixing 6cII, 4cD, and MMA at a ratio of 1/15/500 at 30°C, resulting in 87% 4cD and 69% MMA conversion (run 15). Then, the phenylltellanyl groups at $X_1$, $X_2$, and $X_3$ were selectively reduced by PhSD, giving partially deuterated 19 (Figure 5b). The broad deuterium signals at approximately -1.2 to 2 and -2-4 ppm were assigned to $X_2$ and the sum of the $X_1$ and $X_3$ groups by chemical shift and 2D NMR analyses (see Supporting Information). After the reduction of the remaining phenylltellanyl group at $X_2$ by Bu3SnD, yielding 20, the chemical shifts of the deuterium at $X_2$ and $X_3$ shifted to approximately 0.5 ppm (Figure 5c). The 2D NMR spectrum of 20 indicates that the deuterium derived from the $X_1$ group is negligible (<1%). This is due to the high reactivity of PMMA-end dormant species $X_1$ compared to the alkyl-end dormant species $X_2$ and $X_3$, as discussed below. The $X_1$: $X_2$: $X_3$ ratio was determined to be 0:60:40 from the 2H NMR spectra of 19 and 20 using the CD3 resonance derived from 6cII as an internal standard (Figure 5b and 5c). The DB was determined to be 52%.

The DB in this study was lower than previous results on the synthesis of HB-polyacrylates using 4aA, in which nearly 100% DB was observed.22 The results are explained by the stabilities of the radical species generated from the dormant ends because the activation efficiency of the dormant end is related to the stability of the generated radical species. Alkyl and ester groups stabilize carbon-centered radicals approximately 10-15 kJ mol$^{-1}$, respectively.23 Therefore, the $X_1$ group in 3e generating secondary alkyl radicals is significantly less reactive toward the activation reaction than the $X_3$ group, generating tertiary and ester-substituted radicals. In contrast, in HB-acrylate synthesis using 4aA, the branching carbon from 4aA generates tertiary alkyl radicals, such as 13, while polycrylate-end radicals are less stable than polymethacrylate-end radicals due to the lack of an alkyl group. Therefore, the activation efficiency of the branching point and the polycrylate end in HB-polycrylate synthesis becomes similar to that of the current polymethacrylate synthesis.

The structural effect of the radical intermediate derived from 4aA and 4cD on $\beta$-carbon fragmentation was analyzed by density functional theory (DFT) calculations at the (U)B3LYP/6-31G* level of theory. Model reactions from a model radical 21 ($R^1 = \text{Me or H}$ undergoing $\beta$-carbon fragmentation to yield alkene 22 or propagating to MMA to yield branched radical 23 were examined (Figure 6). The fragmentation takes place with low activation enthalpies of 68.3 and 64.3 kJ mol$^{-1}$ from methyl- and hydrogen-substituted radicals 21a and 21D, yielding 22A and 22D with 23.1 and 24.0 kJ mol$^{-1}$ of endothermicity, respectively. The results suggest that the replacement of methyl with hydrogen in 21 kinetically retards fragmentation, and the calculated trend qualitatively agrees with the experimental results. However, the differences in the activation energy (4.0 kJ mol$^{-1}$) are too small to explain the significant differences between $R^1 = \text{Me and H}$ in the experiments. Consideration of the entropic term at 298.15 K slightly increases the difference in the activation energy (73.3 and 63.6 kJ mol$^{-1}$ for 21a and 21D, respectively), but the difference (9.7 kJ mol$^{-1}$) is still small.

The addition of radicals 21A and 21D to MMA was next examined. Both reactions proceed with very low activation barriers of 44.6 and 22.1 kJ mol$^{-1}$ and yield 23A and 23D with -32.6 and -72.0 kJ mol$^{-1}$ of exothermicity, respectively. The propagation from 21D is 22.5 kJ mol$^{-1}$ kinetically favored over that from 21A, and 23D is 39.4 kJ mol$^{-1}$ more thermodynamically stable than 23A. The kinetic and thermodynamic differences are kept after consideration of the entropic term at 298.15 K (108.4 vs 87.0 kJ mol$^{-1}$ for TS and 34.8 and -2.6 kJ mol$^{-1}$ for the addition product 21). The results suggest that the kinetic preference of the propagation reaction of 21D to yield 23D suppresses the undesired fragmentation reaction. The effect of the methyl group of 21 can be explained primarily by the steric effect, but the higher exothermicity for the formation of 23D than for the formation of 23A also contributes to the lower the corresponding TS.

In summary, vinyl telluride 4cD is an effective comonomer for synthesizing structurally controlled HB-PMMAs under TERRP. In contrast, 4aA and 4aB, which are used for the synthesis of structurally controlled HB-polyacrylates and HB-polystyrenes, respectively, are ineffective for HB-PMMMA synthesis due to the competing $\beta$-carbon fragmentation reaction. Theoretical calculations suggest that the success of the synthesis using 4cD is not mainly due to the rate retardation of the undesired fragmentation but due to the acceleration of the desired propagation reaction. As 4cD is a monomer with hierarchical reactivity, selective chain growth polymerization takes place. Control of the molecular weight, branching number, and branching density are easily attained by changing the 6c/4cD/MMA ratio. Physical properties, such as intrinsic viscosity, can be systematically tuned by tuning the HB structure. Considering the importance of polymethacrylates in polymer materials, the current methods would be useful for designing new polymethacrylate-based polymer materials.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information includes experimental details, SEC traces of resulting polymer samples, MHSK plots, mass spectrum, theoretical calculation results, and NMR spectra of new compounds and is available free of charge on the ACS Publications website at DOI: 10.1021/xxxx.xxxxxxxx.

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Notes
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