Radical Polymerization of Vinyl Boronate Involving Backbiting Chain Transfer and Post-Polymerization Oxidation Affording Branched Poly(vinyl alcohol)s

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Abstract

We found radical polymerization of vinyl boronic acid pinacol ester (VBpin) was accompanied by a back-biting chain transfer reaction to polymer backbone and thus branched chains were generated via the propagation from the mid-chain radical. The subsequent oxidation for the boron pendant afforded a branched poly(vinyl alcohol) (PVA), which was certainly supported by NMR structural analyses. The synthesis of the branched PVA is inaccessible via radical polymerization of vinyl acetate (VAc) and subsequent saponification because the VAc polymerization favors the chain transfer reaction to pendant methyl group over that to the backbone. Our effort was also directed to tuning branch degree via copolymerization of VBpin with VAc for studies in effects of branch degree on the physical properties, such as solubility in water and crystallization in bulk state.

Introduction

Poly(vinyl alcohol) (PVA) is an important class of vinyl polymers not only in chemical industry but also in academic research due to its water-solubility, crystallinity, biocompatibility, biodegradability, and the application as polarizing plating film.[1-5] PVA is generally synthesized through radical polymerization of vinyl acetate (VAc) and saponification because the monomer, i.e., vinyl alcohol, is unstable due to rapid keto-enol tautomerization to acetaldehyde (Figure 1a). Many researchers have made much effort on controlling of polymerization behavior of VAc, which is an unconjugated monomer, as seen in stereospecific polymerization in fluoroalcohol for tacticity control[6] as well as reversible deactivation radical polymerization using thioester-based chain transfer agent[7-9] or cobalt complex.[10,11] Vinyl alcohols protected by silyl or benzyl groups are also usable as the precursor monomers of PVA for cationic polymerization and tacticity control via the stereospecific polymerization has been studied.[12]

Organoboron compounds are used as intermediates for synthesis of functional molecules through C-B bond transformations.[13-18] One of the most reliable transformations is oxidation of boron to hydroxy group, and thus an organoboron compound can be regarded as the precursor of alcohol. For instance, a selective C-H borylation is used for transformation of inert alkane to valuable alcohol,[19] and asymmetric hydroboration is helpful for preparing chiral alcohol.[20,21] Given the transformation feature of carbon-boron bond into carbon-hydroxyl, polymerization of boron-pendant monomer is interesting for synthesis of the precursor for PVA and the related hydroxy-pendant polymers (Figure 1b). Indeed, some types of boron-pendant monomers have been studied for synthesis of PVA and the derivatives. Our group found the radical polymerization ability of isopropenylboronic acid pinacol ester (IPBpin), which is commercially available as the substrate of organic reaction such as Suzuki-Miyaura cross coupling.[22,23] The vinylidene-type monomer

showed high homopolymerization ability as well as copolymerizability with common conjugated monomers such as styrene.[24] Post-polymerization oxidation afforded poly(α-methyl vinyl alcohol) and its copolymer. As for the vinyl-type monomer, VBpin was available as a comonomer in radical copolymerization of conjugated monomers such as styrene.[25] The copolymerization and subsequent oxidation afforded the styrene-VA copolymer, which had been inaccessible due to the poor copolymerization ability of VAc with conjugated monomers. We also found anthranilamide-protected vinylboron monomer was also available in radical copolymerization with styrene.[26] Klausen's group have reported another-type boron monomer bearing azaborine pendant.[27,28] Interestingly, the character of the monomer is like styrene because of the aromaticity of the pendant structure. Thus, the monomer underwent not only radical copolymerization with styrene but also syndio-specific coordination polymerization with titanium catalyst,[29] enabling synthesis of styrene-PVA copolymer and syndiotactic PVA. Chen's group designed pinacol ester -protected boron monomers bearing trifluoromethyl[30] or fluoro groups on the vinyl moiety[31] to synthesize novel PVA-based fluorinated copolymers via radical copolymerization with vinyl acetate aiming at repellency of both water and oil.

As shown above, there are some examples of boron monomers for synthesizing PVA and the derivatives. However, the radical homopolymerization and subsequent oxidation for synthesis of PVA remains unexplored. Our previous study in radical copolymerization of VBpin with styrene revealed the molecular weight of the resultant copolymers was decreased as the feed ratio of VBpin was increased.[25] The trend was not observed in the radical copolymerization of IPBpin with styrene, and thus the vinyl-type monomer presumably triggered some chain transfer reaction. Furthermore, Klausen et al. reported the chain transfer reaction to toluene (i.e., solvent) took place very severely during the polymerization of their vinyl-type monomer.[32] Thus, synthesis of high

molecular weight polymer via radical homopolymerization of vinyl-type boron monomer is likely not so straightforward. In this research, we performed radical polymerization of VBpin under some conditions to examine the effects on the molecular weight (Figure 1c). Subsequently, thus obtained polyVBpin of relatively high molecular weight was converted into PVA via oxidation. We then noticed formation of branched PVA from the structural analyses, and the irregular structure was likely formed via the back-biting chain transfer reaction of VBpin radical species. Such branched PVAs cannot be directly synthesized via radical polymerization of VAc and saponification,[33,34] and the synthetic route with VBpin is rather valuable. Furthermore, we performed the radical copolymerization of VBpin with VAc and the PVA transformation to tune branch degree. The physical properties such as crystallinity and water solubility were also evaluated.
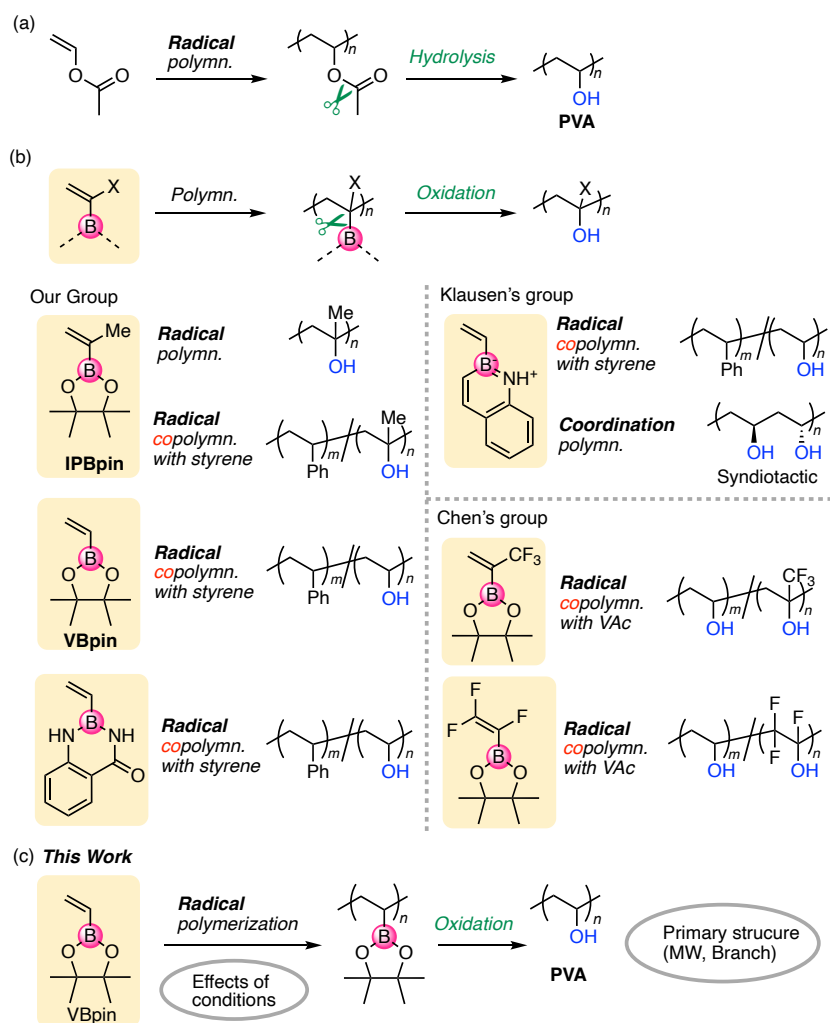
Figure 1. (a) Conventional synthesis of PVA using VAc as a vinyl alcohol precursor, (b) Syntheses of PVAs and their derivatives using boron-pendant monomers, (c) This work: PVA synthesis through radical homopolymerization of VBpin followed by pendant oxidation.

Result and discussion

In radical homopolymerization of VBpin, we investigated effects of temperature, monomer concentration, and the existence of α-methyl group (Figure 2). The polymerization condition of first attempt was as follows; [VBpin]/[AIBN] = 4000/40 in toluene at 60 °C (Figure 2a). Although

the conversion of VBpin reached high value (72%) in 24 h, the poly(VBpin) exhibited low number-average molecular weight (M_n = 3000). In the ^{1}H NMR spectrum, the poly(VBpin) showed peaks at 5.5-5.8 ppm that is likely derived from olefin group, and the peak integration ratio of the olefin group to the sum of peak *b*, *c*, and *d* at 0.5-1.8 ppm attributed to repeating units of poly(VBpin) ($I_{5.5-5.8}/I_{0.5-1.8}$) was 8.7×10^{-3}. These results indicated side reactions such as disproportionation and back-biting followed by β-scission take place during polymerization. The bulk polymerization at 60 ˚C afforded relatively high molecular weight (M_n = 6,600, Figure 2b) and lowering the polymerization temperature to 30 ˚C allowed further increase in molecular weight (M_n = 11,700, Figure 2c and S1). Along with the increase in molecular weight, the olefin ratio $I_{5.5-5.8}/I_{0.5-1.8}$ was decreased (2.4×10^{-3}, 8.7×10^{-4}, respectively). The correlation suggests the suppression of the olefin generation is essential for increasing the molecular weight of the polymer. In the case with α-methyl-type monomer, i.e., IPBpin, the condition of the solution polymerization ([IPBpin]/[AIBN] = 4000/40 in toluene at 60 ˚C) afforded the polymer of apparently high molecular weight (M_n = 30,300). The peaks from olefin protons were hardly observed in the ^{1}H NMR spectrum, although such α-methyl-existing monomer could undergo a disproportionation giving olefin terminal more frequently than the vinyl-type monomer. Thus, the olefin generation for the polymerization of VBpin cannot be attributed to disproportionation. On the other hand, in radical polymerization of acrylate, back-biting reaction of growing radical species to backbone methine carbon can take place unlike that of methacrylate.[35,36] The resultant mid-chain radical species after hydrogen abstraction undergo either chain growth giving branch chain or chain cleavage via β-scission giving olefin terminated chain.[37] The olefin generation and corresponding decrease in molecular weight is likely caused by the back-biting reaction.
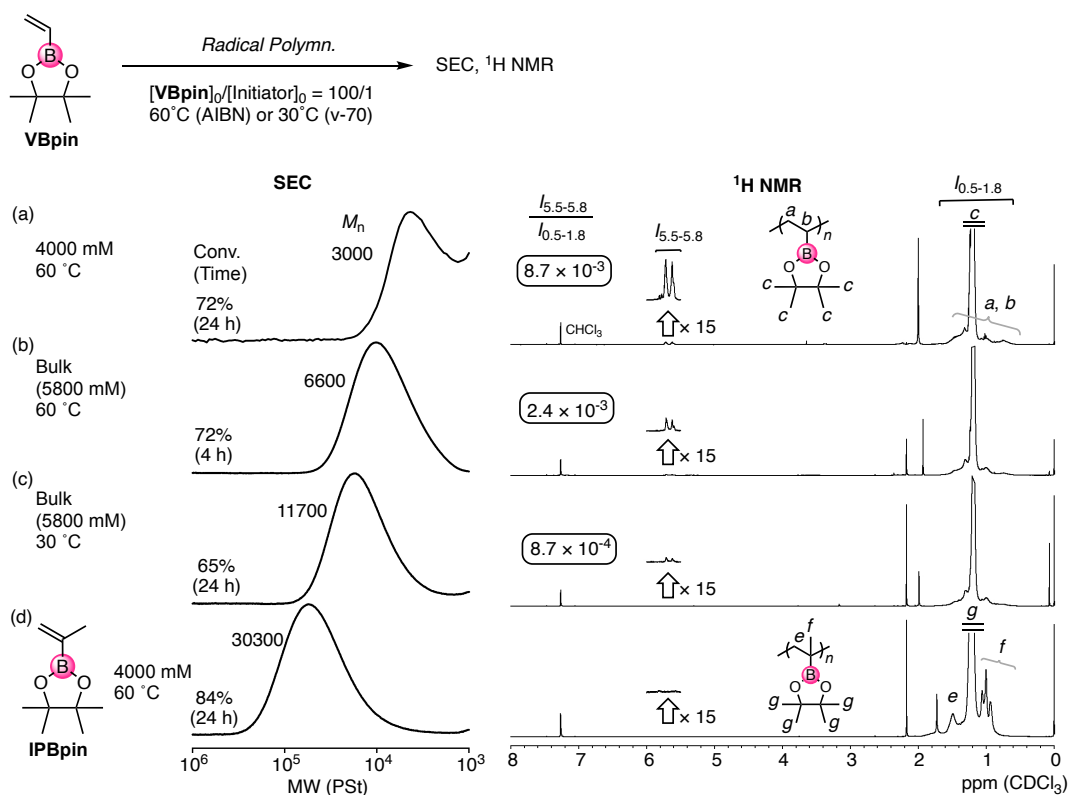
Figure 2. Effects of conditions (concentration and temperature) for radical polymerization of VBpin on molecular weight and structure of the resultant polymer in comparison with that of IPBpin.

We found the backbiting reaction giving branched polymers rather interesting because the following oxidation affords the branched PVA, which cannot be synthesized via radical polymerization of VAc and subsequent saponification. The distinguished feature of the product encouraged us to perform the oxidation of poly(VBpin) ($M_n = 11,700$), which was obtained via the bulk polymerization of VBpin at 30 °C, with H_2O_2 in NaOH aqueous solution. Figure 3a and b showed ^{1}H NMR spectra of the resultant polymer in D_2O and DMSO-d[6] in comparison with those of the common PVA synthesized via radical polymerization of VAc and subsequent saponification.

In D_2O, the polymer gave a spectrum similar to the common PVA, but some additional peaks appeared and in particular a striking peak was observed at 3.5-3.8 ppm. On the other hand, ^{1}H NMR spectra in DMSO-d[6] gave the three peaks characteristic to hydroxy group of PVA[38] and some additional peaks were also observed. The existence of hydroxy group was supported by FT-IR spectrum, where a broad peak corresponding to the stretching vibration of hydroxy group [ν(OH)] was clearly observed around 3200 cm^{-1} (Figure 3c). Importantly, the overall shape of the FT-IR spectrum was quite similar to that of PVA from VAc.
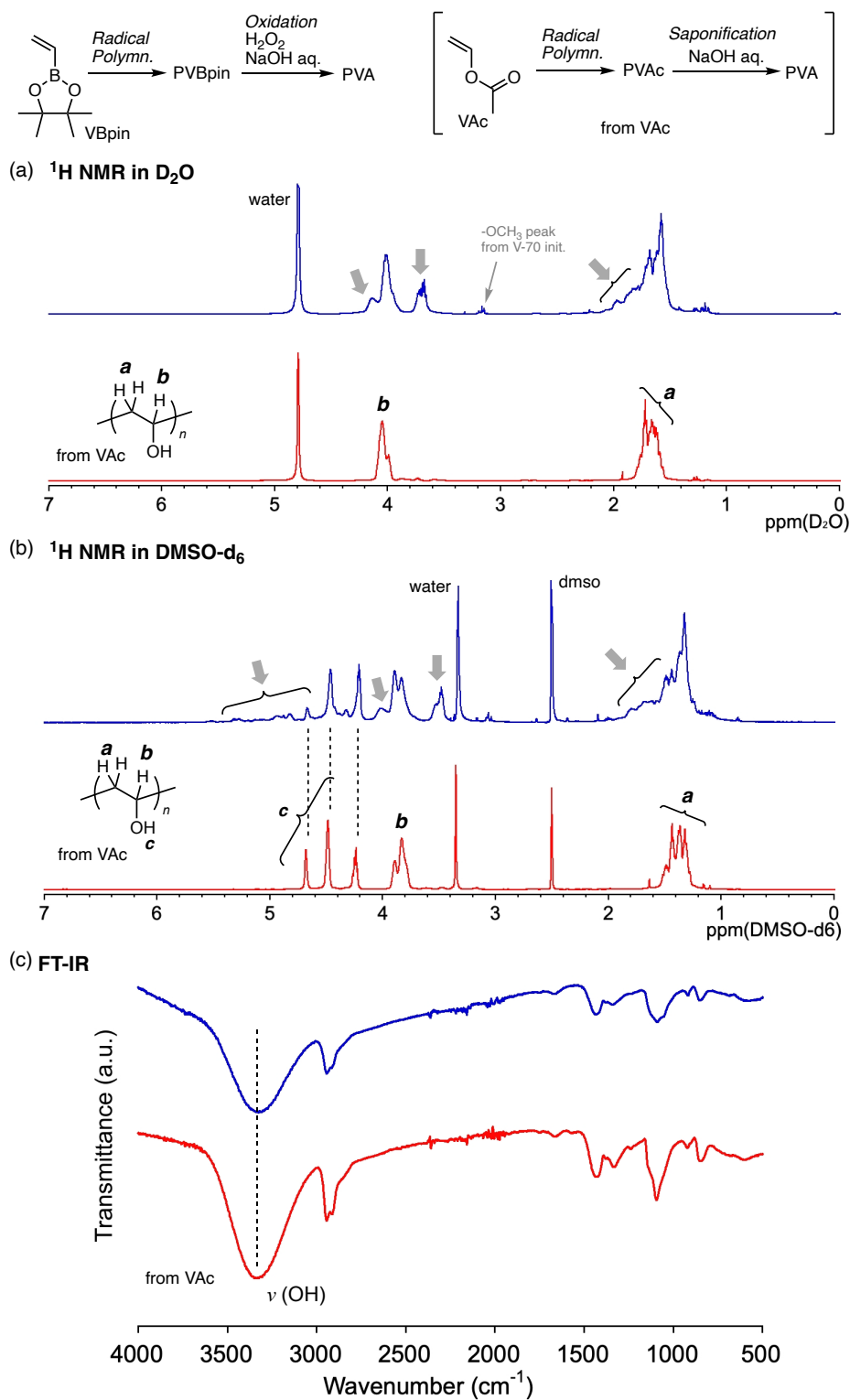
Figure 3. (a) Transformation of poly(VBpin) to PVA and structural analyses by ^{1}H NMR in D_2O (b) and DMSO-d^6 (c), and FT-IR (d) spectra (blue: PVA from VBpin, red: PVA from VAc).

The detailed structure of the polymer obtained through oxidation of poly(VBpin) was further analyzed through ^{13}C and ^{1}H-^{13}C DEPT-HSQC NMR measurements (Figure 4). In ^{13}C NMR spectrum, four peaks were mainly observed, and the corresponding carbon type was clarified thorough DEPT measurement and comparison with PVA from VAc (Figure 4a and S2-4). The peaks around 43-47 ppm and 64-70 ppm were common to PVA: the former was assigned to methylene (2° carbon, **C**a); the latter was to methine protons (3° carbon, **C**b). The two peak groups around 57-60 ppm and 74-77 ppm were specific to the polymer obtained through oxidation of poly(VBpin). The former peak at 57-60 ppm, which was negative in DEPT, was likely assigned to 2° carbon carrying hydroxy group (**C**c). The latter at 74-77 ppm, which was silent in DEPT, was to 4° carbon carrying hydroxy group (**C**d). These assignments were further confirmed by HSQC measurement (Figure 4b). The unknown proton peak c at 3.7-4.0 ppm in ^{1}H NMR spectrum was clearly correlated to the carbon **C**c around 57-60 ppm that is 2° carbon carrying hydroxy group. The plausible reason for the formation of the 2° and 4 ° carbons attaching hydroxy group is that the back-biting reaction occurs during radical polymerization of VBpin. The ratio of the 4° carbon to the whole repeating unit or "Branch Degree (BD)" was estimated by the following equation with the integral ratios [$Int(x), x = a\text{-}c$] of the peak from methylene proton (a) and those from two types of backbone protons (methine b and methylene c) attaching hydroxy pendant: BD = 1 − {(*Int (b)* + *Int (c)*/2) / *Int (a)*/2}. Consequently, BD of the resultant PVA was determined as 10.1 %. Furthermore, the BD of the PVA was also evaluated by quantitative ^{13}C NMR analysis, resulting in the similar value as the aforementioned BD (Figure S7).
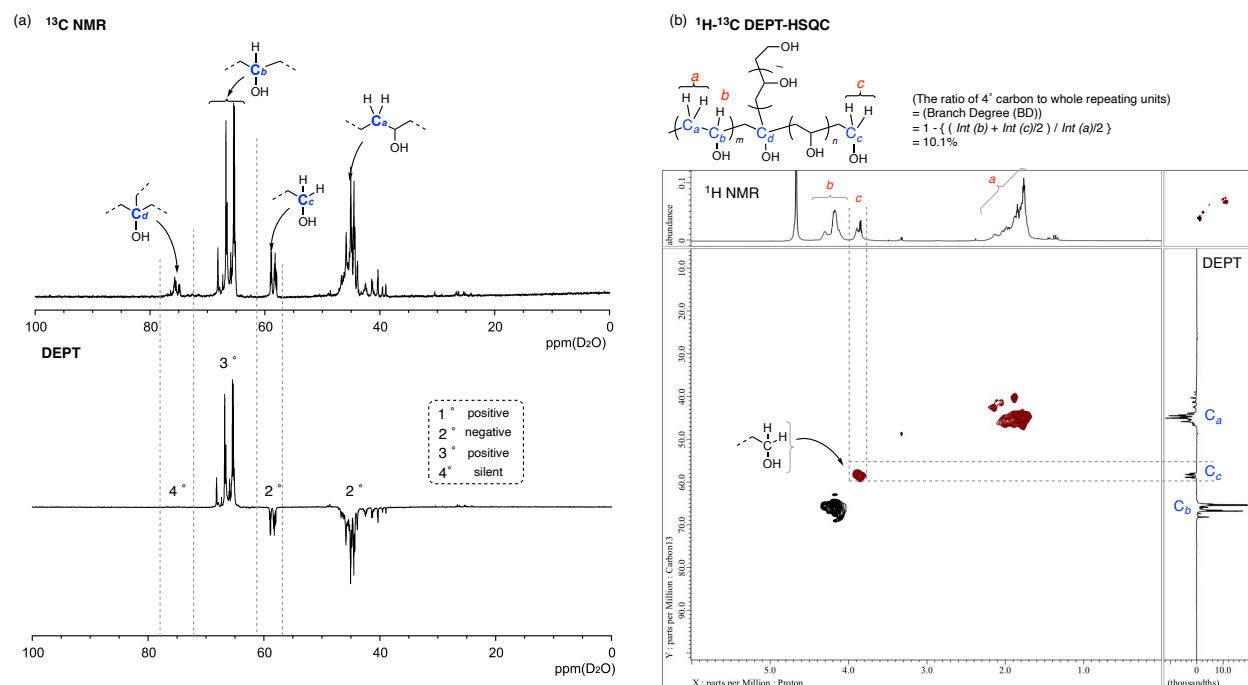
Figure 4. Structural analysis of PVA synthesized from VBpin by NMR in D₂O: (a) ¹³C NMR and DEPT; (b) ¹H-¹³C DEPT-HSQC.

The plausible process for the formation of branched PVA is shown in Figure 5. Chain-transfer reaction of growing radical species occurs to the backbone methine carbon via back-biting reaction like radical polymerization of acrylate monomer. In the reaction, the secondary propagating radical is transferred to tertiary mid-chain radical, which is stabilized by vacant p-orbital of boron side chain. The reaction was found to be exothermic from DFT calculation (Figure S8), and thus the chain-transfer reaction is competitive to the propagation. The tertiary mid-chain radical species via the back-biting reaction undergoes either β-scission causing decrease in molecular weight or initiation giving branched structure. The polymerization at lower temperature and under higher monomer concentration could promote the formation of branched structure rather than β-scission, which causes the higher molecular weight. The branched PVA is inaccessible via radical

polymerization of VAc and saponification, where the chain transfer occurs not to the backbone but to the acetyl pendant yielding branched structures and the following saponification afford linear PVA.[34] It is also supported by DFT calculation that the backbiting to backbone is less favorable in polymerization of VAc (Figure S8).
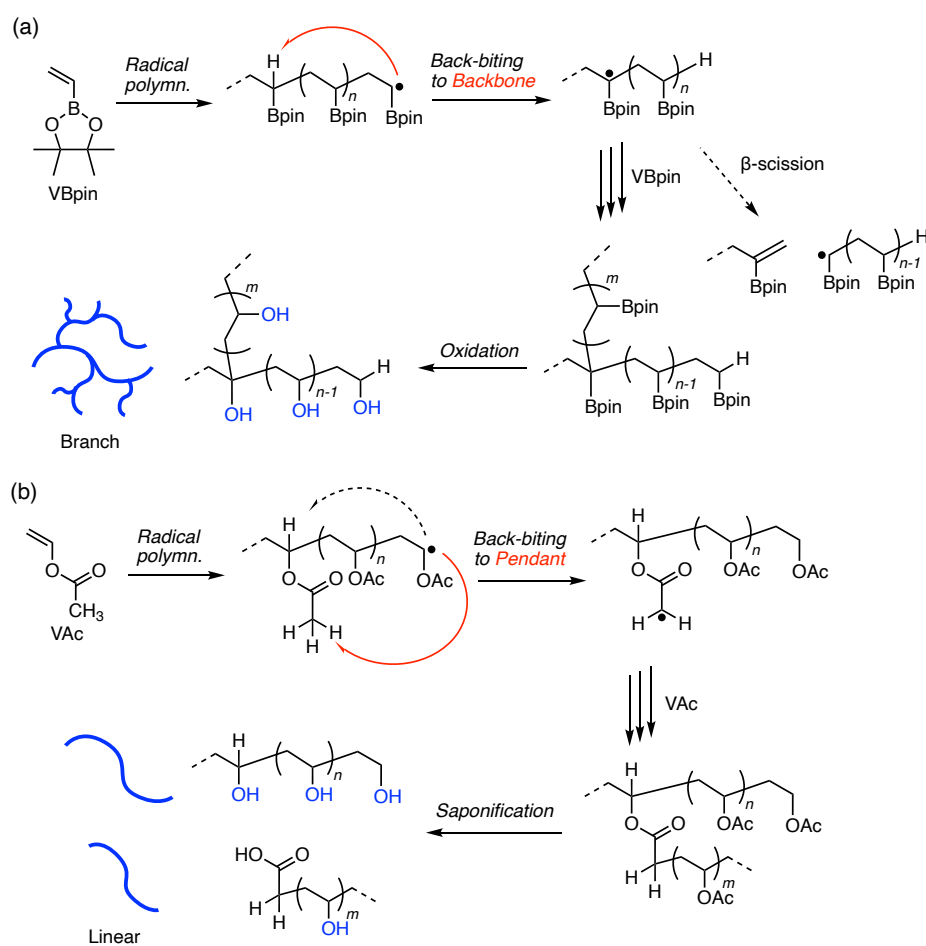

Figure 5. Proposed mechanism for the formation of branched PVA via radical polymerization of VBpin (a) in comparison with VAc (b).

We then came up with the idea of controlling the branch degree in PVA through radical copolymerization of VBpin with VAc (Figure 6a). Radical copolymerization of VBpin with an

excess of VAc ($[\text{VBpin}]_0/[\text{VAc}]_0 = 20/80$) was then performed in toluene at 60˚C. Both monomers were consumed, and the conversion values were gradually increased (Figure S5). The copolymerization in 4 hours gave the copolymer [poly(VBpin-*co*-VAc)] having M_n of 11,100 and almost 1:1 of the unit ratio (Figure S5). We then performed the oxidation reaction with H_2O_2 in conjunction with NaOH for the copolymer expecting conversion of the pendant groups of the both unit into hydroxyl group (Figure S6). ^{1}H NMR spectrum of the resulting polymer was similar to that of the branched PVA obtained via homopolymerization of VBpin. As expected, the BD value became lower (7.6%) than that from the homopolymerization of VBpin (BD = 10.1%), though no difference was observed in FT-IR spectrum (Figure 6b). The quantitative ^{13}C NMR analysis also supported the lower BD (Figure S7).
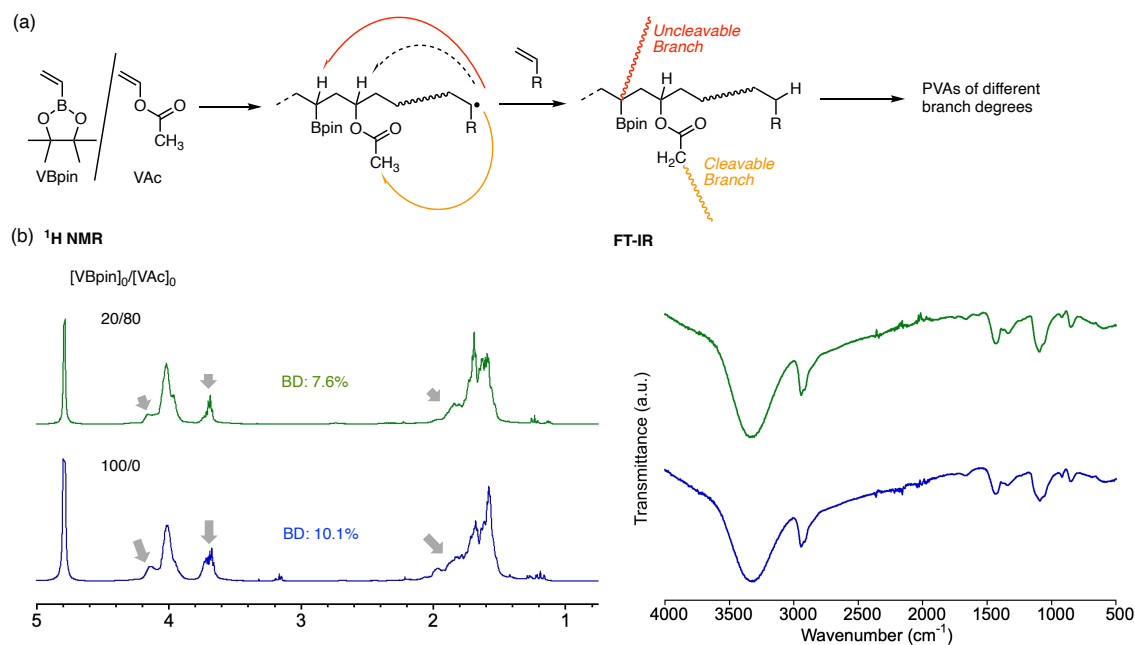
Figure 6. (a) Radical copolymerization of VBpin with VAc for tuning branch degree of PVA. (b) Structural analyses of PVA obtained via radical copolymerization of VBpin with VAc ($[VBpin]_0/[VAc]_0 = 20/80$) by ^{1}H NMR and FT-IR spectra (upper) in comparison with PVA via radical polymerization of VBpin (lower).

Thus, three types of PVA of different BD, i.e., 10.1% (B-PVA$_{10.1}$), 7.6% (B-PVA$_{7.6}$), and 0% (linear, L-PVA), were synthesized via homopolymerization or copolymerization of VBpin and VAc. The difference among three types of PVA was characterized by SEC combined with multi detector of light scattering (LS) and viscosity. Hydroxy groups of the PVA samples were acetylated via the reaction with acetic anhydride for the SEC analyses with THF as eluent and the structures of the resultant PVAc samples, B-PVAc$_{10.1}$, B-PVAc$_{7.6}$, and L-PVAc were identified by ^{1}H-NMR and FT-IR (Figure S9). Figure 7a shows the plots for absolute molecular weight against retention volume and their SEC traces for the three PVAc samples. Figure 7b shows double logarithmic plots of intrinsic viscosity ($[\eta]$) against absolute molecular weight (M_w) fitted by Mark-

Houwink-Sakurada equation ($[\eta] = KM^{\alpha}$) and Figure 7c summarizes the parameters obtained from these measurements. The branched polymers (B-PVAc$_{7.6}$ and B-PVAc$_{10.1}$) showed higher absolute molecular weight than linear counterpart (L-PVAc) at most of retention volumes as seen in Figure 7a. The trend is consistent with the difference of other branched polymers from linear ones due to the more compact conformation of the branching structure.[39,40] The α values of the branched polymers (B-PVAc$_{7.6}$ and B-PVAc$_{10.1}$) were obviously smaller (α = 0.63 and 0.58) than that of L-PVAc (α = 0.83), suggesting the globule-like conformation of the branched polymers. The clear decrease in α depending on the branch degree might indicate an existence of long branched chain, because polyethylene having short branch chains is known to show similar α value to the linear analogue even though the intrinsic viscosity becomes lower.[41].
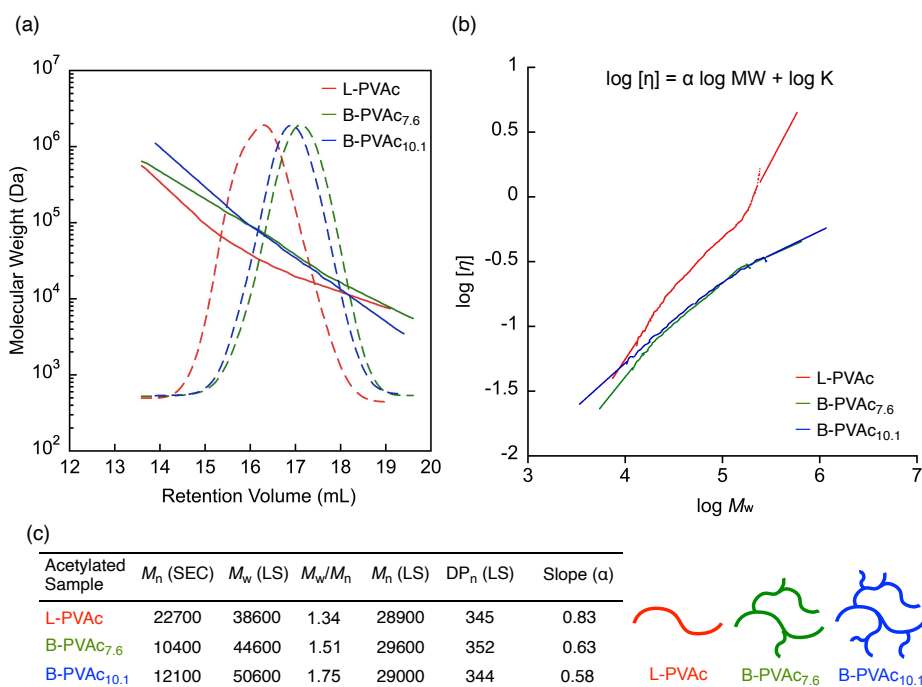
Figure 7. SEC-LS-Viscometry measurement of acetylated PVA samples with different BD: (a) Molecular weight vs. retention volume plots (plain: absolute molecular weight, dashed: SEC curve); (b) Mark-Houwink-Sakurada plots; (c) the summarized data [M_n (LS) was calculated by M_w (LS) and M_w/M_n; DP_n (LS) was caluclated by M_n (LS) and the molecular weight of VAc (86.09 g/mol)]

Finally, we investigated the impact of branched structure of PVA on the physical properties. The thermal properties of the three types of PVAs were evaluated by differential scanning calorimeter (DSC). Figure 8a shows the heating profiles of the samples. Both B-PVA$_{7.6}$ and B-PVA$_{10.1}$ did not show any peaks from the melting point, whereas L-PVA showed the melting point peak (T_m = 221 ˚C) (Figure S10-12). Therefore, the crystalline property of branched PVAs was found to be poor. The low crystallinity of branched PVA was also supported by XRD measurement (Figure 8b); the branched PVAs only showed a broad peak (2θ ~ 18˚) in contrast to the linear analogue giving

sharp diffraction peaks at 11°, 16°, 20°, and 23° corresponding to (100), (001), (101 and 10$\bar{1}$), and

(200) reflections.[42] The branched PVAs did show different solubility in solvents including water

(Figure 8c and S13). In general, heating is required to dissolve PVA in water due to high

crystallinity. However, the branched polymers were dissolved immediately in water without

heating because of the low crystallinity. The branched polymers also showed different solubilities

in DMF (Figure S14); they were easily dissolved in contrast to linear one.
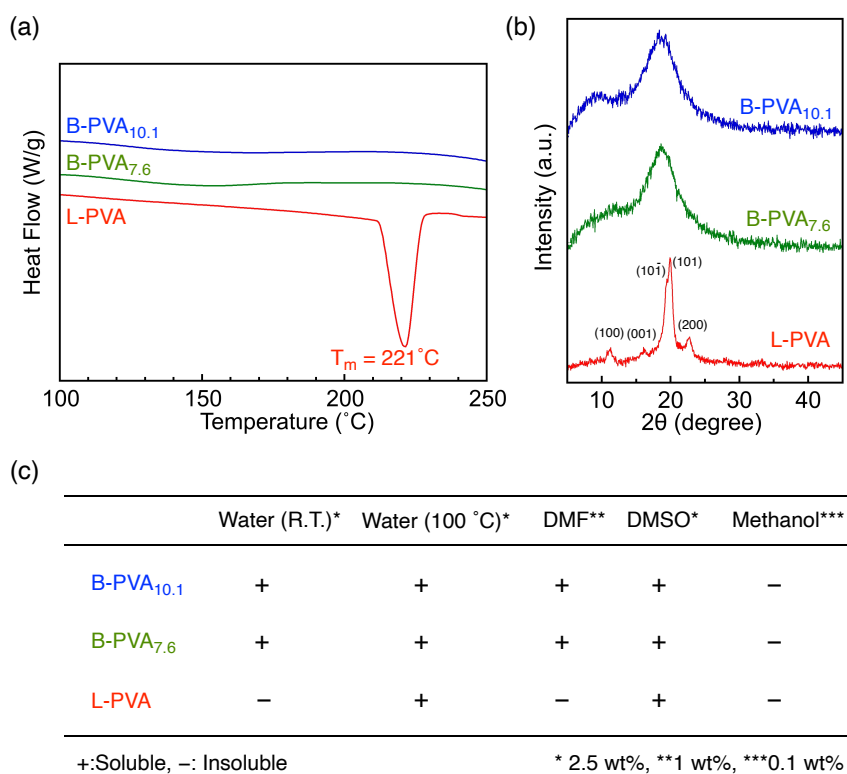

(a) DSC curves showing Heat Flow (W/g) vs Temperature (°C) for B-PVA$_{10.1}$, B-PVA$_{7.6}$, and L-PVA; L-PVA shows $T_m = 221\,°C$.

(b) XRD profiles showing Intensity (a.u.) vs 2θ (degree) for B-PVA$_{10.1}$, B-PVA$_{7.6}$, and L-PVA with reflections (100), (001), (10$\bar{1}$), (101), (200).

(c)

	Water (R.T.)*	Water (100 °C)*	DMF**	DMSO*	Methanol***
B-PVA$_{10.1}$	+	+	+	+	−
B-PVA$_{7.6}$	+	+	+	+	−
L-PVA	−	+	−	+	−

+:Soluble, −: Insoluble   * 2.5 wt%, **1 wt%, ***0.1 wt%

Figure 8. Physical properties of PVAs (B-PVA$_{10.1}$, B-PVA$_{7.6}$, and L-PVA): (a) DSC curves; (b)

XRD profiles; (c) solubility test for water and polar organic solvents.

Conclusion

In conclusion, we found that radical polymerization of VBpin proceeded along with back-biting-type chain transfer affording branched polymers and the branched structure was preserved after oxidation of the boron pendant. Thus, the synthesis of branched PVA, which is inaccessible via radical polymerization of VAc and subsequent saponification, was achieved. VBpin showed the copolymerization ability with VAc leading to syntheses of branched PVAs having different BD. The resultant branched PVAs showed lower crystallinity and better solubility in water than the linear counterpart. Amorphous PVA has potential applications for bio-related researches, and thus the use of VBpin as a precursor for syntheses of PVAs are of great interest.

Supporting Information

The Supporting Information is available free of charge

Detailed description of synthetic procedures, experimental methods, IR, 1H and 13C NMR spectra, GPC analysis, DSC measurement (PDF)

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Notes

The authors declare no competing financial interest.

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References

(1) C. A. Finch *Poly(vinyl alcohol): Properties and Applications* , Wiley, London, 1973.

(2) Teodorescu, M.; Bercea, M.; Morariu, S. Biomaterials of PVA and PVP in Medical and Pharmaceutical Applications: Perspectives and Challenges. *Biotechnol. Adv.* **2019**, *37* (1), 109–131, DOI: 10.1016/j.biotechadv.2018.11.008

(3) Jalal Uddin, A.; Araki, J.; Gotoh, Y. Toward ″strong″ green nanocomposites: polyvinyl alcohol reinforced with extremely oriented cellulose whiskers. *Biomacromolecules* **2011**, *12* (3), 617–24, DOI: 10.1021/bm101280f

(4) Chiellini, E.; Corti, A.; D'Antone, S.; Solaro, R. Biodegradation of poly (vinyl alcohol) based materials. *Prog. Polym. Sci.* **2003**, *28* (6), 963–1014, DOI: 10.1016/S0079-6700(02)00149-1

(5) Choi, M.-C.; Kim, Y.; Ha, C.-S. Polymers for flexible displays: from material selection to device applications. *Prog. Polym. Sci.* **2008**, *33*, 581–630, DOI: 10.1016/j.progpolymsci.2007.11.004

(6) Yamada, K.; Nakano, T.; Okamoto, Y. Stereospecific Free Radical Polymerization of Vinyl Esters Using Fluoroalcohols as Solvents. *Macromolecules* **1998**, *31*, 7598–7605, DOI: 10.1021/ma980889s

(7) Destarac, M.; Franck, X.; Charmot, D.; Zard, S. Z. Dithiocarbamates as Universal Reversible Addition-Fragmentation Chain Transfer Agents. *Macromol. Rapid Commun.* **2000**, *21*, 1035–1039, DOI: 10.1002/1521-3927(20001001)21:15<1035::AID-MARC1035>3.0.CO;2-5

(8) Moad, G.; Rizzardo, E.; Thang, S. H. Living Radical Polymerization by the RAFT Process. *Aust. J. Chem.* **2012**, *65*, 985–1076, DOI: 10.1071/CH12295

(9) Congdon, T. R.; Notman, R.; Gibson, M. I. Synthesis of Star-Branched Poly(Vinyl Alcohol) and Ice Recrystallization Inhibition Activity. *Eur. Polym. J.* **2017**, *88*, 320–327, DOI: 10.1016/j.eurpolymj.2017.01.039

(10) Debuigne, A.; Caille, J. R.; Jérôme, R. Highly Efficient Cobalt-Mediated Radical Polymerization of Vinyl Acetate. *Angew. Chem., Int. Ed.* **2005**, *44*, 1101–1104, DOI: 10.1002/anie.200461333

(11) Demarteau, J.; Debuigne, A.; Detrembleur, C. Organocobalt Complexes as Sources of Carbon-Centered Radicals for Organic and Polymer Chemistries. *Chem. Rev.* **2019**, *119*, 6906–6955, DOI: 10.1021/acs.chemrev.8b00715

(12)   Uchiyama, M.; Satoh, K.; Kamigaito, M. Stereospecific Cationic RAFT Polymerization of Bulky Vinyl Ethers and Stereoblock Poly(vinyl Alcohol) *via* Mechanistic Transformation to Radical RAFT Polymerization of Vinyl Acetate. *Giant* **2021**, *5*, 100047, DOI: 10.1016/j.giant.2021.100047

(13)   Hall, D. G. *Boronic Acids: Preparation and Applications in Organic Synthesis, Medicine and Materials*; Wiley-VCH: Weinheim, Germany, 2011; DOI: 10.1002/9783527639328.

(14)   Sandford, C.; Aggarwal, V. K. Stereospecific Functionalizations and Transformations of Secondary and Tertiary Boronic Esters. *Chem. Commun.* **2017**, *53*, 5481–5494, DOI: 10.1039/C7CC01254C

(15)   Miyaura, N.; Suzuki, A. Palladium-Catalyzed Cross-Coupling Reactions of Organoboron Compounds. *Chem. Rev.* **1995**, *95*, 2457–2483, DOI: 10.1021/cr00039a007

(16)   Matteson, D. S. alpha.-Halo boronic esters: intermediates for stereodirected synthesis. *Chem. Rev.* **1989**, *89*, 1535, DOI: 10.1021/cr00097a009

(17)   Kischkewitz, M.; Okamoto, K.; Mück-Lichtenfeld, C.; Studer, A. Radical-Polar Crossover Reactions of Vinylboron Ate Complexes. *Science* **2017**, *355*, 936–938, DOI: 10.1126/science.aal3803

(18)   Kubo, T.; Scheutz, G. M.; Latty, T. S.; Sumerlin, B. S. Synthesis of Functional and Boronic Acid-Containing Aliphatic Polyesters via Suzuki Coupling. *Chem. Commun.* **2019**, *55*, 5655–5658, DOI: 10.1039/C9CC01975H

(19)   Murphy, J. M.; Lawrence, J. D.; Kawamura, K.; Incarvito, C.; Hartwig, J. F. Ruthenium-Catalyzed Regiospecific Borylation of Methyl C-H Bonds. *J. Am. Chem. Soc.* **2006**, *128*, 13684–13685, DOI: 10.1021/ja064092p

(20)   Collins, B. S. L.; Wilson, C. M.; Myers, E. L.; Aggarwal, V. K. Asymmetric, Synthesis of Secondary and Tertiary Boronic Esters. *Angew. Chem., Int. Ed.* **2017**, *56*, 11700–11733, DOI: 10.1002/anie.201701963

(21)   Thomas, S. P.; Aggarwal, V. K. Asymmetric Hydroboration of 1,1-Disubstituted Alkenes. *Angew. Chem., Int. Ed.* **2009**, *48*, 1896–1898, DOI: 10.1002/anie.200805604

(22)   Nishikawa, T.; Ouchi, M. An Alkenyl Boronate as a Monomer for Radical Polymerizations: Boron as a Guide for Chain Growth and as a Replaceable Side Chain for Post-Polymerization Transformation. *Angew. Chem., Int. Ed.* **2019**, *58*, 12435–12439, DOI: 10.1002/anie.201905135

(23)   Kanazawa, T.; Nishikawa, T.; Ouchi, M. RAFT Polymerization of Isopropenyl Boronate Pinacol Ester and Subsequent Terminal Olefination: Precise Synthesis of Poly(Alkenyl Boronate)s and Evaluation of Their Thermal Properties. *Polym. J.* **2021**, *53*, 1167–1174, DOI: 10.1038/s41428-021-00498-8

(24)   Makino, H.; Nishikawa, T.; Ouchi, M. Elucidating Monomer Character of an Alkenyl Boronate through Radical Copolymerization Leads to Copolymer Synthesis beyond the Limitation of Copolymerizability by Side-Chain Replacement. *ACS Macro Lett.* **2020**, *9*, 788–793, DOI: 10.1021/acsmacrolett.0c00287

(25)   Makino, H.; Nishikawa, T.; Ouchi, M. Vinylboronic Acid Pinacol Ester as a Vinyl Alcohol-Precursor Monomer in Radical Copolymerization with Styrene. *Chem. Commun.* **2021**, *57*, 7410–7413, DOI: 10.1039/D1CC02603H

(26)   Suzuki, H.; Nishikawa, T.; Makino, H.; Ouchi, M. Anthranilamide-Protected Vinylboronic Acid: Rational Monomer Design for Improved Polymerization/Transformation Ability Providing Access to Conventionally Inaccessible Copolymers. *Chem. Sci.* **2022**, *13*, 12703–12712, DOI: 10.1039/D2SC05094C

(27)   van de Wouw, H. L.; Lee, J. Y.; Awuyah, E. C.; Klausen, R. S. A BN Aromatic Ring Strategy for Tunable Hydroxy Content in Polystyrene. *Angew. Chem., Int. Ed.* **2018**, *57* (6), 1673–1677, DOI: 10.1002/anie.201711650

(28)   van de Wouw, H. L.; Awuyah, E. C.; Baris, J. I.; Klausen, R. S. An Organoborane Vinyl Monomer with Styrene-like Radical Reactivity: Reactivity Ratios and Role of Aromaticity. *Macromolecules* **2018**, *51*, 6359–6368, DOI: 10.1021/acs.macromol.8b01368

(29)   Mendis, S. N.; Zhou, T.; Klausen, R. S. Syndioselective Polymerization of a BN Aromatic Vinyl Monomer. *Macromolecules* **2018**, *51*, 6859–6864, DOI: 10.1021/acs.macromol.8b01707

(30)   Zeng, Y.; Zhou, Y.; Quan, Q. Z.; Chen, M. Facile Access to gem-Trifluoromethyl/Boron-Functionalized Polymers via Free-Radical Copolymerization and Cotelomerization. *Macromolecules* **2022**, *55*, 1524–1532, DOI: 10.1021/acs.macromol.2c00023

(31)   Zeng, Y.; Quan, Q. Z.; Wen, P.; Zhang, Z. X.; Chen, M. Organocatalyzed Controlled Radical Copolymerization toward Hybrid Functional Fluoropolymers Driven by Light. *Angew. Chem., Int. Ed.* **2022**, *61* (12), e202215628. DOI: 10.1002/anie.202215628.

(32)   Ji, Y.; Klausen, R. S. Chain Transfer to Solvent in BN 2-Vinylnaphthalene Polymerization. *J. Polym. Sci.* **2021**, *59*, 2521–2529, DOI: 10.1002/pol.20210362

(33)   Markley, T. J.; Pinschmidt, R. K.; Vanderhoff, J. W. Grafting Reactions of Vinyl Acetate onto Poly[(vinyl alcohol)-co-(vinyl acetate)]. *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34*, 2581–2594, DOI: 10.1002/(SICI)1099-0518(19960930)34:13<2581::AID-POLA4>3.0.CO;2-V

(34)   Britton, D.; Heatley, F.; Lovell, P. A. Chain Transfer to Polymer in Free-Radical Bulk and Emulsion Polymerization of Vinyl Acetate Studied by NMR Spectroscopy. *Macromolecules* **1998**, *31*, 2828–2837, DOI: 10.1021/ma971284j

(35)   Junkers, T.; Barner-Kowollik, C. The role of mid-chain radicals in acrylate free radical polymerization: Branching and scission. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46* (23), 7585–7605, DOI: 10.1002/pola.23071

(36)   Chiefari, J.; Jeffery, J.; Mayadunne, R. T.; Moad, G.; Rizzardo, E.; Thang, S. H. Chain Transfer to Polymer: A Convenient Route to Macromonomers. *Macromolecules* **1999**, *32*, 7700–7702, DOI: 10.1021/ma990488s

(37)   Zorn, A. M.; Junkers, T.; Barner-Kowollik, C. Synthesis of a Macromonomer Library from High-Temperature Acrylate Polymerization. *Macromol. Rapid Commun.* **2009**, *30* (23), 2028–2035, DOI: 10.1002/marc.200900536

(38)   The triad tacticity of PVAs is assigned as follows: *mm* at 4.6 ~ 4.8 ppm, *mr* at 4.4 ~ 4.6 ppm, and *rr* at 4.1~4.4 ppm.

(39)   Voit, B. I.; Lederer, A. Hyperbranched and Highly Branched Polymer Architectures-Synthetic Strategies and Major Characterization Aspects. *Chem. Rev.* **2009**, *109* (11), 5924–5973, DOI: 10.1021/cr900068q

(40)   Yamago, S. Practical synthesis of dendritic hyperbranched polymers by reversible deactivation radical polymerization. *Polym. J.* **2021**, *53* (8), 847–864, DOI: 10.1038/s41428-021-00487-x.

(41)   Yu, Y.; DesLauriers, P. J.; Rohlfing, D. C. SEC-MALS Method for the Determination of Long-Chain Branching and Long-Chain Branching Distribution in Polyethylene. *Polymer* **2005**, *46*, 5165–5182, DOI: 10.1016/j.polymer.2005.04.036

(42)   Assender, H. E.; Windle, A. H. Crystallinity in poly(vinyl alcohol). 1. An X-ray diffraction study of atactic PVOH. *Polymer* **1998**, *39*, 4295–4302, DOI: 10.1016/s0032-3861(97)10296-8

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