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# Property Modulation of Poly(vinyl alcohol)s via Controlled Incorporation of $\alpha$-Methyl Groups Using Alkenylboron Monomers

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## Abstract

Radical copolymerization of vinyl- and isopropenyl-type boron monomers followed by side-chain oxidation enabled the synthesis of $\alpha$-methylated poly(vinyl alcohol)s (PVAs), which are difficult to obtain by conventional methods. The composition ratio of the resulting vinyl alcohol (VA)–isopropenyl alcohol (IPA) copolymers was tunable in a wide range (VA/IPA = 84/16 – 7/93 mol%) by adjusting monomer feed ratios in the copolymerization step. All copolymers were amorphous in the bulk state regardless of their composition ratios, despite the semi-crystalline natures of both VA and IPA homopolymers. In solution, copolymers with specific compositions exhibited solvent-dependent thermal-responsive behavior: lower critical solution temperature (LCST)-type transitions in water and upper critical solution temperature (UCST)-type transitions in acetone.

# Introduction

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Poly(vinyl alcohol) (PVA) is an important water-soluble and semi-crystalline polymer that is widely used for adhesives,[1,2] fibers,[3] and polarizing films.[4] The polymer is typically prepared by radical polymerization of vinyl acetate (VAc) followed by saponification (Figure 1A). The properties of PVA, such as hydrophilicity, crystallinity, and thermal stability, have been tailored through various chemical modifications, most commonly by partial derivatization of the hydroxy groups. Among these, the intramolecular acetal formation of PVA with formaldehyde, pioneered by Sakurada to enhance mechanical strength, represents the most classical example; the resulting polymer, known as vinylon, is industrially used as a high-strength fiber material.[5–7] Partial acetylation has also been employed to fine-tune physical characteristics for specific applications.[8,9] In addition, copolymerization of VAc with other monomers provides a versatile route to modulate PVA properties: ethylene–vinyl alcohol (VA) copolymers are widely used as gas-barrier materials,[10–12] while VA–acrylamide copolymers exhibit reduced crystallinity while retaining hydrophilicity.[13]

Poly(isopropenyl alcohol) (PIPA) is a structural analogue of PVA in which a methyl group is introduced at *α*-position of each repeating unit. The presence of this hydrophobic substituent of the isopropenyl alcohol (IPA) unit is expected to influence the physical properties of PVA, particularly decreased crystallinity and hydrophilicity. Consequently, PIPA and its copolymers with PVA are of particular interest as chemically modified PVA derivatives with tunable structural and functional characteristics (Figure 1B). Isopropenyl acetate (IPAc) can be expected as the precursor monomer for constructing the PIPA repeating unit; however, the polymerization is challenging due to its inherently poor (co)polymerization ability. The limitation arises from frequent degenerative chain transfer to the *α*-methyl group of the monomer giving less-reactive allyl radical species.[14–16] To minimize the influence of the degenerative chain transfer process, Nishino and coworkers performed the radical polymerization of IPAc under high-pressure condition (e.g., 1 GPa), successfully obtaining the corresponding polymer.[17] However, such high-pressure conditions require specialized equipment and involve potential safety risks, making this approach less desirable for general use. In previous reports about radical copolymerization of IPAc with VAc under ambient pressure, the increase of IPAc contents caused both significant decrease of the molecular weight of copolymers and increase in structural errors such as 1,2-glycol bonds.[18,19] Even if the copolymerization proceeds under high-pressure condition, systematic control of the composition ratio would be difficult to achieve.

In 2019, our group reported the radical polymerization of isopropenylboronic acid pinacol ester (IPBpin) and post-polymerization oxidation to synthesize PIPA.[20–23] We have also investigated radical polymerization of vinylboron compounds and found their polymerization behavior strongly depends on the protecting group on boron. Pinacol-protected one (VBpin) undewent frequent backbiting during homopolymerization, affording branched polymer that could be converted into branched PVA via post-polymerization oxidation.[24] In contrast, the use of an anthranilamide-type protecting group bearing a substituent on amide moiety effectively suppressed backbiting, enabling the synthesis of linear PVA.[25] These findings led us to envision that the copolymerization of isopropenylboron and vinylboron monomers, followed by post-polymerization oxidation would provide a series of PVAs bearing $\alpha$-methyl group in tunable ratios (Figure 1C). Consequently, we achieved syntheses of VA–IPA copolymers in some ratios and examined impacts of $\alpha$-methyl groups on crystallinity in bulk and solubility/thermoresponsibility in common solvents such as water.

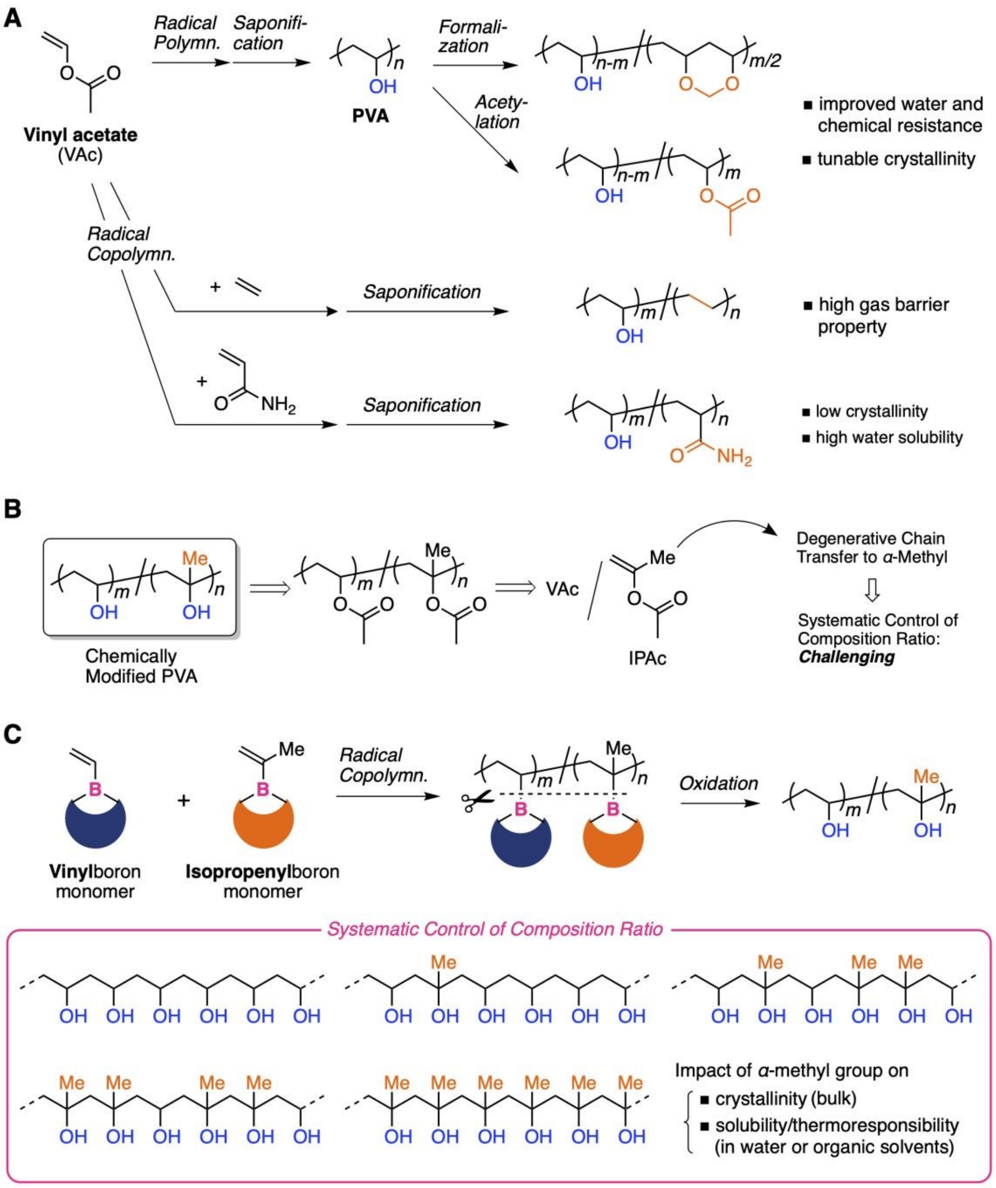


**Figure 1.** (A) Chemical modifications of PVA via post-polymerization functionalization of PVA or copolymerization of VAc with other comonomers. (B) Difficulty in synthesizing vinyl alcohol (VA)–isopropenyl alcohol (IPA) copolymers using acetate monomers. (C) Synthetic route to VA–IPA copolymers through radical copolymerization of vinylboron and isopropenylboron monomers followed by post-polymerization oxidation enabling composition control (This work).

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# Results and Discussion

We performed radical copolymerization of IPBpin as the isopropenyl-type boron monomer with vinyl-type boron monomer and compared their copolymerization behavior with that of acetyl-type monomers (VAc and IPAc) (Figures 2A and S1). As the vinyl-type boron monomer, we selected anthranilamide-protected vinylboron monomer bearing a 2-methoxyethyl substituent on the $N_{amide}$ (VBaam-MOE). In our previous study, we elucidated the key characteristics of VBaam-MOE as a monomer for radical polymerization: i) backbiting chain transfer is effectively suppressed due to the steric effect of $N_{amide}$ substituent; ii) both of the monomer and the resulting polymer exhibit high solubility in organic solvents thanks to methoxyethyl group; and iii) the polymerization proceeds at a higher rate than other anthranilamide-protected boron monomers.[25] The polymerization condition was as follows: [VBaam-MOE]$_0$/[IPBpin]$_0$/[V-70]$_0$ = 750/750/15 mM in DMF at 30 °C. The copolymerization smoothly proceeded giving high conversion, and their consumption speed was almost the same as each other [conv.(VBaam-MOE) = 85%, conv.(IPBpin) = 89%, 48 h]. The number-average molecular weight ($M_n$) of the resultant copolymer was 16,000. On the other hand, when radical copolymerization of two acetyl monomers (VAc and IPAc) was performed under the same condition, they were hardly consumed [conv.(VAc) = 13%, conv.(IPAc) = 8%, 48 h] and the product was oligomer ($M_n$ = 2,400). In the copolymerization under bulk condition, the $M_n$ increased to 7,600, but the monomer conversion was still low [conv.(VAc) = 28%, conv.(IPAc) = 15%, 48 h] (Figure S2). The combinations of boron- and acetyl-monomer, such as VBaam-MOE/IPAc, IPBpin/VAc, were also tested. In these cases, the boron monomers were consumed faster than the acetyl monomers and the conversion of the latter was very low: conv.(VBaam-MOE) = 87% vs. conv.(IPAc) = 18%, conv.(IPBpin) = 46% vs. conv.(VAc) = 5% in 48 h. The boron-containing monomers behave as conjugated monomers, whereas the acetyl monomers are non-conjugated, and there is no significant difference in electron density between the two types of monomers: therefore, the poor copolymerizability of their combination is a reasonable outcome.

The excellent copolymerizability of the VBaam-MOE/IPBpin combination is likely attributed to the fact that VBaam-MOE does not undergo backbiting chain-transfer reactions. To verify this assumption, we examined the copolymerization of VBpin, which is known to promote the backbiting chain-transfer reaction in the homopolymerization, instead of VBaam-MOE. As expected, the molecular weight of the resultant copolymer ($M_n$ = 9,500, Figure S3) was significantly lower despite the comparable conversion to the pair of VBaam-MOE and IPBpin [conv.(VBpin) = 69%, conv.(IPBpin) = 64%, 48 h]. Effects of injection ratio on the molecular weight of the resultant copolymer were also examined. In the case of VBpin, $M_n$ value decreased as the VBpin content in the feed increased, and the $M_n$ became less than 5,000 when injection ratio of VBpin was 80 mol% (Figure 2B and Table S1). The conversions of both monomers also decreased with increasing VBpin injection, becoming below 50% when 80 mol% of VBpin was used. In contrast, when VBaam-MOE was used, an entirely different trend was observed: $M_n$ value rather increased as the monomer feed increased maintaining high conversions (> 90%). The distinct copolymerization behavior clearly reflects the ability of VBaam-MOE to suppress chain-transfer reactions unlike VBpin, confirming the superior copolymerizability of VBaam-MOE with IPBpin. Furthermore, the monomer reactivity ratios for the copolymerization of VBaam-MOE and IPBpin were determined ($M_1$ = VBaam-MOE, $M_2$ = IPBpin, Figure 2C and Table S2). Both $r_1$ and $r_2$ were lower than 1 ($r_1 = 0.302$, $r_2 = 0.567$), indicating that the cross-over propagation between different monomers is rather preferred over the consecutive propagation of same monomers.

2-Cyano-2-propyl dodecyl trithiocarbonate (CPDT) was available as a chain transfer agent (CTA) for control of radical copolymerization of VBaam-MOE and IPBpin via reversible addition-fragmentation chain transfer (RAFT) process. Regardless of the injection ratio, the molecular weights of the resultant copolymers increased linearly with monomer conversion and the molecular weight distributions ($Đ$s) were narrow [$Đ < 1.5$, Figures S4–S7 for [VBaam-MOE]$_0$/[IPBpin]$_0$ = 2/1, 1/1, 1/2 (molar ratio) actual concentrations were shown in the Supporting Information].

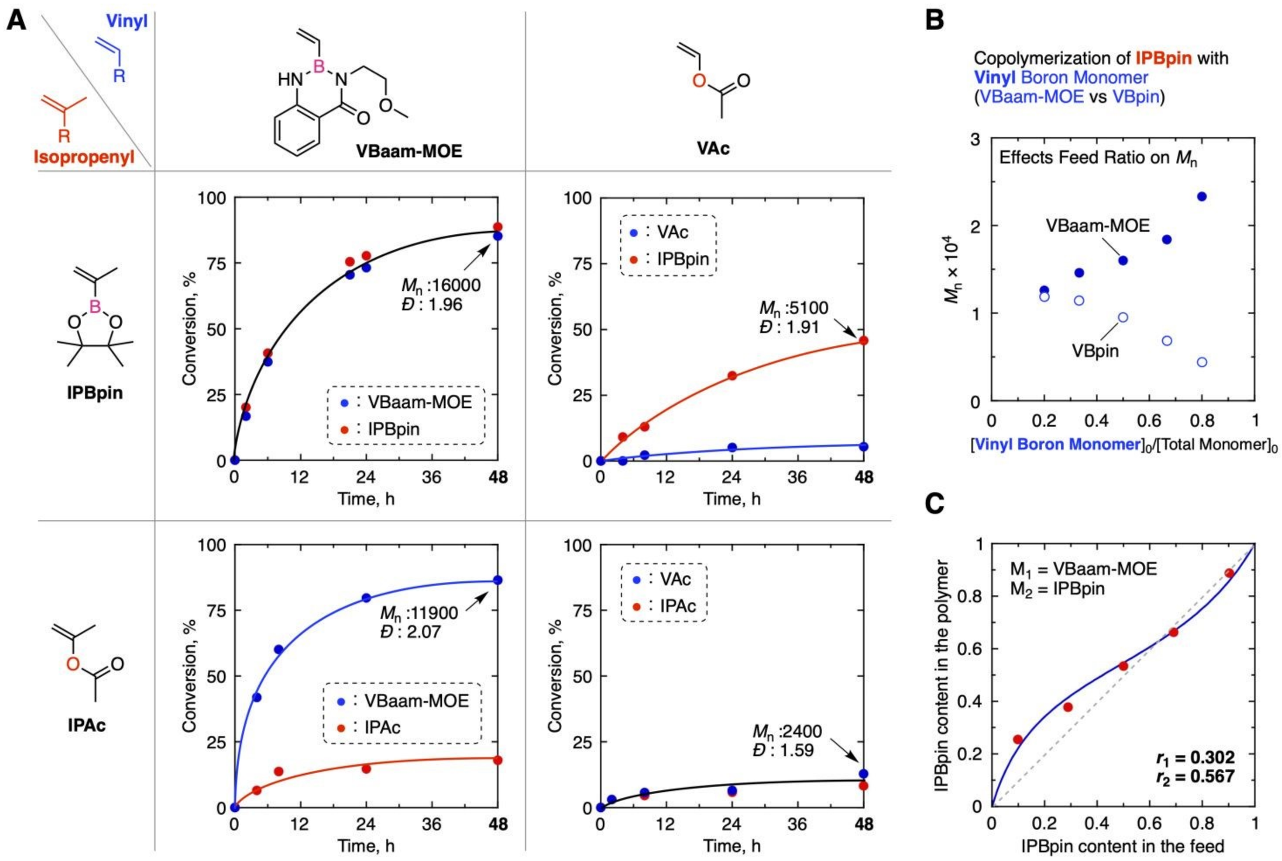


**Figure 2.** (A) Time-conversion plots and molar mass of resulting polymers in radical copolymerization of vinyl monomers (VBaam-MOE or VAc) with isopropenyl monomers (IPBpin or IPAc) in DMF at 30 °C: [vinyl monomer]$_0$ = [isopropenyl monomer]$_0$ = 750 mM and [V-70]$_0$ = 15 mM. (B) Correlation between $M_n$ of the resulting copolymer and the feed ratios of vinyl monomer in radical copolymerization of IPBpin with VBaam-MOE (solid circles) or VBpin (open circles). (C) Copolymer–composition curve for copolymerization of VBaam-MOE ($M_1$) and IPBpin ($M_2$).

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Post-polymerization oxidation was performed for the copolymers and homopolymers. The series of copolymers and homopolymers was prepared through free radical (co)polymerization of VBaam-MOE and/or IPBpin with different monomer injection ratios [$[\text{VBaam-MOE}]_0/[\text{IPBpin}]_0$ = 10/1, 4/1, 2/1, 1/1, 1/2, 1/4, and 1/10 (molar ratio) for copolymerization, actual concentrations were shown in the Supporting Information]. The $^1$H NMR spectra of the resultant copolymers indicated that the IPBpin unit composition ratio could be tuned from 10 mol% to 90 mol% (Figures S8–S16 and Table S3). We attempted the oxidation of the copolymer with $H_2O_2$ and NaOH to convert into VA–IPA copolymers and purification of the product by dialysis. $^1$H NMR spectrum of the product indicated the quantitative transformation, but unidentified peaks from aromatic protons were also detected. The peaks likely arise from byproducts generated by oxidation of anthranilamide pendant and the removal from the copolymers was found difficult.[26] The difficulty in removal of these byproducts by dialysis may be ascribed to the relatively large molecular size and low polarity, making the diffusion in dialysis membrane slow. We then decided to replace the anthranilamide protection with pinacol using *p*-toluenesulfonic acid (TsOH), followed by the oxidation reaction (Figures S17–S25). The two steps transformation was effective for the copolymers containing more than 20 mol% VBaam-MOE units. Consequently, VA–IPA copolymers of various composition ratios were successfully obtained as supported by structural analyses by $^1$H NMR (Figure 3A, DMSO-$d_6$): the peaks from the boron protecting group (i.e., pinacol and anthranilamide) completely disappeared, and the peaks from the byproduct was hardly observed. Most importantly, the signals from hydroxy group ($c_1$ for PVA and $c_2$ for PIPA) were clearly detected at 4.2–4.7 ppm for $c_1$ and 5.1–5.5 ppm for $c_2$ protons. The three sharp peaks arising from the hydroxy group in PVA ($c_1$) are known to correspond to triad tacticity (*mm*, *mr*, *rr*). Although detailed studies have not yet been reported, the hydroxy-derived signals of PIPA ($c_2$) also split into distinct sharp peaks, which are likely due to tacticity. A particularly noteworthy finding was that the NMR spectra of the respective homopolymers (PVA and PIPA) exhibited hydroxyl-derived signals at distinct chemical shifts, while in the copolymers, the hydroxyl peaks shifted to the intermediate position between those of PVA and PIPA (~4.9 ppm) progressively with composition. Taken together with the monomer reactivity ratios, these results suggest that the two repeating units are incorporated in a random fashion with a slight preference for alternating sequence along the polymer chain. When one repeating unit component (VA or IPA) predominated in the copolymer composition, distinct splitting of the hydroxy peaks due to stereoregularity was observed. This is probably due to that continuous sequences of identical units are present. However, as the compositional difference between the two monomers decreased, the proportion of such continuous sequences became smaller, and the hydroxy-derived signals appeared broadened instead. The composition ratio was determined by peak integrations of methine protons in VA unit ($b_1$) and methylene/methyl protons in both units ($a_1$, $a_2$, and $b_2$); VA/IPA = 84/16, 73/27, 57/43, 45/55, 31/69, 18/82 and 7/93 mol%. These values were almost consistent with the composition ratios (VBaam-MOE/IPBpin) before transformation. In contrast to the drastic changes observed in the hydroxy-derived peaks in the

[1]H NMR spectra depending on the VA/IPA composition, the FT-IR absorption band corresponding to the hydroxy groups at around 3300 cm⁻¹ showed almost no noticeable change (Figure 3B).

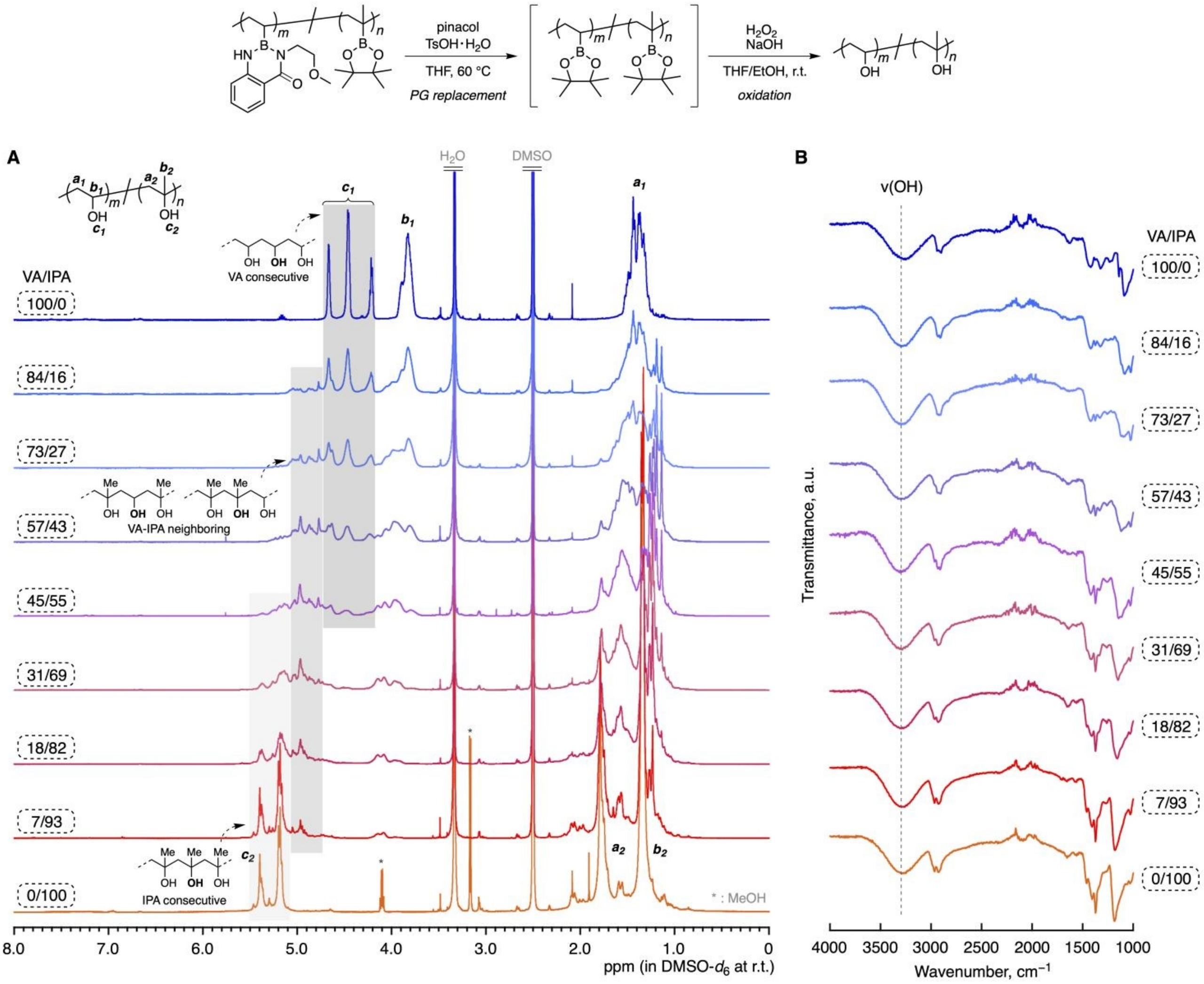


**Figure 3.** Transformation of VBaam-MOE-IPBpin (co)polymers to VA–IPA (co)polymers through protecting group (PG) replacement from anthrnailamide to pinacol and subsequent oxidation. (A) [1]H NMR and (B) FT-IR spectra of the resulting VA–IPA (co)polymers.

We then measured differential scanning calorimetry (DSC) and X-ray diffraction (XRD) of thus-obtained VA–IPA (co)polymers to investigate impacts of $\alpha$-methyl group on the crystallization behavior (Figures 4 and S26–S35). As for the PVA homopolymer obtained from VBaam-MOE, the exothermic peak derived from melting of crystallized polymer was detected at 198 °C. In the XRD profile, the characteristic peaks corresponding to the diffractions of lattice surfaces of PVA crystalline [(100), (10¯ and 101), (200), and (11¯ and 111)][27] were observed. PIPA also showed an endothermic melting peak at 127 °C, indicating the semi-crystalline nature of PIPA. Two sharp peaks in XRD profile also supported the crystallization.[28] On the other hand, PIPA prepared by high-pressure polymerization of IPAc has been previously reported as amorphous polymer.[17] This difference is probably due to the structural defects such as branch structure and head-to-head generated under harsh polymerization condition. Tacticity is also an important factor that may contribute to the distinct crystallization behavior depending on the precursor monomers. However, the investigation on the correlation between tacticity and crystallinity is highly challenging at this stage.

Whereas both homopolymers exhibited crystallinity, all copolymers synthesized in this study were amorphous. Notably, only the copolymer with a composition ratio of VA/IPA = 84/16 showed a small endothermic peak at 148 °C in the DSC trace, which may correspond to melting of crystalline domains; however, the peak was too weak for the polymer to be regarded as crystalline. Instead, baseline shifts from glass transition were observed in the DSC trace, and glass transition temperature ($T_g$) gradually decreased with the increase of IPA content. Intriguingly, the copolymer with a composition ratio of 45/55 specifically exhibited a relatively high $T_g$. Both reactivity ratios are lower than 1 ($r_1$ = 0.302, $r_2$ = 0.567 for $M_1$ = VBaam-MOE, $M_2$ = IPBpin), thus the copolymerization of 1:1 feed ratio is expected to yield a copolymer with a moderately alternating tendency and a limited amount of homosequences. Therefore, the enhanced $T_g$ may result from heterosequence-rich structure, but this speculation will require more precise control of the copolymers. XRD profiles also supported the amorphous character of VA–IPA copolymers; most of the copolymers did not display sharp diffraction peaks in the XRD patterns. Exceptionally, the VA-rich copolymer (VA/IPA = 84/16) gave very tiny XRD peaks suggesting the slight crystallinity corresponding to the small endothermic peak in the DSC trance of the same copolymer. The face distances ($d$) calculated by the most intense peaks increased (4.57 Å $\rightarrow$ 6.11 Å) as the IPA unit ratios (0 mol% $\rightarrow$ 100 mol%) probably because the introduced methyl groups increased the occupied volume of polymers (Table S4).

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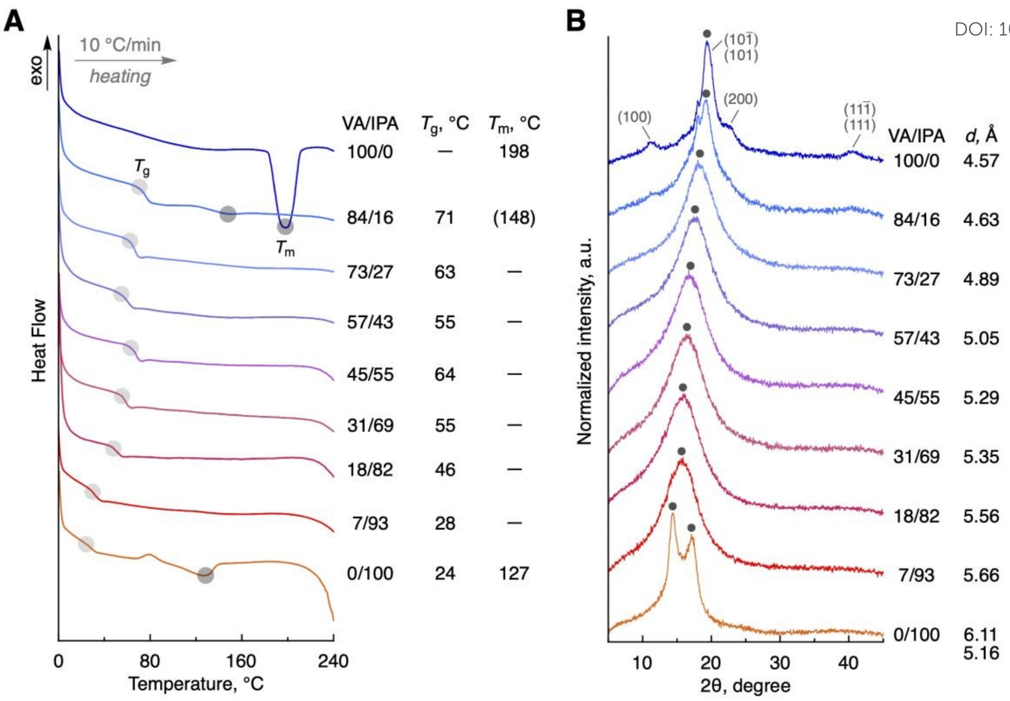


**Figure 4.** Physical properties of VA–IPA (co)polymers: (A) DSC curves (second heating at 10 °C/min) and (B) XRD profiles.

Finally, we investigated the solubility of VA–IPA (co)polymers in various common solvents including water as well as the thermo-responsive behavior of the solution. They showed different solubilities depending on the copolymerization ratio (Figures 5A and S36). PVA was soluble in water, whereas PIPA was insoluble: the hydrophobic methyl group causes decrease in hydrophilicity. The copolymers less than 31mol% of VA units were insoluble in water at any temperature. When the VA ratio increased to 45 mol%, the copolymer was soluble in water at room temperature, and the solution became turbid upon heating (Figure 5B): it exhibited lower critical solution temperature (LCST)-type thermal response. The thermo-responsive behavior was further investigated through variable-temperature transmittance measurement of the solution at 2 mg mL$^{-1}$ (Figures 5C and S37, heating rate: 1 °C min$^{-1}$; λ = 670 nm). The transmittance gradually decreased to 10% around 40–70 °C and the cloud point ($T_{CP,\ 50\%}$: the temperature giving 50% transmittance) was determined as 49.3 °C. The thermal response was also confirmed by temperature-variable dynamic light scattering (DLS) analysis: hydrodynamic diameter ($D_h$) gradually increased from ~50 nm to ~430 nm upon heating (Figure S38). The copolymer is soluble in water due to the hydration of VA-rich segments with water molecules at a lower temperature, and probably, dehydration from polymer chains occurs upon heating due to the entropic driving force. The chains aggregate through the hydrophobic interactions derived from IPA-rich segments giving the turbid solution. The copolymer of 57/43 also showed thermal response at higher temperature (~80 °C) and the transmittance decreased only slightly.

Although PVA is known to insoluble in most organic solvents, the VA–IPA copolymers became soluble in organic solvents such as methanol, ethanol, DMF and chloroform (Figure 5A). The loss of crystallinity observed in the copolymers suggests that the chain-chain interactions through hydrogen bonding among hydroxyl groups are weakened, which likely accounts for their enhanced solubility compared with PVA. Interestingly, the IPA-rich copolymer (IPA content: 55 mol% – 93 mol%) exhibited a distinctive upper critical solution temperature (UCST)-type thermal response in acetone; they were soluble at higher temperature and became insoluble upon cooling (Figure 5D). Both PVA and PIPA homopolymers were insoluble in acetone at any temperature due to their well-packed crystalline structures, indicating that the solubility or UCST behavior of the copolymer are truly unique. Variable-temperature transmittance measurements revealed that the cloud point ($T_{CP,50\%}$) in the UCST behavior did not change monotonically with the unit ratio of the copolymer. Notably, the 18/82 copolymer gave the lowest $T_{CP,\ 50\%}$ among the four copolymers, indicating it exhibits the highest solubility in acetone within a series (Figures 5E and S39). The complicated solubility trend is likely governed by a delicate balance between interactions among polymer chains and interactions with solvent molecules. The solubility uniqueness is reminiscent of the higher solubility of methylated cellulose in water compared with unmodified cellulose and is particularly intriguing as a characteristic unique to hydroxyl-containing polymers.[29] DLS analysis of the 45/55 copolymer (0.9 mg $mL^{-1}$ in acetone) exhibited the formation of huger aggregates than those in aqueous solution: $D_h$ gradually increased from ~200 nm to ~2.4 µm in the cooling process from 50 °C to 10 °C (Figure S40). Thus, the controlled introduction of $\alpha$-methyl groups into PVA was found helpful for modulating the solubility and thermal response not only in water but also in organic solvents.

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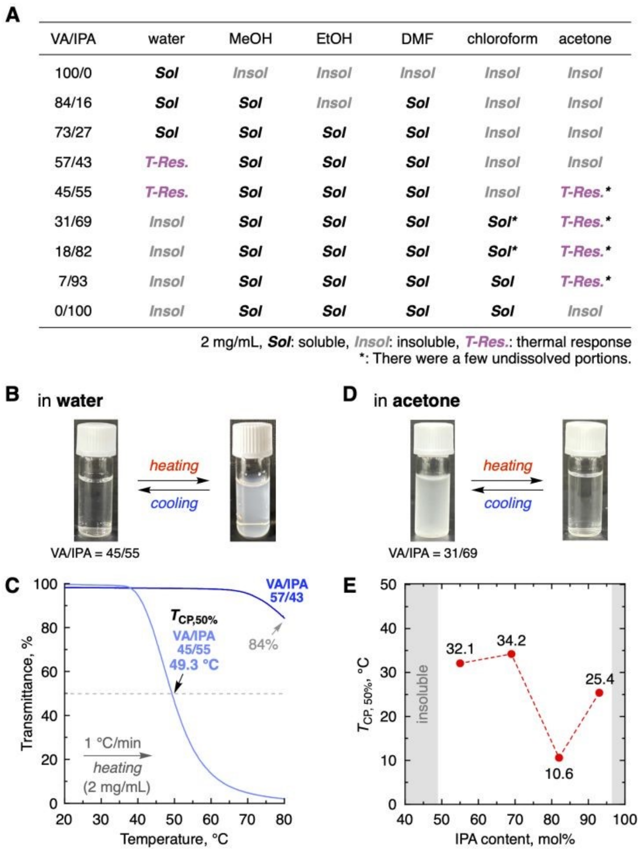

A

| VA/IPA | water | MeOH | EtOH | DMF | chloroform | acetone |
|---|---|---|---|---|---|---|
| 100/0 | *Sol* | *Insol* | *Insol* | *Insol* | *Insol* | *Insol* |
| 84/16 | *Sol* | *Sol* | *Insol* | *Sol* | *Insol* | *Insol* |
| 73/27 | *Sol* | *Sol* | *Sol* | *Sol* | *Insol* | *Insol* |
| 57/43 | *T-Res.* | *Sol* | *Sol* | *Sol* | *Insol* | *Insol* |
| 45/55 | *T-Res.* | *Sol* | *Sol* | *Sol* | *Insol* | *T-Res.** |
| 31/69 | *Insol* | *Sol* | *Sol* | *Sol* | *Sol** | *T-Res.** |
| 18/82 | *Insol* | *Sol* | *Sol* | *Sol* | *Sol** | *T-Res.** |
| 7/93 | *Insol* | *Sol* | *Sol* | *Sol* | *Sol* | *T-Res.** |
| 0/100 | *Insol* | *Sol* | *Sol* | *Sol* | *Sol* | *Insol* |

2 mg/mL, *Sol*: soluble, *Insol*: insoluble, *T-Res.*: thermal response
*: There were a few undissolved portions.



**Figure 5.** (A) Visual solubility test for water and several organic solvents of the resulting VA–IPA (co)polymers. (B) Photos for thermal response behavior of VA–IPA copolymers (VA/IPA = 45/55) in water (2 mg mL$^{-1}$). (C) Temperature-variable transmittance measurement (λ = 670 nm) on the heating process (1 °C min$^{-1}$) with 2 mg mL$^{-1}$ solutions in water. (D) Photos for thermal response behavior of VA–IPA copolymers (VA/IPA = 31/69) in acetone (1.3 mg mL$^{-1}$). (E) $T_{CP,\ 50\%}$–IPA content plot observed in the cooling process (1 °C min$^{-1}$) with saturated (VA/IPA = 45/55: 0.9 mg mL$^{-1}$, 31/69: 1.3 mg mL$^{-1}$, 18/82: 1.7 mg mL$^{-1}$, 7/93: 1.3 mg mL$^{-1}$) solutions in acetone.

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# Conclusion

In conclusion, we established the efficient synthetic route to vinyl alcohol (VA)–isopropenyl alcohol (IPA) copolymers using the two types of alkenylboron monomers. Radical copolymerization of vinyl-type VBaam-MOE with isopropenyl-type IPBpin and side-chain oxidation afforded a series of VA–IPA statistical copolymers with various composition ratios (VA/IPA = 84/16 – 7/93), which were difficult to synthesize from acetyl-type precursors (i.e., VAc and IPAc). The resulting copolymers were found to be amorphous at most composition ratios whereas both VA and IPA homopolymers exhibited distinctive semi-crystalline nature. The introduced *α*-methyl groups dramatically enhanced solubility in organic solvents such as methanol and DMF. The thermal response in solution states depended on the composition ratios; copolymers with 43 – 55 mol% IPA units showed LCST-type thermos-responsive behavior in water, and ones with 55 – 93 mol% IPA units gave UCST-type response in acetone. Since PVA has been widely used for many applications as described above, the unprecedented syntheses of *α*-methylated PVAs of allowing the modulation of physical properties is useful for accessing PVA-based materials with innovative functions in the future.

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# Supporting Information

The Supporting Information is available free of charge

Detailed description of synthetic procedures, experimental methods, $^1$H NMR and FT-IR spectra, GPC analysis, DSC measurements, XRD measurements, UV-vis measurements and DLS measurements (PDF).

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## Notes

The authors declare no competing financial interests.

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26 For the synthesis of PVA homopolymer by boron-pendant oxidation, the resulting polymers spontaneously precipitate during reaction. Then, the most byproducts can be removed by simple filtration, and the residual byproducts are removed by the following dialysis. However, in the case of VA–IPA copolymers, the purification through reprecipitation and filtration does not work due to their high solubility to organic solvent, making the removal of anthranilamide-derived byproducts more difficult.

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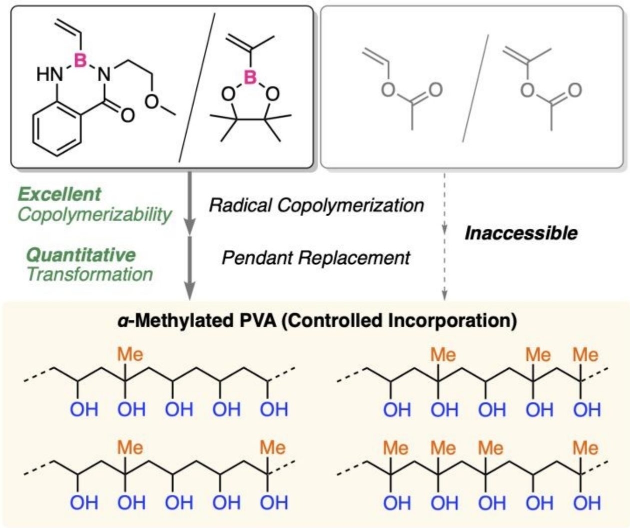

# Data availability statements

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**Property Modulation of Poly(vinyl alcohol)s via Controlled Incorporation of α-Methyl Group Using Alkenylboron Monomers**

Hiroshi Suzuki, Tsuyoshi Nishikawa,* Makoto Ouchi*



**Data availability:**

The data supporting this study have been included as part of the Supplementary Information. In the ESI, detailed description of synthetic procedures, experimental methods, $^{1}H$ NMR and FT-IR spectra, GPC analysis, DSC measurements, XRD measurements, UV-vis measurements and DLS measurements are shown.

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# Property Modulation of Poly(vinyl alcohol)s via Controlled Incorporation of $\alpha$-Methyl Groups Using Alkenylboron Monomers

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KEYWORDS: "Poly(vinyl alcohol)" "Poly(isopropenyl alcohol)" "Vinylboron monomer" "Radical copolymerization" "Crystallinity" "Thermal response"

## Abstract

Radical copolymerization of vinyl- and isopropenyl-type boron monomers followed by side-chain oxidation enabled the synthesis of $\alpha$-methylated poly(vinyl alcohol)s (PVAs), which are difficult to obtain by conventional methods. The composition ratio of the resulting vinyl alcohol (VA)–isopropenyl alcohol (IPA) copolymers was tunable in a wide range (VA/IPA = 84/16 – 7/93 mol%) by adjusting monomer feed ratios in the copolymerization step. All copolymers were amorphous in the bulk state regardless of their composition ratios, despite the semi-crystalline natures of both VA and IPA homopolymers. In solution, copolymers with specific compositions exhibited solvent-dependent thermal-responsive behavior: lower critical solution temperature (LCST)-type transitions in water and upper critical solution temperature (UCST)-type transitions in acetone.

# Introduction

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Poly(vinyl alcohol) (PVA) is an important water-soluble and semi-crystalline polymer that is widely used for adhesives,[1,2] fibers,[3] and polarizing films.[4] The polymer is typically prepared by radical polymerization of vinyl acetate (VAc) followed by saponification (Figure 1A). The properties of PVA, such as hydrophilicity, crystallinity, and thermal stability, have been tailored through various chemical modifications, most commonly by partial derivatization of the hydroxy groups. Among these, the intramolecular acetal formation of PVA with formaldehyde, pioneered by Sakurada to enhance mechanical strength, represents the most classical example; the resulting polymer, known as vinylon, is industrially used as a high-strength fiber material.[5–7] Partial acetylation has also been employed to fine-tune physical characteristics for specific applications.[8,9] In addition, copolymerization of VAc with other monomers provides a versatile route to modulate PVA properties: ethylene–vinyl alcohol (VA) copolymers are widely used as gas-barrier materials,[10–12] while VA–acrylamide copolymers exhibit reduced crystallinity while retaining hydrophilicity.[13]

Poly(isopropenyl alcohol) (PIPA) is a structural analogue of PVA in which a methyl group is introduced at *α*-position of each repeating unit. The presence of this hydrophobic substituent of the isopropenyl alcohol (IPA) unit is expected to influence the physical properties of PVA, particularly decreased crystallinity and hydrophilicity. Consequently, PIPA and its copolymers with PVA are of particular interest as chemically modified PVA derivatives with tunable structural and functional characteristics (Figure 1B). Isopropenyl acetate (IPAc) can be expected as the precursor monomer for constructing the PIPA repeating unit; however, the polymerization is challenging due to its inherently poor (co)polymerization ability. The limitation arises from frequent degenerative chain transfer to the *α*-methyl group of the monomer giving less-reactive allyl radical species.[14–16] To minimize the influence of the degenerative chain transfer process, Nishino and coworkers performed the radical polymerization of IPAc under high-pressure condition (e.g., 1 GPa), successfully obtaining the corresponding polymer.[17] However, such high-pressure conditions require specialized equipment and involve potential safety risks, making this approach less desirable for general use. In previous reports about radical copolymerization of IPAc with VAc under ambient pressure, the increase of IPAc contents caused both significant decrease of the molecular weight of copolymers and increase in structural errors such as 1,2-glycol bonds.[18,19] Even if the copolymerization proceeds under high-pressure condition, systematic control of the composition ratio would be difficult to achieve.

In 2019, our group reported the radical polymerization of isopropenylboronic acid pinacol ester (IPBpin) and post-polymerization oxidation to synthesize PIPA.[20–23] We have also investigated radical polymerization of vinylboron compounds and found their polymerization behavior strongly depends on the protecting group on boron. Pinacol-protected one (VBpin) undewent frequent backbiting during homopolymerization, affording branched polymer that could be converted into branched PVA via post-polymerization oxidation.[24] In contrast, the use of an anthranilamide-type protecting group bearing a substituent on amide moiety effectively suppressed backbiting, enabling the synthesis of linear PVA.[25] These findings led us to envision that the copolymerization of isopropenylboron and vinylboron monomers, followed by post-polymerization oxidation would provide a series of PVAs bearing *α*-methyl group in tunable ratios (Figure 1C). Consequently, we achieved syntheses of VA–IPA copolymers in some ratios and examined impacts of *α*-methyl groups on crystallinity in bulk and solubility/thermoresponsibility in common solvents such as water.

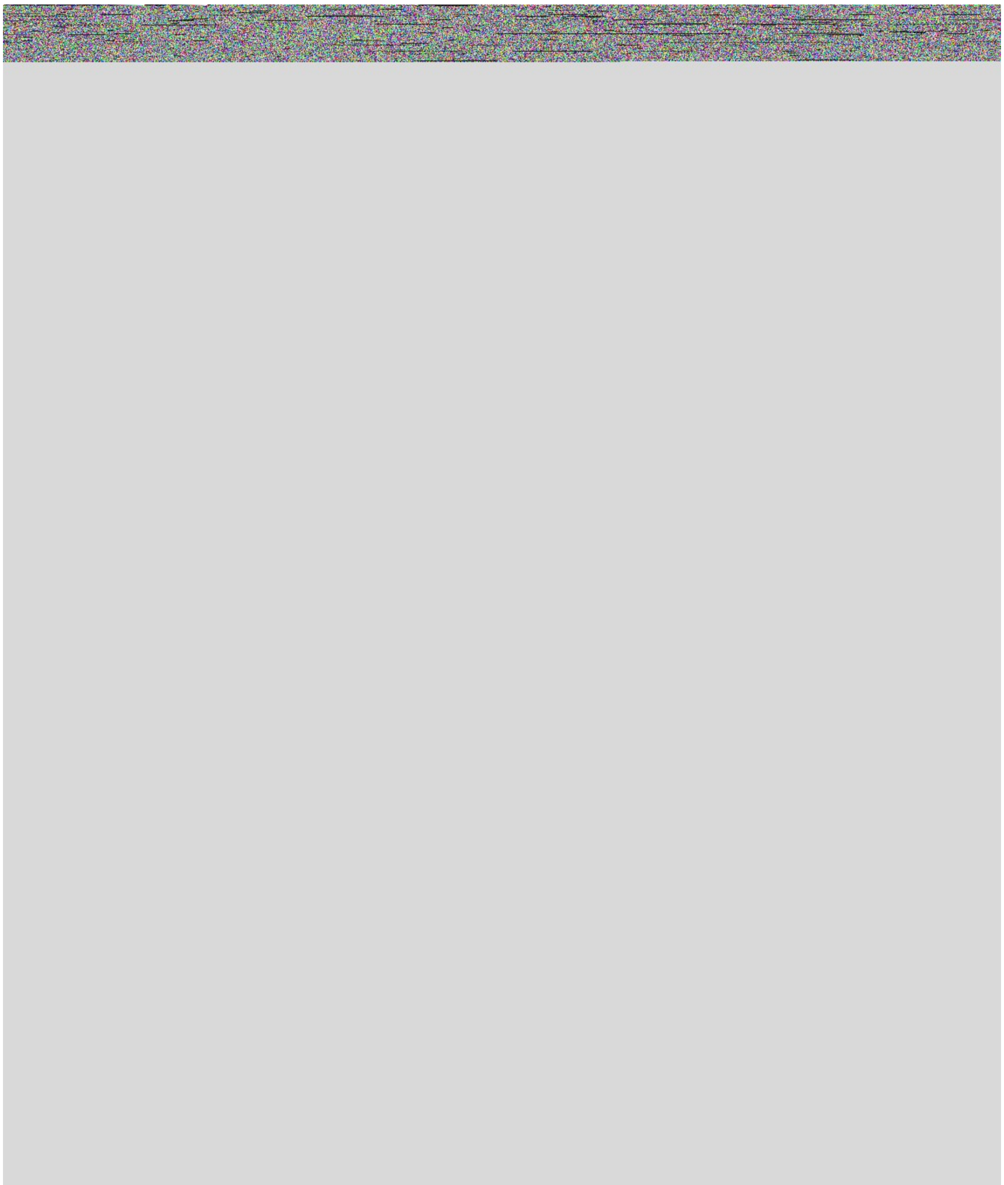

**Figure 1.** (A) Chemical modifications of PVA via post-polymerization functionalization of PVA or copolymerization of VAc with other comonomers. (B) Difficulty in synthesizing vinyl alcohol (VA)–isopropenyl alcohol (IPA) copolymers using acetate monomers. (C) Synthetic route to VA–IPA copolymers through radical copolymerization of vinylboron and isopropenylboron monomers followed by post-polymerization oxidation enabling composition control (This work).

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# Results and Discussion

We performed radical copolymerization of IPBpin as the isopropenyl-type boron monomer with vinyl-type boron monomer and compared their copolymerization behavior with that of acetyl-type monomers (VAc and IPAc) (Figures 2A and S1). As the vinyl-type boron monomer, we selected anthranilamide-protected vinylboron monomer bearing a 2-methoxyethyl substituent on the $N_{\text{amide}}$ (VBaam-MOE). In our previous study, we elucidated the key characteristics of VBaam-MOE as a monomer for radical polymerization: i) backbiting chain transfer is effectively suppressed due to the steric effect of $N_{\text{amide}}$ substituent; ii) both of the monomer and the resulting polymer exhibit high solubility in organic solvents thanks to methoxyethyl group; and iii) the polymerization proceeds at a higher rate than other anthranilamide-protected boron monomers.[25] The polymerization condition was as follows: [VBaam-MOE]$_0$/[IPBpin]$_0$/[V-70]$_0$ = 750/750/15 mM in DMF at 30 °C. The copolymerization smoothly proceeded giving high conversion, and their consumption speed was almost the same as each other [conv.(VBaam-MOE) = 85%, conv.(IPBpin) = 89%, 48 h]. The number-average molecular weight ($M_n$) of the resultant copolymer was 16,000. On the other hand, when radical copolymerization of two acetyl monomers (VAc and IPAc) was performed under the same condition, they were hardly consumed [conv.(VAc) = 13%, conv.(IPAc) = 8%, 48 h] and the product was oligomer ($M_n$ = 2,400). In the copolymerization under bulk condition, the $M_n$ increased to 7,600, but the monomer conversion was still low [conv.(VAc) = 28%, conv.(IPAc) = 15%, 48 h] (Figure S2). The combinations of boron- and acetyl-monomer, such as VBaam-MOE/IPAc, IPBpin/VAc, were also tested. In these cases, the boron monomers were consumed faster than the acetyl monomers and the conversion of the latter was very low: conv.(VBaam-MOE) = 87% vs. conv.(IPAc) = 18%, conv.(IPBpin) = 46% vs. conv.(VAc) = 5% in 48 h. The boron-containing monomers behave as conjugated monomers, whereas the acetyl monomers are non-conjugated, and there is no significant difference in electron density between the two types of monomers: therefore, the poor copolymerizability of their combination is a reasonable outcome.

The excellent copolymerizability of the VBaam-MOE/IPBpin combination is likely attributed to the fact that VBaam-MOE does not undergo backbiting chain-transfer reactions. To verify this assumption, we examined the copolymerization of VBpin, which is known to promote the backbiting chain-transfer reaction in the homopolymerization, instead of VBaam-MOE. As expected, the molecular weight of the resultant copolymer ($M_n$ = 9,500, Figure S3) was significantly lower despite the comparable conversion to the pair of VBaam-MOE and IPBpin [conv.(VBpin) = 69%, conv.(IPBpin) = 64%, 48 h]. Effects of injection ratio on the molecular weight of the resultant copolymer were also examined. In the case of VBpin, $M_n$ value decreased as the VBpin content in the feed increased, and the $M_n$ became less than 5,000 when injection ratio of VBpin was 80 mol% (Figure 2B and Table S1). The conversions of both monomers also decreased with increasing VBpin injection, becoming below 50% when 80 mol% of VBpin was used. In contrast, when VBaam-MOE was used, an entirely different trend was observed: $M_n$ value rather increased as the monomer feed increased maintaining high conversions (> 90%). The distinct copolymerization behavior clearly reflects the ability of VBaam-MOE to suppress chain-transfer reactions unlike VBpin, confirming the superior copolymerizability of VBaam-MOE with IPBpin. Furthermore, the monomer reactivity ratios for the copolymerization of VBaam-MOE and IPBpin were determined ($M_1$ = VBaam-MOE, $M_2$ = IPBpin, Figure 2C and Table S2). Both $r_1$ and $r_2$ were lower than 1 ($r_1 = 0.302$, $r_2 = 0.567$), indicating that the cross-over propagation between different monomers is rather preferred over the consecutive propagation of same monomers.

2-Cyano-2-propyl dodecyl trithiocarbonate (CPDT) was available as a chain transfer agent (CTA) for control of radical copolymerization of VBaam-MOE and IPBpin via reversible addition-fragmentation chain transfer (RAFT) process. Regardless of the injection ratio, the molecular weights of the resultant copolymers increased linearly with monomer conversion and the molecular weight distributions ($Đ$s) were narrow [$Đ < 1.5$, Figures S4–S7 for [VBaam-MOE]$_0$/[IPBpin]$_0$ = 2/1, 1/1, 1/2 (molar ratio) actual concentrations were shown in the Supporting Information].

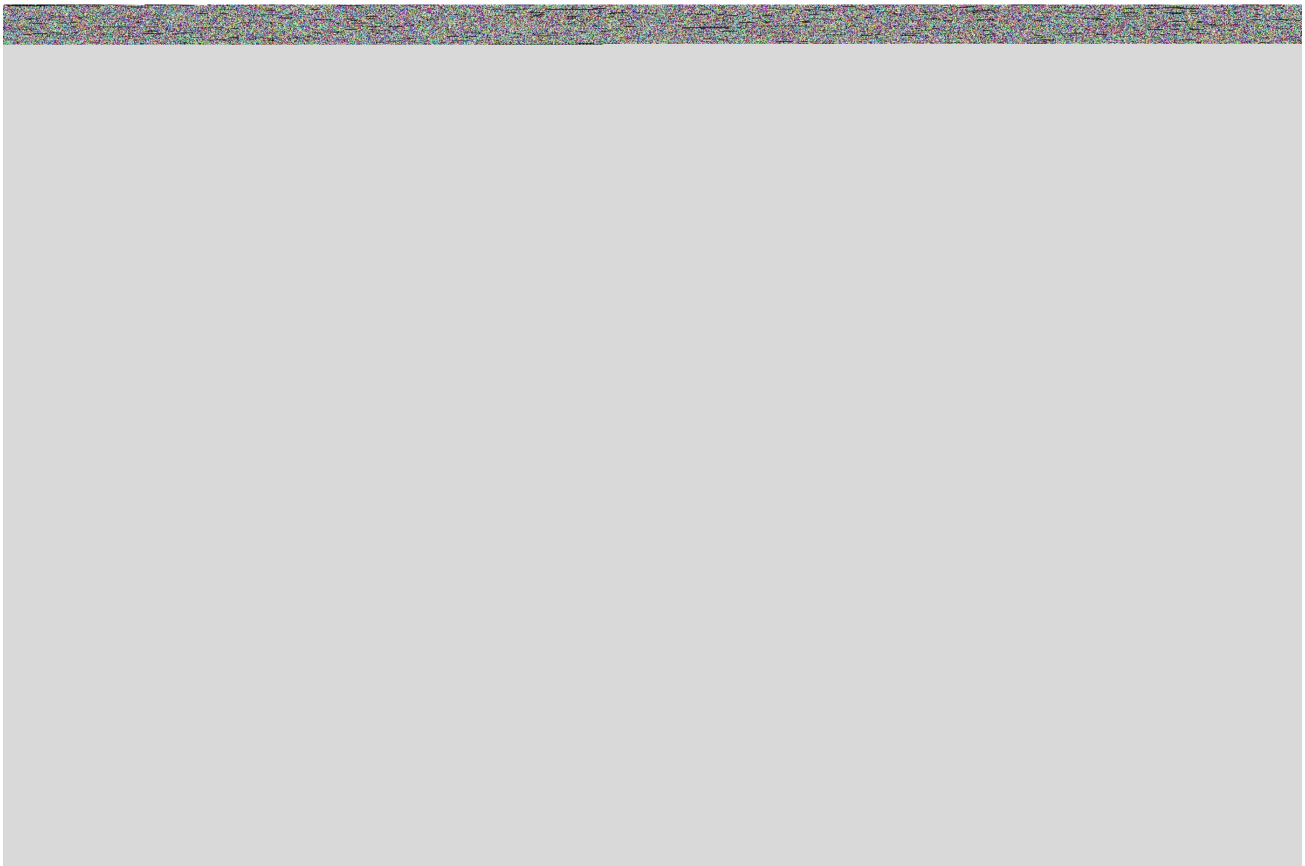

**Figure 2.** (A) Time-conversion plots and molar mass of resulting polymers in radical copolymerization of vinyl monomers (VBaam-MOE or VAc) with isopropenyl monomers (IPBpin or IPAc) in DMF at 30 °C: [vinyl monomer]$_0$ = [isopropenyl monomer]$_0$ = 750 mM and [V-70]$_0$ = 15 mM. (B) Correlation between $M_n$ of the resulting copolymer and the feed ratios of vinyl monomer in radical copolymerization of IPBpin with VBaam-MOE (solid circles) or VBpin (open circles). (C) Copolymer–composition curve for copolymerization of VBaam-MOE ($M_1$) and IPBpin ($M_2$).

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Post-polymerization oxidation was performed for the copolymers and homopolymers. The series of copolymers and homopolymers was prepared through free radical (co)polymerization of VBaam-MOE and/or IPBpin with different monomer injection ratios [[VBaam-MOE]$_0$/[IPBpin]$_0$ = 10/1, 4/1, 2/1, 1/1, 1/2, 1/4, and 1/10 (molar ratio) for copolymerization, actual concentrations were shown in the Supporting Information]. The $^1$H NMR spectra of the resultant copolymers indicated that the IPBpin unit composition ratio could be tuned from 10 mol% to 90 mol% (Figures S8–S16 and Table S3). We attempted the oxidation of the copolymer with $H_2O_2$ and NaOH to convert into VA–IPA copolymers and purification of the product by dialysis. $^1$H NMR spectrum of the product indicated the quantitative transformation, but unidentified peaks from aromatic protons were also detected. The peaks likely arise from byproducts generated by oxidation of anthranilamide pendant and the removal from the copolymers was found difficult.[26] The difficulty in removal of these byproducts by dialysis may be ascribed to the relatively large molecular size and low polarity, making the diffusion in dialysis membrane slow. We then decided to replace the anthranilamide protection with pinacol using *p*-toluenesulfonic acid (TsOH), followed by the oxidation reaction (Figures S17–S25). The two steps transformation was effective for the copolymers containing more than 20 mol% VBaam-MOE units. Consequently, VA–IPA copolymers of various composition ratios were successfully obtained as supported by structural analyses by $^1$H NMR (Figure 3A, DMSO-$d_6$): the peaks from the boron protecting group (i.e., pinacol and anthranilamide) completely disappeared, and the peaks from the byproduct was hardly observed. Most importantly, the signals from hydroxy group ($c_1$ for PVA and $c_2$ for PIPA) were clearly detected at 4.2–4.7 ppm for $c_1$ and 5.1–5.5 ppm for $c_2$ protons. The three sharp peaks arising from the hydroxy group in PVA ($c_1$) are known to correspond to triad tacticity (*mm*, *mr*, *rr*). Although detailed studies have not yet been reported, the hydroxy-derived signals of PIPA ($c_2$) also split into distinct sharp peaks, which are likely due to tacticity. A particularly noteworthy finding was that the NMR spectra of the respective homopolymers (PVA and PIPA) exhibited hydroxyl-derived signals at distinct chemical shifts, while in the copolymers, the hydroxyl peaks shifted to the intermediate position between those of PVA and PIPA (~4.9 ppm) progressively with composition. Taken together with the monomer reactivity ratios, these results suggest that the two repeating units are incorporated in a random fashion with a slight preference for alternating sequence along the polymer chain. When one repeating unit component (VA or IPA) predominated in the copolymer composition, distinct splitting of the hydroxy peaks due to stereoregularity was observed. This is probably due to that continuous sequences of identical units are present. However, as the compositional difference between the two monomers decreased, the proportion of such continuous sequences became smaller, and the hydroxy-derived signals appeared broadened instead. The composition ratio was determined by peak integrations of methine protons in VA unit ($b_1$) and methylene/methyl protons in both units ($a_1$, $a_2$, and $b_2$); VA/IPA = 84/16, 73/27, 57/43, 45/55, 31/69, 18/82 and 7/93 mol%. These values were almost consistent with the composition ratios (VBaam-MOE/IPBpin) before transformation. In contrast to the drastic changes observed in the hydroxy-derived peaks in the

[1]H NMR spectra depending on the VA/IPA composition, the FT-IR absorption band corresponding to the hydroxy groups at around 3300 cm⁻¹ showed almost no noticeable change (Figure 3B).

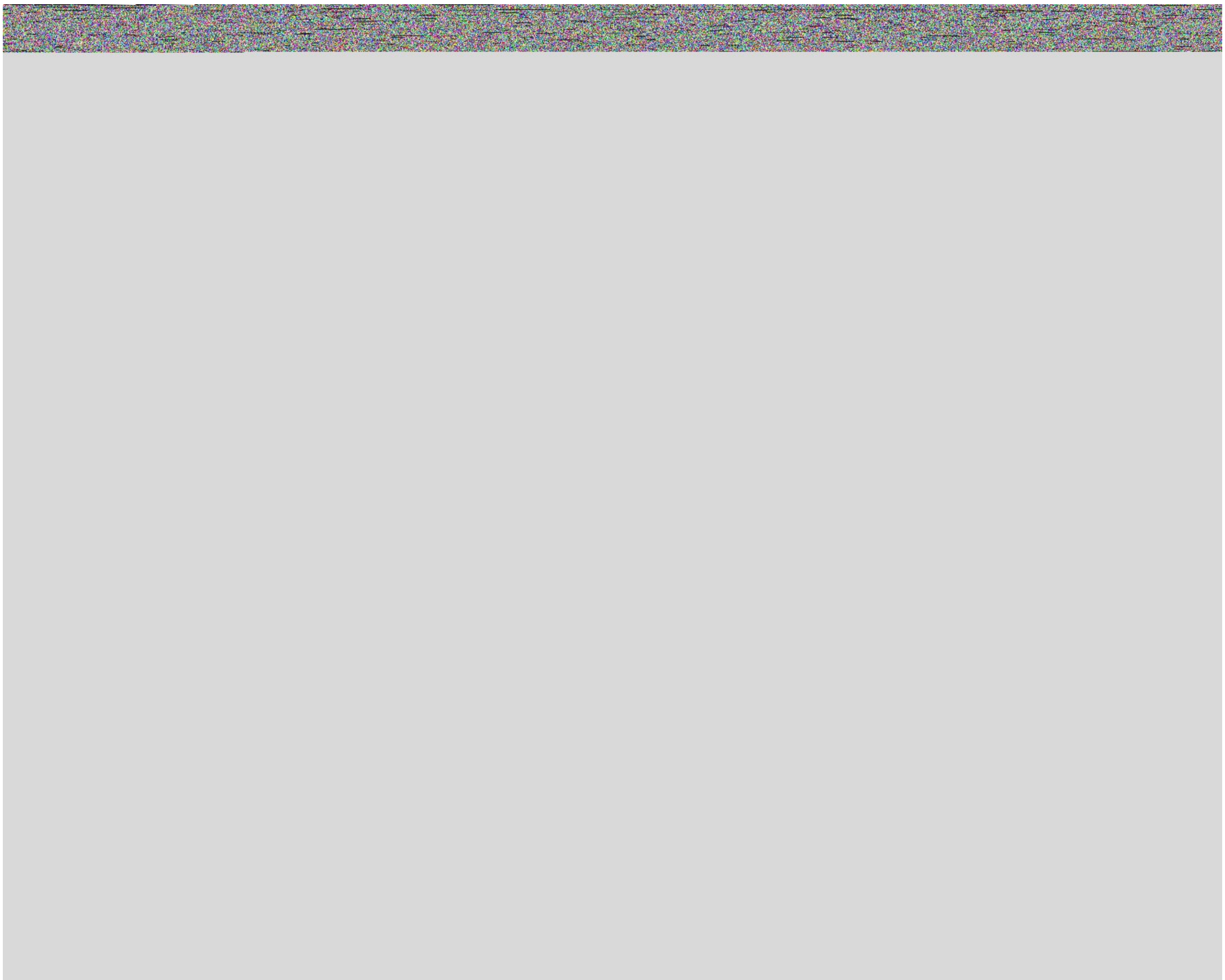

**Figure 3.** Transformation of VBaam-MOE-IPBpin (co)polymers to VA–IPA (co)polymers through protecting group (PG) replacement from anthrnailamide to pinacol and subsequent oxidation. (A) [1]H NMR and (B) FT-IR spectra of the resulting VA–IPA (co)polymers.

We then measured differential scanning calorimetry (DSC) and X-ray diffraction (XRD) of thus-obtained VA–IPA (co)polymers to investigate impacts of $\alpha$-methyl group on the crystallization behavior (Figures 4 and S26–S35). As for the PVA homopolymer obtained from VBaam-MOE, the exothermic peak derived from melting of crystallized polymer was detected at 198 °C. In the XRD profile, the characteristic peaks corresponding to the diffractions of lattice surfaces of PVA crystalline [(100), (10‾ and 101), (200), and (11‾ and 111)][27] were observed. PIPA also showed an endothermic melting peak at 127 °C, indicating the semi-crystalline nature of PIPA. Two sharp peaks in XRD profile also supported the crystallization.[28] On the other hand, PIPA prepared by high-pressure polymerization

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of IPAc has been previously reported as amorphous polymer.[17] This difference is probably due to the structural defects such as branch structure and head-to-head generated under harsh polymerization condition. Tacticity is also an important factor that may contribute to the distinct crystallization behavior depending on the precursor monomers. However, the investigation on the correlation between tacticity and crystallinity is highly challenging at this stage.

Whereas both homopolymers exhibited crystallinity, all copolymers synthesized in this study were amorphous. Notably, only the copolymer with a composition ratio of VA/IPA = 84/16 showed a small endothermic peak at 148 °C in the DSC trace, which may correspond to melting of crystalline domains; however, the peak was too weak for the polymer to be regarded as crystalline. Instead, baseline shifts from glass transition were observed in the DSC trace, and glass transition temperature ($T_g$) gradually decreased with the increase of IPA content. Intriguingly, the copolymer with a composition ratio of 45/55 specifically exhibited a relatively high $T_g$. Both reactivity ratios are lower than 1 ($r_1$ = 0.302, $r_2$ = 0.567 for $M_1$ = VBaam-MOE, $M_2$ = IPBpin), thus the copolymerization of 1:1 feed ratio is expected to yield a copolymer with a moderately alternating tendency and a limited amount of homosequences. Therefore, the enhanced $T_g$ may result from heterosequence-rich structure, but this speculation will require more precise control of the copolymers. XRD profiles also supported the amorphous character of VA–IPA copolymers; most of the copolymers did not display sharp diffraction peaks in the XRD patterns. Exceptionally, the VA-rich copolymer (VA/IPA = 84/16) gave very tiny XRD peaks suggesting the slight crystallinity corresponding to the small endothermic peak in the DSC trance of the same copolymer. The face distances (*d*) calculated by the most intense peaks increased (4.57 Å → 6.11 Å) as the IPA unit ratios (0 mol% → 100 mol%) probably because the introduced methyl groups increased the occupied volume of polymers (Table S4).

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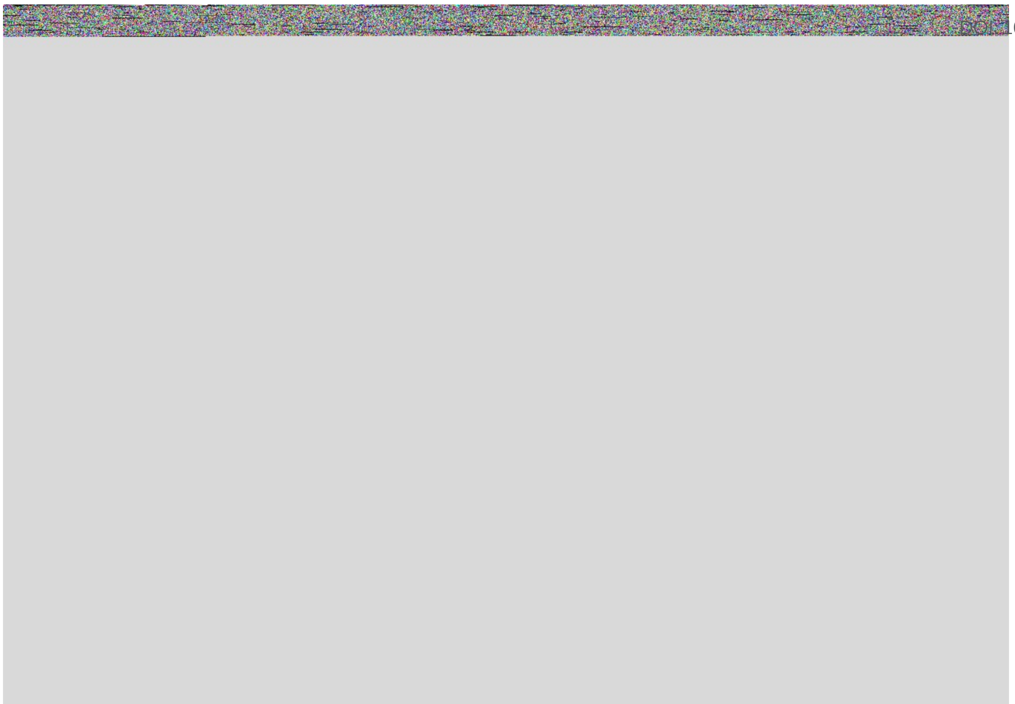

**Figure 4.** Physical properties of VA–IPA (co)polymers: (A) DSC curves (second heating at 10 °C/min) and (B) XRD profiles.

Finally, we investigated the solubility of VA–IPA (co)polymers in various common solvents including water as well as the thermo-responsive behavior of the solution. They showed different solubilities depending on the copolymerization ratio (Figures 5A and S36). PVA was soluble in water, whereas PIPA was insoluble: the hydrophobic methyl group causes decrease in hydrophilicity. The copolymers less than 31mol% of VA units were insoluble in water at any temperature. When the VA ratio increased to 45 mol%, the copolymer was soluble in water at room temperature, and the solution became turbid upon heating (Figure 5B): it exhibited lower critical solution temperature (LCST)-type thermal response. The thermo-responsive behavior was further investigated through variable-temperature transmittance measurement of the solution at 2 mg $mL^{-1}$ (Figures 5C and S37, heating rate: 1 °C $min^{-1}$; λ = 670 nm). The transmittance gradually decreased to 10% around 40–70 °C and the cloud point ($T_{CP,\ 50\%}$: the temperature giving 50% transmittance) was determined as 49.3 °C. The thermal response was also confirmed by temperature-variable dynamic light scattering (DLS) analysis: hydrodynamic diameter ($D_h$) gradually increased from ~50 nm to ~430 nm upon heating (Figure S38). The copolymer is soluble in water due to the hydration of VA-rich segments with water molecules at a lower temperature, and probably, dehydration from polymer chains occurs upon heating due to the entropic driving force. The chains aggregate through the hydrophobic interactions derived from IPA-rich segments giving the turbid solution. The copolymer of 57/43 also showed thermal response at higher temperature (~80 °C) and the transmittance decreased only slightly.

Although PVA is known to insoluble in most organic solvents, the VA–IPA copolymers became soluble in organic solvents such as methanol, ethanol, DMF and chloroform (Figure 5A). The loss of crystallinity observed in the copolymers suggests that the chain-chain interactions through hydrogen bonding among hydroxyl groups are weakened, which likely accounts for their enhanced solubility compared with PVA. Interestingly, the IPA-rich copolymer (IPA content: 55 mol% – 93 mol%) exhibited a distinctive upper critical solution temperature (UCST)-type thermal response in acetone; they were soluble at higher temperature and became insoluble upon cooling (Figure 5D). Both PVA and PIPA homopolymers were insoluble in acetone at any temperature due to their well-packed crystalline structures, indicating that the solubility or UCST behavior of the copolymer are truly unique. Variable-temperature transmittance measurements revealed that the cloud point ($T_{CP,50\%}$) in the UCST behavior did not change monotonically with the unit ratio of the copolymer. Notably, the 18/82 copolymer gave the lowest $T_{CP, 50\%}$ among the four copolymers, indicating it exhibits the highest solubility in acetone within a series (Figures 5E and S39). The complicated solubility trend is likely governed by a delicate balance between interactions among polymer chains and interactions with solvent molecules. The solubility uniqueness is reminiscent of the higher solubility of methylated cellulose in water compared with unmodified cellulose and is particularly intriguing as a characteristic unique to hydroxyl-containing polymers.[29] DLS analysis of the 45/55 copolymer (0.9 mg $mL^{-1}$ in acetone) exhibited the formation of huger aggregates than those in aqueous solution: $D_h$ gradually increased from ~200 nm to ~2.4 μm in the cooling process from 50 °C to 10 °C (Figure S40). Thus, the controlled introduction of $\alpha$-methyl groups into PVA was found helpful for modulating the solubility and thermal response not only in water but also in organic solvents.

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**Figure 5.** (A) Visual solubility test for water and several organic solvents of the resulting VA–IPA (co)polymers. (B) Photos for thermal response behavior of VA–IPA copolymers (VA/IPA = 45/55) in water (2 mg mL$^{-1}$). (C) Temperature-variable transmittance measurement (λ = 670 nm) on the heating process (1 °C min$^{-1}$) with 2 mg mL$^{-1}$ solutions in water. (D) Photos for thermal response behavior of VA–IPA copolymers (VA/IPA = 31/69) in acetone (1.3 mg mL$^{-1}$). (E) $T_{CP,\ 50\%}$–IPA content plot observed in the cooling process (1 °C min$^{-1}$) with saturated (VA/IPA = 45/55: 0.9 mg mL$^{-1}$, 31/69: 1.3 mg mL$^{-1}$, 18/82: 1.7 mg mL$^{-1}$, 7/93: 1.3 mg mL$^{-1}$) solutions in acetone.

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# Conclusion

In conclusion, we established the efficient synthetic route to vinyl alcohol (VA)–isopropenyl alcohol (IPA) copolymers using the two types of alkenylboron monomers. Radical copolymerization of vinyl-type VBaam-MOE with isopropenyl-type IPBpin and side-chain oxidation afforded a series of VA–IPA statistical copolymers with various composition ratios (VA/IPA = 84/16 – 7/93), which were difficult to synthesize from acetyl-type precursors (i.e., VAc and IPAc). The resulting copolymers were found to be amorphous at most composition ratios whereas both VA and IPA homopolymers exhibited distinctive semi-crystalline nature. The introduced $\alpha$-methyl groups dramatically enhanced solubility in organic solvents such as methanol and DMF. The thermal response in solution states depended on the composition ratios; copolymers with 43 – 55 mol% IPA units showed LCST-type thermos-responsive behavior in water, and ones with 55 – 93 mol% IPA units gave UCST-type response in acetone. Since PVA has been widely used for many applications as described above, the unprecedented syntheses of $\alpha$-methylated PVAs of allowing the modulation of physical properties is useful for accessing PVA-based materials with innovative functions in the future.



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# Supporting Information

The Supporting Information is available free of charge

Detailed description of synthetic procedures, experimental methods, $^1H$ NMR and FT-IR spectra, GPC analysis, DSC measurements, XRD measurements, UV-vis measurements and DLS measurements (PDF).

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## Notes

The authors declare no competing financial interests.

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**Data availability:**

The data supporting this study have been included as part of the Supplementary Information. In the Supplementary Information, detailed description of synthetic procedures, experimental methods, $^{1}H$ NMR and FT-IR spectra, GPC analysis, DSC measurements, XRD measurements, UV-vis measurements and DLS measurements are shown.