

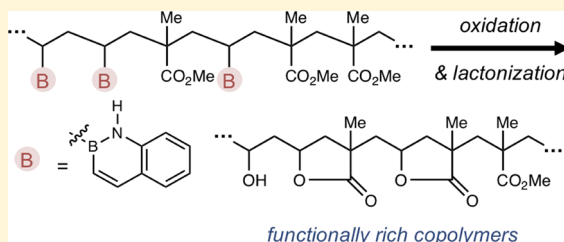
## Organoborane Strategy for Polymers Bearing Lactone, Ester, and Alcohol Functionality

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## Supporting Information

**ABSTRACT:** Vinyl alcohol–methacrylate copolymers have intriguing functionally rich structures but are synthetically inaccessible from vinyl acetate, the traditional precursor to polyvinyl alcohol. We report a solution via BN 2-vinylnaphthalene (BN2VN), an aromatic vinyl borane monomer. Conventional free radical copolymerization of BN2VN and methyl methacrylate (MMA) is facile. Conversion of BN2VN side chains to VA side chains is accomplished in organic solvents with  $\text{Me}_3\text{NO} \cdot 2\text{H}_2\text{O}$  and avoids MMA hydrolysis. The VA–MMA copolymer rapidly lactonizes to give an unprecedented macromolecule bearing both acyclic and cyclic ester residues. Methanolysis furnishes the statistical copolymer bearing vinyl alcohol, methyl methacrylate, and lactone residues. *tert*-Butyl methacrylate–BN2VN copolymers were shown to not lactonize.

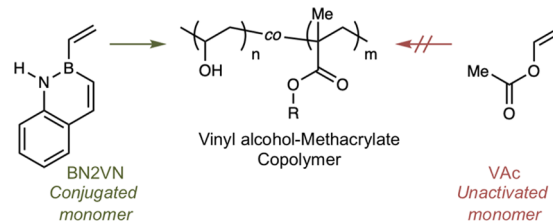


The incorporation of polar functional groups powerfully impacts a polymer's physical properties and applications.<sup>1,2</sup> The hydroxyl functional group (–OH) influences multiple parameters. Hydroxyl-functionalized polyethylene has enhanced barrier properties against water and oxygen, and the ethylene–vinyl alcohol copolymer (EVOH) is used in food packaging.<sup>3</sup> Hydroxyl-functionalization also imparts increased solubility in polar solvents, improved adhesion to polar surfaces, and influences hydrogen bonding<sup>4</sup> with downstream effects on crystallinity, assembly, and phase transitions.

Vinyl acetate (VAc) is the traditional precursor to poly(vinyl alcohol) (PVA) and hydroxyl-functionalized copolymers by alkaline hydrolysis,<sup>5</sup> but this monomer poses significant synthetic challenges. The Lewis basic ester functional group is poorly compatible with early transition metal olefin polymerization catalysts.<sup>6</sup> The propensity of the VAc-derived radical to undergo chain transfer and termination events is a challenge for controlled polymerization techniques like atom transfer radical polymerization (ATRP).<sup>7,8</sup> VAc exhibits poor copolymerization behavior with conjugated monomers like styrene (St), methyl acrylate (MA), and methyl methacrylate (MMA).<sup>9,10</sup>

BN 2-vinylnaphthalene (BN2VN)<sup>11–15</sup> is a recently reported PVA precursor with versatile reactivity arising from its aromatic structure (Scheme 1).<sup>16–18</sup> BN2VN is straightforwardly synthesized, and multigram scale polymerization is reported.<sup>11</sup> It is compatible with titanium-based olefin polymerization catalysts that yield syndiotactic polymer.<sup>14</sup> BN2VN also readily copolymerizes with styrene under radical conditions.<sup>12,13</sup> Nonlinear least-squares (NLLS) statistical analysis showed a dramatic narrowing of the styrene–BN2VN reactivity ratios compared to styrene–VAc ( $r_1(\text{St}) = 2.3$ ,  $r_2(\text{BN2VN}) = 0.42$ ;  $r_1(\text{St}) = 55$ ,  $r_2(\text{VAc}) = 0.01$ ).<sup>10,13</sup> The side chain C–B bond of BN2VN polymers is converted to a C–OH bond with alkaline hydrogen peroxide ( $\text{H}_2\text{O}_2/\text{NaOH}$ ),

## Scheme 1. BN Aromatic Vinyl Monomer for the Synthesis of Linear MMA–VA Statistical Copolymers



which is effective for the synthesis of PVA-*r*-PS<sup>12</sup> and syndiotactic PVA (sPVA)<sup>14</sup> from BN2VN-derived precursors. Nishikawa and Ouchi recently described a similar approach to poly( $\alpha$ -methyl vinyl alcohol) via isopropenyl pinacol boronate polymerization.<sup>19</sup> Postpolymerization borylation, either by hydroboration of alkenyl residues<sup>20–23</sup> or CH activation,<sup>24–26</sup> is a well-explored strategy for polyolefin functionalization.

Like St–VA statistical copolymers, MMA–VA statistical copolymers are an elusive target for polymer synthesis. MMA and VAc have highly mismatched reactivity ratios ( $r_1(\text{MMA}) = 20$ ,  $r_2(\text{VAc}) = 0.015$ ). Significant excess of the vinyl ester is required for high degrees of incorporation.<sup>27</sup> This fact, in combination with the challenge of achieving a high degree of selectivity in the hydrolysis of the vinyl acetate side chain in the presence of an acrylic side chain,<sup>28</sup> complicates the preparation of MMA–VA copolymers from vinyl acetate.

BN2VN is a promising solution. Its conjugated structure is a better reactivity match with MMA. The extensive use of organoboranes in natural product synthesis provides a broad

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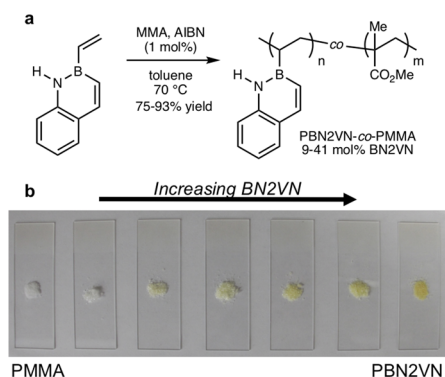
range of conditions for organoborane functionalization in organic solvents. In the context of BN2VN–MMA copolymer oxidation, the typical aqueous  $\text{H}_2\text{O}_2/\text{NaOH}$  oxidation conditions pose risks such as side chain hydrolysis to poly(methacrylic acid) (PMAA) and the formation of acyloxy derivatives.

Herein, we report the statistical copolymerization of MMA and BN2VN, as well as the development of a mild oxidation procedure. Trimethylamine *N*-oxide ( $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$ ) in cyclopentyl methyl ether (CPME) converts PMMA-*co*-PBN2VN to PMMA-*co*-PVA without methyl ester hydrolysis (Scheme 1).<sup>29,30</sup> PMMA-*co*-PVA is not isolable: cyclization to give five-membered butyrolactone substructures is rapid and facile. The incorporation of lactone substructures so closely associated with a polyolefin backbone is unprecedented and may have important consequences for mechanical properties and further postfunctionalization. Lactonization is an equilibrium process, and the vinyl alcohol residues are recovered by methanolysis. We also demonstrate the stability of BN2VN-*tert*-butyl methacrylate (tBMA) copolymers, attributed to the slower rate of lactonization with bulkier ester side chains.

## RESULTS AND DISCUSSION

**BN2VN–MMA Copolymerization.** Azoisobutyronitrile (AIBN)-initiated free radical copolymerization of MMA and BN2VN was performed at different molar ratios of the comonomers (10–50% BN2VN, Scheme 2a). High yields were

**Scheme 2.** Free Radical Copolymerization of BN2VN–MMA and Images of Copolymers<sup>a</sup>



<sup>a</sup>(a) BN2VN–MMA free radical copolymerization. (b) Images of PMMA (left), PBN2VN–PMMA copolymers, and PBN2VN (right). MMA = methyl methacrylate; AIBN = azoisobutyronitrile.

obtained in all cases after precipitation into methanol. The BN naphthalene chromophore absorbs strongly at 320 nm, and PBN2VN is a yellow powder, while PMMA is white. The copolymers become increasingly yellow as the BN2VN content increases (Scheme 2b). The unique absorption at 320 nm of the BN naphthalene chromophore facilitated quantitative determination of the BN2VN content in BN2VN–2VN and BN2VN–St copolymers.<sup>11,12</sup> A similar assay was developed for BN2VN–MMA copolymers (Figures S1 and S2). We find good agreement between mol % BN2VN in the feed compared to isolated samples obtained at high conversion (Table 1).

Copolymer molecular weight properties were determined by gel permeation chromatography (GPC) relative to polystyrene standards and are summarized in Table 2. Unimodal molecular weight distributions were observed, supporting preparation of a

**Table 1.** Copolymer Optical Properties and BN2VN Incorporation in Bulk Samples

sample name	feed ratio (mol % BN2VN)	$\epsilon_{320}^a$	experimental (mol % BN2VN) <sup>b</sup>	yield (%)
PBN2VN <sub>28</sub> - <i>co</i> -PMMA <sub>210</sub>	10.0	4.5	11.5	80
PBN2VN <sub>30</sub> - <i>co</i> -PMMA <sub>138</sub>	20.0	6.9	18.0	75
PBN2VN <sub>38</sub> - <i>co</i> -PMMA <sub>94</sub>	30.0	10.5	28.5	83
PBN2VN <sub>40</sub> - <i>co</i> -PMMA <sub>54</sub>	40.0	14.8	42.7	80
PBN2VN <sub>41</sub> - <i>co</i> -PMMA <sub>37</sub>	50.0	17.5	52.7	93

<sup>a</sup>In L g<sup>-1</sup> cm<sup>-1</sup>. <sup>b</sup>Determined from  $\epsilon_{320}$  (see the Supporting Information for details).

**Table 2.** Copolymer Molecular Weight Properties

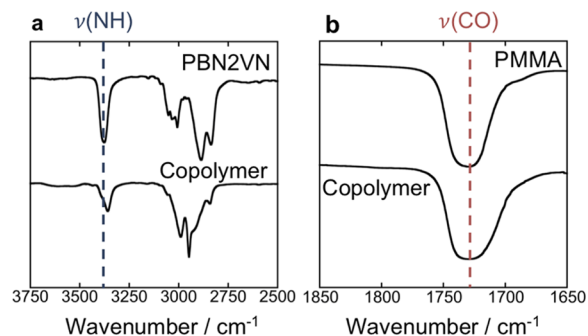
sample name	$M_n$ (kDa) <sup>a</sup>	$\bar{D}$
PBN2VN <sub>28</sub> - <i>co</i> -PMMA <sub>210</sub>	25.3	2.25
PBN2VN <sub>30</sub> - <i>co</i> -PMMA <sub>138</sub>	18.5	2.46
PBN2VN <sub>38</sub> - <i>co</i> -PMMA <sub>94</sub>	15.3	2.54
PBN2VN <sub>40</sub> - <i>co</i> -PMMA <sub>54</sub>	11.6	2.53
PBN2VN <sub>41</sub> - <i>co</i> -PMMA <sub>37</sub>	10.1	2.36

<sup>a</sup>Determined by gel permeation chromatography (GPC) analysis at RI, relative to polystyrene standard (THF, 20  $\mu\text{L}$ , 35 mL min<sup>-1</sup>, 40 °C)

copolymer instead of a mixture of two homopolymers (Figure S3). Diffusion-oriented NMR spectroscopy (DOSY) was also consistent with a single copolymer (Figure S4).

**PBN2VN-*co*-PMMA Structural Characterization.** The copolymers were structurally characterized by <sup>1</sup>H, <sup>11</sup>B, and <sup>13</sup>C nuclear magnetic resonance (NMR) spectroscopy and Fourier transform infrared (FTIR) spectroscopy. All copolymers show resonances diagnostic of both BN2VN and MMA incorporation. Here, we show representative results for PBN2VN<sub>30</sub>-*co*-PMMA<sub>138</sub>, while full spectra for all copolymers are reported in the Supporting Information.

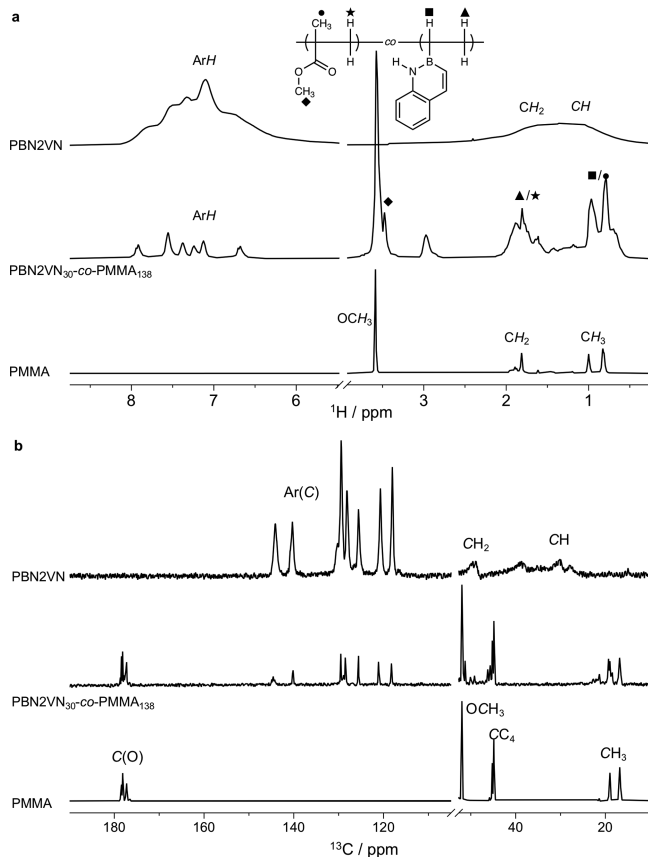
A distinctive FTIR spectroscopy feature of BN2VN incorporation is the presence of a sharp NH resonance at  $\sim 3375$  cm<sup>-1</sup>. This feature was also seen in the copolymers (Figure 1a). Aromatic CH stretching frequencies  $>3000$  cm<sup>-1</sup> were observed in both PBN2VN and PBN2VN<sub>30</sub>-*co*-PMMA<sub>138</sub> as well. A sharp feature at 1727 cm<sup>-1</sup> was observed in both



**Figure 1.** FTIR spectra. (a) Comparison of PBN2VN and the copolymer, showing the presence of NH and aromatic CH stretches. (b) Comparison of PMMA and the copolymer, showing the presence of a carbonyl stretch.

PMMA and PBN2VN<sub>30-co</sub>-PMMA<sub>138</sub> and was assigned to the carbonyl stretch (Figure 1b).

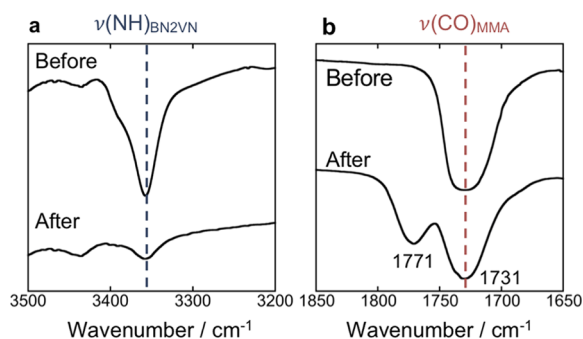
<sup>1</sup>H, <sup>11</sup>B, and <sup>13</sup>C NMR spectra of PBN2VN<sub>30-co</sub>-PMMA<sub>138</sub> were recorded in methylene chloride-*d*<sub>2</sub> at room temperature. The copolymer showed resonances consistent with both BN2VN and MMA incorporation. In the <sup>1</sup>H NMR spectrum, six aromatic resonances consistent with the BN naphthalene side chain were observed (Figure 2a). Sharp singlets ( $\delta$  3.58–



**Figure 2.** (a) <sup>1</sup>H NMR spectra (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) of (top to bottom) PBN2VN, PBN2VN<sub>30-co</sub>-PMMA<sub>138</sub>, and PMMA. (b) <sup>13</sup>C NMR spectra of (top to bottom) PBN2VN, PBN2VN<sub>30-co</sub>-PMMA<sub>138</sub>, and PMMA.

3.48) were assigned to methoxy resonances from the ester side chain. Features at  $\delta$  1.81 and  $\delta$  0.80 were assigned to overlapping backbone resonances, including methylene, methine, and  $\alpha$ -methyl groups from both BN2VN and MMA. The  $\alpha$ -CH<sub>3</sub> resonance of PMMA resolves into *mm*, *mr*, and *rr* triads in chloroform-*d* and tacticity likely contributes to the spectrum of PBN2VN<sub>30-co</sub>-PMMA<sub>138</sub> as well.

The <sup>13</sup>C NMR spectrum of PBN2VN<sub>30-co</sub>-PMMA<sub>138</sub> showed resonances consistent with both BN2VN and MMA incorporation (Figure 2b). Carbonyl ( $\delta$  176–178) and aromatic ( $\delta$  118–144) resonances were readily identified (Figure 3b). The quadrupolar boron-11 nucleus broadens the resonances of carbon atoms attached to boron,<sup>31</sup> and BN2VN backbone resonances were challenging to observe in the copolymer. However, the PMMA methoxy, methyl, and quaternary resonances were identified. Finally, the <sup>11</sup>B NMR spectrum of PBN2VN<sub>30-co</sub>-PMMA<sub>138</sub> showed a broad feature centered at  $\delta$  35 consistent with PBN2VN ( $\delta$  29) (Figure S5).



**Figure 3.** Cropped FTIR spectra of PBN2VN<sub>30-co</sub>-PMMA<sub>138</sub> before and after Me<sub>3</sub>NO/CPME oxidation. (a) BN naphthalene  $\nu(\text{NH})$  diminished, but PVA  $\nu(\text{OH})$  was not apparent. (b)  $\nu(\text{C=O})_{\text{MMA}}$  was retained after oxidation, and a second  $\nu(\text{C=O})$  band at 1771 cm<sup>-1</sup> was observed.

This resonance is comparable to other polymers derived from BN aromatic vinyl monomers.<sup>32–34</sup>

**Oxidation.** In considering the postpolymerization functionalization of BN2VN–MMA copolymers, we were wary of aqueous conditions, which could hydrolyze the MMA side chain. While Carpentier et al. reported aqueous H<sub>2</sub>O<sub>2</sub>/NaOH oxidation of boron-functionalized poly( $\beta$ -hydroxyalkanoate)s, the significant decrease in molecular weight and increase in dispersity after oxidation suggested partial cleavage of the polyester backbone.<sup>35</sup> Williams and coworkers very recently reported the use of 9-BBN followed by *meta*-chloroperbenzoic acid (*m*CPBA) in THF for the hydroboration–oxidation of alternating polyesters and did not report evidence of chain scission.<sup>36</sup> Hydroboration–oxidation resulted in alternating hydrophobic–hydrophilic side chains and nanostructured self-assembly. Organoboranes are versatile intermediates in organic synthesis, and we turned to the literature on molecular organoboranes for alternatives. Kabalka and Hedgcock reported the use of Me<sub>3</sub>NO·2H<sub>2</sub>O as an organoborane oxidant that is compatible with a broad range of organic solvents and provides increased yields relative to H<sub>2</sub>O<sub>2</sub>/NaOH for highly functionalized molecules.<sup>29,30</sup> Me<sub>3</sub>NO·2H<sub>2</sub>O appeared particularly attractive as Me<sub>3</sub>N is volatile, simplifying polymer isolation and purification.

We initiated investigation of Me<sub>3</sub>NO-induced oxidation of BN2VN copolymers in cyclopentyl methyl ether (CPME), a high-boiling ethereal solvent that compatibilized all of the copolymers and Me<sub>3</sub>NO·2H<sub>2</sub>O. For all five copolymers, we observed 85–92% conversion in 24 h of the BN naphthalene side chain based on UV–vis spectroscopy (Table 3). Residual BN2VN could also be detected by NMR spectroscopy (see the Supporting Information). The byproducts of oxidation include boric acid (B(OH)<sub>3</sub>), indole, and trimethylamine (NMe<sub>3</sub>).

**Table 3. Oxidized Copolymers: Molecular Weight Properties**

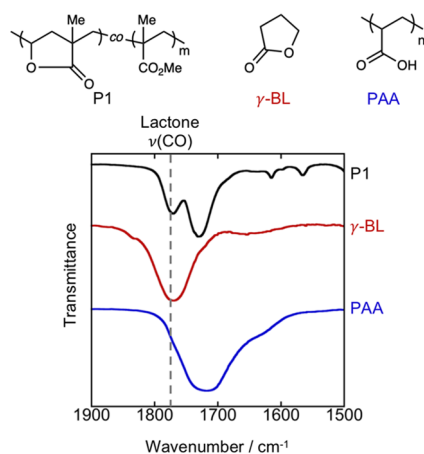
polymer name	$M_n$ (kDa)	$M_w/M_n$	yield (%)	conversion (%)
Oxy. PBN2VN <sub>28-co</sub> -PMMA <sub>210</sub>	23.0	2.25	84	85
Oxy. PBN2VN <sub>30-co</sub> -PMMA <sub>138</sub> (P1)	14.4	2.70	88	87
Oxy. PBN2VN <sub>38-co</sub> -PMMA <sub>94</sub>	13.2	3.08	50	92
Oxy. PBN2VN <sub>40-co</sub> -PMMA <sub>54</sub>	9.89	2.73	35	92
Oxy. PBN2VN <sub>41-co</sub> -PMMA <sub>37</sub>	8.45	2.40	20	92



Indole and  $B(OH)_3$  arise from oxidation of the internal C–B bond of the initially formed BN naphthol and were also the byproducts observed in hydrogen peroxide-mediated oxidations (see Figure S6 for the proposed mechanism of  $Me_3NO$ -mediated oxidation of BN2VN copolymers).<sup>12,14</sup>

While signatures of oxidation were present, structural characterization was not consistent with PVA-*co*-PMMA. In the following discussion, spectra of oxidized PBN2VN<sub>30</sub>-*co*-PMMA<sub>138</sub> (**P1**) are shown as a representative sample. Fourier transform infrared (FTIR) spectroscopy of **P1** showed diminishment of the characteristic BN naphthalene  $\nu(NH)$  after oxidation but not hydroxyl stretching frequencies ( $\nu(OH)$ ) consistent with PVA (Figure 3a). A low intensity feature at  $\sim 3450\text{ cm}^{-1}$  was observed both before and after oxidation and likely corresponds to the overtone of  $\nu(CO)_{MMA}$ .<sup>37</sup>

More insight arose from considering the carbonyl region of the FTIR spectrum. The  $\nu(CO)_{MMA}$  was preserved at  $1731\text{ cm}^{-1}$ , but an additional band was observed at  $1771\text{ cm}^{-1}$  (Figure 3b). The additional carbonyl stretching frequency is very similar to the carbonyl stretch of  $\gamma$ -butyrolactone ( $1770\text{ cm}^{-1}$ , Figure 4). We also considered the possible hydrolysis of



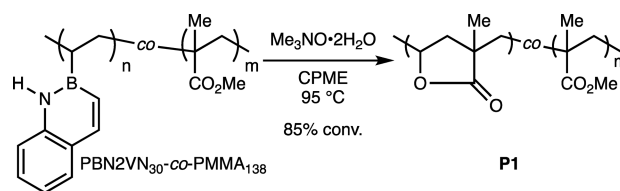
**Figure 4.** Comparison of the carbonyl stretching region in oxidized PBN2VN<sub>30</sub>-*co*-PMMA<sub>138</sub> (**P1**, black) and commercial samples of  $\gamma$ -butyrolactone ( $\gamma$ -BL, red) and poly(acrylic acid) (PAA, blue). The agreement between the  $\gamma$ -BL carbonyl stretch and the new band in **P1** is highlighted with a vertical dashed line. The putative structure of **P1** is shown.

the methyl ester side chain to a carboxylic acid, but poor agreement was observed between the FTIR spectrum of oxidized PBN2VN<sub>30</sub>-*co*-PMMA<sub>138</sub> and poly(acrylic acid) (Figure 4).

Based on the preservation of the methyl ester feature, the appearance of a new band diagnostic of a five-membered lactone, and the diminishment of hydroxyl resonances, we hypothesized that partial lactonization of PVA-*co*-PMMA occurred in CPME (Scheme 3). This hypothesis was supported by  $^{13}C$  NMR spectroscopic data, which showed multiple carbonyl resonances (Figure S7).

**Microstructure and Mechanism of Lactonization.** Ring strain induces characteristic shifts to higher frequency with decreasing ring size in lactones (Figure 5).<sup>38</sup> The strong  $1770\text{ cm}^{-1}$  band observed in our experimental spectrum of **P1** suggests that the  $\gamma$ -butyrolactone substructure is dominant over any other lactone.

### Scheme 3. Oxidation of the BN2VN–MMA Copolymer



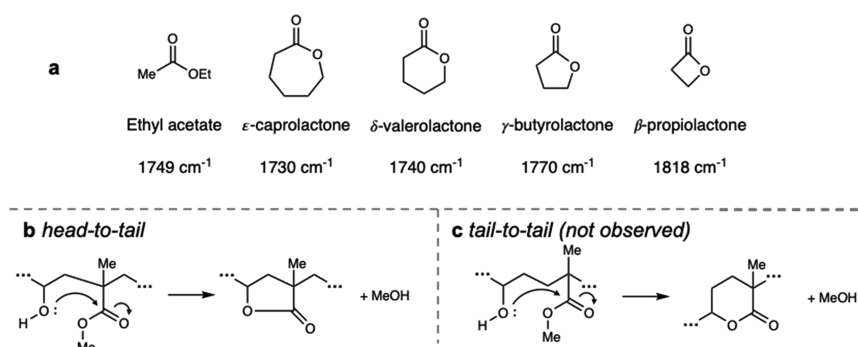
The FTIR spectroscopic data therefore provided revealing insights into the polymer microstructure. The five-membered lactone substructure only arises from adjacent head-to-tail vinyl alcohol and methyl methacrylate monomers (Figure 5b), while head-to-head and tail-to-tail arrangements would form smaller and larger rings, respectively (Figure 5c). Additionally, the intensity of the signal is more consistent with a statistical distribution of monomers along the macromolecular chain, as a blocky structure would result in one butyrolactone substructure per block junction.

Transesterification is an equilibrium process. While exchange can occur simply upon mixing, acid or base catalysis is typically employed for reasonable reaction rates.<sup>39</sup> With respect to lactonization, the conversion of methyl 4-hydroxybutyrate to  $\gamma$ -butyrolactone is rapid and requires only trace acid.<sup>40</sup> Either the trimethylamine or boric acid byproducts of the oxidation reaction are sufficiently basic or acidic to catalyze lactonization of the initially formed VA–MMA statistical copolymer. While  $Me_3N$  might also be expected to buffer boric acid,  $Me_3N$  is also volatile.

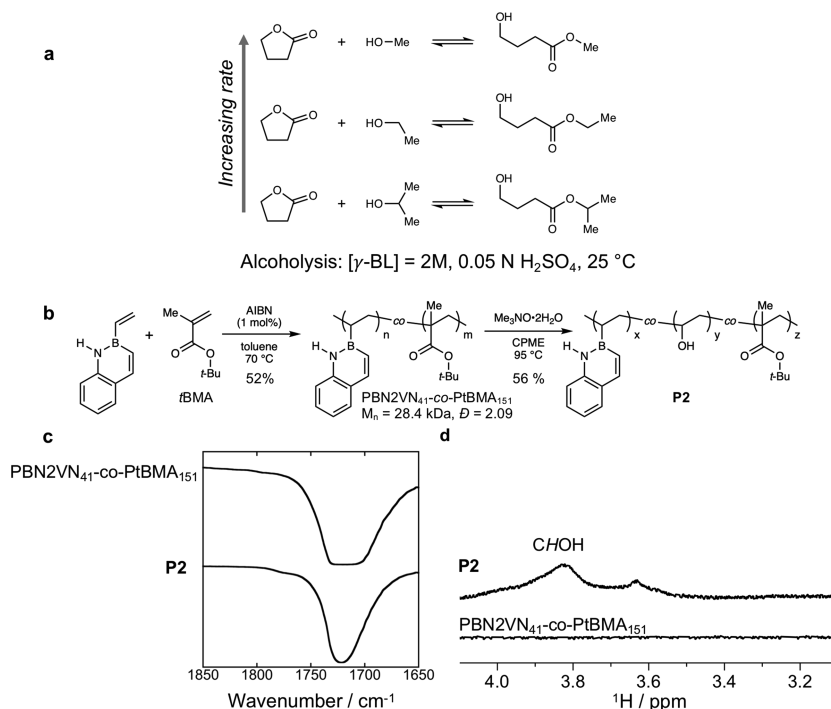
Brown and Keblys studied the rate of  $\gamma$ -butyrolactone alcoholysis at room temperature with methanol, ethanol, and 2-propanol and observed a decrease in the rate of alcoholysis with increasing size of the alcohol (Figure 6a).<sup>40</sup> The effect of alcohol size on the equilibrium constant is much less pronounced than the effect on the rate. By the principle of microscopic reversibility, the rate of lactonization should also decrease with increasing bulk of the ester substituent. We therefore investigated the copolymerization of BN2VN and *tert*-butyl methacrylate (*t*BMA), as well as the  $Me_3NO$ -mediated oxidation (Figure 6b). Free radical copolymerization of *t*BMA and BN2VN yielded a pale yellow polymer in reasonable yield (52%) and molecular weight (28.4 kDa). Comprehensive NMR spectroscopic characterization was consistent with incorporation of both monomers (Figure S8). Oxidation under the typical conditions proceeded in 60% conversion and yielded **P2** in 56% yield.

FTIR spectra of PBN2VN<sub>41</sub>-*co*-*t*BMA<sub>151</sub> and oxidized copolymer **P2** were consistent with suppressed lactonization. A single  $\nu(CO)$  stretch was observed at  $1715\text{ cm}^{-1}$  (Figure 6c) in both materials and was assigned to the *tert*-butyl ester. No  $\gamma$ -BL carbonyl stretch was observed at  $1770\text{ cm}^{-1}$ .  $^1H$  NMR spectra showed signatures of vinyl alcohol residues, including a methine resonance at  $\delta\ 3.83$  (CH–OH, Figure 6d). Assignment of the  $\delta\ 3.83$  resonance to the PVA methine is supported by  $^{13}C$  DEPT NMR spectra and  $^1H$ - $^{13}C$  HSQC spectroscopy (Figure S9).

**Methanolysis of Lactonized PVA-*co*-PMMA.** Prior work on the acid-catalyzed methanolysis of  $\gamma$ -butyrolactone demonstrated that the equilibrium mixture favored the ring-opened form by approximately 3:1.<sup>40</sup> We therefore investigated whether the lactonized PVA-*co*-PMMA initially isolated after oxidation could be enriched in vinyl alcohol subunits. After alkaline methanolysis for 48 h followed by reisolation, the



**Figure 5.** (a) Lactone  $\nu(\text{CO})$  stretching frequency in smaller rings shifts to a higher frequency. (b) Only a head-to-tail arrangement of neighboring vinyl alcohol and methyl methacrylate residues gives rise to the five-membered  $\gamma$ -butyrolactone substructure. (c) Tail-to-tail isomer would give rise to a  $\delta$ -valerolactone substructure. The formation of a  $\beta$ -propionitrile substructure from a head-to-head isomer is not shown.

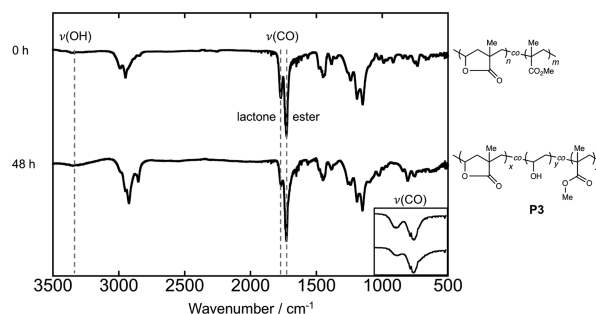


**Figure 6.** Steric influence on lactonization. (a) Influence of alcohol steric parameters on the alcoholysis rate.<sup>40</sup> (b) Synthesis of the BN2VN-*t*BMA copolymer and oxidation to P2. (c) Cropped FTIR spectra of PBN2VN<sub>41</sub>-co-PtBMA<sub>151</sub> (top) and P2 (bottom) showing a single  $\nu(\text{CO})$  band at 1710  $\text{cm}^{-1}$ . No  $\gamma$ -butyrolactone peak at 1770  $\text{cm}^{-1}$  was observed. (d) Appearance of PVA methine (CH-OH) resonance in  $^1\text{H}$  NMR spectrum of P2.

FTIR spectrum showed diminishment of the lactone resonance and preservation of the methyl ester resonance (P3, Figure 7). A broad resonance at  $\sim 3350 \text{ cm}^{-1}$  consistent with the  $\nu(\text{OH})$  also intensified. The broad peak shifted to comparatively low frequency is consistent with a hydroxyl group engaged in extensive hydrogen bonding, as seen in the homopolymer PVA.<sup>41,42</sup> Based on these observations, we assign the methanolysis product to a terpolymer of lactone, methyl ester, and vinyl alcohol units.

## CONCLUSIONS

This study demonstrates the utility of aromatic vinyl borane monomers for the preparation of copolymers inaccessible from traditional feedstocks. We report the free radical copolymerization of BN2VN with both MMA and *t*BMA. Oxidation of MMA copolymers with  $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$  in CPME yielded copolymers bearing both ester and lactone subunits arising



**Figure 7.** Methanolysis of Lactonized PVA-co-PMMA to P3. FTIR spectra before (top) and after (bottom) methanolysis (reflux in 0.5 M NaOMe/MeOH at 70  $^{\circ}\text{C}$  for 48 h) using isolated polymer samples. Spectra are labeled with putative structures. Inset shows the  $\nu(\text{CO})$  region and diminishment of the 1770  $\text{cm}^{-1}$  lactone feature.

from lactonization of the intermediate VA–MMA copolymer, while the bulky side chain of *tert*-butyl methacrylate inhibits lactonization. Alcoholysis returned highly functionalized copolymers bearing vinyl alcohol, lactone, and ester side chains. The VA–MMA statistical copolymer cannot be prepared directly from vinyl acetate and MMA. In combination with Williams' work on *m*CPBA-mediated hydroboration–oxidation of polyesters, this work significantly expands the scope of functionally rich boron-functionalized polymers suitable for oxidative functionalization.<sup>36</sup>

The functionally rich and polar polymers prepared herein are likely to have several potential applications. As both PMMA and PVA are biocompatible polymers, conjugates could be prepared by covalent attachment of a desired small molecule. The lactone substructures may impart unique mechanical properties to the polymers by reducing degrees of freedom along the backbone. Lactones have a rich history in polymer synthesis as monomers;<sup>43</sup> the presence of lactone functionality embedded along the polymer backbone may serve as sites for graft polymerization<sup>44</sup> via ring-opening polymerization.

Access to the novel structures described herein is made possible by an unconventional aromatic organoborane monomer. The incorporation of main group elements into polymeric materials is an active area of research yielding new insights relevant to optoelectronics, material properties, and biology.<sup>45–49</sup>

## ■ ASSOCIATED CONTENT

### ● Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.macromol.9b02201>.

Synthetic procedures, tabulated spectral data, experimental details, copies of NMR spectra (PDF)

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### Notes

The authors declare the following competing financial interest(s): A provisional patent based on this work has been filed (U.S. no 62/573,065).

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