

# Synthesis and Characterization of Ionomeric Poly(vinyl Butyral)

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## SYNOPSIS

A route to synthesizing novel poly(vinyl butyral) ionomers (IPVB), via a condensation polymerization process, has been developed. In the process, ionic groups were permanently incorporated into the poly(vinyl butyral) backbone by using an ion-containing aldehyde in addition to butyraldehyde during the acetalization of poly(vinyl alcohol). The resulting polymers demonstrated properties typical of ionomer systems, i.e., they behaved as "thermally reversible crosslinked thermoplastics" due to the presence of ionic associations present in the polymers. The ionic associations enabled the polymers to behave as crosslinked materials at ambient temperatures, whereas, at higher temperatures (processing temperatures), the ionic associations were lost, thus allowing the polymers to flow. Consequently, at ambient temperatures, the IPVBs demonstrated increased stiffness as determined from the storage modulus of the polymers, whereas, at higher temperatures, the IPVBs demonstrated moduli and stress-relaxation properties comparable to those of conventional poly(vinyl butyral). The IPVBs were characterized by a number of techniques including, high resolution NMR spectroscopy (<sup>1</sup>H, <sup>13</sup>C), dilute solution viscometry, dynamic mechanical analysis, and differential scanning calorimetry (DSC). Characterization was done on plasticized and unplasticized IPVBs.

## INTRODUCTION

Ionomers are a class of polymers that contain ionic groups along the chain.<sup>1,2</sup> These polymers behave as thermally reversible thermoplastics, and this unique property has been attributed to the morphological structures formed due to ionic associations, which have been studied in depth by Eisenberg and co-workers<sup>3-5</sup> and MacKnight.<sup>6-8</sup> In addition, there is extensive documentation on ionomers in the literature.<sup>9-19</sup>

In general, the structure of an ionomer is composed of a hydrocarbon backbone chain containing pendant acid groups which are partially or completely neutralized by an appropriate base to form the ionic component, the concentration of which is usually between 1 and 10 mol %. The ionic associations that appear as a consequence of the ionic

groups enable the polymer to behave as a crosslinked material at ambient temperatures whereas at elevated temperatures the ionic associations disappear, only to reform upon cooling. This thermally reversible behavior allows easy processibility of the polymer at elevated temperatures and high modulus at ambient temperatures, thus making the polymer very versatile. The extent of ionic associations along with the choice of the acid groups and metal (counter) cations effect the final properties of the ionomer. Acid groups such as carboxylic, sulfonic, thioglycolic, and phosphoric have been used along with counterions such as sodium, potassium, zinc, barium, and magnesium. The actual incorporation of the ionic groups onto the polymer backbone can be done either by copolymerizing a monomer containing an acid group with another monomer or by reacting acid functionalities onto an existing polymer via a modification reaction. In either case, ionic groups are introduced upon neutralization of the acid groups. An example of the first approach is a copolymer of ethylene and methacrylic acid where the

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acid groups have been neutralized by magnesium acetate (trade name: Surlyn), and an example of the latter approach is one where sulfonic acid groups are introduced directly into polystyrene at 1–10 mol % levels via a sulfonation reaction, followed by the neutralization of the acid groups to form the ionomer.

Poly(vinyl butyral) (PVB) is a polymer that is extensively used in safety glazings. It is prepared via a conventional acetalization reaction between poly(vinyl alcohol) (PVOH) and butyraldehyde (BA) in the presence of an acid catalyst.<sup>20–35</sup> The reaction conditions are normally controlled to provide the proper balance of residual hydroxyl groups and 1,3-dioxane rings to impart desirable end use properties. The resulting polymer is unique in that the residual hydroxyl groups provide both a high tear resistance and good adhesion to glass while the 1,3-dioxane rings provide chain strength and lack of any detectable crystallinity. These characteristics impart superb optical quality and make it an ideal material for use in preparing laminates suitable for safety glazings. PVB used in safety glazings is plasticized using plasticizers such as dihexyl adipate. The plasticized PVB is then laminated between two sheets of glass to form the final safety glazing.

The aim of this work was to prepare and investigate the properties of ionomeric versions of poly(vinyl butyral) (PVB). The ionomeric PVBs (IPVBs) were prepared by directly reacting ion containing groups onto PVB via the acetalization reaction of an ion-containing aldehyde along with BA with PVOH, following the polymer modification approach. The introduction of the ionomeric groups was expected to provide stiffness at ambient temperatures while maintaining flow characteristics at elevated temperatures.

## EXPERIMENTAL

### Synthesis of Ionomeric Poly(vinyl Butyral) (IPVB)

The sodium salt of *o*-benzaldehyde sulfonic acid (BSNA) obtained from Kodak, was initially reacted with a solution of poly(vinyl alcohol) (PVOH) in deionized (DI) water using nitric acid as the catalyst. The reaction was conducted between 19 and 22°C for periods ranging from 0.5 to 2.0 h, depending upon the extent of ionomer substitution required. Next, butyraldehyde (BA) was introduced to the system; after the resulting polymer precipitated out of solution, the reaction mixture was heated to 30°C and held at this temperature for 4 h, at the end of which the material was washed, neutralized with either

potassium or sodium hydroxide, filtered, and dried. Using this procedure, ionomeric poly(vinyl butyral) (IPVB) containing 1–10 mol % ionomer groups were prepared. IPVBs of different molecular weights (MW, weight average) were also prepared by using PVOHs of different MWs. The following PVOHs were obtained from Nippon Chemical Co. under the trade name Goshenol:

- a. NL-05, DP = 550, MW =  $2.3 \times 10^4$
- b. NM-11, DP = 1275, MW =  $5.6 \times 10^4$
- c. NH-18, DP = 1800, MW =  $7.7 \times 10^4$

Minor adjustments in synthesis conditions were made to facilitate ease of recovery and handling of the resulting IPVBs.

A sample of standard Monsanto Chemical Co. PVB synthesized from PVOH with a DP of approximately 1800 and containing no ionomeric groups was used as a control for comparison with the IPVBs.

### Plasticization of IPVB and PVB

IPVB samples were plasticized by mixing with dihexyl adipate. The levels of dihexyl adipate used were based on the residual PVOH levels of the polymers. The PVB control was mixed with 25 wt % plasticizer.

## Characterization Techniques

### Nuclear Magnetic Resonance (NMR) Spectroscopy

NMR spectra were recorded using a Varian VXR400 NMR spectrometer operating at 400 and 100 MHz proton and carbon frequency, respectively. Spectra were recorded at 50°C using *d*-4 methanol as the solvent.

### Dilute Solution Viscometry

Reduced viscosities ( $\eta_r = t/t_0$ ) were measured on IPVB and PVB samples using an Ubbelohde viscometer. Tetrahydrofuran (THF) was used as the nonpolar solvent, while methanol was used as the polar solvent.

### Thermal Analysis

A Perkin Elmer Model 7 differential scanning calorimeter (DSC) was used to measure the glass transition temperatures ( $T_g$ ) of the polymers.

### Rheological Analysis

Dynamic mechanical analysis of the polymers was carried out using a Rheometrics mechanical spectrometer (Model 605) to measure the storage modulus ( $G'$ ), loss modulus ( $G''$ ), and  $\tan \delta$  ( $G''/G'$ ) in the shear mode at a frequency of 1 Hz from 20 to 230°C, as well as to measure stress relaxation modulus at 150°C (SR150) in the shear mode for an initial step shear strain of 120%. In addition, the storage modulus ( $E'$ ), loss modulus ( $E''$ ), and  $\tan \delta$  ( $E''/E'$ ) were measured in the tensile mode using a Rheometrics solids analyzer at a frequency of 11 Hz from 20 to 180°C.

## RESULTS AND DISCUSSION

### Synthesis of IPVB

The reactions accompanying the synthesis route for IPVB are shown in Figure 1. During the synthesis, the ion-containing aldehyde, BSNA, was first reacted with PVOH [which typically contains 1–2 wt % residual poly(vinyl acetate) groups] prior to the introduction of butyraldehyde (BA). This was done to prevent competitive reactions between BA and BSNA from occurring. The initial acetalization reaction between BSNA and PVOH resulted in a copolymer containing predominantly PVOH groups and some vinylbenzal sulfonic acid groups (Struc-

ture I): The final IPVB was obtained upon completion of the reaction with BA followed by neutralization and was comprised of poly(vinyl butyral), poly(vinyl benzal sodium (or potassium) sulfonate) and residual poly(vinyl alcohol) groups (Structure II): The entire synthesis therefore consisted of a two-step acetalization process.

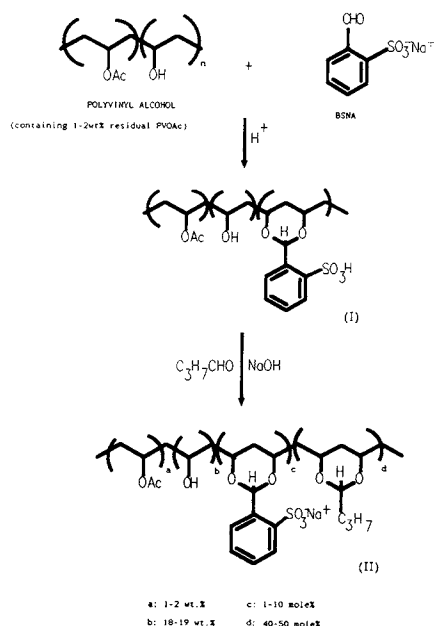
A limitation of the IPVB synthesis process is that the BSNA–PVOH reaction is temperature-limited, i.e., acetal formation is severely hindered above 60°C and hence the reaction is conducted below this temperature. A possible explanation for the lack of acetal formation at higher temperatures is that since the reaction is carried out in water there is a tendency for the reverse of the acetal (hydrolysis) reaction to occur. In the case of the BSNA–PVOH reaction, the hydrolysis reaction would occur to a much greater extent than for the BA–PVOH reaction. At higher temperatures in the presence of water, the hydrolysis reaction would predominate and therefore would result in the disproportionation of vinylbenzal sulfonate groups. Hence, in order to favor the acetal formation, the reaction is carried out at lower temperatures.

### NMR Spectroscopy

Figure 2 is a 1-dimensional 400 MHz NMR proton spectrum of an IPVB sample containing a targeted ionomer level of 5 mol %. Aromatic groups resulting from the vinylbenzal sulfonate moiety are clearly seen between 7.0 and 8.0 ppm, thus confirming the above acetal formation. This is further confirmed from the 100 MHz carbon-13 spectrum shown in Figure 3, where in addition to the conventional features of the NMR spectrum of poly(vinyl butyral) (PVB) reported and discussed previously,<sup>36</sup> two carbon resonances at 99.3 and 103.2 ppm are also seen. These signals have been assigned to benzal groups. From the NMR spectra, the efficiency of the BSNA–PVOH acetal reaction has been calculated at approximately 50%. Figures 4 and 5, on the other hand, show the proton and carbon NMR spectra, respectively, of PVOH acetalized at 75°C. In both spectra there is no evidence of aromatic substitution resulting from the BSNA–PVOH reaction, and the spectra are essentially those of conventional PVB. This confirms that high acetal temperatures do not favor the formation of ionomer groups via the BSNA–PVOH reaction.

### Dilute Solution Viscosity

Evidence of ionomeric behavior in the IPVBs were confirmed from their dilute solution viscosity be-



**Figure 1** Synthesis route for ionomeric poly(vinyl butyral) (IPVB).

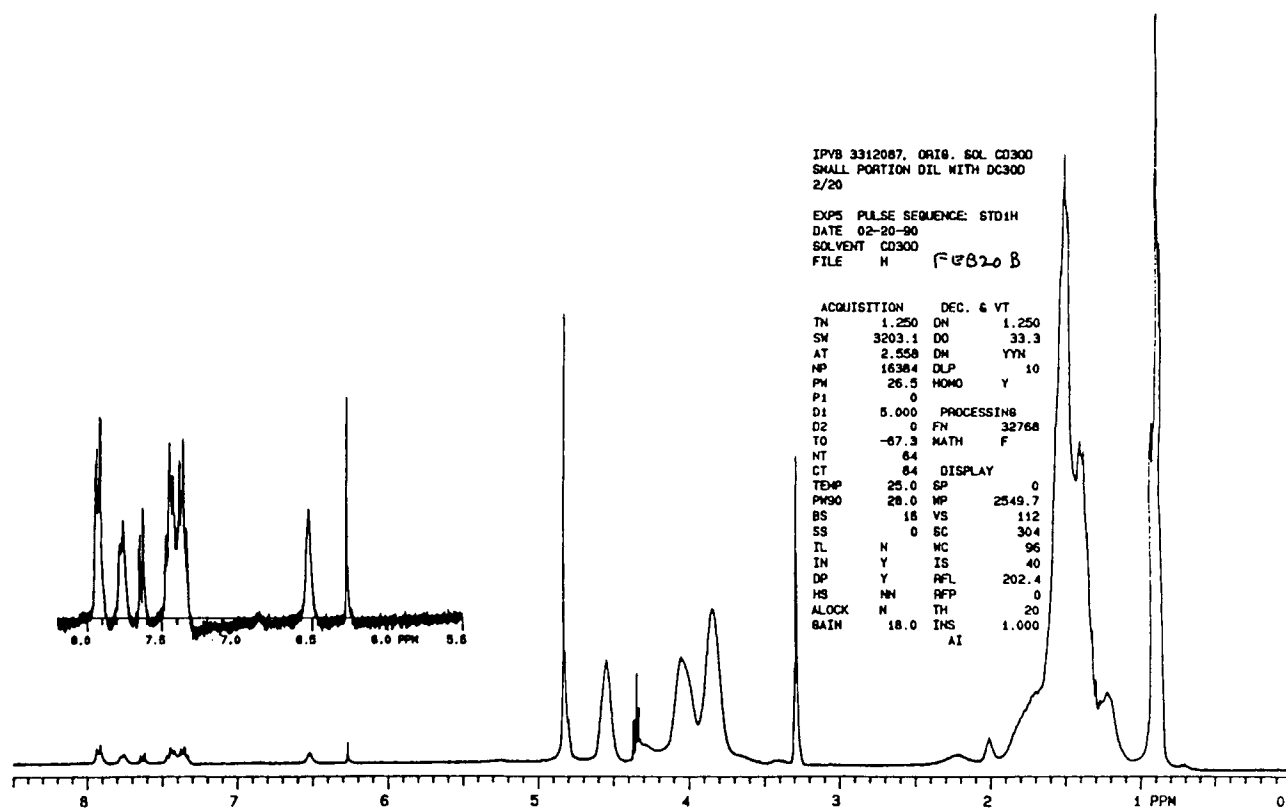


Figure 2 400 MHz <sup>1</sup>H NMR spectrum of ionomeric poly(vinyl butyral).

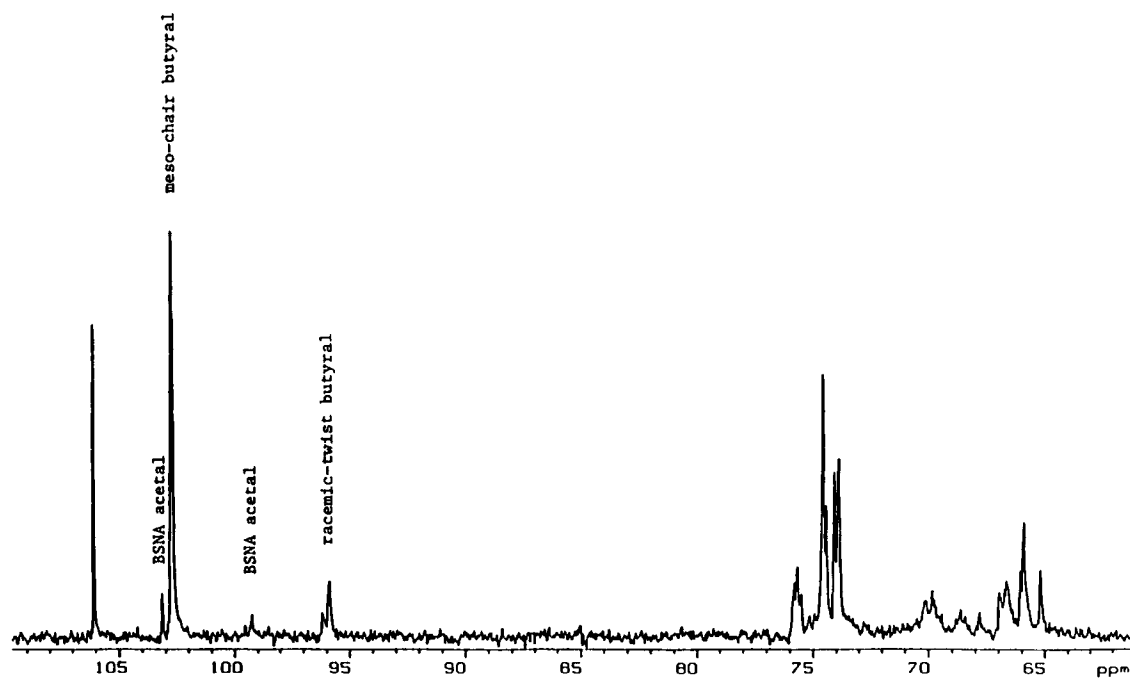


Figure 3 100 MHz <sup>13</sup>C NMR spectrum of ionomeric poly(vinyl butyral).

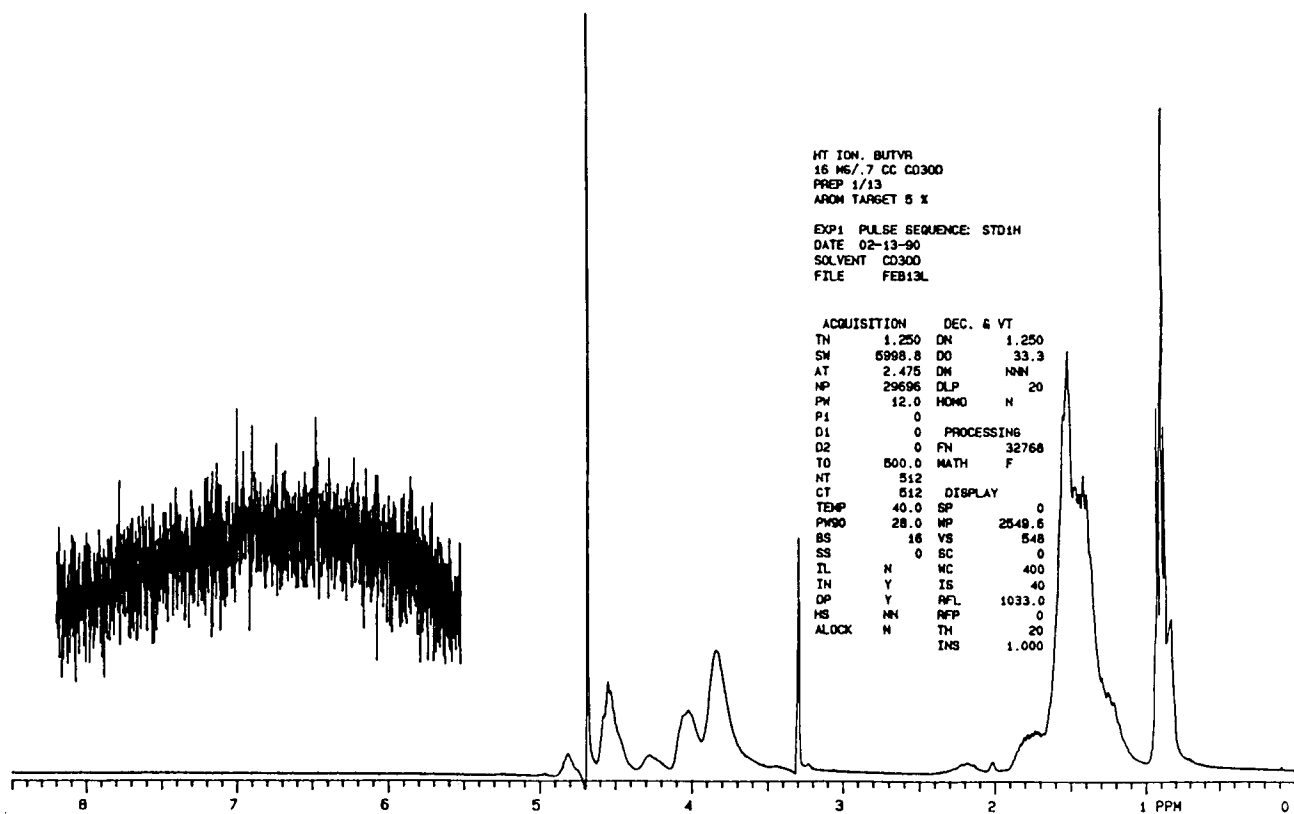


Figure 4 400 MHz <sup>1</sup>H NMR spectrum of polymer prepared at 75°C acetal temperature.

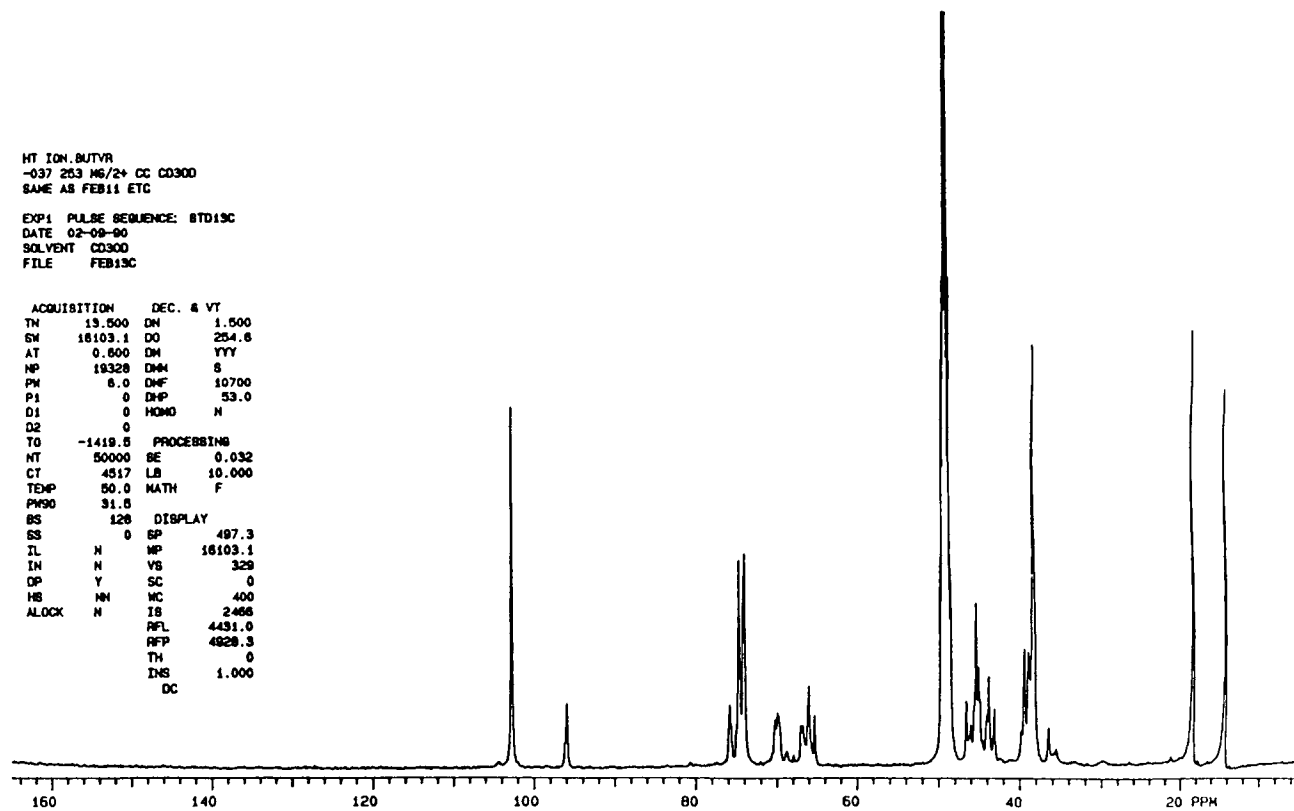


Figure 5 100 MHz <sup>13</sup>C NMR spectrum of polymer prepared at 75°C acetal temperature.

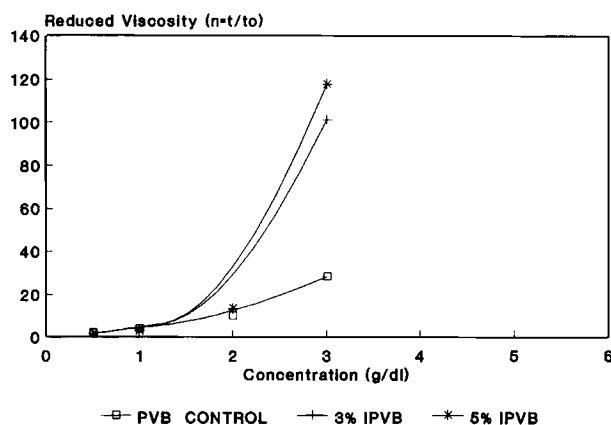
haviors. Figures 6 and 7 illustrate the viscosity behaviors of IPVBs and PVB control in tetrahydrofuran (THF) and methanol, respectively. In a non-polar solvent such as THF, the IPVBs exhibited a sharp rise in reduced viscosity beyond a concentration of 1–2%, ultimately resulting in gels, while the PVB control exhibited normal viscosity behavior. The dramatic increase in viscosity beyond a particular concentration in a nonpolar solvent is typical of ionomers and is due to the high degree of ionic associations.<sup>37,38</sup> On the other hand, in a polar solvent such as methanol, both the IPVBs and PVB exhibited normal viscosity behavior. This is a consequence of the ionic associations breaking apart (solvation) in the polar solvent.

### Thermal Characterization

The glass transition temperatures ( $T_g$ ) of the unplasticized IPVBs and PVB control are presented in Table I. All the samples have residual PVOH levels between 18 and 20 wt %. It can be seen that the  $T_g$  values of all the IPVBs are higher than the PVB control ( $T_g = 73^\circ\text{C}$ ). The  $T_g$ 's of the IPVBs increase with increases in ionomer levels, which is a direct consequence of the ionic associations, which in turn cause the polymers to increase in stiffness with accompanying increases in ionomer levels.

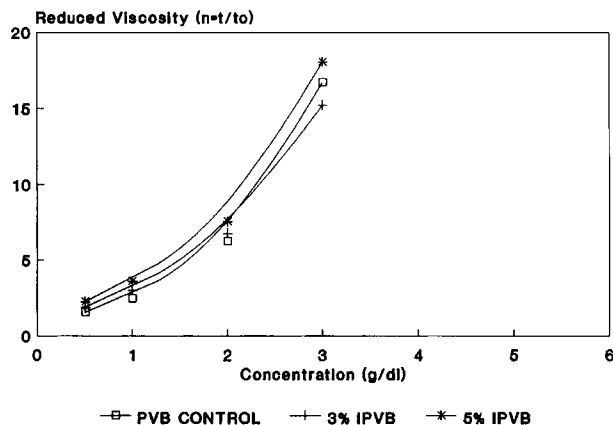
### Rheological Properties

Dynamic mechanical properties including storage modulus ( $G'$ ), loss modulus ( $G''$ ), and  $\tan \delta$  ( $G''/G'$ ) of plasticized IPVB and PVB control samples



IPVB'S synthesized from NH-18 PVOH

**Figure 6** Reduced viscosities of ionomeric poly(vinyl butyral) and poly(vinyl butyral) control, measured in tetrahydrofuran.



IPVB'S synthesized from NH-18 PVOH

**Figure 7** Reduced viscosities of ionomeric poly(vinyl butyral) and poly(vinyl butyral) control, measured in methanol.

were measured to provide information pertaining to the stiffness and flow characteristics of the polymers. Table II compares the  $G'$  values at 25, 40, 60, and  $150^\circ\text{C}$  for high molecular weight (HMW) IPVBs that were synthesized using a PVOH with a degree of polymerization (DP) of 1800, low molecular weight IPVBs (LMW) synthesized using a PVOH with a DP of 550, and a PVB control. The table also contains the residual PVOH levels and the theoretical mole percent of ionomer groups in the polymers. Both the HMW and LMW IPVBs had higher  $G'$  values at ambient temperatures ( $25\text{--}60^\circ\text{C}$ ) than the PVB control, which indicated that the IPVBs possessed greater ambient temperature stiffness than the control. Although higher residual PVOH levels, as in the case of the HMW IPVBs, also contribute towards increased stiffness, the principal source of the stiffness is due to the ionic associations provided by the IPVBs. This is clearly evident in the case of the LMW IPVBs, which have similar PVOH levels as the PVB control but yet are considerably stiffer

**Table I** Effect of Ionomer Groups on the  $T_g$ 's of IPVBs<sup>a</sup>

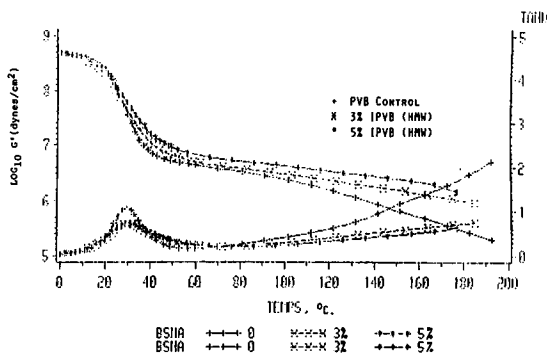
| Sample      | Mol % Ionomer | $T_g$ ( $^\circ\text{C}$ ) |
|-------------|---------------|----------------------------|
| PVB control | 0             | 73                         |
| IPVB        | 3             | 80                         |
| IPVB        | 5             | 85                         |
| IPVB        | 10            | 92                         |
| IPVB        | 15            | 106                        |

<sup>a</sup> PVOH levels of IPVBs = 18–20 wt %.

**Table II Storage Modulus ( $G'$ ) or IPVB and PVB Control**

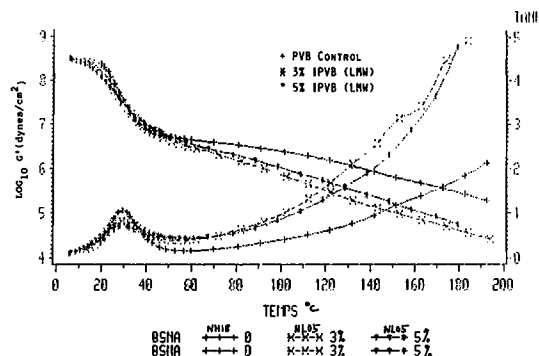
| Sample    | %ION | %PVOH | $G' (\times E-7) (\text{dyn/cm}^2)$ |        |        |         |
|-----------|------|-------|-------------------------------------|--------|--------|---------|
|           |      |       | (25°C)                              | (40°C) | (60°C) | (150°C) |
| PVB-CNTRL | 0.0  | 18.0  | 3.3                                 | 0.57   | 0.41   | 0.06    |
| HMW-IPVB  | 3.0  | 21.5  | 24.0                                | 2.4    | 0.58   | 0.15    |
| HMW-IPVB  | 5.0  | 20.0  | 45.0                                | 21.0   | 1.40   | 0.27    |
| LMW-IPVB  | 3.0  | 18.3  | 42.0                                | 13.0   | 0.66   | 0.015   |
| LMW-IPVB  | 5.0  | 18.4  | 49.0                                | 13.0   | 0.75   | 0.016   |

than the latter. It is also seen, as expected, that the  $G'$  values increase with increases in the ionomer levels. At 150°C, the  $G'$  values of the HMW IPVBs remain higher than the control while the  $G'$  values of the LMW IPVBs are lower than the control and the HMW IPVBs, which would indicate that the LMW IPVBs would have higher flow properties at these temperatures. Both molecular weight and complete dissociation of ionic crosslinks are probable factors here. Plots comparing the  $G'$  and  $\tan \delta$  profiles of the IPVB's and PVB control are shown in Figure 8 (HMW vs. control) and Figure 9 (LMW vs. control). In both the cases, the IPVBs possess  $\tan \delta$  curves (the peak of which corresponds to the  $T_g$  of the plasticized polymer), which are lower in intensity and broader in nature than the  $\tan \delta$  curve for the PVB control. Similar  $\tan \delta$  profiles are seen in crosslinked polymer systems and are attributed to the restricted chain mobility of such systems. In the case of the IPVBs, the crosslinked behavior which accounts for the shape of the  $\tan \delta$  curves is a direct consequence of the ionic associations. Figure 10 compares the  $\tan \delta$  curves of HMW IPVBs at 5 and 10 mol % ionomer levels and a PVB control, measured in the tensile mode. Once again, the IPVBs

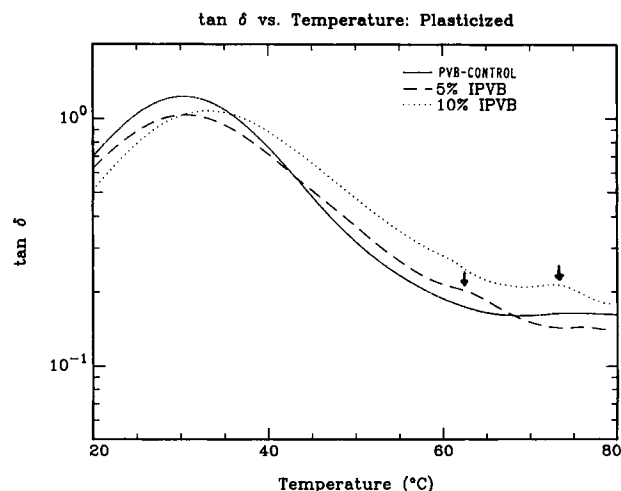


**Figure 8** Shear storage modulus ( $G'$ ) and loss tangent ( $G''/G'$ ) of high molecular weight ionomeric poly(vinyl butyral)s and poly(vinyl butyral) control.

have  $\tan \delta$  profiles similar to those observed in the shear mode. However, in addition, a very important observation can be made in the IPVB curves, namely, the presence of an additional transition between 60 and 80°C. Such additional transitions, ev-



**Figure 9** Shear storage modulus ( $G'$ ) and loss tangent ( $G''/G'$ ) of low molecular weight ionomeric poly(vinyl butyral)s and poly(vinyl butyral) control.



**Figure 10** Loss tangent ( $E''/E'$ ) of ionomeric poly(vinyl butyral) and poly(vinyl butyral) control measured in the tensile mode.

**Table III Storage Modulus ( $G'$ ) and Stress-Relaxation Modulus (SR) of IPVBs**

| Sample   | %ION | %PVOH | $G'$ ( $\times E^{-7}$ ) (dyn/cm <sup>2</sup> ) |        |        |         | SR150<br>$\times$<br>$E^{-3}$ |
|----------|------|-------|---|--------|--------|---------|-------------------------------|
|          |      |       | (25°C)  | (40°C) | (60°C) | (150°C) |                               |
| PVB-CTRL | 0.0  | 18.6  | 6.1   | 0.51   | 0.36   | 0.055   | 6.9                           |
| MMW-IPVB | 3.0  | 17.9  | 7.1   | 0.55   | 0.34   | 0.036   | < 1.0                         |
| MMW-IPVB | 3.0  | 18.6  | 7.5   | 0.58   | 0.35   | 0.004   | < 1.0                         |
| MMW-IPVB | 5.0  | 16.6  | 8.4   | 0.69   | 0.39   | 0.007   | 1.3                           |

ident in  $\tan \delta$  curves, are characteristic of ionomers and are thought to represent the  $T_g$  of the ionic clusters.<sup>14</sup>

Dynamic mechanical properties were also measured for medium molecular weight (MMW) IPVBs synthesized from PVOH with a DP of 1275. These IPVBs also had higher ambient temperature  $G'$  values than PVB control due to their increased stiffness and, like the LMW IPVBs, the MMW IPVBs had lower  $G'$  values at 150°C than the PVB control. Stress-relaxation measurements at 150°C (SR150) also showed lower values for the MMW IPVBs compared to the control (Table III), which along with the lower  $G'$  values at 150°C indicate that the elevated temperature flow properties of the MMW IPVBs are not adversely affected. Both  $G'$  and SR150 values increased with accompanying increases in ionomer concentrations.

## CONCLUSIONS

It has been shown that ionomeric poly(vinyl butyral) (IPVB) can be prepared by the acetalization of poly(vinyl alcohol) (PVOH) using an ionic aldehyde such as the sodium salt of *o*-benzaldehyde sulfonic acid (BSNA) in addition to butyraldehyde (BA), to form side chain groups capable of conversion to their ionomeric form via the addition of metal cations. The presence of the vinylbenzal sulfonate groups on the PVB chain, as a result of the above acetalization, were confirmed by NMR spectroscopy. Dilute solution viscosity and thermal characterization of the IPVBs showed that the polymers displayed typical ionomer properties. Further confirmation of ionomer behavior was obtained from dynamic mechanical property measurements of the IPVBs. It was seen that the ionic associations increased the stiffness of the polymer systems at ambient temperatures. In addition, modulus at processing temperatures similar to PVB control prepared using conventional acetalization procedures could also be obtained by selecting the appropriate IPVB system.

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