

Studies of Thermal Transition Behavior in Plasticized Poly(vinyl Butyral-co-vinyl alcohol) with Solid-State NMR and Thermal Analysis Techniques

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SYNOPSIS

Samples of plasticized poly(vinyl butyral-co-vinyl alcohol) (PVB) are found to exhibit multiple thermal transitions as observed by dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC). Arrhenius plots using DSC and DMA data suggest that two of the transitions are glass-type ones. Variable temperature solid-state ^{13}C -NMR experiments show a temperature-dependent line-broadening pattern for all PVB backbone carbons with maximum broadening at 55°C or at about 50°C above the second-order-type transitions α_1 and α_2 as measured by DSC. Using Arrhenius plots, the NMR transition is found to best correlate with α_1 , which is consistent with glass transition behavior. The solid-state NMR spectra also show that vinyl alcohol tacticity remains unresolved up to a temperature of about 95°C, beyond which line narrowing begins to occur. High-temperature thermal transitions are also observed by DSC and DMA, which suggest that the onset of motion involving vinyl alcohol sequences may be responsible for these transitions.

INTRODUCTION

The glass transition temperature has traditionally been defined as the onset temperature for long-range segmental motion in an amorphous polymer.¹ This transition, although loosely defined, is often used as a phenomenological benchmark for evaluating macroscopic trends such as adhesion, rigidity, impact strength, and permeability. However, complications quickly arise when systems exhibit phase separation.

Extreme phase separation in polymer blends will often result in separate glass transition temperatures that are close to the T_g 's of the individual component polymers. In such cases where the domain sizes are greater than about 10 nm, multiple transitions can be seen by thermal techniques such as differential scanning calorimetry (DSC).² However, when domain sizes become smaller, or when the T_g 's of the component materials are similar, it becomes difficult

to observe phase separation with DSC. This can lead to an incomplete understanding of the miscibility of polymer/polymer or polymer/plasticizer blends. Under such circumstances, the macroscopic differences between polymer systems must be related to more subtle microscopic differences that give rise to phenomena like broadened T_g 's as measured by DSC or multiexponential relaxation rates as measured by NMR.

Thus, the observation of a single T_g by macroscopic techniques does not conclusively prove that miscibility is complete at the microscopic level. In fact, at some level of magnification, and within a certain time scale, phase separation will probably exist in all blended polymer systems. If the phase separation is not static, then it may be dynamic and dependent on the time scale of observation. Even in amorphous homopolymers, dynamic heterogeneity will exist as a result of motional heterogeneity that arises from the distribution of inter- and intramolecular modes of motion.³

Schaefer and Garbow reported phase separation in blends of poly(vinyl butyral-co-vinyl alcohol) (PVB) and di-*n*-hexyladipate (DHA) at the 50 nm

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level using neutron scattering.⁴ We have recently reported results from inversion recovery cross-polarization NMR experiments that are consistent with phase separation in PVB/DHA blends,⁵ and we have also shown that phase separation behavior can be directly correlated with macroscopic properties.⁶ Given the magnitude of phase domains reported for the PVB/DHA system, it is conceivable that multiple transitions should be observable with macroscopic techniques such as dynamic mechanical analysis (DMA) and DSC. We have previously observed multiple thermal transitions in both neat and plasticized PVB systems, and it was found that DHA behaves as an antiplasticizer for PVB in its glassy state.⁷ Although we have identified a localized β -type transition that is antiplasticized by DHA, we have yet to report the identity of the remaining two transitions that we have designated as α_1 and α_2 , respectively, as well as a higher temperature transition that we will designate as α' . To better identify the nature of these transitions, we have used variable-temperature solid-state ^{13}C -NMR in conjunction with DSC and DMA techniques. Taken collectively, these techniques provide a more thorough

understanding of the glass transitional and morphological behavior of the PVB/DHA system.

EXPERIMENTAL

The PVB samples containing 32 phr DHA were studied as received from the Monsanto Co. (trade name Safflex). A Dupont 910 differential scanning calorimeter was used to monitor the transition behavior of PVB over a temperature range of -140 – 80°C . Samples were cooled with a liquid N_2 dewar to -140°C and were then run at $10^\circ\text{C}/\text{min}$ under a dry N_2 purge to 100°C . The samples were then cooled at a rate of approximately $20^\circ\text{C}/\text{min}$ to room temperature by using the chilled N_2 dewar with no liquid N_2 . This was followed by a ramp cooling with liquid N_2 to -140°C for a second run.

The mechanical behavior was studied over a temperature range of -150 – 90°C at fixed frequencies of 0.1, 1.0, and 10 Hz using a DuPont 983 DMA. Samples were vertically mounted and cooled with liquid N_2 from room temperature to -150°C at a rate of $2^\circ\text{C}/\text{min}$ where they were equilibrated for 1 h prior

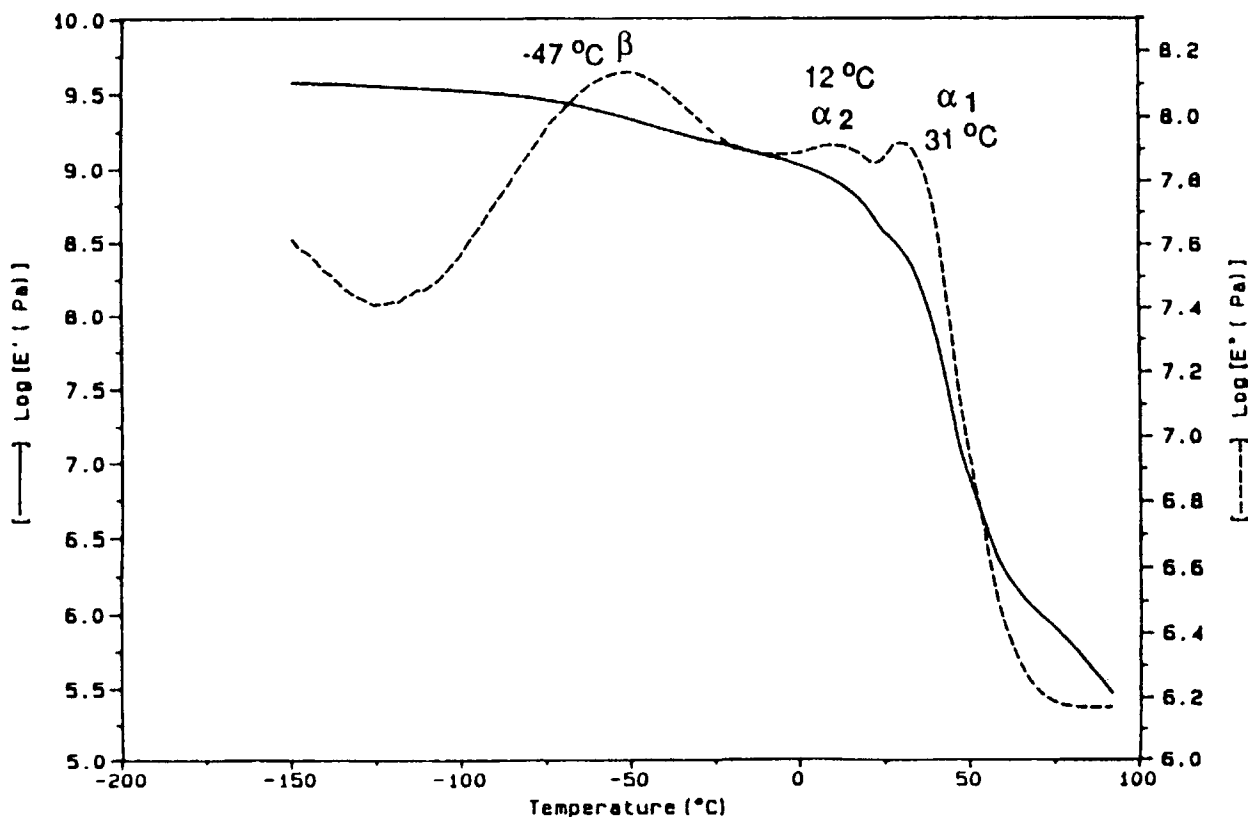


Figure 1 Dynamic storage and loss moduli at 1 Hz vs. temperature for plasticized PVB film.

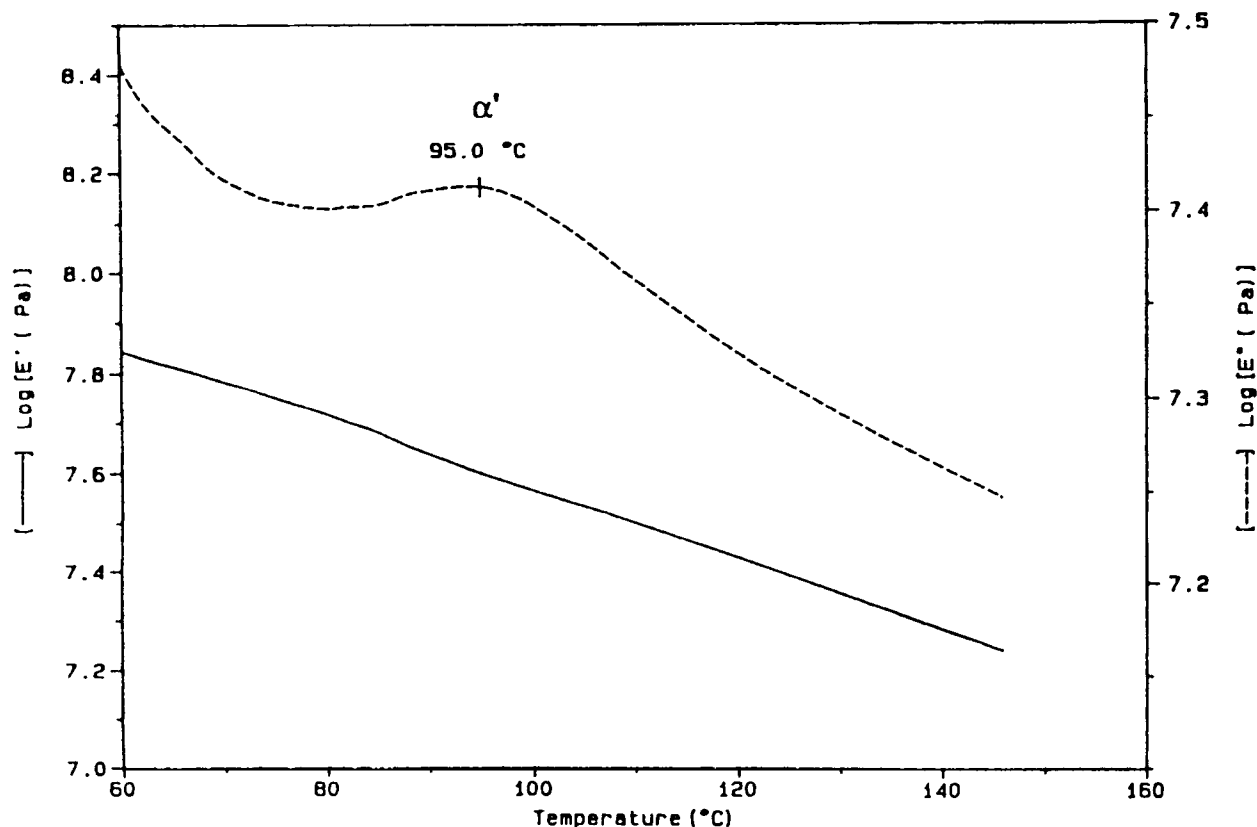


Figure 2 Qualitative dynamic storage and loss moduli at 1 Hz vs. temperature for plasticized PVB film laminated to a fiberglass braid.

to data collection and analysis at a heating rate of 5°C/min. Higher-temperature DMA experiments at 1 Hz were run by using a PVB film that was laminated to a fiberglass braid and mounted horizontally between the DMA clamps. This mode of analysis is qualitative, but can, nevertheless, show relative changes in thermal transition behavior under conditions where materials do not possess the mechanical integrity for vertical mounting.

Solid-state ^{13}C -NMR experiments were performed on a Bruker MSL-400 spectrometer (100 MHz for carbon) using magic angle spinning at 3 KHz to minimize broadening due to chemical shift anisotropy and with broad-band dipolar decoupling at an effective frequency of 57 KHz (^1H 90° pulse of 4.4 μs) to minimize broadening due primarily to carbon-proton dipolar interactions. Carbon single-excitation spectra were obtained over a temperature range of 25–115°C with the sample packed in a ceramic rotor having a ceramic cap glued with a cyanoacrylate adhesive to withstand sample expansion pressure. The spectra are representative of 500 scans at each temperature with a recycle time of 20 s between each scan, which was sufficient to avoid saturation of the ^{13}C spins.

RESULTS AND DISCUSSION

DSC and DMA Studies

DMA scans (1 Hz) of vertically mounted and horizontally mounted plasticized PVB samples are shown, respectively, in Figures 1 and 2. The transition designated as β has been previously identified as a localized backbone process, whereas α_1 and α_2 have been tentatively assigned as glass transitions.⁷ The mechanical transition labeled α' occurs at about 95°C as seen by a maximum in the loss modulus plot. A DSC scan representing a second run of the material is shown in Figure 3 with transitions designated analogously.

Figure 4 shows an Arrhenius plot of $\ln(\text{frequency})$ vs. $1/T$, where transition temperatures were taken as the maxima of loss modulus curves from DMA data and where the effective frequency of the DSC transitions was taken as 10^{-4} Hz.⁸ The slopes yield similar activation barriers of 71 and 70 kcal/mol for α_1 and α_2 , respectively, while the Arrhenius prefactors ($\ln A$) differ at values of 118 and 123 for the respective transitions. This suggests that

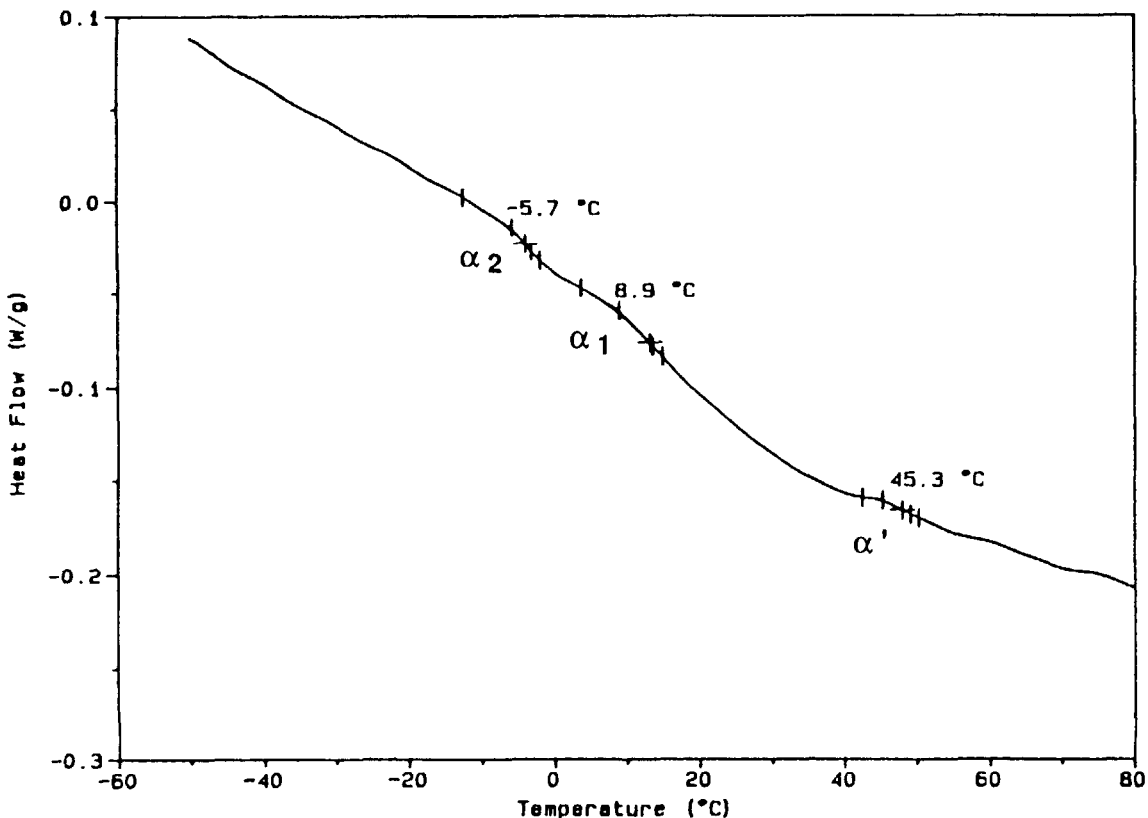


Figure 3 DSC second run of plasticized PVB film.

the motional characteristics of both processes are similar with the only difference being in the effective amplitude of each. The correlation coefficients are greater than .98 in each case, which shows that the

DSC and DMA transitions are correlated to similar motional processes. The magnitude of these activation barriers are also in accord with expectations for glass-type transitions.⁸

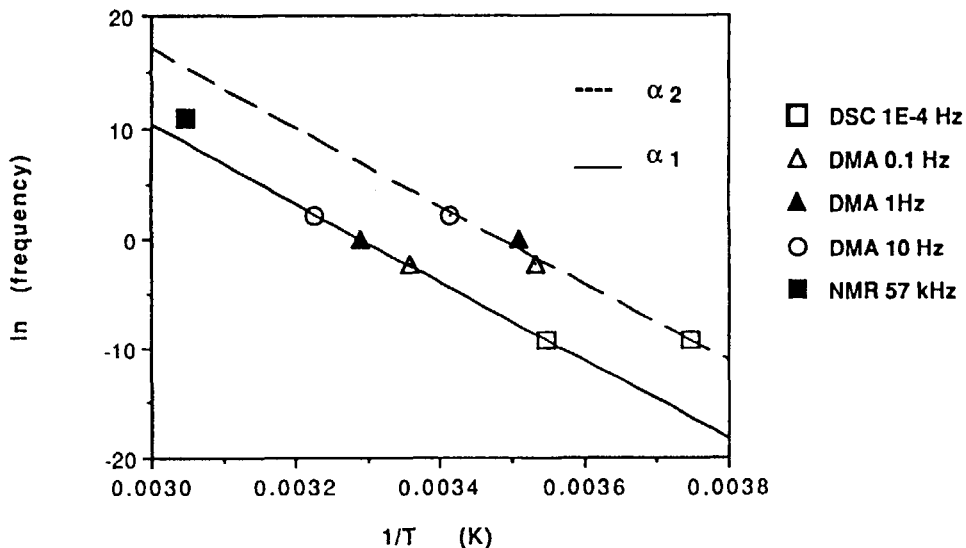


Figure 4 Arrhenius activation energy plot for PVB α_1 and α_2 transitions using DMA and DSC data. The least-squares fit does not include the NMR point at 57 KHz.

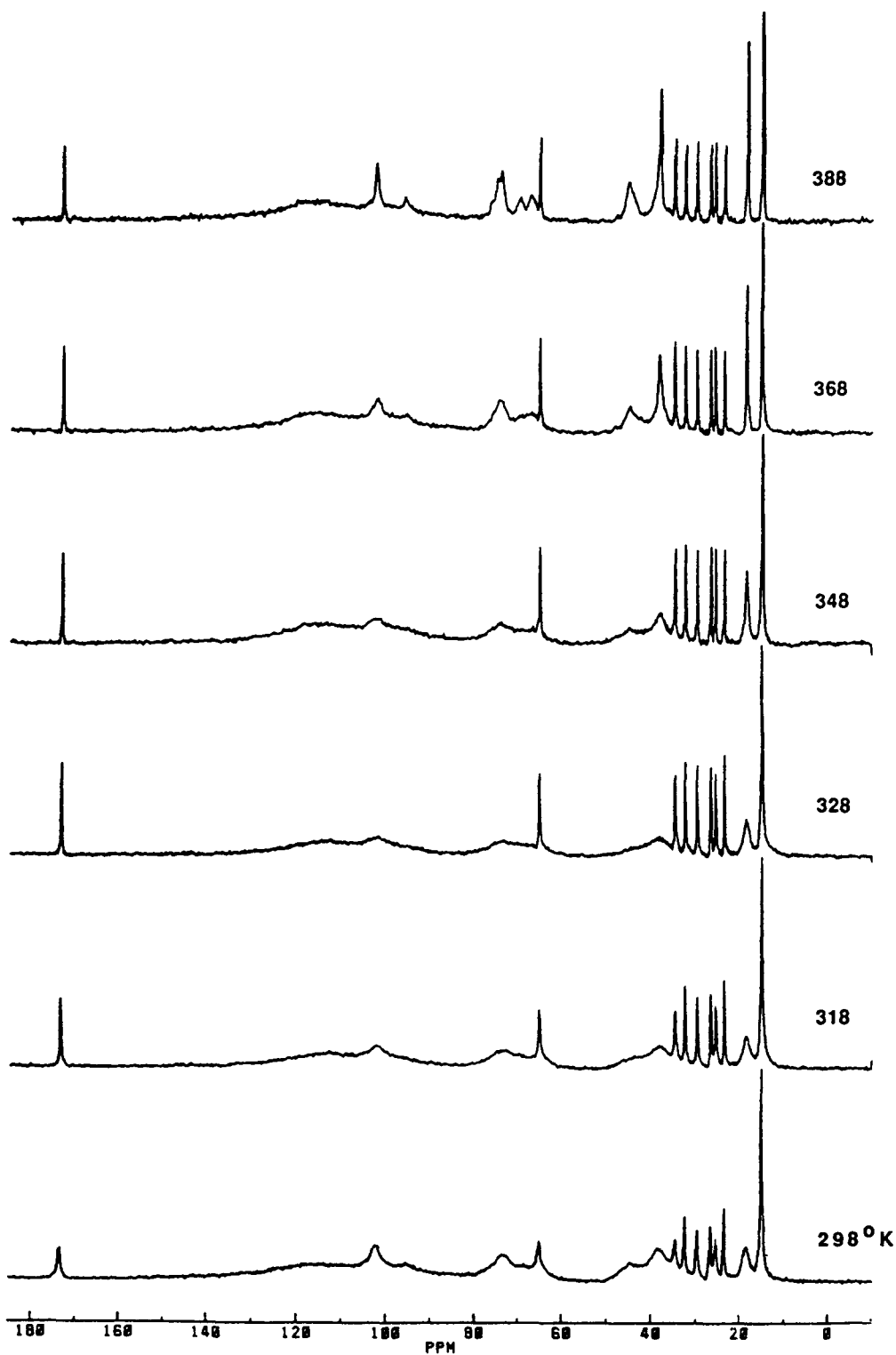


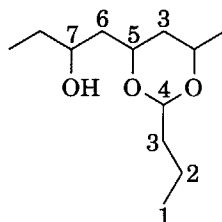
Figure 5 Solid-state ^{13}C -NMR spectra for plasticized PVB film vs. temperature.

The appearance of two T_g 's seems reasonable in light of previous neutron scattering and solid-state NMR results which have shown that PVB polymers

are characterized as having multiphase morphologies.^{4,5} Thus, these transitions are most likely related to phase-separated regions with some of the domains

Table I Structure and ^{13}C Chemical Shift Assignments (ppm) for PVB

Carbon	Chemical Shift
1	15
2	18
3	38
4	102
5	73
6	44
7	68, 66

Structure

being more highly concentrated with plasticizer than are other domains. Apparently, the resultant domains still share motions of similar character.

Solid-State ^{13}C -NMR Studies

Solid-state NMR spectra as a function of temperature are shown in Figure 5. The narrow lines between 20 and 34 ppm as well as the carbonyl at 174 ppm are assigned to the plasticizer carbons,⁹ while the broad resonances are associated with PVB carbons with assignments given in Table I. The broadening of polymer carbon resonances with temperature can be roughly followed by measurements of relative intensity vs. temperature as shown in Figure 6, where the intensity reaches a minimum at about 55°C (328 K).

The phenomenon of line broadening and subsequent renarrowing is not uncommon among polymers above the T_g .² At temperatures below the line-width maximum (or intensity minimum), high power proton-carbon dipolar decoupling tends to efficiently average and null the effective dipole vector to zero within the confines of spin space. However, as the frequency components of motional processes approach the effective dipolar decoupling frequency (which can occur by increasing temperature), the spin-space averaging becomes inefficient and line broadening is the result. With further increases in temperature and, hence, in molecular mobility, the frequency components of dipole motion are high

enough to efficiently average the net carbon-proton dipole interaction to zero by means of thermal energy alone. Thus, the point of maximum dipolar broadening can be a function of frequency and temperature just as mechanical responses like loss and storage moduli are also functions of time and temperature. This analogy will be most applicable when mechanical and NMR relaxation processes are affected by similar portions of the overall distribution of molecular correlation times.

In addition to the DMA and DSC data, the Arrhenius plot in Figure 4 also contains the NMR dipolar broadening maximum temperature at the effective dipolar decoupling frequency of 57 KHz. It appears that the process as measured by NMR correlates best with α_1 . However, given that the two T_g 's have similar activation barriers, the two transitions will tend to converge at higher frequencies.⁸ This makes it difficult to conclusively associate the NMR transition with only one of the mechanical processes. Nevertheless, all the backbone carbons are involved in the broadening process, which supports its association with a glass transition, be it either α_1 or α_2 , or both.

Further inspection of Figure 5 shows that additional narrowing and resolution enhancement occurs for vinyl alcohol carbons (44, 66, and 68 ppm) beginning at about 95°C. The methylene carbon at 44 ppm is still too broad to show tacticity effects, but the tertiary alcohol carbon readily splits into peaks at 66 and 68 ppm, which can be assigned to heterotactic and isotactic triads, respectively.¹⁰ The vinyl alcohol units apparently have enough mobility at this temperature to separate into triad components. The butyral carbons (particularly at 38 ppm) also undergo additional motional narrowing that could also be a result of the dissociation of neighboring hydrogen-bonded hydroxyl sequences. The dissociation of such sequences would lead to higher degrees of motional freedom among all the monomeric units.

If one ignores intermolecular interactions, the intramolecular barrier for chain rotation would be lower among vinyl alcohol sequences than among vinyl butyral sequences. This would follow from a lower effective chain-link length for vinyl alcohol (at least one carbon bond length vs. at least two carbon bond lengths for vinyl butyral) and from the lower steric barrier associated with the smaller size of the alcohol group. A lower steric barrier would, in turn, lead to higher degrees of motional freedom for the vinyl alcohol sequences. Thus, using these arguments, one would expect that the alcohol carbons would be better resolved than butyral carbons

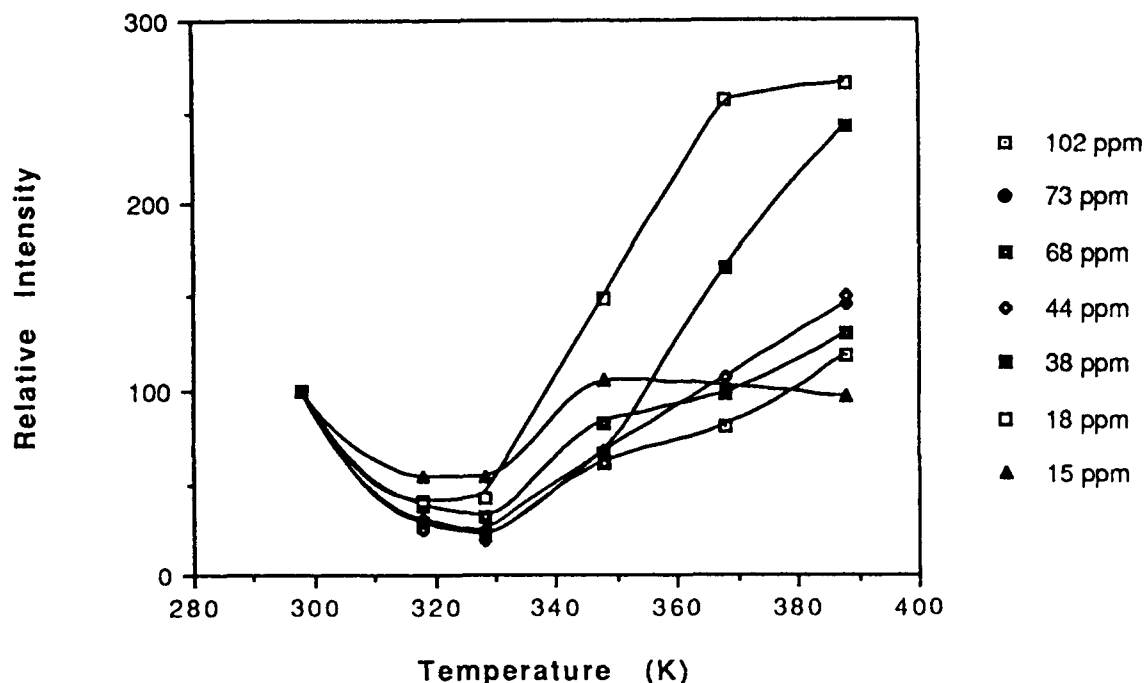


Figure 6 Relative intensity for PVB carbons vs. temperature. Spectra were referenced to spectrum at 298 K.

at any given temperature. However, the tacticity resolution does not occur until elevated temperatures. Thus, intermolecular interactions must prevent extensive hydroxyl carbon motion at lower temperatures, most likely as a result of hydrogen bonding similar to that which would occur in polyvinyl alcohol homopolymers.

Higher-temperature thermal transitions are also observed by both DMA and DSC techniques at 95 and at 45°C, respectively. Although it is likely that these transitions are related to the enhanced vinyl alcohol mobility, more detailed multiple frequency experiments would be needed to validate such a conclusion. Nevertheless, it appears that plasticized PVB has a morphology that is similar to that of other A-B-A block copolymers where hydrogen bonding or other means of self-association (loosely called physical cross-linking) will influence macroscopic properties.

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