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EFFECT OF PLASTICIZER ON PVAc-d3 DYNAMICS USING 2H SOLID STATE NMR

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Introduction

Poly(vinyl acetate) (PVAc) is an important polymer for use in many applications due to its various bulk and surface characteristics. The structure of poly(vinyl acetate) results in a relatively low glass transition temperature (Tg) and makes it important for processing and applications such as paints, adhesives, thin films and surface coatings. Poly(vinyl acetate) can also be easily plasticized, widening its range of applications.

The term "plasticizer" refers to a species that will decrease Tg of a polymer.1 Polymer-plasticizer systems have been studied for years and continue to be of current interest. The effects of polymer-plasticizer interactions2 and plasticizer structure3 on polymer chain motions have been studied extensively, but there is still much to be learned in this area.

Deuterium NMR is an excellent tool for studying the mobility of polymer chains. In this work, we report the investigation of the effect of plasticizer content on the Tg of poly(vinyl acetate) using deuterium nuclear magnetic resonance (2H NMR) spectroscopy. The methyl groups of poly(vinyl acetate) were deuterated in order to probe the mobility of their segments using the 2H NMR technique. Random orientations of the methyl groups, with respect to a magnetic field, are reflected as a powder pattern in the 2H NMR spectrum for segments with little or no motion. Segmental mobility averages the quadrupole couplings and ultimately leads to the collapse of the powder pattern into a single resonance for rubbery polymers when the motion is on the scale of or faster than the interactions.4

Experimental

Vinyl acetate-d3 was prepared via the interchange reaction of acetic acid-d3 and vinyl propionate. A mixture of 0.167 mole of acetic acid-d3, 0.33 mole of vinyl propionate, 2.4 wt% of mercuric acetate, 0.25 wt% of concentrated sulfuric acid and a trace amount of hydroquinone were stirred in three neck flasks at 85-90 °C for 3-4 h. About 4 wt% of sodium acetate was added after reaction appeared to be complete and then the resultant vinyl acetate-d3 was collected by distillation under reduced pressure. The product was then purified using a spinning band column. The yield was about 45% based on the amount of acetic acid used. The weight percentages of the ingredients were based on the mass of acetic acid used.3

Vinyl acetate-d3 was polymerized in a K2S2O5/sodium-dodecyl sulfate/water emulsion. The resulting polymer had a molecular mass and polydispersity of 240 kg/mol and 2.2 respectively. The molecular masses were measured using an OPTILAB DSP Interferometer Refractometer and a DAWN EOS Light Scattering Instrument (Wyatt Technology, Santa Barbara), connected to a gel permeation instrument.

The plasticized samples of PVAc-d3 were prepared by dissolving PVAc-d3, dipropylene glycol dibenzoate in acetone and mixing them for 2-3 h with a mechanical shaker. A thin film was cast from this solution on a clean glass slide and allowed to dry for 24 h. The thin film seemed to have a uniform distribution of plasticizer in the polymer. Samples with 5%, 10%, 15%, 20% plasticizer was prepared. A 0% plasticized sample was prepared in the same way as described above except that the plasticizer was not added. PVAc (Scientific Polymer Products, Mw 235.7 kg/mol, polydispersity 2.0) was used for MDSC. The plasticized samples were prepared in the same manner.

The NMR spectra were obtained on a Varian VX-400/S spectrometer equipped with a wide-line probe (Doty Scientific, Columbia, SC). The 2H resonance frequency was 61.395 MHz, and the pulse sequence was delay-90°-τ-acquisition. The pulse width was 2.8 μs and τ = 30 μs. The Fourier transformation was started at the top of the echo, and no line broadening was applied to the spectra. The number of scans ranged from 700 to 1000. All of the spectra shown were processed using the Mestrec software package (Santiago de Compostela University, Spain) and scaled to the same height for easier comparison. The reported Tg(NMR) was the temperature at which the powder pattern collapsed to form a single narrow peak.

A TA Instruments model 2920 Modulated Differential Scanning Calorimetry (New Castle, DE) was also used for thermal analysis of the plasticized PVAc samples. Two heating scans and one cooling scan were taken from -40 °C to 100 °C, at a rate of 2.5 °C/min, modulation amplitude of ± 0.5 °C and a period of 60 s. The second heating scan was used to determine the glass transition temperature data for the reversing heat flow curves so that all of the samples were subjected to a similar thermal history. The reported Tg was found by using the maximum of the derivative reversible heat flow peak obtained for each sample.

Results and Discussion

Figure 1. 2H NMR spectra for 0% plasticized bulk PVAc-d3

Figure 1. 2H NMR spectra for 0% plasticized bulk PVAc-d3, with different plasticizer amounts, were taken as a function of temperature. The spectra of 0% plasticized PVAc-d3 (Figure 1) showed a powder pattern at 40 °C with a splitting of 44 kHz between the bases of the two horns. This pattern is similar to that expected for a methyl group undergoing fast motions about its symmetry axis. At these temperatures, the backbone motions in the polymer were slow. As the temperature increased, from 45 °C to 80 °C, the powder pattern collapsed with a gradual smoothing of the sharp features to a single narrower resonance. It should be noted that the line shapes observed are single component; i.e., all the different segments in the sample had more or less the same motion. The collapse of the Pake pattern is indicative of the presence of a backbone motion in the polymer that averaged out the residual quadruple interaction. The collapse occurred between 65 °C and 70 °C, and was roughly centered at 68 °C for the 0% plasticized sample. Thus, this can be considered as the "Tg(NMR)".

Figure 1.
The spectra for a 10% plasticized sample are shown in Figure 2. In the case of 10% plasticized PVAc, the collapse of the Pake pattern took place from 55 °C to 60 °C. Similarly, the temperature at which the collapse of the Pake pattern took place shifted to a lower temperature as the percentage of plasticization increased. The T_g decreased by approximately 5 °C for every 5% increment of plasticization. The T_g's (NMR) for the different plasticized samples are given in Table 1. The spectra for the different plasticized amounts remained as fairly single components.

The DSC results for the different plasticized samples are shown in Figure 3 and the T_g's (DSC) for the samples are given in Table 1. The T_g decreased by approximately 6 °C for every 5% increment in the plasticizer. Figure 4 show the plot of glass transition temperature against percentage plasticized samples of PVAc. The graphs are fairly linear which is expected for PVAc-plasticizer systems. Also, the two plots have fairly similar slopes.

The T_g(NMR) is about 35-40 °C above the T_g(DSC). This difference can be attributed to the differences in time scales of the two experiments, with the DSC being on the order of Hertz and the 2H NMR being on the order of kiloHertz.5,6

Table 1. T_g(NMR) And T_g(DSC) For Different Plasticized Samples

<table>
<thead>
<tr>
<th>% Plasticizer</th>
<th>0</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>T_g(NMR) (°C)</td>
<td>68</td>
<td>63</td>
<td>57</td>
<td>53</td>
<td>49</td>
</tr>
<tr>
<td>T_g(DSC) (°C)</td>
<td>36</td>
<td>29</td>
<td>23</td>
<td>15</td>
<td>10</td>
</tr>
</tbody>
</table>

Figure 4. Plot of glass transition temperature vs % plasticized PVAc.

Conclusions

Deuterium NMR is a powerful tool for studying the mobility of polymer chains. The use of labeled methyl groups can provide information about the segmental dynamics of the polymer chains through line shape changes. The glass transition temperature of poly(vinyl acetate) decreases with the increase in the plasticizer content. This was verified with both NMR and MDSC.

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References.

(3) Oosterhout, J. T.; Gilbert, M.; Polymer, 2003, 44, 8081.