Wide Line Nuclear Magnetic Resonance Spectra of Hydrogen-1 and Lithium-7 in an Ethylene–Lithium Acrylate Copolymer

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ABSTRACT: The wide line nuclear magnetic resonance spectra for protons and lithium nuclei in an ethylene–lithium acrylate copolymer were investigated over a wide temperature range. The line widths for both types of nuclei indicate two transitions, supporting the hypothesis that the salt groups are uniformly distributed in the amorphous phase of the polymer.

The extent of association or aggregation of the pendant metal carboxylates in ethylene–metal methacrylate or acrylate copolymers is a point of some controversy.[1-3]

To examine more closely the microheterogeneity of such systems, wide line nuclear magnetic resonance techniques have been employed. Both the ^{1}H and ^{7}Li wide line spectra of a fully neutralized ethylene–acrylic acid (4.9 mol % acid) copolymer were examined. The sample was prepared by titration of the dissolved acid copolymer with freshly prepared $LiOCH_3$ in a manner previously described.[3] The proton spectrum of the parent acid polymer was also studied. For both polymers, melt pressed films were cut into disks with a cork borer, providing a well-filled nmr tube.

The proton magnetic resonance studies were performed on a Varian DP 60 spectrometer. The line widths were taken as the peak-to-peak separations observed in the recorded derivative signal. The lithium resonance line width was determined at 16 MHz, again by the derivative technique. Temperature control in both cases was achieved by circulation of nitrogen gas through the probe.

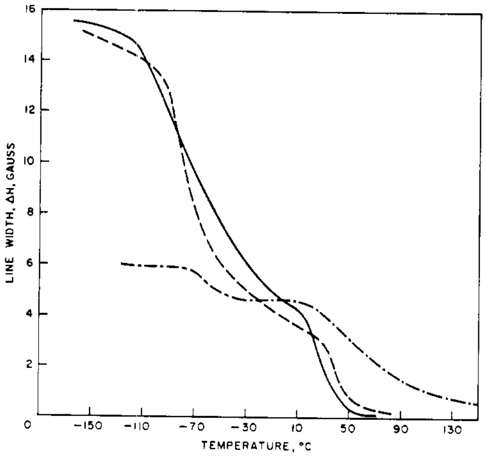

Figure 1. Wide line nuclear magnetic resonances: —, ^{1}H in ethylene–acrylic acid copolymer (60 MHz); – – –, ^{1}H in ethylene–lithium acrylate copolymer (56.5 MHz); –·–·–, ^{7}Li in ethylene–lithium acrylate copolymer (16 MHz).

Figure 1 displays the line widths as a function of temperature for both proton absorptions and the lithium absorption. All three sets of data exhibit two regions where the line width narrows, indicating transitions. The lower temperature transition is identified as the γ transition and the higher temperature transition as the β transition.

The γ transition temperatures as indicated by the protons for both the acid and salt form of the copolymer are about the same, −75°, although this transition is much broader for the acid copolymer. The β transition temperatures for the acid and salt form are about 30 and 40°, respectively. The accurate determination of the transition temperatures from the line-width data is hampered by the lack of a well-defined plateau between the γ and β transitions in the proton data.

For the salt form of the polymer, the lithium resonance indicates γ and β transition temperatures of −60 and 55°. These temperatures are slightly higher than those indicated by the proton spectra. What is important is the fact that the increased motion of the lithium nuclei responsible for the decreased line width at these two temperatures seems to be a direct result of increased matrix mobility. If these lithium nuclei were present in exclusive domains, the matrix mobility would not be transferred effectively.

Above the melting point of the copolymer a finite Li line width persists. This amounts to about 10% of the low-temperature rigid lattice value and may arise either from quadrupolar broadening or weak restraints on salt group mobility. Such a low residual line width, along with the correspondence of the Li nuclear resonance to the matrix transitions, favors the hypothesis that the salt groups are physically well dispersed in the amorphous phase of the copolymer wth dipole–dipole coupling defining the limits of their interaction.

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