

^{133}Cs NMR Investigation of Anisotropic Block CopolymersV. Dessolle,[†] J. P. Bayle,[†] J. Courtieu,[†] J. Rault,[‡] and P. Judeinstein^{*,†}*Laboratoire de Chimie Structurale Organique (URA CNRS 1384)-Bât. 410 and Laboratoire de Physique des Solides-Bât. 510, Université Paris-Sud, 91405 Orsay, France**Received: September 21, 1998; In Final Form: December 9, 1998*

Anisotropic polyamide–polyether block copolymers doped with several cesium salts were studied with ^{133}Cs NMR. These materials are highly hydrophilic. In the first set of experiments the evolution of the spectra was measured as a function of the swelling ratio in $\text{H}_2\text{O}/\text{D}_2\text{O}$ mixtures. The evolution of the spectral parameters (^{133}Cs chemical shifts and the quadrupolar splittings of ^{133}Cs and ^2H) indicates that strong interactions exist between the Cs^+ ions and the polymeric chains. At high swelling ratios the cations freely probe the anisotropic property of the polyether chains. In a second set of experiments dried materials were studied as a function of the sample temperature. Surprisingly, a significant increase in the anisotropic character of the Cs^+ reorientation was measured when the temperature was raised. The increase of the electric field gradient could be considered as a measurement of some “apparent ionic order”, which would be related to the modification of the averaged cation complexation site and to the dynamics of these ions. These measurements may serve as a new approach to the investigation of the nature of ion–polymer interactions.

I. Introduction

Polymers possessing permanent anisotropy are expected to have unusual mechanical, optical, and electrical properties, which is why there is great scientific and technological interest in studying them.¹ Mechanical stretching is a simple method to obtain such oriented structures. Thermoplastic elastomers, such as polyamide–polyether block copolymers (PEBA) can be drawn to give stable anisotropic structures. Their properties arise from the intimate components consisting of polyamide crystallites (PA) and polyether segments (PEO), which produce, respectively, thermoplastic and elastomeric behavior.² Owing to the PEO segments, these blends can absorb water up to 130% of their weight and dissolve organic and/or inorganic compounds. Thus, these materials could be also considered as models for the study of ionic polymer electrolytes, which are commonly based on PEO–XA solid solutions (X^+ is an alkaline ion, generally Li^+ or Na^+ , and A^- an anion, generally ClO_4^- , CF_3SO_3^- , ...).³ NMR spectroscopy provides a tool for the study of ion solvation and dynamics in solutions^{4,5} or in polymer electrolytes⁶ using chemical shifts, quadrupolar splittings, relaxation, and diffusion measurements. These measurements are essential to gauging the mobility of the ions and to monitoring the ionic transport numbers.

This paper presents a new approach for investigating the behavior of ions dissolved in the above-mentioned materials using quadrupolar NMR. The choice of ions with quadrupolar nuclei located inside the anisotropic structures enabled us to measure quadrupolar splittings, which are very sensitive to the geometry of neighboring structures and to the dynamics of the ions⁷ and which can act as a probe of the anisotropic properties. Oriented elastomeric PEBA structures can be swollen with a cesium salt solution. Even if Cs^+ ions are bigger and less solvated than Li^+ and Na^+ ions, ^{133}Cs , which has a spin $I = 7/2$

and a low quadrupolar moment, is then a very adequate probe, since NMR resonance lines are narrow. In these materials a septet can be observed for the ^{133}Cs signal, thus providing evidence for anisotropic reorientational dynamics of the cations because of ion–polymer interactions. The influence of hydration ratio or temperature is presented and compared to the results obtained with ^2H NMR of deuterated probes. These experiments clearly show the differences in interactions between the ions or the probe molecules and the surrounding polymer.

II. Experimental Section

The materials PA6/PEO block copolymers (PEBA) were synthesized by Atochem. Their swelling and mechanical properties have been described previously.² They can be permanently deformed under mechanical stress, producing an anisotropic arrangement.⁸ The dry isotropic samples were drawn and relaxed at room temperature. The resulting permanent drawn ratio $\lambda = l/l_0$ (l_0 and l are, respectively, the lengths before and after stretching) of the samples were measured after relaxation at room temperature. λ was fixed to 3.0 in all our experiments. Next, these oriented materials were dipped in $\text{H}_2\text{O}/\text{D}_2\text{O}$ –CsA solutions (15 wt % deuterated water; salt 5×10^{-2} M; $\text{A}^- = \text{ClO}_4^-$, I^- , Cl^- , NO_3^- , CH_3COO^- , CF_3COO^-), resulting in maximum swelling ratios S_r around 130% ($S_r = 100(m - m_0)/m_0$), where m and m_0 are the masses of the swollen and dried samples). Smaller S_r values were obtained through controlled solvent evaporation. Consequently, the ratio $[\text{O}_{\text{POE}}]/[\text{Cs}]$ is kept constant at 160 during all these experiments (where $[\text{O}_{\text{POE}}]$ is the concentration of oxygen atoms coming from the polymer).

The oligomeric deuterated probe was synthesized as follows. An amount of 3 g of poly(ethylene glycol) (molecular weight 600, 5×10^{-3} mol) was allowed to react overnight at room temperature with deuterated acetyl- d_3 chloride, CD_3COCl (0.98 g, 1.2×10^{-2} mol), in the presence of 0.95 g of pyridine (1.2×10^{-2} mol) in 100 mL of THF. The solution was neutralized and chromatographed on silica gel (60–200 mesh, CH_2Cl_2 eluent). The pure compound bis(acetyl- d_3 , end-terminated)–

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poly(ethylene glycol)₆₀₀ (abbreviation: CD₃COO–PEO₆₀₀–OCOCD₃) was obtained, and the purity was checked by ¹H and ¹³C NMR (1.2 g; purity, >99%).

NMR experiments were performed with a Bruker AM250 spectrometer equipped with a 10 mm broad-band probe without field/frequency lock control. Temperature was controlled in the range 293–400 K by a Bruker VT100 system (±1 °C regulation). ²H spectra were recorded following the usual conditions at 38.376 MHz. ¹³³Cs NMR spectra were recorded at a frequency of 32.792 MHz. The transients (FID) were obtained using a 10 μs pulse width (π/2 pulse is 15 μs) and a recycle delay of 0.2 s. For swelled materials FID signals were typically sampled with 2K real data points over a 3350 Hz spectral width. Zero-filling to 4K points was applied to increase the digital resolution to 0.82 Hz/point, and an exponential line broadening of 1 Hz was used. Under these conditions 3000–5000 transients were usually added to obtain spectra with good signal-to-noise (S/N) ratio. Chemical shifts were referenced to an aqueous 10^{−2} M CsNO₃ solution and positively downfield. Owing to the broad signals of the dried material, the ¹³³Cs FIDs were sampled using 1K real data points over 10 kHz spectral width. Zero-filling to 2K points was applied to achieve a 4.88 Hz/point digital resolution. Under these conditions 4000–7000 interferograms and exponential line broadening (8 Hz) were usually necessary to obtain spectra with reasonable signal-to-noise (S/N) ratio.

III. Analysis

Extensive discussions of the spectral line shape of quadrupolar nuclei in anisotropic media (liquid crystals, amphiphiles, anisotropic polymers) have been discussed elsewhere.^{9,10}

In an isotropic solvent, the averaged electric field gradient (efg) is null and each nonequivalent nuclei gives a single line in the fast reorientation regime. When molecules or ions are dissolved in anisotropic media, guest–host interactions may lead to the partial orientation of the molecules and to a polarization of the electronic cloud for an ion, leading to a partially ordered electric field gradient. The anisotropic interaction between the nuclear quadrupolar moment (spin $I > 1/2$) and the efg removes the degeneracy in the Zeeman energy levels. This leads to 2I equally spaced lines with respective intensities calculated from the transition probabilities. From the value of the measured quadrupolar splitting, Δν_Q, we can relate the order parameter of the principal component of the electric field gradient at the nucleus site with respect to the magnetic field.⁹ With the approximation of a small deviation from cylindrical symmetry (disregarding the asymmetry parameter) the following expression applies:¹¹

$$\Delta\nu_Q = \frac{3}{2I(2I-1)} P_2(\cos \Omega) S_{\text{polym}} |\bar{q}_{nm}|_S S_{\text{probe}} \quad (1)$$

where Ω is the angle between the polymer-drawing direction and the magnetic field (fixed to zero in our experiments), P₂ is the second-order Legendre polynomial, S_{polym} is the order parameter characterizing the anisotropic reorientation of the polymer chain segments relative to the stress direction, S_{probe} is the order parameter characterizing the behavior of the probe toward the polymer chain, and | \bar{q}_{nm} |_S is the average over all the possible sites S of the components of the quadrupolar tensors. Two simplified expressions can then be used to describe the quadrupolar splitting.

(a) For a deuterium atom linked to an oxygen or a carbon atom, the electronic field gradient lies along the O–D or the

C–D directions, respectively, and the expression for Δν_Q^(D) becomes⁹

$$\Delta\nu_Q^{(D)} = \frac{3}{2} S_{\text{polym}} \nu_q \langle P_2(\cos \theta_{OD}) \rangle \quad (2)$$

where ν_q is the quadrupolar coupling constant, which is about 210 kHz for O–D bonds in water (180 kHz for C–D), ⟨P₂(cos θ_{OD})⟩ is the order parameter of the O–D bonds (C–D) relative to the polymer chain, and ⟨...⟩ denotes an ensemble average over all the relative orientations sampled on the NMR time scale.

(b) For a cesium cation that is bound or solvated by the surrounding media, the electronic field gradient is polarized or deformed from the spherical symmetry when the “average complexation site” becomes anisotropic. A rapid exchange regime (in regard to the reciprocal of the quadrupolar interaction) between different sites is generally satisfied and can be used to describe the behavior of the ions. The quadrupolar splitting is then expressed as¹²

$$\Delta\nu_Q^{(\text{Cs})} \propto S_{\text{polym}} \bar{\chi} S_{\text{ion}} \quad (3)$$

where S_{ion} represents the averaged order parameter of the ion toward the polymer and $\bar{\chi}$ is the mean quadrupolar coupling constant of the cesium ions. Thus, Δν_Q^(Cs) represents the averaged apparent ionic orientation and can be called “apparent ionic order”. It states that distorted ions are oriented inside an anisotropic media. Some physical possible models to detail this expression are proposed in the following sections.

²H quadrupolar splitting is measured through the doublet separation in the deuterium spectrum. For ¹³³Cs spectra it is necessary to deconvolute the spectra into seven dependent Lorentzian shaped curves that are equally spaced by the quadrupolar splitting Δν_Q^(Cs). The procedure we used is given by

$$\text{NMR spectrum} = \sum_{i=-3}^3 \text{Lorentzian}\{(\nu_0 + i\Delta\nu_Q^{(\text{Cs})}), A_i, \omega_{1/2,i}\} \quad (4)$$

where ν₀ is the central frequency of the spectra, Lorentzian-{(ν₀ + iΔν_Q^(Cs)), A_i, ω_{1/2,i}} represents the *i*th Lorentzian curve centered at frequency ν₀ + iΔν_Q^(Cs). The intensities of the seven lines, A_i, are determined from the transition probabilities in the proportion 7:12:15:16:15:12:7. The half-height line widths ω_{1/2,i} are taken as a linear function of the frequency shift from the central line as ω_{1/2,i} = ω_{1/2,0} + |F(ω_i − ω₀)|, taking into account the order inhomogeneities of Cs⁺ ions inside the material.

The fitting parameters are therefore the following.

(1) The central line chemical shift ν₀ is one parameter, which is related to the Cs⁺ ion coordination shell (δ = 0 ppm for a 10^{−2} M CsNO₃ solution). Cesium chemical shifts are very sensitive to the coordination shell and also to the nonspherical deformation of the electronic distribution, since the Sternheimer antishielding factors is rather large.¹⁵

(2) The line splitting, Δν_Q^(Cs), is another parameter, which is connected to the averaged “apparent ionic order”.

(3) A third parameter is the line width of the central line, ω₀, which is insensitive to the first-order quadrupolar effect and is directly related to the T₂^{*} relaxation time.

(4) F is a constant that takes into account the broadening of the satellite peaks. The shape of all satellite peaks is symmetric,

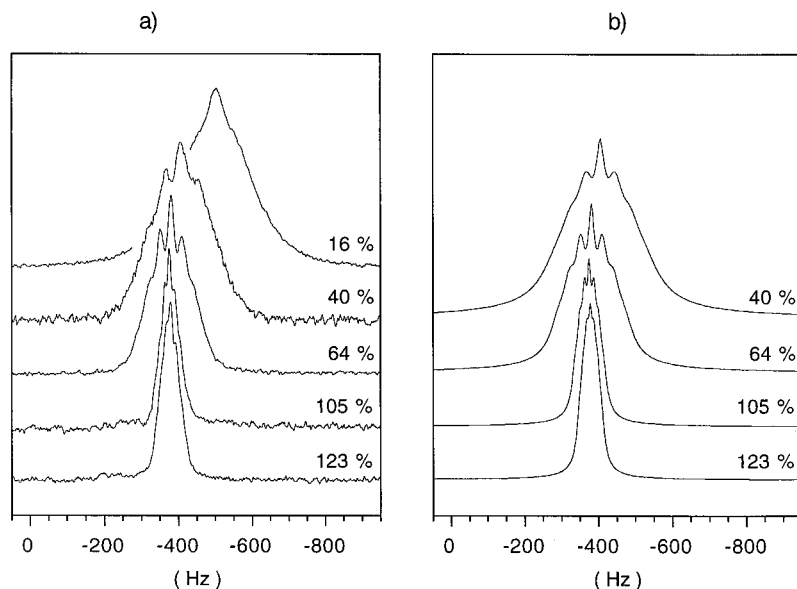


Figure 1. ^{133}Cs NMR spectra of anisotropic PA6/PEG-H₂O/D₂O-CsNO₃ ($\lambda = 3.0$) material as a function of swelling ratio, where, for the sake of clarity, the intensities of the spectra are in arbitrary units: (a) experimental spectra for swelling ratio $S_r = 16\%$, 40%, 64%, 105% and 123%; (b) fitted spectra (eq 4) (because of the signal broadness, spectrum obtained for $S_r \leq 16\%$ is not deconvoluted). Parameters are expressed (in Hz) for the following sequence. S_r swelling ratio: $[\Delta\nu_Q^{(\text{Cs})}]$ quadrupolar splitting; $\omega_{1/2,0}$ central line width; F -order distribution factor; ν_0 chemical shift in reference to 10^{-2} M CsNO₃-H₂O]. 40%: [43; 20.0; 0.21; -406.4]. 64%: [31; 11.5; 0.16; -381.8]. 105%: [13; 7.0; 0.09; -375.2]. 123%: [10; 7.0; 0.08; -378.5].

and thus, this broadening arises mainly from a distribution of a motionally averaged quadrupolar coupling constant¹⁶ even if the orientational distribution of the local director orientation and contributions from magnetic field homogeneities cannot be excluded.¹⁷

IV. Swollen Materials

Figure 1 shows the evolution of NMR ^{133}Cs spectra as a function of swelling ratio for the anisotropic PEBA-H₂O/D₂O-Cs⁺NO₃⁻ system ($\lambda = 3.0$). Each spectrum presents a complex shape that can be deconvoluted using eq 4 (correlation factor $R > 0.98$). The calculated spectra are displayed on the right side in Figure 1. These deconvolutions point out the anisotropic reorientation of the Cs⁺ ions inside the swollen polymer matrix except for very low water content ($S_r < 5\%$) where the signals are rather broad. Figure 2 presents the evolution of the spectral parameters ν_0 , $\Delta\nu_Q^{(\text{Cs})}$, and $\omega_{1/2,0}$ (obtained after fitting), which are observed during the drying process. These data are also presented for anisotropic materials swollen with different H₂O/D₂O-Cs⁺A⁻ solutions by changing the nature of the anion A ($\text{A}^- = \text{ClO}_4^-$, Cl^- , I^- , CH_3COO^- , CF_3COO^-). Similar evolutions of the different parameters were observed for the various polymers, thus providing evidence that the counterions do not influence too much the behavior of the cesium cations inside the swollen materials. For comparison in isotropic PEBA-H₂O/D₂O-Cs⁺A⁻ samples, we observed a single NMR ^{133}Cs Lorentzian signal ($\Delta\nu_Q^{(\text{Cs})} = 0$ Hz) showing similar evolutions for the two other parameters (ν_0 and $\omega_{1/2,0}$). In Figure 2b, the evolution of the ^2H quadrupolar splitting, $\Delta\nu_Q^{(\text{D})}$, of the water molecule is also reported in order to compare the behavior of ions and solvent molecules inside this anisotropic matrix.

Figure 2a shows the gradual shift of the ^{133}Cs resonance, ν_0 , which is measured when the polymers are gradually dried. ν_0 is nearly constant until the $[\text{H}_2\text{O}]/[\text{O}_{\text{PEO}}]$ ratio reaches values between 1 and 3, depending on the anion, for I^- , ClO_4^- , and NO_3^- . Upon further drying, a remarkable decrease of the

chemical shifts is measured. These shifts correspond to the screening of the nucleus and reflect the changes of the Cs⁺ binding shell from mostly water molecules in the highly swelled materials to the oxygen atoms of the PEO ether linkages inside the dried materials. Such chemical shift effects have been already described for Cs⁺ ions probing micellar systems and are related to the fraction of Cs⁺ atoms bound to the polar headgroups and to those that are solvated by the water.^{13,18}

Parts b and c of Figure 2 respectively present the evolution of the quadrupolar splitting, $\Delta\nu_Q^{(\text{Cs})}$, and the central line width, $\omega_{1/2,0}$, of the $^{133}\text{Cs}^+$ ions that are observed by varying the swelling ratio. When the samples are dried from 130% to 25%, these two parameters increase monotonically. When S_r values are below 20%, a single broad line is observed, which does not allow any further deconvolution of these spectra. These results illustrate that two mechanisms are involved in the polymer-cation interactions. They can be explained by the classical physical model of a two-site system similar to those used for membranes or lyotropic systems.¹⁴ The first mechanism, manifested by the increase of quadrupolar interactions, corresponds to a rapid exchange regime between bound ions, which are strongly oriented by the polymer segments, and unbound ions, which are free to move in the anisotropic solvating medium.¹⁴ The fraction of ions strongly bound to the polymer increases when the solvent volume is lowered, and this leads to an increase of the apparent orientational order. This rather common behavior is also observed for water molecules in the entire range of the swelling ratio. The second mechanism is connected to some increase of the central line width, $\omega_{1/2,0}$ (Figures 2c). Such line broadening trends to originate from a decrease in T_2^* associated principally with the decrease of the ion mobilities, as reported in many swelled polymers or gels.¹⁹ In fact during drying the solvating medium for the Cs⁺ ions changes from solvent to polymer sites and a noticeable hindrance of mobility occurs when cations are mainly complexed by polymer segments. The change in the solvation shell of the Cs⁺ ions (the nature and geometry of the bonds) also influences the

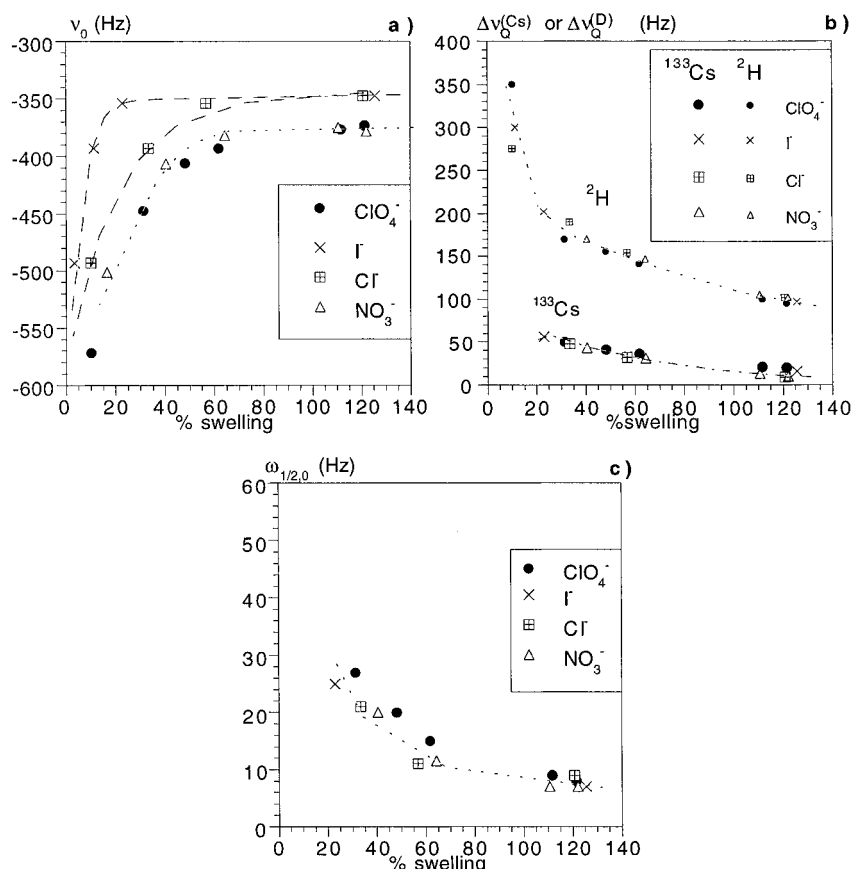


Figure 2. Evolution of different ^{133}Cs spectral parameters with swelling ratio: (a) chemical shift (ν_0); (b) quadrupolar splitting ($\Delta\nu_Q^{(\text{Cs})}$) and ^2H quadrupolar splitting, $\Delta\nu_Q^{(\text{D})}$, of deuterated water; (c) central transition line width ($\omega_{1/2,0}$).

shape and polarizabilities of the electronic cloud; this is also illustrated by the change in the chemical shift of the central line (Figure 2a). Consequently, the changes in the spectra come from both dynamical and structural effects. Some of these effects are clarified in the following sections.

V. Dried Materials

Varying the temperature of dried materials appears to be a simple way to change the molecular and ionic dynamics without affecting the material structure. To avoid residual humidity, the PEBA samples were vacuum-heated (70 °C, 10^{-2} mmHg, 72 h) prior to any measurements until a constant weight was obtained. This process was also controlled by IR spectroscopy, presenting the absence of any ν_{OH} bonds. Next, the NMR tube containing the pieces of PEBA was sealed in order to avoid any moisture.

Figure 3 presents the set of ^{133}Cs NMR spectra recorded between 290 and 380 K for the PEBA- $\text{Cs}^+\text{ClO}_4^-$ material. The areas of these different signals are nearly constant even though for the sake of clarity these spectra have also been normalized to constant intensities. At temperatures below 320 K the spectra appear as a broad line and a complex structure is observed above 330 K, leading to a well-resolved septet around 355 K. The spectra have been fitted using eq 4 with good correlation factors ($R > 0.98$).

The evolution of the quadrupolar splitting as a function of material temperature is presented in Figure 4. At low temperatures the quadrupolar splittings are nearly zero, or at least smaller than the central line width. When the temperature is increased, a significant evolution of the fitted parameters is measured.

There is a noticeable change in the chemical shift of the ^{133}Cs signal, ν_0 , from -650 Hz (-19.8 ppm) down to -1000 Hz (-30.5 ppm) within the temperature range of 290–380 K. It should correspond to the modification of the averaged coordination site with the change of temperature. This effect is enlarged by the considerable Sternheimer shielding factor of the ^{133}Cs nuclei and reflects the strong polarizability of the valence shell of the nuclei.

Figure 4 presents the regular increase of the cesium quadrupolar splitting, $\Delta\nu_Q^{(\text{Cs})}$, which is observed over a more than 70 °C range. The “apparent ionic order” measured from the ^{133}Cs quadrupolar splittings inside these polymeric structures has a rather specific feature because it increases greatly with temperature. These measurements support the idea of the anisotropic reorientation of cations, as was previously observed in oriented Cs–DNA structures.^{20,21} In parallel, the decrease of the line width shows the increase of T_2^* , which is associated with faster reorientational dynamics of ions at higher temperatures.

The same materials have also been investigated using ^2H NMR by dissolving deuterated solvents ($\text{CDCl}_2\text{CDCl}_2$) or poly(ethylene glycol) oligomers end-terminated by acetyl- d_3 groups ($\text{CD}_3\text{COO}-\text{PEO}_{600}-\text{OCOD}_3$) (less than 1 wt %) inside the materials. Next, the ^2H splittings of the $\text{CD}_3\text{COO}-\text{PEO}_{600}-\text{OCOD}_3$ oligomers are reported in Figure 4. They show a plateau until 335 K ($\Delta\nu_Q^{(\text{D})} = 240$ Hz), while at higher temperatures a moderate decrease of the quadrupolar interactions is observed ($\Delta\nu_Q^{(\text{D})} = 210$ Hz at 390 K). Such probes are good solvents of the PEO phase or have a structure similar to that of the PEO itself, and they are known to replicate the reorientational behavior of the polymer segments fairly accurately. It means that S_{probe} has a constant value (which depends on the

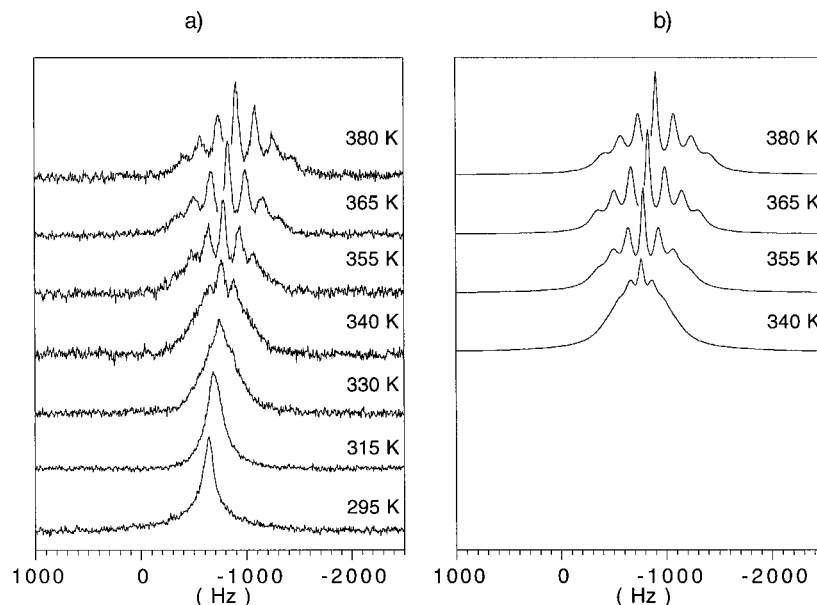


Figure 3. Evolution of ^{133}Cs NMR spectra of anisotropic dried PEBA- CsClO_4 materials ($\lambda = 3.0$) as a function of temperature, where, for the sake of clarity, the intensities of the spectra are in arbitrary units: (a) experimental spectra; (b) fitted spectra (eq 4) (because of to the signal broadness, spectrum obtained for $T \leq 330$ K is not deconvoluted). Parameters are expressed (in Hz) in the following sequence. T sample spectrum: $[\Delta\nu_Q^{(\text{Cs})}$ quadrupolar splitting; $\omega_{1/2,0}$ central line width; F -order distribution factor; ν_0 chemical shift in reference to 10^{-2} M $\text{CsNO}_3\text{-H}_2\text{O}$]. 340 K: [105; 30; 0.24; -765]. 355 K: [147; 30; 0.14; -785]. 365 K: [163; 28; 0.10; -830]. 380 K: [171; 27; 0.12; -906].

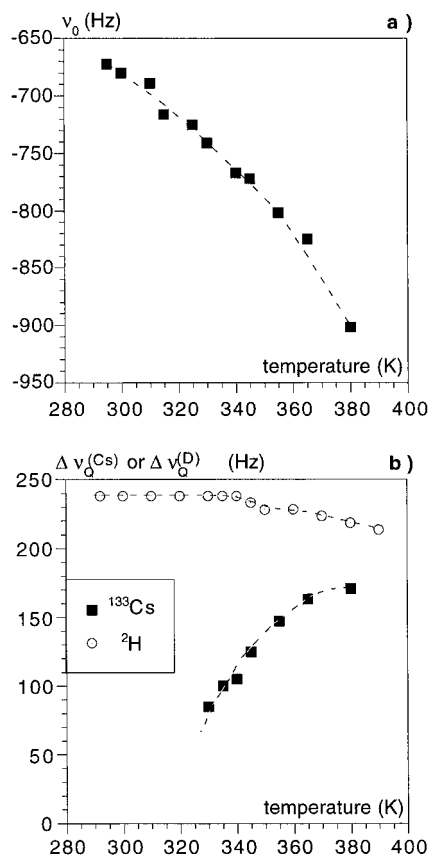


Figure 4. Evolution of different ^{133}Cs spectral parameters with temperature: (a) chemical shifts (ν_0); (b) splitting ($\Delta\nu_Q^{(\text{Cs})}$) and ^2H splitting, $\Delta\nu_Q^{(\text{D})}$, of $\text{PEO}_{600}\text{-bis}(\text{acetyl-}d_3)$ terminated $\{\text{CD}_3\text{COO-PEO}_{600}\text{-OCOCD}_3\}$.

polymer-solvent system),²² and then $\Delta\nu_Q^{(\text{D})}$ reflects directly the behavior of the polymeric segments. Then these measurements show that the order parameter of the polymer chains, S_{polym} , is nearly constant within this temperature range. The

moderate decrease observed at higher temperatures could account for the increase of molecular motion or a moderate mechanical relaxation of the material at higher temperatures.

If the polymer order parameter is nearly constant during these experiments, then the ^{133}Cs NMR quadrupolar measurements depict only strictly the behavior of the cations toward the PEO matrix, as observed in eq 3. Obviously, the significant changes of both chemical shift and "apparent ionic order" are related to some changes in the symmetry of the averaged valence shell of the cations with changes in temperature. To override the averaging, the behavior of ionic species in complex structures is generally described by a multisite model in which ions could be located in j distinct sites, presenting particular host-guest interactions. Then the expression $\bar{\chi}S_{\text{ion}}$ can be expanded as $\bar{\chi}S_{\text{ion}} = \sum_j p_j \chi_j S_j$ where p_j is the fraction of Cs ions at site j , χ_j is the quadrupolar coupling constant at the given j th site and is related to the electronic density distortion from spherical symmetry at this site, and S_j characterizes the order parameter of the j th site, which is defined as $S_j = \langle 3 \cos^2 \theta_{\text{PM}} - 1 \rangle_{\text{PM},j}$ where θ_{PM} is the angle between the normal to the director and the main component of the efg tensor. Such a model has been used in studying cations in oriented DNA fibers.^{14,20} These different sites are characterized by their specific interactions with the surrounding location. From discussions in the literature on polymeric ionic conductors, two principal situations can be considered in our materials.²³ The first one corresponds to cations that are in the complexation site of the PEO chains. The second one corresponds to cesium ions that pair with the counterions. However, a third position could be envisaged: cesium ions in a weak interaction with either the complexation PEO site or the anions. Obviously, from the shape of these signals the exchange rate between the different sites is rapid on an NMR time scale, thus leading to an "averaged" contribution. Assuming that order parameters and efg's for each j site are approximately independent of temperature, the evolution of quadrupolar splitting may reflect the ratio of population in each site, a ratio that should be governed by the free energy difference between sites.¹⁴ These experiments, then, seem to reveal the

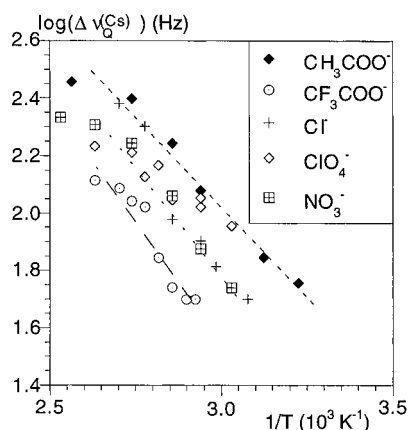


Figure 5. Evolution of ^{133}Cs quadrupolar splittings with temperature for numerous PEBA–CsA materials ($\text{A}^- = \text{ClO}_4^-, \text{Cl}^-, \text{Br}^-, \text{CH}_3\text{COO}^-, \text{NO}_3^-, \text{CF}_3\text{COO}^-$). The choice of scale $\log_{10}(\Delta\nu_Q^{(\text{Cs})}) = f(1/T)$ helps in following the tendency.

change of the averaged complexation mode of the Cs^+ cations with temperature.

Similar experiments have been performed with polymers doped by different Cs^+ salts, and the same effects were measured: the upfield chemical shifts and the unusual increase of “apparent ionic order” with temperature were observed for different systems. Also, the $\Delta\nu_Q^{(\text{Cs})}$ measured around 390 K varied from 140 Hz for $\text{CF}_3\text{COO}^-\text{Cs}^+$ up to 300 Hz for $\text{CH}_3\text{COO}^-\text{Cs}^+$. The variations of $\Delta\nu_Q^{(\text{Cs})}$ for the different materials show a strong dependence with the temperature ($1/T$) (Figure 5). Such an evolution could suggest some similarity to Arrhenius or free volume plots, which are used to describe thermally activated processes of ions inside some polymeric networks.²³ This is also fully compatible with the evolution of equilibrium constants for ions inside a multisite system. This feature serves as additional support to our contention that quadrupolar splittings measured on ^{133}Cs spectra are closely associated with the jump of the cesium ion from site to site.

A contribution to the equilibrium state between the different species (sites) is evidently related to the dynamics of the polymer chains and ions. Reorientation of the polymer segments, occurring between the cross-linking nodes (PA crystallites), is extremely localized in space and is thermally activated.²⁴ Yet, ions have reorientational and diffusional degrees of freedom and are expected to diffuse over the whole structure by successive hopping from one complexation site to the next. These displacements are correlated with the motions of the polymer segments.^{3,6,25,26} The increase of mobility of all species with temperature is evidenced by the line width evolutions. The neighborhood of the cations is affected by the change of temperature. The nature of the complexing ligands of Cs^+ is guided by a competition between the proximity of ClO_4^- anions in the ionic shell (related ion pairing) and the solvation of ionic species inside the polymer, thus acting as a charge separation process.²⁷ These effects are also correlated with dynamical contributions arising from the chain segment motion and the ion diffusion, which could severely change the geometry of the cation coordination cage²⁸ and the consequence of large chemical shifts.

VI. Conclusion

This paper presents, to the best of our knowledge, the first report of quadrupolar NMR measurements of Cs^+ cations dissolved inside an anisotropic synthetic polymeric structure.

The moderate magnitude of the quadrupolar interaction enabled us to observe narrow septets using ^{133}Cs NMR spectroscopy inside these oriented media. We contend that cations experience an anisotropic motion related to that of polymeric segments in both swelled materials (gel-like) or dried structures (polymer-electrolyte-like). Actually, the behavior of these cations may be quite complex and depends greatly on the solvation shell. These measurements appear to provide a way to monitor the complexation state of cations in a complex medium such as swelled amorphous materials. In dried materials, the “apparent ionic order” increases as the temperature is raised. Such unusual behavior demonstrates that quadrupolar splittings reflect the population change of ions that can be solvated, complexed, or ion-paired (etc.) inside an anisotropic polymeric backbone. The equilibrium is modified by the sample temperature, which also plays a role in the local dynamics.

The comparison between molecules and alkali ions indicates they act differently in the polymeric medium. These observations are very likely related to the differences between polymer–molecule interactions and polymer–ion interactions. Molecules are dissolved inside the anisotropic structures and are guided by the macromolecular anisotropic backbone. Yet ions are complexed by specific assemblies of oxygen atoms in the PEO chains, and the electrostatic binding forces compete with Coulombic ion pair interactions. The measurement of quadrupolar splittings of selected probes may finally provide an approach to characterize reorientational anisotropic behavior that reflects probe–backbone relationships.

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