Direct NMR Evidence for a Local Restriction in the Segmental Chain Mobility of a Model Ionomer

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ABSTRACT: To probe the local mobility of the chain segments directly attached to ionic multiplets, two model ionomers have been synthesized. The first one is a carboxylato-telechelic deuterated polystyrene in which the chain segments bearing the sodium carboxylate end groups have been selectively protonated; the second one has a protonated polystyrene backbone terminated at both ends with a deuterated polystyrene segment bearing the sodium carboxylate groups. Both polymers have been studied by high-resolution solid-state ^{13}C NMR. Line-width measurements of the protonated units have clearly shown that the dipolar interactions of the sodium carboxylate end groups are responsible for a mobility restriction of the chain end segments. This experiment is thought to be the first direct evidence for the model recently proposed by Eisenberg *et al.* for ionomer morphology according to which the ionic multiplets are surrounded with a shell of constrained polymer segments.

Introduction

Over the last 30 years, a number of ion-containing plastics and elastomers, designated as ionomers, have been developed. Their unique mechanical, rheological, and transport properties result from the intermolecular interactions of the ionic moieties. The specific advantages of ionic interactions have been exploited in a large range of applications including thermoplastic elastomers, polymer impact modification, oil-based drilling fluids, adhesives, lubricants, antistatics, magnetic recording and imaging systems, and permselective and microencapsulation membranes.[1-3]

The basic question addressed to the scientist is the following: what are the morphological changes promoted by the ionization of the base polymer? In other words, what is the spatial arrangement of the few ionic groups responsible for the original properties of the ionomers?

A considerable body of experimental and theoretical work has focused on the structure of ionomers. Several experimental techniques have been used, among which electron microscopy has usually failed to give a direct and reliable image of the ionomer morphology.[4,5] Extensive studies by dynamic mechanical analysis (DMA)[1,6] and dielectric spectroscopy[7-10] have indicated that ionomers are two-phase materials, consisting of a major phase with the characteristic features of the nonionic precursor and a minor phase with a much higher glass transition temperature, T_g, in which ion pairs are concentrated. Small-angle X-ray and neutron scattering have been of the utmost importance in the interpretation of the structure of ionomers.[1,11-16] The main feature of the diffraction profiles is the so-called "ionic peak", the position of which allows Bragg distances in the range of 1-15 nm to be calculated. The morphological information provided by SAXS and SANS is not equivalent to the two-phase behavior evidenced by DMA, since this method cannot detect domains smaller than 50 mm.

Very early, the ionic peak was considered as a signature for ionic aggregation. Several models have been proposed that give a geometrical description of the aggregates and of their spatial organization. They usually refer to two kinds of ionic aggregates, designated as multiplets and clusters. Multiplets contain up to ca. 10 ion pairs,[17,18] whereas clusters are larger structures rich in ion pairs, phase-separated from the continuous polymer and responsible for the mechanical properties. As a rule, in all the models that have been proposed to account for the SAXS data, multiplets are the basic scattering units. The ionic peak is assigned either to an interference between aggregates or to the internal structure of the noninteracting particles.[2]

The understanding of the ionomer morphology has been greatly improved by the study of halato-telechelic polymers (HTP's). HTP's are model ionomers consisting of short linear chains terminated by an ionic group at each extremity. They have very well-controlled molecular characteristics and clean architecture. The important conclusions of the HTP investigation are the following:[15] the ionic domains, typically multiplets, are small and their dimensions, on the order of 6-9 Å, do not depend much on the nature of the cation in a given series of carboxylato-telechelic polymers. The microphase separation between ionic and nonionic moieties is sharp and tends to be complete when the polymer polydispersity is small. The average distance between domains is determined by the molecular weight of the subchains between the domains, which adopt a coiled configuration. Finally, the domains are likely to be organized in a liquidlike manner, with a "correlation hole" surrounding each ionic aggregate from which all other ionic domains are excluded.

The model for the ionomer structure, recently proposed by Eisenberg *et al.*,[19] is quite consistent with most of the available experimental data, including dynamic mechanical results. The authors assume that the ionic groups are aggregated into multiplets and that chains in close proximity to their points of attachment to a multiplet experience a restriction in mobility. Each multiplet is thus surrounded by a region of restricted mobility, the

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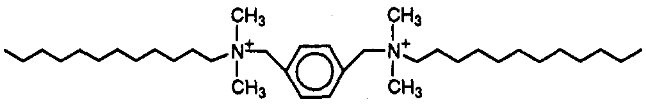
thickness of which is assumed to be on the order of the persistence length of the chains. Above a critical ion content, the low-mobility regions overlap and form domains large enough to have their own glass transition temperature. These domains constitute clusters. Under these conditions, the ionomer exhibits a typical two-phase behavior. Of course, the ion-pair content in the HTP's is too small for clusters to be formed, in agreement with experimental observations.[20]

At the present time, no direct experimental evidence for a local restriction in the chain mobility has been reported. Recent measurements performed by Yano *et al.* on a model HTP using dielectric spectroscopy have shown the existence of an α relaxation characteristic of the micro-Brownian motion of chain segments directly attached to the quaternary ammonium end groups.[21] As compared to the α relaxation of the nonionic material, this α relaxation is shifted toward higher temperatures and its amplitude is an order of magnitude higher. However, the model cationic ionomer used by Yano *et al.* has two quaternary ion pairs covalently bonded to each other by a *p*-xylyl bridge:



In addition to the ionic aggregation, the rigidity of the aromatic bridge may also contribute to the mobility restriction observed by dielectric spectroscopy.

NMR spectroscopy is an alternative and versatile method for probing local dynamics.[22-25] To detect regions having an eventual restricted mobility in ionomers, it is necessary to obtain selective NMR spectra of the chain segments in the close vicinity of the ionic groups. In this paper, the ability of the high-resolution solid-state ^{13}C NMR technique to obtain different responses from the central and end segments, that have identical chemical shifts, is based on the different behaviors of protonated and deuterated carbons in a cross-polarization experiment. The model ionomers studied in this work are well-characterized carboxy-telechelic polystyrenes in which either the central units or the end segments have been deuterated. It must be noticed that the deuteration is not expected to modify the ionomer behavior significantly. Moreover, polystyrene-based systems have been extensively investigated by NMR.[24-28]

Experimental Section

Polymer Synthesis. α,ω-Carboxylic acid polystyrene was synthesized by living anionic polymerization, as detailed elsewhere.[29] Styrene was carefully dried just before use, and freshly prepared naphthalene–lithium was used as a difunctional initiator. Typically, the required amount of initiator was added to freshly dried THF in a previously flamed glass reactor under nitrogen at room temperature. After cooling to −78 °C, styrene (or styrene-d_8) was added dropwise. Polymerization was allowed to proceed for 30 min, and a sample was withdrawn for characterization. The appropriate amount of styrene-d_8 (or styrene) was finally added dropwise, and the polymerization was allowed to proceed for an additional 20 min. The living anionic species were deactivated by bubbling dry CO$_2$ into the reaction medium kept at −78 °C. Bubbling was maintained for 15 min, and the polymer was twice precipitated in acidified methanol.

α,ω-Carboxylic acid polystyrene was converted into the corresponding sodium salt by end neutralization with sodium methoxide in anhydrous toluene, as reported elsewhere.[29] Molecular weights were measured by size-exclusion chromatography in THF (calibrated with polystyrene standards). Functionality was calculated from the molecular weight data and potentiometric titration of the acid end groups with tetramethylammonium hydroxide in a toluene/methanol 9/1 mixture.

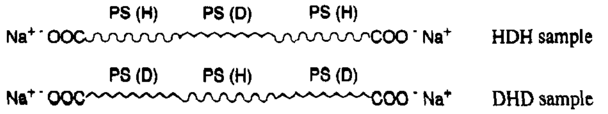


Figure 1. Schematic drawing of the two selectively deuterated HDH and DHD α,ω-sodium carboxylate polystyrenes.

Table 1. Molecular Characteristics of the HDH and DHD Samples

sample	$\bar{M}_n{}^a$	$\bar{M}_n{}^b$	$\bar{M}_n$, total	$\bar{M}_w/\bar{M}_n$	f (%)^c	T_g (K) (DTA)
HDH	9500	500	10 500	1.15	99	376
DHD	9000	500	10 000	1.15	100	373

[a] $\bar{M}_n$ of the central part of polystyrene. [b] $\bar{M}_n$ of each polystyrene terminal segment. [c] Carboxylation efficiency of the polystyrene chain ends.

NMR Measurements. High-resolution solid-state ^{13}C NMR spectra were recorded by combining the techniques of cross-polarization (CP), proton dipolar decoupling (DD), and magic-angle spinning (MAS) at an operating frequency of 75.47 MHz on a Bruker CXP 300 spectrometer. The strength of the ^{13}C and ^{1}H fields used in cross-polarization was 63 kHz, and the contact time was 100 μs. A variable-temperature Doty probe was used for all the measurements. Alumina spinners were of the cylindrical double-bearing type. The spinning speed ranged from 3500 to 4000 Hz, which did not allow complete disappearance of the spinning side-bands associated with the polystyrene ^{13}C aromatic resonances. Usually 2000 transients were accumulated to provide an acceptable signal-to-noise ratio. Measurements were performed at temperatures up to 443 K for the DHD polymer. Owing to the low percentage (10%) of protonated material in the HDH sample and the rapid decrease of ^{13}C sensitivity upon increasing temperature, measurements were not reported at temperatures above 433 K for this sample.

Results and Discussion

Two selectively deuterated α,ω-sodium carboxylate polystyrenes were synthesized, as schematized in Figure 1. Their abbreviated names and characteristics are summarized in Table 1. The total molecular weights of the HDH and DHD samples are 10 500 and 10 000, respectively. The glass transition temperatures are close to 373 K, which is the usual value for polystyrene chains.

The length of the terminal segments has been designed to match as closely as possible the thickness of the shell surrounding each multiplet. For polystyrene, this shell should be *ca.* 10 Å thick, which is the polystyrene persistence length, corresponding to 5–6 styrene units. Accordingly, each terminal segment in the HDH and DHD samples has a molecular weight of 500.

The protonated sequences of the HDH and DHD polymers were selectively detected by using a cross-polarization pulse sequence with a short contact time. The cross-polarization technique takes advantage of magnetization transfer from ^{1}H to ^{13}C in order to improve the ^{13}C sensitivity. During the first tens of microseconds of the contact, the energy transfer occurs between a carbon and its directly bonded protons. Then, at longer times, more remote protons transfer a part of their magnetization via the mechanism of ^{1}H–^{1}H spin diffusion. The delay necessary for the spin diffusion to be efficient on a length scale of 10 Å is on the order of 10 ms in solid polymers.[30] Therefore, a contact time as short as 100 μs insures that the carbons benefit from the magnetization transfer from nearby protons only, and only the carbons located in the protonated segments of the PS chains give rise to a significant signal. In contrast, as no significant spin diffusion can occur on a 10-Å scale, which is the size of the smaller deuterated domains in the PS chains, the carbons in the deuterated segments are not expected to gain a significant magnetization. The selectivity of the method has been checked by comparing the signal-to-noise ratio observed for the HDH and DHD polymers. Under similar experimental conditions, the signal-to-noise ratio is much higher in the DHD polymer than in the HDH polymer. The signal intensity is in qualitative agreement with the relative number of protons in these two samples.

Analysis of the temperature dependence of polystyrene (PS) spectral line widths is a usual way of probing the segmental mobility of this polymer.[24,31] Under suitable conditions of magic-angle sample spinning and proton decoupling irradiation, line broadenings that exceed a few ppm are promoted by relaxation mechanisms. The relaxation mechanism depends, however, on the chemical environment of the carbon considered. For carbons having a high chemical shift anisotropy, motional modulation of the chemical shift anisotropy gives rise to a line broadening that is maximal when the rate of molecular motion is equal to the sample spinning speed,[32] that is, around 4000 Hz. In contrast, the motional modulation of the dipolar carbon–proton coupling leads to line broadening for carbons having strong dipolar carbon–proton coupling. In the latter case, line broadening is maximal when the rate of molecular motion is equal to the proton-decoupling radio-frequency field strength,[33] that is, close to 60 kHz. As shown in the NMR study of PS/poly(vinyl methyl ether) blends, the motional broadening of the PS aliphatic carbon line arises from motional modulation of the dipolar coupling. For the PS protonated aromatic carbon resonance, motional modulations of both the dipolar coupling and chemical shift anisotropy are active relaxation mechanisms. However, although these two mechanisms probe motions in a somewhat different frequency range, this frequency difference corresponds to a temperature difference of only a few degrees.[24] These line-broadening measurements have proved most useful to investigate the local motions associated with the glass transition phenomenon in the PS/poly(vinyl methyl ether) compatible blends. The observation of a parallel temperature dependence for the PS aromatic and main-chain carbon line broadenings has led to the conclusion that the PS main chain and side rings are involved in correlated motions.[24]

As an example, the temperature dependence of the DHD ^{13}C NMR spectra is illustrated in Figure 2. The solid-state ^{13}C chemical shifts are close to those observed for the polymer in solution. However, the lines are broader. The unprotonated and protonated aromatic carbon resonances are centered around 145 and 127 ppm, respectively. The peak located around 40 ppm is a composite line resulting from the superposition of the relatively narrow resonance of the methine carbon and the broader resonance of the methylene carbons, which is sensitive to tacticity effects. The first-order spinning sidebands of the aromatic carbons (star-labeled in Figure 2) are well-separated from the ^{13}C main lines.

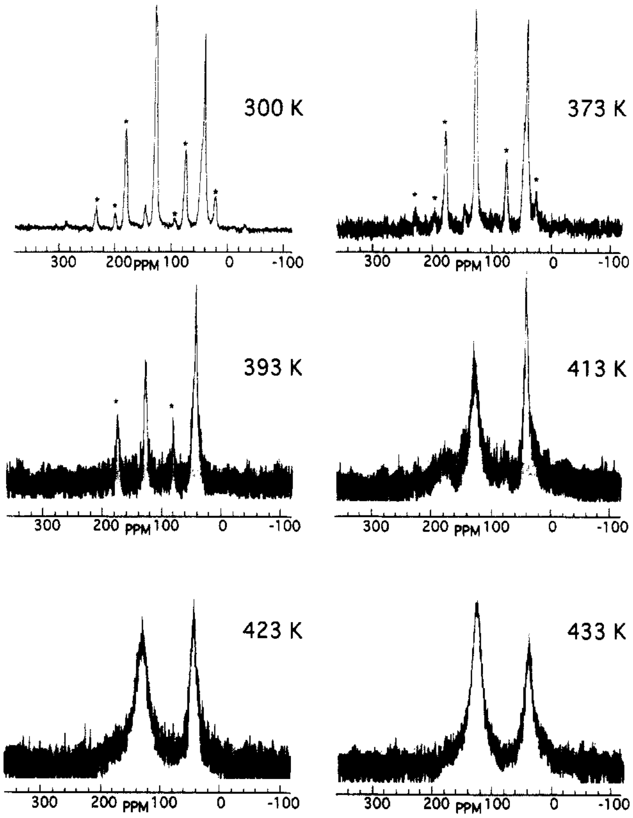


Figure 2. High-resolution solid-state CP/MAS/DD ^{13}C NMR spectra of the DHD sample, recorded at 75.47 MHz as a function of temperature, *T*.

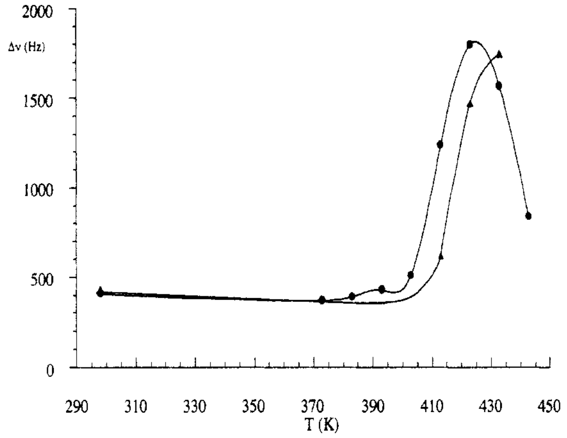


Figure 3. Variation of the PS protonated aromatic carbon line width as a function of temperature, *T*, for the HDH (▲) and DHD (●) samples. Lines are guides for the eyes.

As shown in Figure 2 for the DHD polymer, at temperatures above 410 K, large line-broadening variations are observed for both the aromatic and aliphatic lines. Simultaneously, the spinning sidebands tend to disappear. Figure 3 illustrates, for both polymers, the temperature dependence of the line width at mid-height of the protonated aromatic carbon line. For the DHD polymer, there is, initially, a large line broadening with increasing temperature, followed by a subsequent narrowing at higher temperatures. The order of magnitude of the maximum line broadening is beyond the static line broadenings. These line-width variations are comparable to those observed for the PS protonated aromatic carbon resonance in PS/poly(vinyl methyl ether) above the glass transition temperature.[24] They are a clear indication of aromatic carbon motions associated with the glass transition phenomenon and having frequencies on the order of 4–60 kHz, depending on the exact line-broadening mechanism of interest for the PS protonated aromatic carbons.

As shown in Figure 3, in the temperature range investigated, the line widths at mid-height of the protonated aromatic carbon line have parallel temperature dependences in the HDH and DHD polymers. The only observed difference is a systematic shift of 7–10° toward high temperature of the HDH curve with respect to the DHD one. For example, the maximum line broadening is reached at 423 and 433 K in the DHD and HDH samples, respectively. This result indicates that the motions of the aromatic carbons are somewhat slower in the end chain

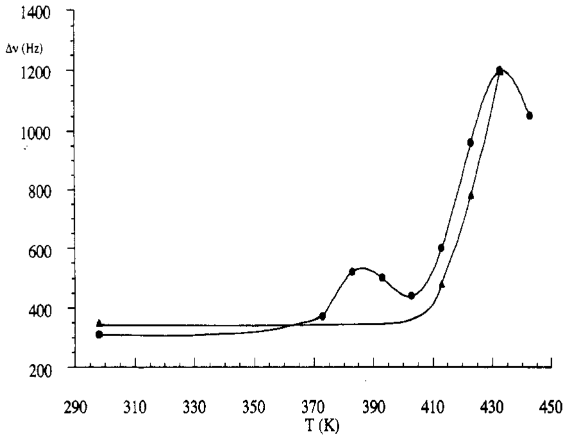


Figure 4. Variation of the PS aliphatic line width as a function of temperature, *T*, for the HDH (▲) and DHD (●) samples. Lines are guides for the eyes.

segments of the HDH polymer than in the central units of the DHD compound.

In Figure 4 are shown the temperature variations of the line widths at mid-height of the composite resonance of the aliphatic carbons. At temperatures below 413 K, the data dispersion is not significant. It reflects the fact that the overlap of the methine and methylene carbon lines is not strictly identical at the temperatures considered. In this temperature range, the line width is essentially of static origin. Its value originates mainly from tacticity effects. In contrast, at temperatures above 413 K, the much higher values of the line widths indicate the occurrence of motions of the aliphatic carbons associated with the glass transition phenomena and with a frequency on the order of some tens of kilohertz. It must be noted that the maximum line broadening in the DHD polymer is observed at a temperature lower by 10° for the aromatic carbon resonance than for the aliphatic carbon line, in agreement with the underlying relaxation mechanisms. Moreover, as noted for the PS chains in PS/poly(vinyl methyl ether) compatible blends above the glass transition temperature,[24] the parallel behavior of the aromatic and aliphatic resonances indicates that the observed motions of the chain and side rings are correlated.

As for the aromatic carbon line widths, the behavior of the aliphatic lines is very similar for the HDH and DHD samples, except for a temperature shift of 7–10° toward high temperature of the HDH curve with respect to the DHD one. The fact that the maximum line broadening is reached at a temperature 10 K higher for the end segments than for the central sequences is clear evidence of mobility restriction in the close vicinity of the ion pairs. Local motions are slower in the PS segments directly attached to the carboxylate end groups than in the less-constrained central segments. This result is in sharp contrast with data obtained on nonionic PS chains. In this case, the chain ends are dangling and thus more mobile than the central polymer segments. This behavior is supported by recent ^{2}H NMR measurements performed by Kornfield *et al.* on selectively deuterated polystyrene chains.[27] These authors have shown that the onset of mobility occurs 20 K earlier in the chain ends than in the central segments. On this basis, the presence of one sodium carboxylate group at each extremity of a polystyrene chain is responsible for an estimated 30 K increase in the temperature at which the local motions associated with the glass transition phenomenon manifest themselves in ^{13}C NMR experiments.

The NMR measurements reported in this paper, that give direct evidence for a shell of restricted polymer mobility surrounding each multiplet, are in complete agreement with the model proposed by Eisenberg *et al.*[19] It must be pointed out that the mobility restriction is expected to be less drastic in HTP's than in random ionomers. Indeed, in HTP's, the ion pairs are attached to only one chain segment, whereas in ionomers, they are randomly attached to the polymer backbone as pendent groups, so that two polymer segments per ion pair emerge from the multiplet. Steric hindrance and mobility restriction should thus be more severe in the shell surrounding multiplets formed in ionomers. Furthermore, the ionic interactions in carboxylic ionomers are known to weaken above 410 K.[1–6] Since, in the above example of the HDH and DHD carboxylato-telechelic polystyrenes, the mobility restriction has been observed above 410 K, its magnitude has been more than likely underestimated. This adverse effect could be avoided by substituting either the metal carboxylate ion pairs by metal sulfonate ones or the polystyrene backbone by a low-T_g polymer (a polydiene, for example).

Conclusions

In the selectively deuterated α,ω-sodium carboxylate polystyrenes, the segmental motions associated with the glass transition phenomena have been detected by ^{13}C NMR at a higher temperature for the terminal segments than for the central units. This behavior is in sharp contrast with previous results obtained on nonionic polystyrene[27] in which the chain ends have proven to be more mobile than the central part of the chain. Thus, the ion-pair aggregation into small multiplets results in the buildup of a shell of constrained polymer segments around the ionic domains. To the best knowledge of the authors, this experiment is the first direct evidence of local mobility restriction which is the characteristic feature of the model recently proposed by Eisenberg *et al.* for the structure of traditional ionomers.[19]

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