

Methyl Ester Carboxylates: A Nuclear Magnetic Resonance Study

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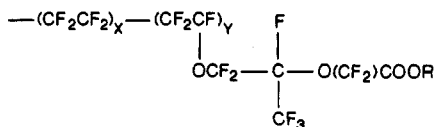
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ABSTRACT: Nuclear magnetic resonance has been used to investigate relaxation in the methyl ester precursor of a perfluorocarboxylate ionomer. Whereas the findings are broadly consistent with earlier interpretations of dynamic mechanical relaxation, minor interpretative changes are indicated, principally a revision of the assignment of the γ relaxation peak in the DMA data. Further insight is also obtained into the way in which even quite small amounts of water can influence in an important way the overall relaxation response of the system.

Introduction

A sustained interest in perfluorinated sulfonate and carboxylate ionomers attests both to their intriguing properties and to their commercial importance. Several studies^{1,2} have thus far exploited a wide variety of techniques in an attempt to unravel their complex molecular behavior which depends sensitively upon a number of important parameters, including equivalent weight, water content, nature of the cation, and degree of neutralization. It is noted, in addition, that interpretive difficulties have arisen through inadequate sample characterization.^{3,4}

This paper forms part of a continuing series on carboxylate systems having the structure



In an earlier paper,⁵ dynamic mechanical data were analyzed for the methyl ester precursor ($R \equiv \text{CH}_3$) and for a number of salts ($R \equiv \text{Na}, \text{K}, \text{Cs}, \text{Ag}, \text{N}(\text{C}_4\text{H}_9)_4, \text{Mg}, \text{Ba}, \text{Zn}$). Two ion-exchange capacities (IEC) of 1.25 and 1.8 mequiv/g were considered. The Na salt exhibited five peaks in the $\tan \delta$ vs. temperature response. In order of decreasing temperature, the α peak was assigned to motions associated with the glass transition in the ionic phase, the β relaxation reflected micro-Brownian segmental motions accompanying T_g of the fluorocarbon phase, β' was tentatively assigned to motions of the long-chain side groups, the γ' relaxation was assigned to local motions of those parts of the polar side groups that were not separated from the fluorocarbon matrix, and the γ relaxation, not unexpectedly, was considered to originate from local CF_2 motions in the main chain. Phase separation was a characteristic of the 1.25 IEC material excepting the dry acid, although, significantly, phase separation could be induced even in this sample upon hydration, as evidenced by the effects of water on the mechanical relaxation peaks.⁵ This is an important observation. In contrast, the 1.8 IEC material appeared essentially to be a dominant single ionic phase with the less polar fluorocarbon as a minor phase, if present at all. This was attributed to the high concentration of polar groups (ca. 36 mol %).

The methyl ester precursors are singled out for further study in this paper. Only two peaks were observed in the dynamic mechanical data, attributed respectively to the β and γ relaxations. An interesting feature of these data was the unusually high temperature quoted for the " γ

peak" compared with the acid and salt forms or indeed compared with other related fluorocarbon polymers.⁶ A nuclear magnetic resonance study was carried out in order to explore further this somewhat puzzling aspect and, more generally, to gain greater insight into the general molecular dynamics of the precursors. NMR has generated a substantial body of important data, yielding detailed and occasionally unique insight into heterogeneous systems such as the ones of interest in this paper.^{7,8}

Experimental Section

The materials under investigation were obtained from Asahi Glass Co. and have been fully described elsewhere.⁵ About 1 g of the completely amorphous polymer film was cut into small pieces, placed in an NMR tube, and sealed after evacuation for a period of about 14 h. NMR data for both ^1H and ^{19}F nuclei were recorded over the temperature range 150–400 K on a Bruker SXP spectrometer operating at 40 MHz and interfaced to a Commodore PET computer via a Biomation digitizer. Sample temperature was controlled to ± 1 K. The spin-lattice relaxation time, T_1 , was determined by means of the $180^\circ\text{--}\tau\text{--}90^\circ$ pulse sequence.⁹ The spin-spin relaxation time T_2 was deduced from the free induction decay following a 90° pulse or from the $90\text{--}\tau\text{--}180^\circ$ sequence as appropriate,⁹ and the spin-locking sequence $90^\circ\text{--}90^\circ$ (90° phase shift) yielded the rotating frame relaxation time $T_{1\rho}$ at a selected H_1 radio-frequency field of 10 G.¹⁰ Data analysis followed established procedures.^{7,11} The two samples with ion-exchange capacities (IEC) of 1.8 and 1.25 mequiv/g are hereafter denoted S(1.8) and S(1.25), respectively.

Results and Discussion

T_1 , T_2 , and $T_{1\rho}$ ^{19}F and ^1H resonance data are portrayed for S(1.25) and S(1.8) in Figures 1 and 2. Results for the two samples are superimposed for ease of comparison. In analysis of the data, a number of general observations are first drawn and then more detailed assignments are considered through exploitation of transition maps which compare the NMR results with those of other relaxation experiments.

^{19}F relaxation times exhibit behavior that is broadly typical of related polymers.^{3,4,12} T_2 in the higher temperature region reflects a predominantly bimodal distribution of relaxation times, and one can visualize part of the polymer to be more constrained than the other but with significant cooperativity between components as evidenced by the way in which the two T_2 components increase in consort with increasing temperature. This is not unlike the observed response in another nominally amorphous polymer, PVC, which has been shown to have appreciable small-scale heterogeneity and is in keeping with the earlier predictions of extensive phase mixing of

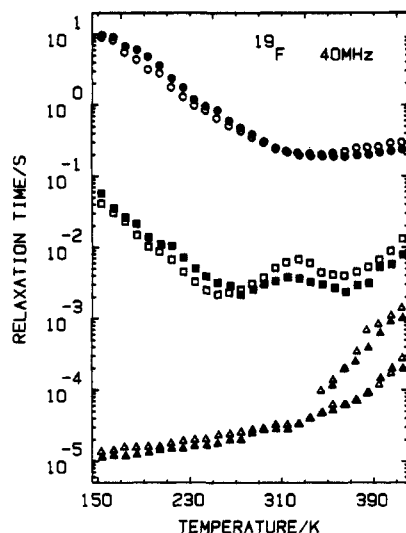


Figure 1. T_1 (○, ●), $T_{1\rho}$ (□, ■), and T_2 (△, ▲) data for ^{19}F resonance as a function of temperature in S(1.25) (unfilled points) and S(1.8) (filled points).

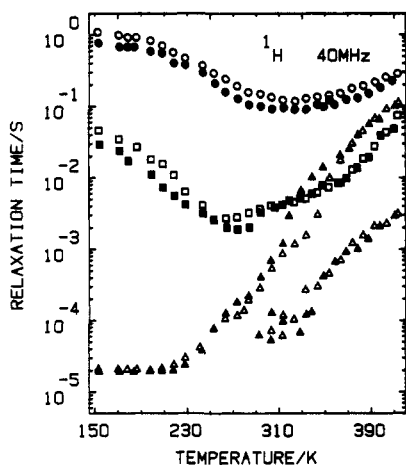


Figure 2. T_1 (○, ●), $T_{1\rho}$ (□, ■), and T_2 (△, ▲) data for ^1H resonance as a function of temperature in S(1.25) (unfilled points) and S(1.8) (filled points).

Table I
NMR T_2 Intensity Data

| sample | $T_{2L} (^1\text{H})$ | $T_{2L} (^{19}\text{F})$ | calcd fractn ^{19}F nuclei in side chain |
|---------|-----------------------|--------------------------|---|
| S(1.25) | 0.20 ± 0.10 | 0.38 ± 0.08 | 0.28 |
| S(1.80) | 0.48 ± 0.10 | 0.56 ± 0.08 | 0.42 |

the fluorocarbon matrix and the polar groups.⁵ Note, too, that T_1 and $T_{1\rho}$ are single valued over the entire temperature range. The long T_2 component, T_{2L} , is assigned to side-group motions on the basis of a quantitative comparison of the relative numbers of ^{19}F nuclei in the side group and main chain, respectively, with the observed T_2 component intensities (Table I). The short T_2 component, T_{2s} , has a magnitude that is comparable to the amorphous T_2 in a related member of the fluorocarbon family, the tetrafluoroethylene/hexafluoropropylene copolymer (FEP),¹⁵ and in all probability reflects backbone motion.

Inasmuch as there are no ionic species present, clustering is not anticipated. As observed in Figure 3, the increase in T_2 with temperature exhibits no intermediate plateau region typical of clustering and is closely similar to that observed in the perfluorosulfonate "Nafion" precursor,¹² confirming that clustering is absent in S(1.8) and S(1.25). The temperature at which T_2 begins to increase is higher

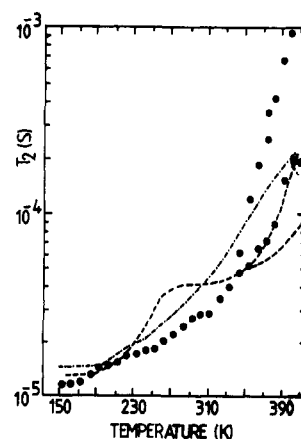


Figure 3. Comparison of ^{19}F T_2 data for S(1.8) (●) with the T_2 response for the Nafion precursor³ (---) and the amorphous component in FEP (---).¹⁵

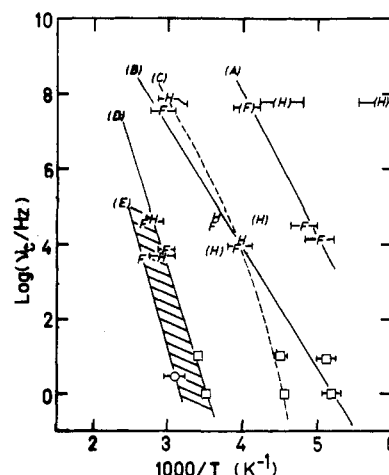


Figure 4. Transition map for S(1.8). (H) denotes ^1H NMR data; (F) denotes ^{19}F resonance data; (○) and (□) derive from DSC and DMA data, respectively. Points in parentheses signify that the transition is barely detectable and is therefore doubtful. The various loci are discussed in the text.

than in the Nafion precursor,¹² indicating a somewhat higher glass transition temperature in S(1.8) and S(1.25).

For the ^1H resonance data, it is significant that two T_2 components are resolved over a wide temperature range. The behavior of T_2 indicates the onset of general motions beginning at ~ 230 K, achieving liquidlike character at high temperatures. It is most probable that the supposedly dry polymers in fact contain small amounts of water that behave in the same complex way as, for example, water in Nafions.^{3,16} The T_{2s} component is assigned to the only other source of protons, namely the methyl groups. This assignment of the two T_2 components, though highly probable and consistent with earlier observations in ionomers, is not unequivocal since methyl groups themselves can exhibit complex relaxation profiles leading to multi-component T_2 decays.¹⁷ On the basis of the T_2 (^1H) component intensity data in Table I it is estimated that S(1.8) and S(1.25) contain 4.4 and 0.8 wt % of water, respectively. These estimates are entirely plausible in view of the greater propensity of the higher IEC sample to absorb water.

Correlation frequencies, ν_C , extracted from the NMR data in the usual way⁶⁻⁸ are compared with dynamic mechanical⁵ and DSC data in Figures 4 and 5. As with similar systems it is a major task to decide upon appropriate loci; the loci as drawn are tentative. On closer inspection of the earlier DMA results it would appear that there is a shoulder on the low-temperature side of the " γ

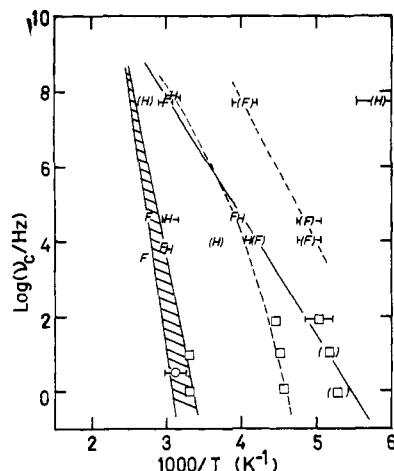


Figure 5. Transition map for S(1.25). The notation is the same as in Figure 4.

peak". This has been afforded the status of a separate relaxation on the transition maps of Figures 4 and 5.

Consider the relaxations in S(1.8) in order of increasing temperature. There is evidence of a shallow T_1 (^1H) minimum in the vicinity of 170 K which may well reflect terminal methyl group motion. The relaxation denoted A in Figure 4, although weak, was also observed in the perfluorosulfonate precursor and acid¹² and was tentatively assigned to the onset of motion of the perfluoromethyl groups in the side chain. This would appear to be reasonable. Locus B is assigned to the γ relaxation associated with CF_2 motions in the main chain. The position of this locus and the activation energy are generally consistent with the γ relaxation in a number of related polymers and, coincidentally, is consistent with the assignment of the DMA shoulder peak rather than the main peak to the γ relaxation.^{5,6,12,15} The dashed locus, labeled C, may well reflect the glassy behavior of the water present.¹⁶ It can be fitted to the WLF equation¹⁸ with $T_g = 200$ K and $\log \nu_0 = -4.8$. The two proton relaxation points between loci B and D at $1000/T = 3.66$ are consistent with the presence of free water in the sample. On the basis of T_2 component intensity assignments, locus D is associated with general

side-group motions, while locus E predominantly reflects the onset of general motions of the main chain. The shading between the two high-temperature loci implies a region of significant cooperativity between the onset of the glass transition for the main chain and side groups. This general scheme of interpretation is considered also to describe the S(1.25) data.

In summary, it is clear that the NMR results provide detailed additional perspective on the behavior of the methyl ester carboxylate precursors at a molecular level. Interpretations are largely consistent with the conclusions of the earlier report on these materials⁵ but indicate, in addition, the way in which even small amounts of water in the sample can influence the observed relaxation response. The assignment of the γ relaxation in the previous work has been revised in the light of the NMR data.

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