The Interaction of Water with Polyurethanes Containing Block Copolymer Soft Segments

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SYNOPSIS

The saturation water uptake and nonfreezing water, determined as a function of temperature in a polyurethane containing the pure polyethylene oxide soft segment (I) and in polyurethanes containing block copolymer polyethylene oxide/polypropylene oxide soft segments (II), show significantly different behavior. In sample I, the water content and nonfreezing water are only weakly dependent on temperature from 276 to 333 K. In the samples based on II, with various ratios of the hydrophilic and hydrophobic segments, there is a strong decrease in solubility with temperature and a steep drop above 303 K. The nonfreezing water exhibits a parallel trend. This behavior is interpreted in terms of the temperature-dependent phase compatibility of the polyethylene oxide and polypropylene oxide segments of II. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Polyurethanes based on the incorporation of a polyethylene oxide (PEO) soft segment exhibit substantial water uptake and, therefore, high moisture vapor transmission rates (MVT). The high MVT could be an advantage as a fabric coating for rainwear and sports clothing[1] and in certain biomedical applications. The interaction of water with PEO is also of interest in the use of ionic complexes of PEO for battery applications.[2] In earlier work, Tobolsky and co-workers[3] described the properties of a series of hydrophilic polyurethanes prepared for possible reverse osmosis separations. The water solubility was controlled by varying the proportion of PEO and polypropylene oxide (PPO) used to form the mixed soft segment. Significantly, it was shown that the saturation water concentration was directly proportional to the PEO concentration. A variation on this approach in the preparation of hydrophilic polyurethanes was undertaken in studies by Illinger et al.[4] In this work, the soft segment consisted of a

block copolymer containing a central segment of PPO and terminal segments of PEO. Samples were prepared in which the proportions of these two components in the soft segment were varied. In addition, the effect of increasing hard-segment content was examined for a set of samples in which the soft-segment composition was fixed at equal amounts by weight of the two components. Some of the results of this work have been published earlier.[5] However, in a recent review of this study, it was realized that the dependence of the saturation water concentration and the state of the sorbed water on temperature were unusual and deserved more detailed consideration. This paper reports on an analysis of the earlier data in an attempt to clarify the unique aspects of the behavior and to suggest an explanation for those results.

EXPERIMENTAL

Polyurethane samples were prepared by a two-step procedure, with MDI and butanediol forming the hard segment and with pure polyethylene oxide (PEO) (Union Carbide), pure polypropylene oxide (PPO), or block copolymers of PPO and PEO (Wyandotte Corp.) as the soft segment. Details of

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Table I   Composition of Polyurethane Samples

| Sample | Soft Segment | | Mole Ratio (MDI/BD/SS)[b] | Wt % HS[c] | T_g (K) |
	Mol. Wt.	a/b[a]			
10PE33	1540	36/0	4.20/3/1	46.2	242
5PE33	1954	11/17	4.20/3/1	39.8	236
3PE33	1950	7/23	4.20/3/1	39.8	230
1PE33	2134	2.5/33	4.20/3/1	39.8	n.d.
0PE33	2010	0/35	4.20/3/1	39.8	232
5PE28	1954	11/17	3.15/2/1	32.6	236
5PE33	1954	11/17	4.20/3/1	39.8	236
5PE40	1954	11/17	6.30/5/1	50.3	236

n.d., not determined.

[b] In the ratio a/b, a is the number of EO units; b is the number of PO units.

[b] MDI, diphenyl methyl diisocyanate; BD, butanediol; SS, soft segment.

[c] HS, hard segment.

the synthesis have been reported earlier.[4] The composition and certain properties of the polyurethanes are summarized in Table I. In calculating the molecular weight of the block copolymers from the size of the segments, given as the number of ethylene oxide (EO) and propylene oxide (PO) units, a/b, it is necessary to double the EO contribution since the polymer consists of a central PPO segment terminated by PEO segments of equal length.

Equilibrium sorption measurements were performed on a preweighed sample of polymer immersed in distilled water that was maintained at the proper temperature, as required. The sample was removed from the water, blot dried, and placed in a tared weighing bottle to determine the weight gain. The immersion procedure was repeated until the sample was at constant weight.

DSC runs were made using a Perkin-Elmer DSC-2 with subambient accessory cooled with liquid nitrogen and purged with helium. Samples were prepared from films cast from DMF solution and dried under vacuum for 48 h at 50°C. The polymer discs of known dry weight were equilibrated with water, transferred to large diamenter, and custom-fashioned, gold-foil pans and the excess water was allowed to evaporate on the microbalance to the desired water content before the pans were hermetically sealed. Samples were equilibrated at 10 K intervals from 273 to 323 K (T_{eq}) in a constant temperature bath or in the DSC. The rate of approach to equilibrium depended on the temperature. The equilibration times were varied from 4 h at 323 K to 24 h at 273 K. Following equilibration, a sample from the constant temperature bath was placed in the DSC held at the equilibrium temperature. The

DSC was quenched at a setting of 320 K per min to 150 K, then scanned at 20 K per min to T_{eq}.

RESULTS

Immersion Uptake at 30°C

The water uptake in the polyurethanes of varying composition determined at 30°C by immersion is listed in Table II, both for the series of samples of fixed hard-segment content and various soft-segment compositions and for the three samples of fixed soft-segment composition and varying hard-segment content. The first column of water data lists the values as grams of water per 100 grams of polymer. These results are consistent with the general expectation that the water uptake will reflect the amount of the hydrophilic component, PEO, and, therefore, decrease with increasing PPO in the soft segment or with increasing hard-segment content. However, the results in the next column indicate that the amount of sorbed water is not simply proportional to the PEO content. The ratio, grams of water per 100 grams of PEO, decreases with decreasing PEO content and with increasing hard-segment content. In the last column, the results are presented as moles of water per EO repeat unit. The ratio in 10PE33 is close to three, the value determined as the water of hydration per EO unit.[6] Therefore, in this case, it is expected that the water molecules would be bound to EO units. This expectation can be tested by examining the DSC trace to determine the fraction of nonfreezing water and will be discussed later.

Table II   Immersion Water Uptake Determined at 30°C

Sample	Wt % HS[a]	PEO/SS[b] (wt %)	PEO/Poly.[c] (wt %)	H_2O/Poly. (g/100g)	H_2O/PEO (g/100g)	H_2O/EO[d] (mol/mol)
10PE33	46.2	100	54.0	58	107	2.62
5PE33	39.8	49.5	29.8	25	84	2.05
3PE33	39.8	30.6	19.0	8	43	1.04
1PE33	39.8	10.3	6.3	3	48	0.49
0PE33	39.8			2		
5PE28	32.6	49.5	33.3	40	121	2.96
5PE33	39.8	49.5	29.8	25	84	2.05
5PE40	50.3	49.5	24.6	15	61	1.49

[a] HS, hard segment.
[b] PEO, polyethylene oxide; SS, soft segment.
[c] Poly., polymer.
[d] EO, ethylene oxide repeat unit.

The observation that the ratio, moles of water/moles of EO, decreases as the amount of PPO increases suggests that there is some interaction between the PPO and PEO blocks of the soft segment that influences the water uptake, but it is difficult at this point to be specific about the exact nature of the interaction. In the samples of differing hard-segment content, the effect of increasing hard segment is also to reduce the sorbed water by an amount that exceeds the proportional reduction in PEO content. In this case, the effect can be attributed to the reduction in swelling that is expected as a result of the increase in the effective degree of cross-linking with an increase in hard-segment content. However, there may be secondary effects associated with changes in the complex morphology of the segmented polyurethanes that are difficult to quantify.

Immersion Water Uptake as a Function of Temperature

Measurements of water uptake made at several temperatures over the range 276–333 K were instructive about the nature of the interactions determining the sorption levels. The results are summarized in Table III as the ratio of moles of water to moles of the EO repeat unit. In almost all cases, the values are highest at the lowest temperature, 276 K, and decrease with increasing temperature. The exception is 1PE33, where the value at 303 K seems to be lower than at the other temperatures. Note, however, that, otherwise, 1PE33 follows the same trend, the values decreasing with increasing temperature. For 0PE33, the water uptake is essentially constant except for a somewhat lower value

Table III   Immersion Water Uptake as a Function of Temperature

	Immersion Water Uptake[a]					
Sample	276 K	288 K	303 K	323 K	333 K	Ratio[b]
10PE33	3.08	2.93	2.62	2.00	1.63	1.89
5PE33	4.01	3.12	2.05	0.76	0.68	5.89
3PE33	4.01	2.32	1.04	0.71	0.67	5.89
1PE33	2.37	1.59	1.18	1.42	1.42	1.67
0PE33	0.15	0.13	0.11	0.15	0.15	1.0
5PE28	5.92	4.40	2.96	0.88	0.73	8.11
5PE33	4.01	3.12	2.05	0.76	0.68	5.89
5PE40	2.98	2.30	1.49	0.67	0.61	4.89

[a] Expressed as moles water per moles of EO unit.
[b] Ratio of the values for moles of water to moles of EO at 276 K to that at 333 K.

at 303 K. A measure of the change in the water up-take with temperature is given by the values in the last column, which represent the ratio of the water uptake at 276 to that at 333 K.

There are two other aspects of the data in this table that are noteworthy. First, the number of moles of water to EO at 276 K is about 30% higher for 5PE33 and 3PE33 than for the pure PEO-containing polymer, 10PE33. It should be noted, however, that the latter sample has a higher hard-segment content, because of the lower soft-segment molecular weight (see Table I). Comparison with the results for the three samples with different hard-segment content in the bottom section of Table II shows that reducing the hard-segment content from 50.3% in 5PE40 to 39.8% in 5PE33 also increases the saturation water content by 30%. Second, the values for these two polymers decrease to a much larger extent with increasing temperature. This result is indicated by the values in the last column of Table II, which are close to 6 for 5PE33 and 3PE33, compared with 1.9 for 10PE33. The trend in the data is illustrated in Figure 1 (a) and (b), where the solubility, S, is plotted as moles of H_2O per EO against the reciprocal of absolute temperature, T, in the manner appropriate for determining the heat of solution, ΔH, according to the usual relation:

$$\Delta H = -Rd \ln S / d(1/T)$$

The heats of solution are negative throughout the temperature range with the possible exception of 0PE33. The contrast between the behavior of 10PE33 and that of the other polymers is clearly indicated. The solubility for samples that have a block copolymer soft segment changes more rapidly with temperature and drops markedly in the temperature range of 303–323 K. This behavior is especially well defined in the data for the three samples with different hard-segment contents, as illustrated in Figure 1(b).

DSC Measurements of the State of Sorbed Water

DSC measurements were made on samples with a defined amount of added water at various equilibration temperatures, T_{eq}. An example of results obtained for 10PE33 with 48% added water is shown in Figure 2 taken from Ref. 5. For these conditions, there is a broad endotherm at all T_{eq} with an onset temperature of approximately 260 K. A second sharp endotherm appears in the samples equilibrated at 303 K and higher. It is customary to identify the broad endotherm as bound freezing water, implying
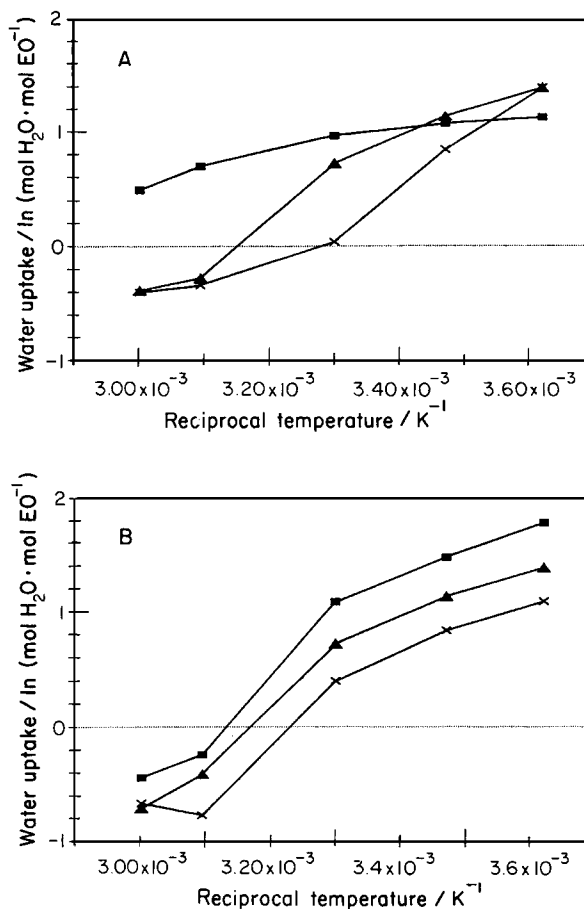

Figure 1 (a) Water uptake as a function of temperature for samples with various EO contents at fixed hard-segment content: (■) 10PE33; (▲) 5PE33; (✖) 3PE33. (b) Water uptake as a function of temperature for samples with various hard-segment contents at fixed EO content: (■) 5PE28, (▲) 5PE33, (✖) 5PE40.

that the behavior is influenced by strong interactions with the matrix. The water contributing to the sharp endotherm has been labeled free water. NMR measurements have shown that the mobility of dissolved free water is much lower than that of bulk water.[7] However, this endotherm could be due to water that is dissolved in the polymer matrix or water that exists in the free space within the sample cell. In the present case, the added water exceeds the solubility at 323 K and is borderline at 313 K, so the sharp endotherm must be due to the excess water.

The amount of bound nonfreezing water was calculated by subtracting the total amount of water represented by the endotherms, assuming the applicability of the heat of fusion for bulk water, 79.8 calories per gram. It was noted that the T_g increases with the increase in the fractional amount of water represented by the endotherms, but these results will not be discussed here. In all cases, the amount of
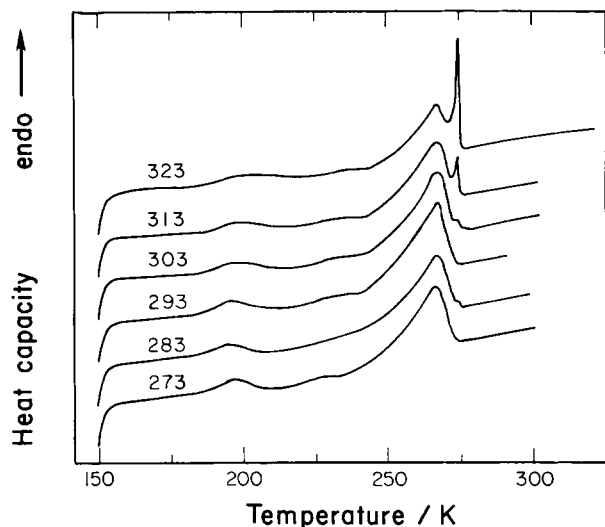
Figure 2 DSC scans of 10 PE33 with 48% added water following equilibration at various temperatures as labeled. The individual scans are arbitrarily displaced on the heat capacity axis for clarity. (From Ref. 5; used with permission.)

added water was well below saturation at 273 K. Therefore, it can be assumed that where the nonfreezing water values are close to the amount of added water that no endotherm was observed.

Data for 10PE33 and for 5PE33 as a function of equilibration temperature, in 10 K intervals from 273 to 323 K, are shown in Table IV. All data are normalized to the PEO content of the polymer, i.e., grams of water per 100 grams of PEO. Results were obtained at two levels of added water. For 10PE33, the added water levels were 42% (which is below the saturation concentration of 44% water at 323 K) and 67% water (which exceeds the saturation concentration above 283 K). For 5PE33, the added water levels were 9% water (which is below the saturation concentration of 9.2% at 323 K) and 33% water (which exceeds the saturation concentration above 303 K). The behavior in the two samples is very different. In 10PE33, the amount of nonfreezing water decreases slowly with increasing equilibration temperature and does not change significantly with the added water level. Thus, at 283 K, the amount of nonfreezing water is 60% of the lower amount of added water and 42% of the higher amount of added water. In 5PE33, at the lower added water content, the amount of nonfreezing water is essentially constant up to 303 K and then decreases sharply between 303 and 313 K. At the higher added water level, the amount of nonfreezing water has increased significantly and shows a somewhat stronger dependence on equilibration temperature in the range 273–303 K. The amount of nonfreezing water decreases

sharply above 303 K, behavior similar to that seen for the saturation water content in the immersion experiments. As the results in Table IV show, the nonfreezing water represents an appreciable fraction of the saturation concentration at each temperature, amounting to 85% at 303 K, whereas the 33% added water content just exceeds saturation.

Data are also presented in Table IV on 5PE40 at an added water level of 7%, which is slightly higher than the saturation concentration of 6.7% at 323 K, and at an added water level of 19%, which just exceeds the saturation concentration at 303 K. At the lower concentration, the nonfreezing water content shows little change with temperature up to 323 K. At the higher water content, the nonfreezing water has increased by nearly threefold, essentially in proportion to the increase in added water, and equals the added water at 273 and 283 K. Above 293 K, there is a sharp drop in nonfreezing water, although the level is still well below saturation at 303 K. The nonfreezing water at 303 K is equivalent to 5 g/100 g polymer compared to a saturation concentration of 15 g/100 g polymer at this temperature. Therefore, the change is not due to the marked decrease in saturation concentration that occurs in this temperature range although it probably reflects the same cause. Results for 5PE28 are similar but somewhat more scattered.

DISCUSSION AND CONCLUSIONS

This study has shown that there are marked differences in the interaction of water with the polyurethane based on the pure PEO soft segment compared with the samples containing the block copolymers consisting of PEO and PPO. In 10PE33, the saturation water content is only weakly dependent on temperature. This finding is consistent with the results of NMR studies of aqueous PEO solutions showing that the state of hydration is stable to temperatures as high as 80°C.[6] In the polymers containing the block copolymer soft segment, the saturation concentration decreases rapidly with increasing temperature and drops abruptly above 303 K. When plotted in the Arrhenius form, the behavior of the saturation concentration suggests the occurrence of a transition above 303 K. The two types of polymer show equally marked differences in the temperature dependence of the nonfreezing water determined by DSC. In 10PE33, the amount of nonfreezing water shows little sensitivity to changes in temperature or, within limits, to the amount of added water. In 5PE33 and 5PE40, as examples, the nonfreezing water increases with the amount of added water and shows a marked change above 303

Table IV   Nonfreezing Water at Various Equilibration Temperatures

Sample	Added Water[a]		Nonfreezing Water (K)					
			273	283	293	303	313	323
10PE33	42/78	Rel. to PEO[b]	55	46	51	50	48	39
		Rel. to sat.[c]	44	37	44	47	46	48
	67/124	Rel. to PEO	62	52	54	57	50	19
		Rel. to sat.	49	42	46[d]	53[d]	53[d]	23[d]
5PE28	10/31	Rel. to PEO	31	31	27	29	27	10
		Rel. to sat.	12	15	17	24	36	26
	52/157	Rel. to PEO	120	116	42	102	85	28
		Rel. to sat.	46	57	26	84[d]	110[d]	72[d]
5PE33	9/31	Rel. to PEO	31	31	31	28	12	11
		Rel. to sat.	17	22	28	33	21	34
	33/111	Rel. to PEO	105	98	66	71	19	16
		Rel. to sat.	59	70	59	85[d]	33[d]	52[d]
5PE40	7/29	Rel. to PEO	29	29	26	26	26	13
		Rel. to sat.	23	27	32	42	60	49
	19/79	Rel. to PEO	79	79	68	23	37	22
		Rel. to sat.	63	75	83	37[d]	86[d]	80[d]

[a] Added water; g water per 100 g polymer/g water per 100 g PEO.
[b] Percent nonfreezing water relative to PEO; g nonfreezing water/100 g PEO.
[c] Percent nonfreezing water relative to saturation; g nonfreezing water/100 g saturation water at T_{eq}.
[d] Indicates that the added water exceeds the saturation concentration at that temperature.

K, analogous to that seen for the drop in the saturation concentration in this temperature range.

The complex morphology of these phase-segregated polyurethanes makes it difficult to interpret these data in quantitative terms. Phase mixing, which involves mixing of hard segments with the soft-segment phase and soft segments with the hard-segment phase, will affect the behavior. However, no data were collected to define the extent of phase mixing. Since the measurements that were carried out on model hard-segment copolymers indicated that there was negligible water solubility in this material, it will be assumed that water is only soluble in the soft-segment phase and that all of the soft segment is accessible to water.

The sorption of water can affect the properties of the polymer. One such effect is the lowering of the glass transition temperature with increasing water uptake. But it is also possible that the presence of water could affect the morphology, especially with increasing temperature. Thus, it might be suggested that the transition in solubility that occurs in the samples with the block copolymer soft segments is due to a change in the hard-segment morphology. There are two arguments against this. First, any such change would increase the mobility of the hard-

segment domains and, therefore, increase the accessibility to water and the solubility. However, the transition is marked by a large drop in solubility. Second, the solubility–temperature plots for the three 5PE samples show identical transition behavior independent of the hard-segment content. These considerations suggest that the abrupt change in solubility might be related to some type of change in the soft-segment phase.

Although only a single glass transition temperature is observed in these samples, it is not possible to conclude, on this basis, that the PPO and PEO segments are compatible. The *Polymer Handbook* records a T_g of 198 K for PPO but notes that there is conflicting data.[8] However, this value is close to the 202 K value reported by Camberlin et al.[9] Unfortunately, there is considerable uncertainty in the value for PEO. The *Polymer Handbook* records a value of 232 K, a full 30 K higher than that of PPO, but lists a range of 158–233 K. The difficulties may be due to the high degree of crystallinity in PEO. The soft-segment glass transition temperature in PE1033 (Table I) is only 10 K higher than that of 0PE33. Even this difference should be discernible by DSC if the segments in the block copolymer are incompatible. However, the true glass transition

could be even closer since the lower molecular weight and greater polarity of the PEO soft segment should lead to a greater concentration of hard-segment units mixed with the soft-segment phase, thus raising the glass transition temperature of the PEO in PE1033. It seems reasonable to conclude that the glass transition temperatures of the PEO and PPO soft segments are probably close enough not to be distinguishable by DSC.

Measurements have recently been reported on the compatibility of mixtures of PEO and PPO.[10] Polymers of sufficiently high molecular weight are incompatible. The phase separation–temperature curve is quite flat and the upper critical consolute temperature is strongly dependent on the molecular weight of the two polymers. For a PPO molecular weight of 2000 and PEO molecular weights of 550 and 750, the critical consolute temperatures were 67°C and about 112°C, respectively. On the basis of these results, it can be assumed that the segments of the block copolymer corresponding to 5PE55 and 3PE33 would also exhibit incompatibility. The phase-separation temperature would be lower as a result of the linkage between the segments and the lower molecular weight of the segments: 484 and 986 for the molecular weights of the PEO and PPO segments in 5PEO, and 308 and 1334, in 3PEO. Therefore, the transition in water solubility occurring above 303 K in these two polymers could be a result of a transition from incompatibility to compatibility in the soft-segment phase. Given the higher concentration of PPO, the PEO segments would be dispersed in a continuous PPO matrix. The problem is to explain why this type of organization leads to normalized saturation water concentrations comparable to that in the pure PEO at 273 K but shows a much stronger reduction with increasing temperature and a sudden drop with the onset of the suggested phase compatibility.

Based on the preceding model, the drop in water solubility at the temperature of soft-segment-phase compatibility must be due to the more hydrophobic nature of the PPO and to a reduction in the possibility of water molecules bridging EO segments. There might also be secondary effects arising from PO/EO interactions. The strong temperature dependence of the saturation water content would be similarly related to the progressive homogenization of regions of different stability in the soft-segment phase with increasing temperature. However, a troubling result, which cannot be explained, is the high water content of 1PE33, normalized to EO, at temperatures of 303 K and higher.

Attempts have sometimes been made to account for the decrease in the glass transition temperature of the soft-segment phase with increasing water uptake by using a free-volume expression in which the nonfreezing water, rather than the total water content, is used.[11] If the nonfreezing water is strongly bound to EO, then in the two-phase region for the block copolymer soft segment, the glass transition temperature of the PEO segment should be lowered selectively. Accordingly, the individual PEO and PPO should become distinguishable. This result has not been observed. It is not known whether there is evidence of broadening of the glass transition consistent with this idea.

In seeking a better understanding of the state of water in these polymers, it is also necessary to have a clearer understanding of the nature of the so-called freezing bound water. It is curious that in 10PE33 there seems to be a partition of the water between the nonfreezing and freezing bound water that is relatively independent of temperature or of the amount of added water. The freezing bound water is distinguished by the low onset temperature of the melting endotherm and its broad temperature range. This finding suggests that the freezing bound water exists in a range of environments. Correlation of these observations with the effect on the polymer properties, such as the glass transition, and with measurements by other means, especially deuterium NMR, would be helpful.

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