Macromolecules **1984,** *17,* 449–452

isotropic and a second model of motion that is essentially static and accounts for the remainder of the spatial averaging. These two models could be distinguished in a coherent averaging experiment if we were able to distinguish two limiting cases: (a) a bimodal population could give rise to a spectrum consisting of $\sim$99% of the total intensity in a very narrow line and $\sim$1% of the total intensity in a very broad line, and (b) a uniform population would give rise to a spectrum consisting of 100% of the total intensity on a very narrow line. Differentiation of these two possibilities would require a detection linearity and dynamic range greater than 10^6, which is beyond the capabilities of our present instrumentation. A third model, similar to the first, but invoking spin diffusion as the exchange mechanism, is excluded. The compound effects of the rate and amplitude of motion as observed here in proton and carbon-13 NMR experiments have been previously observed in NMR studies of other solid polymers such as poly(tetrafluoroethylene) and its copolymers,[5] poly(methyl methacrylate),[24] polyethylene,[25] and polystyrene.[26] The importance of recognizing the temperature dependence of both the amplitudes and rates of motions, which are both reflected in NMR line width and relaxation data, cannot be underestimated.

Note Added in Proof: Recent results for slow coherent averaging experiments and recently published results for the characteristic time of chain diffusion indicate that only the model of anisotropic segmental motion is reasonable (manuscript in preparation).

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^{13}C-NMR Relaxation of Polysaccharides: Dextran and Amylose in Dimethyl Sulfoxide and Water

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ABSTRACT: ^{13}C-NMR spin–lattice relaxation times and nuclear Overhauser enhancements are reported for dextran and amylose in dimethyl-d_6 sulfoxide and D_2O over the temperature range 40–105 °C at 15 MHz. The α-D(1,6)-glycosidic rings of dextran are found to move somewhat more rapidly than the α-D(1,4)-glycosidic rings of amylose in both solvents, and both are somewhat more mobile in water than in dimethyl-d_6 sulfoxide. The derived energy barriers to segmental motions of dextran in both solvents and of amylose in Me_2SO-d_6 are 23 ± 4 and 16 ± 3 kJ/mol, respectively. These figures are slightly higher than those for typical linear-chain molecules.

Introduction

Motional studies of dissolved polymer chains by means of ^{13}C-NMR spin–lattice relaxation time (T_1) and nuclear Overhauser enhancements (NOE) have become significant in addition to other dynamical techniques such as dielectric relaxation, electron spin resonance, and fluorescence depolarization. The method can be applied to almost all polymer solutions, while the other experiments require special labels such as polar groups, free radicals, or fluorescent groups.

Conformational studies[1-3] and solution properties[4,5] of dextran, amylose, and other polysaccharides are described

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Table I
Observed ^{13}C-NMR T_1 (ms) and NOE Values of Dextran and Amylose in Me_2SO-d_6 and D_2O^a

(a) Dextran in Me_2SO-d_6

t, °C	C-1	C-3	C-4,5	C-6
105	114 (2.7_4)	103 (2.5_4)	92 (2.5_4)	60 (2.7_2)
89	87 (2.7_6)	78 (2.1_7)	73 (2.3_7)	48 (2.2_9)
73	67 (2.5_6)	60 (2.0_3)	55 (2.1_0)	33 (2.3_2)
58	47 (2.3_1)	47 (1.9_5)	43 (2.0_4)	26 (2.0_3)
40	38 (1.9_0)	39 (1.6_9)	37 (1.7_3)	20 (1.9_7)
28	32 (1.5_0)		33 (1.5_1)	19 (1.7_5)

(b) Amylose in Me_2SO-d_6

t, °C	C-1	C-2,3,5	C-6
105	59	70 (2.3_2)	48
89	60 (2.4_9)	60 (2.1_5)	44 (2.2_4)
81	57	56	36
73	39 (1.8_1)	48 (2.1_4)	32 (2.2_8)
58	38 (1.9_2)	42 (1.7_8)	28 (1.8_0)
54[b]	37 (2.0_4)	41 (1.7_3)	27 (1.9_4)
40	33 (1.5_4)	37 (1.7_0)	23 (1.7_7)
28	33	36 (1.5_9)	20 (1.5_5)

(c) Dextran in D_2O

t, °C	C-1	C-3	C-4,5	C-6
71	121 (2.8_3)	110 (2.6_9)	103 (2.9_5)	60 (2.7_9)
50	79 (2.5_5)	75 (2.4_5)	70 (2.4)	43 (2.3_5)
40	69 (2.4)	61 (2.1)	60 (2.2)	35 (2.2)
32	56	52	51	28

(d) Amylose in D_2O (Synthetic)

t, °C	C-1	C-2,3,5	C-6
98	116 (2.7_1)	113 (2.2_7)	85 (2.2_5)
84	97	91	58

[a] ^{13}C peaks assigned according to Allerhand.[8]
[b] Synthetic.

in several reviews. ^{13}C-NMR chemical shifts and ^{13}C T_1 values are given in the literature[6-17] for various polysaccharides. Here we report on a comparative dynamical study of *dextran* and *amylose*, which have predominantly α-D(1,6)- and α-D(1,4)-glycosidic linkages, respectively, in (deuterated) dimethyl sulfoxide and water.

Experimental Section

Dextran (Nutritional Biochemical Corp.) and a cornstarch amylose (Sigma Chemicals, amylopectin free) had nominal molecular weights of 1×10^5 and 5×10^4, respectively. The commercial amylose had very low solubility in water, but we were fortunate to receive a gift of synthetic amylose[18] from Dr. B. Pfannemüller of the University of Freiburg. The sample, with a molecular weight exceeding 10^5, had higher water solubility. Each of the following solutions was sealed in a 10-mm NMR tube after five (freeze-pump-N_2 flush-thaw) cycles: dextran, 15% (w/w) in Me_2SO-d_6 (Aldrich) and 14% (w/w) in D_2O (Aldrich); potato amylose, 13% (w/w) in Me_2SO-d_6; synthetic amylose, 3% (w/w) in D_2O. The ^{13}C T_1 measurements were performed by the inversion-recovery method with a pulse sequence π–t–$\pi/2$–τ with τ = 0.5 s, at 15 MHz in a JEOL-60Q spectrometer, with complete noise decoupling of protons. The NOE's were evaluated from ratios of the peaks obtained with complete noise decoupling of protons and those obtained under gated decoupling only during data acquisition following each pulse. The magnetic field was locked on the deuterium resonance. The reproducibilities of ^{13}C T_1 and NOE are considered to be ±10%.

Results and Discussion

Table I lists the observed ^{13}C T_1 and NOE for several carbon atoms in dextran and amylose in the two solvents at various temperatures. Where the figures for different carbons were indistinguishable or differed by less than 10%, only certain representative values are reported. Peaks in the spectra were assigned to the individual carbons according to Allerhand.[8]

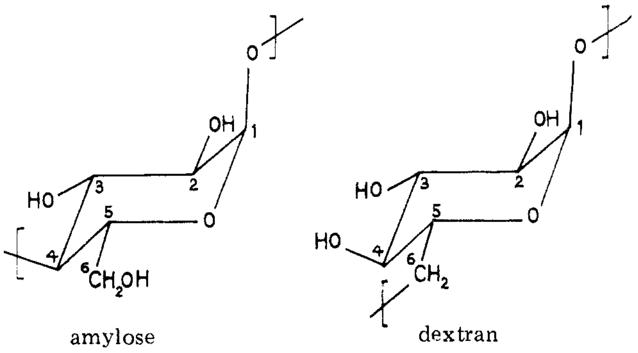

Figure 1. Principal repeat-unit structures of amylose and dextran.

The observed NOE values generally fall well below the extreme-narrowing limit of 2.99, indicating the need for a model with at least two parameters to describe the results. For convenience we used the limited-correlation scheme of Jones and Stockmayer (JS),[19] which enables us to match the observed NOE values and to report harmonic mean correlation times for C–H axis reorientation. These are shown in Table II for the JS model with s = 4 and also with s = 1, which corresponds to a simple exponential time-correlation function but which fails to match the observed NOE values.

Several alternative two-parameter correlation functions are available for treating data of this kind. Three of them[19-21] are based on more or less the same local process, typified by (though not required to match in detail) a three-bond crankshaft rearrangement in a chain confined to a diamond lattice. They differ in certain details (e.g., imposition of short-time and/or long-time cutoffs, passage to a continuous chain limit), but it has been shown[22] that all three of the models are about equally successful in fitting typical NMR relaxation data, and the physical meaning of the model parameters is at least roughly similar. More recently, Hall and Helfand[23] have presented a new two-parameter function based in part on the molecular nonlattice theory of Skolnick and Helfand,[24] which is quite realistic for an alkane-type chain but not especially relevant to polysaccharides. Viovy[25] has compared all these functions, and still another one[26] allowing for inertial effects, with respect to fitting some recent synchrotron-radiation-excited fluorescence polarization decay experiments[27] and has found that the JS,[19] BY,[21] and VF[26] models are somewhat superior to the others in this relatively demanding test. There are to our knowledge no models based more directly on polysaccharide structural types. We therefore do not apologize for our present use of the JS model, recognizing of course that the model parameters cannot be given strict meaning with respect to actual motions of polysaccharide segments.

From the figures reported in Table II, we draw the following conclusions:

(1) At lower temperatures the rates of segmental motions of the two types of glycosidic ring are quite similar, but at higher temperatures the rates of segmental motion of the dextran rings become somewhat faster than those of the amylose rings. From Figure 1, which shows the structures of dextran and amylose, with carbons numbered conventionally, one may suppose that the –O–CH_2– linkages connecting the dextran rings offer somewhat greater motional freedom than the simple –O– linkages connecting the amylose rings. In both polymers, all the ring carbons show essentially the same behavior, with C_1 of dextran as a possible exception.

Table II
Calculated Harmonic Mean Correlation Times (τ_h/ns) and Calculated NOE Values from ^{13}C T_1

(a) Dextran in Me_2SO-d_6

	C-1		C-3		C-4,5		C-6	
t, °C	*s* = 1	*s* = 4	*s* = 1	*s* = 4	*s* = 1	*s* = 4	*s* = 1	*s* = 4
105	0.42 (2.95)	0.10 (2.74)	0.46 (2.94)	0.12 (2.66)	0.52 (2.93)	0.14 (2.57)	0.40 (2.96)	0.1 (2.75)
89	0.56 (2.92)	0.16 (2.50)	0.63 (2.91)	0.19 (2.39)	0.68 (2.90)	0.22 (2.30)	0.50 (2.94)	0.14 (2.57)
73	0.74 (2.88)	0.26 (2.20)	0.85 (2.85)	0.33 (2.04)	0.95 (2.81)	0.40 (2.02)	0.78 (2.87)	0.28 (2.16)
58	1.2 (2.73)	0.58 (1.96)	1.2 (2.73)	0.60 (1.96)	1.3 (2.69)	0.79 (1.97)	1.0 (2.80)	0.45 (2.00)
40	1.6 (2.57)	1.5 (2.01)	1.6 (2.60)	1.2 (2.00)	1.7 (2.52)	1.9 (1.99)	1.5 (2.62)	1.0 (1.99)
28	2.3 (2.30)				2.2 (2.33)	6.4 (1.55)	1.6 (2.57)	1.5 (2.01)

(b) Amylose in Me_2SO-d_6

	C-1		C-2,3,5	
t, °C	*s* = 1	*s* = 4	*s* = 1	*s* = 4
105	0.87 (2.84)	0.34 (2.08)	0.71 (2.88)	0.24 (2.25)
89	0.85 (2.85)	0.33 (2.09)	0.86 (2.84)	0.34 (2.08)
81	0.92 (2.83)	0.38 (2.04)	0.94 (2.82)	0.40 (2.02)
73	1.6 (2.57)	1.4 (2.01)	0.98 (2.81)	0.57 (1.97)
58	1.6 (2.57)	1.6 (2.01)	1.1 (2.80)	0.89 (1.98)
54[a]	1.6 (2.57)	1.9 (2.00)	1.4 (2.65)	0.96 (1.97)
40	2.2 (2.33)	5.0 (1.66)	1.7 (2.53)	1.7 (2.00)
28	2.2 (2.33)	5.0 (1.66)	1.8 (2.49)	2.5 (1.94)

(c) Dextran in D_2O

	C-1		C-3		C-4,5		C-6	
t, °C	*s* = 1	*s* = 4	*s* = 1	*s* = 4	*s* = 1	*s* = 4	*s* = 1	*s* = 4
71	0.39 (2.96)	0.09_5 (2.75)	0.43 (2.95)	0.11 (2.70)	0.47 (2.94)	0.12 (2.66)	0.40 (2.96)	0.10 (2.75)
50	0.66 (2.90)	0.19 (2.39)	0.66 (2.90)	0.21 (2.30)	0.72 (2.89)	0.25 (2.22)	0.56 (2.92)	0.16 (2.50)
40	0.72 (2.88)	0.24 (2.25)	0.84 (2.85)	0.33 (2.10)	0.86 (2.84)	0.34 (2.08)	0.71 (2.88)	0.24 (2.2_5)
32	0.92 (2.83)	0.38 (2.04)	1.0 (2.80)	0.46 (1.99)	1.1 (2.75)	0.50 (1.98)	0.93 (2.82)	0.39 (2.0_2)

(d) Amylose in D_2O (Synthetic)

	C-1		C-2,3,5	
t, °C	*s* = 1	*s* = 4	*s* = 1	*s* = 4
98	0.41 (2.96)	0.10 (2.74)	0.42 (2.95)	0.11 (2.73)
84	0.49 (2.94)	0.13 (2.60)	0.53 (2.93)	0.15 (2.53)

[a] Synthetic.

Table III
Comparison of $\tau_h/\eta_{solvent}$ of Polysaccharides in the Two Solvents

t, °C		τ_h, ns	$\eta_{solvent}$, cP	$\tau_h/\eta_{solvent}$
		Dextran		
40	Me_2SO-d_6	1.2	1.51	0.79
40	D_2O	0.33	0.832	0.40
73	Me_2SO-d_6	0.39	0.895	0.44
71	D_2O	0.12	0.672	0.18
		Amylose		
84	Me_2SO-d_6	0.53	0.768	0.69
84	D_2O	0.17	0.625	0.27

(2) The C_6 carbons of both polymers are somewhat more mobile than the others, since they are outside of the rings and less hindered. Correlation times for the C_6 of amylose are not reported here, since it is on a side group whose dynamical analysis is somewhat more complicated.[28] We hope to discuss such motions at a later time.

(3) Segmental motions of both dextran and amylose rings in water are several times faster than those in Me_2SO even when adjusted for the difference in solvent viscosities.[29] From Table III, the quotients τ_h/η_0 of dextran and amylose rings in water are only 40–50% of those of both rings in Me_2SO. According to Burchard's study[30] of the viscosity behavior of amylose in several solvents, the Mark–Houwink–Sakurada exponents are 0.82 and 0.68 in Me_2SO and water at 25 °C, and the intrinsic viscosities of amylose at 25 °C in Me_2SO are twice as large as those in water. This difference of chain dimensions, which may reflect differences in hydrogen-bonding strengths in the two solvents,[31,32] is in the same direction as the difference in dynamical flexibility reported in the present study.

(4) The observed correlation times in Me_2SO-d_6 follow Arrhenius relations quite well as functions of temperature, with apparent activation energies of 30 ± 3 and 37 ± 4 kJ mol^{-1} in amylose and dextran ring carbons, respectively. Subtracting a viscous-flow activation energy of 14 kJ/mol^{-1} for Me_2SO, we obtain barrier heights U^* of 16 ± 3 and 23 ± 4 kJ mol^{-1} of amylose and dextran rings, respectively. These values are slightly higher than those for typical vinyl polymers. However, the actual magnitudes of the correlation times are not greatly different from those for polystyrene.

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Registry No. Dextran, 9004-54-0; amylose, 9005-82-7.

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Poly(methacrylic acid) Derivatives. 8. Effects of Solvent- and pH-Induced Conformational Transition on the Chiroptical Properties of Hydrophilic–Hydrophobic Poly(*N*-methacryloyl-L-alanine-*co*-*N*-phenylmethacrylamide) Copolymers

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ABSTRACT: CD spectra of poly(*N*-methacryloyl-L-alanine) (PNMA), of its model molecule *N*-isobutyryl-L-alanine (NIBA), and of a random copolymer of *N*-methacryloyl-L-alanine and *N*-phenylmethacrylamide (P50) were recorded in water at different values of the degree of neutralization $\bar{\alpha}$ of the carboxylic functions. Upon ionization, PNMA behaves like a normal polyelectrolyte and undergoes a progressive expansion of the macromolecular conformation. On the contrary, P50 shows a transition from a compact conformation at $\bar{\alpha} < 0.3$ to a more expanded conformation at $\bar{\alpha} > 0.7$. These differences in the conformational behavior of PNMA and P50 were not reflected in the chiroptical properties. The changes in the CD spectra upon neutralization are mainly attributed to the perturbation of all the electronic transitions (carboxyl, amide, and aromatic chromophores) of both kinds of residues due to the ionization of the carboxyl group.

Introduction

During the past decades, it has been widely demonstrated that the chiroptical properties of poly(α-amino acids), proteins, polynucleotides, etc. are very sensitive to the existence of secondary structures in solution and they have been used to study conformational transitions such as the helix-to-coil transition.[1] More recently, other kinds of synthetic optically active polymers have been synthesized and studied.[2–4] In some cases, these polymers are highly stereoregular and the presence of ordered structure is likely. The chiroptical properties may then be interpreted in terms of macromolecular conformation.[5]

Nevertheless, in most cases, synthetic optically active polymers are stereoirregular and no ordered structure can be predicted. Chiroptical properties are then mainly dependent on the effect of external factors, e.g., solvent, temperature, added salt, ionization, etc.,[3,4] on the different chromophores present in the macromolecule. When dealing more especially with polyelectrolytes, an interesting case is that of hydrophobic–hydrophilic polyelectrolytes in which the balance between the hydrophobic cohesive interactions and the repulsive electrostatic interactions governs the conformation taken by the polyelectrolyte in aqueous solution.[6–8] At low values of the degree of ionization $\bar{\alpha}$ and when the amount and/or the size of the hydrophobic groups is sufficient, the cohesive interactions are predominant and the macromolecule takes a compact, tightly coiled conformation in which the hydrophobic groups are clustered in microdomains without contact with water. As $\bar{\alpha}$ increases, the repulsive electrostatic interactions also increase, leading to the unfolding of the compact conformation. This well-known compact → coil conformational transition may also be induced by addition of an organic solvent to the aqueous solution in order to weaken the hydrophobic interactions.

In recent years, a number of papers have been devoted to the study of such hydrophobic polyelectrolytes, having a chiral center in their side chain, in order to determine whether or not their special conformational behavior is reflected in the chiroptical properties (optical rotatory

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