static and dynamic light scattering to determine molecular weight distributions would benefit from the evaluation of ξ using monodisperse amylose preparations. Estimates of molecular stiffness are sensitive to polydispersity. Values corrected for polydispersity are consistent with $C_\infty = 11.7$ and $a = 27.8$ Å, in dilute aqueous solution. Corrections for chain expansion yield $C_\infty' \approx 4.5$ for the unperturbed state consistent with the data obtained in the Θ solvent 0.33 M KCl.

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Registry No. Amylose, 9005-82-7.

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^{13}C Relaxation of Dissolved Polymers Containing In-Chain Six-Membered Alicyclic Rings

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ABSTRACT: Spin-lattice relaxation times and nuclear Overhauser enhancements are reported for ^{13}C nuclei in 5% *m*-cresol solutions of six polyethers containing 1,4- or 1,2-cyclohexylene rings in the chain backbone. The rings appear to move as rigid units and are opposed by low barriers to internal rotation, thus being rather more mobile than the hexose rings of polysaccharides.

Introduction

We report here some ^{13}C spin-lattice relaxation measurements on several polyethers containing cyclohexylene rings in the chain backbone[1-3] and briefly compare their revealed motional behavior to those of polymers with different backbone rings. Dynamical mechanical measurements have already been reported[4,5] for some of our polymers and are summarized in Table I. The structures of the repeat units are displayed in Figure 1.

Experimental Section

Samples of the six polyethers shown in Figure 1 were kindly supplied by Dr. J. Kops of the Instituttet for Kemiindustri. Molecular weights were estimated either from GPC or intrinsic viscosities and in all cases were sufficiently high to suppress overall tumbling (rotatory diffusion) as contributor to NMR relaxation.

Polymer solutions at about 5% (w/w) concentration were prepared in freshly distilled *m*-cresol, which, unlike other common solvents, can dissolve all six polymers at suitable temperatures. The ^{13}C NMR measurements were made at 15.04 MHz with a JEOL 60Q spectrometer. An external lock signal was employed: a small tube containing dimethyl-d_6 sulfoxide (or acetone-d_6 for polymer A) was positioned concentrically within the 5-mm tube containing the polymer solution. The method of assigning chemical shifts under these circumstances is described below. Spin-lattice relaxation times T_1 were measured with the standard technique described previously:[6] inversion-recovery with the pulse sequence π–t–$\pi/2$–τ, where the waiting time τ is chosen to be at least $5T_1$ (i.e., ca. 1 s), and with complete noise decoupling of the protons. The $\pi/2$ pulse width was 25 μs. Overhauser enhancement factors, NOE, were evaluated from ratios of the peaks

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Table I
Structures of Alicyclic Ring-Containing Polymers

name	structure	viscoelastic relaxation peaks	ref
(A) poly(1,4-cyclohexylene ether)	Figure 1a	12 °C, 1 Hz	5
		32 °C, 5.26 kHz	4
		−93 °C, 6.38 kHz	4
(B) poly(*endo*-2-methyl-7-oxabicyclo[2.2.1]heptane)	Figure 1b	65 °C, 1 Hz	5
(C) poly(*exo*-2-methyl-7-oxabicyclo[2.2.1]heptane)	Figure 1c	72 °C, 1 Hz	5
(D) poly(*trans*-8-oxabicyclo[4.3.0]nonane)	Figure 1d		
(E) poly(*trans*-7,9-dioxabicyclo[4.3.0]nonane)	Figure 1e		
(F) poly(*trans*-7-oxabicyclo[4.3.0]nonane)	Figure 1f		

Table II
Viscosity of *m*-Cresol

temp/°C	η/(mN s m^{-2})[a]	temp/°C	η/(mN s m^{-2})[a]
25	13.6	65	2.75
35	7.9	75	2.08
45	5.23	80	1.83
55	3.72		

[a] 1 mN s m^{-2} = 1 cP.

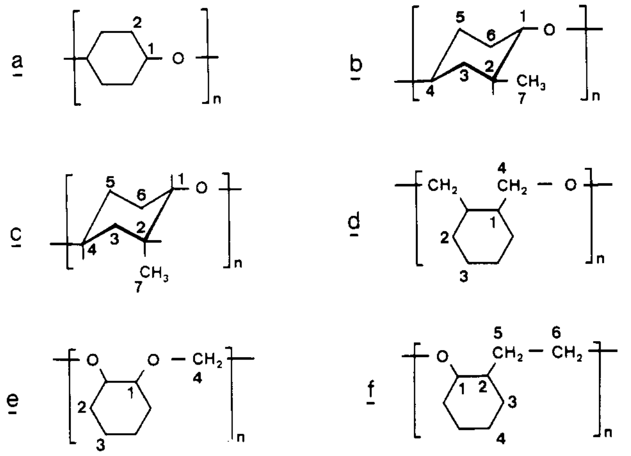

Figure 1. Repeat-unit structures of the polymers studied.

obtained with complete noise decoupling of protons and those obtained under gated decoupling only during data acquisiton following each pulse. Reproducibility of T_1 is about 10% and that of the NOE factor of the order of 15%.

Finding no viscosity data for *m*-cresol in the literature, we used a capillary viscometer to obtain the values shown in Table II. The corresponding Arrhenius plot is somewhat curved yielding apparent activation energies ranging from 27 to 35 kJ mol^{-1}, with an average value of 31 kJ mol^{-1} over the range 25–80 °C.

Results and Discussion

Chemical shifts with respect to Me_4Si were assigned to the various ^{13}C nuclei on the basis of the spectrum reported for polymer D by Kops, Hvilsted, and Spanggaard;[7] in effect, we used our measurements for this polymer as the reference for the other samples. The resulting chemical shifts (with respect to Me_4Si) are listed in Table III. Our measurements for polymer F are then also in good accord with the data of Kops et al. It should be remarked that the spectra were of relatively low quality for polymers B and C, for which every ring carbon is different and the intensities of individual resonances are therefore lower. It may be observed in Table III that a splitting of 2–3 ppm is found for the C_1 and C_4 resonances of polymer E, and this is attributed to stereoisomerism at the ring junction, as already noted by Kops et al.[7] for similar polymers. The cis/trans ratio of polymers D, E, and F is otherwise not specified. However, polymers B and C are isomerically pure, being all equatorial and diequatorial–monoaxial, respectively. For polymer E, where the small splitting was observed, it was not possible to measure separate relaxation times for the individual isomers.

Table III
NMR Assignments

polymer	numbered carbon[a]	chem shift,[b] ppm	polymer	numbered carbon[a]	chem shift,[b] ppm
A	1	123	D	1	40
	2	32		2	30
				3	25
				4	74
B	1	82	E	1	72, 74
	2	37		2	24
	3	40		3	17
	4	77		4	86, 89
	5	30			
	6	31			
	7	18			
C	1	76	F	1	68
	2	31		2	33
	3	36		3	31
	4	72		4	25
	5			5	
	6			6	83
	7				

[a] See Figure 1. [b] Relative to Me_4Si (see text).

The measured spin–lattice relaxation times and NOE factors are listed in Table IV, the former being given as nT_1, where n is the number of attached protons. Note also that a single NOE figure is quoted for all the ^{13}C nuclei of a given polymer at any temperature, individual differences being no greater than the general reproducibility. The NOE factors are in most cases well below the extreme narrowing limit of 2.99. It was not possible to simulate both T_1 and the NOE factor with any single value of correlation time in a simple exponential correlation function, and thus a more complicated motion is at hand. Nevertheless, several general features of the polymer motions can be discerned directly from the nT_1 values of Table III:

(1) In polymer A, all the carbon nuclei move in concert; and the same is true, within the relatively large experimental uncertainly, for the other polymers.

(2) The methyl ring substituent in polymers B and C reduces the mobility relative to polymer A. This observation is consistent with the low-frequency dynamic mechanical data[5] (Table I) for these materials in the bulk state.

(3) In polymers D and E, the motions of the inter-ring bridging methylene carbons are, within experimental uncertainty, neither slower nor faster than those of the rings. In polymer F, however, it is quite clear that the bridging groups have a higher mobility than the ring.

(4) There is no great difference, if any, in mobility between 1,2- and 1,4-cyclohexylene rings.

For more quantitative discussion we restrict ourselves to polymer A, for which the results are most extensive and

Table IV
^{13}C NMR Relaxation Data in *m*-Cresol[a]

polymer	temp/°C	nT_1/ms						NOE
		C_1[b]	C_2	C_3	C_4	C_5	C_6	
A	32	60	65					1.7 (?)[c]
	53	95	94					2.3
	67	119	122					2.4
	85	189	156					2.5
B	84	94	73	69	60	88	(88)	2.0
C	100	177	123	158	198	164	(164)	2.0
D	30	31	32	32	29			
	44	50	48	46	67			2.3
	56	80	77	87	110			2.6
	83	227	217	239	286			2.9
E	30	63	63	78	52			2.0
	55	85	78	71	78			2.5
	70	156	117	126	106			
	98	238	290	374	257			2.7
F	46	40	37	61	58	107	118	2.2
	69	102	76	94	57 (?)	220	224	

[a] Parentheses indicate weak signals. (?): data appearing to be spurious. [b] Carbon atoms numbered as in Figure 1. [c] This figure seems too low to reconcile with those at the higher temperatures.

accurate. Here we need a two-parameter model to accommodate both the nT_1 and NOE observations, and for convenience we choose that of Jones and Stockmayer,[8] which has previously often been used by several of us.[6] In this model, the orientational time correlation function, $\phi(t)$ is a superposition of a small number, s, of exponential processes:

$$\phi(t) = \sum_{k=1}^{s} G_k \exp(-t/\tau_k); \qquad \sum G_k = 1 \tag{1}$$

so that the harmonic and arithmetic mean correlation times respectively are given by

$$1/\tau_h = \phi'(0) = \sum \tau_k^{-1} G_k$$

$$\tau_a = \int_0^\infty \phi(t)\,dt = \sum \tau_k G_k \tag{2}$$

where the prime refers to the time derivative.

The individual correlation times, τ_k, are all related to a common rate parameter, and for this model the relation

$$\tau_a = s\tau_h \tag{3}$$

is always obeyed. Customarily the harmonic mean τ_h has been reported,[6] but actually the arithmetic mean τ_a is much less sensitive to the selected value of the parameter s, which is largely dictated by the NOE. We therefore elect to work with τ_a, and for polymer A the derived values (for s in the range 3–6) are shown as a function of temperature in Figure 2, in which we also include the single points for polymers B and C. The apparent activation energy for polymer A is 36 kJ/mol. If the process conforms to the diffusion limit of Kramers' theory, subtraction of the solvent viscous-flow activation energy of 31 kJ mol^{-1} leaves a mere 5 kJ mol^{-1} for the barrier height. Such a low value is surprising, but it is exactly the figure obtained for another polyether, poly(oxytetramethylene), from both dielectric and NMR measurements,[9] and not much below the 11 kJ mol^{-1} found[10] for the backbone motion in poly(styrene oxide). We have insufficient data to determine activation barriers for the other polymers, but Table IV shows that the ring motions are nowhere faster than in polymer A, so its activation energy is presumably a lower limit. The bridging methylene groups do move faster, but they have much smaller frictional radii, so that a direct comparison with polymer A is again not possible with the limited data base at hand.

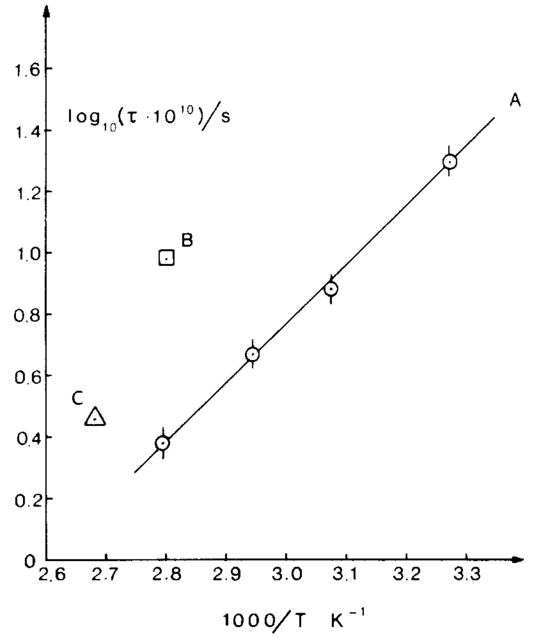

Figure 2. Mean orientational correlation times τ_a for polymers A, B, and C.

The low potential barrier is polymer A allows the cyclohexylene ring to move as a unit relatively rapidly as compared to other backbone rings that have been observed. Thus, for example, amylose[6] at 84 °C has a τ_a in D_2O (viscosity 0.63 cP) of 0.7 ns, as compared to a figure of only 0.24 ns for polymer A at 85 °C in the much more viscous solvent *m*-cresol (1.7 cP). Some of this difference might be ascribable to the larger frictional resistance of the saccharide ring with its several substituents, but the barrier height (16 kJ mol^{-1} in amylose) clearly must play a large role. Jones and his students[11,12] have made NMR studies of polymers containing 1,4-phenylene rings in the chain backbone and have been able to distinguish both rotations of the rings about their 1,4-axes as well as segmental backbone motions. In the polycarbonate of bisphenol A, both motions are rapid enough to invite comparison with our polyether; for example, in $CDCl_3$ at 40 °C Jones and Bisceglia[11] report a correlation time of 0.087 ns for the phenylene rotation and $\tau_a = 3\tau_h = 0.33$ ns for the backbone

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segmental motion. Of course their solvent is far less viscous, and their observed activation energies correspond to energy barriers of over 10 kJ mol^{-1}. In poly(2,6-dimethyl-1,4-phenylene oxide) and poly(2-methyl-6-phenyl-1,4-phenylene oxide) the phenylene ring rotations are only slightly slower than in the polycarbonate while the segmental motions are considerably slower.[12] Our cyclohexylene rings thus appear to be especially mobile.

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Spectrum of Light Quasi-elastically Scattered from Dilute Solutions of Very Long and Slightly Bendable Rods. Effect of Hydrodynamic Interaction

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ABSTRACT: The effect of the hydrodynamic interaction on the spectral shape of light quasi-elastically scattered from dilute solutions of very long and slightly bendable rods was considered theoretically on the basis of a spherically averaged interaction tensor. Numerical simulation of the field correlation function of polarized scattered light for dimensions appropriate to fd virus showed a definite effect of the hydrodynamic interaction on the spectral shape. The method presented here will provide an approximate but practical procedure to estimate the flexibility parameter of very long and semiflexible filaments from experimental spectra for dilute solutions.

Introduction

On the basis of the Harris and Hearst (HH) model of polymer dynamics,[1] we have presented a theory of the spectrum of light quasi-elastically scattered from solutions of very long filaments.[2-6] There are two kinds of criticisms to our model. One is that the HH model has some unphysical properties.[7] Another is that our treatment does not include the hydrodynamic interaction. For the first criticism, we would like to stress that the HH model is mathematically tractable and that the model has afforded some valuable insights into semiflexible chain dynamics and should not be dismissed too lightly.[8] For the second criticism, we would like to discuss here approximately the effect of the hydrodynamic interaction on the spectrum of light in the framework of the Hearst, Beals, and Harris (HBH) model.[9]

HBH Model

We adopt the notation used in our previous papers, although it has one-to-one correspondence to that in the HH paper. The operator describing the free-draining force per unit length is $A(s)$, where

$$A(s) = \epsilon(\partial^4/\partial s^4) - \kappa(\partial^2/\partial s^2) \tag{1}$$

The quantity s is a continuous contour parameter whose range is $-L/2 \leq s \leq L/2$ where L is the contour length of the chain. The quantity ϵ is a bending force constant and κ is the Lagrange multiplier introduced as a means of establishing the constraint that the contour length of the chain be a constant equal to L. HBH treated the hydrodynamic interaction between beads in its spherically averaged form, as was done by Zimm.[10] The interaction tensor has been introduced as

$$H(s,s') = \delta(s - s') + (\zeta/6\pi\eta)f(|s - s'|) \tag{2}$$

The quantity ζ is the friction constant per unit length of the chain, which is assigned the value $3\pi\eta$ throughout by analogy to a string of touching spherical beads. The solvent viscosity is η.

The eigenvalue problem which has to be solved now has the form

$$A(s)\Psi(n,s) + {}^1\!/_2\int_{-L/2}^{L/2} f(|s - s'|)A(s')\Psi(n,s')\,\mathrm{d}s' = \sigma_n\Psi(n,s) \tag{3}$$

For the function $f(|s - s'|)$, HBH followed the method of Hearst and Stockmayer[11]

$$f(|s - s'|) = (6/\pi)^{1/2}\gamma^{(1-\nu)/2}|s - s'|^{-(1+\nu)/2}$$

where $\gamma|s - s'| > a$ ($\simeq 2$) and

$$f(|s - s'|) = |s - s'|^{-1}(1 + {}^1\!/_3\gamma|s - s'| + c\gamma^2|s - s'|^2 + d\gamma^3|s - s'|^3) \tag{4}$$

where $\gamma|s - s'| < a$. The quantity γ is the flexibility pa-

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