in contrast to aliphatic alcohols (either monohydric or polyhydric). This is obviously not due to the presence of a ring structure in itself, as can be seen by comparison with cyclohexanol; evidently the aromaticity of the ring is necessary. Phenol is so strongly absorbed that it can only be used in dilute solution. A phenol solution of 0.25 M in CCl_4 is only about 2.5 wt %; concentrations double this or higher will totally dissolve nylon 6, indicating a total penetration of the crystalline phase. A more detailed study of the absorption behavior of substituted phenols of various types in nylon 6 is also being carried out and will be reported separately.

Communications to the Editor

Nuclear Magnetic Resonance Spin-Lattice Relaxation in the Lyotropic Polypeptide Liquid Crystal[1]

In this communication, we report preliminary measurements of the proton nuclear magnetic resonance (nmr) spin-lattice relaxation times of the solvent molecules in the two component lyotropic polypeptide liquid crystal dichloromethane-poly(γ-benzyl L-glutamate) solution (CH_2Cl_2-(BzlGlu)$_n$). Synthetic polypeptides, (NHCHRCO)$_n$ (for (BzlGlu)$_n$, R = $CH_2CH_2COOCH_2C_6H_5$), spontaneously form a birefringent liquid crystalline phase above a limiting concentration in various helicogenic solvents. With increasing polypeptide concentration, the solution passes from a normal isotropic fluid through a two-phase region (isotropic plus anisotropic liquid crystal) resulting in a homogeneous liquid crystal. The equilibrium *supramolecular* structure in polypeptide liquid crystals is cholesteric; the α-helical, rodlike polymer molecules assume a helicoidal arrangement in the solution.[2a] This colesteric arrangement is, however, untwisted in a magnetic field yielding a nematic *supramolecular* structure with the helical molecules aligned parallel to the field.[2b-4] This lyotropic liquid crystal is unique in that no specific interactions are required for its formation; it is a consequence of the high axial ratio of the rodlike polypeptide. An extension of the lattice theory of solutions, which incorporates the constraints involved in packing rodlike molecules with noninteracting solvent molecules, satisfactorily predicts the concentrations at which the phase boundaries occur as a function of the axial ratio.[5]

In this study, two (BzlGlu)$_n$ molecular weights were used, mol wt 550,000 and 13,000. This corresponds to axial ratios of p = 151 and 3.56, respectively, using a polypeptide diameter of 25 Å (obtained from a molecular model with a radially extending side chain) and a length = 1.5 (mol wt/M_w) Å, where M_w is the (BzlGlu)$_n$ peptide residue molecular weight (219) and 1.5 Å is the projection of a peptide residue along the helix axis. With these axial ratios and the above-mentioned lattice theory, we calculate the isotropic two-phase boundary to occur at N_p/N_s = 0.019 (0.355) and the two-phase liquid crystal boundary at N_p/N_s = 0.031 (0.375) for p = 151 (3.56); N_p/N_s is the ratio of peptide residues to solvent molecules.

Measurements of the spin-lattice relaxation, T_1, were made using a saturation-90° sequence at 8 and 30 MHz. The polymer solutions were degassed using conventional freeze-pump-thaw cycles. The large differences between the T_1 for the solvent (4–28 sec) and T_1 for the polymer (~0.5 sec) enabled us to extract CH_2Cl_2 T_1 values from the solution relaxation data. Our value for neat CH_2Cl_2, T_1 = 28 sec at 20°, is in good agreement with reported values (T_1 = 32 sec at 35°).[6] Relative rates of flow of the polypeptide solutions in the nmr sample tubes were compared with glycerine (η = 14.9 P at 20°) in order to make qualitative estimates of the viscosity.

In Figure 1a, the CH_2Cl_2 spin-lattice relaxation rate, $1/T_1$, is shown as a function of polypeptide concentration for the two values of (BzlGlu)$_n$ molecular weight. The calculated phase boundaries for the high molecular weight polymer are indicated. These boundaries are in agreement with polarizing microscope observations; *i.e.*, the sample with N_p/N_s = 0.025 is birefringent whereas the sample with N_p/N_s = 0.017 is not. In addition, the position of the isotropic-two phase boundary is consistent with the dramatic change in solution viscosity. The solid curve shown in Figure 1b is derived from previously reported studies of this phenomenon.[7] The position of the two-phase liquid crystal boundary is not easily amenable to similar experimental verification.

The gradual monotonic increase in the relaxation exhibited by the low molecular weight (BzlGlu)$_n$ solutions with increasing polymer concentration is characteristic of ordinary isotropic polymer solutions.[6,8] $1/T_1$ for the low molecular weight polypeptide solutions is independent of frequency over the concentration range investigated. Consideration of the relaxation data for the high molecular weight and low molecular weight polypeptide solutions separately, as a function of N_p/N_s, and together, at a single value of N_p/N_s, reveals a conspicuous absence of correlation between solvent relaxation rates and solution viscosities. This indicates that unlike simple liquids, macroscopic polymer solution viscosity does not reflect microscopic dynamics. There is an anomalous increase in the solvent relaxation rate at the two-phase liquid crystal boundary. Concomitantly, $1/T_1$ becomes frequency dependent. In the liquid crystalline phase, the oriented nematic solutions exhibited angular-dependent free induction decays. (The high viscosity of the polypeptide liquid crystal relative to that of thermotropic liquid crystals enables one to rotate the nematic axis away from the magnetic field direction without immediate reorientation of this axis.) When the nematic axis is at an angle of $\cos^{-1}(1/(3)^{1/2})$ with the magnetic field, dipolar interactions are removed and the free induction decay is inhomogeneity

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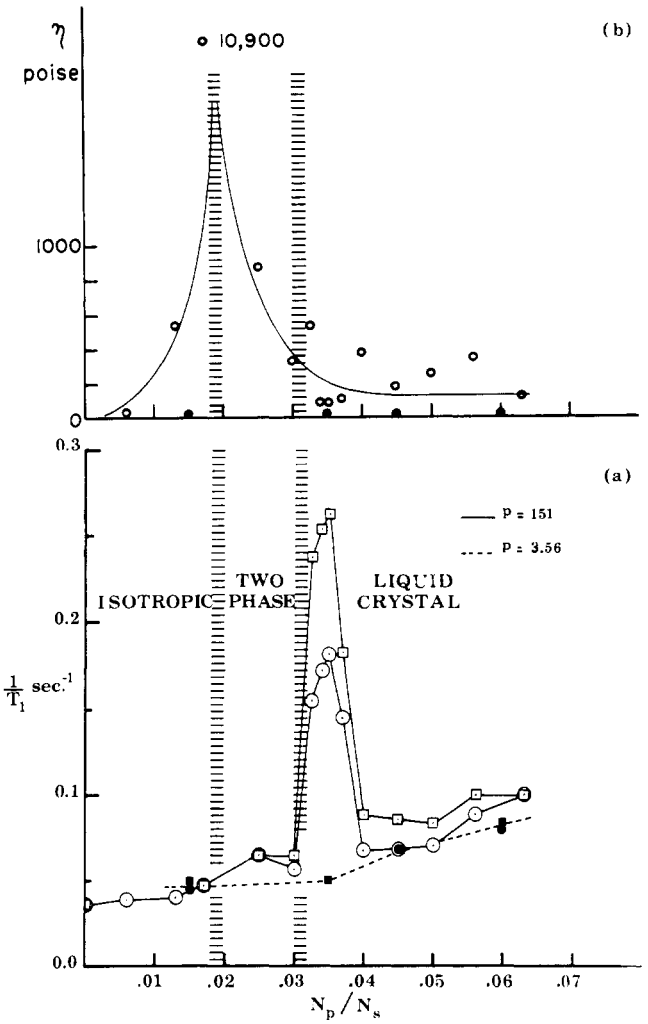

Figure 1. (a) CH_2Cl_2 proton spin-lattice relaxation rate ($1/T_1$) *vs.* polypeptide concentration (N_p/N_s); open symbols correspond to the high molecular weight (p = 151) $(BzlGlu)_n$ (□, 8 MHz; ⊙, 30 MHz) and closed symbols correspond to the low molecular weight (p = 3.56) $(BzlGlu)_n$ (■, 8 MHz; ●, 30 MHz). (b) Relative viscosity (η) *vs.* polypeptide concentration (N_p/N_s); (○) high molecular weight $(BzlGlu)_n$; (●) low molecular weight $(BzlGlu)_n$. Solid curve is derived from previously reported data (see ref 7).

limited. This effect is most pronounced for the rapidly decaying polymer component of the free induction decay.

There are several examples of frequency-dependent spin-lattice relaxation in the literature. The presence of the macromolecule in the polypeptide liquid crystal prompts us to remark on the reported frequency dependence of solvent T_1's in aqueous protein solutions. Frequency dependent spin-lattice relaxation in protein solutions is attributed to specific interactions (hydrogen bonding) between the protein and H_2O; in the "bound" state, the H_2O molecule's rotational correlation time is increased approaching that for reorientation of the macromolecule.[9] There are no comparable interactions between macromolecule and solvent in the $(BzlGlu)_n$-CH_2Cl_2 solution. The lack of frequency dependence in the low molecular weight polypeptide solutions at N_p/N_s values for which frequency dependent T_1's are found in the high molecular weight polypeptide solutions is in agreement with the absence of such specific polymer-solvent interactions. Similar to observations in CH_2Cl_2-polystyrene solutions,[6] the gradual increase in $1/T_1$ with increasing N_p/N_s in the low molecular weight polypeptide solutions (paralleled in the high molecular weight polypeptide solutions in the isotropic phase and later in the liquid crystal) probably reflects increasing contributions to the relaxation rate from less specific solvent-polymer interactions.

T_1 is frequency dependent if the correlation time for relevant molecular motion is the order of the Larmor frequency. Our findings suggest that a relaxation mechanism intrinsic to the formation of an ordered *supramolecular* structure in the solutions is responsible for the solvent relaxation anomalies. Previous high-resolution nmr studies indicated that the solvent molecules are partially oriented in the polypeptide liquid crystal (order parameter, $S \approx 0.001$).[10] In the liquid crystal one might expect the anisotropic solvent reorientation to modify intramolecular dipole-dipole contributions to solvent relaxation in a manner different from that found in isotropic polymer solutions. However, further experiments with partially deuterated solvent will be required to determine if the behavior of the CH_2Cl_2 relaxation at the two-phase liquid crystal transition is intramolecular in origin. Below we mention several possible sources of frequency-dependent solvent spin-lattice relaxation including one derived from the supramolecular arrangement of the polymer in the polypeptide liquid crystal.

Frequency dependent spin-lattice relaxation in thermotropic nematic liquid crystals is currently a subject of considerable interest. Hydrodynamic fluctuations which modulate the intramolecular dipolar interaction are thought to be the source of frequency-dependent relaxation in thermotropic liquid crystals. There is general agreement between experimental relaxation data and the predictions of the hydrodynamic theory:[11] $1/T_1 \propto \omega_0^{-1/2}$, where ω_0 is the Larmor freqquency. We have insufficient data at this time to comment on the validity of this theory in polypeptide liquid crystals. Another possible source of frequency dependent relaxation has its origin in intermolecular interactions. For certain values of the self-diffusion constant, D_t, in ordinary liquids[12] and some liquid crystals,[13] it has been shown that $1/T_1 \propto \tau(1 - C(\omega_0\tau)^{1/2}$, where C is a constant of the order unity and τ is related to the mean-squared jump distance $\langle r^2 \rangle$ by $\tau = \langle r^2 \rangle / 6D_t$.[14] An appropriate change in D_t for the solvent at the two-phase liquid crystal transition could introduce a contribution to the spin-lattice relaxation rate *via* this mechanism. We are currently constructing pulse field gradient equipment to measure solvent self-diffusion in this system. Also, consideration should be given to a recent theoretical description of molecular dynamics in the liquid state which suggests that anisotropic mediums impart a distribution of reorientational relaxation times to the liquid which may result in frequency-dependent nuclear relaxation times.[15] The CH_2Cl_2 molecules are situated in an anisotropic environment in the polypeptide liquid crystal (between the matrix of parallel helices). Lastly, we present below a possible source of frequency dependence which is unique to the polypeptide liquid crystal.

X-Ray studies of the polypeptide liquid crystal have shown that the rodlike molecules pack in a hexagonal arrangement. It was found experimentally that the concentration dependence of the distance between the $(10\bar{1}0)$ planes of the hexagonal net, d, is in good agreement with theoretical expectations for expansion of the net if it is assumed that no dilution parallel to the long axis of the

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molecules occurs.[16] On the hexagonal net, the long rodlike molecule is only allowed to execute a very small rotation about an axis through its center and perpendicular to its length before contracting a nearest neighbor. The rotary diffusion coefficient, D_r, of a rodlike particle in a medium of vicosity η can be obtained by suitable modification of the Stokes or Einstein relation.[17] The mean-square angular displacement of the rod, θ^2, in a time t is given by the random walk formulation, $\theta^2 = 4D_r t$. Since θ can be estimated from the lattice constant d at a given concentration and the length of the helix, we can calculate t, the average time between polymer collisions for a single polymer molecule. Using published values of d, we find that the helical polypeptide molecule in the liquid crystal executes oscillatory motion about its mean direction of orientation on a time scale comparable to the Larmor frequency. For example, using the high molecular weight polypeptide with $N_p/N_s = 0.035$ and $N_p/N_s = 0.060$ we find that $1/t = 11.9$ and 45.2 MHz, respectively. Hence, in addition to being a potential source of frequency-dependent solvent relaxation, the origin of the oscillatory fluctuations, *i.e.*, macromolecular motion, suggests that it would be very useful to look for frequency-dependent spin–lattice relaxation of the polymer protons in the lyotropic polypeptide liquid crystal.

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^{13}C, ^{19}F, and ^{1}H Nuclear Magnetic Resonance Studies of Hydroxy-Terminated Polybutadienes

Although hydroxy-terminated poly(butadienes)[1] have been studied in detail by a variety of analytical techniques, including infrared[2,3] and nmr spectroscopy,[4] as well as chemical,[5] the exact nature of the terminal groups has remained in doubt.

In this communication we report new data on the terminal groups which strongly suggest that they are predominantly primary alcohols, >95%, and that these are further divided into three types: adjacent to cis and trans double bonds, and adjacent to a saturated carbon which has a vinyl group attached.

In general, it appears that most hydroxy-terminated polybutadienes[1] possess two or more functional groups per molecule; the average is about 2.3. This number arises from the product of the number-average molecular weight as determined by vapor pressure osmometry (VPO) and the hydroxyl content from either acetic anhydride or toluene–sulfonyl isocyanate titrations. This average value of 2.3 indicates that tri- or higher functional materials are present and the extra hydroxyl groups could take the form of either primary or secondary alcohols depending upon the termination steps of the polymerization. Considerable data have been accumulated on attempts to separate the various species. The results are, however, open to question.

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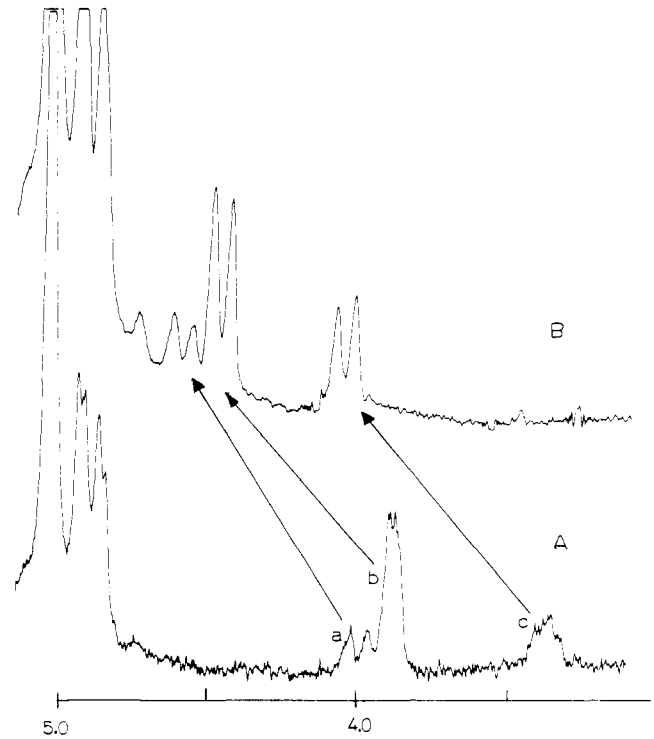
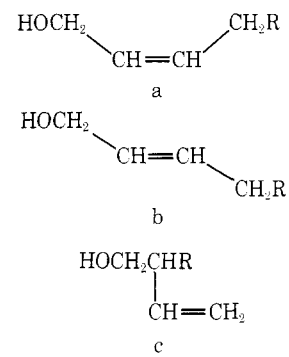


Figure 1. Portion of ^{1}H nmr spectrum, 100 MHz, of: (A) sample of poly BD in C_6D_6 and (B) CF_3COOH derivative.

The ^{1}H nmr spectrum of sample A[6] yields, in addition to the expected olefinic and CH_2 resonances, three small bands at 3.4, 3.9, and 4.0 ppm and these are depicted in Figure 1. The three fractions from solvent precipitation A–C yield essentially the same spectra, except for intensities, and they are consistent with typical commercial samples of R-45M.[1] The first resonance corresponds to a primary alcohol ($-CH_2OH$) adjacent to a saturated carbon while the 3.9 and 4.0 bands were assigned to primary alcohols adjacent to olefins. Their relative intensities are in rough agreement with the overall composition of the backbone chain, 55% trans, 20% cis, and 25% vinylic. This, in turn, led to the assignment of the above ^{1}H resonances to structures a–c, with increasing field strength, respectively.



Further evidence supporting the above assignments was obtained from the reaction of the OH groups with CF_3COOH. At room temperature the reaction is quite slow, but requires less than 1 hr for completion at 70°, as defined by nmr. The resulting $-CH_2OOCCF_3$ resonances (Figure 1B) are shifted about 0.5 ppm downfield from the corresponding alcohol.

(6) Sample A corresponds to the low molecular weight fraction, M_n = 1800, obtained by solvent precipitation from lot no. 110225 (ARCO Chemical Co., Glenolden, Pa.).