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Nature of the Water–Epoxy Interaction

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ABSTRACT: Absorption of small amounts (1–3 wt %) of water by epoxy resins effects a substantial plasticizing action and degradation of their mechanical properties. We present results that provide new insight into the molecular details of the interaction of epoxy resins with water. These results show (1) that the water in epoxy resins is impeded in its movement, with the molecules hopping from site to site with an approximate residence time per site of 7×10^{-10} s, (2) that there is no "free" water, (3) that there is no evidence for tightly bound water, and (4) that it is unlikely that the water disrupts the hydrogen-bond network in the epoxy resin. These results are consistent with the notion that water acts simply as a plasticizer for these hydroxyl-containing systems, just as it does for polymers which contain no exchangeable protons.

Water is known to plasticize certain amorphous,[1,2] semicrystalline,[3] and cross-linked polymers.[4–6] In particular absorption of small amounts (1–3% by weight) of water causes a large reduction in the glass transition temperature (T_g) of epoxy resins,[5,6] often considered to reduce the temperature threshold of utility and general mechanical integrity of this class of materials by a considerable margin. This feature of water plasticization in this and other systems has led to some speculation with regard to the nature of the interaction of water molecules with polar polymeric substrates. Here we present results which not only clarify this situation but improve the fundamental understanding of the molecular details concerning the interaction of water with these materials.

Some early spectroscopic and calorimetric data have been interpreted to indicate a highly specific "binding" between the water molecules and the polar groups of the epoxy resin,[7,8] proposing that the water disrupts the hydrogen-bonding network.[9] However, recent work[4,10–12] shows that the plasticization of epoxy resins by water can be explained simply by treating the T_g depression as arising from the expected composition dependence of miscible polymer–diluent systems. The latter treatment has the virtue that it successfully predicts the depression of T_g for polymer systems that contain polar groups such as OH residues,[12] as well as for those that are considered relatively inert.[11]

In a preliminary communication on the interaction of water (D_2O) with epoxy resins,[13] quadrupole echo deuterium NMR spectroscopy was used to show (1) that although the absorbed water is very mobile, it is not identical with bulk water in this respect, (2) that the water is distributed homogeneously throughout the sample, (3) that approximately one water molecule is entrained for every six OH/OD sites on the polymer backbone, and (4) that the water exchanges with the OH/OD groups on the polymer backbone, but the time scale of this exchange was not determined. The communication also established that solid-state deuterium NMR spectroscopy shows particular promise for the further investigation of plasticization phenomena in these and other systems.

We report here an extension of the early study.[14] The present work is designed to clarify and further establish the molecular details of the interaction between water and epoxy resins. In particular, the experiments described here are intended to (1) obtain in residence time for the mobile water molecules, (2) examine the effect of water plasticization on the backbone mobility of the epoxy resin, (3) determine whether any fraction of the water can be considered to be tightly bound to the epoxy resin, and (4) establish upper limits on the rate of exchange between the water molecules and the OH/OD groups on the epoxy backbone.

Materials and Methods

Epoxy Resins. The epoxy samples used in this study are based on the diglycidyl ether of bisphenol A. The sample we designate as EX4 was prepared as a stoichiometric cure of Epon 825 (Shell Co.) (epoxy equivalent weight (eew) 175; theoretical eew of pure monomer is 170) with *m*-phenylenediamine. The calorimetrically determined onset T_g of this completely dry, fully cured sample is 424.2 K and the midpoint is 432.0 K (heating rate 20K/min). The depression of T_g with water plasticization[4] shows no discontinuity in the depressed T_g up to a water content of approximately 3.5% w/w.

Sample NX2 was made according to literature methods[15] using Epon 825 and nadic methyl anhydride (Aldrich Chemical Co.). This sample has an approximate stoichiometry of 1.0:0.75 epoxide to anhydride groups. An IR spectrum shows no evidence of residual anhydride or epoxide moieties, although a small number of OH groups are present in this sample. The onset T_g is 386 K and the midpoint is 392.6 K (heating rate of 20°/min).

Poly(*N*-vinylpyrrolidone) (M_n 360 000) was obtained from Aldrich Chemical Co. This material was dried in a vacuum oven at 180 °C for 24 h prior to use.

Figure 1 shows the chemical structures of the materials used in this study.

Exchange with Deuterium. The epoxy samples were exchanged with D_2O in one of two ways. In the first method, an ampule of D_2O was placed in a glass tube containing the epoxy. After evacuation and sealing, the ampule was broken by shaking and the whole assembly was placed in an oven at 160 °C. This process was repeated 5 times, each time with a fresh ampule of D_2O, to ensure complete exchange. After the final cycle a given amount of D_2O was introduced into the system and the final weight percent D_2O was determined gravimetrically. The samples plasticized in this manner contained between 1 and 3 wt % D_2O, with the exception of NX2, which absorbed less than 0.5 wt % D_2O.

In the second method, 2 × 2 × 2 mm cubes of the dried epoxy samples were soaked in D_2O at room temperature for a period of 1 week. At the end of the soaking period, the samples were blotted dry and allowed to equilibrate in a 100% relative humidity D_2O atmosphere[16] for 2 days prior to NMR measurement. This method produced samples containing approximately 2 wt % D_2O. Samples prepared by either method produced equivalent NMR results.

Nondeuterated epoxy resins were plasticized with Me_2SO-d_6 by soaking the resin in this material for 48 h. The samples were blotted dry prior to NMR measurement. They contained 5% by weight Me_2SO-d_6.

The poly(*N*-vinylpyrrolidone) was plasticized with D_2O by exposing the dried polymer to D_2O in the 100% relative humidity chamber for 24 h. This produced a sample containing ~40 wt % D_2O. Several hours of drying under a slight vacuum at room temperature reduced this to 21% by weight of D_2O.

Exchanged and Dried Samples. Some of the samples that had been previously exchanged with D_2O were dried to provide reference samples. The dried samples were produced by heating

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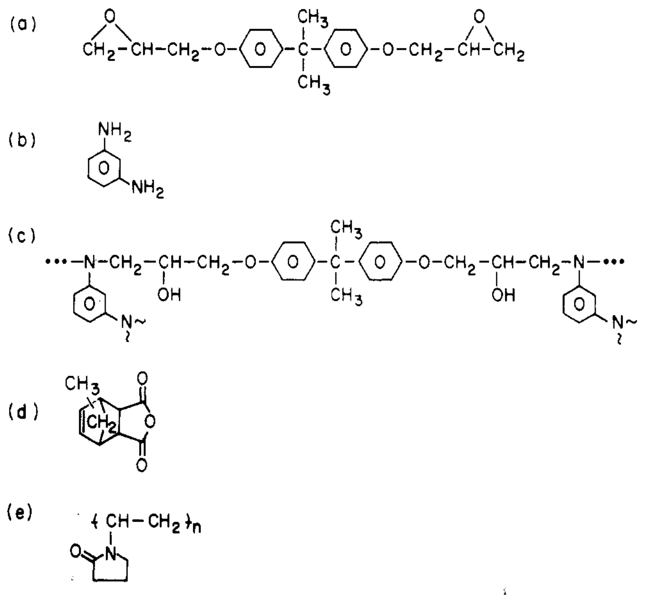

Figure 1. Chemical formulas of materials used in this study: (a) diglycidyl ether of bisphenol A; (b) *m*-phenylenediamine; (c) epoxy resin EX4; (d) nadic methyl anhydride; (e) poly(*N*-vinylpyrrolidone).

the deuterium-exchanged resin to 170 °C in vacuo for 2 days in the presence of phosphorus pentoxide. These samples were sealed under dry nitrogen until the NMR experiments were performed.

NMR Measurements. Each NMR measurement was performed on a fresh sample (approximately 100 mg) of the appropriate polymer unless noted otherwise. NMR experiments were performed by using a home-built solid-state deuterium NMR spectrometer operating at 55.26 MHz for deuterium. The spectrometer[17] and its sample temperature control[18] have been described previously. The quadrupole echo pulse sequence[19,20] was used for most experiments. Relaxation data were obtained by using an inversion–recovery pulse sequence prior to the quadrupole echo sequence. T_1 values were measured from the null points in the inversion–recovery spectra. The 90° pulse width was 3.2 μs and data were obtained in quadrature by using 2K points per channel. For most experiments the digitization rate was 100 ns/point (10 MHz).

Results

General Description of NMR Spectra. Figure 2 shows a typical quadrupole echo solid-state deuterium NMR spectrum of the exchanged epoxy resin EX4 when it contains 2 wt % D_2O (a) and when this same sample is dried (b). We have previously shown that the sharp central line arises from the sorbed D_2O, at this peak disappears when the sample is heated or dried.[13] The outer, broad part of the NMR spectrum is attributed to OH residues that have undergone exchange with D_2O and have become OD groups on the polymer backbone. The quadrupolar splitting between the outer peaks (125 kHz) indicates that the OD groups are not undergoing any large-amplitude motions on the NMR time scale.

The line width of the central sharp peak is somewhat broader than that of free water. This broadening may be attributed to contributions from sample inhomogeneities. In addition, the line width decreases as the weight percent of D_2O increases.

Because sample EX4 contains OD residues on the backbone (i.e., OH groups that have exchanged with D_2O) which produce a static-like pattern, such a broad pattern would obscure the signal from a small amount of tightly bound water, if it were present. Two experiments were designed to circumvent this problem. In the first, sample NX2 (which contains very few OH groups) was exchanged with D_2O. It absorbed less than 0.5 wt % D_2O, and this level of deuterium was not detected in the NMR experiment. A model polymer, poly(*N*-vinylpyrrolidone), was used in the second experiment. Poly(*N*-vinylpyrrolidone) is a hydrophilic polymer that does not contain exchangeable OH groups. The deuterium NMR spectrum of a sample of poly(*N*-vinylpyrrolidone) containing 21 wt % D_2O shows no evidence for bound or static-like water. At this content of deuterium, a broad component arising from bound water would be clearly observed.

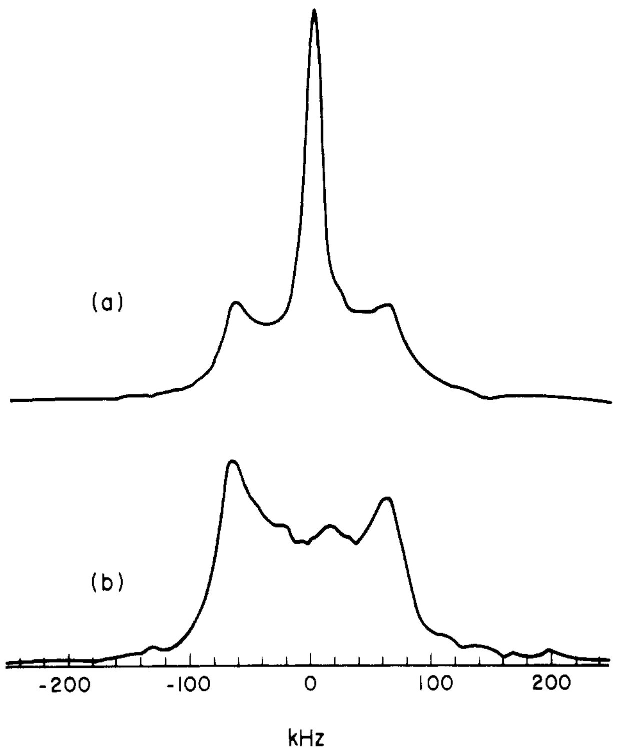

Figure 2. Quadrupole echo deuterium NMR spectra of epoxy resin EX4: (a) containing 2 wt % D_2O; and (b) the EX4 sample in a after it has been dried. The spectra were obtained at 20 °C and 55.26 MHz for deuterium.

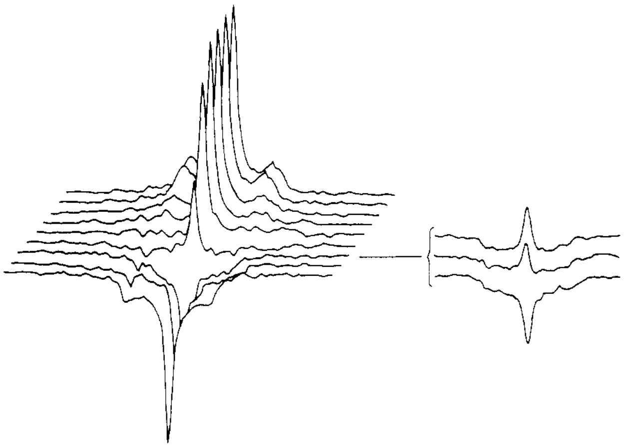

Figure 3. Inversion–recovery quadrupole echo NMR spectra for epoxy resin EX4 containing 2 wt % D_2O. From top to bottom, the inversion–recovery delay times are 5000, 500, 200, 100, 50, 10, 1, 0.5, and 0.1 ms. The enlargement on the right shows data obtained at inversion–recovery delay times of 9 (top), 7, and 3 ms. All data were obtained at 20 °C and 55.26 MHz for deuterium.

Relaxation Data. Typical inversion–recovery relaxation data for an EX4 resin containing 2 wt % D_2O are shown in Figure 3. It is clear that the OD groups and the signal due to D_2O relax at significantly different rates.

Relaxation data for EX4 (both "wet" and dried) at various temperatures are reported in Table I and are

Table I
Deuterium NMR Relaxation Data[a] for Epoxy-D_2O and Related Systems

sample	measurement temp, °C	T_g - measurement temp, °C	T_1, ms
EX4-backbone OD			
dry EX4	20	139	203
	60	99	44
wet EX4[b]	20	116	63
	65	71	36
D_2O			
in EX4	20		12[c]
in poly(vinylpyrrolidone)	20		12
neat	20		362
plus $Fe(AC)_2$	20		362
Me_2SO-d_6			
in EX4[d]	20		73
neat	20		306

[a] All data were obtained at 55.26 MHz for ^2H. [b] Sample contained 2% D_2O by weight. [c] This value obtained by using a quadrupole-echo inversion-recovery pulse sequence. T_1 of 12 ms also obtained by using standard high-resolution inversion-recovery sequence. [d] Sample contained 5% Me_2SO-d_6 by weight.

compared to the relaxation times of pure and paramagnetically doped D_2O. Several points are apparent from inspection of the data in Table I.

First, the T_1 of the mobile water in sample EX4 is substantially different from that of pure D_2O. It is unlikely that this difference is due to small amounts of paramagnetic impurities, as paramagnetic doping of D_2O (Table I) does not change its relaxation time.

Second, the relaxation times for the static component of the wet and dried EX4 samples are significantly different when measured at 20 °C. The glass transition temperatures for the wet and dried EX4 sample are different, which could account for the differences in the T_1 of the static component. The relaxation times for the static-like component of these two samples become similar when measured at a constant ΔT below T_g (i.e., at 20 °C for the wet EX4 and at 60 °C for the dried sample).

Figure 4 shows a plot of the T_1 data for the backbone OD group. Data for both the dry (triangles) and wet (circles) EX4 samples are shown. The abscissa corresponds to the difference in temperature between T_g and the measurement temperature. Data from both the wet and dry samples fall on this line, suggesting that the T_1 differences between the wet and dry epoxy samples (Table I) are due primarily to plasticization effects.

Discussion

Question of "Free" Water. Several lines of evidence argue against the presence of "free" water. (We define "free" to mean water that is isotropically mobile and thus has the same relaxation time as pure water.)

First, in our previous work[13] we showed that the water in resin EX4 did not freeze at temperatures down to -20 °C. This experiment is not unequivocal, however, because the signal for the water resonance did broaden, and a small amount (less than 10%) of free water could have been obscured by the OD signal from the polymer backbone.

In contrast to the above experiment, relaxation data provide a clear indication that there is no free water in this system. The spin-lattice relaxation time of pure D_2O under our conditions is 362 ms, whereas the corresponding relaxation time of the sharp signal in the spectrum of EX4 is 12 ms (Table I). This finding provides strong evidence that the motion of the water molecules in the epoxy resin is impeded. In addition, the relaxation data are described by a single exponential, consistent with there being only one species contributing to this signal. Finally, to eliminate the possibility that the signal from free water is suppressed by the quadrupole echo NMR experiment, the T_1 of this sharp component was measured by using a standard inversion-recovery Bloch decay experiment. This experiment also produces a 12-ms T_1 for the sharp component (Table I).

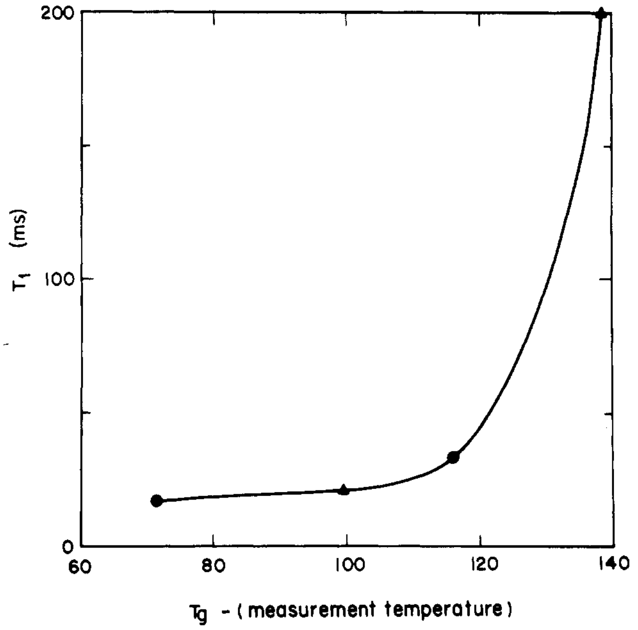

Figure 4. Plot of T_1 data for the OD backbone group in epoxy sample EX4 vs. the difference between T_g and the temperature of measurement. The triangles represent the dry samples; circles represent the sample containing 2 wt % D_2O.

Calorimetric studies down to -80 °C on differently prepared samples have also failed to reveal thermal phenomena associated with free water. Taken together, the data from the low-temperature experiments, the relaxation data, and the line width data support the conclusion that there is no isotropically free water in this epoxy-water system. This obviates the presence of the water in macroscopic voids, a situation which has been seen to occur in a different epoxy system.[8] Instead, the water appears to be distributed homogeneously throughout the system.

These data also show that the motion of the water is impeded. When the standard relationship between correlation time and relaxation times is used,[21] the 12-ms T_1 translates into a correlation time of 7×10^{-10} s. (The correlation time of free water is 2×10^{-11} s at this temperature.) This correlation time can be interpreted as the residence time of the water as it hops from site to site. It is likely that the OD or residual ND groups act as the impeding sites.

Question of Tightly Bound Water. Although it is clear that essentially all of the water is very mobile, we are unable to directly eliminate the possibility that there is a small amount of bound water. This situation arises because the signals from the OD of the epoxy resin backbone would obscure any static water, if it were present. However, the following experiments and considerations indicate that it is highly unlikely that there is a significant amount of bound water. (We define "bound" water as water with a residence time of 10^{-3} s or longer, or water whose only motion consists of a flip about the molecular symmetry axis.)

Firstly, the depression of T_g in the EX4 system by water exhibits a monotonic decrease from 0% moisture content.[4] If tightly bound water does not exercise the same plasticizing action as normal "dissolved" water, then some discontinuity may be anticipated. However, evaluation of the depression of T_g is obviously determined at the respective temperature of the transition and not at ambient conditions. We know from our experiments here that T_1 times of water molecules in the epoxy matrix vary significantly with temperature and hence the water molecules have different mobilities at different temperatures. This in fact forms the very basis of the great utility of the deuterium NMR technique used here since molecular interactions are determined at the temperature in question and are not inferred from property measurements at a temperature far removed from the point of interest.

Further evidence against the presence of bound water at ambient conditions comes from the fact that the composite line shape of Figure 2a can be simulated satisfactorily by assuming that there are only two components—a static pattern and a Lorentzian line.[13]

Thirdly, evidence comes from experiments on a model polymer, poly(*N*-vinylpyrrolidone). This material is known to be exceptionally hydrophilic, yet it contains no exchangeable NH or OH groups. When plasticized with D_2O, the deuterium NMR spectrum of this polymer shows only a single line and no evidence of bound water.

A final line of reasoning comes from examination of the crystal structures of inorganic molecules that contain water of crystallization. Gypsum, or $CaSO_4 \cdot 2H_2O$, provides a relevant example. Although the water in $CaSO_4 \cdot 2H_2O$ forms part of the structure in the solid state, NMR experiments show that it is actually undergoing two-site flips about the c_2 axis.[22] The NMR pattern for water that is involved in two-site flips consists of a tentlike pattern that is approximately 120 kHz in breadth. This line shape would not be obscured by the signals from the OD groups, and hence we can rule out the presence of bound, but flipping, water molecules.

These experiments and lines of reasoning suggest that it is highly unlikely that the epoxy–water system contains tightly bound water.

Question of D_2O Disruption to the Hydrogen-Bonding Network. In this section we obtain an upper limit for the OD/D_2O exchange rate and show that the water molecules are hopping from site to site at least 6 orders of magnitude faster than this.

The two-component nature of the spectrum of EX4 plasticized with water (Figure 2a) indicates that the OD/D_2O exchange rate is slow compared to the frequency separation between the OD signal and the D_2O signal. If the exchange rate were faster than this separation in frequency units (ca. 100 kHz), we would not observe these two components. Instead, the signals would be averaged together, producing only a sharp signal in the center of the spectrum. This observation sets an upper limit on the exchange rate of 10^5 s^{-1}.[23]

This upper limit can be lowered to ca. 10^3 s^{-1} if we can rule out the possibility of intermediate exchange. The T_1 data indicate that the OD and D_2O are not exchanging at an intermediate rate on the NMR time scale. If intermediate exchange were the case, we would expect that the hopping water molecules could communicate their efficient relaxation to the OD groups. We would predict that the relaxation time of the OD groups would be shorter in the EX4 sample that contains water than in the one that is dry. T_1 measurements performed at fixed temperatures below the respective T_g of the dry and wet samples (Table I) show that the static components have identical relaxation times. This finding provides strong evidence that the OD/D_2O exchange rate is much slower than 100 kHz, allowing us to rule out the possibility of exchange at an intermediate rate.

We therefore have an upper limit for chemical exchange of 10^3 s^{-1}, and a hop rate of the water molecules of 10^9 s^{-1}. Because the water molecules hop from site to site *at least* 6 orders of magnitude faster than they undergo chemical exchange, it is unlikely that the water molecules serve to disrupt the hydrogen-bonding network in the epoxy resin.

These conclusions are supported by water relaxation measurements on poly(*N*-vinylpyrrolidone). The T_1 of water is the same in this system as it is in the epoxy–water system (Table I). As poly(*N*-vinylpyrrolidone) does not have the possibility of forming a hydrogen-bonded network, the similarity in relaxation times suggests that the water is acting merely as a plasticizer in both of these systems.

Summary

The results presented here provide new insight into the molecular details of the interaction of epoxy resins with water. In particular, these results establish (1) that the water is impeded in its movement, with the molecules hopping from site to site with an approximate residence time per site of 7×10^{-10} s, (2) that there is no free water, (3) that there is no evidence for tightly bound water, and (4) that it is unlikely that the water disrupts the hydrogen-bond network in the epoxy resin.

These results are consistent with the notion that water is simply a plasticizer for these systems, just as it is for polymers that contain no exchangeable protons. However, these results clearly demonstrate that the water *does* interact with specific sites or traps on the epoxy backbone, insomuch as the water molecules hop from site to site, rather than behaving as a gas in an inert matrix. However, these results do not connect the hopping water molecule with specific hydrogen-exchange mechanisms.

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Exposure of Hydroxyl Groups in Phenol–Acetaldehyde Oligomers, As Investigated by Photo-CIDNP ^{1}H NMR and Infrared Spectroscopy

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ABSTRACT: A number of oligomers related to phenol–acetaldehyde novolac resins possessing different stereoregularity are investigated by conventional and photochemically induced dynamic nuclear polarization (photo-CIDNP) ^{1}H NMR and IR spectroscopy. Complete assignment of NMR spectra is achieved by double-resonance techniques, spin-echo multiplet selection, use of shift reagents, and comparison with spectra of two monomeric model compounds. For each oligomer, the spectral parameters can be directly related to the tacticity of the molecule (i.e., to the sequence of meso and racemic units). The photo-CIDNP technique provides information on the accessibility of the phenolic moieties. In both monomers access to the OH's is hindered. From the dimer to the pentamer, a gradual reduction of the exposure of the OH groups from the external rings is observed, whereas those from the inner rings are always accessible, irrespective of the number of units. This indicates the absence of the isodromic intramolecular H bonds which were observed in the X-ray structure. In the IR experiments the OH···OH absorption band shifts to lower frequencies and broadens by increasing the molecular weight. Combined with the photo-CIDNP results, this suggests a progressive strengthening of the H bonding of the outer functional groups. Two empirical rules are proposed, which correlate the intensity of the aromatic signals with the number of internal phenolic units.

Introduction

All-ortho alkylidene-bridged oligophenols (novolacs) have been the subject of several investigations.[3-5] IR studies have shown that in carbon tetrachloride these molecules adopt well-defined conformations, involving OH---OH intra- and intermolecular hydrogen bonds.[6,7] The X-ray structure analysis of a number of oligomers indicates that the conformation in the crystal is mainly determined by an isodromic, intramolecular H-bonding system, formed by the phenolic functional groups.[5] The H-bond stabilization defines two domains, one highly polar, containing all OH groups, the other strongly hydrophobic, in which the aromatic rings form a lipophilic matrix.

The present communication is focused on the aromatic resonances of a number of oligophenols (number of internal rings $0 < n < 3$) having different steric regularity. The accessibility of the phenolic groups is investigated by photochemically induced dynamic nuclear polarization (photo-CIDNP) and IR spectroscopy, in order to obtain some evidence on the molecular structure, in particular on the stabilizing role of the hydrogen bonds.

Materials and Methods

The two monomers and the oligomers in this study were obtained as described elsewhere.[5] The methyl ester of 3-*N*-(carboxymethyl)lumiflavin was the kind gift of Dr. F. Müller (Wageningen). C^2HCl_3 was from Merck Isotopes.

The conventional NMR spectra were recorded with a Bruker HX-270 spectrometer, controlled by an Aspect 2000 computer. Chemical shifts are quoted in ppm from internal tetramethylsilane (Me_4Si). Typically 64 scans were accumulated for each spectrum. The spin-echo experiments shown in Figure 6 were performed according to the pulse sequence ($90°–t_1–180°–t_1–\pm 90°–t_2–90°$–acquisition), where t_1 is $1/2J$ and t_2 allows for partial relaxation.[8]

Photo-CIDNP spectra were obtained with a Bruker HX-360 spectrometer, also equipped with an Aspect 2000 computer. The sample concentrations ranged between 6 and 12 mM in C^2HCl_3. Difference spectra were obtained by taking "light" and "dark" free induction decays (see text) and subtracting the spectra after Fourier transformation. A Spectra Physics Model 171 argon ion laser was employed as the light source. A 0.6-s light pulse (4 W, multiline) was used, with a 0.05-s delay before the 90° rf pulse. Four scans were accumulated for each spectrum. All spectra were resolution enhanced via the Gaussian convolution.[9] The line at 7.23 ppm in the photo-CIDNP difference spectra results from incomplete cancellation of the $CHCl_3$ signal.

IR spectra were obtained with a Perkin-Elmer 457 spectrometer, the sample concentrations varying between 0.2 and 2.0 mM in C^2HCl_3. The cell paths ranged between 75 and 500 μ.

Results and Discussion

Resonance Assignment. The phenol–aldehyde oligomers of this study are listed in Chart I. The monomers I and I′ are models for inner and outer rings in the oligomers, respectively. Figure 1 shows the aromatic region of the ^{1}H NMR spectra of I and I′, after resolution enhancement. The axial symmetry of compound I prevents the observation of J couplings across more than three

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