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An Infrared Spectroscopic Study of a Hyperbranched, Dendrimer-like, Polyester and its Blends with Poly(4-vinyl Phenol)

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SUMMARY: A dendrimer-like hyperbranched polyester is characterized by infrared spectroscopy. By converting and labeling the terminal groups by acetylation with ^{13}C acetic anhydride, the relative accessibility of core and terminal functional groups to solvents and linear polymers can be measured by counting the number of hydrogen bonds formed between the complementary functional groups found in these materials. The terminal groups form hydrogen bonds as readily as the same groups in linear polymers, but the core groups are highly screened. These results suggest that in these mixtures the dendrimer is extended, with the terminal groups located near the periphery of the molecule.

Introduction

Dendrimers are highly branched molecules consisting of a central core from which tree-like arms extend three-dimensionally into space. Topologically, the branching is regular, increasing systematically from the core of the molecule and each successive layer of branches is called a generation.

The unusually compact shape of these macromolecules and the multiplicity of end-groups results in some novel properties and the potential for a wide-range of applications. For example, the unusually low viscosity of these polymers suggest uses as viscosity modifiers,

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lubricants or coatings. The globular protein like shape suggests uses in catalysis, drug encapsulation, various types of guest-host chemistry; and so on.

These properties naturally depend upon the conformation and shape of the molecules. Initial theoretical work by de Gennes and Hervet [1)] suggested a dense-shell model, where the end-groups are located near the periphery of the molecule with a density that increased sharply with generation number. More recent simulations using a variety of approaches[2-6)] suggest that the lower generations ($g \leq \approx 4$) indeed have an open structure with the chain ends located near the periphery, but by the fifth generation there is a more spherical three-dimensional structure with an approximately uniform density of end groups found throughout the molecule. This inward folding of the chain-ends is supported by recent experimental nmr work by Wooley et al.[7)] on a fifth generation dendrimer.

The conformation and hence properties of dendrimers will obviously depend upon the generation number, the functionality of the cross-link points and their spacing, the nature of the end-groups, and so on. In recent work in this laboratory we have found that even in linear polymers there are what we call screening and spacing effects.[8-14)] Essentially, a chain bends back on itself, largely through local as opposed to long-range effects, such that there are a greater number of like-like contacts in blends and solutions than would be predicted on the basis of a random mixing of segments.[9)] Similarly, we determined that the ability of functional groups to hydrogen bond to partners on different chains depend upon their topological “spacing”. For example, the equilibrium constant describing the number of hydrogen bonds formed between the OH groups of poly(4-vinyl phenol) (PVPh) and the carbonyl groups of ethylene-co-vinyl acetate copolymers increases as the amount of ethylene in the latter increases, spacing the vinyl acetate groups along the chain (we believe this increase in accessibility is related to the increase of rotational freedom of a vinyl acetate group relative to its acetate neighbors along the same chain).[11,12)] These conclusions were based on the unique ability of infrared spectroscopy to “count” contacts in hydrogen bonded systems.[8)] Because many dendrimers contain internal functional groups and chain ends that hydrogen bond, this immediately suggests that infrared spectroscopy should prove to be a powerful tool for the investigation of conformation, accessibility and interactions in these systems. In this paper we will explore this idea through an initial infrared spectroscopic study of a hyperbranched dendrimer-like polymer and its solution and blends.

Experimental

A generation 5 aliphatic hyperbranched polyester with hydroxyl terminal groups was obtained from Perstorp Polyols Inc. In these materials dendritic growth is controlled through the stoichiometry of the reactants and the polymer is presumably polydisperse.

Nevertheless, as we will show below, the ratio of end-groups to "internal" functional groups is close to what would be expected for a perfect dendritic structure.

Acetic anhydride and 4-ethyl phenol (EPh) were obtained from Aldrich, PVPh (M_n = 30,000 g/mol) from Polysciences, and ^{13}C acetic anhydride from Cambridge Isotope Laboratories, Inc. Acetylation of the terminal OH groups to form esters was accomplished by refluxing in THF overnight at 80°C. The product was precipitated in water, collected and dried under vacuum at room temperature.

Samples for infrared analysis were obtained by casting from 2% (wt/vol) solutions in THF onto KBr windows. After initial evaporation of the THF, residual solvent was removed by heating in a vacuum oven at 70° C for 48 hours. Great care has to be taken to ensure that infrared absorption is within the Beer-Lambert law range and that the films are of even thickness, otherwise band distortions are likely to occur.15) Blends with PVPh were annealed at 160°C overnight (above the T_g of the mixture). Infrared spectra were recorded on a Digilab FTS-45 Fourier transform infrared spectrometer at a resolution of 2 cm^{-1}.

Results and Discussion

Even a cursory examination of a schematic representation of the hyperbranched material used in this study, shown in Figure 1, suggests that infrared spectroscopy should be a useful probe of structure.

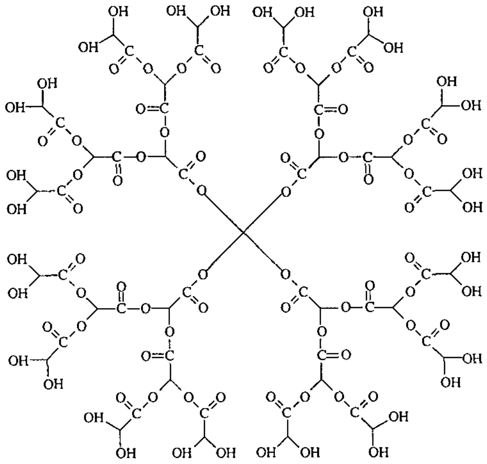

Figure 1. Schematic representation of a dendrimer

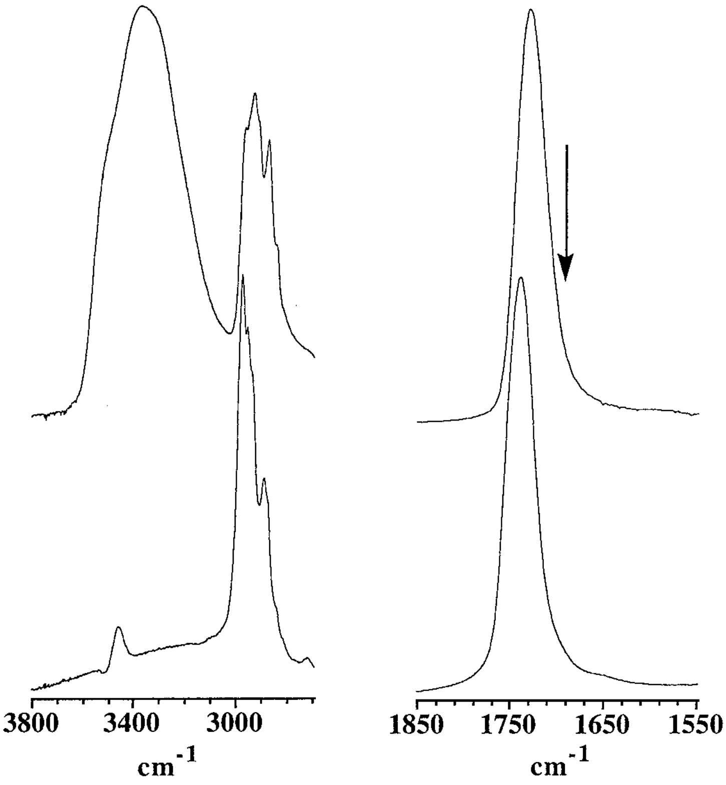

Figure 2. Infrared spectra in the O–H and C=O stretching region. Top: Original G5 hyperbranched polyester with terminal hydroxyl end groups. Bottom: After acetylation of the terminal O–H groups.

In the solid state the terminal OH groups can obviously hydrogen bond to one another or their partners on adjacent molecules, or they can "bend back" into the molecule to hydrogen bond to carbonyl groups within the core, or interpenetrate their neighbors to again hydrogen bond to available ester groups. These possibilities can be probed by examining the infrared spectrum in the OH and carbonyl stretching region, as shown in Figure 2. The OH stretching region clearly consists of a number of overlapping bands, consistent with the presence of some "free" (non hydrogen bonded) groups, together with the various hydrogen bonded structures mentioned above. The carbonyl stretching region also shows evidence of hydrogen bonding, but because aliphatic hydroxyls strongly self-associate and the alkyl O–H/ester carbonyl interaction is not as strong as, say, the corresponding phenolic O–H/ester carbonyl interaction, the hydrogen bonded component only appears as a weak band on the low wavenumber side of the free mode.16) Accordingly, all that is observed is a band profile centered near 1730 cm^{-1} that appears asymmetrically broadened. That this band is indeed present becomes clear when the terminal O–H groups are acetylated, converting them to ester groups. This results in the appearance of a single symmetric band near 1740 cm^{-1}, as also shown in Figure 2. The acetylation appears almost complete, in that only very weak bands remain in the OH stretching region (and these could be overtone or combination modes).

This immediately tells us that there must be some interpenetration of terminal OH groups into the core of its own and/or neighboring molecules, but the extent of this is not clear, because alkyl O–H/ester hydrogen bonds are too weak to be good quantitative probes. Furthermore, our previous work on blends has demonstrated that PVPh is miscible with a wide range of polyesters and gives free and hydrogen bonded carbonyl bands that are well-separated and (relatively) easily measured. Forming blends with PVPh should tell us the extent to which a linear polymer can interpenetrate the core of a dendrimer, relative to a low molecular weight analogue such as EPh, presuming that the carbonyl ester groups are sufficiently accessible that enough hydrogen bonds can be formed to drive mixing and the formation of a single phase system. However, we would not want to mix these phenolic materials with the original OH terminated dendrimer, as the various combinations of allowed hydrogen bonds would be too complex for analysis. At the same time, we would like to distinguish between the terminal groups and those in the core, as this would provide some intriguing information on functional group accessibility. Accordingly, we acetylated a sample using ^{13}C labeled acetic anhydride. The carbonyl stretching region of the infrared spectrum of this sample is compared to that of the non-labeled sample in Figure 3, showing the appearance of a ^{13}C carbonyl stretching mode near 1700 cm^{-1}, well separated from the "core" unlabeled groups near 1740 cm^{-1}. Furthermore, if we assume that ^{13}C labeling does not change absorption coefficients significantly, then the number of terminal groups is almost equal to the number of core groups (the intensities of the ^{12}C and ^{13}C modes are almost equal) indicating that this hyperbranched material does not have a large number of defects and is indeed dendrimer-like in its structure.

We first measured the relative accessibility of the terminal and core groups using EPh as a probe. The carbonyl stretching region of the spectra of the original ^{13}C acetylated dendrimer and a 75/25 by weight (75% EPh) mixture are also compared in Figure 3.

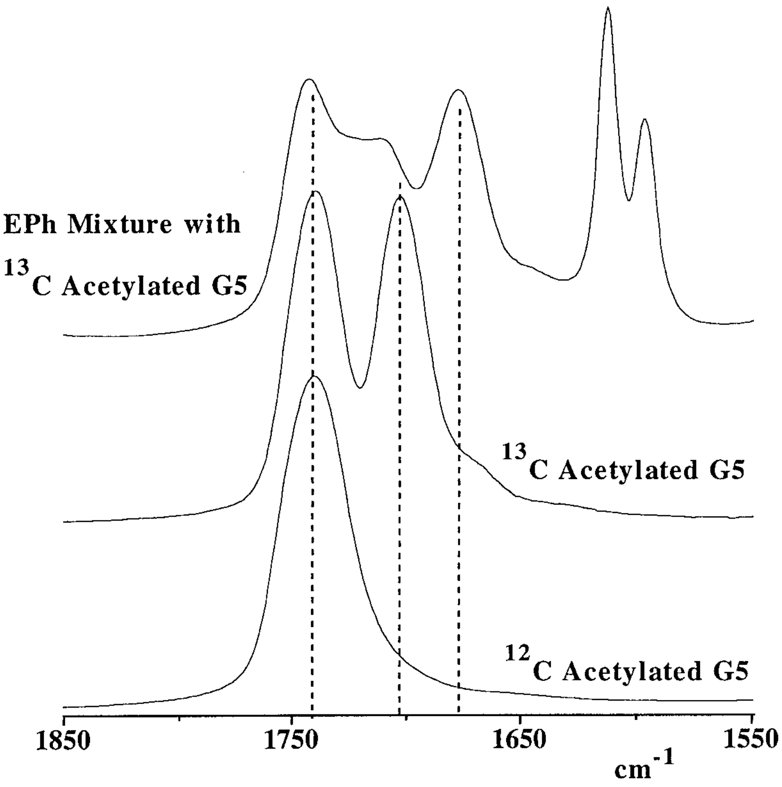

Figure 3. Infrared spectra in the C=O stretching region. Bottom: G5 hyperbranched polyester after ^{12}C acetylation of the terminal O–H groups. Middle: G5 hyperbranched polyester after ^{13}C acetylation of the terminal O–H groups. Top: 75:25 wt % EPh mixture with ^{13}C acetylated G5.

We would anticipate the presence of four bands in the spectrum, free modes near 1740 and 1700 cm^{-1} (^{12}C and ^{13}C, respectively) and hydrogen bonded bands that are shifted $\approx$ 25 cm^{-1} from these positions. The hydrogen bonded ^{13}C band is clearly resolved near 1678 cm^{-1}, but the hydrogen bonded ^{12}C band and the free ^{13}C carbonyl mode overlap considerably. Nevertheless, the sum of these two bands is clearly less than either the free ^{12}C band and the hydrogen bonded ^{13}C band, immediately demonstrating that the peripheral or terminal carbonyl groups are much more accessible than those in the core.

In order to quantify this we need to curve resolve that spectrum of the blend. Great care must be taken here, because it is very easy to get spurious or meaningless results unless you can fix the parameters, (number of bands, peak positions, width at half-height and band shape) that are used in the fit. Fortunately, in this case, we know that characteristics of the free bands from the spectrum of the pure dendrimer. Also, by making mixtures of the ^{12}C acetylated dendrimer with EPh we were able to fix the characteristics of the ^{12}C hydrogen bonded band.

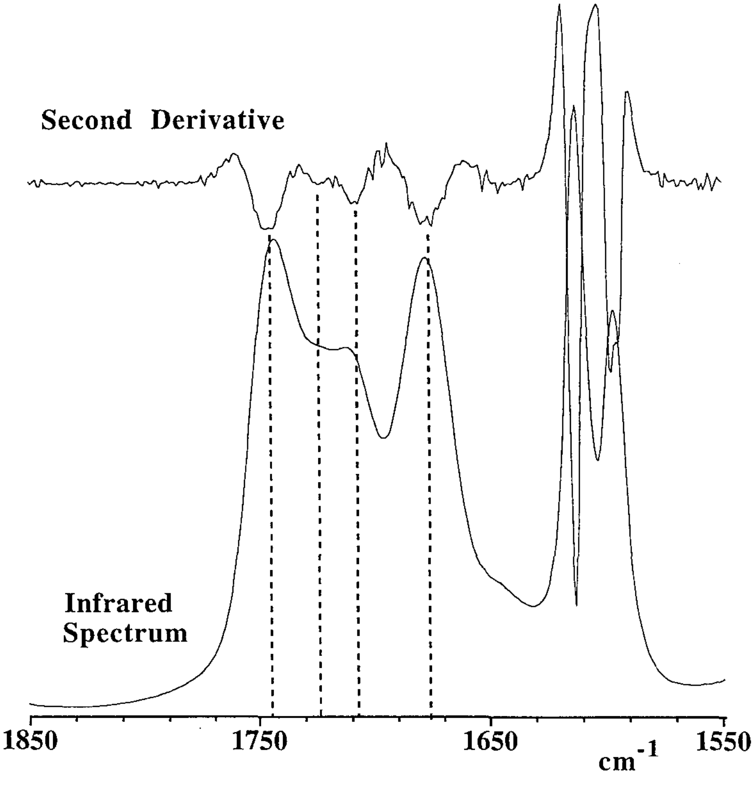

Figure 4. Bottom: Infrared spectrum of the 75:25 wt % EPh mixture with ^{13}C acetylated G5 in the C=O stretching region. Top: Second derivative of the spectrum.

A second derivative of the spectrum of the 13C acetylated spectrum, shown in figure 4, confirmed the peak positions and we were able to obtain the results shown in figure 5. (A complete discussion of our curve-resolving protocols, including how we set the baseline, the cut-offs we use to define the region to be analyzed, etc., are given in reference 15).

The curve-resolved bands shown in figure 5 can be considered as two pairs, free and hydrogen bonded ^{12}C (core) carbonyl groups (1745 and 1724 cm^{-1}, respectively) and free and bonded ^{13}C (terminal) groups (1707 and 1678 cm^{-1}, respectively). Because we start with practically equal concentrations of each type of group, the relative intensities of the bands are a measure of the fraction of hydrogen bonds of each type. Accounting for the difference in absorption coefficients according to previous studies[8)], we calculate that 64% of the terminal groups are hydrogen bonded, while only half of this figure, 32% of the core groups, hydrogen bond.

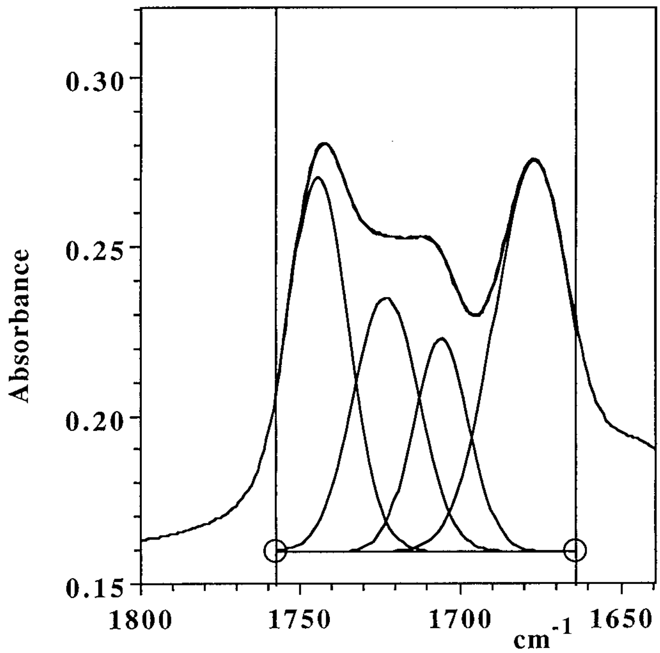

Figure 5. Result of curve fitting the infrared spectrum of the 75:25 wt % EPh mixture with ^{13}C acetylated G5 in the C=O stretching region.

This would suggest an extended conformation for this molecule with the terminal groups near the periphery, as opposed to the compact shape found in simulations, where the terminal groups for generation 5 and larger dendrimers are distributed more-or-less uniformly throughout the structure.[2-6] However, these simulations were performed for mixtures or solutions that were at best athermal. Here we have significant negative contributions to the free energy of mixing from hydrogen bonds. Although chains are thought to be close to ideal in the concentrated regime, the highly branched and compact nature of these molecules coupled to the strong driving force for forming contacts with EPh could well lead to a significant conformational change relative to the pure state.

It is now interesting to compare the accessibility of the dendrimer ester groups to a linear polymer, as opposed to a low molecular weight solvent. Because of screening effects we have found that there are significantly fewer hydrogen bonds formed between identical functional groups in blends than in polymer solutions or mixtures of low molecular weight analogues.[8] Blends with PVPh were therefore prepared. DSC results showed a single Tg between those of the pure components, indicating that mixture is miscible. The curve resolved spectrum of a PVPh/^{13}C acetylated dendrimer blend (75/25) is shown in figure 6 (obtained using the same protocols as above). The fraction of hydrogen bonds formed by the terminal groups, ≈ 56%, is indeed less than found in EPh mixtures, but the fraction of hydrogen bonds formed by the core ^{13}C esters is, within error about the same (~34%). Care must be taken here, however, because there is a difference in the molar volume of EPh and the repeat unit of PVPh that will affect the number of hydrogen bonds that can be formed (i.e. a weight % concentration scale does not make for an equivalent concentration of functional groups). The best way to compare these results is to calculate a equilibrium constant for phenolic O–H/ester carbonyl groups, K_A . Usually, we employ data over a range of compositions, so that the one point calculations presented in this initial study only allow "ball-park" comparisons. However, for the terminal groups we find that K_A is close to 110 for EPh mixtures and 52 for PVPh blends (dimensionless units normalized to a common molar volume of 100 cc/mol, see reference 8 and citations therein). These correspond to values found for poly(vinyl acetate)/EPh mixtures and poly(vinyl acetate)/PVPh blends, respectively, indicating that the terminal groups are essentially as accessible as equivalent functional groups in linear polymers. The core groups have a value of K_A near 15, and are thus highly "screened".

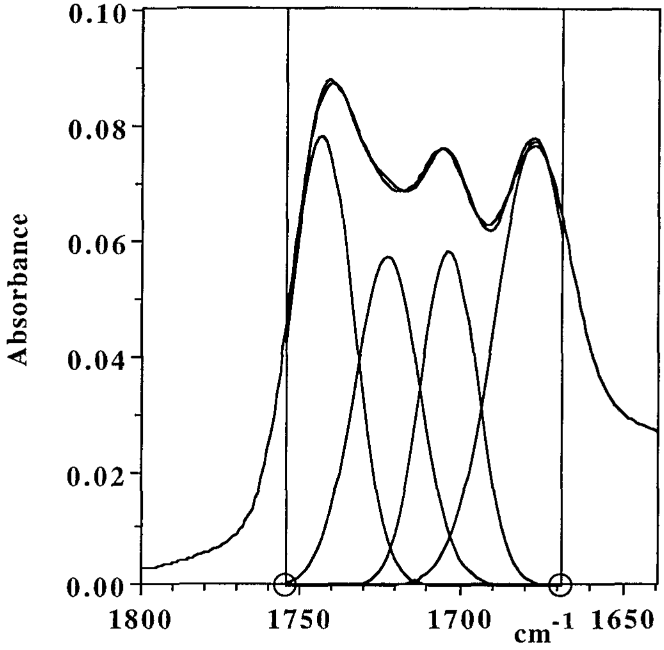

Figure 6. Result of curve fitting the infrared spectrum of the 75:25 wt % PVPh blend with ^{13}C acetylated G5 in the C=O stretching region.

Conclusions

First, we would emphasize that these are preliminary results and studies over a range of compositions are necessary for accurate work. Our main conclusions are obvious, however, because the observed difference in the degree of hydrogen bonding is well-outside any experimental errors. The terminal groups in these mixtures are clearly more accessible than the core groups, suggesting a conformation with the terminal groups located near the periphery of the molecule. Given that previous work strongly indicates a compact structure in the solid state or athermal solvents, there must presumably be a significant conformational change driven by the favorable free energy associated with hydrogen bond formation.

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