



SOLID STATE NMR CHARACTERIZATION OF STRUCTURAL AND MOTIONAL PARAMETER DISTRIBUTIONS IN POLYAMIDONAMMONIUM DENDRIMERS

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Abstract

The characterization of narrow distributions of structural and motional parameters, and their evolution during the broad glass transition, is performed for deuterated PAMAM dendrimer slats using solid state NMR. The broadening of deuteron quadrupole echo (QE) lineshapes is consistent with the presence of narrow hydrogen bond length distribution ($\sigma_r < 0.25 \text{ \AA}$) at the spacer amide and branching tertiary amine sites. The temperature dependent averaging of the experimental lineshapes is explained on the basis of fast planar librations in the dendrimer interior, and fast rotation and intermediate regime libration (in an asymmetric cone) of the dendrimer termini. The amplitudes of libration are temperature dependent and higher for low generation dendrimers, while librational rates show Arrhenius behavior only within the glass transition region. In this region, the width of the log-normal distribution rates increases with temperature at sites associated with chlorine counterions. The largest distributions are still less than one order of magnitude wide, unlike the dendrimer in solution or the linear polymers. Interpenetrated low generations ($G < 3$), uniform intermediate generations ($G = 3-5$) with surface network, and backfolded high generations ($G > 5$), are distinguished by interior and termini dynamics.

In the regime of fast motion QE lineshapes are highly sensitive to the presence of narrow structural and motional parameter distributions, and provide constraints on motional geometry independent of rates. The precise characterization of narrow log-normal rate distributions in the intermediate regime can be done using ^2H magic angle spinning (MAS). Deuteron inversion-recovery techniques provide quantitative information on the rates of fast motion. For PAMAM salts, the influence of narrow distributions of structural and motional parameters, and fast planar libration, is negligible for distance determination using Rotational Echo Double Resonance (REDOR). The discrimination between inter- and intra-molecular hydrogen bonding can be done through selective labeling of dendrimer core and termini dilution in natural abundance samples according to developed strategies. The internuclear distances evaluated on the basis of QE results are 3.4-4.0 \AA . These fall within the sensitivity range of ^{13}C - ^{15}N REDOR, as exemplified by the measurements on small amino acids according to analytically predicted optimum dephasing scheme.