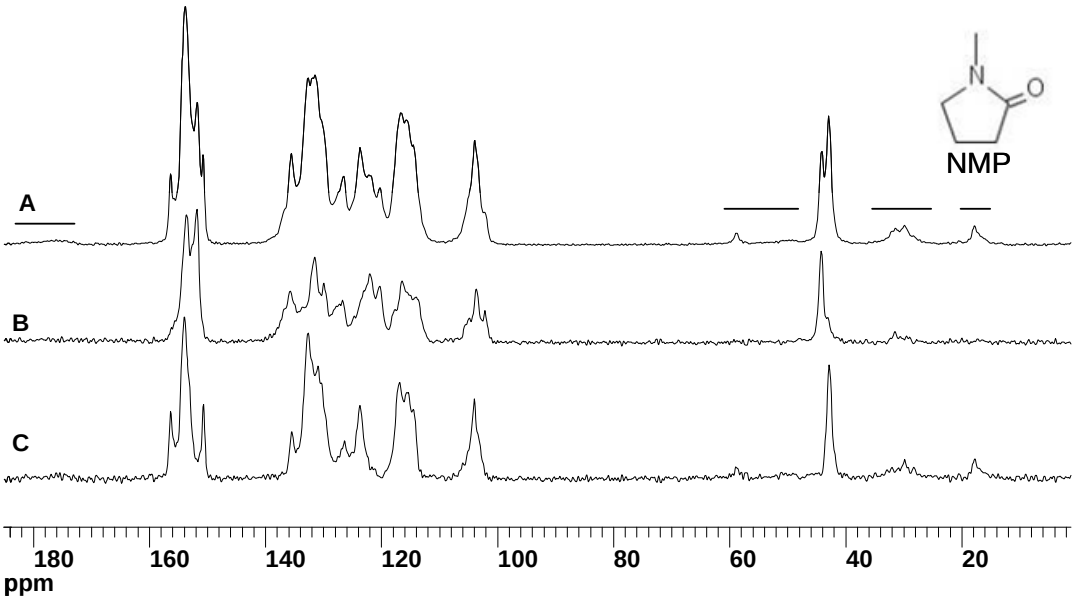

Figure S1. 25 MHz ^{13}C cross-polarization, magic-angle-spinning (CPMAS) spectrum of HR-0. This crystalline sample shows two types of domains whose domain sizes exceed 100 nm. B and C are spectra associated with each of the two domains and these spectra have been separated based on having differing proton longitudinal relaxation times, T_1^H; B represents the shorter-T_1^H component (42% of the intensity; T_1^H <0.5 s) and C the longer-T_1^H component (58 % of the intensity; $T_1^H = (2.0 \pm 0.2)$ s). Very weak resonances near 18, 30, 51 and 176 ppm are associated with the impurity, N-methyl 2-Pyrrolidinone (NMP) whose structure is shown; the majority of that impurity is found in spectrum C. The intensity of the NMP resonances in C corresponds to between 1 and 2 HR-0 molecules per NMP molecule. Resonance assignments for HR-0: 4 tetrahedral C's (40 ppm to 44 ppm), 48 aromatic C's 100 ppm to 160 ppm [24 protonated ring C's (100 ppm to 134 ppm), partially overlapping with 12 unprotonated, C-substituted ring C's (130 ppm to 140 ppm) and 12 unprotonated, OH-substituted ring C's (150 ppm to 158 ppm)]. Regions for the NMP resonances are indicated by the horizontal bars in spectrum A. The fact that the NMP signal cross polarizes indicates that the NMP has solid-state character and is not in a phase by itself (as a liquid); thus, the NMP and HR-0 coexist in the same phase.

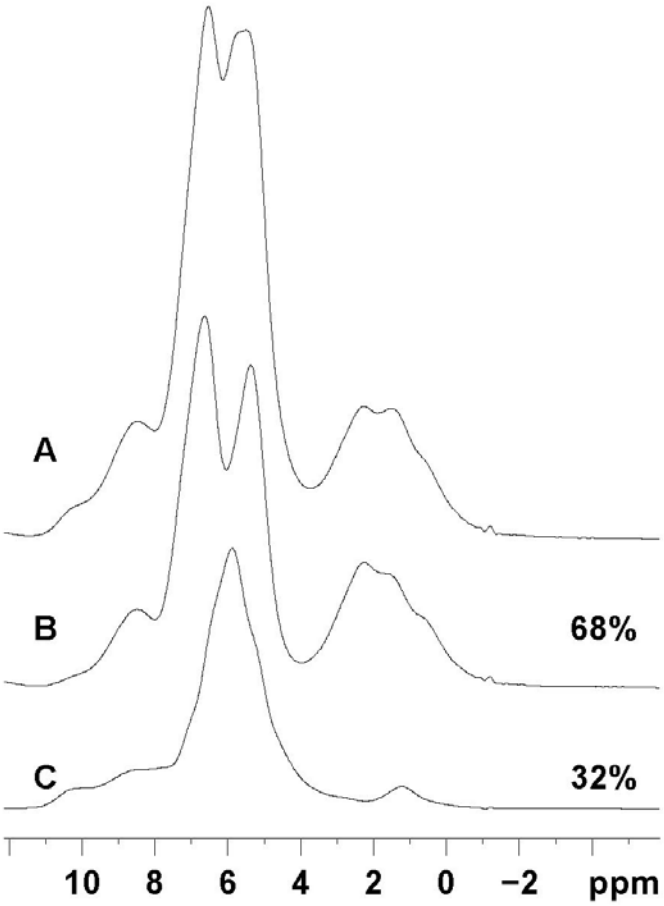

Figure S2. Proton CRAMPS spectrum of HR-0 (A) and its components (B,C) based on a separation of lineshapes exhibiting T_1^H differences. The apparent proton fraction associated with each component is indicated in the figure. Note the much stronger aliphatic contribution in B relative to C, mainly arising from the selective presence of the NMP impurity in the former. Note also the minor intensities in C in the 8 ppm to 10 ppm region, indicative of hydroxyl protons involved in strong H-bonds. Attribution of the excess aliphatic intensity in B to the solvent NMP results in a ratio of NMP molecules to HR-0 molecules of 1.07:1, i.e. essentially 1:1. Taking into account the NMP intensity in B, the actual fractions of HR-0 molecules in B and C are, respectively, 0.63 and 0.37. These fractions are in good agreement with the reported fractions of rccc (0.70) and rctt (0.30) stereoisomers in the synthesis of HR-0. The suggestion is therefore strong that the most symmetric caged stereoisomer of HR-0 has the strong preferential affinity for NMP while the less symmetrical rctt stereoisomer has no special affinity. ^{13}C spectra in Figure S1 provide additional support for the strong partitioning of NMP into the major phase.

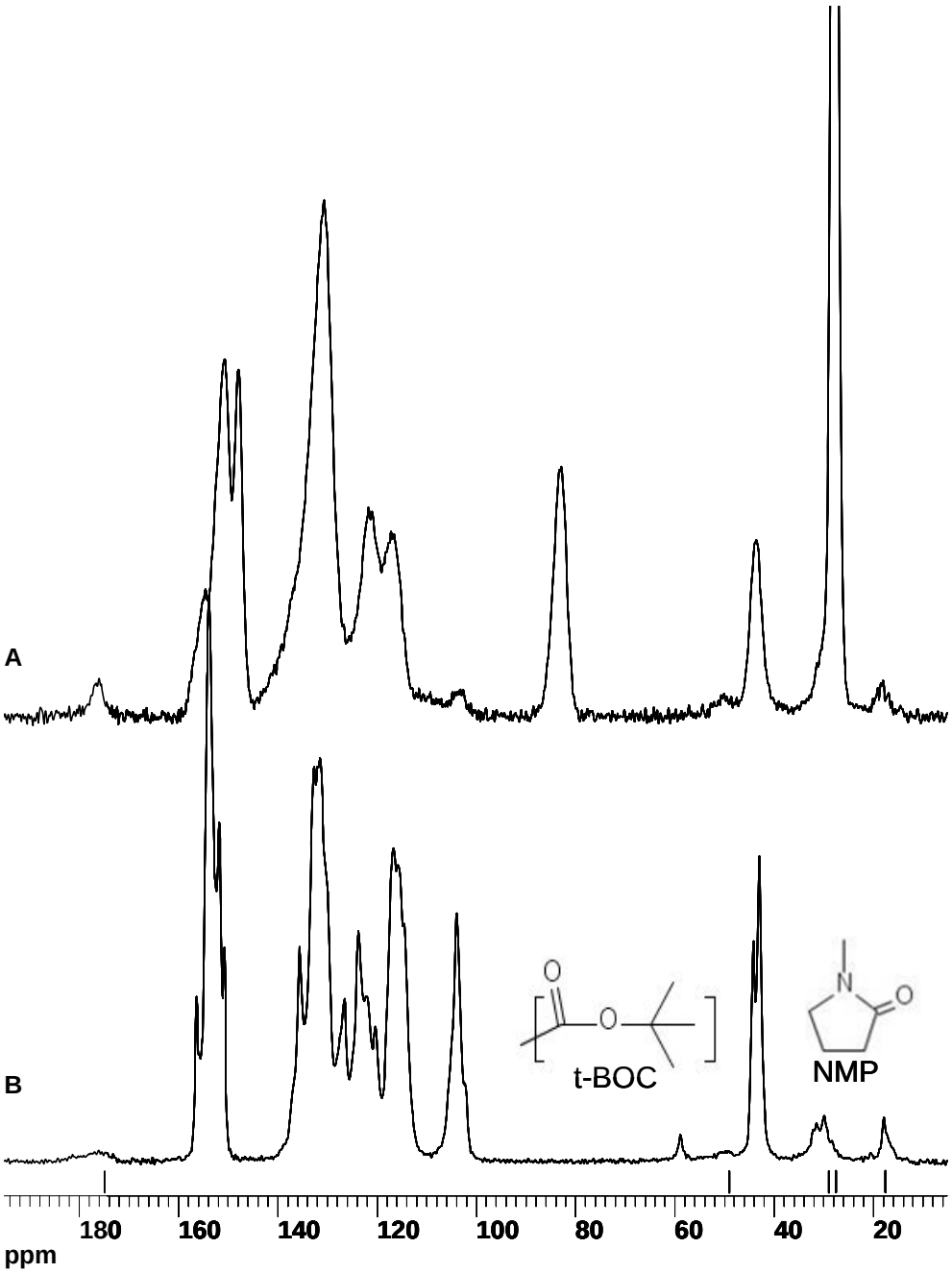

Figure S3. Comparison of CPMAS spectra of samples HR-70 (A) and HR-0 (B). Increase in linewidth from B to A is typical of going from an ordered, crystalline state to a disordered glassy state. In spectrum A one can identify resonances associated with t-BOC substituents (t-butyl methyls at 28 ppm, the quaternary ether carbon at 82 ppm and the carbonyl in the 145 ppm to 158 ppm range. Note also that a lot of shifting of aromatic intensity is seen in the range 100 to 125 ppm. Of particular interest is the change in lineshape for the NMP impurity resonances in the 50 ppm to 60 ppm region (the N-methylene resonance) and in the 170 ppm to 185 ppm region (the N-carbonyl resonance). Changes in these lineshapes indicate that the ^{14}N quadrupolar coupling of the NMP is changing, at least in orientation if not in magnitude, upon going from the crystalline, underivatized state of HR-0 to the glassy, derivatized state of HR-70. Positions of NMP resonances in chloroform solution are given by vertical bars above the shift axis.

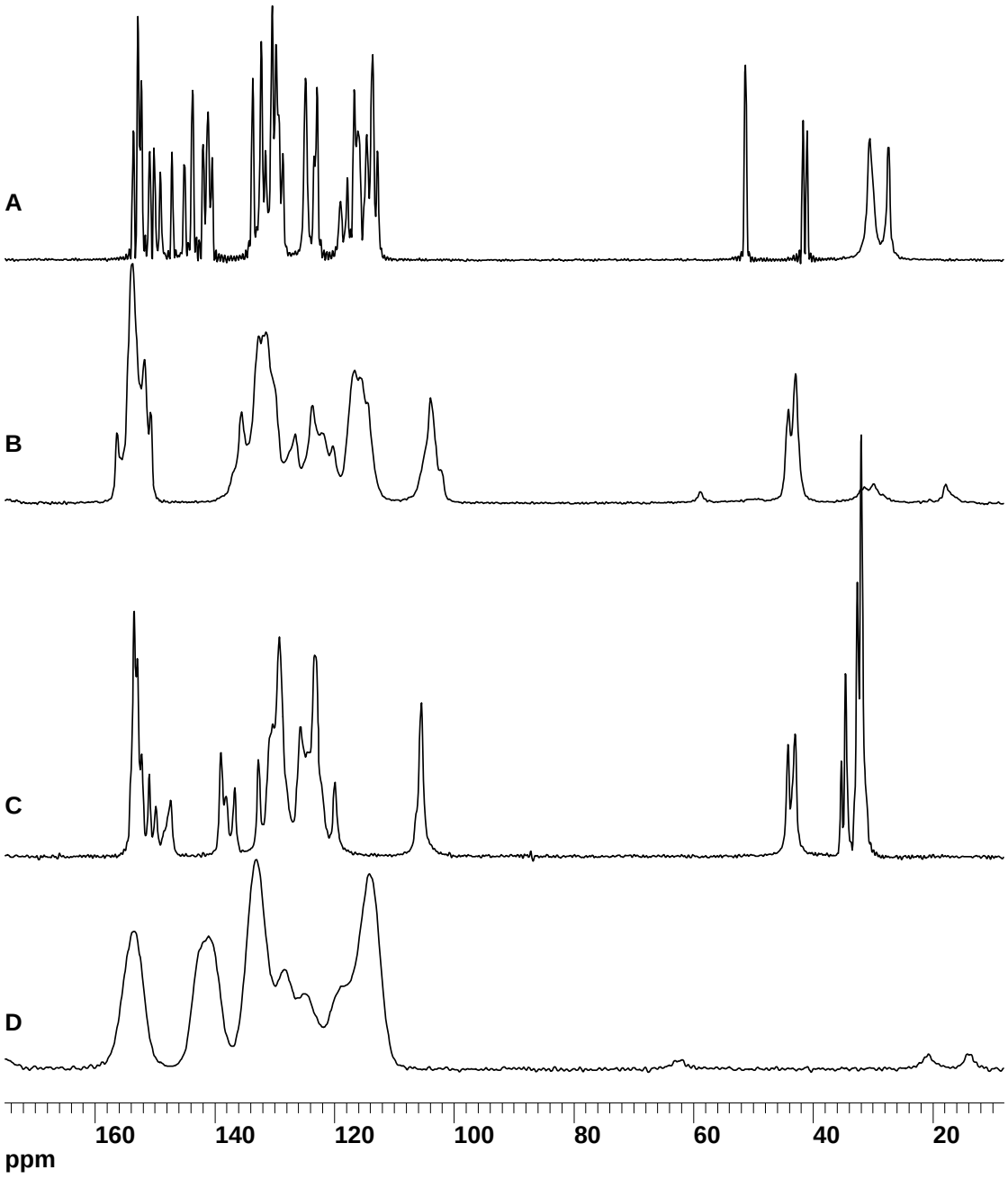

Figure S4. 25 MHz CPMAS spectra (4 kHz spinning frequency, 2 ms CP time) of underivatized MGs. A: TS-0; B: HR-0; C: tBR-0; D: PB-0. The poor resolution in D suggests a lack of crystallinity in PB-0. The remainder are assumed crystalline on the basis of much better resolution where the differences in resolution among those three spectra probably reflect differences in magnetic susceptibility anisotropy with TS-0 expected to have the smallest anisotropy. The weak resonances in D are from the entrained solvent impurity, ethyl acetate.