Electronic supplementary information (ESI):

Solid State NMR Investigation of Photoresist Molecular Glasses Including Mixing Behavior with a Photoacid Generator[1]

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NMP affinity for HR samples

A secondary issue that initially caught our attention in this investigation was the apparent affinity of 1-methyl-2-pyrrolidinone (NMP) for HR-0. This sample showed two different domains having dimensions that exceeded 100 nm owing to the fact that each domain had a different longitudinal proton relaxation time, T_1^H. Moreover, these domains were both judged to be crystalline on the basis of ^{13}C CPMAS linewidth differences between the glassy HR-70 and HR-0. Figure S1 shows the HR-0 CPMAS spectrum (S1A) along with the component spectra, based on differing T_1^H values. The figure caption gives details about the component spectra, the relative amounts of each and some information about spectral assignments. Of interest is the fact that most of the NMP is found in one of the phases and that, based on the attempts to integrate the NMP and the HR-0 intensities, it is estimated that the ratio of HR-0 molecules to NMP molecules is between 1 and 2.

A more accurate estimate of this latter ratio comes from a similar comparison of the proton CRAMPS spectra shown in Figure S2. If the HR-0 sample were without impurity, then the only aliphatic protons would be the 4 methine protons and these would represent 10 % of the total protons since, in these materials, the phenolic hydroxyl protons strongly overlap the aromatic protons. However, the aliphatic region of the HR-0 spectrum (S2A) contains much more than 10 % of the intensity. If one looks at the T_1^H-separated component spectra, S2B and S2C, it is clear that spectrum S2B, representing 68 % of the total intensity, is the only one with excess aliphatic intensity. If one separately integrates the aliphatic and "aromatic-plus-hydroxyl" intensities, one can deduce that the ratio of HR-0 to NMP molecules is (0.94 ± 0.10, i.e. very close to unity. This assay is significantly more accurate than that obtained from the noisier ^{13}C intensities in Figure S1. Hence, we conclude that the major phase is both crystalline and a near-stoichiometric 1:1 combination of HR-0 and NMP molecules. Moreover, making adjustment for the contribution of NMP to the proton spectrum of S2B, we conclude that the major phase has 63 % and the minor phase 37 % of the HR-0 molecules.

We did not pursue this further; however, we assume that the underlying reason for the 2-phase behavior and for the strong affinity of NMP for only one of the phases is that in the synthesis of HR-0, there was no attempt to isolate the stereoisomers of HR-0. In a report dealing with the analysis of isomers for several synthesized resorcinarenes, Weinelt, et al. [1]indicate that two of the four possible stereoisomers of HR-0 were found in their synthetic product of HR-0; the breakdown was 70 % of the rccc stereoisomer and 30 % of rctt. Our (63/37) % ratio is very similar and that provides us with good reason to believe that our HR-0 sample crystallized into two regions based on the two dominant stereoisomers and that the high affinity for NMP is associated with the most symmetric rccc stereoisomer. This stereoisomer is bowl-shaped[1] having the planes of the four tetrasubstituted rings forming the sides of the bowl and the four remaining rings pointing straight down from the base of the bowl. Weinelt, et al. also synthesized tBR-0 and detected only the non-bowl shaped rctt isomer. Since NMP was not used as a solvent for tBR-0 in our studies we do not expect to garner parallel information about any possible affinity between NMP and tBR-n materials.

Change in NMP/HR interactions upon derivatizing the HR

Given the strong interaction between HR-0 and an NMP molecule, one might expect to see evidence for this in the solid state spectra. Two potential observations are among those that might be indicative of a strong interaction. First, proximity to an aromatic ring could shift NMP resonances either slightly upfield or downfield, depending on that atom's distance from and orientation to the planes of the aromatic rings.[2] Secondly, the existence of a ^{14}N atom having spin = 1, in NMP offers the possibility that the ^{14}N nuclear quadrupolar interaction could be modified by association with the HR-0 molecule. It is this second possibility that we will briefly pursue in a very qualitative way, given that the details of the NMP/HR-0 are not the primary focus of this paper.

The way in which the ^{14}N quadrupolar interaction shows up in proton or ^{13}C spectra is through the dipolar couplings of those ^{14}N nuclei to the observed nuclei[3-6]. Under magic angle spinning, in the absence of ^{14}N quadrupolar interactions, these heteronuclear dipolar couplings should average to zero. However, if the ^{14}N quadrupolar coupling competes, energetically, with the Zeeman energy of the ^{14}N nucleus, then, as the rotor turns through different angles in its rotation, the quantization axis of the ^{14}N nucleus can modestly move away from the direction of the applied magnetic field. In that

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case, it appears to the nearby ^{13}C (or proton) nuclei that the ^{14}N has a magnetic moment which, in magnitude and direction, is a function of the rotor angle. This is a recipe for not fully averaging to zero the dipolar interactions with the ^{14}N. Since dipolar interactions are, among other dependences, proportional to the inverse cube of the associated internuclear distances, the influence of the ^{14}N quadrupolar interaction on the spectrum of protons or ^{13}C nuclei will depend[5] strongly on the internuclear distances as well as on a) the ratio of Zeeman to quadrupolar interactions for the ^{14}N nucleus, b) the asymmetry parameters of the quadrupolar interaction and c) the orientation of the internuclear ^{14}N-^{13}C vector with respect to the principal axis directions for the quadrupolar tensor. For a given system, this means that spectra will also be more strongly perturbed 1) for those nuclei bonded to the ^{14}N and 2) when spectra are taken at lower applied fields where the quadrupolar interaction becomes more influential. Following this line of reasoning, we examine the 25 MHz (2.35T) ^{13}C CPMAS spectra of HR-0 and HR-70 for evidence of changes in the ^{14}N quadrupolar coupling as reflected in the ^{13}C nuclei bonded to the ^{14}N nucleus. The foregoing samples are also favorable candidates for comparison because they had comparable molecular ratios of NMP to either HR-0 or HR-70.

The structure of NMP is given in Figure S3 along with a comparison of 25 MHz ^{13}C spectra for samples HR-0 and HR-70. Spectra are normalized to give the same intensities for the strongly-cross-polarizing methine carbons near 44 ppm. This normalization corresponds to equivalent numbers of HR-0 and HR-70 molecules. Solution-state NMP resonances in chloroform are reported[7] to occur at (17.7, 29.5, 30.7, 49.4 and 174.5) ppm. In spectrum 9B, minor resonances for HR-0 are observed in those same general areas with the most intense resonance(s) near 30 ppm, as expected. While we could not find a reference to the definitive assignment of these high resolution resonances to various carbons in NMP, it is pretty clear from an inspection of assigned shifts for related compounds[8] that the solution chemical shifts assigned to the three carbons directly bonded to the nitrogen are as follows: N-methyl (29.5 or 30.7), N-methylene (49.4) and N-carbonyl (174.5). Given that the t-BOC resonances overwhelm the region near 30 ppm for the HR-70 sample, we cannot compare lineshapes for the methyl carbon. In contrast, the low-field N-carbonyl and N-methylene resonances allow for some comparison. The first qualitative conclusion to be drawn is that in the HR-0 sample, these latter resonances show asymmetric doublets. The existence of such doublets, often in a 2:1 ratio, tends to be associated with the (S= +1,-1) and (S= 0) spin states of the ^{14}N nucleus. In addition, such a doublet may also be taken as evidence of the “solid state” character of the spectra, i.e. of the *reorientational immobility* of the NMP molecules on the time scale of a few μs. Secondly, while we recognize that HR-0 is crystalline and HR-70 is glassy, if the NMP had similar interactions with the MG in both samples, one impact on these two NMP resonances would be that the resonances in the HR-70 should become broader. What is observed, however, is that the carbonyl resonance becomes a bit narrower and more symmetric. More informative is the change in the N-methylene lineshape which shows, for HR-0, a significant narrow feature near 59 ppm along with a broad shoulder extending at least to 48 ppm, but for HR-70, the feature near 59 ppm disappears in favor of a more intense resonance near 50 ppm. Given that these lineshape changes occur at what we presume to be constant C-N bond length in NMP, and given that changes only in the strength (not in the orientation) of the quadrupolar coupling tensor should, to a first approximation, change the overall width but not the shape of the resonances, the substantial change in shape seen for the N-methylene carbon suggests that at least the direction (and possibly the amplitude as well) of the N^{14} quadrupolar coupling is changed upon going from the HR-0 crystalline state to the HR-70 glassy state.

For the sake of completeness, one has to recognize the possibility, for highly aromatic solids like the HR samples, that ring-current shifts [[cross ref. to ref #2]] can also play a role in dictating lineshapes. These shifts depend on the position of carbons with respect to the planes of the nearby aromatic rings. Without going into a more extended argument about how ring current shifts might influence the NMP resonances in the HR-0 and HR-70 sample, it is our contention that, especially for the N-methylene carbon, ring current shifts are inadequate for producing the observed 5 ppm to 8 ppm lineshape changes if we assume that the NMP occupies exactly the same geometry with respect to the bowl-like structure of the rccc isomer of HR in both HR-0 and HR-70. Under this latter assumption, the most important ring current shifts, associated with the rings forming the bowl, would be preserved. Therefore, the qualitative conclusion of the previous paragraph remains.

As noted in the main text, HR-0 exhibits some very strong H-bonds whereas, for HR-70, those bonds do not form. Hence the charge distribution seen by the NMP in the bowl-like structures of HR-0 and HR-70 may well be altered in a way that creates a modest change in the ^{14}N quadrupolar interaction, even though one expects that the most important considerations for determining the quadrupolar interaction can be attributed to the intrinsic structure of the isolated NMP molecule. At the same time, it is also a possibility that, for reasons of steric hinderance or of changed polarity, the NMP may not occupy the same region of the HR molecule that it did in the crystalline HR-0 sample. In fact, the ability of the glassy HR-25 sample to hold a substantially higher amount of NMP might be taken as a commentary on the non-specific interaction between NMP and the glassy, derivatized forms of HR. Further support for this idea might also reside in the observation that the NMP resonances in the glassy HR-70 and HR-25 preparations, with or without PAG present, have lineshapes which are reasonably symmetric and centered at values close to those observed in solution. We emphasize, however, that the NMP in the HR-70 sample **cannot** have fast-isotropic, liquid-like mobility in these glasses and still cross polarize with the observed strength. Recall also that the NMP cannot be removed from these samples by pumping in vacuum at 40 °C.

Miscellaneous Observations

Evidence for crystallinity, indicated by a higher achievable resolution, is seen in both ^{13}C and proton spectra of the underivatized materials, except for PB-0. In Figure 5, CRAMPS spectra in the left column, except for PB-0, have superior resolution compared to all remaining samples. Figure S4 shows ^{13}C spectra of the four underivatized materials; again the PB-0 sample has poorest resolution, while the TS-0 sample has the best resolution in both the ^{13}C and proton spectra. Recall that PB-0 is a mixture of two isomers. X-ray scattering (not shown) of PB-0 shows some peaks; hence this material is not simply an amorphous glass. However, by DSC there is no observed melting point for this material, nor can one find any glass transition temperature when scanning to 300 °C. The broader proton and ^{13}C resonances in PB-0 and the peaks in the X-ray scattering are probably indicative of 2 dimensional order, rather than 3-dimensional crystalline order. The superior resolution of the TS-0 among the three crystalline samples in Figure S4 probably arises from the differing values of magnetic susceptibility anisotropy for each of the crystals. In highly aromatic materials, the susceptibility anisotropy depends, to a large extent, on the vector sum of the normals to the aromatic rings in the crystal. The larger that sum, the larger this anisotropy tends to be and the lower the resolution becomes[9] in a polycrystalline sample. ^{13}C spectra of the derivatized samples will not be shown, beyond what has already been shown. Spectrum S3A is a good example of the typical resolution seen in the glassy, derivatized materials.

^{13}C CPMAS experiments on each material surveyed herein included collecting spectra both with and without a 7 ms spin locking time just prior to cross polarization. If multiple phases are present, each with a different proton rotating frame relaxation time, $T_{1\rho}^{H}$, then it is possible to identify the presence of multiple phases if the lineshapes, with and without prior spin locking differ in shape as well as amplitude. We did not find any cases where the lineshape changed in this way, so, on this basis we have no reason to suspect multiple phases in any of these samples. The multiple phases seen in HR-0 exhibited themselves as differences in T_1^{H} and not in $T_{1\rho}^{H}$. Whereas non-uniform $T_{1\rho}^{H}$'s within a sample imply multiple phases, uniform $T_{1\rho}^{H}$'s within a sample do not necessarily imply a single phase in the event that both phases exhibit similar $T_{1\rho}^{H}$'s.

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