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Development of Direct and Optical Polarized Nuclear Magnetic Resonance (NMR) Methods for Characterization and Engineering of Mesophased Molecular Structures

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Abstract

The development of NMR methods for the characterization of structure and dynamics in mesophase composite systems was originally proposed in this LDRD. Mesophase systems are organic/inorganic hybrid materials whose size and motional properties span the definition of liquids and solids, such as highly viscous gels or colloidal suspensions. They are often composite, ill defined, macromolecular structures that prove difficult to characterize. Mesophase materials are of broad scientific and programmatic interest and include composite load bearing foams, aerogels, optical coatings, silicate oligomers, porous heterogeneous catalysts, and nanostructured materials such as semiconductor quantum dot superlattices. Since mesophased materials and precursors generally lack long-range order they have proven to be difficult to characterize beyond local, short-range order. NMR methods are optimal for such a task since NMR observables are sensitive to wide ranges of length (0-30Å) and time (10^{-9}-10^{0}sec) scales. We have developed a suit of NMR methods to measure local, intermediate, and long range structure in a series of mesophase systems and have constructed correlations between NMR observables and molecular size, topology, and network structure. The goal of this research was the development of a strong LLNL capability in the characterization of mesophased materials by NMR spectroscopy that will lead to a capability in rational synthesis of such materials and a fundamental understanding of their structure-property relationships. We demonstrate our progress towards attaining this goal by presenting NMR results on four mesophased model systems.

Introduction

There is intense scientific interest in the rich potential of directing agents (templates and linkages of polymers or surfactants, for example) to control the nucleation and growth, and thus the morphology and structure of, organic/inorganic nanoscale macromolecular structures. Potential applications of these organic/inorganic structures include their use as structural materials, as chemical catalysts, as critical components in advanced electronic architectures, and as biomedical implants [1-8]. These materials often possess structural heterogeneity over many length scales. In the short range (angstroms) disorder can occur in the local bonding structures. In the nanometer range, the materials may be characterized by disorder in the spatial proximity of structural and functional domains. On the micron range, disorder can be found in larger features such as pore structure. Unfortunately, many nanostructured materials, or important precursors in their production, have proven difficult to characterize beyond local, short-range order due to this inherent disorder. Characterization can further be hampered by complex motional properties that span timescales between that of solid and liquid phases.

A number of important materials fall into this gap, and are known as mesophased materials. For example, high molecular weight elastomers, polymers above their glass transition temperature, sols, gels, cell membranes, colloidal aggregates and silicate oligomers all can be characterized by long range structure with out long range order, and cannot truly be characterized in their natural state as solids. *As a result, rational design and detailed understanding of the chemistry and physics behind any novel materials properties becomes difficult to predict in the absence of detailed structural insight.*

Small Angle X-ray and Neutron Scattering (SAXS and SANS) are currently one of the only characterization techniques for these systems. However, SAXS and SANS have burdensome equipment, data analysis, time and, consequently, cost constraints. The development of routine analytical methods to investigate and characterize the long-range structure and dynamics of mesophase systems is of increasing importance and Nuclear Magnetic Resonance (NMR) spectroscopy holds much promise for this task. NMR observables are sensitive to short, intermediate, and long-range structure without the need for long range order. NMR can, in principle, measure structural parameters from 0-30Å and NMR observables are uniquely sensitive to motional timescales over 9 decades (10^{-}

$^{9} \geq \tau_c \geq 10^0$ sec) [9-14]. The measurement of motional processes over multiple timescales can often be correlated to size and chemical properties. In addition, by exploiting recently developed optical polarization capabilities at the Laboratory, we can also investigate long-range structures with low concentrations or with surface specificity unheard of in standard NMR methodology.

We are developing novel Nuclear Magnetic Resonance (NMR) methods that will provide structural and dynamic characterization over wide size and time scales. This project exploits LLNL expertise in the production of nanoscale materials, ongoing multiscale computational efforts, and expertise in applying nuclear magnetic resonance (NMR) spectroscopy to disordered systems to develop a strong LLNL capability in the characterization of mesophased materials. The work described in this report details the the initial development of some NMR methods to measure local, intermediate, and long range structure in a series of mesophase systems. The methods developed in the course of this study will be of practical application to soft materials research in stockpile stewardship and bioscience research at the laboratory. For example, the techniques developed could be applied to the characterization of composite foams and HE/binder systems, Aerogel target materials, and energetic materials (DNT), membrane proteins and large molecular weight biomolecules (BBRP), sol-gel optical coatings (Lasers), and colloidal silicate oligomers (EES).

Experimental

Materials: Four model materials were synthesized for this work, a filled polydimethyl – polydiphenylsiloxane block copolymer composite, polymeric organic materials with nanometer size heterogeneities (an organic aerogel synthesized with ^{13}C enriched formaldahyde and a polyurethane elastomer), and functionalized germanium and silicon quantum dots. Details of the synthesis of these materials can be found elsewhere [16-23]. All these materials were synthesized at LLNL utilizing the advanced synthetic capabilities available in CMS.

NMR methods: Experiments were performed on either a Chemagnetics CMX-300 or a Bruker DRX-500 spectrometer. Commercially obtained magic angle spinning and wideline probes were used in these experiments. Pulse widths were calibrated on either the material of interest, or in cases where insufficient signal to noise was available in 4 scans, a concentrated reference solution. ^{1}H, ^{13}C, and ^{29}Si chemical shifts were referenced to the respective resonance of TMS at room temperature.

Magic angle spinning (MAS) and cross-polarization magic angle spinning (CPMAS) NMR were performed with spinning speeds of 5-10 kHz and with RF power levels of 40-70 kHz. Hartmann-Hahn matching was verified on the sample of interest. High powered proton decoupling was used in all cases. Two dimensional WIdeline SEparation (2D-WISE) and one-dimensional spin-diffusion experiments were performed using the standard CPMAS pulse sequence with a ^{1}H frequency precession period or a ^{1}H magnetization filter inserted after the first pulse and a spin-diffusion period added afterward. Double quantum NMR was performed using well established methods for creating and detecting multiple quantum coherences [9,10,24].

Results

Short range structure of model materials.

Standard magic angle spinning (MAS) NMR is a well established method able to measure short range structure in a quantitative manner without the need for long range order [11]. This is highly advantageous in soft materials which lack long range order and are often to mobile for X-Ray based spectroscopic methods. Competing spectroscopic approaches such as IR also meet this requirement but do not offer the ability to sort spectroscopic resonances by the timescales of motional processes. NMR, however, is quite capable of separating spectroscopic signatures by motional lifetimes. MAS NMR it self is unable to distinguish directly between nano- or micro-scale domains within the bulk that are characterized by differing motional properties, but Cross-polarization methods can be used to filter NMR sensititivity of rare nuclei (^{13}C, ^{29}Si, for example) by motional properties. CPMAS operates by transferring spin polarization from abundant protons to the rare nuclei via the dipolar coupling mechanism [9]. The dipolar coupling mechanism is a sensitive probe of internuclear distances and timescales on the

millisecond range [9] and, as a result, cross-polarization can be used to filter the MAS spectra according to motional properties. We have used such an approach to study short-range structure in three of our model systems.

To illustrate this point, we prepared an organic aerogel material with isotopically enriched formaldahyde to test theories of the gelation mechanism. According to previously reported studies, during the gelation stage, sol particles crosslink via both methylene and ether linkages, as shown schematically in Figure 1A [19-22]. A ^{13}C MAS NMR spectrum of this sample is shown in Figure 1B. As can be seen a series of sharp resonances at 80-100 ppm were observed and no broad resonances due to aromatic components, ether linkages, or methylene linkages are seen. We have assigned the narrow resonances to mobile, unreacted intermediate species, likely low molecular weight alcohols that have retained the ^{13}C isotopic label from the formaldahyde. These residual species have been trapped in the pore structure and in interstitial sites in the aerogel matrix. Figure 1C shows the short contact time CPMAS spectrum. The CPMAS spectrum shows a strong broad resonance at 45 ppm and a small broad peak at 65 ppm and has filtered out the narrow peaks due to mobile species. The broad peak at 45ppm is consistent with the methylene crosslink sites arising from incorporation of the 13C labeled formaldahyde. On the other hand, if ether linkages were formed to a significant extent during crosslinking, then a sizeable resonance at ~65 ppm would be expected. The intensity of the ether crosslinking sites at 65 ppm is far below what has been reported previously and suggests that the previously accepted crosslinking mechanism is in error and needs to be reevaluated.

We have employed a similar methodology to a polyurethane elastomer that is composed of very mobile, long chain ether domains connecting aromatic rich segments that are significantly less mobile. These aromatic rich domains order spontaneously during the curing stage of synthesis forming hard segments within the soft segments bath (see figure 2A) and provide effective crosslinks to provide an avenue for tailoring mechanical properties [23]. The ^{13}C MAS spectrum shown in Figure 2B is dominated by the mobile ether chains, in a similar fashion that the ^{13}C MAS spectrum of the aerogel was dominated by the narrow mobile impurities. By applying ^{13}C CPMAS methods, the resonances due to the hard, ordered aromatic rich segment, are enhanced, as shown in

Figure 2C. At sufficiently short contact time, shown in Figure 2D, the hard segment species clearly dominate the spectrum.

In the case of functionalized nanoparticles, it is of significant interest to detect and characterize the surface functionalized species as well as detect the surface bonding mechanisms. These questions are fundamentally questions of short range order. We have applied the MAS/CPMAS method to a silicon nanoparticle terminated with $CH_3(CH_2)_4$-groups. Figure 3A and 3B show the ^{29}Si and the ^{13}C MAS spectra obtained for this sample. The spectra are dominated by sharp resonances of organosiloxanes. Upon the application of CPMAS, shown in Figure 3C and 3D, one set of the ^{13}C sharp resonances has vanished leaving only two resonances, presumably due to surface immobilized organic groups, and the narrow ^{29}Si resonances vanish altogether. A broad ^{29}Si peak at –100 ppm remains in the ^{29}Si NMR characteristic of silicon-oxide polymorphs. This result indicates that the particle surfaces have been oxidized to a significant extent and that the narrow peaks that remain are likely due to a surface bonded organosiloxane, >Si-O-R rather than >Si-R species.

Intermediate range structure of model materials

In order to build a complete picture of soft material structure, structural insight beyond the first coordination sphere is required. In order to develop methods to investigate this intermediate range structure, we have investigated the block copolymer structure of a polydimethyl-polydiphenyl (PDMS-PDPS) coblock polymer. The structure of block copolymers is an area of significant scientific interest and few methods are as perfectly suited to address this issue as NMR. The spatial proximity of polymer blocks is obtainable if the intermediate range structure of the polymer can be determined.

We have applied a double quantum (DQ) NMR approach to measure the spatial proximity of the PDMS and PDPS blocks of our fourth model system. Some initial experiments have suggested that the PDMS and PDPS blocks were separated at length scales exceeding 10 nm, and thus effectively phase separated [25]. We chose to investigate the applicability of a DQ sequence to filter out responses due to uncoupled spins and provide a a correlation map of the presence of couplings between spins. If detectable couplings existed between the phenyl resonances (~7 ppm) and the methyl

resonances (~0 ppm) this would establish the spatial proximity of the domains. Evaluation of the dipolar couplings could, then be used to quantify the proximity.

Figure 4A shows the 2D double quantum (DQ) filtered spectrum of the coblock polymer. The figure clearly shows signal intensity along the diagonal representing coupling between methyl and phenyl spins within each block. The figure also shows off-diagonal signal intensity connecting the methyl and phenyl regions. This signal intensity establishes the existence of dipolar couplings between these polymer blocks and that they are within a few 10s of Angstroms of each other. Figure 4B shows the double quantum growth curve and clearly show the development of DQ intensity in 1 ms and, thus, the existence of homonuclear dipolar couplings in the range of 1-10 kHz. This observation strongly suggests intermixing of the polymer blocks.

Long Range structure

NMR measurement beyond the intermediate range (>10Å) become increasingly difficult even in crystalline, immobile materials. In soft materials, the problem becomes increasingly difficult because the dipolar couplings that are sensitive to internuclear distances are pre-averaged to a reduced value due to rapid motions. One potential method for measuring structural features on the nanoscale is to rely on enhanced sensitivity of either optically polarized spins [26-27] or on groups of spins found with in phase separated domains [10]. Our optical polarization efforts still remain in their infancy, but we have used two-dimensional wideline separation experiments (WISE) and spin-diffusion measurements to measure nanoscale inclusions in bulk soft material and these results are discussed here.

We have already mentioned above that aerogel samples synthesized with isotopically labeled formaldahyde show evidence for low molecular weight inclusions in the pore structure formed during gelation. We have applied 2D-WISE NMR to gain insight into the size of the inclusions and their proximity to the bulk aerogel structure. The ^{13}C-^{1}H 2D WISE spectrum with 10us and 1ms spin diffusion times are shown in Figure 5. As can be seen, at small spin diffusion times, the peaks in the ^{1}H dimension, which are correlated to the motional properties of the system investigated, are all quite broad and show no evidence of the narrow peaks due to the mobile inclusions. As the

spin diffusion time is increased, however, the width of the peaks in the ^{1}H dimension narrow considerably so that at 1ms the ^{1}H linewidths are all significantly narrowed and a narrow peak at 85 ppm in the ^{13}C dimension has appeared. These changes are, in fact, due to transfer of spin polarization from the mobile inclusions to the immobile walls of the aerogel structure. Due to the rate at which this transfer occurs we have determined that the domain sizes of the inclusions are on the order of 1 nm. This measurement is consistent with measurements of the average pore size determined by BET methods [19-22]. Further experiments to refine these measurements are underway.

In a previous section we also pointed out that for the polyurethane model system, the structure of the elastomer could be described as phase separated in to hard and soft domains. The ^{13}C CPMAS data, while able to selectively observe either the hard or the soft domain, however, were unable to provide information on the size of the hard segment domains within the soft segment bath. In order to measure the hard segment domain we employed a one-dimensional version of the 2D-WISE spin diffusion experiment discussed above. In this experiment, the spin-polarization of the hard segment domain is destroyed using a special filter and is gradually reestablished by spin-diffusion from the soft segment domain protons. The rate at which this occurs, again, is related to the domain size. Results of the spin-diffusion NMR experiment on one formulation of a polyurethane elastomer is shown in Figure 6 along with a fit derived from considering the mechanisms of diffusion [28]. The data is consistent with a hard segment domain approximately 20 nm in diameter. We have demonstrated that NMR would be able to measure these domain sizes and correlate them directly to chemical speciation and provide unique insight into any effort to engineer such materials. By modification of the synthetic protocol, for example, it is expected that the size of the hard segment could be modified, and by NMR in a measurable manner, to tailor the physical properties of the elastomer.

Discussion and Conclusions

` The results described above demonstrate the ability of NMR spectroscopy to characterize the structure of a variety of mesophased materials. Additional results describing the ability of NMR to characterize dynamics over a wide range of timescales

are reported elsewhere [25]. Combined with molecular modeling, the data provided by NMR combined with additional characterization methods, will allow for detailed structure and dynamic characterization of soft, meso-phased materials. The detailed characterization of these soft materials will allow for detailed understanding of the structure-property relationships that will form the basis of rational synthetic efforts in CMS.

The results described here set the foundation for a new capability in CMS-LLNL-the ability to perform structural characterization of soft materials over many length and time scales. This capability can provide detailed insight into structure and dynamics of such materials and provide a unique source of data for modeling validation. Such work has already been demonstrated out side the scope of this report [25,29]. The results reported here have proven to be beneficial to both ongoing cutting edge research in nanotechnology and in bioscience applications and to programmatic endeavors, primarily in the Stockpile Stewardship Program. In it believed that continuing work in this area will lead to further demonstrations of the utility of this approach. Important developments in the ability of NMR methods to characterize disordered large molecular weight mesophased macromolecules have been the result.

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Figure 1. Results of short range structural determination of aerogel model sample. A) schematic of proposed aerogel structure. B) ^{13}C MAS spectrum showing contribution of mobile, low molecular weight inclusions. C) ^{13}C CPMAS spectrum showing immobile components created during gelation with ^{13}C labeled formaldahyde.

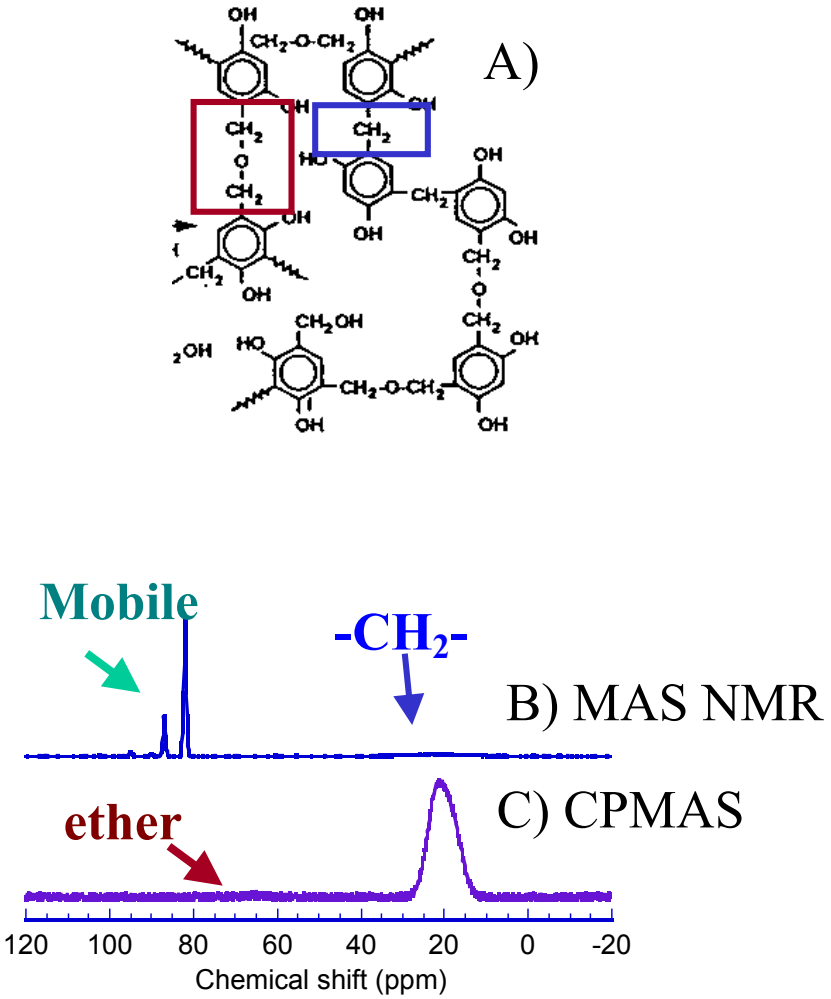

Figure 2. ^{13}C MAS and CPMAS spectra of polyurethane elastomeric material. A) Schematic of proposed polymer structure. B) ^{13}C MAS spectrum dominated by mobile ether chains. C) long contact time CPMAS spectrum showing both hard domain and soft domain resonances. D) short contact time CPMAS spectrum showing predominately hard segment domain resonances.

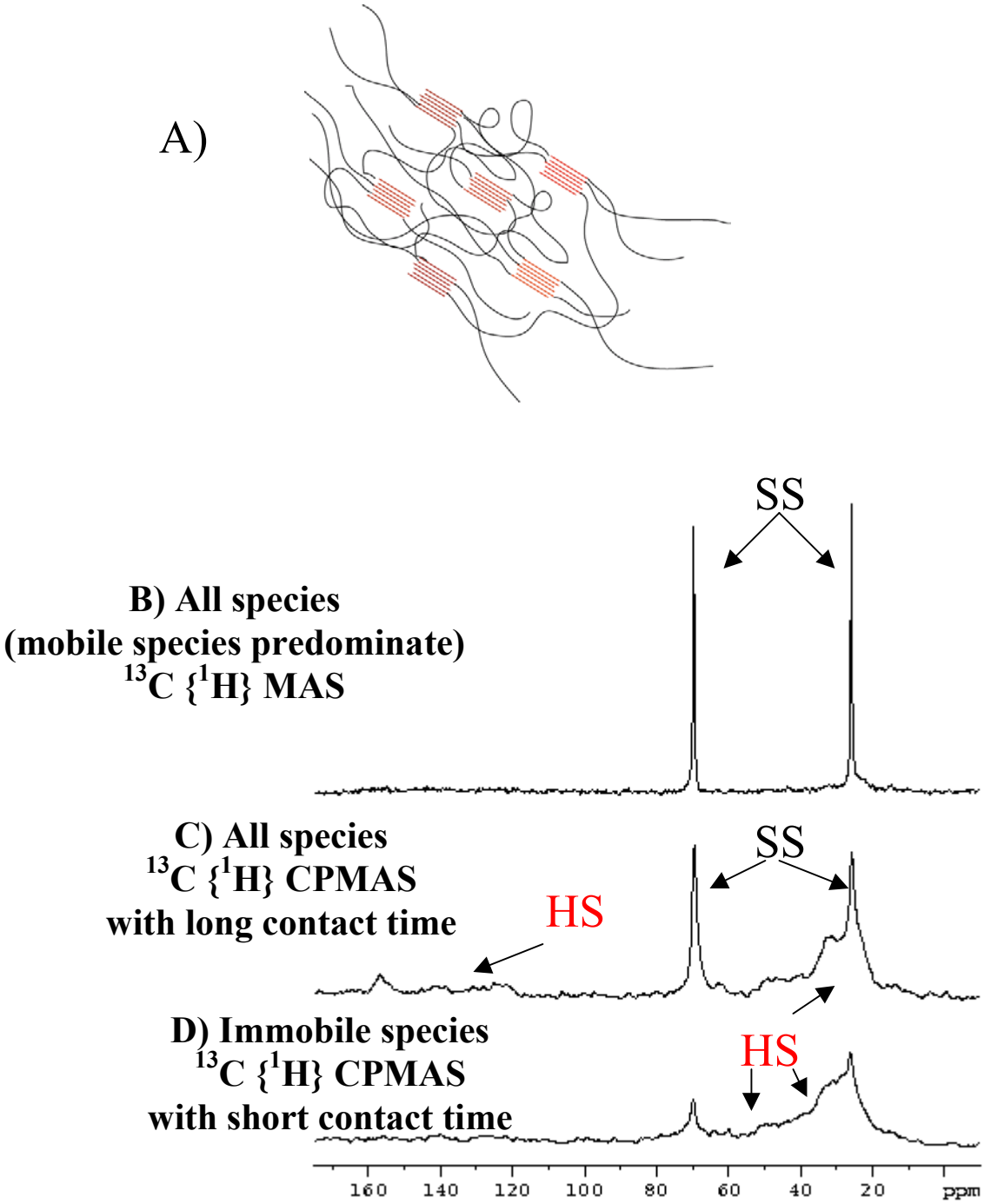

Figure 3. ^{29}Si and ^{13}C MAS and CPMAS NMR spectra of $CH_3(CH_2)_4$-(Si) nanoparticle.

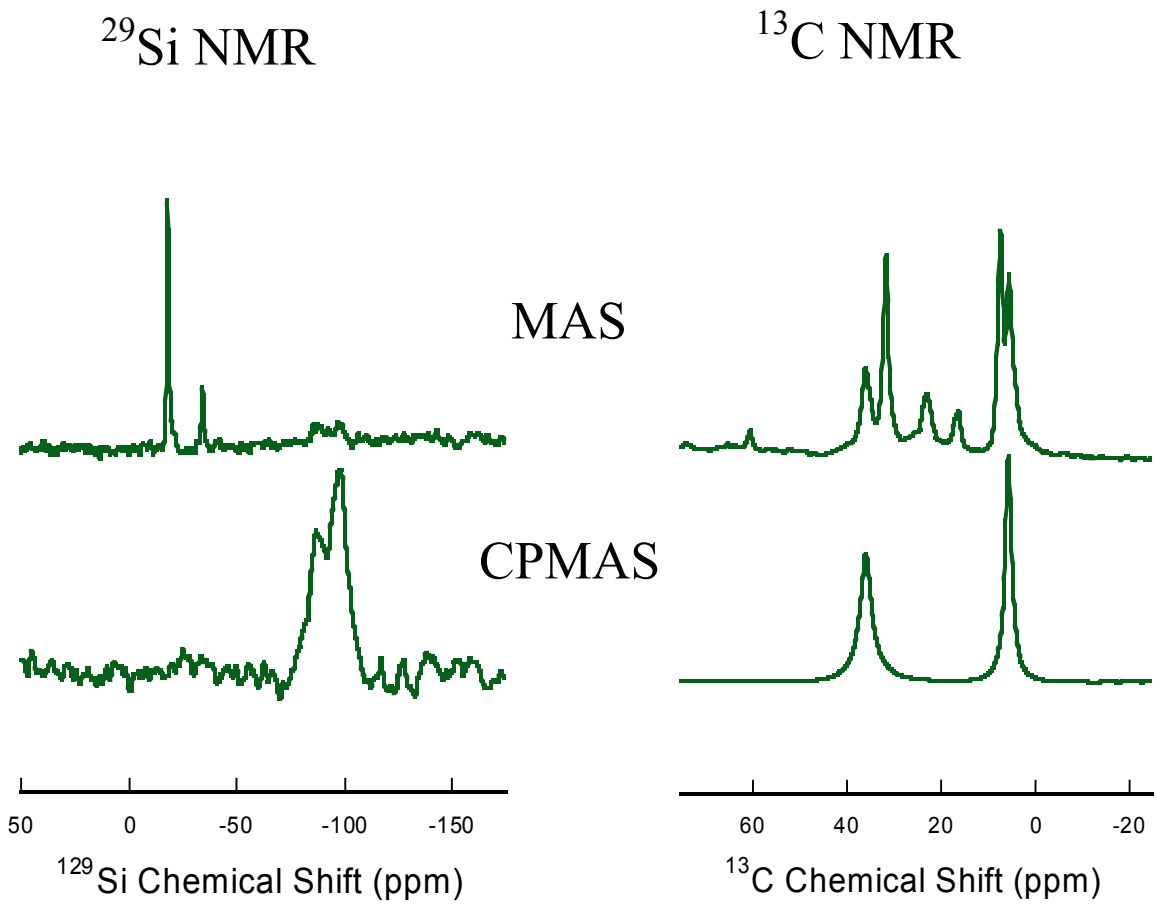

Figure 4. Results of DQ NMR of PDMS/PDPS coblock polymer. A) Schematic of polymer structure. B) 2D DQ NMR correlation map showing DQ intensity along diagonal and off diagonal. Results establish spatial proximity of polymer blocks. C) DQ intensity growth curve from which quantitative value of dipolar coupling can be obtained [~ 2 10^6 rad^2 sec^{-2}].

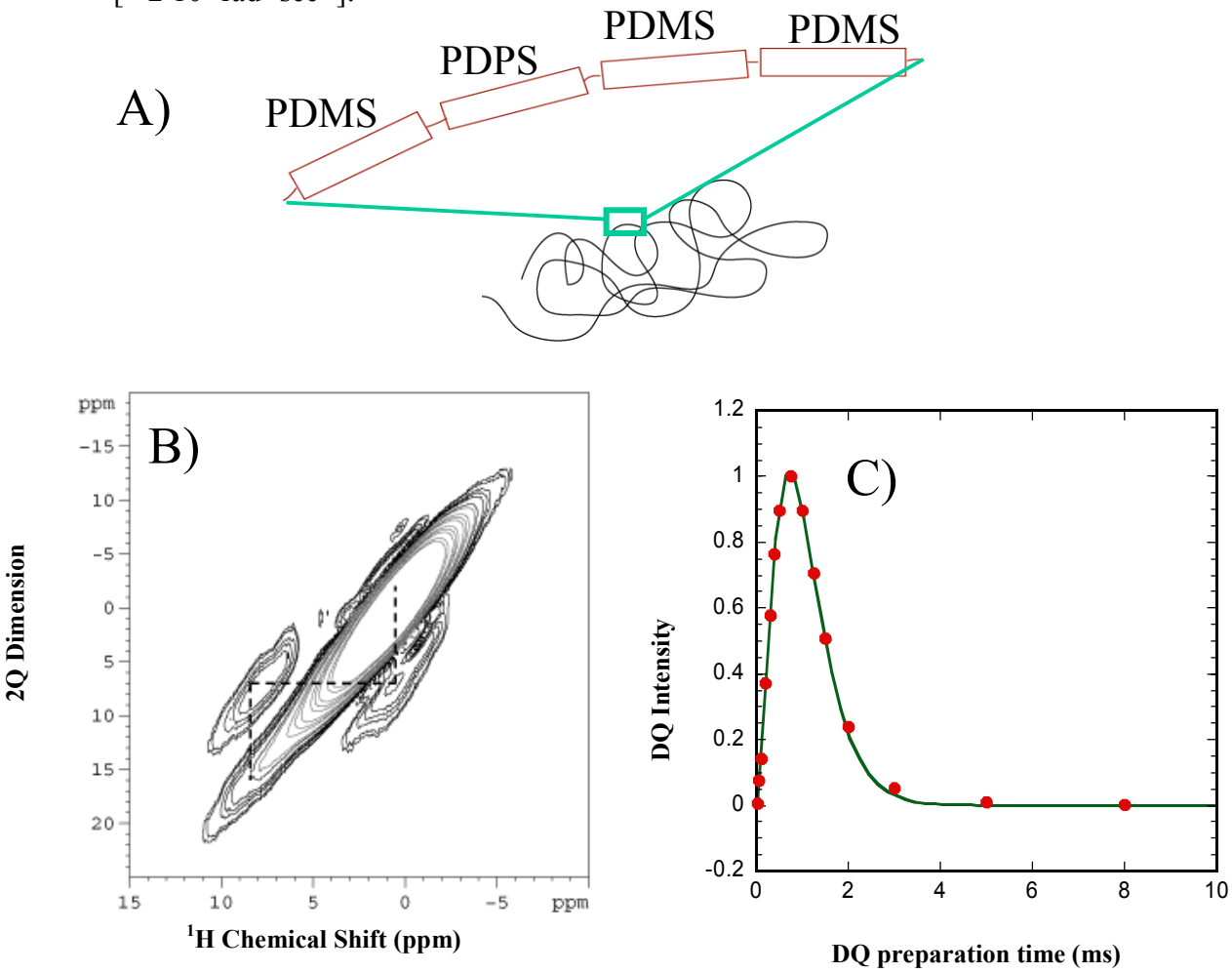

Figure 5. 2D-WISE NMR of organic aerogel. A) spin diffusion time of 10 ms; ^{13}C resonances due to aromatic and aliphatic species observable while ^{1}H linewidths are broad due to slow motion associated with bulk aerogel structure. B) spin diffusion time of 1ms; ^{13}C resonances due to low molecular weight inclusions can be observed and ^{1}H linewidths have narrowed considerably due to spin-diffusion with mobile components. C) schematic of pore structure showing mobile inclusions at the nm scale.

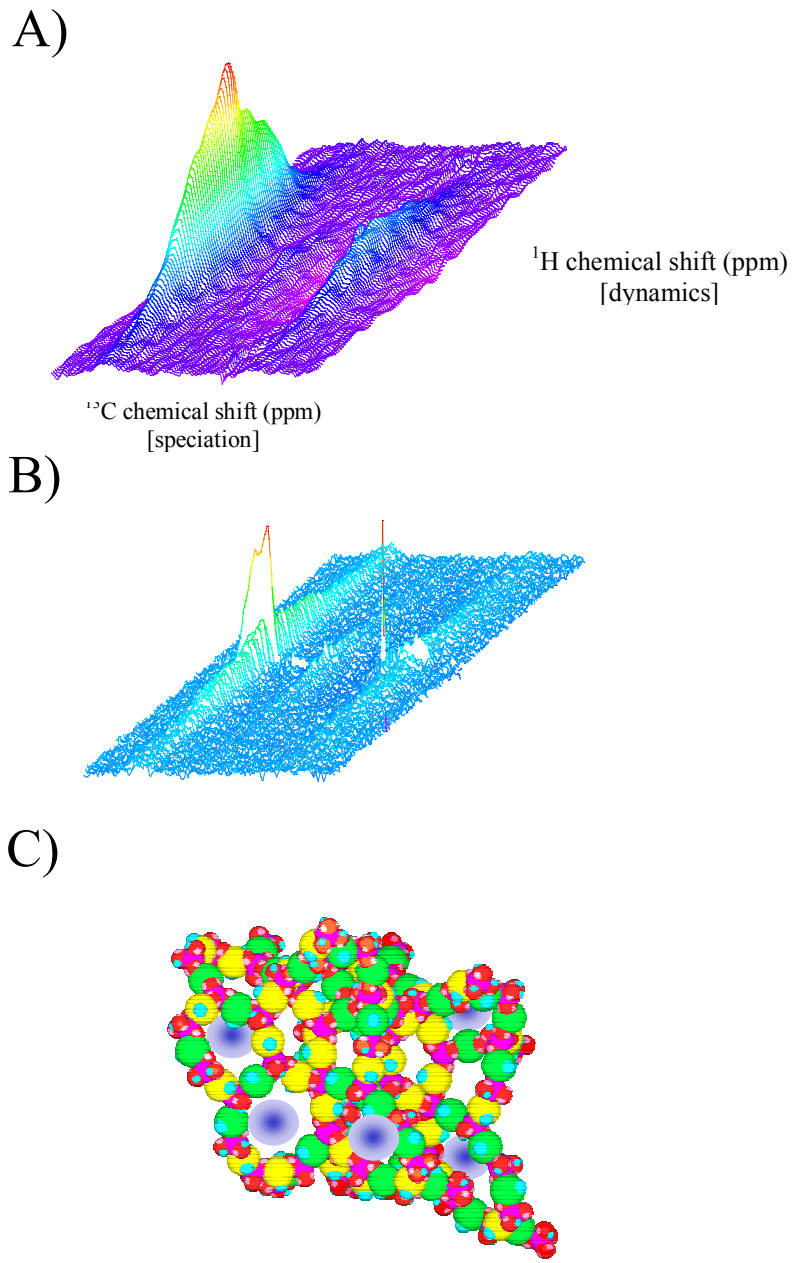
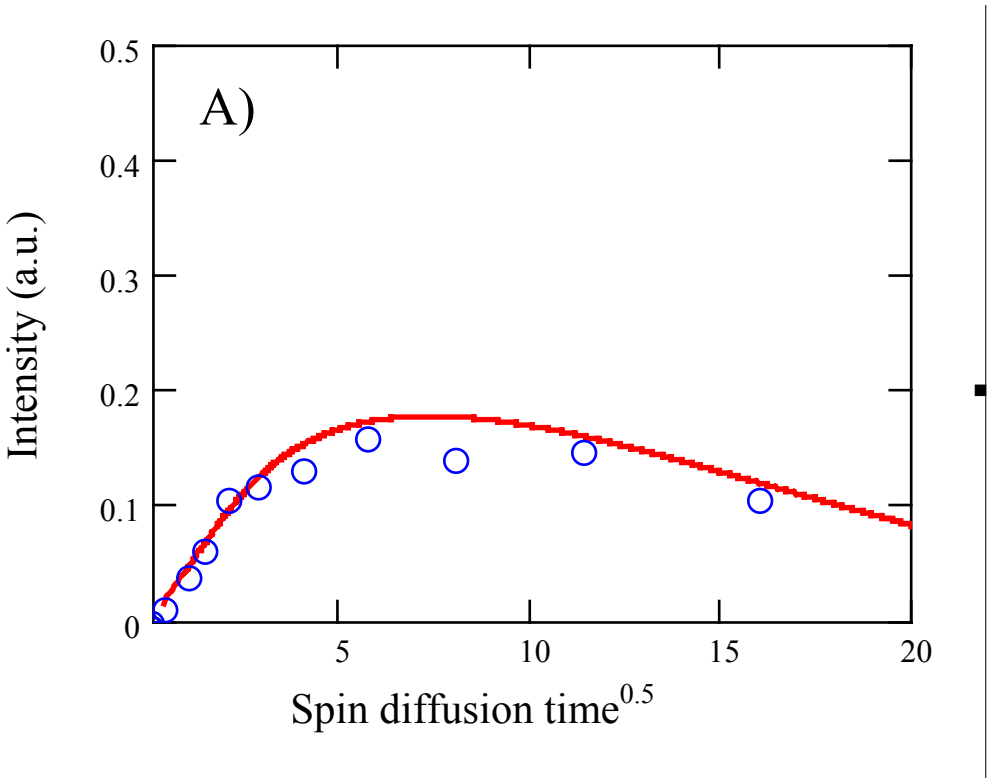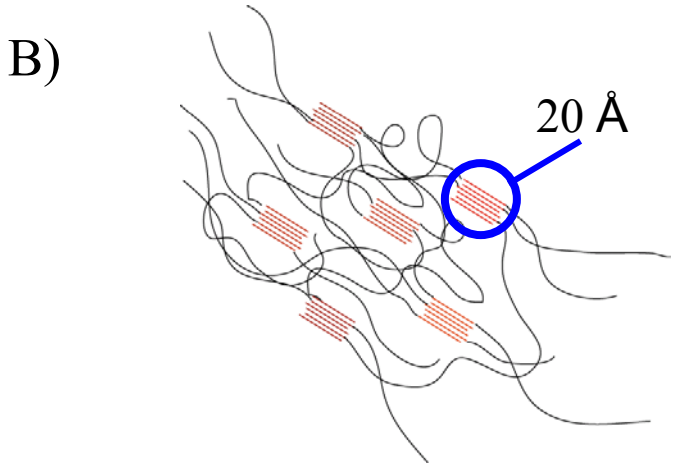
Figure 6. A) Plot of regained signal intensity as a function of spin-diffusion time from 1D ^{13}C detected spin-diffusion experiments on polyurethane model compound after destruction of ^{1}H and ^{13}C magnetization of the hard segment domain. Displayed solid curve derived for hard segment domain size of ~20 nm. B) Schematic of elastomer structure.