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Engineered Monodisperse Mesoporous Materials

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Engineered Monodisperse Mesoporous Materials

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Abstract

Porous materials technology has developed products with a wide variety of pore sizes ranging from 1's of angstroms to 100's of microns and beyond. Beyond 15Å it becomes difficult to obtain well ordered, monodisperse pores. Materials of this type would be of great use to industry. In this report we describe our effort in making novel porous materials having monodisperse, controllable pore sizes spanning the mesoporous range (20-500Å). We set forth to achieve this by using unique properties associated with block copolymers - two linear homopolymers attached at their ends. Block copolymers phase separate into monodisperse mesophases. We desired to selectively remove one of the phases and leave the other behind, giving the uniform monodisperse pores.

To try to achieve this we used ring-opening metathesis polymerization (ROMP) to make the block copolymers. We synthesized a wide variety of monomers and surveyed their polymers by TGA, with the idea that one phase could be made thermally labile while the other phase would be thermally stable. We were able to down select to two monomer types that were used to create the thermally stable phase, and one monomer type to create the thermally labile phase. Block copolymers were made incorporating one of the stable monomers with the other labile monomer. These polymers were processed either by precipitation, film casting, or by sol-gel techniques, and then thermally treated to remove the labile phase. In the precipitated and sol-gel processed materials, we determined by porosimetry measurements that micropores, mesopores, and macropores were created. In the film processed sample there was not much porosity present. We moved to a new system that required much lower thermal treatments to thermally remove over 90% of the labile phase. This approach involves making a peculiar heat sensitive monomer whose polymer repeat unit will fragment off over 90% of its weight when heated at 130°C. We were successful in making these block copolymers where one block was thermally stable and the other incorporated this thermally sensitive monomer. Film casting followed by thermal treatment and solvent extraction produced the desired monodisperse materials (based solely on SEM results).

Modeling using Density Functional Theory was also incorporated into this project. The modeling was able to predict accurately the domain size and spacing vs. molecular weight for a model system, as well as accurate interfacial thicknesses. For real life systems, solubility parameters and radii of gyration (R_g) are important pieces of information. Therefore we included a detailed study of determining R_g for our ROMP type polymers. This can be done using small-angle neutron scattering by mixing deuterated with non-deuterated polymers and analyzing the resulting scattering curve. These experiments were performed at OakRidge National Labs and the results are reported herein.

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Engineered Monodisperse Mesoporous Materials

I. Introduction

Porous materials technology has developed products with a variety of pore sizes ranging from 1's of angstroms to 100's of microns and beyond. Applications for porous materials are very broad, and include such areas as molecular separations, bio-sensing devices, gas adsorption, and insulating materials. In the 1 - 15Å pore size range, zeolites have been prepared with very uniform morphology and pore-size distribution (figure 1). However, beyond about 15Å, it becomes difficult to obtain well ordered, monodisperse pores. A facile control of the pore size with very narrow pore-size distribution beyond the 15Å size would be advantageous for several reasons. On a fundamental basis these kinds of materials would aid in determining the effect of pore sizes on the performance for any particular application. Second, separation applications would greatly benefit due to very high selectivity, which ultimately leads to energy savings.

Figure 1. Representative structures of a 4Å (left) and 5Å (right) zeolite.

In this report we describe our effort in making novel porous materials having monodisperse, controllable pore sizes, spanning the mesoporous range (20-500Å). In order to achieve such a high degree of control over pore size and size distribution, we set forth to use the unique properties associated with block copolymers. A block copolymer consists of two differing polymers chemically attached at their ends (figure 2).

Figure 2. Animated structure of an A-B type block copolymer. Each bead is roughly 5Å

Since the two polymers are different, they almost always phase separate from each other much like oil and vinegar. Due to the chemical attachment, they can only separate out on a scale equivalent to the end-to-end distance of the polymer blocks (figure 3).

Figure 3. Animated figure of phase separation that occurs in block copolymer systems

The result is a material consisting of monodisperse, meso-size domains of one type of polymer surrounded by the other (figure 4). We proposed to design these block copolymers in such a way that one of the phases can be highly crosslinked to impart structural integrity (and prevent collapse during further processing), and the other phase can be selectively removed by thermal, chemical, or ultraviolet means. This process would generate the desired controllable mesoporous materials. Block copolymers are also advantageous in that they can create a number of different morphologies, as shown in figures 4 and 5, depending on the ratio of the polymer blocks. We planned to exploit this fact to obtain controllable and novel mesoporous architectures. The size of the "meso" domains should be easily tailored by adjusting the length of the polymer blocks, and generally can be made in sizes ranging from 20-500Å; thus the facile control of domain size and ultimately pore size.

Figure 4. Different structures obtained in a diblock copolymer system for varying amounts of block A vs. block B

Figure 5. TEM pictures of real-life block copolymer systems. a) annular morphology of a triblock copolymer system. b) tetrahedral morphology. c) cylindrical morphology (head-on view). d) cylindrical morphology (side-view).

Another important aspect of our project is the modeling that was performed by John McCoy at New Mexico Tech. In conjunction with the synthesis of these materials, Prof. McCoy worked on using Density Functional Theory to accurately predict domain morphology and size based on a block copolymers chemical composition, chain length, and block ratio. The main conclusions of the modeling will be discussed in this report, and the reader is referred to a published paper for further details.²¹

Synthesis of these diblock materials was performed using a specialized synthetic technique called Ring-Opening Metathesis Polymerization. This living polymerization technique is extremely versatile in that it can tolerate a wide variety of chemical groups on monomers, and also gives us tremendous control over block length and ratio. The wide variety of chemical groups that can be introduced allows us to make one block that can be thermally or chemically crosslinked while the other block can be thermally or chemically removed.

In this report we discuss our results on the synthesis, characterization, treatment, and modeling of these block copolymer systems to obtain monodisperse mesoporous materials. We end by offering suggestions for further work if further funding arises.

II. Experimentals

A. Instruments

Gel Permeation Chromatography (GPC) was performed using a Polymer Labs PL210 with a refractive index detector and a PD2000 dual-angle laser light scattering detector. The columns were two linear ultrastrogel columns in series using thf as the eluent running at 1 ml/min. Small-Angle X-Ray Scattering (SAXS) was performed using a Rigaku instrument with a 1.54Å Cu K α rotating point source, Charles Supper double mirror focusing optics, and a Nicolet two-dimensional detector. Small-Angle Neutron Scattering (SANS) was performed at Oakridge National Labs using their High-Flux Isotope Reactor. Nuclear Magnetic Resonance was performed using a Bruker 300 Mhz instrument. Thermal Gravimetric Analysis (TGA) was performed on a Perkin Elmer Instrument with a TGA 7 module, using a nitrogen stream and heating rate of 10°C/min. Scanning Electron Microscopy was performed using a Hitachi S4500 with field emitter gun. Gas Adsorption Porosimetry measurements were obtained on a Micromeritics ASAP 2000 at 77 and 87 K, respectively for nitrogen and argon. Pyrolysis of samples was performed using a quartz tube with a slow nitrogen flow inside a controlled temperature furnace.

B. Monomer synthesis

All chemicals for monomer synthesis were purchased from Aldrich, Acros, or Fisher, and typically used without further purification. Due to the large number of monomers synthesized, only a generalized scheme will be shown here. All norbornene type monomers are synthesized using traditional Diels-Alder chemistry where cyclopentadiene (Cp) reacts with a dienophile:

Refer to figures 8, 12, 24, and 28 for all the monomers made for this project. Deuterated monomers were made by starting with deuterated Cp and/or deuterated dienophiles. Deuterated Cp was made by stirring freshly cracked Cp with a 15 wt% solution of potassium hydroxide in deuterated water using a phase transfer catalyst over several stages. Deuterium levels on the Cp typically ended up being 90%.

C. Polymer Synthesis

Monomers were purified for polymerization by distilling from calcium hydride or sodium hydride, and passing through a small plug of alumina immediately prior to use. THF was used as the polymerization solvent, and was purified by distilling from sodium hydride, followed by vacuum transferring from a purple sodium/benzophenone ketyl immediately prior to use. All polymerizations were performed inside a Vacuum Atmospheres glovebox with nitrogen as the atmosphere. Homopolymer and block copolymer synthesis schemes are shown in figure 6.

III. Results and Discussion

A. Monomer/Polymer Survey for Stable and Labile Polymers

1. Introduction to Ring-Opening Metathesis Polymerization (ROMP).

ROMP is a relatively new polymerization technique whereby a strained cyclic olefin monomer is ring-opened, and further monomer is continually ring-opened onto the end to propagate the polymer chain end, giving a homopolymer (see figure 6).

Figure 6. ROMP polymerization scheme of homopolymers and block copolymers. The asterix designates an active polymer chain end capable of adding more monomer to the chain. The benzaldehyde step is used to terminate the polymerization and kill the chain end

A block copolymer can then be made by adding a second type of norbornene to the polymerization reaction, once the first type of monomer has been completely consumed (see figure 6). There are a few types of cyclic olefin monomers that are quite amenable to ROMP (see figure 7).

Figure 7. Monomers amenable to ROMP polymerization: a) norbornene type structures. b) Ninetzenscu hydrocarbons. c) quadricyclane adducts.

The first is a very common type known as a norbornene type structure. ROMP of these monomers is very well known^{1,2} and will not be described in detail here. The second type are known as Ninetzenscu hydrocarbons, and have been used recently in ROMP to create conductive polyacetylene polymers.^{3,4} The third type is a modified norbornene structure which is designated here as a quadricyclane adduct. Quadricyclane adduct monomers have never been studied before as a ROMP monomer. We therefore considered it worthwhile to study the polymerization characteristics of these new monomers in detail. The next section was published as a communication in *Macromolecules* and reproduced here for completeness.⁵

2. Quadricyclane Adduct Monomers/Polymers.

Ring-Opening Metathesis Polymerization (ROMP) has been known for quite some time. With the recent contributions of Grubbs¹ and Schrock,² organometallic initiators have been developed that are known to perform ROMP on norbornene-type compounds in a well-behaved and living fashion, resulting in monodisperse homopolymers and block copolymers. The polymerization of norbornenes made from cyclopentadiene (Cp) adducts has extensively been studied using these initiators. However, the polymerization of norbornene compounds from quadricyclane adducts (see below)⁶⁻⁸ has not yet been studied.

It has been observed with certain polymer systems that thermal treatment converts them to electrically conductive carbon.^{9,10} Our initial intention was to identify norbornene-type polymers that could similarly be converted to carbon upon thermal treatment. We therefore turned our attention to the polymerization and thermal treatment of quadricyclane adducts. It has been reported previously that quadricyclane undergoes a $2_{\pi}+2_{\sigma}+2_{\sigma}$ cycloaddition with strongly electron withdrawing dienophiles to give norbornene-type compounds having a fused cyclobutene or cyclobutane ring.⁶⁻⁸ It was our hope that the fused cyclobutene ring could undergo a thermal ring-opening to form a diene, which would undergo further crosslinking through a Diels-Alder mechanism with existing double bonds

in the backbone. This highly crosslinked system would hopefully promote the conversion of the polymer in high yield to carbon. This thermal ring-opening of cyclobutenes is well known,¹¹ and is most familiar in the new benzocyclobutene materials currently available from DOW Chemical Company. Apart from our desire to identify high-yield carbon forming materials, we have observed in some circumstances that adducts with quadricyclane are readily polymerized by ROMP, whereas the analogous Cp adducts cannot be polymerized. These new polymers may therefore also prove useful where certain stereospecific¹² functionalities on the polymer are required, but these functionalities are not tolerated as Cp adducts. Therefore we wish to report in this communication the polymerization of these quadricyclane adducts using a Schrock-type molybdenum based initiator, and their comparison to analogous Cp adduct polymerizations.

The monomers synthesized for this study are shown in figure 8, and are readily synthesized using quadricyclane and the appropriate dienophiles.^{6-8,13}

Figure 8. Different quadricyclane adduct monomers synthesized and studied

a) **Monomer 1**

The polymerization of monomer 1 proceeded smoothly and quantitatively. A proton NMR spectrum was taken of the final product after 1 hr (Figure 9a), and showed no remaining peak at 6.2 ppm which would correspond to the strained double bond of the monomer. Instead, a broader bimodal peak from 5.2 to 5.5 ppm was observed, and indicated the formation of a polymer having a high trans double bond content¹⁴ (82%) in the backbone. A number of broad peaks appear in the range of 1.0 to 4.0 ppm., which indicates the existence of a polymer in a multitude of isomeric states. A ¹³C NMR spectrum was taken of the final polymer and the spectrum is shown in Figure 9b. In comparison to the carbon NMR spectrum of the cyclopentadiene (Cp) adduct,¹⁵ the analogous carbon peaks of poly-1 are broader, indicating a lack of stereoregularity in the polymer. Polymerization of the Cp adduct with classical ROMP catalysts yields even broader peaks. We therefore conclude that there may be some degree of tacticity in poly-1, but not to the extent that it

exists in the Cp adduct polymer. This is consistent with a less than quantitative trans content observed in poly-1. A closer inspection of the $-\text{CF}_3$ carbon signal in the

Figure 9. ^1H and ^{13}C NMR spectra of poly-1 (a,b) and poly-2 (c,d) in CDCl_3

polymer (see insert of Figure 9b) reveals that each signal of the quartet is split into two peaks, which occur in a ratio of 80:20. This is nearly identical to the trans/cis ratio determined from the proton NMR spectrum. We therefore conclude that the splitting of the quartet peaks is associated with the cis/trans configuration of the double bonds in the backbone. The resulting polymer was readily soluble in most organic solvents, indicating a lack of crystallinity (and therefore a lack of tacticity). This is in contrast to the polymerization of the analogous Cp adduct with the same initiator, which shows a crystalline melting point at 200°C .¹⁵

Poly-1 was analyzed by GPC and the trace is shown in Figure 10. From these results, we conclude that the polymerization of monomer 1 is living and well-behaved. A

Figure 10. GPC traces of poly-1 (left) and poly-2 (right). Molecular weights are relative to narrow polystyrene standards.

molecular weight of 22,800 g/mol (vs. polystyrene standards) and a polydispersity of 1.05 for this polymer were obtained, indicating that the polymerization is controlled and the resulting polymer is essentially monodisperse. A small shoulder at double the molecular weight can be seen and is associated with minute amounts of impurities terminating two

living chains by linking them together. This phenomena has often been seen in other systems.¹⁶ It has been observed previously that the polymerization of the Cp adduct is quite slow, taking up to 5 hours under identical conditions.

b) Monomer 2

Monomer 2 was also polymerized and analyzed by proton NMR (Figure 9c), ¹³C NMR (Figure 9d), and by GPC (Figure 10). Again, within the course of one hour, the NMR spectrum shows the polymerization to be complete: the strained double bond signal at 6.09 ppm has completely disappeared and has been replaced by a broader doublet centered around 5.5 ppm. The double bonds in the backbone are observed to be 75% trans from this spectrum. The ¹³C NMR spectrum again shows broad peaks, indicating the lack of tacticity in this polymer. The GPC trace shows a molecular weight of 23,100 g/mol (vs. polystyrene) and a polydispersity of 1.06. This is close to the target weight of 20,000 g/mol, again indicating that the polymerization of this monomer is well-behaved and the resulting polymer is essentially monodisperse (the small double molecular weight shoulder is also observed for this polymer). Similar reaction times were observed for the analogous Cp adduct with the same initiator.¹⁵

It is interesting to note here that similar trends are observed when comparing poly-1 to poly-2, and when making comparisons between the analogous Cp adduct polymers. Specifically, the trans double bond content in the backbone is decreased when switching from the -CF₃ group to the less polar -CO₂Me substituted systems.

c) Monomer 3

Monomer 3 was swiftly polymerized, forming an insoluble precipitated polymer. Due to the intractability of this polymer it was not further characterized.

b) Monomer 4

The polymerization of monomer 4 is quite interesting. Ten minutes after addition of the initiator a precipitated polymer starts to form, and the amount increases with time. Upon termination of the polymerization after 1 hour, the polymer was precipitated in water, dried, and a proton NMR spectrum was taken in d-6 DMSO (Figure 11 top).

Figure 11. ¹H NMR (top) and ¹³C NMR (bottom) of poly-4 in DMSO-d₆

The spectrum indicates the presence of a small amount of unreacted monomer (singlet at 6.18 ppm) and of polymer (broad singlet centered around 5.6 ppm). Upon closer examination the spectrum between 5.0 and 6.0 ppm, a small shoulder is observed upfield from the broad singlet. We associate the broad singlet with trans double bonds in the backbone,¹⁴ and the small shoulder upfield with cis double bonds. Therefore this polymer contains a highly trans double bond content in the backbone (>99%). The simpler and slightly more resolved peaks for poly-4 in the region of 1.5 to 3.5 ppm (as compared to poly-2 in d-6 DMSO) would also indicate a more stereoregular polymer. The ¹³C NMR (d-6 DMSO, Figure 11 bottom) of poly-4 shows fairly sharp peaks for the carbon signals, again indicating a high degree of stereoregularity in this polymer. Qualitatively it is observed that poly-4 is difficult to dissolve in DMSO, and is insoluble in most other solvents. It is therefore possible that this polymer has some degree of crystallinity. Several attempts have been made to polymerize the analogous Cp-tetracyanoethylene (TCNE) adduct without success.¹⁷ It is intriguing, therefore, that the quadricyclane adduct of TCNE can readily be polymerized.

e) Monomer 5

Attempted polymerization of monomer 5 and its analogous Cp-maleic anhydride adduct were both unsuccessful. In both cases, a dark brown, gelatinous precipitate forms over time. In this case we assume that there is a competition between ROMP of the monomer and reaction of the catalyst with the anhydride functionality. Difficulty with polymerizing other anhydride functionalized monomers has been observed elsewhere.¹⁸

f) Conclusion

This work has demonstrated the first living ROMP of quadricyclane adducts. We have shown that the polymerizations can proceed readily in a well-controlled fashion to yield monodisperse polymers. In several instances, the polymerization of the quadricyclane adducts appears to proceed more quickly and with less stereospecificity. For the TCNE-quadricyclane adduct a polymer could be readily formed, and with stereoregularity, whereas in the Cp adduct polymerization does not occur. This selective polymerization of quadricyclane adducts over CP adducts was also observed for adducts with the diethylazodicarboxylate dienophile.^{19,20} ROMP of quadricyclane adducts therefore promises to be a useful tool for the polymerization of stereospecifically¹² functionalized monomers that cannot be tolerated as Cp adducts.

We are currently studying the interesting thermal and photochemical properties associated with these new quadricyclane-adduct polymers, as well as synthesis and polymerization of other quadricyclane adducts.

3. Thermal Study of Polymers using TGA

TGA is used to measure weight loss of a sample versus temperature. It is a very useful technique for determining what kind of temperatures the polymers can withstand and at what temperatures they start burning off volatiles. It was our hope that we could use this technique to determine which polynorbornenes could be used as one block that could be thermally removed, and which ones could be used as the second block that could be crosslinked and rendered thermally stable. We synthesized a wide variety of norbornene monomers, and also obtained some commercially available ones. Figure 12 shows the chemical structures of all the monomers surveyed. Table 1 lists the thermal properties of these polymers based on TGA. It was observed that the ethoxymethyl norbornene monomer (monomer 7) had the most attractive thermal removability properties. This was based on the fact that 95% of the polymer had burned off before 450°C. In table 1 we report the final plateau temperature (the temperature beyond which there is virtually no more weight loss), and percent polymer remaining at this temperature. We also report the amount of polymer remaining at 450°C. These last data are reported so that we can

Figure 12. Chemical structures of monomers whose polymers were surveyed using TGA

determine which polymer has the most weight remaining by the time the temperature reaches 450°C . This gives us an idea about which polymers are the most likely candidates for incorporating into the second thermally stable block. Figure 13 shows a few representative TGA's, which were chosen based on percent polymer remaining at 450°C .

Table I. TGA thermal properties of monomers surveyed¹

polymer	final plateau temp (°C)	% remaining at plateau temp	% remaining at 450° C
1	575	40	75
3	575	48	70
4	900	55	80
6	500	30	35
7	435	5	5
8	500	5	40
9	435	9	8
10	515	20	62
11	550	20	45
12	500	7	55
13	625	55	89
14	600	40	93
15	540	26	90
16	650	37	56
17	600	33	50
18	525	28	39

1. Numbers not shown are monomers that were made but not studied by TGA

Figure 13. TGA's of representative polynorbornenes that demonstrate thermal lability and thermal stability

Figure 14. GPC trace of poly-14

It is clear from the data in the table, and from the TGA figures, that the best polymers for thermal stability are poly-4, poly-13, and poly-14. Among these three thermally stable polymer systems we downselected to one for several reasons. As stated in the quadricyclane adduct polymerization section, monomer 4 polymerized into a semi-crystalline homopolymer. Attempts to incorporate this into a block copolymer failed due to gelation of the polymerization reaction, creating an uncharacterizable polymer system - we could not determine if we were creating a well-defined block copolymer system. Polymerization of monomer 13 was straightforward, however characterization of this final polymer was hampered by its extreme moisture sensitivity. It was used in a few experiments, but the final block copolymer was not characterized before further processing. We proceeded to use monomer 14 - trimethoxysilylnorbornene. In analyzing the homopolymerization of this monomer we obtained some interesting results. Figure 14 shows the GPC trace of a 20,000 g/mol homopolymer of this monomer. From the trace we see a couple broad shoulders at higher molecular weight, indicating that we get coupling of chains to make double and triple molecular weight species. This monomer was extensively purified, and thus impurities are not the cause for these coupling reaction. We concluded that the polymerization initiator is somehow coupling chains together to give the double and triple molecular weight species seen here. We therefore decided to use a new monomer analogous to this one - triethoxysilylnorbornene (figure 15).

Figure 15. Structure of now polynorbornene used. Designated as monomer 19.

Figure 16. GPC trace of poly-19

The polymer of this monomer, when chemical crosslinked, creates virtually the same type of thermally stable material as the polymer of monomer **14**. We studied the polymerization of this new triethoxysilyl norbornene, and the GPC trace is shown in figure 16. As can be seen, polymerization of this monomer still produces a double molecular weight shoulder, but is not quite as pronounced as with poly-**14**. We decided to proceed with this monomer for most of our other studies. It has been observed in other block copolymer systems that a small amount of this kind of double molecular weight species does not greatly affect the ability of the block copolymer to phase separate on the meso-scale.

B. Homopolymer and Block copolymer Synthesis

Figure 17 summarizes the three monomers chosen based on the thermal properties of their polymers.

Figure 17. Summary of monomers chosen for thermal lability (poly-7) and for thermal stability (poly-13 and poly-19)

1. **System A - poly-13/poly-7 block copolymers.** One block copolymer length and block ratio were made with this system: the first block is a 22,500 g/mol poly-13 and the second block is a 7,500 g/mol poly-7. We designate this as **22.5/7.5 13-7**. This kind of system should create a cylindrical morphology of the thermally removable block surrounded by the thermally stable block. This system was not characterized due to its high moisture instability. The system was processed in two different ways. The first processing involved taking the polymerization solution (0.5g of block copolymer in 10 mls thf) and precipitating it into a flask of distilled water. This processing creates an ill-defined aerogel type system which is immediately crosslinked in the thermally stable phase. We desired to see if we still get phase separation of the thermally labile block. This material was pyrolyzed in a tube furnace at 5°C/minute up to 550°C and held there for 10 minutes (in the future we should use 450°C).

Figure 18. SEM of poly-13/poly-7 precipitated system a) before pyrolysis, b) after pyrolysis

We analyzed this material by high-resolution SEM and by porosimetry. Figure 18 shows the SEM before and after pyrolysis. As can be seen from this picture, the morphology definitely changes after pyrolysis. Fairly well-defined pores are created from the pyrolysis processing. Upon closer analysis the pore sizes are in the range of 2000 to 4000Å, which are too large to be associated with pores that would have been created by removal of the thermally labile block. Porosimetry sheds some light on this issue as well. Before pyrolysis the sample possesses a surface area of 24 m²/g. After pyrolysis it has a surface area of 620 m²/g. Therefore substantial porosity is created by the pyrolysis of this material. Analysis of the pore-size distribution reveals that there exists micropores, mesopores, and macropores. The micropores are in the range of 5 - 20Å, the mesopores are in the range of 100-500Å, and the macropores are in the range greater than 1000Å. We have therefore concluded that with this type of processing we do create mesopores, but we also create micropores and macropores, and the pore-size distribution is not very narrow at all. We therefore abandoned this processing approach and went to thin film processing. A thin film of this same kind of material was formed by taking the block copolymer polymerization solution and placing it in a small teflon-coated aluminum boat and allowed the solvent to slowly evaporate leaving behind a thin film, roughly 0.5mm in thickness. This film was then submersed in distilled water for 1 week. This creates chemical crosslinks between chains of the thermally stable block through -SiOSi- linkages that will occur. This material was analyzed by SAXS (see figure 19).

Figure 19. SAXS pattern for the poly-13-poly7 block copolymer film system

The results show that there is clear meso-phase separation, as witnessed by the existence of the scattering peak at a scattering vector value of 0.02Å⁻¹. This sample was pyrolyzed in a manner similar to the precipitated sample described previously. Porosimetry results showed this sample to have virtually no porosity. We therefore concluded that the pores must have collapsed during processing. We therefore went to different polymer systems and processing techniques, as described in the next block copolymer system.

2. **System B - poly-19/poly-7 block copolymer systems.** Due to the assumed collapse of the pores in the previous system, we decided on a different approach for this system. We decided the collapse was caused by a lack of a high degree of crosslinking - the moisture that creates the chemical crosslinks in the system was not able to diffuse substantially through the film to create a bulk crosslinked material. Our next approach was designed to allow moisture to reach all sites for potential crosslinking. This was done by processing the system as an aerogel: A block copolymer was synthesized in thf consisting of 22,500g/mol poly-19 as the first block and 7,500 g/mol poly-7 as the second block. We characterized a small aliquot of this system by GPC and the results are shown in figure 20.

Figure 20. GPC traces of the poly-7 homopolymer and the poly-19/poly-7 block copolymer

This figure shows that we do indeed have a block copolymer, and a small portion of this block copolymer consists of double molecular weight chains - this was expected in light of previous discussions in this report. After the synthesis of the block copolymer in thf, a small amount of 1N hydrochloric acid was added and thoroughly mixed with this solution. The result is a material that is analogous to an aerogel, however, the large dangling thermally labile block does not participate in the sol-gel reaction, and we proposed that this may form a small meso-sized ball tucked away within the matrix of the sol-gel. We observed that these systems gelled within 30-45 minutes, indicating that we are getting the sol-gel that we expected. We then supercritically extracted the thf from the gel to leave behind this novel kind of aerogel. This aerogel was then exposed to pyrolysis identical to that of the previous block copolymer system - a thermal ramp at 5°C/min to 550°C, and then held there for 10 minutes before cooling down again. Figure 21 shows high-resolution SEM analysis of this sample before and after pyrolysis.

Figure 21. SEM of poly-19/poly-7 sol-gel sample a) before pyrolysis, b) after pyrolysis

By SEM virtually no difference was observed before and after pyrolysis. Porosimetry was performed on this sample, and demonstrated that a substantial difference occurred due to the pyrolysis of the sample. The pre-pyrolyzed sample showed a surface area of $152 \text{ m}^2/\text{g}$ and an average pore diameter of $66 \text{ \AA}$. After pyrolysis the sample showed a surface area of $635 \text{ m}^2/\text{g}$ and an average pore diameter of $36 \text{ \AA}$. A pore-size distribution before and after pyrolysis is shown in figure 22.

Figure 22. Pore size distribution of poly-19/poly-7 sol-gel sample before and after pyrolysis

This figure shows that before pyrolysis there exists a mesoporous system with a broad pore-size distribution. After pyrolysis we obtain a bi-modal pore-size distribution, with a narrow size centered around 35Å and a broader distribution ranging from 40-100Å. Therefore we are creating narrowly dispersed mesopores, but also more broadly dispersed, slightly larger mesopores. We conclude that this is a result of a combination of burning away the thermally labile block, and some rearrangement and collapse of the aerogel. Since this approach still does not create the monodisperse mesoporous material we were trying to create, we have gone to an entirely new approach.

C. New approach to monodisperse meso-porous materials.

We have concluded from the previous materials and experiments that perhaps this kind of thermal processing is a little too harsh. We therefore sought systems that would be thermally labile at much lower temperatures. We turned our attention to the Ninetescu hydrocarbons, as described in figure 7. As previously discussed, these monomers are used to create polymers, by ROMP techniques, that thermally convert to conductive polyacetylene by fragmenting off a small molecule in a "Retro" Diels-Alder reaction. This is shown schematically in figure 23.

Figure 23. Schematic representation of the polymer formation and Retro Diels-Alder reaction to form polyacetylene and kick off an aromatic fragment

We decided that we could make a monomer whose polymer, when thermally treated at 130°C, would fragment a substantial portion of each repeat unit. We were successful in making the monomer shown in figure 24, designated as di-dodecoxybenzo precursor, or monomer **20**. The thermal treatment of this polymer at 130°C should create a fragment from each repeat unit that, when extracted out, will take 91% of the repeat unit weight with it. This translates to a total weight loss of 91% of this polymer when heated at 130°C. This temperature treatment was based on previously published papers on the subject of polyacetylenes made by this approach.^{3,4}

Figure 24. Chemical structure of new Ninetescu hydrocarbon synthesized for creating large aromatic fragments.

The polymerization of this polymer into a homopolymer, and subsequently a block copolymer, was successful, and the GPC traces are shown in figure 25.

Figure 25. GPC traces of homopolymer poly-20 (right) and block copolymer poly-19/poly-20 (left)

The thermally stable block was the poly-19 block, as used in the previous section. The molecular weight of the block copolymer was as follows: the poly-19 block was 32,500 g/mol, and the poly-20 block was 17,500 g/mol. As seen from the GPC trace, a small

amount of the double molecular weight species occurs in this sample also. We analyzed this material by SAXS, and the results are shown in figure 26.

Figure 26. SAXS curve for the poly-19/poly-20 system.

As can be seen from this figure, there is a scattering peak at $q = 0.29$, which indicates that there is indeed phase separation, and the domain spacing between identical phases is $200\text{\AA}$. This sample was cast into a thin film as previously described for other samples. This film was treated in a 1N HCl solution for two weeks, with the desire to crosslink the thermally stable phase. This sample was then heated at 130°C for 10 minutes, and the sample was extracted in a soxhlet extractor overnight using chloroform as the solvent. This was done to extract all the fragments that were cleaved off in the Retro-Diels-Alder thermal treatment. A weight loss analysis demonstrated that the amount of weight extracted from the film was nearly identical to the theoretical weight loss that would occur from each repeat unit of the thermally labile block losing its aromatic fragment. We only had time and money to analyze this sample by high-resolution SEM, and this is shown in figure 27. The SEM figure is very encouraging, showing a spaghetti like morphology, with the pores nearly monodisperse at a size of nearly $200\text{\AA}$. This corresponds quite well with the domain spacing observed by SAXS. Therefore this approach to creating mono-disperse mesoporous materials was quite successful. Apparently the crosslinking treatment was sufficient to give the thermally stable phase structural integrity, and the mild thermal treatment of this system did not cause collapse of the pores. This method should be the method of choice for further studies.

Figure 27. SEM of poly-19/poly-20 film after thermolysis and extraction

D. Modeling Efforts

An integral part of this project involves modeling of the phase separation of block copolymers. This was included in the project with the hopes that if we can predict domain size and morphology vs. block copolymer molecular weight, block ratio, and chemical composition, we could predict what the pore sizes of our systems would ultimately be. We employed the expertise of Prof. John McCoy at New Mexico Tech. to participate in the modeling effort on this project. He used Density Functional Theory (DFT) in conjunction with PRISM theory developed by John Curro at Sandia Labs, to determine the thermodynamics of block copolymer systems - i.e. at what molecular weights do certain block copolymer systems phase separate, and what are the domain sizes and interfacial thicknesses of these systems. He analyzed theoretical lamellar-type block copolymer systems using DFT. The details of this modeling effort are outside the expertise of the author of this report, and therefore only the final conclusions are reported here. The reader is directed to the journal article that was published for further details.²¹

1. **Summary of DFT Modeling Results.** Professor John McCoy has demonstrated that the DFT modeling of theoretical lamellar block copolymer systems predicts accurate behavior of the dependence of domain spacing vs. molecular weight, as observed both by other modeling approaches and by experimental results.²¹ In general, this dependence can be expressed by the following equation:

$$D = AN^{\delta}$$

where D corresponds to the spacing between mesophase separated domains, A is a proportionality constant, N is the number of repeat units in the polymer chain, and δ is the exponential constant describing the dependence. Experimental results predict that for large N the value of δ is near 0.65, and this is exactly what is predicted by the DFT modeling results employed by John McCoy. for small N, where the chains are just long enough to promote phase separation between the two blocks, δ is found to be 0.5.

When block copolymers phase separate, they do not do so with sharp interfaces between the two phases, but rather with a gradual transition from one type of polymer to the other. This transition region is designated as the interface, and has a characteristic thickness. The DFT modeling has been able to accurately predict these interfacial thicknesses when compared to real-life systems such as poly(ethylene)/poly(propylene) block copolymer systems and polystyrene/polymethylmethacrylate block copolymer systems. This is in contradiction to previous modeling approaches used by other researchers, which predict artificially smaller interfacial thicknesses than are observed experimentally.²¹ Therefore this modeling approach has definitely contributed to the field of block copolymer thermodynamics predictions. In order to determine real domain sizes and spacings in real polymer systems, crucial pieces of information on the real system are needed, such as radii of gyration (R_g) and solubility parameter (δ). We therefore sought to determine these values experimentally for our norbornene-type polymer systems. Due to lack of time and funding, we have only been able to determine R_g for several types of polynorbornenes. This can be done by using Small-Angle Neutron Scattering (SANS) experiments, and our results on R_g determinations are described in detail in the next section.

2. Small-Angle Neutron Scattering of Polynorbornenes.

a) **Introduction:** As stated previously, the radius of gyration (R_g) of a polymer system vs. Its molecular weight is an important piece of information needed for modeling of real-life polymer systems. R_g can be determined for a polymer chain by mixing a partially or fully deuterium labeled polymer with the non-deuterated polymer of identical molecular weight. Small-Angle Neutron Scattering (SANS) can then be used to get a scattering between the deuterated and non-deuterated chains. A scattering curve is obtained that is fit to a curve based on Debye Coil Theory. An R_g value can then be extracted from this curve for the particular polymer of its given molecular weight. If a series of molecular weights are studied, we can obtain R_g vs. Molecular weight and can compare this to the dependence predicted by theory. We therefore set out to make a series of deuterated and non-deuterated polymer molecular weights for a variety of polynorbornenes.

b) **Results and Discussion:** For each type of polynorbornene, we synthesized a 15K, 25K, 35K, and 45K sample of non-deuterated chains, and of varying levels of deuterated chains. Figure 28 shows all the monomers synthesized for the SANS study, including the differing levels of deuterium labeling.

Figure 28. Chemical structures of monomers whose polymers were used in the SANS study. The letter d with the subscript designates the amount of deuteriums replacing hydrogens on each monomer.

1) GPC Stydy: In order to ensure that these systems are well behaved, we analyzed them extensively using GPC. Figure 29 shows representative sets of GPC traces. Part a shows the non-deuterated set of poly-**22** and part b shows a deuterated set of poly-**22-d_{8.3}**.

Figure 29. GPC traces of molecular weight sets of poly-22 (a) and poly-22-d_{8.3} (b)

As can be seen by these traces, this polymerization technique produces well-defined polymer chains with narrow molecular weight distribution, with increasing molecular weights eluting at earlier times. This is exactly what would be expected for living polymerization systems, as our technique is proposed to be. All the data for these systems obtained by GPC analysis are shown in table 2. For each system, the table shows targeted molecular weights, GPC calculated molecular weights, polydispersities, and retention times, for the series of molecular weights. At this point a comment is warranted about GPC calculated molecular weights. Our GPC operates with a two-angle laser light scattering detector, which allows absolute molecular weights to be calculated. However, in order for these values to be accurate, another polymer property is needed to be known accurately - the incremental refractive index change with concentration for the particular polymer in the GPC solvent, which is thf in our case. This value is commonly known as dn/dc . The GPC setup has capabilities of determining dn/dc , but not very accurately. We have experienced errors in molecular weights as much as 20% off using the GPC calculated dn/dc . We don't have capabilities in our lab to accurately determine dn/dc , and therefore took a different approach. Based on our vast experience with ROMP we assumed that one of the molecular weights in the series was accurate according to the targeted molecular weight. We chose the 25K sample for each type of polynorbornene. We then fit the dn/dc to a value that made the GPC calculated molecular weight closely match the targeted molecular weight. We then used this dn/dc (this value is independent of molecular weight) to calculate all other molecular weights in the series. As can be seen from table 2 this proved to be quite accurate once the 25K dn/dc was determined. For completeness, we report all the determined dn/dc values for each type of polynorbornene in table 3.

Table II. GPC information for polymers used in SANS study

homopolymer	Mw(g/mol)-targeted	Mw - from GPC	Polydispersity	Retention Time (min)
7	15,000	14,930	1.06	12.49
	25,000	24,730	1.05	11.87
	35,000	35,330	1.06	11.47
	45,000	45,580	1.07	11.18
7-d7.3	15,000	17130	1.04	12.31
	25,000	24290	1.04	11.35
	35,000	36330	1.07	11.00
	45,000	47806	1.08	10.64
15	15,000	15,530	1.04	12.09
	25,000	25,320	1.04	11.55
	35,000	35,450	1.04	11.20
	45,000	44,920	1.04	10.96
15-d3	15,000	15,260	1.05	12.13
	25,000	25,400	1.05	11.56
	35,000	36,460	1.05	11.20
	45,000	47,280	1.07	10.96
15-d4.8	15,000	15,500	1.05	12.09
	25,000	25,220	1.04	11.56
	35,000	35,100	1.04	11.23
	45,000	46,750	1.05	10.99
21	15,000	15,500	1.04	12.29
	25,000	25,110	1.04	11.71
	35,000	35,000	1.05	11.34
	45,000	46,980	1.05	11.02
21-d5	15,000	15,030	1.04	12.39
	25,000	25,290	1.04	11.77
	35,000	34,710	1.04	11.41
	45,000	45,280	1.04	11.13
21-d10.3	15,000	14,850	1.05	12.40
	25,000	25,280	1.04	11.79
	35,000	35,920	1.04	11.37
	45,000	47,170	1.05	11.05
21	15,000	15,460	1.04	12.32
	25,000	25,700	1.04	11.75
	35,000	34,820	1.04	11.37
	45,000	45,320	1.05	11.11
21-d3	15,000	14,900	1.05	12.44
	25,000	25,300	1.04	11.82
	35,000	34,580	1.04	11.47
	45,000	44,180	1.04	11.19
21-d8.3	15,000	14,460	1.05	12.38
	25,000	25,250	1.04	11.76
	35,000	35,440	1.04	11.36
	45,000	45,620	1.04	11.09

Table III. dn/dc values¹ for the SANS study polymers

<u>polymer</u>	<u>dn/dc</u>
7	0.113
7-d7.3	0.120
15	0.176
15-d3	0.172
15-d4.8	0.168
21	0.143
21-d5	0.133
21-d10.3	0.129
22	0.142
22-d3	0.130
22-d8.3	0.135

1. Values are for solutions in thf at 31°C, at a wavelength of 640nm.

Another test for a true, well-defined, living polymerization system is that, when the log of molecular weight is plotted vs. GPC retention time, a linear relationship is observed, where the slope of the line is negative (larger molecular weights elute at earlier times on GPC systems). We analyzed the GPC data in this way for all our polynorbornene systems, and we observed nearly perfect linear relationships in all cases. Two representative plots are shown in figure 30 corresponding to the two GPC data set traces in figure 29.

Figure 30. Plots of $\ln(\text{molecular weight})$ vs GPC retention time for: a) poly-22, and for b) poly-22-d_{8.3}

These straight line relationships of $\log(\text{molecular weight})$ vs. GPC retention time again show that all of our systems are well behaved and the polymerization technique is a true

living polymerization system. One final comment relates to an omission in the tables, that of poly-14 and poly-14-d₃ systems. These data were omitted because we thought that the double and triple molecular weight species would throw off both the GPC and SANS-Rg calculations.

2) SANS Study: Now that we have proved that we have well behaved systems using GPC analysis arguments, we proceeded to prepare samples for SANS analysis. This was done by mixing the non-deuterated chain of a given molecular weight of a particular polynorbornene system with one of the partially deuterated samples of identical molecular weight and polymer type, usually at about 50 wt% of each. For example, 0.25g of 25K poly-22 and 0.25g of 25K poly-22-d_{8.3} would be dissolved together in thf or chloroform and mixed thoroughly by shaking. The mixed solution is then poured into a teflon-coated aluminum, boat, and the solvent allowed to evaporate slowly to leave behind a film of the mixed 25Kpoly-22, 25Kpoly-22-d_{8.3}. This sample is then analyzed by SANS to get the scattering curve. A representative curve for this mixture is shown in figure 31.

Figure 31. SANS scattering curve for 25K poly-22 mixed in 25K poly-22-d_{8.3}

The decreasing curve is fit to a Debye coil expression to extract out Rg. In this way, Rg was calculated for several systems. Table ___ summarizes Rg vs. Molecular weight for all these systems.

For all these systems, a relationship can be determined between Rg and molecular weight. Theoretically, this relationship can be described by the following equation:

$$Rg \propto MW^{1/2}$$

where Rg is the radius of gyration and MW is the molecular weight of the chain. By plotting log(Rg) vs. log(MW) we should obtain a straight line with a slope of 0.5. This was done for all the systems studied, and a representative plot for the poly-22/poly-22-d_{8.3} mixture is shown in figure 32.

Table IV. Data of Radius of Gyration (Rg) vs. Molecular Weight
for the SANS study polymers¹

polymer mix	Molecular Weight	Rg (Å)
7 / 7-d7.3	15,000	52
	25,000	64
	35,000	71
	45,000	73
14 / 14-d9	15,000	34
	25,000	47
	35,000	68
	45,000	78
15 / 15-d3	15,000	33
	25,000	44
	35,000	56
	45,000	65
15 / 15-d4.8	15,000	56
	25,000	80
	35,000	90
	45,000	114
21 / 21-d5	15,000	39
	25,000	53
	35,000	
	45,000	75
21 / 21-d10.3	15,000	48
	25,000	64
	35,000	79
	45,000	92
22 / 22-d3	15,000	66
	25,000	63
	35,000	81
	45,000	86
22 / 22-d8.3	15,000	53
	25,000	69
	35,000	84
	45,000	96

1. Rg values correspond to the deuterated chains in the non-deuterated matrix

Figure 32. Plot of $\ln(R_g)$ vs. $\ln(\text{Molecular Weight})$ for the poly-22/poly22-d_{8.3} system

As can be seen from this figure, a straight line relationship exists, and the slope of this line is 0.54. These plots were done for all the SANS polymer systems studied, and the slopes of these lines are shown in table 5. As can be seen from the data, most of the slopes are near the theoretical value of 0.5. Factors that add to erroneous results (such as for set 22 / 22-d3) are typically levels of deuterium that are too low, where background scattering becomes significant enough to alter the analysis. The samples that were the closest to theoretical were the monodisperse homopolymer systems with the highest levels of deuterium labeling, for example the 21 / 21-d10.3 system and the 22 / 22-d8.3 system.

Now that we have a reasonably good idea about what R_g values are for polynorbornene systems, we can use this information to input into the Density Functional Theory modeling theory to help predict thermodynamic properties of real-life polynorbornene systems.

c) **SANS Experiment Conclusions:** GPC demonstrated our polynorbornene systems to be well-behaved and the polymerization technique to be living. The SANS experiments were a powerful tool for determining R_g for these polynorbornene systems, and have brought us one step closer to employing the DFT modeling theory to real-life systems, which was shown to be accurate for theoretical systems. If further funding were to arise, δ 's (solubility parameters) could be determined for these systems, which would give us a complete picture for helping the DFT to be successfully applied to real-life polynorbornene systems.

Table V. Slopes of the curve fits to the plots of $\ln(R_g)$ vs. $\ln(\text{Molec. Wt.})$ for the deuterated/non-deuterated homopolymer mixtures studied.

polymer system	slope of $\ln(R_g)$ vs. $\ln(\text{Molec. Wt.})$
7 / 7-d7.3	0.371
14 / 14-d9	0.783
15 / 15-d3	0.623
15 / 15-d4.8	0.618
21 / 21-d5	0.595
21 / 21-d10.3	0.573
22 / 22-d3	0.241
22 / 22-d8.3	0.543

IV. Overall Summary and Conclusion

In this work, we successfully synthesized a wide variety of norbornene-type homopolymers and surveyed them for thermal stability and thermal lability. We were able to down select to a couple monomer types whose polymers create quite stable phases when heated to 450°C, and a monomer type whose polymer is almost completely labile by 450°C. Block copolymers of these systems were successfully made and showed mesophase separation by SAXS. Precipitation or sol-gel processing of these materials followed by pyrolysis created the desired mesopores, but these were not monodisperse, and the samples contained micropores and macropores as well. Film processing followed by crosslinking and pyrolysis created very low porosity, indicating a collapse of the pores. If further time and funding were available, we feel that we could determine optimal processing conditions for these types of materials that would impart a high degree of crosslinking to prevent collapse of the pores, and thus give us the desired monodisperse materials once the labile phase is removed. In moving to a new system based on the precursor route to polyacetylene, we demonstrated that we could remove over 90% of the thermally labile phase by only heating at 130°C for 10 minutes. By SEM we showed that we did get the desired monodisperse mesopores. Again if further time and funding were available we could explore this avenue more fully, such as confirming this monodisperse mesoporosity by porosimetry.

Modeling of theoretical block copolymer systems using Density Functional Theory was also very successful, as demonstrated by the accurate determination of the dependence of domain spacing and size on the molecular weight and block ratio of the block copolymer. The accurate prediction of interfacial thicknesses also demonstrates that the modeling was successful. For our real-life polynorbornene type systems, we needed to know solubility parameters, and radii of gyration. We were successful in determining R_g for several types of polynorbornenes, and their molecular weight dependence was accurate as long as the level of deuterium labeling was quite high. Again, If further time and funding were available, we would be able to determine solubility parameters for these polynorbornenes, and thus be one step closer to being able to accurately predict domain size and spacing, and thus ultimately pore size.

In general, this approach shows a lot of promise in being able to predict pore sizes of a system based solely on block copolymer chemical structure, molecular weight, and block ratio. It also promises to be able to make these ordered monodisperse porous materials in the mesoporous range. Much further study is required to be able to actually attain this ultimate goal.

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