

MAY 29 1997

# SANDIA REPORT

SAND97-1030 • UC-704

Unlimited Release

Printed May 1997

## New Adhesive Systems Based on Functionalized Block Copolymers

RECEIVED

JUN 26 1997

OSTI

M. Kent, R. Saunders, M. Hurst, J. Small, J. Emerson, D. Zamora

Prepared by  
Sandia National Laboratories  
Albuquerque, New Mexico 87185 and Livermore, California 94550

Sandia is a multiprogram laboratory operated by Sandia  
Corporation, a Lockheed Martin Company, for the United States  
Department of Energy under Contract DE-AC04-94AL85000.

Approved for public release; distribution is unlimited.

MASTER



Sandia National Laboratories



Issued by Sandia National Laboratories, operated for the United States Department of Energy by Sandia Corporation.

**NOTICE:** This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government, any agency thereof, or any of their contractors or subcontractors. The views and opinions expressed herein do not necessarily state or reflect those of the United States Government, any agency thereof, or any of their contractors.

Printed in the United States of America. This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from  
Office of Scientific and Technical Information  
P.O. Box 62  
Oak Ridge, TN 37831

Prices available from (615) 576-8401, FTS 626-8401

Available to the public from  
National Technical Information Service  
U.S. Department of Commerce  
5285 Port Royal Rd  
Springfield, VA 22161

NTIS price codes  
Printed copy: A04  
Microfiche copy: A01

**DISCLAIMER**

**Portions of this document may be illegible  
in electronic image products. Images are  
produced from the best available original  
document.**

## **DISCLAIMER**

**This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.**

## **New Adhesive Systems Based On Functionalized Block Copolymers**

M. Kent, R. Saunders, M. Hurst, J. Small  
Material and Process Sciences Center  
Sandia National Laboratories  
P.O.Box 5800  
Albuquerque, NM 87185-1407

J. Emerson, D. Zamora  
Manufacturing Technologies Center  
Sandia National Laboratories  
P.O.Box 5800  
Albuquerque, NM 87185-0958

### **Abstract**

The goal of this work was to evaluate chemically-functionalized block copolymers as adhesion promoters for metal/thermoset resin interfaces. Novel block copolymers were synthesized which contain pendant functional groups reactive toward copper and epoxy resins. In particular, imidazole and triazole functionalities that chelate with copper were incorporated onto one block, while secondary amines were incorporated onto the second block. These copolymers were found to self-assemble from solution onto copper surfaces to form monolayers. The structure of the adsorbed monolayers were studied in detail by neutron reflection and time-of-flight secondary ion mass spectrometry. The monolayer structure was found to vary markedly with the solution conditions and adsorption protocol. Appropriate conditions were found for which the two blocks form separate layers on the surface with the amine functionalized block exposed at the air surface. Adhesion testing of block copolymer-coated copper with epoxy resins was performed in both lap shear and peel modes. Modest enhancements in bond strengths were observed with the block copolymer applied to the native oxide. However, it was discovered that the native oxide is the weak link, and that by simply removing the native oxide, and then applying an epoxy resin before the native oxide can reform, excellent bond strength in the as-prepared state as well as excellent retention of bond strength after exposure to solder in ambient conditions are obtained. It is recommended that long term aging studies be performed with and without the block copolymer. In addition, the functionalized block copolymer method should be evaluated for another system that has inherently poor bonding, such as the nickel/silicone interface, and for systems involving metals and alloys which form oxides very rapidly, such as aluminum and stainless steel, where bonding strategies involve stabilizing the native oxide.

## I. Introduction

The need to control and optimize the properties of interfaces between solids and thermoset polymeric resins is critical in a host of technologies. Often the adhesive strength of the interface, the resistance to moisture and corrosion (metals), and the ability to transfer stress through the interface are critical to the overall performance of a product or device. Some examples include layers of conducting metals and polymer dielectrics in the electronics packaging industry, adhesive joints involving aluminum or stainless steel and epoxy in the aerospace and automotive industries, and carbon black- or silica-filled rubber in the tire industry. In Defense Programs (DP) applications, epoxy, silicone, and polyurethane adhesives and encapsulants are commonly found in contact with stainless steel, aluminum, nickel and various other metal surfaces.

Etching and controlled pre-oxidation treatments are commonly used to promote adhesion and durability of metal/thermoset interfaces. While excellent performance can often be achieved, these processes are time consuming, costly, and involve harsh chemicals detrimental to the environment. In addition, in certain technologies the roughness of the solid surface, which is an essential element of the etching and pre-oxidation treatments, is limiting to the product or process. One such example is the electronic circuit board industry, where copper line spacings and widths can become limited by the roughness of commercial foil treatments. Moreover, in the subtractive process of manufacturing circuit boards, copper must be etched away to pattern the circuit. The difficulty of this processing step increases substantially with the roughness of the copper.

Several obstacles must be overcome to provide a strong, durable bond between a solid surface and a thermoset resin which does not rely upon physical roughness. First, the thermoset resin and the solid surface must be linked through a chain of chemical bonds. This can be especially difficult for certain metals, such as nickel, which are unreactive toward most functional groups. Second, for metals, the surface of the metal must be protected from oxidation and corrosion in the presence of heat, oxygen, and water. This criterion is especially severe for copper foil exposed to molten solder in the manufacture of printed circuit boards. Copper oxidizes rapidly when heated in air to produce a weak surface oxide layer which leads to failure at low loadings. Third, the properties of the interface region must be such that the stresses that build up during thermal cycling due to differences in coefficients of thermal expansion (CTE) can be dissipated nondestructively.

Primer formulations involving small-molecule silane coupling agents work extremely well for glass, silica, and certain metal substrates [1]. However, there are many metals and other inorganic substrates to which silane coupling agents will not bond. Another problem with silanes is that they do not protect metal surfaces from oxidation and corrosion. Small-molecule chelating agents have been proposed as a resolution to this latter problem [2]. These materials, which possess a functional group which chelates to the metal and another functional group that bonds to the polymer resin, have been shown to inhibit oxidation of certain under ambient conditions. However, in contrast to silane coupling agents, these do not possess the ability to form a three-dimensional interpenetrating network and entangle with the resin. Moreover, they are susceptible to attack by moisture and are not stable at elevated temperature. Polymers containing chelating agents have demonstrated improved passivation at elevated temperature, but with only a small increase in adhesive strength [3], likely due to limited reactivity of the chelating agent with the thermoset resin.

Recently, polymeric coupling agents have been proposed [4] which possess a single chemical functionality capable of bonding to both the metal and to the thermoset resin. This reactive group is incorporated at set intervals along the backbone of the polymer. The advantages cited in this method are that the backbone of the polymer can be made hydrophobic to provide increased resistance to water, that attachment of the functional groups to a polymeric backbone adds stability and strength to the interphase, and that polymeric coupling agents can be more efficient than low molecular-weight compounds

in dissipating stresses. However, it has not been demonstrated that the level of passivation is sufficient to protect copper from destructive oxidation after exposure to elevated temperatures such as occurs in soldering operations. In addition, the method involves the use of multilayer coatings that can lead to cohesive failure between the layers. Also, the fact that only one type of functional group is present in the polymer makes it unlikely that both functions, bonding to and passivating metal or metal oxide surfaces and bonding to thermosets, can each be accomplished in an optimal fashion for a variety of metals and thermosets. None of the above performs well enough to replace the etching and oxidation treatments for most applications.

The purpose of this investigation was to assess the performance of chemically functionalized block copolymers as adhesion promoters for metals and thermosetting polymer resins. In contrast to the polymeric coupling agents described in [4] in which one type of functional group must be chosen to perform both functions, in this method two types of functional groups are employed to perform the two essential functions. Since two types of functional groups are present, each can be chosen to perform its function in an optimal fashion. For certain metals such as nickel, which form bonds with only a select few functional groups, this flexibility in the design of the copolymer is essential. Since these materials promote adhesion due to chemical bonding, the need for surface roughness should be dramatically decreased or eliminated. In addition, the process described below does not involve harsh chemicals detrimental to the environment.

The fact that the two types of chemical functionalities are present in blocks rather than randomly distributed along the backbone of the polymer has a profound significance for the structure of the interphase region, for adhesion, and for passivation of metals. If the two types of functional groups were distributed randomly along the backbone, as in a random copolymer, both groups would be present at the solid surface and also at the interface with the resin. On the other hand, with block copolymers the two blocks are able to segregate at the interface. This is illustrated in Figure I.1. Thus each block can perform a unique function which is not impeded or diluted by the presence of the other functional group. For example, it is possible that a metal or metal-oxide surface can be exposed only to chelating functional groups, which inhibit oxidation, while the second block can be designed to have a high degree of compatibility with the thermoset resin, and thus penetrate into and entangle with the resin, as well as chemically react with it. Thus it is proposed that block copolymers can lead to better passivation of the metal-oxide surface and better compatibility with the resin than their random copolymer counterparts.

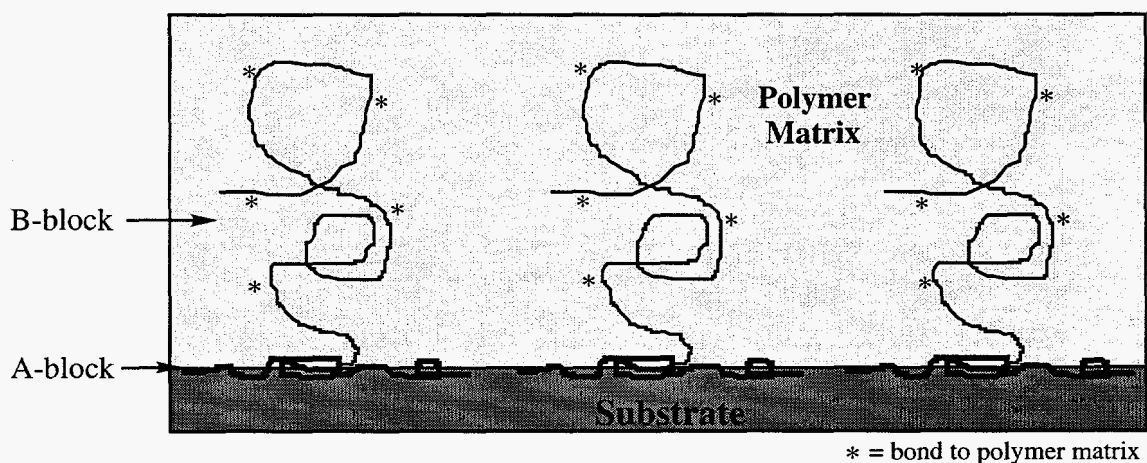


Figure I.1

A further advantage of the present method is that only a monolayer of the block copolymer coupling agent is present at the interface. This eliminates the possibility of failure between layers. Another advantage of block copolymers, and polymeric coupling agents in general,

is that there are many attachment points per molecule both to the solid substrate and to the resin. In addition, the present block copolymers have excellent temperature stability. Another important advantage is that the synthetic method is very general, allowing a wide variety of functional groups to be incorporated. This enables one to tailor the functionality to specific substrates. Finally, it is also possible to prepare triblock copolymers, where the middle block can be designed to impart additional properties, such as moisture resistance. Adhesion promoters such as those described herein have not been made previously due to restrictions related to conventional synthetic techniques.

The limited duration of this program only allowed for the detailed investigation of one metal/resin system. The system chosen for study was copper/epoxy, due to its relevance to the printed circuit board industry. The work focused on a block copolymer functionalized with imidazole groups, which are known to chelate with copper and inhibit oxidation, and amines that bond with epoxies. At the start of this program, it was believed that the inherent bond strength of copper to epoxy was poor, and thus that this interface would be a good candidate for testing block copolymer coupling agents. This conclusion was based on our own initial testing, literature data, and communications with industry representatives. In fact, we discovered through the course of this program that the inherent bond strength of epoxy to bare copper, in the absence of oxide, is quite strong. Thus only small enhancements in adhesion strength are observed with the block copolymer. While much has been learned regarding the synthesis, reactivity, and adsorbed conformation of the block copolymer coupling agents, further work involving an inherently poorly bonding interface should be explored to definitively assess the efficacy of this method.

The outline of this report is as follows. Section II describes the synthesis of the block copolymers. Section III provides evidence for the reactivity of the secondary amine functionality toward epoxy. (The reactivity of the imidazole functionality toward copper is well documented in the literature [2,3].) The characterization of the adsorbed conformation of the block copolymer is reported in Section IV. Adhesion testing using both lap shear and peel test methods are reported in Section V. A brief summary of the entire project is provided in Section VI.



## II. Synthesis

### Introduction

There are several challenging requirements for the synthesis of block copolymer coupling agent systems. The synthesis of block copolymers requires a "living" polymerization technique, where the reactive end of the growing chain remains active after complete consumption of monomer. This enables the sequential addition of different monomers to form a block copolymer. To serve as a coupling agent, the copolymer must be functionalized with a group that reacts with an epoxy resin, such as a primary or secondary amine, and another group which interacts strongly with the substrate. Very few living polymerization techniques can tolerate such functionalities, due to their interaction with the initiator. One particular technique, Ring-Opening Metathesis Polymerization (ROMP), has been shown to be tolerant toward secondary amine functionalities using classical ROMP catalyst systems [5]. However, these polymers tended to be crosslinked and insoluble. Recently Schrock has developed a living molybdenum based ROMP catalyst system that has been shown to tolerate a wide variety of chemical functionalities [6]. We therefore set out to try this catalyst system for polymerizing primary and secondary amine functionalized monomers. In this section we report the successful synthesis of amine functionalized homopolymers and block copolymers using this catalyst system. We also discuss the synthesis of the amine functionalized monomers, and improvements over literature preps.

### Results and discussion

#### Monomer Synthesis

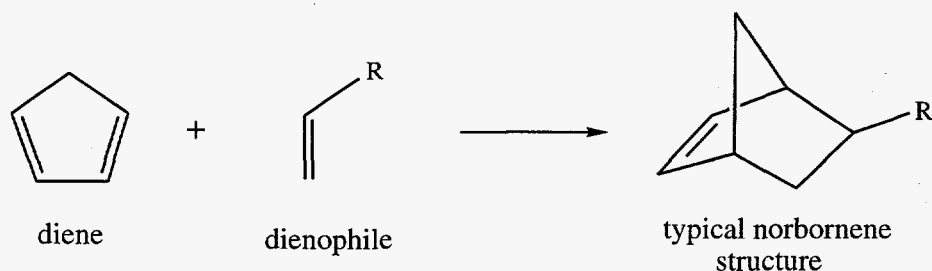


Figure II.1. Diels-Alder reaction of a diene with a dienophile to make a typical norbornene structure.

In order for ROMP to work with the Schrock catalyst, the monomer must have a strained double bond. The most common structure that possesses this is the norbornene structure. Norbornenes are readily synthesized via Diels-Alder reactions of cyclopentadiene and a dienophile (see Figure II.1). There have been a few literature preps describing the synthesis of amine functionalized norbornenes [5,7]. These involved typically a one-to-one reaction of the cyclopentadiene with an allyl or vinyl amine compound. The workup involved an aqueous acid extraction of the reaction mixture followed by basification and an organic extraction, and finally distillation to get pure product. We have devised a much better and simpler approach to making these amine functionalized norbornene monomers (see Figure II.2).

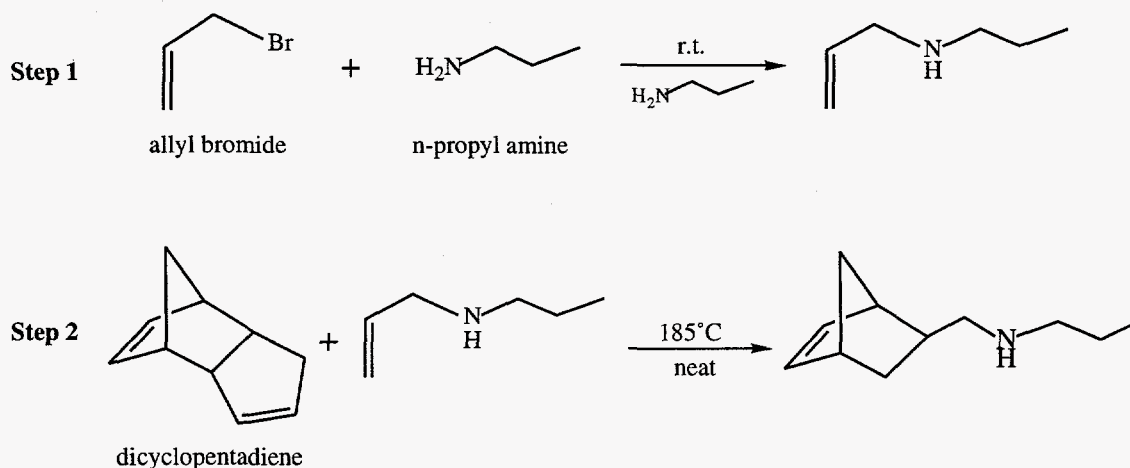


Figure II.2. Two step synthesis for making amine functionalized norbornenes, using the n-propyl monomer as an example.

Our first step is to make the allyl amine compound. This is done by reacting allyl bromide with a large excess of the primary amine. The excess of the amine suppresses undesirable side reactions, and gives yields of the intermediate in the range of 60 to 70 %. Any unreacted amine is recovered in the distillation process and can be reused for future reactions. The next step involves the reaction of the allyl amine with uncracked cyclopentadiene (dicyclopentadiene). The amine intermediate is added in excess of the cyclopentadiene (Cp) by a ratio of 2.5 to 1. The reaction is carried out in a PARR high pressure reactor at 185°C for 15 hours. The excess amine helps suppress undesirable side reactions that form multiple Cp adducts. Also, no acid extraction is needed - the final product is recovered by simple distillation of the reaction mixture. Any excess of the allyl amine intermediate is recovered and reused. There is therefore little or no waste of reactants, and much workup time is saved. Yields of the second step are typically in the range of 55 to 75 %. Figure II.3 shows all the monomers synthesized and used in this study. There are two exceptions to this general reaction scheme. For the imidazole functionalized norbornene (monomer 6), allyl imidazole is already commercially available and does not need to be synthesized. The reaction of the allyl imidazole is carried out at atmospheric pressure and at reflux temperatures instead of in the PARR bomb. The pyridine functionalized norbornene (monomer 5), which is not of use for the adhesives but was made for comparison to the amine-functionalized monomers, was synthesized according to the literature prep because excess vinyl pyridine in the bomb at the desired temperatures tended to polymerize and make product isolation virtually impossible.

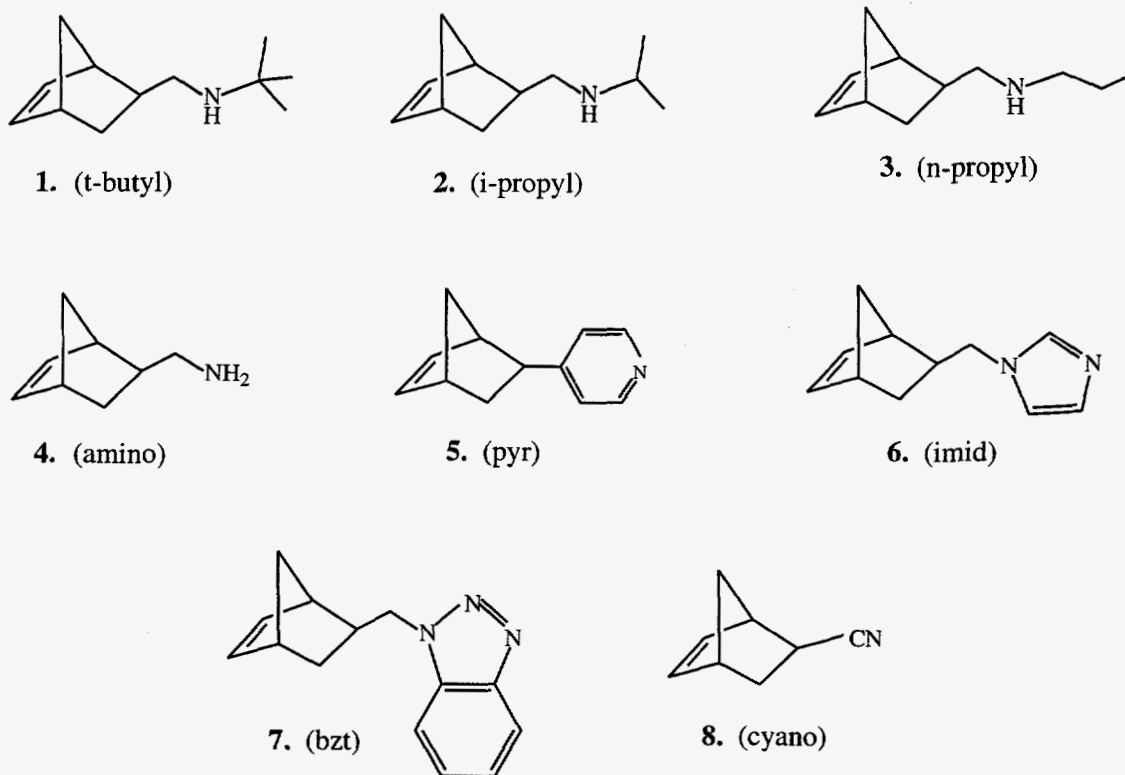


Figure II.3. Monomers synthesized and used in this study. Monomer 8 was included as a comparison to the amine monomers.

Corresponding deuterated monomers are made in a similar manner by starting with deuterated reagents such as deuterated isopropylamine and deuterated cyclopentadiene. Deuterated cyclopentadiene is made by stirring freshly cracked cyclopentadiene with deuterated water with some potassium hydroxide present. Figure II.4 shows the deuterated monomers that were made for this study.

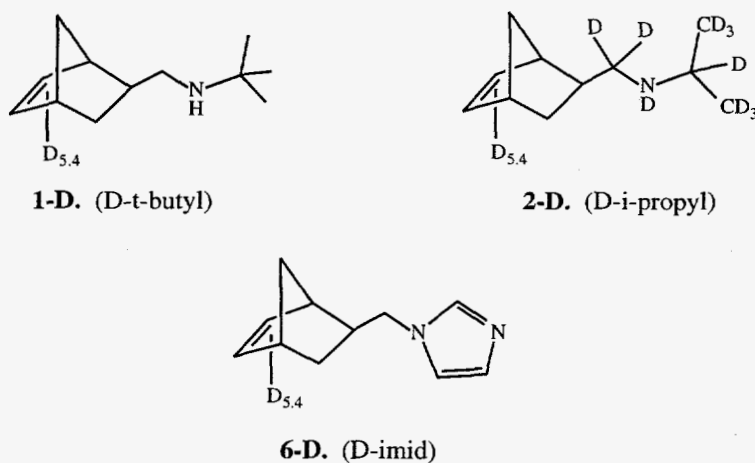


Figure II.4. Deuterated monomers synthesized and used in this study

## Polymerization kinetics

Figure II.5 shows the structure of the initiator and the general polymerization scheme.

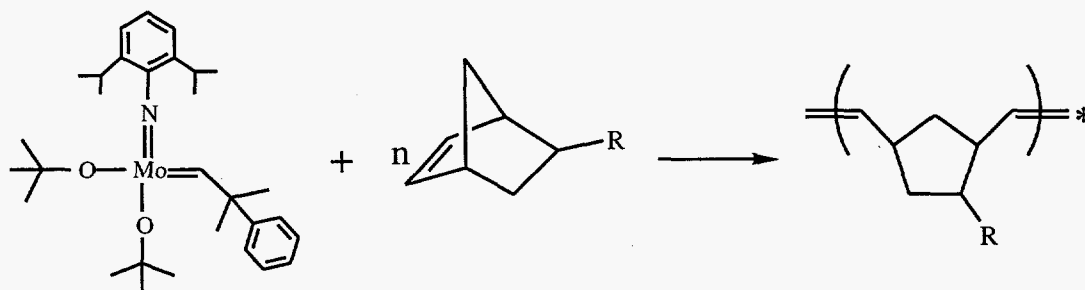


Figure II.5. Structure of the molybdenum based initiator, and polymerization scheme of norbornenes. The asterisk represents the living chain end of the polymer.

The polymerization involves two steps: an initiation step where the first monomer is inserted to start the polymer chain, and propagation step where additional monomer units are inserted to continue the growth of the chain. To simplify the analysis, we assume first order kinetics, which will be the case after all the initiator has inserted the first monomer unit.

In order to know how long to let the polymerization proceed to insure complete consumption of monomer, the kinetics of polymerization must be determined. This is done using NMR and following the disappearance of monomer peaks and the appearance of polymer peaks over time. For functionalized norbornene polymerizations this is quite easy, since the protons associated with the strained double bond always appear in the spectrum between 5.8 to 6.5 ppm, and the corresponding protons in the polymer occur between 5.0 and 5.8 ppm (see Figure II.6). Usually no other proton signals appear at these shifts.

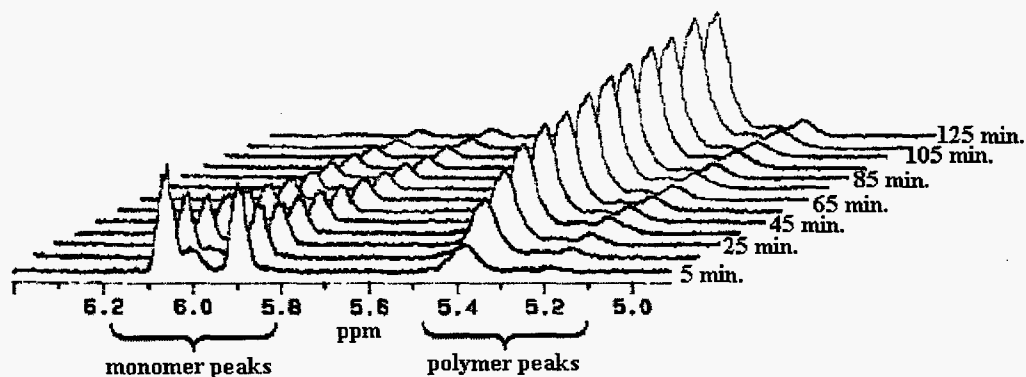


Figure II.6.  $^1\text{H}$  NMR spectra vs. time for the polymerization of the n-propyl monomer.

We can therefore observe monomer consumption by the disappearance of the peaks from 5.8 to 6.5, and polymer formation by the growing peaks from 5.0 to 5.8. To determine rate constants, we have assumed pseudo first order reaction kinetics. Table II.1 shows a representative data set for monomer concentration and  $\ln(\text{monomer concentration})$  vs. time for the n-propyl monomer. A plot of  $\ln(\text{monomer concentration})$  vs. time is shown in Figure II.7. The excellent linear relationship validates the assumption of first order reaction

Table II.1. Data of monomer concentration vs. time for the polymerization of the n-propyl monomer.

<u>time (hours)</u>	<u>concentration</u>	<u>ln(concentration)</u>
0.200	0.479	-0.736
0.283	0.395	-0.928
0.367	0.369	-0.997
0.450	0.307	-1.182
0.700	0.228	-1.478
0.867	0.184	-1.694
0.950	0.174	-1.749
1.033	0.157	-1.855
1.117	0.149	-1.905
1.283	0.130	-2.041
1.367	0.116	-2.154
1.450	0.104	-2.265
1.533	0.089	-2.415
1.617	0.088	-2.423
1.867	0.071	-2.642
1.950	0.058	-2.854
2.033	0.054	-2.915

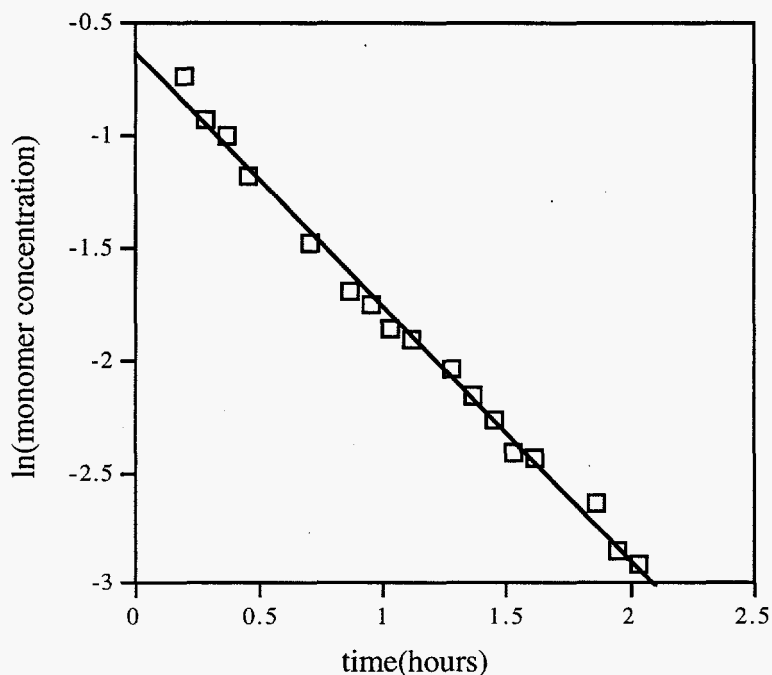


Figure II.7. Plot of ln(monomer concentration) vs. time for the polymerization of the n-propyl amine monomer.

kinetics. Table II.2 lists all the rate constants determined by NMR for the polymerization of the monomers studied. Also included is the time it takes for 99% consumption of each monomer based on these rate constants:

Table II.2. Polymerization rate constants, in decreasing order, for the monomers used in this study, along with time to reach 99% conversion. These constants are for polymerization in deuterated tetrahydrofuran (d8-THF).

monomer	rate constant (hr <sup>-1</sup> )	time to 99% conversion
bzt	27.18	10 min.
cyano	16.06	17 min.
t-butyl	13.74	20 min.
i-propyl	10.46	26 min.
pyr	7.04	39 min.
n-propyl	1.13	244 min.
imid	0.43	650 min.
amino	0.00	-
cyano <sup>a</sup>	0.00	-

a. this polymerization was carried out in the presence of n-methyl imidazole.

For comparison, cyano norbornene was studied (monomer 8) since it contains a non-coordinating nitrogen functionality, as opposed to the amines which have a coordinating nitrogen. For nitrogen containing monomers, the lone pair of electrons have the potential to bind to the active site of the initiator and thus slow down the polymerization. From looking at the rate constant data in the table, we can make a couple of observations. First of all the imidazole functionalized norbornene is by far the slowest by almost two orders of magnitude. The next slowest is the n-propyl functionalized norbornene, which is roughly one order of magnitude slower than the others. The remaining monomers are roughly the same, with the exception of the benzotriazole functionalized norbornene, which is nearly double the rate of the other amine monomers. The cyano norbornene rate constant falls in the range of the average norbornene monomers. From these observations we can make several conclusions. The monomer with the highest basicity is the t-butyl amine norbornene, and the monomer with the lowest is the benzotriazole norbornene. We can therefore say that the lower the basicity of the amine on the monomer, the more likely it is to polymerize faster. However, a higher basicity does not necessarily mean a slower polymerization. The t-butyl amine monomer has the highest basicity, but does not have a correspondingly low rate constant. Therefore steric hindrance must also play a role. This is borne out by the fact that the n-propyl amine monomer is less sterically hindered than the t-butyl amine monomer and has a correspondingly lower rate constant by an order of magnitude. However, the basicity of the n-propyl amine is nearly identical, and may be even slightly lower than the t-butyl amine, which should cause an increase in the rate constant. The imidazole, being sterically unhindered at the amine, and having a higher basicity than the benzotriazole, polymerizes the slowest of all the monomers. We therefore conclude that the higher the steric hindrance at the amine functionality, the higher the polymerization rate constant, and the higher the basicity of the amine, the lower the rate constant, except where steric hindrance is the primary factor affecting the rate. With these data we can conclude that the isopropyl amine and t-butyl amine monomers only need roughly 15 minutes for consumption, and the imidazole monomer needs at least three hours.

As a comparison, we attempted the polymerization of the cyano norbornene in the presence of n-methyl imidazole to see the effect of the presence of an imidazole functionality on the polymerization rate of an otherwise "fast" monomer. As can be seen from the table, n-methyl imidazole completely stopped the polymerization of the cyano norbornene. In order to make a useful block copolymer for copper/epoxy adhesion, we need to incorporate the imidazole functionalized monomer or the benzotriazole monomer

into one block, and the isopropyl or t-butyl amine monomer into the second block, and we now know how long to let each block grow.

#### Polymer Synthesis and Characterization

Figure II.8 shows the scheme to make block copolymers using ROMP:

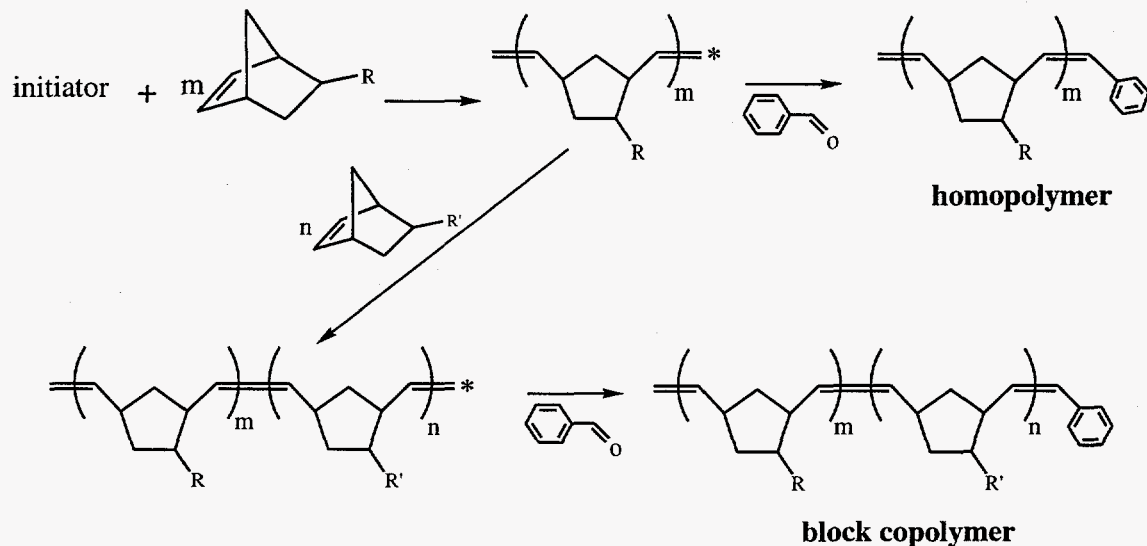


Figure II.8. General scheme for homopolymer and block copolymer synthesis using ROMP.

The initiator is intolerant of impurities such as moisture and oxygen, and therefore the polymerization is carried out in an inert nitrogen atmosphere in a glove box, using bone-dry tetrahydrofuran and extremely pure monomer. A homopolymer can be made by polymerizing one type of monomer and then terminating the polymerization with benzaldehyde. A block copolymer can be made by polymerizing one monomer, and then upon complete consumption of this monomer adding the second type of monomer. Upon consumption of the second monomer the polymerization is then terminated by addition of benzaldehyde. Molecular weights of the polymers are determined solely by the monomer/initiator ratio. Figure II.9 shows the three block copolymer systems that have been made and their corresponding molecular weights and block ratios. For the imid/t-butyl block copolymer we show a representative NMR spectrum in Figure II.10 of the homopolymer of each, and the corresponding block copolymer, to show that the block copolymer spectrum is a composite of the two homopolymers. This indicates that we have the block copolymer that we desired to make.

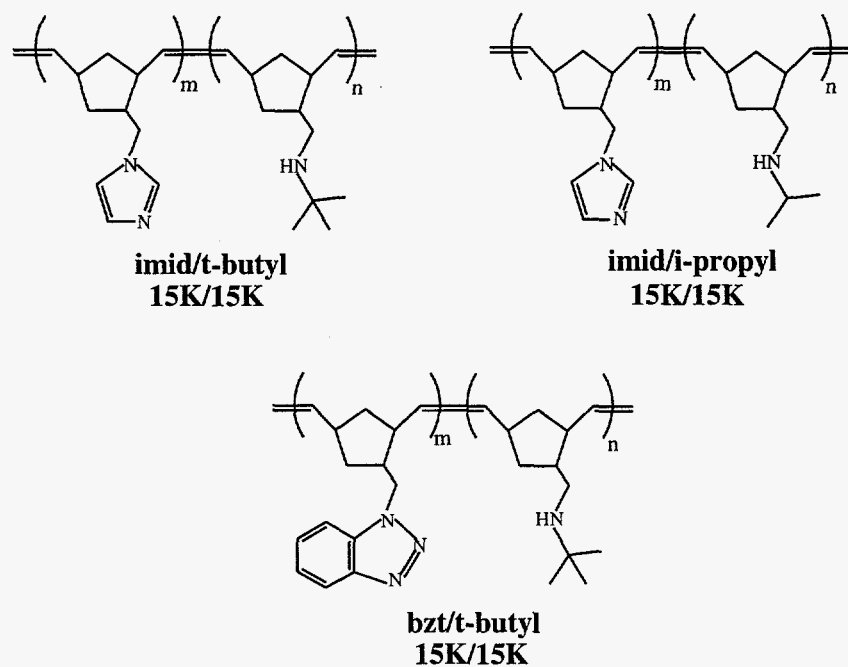


Figure II.9. Block copolymers synthesized for this study

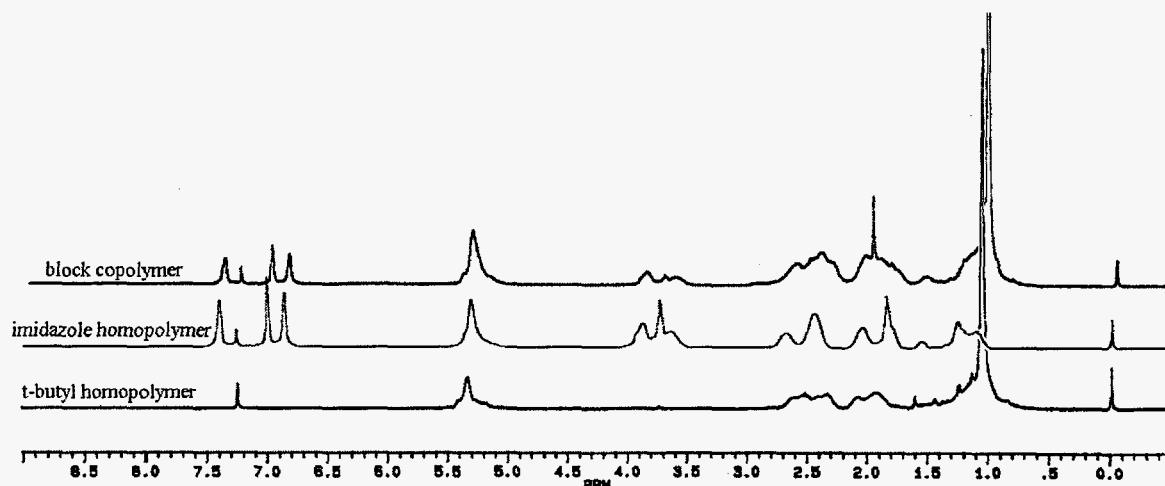


Figure II.10.  $^1\text{H}$  NMR of the t-butyl homopolymer, imidazole homopolymer, and the block copolymer, all in  $\text{CDCl}_3$ .

Gel Permeation Chromatography (GPC) was attempted on these block copolymers. However, amine functionalities tend to stick to GPC columns, and therefore no polymer peaks could be observed with the exception of the benzotriazole (bzt) polymer. The bzt polymer does not stick to the columns and can thus be analyzed by GPC. A homopolymer of the bzt monomer was synthesized along with a block copolymer with the other block being unfunctionalized polynorbornene. The GPC traces are shown in Figure II.11:



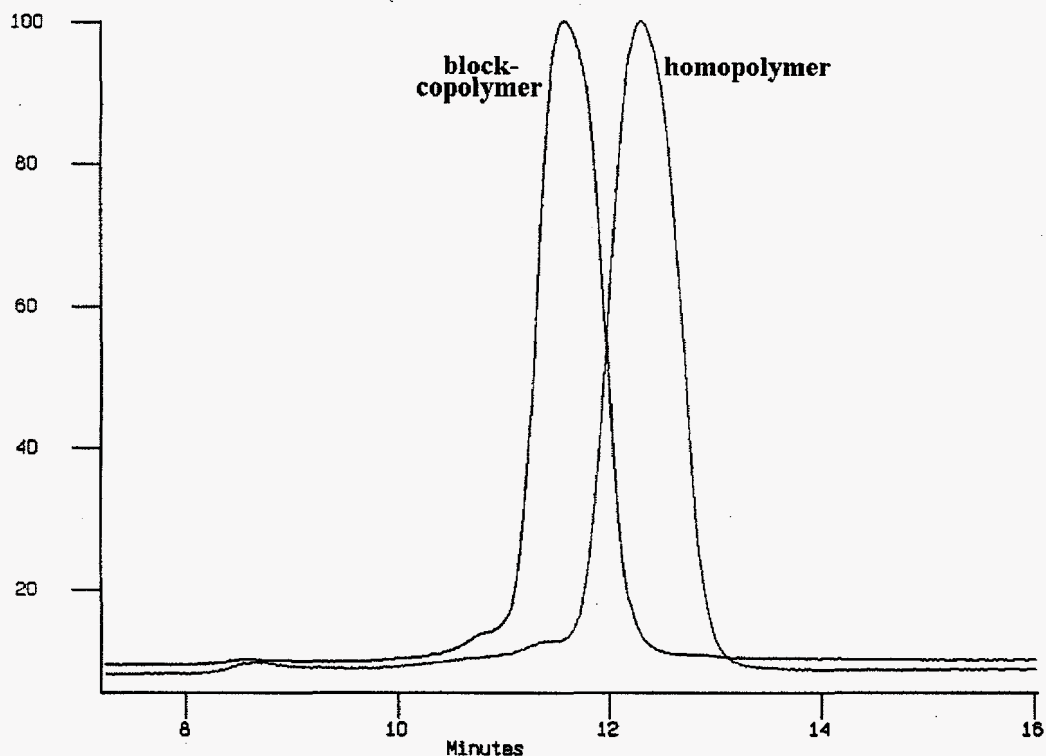
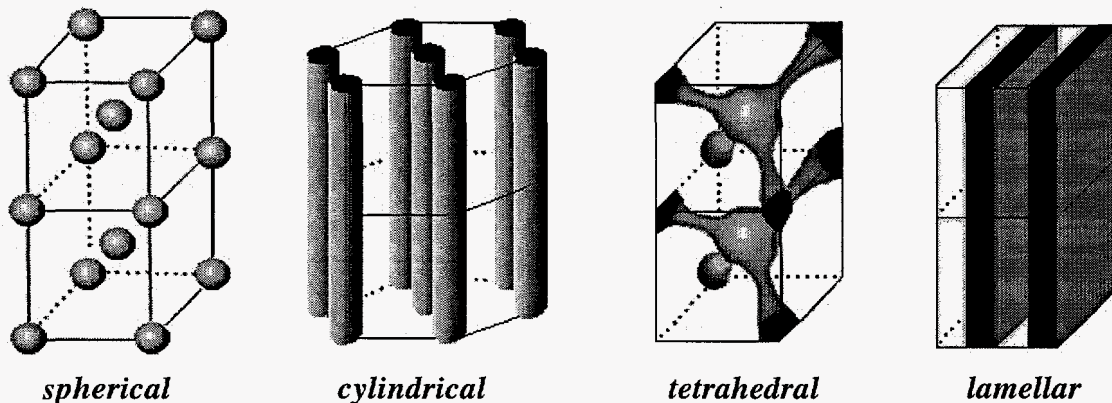


Figure II.11 GPC trace of the benzotriazole homopolymer and the benzotriazole/norbornene block copolymer.

This experiment demonstrates that the bzt homopolymer has a very narrow molecular weight distribution (1.02), and the block copolymer elutes at a higher molecular weight than the homopolymer, with no remaining homopolymer in it. These results indicate that the polymerization of the bzt monomer is a living polymerization. We extrapolate these findings, along with the fact that practically all previous monomers reported in literature were polymerized by this initiator in a living fashion, to our belief that the remaining amine functionalized norbornenes are polymerized in a living fashion, and thus can be used to make block copolymers.

Small-Angle X-Ray Scattering (SAXS) can also be used to characterize block copolymers. Due to thermodynamic incompatibilities of the two blocks in a block copolymer, they tend to phase separate in bulk into well ordered structures on a nano-scale, as shown below:



These phase separated structures cause scattering of X-rays into well defined diffraction patterns. Thus a peak in intensity in a SAXS pattern indicates the presence of ordered structures, and is conclusive proof that the polymer system is a true block copolymer. If the two polymers do not form a well-defined block copolymer, they will not phase separate on this scale and will not show a scattering peak. Figure II.12 shows a representative SAXS pattern for these types of block copolymers. Clear scattering peaks are observed, indicating that this polymer system forms a true block copolymer.

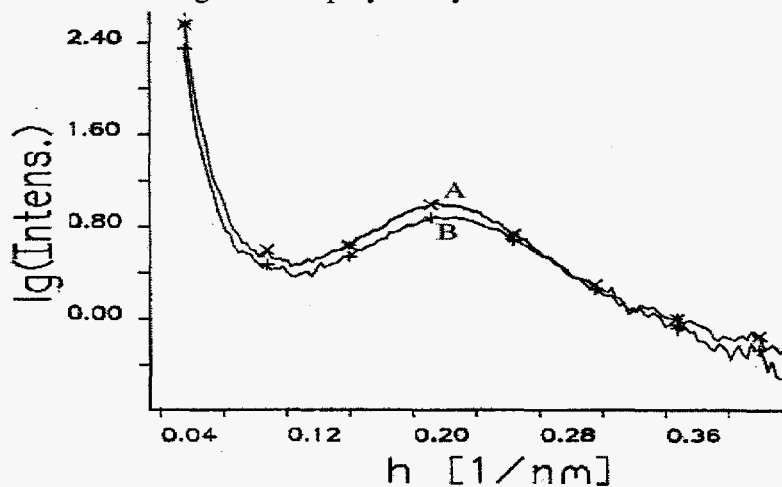


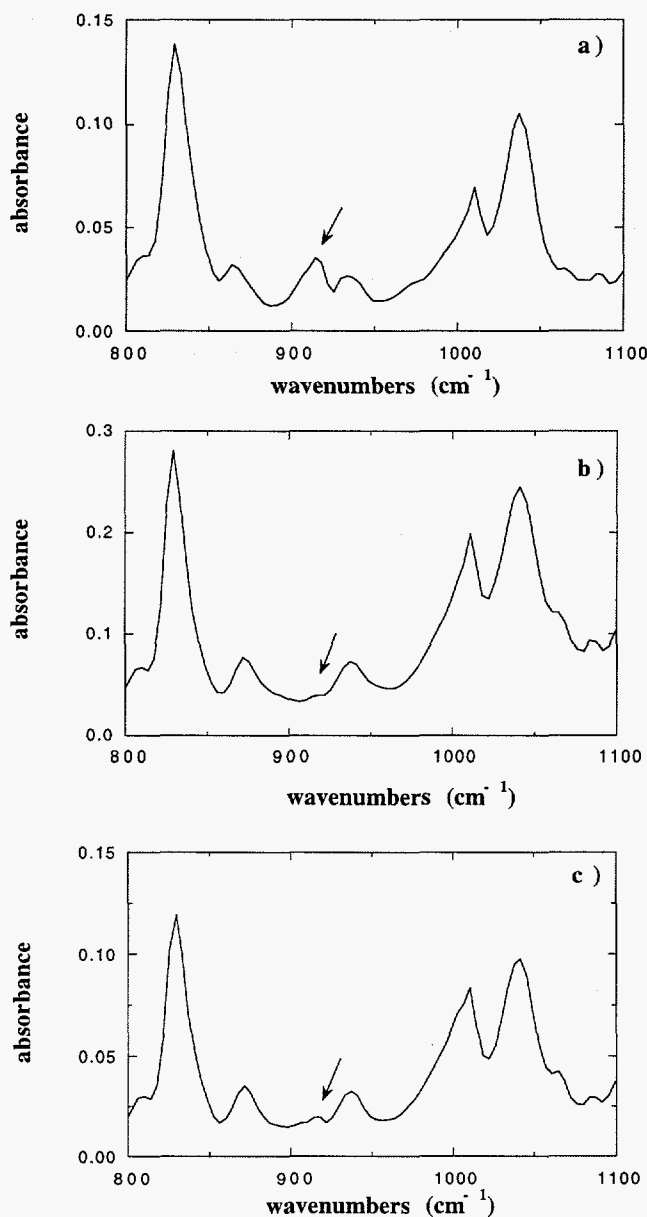
Figure II.12. SAXS patterns for two typical adhesive block copolymers

### Summary and Conclusion

We have been able to synthesize several different types of amine functionalized norbornene monomers, and have significantly improved on yield and ease of synthesis of these monomers. We were able to determine polymerization kinetics of all of these monomers, and have concluded that both basicity and steric hindrance at the amine has an effect on the rate of polymerization - the higher the basicity of the amine, the slower the polymerization, except where steric hindrance is significant. We have also demonstrated through GPC, NMR, and SAXS, that these polymerizations are living in nature, and thus we can make secondary and tertiary amine functionalized block copolymers. This is significant in that no other living polymerization technique can tolerate secondary amine functionalities on monomers and thus cannot be used to synthesize the kind of block copolymers that have been prepared in this project.

### III. Characterization of reactivity of amine functionalized block with epoxy

We have examined the reactivity of the secondary amine functionalized monomer toward FR4 epoxy with FTIR. A peak at  $920\text{ cm}^{-1}$  is characteristic of the epoxide ring vibration and is used to detect the extent of the crosslinking reaction. In Figure III.1a we



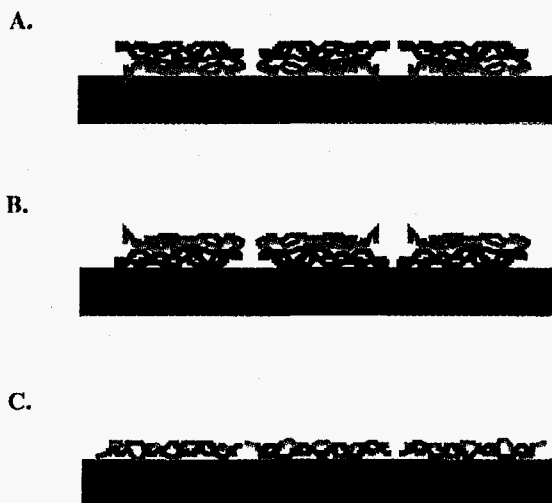
**Figure III.1** FTIR spectra for a) uncured FR4 epoxy, b) cured FR4 epoxy, and c) cured FR4 with dicyandiamide (DICY) replaced by the amine functionalized monomer.

show the spectra for the uncured FR4 epoxy resin. For this sample, all components of the FR4 resin were present (Shell EPON 1124-A-80, dicyandiamide (DICY), 2-methyl imidazole) but the sample was not yet heated. We observe a strong peak at  $920\text{ cm}^{-1}$ ,

which indicates that very little reaction of the epoxide groups with DICY has occurred. In Figure III.1b, we show the spectra for the fully cured FR4 epoxy resin. The sample is identical to that in Fig. III.1a except that the sample has been heated to 177 °C for 2 hours. The peak at 920  $\text{cm}^{-1}$  is now absent, which indicates that nearly all the epoxide groups have reacted. In Figure III.1c we show the spectra for a sample identical to that in Figure III.1b, except that DICY has been replaced by the amine functionalized monomer. We observe in Figure III.1c that the epoxide peak at 920  $\text{cm}^{-1}$  has almost completely disappeared, indicating that the amine functionalized monomer is indeed highly reactive toward the epoxy resin.

#### IV. Characterization of adsorbed conformation

The ability of a block copolymer to chemically couple two materials must surely depend upon the conformation that it adopts at the interface. Since many applications will involve first adsorbing the copolymer from solution onto a substrate and then contacting the copolymer-coated substrate with the resin, the adsorbed conformation is expected to be critical. Because both blocks of the block copolymers are functionalized, each can have specific attractive interactions with the substrate. Such interactions would tend to cause both blocks to adsorb to the surface. However, it is well known that the interaction between different monomers is usually unfavorable, even for monomers which differ only slightly in chemical structure. These monomer-monomer interactions will tend to cause the two blocks to segregate in space [8]. The conformation that results is not obvious, and will depend upon the relative strengths of the two types of interactions. The three possible conformations of the copolymer are illustrated in Figure IV.1. Only one of these, conformation A, can be expected to lead to optimal coupling. In this conformation,



**Figure IV.1** Red = substrate-bonding block (imidazole), green = resin-bonding block (amine)

the blocks form separate layers with the resin-bonding block exposed at the air surface. To investigate the adsorbed conformation of the block copolymers, we have used neutron reflectivity and time-of-flight secondary ion mass spectroscopy (TOF-SIMS) along with selective deuteration of individual blocks of the copolymer.

#### **Sample preparation**

For characterization purposes, the copolymers were adsorbed from solution onto silicon wafers that had previously been coated with thin 150-400 Å copper films. The copper films were deposited by sputtering at Sandia (J. Ruffner and coworkers, Dept. 1831). Typically, the copper-coated wafers were submerged in the adsorbing solution, either pure methanol or a methanol/water mixture, then removed and rinsed exhaustively with methanol to remove any nonbonded material. In the following we will refer to each copolymer sample using the code XX-YY, which corresponds to the molecular weight of the imidazole (XX) and amine (YY) blocks, respectively. The letter "d" is included to indicate which block was deuterated.

## Procedures

### *Neutron Reflection*

In this technique, a collimated beam of neutrons is impinged onto the samples at grazing incidence ( $\sim 0.5$  deg). The intensity of neutrons reflected at the specular angle is determined as a function of the momentum transfer vector  $k$  (or  $q = 2k$ ), which is varied by either changing the wavelength of the neutrons or by changing the angle. Such a curve is very sensitive to the neutron refractive index profile normal to the surface. For most cases the adsorption of neutrons is low, and the neutron refractive index is simply a function of the neutron scattering length density (SLD). The neutron scattering length density is a function of the density and atomic composition of the material. In particular, there is an enormous difference in the scattering power of H and D atoms, and therefore selective deuteration is commonly used with organic materials to optimize sensitivity to desired structural details. The spacial resolution normal to the surface is roughly 5 Å. Detailed profiles can be obtained for films up to several thousand angstroms. Neutron reflection was performed on the SPEAR reflectometer at the Los Alamos Neutron Science Center (LANSCE), Los Alamos NM, and on the POSYII reflectometer at the Intense Pulsed Neutron Source (IPNS) at Argonne National Labs., Argonne, Ill. Both reflectometers operate in the time of flight mode. Details regarding the technique of neutron reflectivity can be found elsewhere. [9]

### *Time of Flight Secondary Ion Mass Spectrometry (TOF-SIMS)*

In this technique, the sample is bombarded with successive pulses of heavy ions, gallium ions in the present case, and the charged ions dislodged from the sample are accelerated to a detector. Extremely high mass resolution allows identification of the individual species sputtered off by each pulse. The intensity of each species is determined as a function of sputtering time, and thus, increasing depth into the sample. TOF-SIMS was performed at Sandia (Gerald Nelson, Dept. 1823).

## Results - neutron reflectivity

### **a) Imidazole block deuterated, different amine block lengths**

The first reflectivity experiments were performed using copolymers with the imidazole block partially deuterated, and the amine block protonated. The length of the amine block was varied from 15 (kg/mol) to 40 while the imidazole block was held constant at  $\sim 10$ . Assuming melt density, the SLD of the imidazole block is calculated to be  $2.7 \times 10^{-6} \text{ \AA}^{-2}$  and that of the protonated amine functionalized block is  $0.4 \times 10^{-6} \text{ \AA}^{-2}$ . The copper coated wafers were soaked for 2 hr in a 0.002 g/ml solution in pure MeOH, which is a good solvent for both blocks of the copolymer. For the first sample, the 10d-15 copolymer was adsorbed onto a  $\sim 250$  Å copper film. The reflectivity data are shown in Figure IV.2a and the SLD profiles

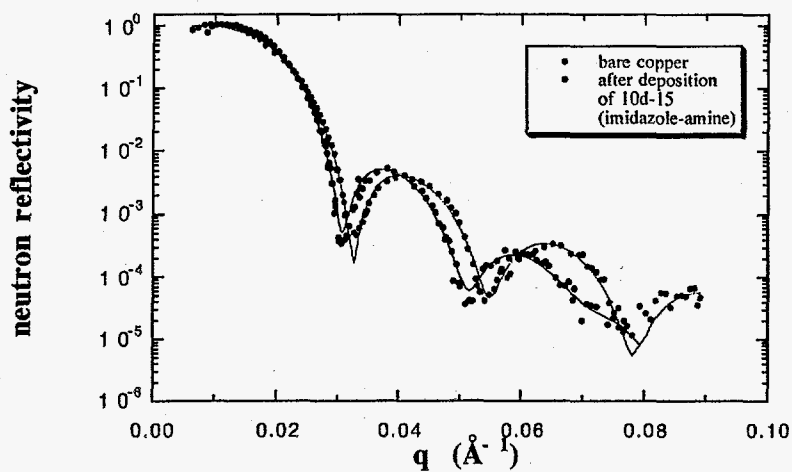


Figure IV.2a

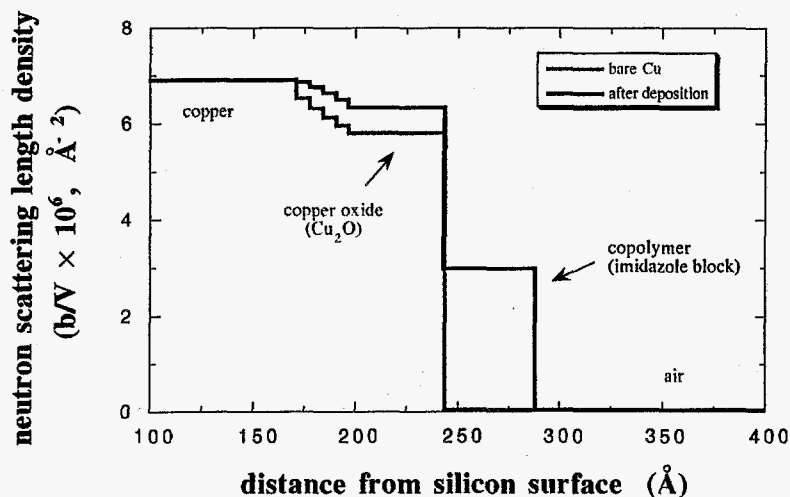


Figure IV.2b

obtained from these data are shown in Figure IV.2b. The main effect of the adsorbed copolymer on the reflectivity is to shift the fringes to lower  $q$ . This can be modeled using a single layer on the copper film with a SLD of  $3.0 \times 10^{-6} \text{ \AA}^{-2}$  and a thickness of 44 Å. This SLD is close to that expected for the pure imidazole block ( $2.7 \times 10^{-6} \text{ \AA}^{-2}$ ). The thickness is consistent with that of a polymeric monolayer. A second experiment was performed using

the 10d-40 copolymer. The data for this experiment are shown in Figure IV.3, along with

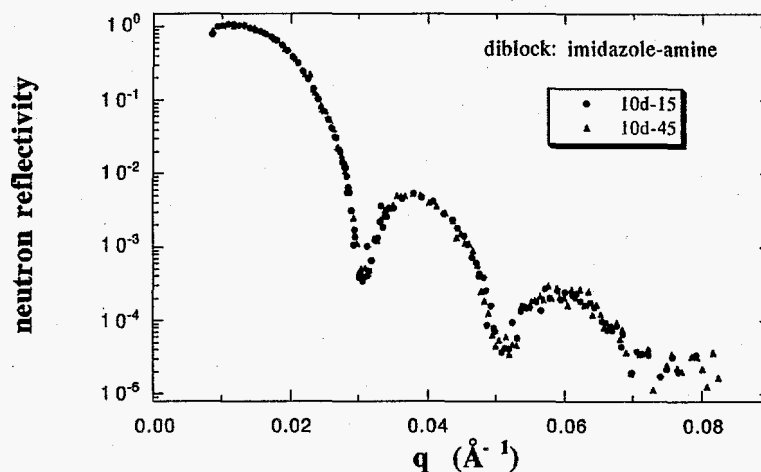


Figure IV.3

the data for the 10-15 sample. The fact that the data for the two copolymers are nearly identical is important. If the two blocks formed a mixed layer as in Figure IV.1c, the thickness of the layer would vary with the total molecular weight of the copolymer, and a variation in the reflectivity would result.

The data in Figures IV.2 and IV.3 are consistent with two possible scenarios. First, the data are consistent with the conformation in Figure IV.1a. Since the SLD of the amine block in the fully protonated form is close to zero ( $0.4 \times 10^{-6} \text{ \AA}^{-2}$ ), a pure layer of this block would be nearly invisible to neutrons. Therefore, no effect on the reflectivity curve would result from increasing the length of this block. The second scenario is based on the small but finite polydispersity within the block copolymer samples. It is possible that only those copolymers that have a very short amine block adsorb onto the surface in each experiment. Even though the weight average molecular weights of these two copolymer samples are quite different, it is possible that the copolymers actually adsorbed onto the surfaces may be very similar, and in fact, may have little or no amine functionalized block. This second interpretation is indeed the one we believe to be correct. This conclusion is based upon the data from experiments involving copolymers with deuterated amine blocks, which are described in the next section.

#### b) Varying solvent composition: MeOH versus MeOH+H<sub>2</sub>O

The next series of experiments utilized copolymers with fully deuterated amine blocks ( $\text{SLD}=5.3 \times 10^{-6} \text{ \AA}^{-2}$ ) and protonated imidazole blocks ( $\text{SLD}=1.4 \times 10^{-6} \text{ \AA}^{-2}$ ), as well as copolymers with protonated amine blocks ( $\text{SLD}=0.4 \times 10^{-6} \text{ \AA}^{-2}$ ) and deuterated imidazole blocks ( $\text{SLD}=2.7 \times 10^{-6} \text{ \AA}^{-2}$ ) as in the previous experiments. The first experiment of this series involved the 15d-15 copolymer adsorbed from a 0.002 weight fraction solution in pure methanol. The copper-coated silicon wafers were exposed to the solution for 2 hours, and then rinsed with methanol. The reflectivity results are shown in Figure IV.4a, and the SLD profile is shown in Figure IV.4b. This experiment is thus similar to that in Figure IV.2, although the copolymer sample came from a different synthesis batch and thus may have slightly different characteristics. Again we find that the reflectivity can be described by



a single layer (SLD =  $2.3 \times 10^{-6} \text{ \AA}^{-2}$ , thickness =  $24 \text{ \AA}$ ). The SLD of the layer is again close to that expected for a pure imidazole layer.

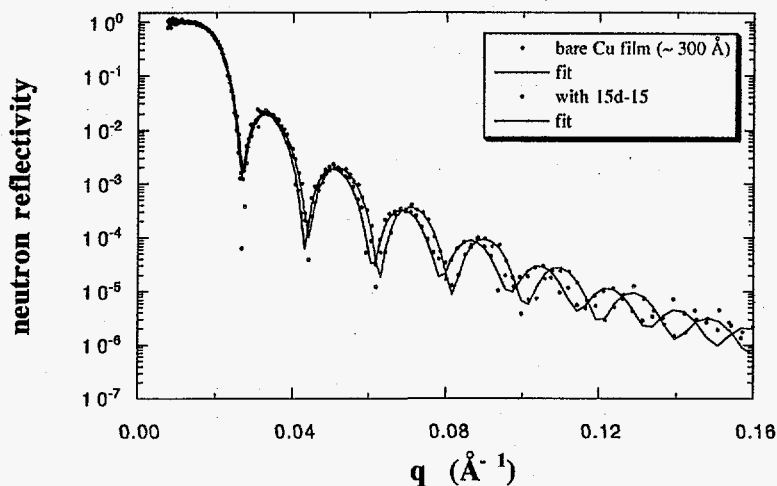


Figure IV.4a

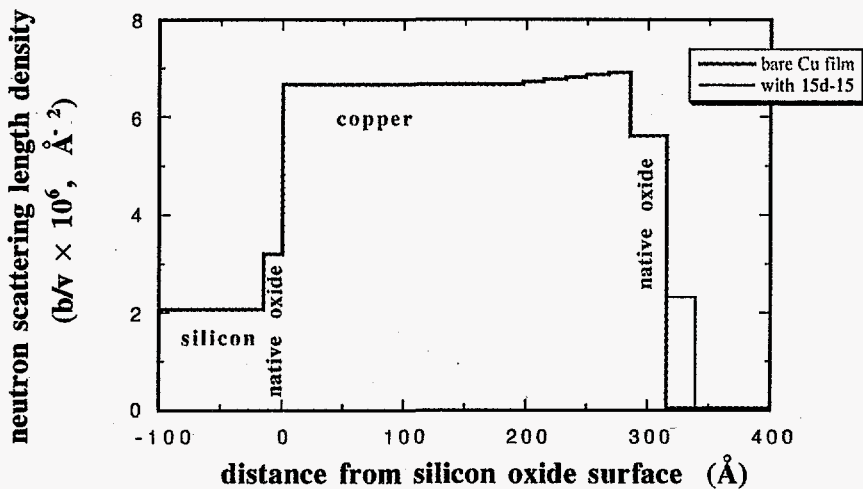


Figure IV.4b

The next experiment involved the 15-15d copolymer, adsorbed under the same conditions. The reflectivity data and SLD profiles are shown in Figure IV.5a and IV.5b. Surprisingly, almost no variation in reflectivity is observed upon adsorption of this copolymer sample under these conditions. The presence of the highly deuterated amine block, even if it were mixed with the imidazole block, would lead to a significant variation in the reflectivity. Thus, these data seem to suggest that there is very little, if any,

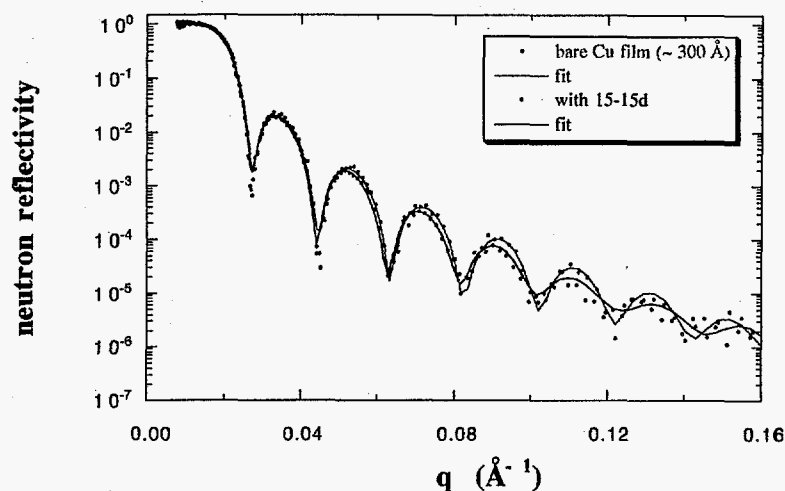


Figure IV.5a

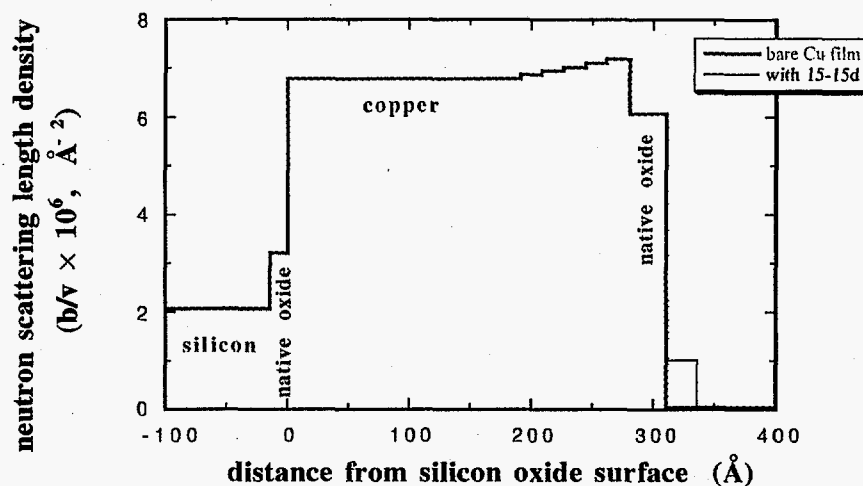


Figure IV.5b

deuterated amine block on the copper surface. The data can be fit with a single layer model, with thickness of 16 Å and SLD of  $1.0 \times 10^{-6} \text{ \AA}^{-2}$ . The latter is reasonably consistent with that expected for the pure imidazole block ( $1.4 \times 10^{-6} \text{ \AA}^{-2}$ ).

The same experiments were then repeated using a mixture of methanol and water (80/20 by weight). The addition of water decreases the solvent quality and increases the thermodynamic driving force for adsorption. Data for 15d-15 are shown in Figure IV.6a and the SLD profile is shown in Figure IV.6b. The data can again be fit with a single layer model, with thickness of 37 Å and SLD of  $1.8 \times 10^{-6} \text{ \AA}^{-2}$ . In this case, the SLD is significantly lower than that expected for the pure imidazole block ( $2.7 \times 10^{-6}$ ). Also, the

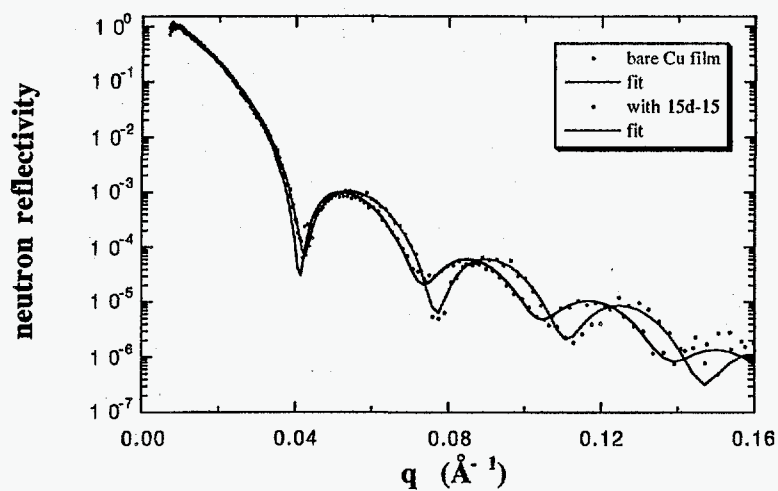


Figure IV.6a

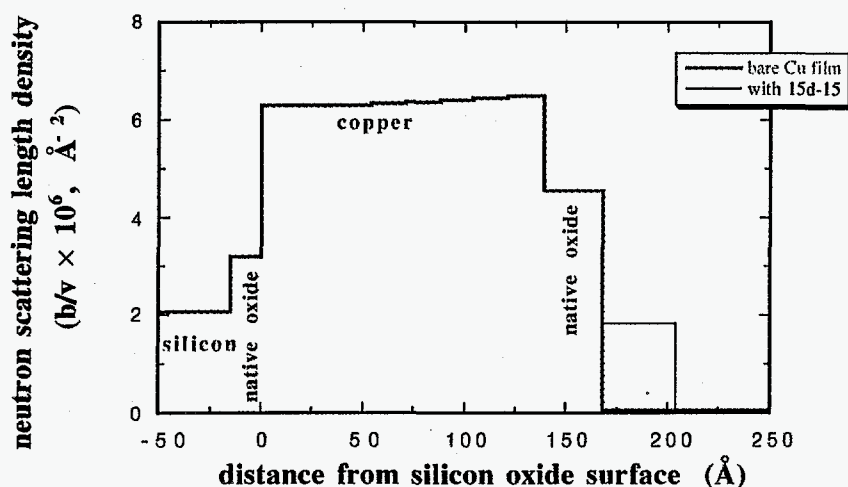


Figure IV.6b

thickness is about twice that obtained using pure MeOH (Figure IV.4b). Thus the layer is thicker but with lower SLD when the mixed solvent is used than when pure MeOH is used. This could indicate that the amine block leads to a decreased coverage and prohibits the imidazole block from lying flat on the surface, or could possibly indicate some mixing of the amine block with the imidazole block.

The reflectivity and SLD profiles for a sample with the 15-15d copolymer from the 80/20 methanol/water mixture are shown in Figure IV.7a and Figure IV.7b, respectively.

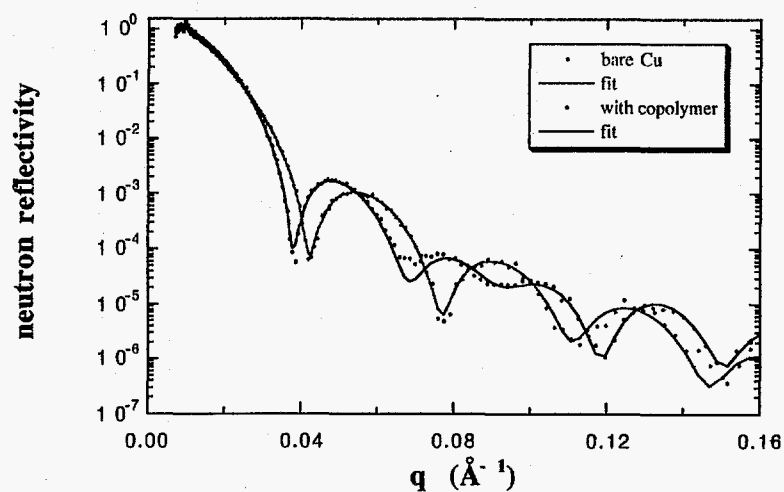


Figure IV.7a

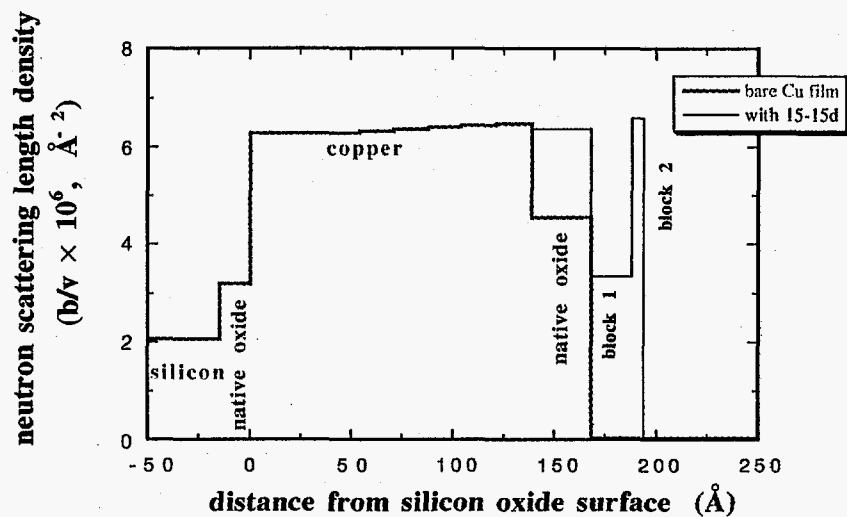


Figure IV.7b

In this case, the form of the reflectivity curve is dramatically different than those obtained in the previous experiments. The fringe pattern is entirely changed, rather than just simply shifting to lower  $q$  as observed previously. In this case a two layer model is required to describe the reflectivity data. The layer adjacent to the copper surface has  $SLD=3.33 \times 10^{-6}$  and a thickness of 19 Å, while that at the air surface has  $SLD=6.56 \times 10^{-6}$  with a thickness of 6 Å. Some mixing of the amine block or copper oxide into the imidazole layer may explain the high SLD value of the layer adjacent to the copper surface relative to that calculated for a pure layer of the imidazole block. Most importantly, note the dramatic difference with Figure IV.5 (pure MeOH). It is clear that with the methanol and water mixture, the deuterated amine block is present in the adsorbed layer at the air surface, and that it is absent when pure MeOH is used. Thus, this series of experiments shows that

when pure methanol is used there is very little, if any, amine block present and a relatively high coverage of the imidazole block. On the other hand, when the 80/20 MeOH/H<sub>2</sub>O mixture is used, the amine block is clearly present along with a somewhat reduced coverage of the imidazole block. Thus, we find that different portions of the molecular weight distribution adsorb onto the surface when different solvent compositions are used.

**c). Different amine block lengths, each block deuterated in separate experiments**

In the next series of experiments, the amine block lengths were varied from 15 to 40 (kg/mol). Copolymers with only the imidazole block deuterated as well as copolymers with

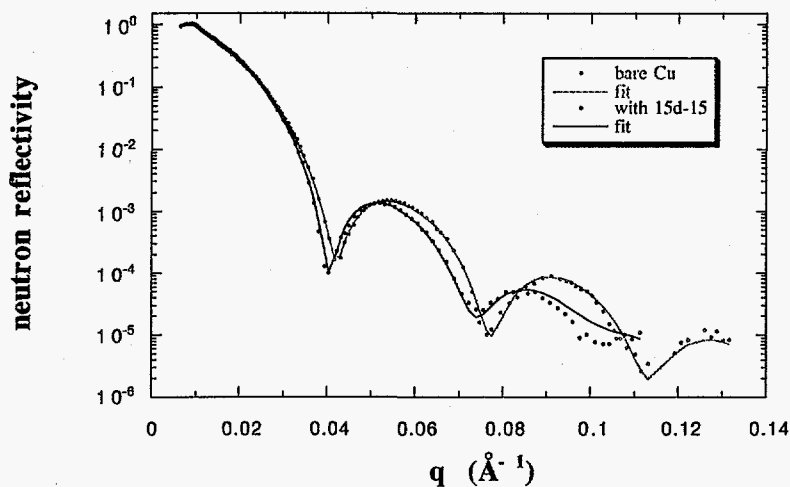


Figure IV.8a

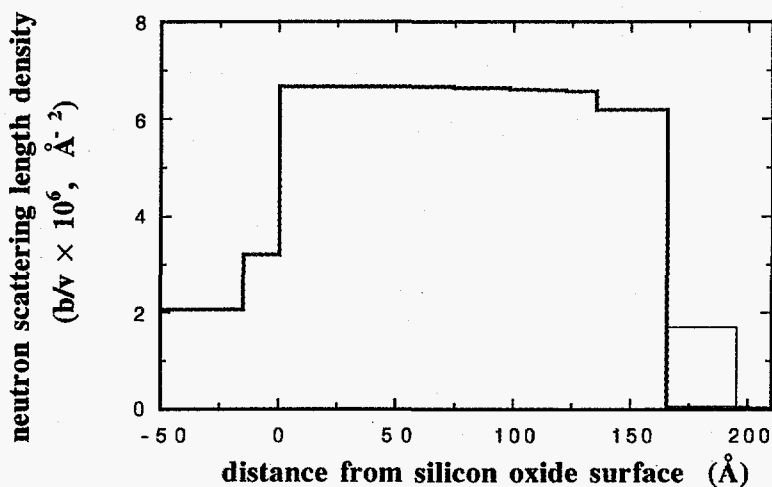


Figure IV.8b

only the amine block deuterated were again employed. In addition, the exposure time of the samples to the block copolymer solution was reduced to 5 minutes. Reflectivity data and SLD profiles for the 15d-15 copolymer adsorbed from the 80/20 MeOH/water solution are shown in Figure IV.8a and Figure IV.8b. Again the familiar result is obtained with this copolymer in which the fringe pattern is simply shifted to lower  $q$ . Fitting the data with a single layer yields a SLD of  $1.72 \times 10^{-6}$  and a thickness of 30 Å, in fairly good agreement with the results obtained for the longer soaking time (Figure IV.6).

In the subsequent experiment, the 15-15d copolymer was used. Reflectivity data and SLD profiles are shown in Figures IV.9a and IV.9b. As observed previously for

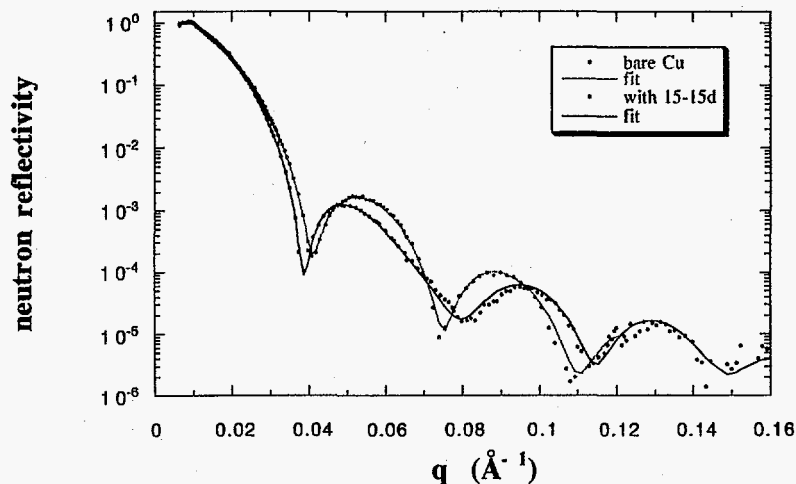


Figure IV.9a

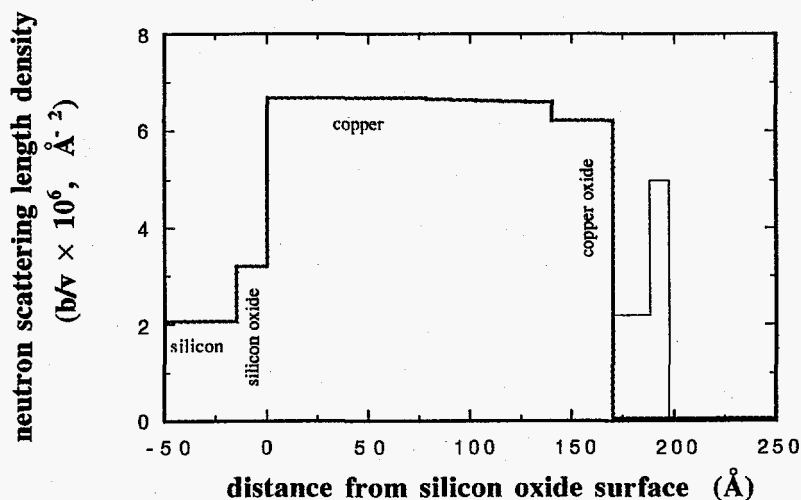


Figure IV.9b

the longer soak time (Figure IV.7), the fringe pattern is altered with adsorption of the copolymer. The data correspond to a bilayer profile with a layer of high SLD at the air surface. The thicknesses and SLD values are  $2.2 \times 10^{-6}$  and 18 Å for the first layer, and

$5.0 \times 10^{-6}$  and  $9 \text{ \AA}$  for the layer at the air surface, qualitatively consistent with Figure IV.7b.

The experiment was then repeated using the 15d-40 and 15-40d copolymers. The

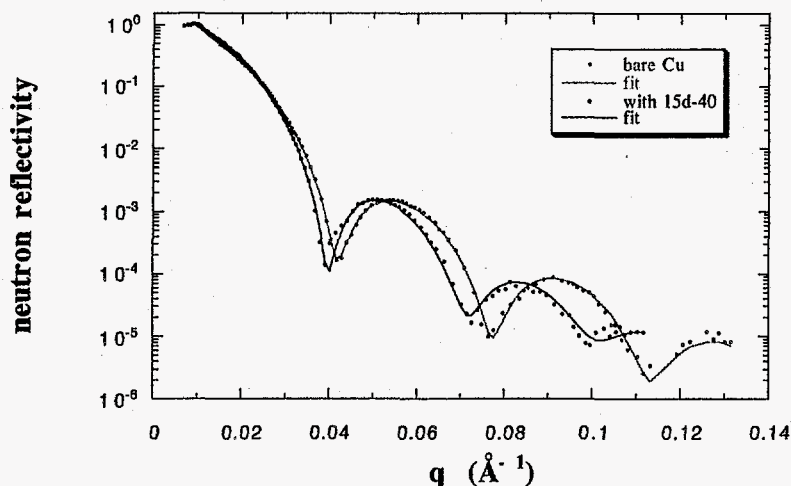


Figure IV.10a

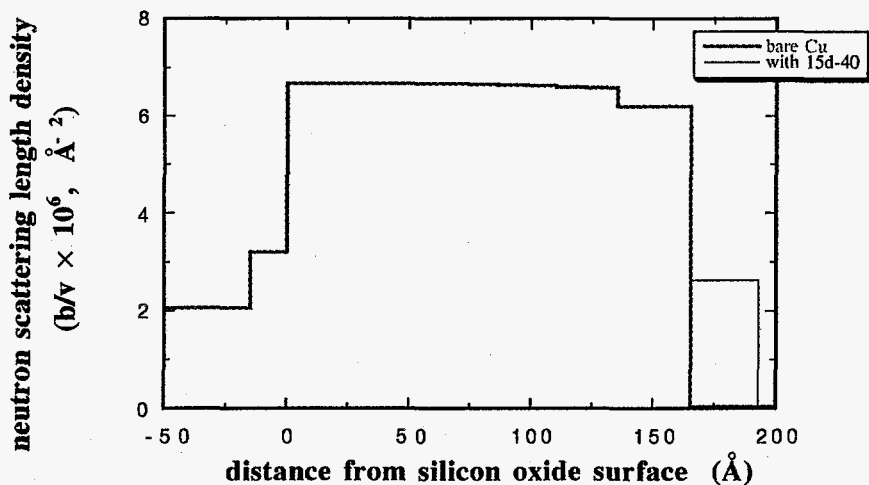


Figure IV.10b

reflectivity and SLD profiles for the 15d-40 copolymer are shown in Figures IV.10a and IV.10b, and those for the 15-40d copolymer are shown in Figures IV.11a and IV.11b. For the 15d-40 copolymer, we observe again the same fringe pattern shifted to lower  $q$ . These data are consistent with a single layer with SLD of  $2.64 \times 10^{-6}$  and thickness of  $28 \text{ \AA}$ , similar to the data in Figure IV.8b, although the SLD is slightly higher with 15-40d.

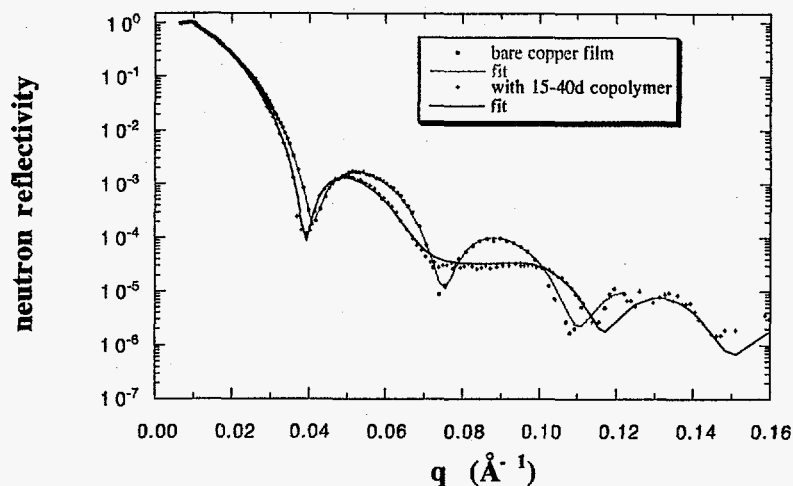


Figure IV.11a

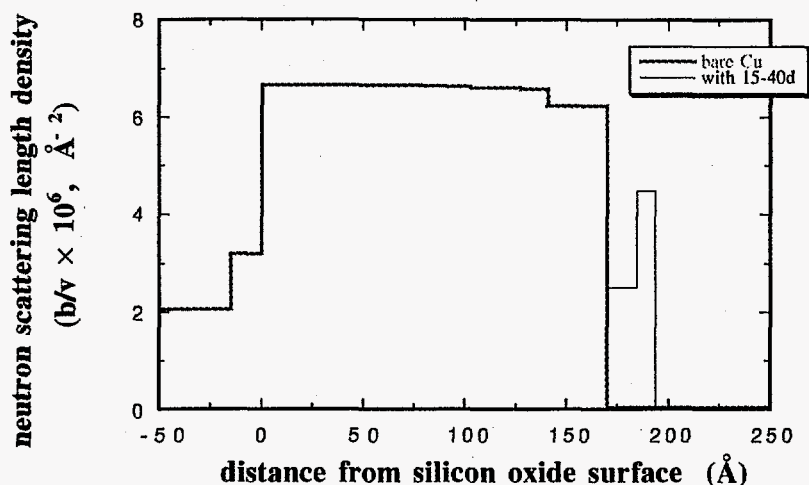


Figure IV.11b

As for the 15-15d copolymer, the fringe pattern is also dramatically altered with the 15-40d copolymer. The results are consistent with a bilayer model, with SLD of  $2.5 \times 10^{-6}$  and thickness of 15 Å for the first layer, and SLD of  $4.5 \times 10^{-6}$  and thickness of 10 Å for the layer at the air surface. The monolayer is thus very similar in structure to that obtained with the 15-15d copolymer.

From this series of experiments we confirm that the bilayer structure is consistently obtained when the 80/20 methanol water solution is used, even for only 5 minutes exposure time. By using selective deuteration, we have confirmed that this structure is consistent with that of Figure IV.1a, with the imidazole block on the copper surface and the amine block exposed at the air surface. The size of the amine block appears to be significantly smaller than that of the imidazole block. Alternatively, there may be some mixing of the amine block into the imidazole block layer. Finally, we observe that the



structure of the adsorbed layer is similar for the 15-15 and 15-40 copolymers. The thickness of the amine block layer does not appear to vary strongly with the average molecular weight of the amine block in the sample. This is further evidence that only a fraction of the total copolymer molecular weight distribution, and not necessarily the weight average, is selected for adsorption.

#### d). Concentration dependence, amine block deuterated

The next series of experiments was designed to investigate the variation of the adsorbed monolayer structure with the concentration of copolymer in solution. In each case, the 15-15d copolymer was used in 80/20 methanol/water mixtures. The exposure time was fixed at 5 minutes. Reflectivity data and SLD profiles for samples exposed to solutions of 0.0002, and 0.062 weight fraction copolymer are shown in Figures IV.12 and IV.13. Data for a sample exposed to a solution of 0.002 weight fraction copolymer were shown previously in Figure IV.9. We find a very strong dependence of the adsorbed monolayer structure on concentration. Indeed, almost no adsorption occurs for 0.0002 wt fraction in a 80/20 methanol/water mixture. Data obtained at a weight fraction of 0.002 indicated a bilayer profile in which the thickness of the amine block was significantly less than that of the imidazole block. At a relatively high weight fraction of 0.062, not only is the adsorbed amount increased, but the size of the amine block layer is much greater than that of the imidazole block layer.

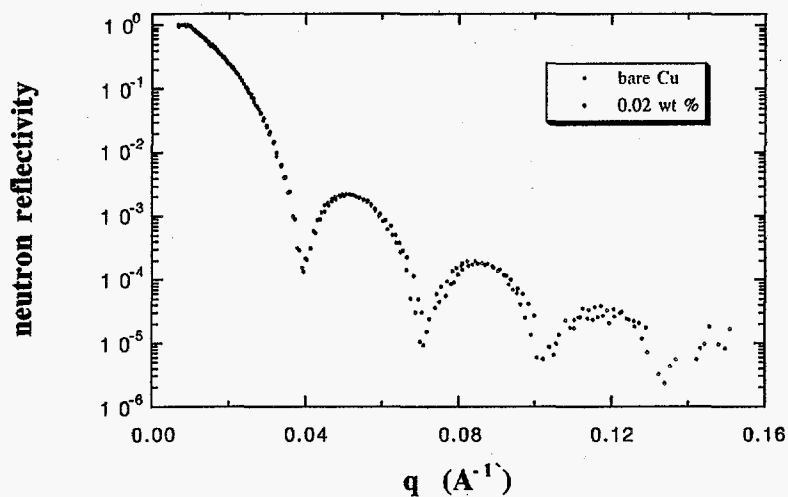


Figure IV.12

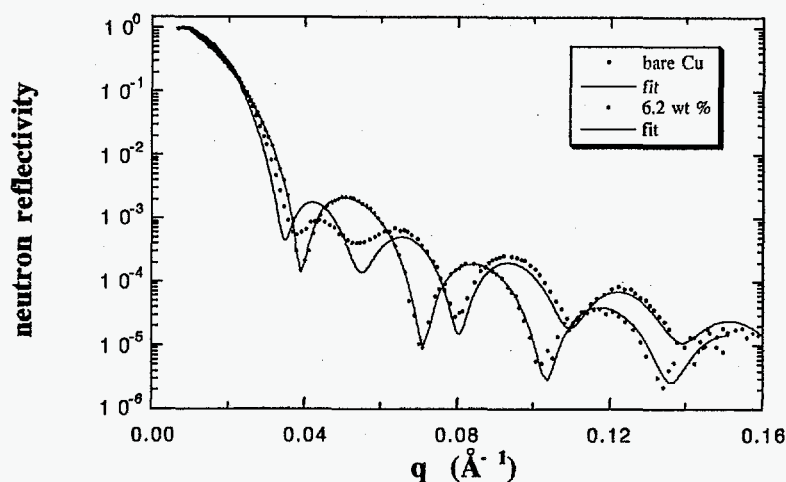


Figure IV.13a

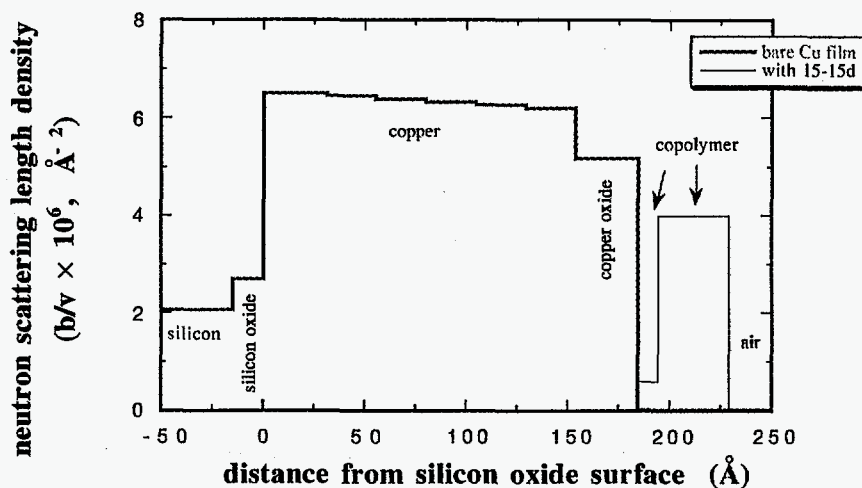


Figure IV.13b

e) **Allowing the copolymer solution to dry on the face of the wafer**

The final experiment was designed to see if dense adsorbed layers, with high amine block content, such as in Figure IV.13b, could be obtained without using highly concentrated solutions. Such high concentrations will no doubt be impractical for economic reasons in many cases. The method which we investigated was to expose the sample to a dilute solution, remove the sample from the adsorbing solution, and then allow the solution to dry on the face of the wafer before rinsing with methanol. As the solution on the face of the wafer dries, it becomes concentrated. The hope is that in this way, only very low concentrations would be required to produce a dense adsorbed layer with high

amine block content. For this experiment we used the 15-15d copolymer at a weight fraction of 0.0002 in the 80/20 methanol/water solution. The reflectivity data and SLD profile from this experiment are shown in Figure IV.14a and IV.14b. In Figure IV.14a, the reflectivity at high  $q$  values is elevated above that of the bare copper film. This is indicative of a relatively thick deuterated amine block (cf. Figure IV.13a). Indeed, with this method the copolymer monolayer appears to be similar in structure to that obtained using a concentrated solution (Figure IV.13b).

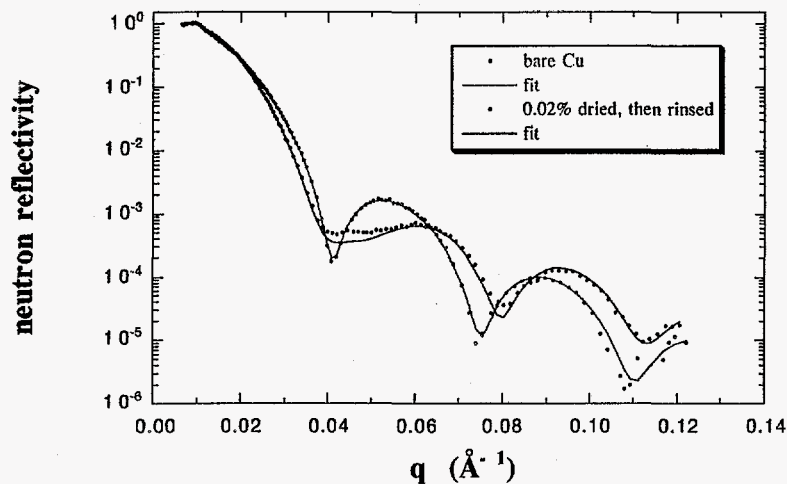


Figure IV.14a

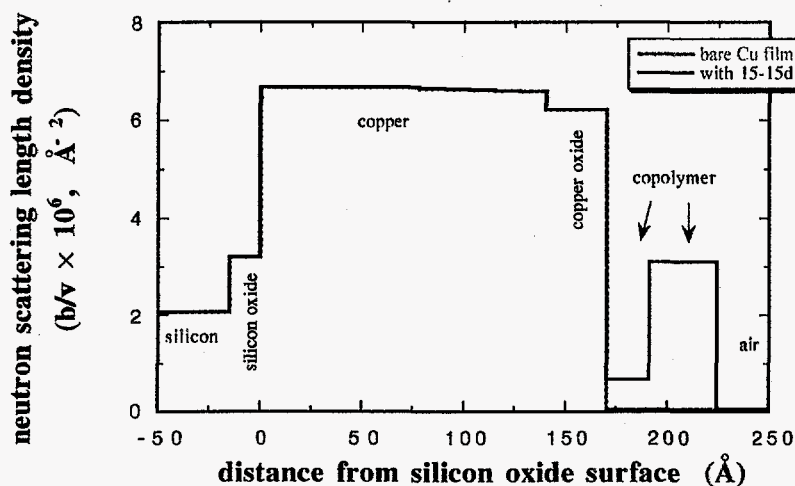


Figure IV.14b

## Results - TOF-SIMS

To confirm the reflectivity results, we have also performed TOF-SIMS on selected samples. In the first series of TOF-SIMS experiments, the concentration was fixed at 0.002 g/ml. Samples were prepared using solutions of the 15-15d copolymer in pure methanol and also in the 80/20 methanol/water mixture. Soak time was varied between 1 minute and 2 hours. TOF-SIMS data for the samples soaked for 5 minutes are shown in

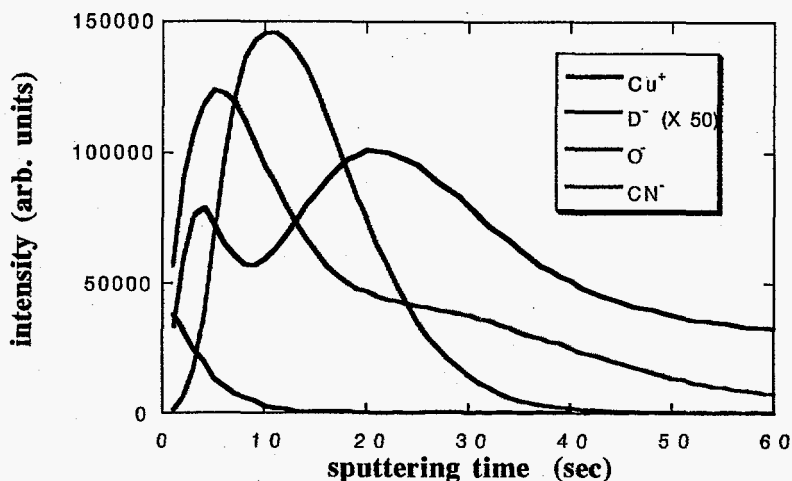


Figure IV.15a

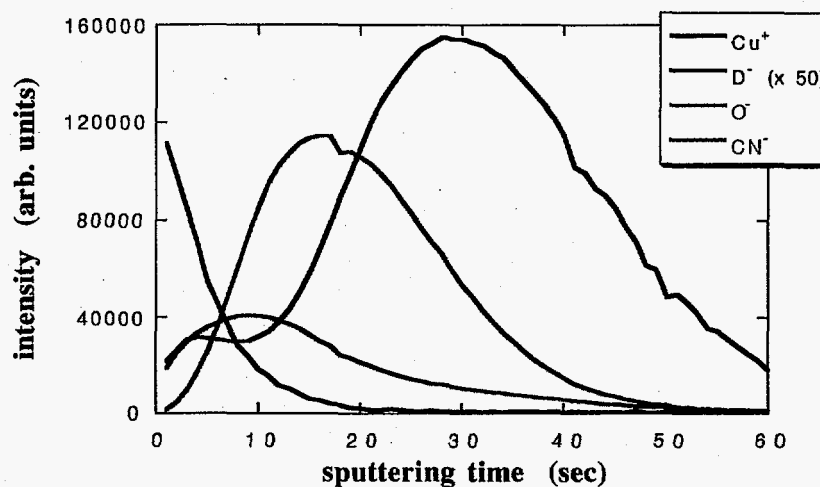


Figure IV.15b

Figure IV.15a (methanol only) and Figure IV.15b (80/20 methanol/water solution). These data confirm the reflectivity results in Figures IV.5 and IV.7. First, we find that the intensity of all deuterated species (only  $\text{D}^-$  shown) peak in the limit of zero sputtering time. This indicates that the deuterated amine block is indeed at the air surface. Second, the ratio of  $\text{D}^-$  ions to  $\text{CN}^-$  ions is indicative of the relative mass of the two blocks. We find that this

ratio is much lower when the pure methanol solution was used than when the methanol/water solution was used. The ratio of the intensity of  $D^-$  normalized to that of  $Cu^+$  is shown in Figure IV.17 as a function of soak time for samples exposed to the methanol/water and pure methanol solutions. It is clear from this plot that for a 5 minute exposure, the amount of deuterated species in the adsorbed layer is far lower for the pure methanol case than for the methanol/water case. Interestingly, a much smaller difference in the amount of deuterated material results when the samples are only exposed for 1 minute. However, for the 1 minute soak in the methanol/water solution the level of deuterium is far lower than that obtained for the 5 minute soak. Further work is required to understand the fundamental basis for these trends.

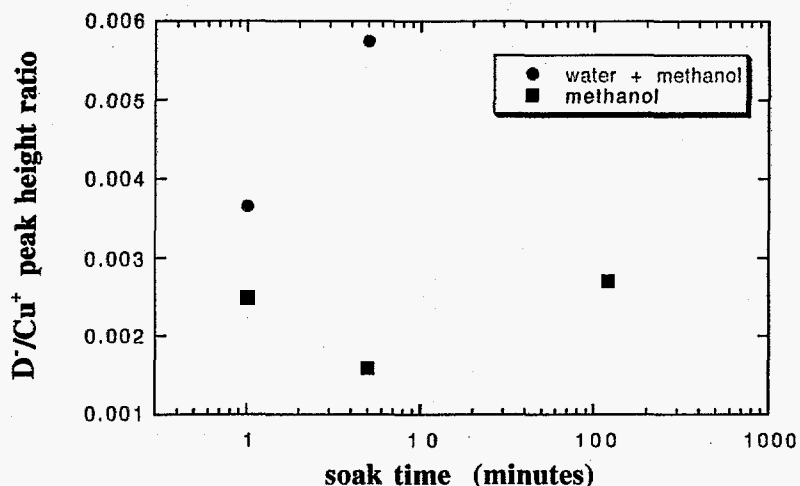


Figure IV.16

TOF-SIMS data were also obtained from a sample exposed to a 0.0002 wt fraction solution which was allowed to dry on the wafer before rinsing. This sample is analogous to that used in the reflectivity experiment in Figure IV.14. The TOF-SIMS data are shown in Figure IV.17. In this case, we find a high ratio of  $D^-$  to  $Cu^+$ , much higher than that observed in Figure IV.15.b. This indicates that even though a low concentration was used, the method of allowing the solution to dry on the face of the wafer yields layers with a large amine block layer. This confirms the conclusion from the reflectivity data in Figure IV.14.

One final note from the TOF-SIMS data regards the observation of oxygen between the  $CN^-$  layer and the  $D^-$  layer in Figures IV.15a and IV.15b. This seems to imply that copper oxide has migrated into the copolymer layers, or else that the imidazole block of the copolymer has penetrated into the oxide of the copper. Another alternative is that either methanol or  $H_2O$  has not been completely removed. Further work is required to discriminate between these possibilities. We note that in the final case, where the adsorption was done from a 0.0002 wt fraction solution which was allowed to dry on the wafer before rinsing, the oxygen peak was between the  $CN^-$  peak and that of copper, as expected for a structure like that in Figure IV.1a. More work needs to be done to firmly establish changes in the oxide layer with soaking conditions.

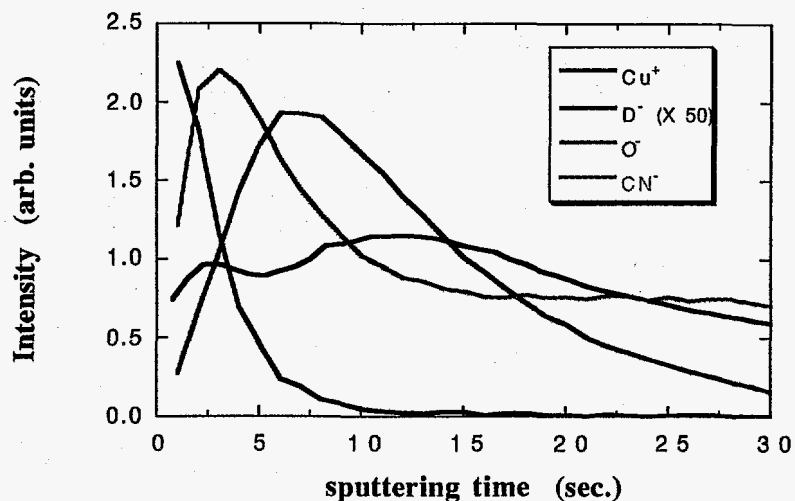


Figure IV.17

### Summary

It was found that under appropriate conditions, an adsorbed copolymer monolayer structure like that in Figure IV.1 is obtained. However, it was discovered that the structure of the copolymer monolayer is a very strong function of the solution conditions and adsorption protocol. When the copolymer is adsorbed from a methanol solution, the resulting adsorbed monolayer appears to have only a very small amine block relative to the imidazole block (Figure IV.18a). This should strongly affect its performance as a coupling agent since only the amine block can covalently bond to the epoxy. This result must be due to the polydispersity of the copolymer sample. Apparently, only polymers from one end of the molecular weight distribution are adsorbed. The kinetic or thermodynamic reasons for this have not been determined. By adding water, the solution becomes a poorer solvent for the copolymer and the driving force for adsorption is increased. However, adding water may also change the form of the copolymer in solution (formation of micelles is likely). When the copolymers are adsorbed from a 80/20 methanol/water mixture, the adsorbed monolayer structure is a bilayer, with sizable layers of each block. Somewhat surprisingly, no dramatic variation in the copolymer monolayer structure was observed when the molecular weight of the amine block was varied. This is likely due again to the polydispersity of the sample and selective adsorption of only a fraction of that distribution. There is a strong variation in the adsorbed monolayer structure with concentration. Under "normal" conditions in which the copolymer solution is immediately rinsed from the surface of the wafer upon removal from the bath, little or no adsorption is detected using a weight fraction of 0.0002. As the weight fraction is increased, the bilayer monolayer structure passes from one in which the size of the amine block is less than that of the imidazole block (0.002 wt fraction, Figure IV.18b), to one in which the size of the amine block is much greater than that of the imidazole block (0.062 wt fraction, Figure IV.18c). Finally, it was found that a monolayer with structure similar to that obtained using the concentrated solution could be obtained with a very dilute solution (0.0002 wt fraction) if the solution was allowed to dry on the wafer before rinsing with methanol. This could be very important for economic reasons, since the amount of copolymer required is reduced

by more than a factor of 100. Finally, we note that all the characterization work was performed on copper with the native oxide. In the following section, results from adhesion



**Figure IV.18** Illustration of relative block sizes for adsorbed copolymers using a) pure methanol, b) 80/20 by weight methanol/water solution, 0.002 wt fraction, c) 80/20 by weight methanol/water solution, 0.062 wt fraction. Red = imidazole block, Blue = amine block

testing are reported which demonstrate much more favorable results in the absence of the native oxide. Therefore, it is recommended that some of the characterization work be repeated for adsorption onto bare copper.

## V. Adhesion testing

Adhesion tests were performed in both lap shear and peel modes. In each case, two controls were typically used, in order that conclusions could be made without having to rely upon the consistency of absolute strength values from test to test. However, the absolute reproducibility was indeed reasonably good. The first control sample involved copper that was treated with only a microetch and deionized water rinse and then left in air to allow the native oxide to form. For the second control sample, an industry standard "brown oxide" treatment was applied. This is the method currently in use in the PWB industry, and the strength values from this treatment served as a benchmark for performance evaluation. Below, the data from each test are presented in separate sections, and in chronological order in each case. Since the characterization of the copolymer layer structure was being conducted concurrently with the adhesion testing, the conditions used for adsorption of the block copolymer (concentration of copolymer, solvent composition, soaking time) for the adhesion test samples varied from test to test, and indeed, were not optimized in any of the tests. Nevertheless, a number of important conclusions were obtained.

### **Lap Shear Tests**

Lap shear coupons were machined from copper blocks. The bonding surfaces of all samples were milled to a 0.8  $\mu\text{m}$  average roughness finish, microetched using Shipley's PREPOSIT ETCH 748 solution, and then rinsed exhaustively with deionized water. The FR4 (4-component flame retardant) epoxy used was Shell EPON 1124-A-80 resin with dicyandiamide (DICY) and 2-methylimidazole (2MI) dissolved in 2-methoxy ethanol (2ME) or dimethyl formamide (DMF). The following parts by weight of resin, DICY, 2ME (or DMF), and 2MI were used: 125/3/47/0.06. This resin was chosen because of its relevance to the printed circuit board industry. The mixture was applied with a roller. The cured thickness ranged from 3 to 9 mils, and was not precisely controlled. The lap shear strength is not expected to vary significantly with bond thickness over this range. Where comparisons can be made, the lap shear strengths obtained here fall in the same range as similar studies reported in the literature [10].

The first test involved the two control sets mentioned in the introduction to this section and three sets of samples with the imidazole-amine block copolymer applied. For this series of tests, DMF was used as the solvent for the epoxy resin. For the samples containing the block copolymer, the first set (set c) in Figure V.1) was immediately placed into a 0.002 g/ml methanol solution of the block copolymer after microetching in order to test the adhesion to bare copper. Xue, et al. [11], have examined the growth of the native oxide on copper after acid etching by surface enhanced Raman spectroscopy. They showed that the native oxide on copper becomes observable after  $\sim 30$  minutes, and reaches a limiting thickness after  $\sim 2$  hours. In the present sample set, the samples were submerged in the copolymer solution within  $\sim 5$  minutes after microetching. For the second set of samples with block copolymer (set d) in Figure V.1), the coupons were left in air for 3 hours after microetching and rinsing, and then placed into the methanol solution of the block copolymer. Both sets c) and d) were left in the block copolymer solution overnight ( $\sim 16$  hours), then washed exhaustively with methanol, and roll-coated with FR4. For the third set of samples with block copolymer (set e) in Figure V.1), the block copolymer was dissolved into the FR4 resin at 1.8 wt %, and the accelerator, 2-methyl imidazole, was omitted since the block copolymer contains an imidazole functionality. This test was performed because it may be more advantageous in an industrial production process to simply include the copolymer in the resin mixture rather than adding an extra processing step for adsorption of the copolymer onto the foil. Since the copolymer would not dissolve in DMF, 2ME was used as the solvent for the epoxy resin for the third block copolymer sample set. After curing (10 mins. at 60  $^{\circ}\text{C}$ , 2 hrs. at 177  $^{\circ}\text{C}$ ), the samples were cooled to



room temperature and pulled with an Instron. All sample sets were composed of 5 coupons.

The results are displayed in Figure V.1. The error bars indicate the standard deviation of the five samples in each set. We observe that i) the lap shear strengths for sample sets d) and e) were significantly higher than that for the brown oxide treated control samples (set b), and far greater than the control set with only the microetch treatment (set a), and ii) the adhesion enhancement was slightly greater when the copolymer was bonded to the native oxide (set d) rather than to bare copper (set c). The first point is the major result of this test, demonstrating significant enhancement with the block copolymer adsorbed onto the native oxide. The second observation is somewhat anomalous, running counter to the data obtained in subsequent tests, as presented below. Indeed, a major

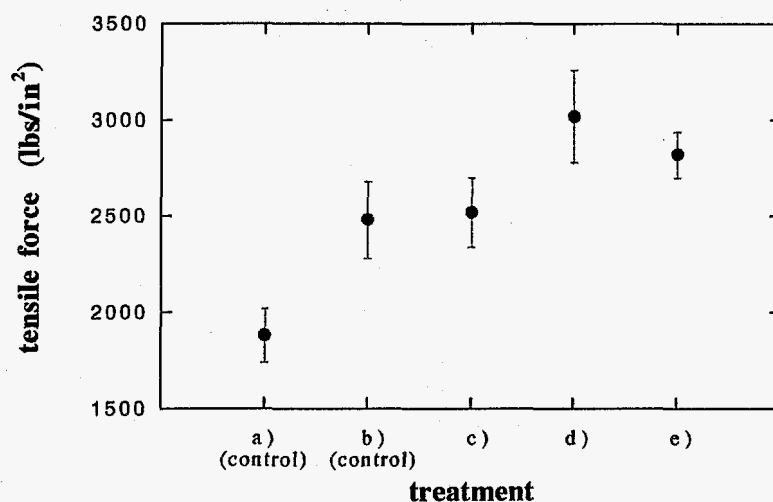


Figure V.1 a) native oxide, b) brown oxide, c) block copolymer (BC) on bare Cu, d) BC on native oxide, e) BC in resin, applied onto native oxide

conclusion of this study (demonstrated below in Figures V.5 and V.10) is that excellent performance can be obtained by applying the epoxy or block copolymer to copper before the oxide can form. The slightly poorer performance in the present test for the samples which were submerged in the block copolymer solution soon (within 5 minutes) after microetching, may be due to the fact that an excessively long soaking time (~ 16 hours) was used. The long exposure to the methanol solution may weaken the surface layers of the copper. In support of this assertion is that fact that dissolution of the surface layers of copper into the adsorbing solution was observed by X-ray reflection. It is possible that the adverse affect of the long exposure to the methanol solution may be more pronounced for the bare copper surface than for the native oxide. This could explain the trend in Figure V.1. The comparison of samples with and without the native oxide was repeated later on in this study (Figure V.5) using a greatly reduced soak time. Those experiments show that the performance is far superior when the oxide is not allowed to form.

The second test was designed to examine the effect of soak time, once again using methanol solutions at 0.002 g/ml. Initially, the two control sets were repeated along with sets of samples with the block copolymer adsorbed onto the native oxide during 15 minute and 24 hour soaks. DMF was again used as the solvent for the resin. The results are shown in Figure V.2. The measured strengths of the control samples were reasonably consistent with those in the previous test. However, the two sets with the block copolymer (sets c) and d)) gave poor strengths, only at the level of the samples with just the microetch treatment (set a)). This poor performance was determined to be due to the fact that the

methanol solutions of the block copolymer had been used previously. It had been hoped that the solutions could be used repeatedly in order to conserve the specially synthesized block copolymer. However, these data showed that multiple uses of the same solution results in poor performance. It was also noticed that the solutions had become cloudy after the initial soaks. This is likely due to complexation of the copolymer with copper ions that had dissolved into the solution from the surfaces of the coupons. The layer which deposited from this complex mixture was clearly detrimental, and therefore this test precludes multiple uses of the same solutions. However, it should be noted that the foils were soaked for 24 hours, and that multiple uses of the same solution may be possible if the soak time were limited to only several minutes. When the experiment was repeated with freshly prepared solutions (sets e) and f)), strengths in the range of 3000 lbs/in were again obtained, independent of soak time, for exposure times ranging from 2 to 18 hours. While no variation in strength is observed for samples with the block copolymer adsorbed onto the native oxide over this range of exposure times, the corresponding comparison for samples without the native oxide (set c) in Figure V.1 and set b) of Figure V.5) indicates a large effect of soak time.

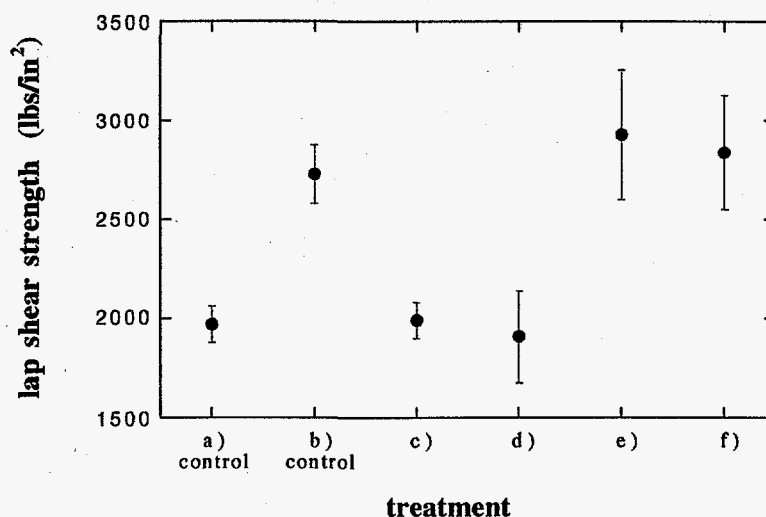
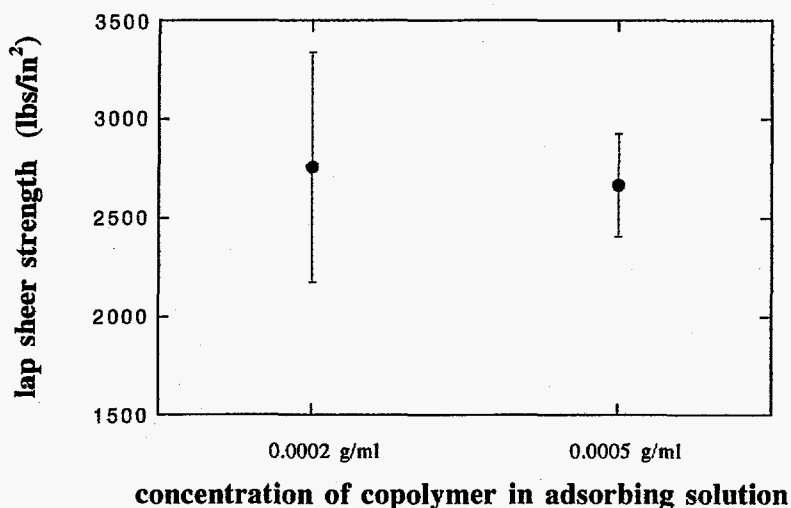


Figure V.2 a) native oxide, b) brown oxide, c) used BC solution, 15 min. soak, d) used solution, 24 hr soak, e) fresh solution, 2 hr soak, f) fresh solution, 18 hr soak

The following test was designed to examine the effect of the concentration of copolymer in the methanol soaking solution. Sample sets with native oxide were soaked in methanol solutions at concentrations of 0.0005 and 0.0002 g/ml, again in hopes of reducing the quantity of block copolymer consumed. For this, and all subsequent tests, 2ME was used as the solvent for the resin. The results are shown in Figure V.3. Within the rather large scatter in the data, the strengths for each sample were in the range of that obtained at a concentration of 0.002 g/ml. Thus no variation in lap shear strength was observed over this range of concentration. We now know, based on the results of Section IV, that the adsorbed monolayers obtained using pure methanol solutions of the copolymer contain little if any of the amine-functionalized block. The dependence on concentration may be different when adsorption is done from a methanol/water mixture.



**Figure V.3**

The next test was designed to evaluate the durability of the joint after brief exposure to molten solder, which occurs during processing of PWBs. To accomplish this, the lap shear samples were entirely submerged in molten solder (260 C) for 20 seconds following the cure. The samples were prepared as in the Figure V.1, except that the soaking time in the copolymer solution was only 2 hours. The data are shown in Figure V.4 (blue circles), along with the as-prepared strengths from Figure V.1. The samples with only the microetch treatment all failed in the solder pot. However, samples with the brown oxide treatment and the adsorbed block copolymer both survived submersion in solder and yielded similar strengths (evaluated after cooling to room temperature). This test demonstrates that the block copolymer enhances durability, presumably by inhibiting growth of a weak, low density oxide during solder exposure.

In order to test the assumption that oxidation of the copper, rather than the thermal spike, plays the major role in the loss of strength of the joint during solder exposure, sample sets were prepared in the same fashion as those in Figure V.4 (2 hour soak in copolymer solution) and then submerged in a solder pot that was placed inside a glove box in an argon atmosphere devoid of oxygen. After curing, the samples were placed in the glove box for several days before submersion in solder, to allow dissolved oxygen to diffuse out of the epoxy. After submersion in solder the samples were removed from the glove box and pulled in ambient conditions. The results are shown in Figure V.4 (green circles). All samples sets, including the set with only the microetch treatment, showed excellent retention of strength when the submersion in solder was performed in an atmosphere devoid of oxygen. The strengths of the sample sets were comparable. This test proves that the loss of strength for samples submerged in solder under ambient conditions is linked to the presence of free oxygen. It is most likely due to growth of a weak oxide. The primary effect of the block copolymer leading to improved durability is apparently to inhibit further oxidation, rather than providing a chemical bond between epoxy and copper. The reason the block copolymer inhibits further oxidation, however, is likely linked to its ability to interact strongly with the surface and block access of oxygen to surface sites.

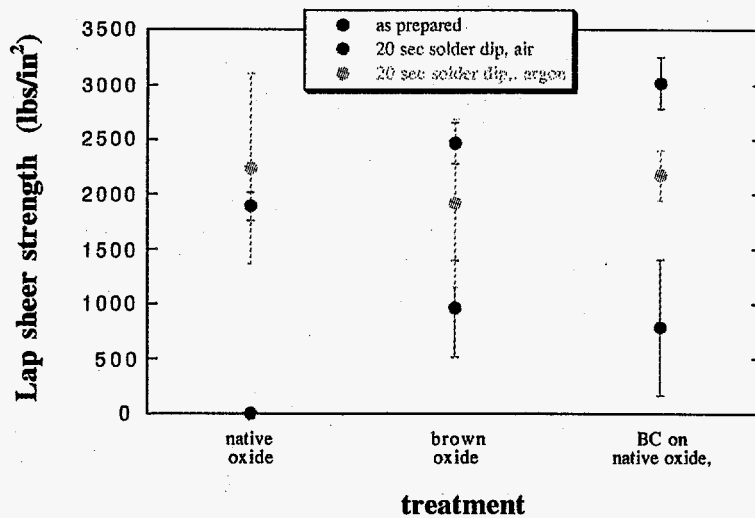


Figure V.4

Following the above results, a further test was performed in which two sample sets were prepared without allowing the native oxide to form, by coating the copper surfaces with either the epoxy resin or the block copolymer (0.002 g/ml in methanol, soaked for 2 hours) within approximately 1 minute after microetching and rinsing. Samples were evaluated as-prepared and after submersion in solder. The data are shown in Figure V.5. This plot, which is the most important result of the lap shear testing, shows that i) the as-prepared strengths are enhanced relative to the strengths obtained when the native oxide is present (Figure V.4), ii) excellent retention of the strength is obtained after submersion in molten solder under ambient conditions, and iii) only a slight enhancement is observed with the block copolymer over that obtained with only FR4 coated onto the bare copper.

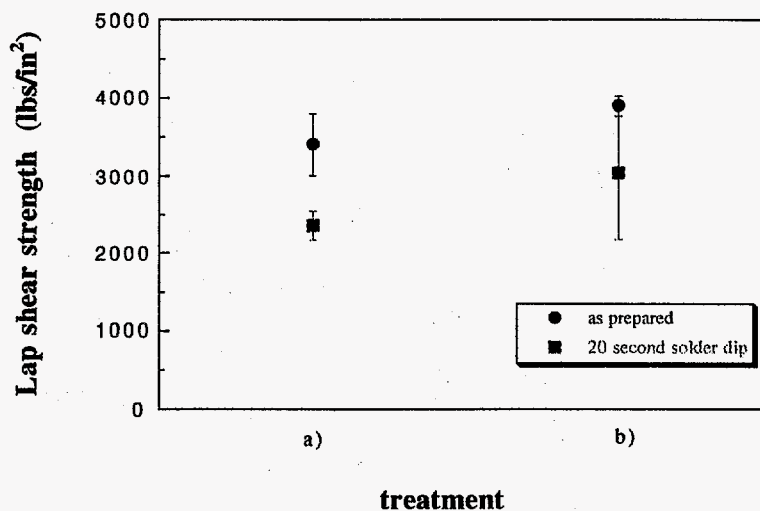


Figure V.5 a) no oxide, b) no oxide, with block copolymer

Observation i) shows that the native oxide weakens the joint relative to an interface of epoxy with bare copper. Perhaps even more importantly, observations ii) and iii) indicate that the epoxy alone can protect the bare copper surface from oxidation. This is in contrast to the results with the native oxide in Figure V.4, where the epoxy alone apparently did not protect the native oxide from further oxidation during solder exposure in an oxygen atmosphere. The fact that only a slight enhancement is observed with the block copolymer suggests that the bonding of epoxy to copper is, in fact, quite good, and that inhibition of oxide growth may be accomplished with the epoxy resin alone to nearly the same extent as when the block copolymer is applied. Finally, we note that the strength levels in Figure V.5 exceed those obtained by the current standard treatment (brown oxide) in the PWB industry (Figure V.4).

One final lap shear test was performed in which the block copolymer was coated (18 hour soak in 0.0005 g/ml methanol solution) onto brown oxide-treated copper coupons. A second set of brown oxide treated samples were prepared as a control. Both sets of coupons were then evaluated in the as-prepared state. The results are shown in Figure V.6. We observe a severe loss of strength for the samples which were soaked for the extended period in the block copolymer solution. This is believed to be due to the methanol solution attacking and weakening the oxide. Evidence for this is that a pink, apparently pure copper, surface was observed on the fracture surfaces indicating that failure occurred between the brown oxide and the underlying pure copper, rather than within the brown oxide, epoxy, or at the brown oxide/epoxy interface. This test demonstrates that extended contact with the soaking solution can have a detrimental effect on the copper oxide layer.

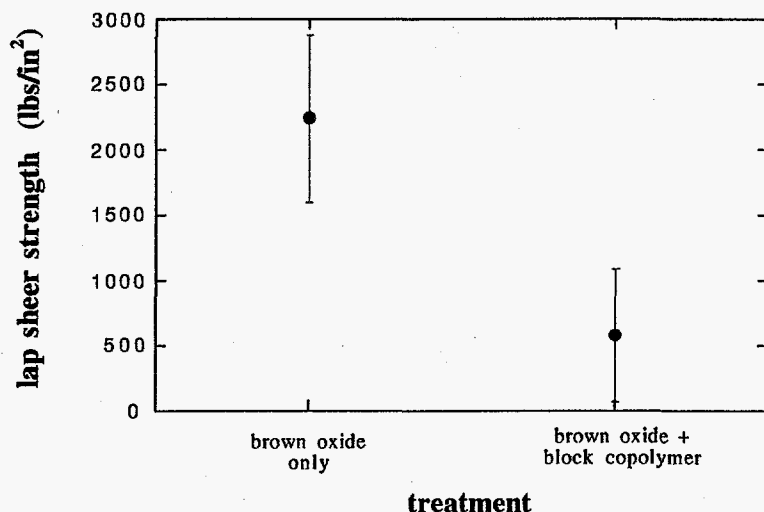


Figure V.6

### Summary - lap shear testing

Failure in the lap shear tests is strongly affected by the nature of the oxide. When the native oxide is present, the block copolymer provides some protection against further

oxidation during solder exposure in an oxygen atmosphere. The epoxy alone provides little or no protection under the same circumstances. When the joint is prepared without allowing the native oxide to form, the as-prepared strength is higher than that when the native oxide is present. In addition, the epoxy alone provides excellent protection against oxidation of the bare copper/epoxy interface, comparable to that when the copolymer is applied.

The characterization work in the previous section indicates that for the adsorption conditions of these experiments (pure MeOH solutions), only copolymers with small amine-functionalized blocks adsorb. These are not favorable conditions from the point of view of improving the chemical coupling. The fact that under these conditions the block copolymer provided some enhanced performance, at least on the native oxide, argues that inhibiting oxidation is the key to improved performance rather than improving the chemical coupling. Finally, we note that the above interpretations regarding failure modes were made through indirect evidence, and that additional work should include spectroscopic and microscopic studies of the fracture surfaces.

### Peel tests

Peel test data are presented in this section, again in the chronological order in which they were obtained. The tests conditions varied initially until a final protocol was established. In particular, the first test involved a different resin system and test geometry than all subsequent tests (FR4-based laminates). The second test involved a much thicker copper foil than all subsequent tests.

The initial peel test samples were prepared by pouring a thick plaque (~1/4 inch) of epoxy onto copper foils that had previously been microetched and left in air to allow the native oxide to form. The copper foil was then slit into strips and peeled from the plaque with an Instron. For this initial test, Shell EPON 828 (bisphenol-A based bifunctional) resin was used along with Versamid 140 curative. Two control samples were prepared along with one foil coated with the block copolymer (0.00286 g/ml in methanol, foil soaked for ~2 hours). The peel strengths are shown in Figure V.7.

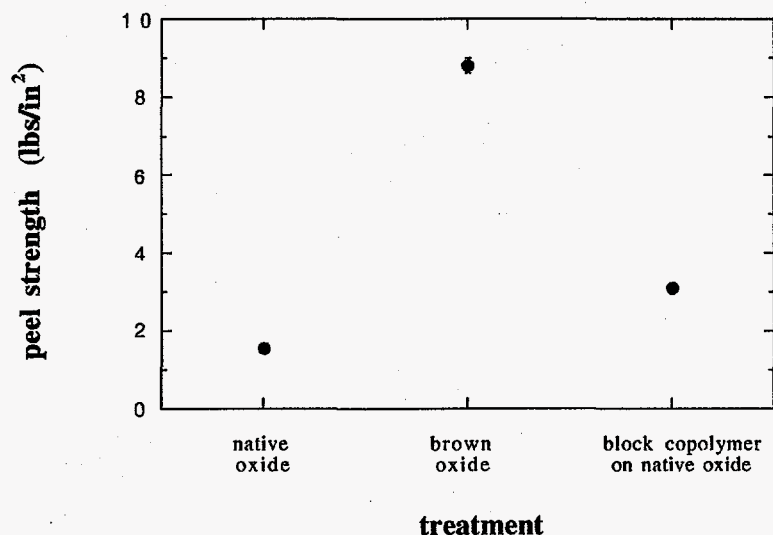


Figure V.7

The strength with the adsorbed block copolymer was twice that for the sample with only the microetch treatment, however, the strength was far lower than that obtained with the brown-oxide treatment.

In all subsequent peel tests, the FR4 resin was used, formulated as described in the lap shear section using 2ME as solvent. Samples were prepared by laminating the foils to 3 sheets of FR4-based prepreg obtained from Allied Signal Corp (ED130, 7628 style glass cloth). The laminating temperature and pressure were 350 °F and 300 psi, respectively.

In the peel tests, it was determined that the thickness of the copper foil had a surprisingly strong effect on the measured peel strength values. In the first laminate peel test, 13 oz. copper foil was used, which is significantly thicker than foil normally used for PWB laminates. Two control samples were again prepared: one with only the microetch treatment followed by exposure to air to allow for growth of the native oxide, and another with the brown oxide treatment. The brown oxide samples yielded peel strengths in the range of 30 lbs/in., compared to the range of 4-7 lbs/in. typically reported in the industry. The elevated peel strength was found to be due to the thickness of the copper foil. Nevertheless, the data obtained with this unusually thick copper foil, shown in Figure V.8,

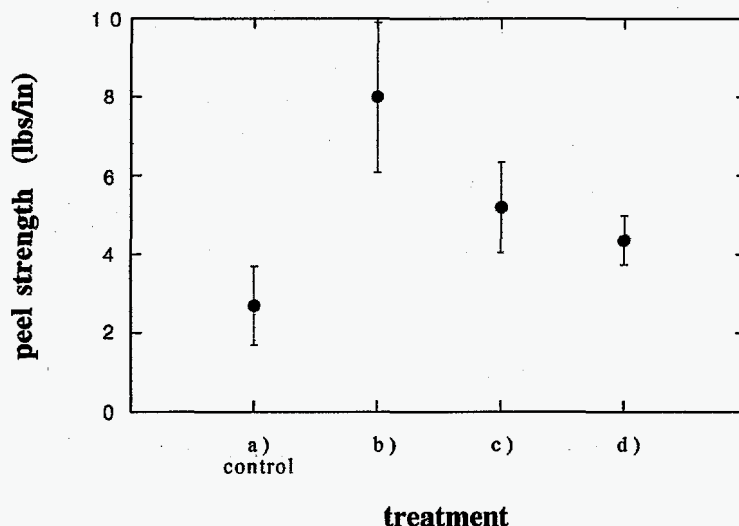


Figure V.8 Block copolymer on native oxide adsorbed from b) pure MeOH, c) 80/20 MeOH/H<sub>2</sub>O, and d) 50/50 MeOH/H<sub>2</sub>O. a) native oxide control

still reveals qualitative trends. Three block copolymer-coated samples were examined, which varied in the quantity of H<sub>2</sub>O mixed with the methanol. Such mixtures were explored following the characterization work (Section IV) which revealed that the structure of the adsorbed copolymer layer varied greatly depending upon the quantity of water mixed with methanol. In particular, the thickness of the amine-functionalized block was much greater when water was included. The concentration of block copolymer was fixed at 0.002 g/ml. In addition, after adsorption of the block copolymer, a "primer" layer was applied by brush. The primer was composed of the normal FR4 resin formulation given above diluted to 1/4 of the total weight fraction with 2ME. The primed surfaces were then partially cured, or "B-staged", by heating in an oven at 125 °C for 15 minutes. The foils were then laminated as above. The data in Figure V.8 show a tripling of the peel strength for the block copolymer coated from pure methanol solution relative to the sample with only the microetch treatment. However, the peel strength is still far below that obtained with the brown oxide treatment (~ 30 lbs/in). We also observe that the peel strength decreases with increasing concentration of water in the adsorbing solution. This is in

contrast to our expectations based on the layer structure revealed for these conditions in Section IV. We expected better performance when the adsorbed copolymer structure contains sizable layers of each block. One sample from the set involving the 50/50 MeOH/H<sub>2</sub>O solution was peeled roughly 6 weeks after lamination, and a value of 9 lbs/in was obtained, much higher than that obtained shortly after lamination (~4.3 lbs/in). The variation with H<sub>2</sub>O content shown in Figure V.8 may be due to adsorption of micelles or other aggregates rather than single copolymer chains. The 50/50 solution was visibly cloudy, indicating the presence of aggregates. In the micellar state, only one block is exposed and the copolymers would be unlikely to enhance bonding across the interface. A relatively slow rearrangement of the block copolymers at the interface from micelles to a conformation of single chains straddling the interface may account for the increase in the peel strength with time for the 50/50 sample.

The next experiment was designed to further test the effect of the solution composition as well as soak time, once again motivated by our observations of variations in copolymer layer structure. Foils were microetched, left in air overnight to allow the native oxide to form, and then soaked for either 5 minutes or 1 hour in solutions of the block copolymer. The adsorbing solutions were prepared using either pure methanol or an 80/20 mixture of methanol and water as solvent. The copolymer concentration was fixed at 0.0005 g/ml. Such a low concentration was chosen following the results in Figure V.3, which showed no variation in lap shear strength with concentration down to this low value. However, those tests were done using pure methanol. It is now known from the results of Section IV that for MeOH/H<sub>2</sub>O solutions this concentration is too low to ensure a high coverage of copolymer. Following adsorption, the primer was again applied by brush and B-staged. The foils were then laminated as above. For these tests, 1 oz. copper foil was used, which corresponds to a weight (thickness) of foil commonly used in PWB laminates. Two control samples were included: a sample with only the microetch treatment followed by exposure to air to allow the native oxide to form, and a sample with the brown oxide treatment. Both electrodeposited (ED) copper foil and rolled-annealed (RA) foils were used for each control. Peel strengths were evaluated for as-prepared laminates and also after a 10 second float on molten solder (260 C). The data are shown in Figure V.9. With the

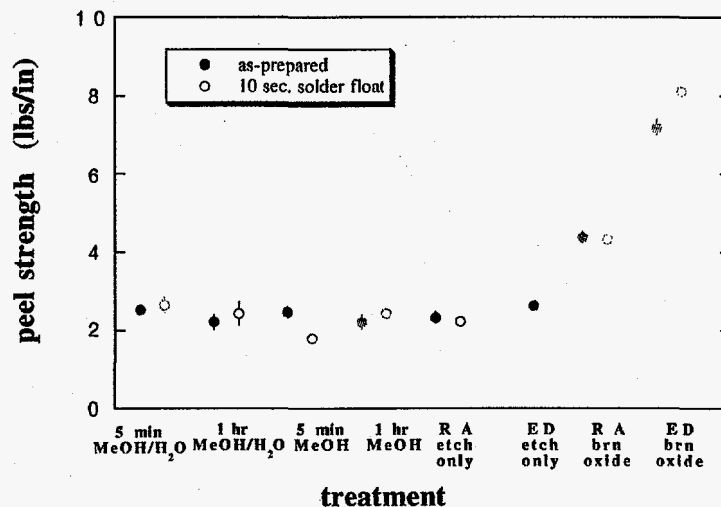


Figure V.9

1 oz. copper foil, the scale defined by the control samples is reduced relative to that with the thicker foil in Figure V.8, with strengths ranging from 2.2 lbs/in for samples with only



the microetch treatment to 8.0 lbs/in for the brown oxide on ED foil. These values are in excellent agreement with the values commonly reported in the PWB industry. The main result of this test (native oxide present) is that no adhesion promotion is observed with the block copolymer on this scale, and there is no significant dependence on soaking time or H<sub>2</sub>O concentration. We note that the neutron reflectivity work has indicated that very little block copolymer is adsorbed at the concentration used, which may explain the insensitivity to adsorbed copolymer layer structure. Also surprising is the fact that no decrease in peel strength was observed after 10 sec. solder float, in contrast to the lap shear data in Figure V.4 where the as-prepared strength was fairly high but dropped to zero upon solder exposure. This will be discussed in more detail in relation to Figure V.12.

The subsequent peel test was designed to examine the effect of laminating without allowing the native oxide to form. For this test, the copper foils were placed into the block copolymer solution (0.0005 g/ml) within 1-2 minutes after microetching and rinsing. Samples were prepared which varied in the exposure time (1 or 5 minutes) to the copolymer solution and also in the H<sub>2</sub>O composition of the solution. The primer coat was brushed onto each foil after removal from the copolymer solution. A further set of samples was prepared in which the primer alone was applied within 1-2 minutes after microetching and rinsing, without adsorption of the block copolymer. Samples were evaluated as-prepared, and after a 10 sec. solder float. The results are shown in Figure V.10. These

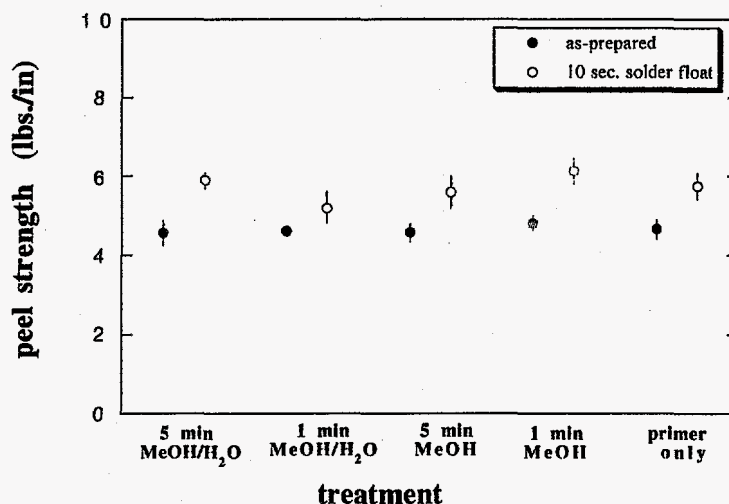


Figure V.10

data are the most important results of the peel testing. All values are in the range from 4-5 lbs/in. in the as-prepared state, and increase to 5-6 lbs/in. after the solder float. In comparing with Figure V.9, the peel strength after solder float has nearly tripled. The level of performance in Figure V.10 exceeds the specifications set by the PWB industry (> 5 lbs/in after 10 sec. solder float). Somewhat surprisingly, no variation is observed with soak time or solution composition. In fact, the samples with only the primer show the same level of strength as those with both block copolymer and primer. As in the lap shear tests, we again conclude that the principle requirement for achieving good bond strength as-prepared and after solder exposure is to inhibit the formation of oxide. This is apparently accomplished by the primer alone to the same extent as when the block copolymer is also applied. However, we again emphasize that the concentration of the block copolymer solutions (0.0005 g/ml) was too low to ensure a high coverage of block copolymer.

An initial attempt was made to determine the durability of the interfaces prepared without the native oxide. The test involved one set of samples with the primer-coated foil and one set with adsorbed block copolymer followed by coating with primer. The as-prepared samples were heated in an oven at 125 °C for 2 weeks, cooled to room temperature, floated on solder for 10 sec, cooled again to room temperature, and then peeled. The results are shown in Figure V.11. The peel strengths of both sample sets dropped from nearly 5.0 (Figure V.10) to 1.2 lbs/in with the extended period of heating.

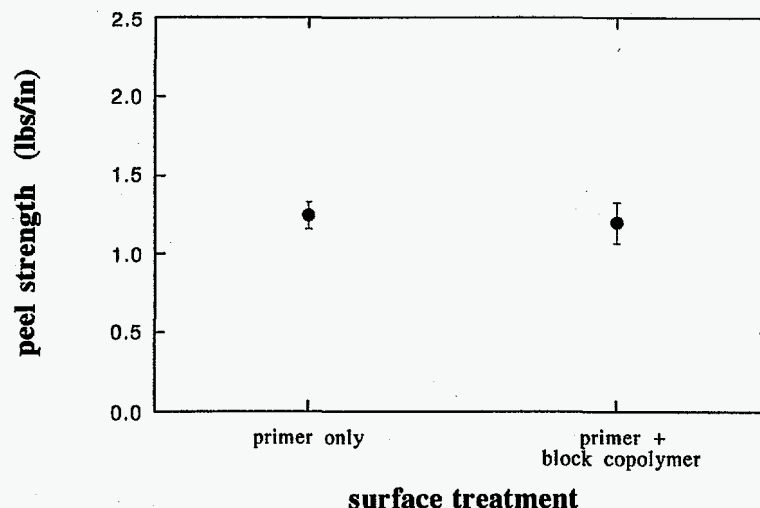


Figure V.11

Unfortunately, no brown oxide control samples were included for comparison. No improvement in strength retention was observed with the block copolymer, however, once again we note that the concentration of the adsorbing solution was too low to achieve a dense adsorbed layer. In addition, the failure mode was not precisely determined. If the samples failed within the prepreg layer, this could also explain why there was no dependence on the interface treatment.

The next series of samples was designed to determine whether the peel strengths showed any dependence on the time between etching and laminating, and in particular, to compare with the lap shear results in Figure V.4. In this case, no block copolymer or primer were used. The samples were left in air for 0, 3, and 24 hrs. between microetching and lamination. However, the  $t=0$  hrs samples were exposed to air for as much as 5 minutes before lamination, the time required for lay-up in the lamination process. The data are displayed in Figure V.12. Two surprising results are observed. The first is that there is only a slight dependence on the delay time, all samples showing very poor strength. Apparently epoxy prepreg does not provide the protection of the bare copper surface that is afforded by the dilute epoxy primer. Alternatively, the longer delay time (~ 5 min.) between microetching and lamination may have allowed some oxide growth. However, since a delay time will likely always be present before lamination, this argues strongly for the use of the primer or block copolymer. Second, the samples did not fail during the solder exposure, as did the analogous lap shear samples in Figure V.4. Apparently the lamination process adds a low level of durability that is not obtained in the lap shear coupons. Alternatively, the stress fields developed in the peel samples during solder float may be significantly different than those arising in the lap shear samples during total submersion. The difference in exposure time (10 sec. solder float for peel samples versus 20 sec. submersion for lap shear coupons) might also contribute to this difference.

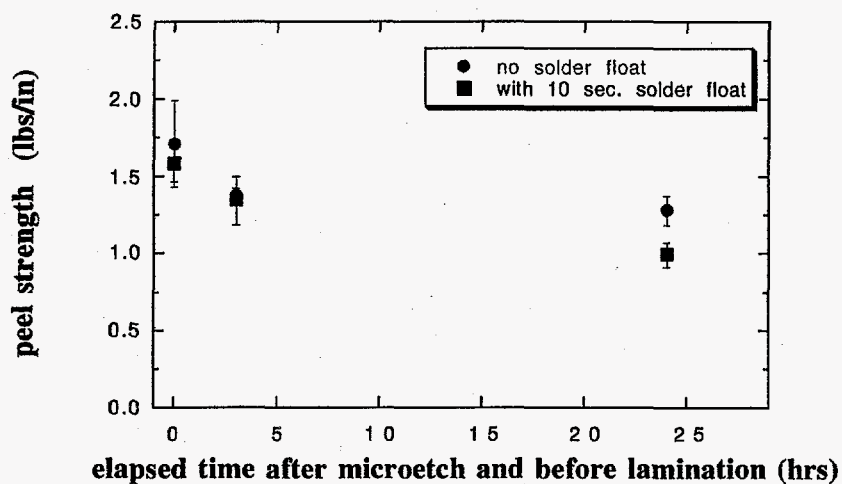


Figure V.12

Figure V.13 shows the results from a final test which compares the cases where the block copolymer and the primer treatments were each applied onto foils with fully formed native oxide. The block copolymer was adsorbed from a 0.0005 g/ml solution in methanol. Data are shown in the as-prepared state, and also after solder float. Once again, both sets of samples survived the solder float, albeit with only a minimal amount of strength, in contrast to the lap shear data in Figure V.4. No difference is observed in the performance for these two treatments, also in contrast to the lap shear results in Figure V.4.

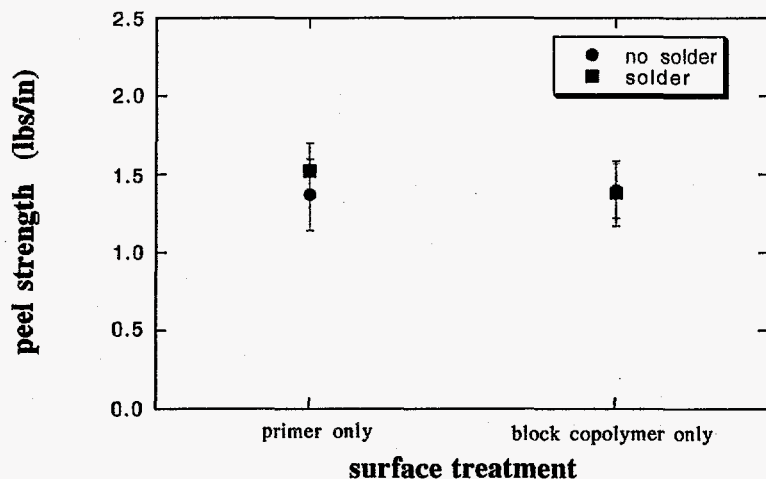


Figure V.13

## Summary of peel testing

Failure in the peel tests is strongly affected by the presence of copper oxide. When the joint is prepared without allowing the native oxide to form, the as-prepared strength is higher than when the native oxide is present (cf Figure V.9 and Figure V.10). In addition, the epoxy primer alone provides excellent protection against oxidation of the bare copper/epoxy interface, equal to that when the copolymer is applied. On the other hand, prepreg alone apparently does not afford such protection.

When the native oxide is present, the block copolymer provides some enhancement (Figure V.7 and Figure V.8) to the as-prepared strength. However, this enhancement is relatively minor compared to the effect of disallowing oxide formation.

The characterization work in the previous section indicates that the structure of the copolymer layer varies greatly with the different adsorption conditions used in the peel tests. The lack of variation in the peel strengths under these conditions (Figure V.9, Figure V.10) may be due to poor coverage. It is now known that the copolymer concentration used (0.0005 wt fraction) is too low to ensure a dense coverage. However, the fact that the epoxy primer alone provides good performance when no oxide is present establishes that the bond between epoxy and copper is strong, and thus that a coupling agent is not needed. An important but unanswered question is the durability of the oxide-free bond, with or without the block copolymer, with long term thermal cycling or exposure to humidity. Finally, we again note that the above interpretations regarding failure modes were made through indirect evidence, and that additional work should include microscopy and spectroscopic studies of the fracture surfaces.

## Summary of adhesion testing

The main result of both adhesion tests is that by simply applying the epoxy resin immediately after microetching and rinsing, excellent bond strength in the as-prepared state as well as excellent retention of bond strength after exposure to solder can be obtained (Figure V.5, Figure V.10). Under these conditions, the level of performance exceeds that specified by the PWB industry. The epoxy apparently bonds to the copper surface and inhibits the growth of copper oxide during the solder exposure. The native oxide of the copper is believed to be the weak link. When either the block copolymer, the primer, or both are applied onto the native oxide, much poorer performance results.

When the joints are prepared without the native oxide, no additional enhancement is observed with the block copolymer. The epoxy primer apparently provides adequate bonding to and protection of the bare copper surface. Epoxy prepreg, on the other hand, does not afford such protection. However, we note that the block copolymer was never applied in the proper fashion to ensure a dense coverage. Such a test must be performed before a definitive conclusion can be made about the efficacy of the block copolymer as an additive. In addition, the durability of the bond with respect to short term exposure to acids, as well as long term thermal cycling and humidity conditioning has not been determined. It is possible that the block copolymer may be required to impart improved resistance to these factors.

In addition to the main result above, a number of minor conclusions can also be made from these experiments. First, no variation in adhesive strength was observed with copolymer solution conditions (concentration, quantity of H<sub>2</sub>O), even though the conformational studies indicate that the structure of the copolymer layer is a strong function of solution conditions. This likely indicates that i) the adsorption conditions were not appropriate to yield a dense adsorbed monolayer containing both blocks, ii) failure initiates within the weak copper oxide when present, and iii) low molecular weight epoxy resin (as opposed to partially cured prepreg) apparently occupies all the surface sites, bonds very strongly to bare copper, and inhibits oxidation. Apparently, the key requirement for good

performance is to inhibit the growth of the oxide, rather than to enhance chemical coupling. Since this can be accomplished by the epoxy primer alone, there is little dependence on the copolymer conformation. Once again, however, it is essential to perform tests under conditions which ensure a dense copolymer layer before firm conclusions can be made. In addition, it would be interesting to apply the copolymer without primer in the laminate peel test. If the copolymer alone can afford adequate protection against oxide formation, it may provide an advantage over the epoxy primer for ease of foil handling during the delay between microetching and lamination.

The application of the block copolymer did lead to modest improvements in performance when applied to the native oxide. In the lap shear test, the application of block copolymer led to modest improvements in the as-prepared state (Figure V.1) as well as improved strength retention after submersion in solder (Figure V.4). In the peel tests, significant enhancement was observed in the as-prepared state for the Versamid cured system (Figure V.7) and for the FR4 resin system when the thick copper foil was used (Figure V.8). When the 1 oz. copper was used, which led to a much compressed scale, this enhancement was no longer observed (although a much lower copolymer concentration was used). The abovementioned modest enhancements in performance, however, were small compared to the improvements when the native oxide was not allowed to form.

Some interesting differences in performance were observed in peel and lap shear modes. The lap shear strength when the block copolymer was applied to the native oxide exceeded that of the brown oxide control (Figure V.1, Figure V.4), however the peel strength for the analogous sample was far lower than that of the brown oxide control (Figure V.7, Figure V.9). This is likely due to different modes of failure in the two tests. In addition, while the lap shear samples with only the native oxide failed in the solder pot (20 sec submersion, Figure V.4), the corresponding laminate peel samples survived the solder pot with little or no loss of peel strength (10 sec. float, Figure V.9, Figure V.12, Figure V.13). This is attributed to the high pressure lamination process adding a low level of durability that is not obtained in the lap shear coupons, to differences in the stress fields developed in the peel/lap shear samples during solder float/submersion, or to the difference in exposure time (10 sec. solder float versus 20 sec. submersion).

Finally, it would be interesting to investigate the addition of the copolymer to the primer formulation as an alternative approach to the two step process of copolymer adsorption followed by primer coating. The lap shear data in Figure V.1 indicates that the copolymers can indeed migrate to the interface from within the epoxy resin.

## VI. Summary and Conclusions

Novel block copolymers were synthesized which contain pendant functional groups reactive toward copper and epoxy resins. In particular, imidazole and triazole functionalities which chelate with the copper were incorporated onto one block while secondary amines were incorporated onto the second block. This is the first time that amine groups have been incorporated into this type of copolymer. The secondary amine was shown to be reactive toward epoxy resins. Copolymers with fairly narrow molecular weight distributions were synthesized with a range of weight average molecular weights. In addition, copolymers with individual blocks selectively deuterated were prepared to enable characterization of the adsorbed monolayer structure.

These copolymers were found to self-assemble from solution onto copper surfaces to form monolayers. The structure of the adsorbed monolayers was studied in detail, and was found to vary markedly with solution conditions and adsorption protocol. This strong dependence is likely due to the finite polydispersity of the samples, to complex mixtures of single chains and micellar structures coexisting in the solution, and to both kinetic and thermodynamic factors influencing the adsorption process. Each of these requires further study to obtain a complete understanding. Using neutron reflection and time-of-flight SIMS, it was shown that under certain conditions the two blocks form separate layers on the surface with the amine functionalized block exposed at the air surface. This conformation is expected to provide optimal coupling. However, the total amount of copolymer adsorbed, as well as the relative amounts of the two blocks, varied strongly with solution conditions. Unfortunately, these results have also shown that most of the adhesion testing was performed for samples that had a low surface coverage of copolymer (peel) or that had only a small amount of the amine functionalized block (lap shear).

Adhesion testing was performed in both lap shear and peel modes. The principle conclusions were the same in both tests. The main result was somewhat surprising. By simply applying the epoxy resin immediately after microetching and rinsing, which removes the native oxide, excellent bond strength in the as-prepared state as well as excellent retention of bond strength after exposure to molten solder were obtained. Under these conditions, the level of performance exceeds that specified by the PWB industry. The native oxide of the copper was clearly determined to be a weak link. When either the block copolymer, an epoxy primer, or both were applied onto the native oxide, much poorer performance resulted.

The excellent performance is apparently due to the ability to form the epoxy/copper interface without allowing the native oxide to form. This is only possible because of the relatively low rate of oxide growth on copper. This contrasts with many other common metals and alloys, such as aluminum and stainless steel, for which rapid oxide growth rates preclude formation of oxide-free surfaces in an industrial setting.

Surprisingly, when the joints were prepared without the native oxide, little or no additional enhancement was observed with the block copolymer. Furthermore, no variation in adhesive performance was observed over conditions for which the adsorbed copolymer monolayer structure should have varied dramatically. All these observations point to the fact that the presence (or absence) of the oxide is the controlling factor. However, we reiterate that the conditions for adsorption of the copolymer were far from optimized in the adhesion testing.

Some modest enhancements in bond strengths were observed with the block copolymer applied to the native oxide, despite the less-than-optimal adsorption conditions. However, these enhancements were small compared to that obtained by forming the joint without allowing the native oxide to form. The epoxy apparently bonds extremely well to the bare copper surface. Under these conditions, no coupling agent is required. The key to a durable bond with this system appears to be avoiding oxide formation. For brief exposures to molten solder, the epoxy primer apparently provides adequate protection of the bare copper surface, equivalent to that obtained with the block copolymer. Epoxy

prepreg, on the other hand, does not afford such protection. Long term aging studies (thermal cycling, exposure to humidity) must be performed to determine if the epoxy primer affords robust protection against oxide formation. The block copolymer could possibly provide some enhancement to the long term durability, but time did not allow such a study to be completed.

Thus we recommend that further testing be performed using optimal adsorption conditions, and including long term aging studies. In addition, the functionalized block copolymer method should be evaluated for another system which has inherently poor bonding. One excellent candidate is the nickel/silicone interface, which has applications in DP and which is known to have exceptionally poor inherent bond strength. Furthermore, this method should be examined for interfaces involving metals which form oxides very rapidly, such as aluminum and stainless steel. Since it is not possible to prepare interfaces with oxide-free surfaces for these materials, bonding strategies typically focus on stabilizing the existing oxide. In this work it has been shown that block copolymers improve the stability of the native oxide on copper, and it is likely that block copolymers could be designed to stabilize the oxides of these other metals as well. Block copolymer coupling agents are likely to have a greater impact on joints involving these metals than for copper, since it is possible to bond directly to oxide-free copper. It is also recommended that this method be explored for interfaces between two thermosetting polymers, such as are often used in multilayer paint and corrosion resistance coatings for metals.

## References

1. E. P. Pleuddemann, "Silane Coupling Agents", 2nd Ed., Plenum Press, New York, 1991.; L. H. Lee, "Fundamentals of Adhesion", Plenum Press, New York, 1991.
2. U.S. Pat. Nos. 3,837,964; 4,428,987; and 4,448,847.
3. Eng, F.; Ishida, H. *J. Electrochem. Soc.*, **1988**, *135*, 603.; Hansen, J.; Kumagai, M.; Ishida, H. *POLYMER*, **1994**, *35(22)*, 4780.
4. U.S. Pat. No. 4,812,363
5. Larroche, C.; Laval, J.P.; Lattes, A. *J. Org. Chem.*, **1984**, *49*, 1886.
6. Bazan, G.C.; Schrock, R.R.; Cho, H.N.; Gibson, V.C. *Macromolecules*, **1991**, *24*, 4495.
7. Bristol, J.A.; Brambilla, R. *J. Org. Chem.*, **1979**, *44(11)*, 1889-1891
8. "Block copolymers: Overview and Critical Survey", A. Noshay and E. McGrath, Academic Press N.Y., N.Y., 1977.
9. Russell, T.P. *Mat. Sci. Rep.* **1990**, *5*, 171.
10. Guo, S., Xue, G., Qian, Y. *Applied Surface Science* **1995**, *84*, 351.
11. Xue, G., Lu, Y., and Shi, G. *POLYMER* **1994**, *35(12)*, 2488.



## Distribution List

1	MS 0958	J. Emerson	1492	
1	MS 0958	C. Adkins	1472	
1	MS 1407	M. Kent	1832	
1	MS 0343	W. Cieslak	1832	
1	MS 0367	R. Saunders	1815	
1	MS 1407	J. Aubert	1815	
1	MS 9018	Central Technical Files		8940-2
1	MS 8099	Technical Library	4414	
1	MS 0619	Review and Approval Desk		12690
1	1380	Technology Transfer	4212	