FUNCTIONALIZED BLOCK COPOLYMERS AS ADHESION PROMOTERS

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INTRODUCTION

The goal of this work is to develop novel functionalized block copolymers to promote adhesion at inorganic substrate/polymer interfaces. We envision several potential advantages of functionalized block copolymers over small molecule coupling agents. Greater control over the structure of the interphase region should result through careful design of the backbone of the copolymer. The number of chains per area, the degree of entanglement between the copolymer and the polymer matrix, the number of sites per chain able to attach to the substrate, and the hydrophobicity of the interphase region can all be strongly affected by the choice of block lengths and the monomer sequence. In addition, entanglement between the copolymer and the polymer matrix, if achieved, should contribute significantly to adhesive strength.

Our program involves four key elements: the synthesis of suitable functionalized block copolymers, characterization of the conformation of the copolymers at the interface by neutron reflectivity and atomic force microscopy, characterization of the degree of bonding by spectroscopy, and measurement of the mechanical properties of the interface. In this paper we discuss block copolymers designed as adhesion promoters for the copper/epoxy interface. We have synthesized a diblock with one block containing imidazole groups to bond to copper and a second block containing secondary amines to react with the epoxy matrix. We have also prepared a triblock copolymer containing a hydrophobic middle block. Below we describe the synthesis of the block copolymers by living, ring-opening metathesis polymerization (ROMP) and the first characterization data obtained by neutron reflectivity.

EXPERIMENTAL

Synthesis

ROMP has been known for many years. However, the synthesis of block copolymers by ROMP became possible only recently when Grubbs [1] and Schrock [2] developed molybdenum and titanium based initiators capable of living polymerization. The molybdenum based initiator is capable of tolerating a wide variety of chemical functionalities on norbornene-type monomers, and thus lends itself to the synthesis of well-defined, functionalized block copolymers that can be tailored to a wide variety of interfaces.

All reactants were purchased from Aldrich Chemical Company. Tetrahydrofuran was used as the polymerization solvent, and was vacuum distilled from a sodium/benzophenone solution immediately prior to use. The molybdenum based initiator ((2,6-diisopropylimido)neophylidine-molybdenum-bis-t-butoxide) was purchased from Strem and used without further purification. All polymerizations were performed under an inert atmosphere in a Vacuum Atmospheres dry box.

The synthesis of the three monomers (5-(n-methylimidazole)-2-norbornene, 5-(t-butylaminomethyl)-2-norbornene, and 5-(octaoxymethyl)-2-norbornene) will be described in detail elsewhere. All three were dried by distilling from and storing over calcium hydride or sodium hydride, and filtering through activated neutral alumina immediately prior to use.

A partially deuterated form of the imidazole monomer, used in the neutron reflection experiments, was prepared following the same reaction scheme as that for the protonated imidazole monomer, but starting with a partially deuterated dicyclopentadiene precursor. This sample contained 4 to 5 deuterium atoms per repeat unit.

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The two block copolymers synthesized for this study are shown below.
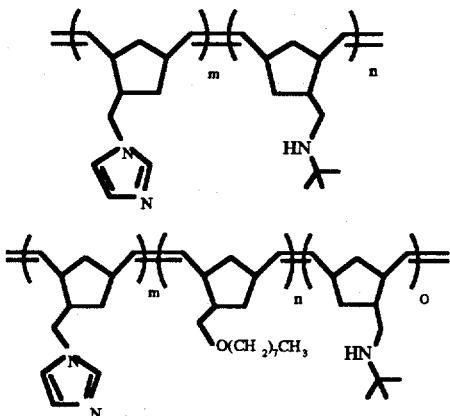
Typically a total of 1g of copolymer was formed in about 15 mls. dry THF. An appropriate amount of the first monomer was initially stirred with the molybdenum initiator. Upon complete consumption, the second monomer was then added. After the polymerization of the final block, the living chain ends were terminated by the addition of benzaldehyde. The copolymers were characterized by proton nmr, which showed complete consumption of all monomer except in the case of the imidazole monomer. This was the last block in the polymerization sequences, and thus did not destroy the continuity of the other blocks. The block copolymers were precipitated from acetonitrile, dried, and redissolved in chloroform for future use.

Each block in the copolymers had a targeted molecular weight of 15,000 g/mol. The actual molecular weight of the immidazole block is roughly 10,000 g/mol, whereas the other blocks are assumed to have the targeted molecular weight based upon the observation of total monomer consumption.

Characterization of adsorbed films by neutron reflectivity

Since both the imidazole and amine functionalities have an affinity for the copper surface, it is essential to determine whether the blocks order into layers upon adsorption to a copper substrate, with one block adsorbing preferentially, or whether they adsorb in a

disordered conformation with both blocks adsorbing at the surface. To address this question we prepared copolymer samples with partially deuterated imidazole blocks and examined adsorbed films of these copolymers by neutron reflectivity. With this technique the neutron refractive index profile normal to the surface is obtained with ~ 5 Å resolution. The selective deuteration allows one to distinguish between the two blocks. The copolymers were adsorbed from solution onto silicon wafers which had been previously sputter-coated with smooth, thin (~ 250 Å) copper films. Following the adsorption step, the samples were thoroughly washed with MeOH and THF to remove any copolymer not strongly adsorbed to the surface.

Results for the diblock copolymer (with targeted block lengths 15K-15K) adsorbed from 0.002 g/ml solution in MeOH are shown in Figure 1a. The main effect of the adsorbed copolymer on the reflectivity is to shift the fringes to lower q. This is consistent with the imidazole block selectively adsorbing to the surface, as shown in Figure 1b. The curves in Figures 1b-1d were calculated using the known atomic compositions of the blocks and assuming a 30 Å thickness for the layers formed by each block, which is consistent with the size of the shift observed in Figure 1a. Thus, these data suggest that the copolymer adsorbs in a monolayer film, and that the blocks form separate layers with the imidazole block adsorbed to the surface. Work involving atomic force microscopy is in progress to further characterize the structure of the adsorbed films.

References:
1.   R. H. Grubbs and W. Tumas, Science 243, 902, 1989.
2.   R. R. Schrock, Acc. Chem. Res., 23, 158, 1990.
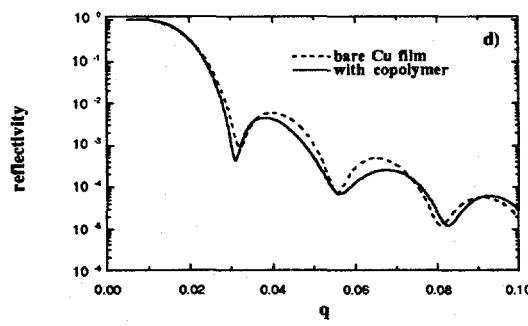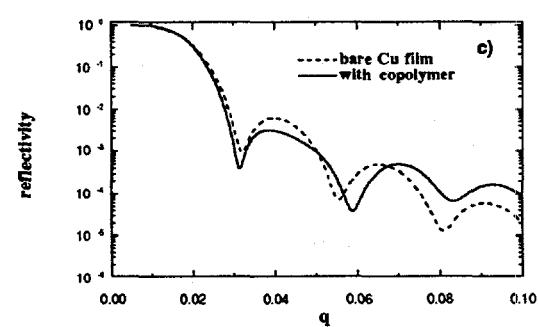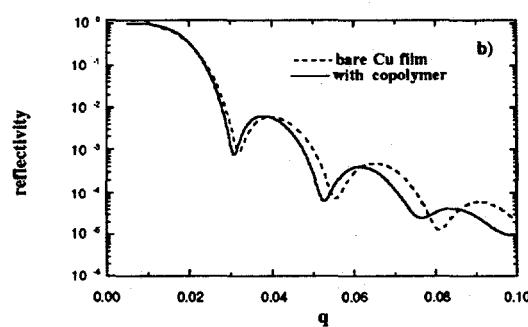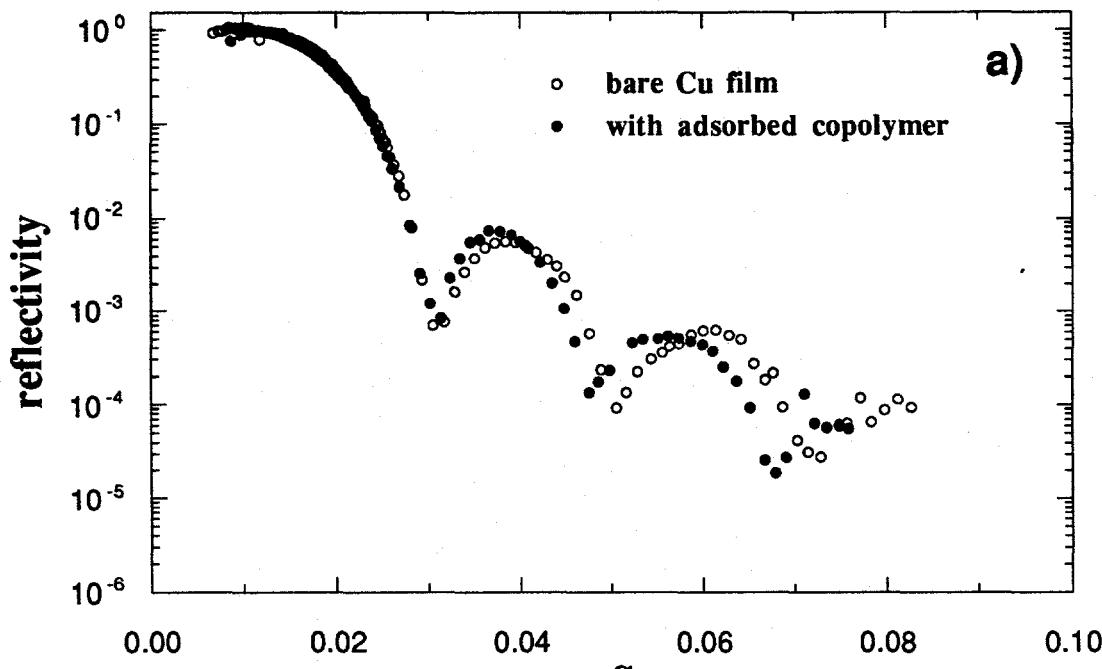
Figure 1. a) Neutron reflectivity for a bare Cu film and after adsorption of the block copolymer. Also shown are calculated reflectivity curves for the cases in which b) the imidazole block selectively adsorbs, c) the amine block selectively adsorbs, and d) the two blocks are randomly mixed in a single layer. These comparisons strongly suggest that the imidazole block selectively adsorbs.