

# Strategies for Covalent Multilayer Growth. 1. Polymer Design and Characterization

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We describe the synthesis and characterization of several maleimide–vinyl ether and maleimide–primary alkene alternating copolymers capable of being incorporated into covalently bound multilayer assemblies. Synthetic control over the monomer substituents allows substantial versatility in the choice of layer formation chemistry and in polymer properties. We report on the copolymerization of substituted allyl-, allyloxy-, vinyl-, and vinyloxy- monomers with a variety of *N*-substituted maleimides. The substituted maleimides were prepared by reaction of maleic anhydride with selected aromatic amines. Polymerization yields are typically in the range of 75–95% consumption of the monomers. <sup>1</sup>H NMR, FTIR, and UV–visible spectroscopies were used to characterize the polymers.

## Introduction

A major effort in the materials community lies in the design, construction, and characterization of novel interfacial thin films, with the goal being the ability to control the resultant macroscopic interface properties. Such materials have been designed and demonstrated for specific target applications, including chemical separations,<sup>1,2</sup> nonlinear optics,<sup>3–5</sup> chemical and biological sensing,<sup>6–9</sup> and heavy-metal analysis and remediation.<sup>10–12</sup> These interfacial materials have been applied to surfaces by spin coating, Langmuir–Blodgett film formation, monolayer self-assembly,<sup>13–16</sup> (SAMs) and metal phosphonate chemistry.<sup>17–19</sup> To extend the utility of interfacial chemistry into new areas and to improve

upon current technology, the development of a range of chemical approaches that are easy to implement and that result in chemically and physically robust materials will be required. We report here on the synthesis and characterization of several alternating copolymers that can be used for layered interface growth. The chemical identity of the side groups of these alternating copolymers renders them capable of discrete layer growth, where the interlayer linkages are covalent. In addition to having control over the interlayer linking chemistry, we can also demonstrate control over the resulting properties of the interface through the judicious choice of maleimide monomer functionality.

The primary point of the work we present here is the demonstration of two distinct levels of synthetic and structural control we exercise over the properties of alternating copolymers. We design alternating copolymers with specific pendant side groups to gain explicit control over the way in which individual polymer layers can be assembled or cross-linked into multilayers. The functionality incorporated into the polymers allows control over the macroscopic properties of the resulting interface.

We report here on the synthesis of polymers capable of covalent interlayer attachment. Because of the number of different functionalities we use in achieving this goal, we report in this paper on the synthesis and characterization of the polymers that comprise the individual layers. The work we present here is intended to demonstrate the structural control and versatility of selected alternating copolymer systems. The chemistry we use to synthesize the polymers is based on established maleimide–vinyl ether alternating copolymerization and we demonstrate here that vinyl and vinyl ether monomers can be used with equal success. These polymers are robust and afford substantial control over their properties through the identity of the monomer

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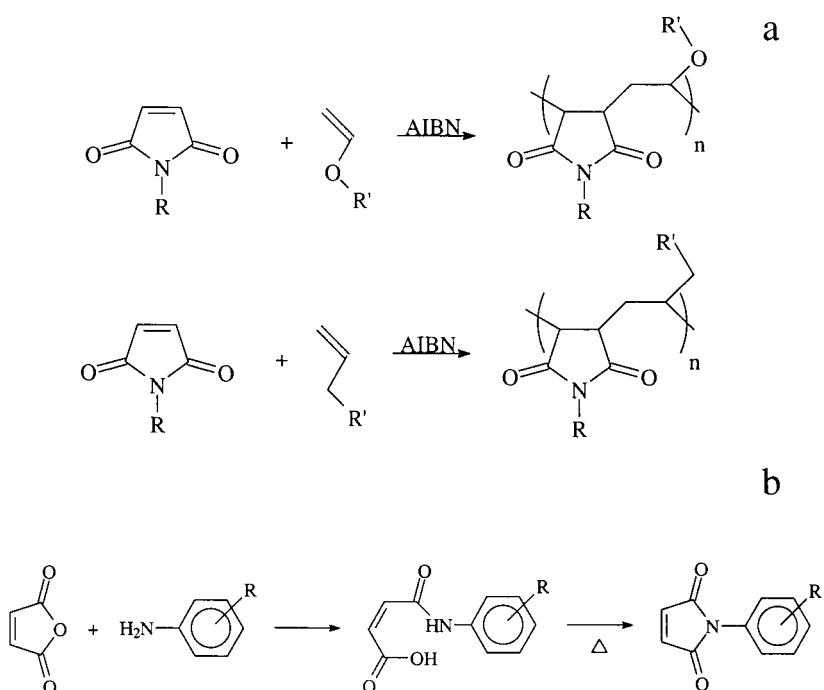
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**Scheme 1. (a) Synthetic Route for Polymerization of Maleimide and Vinyl Ether Monomers (Top) and for Maleimide and Vinyl Monomers (Bottom). Both Reactions Are Initiated with AIBN. (b) Reaction of Maleic Anhydride with an Aromatic Amine To Produce the Maleamic Acid, Followed by Ring Closure to the Maleimide**



substituents. We use vinyl and vinyl ether monomers possessing terminal functionalities capable of participating in amide, ester, ether, urea, and urethane formation chemistry. We report the assembly of these polymers into discrete multilayer structures in the accompanying paper.<sup>20</sup> A portion of this work is dedicated to the synthesis of substituted maleimide monomers because these moieties influence the properties of the bulk polymer significantly.

## Experimental Section

We have designed two categories of monomers and polymers that we use and build upon the maleimide–vinyl ether polymerization chemistry reported previously by our group.<sup>21–23</sup>

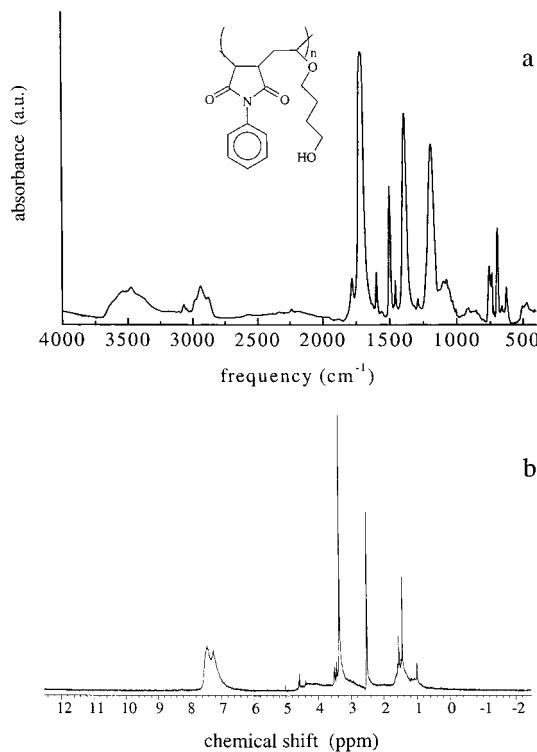
**Syntheses.** Alternating copolymers were prepared by radical polymerization of the various monomer units as indicated in Scheme 1a. In the first group of syntheses, substituted maleimide monomer units are copolymerized with a variety of vinyl and vinyl ether comonomers possessing functionalities capable of participating in several different interlayer linkage schemes.<sup>20</sup> In the second group of syntheses, the functional groups of the maleimide moiety are capable of participating in interlayer linkage chemistry. These substituted maleimides are copolymerized with the ethyl vinyl ether-2-diisopropylphosphonate (VEP) to form a polymer that is also capable of participating in ionic interlayer linking chemistry. For this type of multilayer growth, control over the extent of ionic bonding within these materials is determined by stoichiometric deprotection chemistry<sup>24,25</sup> and can potentially be used to mediate (ionic) conductivity in these materials.

**Maleimide Monomer Preparation.** The maleimide monomers were prepared by reacting maleic anhydride with a substituted aniline. This reaction results in the formation of the corresponding maleamic acid with typical yield of >95% for all monomers reported here (Scheme 1b). Cyclization of the maleamic acid is accomplished by reaction with sodium acetate in acetic anhydride at 70 °C for 2–3 h (Scheme 1b). Typical yield for the ring-closing reaction is >75%. After ring closure, the maleimide monomers are collected from ice-cold water with stirring, followed by filtration and rinsing with cold water. Ring closure was confirmed by the absence of a carboxylic acid proton in the <sup>1</sup>H NMR spectrum. The resulting substituted maleimide is used in copolymer preparation. Substituted vinyl and vinyl ether monomer were available commercially (Aldrich), except ethyl vinyl ether diisopropylphosphonate, which was prepared as described elsewhere.<sup>24</sup>

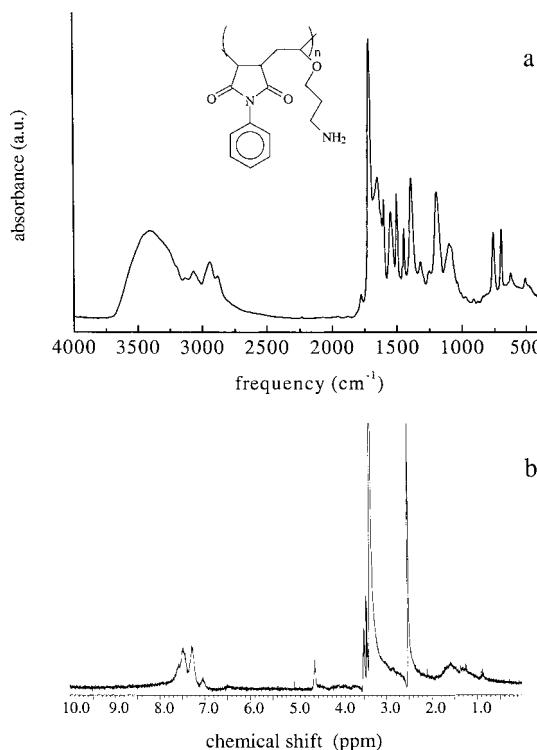
Copolymerization of the monomer units (Scheme 1a) was performed according to the following procedures unless otherwise noted. The constituent monomers were dissolved in chloroform and 10–25 mol % of the radical initiator 2,2'-azobisisobutyronitrile (AIBN) was added to the solution. The reaction mixtures were refluxed with stirring at ≈60 °C for 2–24 h, as determined by observation of a change in solution viscosity or, in the case of the *N*-phenylmaleimide acrylic acid polymer, a white suspension/precipitate was obvious after about 2 h and the yield was ≈95%. Reactions were carried out under an argon atmosphere. Upon completion of the reaction, excess solvent was removed by rotary evaporation and the resulting solution was diluted with hexanes and stirred for ≈30 min to separate residual monomer from the polymer product. The resulting polymer was collected by filtration, air-dried, and characterized by UV-visible, FTIR, and <sup>1</sup>H NMR. Purification of the polymers was achieved by redissolving the product in a small amount of chloroform and collection from ether or hexane once or twice as necessary.

**Poly(*N*-phenylmaleimide–1-vinyloxy-4-butanol).** Poly(*N*-phenylmaleimide–1-vinyloxy-4-butanol) (poly(NPM–VOB), 1, Figure 1 inset) was prepared by reacting equimolar amounts of *N*-phenylmaleimide with 1-vinyloxy-4-butanol in the presence of the initiator. Typical yield for this polymerization is

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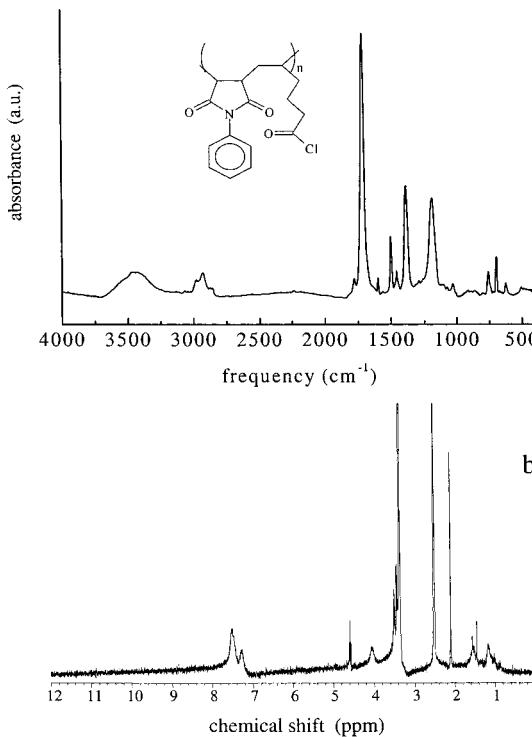
**Figure 1.** Inset: Structure of poly(NPM-VOB). (a) IR spectrum of poly(NPM-VOB). (b)  $^1\text{H}$  NMR spectrum of poly(NPM-VOB).



**Figure 2.** Inset: Structure of poly(NPM-APVE). (a) IR spectrum of poly(NPM-APVE). (b)  $^1\text{H}$  NMR spectrum of poly(NPM-APVE).

≈80%. Purification of the product was accomplished by dissolution in chloroform and collection from hexane.

**Poly(N-phenylmaleimide-3-aminopropyl-1-vinyl ether).** Poly(N-phenylmaleimide-3-aminopropyl-1-vinyl ether) (poly(NPM-APVE), **2**, Figure 2 inset) was prepared by reacting equimolar amounts of *N*-phenylmaleimide and 3-aminopropyl-



**Figure 3.** Inset: Structure of poly(NPM-4-PC). (a) IR spectrum of poly(NPM-4-PC). (b)  $^1\text{H}$  NMR spectrum of poly(NPM-4-PC).

1-vinyl ether in chloroform in the presence of AIBN. Reaction procedures and conditions are the same as those reported above. Typical yield for this polymerization is ≈75%.

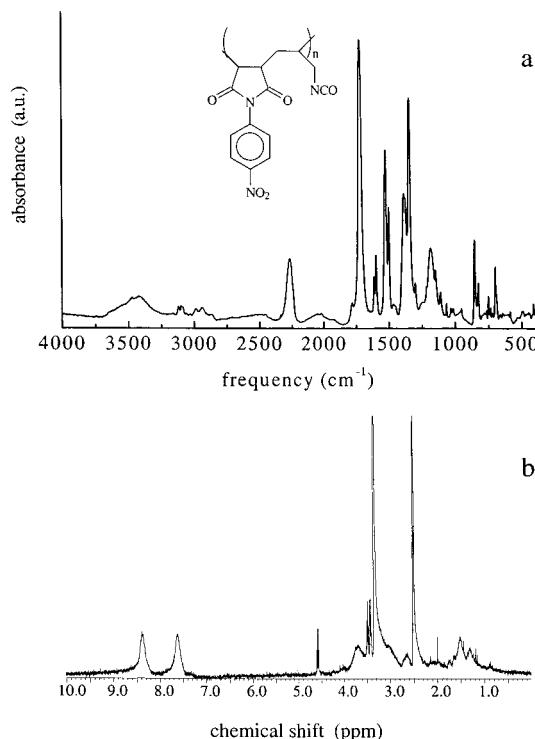
**Poly(N-phenylmaleimide-4-pentenoyl chloride).** Poly(*N*-phenylmaleimide-4-pentenoyl chloride) (poly(NPM-4PC), **3**, Figure 3 inset) was prepared by reacting equimolar amounts of *N*-phenylmaleimide and 4-pentenoyl chloride in chloroform in the presence of AIBN. Reaction procedures and conditions are the same as those reported above. Typical yield for this polymerization is 50% with 10 mol % AIBN initiator and >85% with 20 mol % AIBN. Polymer purification was accomplished by redissolving the product in a small amount of chloroform and collecting from hexane. The polymer possesses acid or acid chloride side groups and the spectroscopic data do not show evidence for hydrolysis of the acid chloride group even after air-drying the product for extended periods.

**Poly(4-nitrophenylmaleimide-allylisocyanate).** Poly(4-nitrophenylmaleimide-allylisocyanate) (poly(4NAI), **4**, Figure 4 inset) was prepared by reacting equimolar amounts of 4-nitrophenylmaleimide and allylisocyanate monomers in chloroform in the presence of AIBN initiator. Reaction conditions and procedures are the same as those reported above, except the reaction time required for this polymerization was 12–18 h. Typical yield for this polymerization is ≈80%.

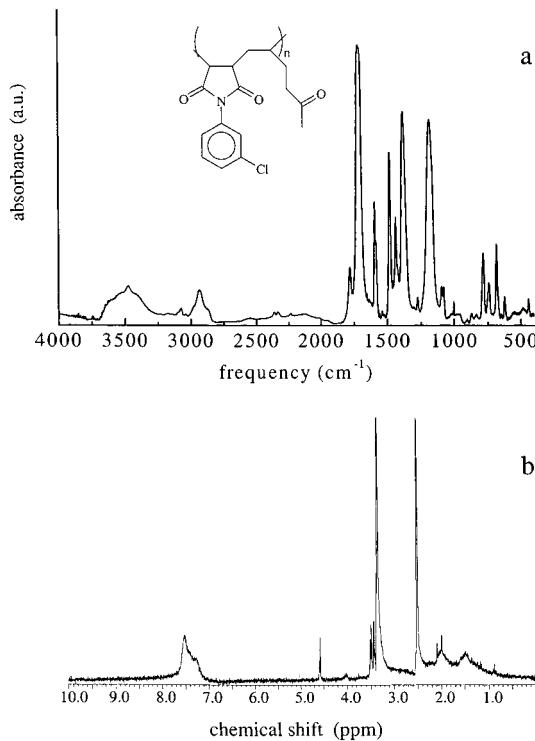
**Poly(3-chlorophenylmaleimide and 5-hex-2-one).** Poly(3-chlorophenylmaleimide and 5-hex-2-one) (poly(3CPM-hex), **5**, Figure 5 inset) was prepared by reacting equimolar amounts of 3-chlorophenylmaleimide and 5-hex-2-one in chloroform in the presence of AIBN (20 mol %). Reaction conditions were the same as those reported above. Typical yield for this polymerization is ≈50%.

**Poly(1-maleimidopyrene and 3-aminopropyl-1-vinyl ether).** Poly(1-maleimidopyrene and 3-aminopropyl-1-vinyl ether) (poly(MP-APVE), **6**, Figure 6 inset) was prepared by dissolving equimolar amounts of both monomers in chloroform using AIBN as initiator (10 mol %). Reaction conditions were the same as those reported above. Typical yield for this polymerization is 90%.

**Poly(4-hydroxyphenylmaleimide-vinyl ether diisopropylphosphonate).** Poly(4-hydroxyphenylmaleimide-vinyl ether diisopropylphosphonate) (poly(4-HPM-VEP), **7**,



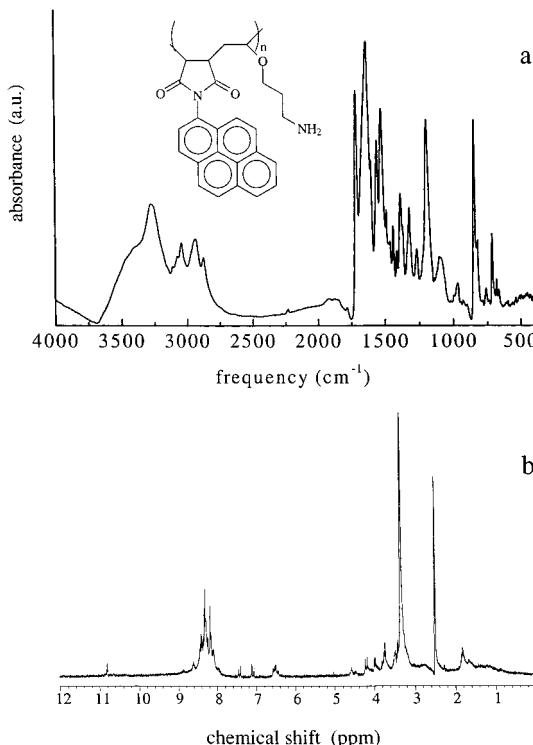
**Figure 4.** Inset: Structure of poly(4NAI). (a) IR spectrum of poly(4NAI). (b)  $^1\text{H}$  NMR spectrum of poly(4NAI).



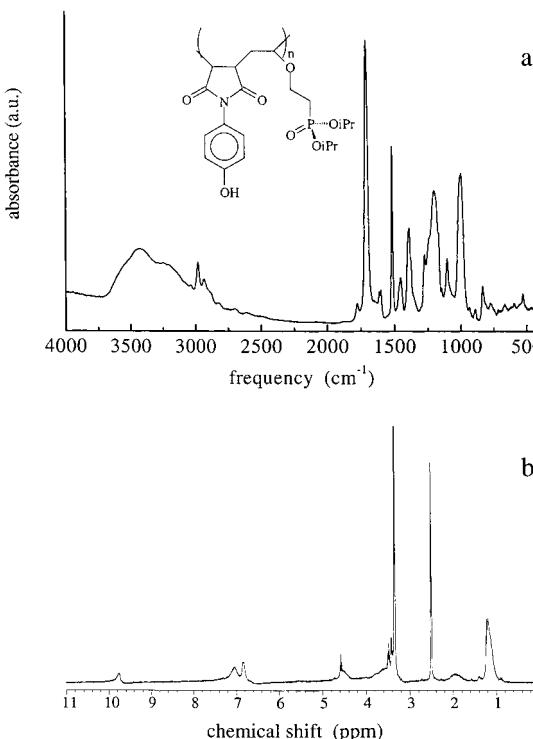
**Figure 5.** Inset: Structure of poly(3CPM-hex). (a) IR spectrum of poly(3CPM-hex). (b)  $^1\text{H}$  NMR spectrum of poly(3CPM-hex).

Figure 7 inset) was prepared by reaction of equimolar amounts of 4-hydroxyphenylmaleimide and vinyl ether diisopropylphosphonate in chloroform, with the addition of AIBN initiator (10 mol %). Typical yield for this polymerization is 75%.

The reactive functionalities introduced into these alternating copolymers makes the resulting materials amenable to a variety of deposition strategies where interlayer linking chemistry can be accomplished by the formation of amide,



**Figure 6.** Inset: Structure of poly(MP-AVE). (a) IR spectrum of poly(MP-AVE). (b)  $^1\text{H}$  NMR spectrum of poly(MP-AVE).



**Figure 7.** Inset: Structure of poly(4-HPM-VEP). (a) IR spectrum of poly(4-HPM-VEP). (b)  $^1\text{H}$  NMR spectrum of poly(4-HPM-VEP).

ester, ether, urea, or urethane functionalities. The functionalized maleimide monomers employed in this work were prepared in-house as reported previously,<sup>26</sup> except *N*-phenylmaleimide, which is available commercially, and was used after recrystallization from absolute ethanol. The reaction schemes for substrate preparation and multilayer assembly

are presented and discussed more extensively in the accompanying paper.<sup>20</sup>

## Results and Discussion

The primary goal of this paper is to report the synthesis and characterization of several alternating copolymers that can be used as layer constituents in the construction of discretely layered interfacial structures. We have synthesized and characterized an extensive library of these compounds and report on a representative selection of seven alternating copolymers here. The structural versatility of the polymers we report here allows us to achieve control over the identity of the reactive polymer side group used in covalent interlayer linkage formation. We also have control over polymer properties by maleimide substitution to incorporate a variety of functional groups that can be used to determine the properties of the polymer matrix. The alternating copolymer structural motif of these materials removes the substantial structural variability associated with random block copolymers and thus affords control over the properties of the polymer and resulting interface.<sup>22</sup>

For all of the polymers, <sup>1</sup>H NMR and FTIR show no evidence of unreacted C=C–H groups, indicating that separation of the monomer reactants from the polymer product was essentially complete. The IR data exhibit no bands for the vinyl ether C=C stretch in the 1660–1610-cm<sup>−1</sup> region nor any =C–H wagging resonance in the 900–1000-cm<sup>−1</sup> region. Previous GPC results for polymers prepared under similar conditions indicated molecular weights of approximately  $M_w = 10800$ .

**Poly(NPM–VOB).** The infrared spectrum of poly(NPM–VOB) contains several characteristic bands that are useful to the structural characterization of this polymer (Figure 1a). First are the aromatic methylene stretches associated with the *N*-phenyl ring between 3000 and 3100 cm<sup>−1</sup>. The aliphatic CH<sub>2</sub> stretches between 2850 and 2950 cm<sup>−1</sup> are associated with the butyl group and the band centered around 3475 cm<sup>−1</sup> is characteristic of hydroxyl stretching. The width of this band is indicative of intermolecular hydrogen bonding within this polymer.<sup>27</sup> There are two carbonyl stretches, the first centered at 1775 cm<sup>−1</sup> and the second at  $\approx 1710$  cm<sup>−1</sup>. This spectral signature is characteristic of the presence of the maleimide groups and is evident in all of the polymers we report here. The band at 1775 cm<sup>−1</sup> is associated with the symmetric C=O stretch and the band at 1710 cm<sup>−1</sup> is associated with the asymmetric C=O stretch in the succinimide moiety. We also observe the characteristic C=C stretching modes of the phenyl ring at 1597, 1500, and 1457 cm<sup>−1</sup> and out-of-plane ring bending at 692 cm<sup>−1</sup>.<sup>27</sup> The band centered at 1387 cm<sup>−1</sup> has been assigned to the C–N bond of the tertiary aromatic amine (aniline).<sup>27</sup> This band is centered at 1387 cm<sup>−1</sup> rather than the expected 1360 cm<sup>−1</sup> due to resonance stabilization of the amine group with the phenyl ring as well as the presence of the succinimide carbonyl functionalities. The 1189-cm<sup>−1</sup> band has been

assigned to the maleimide C–N–C stretch.<sup>28</sup> Because C–O–C stretches also occur in this region, it is possible that the intensity of this band is the result of overlap of the C–N–C and C–O–C vibrations. This is likely the case based on the noticeably higher intensity of this band in the vinyloxy– copolymers. We hasten to point out, however, that these band intensity comparisons are only qualitative owing to the structural complexity of the samples. The bands at 1073 and 1090 cm<sup>−1</sup> are also associated with the C–O–C stretch. The bands at 755 and 734 cm<sup>−1</sup> have been assigned to the C–N symmetric stretching modes.

<sup>1</sup>H NMR spectroscopy has also been useful in characterizing the polymers we report here. An important indicator of the polymerization process is the disappearance of C=C–H bands of both monomers ( $\delta = 7.1$  ppm for the maleimides and  $\delta = 6.2, 3.95$ , and 4.05 ppm for the protons adjacent to the ether oxygen and the two terminal protons of 1-vinyloxy-4-butanol, respectively), consistent with essentially complete separation of the polymer product from the monomers (Figure 1b). We see no evidence of homopolymerization of any monomers. Extensive overlap and broadened peaks in some regions of the spectra makes unequivocal peak assignment impossible, particularly for aliphatic methylene groups. We observe the protons of the NPM aromatic ring at  $\delta = 7.2$ –7.6 ppm. The butyl protons adjacent to the hydroxyl oxygen are found at  $\delta = 4.2$ –4.6 ppm and both the aliphatic protons of the butyl group and the bridging protons between the maleimide and the vinyloxy– groups are seen as a broad resonance between  $\delta = 1.0$  and  $\delta = 1.6$  ppm. The succinimide protons are seen at  $\delta = 3.3$  ppm and the multiplet feature at  $\delta = 3.6$  ppm is assigned to the methine protons adjacent to the ether oxygen. The alcoholic proton is not seen in the spectrum because of facile proton exchange.

**Poly(NPM–APVE).** The FTIR spectrum of this polymer reveals several characteristic bands in addition to those seen for all of the polymers we report here, as noted above (Figure 2a). The band centered at 3408 cm<sup>−1</sup> has been assigned to the associated NH<sub>2</sub> stretches of the amino group. We also see the NH bending mode resonance at 1648 cm<sup>−1</sup>.

The <sup>1</sup>H NMR spectrum of poly(NPM–APVE) (Figure 2b) contains the expected features such as the C–H resonances associated with the phenyl ring between  $\delta = 7.2$  and  $\delta = 7.6$  ppm. The aliphatic methylene bands are contained in the broad resonance between  $\delta = 1.2$  and  $\delta = 1.8$  ppm, succinimide protons are found at  $\delta = 3.2$  ppm, and the propyl methylene protons adjacent to the ether oxygen are at  $\delta = 4.45$  ppm. The proton exchange rate for the amino proton precludes observation of this resonance, analogous to the hydroxyl proton resonance for poly(NPM–VOB).

**Poly(NPM–4–PC).** Much of the vibrational and electronic spectral signature of poly(NPM–4–PC) is the same as that of the other copolymers we report here (Figure 3a). We also see the characteristic aliphatic methylene stretches associated with the pentenyl– portion of the polymer. There are several additional features associated with the acid chloride moiety in this

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polymer. For poly(NPM-4-PC), the  $1189\text{-cm}^{-1}$  band is weaker than that seen for poly(NPM-AVPE) because there are only the C-N-C stretches for poly(NPM-4-PC). The absence of contributions from the vinyloxy C-O-C band accounts for the attenuation of this feature. For poly(NPM-4-PC) there is a resonance at  $\approx 3450\text{ cm}^{-1}$ , suggesting intermolecular hydrogen bonding of the hydrolyzed acid chloride functionality. The carbonyl stretching region is characterized by bands associated with the succinimide, the acid chloride, and some carboxylic acid (hydrolyzed acid chloride). The  $^1\text{H}$  NMR spectrum of poly(NPM-4-PC) (Figure 3b) shows no evidence of hydrolysis of the acid chloride to the acid even after extensive periods of atmospheric exposure, and this finding is not consistent, at face value with the IR spectra. These two pieces of information suggest that the FTIR (KBr crystals) sample may have been wet. Aromatic, aliphatic, and succinimide protons occur in the same region as seen for the other polymers.

**Poly(4-NAI).** The IR band of the isocyanate group at the  $2265\text{-cm}^{-1}$  region is characteristic of this polymer (Figure 4a). We also observe the characteristic aromatic and aliphatic methylene stretches and the succinimide C=O stretches at  $1775$  and  $1720\text{ cm}^{-1}$ . In addition, we observe the asymmetric  $\text{ArNO}_2$  stretch at  $1523\text{ cm}^{-1}$  and the symmetric  $\text{ArNO}_2$  stretch at  $1347\text{ cm}^{-1}$ . We note the lower frequencies of the phenyl ring as well as the splitting of some of these bands into doublets due to ring substitution. The  $854\text{-cm}^{-1}$  band is associated with the aromatic C-N stretch of the nitro group. We observe a symmetric splitting of the aromatic protons peak in the  $^1\text{H}$  NMR spectrum of poly(4-NPM-AI) which is expected because of the presence of the  $\text{NO}_2$  group in the 4-position. Para substitution of the phenylmaleimide leads to equivalence of the two protons adjacent to the substituent, leading to one peak for both protons (Figure 4b). The resonance for the methylene group protons adjacent to the isocyanate group is in the same region as the bridging methine and succinimide protons,  $\delta = 3.15\text{--}3.5\text{ ppm}$ .

**Poly(3CPM-hex).** For this polymer, the IR band centered at  $3475\text{ cm}^{-1}$  is likely an overtone of the carbonyl band (Figure 5a). We make this assignment because of the absence of amino or hydroxyl functionality in this polymer. We observe characteristic aromatic and aliphatic methylene stretches between  $2850$  and  $3100\text{ cm}^{-1}$  and maleimide C=O stretches are seen at  $1780$  and  $1715\text{ cm}^{-1}$ . The broadened carbonyl band at  $1715\text{ cm}^{-1}$  is the result of spectral overlap between the maleimide C=O stretch and the ketone C=O stretch. Aromatic C=C stretches are at slightly lower frequencies than those for *N*-phenylmaleimide because of the presence of the Cl- substitution at the 3-position. The C-N stretch of the tertiary amine is seen at  $1382\text{ cm}^{-1}$  for poly(3CPM-hex).

$^1\text{H}$  NMR spectroscopy of poly(3CPM-hex) (Figure 5b) shows the expected aromatic protons at  $\delta = 7.2\text{--}7.6\text{ ppm}$ . The aliphatic methylene resonances are seen at  $\delta = 1.5\text{ ppm}$  with the methyl protons adjacent to the C=O functionality occurring at  $\delta = 2.05\text{ ppm}$ . The succinimide resonances are found at  $\delta = 3.3\text{ ppm}$ , consistent with the NMR spectra of the other polymers we report here.

**Poly(MP-APVE).** The IR spectrum of poly(MP-APVE) contains several features unique to this polymer (Figure 6a). We observe the  $-\text{NH}_2$  stretch at  $3277\text{ cm}^{-1}$ . The position of this band suggests that the  $\text{NH}_2$  groups exist primarily in the associated form. We note the presence of a high-frequency shoulder on the  $-\text{NH}_2$  band, indicating some free  $-\text{NH}_2$  groups. The aromatic C-H stretches are consistent with the pyrenyl ring structure. We also observe the characteristic maleimide C=O bands and a broad band at  $1632\text{ cm}^{-1}$ , which we assign to the N-H bending mode(s). This band could also be present because of some amount of maleimide ring opening during polymerization. We observe a relatively strong band at  $1194\text{ cm}^{-1}$  that we attribute to the presence of both the C-O-C and C-N-C functionalities in the polymer. The intense band at  $844\text{ cm}^{-1}$  has been assigned to the out-of-plane C-H bending modes of the polynuclear aromatic moiety.<sup>27</sup>

Examination of the  $^1\text{H}$  NMR spectrum (Figure 6b) reveals a complex spectral signature for the aromatic proton resonances at  $\delta = 8.0\text{--}8.8\text{ ppm}$ , consistent with the ring structure of the pyrene moiety. We observe the methylene and succinimide protons at the same chemical shifts as those seen for the other polymers we report here. There is a small resonance at  $\delta = 10.8\text{ ppm}$ , suggesting some succinimide ring opening occurring either as the result of incomplete ring closure of the monomer or as a result of the polymerization reaction. Given the integration of this band for 0.3 protons, it appears that ring opening, if it is proceeding, is not a dominant process. As a point of reference, the  $^1\text{H}$  NMR spectrum of the pyrene maleimide monomer shows no evidence of incomplete ring closure.

**Poly(4-HPM-VEP).** The IR spectrum of this polymer shows intermolecular hydrogen bonding on the basis of the  $-\text{OH}$  stretching resonance of the phenol hydroxyl group at  $\approx 3430\text{ cm}^{-1}$  (Figure 7a). The strength and spectral width of this band obscures the aromatic methylene stretches. We note the presence of the maleimide C=O stretches. This polymer exhibits several IR bands that are characteristic of phosphate or phosphonate. The phosphoester P=O stretch is superimposed on the phenol ring C-O stretch at  $\approx 1200\text{ cm}^{-1}$ . We also see the P-O-C stretch at  $995\text{ cm}^{-1}$ . This band is important in structural assignment because it demonstrates the absence of the oxidation of the phosphoester groups to the corresponding phosphorus acid. We deliberately keep the phosphonate groups protected during multilayer assembly so they can be used for metal ion sequestration once the multilayer structure is formed.<sup>29</sup> The  $^1\text{H}$  NMR spectrum (Figure 7b) of this polymer reveals an aromatic resonance centered at  $\approx 7.0\text{ ppm}$ . Again, we observe the splitting of this peak due to the presence of the *p*-hydroxyl group, where the splitting is a result of ring substitution at the 4-position. We also observe a peak centered at  $\approx 9.8\text{ ppm}$ , which may be due to ring opening or, possibly, to hydrolysis of some of the phosphonate groups. However, either of these processes contribute negligibly because of the integration of the peak for  $\approx 0.3$  relative to the other peaks. The spectral signature between 1.0 and 4.6 ppm has been assigned to the various contributions of the

vinyl ether phosphonate resonances as reported previously.<sup>24</sup>

### Conclusions

We have reported on the synthesis and characterization of a family of alternating copolymers possessing a variety of functional side groups capable of forming covalent linkages for controlled multilayer assembly. Some of the polymers we have prepared are capable of participating in either ionic or covalent interlayer linking chemistry. We have demonstrated the ability to

introduce a variety of functional groups into the matrix through substitution of the maleimide *N*-substituent. This substantial structural versatility is put to use in a companion paper and we anticipate using these polymers in the design of chemically selective interfaces.

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