Bis(trifluoromethyl)carbinol-Substituted Polynorbornenes: Dissolution Behavior

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ABSTRACT: Alicyclic polymers, such as substituted polynorbornene (PNB), are expected to be one potential material solution for providing transparent photoresist polymer resins for photolithography at 193 and 157 nm wavelengths. In this work, the dissolution behavior of bis(trifluoromethyl)carbinol-substituted polynorbornene (HFAPNB) in aqueous alkaline solutions as a function of polymer molecular weight is explored. Surprisingly, it was found that the dissolution rate of bis(trifluoromethyl)carbinol-substituted polynorbornene increased with increasing molecular weight over the range from approximately 10,000 to 100,000 M_w. Experimental results show that this polymer displays strong hydrogen bonding in the solid film form and that such hydrogen bonding is disrupted as the polymer molecular weight is increased. On the basis of this evidence, an explanation for this unusual dissolution behavior based upon disruption of hydrogen bonding is presented.

Introduction

As feature sizes in semiconductor devices continue to shrink below 100 nm, there is a tremendous need to develop future lithographic technologies that can pattern features at these diminishing size scales.[1−3] Projection optical lithography continues to be the workhorse for semiconductor fabrication, and one of the primary methods for increasing the resolution of such projection stepper and scanner tools is to reduce the wavelength of light used to expose patterns. Recently deep ultraviolet (DUV) lithography at 248 nm has become a primary technology for critical level patterning, and 193 nm lithography is currently growing in use. One of the crucial challenges for each new lithographic technology generation is the development of photoresist materials that can be used at each new exposure wavelength.[1,4,5] As the wavelength is decreased, typically one finds that the polymer resins used for the previous exposure tools at higher wavelengths are too strongly absorbing to be used at lower exposure wavelengths.[1,4,5] For example, when the exposure wavelength was reduced from 365 to 248 nm, phenolic novolac resins were replaced by polymers such as poly(hydroxystyrene) (PHOST).[6,7] Development of 193 nm lithography has required that PHOST be replaced by other polymers that avoid aromatic rings in order to provide sufficient transparency at the exposure wavelength for acceptable lithography.[8,9] However, designing new polymer resins for photoresists is not a trivial task since the polymer resin must satisfy a variety of challenging and sometimes conflicting requirements. For example, the polymer resin is responsible for providing the plasma etch resistance of the photoresist, which is critically important if the resist is to be successfully used to pattern underlying layers. The use of aromatic rings in the polymer typically benefits the etch resistance,[10−13] but aromatic groups are generally detrimental to the transparency of the polymer in the deep ultraviolet.[14] The polymer must also possess a functionality, typically a group that provides solubility in aqueous alkaline developers, that can allow for the formation of a relief image in the material. In the case of modern chemically amplified resists this is commonly achieved by the presence of hydroxyl groups on the polymer that can be protected to render the polymer initially insoluble in aqueous base developers and later deprotected thermally upon exposure to photogenerated acid to yield a soluble material. Potential polymer matrix resins for 193 nm lithography include (meth)acrylates, norbornene−maleic anhydride copolymers, norbornene−maleic anhydride−(meth)acrylate copolymers, and vinyl addition norbornene polymers. The base-soluble group of choice has been the protected carboxylic acid. However, incorporation of a pendant carboxylic acid functionality in the vinyl addition norbornene polymers yields matrix resins that can exhibit extremely fast dissolution or swelling in aqueous-based developer depending on the composition, neither of which is desirable.[15] It is proposed that 157 nm lithography will serve as the next optical lithography technology after the incoming 193 nm generation. At these extremely low ultraviolet wavelengths, the design of transparent polymers is an even more difficult problem due to the tendency for a wide variety of organic groups to absorb strongly in this wavelength range.[1,4,5] The incorporation of fluorine into polymer resins has been identified as one promising route to the production of polymers that are sufficiently transparent to serve as 157 nm resist resins.[16] In addition to the transparency of the polymer backbone, significant work has been required in identifying appropriate base-soluble functional groups. One class of promising transparent base-soluble functional groups are the bis(trifluoromethyl)carbinols. These groups

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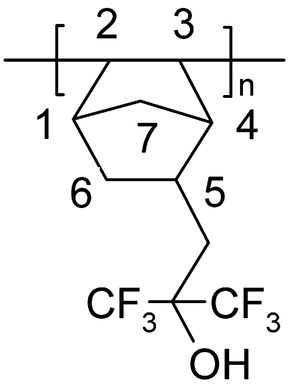

Figure 1. Representative structure of the bis(trifluoromethyl)carbinol-substituted polynorbornene (HFAPNB) used in this work.

have been shown to offer an ideal combination of transparency and acidity for use in 157 nm resist materials.[17]

A promising set of candidate matrix resins that may meet these demanding requirements for a transparent polymer, inclusion of a base soluble functional group, and good etch resistance for 157 nm lithography are functionalized polynorbornenes (PNBs) containing pendant bis-trifluoromethyl carbinols (see Figure 1).[18] Polynorbornenes, which are currently being explored for resist applications at 193 nm, offer a transparent alicyclic polymer structure that has improved plasma etch resistance as compared to other potential resin polymers such as (meth)acrylates.[10,13] Thus, one of the goals of this work has been to explore the use of such substituted polynorbornenes for use in 157 nm photoresists.

One of the most important characteristics of a polymer resin in terms of its suitability for use in photoresist applications is its dissolution behavior. Resist polymers must dissolve cleanly into an appropriate developer without forming a gel or swelling to any significant degree. It is also critical that resist resins which exhibit a controlled and constant dissolution rate can be manufactured in order to minimize batch to batch resist performance variation. Such control over polymer dissolution behavior is commonly achieved by methods such as blending various molecular weight polymer fractions together to achieve a composite resin with optimized performance.[19] Therefore, to gain a better understanding of the basic polymer resin behavior and to aid in polymer design and resist formulation, a detailed investigation of the dissolution behavior of bis(trifluoromethyl)carbinol-substituted polynorbornene is reported.

Experimental Section

Materials. The monomer α,α-bis(trifluoromethyl)bicyclo[2.2.1]hept-5-ene-2-ethanol (HFANB) has been prepared previously.[18] The vinyl addition norbornene polymers investigated herein were provided by Promerus LLC and were synthesized using cationic palladium catalysts as described previously.[20−22] The polymerizations involving palladium used increasing amounts of hexene to lower the molecular weight.

Gel Permeation Chromotagraphy. Polymer molecular weights were analyzed by gel permeation chromatography (GPC) using a Waters model 590 GPC equipped with four Ultrastyragel columns in tetrahydrofuran at 50 °C. The molecular weight values reported here were determined using a polystyrene calibration curve. The weight-average molecular weight (M_w) for the HFAPNB samples varied from 5000 to 474 000, with polydispersities ranging from 2 to 9.21 (see Table 1).

Table 1. Molecular Weight and Polydispersity Data for the Bis(trifuoromethyl)carbinol-Substituted Polynorbornene (HFAPNB) Polymers Used in This Work

sample no.	M_w (g/mol)	PDI	sample no.	M_w (g/mol)	PDI
1	4 750	2.05	7	23 900	4.04
2	5 670	1.91	8	39 600	4.61
3	8 550	2.27	9	71 800	2.43
4	9 430	2.73	10	94 200	9.21
5	11 700	3.04	11	182 100	2.43
6	16 300	3.53	12	474 400	3.70

General Polymer Film Preparation Methods. The HFAPNB polymers are soluble in a variety of common film casting solvents. In this work, propylene glycol methyl ether acetate (PGMEA) purchased from Aldrich Chemicals (Aldrich, 98% purity) was used as the casting solvent. Polymer solutions were made by dissolving the appropriate polymer in PGMEA to create 10 wt % polymer solutions that were mixed overnight. Polymer films were prepared by spin casting. Spin coating was performed using a CEE 100 CB spin coat and bake system (Cost Effective Equipment, Brewer Science).

Fourier Transform Infrared Spectroscopy. Fourier transform infrared spectroscopy was performed in transmission mode using a Bruker KLS/088 FTIR. The optics and sample chamber were maintained under vacuum throughout the measurement. Resist solutions containing 10 wt % polymer in PGMEA were spin-coated onto ZnSe crystals at 2000 rpm for 30 s. All films were baked at 130 °C for 90 s and then dried in a vacuum oven overnight at 180 °C to achieve maximum removal of residual casting solvent.

Dissolution Rate Measurements. Polymer films were prepared by spin-coating onto 2 in. ⟨100⟩ silicon wafers (NOVA Electronic Materials). Films were baked using a hot plate at 130 °C for 90 s. The polymer solution concentration and spin speeds were adjusted to achieve an approximate thickness of 1 μm for the coated and baked film. The dissolution rate of HFAPNB films was measured using a custom-made, spectroscopic reflectometer based dissolution rate monitor (DRM).[23,24] For these dissolution experiments, 0.19 N tetramethylammonium hydroxide (TMAH) was used (AZ Electronic Materials). Unless otherwise specified, the dissolution rate cited is measured at 50% remaining film thickness during development in order to eliminate any interfacial effects such as surface inhibition or acceleration.

Wide-Angle X-ray Diffraction (WAXD). Wide-angle X-ray diffraction (WAXD) studies were performed at room temperature using a Philips PW1800 X-ray diffractometer. Copper radiation with a wavelength of 1.54 Å was used with the X-ray source generator tension and current set at 40 kV and 30 mA, respectively.

Polymer films were prepared for various molecular weight HFAPNB samples on Si ⟨100⟩ 2 in. wafers. The spin-coated films were all spun at 500 rpm for 30 s, then 2000 rpm for 90 s, and then soft baked at 130 °C for 90 s. Both types of films were then annealed in a vacuum oven for 24 h at 180 °C.

All samples were scanned continuously with a step size of 0.010° and the intensity measured at each step for 5 s. The raw data are then smoothed using a moving average to obtain the final WAXD patterns for all samples.

Results and Discussion

Figure 2 shows a log−log plot of the dissolution rate of bis(trifluoromethyl)carbinol polynorbornene (HFAPNB) polymer films cast from propylene glycol monomethyl ether acetate (PGMEA) vs molecular weight in 0.19 N aqueous tetramethylammonium hydroxide. At low molecular weights, less than approximately 10 000 M_w, the dissolution rate of the polymer decreases with increasing molecular weight as one might expect. How-

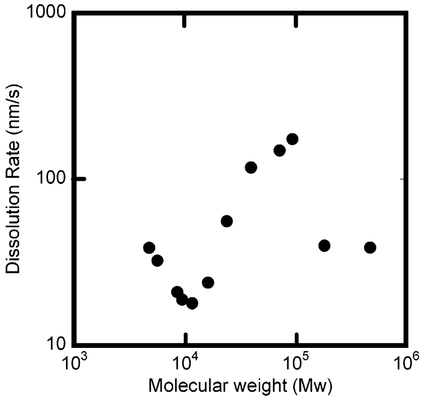

Figure 2. A log−log plot of the dissolution rate behavior of bis(trifluoromethyl)carbinol-substituted polynorbornene films cast from propylene glycol methyl ether acetate solvent in 0.19 N tetramethylammonium hydroxide.

ever, it is observed that the polymer dissolution rate increases with increasing molecular weight over an intermediate molecular weight range from approximately 10 000 M_w to 100 000 M_w. Finally, at higher molecular weights, the dissolution rate again decreases and eventually appears to plateau to a relatively constant value.

The dissolution behavior and dissolution rates of a variety of conventional polymer resins used in photoresists have previously been studied. It is often customary to plot such dissolution rate data on a log−log scale as shown in Figure 2, which generally reveals a linear relationship between the logarithm of the dissolution rate and the logarithm of the polymer molecular weight.[25,26] For common photoresist resins, it has been observed that the slope of such a log−log plot typically varies between approximately −0.3 and −4.[25] For example, the slope for novolac resins has been measured as −3.55,[25] and the slope for poly(hydroxystyrene) or PHOST is −2.3.[27] Recent tests with a fluorinated base-soluble styrenic polymer yielded a slope of −0.55.[27] Figure 2 shows the dissolution rate data obtained for HFAPNB films cast from PGMEA solvents also on such a log−log scale. It is obvious that, except for perhaps in very low molecular weight HFAPNB polymers (less than ~9000 M_w), no such linear decreasing trend with molecular weight is observed. An estimate for the slope of the linear region below 10 000 M_w can be made from the limited number of data points available in that region, and such an analysis yields a slope of approximately −1.05 for the HFAPNB materials studied in this work. Even though the observed trend is not a single linear function in log−log space, the dissolution rate data do follow a systematic trend of decreasing, then increasing, and finally decreasing as a function of molecular weight as described earlier.

A recent publication by Ito and co-workers reports that the dissolution rate of HFAPNB polymers in TMAH developers does not seem to be governed by molecular weight, in contrast to the clear trend observed in Figure 2.[28] This apparent contradiction can be explained, however, since the HFAPNB materials studied by Ito and co-workers were made using a variety of different metal catalysts (including both Pd and Ni materials). As will be discussed later in this paper, the choice of catalyst used in making the HFAPNB is believed to result in different stereochemical conformations for the polymer. The current work shows that this stereochemical conformation and the resulting secondary structure of the polymer greatly influences the dissolution behavior of HFAPNB homopolymers. Thus, the combination of dissolution rate data for HFAPNB materials made using different catalysts made any clear molecular weight dependence difficult to observe in the previous studies.

The atypical increase in dissolution rate with increasing molecular weight for HFAPNB (made using the Pd catalyst) observed in this work was believed to be directly correlated to the polymer molecular weight. However, because of differences in the polydispersity (see Table 1) of the various polymer samples, the influence of polydispersity could not be immediately ruled out. If the varying polydispersity of the samples, as measured by the polydispersity index (PDI = M_w/M_n), listed in Table 1 could be strongly correlated with the dissolution rate, then this unusual behavior could have simply been a manifestation of the differences in the molecular weight distributions of the samples. Linear regression of the logarithm of the dissolution rate vs the logarithm of both the polydispersity index and molecular weight was performed in the molecular weight regime in which the dissolution rate was increasing with increasing molecular weight (data points 5−10, corresponding to M_w between 10^4 and 10^5 in Figure 2). The 99% confidence interval about the slope for the best fit line of the log dissolution rate vs log molecular weight plot was 1.18 ± 1.15, indicating that this slope differed from zero to $p < 0.01$. In other words, the dissolution rate strongly correlates with molecular weight in this region. In contrast, the same correlation of dissolution rate vs PDI in log−log space produced a slope with a 99% confidence interval of −0.012 ± 0.17, where this value of the slope differs from zero to only $p < 0.43$. This means that the observed increase in dissolution rate with molecular weight is not strongly correlated with the polydispersity of the samples. While polydispersity may play some role, the significant difference in the correlation for these two variables clearly indicates that the molecular weight is the most significant variable in Figure 2.

This unusual dissolution behavior observed in the HFAPNB was quite surprising and led us to consider more deeply a variety of factors that could influence the dissolution rate and other properties of polynorbornene resins. The first issue to consider is the detailed stereochemical configuration of the polymer and its potential influence on the polymer behavior. Vinyl addition polymerization of norbornene typically results in a 2,3 exo−exo enchained polynorbornene.[29] Given this, the only remaining structural degree of freedom is the stereochemical orientation of the bridging carbon (carbon 7 in Figure 1). Previous simulations of various stereochemical configurations suggest that pure poly(norbornene) synthesized with a Pd catalyst is comprised mainly of the erythro diisotactic isomer.[30,31] The bridging carbons in this stereoisomer have a completely alternating orientation in the fully extended cis conformation. Two-dimensional NMR studies produce consistent results that suggest this particular catalyst produces a structurally regular isomer.[32]

Previous simulation work also provides useful information regarding the conformational behavior of this particular poly(norbornene) isomer. Because the bulky norbornene backbone groups create such a large rotational energy barrier,[33] it is reasonable to assume that the additional steric hindrance provided by the side

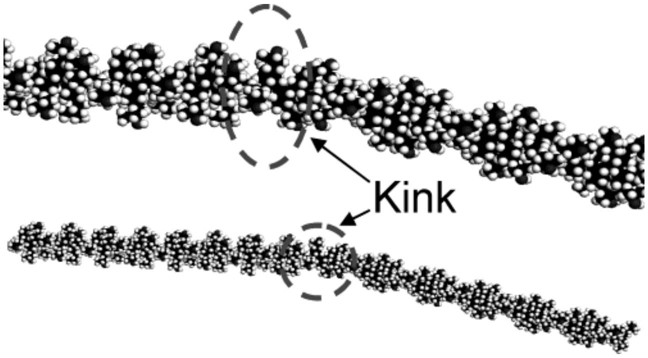

Figure 3. An illustration of bis(trifluoromethyl)carbinol-substituted polynorbornene placed in the helical conformation as observed from previous simulations of unsubstituted polynorbornene (top structure is close up of kink).

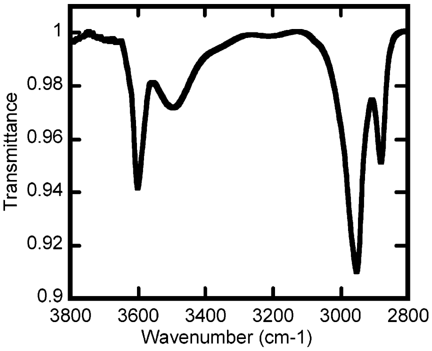

Figure 4. FTIR spectrum for bis(trifluoromethyl)carbinol-substituted polynorbornene homopolymer.

chain has a negligible effect on the backbone conformation. Assuming HFAPNB adopts a conformation similar to the PNB homopolymer suggests a mechanism for the increase in dissolution rate with increasing molecular weight. This stereoregular isomer adopts a helical conformation that is occasionally interrupted by a "kink".[30,31,33] This kink occurs randomly with a probability of less than 1% per repeat unit.[33] This suggests that the dominant polymer conformation at very low molecular weight is helical, which causes the polymer to adopt many of the characteristics of a rigid-rod polymer. More recent simulations indicate that kinks occur due to a reversal of this helical symmetry from left- to right-handed and back again.[34] An idealized illustration of this helix with a single kink, for the HFAPNB studied here, appears in Figure 3. One should note that this helical conformation is actually less regular than the illustration in Figure 3, owing to the flexibility about this low-energy helical angle in the polymer backbone.[30,34]

It was suspected that this unusual secondary structure plays a major role in producing the unusual dissolution rate behavior for polymers made using the catalysts described in this work. Because of the propensity for the polymer to kink as the molecular weight is increased, it was initially hypothesized that one possible explanation for the increasing dissolution rate with molecular weight may be differences in the polymer density introduced by such kinks. These kinks disrupt order and packing of the polymer chains which in turn affects properties such as the density and free volume of the polymer. For example, differences in density could lead to variation in the ability of a polymer chain to remove itself or disentangle from the bulk polymer film during dissolution. Differences in density or free volume may also influence the rate and ability of developer molecules to penetrate into the film and deprotonate the polymer. A variety of polymer density measurements were attempted including quartz crystal microbalance methods and density gradient columns. These measurements indicated that there was in fact minimal change in the polymer density over the molecular weight range of the polymer studied in this work. These results do not rule out small changes in density due to such effects and their potential contribution to the observed dissolution phenomena, but such a dramatic change in dissolution rate was deemed hard to reconcile with such small changes in film density.

It was suspected that a much stronger potential influence on the dissolution rate could be hydrogen bond formation between the bis(trifluoromethyl)carbinol substituent groups on neighboring polymer chains. It is known from prior work on photoresist polymers that the ability to form hydrogen bonds can significantly impact the dissolution rate of polymer resins. Dissolution inhibition through hydrogen bonding has been relatively well established in the case of diazonaphthoquinone (DNQ)−novolac resists.[15,35] The combination of DNQ and novolac polymers is believed to create extensive hydrogen-bonding networks in the polymer which serve to retard the dissolution rate of the material. Inductive cluster polarization is one of the more popular interpretations of the mechanism by which the dissolution inhibition occurs in these materials. The mechanism postulates that the DNQ molecule starts a small string or cluster of hydrogen bonds within the novolac chain and potentially between neighboring chains. The cluster originates with the formation of a hydrogen bond between a DNQ molecule and a novolac segment in the polymer chain. The initial hydroxyl group that is hydrogen bonded then forms hydrogen bonds with the next closest hydroxyl group in the polymer matrix. This process repeats itself to extend the hydrogen-bonding network down the polymer chain or through the polymer matrix some number of repeat units. Dissolution inhibition is then hypothesized to be the result of the increase in $\mathrm{p}K_a$ of the phenolic hydrogen while it participates in the hydrogen-bonding network.[36] Likewise, although attempts were made to produce similar inhibitor additives for PHOST materials, very little success was achieved in developing inhibitors for PHOST. It is believed that this difficulty in developing inhibitors for PHOST materials stems partially from the fact that the hydroxyl groups in PHOST can exhibit much greater spacing than in the novolac case, thus reducing substantially any hydrogen bond network formation.

The propensity for bis(trifluoromethyl)carbinol groups to participate in hydrogen bonding has been reported previously in the literature.[37] Therefore, the hydrogen bonding in the HFAPNB polymers used in this work was studied extensively using transmission FTIR measurements. Figure 4 shows a portion of the FTIR spectrum for a low molecular weight HFAPNB polymer used in this work. The two peaks of most interest in this spectrum occur at approximately 3600 and 3500 cm^{-1}. The 3600 cm^{-1} peak corresponds to the normal position observed for hydroxyl peaks and represents the "free" (non-hydrogen-bonded) OH peak.[37,38] Hydrogen bonding would be expected to result in a spectroscopic shift in the OH peak to lower wavenumbers, and the presence of such a shift in bis(trifluoromethyl)carbinol-substituted polystyrenes has previously been demon-

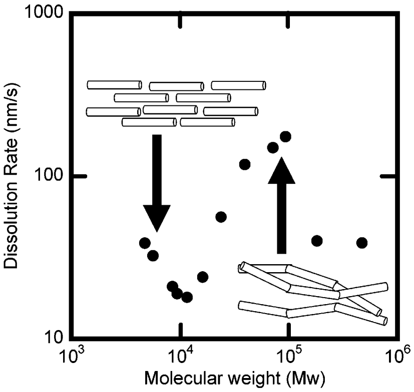

Figure 5. Schematic explanation of HFAPNB dissolution behavior as a function of molecular weight. At low molecular weight, a lack of kinks in the polymer helix allows regular packing of chains that increases intermolecular hydrogen bonding and thus slows dissolution rates. As molecular weight increases, the presence of kinks reduces the chain packing efficiency, disrupts intermolecular order and hydrogen bonding, and results in an increase in the polymer dissolution rate.

strated in the literature.[38] In the case of HFAPNB materials, it is clear that such a hydrogen-bonded OH peak at approximately 3500 cm^{-1} is present. This hydrogen bonding in the polymer must occur between bis(trifluoromethyl)carbinol substituted on adjacent HFAPNB polymer chains. The steric hindrance caused by the fluorines in the bis(trifluoromethyl)carbinol group and the large distances between neighboring carbinol groups on the same polymer chain due to its rigid extended secondary structure make intramolecular hydrogen bonding difficult or impossible.

Our hypothesis is that it is the secondary structure of the metal-catalyzed polynorbornenes studied in this work that is responsible for the unusual dissolution rate behavior due to the disruption of interchain hydrogen bonding in the polymer film as the polymer molecular weight is increased. As the polymer molecular weight increases, the probability of a kink rises dramatically. In fact, at extremely high molecular weight, sufficient kinks will occur to produce essentially random coil conformations in the polymer.[34] These additional kinks as the molecular weight increases prevent the polymer chains from packing as easily, making alignment between groups on neighboring chains difficult and increasing the separation between such groups and thus reducing the ability to form intermolecular hydrogen bonds. This reduction in hydrogen bonding subsequently results in an increase in dissolution rate through either pK_a shifts in the bis(trifluoromethyl)carbinol groups which are responsible for rendering the polymer soluble in aqueous base or other similar effects. Schematically our theory to explain the origin of the increased dissolution rate with increasing molecular weight is seen in Figure 5.

Detailed molecular simulations of poly(norbornenes) have been able to reproduce the wide-angle X-ray diffraction (WAXD) pattern for unsubstituted poly(norbornene). These WAXD patterns contain a split of the amorphous halo which is commonly associated with some level of structural order intermediate between the crystalline and amorphous region.[39] Previous simulations indicate that the low-angle peak in this split is strongly associated with intermolecular order while the high-angle peak is more indicative of intramolecular order.[31] This supports the idea that measurements of the WAXD pattern for this polymer system can be used as a way to measure the degree of intermolecular order in these materials. Therefore, it was expected that a decrease in the low-angle peak of the WAXD pattern for the HFAPNB materials used in this work would be observed as the molecular weight was increased. WAXD results do in fact suggest that a decrease in the intermolecular order of the bis(trifluoromethyl)carbinol-substituted polynorbornene occurs as the polymer molecular weight increases (see Figure 6). A more extensive study is currently underway to further validate this idea.

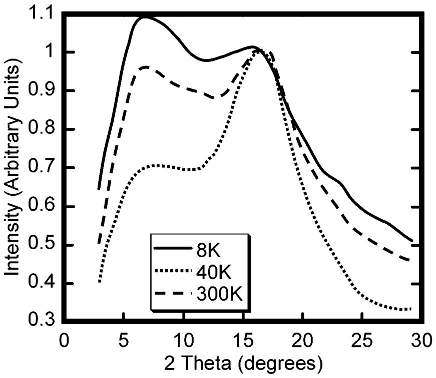

Figure 6. WAXD patterns for spin-coated HFAPNB films at low, mid, and high molecular weights. The intramolecular peak height for these patterns was normalized to an arbitrary value of 1.

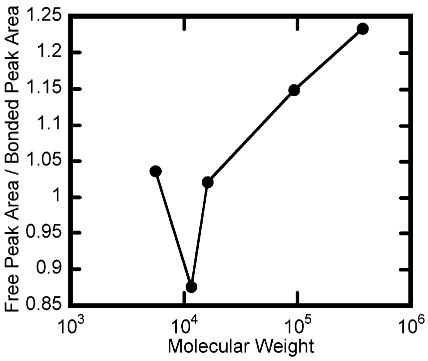

Figure 7. Ratio of deconvoluted free OH peak area (3600 cm^{-1}) to hydrogen-bonded OH peak (3500 cm^{-1}) area ratio as a function of molecular weight.

Even more directly, it was expected that a decrease in the extent of hydrogen bonding with increasing molecular weight would be observed in the HFAPNB materials if an increase in kinks in the chain disrupts interchain hydrogen bonding. Figure 7 shows a plot of the ratio of the FTIR peak area of the “free” OH peak ($\sim$3600 cm^{-1}) to the peak area of the “bonded” OH peak ($\sim$3500 cm^{-1}) as a function of molecular weight. As expected, the ratio of the non-hydrogen-bonded or free OH groups increases with increasing molecular weight above molecular weights of 10 000. This supports the idea that the ability of the polymer to form hydrogen bonds is disrupted as the polymer molecular weight increases, and thus the polymer dissolution rate increases as a result. Once hydrogen bonding has been substantially disrupted due to a large number of kinks being formed in the chain, it would be expected that the polymer dissolution rate would again decrease due to the influence of polymer size effects. Such a decrease is observed in the polymer dissolution rate for molecular weights above 100 000 as shown in Figure 2. Finally, in addition to the kinks that naturally occur in the HFAPNB polymer made using the Pd catalysts employed in this work, it should be possible to introduce "kinks" into the polymer by copolymerizing the HFAPNB with small amounts of a monomer that can introduce flexibility into the backbone. Experiments are currently in progress to test this idea and will be the subject of a future paper.

Conclusions

It has been observed that bis(trifluoromethyl)carbinol-substituted polynorbornene materials, which are promising candidates for future 157 nm photoresist resins, can exhibit unusual dissolution rate behavior. Specifically, this work reports the dissolution behavior of HFAPNB materials polymerized using Pd metal catalysts. It has been observed that the Pd made HFAPNB materials exhibit an increasing dissolution rate in aqueous alkaline solutions as a function of molecular weight for molecular weights in the range from approximately 10 000 to 100 000 M_w. Polynorbornene polymers synthesized using Pd metal catalysts are believed to form unusual helix–coil conformations based on prior simulation and experimental work. It was hypothesized that this unusual stereochemical conformation creates an increase in the extent of disorder in chain packing for these polymers as the molecular weight of the polymer is increased. It was also observed that the bis(trifluoromethyl)carbinol functional groups have a strong propensity to form hydrogen bonds in the HFAPNB materials studied in this work. This ability to form hydrogen bonds, which are thought to occur primarily between groups on neighboring chains, is disrupted by the slight disruptions in packing created as the number of kinks in the polymer chain increases as a result of increasing the polymer molecular weight. WAXD data were presented which support the conclusion that interchain packing and order are disrupted as the polymer molecular weight is increased. FTIR data, which show an increase in the nonbonded hydroxyl to total hydroxyl peak area ratio as the molecular weight is increased, also support this conclusion. This research thus provides a framework within which to think in detail about the molecular level events that control the dissolution behavior in HFAPNB polymers and begins to offer a guide for the rational design of improved resist materials based on this type of material platform. It is easy to imagine that this propensity for bis(trifluoromethyl)carbinol functional groups to exhibit strong hydrogen bonding also has rather strong implications for the potential interaction and influence of photoacid generators and other relatively polar additives used in photoresist formulations on resist film behavior. Further studies are in progress to elucidate such interactions and their impact on resist performance.

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