Thermally Stable and Processible Norbornene Copolymers

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Abstract: Processible norbornene copolymers were realized by judiciously designing norbornene comonomers, which were themselves prepared by the Diels-Alder reaction of cyclopentadiene and benzoquinone followed by the isomerization and alkylation of alcohols. The norbornene copolymers containing these derivatized comonomers, prepared by $[Pd(NCCH_2CH_3)_4][SbF_6]_2$ catalyst, exhibited excellent solubility in many organic solvents as well as good thermal stability, as evidenced by their high glass transition (T_g) and decomposition (~350 °C) temperatures. In addition, fairly strong adhesion to substrates such as glasses and silicon wafers was also achieved with these copolymers to overcome the limitations experienced by polynorbornene homopolymers and to make them attractive for many important industrial applications.

Keywords: polynorbornene copolymers, solubility, thermal stability, adhesion.

Introduction

Polyimides have dominantly been used in many semiconductor electronic devices as an insulating material owing to their excellent thermal stability along with relatively low dielectric constant.[1-3] It was, however, pointed out that there are several intrinsic drawbacks of polyimides such as high moisture absorption, optical and electrical anisotropies, and yellowish color, which make their usage limited in many next-generation optoelectronic applications.[4] Polynorbornene (PNB) has recently attracted much attention as one possible alternative of polyimides due to their unique features such as high transparency in visible and near UV regions, low dielectric constant, high thermal and chemical stabilities, and optical and electrical isotropic properties.[5] Although addition-polymerized PNBs have superior optical and mechanical properties with higher thermal stability compared with other types of PNBs, which are typically synthesized from ring-opening metathesis polymerization (ROMP), cationic polymerization, or cyclic olefin copolymerization (COC), they usually possess limited solubility in many organic solvents and very poor adhesion to substrates to cause serious problems in real applications.[6] These problems are believed to originate from their molecular structure. Since PNB homopolymers obtained from the addition

polymerization are fully saturated and do not have any polar functional groups in the polymer, they obviously have poor adhesion to substrates like glasses or silicon wafers. Also, due to the rigid backbone structure of PNBs, they are also very difficult to swell and eventually dissolve in many common organic solvents. Derivatized norbornene comonomers with long alkyl chains have been prepared and copolymerized with the parent norbornene[7] in order to improve the processability of PNB homopolymers, but the large amount of such comonomers incorporated into the copolymer to achieve reasonable solubility in organic solvents tends to deteriorate all the merits of the PNB homopolymers such as high thermal stability.[8] In present report, we describe the synthesis and characterization of a series of PNB copolymers with excellent solubility in common organic solvents and good thermal stability at the same time as well as with fairly good adhesion to substrates by employing newly designed norbornene comonomers.

Experimental

Materials. 1,4-Benzoquinone (98%), chlorobenzene (anhydrous grade), nitromethane (96%), dicyclopentadiene, norbornylene (99%), toluene, Pd sponge, propionitrile (99%), nitrosonium hexafluoroantimonate, ethyl bromide, benzyl bromide and octyl bromide were purchased from Aldrich. Methylene chloride, HCl, *n*-hexane and methanol were pur-

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chased form Daejung Chemical.

Instruments. ^{1}H- and ^{13}C-NMR data were measured by Bruker DPX-300 MHz. Molecular weights were determined by FAB-Mass Jeol JMS-AX505WA and elemental analysis was performed by EA1110 (CE instrument). The Molecular weights for the polymers were measured by GPC from Yonglin instrument (eluent : toluene, rate: 1 mL/min, based on PS standard). Thermal stability was measured by TGA 2050 (TA instrument). And the detection of T_g was done by DMA 2980(TA instrument).

Synthesis of Comonomers.

Endo-tricyclo [6.2.1.0^{2,7}] undeca-4, 9-diene-3,6dione (1): In 250 mL 2-neck RBF, 1,4-benzoquinone 8.0 g (74 mmol) was solved in 50 mL methylene chloride and then cooled to 0 °C. Cyclopentadiene (5.1 g, 77 mmol) in 20 mL methylene chloride was dropwised into the flask by addition funnel for 10 min. And then, the mixture was stirred in ice bath for 1 hr and at room temperature for 30 min. The solvent was evaporated, and 50 mL *n*-hexane was added to the mixture. The flask was put in ice bath for 30 min, and then the pale-yellow solid was formed. After two times of recrystallization, pure solid product was obtained. Yield: ~93%. ^{1}H-NMR (CDCl$_3$, 300 MHz): 1.42, 1.57. 3.23, 3.56, 6.07, 6.58 ; ^{13}C-NMR (CDCl$_3$, 75 MHz) : 15.3, 47.2, 65.1, 70.0, 111.6, 141.0, 143.0, 148.2 ; FAB-mass (m/z) : 174 ; Elemental analysis(%) calcd. for C$_{11}$H$_{10}$O$_2$: C 75.84, H 5.79, O 18.37; found : C 76.02, H 5.93, O 18.11.

1,4-Dihydro-1,4-methanonaphthalin-5,8-diol (2): 100 mL of ethyl acetate solution of **1** was stirred with Al$_2$O$_3$ (20 g, Fulka, basic: pH 9-9.5, activity I) at room temperature for 3 hr. The color of solution turned to yellow. After Al$_2$O$_3$ was filtered out, solvent was evaporated to leave brown sticky liquid. Chloroform was added and the mixture was sonicated to give a pure solid product. Yield: ~75%. ^{1}H-NMR (CD$_3$COCD$_3$, 300 MHz) : 2.13, 4.11. 6.29, 6.73, 7.42 ; ^{13}C-NMR (CD$_3$COCD$_3$, 75 MHz) : 47.6, 69.8, 114.8, 137.9, 143.4, 145.8, 206.7 ; FAB-mass (m/z) : 174 ; Elemental analysis(%) calcd. for C$_{11}$H$_{10}$O$_2$: C 75.84, H 5.79, O 18.37; found : C 75.81, H 5.61, O 18.17.

5, 8-Diethoxy-1, 4-dihydro-1, 4-methano-naphthalene (EDMN): In 10 mL DMSO, **2** and KOH was solved and stirred for 15 min. Ethyl bromide in 5 mL DMSO was added dropwisely into the solution. After 30 min, 20 mL of brine and 20 mL of methylene chloride were poured into the solution and the organic layer was separated. The expected product was obtained as a white powder from the organic layer. Yield: ~85%. ^{1}H-NMR (CDCl$_3$, 300 MHz): 1.41, 2.24, 3.9~4.05, 4.19, 6.51, 6.86 ; ^{13}C-NMR (CDCl$_3$, 75 MHz) : 15.33, 47.20, 65.13, 70. 06, 111.56, 141.04, 143.08, 148.16 ; FAB-mass (m/z) : 230 ; Elemental analysis(%) calcd. for C$_{15}$H$_{18}$O$_2$: C 78.23, H 7.88, O 13.89; found : C 78.55, H 7.90, O 13.88.

Copolymerization of Norbornene and EDMN: [norbornene] : [EDMN] = 90 : 10 (mol%) [monomer] : [cat.] =

500 : 1. In 100 mL RBF, catalyst (20 mg, 2.5×10^{-5} mol), EDMN (0.288 g, 1.25 mmol), nitromethane (2 mL) and chlorobenzene (10 mL) were mixed and stirred. To this solution, norbornene (1.06 g, 11.3 mmol) in chlorobenzene (5 mL) was slowly added. The solution was stirred at room temperature for 12 hr. After the reaction was completed, the mixed solution of methanol (50 mL) and HCl (1 mL) was poured to quench the reaction. The mixed solution was stirred for 5 hr, and the precipitated polymer product was filtered and dried in vacuum oven. Yield: 55% ; M_w = 77 K ; PDI = 1.91. All the polymerization reactions for other compositions were similar to the above procedure.

Stud Pull-off Test for the Adhesion Property.

Surface Treatment of Stud: Hydrocarbon-based surface contaminants were removed by. solvent degreasing with acetone, and the stud was immersed for 12 min (at 70 °C) in an etching solution prepared from deionized water (100 g), H$_2$SO$_4$ (30 g) and Na$_2$Cr$_2$O$_7$ (6 g). Finally, the studs were washed in running deionized water and dried at 60 °C for 30 min.

Metal Deposition and Spin Coating of PNB-Based Polymer: Metal was deposited onto one inch diameter wafer and the PNB-based polymer was spin coated onto the metal layer.

Stud Pull-off: After a pre-cleaned stud was attached on the PNB-based thin film by employing epoxy resin, the adhesion between polymer and metal layers was tested by pulling the stubs apart in an Instron at 50 mm/min crosshead speed. The adhesion strength was calculated by dividing the force necessary to separate the stubs by the area of the upper stub. The adhesion of norbornene copolymers to aluminum and copper was tested.

Results and Discussion

Synthesis of Monomers and Copolymers. New norbornene-based comonomers with rigid chemical structure, yet containing different alkyl side chains, can be effectively synthesized from the Diels-Alder reaction between cyclopentadiene and benzoquinone followed by the isomerization and alkylation of alcohols (Scheme I).[9] Alkyl side chains and polar ether linkages are introduced close to the rigid benzene ring to improve the solubility of resulting copolymers and also to enhance film-forming ability with good adhesion to substrates. In this scheme, a rigid and planar aromatic ring is fused into the norbornene backbone unit to maintain high glass transition temperature or thermal stability while improving solubility in common organic solvents. The incorporation of bulky and stiff cyclic chemical structure into polymer backbones has been reported as a useful method for increasing the glass transition temperature (T_g) of polymers, because such cyclic groups generally increase the energy to trigger the onset of molecular motions of such polymers.[10]

A typical Diels-Alder reaction between cyclopentadiene
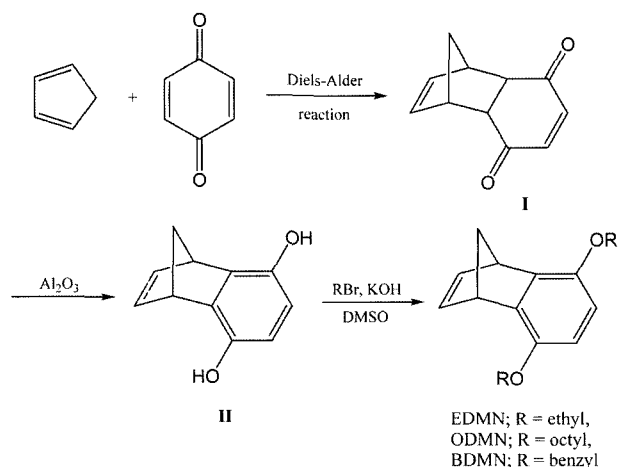
Scheme I. Synthetic scheme of norbornene-based comonomers used in this study.

and benzoquinone yielded the expected product **I** quantitatively, and the isomerisation of **I** to aromatic compound **II** was achieved by treating with Al_2O_3 in an isolated yield of 75%. The compound **II** was then easily deprotonated with KOH and coupled with various alkyl halides to yield comonomers, EDMN (5,8-diethoxy-1,4-dihydro-1,4-methanonaphthalene), ODMN (5,8-dioctyloxy-1,4-dihydro-1,4-methanonaphthalene), and BDMN (5,8-dibenzyloxy-1,4-dihydro-1,4-methanonaphthalene) with high isolated yields (typically, 80~85%).

These norbornene-based comonomers were copolymerized with different amounts of norbornene in the presence of [Pd(NCCH$_2$CH$_3$)$_4$][SbF$_6$]$_2$ catalyst,[11] and the optimum ratio for the norbornene (NB)/comonomer to show reasonable solubility in many common organic solvents was determined to be 9/1. As previously reported from Risse *et al.*,[12] the catalyst employed in this study enables a good control over

the molecular weight with fairly small polydispersity values, as summarized in Table I. When the ratio of [monomers]/[catalyst] is increased, the molecular weight of the copolymer increases almost linearly. It is, however, noted that the polydispersity index becomes larger and the isolated yield is decreased.

Reactivity Ratio. In general, the degree of polymerization (DP) in the addition polymerization is known to be proportional to the reaction time. While the homopolymerization of norbornene with the same catalyst reached the gel point within several minutes, we noted that the reaction time for the copolymerizations shown in Table I was longer than 12 hr without any detectable gel formation. Consequently, this longer reaction time allows us to carry out several experiments to determine the reactivity ratios of norbornene (NB) and the EDMN comonomer, which are typically obtained by the Fineman-Ross method.[13,14] Figure 1(a) shows a plot of the instantaneous copolymer composition (F_{NB}) against the initial comonomer feed ratio (f_{NB}). Each copolymerization was terminated at about 10% of monomer conversion to avoid any composition drift due to the difference in reactivity ratios of the monomers involved. The mole fraction of the comonomer EDMN in each polymer was determined by ^{1}H NMR to calculate the reactivity ratios of the monomers involved and the χ value (F_{NB}/f_{NB}), which is a measure of the randomness of the copolymer prepared. The χ value, which is obtained from the slope of Figure 1(a), is close to unity, implying that the distribution of two different monomers in the copolymer is almost random. Using the values of f_{NB} and F_{NB}, the reactivity ratios of norbornene (NB) and EDMN can be estimated from x(1-X) $= r_{EDMN} - r_{NB}(x^2/X)^{14}$ where X and x are the molar ratios of norbornene in the copolymer and in the feed solution, *i.e.*, $x = f_{NB}/(1-f_{NB})$ and $X = F_{NB}/(1-F_{NB})$, and r_{NB} and r_{EDMN} are the reactivity ratios of norbornene and EDMN, respectively. From the plot shown in Figure 1(b), the reactivity ratios are

Table I. PNB Copolymers Prepared from Different Ratios of Monomer and Catalyst

Sample Notation[a]	[monomers] / [catalyst]	MW[b]	PDI	Yield (%)
NB9EDMN1-125[c]	125 / 1	19 K	2.07	85
NB9EDMN1-500	500 / 1	77 K	1.91	55
NB9EDMN1-1000	1000 /1	119 K	2.60	38
NB9ODMN1-125[d]	125 / 1	21 K	2.11	69
NB9ODMN1-500	500 / 1	53 K	1.94	53
NB9ODMN1-1000	1000 /1	140 K	2.27	40
NB9BDMN1-125[e]	125 / 1	27 K	1.53	76
NB9BDMN1-500	500 / 1	44 K	1.76	68
NB9BDMN1-1000	1000 /1	122 K	1.91	60

[a]NB9EDMN1 denotes the molar ratio of [NB]/[EDMN]=9/1. The number 125 implies the ratio of [monomer]/[cat] = 125/1.
[b]MWs were determined by GPC with reference to PS standards. [c,e]Reaction time : 12 hr. [d]Reaction time : 48 hr.
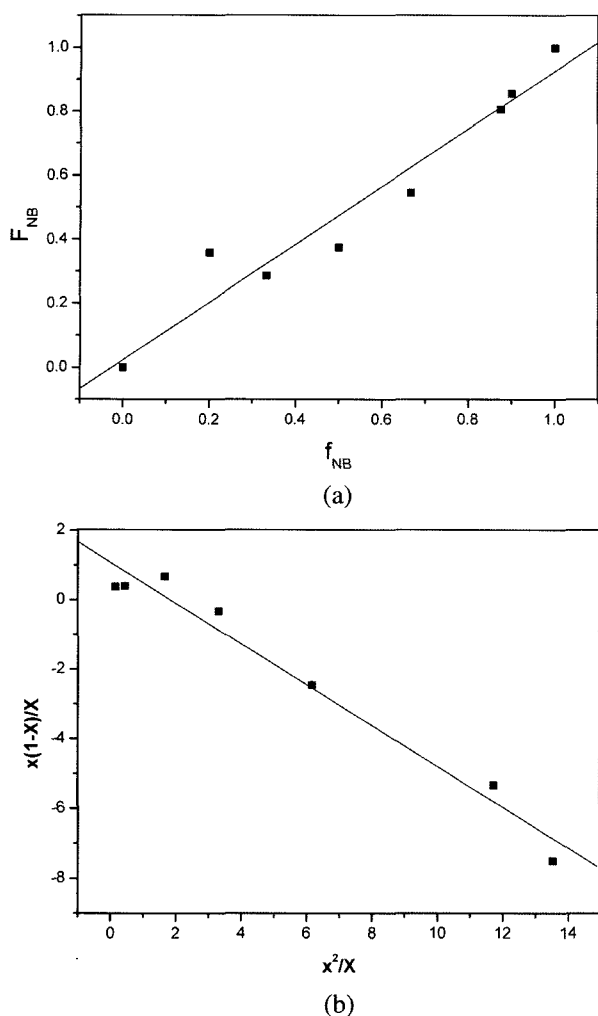
(a)

(b)

Figure 1. (a) A plot of the instantaneous copolymer composition (F_{NB}) against the initial comonomer feed composition (f_{NB}) and (b) the Fineman-Ross plot to determine the reactivity ratios of NB and EDMN comonomer.

calculated to be 0.587 for norbornene and 1.078 for EDMN with a correlation coefficient (R^2) of 0.9811.

The results from the Fineman-Ross plot show the reactivity ratio, which is defined as the ratio of cross polymerization over homopolymerization, of EDMN comonomer is higher than the value for norbornene, implying that the polar sites

in the EDMN comonomer could enhance the coordination tendency toward Pd catalysts. The extra coordination of the polar sites in the comonomer along with the coordination of olefinic moieties can stabilize the intermediate complexes and thus reduce the activity of catalysts to enable the copolymerization to proceed much slower than the homopolymerization of norbornene itself. The linear alkyl chains and the fused extra aromatic ring in the EDMN comonomer, as known in other cases, can also increase the steric hindrance for the access of other monomers to the core metal in the catalyst.[15] When the size of substituents attached to the fused aromatic ring of derivatized comonomers is increased from ethyl to benzyl and to octyl, it was found that the polymerization yield is decreased.

Solubility in Organic Solvents. Owing to different microstructures of polymers prepared, norbornene homopolymers prepared with Pd catalysts are usually less soluble in organic solvents compared with norbornene homopolymers prepared with Ni catalysts.[15,16] Pd catalysts are, however, known to be more tolerant to functional groups than Ni catalysts such that Pd catalysts are typically used to prepare PNB polymers with functional groups. Although norbornene homopolymers with a molecular weight of about 100 K are only soluble in warm chlorobenzene, the norbornene-based copolymers prepared in present study have excellent solubility in many organic solvents, as demonstrated in Table II. Unlike previously reported alkyl-substituted norbornene comonomer system, where more than 30 mol% of the alkyl-derivatized comonomer is necessary to be soluble in common organic solvents,[17] only 10 mol% incorporation of comonomers such as EDMN, ODMN, or BDMN could make the norbornene-based copolymers quite soluble in many organic solvents such as toluene, chloroform, methylene chloride and THF. Even a few mol% incorporation of the comonomer into the PNB chains can show reasonable solubility in many organic solvents, implying that enhanced solubility could originate not only from the alkyl substituents but also from the random nature of the copolymer structure (the irregular structure of polymer backbones in the form of structural defects or kinks) which would suppress tight interchain interactions.

Thermal Behavior. The thermal behavior of these norbornene-based copolymers is evaluated by thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA). As shown in Figure 2(a), the NB9EDMN1 copolymers with

Table II. Solubility of Copolymers in Common Organic Solvents

Entry	Chlorobenzene	Toluene	THF	CH_2Cl_2	$CHCl_3$
PNB	+ [a]	-	-	-	-
NB9EDMN1-1000	++	++	++	++	++
NB9ODMN1-1000	++	++	++	+	++
NB9BDMN1-1000	++	++	++	++	++

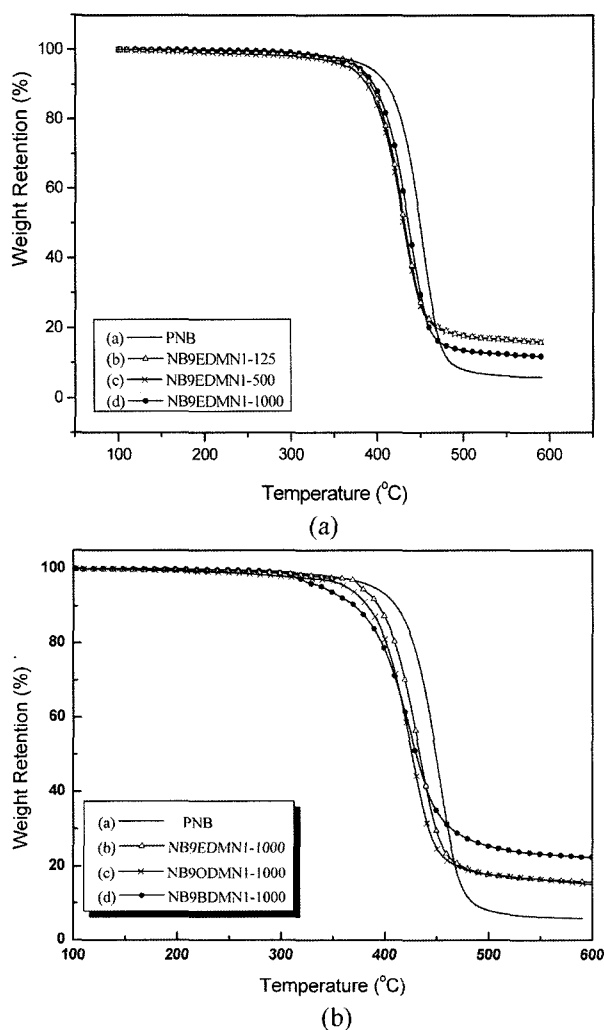[a] ++ : quite soluble, > 0.5 g/ml of solvent; + : soluble, > 0.1 g/mL of solvent; - : insoluble.

Figure 2. TGA data of (a) NB9EDMN1 copolymers with different molecular weights and (b) NB9EDMN1, NB9ODMN1, and NB9BDMN1 containing about 1000 mers.

different average molecular weights show fairly good thermal stability and start to decompose at around 350 °C, which is about 10 °C lower than the parent PNB homopolymer (M.W.=110 K). The residue amount for the NB9EDMN1 copolymers above 500 °C, which is within 12 to 18 wt%, is slightly higher than the value for the PNB homopolymer (about 6 wt%) presumably due to the incorporation of thermally stable aromatic moieties. In Figure 2(b), the thermal behavior of norbornene-based copolymers containing different types of comonomers at the same molar ratio is also shown. When the size of substituent in the comonomer is increased, it is noted that the thermal decomposition starts at a slightly lower temperature than the PNB homopolymer and the residue amount after heating the sample above 500 °C is increased to ~20 wt%. However, all the copolymers, except NB9BDMN1, show good thermal stability without showing significant thermal degradation up to 350 °C.

The glass transition temperature (T_g) of norbornene-based copolymers were also measured by DMA. The measured T_g of the PNB homopolymer is in good agreement with the reported value of 350 °C,[18] while those for NB9EDMN1-1000 and NB9ODMN1-1000 were measured to be 342 and 250 °C, respectively. As expected from long alkyl substituents in the NB9ODMN1 copolymer, we note that the T_g value was significantly decreased. In order to compare with previously reported comonomer systems, 5-ethyl-2-norbornene (EN) was copolymerized with norbornene in different compositions and their solubility and T_g were investigated. If the incorporation ratio of [EN] in the copolymer is lower than 30 mol%, the T_g remains higher than 300 °C while solubility in common organic solvents was found to be quite poor. The incorporation ratio of [EN] should be higher than 30 mol% in order to show reasonable solubility in organic solvents, but the T_g of the copolymers in this cases rapidly decreases below 250 °C. From the viewpoint of balanced solubility and thermal properties of norbornene-based copolymers, it is believed that the NB9EDMN1 copolymer has promising properties: enhanced solubility in various organic solvents with only 10 mol% incorporation of the comonomer while maintaining high T_g, fulfilling major requirements for processable PNB copolymers.

Adhesion Property. Another important issue for practical applications of PNB copolymers to packaging is the adhesion property. The adhesion force of the copolymers onto a substrate (typically, silicon wafer) is qualitatively tested by the tape test and the stud-pull test, as documented in the ASTM (American Society for Test and Materials) D335997 and ASTM D517902, respectively. Although the tape test does not yield any quantitative adhesion values, it is regarded as a simple and easy method to check preliminary adhesion against a substrate of interest to screen many possible candidate materials. For the tape test, the norbornene-based copolymers were spin-coated on silicon wafers. Scotch tape was then applied firmly to a fixed area of the film and removed quickly from the surface of the film. The copolymer film after removal of a scotch tape was checked under a microscope to check any delamination that could occur as a result of the adhesive failure at the interface between the copolymer film and the substrate. In the case where no delamination was observed under the microscope, the copolymer films were immersed in boiling water for one hour. If the copolymer film is not peeled off the substrate during the test, the copolymer film is classified as a film with good adhesion. From this tape test (reliability was confirmed with repeated experiments more than 3 times with freshly prepared), we are able to compare the relative adhesion property among PNB, NB9EDMN1-1000, NB9ODMN1-1000 and NB9BDMN1-1000, as summarized in Table III.

More quantitative data for the adhesion of the copolymers were obtained from the stud-pull test by ASTM D 517902. The adhesion between polymer and metal was tested by

Table III. Relative Adhesion of PNB Homopolymer and Copolymers from the Tape Test

Entry	Film Thickness (μm)	Tape Test
PNB	0.8 ± 0.05^a	Fail
NB9EDMN1-1000	1.2 ± 0.07	Pass
NB9ODMN1-1000	0.9 ± 0.05	Pass
NB9BDMN1-1000	0.6 ± 0.05	Pass

^{a}The tickness of films was determined from SEM images.

pulling the stubs apart in an Instron at a crosshead speed of 50 mm/min. The adhesion strength was calculated by dividing the force necessary to separate the stubs by the area of the upper stub. The adhesion of norbornene copolymers to aluminum and copper was tested by detection of failure at the interface between the polymer and metal. In Figure 3, the copolymers have stronger adhesion strength than norbornene homopolymer because of the oxygen functional group in the comonomer. And ODMN and BDMN copolymers have less strength than EDMN copolymer. This indicates that the bulky groups may be decreasing the number of the functional group interacting with the metal as a substrate. As the bulky groups increase the free volume of the polymer, it is conceivable that there are less functional groups actually present at the interface to participate in reactions with metal. The adhesion strength of polyimide and BCB (benzocyclobutene) which are mainly used in electronic packaging materials are about 1,050 and 800 psi each other. In a point of an amount of polar groups which bring fatal defects to the chip, although the adhesion property is somewhat weak, the PNB copolymers which don't have much polar group will be a good candidate in the advance of microelectronic packaging. And also, because compared with polyimide ($k \sim 3.0$) or BCB ($k \sim 2.7$), the dielectric constant of the PNB copolymer may be relatively very low, it can have the other merit for the application in the microelectronic packaging. Actually, the dielectric constant of NB9E1-1000 was confirmed to be 2.40 from the average-calculation of refractive indices which were detected by 1 nm scanning of 8 inch wafer film with ellipsometer.

Conclusions

In summary, we rationally designed and synthesized derivatized norbornene comonomers and copolymerized with the parent norbornene monomer to yield thermally stable and processable PNB copolymers. These PNB copolymers are shown to have excellent solubility in many organic solvents as well as good thermal stability, equivalent to the thermal degradation of the PNB homopolymer as evidenced by TGA and DMA experiments. These copolymers also demonstrate quite promising adhesion characteristics which could not be achieved by PNB homopolymer alone. Based on these novel properties of norbornene-based copolymers, we believe that many interesting optoelectric applications including high density MCM (Multichip Packaging Module), new generation photoresists, and waveguide materials are possible while basic studies to understand the detailed mechanism of copolymerization are still under way.
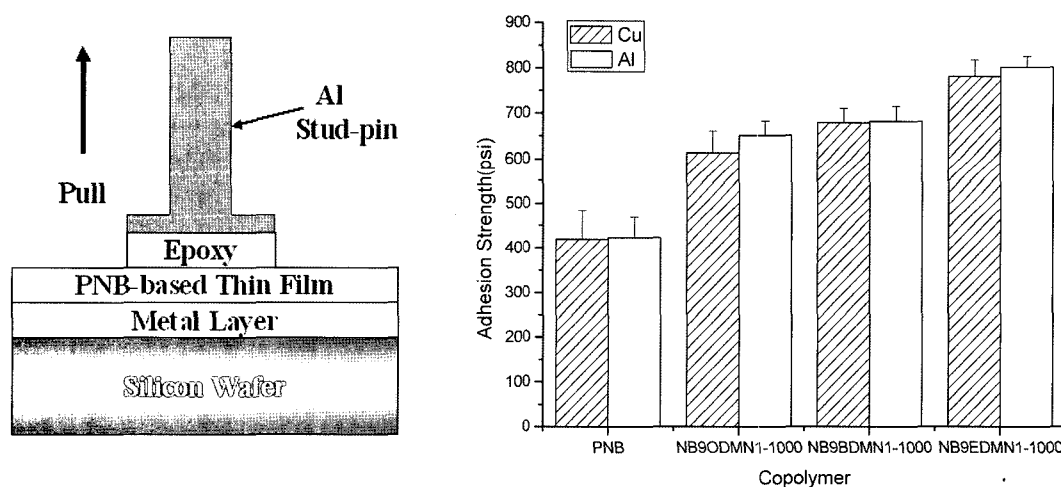
Figure 3. Schematic illustration of stud-pull test and adhesion strengths obtained for PNB homopolymer and copolymers.

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