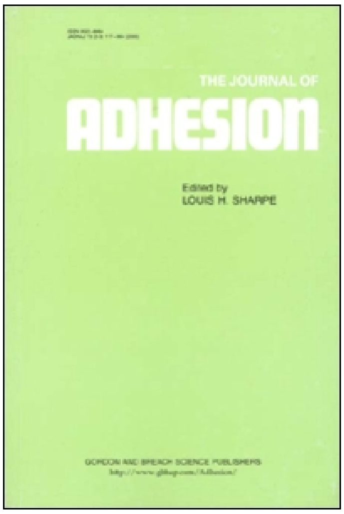

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Photo-Reactive Polyimides and Poly(siloxane imide)s as Reversible Polymeric Interfaces

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Photo-Reactive Polyimides and Poly(siloxane imide)s as Reversible Polymeric Interfaces

Stephen M. June[1], Takeo Suga[1], William H. Heath[1], Timothy E. Long[1], Qin Lin[2], and Rama Puligadda[2]
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Polyimides and poly(siloxane imide)s containing photo-active cyclobutane diimide units were developed as reversible adhesives for temporary bonding in micro-fabrication processes. Poly(amic acid) formation in dipolar aprotic solvents and subsequent chemical or thermal solution imidization yielded the corresponding organic soluble polyimides. Incorporation of nonplanar (alicyclic or bicyclic) structures and poly(dimethyl siloxane) blocks into the main chain improved the solubility. The synthesized poly(siloxane imide)s afforded tough and ductile films, which exhibited a rubbery plateau in the storage modulus, as observed using dynamic mechanical analysis. This plateau was attributed to the microphase-separation of the poly(dimethyl siloxane) segments and the polyimide segments. Spin-coated thin films on silicon substrates were photo-degraded with ultraviolet-C (UVC) light (254 nm). Nuclear magnetic resonance (NMR) spectroscopy demonstrated a growth in the proton resonance corresponding to the formation of maleimide functionality upon photo-cleavage. This observed photo-cleavage suggests possible applications as temporary structural adhesives.

Keywords: Micro-fabrication processes; Photo-reactive; Polyimides; Reversible adhesives; Siloxanes; Structural adhesives; Temporary bonding

INTRODUCTION

As electronic devices become increasingly advanced and miniaturized, the need has arisen for a temporarily bound support substrate during

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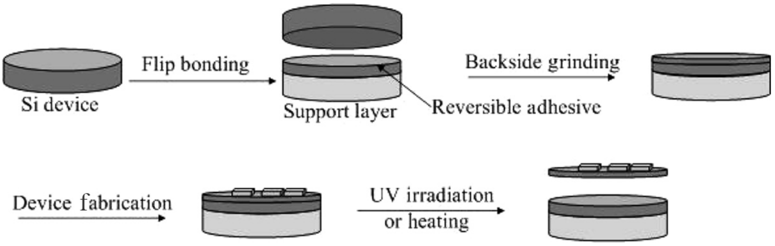


FIGURE 1 Scheme demonstrating temporary bonding for fabrication of electronic devices.

the fabrication process. Utilization of a support substrate allows for device stability throughout a relatively rigorous fabrication process such as backside grinding, lithography, or deposition [1].

Figure 1 demonstrates a scheme for the fabrication of an electronic device utilizing temporary bonding. A device substrate, such as a silicon wafer, is bonded to a support substrate with an adhesive. This allows for grinding, machining, and other fabrication of the device substrate without any risk of damaging the device itself. Thermal softening or degradation of the adhesive permits removal of the device from the support substrate upon completion of device fabrication. However, the thermal process is less controlled and requires extremely high temperatures, thus increasing the difficulty of handling and process complexity. Furthermore, repeated heating and cooling of thin and ultrathin wafers leads to deformation, cracking, warping, and folding [2,3]. For this reason, we have developed a model for an alternative photo-degradable structural adhesive, in lieu of an adhesive which is releasable upon thermal softening or degradation. Our model compound is photolytically degraded, thus potentially allowing for a diminishment of adhesive properties upon exposure to ultraviolet light. This will potentially allow for the facile removal of the device from the support substrate without the need for heating.

As structural adhesives, polyimides are promising materials for device applications and are widely utilized as low static permittivity materials in microelectronic devices, such as integrated circuits, due to their high thermal stability, chemical resistance, and dielectric properties. A wealth of research exists towards the development of photo-reactive polymers as photo-resists for the microelectronics industry [4–16]. For instance, *o*-nitro benzyl (ONB) esters, alcohols, and amides have demonstrated utility as photo-cleavable linkers in polymers [6,8]. Photo-reversible groups such as the photodimer of maleic anhydride, 1,2,3,4-cyclobutane-tetracarboxylic dianhydride

(CBDA), have proven effective as positive photoresist materials in the mid-1980s [7]. Such photo–reversible [2 + 2] cycloaddition/cleavage units have also shown utility as photo-crosslinking, photo-chain extension, or photo–cleavable sites in polymers and polymeric materials [10–12,15–18]. Our group has significant experience in developing thermally and photolytically reversible adhesives [11–13,17,19,20]. In particular, our group has developed the coumarin-functionalized poly(2-ethylhexyl acrylate-*co*-hydroxyethyl acrylate) and demonstrated a photo-reversible pressure-sensitive adhesive system [11].

Requirements for the backbone polymer matrix for an adhesive as described include thermal and photolytic stability, solubility, and adequate adhesive performance. Other requirements include formation of uniform films and effective adherence to a variety of substrates [3]. It is for this reason that poly(siloxane imides) were utilized. McGrath and others previously demonstrated enhanced solubility and adhesive performance, relative to the corresponding polyimide homopolymer [4,21–29]. Furthermore, incorporation of poly(dimethyl siloxane) blocks into polyimides does not decrease the thermal, oxidative, or UV stability of the polymer [25–29]. In addition, incorporation of oligo(dimethyl siloxane) blocks allows for microphase separation and elastomeric mechanical properties [27,28,30].

EXPERIMENTAL

Materials

Aminopropyl-terminated poly(dimethylsiloxane) (Gelest DMS-A12, $M_n = 1{,}600$, $T_g = -122°C$) was purchased from Gelest, Inc. (Morrisville, PA, USA) and used without further purification. Bicyclo[2.2.2]oct-7-ene-2-exo,3-exo,5-exo,6-exo-tetracarboxylic-2,3:5,6-dianhydride (BOEDA) and 4,4′-(1,3-phenylenedioxy)dianiline (PDDA) were purchased from TCI America (Portland, OR, USA) and repeatedly recrystallized, prior to use, from acetonitrile and toluene, respectively. Anhydrous *N*-methyl-2-pyrrolidinone (NMP) equipped with an AcroSeal^{TM} was purchased from Acros (Geel, Belgium) and was used as received. 1-Cyclohexyl-2-pyrrolidinone (CHP) and maleic anhydride were purchased from Aldrich (St. Louis, MO, USA) and used as received. Tetrahydrofuran (THF), *N,N′*-dimethyl formamide (DMF), and toluene were purchased from Fisher Scientific (Pittsburgh, PA, USA) and purified using an MBraun (Garching, Germany) MB-SPS solvent purification system. All other solvents and reagents were purchased commercially and used as received.

Instrumentation

^{1}H NMR spectroscopy was performed in THF-d_8, DMSO-d_6, DMF-d_7, or $CDCl_3$ at 23°C with a Varian (Palo Alto, CA, USA) 400 MHz INOVA, UNITY, or MR400 spectrometer. Thermogravimetric analysis (TGA) was performed using a TA Instruments (New Castle, DE, USA) Hi-Res TGA 2950 in a platinum pan under a constant nitrogen purge of 50 mL/min and a ramp rate of 10°C/min. Differential scanning calorimetry (DSC) was conducted in a TA Instruments Q1000 DSC at a heating rate of 10°C/min and a cooling rate of 50°C/min under a constant nitrogen purge of 50 mL/min. Glass transition temperatures (T_g) were reported as mid-point temperatures from the second heat. Dynamic mechanical analysis (DMA) data were obtained using a TA Instruments Q800 dynamic mechanical analyzer in tension mode at a frequency of 1 Hz and temperature ramp of 3°C/min. Tensile experiments were performed on an Instron (Norwood, MA, USA) 4411 universal testing instrument utilizing sample strips and a crosshead speed of 2 mm/min with manual grips at ambient temperature.

Size-exclusion chromatography (SEC) was performed at 40°C in THF (HPLC grade) at 1 mL/min using polystyrene standards on a Waters 707 autosampler equipped with three in-line PLgel 5 mm MIXED-C columns (Polymer Laboratories, Amherst, MA, USA), a Waters 410 refractive index detector (Waters Co., Milford, MA, USA), and an in-line Wyatt Technology Corp. mini-DAWN multiple-angle laser light scattering (MALLS) detector (Wyatt Technology, Santa Barbara, CA, USA). Reported number-average and weight-average molecular weights are relative to polystyrene standards.

Atomic force microscopy (AFM) was performed using a Veeco (Plainview, NY, USA) MultiMode AFM equipped with a low modulus tip. Sample films were solution-cast from THF into a PTFE mold, and annealed at 80°C *in vacuo* for 18 h prior to testing. UV/Visible spectra were obtained using an Analytical Instrument Systems Inc. spectrometer (Flemington, NJ, USA) equipped with fiber-optic light guides, a DT1000CE light source, and an Ocean Optics (Dunedin, FL, USA) USB2000 UV-Vis detector.

UV irradiation was performed using either a ThermoOriel (Newport Stratford Inc., Stratford, CT, USA) mercury arc lamp, a Fusion UV Systems, Inc. (Gaithersburg, MD, USA) F300 s series microwave powered electrodeless lamp source coupled with a LC-6B bench top conveyer at an intensity of 0.211 W/cm^2 in the UVC region, 1.513 W/cm^2 in the UVB region, and 2.044 W/cm^2 in the UVA region, or a R-52 Mineralight® Grid Lamp obtained from UVP (Upland, CA, USA) irradiating at 254 nm with an intensity of 0.814 mW/cm^2. Gel fraction studies were performed utilizing a soxhlet extraction apparatus, with THF as a solvent and a 10 h exposure.

Synthesis

Cyclobutane-1,2,3,4-Tetracarboxylic Dianhydride (CBDA)

The synthesis of CBDA was performed according to a literature procedure [9]. Briefly, maleic anhydride (40 g, 408 mmol) was dissolved in 400 mL ethyl acetate and placed inside a photo-reactor. Photo-dimerization was carried out in a Pyrex® photo-reactor system equipped with a 450 W high-pressure mercury lamp (180–450 nm), and a Pyrex water jacket for cooling. The utilization of Pyrex for the reactor was beneficial, as Pyrex effectively filters out light wavelengths below 280 nm, diminishing the effects of the reverse reaction. CBDA precipitated out of solution as it was formed. After 24 h, the product was filtered, dried at 50°C at reduced pressure, and recrystallized from acetic anhydride with an isolated yield of 50%. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): 3.86 (s, 4H, CH); ^{13}C-NMR (100 MHz, DMSO-d_6, ppm) : 170.9, 41.9.

Polymerization of CBDA and 4,4′-Oxydianiline (Thermal Bulk Imidization Method)

Step-growth polymerization of CBDA and 4,4′-oxydianiline was performed according to the literature [7]. CBDA and oxydianiline were dissolved in a 1:1 molar ratio in *N*,*N*′-dimethyl acetamide (DMAc) (30 wt%) in a three-necked, round-bottomed flask equipped with mechanical stirring under nitrogen. The reaction solution was allowed to stir at ambient temperature, under nitrogen for 18 h to give the corresponding poly(amic acid). The resulting poly(amic acid) was solution cast from DMAc into a Teflon® mold. The film was clear and colorless, and uniform in thickness. Bulk thermal imidization was performed first at 150°C for 3 h and, subsequently, at 220°C for 18 h *in vacuo*. As expected, the resulting film was insoluble in organic solvents such as DMAc, DMF, NMP, THF, or $CHCl_3$. Furthermore, upon imidization the film had yellowed significantly, shrunk, and warped. These results confirmed the findings that Moore and Dasheff had demonstrated previously [7].

Polymerization of CBDA, BOEDA, and PDDA (Chemical Imidization Method)

CBDA, BOEDA, and PDDA (0.1/0.9/1.0) were dissolved in DMAc (30 wt%) in a three-necked round-bottomed flask equipped with mechanical stirring under nitrogen. The reaction solution was allowed to stir at 85°C for 24 h. Chemical solution imidization was utilized to perform imidization on the corresponding poly(amic acid). Triphenyl phosphite (0.8 equivalents; relative to diamine) and 1.26 equivalents of pyridine were added to the reaction flask. The reaction was allowed to stir for 24 h at 85°C. Finally, six equivalents each of acetic anhydride and triethylamine were added to the reaction solution and the solution was allowed to stir for an additional 24 h at 85°C. The polymer was precipitated into methanol and the precipitate was collected. The collected polymer was dried at 85°C *in vacuo* (yield 94%). $M_n = 47{,}000$; $M_w/M_n = 2.33$. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): 7.41 (t, 8.4 Hz, 1H, Ph), 7.14 (m, 8H, Ph), 6.80 (d, 8.4 Hz, 2H, Ph), 6.75 (s, 1H, Ph), 6.27 (s, 1.8H, BOEDA olefin), 3.67 (s, 0.3H, CBDA methine), 3.49 (s, 1.8H, BOEDA bridgehead), 3.42 (s, 3.6H, BOEDA methine). The composition (CBDA/BOEDA) was 0.08/0.92. Similar methods were utilized to synthesize polymers containing 0 and 20% CBDA, relative to BOEDA.

Cyclobutane Diimide-Containing Poly(Siloxane Arylene Imide)s (Thermal Solution Imidization Method)

CBDA and BOEDA were dissolved in a NMP/THF (1/1, 30 wt% solids) co-solvent system in a 0.7:0.3 ratio and stirred under nitrogen at 55°C. Aminopropyl-terminated poly(dimethylsiloxane) ($M_n = 1{,}600$) was added drop-wise in a 0.5 molar equivalent (respective to the anhydride functional group). A solution of 0.5 molar equivalents of PDDA in the reaction solvent was added to the reaction solution. The reaction was stirred under nitrogen for 24 h at 55°C. After 24 h, the temperature was increased to 160°C, removing the THF, and cyclohexyl pyrrolidinone (CHP) was added as an azeoptrope agent (25%, relative to NMP) in order to perform thermal solution imidization. The imidization was allowed to take place for 24 h. The product was precipitated into methanol, vacuum-filtered, and dried at 50°C at reduced pressure (yield 89%). ^{1}H-NMR (400 MHz, DMSO-d_8, ppm): 7.37 (br, 3H, Ph), 7.21 (br, 2H, Ph), 7.06 (br, 4H, Ph), 6.77 (br, 3H, Ph), 6.28 (s, 0.6H, BOEDA olefin), 6.14 (s, 0.4H, BOEDA olefin), 3.71 (br, 2H, PDMS endgroup methylene), 3.49 (br, 6H, CBDA methine), 3.28 (br, 4H, BOEDA methine), 3.07 (br, 1H, BOEDA bridgehead), 1.62 (br, 4H, PDMS endgroup methylene), 0.57 (br, 4H, PDMS endgroup methylene), 0.10 (s, 123H, PDMS methyl). Polymers containing 30 and 50 mol% CBDA, relative to BOEDA, were also synthesized as outlined above.

Poly(N-Cyclohexyl Maleimide)

N-cyclohexyl maleimide was dissolved in degassed DMF (30 wt%). Azobisisobutyronitrile (AIBN) was added to the solution (0.5 mol %).

The solution was allowed to stir under inert atmosphere for 24 h at 60°C. The solution was precipitated into ultrapure water and the precipitate was collected. The collected polymer was dried overnight *in vacuo* at 60°C. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): 3.0–4.0 (br, 3H, backbone and cyclohexyl methine), 1.98 (br, 2H, cyclohexyl methylene), 174 (br, 3H, cyclohexyl methylene), 1.56 (br, 3H, cyclohexyl methylene), 1.19 (br, 3H, cyclohexyl methylene).

RESULTS AND DISCUSSION

Polymer Synthesis

Synthesis of Aromatic Polyimides Containing Cyclobutane Diimide

Synthesis of maleic anhydride dimer (CBDA) was perfomed using methods previously reported in the literature [9]. The obtained crude dimer was purified by recrystallization in acetic anhydride under nitrogen purge to afford pure product. The ^{1}H NMR of CBDA in DMSO-d_6 demonstrated a single resonance at 3.86 ppm, which was distinctly shifted from the olefin peak for maleic anhydride (7.45 ppm), confirming photo-dimerization. Figure 2 demonstrates the reaction apparatus utilized for the synthesis of CBDA [9]. All dianhydrides were subjected to a thermal treatment at 100°C at reduced pressure prior to polymer synthesis in order to reverse any prior hydrolysis of anhydride functionality.

Initial attempts at incorporating cyclobutane diimide functionality into polyimides included only the use of CBDA and 4,4′-oxydianiline. However, as previously reported in the literature, the wholly aromatic polyimides obtained were not readily soluble in any common organic solvent such as THF, $CHCl_3$, DMF, or NMP. In order to evaluate the effectiveness of this polymer for film or coating applications, the poly(amic acid) precursor was cast from the solution, and subsequent bulk thermal imidization yielded the corresponding polyimide film. However, bulk imidization induced a significant shrinkage and warping of the film. This was not appropriate to ensure uniform bonding, because film homogeneity is a crucial requirement for adhesives [2,3].

Soluble Alicyclic Polyimides Containing Cyclobutane Diimide

For improved solubility of the polyimides, the combination of dianhydrides and diamine were investigated. Previous literature studies have shown that incorporation of alicyclic dianhydrides such as bicyclo-[2.2.2]oct-7-ene-2-exo,3-exo,5-exo,6-exo-tetracarboxylic-2,3:5,6-dianhydride

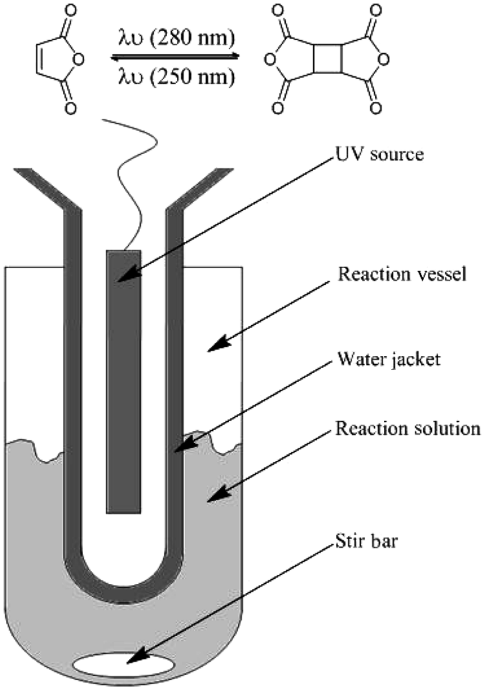
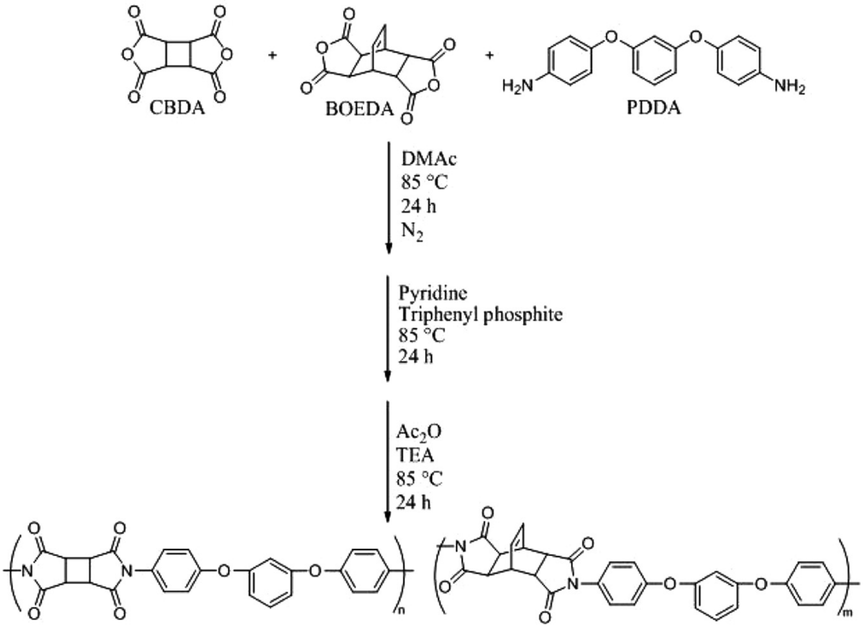


FIGURE 2 Reaction scheme and reactor setup for synthesis of CBDA.

(BOEDA) enhances solubility without significant loss of mechanical properties relative to aromatic dianhydrides [31,32]. Incorporation of *m*-linked aromatic diamines also increases solubility. Therefore, 4,4′-(1,3-phenylenedioxy)dianiline (PDDA) was selected as a co-monomer [32–34].

Syntheses of polyimides containing CBDA, BOEDA, and PDDA were performed using chemical solution imidization (Scheme 1). Table 1 gives the molecular weights and thermal properties of the obtained polymers. Chemical imidization with acetic anhydride in the presence of triphenylphosphite and pyridine yielded the colorless and highly transparent polyimides, which is favorable for efficient photo-irradiation of cyclobutane diimide units. Thermo-gravimetric analysis (TGA) of the obtained polyimides exhibited high thermal stability with a 5% weight loss occuring at approximately 400°C. The retro-Diels Alder degradation of BOEDA does not occur until approximately 360°C, well beyond the required debonding temperature for our photo-releasable adhesives [31].



SCHEME 1 Synthesis of soluble polyimides containing CBDA and BOEDA via chemical imidization.

The obtained polymers were slightly soluble in NMP, DMSO, and DMF with a low loading of CBDA, but as chromophore (CBDA) loading increased, the solubility decreased markedly. The observed solubility of the polyimides effectively limited the usable chromophore loading into the mainchain of the polymer. Thus, it was evident that further solubility enhancements were necessary.

TABLE 1 Polymerization of Soluble Polyimides Containing CBDA and BOEDA

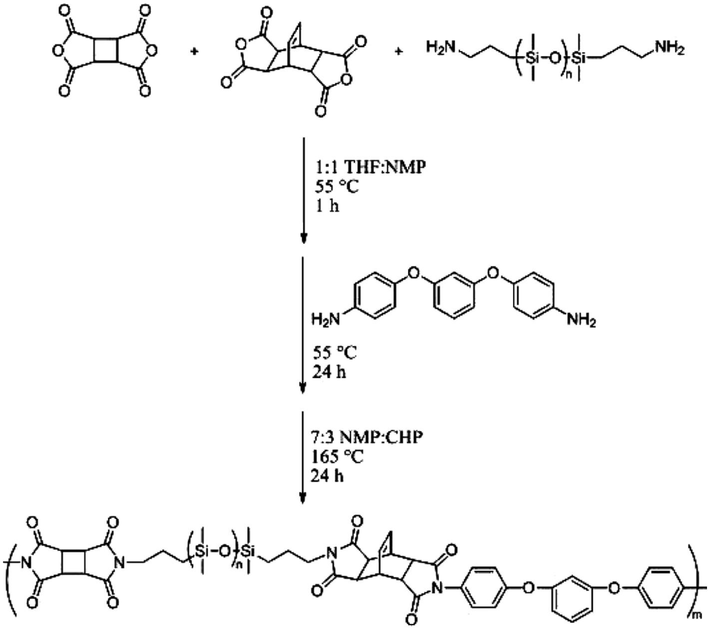
Molar feed ratio CBDA:BOEDA	Composition CBDA:BOEDA	M_n[a]	M_w/M_n	$T_{d5\%}$[b] (°C)	T_g[c] (°C)	Yield (%)
0.2:0.8	0.15:0.85	12,300	2.08	406	268	95
0.1:0.9	0.08:0.92	47,000	2.33	404	281	94
0:1.0	0:1.0	147,000	1.63	416	293	97

[a] SEC – DR1, MALLS, NMP, 50°C, 1 mL/min.
[b] TGA – TA Instruments 2950 TGA, 10°C/min, N, purge 50 mL/min.
[c] DSC – TA Instruments Q1000 DSC, 10°C/min, N_2 purge 50 mL/min, 2nd heat.

Poly(siloxane imide) Containing Cyclobutane Diimide

Subsequent efforts included the use of aminopropyl-terminated PDMS as a solubility enhancer, and as an enhancer of adhesive properties. McGrath *et al.* previously demonstrated that it is possible to increase the solubility of polyimides dramatically through incorporation of PDMS blocks in the polyimide mainchain [25–29,35]. Furthermore, several literature sources document that segmented poly(siloxane imides) will microphase separate into domains containing the polyimide blocks and domains containing the PDMS blocks, leading to favorable elastomeric properties [21,23,24,30]. Initially, chemical imidization was utilized in an attempt to yield soluble materials, as was the case with polyimides without PDMS blocks. However, this proved unsuccessful and another synthetic route was necessary.

McGrath and others demonstrated the use of thermal solution imidization in a mixed solvent system that included an azeoptrope such as CHP [4,21–30]. This method proved successful and was utilized for the synthesis of a series of poly(siloxane imides) containing cyclobutane diimide units. Scheme 2 demonstrates the synthesis of poly(siloxane



SCHEME 2 Synthesis of poly(siloxane imides) containing cyclobutane diimide functionality.

imides) containing cyclobutane diimide functionality. The subsequent polymers were readily soluble in THF, NMP, cyclopentanone, and DMF.

Characterization

Table 2 demonstrates compositions and molecular weight data for the series of synthesized cyclobutane diimide-containing poly(siloxane imides), as well as TGA and DSC analysis of the synthesized cyclobutane diimide-containing poly(siloxane imides). Molecular weights of the polymers obtained ranged from M_w of 27,000 to 47,000 with molecular weight distributions ranging from 2.3 to 2.7, and the polymers formed good films when solution cast from THF. The resulting films were tough, creaseable, and relatively transparent, albeit slightly colored. ^{1}H NMR confirmed in all cases that the feed composition closely matched the final composition of the polymer.

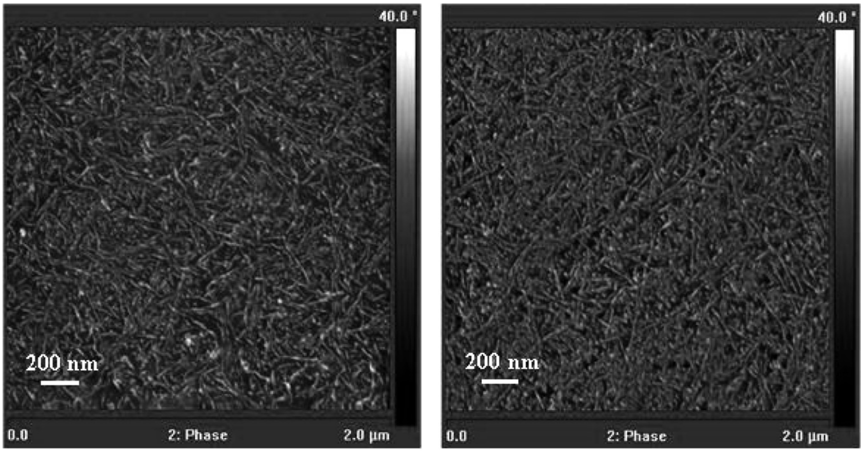
TGA and DSC were utilized to study the effects of composition on thermal properties of the synthesized polymers, as well as to evaluate thermal stability. TGA indicates that all polymers exhibit insignificant weight loss below 400°C, suggesting thermal stability sufficient for flip bonding. The observed that the T_g of the poly(siloxane imide) was identical to that of the poly(dimethyl siloxane) macromonomer ($T_g = -122°C$). This suggests microphase separation of the material into a polyimide domain (hard segment) and a PDMS domain (soft segment).

Atomic force microscopy (AFM) was utilized in order to confirm microphase separation of the poly(siloxane imides). The polymers were spin-coated from THF onto thin silicon wafers and annealed under reduced pressure at 80°C. The obtained micrographs of two CBDA: BOEDA compositions are shown in Fig. 3, with lighter portions being

TABLE 2 Molecular Weight and Thermal Analysis Data for Cyclobutane Diimide-Containing Poly(siloxane Imides)

	Molar feed ratio						
PDMS	PDDA	CBDA	BOEDA	M_n^{a} (g/mol)	M_w^{a} (g/mol)	T_g^{b} (°C)	$T_{d5\%}$^{c} (°C)
0.5	0.5	0.7	0.3	17,000	47,000	−119	406
0.5	0.5	0.5	0.5	11,000	27,000	−121	420
0.5	0.5	0.3	0.7	13,000	30,000	−120	411

[a] SEC – DRJ, MALL S, THF, 40°C, 1 mL/min; values relative to polystyrene standards.
[b] DSC – TA Instruments Q1000 DSC, 10°C/min, N_2 purge 50 mL/min, 2nd heat.
[c] TGA – TA Instruments 2950 TGA, 10°C/min, N_2 purge 50 mL/min.



CBDA:BOEDA 5:5 CBDA:BOEDA 3:7

FIGURE 3 Atomic force micrographs showing phase images of cyclobutane diimide-containing poly(siloxane imides), which confirm microphase separation.

the polyimide domain (hard segment), and the darker portions being the PDMS domain (soft segment). Although only one scale is shown, the surface properties do scale with variations in magnification. As expected, the surface morphology is microphase separated.

Tensile testing (Fig. 4 and Table 3) and dynamic mechanical analysis (DMA) confirmed that the synthesized poly(siloxane imides) exhibited elastomeric properties. Representative DMA data is shown in Fig. 5. As expected with elastomers, the DMA storage modulus demonstrated a marked decrease at approximately −110°C. After the decrease, the storage modulus leveled off into a "rubbery plateau"

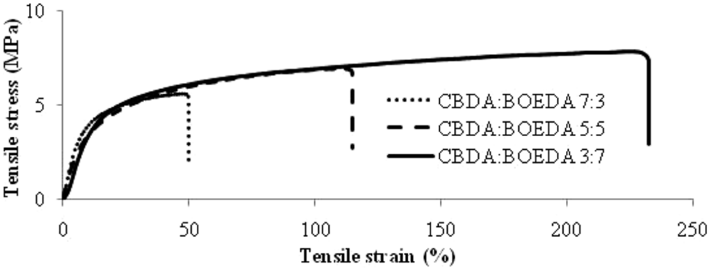


FIGURE 4 Tensile analysis of cyclobutane diimide-containing poly(siloxane imides).

TABLE 3 Tensile Data for Cyclobutane Diimide-Containing Poly(siloxane Imides)

CBDA:BOEDA	Tensile stress at break (MPa)	Tensile strain at break (%)	Tensile stress at yield (MPa)	E modulus (MPa)
7:3	4.6 ± 0.5	55 ± 11	5.4 ± 0.6	49.6 ± 9.9
5:5	6.2 ± 0.4	114 ± 9	6.5 ± 0.7	46.0 ± 5.0
3:7	6.5 ± 2.4	234 ± 67	7.6 ± 1.4	38.2 ± 3.3

which suggested elastomeric properties. This plateau is maintained until approximately 100°C, giving these polymers an extremely wide temperature range during which the mechanical properties do not change significantly. From −50 to 100°C the storage modulus diminished less than 100 MPa. This may prove exceptionally useful for adhesive applications that require little change in adhesive properties over a wide temperature range, such as flip bonding.

UV Irradiation Studies and Analysis

Decker *et al.* have previously demonstrated that bis-maleimides such as those formed upon the expected photo-degradation of cyclobutane diimide containing polyimides crosslink upon UV irradiation in the absence of a photo-initiator [5]. In order to ensure photo-cleavage in the absence of crosslinking, a model study was undertaken utilizing *N*-cyclohexyl maleimide (CyMI), and the AIBN initiated homopolymer of the same (poly(CyMI)). Qualitative UV-visible spectroscopy of CyMI

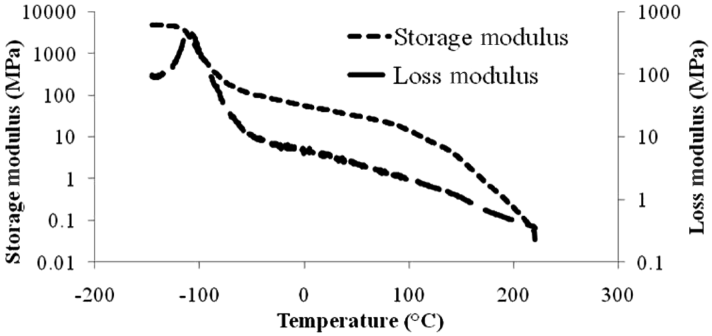


FIGURE 5 DMA of a representative cyclobutane diimide-containing poly(siloxane imide) demonstrates a rubbery plateau.

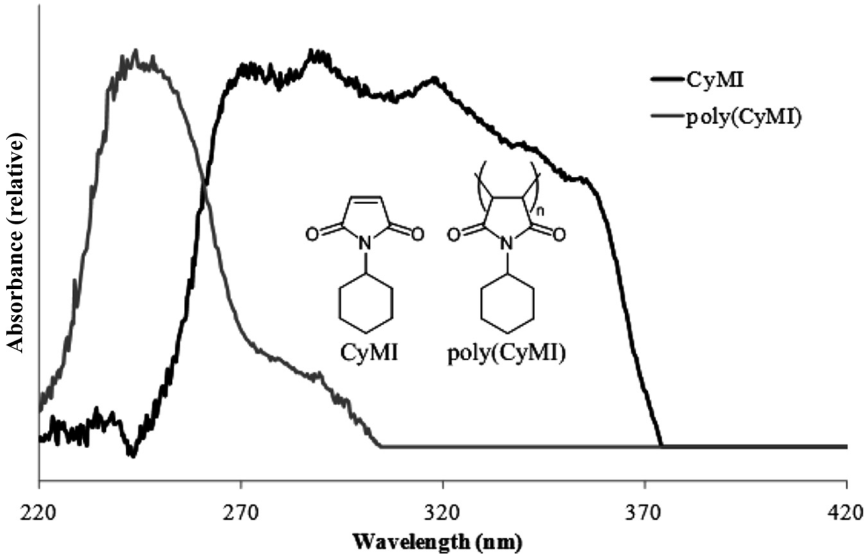


FIGURE 6 UV/Vis spectra of CyMI and poly(CyMI).

and poly(CyMI) is shown in Fig. 6. Based upon these data, it is clear that imide and anhydride absorbances are distinctly different from those of maleimides. In order to photo-cleave the cyclobutane diimide units efficiently within the poly(siloxane imide) mainchain and prevent subsequent crosslinking of the formed maleimide residues, it is important to irradiate with a narrow bandwidth UV light centered in the region in which the anhydride and imide residues absorb but maleimides demonstrate no absorbance. For this purpose, all subsequent experiments were performed utilizing a lamp which provides a narrow source of UV light at 254 nm.

In order to obtain photo-cleavage in the absence of crosslinking, a narrow band UV source was utilized. CBDA-containing poly(siloxane imides) (0.7:0.3 CBDA:BOEDA) were exposed to UVC light at 254 ± 10 nm in dosages ranging from 2.2–26 J/cm^2 UVC. The resulting films were entirely soluble in THF and indicated no evidence of cross-linking. This finding confirmed the hypothesis obtained from the UV/Vis data as discussed above. Figure 7 demonstrates a dramatic growth as a function of irradiation dosage in the peak corresponding to the formation of maleimide functionality in the ^{1}H NMR. As indicated in Fig. 7, maleimide functionality forms as a function of irradiation dosage, confirming cleavage of the CBDA units in the polymer mainchain.

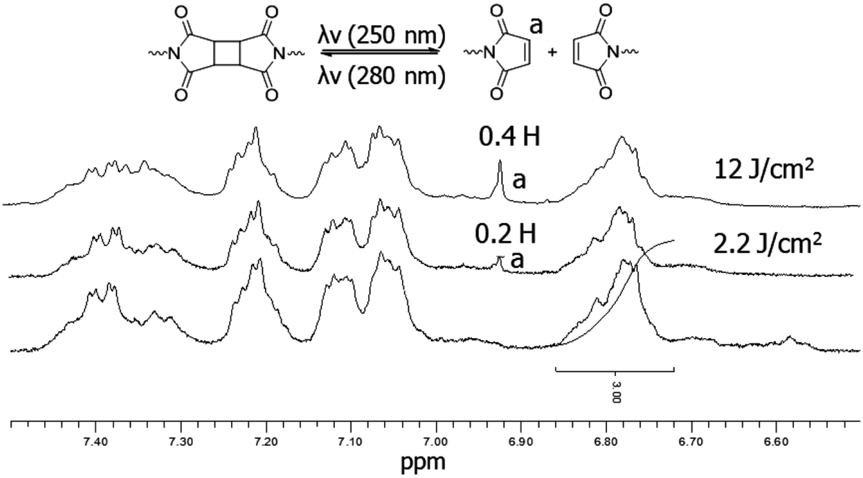


FIGURE 7 ^{1}H NMR spectroscopy demonstrates growth in peak corresponding to maleimide functionality as a function of UVC dose.

CONCLUSIONS

Photo-cleavable reversible structural adhesive poly(siloxane imides) containing photo-active cyclobutane diimide units within the mainchain were prepared *via* thermal solution imidization step-growth polymerization of CBDA, BOEDA, PDDA, and aminopropyl-terminated poly(dimethyl siloxane). Polymers were synthesized with varying compositions of CBDA, relative to BOEDA. Incorporation of PDMS blocks within the polyimide mainchain was necessary for solubility, adequate adhesion, and homogeneous film formability. Thermal and morphological testing indicated micro-phase separation, leading to the observation of elastomeric properties. Upon broad-spectrum UV irradiation, some crosslinking was observed. Model compound studies demonstrated the necessity for irradiation with a narrow UV band, centered at approximately 250 nm. Photo-cleavage in the absence of crosslinking was obtained from the use of a narrow-spectrum UV source. Upon irradiation, ^{1}H NMR demonstrated an increase in the resonance corresponding to the formation of maleimide functionality, confirming cleavage of cyclobutane diimide functionality. These findings indicate that this system may provide a highly effective route for photo-reversible adhesion.

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