

method to carbohydrates, we examined the nucleophilic substitution of **5** with several nucleophiles under the similar conditions (Eq. 3). **5** was generated by treatment of 3,4-dihydro-2H-pyran with 1.0 equiv of triflic acid in the presence of 1.5 equiv of dimethyl sulfide at -78°C in dichloromethane. **5** worked well with Grignard reagents, silyl enol ethers and phenylthiotrimethylsilane but failed to react with allyltrimethylsilane.

In conclusion, we have shown that previously unknown α -alkoxysulfonium salts are very reactive species and undergo facile nucleophilic substitution reactions with a variety of nucleophiles under mild conditions.

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5. **3** ($R = n\text{-C}_3\text{H}_7$, $R' = \text{Me}$): $^1\text{H NMR}$ (CDCl_3 , -40°C) δ 0.20 (s, 9H), 0.90-1.00 (b, s, 3H), 1.40-1.65 (m, 2H), 1.65-1.90 (m, 2H), 2.70 (s, 3H), 2.85 (s, 3H), 3.60 (s, 3H), 5.41 (b, s, 1H).
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Synthesis and Properties of Photosensitive Polyimides Containing Cyclobutane Ring Structure

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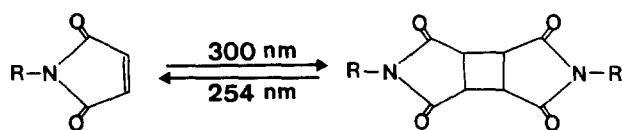
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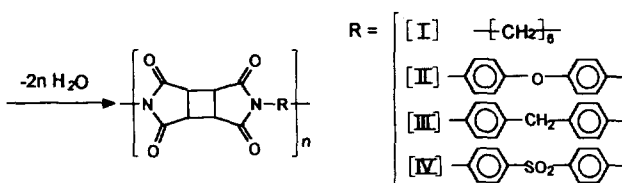
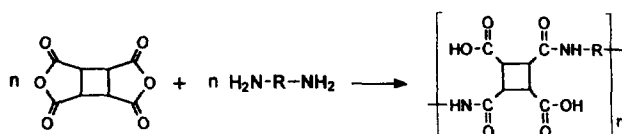
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Polyimides are well known not only for their chemical and thermal stabilities but also for their excellent electrical and mechanical properties. They are used as encapsulants, insulators and flexible substrates for printed circuits in the



Scheme 1.



Scheme 2.

electronics industry. Recently, the use of polyimides as polymer materials for electronic applications has become increasingly important because it not only has many excellent properties but also simplifies the VLSI fabrication processes.¹⁻³ For these purposes, solvent soluble⁴⁻⁵ and/or photosensitive polyimides⁶⁻¹⁰ have been developed.

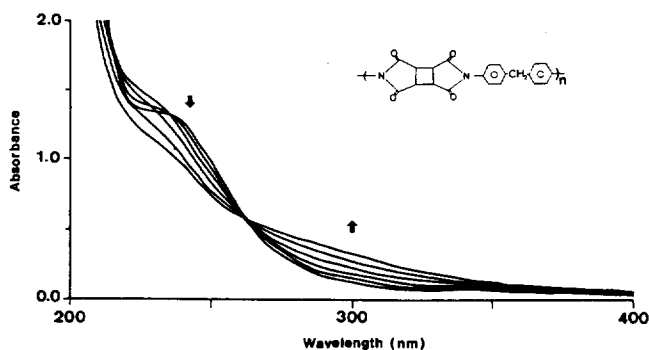
Irradiation of maleimide derivatives with 300 nm UV light produces cyclobutane photodimers,¹¹ and photolysis of these photodimers with 254 nm UV light results in original maleimide derivatives by the cycloreversion process as shown in Scheme 1. In continuation of our studies on the application of photochemical reactions to the polymer systems,¹² the present communication reports a synthesis and properties of photosensitive polyimides containing cyclobutane ring in the main chain. This type of polyimides may be used as a promising positive deep UV photoresist that can be developable in organic solvents.¹³

The synthetic method of polyimides containing cyclobutane ring is shown in Scheme 2. Maleic anhydride cyclobutane dimer was obtained by irradiation of maleic anhydride with 300 nm UV light in CHCl_3 or CH_2Cl_2 .¹¹ Polyamic acid [I]-[IV] was synthesized by the reaction of maleic anhydride cyclodimer (5 mmol) with corresponding diamine (5 mmol) in 20 ml dimethylacetamide (DMAc) at room temperature. The polyamic acid was purified by precipitation of the reaction mixture in MeOH. The polyimide was obtained by heating the polyamic acid stepwise at 150°C for 5 hrs, 200°C for 5 hrs, 250°C for 2 hrs, and 300°C for 2 hrs.

Physical properties of the polyamic acid and polyimide are summarized in Table 1. The precursor of the polyimide, polyamic acid was soluble in polar aprotic solvents such as DMAc or N-methyl-2-pyrrolidinone (NMP) and inherent viscosity of the polyamic acid measured in DMAc solution ranged between 0.5-0.9 dl/g indicating relatively high molecular weights. DSC analysis shows that the decomposition of poly-

Table 1. Physical Properties of Polyamic acids and Polyimides

Polymer	Polyamic acid		Polyimide		
	T_d^a	$[\eta]^b$	T_d^a	Temp.(°C) of 5% wt. loss ^c	Temp.(°C) of 50% wt. loss ^c
[I]	378	0.56	392	408	541
[II]	458	0.92	459	469	658
[III]	425	0.66	436	439	749
[IV]	439	0.51	454	431	596

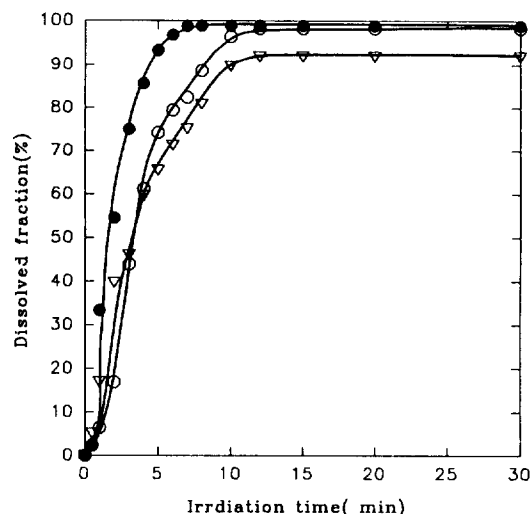
^aDecomposition temperature (T_d) by DSC: Scan speed, 10°C/min.^bIntrinsic viscosity in DMAc at 25°C.^cThermal gravimetric analysis under nitrogen atmosphere.**Figure 1.** UV absorption changes of polyimide [III] film on irradiation at 254 nm UV light. Irradiation times: 0, 10, 20, 30, 60, 120 min. The arrow at 300 nm shows the increase in absorbance with irradiation time.

imide takes place in the range 390-460°C and thermal gravimetric analysis indicated the temperature of 50% weight loss to be around 540-750°C which shows relatively high thermal stability.

UV absorption changes of a polyimide [III] film coated on quartz plate upon irradiation at 254 nm UV light are shown in Figure 1. The absorbance around 300 nm increased with irradiation time and an isosbestic point was observed at 273 nm. Similar results were obtained for *N*-phenylmaleimide cyclobutane dimer, a model compound of polyimide containing the cyclobutane ring. This result shows that cyclobutane ring of the polymer was splitted into two ethylene bonds to form maleimide derivatives upon irradiation with short wavelength UV light.

These polyimides were not soluble in any organic solvents even in very polar solvents such as DMAc or NMP but become soluble in THF or DMAc upon irradiation with 254 nm UV light except polyimide [I]. Polyimide [I] could not be photosplitted because it has no absorption at 254 nm. This result suggests that the polyimide [II]-[IV] was photodegraded to low molecular weight compounds by photosplitting of cyclobutane ring.

Dissolution properties of polyimide films with time of irradiation at 254 nm were observed. The polyimide film coated on a quartz plate was irradiated and developed in DMAc for 1 min. Dissolved fraction was monitored by absorbance changes upon irradiation. Figure 2 shows dissolved fraction

**Figure 2.** Plot of dissolved fraction vs. irradiation time for photolysis of polyimide films with 254 nm UV light in air. Dipping solvent; DMAc. (○), polyimide [I]; (●), [II]; (●), [III]; (▽), [IV].

of polyimide film with time of irradiation in air. About 98% of polyimide film was dissolved after 7 min of irradiation and the relative dissolution rate of polyimide film increased in the order [III]>[II]>[I]. When the experiment was carried out under N₂, the order of increase in dissolution rate was same but the rate was slower. The results suggest that a photodegradation mechanism other than photosplitting of cyclobutane ring is operating in the photolysis of polyimide under aerobic conditions.

To understand the difference of photodegradation mechanism in air and N₂. IR spectral changes of polyimide [III] film before and after the photolysis with 254 nm UV light were studied. All the absorption bands decreased in intensity with increasing irradiation time and the IR spectra of polyimide photolysed in N₂ show much less change than in air. This polymer shows absorption bands at 1777 and 1720 cm⁻¹ from the two carbonyl stretching modes, 1375 cm⁻¹ from C-N stretching mode, and 839 cm⁻¹ from cyclobutane ring deformation mode. Plot of the ratio of absorbance $A(t)/A(0)$ with irradiation time showed that both of the bands at 839 and 1375 cm⁻¹ decreased faster than 1777 and 1720 cm⁻¹ bands in air, while the band at 839 cm⁻¹ decreased faster than all the imide bands in N₂. This implies that not only photosplitting of cyclobutane ring but also photooxidation of C-N bond take place when the reaction is run in aerobic conditions, as reported by Hoyle *et al.*¹⁴

The present results show that the polyimides containing cyclobutane ring in the main chain is thermally stable and can be developed in organic solvents after photolysis with 254 nm UV light. Photooxidation of imide bond as well as photosplitting of cyclobutane ring are considered to be major photodegradation processes for these polyimides. Further studies on the details of photodegradation mechanism of polyimides are in progress.

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Orientational Effect of N₂ on Nitrogen Fixation

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We have reported the effect of water on nitrogen fixation, and tried to investigate the nitrogen reduction processes by inserting the water cluster. One atom of N₂ molecule participates in constructing the ring structure with waters and Fe-substrate discussed in our previous paper¹. With such a model, the reduction mechanisms could be explained fairly well in some respects.

In this work, we tried to find out another possible process

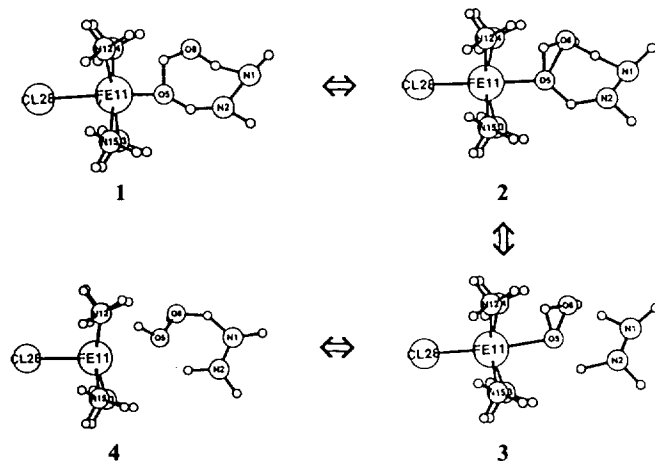


Figure 1. Reduction processes to amine species with using 2H₃ O⁺ during the INDO optimization. N₂ molecule is bonded to the intermediate water cluster as parallel (side-on bonding). Structure 1 is the starting model and others are intermediate structure obtained during the optimization. The electronic energy (in au) of each structure is -144.8158 for 1, -145.0508 for 2, -145.1660 for 3, and -145.6871 for 4.

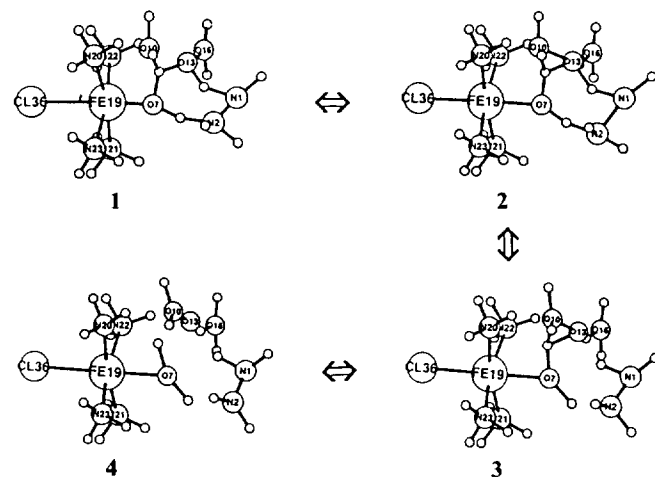


Figure 2. Reduction processes to amine species with using 4H₃ O⁺ during the INDO optimization. N₂ molecule is bonded to the intermediate water cluster as parallel (side-on bonding). Structure 1 is the starting model and others are intermediate structure obtained during the optimization. The electronic energy (in au) of each structure is -180.1048 for 1, -180.6503 for 2, -181.1508 for 3, and -181.4186 for 4.

on the basis of the previous work, and to concentrate our attention on directional effect of nitrogen molecule which approaches to the complex of water-substrate. Lots of tests were done with changing the orientation of nitrogen molecule perpendicular to that of the structure employed in the previous work. Actually, Fe-substrate not constructing the ring structure with water molecule repels the nitrogen molecule, and it doesn't show any reduction process. But, under the situation constructing the complex with water and Fe-substrate, we could observe the unexpected phenomena even though we varied the direction of N₂ to form a side-on bonding. At certain respects, similiar or more reasonable reduc-