4. Meyer, J. W.; Hammond, G. S. *J. Am. Chem. Soc.* **1972**, *94*, 2219.

5. Shine, H. J.; Subotkowski, W. *J. Org. Chem.* **1987**, *52*, 3815.

6. Horspool, W. M.; Pauson, P. L. *J. Chem. Soc.* **1965**, 5162.

7. Finnegan, R. A.; Mattice, J. J. *Tetrahedron.* **1965**, *21*, 1015.

8. Lappin, G. R.; Zannucci, J. S. *J. Org. Chem.* **1970**, *35*, 3679.

9. Veglia, A. V.; Sanchez, A. M.; de Rossi, R. H. *J. Org. Chem.* **1990**, *55*, 4083.

10. Ramamurthy, V.; Eaton, D. F. *Acc. Chem. Res.* **1988**, *21*, 300.

11. Newkome, G. R.; Moorefield, C. N.; Keith, J. M.; Baker, G. R.; Escamilla, G. H. *Angew. Chem. Int. Ed. Engl.* **1994**, *33(6)*, 666.

12. Xu, Z.; Kahr, M.; Walker, K. L.; Wilkins, C. L.; Moore, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 4537.

13. Hawker, C. J.; Frechet, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 8405.

14. UV absporption spectrum of **1** was not presented in ref. 13: UV (MeOH), λ_{max} 277, 235, 206 nm.

15. Spectral data of **2**: UV (MeOH), λ_{max} 309, 256, 240, 216, 212, 205, 201 nm; Fluorescence (MeOH), λ_{em} 322, 308, 297 nm (λ_{ex} 255 nm); IR (KBr), 3254 (br), 3064, 2959, 1735, 1630, 1567, 1447, 1370, 1250, 1208, 1068, 941, 899, 821, 763, 702 cm^{-1}; ^{1}H NMR (CDCl$_3$), δ 10.13 (bs, 1H, 1 x OH), 7.77 (s, 1H, 1 x ArH), 7.64-7.23 ppm (m, 11H, 10 x PhH and 1 x ArH), 5.00 ppm (s, 2H, CH$_2$CCl$_3$), ^{13}C NMR (CDCl$_3$), δ 163.18, 160.72, 150.07, 138.79, 133.76, 132.77, 129.75, 128.65, 128.30, 128.03, 117.26, 115.28, 94.55, 74.78 ppm; Mass (EI), m/e 492 (M), 345 (M-147), 105 (100%, PhCO), 77 (Ph).

16. Spectral data of **3**: UV (MeOH), λ_{max} 309, 254, 238, 213, 210, 209, 203 nm; Fluorescence (MeOH), λ_{em} 322, 308, 297 nm (λ_{ex} 255 nm); IR (KBr), 3254 (br), 3065, 2959, 1743, 1665, 1588, 1440, 1370, 1320, 1250, 1124, 1060, 927, 772, 709 cm^{-1}; ^{1}H NMR (CDCl$_3$), δ 9.50 (bs, 1H, 1 x OH), 8.22 (2 d's, 2H, 2 x ArH), 7.75-7.40 (m, 10H, 10 x PhH), 4.31 ppm (s, 2H, CH$_2$CCl$_3$); ^{13}C NMR (CDCl$_3$), 164.04, 159.92, 153.90, 138.76, 134.19, 133.84, 133.22, 130.36, 128.76, 128.68, 115.65, 115.52, 94.09, 74.54 ppm; Mass (EI), m/e 492 (M), 345 (M-147), 239 (M-PhCHO-OCH$_2$CCl$_3$), 105 (100%, PhCO), 77 (Ph).

17. Spectral data of **4**: UV (MeOH), λ_{max} 316, 266, 250, 219, 215, 203 nm; Fluorescence (MeOH), λ_{em} 322, 308, 297 nm (λ_{ex} 255 nm); IR (KBr), 3332 (br), 3064, 2924, 1743, 1616, 1447, 1377, 1264, 1215, 1131, 1025, 920, 860, 818, 770 cm^{-1}; ^{1}H NMR (CDCl$_3$), δ 10.62 (bs, 2H, 2 x OH), 7.64 (d, 4H, 4 x PhH), 7.47 (d, 2H, 2 x PhH), 7.42 (dd, 4H, 4 x PhH), 6.93 (s, 1H, ArH), 4.94 ppm (s, 2H, CH$_2$CCl$_3$); Mass (EI), m/e 492 (M), 239 (100%, M-PhCHO-OCH$_2$CCl$_3$), 105 (PhCO), 77 (Ph).

Preparation of Photosensitive Poly(urethane-imide)s Having Cyclobuthane Rings and Their Properties

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Polymer materials for electronic applications are required to have the properties of both easy processibility and thermal stability with low water absorption. Recently, the use of polyimides as polymer materials for electronic applications has become increasingly important because it simplifies the VLSI fabrication process.[1-3] Polyimides are well known not only for their chemical and thermal stabilities but also for their excellent electrical and mechanical properties. However, polyimides usually suffer from processing problems due to their insolubility and infusibility. In order to overcome these drawbacks, solvent soluble[4] or modified polyimides[5] have been developed.

In the previous studies at this laboratory we have reported the preparation and properties of photosensitive polyimides having cyclobutane ring structure.[6] The present communication deals with the preparation method and properties of a modified photosensitive polyimide, poly(urethane-imide)s, having cyclobutane rings in the main chain.

The synthetic route of poly(urethane-imide)s (PUIs) having cyclobutane ring is shown in Scheme 1. The N-methylol maleimide cyclobutane dimer (MCD)[7] was obtained by irradiation of N-methylol maleimide[8] with 350 nm UV light in CH$_2$Cl$_2$. PUI was prepared by reacting 1.27 g (5 mmol) of MCD with an equimolar amount of corresponding diisocyanate in 10 mL of N-methyl-2-pyrrolidone (NMP) at 60-110 ℃ for 2 hours. The polymer was purified after precipitation

Scheme 1.

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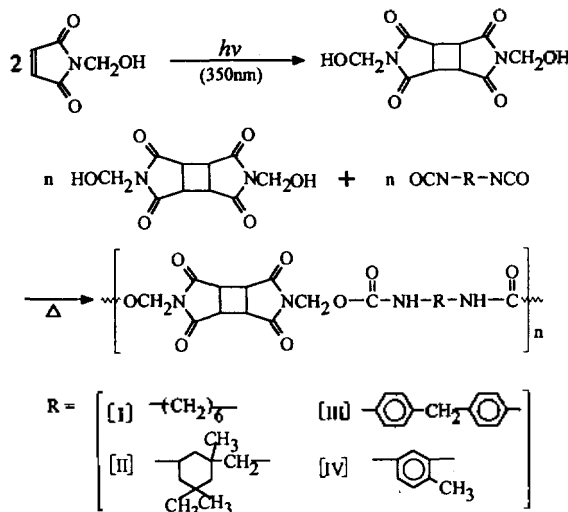
Table 1. Physical Properties of Poly(urethane-imide)

Abbr.	Polymerization		Yield	T_d	Temp. of	Solubility[c]			η_{int}
	Temp. (℃)	Time (h)	(%)	(℃)[a]	50% wt loss (℃)[b]	H_2O base	THF DMF	DMAc NMP	(dl/g)[d]
PUI [I]	110	2	85	334	450	X	X	+	0.30
PUI [II]	80	2	79	240	435	X	X	+	0.21
PUI [III]	60	2	96	336	485	X	+	+ +	0.46
PUI [IV]	60	2	93	405	424	X	+	+ +	0.44

[a] Obtained from DSC thermogram under nitrogen atmosphere; scan speed, 10 ℃/min. [b] Obtained from TGA thermogram under nitrogen atmosphere; scan speed, 10 ℃/min. [c] Solubility; X (insoluble), + (slightly soluble), + + (good soluble). [d] Intrinsic viscosity in NMP at 25 ℃.
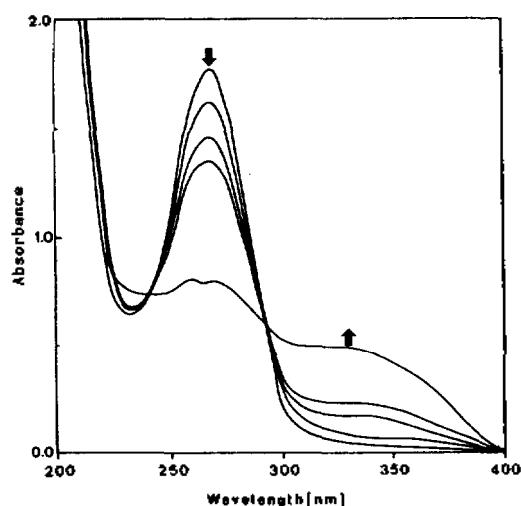

Figure 1. UV absorption spectral changes of poly(urethane-imide) [III] film upon irradiation with 254 nm light. The arrow at 330 nm shows increase in absorbance with irradiation time, 0, 1, 3, 5, 20 min.
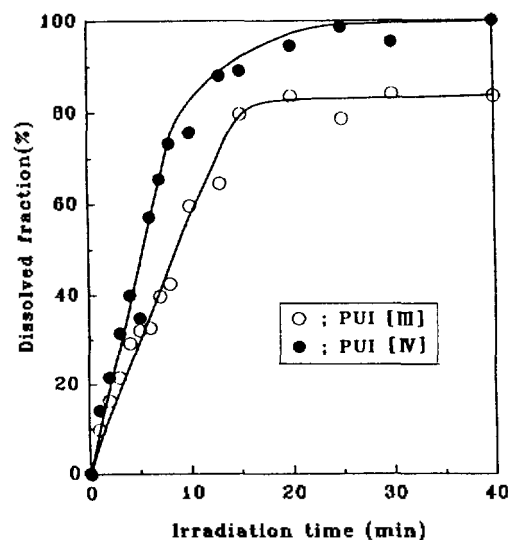

Figure 2. Plot of dissolved fraction as a function of irradiation time for photolysis of poly(urethane-imide) films with 254 nm light: dipping solvent, 3 N NaOH solution; time, 2 min.

in methanol or water. The structure of PUI was confirmed by FT-IR spectroscopy.

The preparation conditions and physical properties of the PUIs are summerized in Table 1. They are not soluble in water, alkali, or non-polar organic solvents but fairly soluble in polar aprotic solvents such as dimethylacetamide or NMP. Intrinsic viscosities measured in NMP in the range of 0.21-0.46 dL/g. DSC analysis shows that the PUIs begin to decompose at the temperatures between 240-400 ℃.

Figure 1 shows UV absorption spectral changes of the PUI [III] film on the quartz plate upon irradiation with 254 nm UV light. An isosbesitc point is observed at 293 nm and the absorbance around 320 nm increases with irradiation time. Similar results were observed in THF solution. This result shows that cyclobutane ring of the polymer was split-ted into two ethylene bonds to form maleimide derivatives upon irradiation with short wavelength UV light.

The PUIs are not soluble in acetone or THF before the irradiation. However, polymer [III] and [IV] become soluble after the irradiation. This result suggests that the PUI [III] and [IV] photodegraded to low molecular weight compounds as a result of photosplitting of cyclobutane rings. Also, the

aromatic PUI [III] and [IV] becomes soluble in alkali medium after the irradiation, while they are not soluble in alkali before the irradiation. This is likely due to the photooxidation of a C-N bond in the imide group[9] to produce carboxylic acid. Polymer [I] and [II] are not affected by the irradiation because they do not absorb the light at 254 nm.

Dissolution properties of PUI films in alkali as a function of irradiation time at 254 nm were investigated. The PUI films were casted on the quartz plate. Dissolved fraction of the films after the irradiation were determined from the difference between absorbance at the isosbestic point of UV spectra before and after dipping the quartz plate in 3 N NaOH solution for 2 min at room temperature. Figure 2 shows the change in the dissolved fraction of PUI film as a function of irradiation time in air. Most of the PUI [IV] films were dissolved after 25 min irradiation. The relative dissolution rate of PUI [IV] film was faster than that of PUI [III] film.

To understand the photochemical reaction of PUI upon irradiation, IR spectral changes of PUI [III] films casted on KBr pellet before and after the photolysis with 254 nm UV light were studied. The difference of IR spectra obtained

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before and after the irradiation showed the increase in the absorption band around 3,300-2,500 cm^{-1} and 1,699 cm^{-1}, indicating the formation of carboxylic acid. The decrease of the absorption band at 1,780 cm^{-1} indicates the photodecomposition of a C-N bond in the imide group. The increase of absorption band at 1,577 cm^{-1} indicates the formation of primary aromatic amine by photodecomposition of the urethane bond. The increase of the absorption band at 670 cm^{-1} is due to the photosplitting of cyclobutane ring to form maleimide derivatives.

The results presented so far show that the PUIs containing cyclobutane rings in the main chain are somewhat thermally stable and soluble in aprotic organic solvents unlikely known polyimides. It can be developed in an alkali after photolysis with 254 nm light. Photodecomposition of imide and urethane bonds as well as photosplitting of cyclobutane rings are considered to be the major photodegradation process for these PUIs.

References

1. Makino, D. *Polymers for Microelectronics*; ACS Symposium Series 537, Thomson, L. F.; Willson, C. G.; Tagawa, S. Eds.; American Chemical Society: Washington D. C., 1994; p 380.
2. Davis, G. C. *Polymers in Electronics*; ACS Symposium Series: Davidson, T. Ed.; American Chemical Society: Washington D. C., 1984; p 259.
3. Ahne, H.; Kruger, H.; Pammer, E.; Rubner, R. *Polyimides: Synthesis, Characterization, and Applications*; Mittal, K. L. Ed.; Plenum: New York, 1982; p 905.
4. (a) Kanna, D. N.; Mueller, W. H. *Polym. Eng. Sci.* **1989,** *29*, 954. (b) Khanna, D. N.; Mueller, W. H. *Polym. Eng. Sci.* **1989,** *29*, 954. (c) Jeong, H.-J.; Kakimoto, M.-A.; Imai, Y. *J. Polym. Sci. Polym., Chem. Ed.* **1991,** *29*, 1691. (d) Matsuura, T.; Hasuda, Y.; Nishi, S.; Yamada, N. *Macromolecules* **1991,** *24*, 5001.
5. (a) Yu, X.; Song, C.; Li, C.; Cooper, S. L. *J. Appl. Polym. Sci.* **1992,** *44*, 409. (b) Becker, K. H.; Schmidt, H.-W. *Macromolecules* **1992,** *25*, 6784. (c) Litauski, L.; Karasz, F. E. *J. Appl. Polym. Sci.* **1993,** *48*, 1023. (d) Parthban, A.; Sundaram, N. *J. Polym. Sci., Polym. Chem. Ed.* **1993,** *31*, 1233.
6. Chae, K. H.; Park, J. S.; Chung, J. S. *Bull. Korean Chem. Soc.* **1993,** *14*, 657.
7. Yield=46%; mp >300 ℃ ; ^{1}H NMR (D$_2$O) 3.75 (S, 4H), 5.2 (s, 4H); IR (KBr) 3420 (OH), 1770 (C=O), 1720 (C =O), 1370 (C-N), 1180, 1060 cm^{-1}. Elemental analysis (%): Calcd. for C$_{10}$H$_{10}$N$_2$O$_6$: C, 47.25; H, 3.97; N, 11.02. Found: C, 47.09; H, 3.50; N, 10.72.
8. Tawney, P. O. *U. S. Pat.* 2,526,517, 1950.
9. Hoyle, C. E.; Creed, D.; Nagarajan, R.; Subramanian, P.; Anzures, E. T. *Polymer* **1992,** *33*, 3162.

Structure Elucidation of Methicillin-Resistant Peptidoglycan Monomer by Tandem Mass Spectrometry

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Antibiotics which interrupt peptidoglycan synthesis have been effective since the peptidoglycan heteropolymer surrounding the cytoplasmic membrane is unique to bacterial cell walls.[1] However, many *beta*-lactam antibiotics are no longer effective due to the acquired resistance.[2] This resistance has been known to be related to the altered structure of peptidoglycan, even though the functional relationship is not yet clear.[3-5] Peptidoglycan is composed of repeating units of 1,4-linked N-acetylglucosaminyl-N-acetylmuramic acid. From the latter monosaccharide residue is typically attached a short peptide chain that can vary from species to species; there can be significant heterogeneity in the peptide sequences and further, the peptide chains can be linked to one another directly.

The fragments of the individual peptidyl disaccharide residues can be obtained by treating the peptidoglycan with muramidase to hydrolyze the 1,4-glycosyl bond between the muramic acid and N-acetylglucosamine, followed by purification using HPLC.[6] In this way the individual muropeptide monomers, dimers, trimers and higher oligomers (*i.e.*, monomers connected *via* their peptide chains) have been isolated. The fine structures of bacterial cell wall are then studied by tandem mass spectrometry (MS/MS).[7] The role of tandem mass spectrometry here is to provide precise determinations of molecular size and also sequence on the same ultrafine scale of resolution.[8] An important aspect of a high performance tandem mass spectrometer is the ability to select a single mass from MS 1 for collisionally induced dissociation. The resulting sequencing-characteristic fragment ions are then mass analyzed by scanning MS 2.

Previously, we have reported our mass spectral results on several highly purified peptidoglycans isolated from various bacteria strains.[9-13] Analysis by MS/MS yielded sufficient information to provide the complete structure of monomers. Assignments for some of the peaks were confirmed by amino acid analysis. Inferences based on the monomer structures and molecular weights allowed most of the dimers and higher oligomers to be tentatively identified. The question addressed was to determine the nature of the peptidoglycan modification in reduced resistance transposon mutants of a methicillin resistant strain of the bacterium *Staphylococcus aureus*, a major pathogen in hospital-born infections. We describe, in this paper, the complete structure determination of peptidoglycan monomer of a new strain, Tn551 mutant of *Staphylococcus aureus* (RUSA208) selected for reduced methicillin resistance by tandem mass spectrometry.

Peptidoglycan of RUSA208 was isolated and enzymatically