

Novel Polyureas Having Isobutenyl Bis(aryl ether) Moieties in the Polymer Main Chain: Synthesis, Tandem Claisen Rearrangement, and Thermal Patterning on Polymer Film Surface Using Microthermal Analyzer

GANG YANG, HIDEO TOKUHISA, EMIKO KOYAMA, SHIN-ICHIRO MATSUZONO, KAZUHISA HIRATANI

Nanoarchitectonics Research Center, National Institute of Advanced Industrial Science and Technology, Tsukuba Central 4, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8562, Japan

Received 1 June 2001; Accepted 13 September 2001

ABSTRACT: Two kinds of new polyureas **2a** and **2b** were synthesized by polyaddition of 1,4-phenylene diisocyanate with 2-{2-[(2-amino-4-methyl-phenoxy)methyl]allyl}oxy-5-methyl-aniline (diamine **1a**) and 2-{2-[(2-amino-4-*tert*-butyl-phenoxy)methyl]allyl}oxy-5-*tert*-butyl-aniline (diamine **1b**), respectively. The isobutenyl bis(aryl ether) moiety, capable of yielding plural phenolic hydroxyls by means of tandem Claisen rearrangement (TCR), was successfully incorporated into the resulting polymer main chain. TCR at isobutenyl bis(aryl ether) moieties readily occurred by heating in the bulk state, affording phenolic hydroxy groups ortho to urea linkages. Subsequent intramolecular cyclization between the hydroxy groups and the urea groups gave the bis(2-benzoxazolinone) derivatives, with loss of 1,4-phenylenediamine, resulting in degradation of the polymers. At the same time, the thermal properties were investigated by TG/DTA. The degradation of these new polymers in the bulk state was shown to proceed smoothly by heating at 230°C. Using a microthermal analyzer (μ TA), a preliminary study of thermal patterning on polyurea **2b** film surface was carried out, and precise spot patterns were successfully processed with diameters of less than 1 μ m. Two kinds of novel polyureas, containing isobutenyl bis(aryl ether) moieties ortho to the urea linkages were successfully synthesized. These results imply that these easily decomposable polymers might be used as patterning materials. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 2287–2293, 2002

Key words: polyether; pyrolysis; thermal properties; lithography; tandem Claisen rearrangement

INTRODUCTION

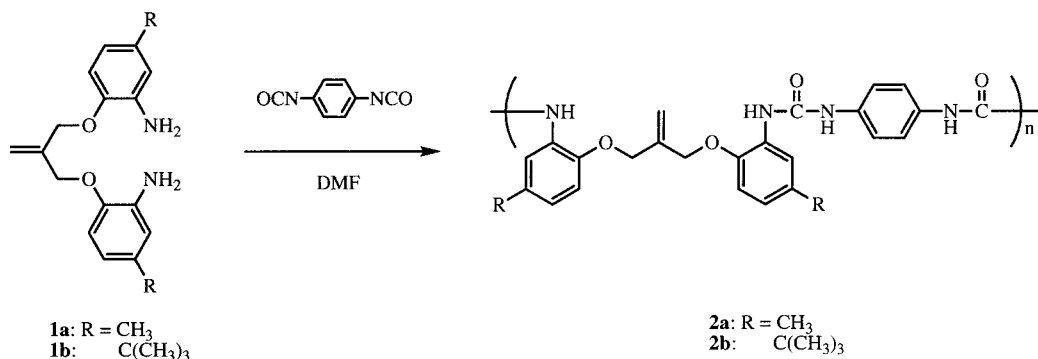
Claisen rearrangement has held the interest of chemists for decades because of its extensive applications for organic synthesis,^{1,2} which was further extended by the observation that tandem sequences can also be effected.^{3,4} Recently, using isobutenyl bis(aryl ether) moiety as the tandem sequence for

the Claisen rearrangement [called tandem Claisen rearrangement (TCR), leading to formation of plural phenolic hydroxy groups], a series of calixarene-like compounds and novel crownphanes were synthesized in our laboratory.^{5–7} Gutsche also applied this procedure to biscalix[*n*]arenes.⁸

In the case of polymers, unusual changes in properties are also expected to take place after the TCR of isobutenyl bis(aryl ether) moiety in the polymer structure. Isard² reported an oligomeric polyether (<1150) containing isobutenyl bis(aryl ether) moiety, which was synthesized by

Correspondence to: K. Hiratani (k.hiratani@aist.go.jp).

Journal of Applied Polymer Science, Vol. 84, 2287–2293 (2002)
© 2002 Wiley Periodicals, Inc.



Scheme 1 Synthesis of polyureas.

the Williamson reaction of bis(*p*-hydroxyphenyl)-2,2-propane (bisphenol A) and 3-chloro-2-chloromethyl-1-propene in the presence of sodium carbonate as a base. The TCR of isobutenyl bis(aryl ether) moiety occurred by heating. As a result of the formation of two phenolic hydroxy groups in each repeat unit, the parent polyether converted to a phenolic polymer with different properties.

It is well known that *o*-hydroxyphenylureas can be pyrolyzed to 2-benzoxazolinones with loss of ammonia by the cyclization reaction between the hydroxy and urea groups.⁹ According to this reaction, we reported a successful synthetic application of the TCR for two kinds of bis(2-benzoxazolinone) derivatives,¹⁰ in which the TCR produced hydroxy groups ortho to urea groups, and subsequent intramolecular cyclization between hydroxy and urea groups afforded oxazolinone structure with loss of aniline.

In the present study we demonstrate that these consecutive reactions could be effected in a new polyurea system. Two kinds of new polyureas **2a** and **2b** (Scheme 1), containing isobutenyl bis(aryl ether) moiety ortho to urea linkage in the polymer main chain, were synthesized, as

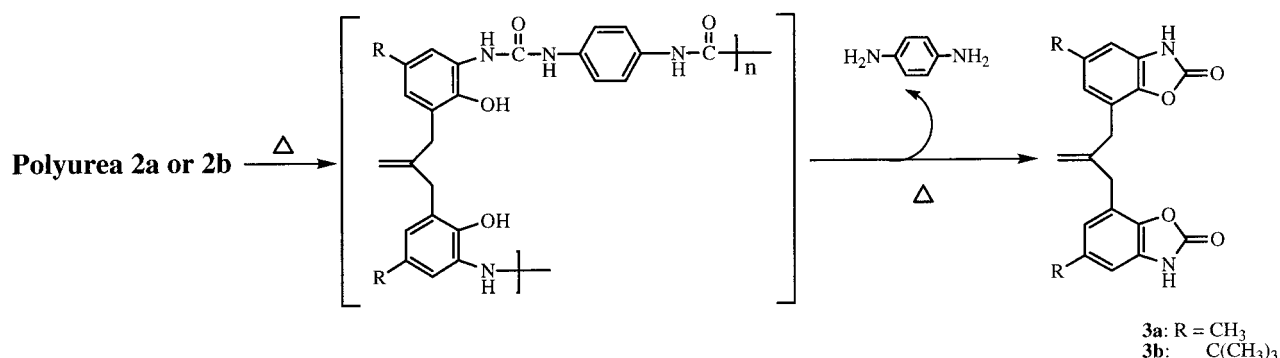
shown in Scheme 1. During thermal treatment of the resulting polymers at 230°C, the TCR of isobutenyl bis(aryl ether) moiety easily occurred, to form phenolic hydroxy groups ortho to the urea groups; the subsequent intramolecular cyclization between the hydroxy groups and the urea groups afforded bis(2-benzoxazolinone) derivatives (**3a**, **3b**) with loss of 1,4-phenylenediamine, resulting in degradation of polyureas **2a** and **2b** (see Scheme 2).

Because of the thermal degradable property of the new polymers, thermal patterning on the film surface of polymer **2b** was carried out on a microthermal analyzer (μ TA). Using the thermal probe tip as a heat source to treat the film surface, precise spot patterns were obtained with diameters of less than 1 μ m.

EXPERIMENTAL

Materials

All the chemicals used in this study were obtained from Tokyo Chemical Industry Co., Japan and used without further purification. Synthesis of



Scheme 2 Pyrolysis of polyureas.

2-[2-[(2-amino-4-methyl-phenoxy)methyl]allyl]oxy-5-methyl-aniline (diamine **1a**) and 2-[2-[(2-amino-4-*tert*-butyl-phenoxy)methyl]allyl]oxy-5-*tert*-butyl-aniline (diamine **1b**) was described in our previous work.¹⁰

Measurements

¹H- and ¹³C-NMR spectra were obtained using a Bruker AF-500 spectrometer. Shifts were measured in parts per million from tetramethylsilane (TMS). Infrared (IR) spectra were recorded on a Jasco FTIR-420 Fourier transform infrared spectrophotometer. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out with a Seiko TGDTA6200-S using a heating rate of 5 K min⁻¹ in nitrogen. Gel-permeation chromatography (GPC) was performed on a Shimadzu Class-LC10 (Shimadzu, Japan) fitted with polystyrene-divinylbenzene columns (two Shodex KD803 and KD804) and a Shodex RID-10A refractive index detector in *N,N*-dimethylformamide containing 0.42 g/L of lithium chloride as an eluent using polystyrene as standard.

Polymer Synthesis

The polyureas **2a** and **2b** were synthesized at room temperature under nitrogen by polyaddition of 1,4-phenylene diisocyanate with the corresponding diamines **1a** and **1b**, respectively, as shown in Scheme 1.

A typical procedure for polyurea **2a** is as follows. In a flask, diamine **1a** (1.00 g, 3.35 mmol) was dissolved into dry DMF (8 mL) under nitrogen. The solution was then cooled down to 0°C using an ice-water bath, and 1,4-phenylene diisocyanate (0.54 g, 3.35 mmol) was charged into the flask. After the reaction mixture was stirred at 0°C for 1 h, the temperature was increased slowly up to room temperature and the reaction was continued for another 3 h. Polyurea **2a** was precipitated by pouring the reaction mixture into methanol and collected by filtration. Final purification was achieved by reflux in methanol, to give polyurea **2a** (1.51 g, 98.5%). IR (KBr): 3348 (N—H), 1656 (C=O), 1199, 1016 (C—O—C) cm⁻¹. ¹H-NMR (DMSO-*d*₆): δ 2.22 (s, 6H, —CH₃), 4.75 (s, 4H, —CH₂—), 5.37 (s, 2H, =CH₂), 6.65 (s, 2H, Ar), 6.98 (s, 2H, Ar), 7.37 (s, 4H, Ar), 7.97 (s, 2H, Ar), 8.05 (s, 2H, —CONH—), 9.60 (s, 2H, —CONH—). ¹³C-NMR (DMSO-*d*₆): δ 152.40, 144.39, 140.13, 134.03, 129.40, 128.52, 121.85, 119.65, 118.74, 115.43, 111.96, 68.52, 20.61. Weight-average molecular weight (*M_w*) and poly-

dispersity index (*M_w*/*M_n*) were determined as 153,000 and 1.51, respectively. ANAL. calcd for C₂₆H₂₆N₄O₄· $\frac{1}{2}$ H₂O: C, 66.80%; H, 5.80%; N, 11.98%. Found: C, 67.14%; H, 5.64%; N, 11.83%.

Polyurea **2b** was synthesized with a yield of 96.5%. IR (KBr): 3406 (N—H), 1656 (C=O), 1199, 1016 (C—O—C) cm⁻¹. ¹H-NMR (DMSO-*d*₆): δ 1.18 (s, 18H, —C(CH₃)₃), 4.76 (s, 4H, —CH₂—), 5.43 (s, 2H, =CH₂), 6.83 (s, 2H, Ar), 6.90 (s, 2H, Ar), 7.34 (s, 4H, Ar), 8.00 (s, 2H, Ar), 8.20 (s, 2H, —CONH—), 9.34 (s, 2H, —CONH—). ¹³C-NMR (DMSO-*d*₆): δ 152.51, 144.33, 142.88, 140.17, 134.04, 128.21, 118.73, 118.10, 116.42, 115.47, 111.49, 68.47, 33.85, 31.22. *M_w* and *M_w*/*M_n* were determined as 95,000 and 1.53, respectively. ANAL. calcd for C₃₂H₃₈N₄O₄· $\frac{1}{2}$ H₂O: C, 69.67%; H, 7.13%; N, 10.16%. Found: C, 69.91%; H, 7.04%; N, 10.20%.

Pyrolysis of Polymer

Pyrolysis of polyureas **2a** and **2b** were carried out under almost identical reaction conditions as shown in Scheme 2. Into a reaction tube was added 0.50 g of **2a**. The tube was flushed with argon and evacuated three times, then heated at 230°C under reduced pressure with the use of a rotary pump for 3.5 h. The reaction residue was extracted by reflux in acetone (200 mL), and the product dissolved into acetone was collected and recrystallized from an acetone/water (1 : 3 v/v) mixture, to give slightly brown crystals of the bis(2-benzoxazolinone) derivative (**3a**) (0.28 g, 72%). IR (KBr): 3211 (N—H), 1771 (C=O), 1174, 934 cm⁻¹. ¹H-NMR (DMSO-*d*₆): δ 2.28 (s, 6H, —CH₃), 3.33 (s, 4H, —CH₂—), 4.85 (s, 2H, =CH₂), 6.65 (s, 2H, Ar), 6.72 (s, 2H, Ar), 11.46 (brs, 2H, —NHCOO—). ¹³C-NMR (DMSO-*d*₆): δ 154.90, 144.75, 140.27, 133.12, 130.38, 123.36, 120.64, 114.12, 108.56, 35.30, 21.25. ANAL. calcd for C₂₀H₁₈N₂O₄: C, 68.56%; H, 5.18%; N, 8.00%. Found: C, 68.55%; H, 5.30%; N, 7.70%.

After pyrolysis of polyurea **2b** at 230°C under reduced pressure for 3.5 h, the reaction residue was extracted with acetone and filtered to remove the insoluble fraction. A powdery and slightly brown colored bis(2-benzoxazolinone) derivative (**3b**) was obtained in a yield of 86% from the filtration after removing the acetone. IR (KBr): 3231 (N—H), 1766 (C=O), 1157, 943 cm⁻¹. ¹H-NMR (DMSO-*d*₆): δ 1.26 (s, 18H, —C(CH₃)₃), 3.36 (s, 4H, —CH₂—), 4.89 (d, *J* = 10.65 Hz, 2H, =CH₂), 6.82 (s, 2H, Ar), 6.85 (s, 2H, Ar), 11.35 (brs, 2H, —NHCOO—). ¹³C-NMR (DMSO-*d*₆): δ 153.43, 145.09, 143.13, 138.65, 128.67, 118.68, 118.03,

Table I Data of Polymerization and Polyurea Solubility

Polyurea	Yield (%)	M_w^a	M_w/M_n	Solubility ^b					
				DMF	DMAc	DMSO	NMP	CHCl ₃	THF
2a	98.5	153,000	1.51	+	+	+	+	-	-
2b	96.5	95,000	1.53	+	+	+	+	-	+

^a Measured by GPC using polystyrene as standard in DMF containing lithium chloride at a concentration of 0.42 g/L as an eluent.

^b +, soluble; -, insoluble.

112.63, 103.52, 34.03, 33.15, 30.09. ANAL. calcd for C₂₆H₃₀N₂O₄: C, 71.87%; H, 6.96%; N, 6.45%. Found: C, 71.77%; H, 7.09%; N, 6.16%.

Preparation of Casting Film of Polyurea 2b

The resulting polyurea **2b** was purified by repeat precipitation from a tetrahydrofuran (THF) solution (5 wt %) into methanol three times, and the collected polymer was washed by reflux with methanol and dried at 60°C under vacuum for 36 h. Then a solution of the sample in THF (5 mg/ml) was prepared and stirred at room temperature for 24 h and was finally filtered through a syringe-driven filter unit (0.45 μm). The polymer solution was directly used for film spin-casting onto a glass plate. The glass plate was carefully cleaned before applying the polymer by subsequently sonicating it in acetone, a 10 wt % sodium hydroxide solution, and distilled water. After this

treatment, the glass plate was carefully dried with nitrogen.

Using a Kyowariken K-359 S-1 apparatus, a thin film of polyurea **2b** on the glass plate for microthermal analysis was prepared by spin-casting the THF solution of this polymer at 700–2000 rpm. After being dried at 50°C for 8 h, the film was dried at 80°C for a further 12 h under vacuum. This film was then used for thermal surface patterning on a micro-thermal analyzer (see the next section).

RESULTS AND DISCUSSION

In our previous work,¹⁰ diamines **1a** and **1b** with an isobutenyl bis(aryl ether) moiety capable of TCR, were synthesized. For the structure of **1a** or **1b**, TCR is allowed to take place only to the ortho

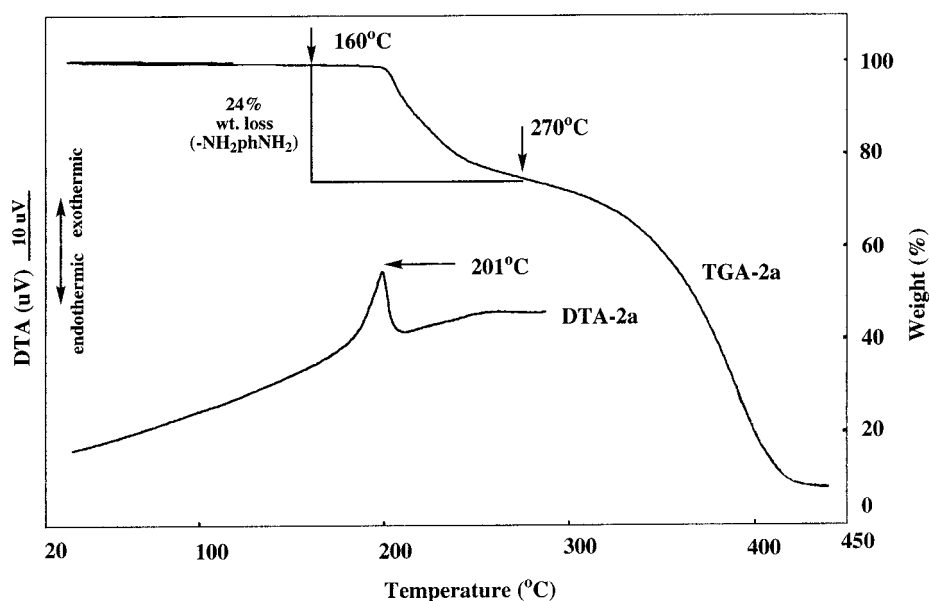


Figure 1 TG/DTA analysis in nitrogen (heating rate 5°C/min) of polyurea **2a**.

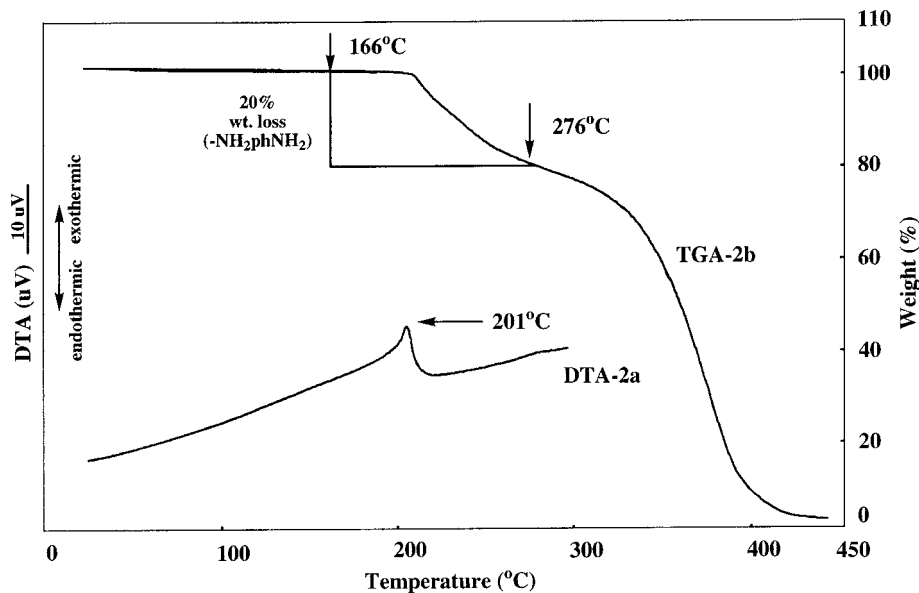


Figure 2 TG/DTA analysis in nitrogen (heating rate 5°C/min) of polyurea **2b**.

position of isobutenyl bis(aryl ether) moiety because of the presence of the para substituent.⁵ Based on these two kinds of monomers, polyureas **2a** and **2b** were synthesized as shown in Scheme 1. The structures of the polymers were identified by IR, ¹H-NMR, and ¹³C-NMR measurements. The details of the polymerization and solubility of polyureas **2a** and **2b** are summarized in Table I. Weight-average molecular weights (M_w), determined by GPC, were 153,000 and 95,000 for polyureas **2a** and **2b**, respectively, and the corresponding polydispersities (M_w/M_n) were 1.51 and 1.53. These polymers were soluble in DMSO and amide solvents. Polyurea **2b** was readily soluble in THF, whereas polyurea **2a** was insoluble, which indicates that the solubility of **2b** was facilitated by tertiary butyl groups in the polymer structure.

Thermal behaviors of the polyureas (**2a**, **2b**) were investigated by thermogravimetric analysis (TGA) and DTA, as shown in Figures 1 and 2. The analysis results are summarized in Table II.

In TGA-**2a** and TGA-**2b** curves, the theoretical weight losses 24 and 20%, corresponding to one 1,4-phenylenediamine per compositional repeat unit, were found between 160 and 270°C and 166–276°C for polyureas **2a** and **2b**, respectively. In DTA-**2a** and DTA-**2b** curves, exothermic peaks at 201 and 204°C, caused by TCR and the following cyclizations, were observed for polyureas **2a** and **2b**. This indicates that the TCR and the subsequent cyclization could proceed between 201 and 270°C and 204–276°C for polyureas **2a** and **2b**, respectively.

Practical thermal treatment of polyureas **2a** and **2b** was carried out at 230°C for 3.5 h under

Table II Results of Thermal Treatment of Polyureas and Model Compounds

Polyurea	Yield ^a (%)	Exotherm ^b (°C)	Weight Loss	
			Calculated ^c (%)	Temperature region ^d (°C)
2a	72	201	24	160–270
2b	86	204	20	166–276

^a Pyrolysis conversions of polyureas (**2a**, **2b**) to bis(2-benzoxazolinone) derivatives (**3a**, **3b**) at 230°C under reduced pressure for 3.5 h.

^b Temperatures corresponding the tops of exothermic peaks attributed to the TCR and intramolecular cyclization observed by DTA using a heating rate of 5 K min⁻¹ under nitrogen.

^c Theoretical weight losses of 100% conversion from the polymers and their model compounds to **3a** and **3b**.

^d Temperature regions corresponding to 100% conversions to **3a** and **3b** observed by TGA using a heating rate of 5 K min⁻¹ under nitrogen.

reduced pressure using a rotary motor equipped with a gas trap. Interestingly, pyrolysis of these polymers gave the respective bis(2-benzoxazolinone) derivatives **3a** and **3b** with the loss of 1,4-phenylenediamine, which was found in the gas trap after pyrolysis, resulting in degradation of **2a** and **2b**, as shown in Scheme 2. The high yields of **3a** and **3b** imply that the reactions proceeded smoothly under the reaction conditions.

Hence, it is clear that, during the thermal treatments, *in situ* tandem Claisen rearrangement (formation of hydroxy groups) followed by cyclization (between the hydroxy groups and ortho urea groups), with loss of 1,4-phenylenediamine, led to the formation of bis(2-benzoxazolinone) derivatives, resulting in degradation of the polymers.

As one application using the polyurea, we did a preliminary study to assess the polymer as a material for use in lithography by using μ TA. In general, μ TA, a technique combining the visualization power of atomic force microscopy (AFM) with the characterization ability of thermal methods, is used to obtain spatially resolved information about the morphology and composition of polymer films. In this case, we applied it as a tool to modify the thermally decomposing polymer film with the thermal probe tip.

A film was prepared by spin-casting a THF solution of polymer **2b** onto a glass plate (see Experimental section). Micro-TMA and DTA were carried out to measure the decomposition temperature on the polymer film, where the thermal probe tip is thought to descend and detect a thermal flow. Almost consistent with the results for the bulk experiments, the tip started sinking into the film from 200°C and an exo/endothermic curve was observed

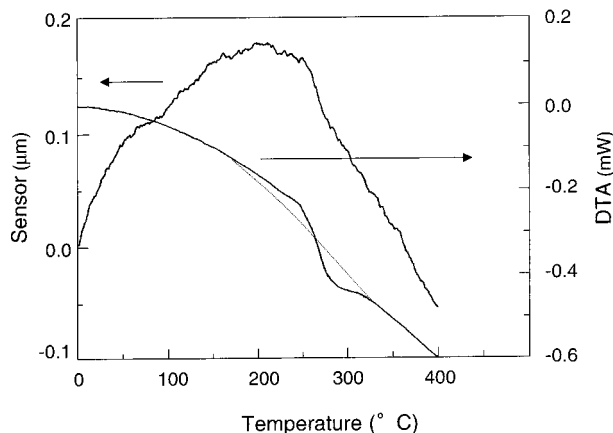


Figure 3 Micro-TMA and DTA curves for a scan location of the polyurea film.

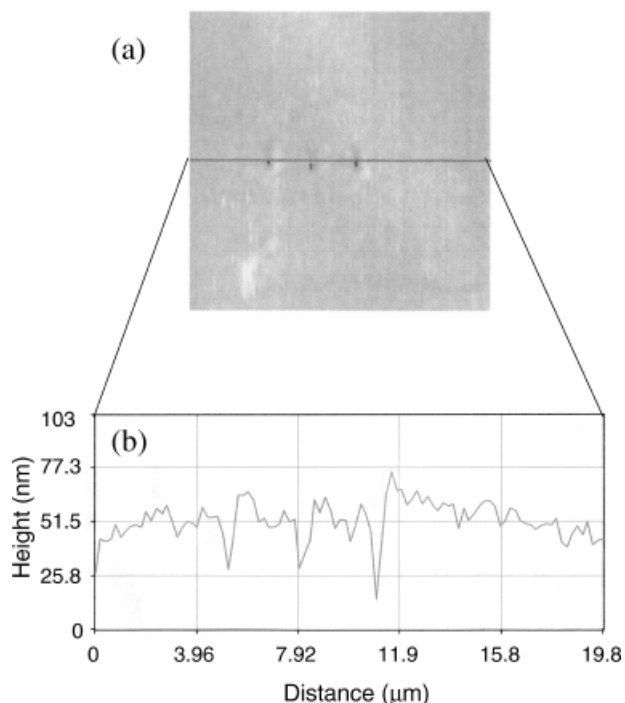


Figure 4 (a) A contact-mode AFM image of modified polyurea film by the thermal probe tips of μ TA. (b) Cross section of the features identified by the solid lines.

in the region of 200–300°C, although the curve was broadened and shifted to higher temperatures, overall (Fig. 3). This might be caused by the difference in the efficiency of the thermal conductivity to the sample between the microsized probe of μ TA and the heating stage of conventional DSC. Then, we attempted to create holes on the surface using the tip as follows: the probe tip was contacted with the surface, scanned the temperature from 25 to 275°C at 25°C/s, and moved up and toward the other locations. Figure 4 shows an AFM image of the polyurea surface after the process was conducted three times. As shown in the figure, there are three distinctive features of ellipsoidal shape. Those features had reproducible cross sections with about 0.70 μ m width. Taking into account the 5 μ m diameter of the probe tip, the width is very small. This result suggests that this polymer might be applicable to microlithography

CONCLUSIONS

1. Two kinds of novel polyureas, containing isobutenyl bis(aryl ether) moieties ortho to the urea linkages, were successfully synthesized.

2. Tandem Claisen rearrangement at isobuteryl bis(aryl ether) moieties readily occurred by heating in the bulk state, affording phenolic hydroxy groups ortho to urea linkages. Subsequent intramolecular cyclization between the hydroxy groups and the urea groups yielded the bis(2-benzoxazolinone) derivatives, with loss of 1,4-phenylenediamine, resulting in degradation of the polymers.
3. By microthermal analysis, a preliminary study of thermal surface patterning of polyurea **2b** film implied that the easily decomposable polymer might be used as a thermal patterning material, given that precise spot patterns were obtained with diameters of less than 1 μm .

REFERENCES

1. Claisen, L. *Ber Dtsch Chem Ges* 1912, 45, 3157.
2. Lutz, R. P. *Chem Rev* 1984, 84, 205.
3. Weiss, F.; Isard, A. *Bull Soc Chim Fr* 1967, 6, 2033.
4. Tyhagarajan, B. S.; Balasubramanian, K. K.; Rao, R. B. *Chem Ind (London)* 1967, 401.
5. Hiratani, K.; Takahashi, T.; Kasuga, K.; Sugihisa, H.; Fujiwara, K. *Tetrahedron Lett* 1995, 36, 5567.
6. Hiratani, K.; Uzawa, H.; Kasuga, K.; Kambayashi, H. *Tetrahedron Lett* 1997, 38, 8993.
7. Hiratani, K.; Kasuga, K.; Goto, M.; Uzawa, H. *J Am Chem Soc* 1997, 119, 12677.
8. Wang, J.; Gutsche, C. D. *J Am Chem Soc* 1998, 120, 12226.
9. Nachman, R. J. *J Heterocycl Chem* 1983, 20, 1423.
10. Yang, G.; Koyama, E.; Gestermann, S.; Matsuzoro, S. I.; Hiratani, K. *J Heterocycl Chem*, to appear.