

Side Reactions of Phenylisocyanate in *N,N*-Dimethylacetamide

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SYNOPSIS

Side reactions of isocyanate groups in *N,N*-dimethylacetamide (DMAC) were studied. Although 4,4'-diphenylmethane diisocyanate (MDI) in DMAC was stable and no changes occurred at 3°C, the isocyanate content decreased and a gel was finally formed at 40°C. Using phenyl isocyanate (PI) as a model compound of MDI, the identification of PI side-reaction products in DMAC were studied. From these experiments, the following five products were identified; (1) 1,3-diphenylurea (DPU), (2) 1,3-diphenyl-5-phenylcarbonyl-6-dimethylaminouracil (PUR), (3) 1,3,5-triphenylbiuret (TPB), (4) triphenyl-*s*-triazine-2,4,6-trione (TTT), and (5) 1,1-dimethyl-3-phenylurea (DMPU). Among these identified products, the novel side reaction product PUR, which was formed between PI and DMAC as solvent, was found along with TPB and TTT, which were already known to cause three-dimensional network formation.

INTRODUCTION

Isocyanate groups have high reactivity; hence, polyisocyanates are used as raw materials in many fields such as coating materials, adhesives, plastics, and elastomers. In the case of industrial production, it is well known that small amounts of side reactions are not inevitable considering the high reactivity of isocyanate groups.¹⁻³ So far, the following typical side reactions are well known: (1) allophanate group formation between urethane and isocyanate groups; (2) biuret group formation between urea and isocyanate groups; (3) trimerization reaction of the isocyanate group itself; and (4) urea group formation between the isocyanate group and contaminated trace water. Therefore, to avoid side reactions, polyurethanes should be synthesized without solvents. However, in case of the necessity of employing solvents, polar solvents such as DMAC, *N,N*-dimethylformamide, and dimethyl sulfoxide are used.⁴ In industrial raw materials, trace contaminants are in-

cluded. Therefore, trace side reactions are inevitable as mentioned above, but industrial production is carried out within the limit of acceptable process trouble or within the properties of polyurethanes (PU). PU can usually be produced without any trouble using DMAC as solvent by conventional methods. However, PUs are inclined to gel in the case of using MDI dissolved in DMAC for a long time. Therefore, side-reaction products of isocyanate formed in DMAC were studied.

In this report, PI was used as the model compound of MDI, and these side-reaction products produced in DMAC solution are described.

EXPERIMENTAL

Materials

MDI (Nippon Polyurethane Industry Co., Ltd.) distilled at 183°C/3 Torr, DMAC (Mitsubishi Rayon Co., Ltd.) containing 150 ppm water measured by the Karl Fischer method, and 10 ppm dimethylamine measured by gas chromatography and PI (Nacalai Tesque Inc.) distilled at 46°C/10 Torr were used.

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Side Reactions of Isocyanates in DMAC and Separation of Side-Reaction Products

Side Reactions of MDI in DMAC

A mixture of 27.5 g (0.11 mol) of MDI and 27.5 g (0.31 mol) of DMAC was placed in a two-necked 200 mL flask at 3 or 40°C and protected from moisture in the atmosphere by passing nitrogen gas. The isocyanate content was measured at certain intervals.

Side Reactions of PI in DMAC

A mixture of 27.5 g (0.23 mol) of PI and 27.5 g (0.31 mol) of DMAC was also placed in a 200 mL flask and protected from moisture in an atmosphere by nitrogen gas. After maintaining this mixture at 40°C for 9 days, the unchanged PI and DMAC were distilled at a reduced pressure (50°C, 0.15 Torr), and this residue was analyzed as side-reaction products of PI.

Characterization of Side Reaction

Measurement of Isocyanate Content

The isocyanate content of the mixture of MDI and DMAC was measured by the dibutylamine titration method reported by Stagg.⁵

Measurement of IR Spectra

The chemical changes of MDI in DMAC were measured with a Hitachi 270-30-type infrared spectrophotometer with the use of KBr plates.

Measurement of NMR Spectra

NMR spectra were obtained with a Varian XL-300 (¹³C: 75.5 MHz) and Gemini 200 (¹³C: 50.0 MHz) at room temperature. Solvents used in these measurements were CDCl₃ and DMSO-*d*₆. ¹³C-NMR by the gated decoupling method was especially used for quantitative measurement, and the APT method was used for separative analysis between quaternary carbon and methin carbon.

Measurement of Mass Spectra

Mass spectra were obtained with a Shimadzu GC MS 9100 MK/PAK-1500, and the measured conditions were as follows:

- Direct induced method (DI)
- Accelerate voltage: 3 kV
- Ionizing voltage: 70 eV
- Reaction gas: isobutane
- DI temperature: RT–320°C (40°C/min)

High-Performance Liquid Chromatography (HPLC)

Qualitative analyses of side-reaction products of PI in DMAC were performed by measuring with a high-performance liquid chromatograph (Shimadzu LC-3A) and detected at 254 nm. Measurements were performed using chloroform as the mobile phase and with a Styragel column (Shin-Pack CLS-SIL Φ = 6 mm L = 15 cm) at a flow rate of 0.8 mL/min at 25°C.

Preparative Liquid Chromatography (PLC)

A preparative liquid chromatograph (Yamazen Co. Ltd.) equipped with an ultraviolet detector (254 μ m) was used for separation of side-reaction products of PI. The separation was performed using the following conditions:

Condition 1: solvent as mobile phase; *n*-hexane/dioxane = 70/30 column; silica gel Si60 25–40 μ m Φ = 20 mm L = 300 mm flow rate; 3 mL/min.

Condition 2: solvent as mobile phase; methanol/water = 75/25 column; ODS-silica 25–40 μ m Φ = 20 mm L = 300 mm flow rate; 3 ml/min.

Condition 3: solvent as mobile phase; *n*-hexane/dioxane = 60/40 column; silica gel Si60 25–40 μ m.

RESULTS AND DISCUSSION

Side Reaction of MDI in DMAC

Figure 1 shows the residual percent of the MDI isocyanate content in DMAC at 3 and 40°C. It is clear that isocyanate groups are stable at 3°C but unstable at 40°C. Figure 2 shows the IR spectra of the MDI-DMAC solution just after mixing and after 5 days. The absorption at 2250 cm⁻¹ due to isocyanate groups are decreasing after 5 days, and novel absorptions can be identified at 3372, 1708, 1512, 1416, 1306, 1234, 818, and 762 cm⁻¹. These absorptions are not observed in the original MDI and DMAC spectra. This solution finally becomes a gel. From these absorptions, it can be presumed that urea groups (3372 cm⁻¹) and trimer of MDI or biuret groups (1708 cm⁻¹), which were already known as side-reaction products due to trace impurities, were produced. However further detailed identification of side reactions are difficult without analysis of decomposition products of the gel or of the studies of model reactions. Therefore, side reactions using PI as the model compound were studied.

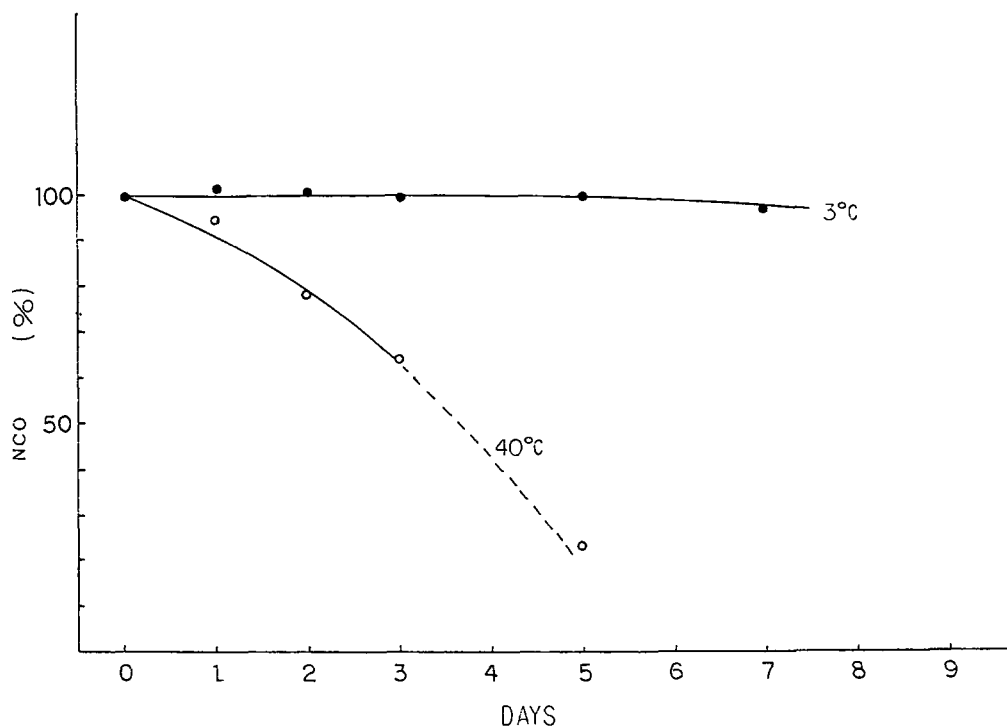


Figure 1 Residual percent of isocyanate content in MDI and DMAC mixture.

Side Reaction of PI in DMAC

The conversion of side reactions of PI in DMAC predicted in the experimental section was 32%. Sixteen peaks of the reaction products including trace peaks were separated by HPLC. However, there were five main peaks. The elution time and peak area percent of the main five peaks against total peaks

are shown in Table I. It was confirmed that the main five products were not produced during the reduced pressure distillation procedure by the following method. At the end of the same reaction between PI and DMAC, excess ethyl alcohol was added to react the unreacted PI.

This reaction mixture was analyzed by the same HPLC. From this analysis, the same peaks except

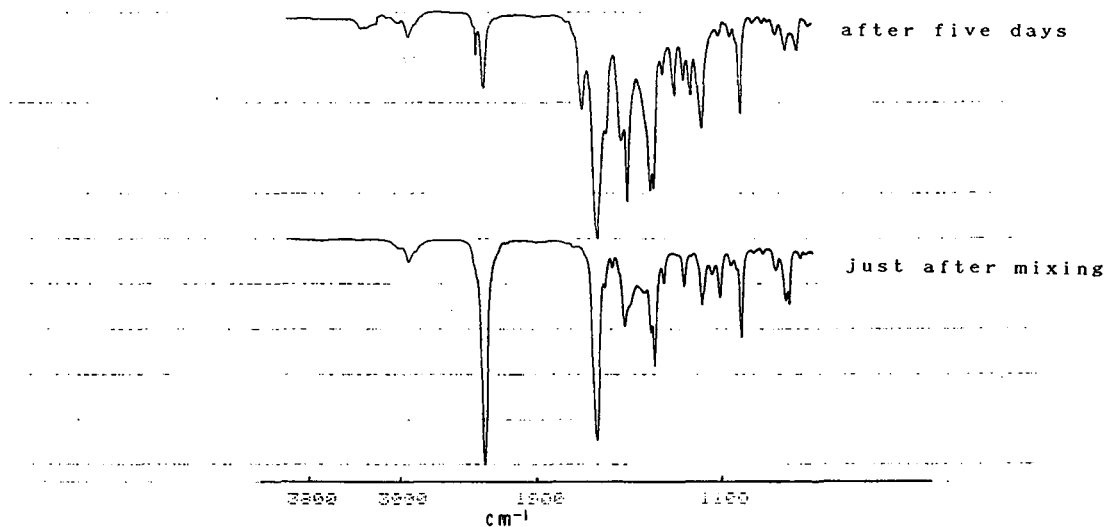


Figure 2 IR spectra of MDI and DMAC mixture.

ethylphenyl urethane from unreacted PI were identified. These five reaction products were separated by the following procedure:

Product 1: One part of the reaction mixture was dissolved into four parts of chloroform by weight and separated from the undissolved portion. This crude product recrystallized using acetone.

Product 2: Removing the chloroform after taking out Product 1, the residual mixtures dissolved in boiling ethyl alcohol, and after removing the undissolved portion and after cooling the mixture, they were recrystallized three times using ethyl alcohol.

Products 3 and 4: After removing products 1 and 2, products 3 and 4 were separated by PLC using conditions 1 and 2 in the Experimental section above.

Product 5: This product was obtained by condition 3.

The flow chart of the separations is shown in Figure 3. The isolated products indicated the same elution time as in Table I. It was confirmed that the isolated product 1 was DPU by it showing the same spectrum as the authentic DPU Sadler IR spectrum No. 3899 and that products 4 and 5 were TTT and DMPU from being similar to No. 33139 of the authentic TTT and No. 3910 of DMPU Sadler IR spectra, respectively. Product 3 was confirmed by showing the same IR and NMR spectra of TPB, which was synthesized by the same method as that of Spirkova et al.⁶ These spectra are shown in Figures 4 and 5, and the molecular weight of product 3 showed the same molecular weight as did 331 of TPB by mass spectra analysis.

Product 2 was identified to be PUR by the following analysis: Figure 6 shows the proton NMR spectrum of product 2. From this spectrum, the signals at 10.3, 7.0–7.7, and 3.3 ppm correspond to NH amide proton, phenyl proton, and N—CH₃ (equiv-

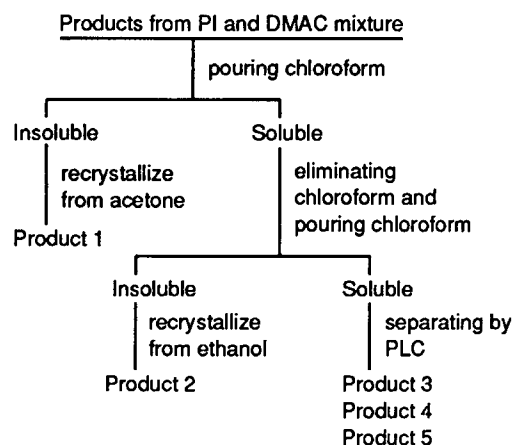
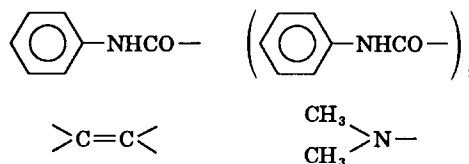


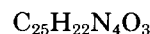
Figure 3 Flow chart of the separations.

alent) proton, respectively. The proton ratio, NH/phenyl proton/N—CH₃, is 1/15/6. This suggests the presence of three monosubstituted benzenes and one dimethylamino group.

Figure 7 shows the ¹³C-NMR spectrum. The signals at 160–165 ppm show the presence of the three carbons due to the amide carbonyl. The signals at 118–155 ppm show 19 carbons due to the phenyl group and one other carbon and 15 carbons bonding to proton. The peak at 42.3 ppm having the intensity of two carbons may be due to the dimethylamino group. The left 94.2 ppm signal is a quaternary carbon signal. From this consideration, the presence of the following structures can be presumed:



The molecular weight of product 2 was 426 by mass spectra analysis, and elementary analyses are shown in Table II. From the results of the molecular weight and elementary analyses, the following molecular formula can be written:



Also, the following two structures can be presumed:

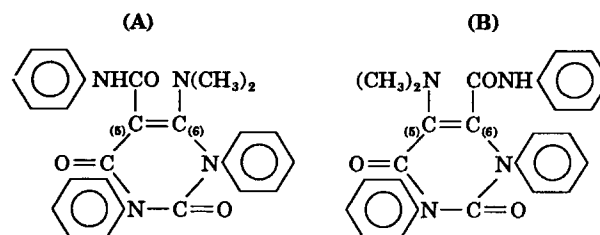


Table I Elution Times of Main Products from PI and DMAC Mixture

Product No.	Elution Time (min)	Area (%)
1	13.60	42.4
2	6.82	24.2
3	4.78	7.4
4	5.52	6.7
5	24.33	5.5

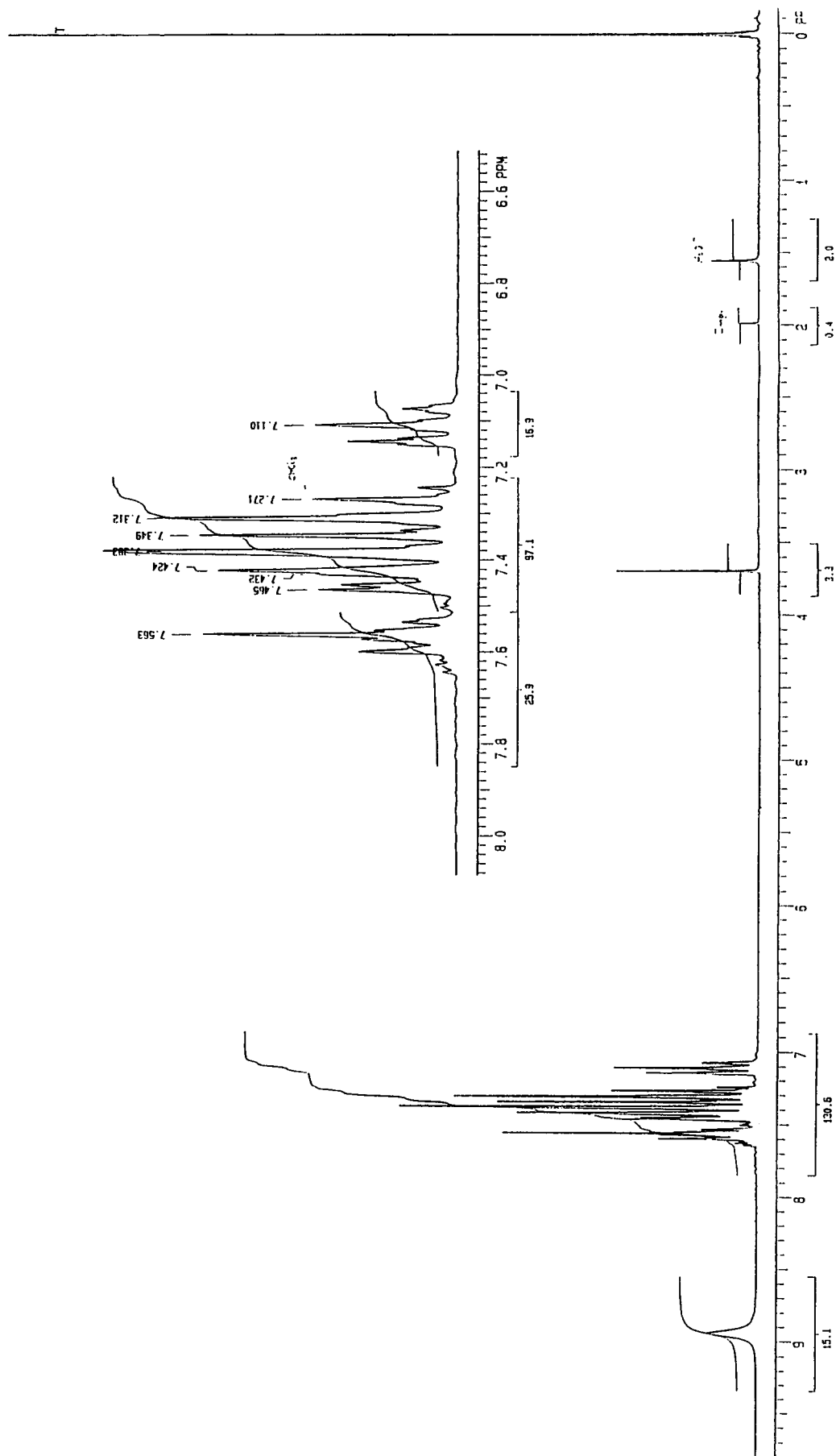


Figure 4 NMR Spectrum of TPPB.

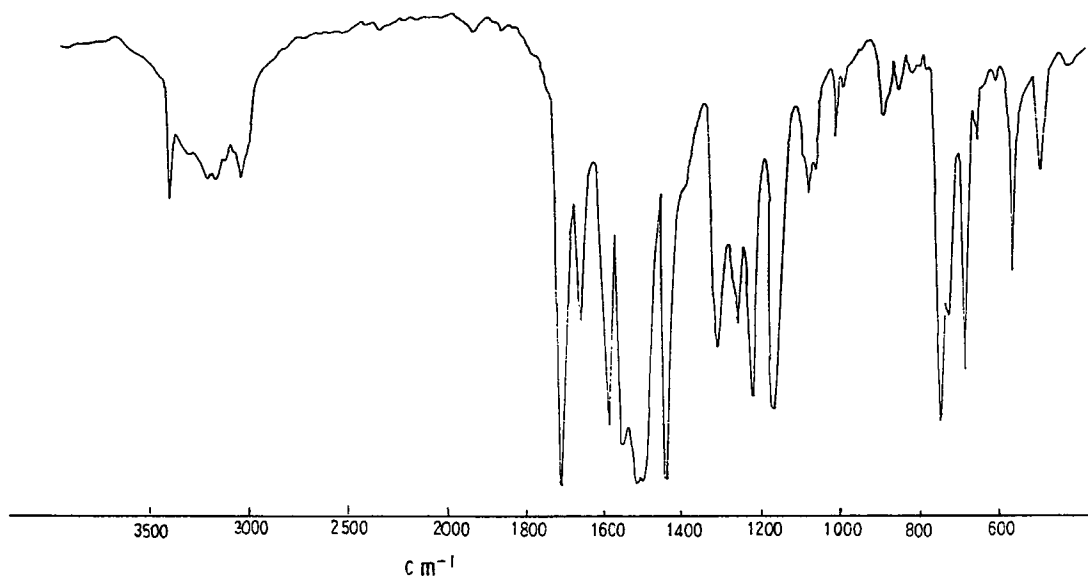


Figure 5 IR Spectrum of TPB.

In Figure 7, signals at 94.2 and 160–165 ppm are left after leaving the signal due to PI. The carbon signals at positions 5 and 6 of 1,3-dimethyl uracil are 100 and 142 ppm. Meanwhile, substitution effects of the *N*-phenylcarbamyl group and the dimethylamino group are -4.8 and 14.5 ppm as calculated by the Sadtler Guide to Carbon-13 NMR Spectra.⁷ Based

on these data, carbon signals at positions 5 and 6 were calculated as follows:

$$\text{Position 5 in (A)} = 100 - 4.8 = 95.2 \text{ ppm}$$

$$\text{Position 5 in (B)} = 100 + 14.5 = 114.5 \text{ ppm}$$

$$\text{Position 6 in (A)} = 142 + 14.5 = 156.5 \text{ ppm}$$

$$\text{Position 6 in (B)} = 142 - 4.8 = 137.2 \text{ ppm}$$

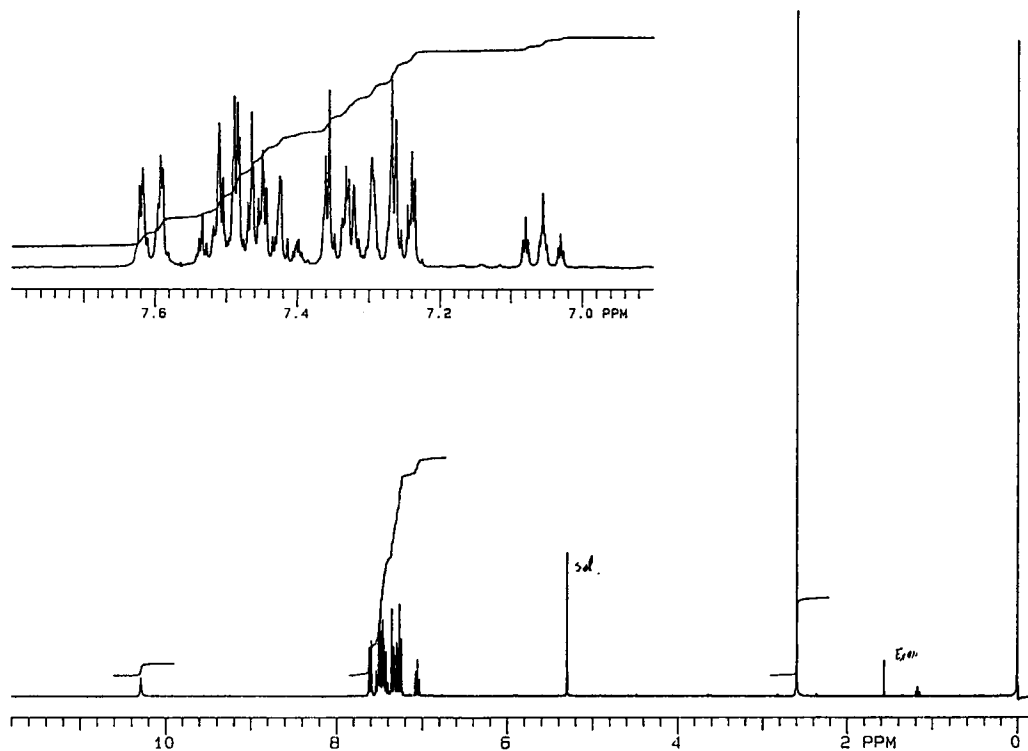


Figure 6 NMR Spectrum of Product 2.

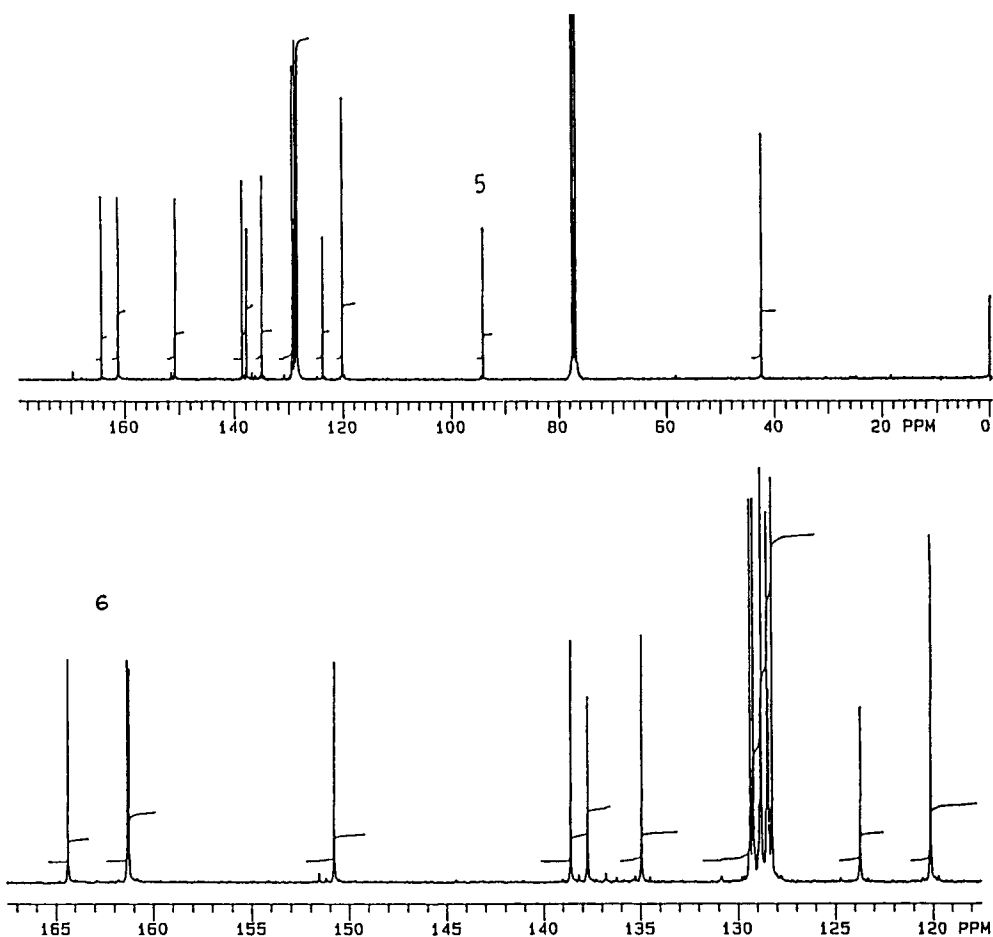


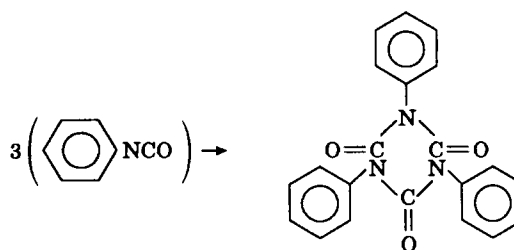
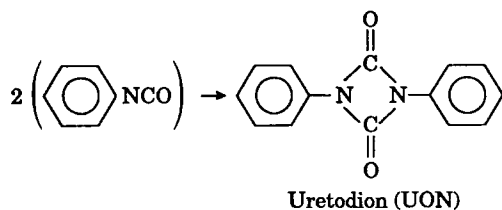
Figure 7 ^{13}C -NMR Spectrum of Product 2.

From this consideration, the structure of product 2 PUR is identified to be (A).

Table III shows the above five products identified from PI and DMAC mixture and estimated products from the MDI and DMAC mixture. In this table, products 2, 3, and 4 cause the three-dimensional network in the case of MDI.

The Presumption of Reaction Mechanisms

The cyclization of the isocyanate group is well known as follows⁸:



Triphenyltriazinetriion (TTT), product 4 (Triphenylisocyanurate)

These reactions are catalyzed with base or metal. However, they can take place slowly even without any catalyst. DMAC, a slightly basic solvent, may enhance these reactions. Uretodion was not found in the products. It might be hydrolyzed into product 1 during the analysis.

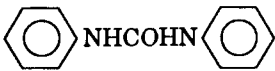
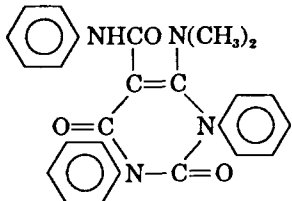
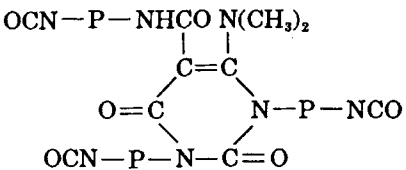
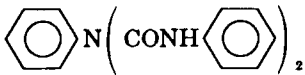
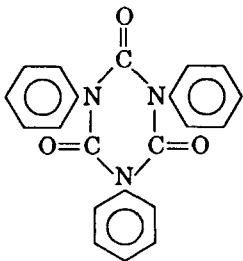
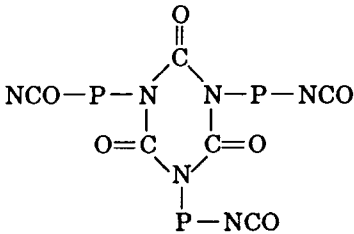

Table II Elementary Analyses of Product 2

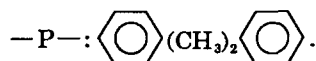
	C	H	N	(O)
Found (%)	70.33	5.25	12.99	(11.43)
Calcd (%)	70.41	5.20	13.14	(11.24)

The formations of products 1, 2, 3, and 5 are presumed to be as shown in Scheme I. The first step of these reactions are the reaction of DMAC with PI.

DMAC itself may play as a catalyst. When the first PI reacted with DMAC, the second PI can be added easily ([A] → [B]). The product may transform into a diene compound ([C]). Then, the Diels–Alder addition with the other PI gives [D].⁷ The elimination of water from [D] yields product 2. The eliminated water can react with the other PI, yielding equimolar product 1. Product 1 also react with the other PI, giving product 3. If dimethylamine was eliminated from [D] instead of water, it could react

Table III Identified Main Products from PI and DMAC Mixture and Corresponding Products stimated from MDI and DMAC Mixture

Product no.	Product From PI	Estimated product from MDI
1	 1,3-diphenyl urea	OCN—P—NHCONH—NCO
2	 1,3-diphenyl-5-phenylcarbonyl-6-dimethyl aminouracil	 OCN—P—NHCO N(CH ₃) ₂ OCN—P—N—C=O
3	 1,3,5-triphenyl biuret	OCN—P—N(CONH—P—NCO) ₂
4	 triphenyl- <i>s</i> -triazine-2,4,6-trion	 NCO—P—N—C(=O)—N—P—NCO O=C—N—C(=O)—N—P—NCO
5	 1,1-dimethyl-3-phenylurea	OCN—P—NHCON(CH ₃) ₂



identified products. No catalyst were added or found in the reaction mixture. DMAC itself may be a catalyst of the reactions.

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