First Evidence of Polyimide Elastomer Prepared from Polyurea and Pyromellitic Dianhydride

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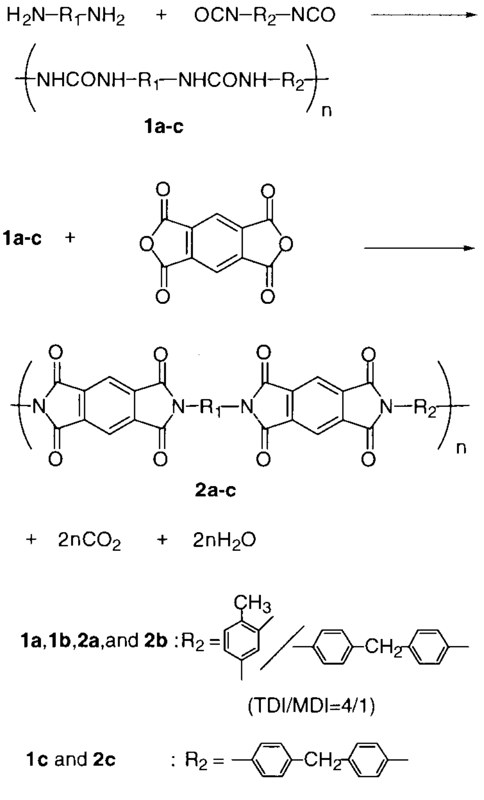
The reaction of polyureas, prepared from the conventional diisocyanates and the α, ω- diaminopolyoxyalkylenes, with pyromellitic dianhydride in N-methyl-2-pyrolidone (NMP) at 165 °C leads to the formation of polyimide elastomers. The polyimide elastomers exhibited excellent physical properties.

Having recently been the subject of a few papers[1] and patents,[2] elastic polyimides with the polyimide hard segments and the soft segments such as the polyoxyalkylene and the polysiloxane are elastomer block copolymers noteworthy for the application to high-performance adhesive, speciality coating, gas separation membrane and pervaporation membrane. The elastic polyimides are known to be polyurethaneimide, polyureaimide and polyimide elastomers. Polyimide elastomers are usually prepared by imidization of polyamic acids.[3] Accordingly, the conventional diisocyanates cannot be used as the starting materials of polyimide elastomers.

Takahashi[4] reported that an important consideration in the successful synthesis of polyimide is a design of proper composition and proper choice of synthesis method because of general difficulty in processing polyimides and their high cost. We report here the first evidence of polyimide elastomer, prepared from polyurea and pyromellitic dianhydride. The use of polyurea is a novel and simple synthesis method with good cost performance utilizing the organic reaction[5] of urea with carboxylic anhydride. Polyureas, prepared from the conventional diisocyanates, such as 2,4-tolylenediisocyanate (TDI-100) and 4,4'-methylenedi (phenylisocyanate) (MDI), and the polytetramethyleneoxide-di-*p*-aminobenzoate (Elasmer 1000), reacted with pyromellitic dianhydride to give polyimide elastomers (Scheme 1).



Scheme 1.

The polyurea (**1a**) was obtained by a solution polymerization of Elasmer 1000 and the mixed diisocyanate (TDI-100 : MDI molar ratio = 4 : 1). **1b** (TDI-100 : MDI molar ratio = 4 : 1) and **1c** (MDI) were obtained by a bulk polymerization in the same reaction conditions. The mixed diisocyanate was used to obtain polyimide elastomer which was soluble in NMP at 23 °C. Polyimide elastomer (**2a**) was prepared by reacting **1a** with pyromellitic dianhydride in 35 wt% NMP solution at 165 °C for 3 h, during which the reactor was swept with argon gas to distill out the NMP containing water formed by imidization. **2b** and **2c** were prepared under similar conditions in 20 wt% NMP solution. The evolution of carbon dioxide gas was not observed after 3 h of reacting at 165 °C in any imidization reaction. The degrees of an imidization were approximately calculated from the amount of water in the distillates. In the reactions of **1b** and **1c** with pyromellic dianhydride, the amounts of water to be distilled out were 48 and 92% in comparison with the theoretical amount. Considering that carbon dioxide gas was no longer evolved toward the end of the process, the degrees of an imidization were assumed to be over 70% in **2b** and over 95% in **2c**. The physical properties of product solutions are summarized in Table 1.

Films of polyurea (**1a-c**) and polyimide elastomers (**2a-c**) were obtained by the method cited in the footnote of Table 2.

Table 1. The physical properties of polyurea (**1a-c**) and polyimide (**2a-c**) solutions[a]

polyurea and polyimide	appearance	non volatile	viscosity
		wt %	mPas/23°C
1a	light yellow, clear	29.6	2170
2a	dark brown, clear	19.2	60
1b	light yellow, clear	19.9	31250
2b[b]	dark brown, clear	20.3	200
1c	light yellow, clear	20.0[c]	8920
2c	dark brown, clear	20.0[c]	gel

[a] The solvent was NMP. [b] The polymer powder was obtaind by pouring the product solution (**2b**) in methanol, and then it was dried for 24 h at 80 °C in vacuo. The yield was 91.1% and the reduced viscosity was 0.30 dL/g (0.1g/dL NMP at 30 °C). [c] Calculated by material balance data.

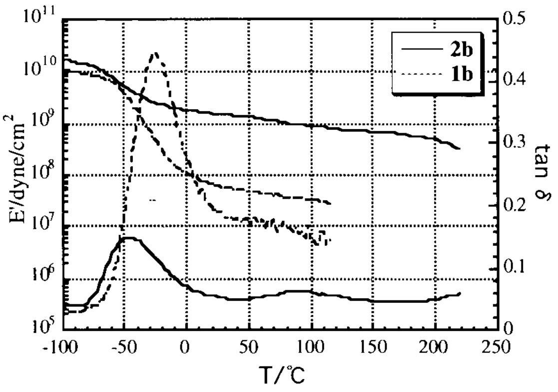


Figure 1. Temperature dependence of the dynamic mechanical storage modulus (E') and the dissipation factor (tan δ) at 10 Hz at heating rate of 5 °Cmin^{-1} for polyureas (**1b**) and polyimide (**2b**) elastomers.

The infrared spectrum of the film of polyimide elastomer (**2b**) by ATR method exhibits remarkable absorption around 1780 and 1380 cm^{-1} which are characteristic absorption bands of imide.

Thermogravimetric analysis (TGA) was carried out to investigate the thermal stability of the films of polyurea (**1a**) and polyimide elastomers (**2a**). The profile of TGA in air shows that **1a** has the temperatures of initial (T_0) weight loss at 234 °C and 10% (T_{10}) weight loss at 317 °C and that **2a** has T_0 at 280 °C and T_{10} at 377 °C. The thermal stability increases due to the imidization, although T_0 and T_{10} are considered to depend upon thermooxidative degradation of the polyoxytetramethylene segment which is the most unstable segment in the polymer.

Table 2. Tensile properties of films[a] of polyurea (**1a-c**) and polyimide (**2a-c**) elastomers

polyurea and polyimide	Modulus, %				TB	EB
	50	100	200	300		
	MPa				MPa	%
1a	1.3	1.5	1.7	1.9	2.4	1100
2a	16.3	17.8	19.2	25.0	61.6	550
1b	1.7	1.9	2.4	2.8	12.3	1090
2b	17.4	17.6	18.5	19.4	40.1	500
1c	5.3	5.6	6.1	6.7	12.9	900
2c	17.5	16.5	16.5	16.5	48.5	750

[a] The product solution was cast on a polypropylene sheet, and then solidified in argon gas at 150 °C for 2 h. The film was allowed to stand for 16h at 150 °C in vacuo. The final thickness of the film was adjusted about 200 μm.

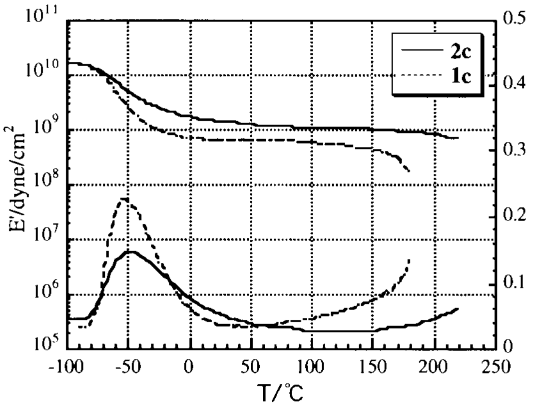


Figure 2. Temperature dependence of the dynamic mechanical storage modulus (E') and the dissipation factor (tan δ) at 10 Hz at heating rate of 5 °Cmin^{-1} for polyureas (**1c**) and polyimide (**2c**) elastomers.

The tensile strength at break (T_B) of polyurea (**1a**) was 2.4 MPa and that of the corresponding polyimide (**2a**) was 61.6 MPa. The imidization of polyureas brought a substantial improvement of tensile properties and an essential degradation of polyurea chain during the imidization reaction did not occur. The tensile properties of **1a-c** and **2a-c** are indicated in Table 2.

The dynamic mechanical storage modulus (E') and the dissipation factor (tan δ) plotted as a function of temperature are given in Figures 1 and 2. The values of E' and tan δ in **2b** showed that the microphase separation between the soft segment and hard segment was increased due to the imidization. As shown in Figure 2, the range of rubbery plateau of **2c** is equal to or wider than that of this class of elastomers obtained by other synthesis methods.[3,6] These results suggest that the synthesis method described here is a greatly improved method producing of polyimide elastomers.

References

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