Thermodegradable Polyurethanes Having Azo Groups in the Main Chains. 1. Synthesis and Thermal Properties

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ABSTRACT: Thermodegradable polyurethanes were synthesized from α,ω-dihydroxypolycaprolactone (PCL), 4,4′-methylenediphenylisocyanate (MDI), and 2,2′-azobis(2-cyanopropanol) (ACP) in a two-step polyaddition reaction. The thermodegradations of ACP and the polyurethanes were investigated by thermogravimetric analysis and FTIR. The molecular degradation processes of the polyurethanes were followed by GPC. Degradation kinetics were discussed based on the disproportionation termination of radicals generated by the scission of an azo group. The experimental results showed a more complex mechanism.

Introduction

With increasing uses of synthetic polymers, treatment and disposal of polymer wastes are important concerns to ensure preservation of the environment around the world. Many studies have focused on the design and development of new polymers with photo- and biodegradable properties. Comparatively less attention has been paid to thermodegradable polymers. Since many symmetrical, difunctional azo compounds (XRN═NRX with X's as functional groups like OH, COOH, and COOMe) have been developed, the synthesis of thermodegradable polymers with controllable thermodecomposition characteristics becomes possible. Polymers containing such azo compounds, which can be macroinitiators for radical polymerization or microcapsules for thermotransfer printing, have been extensively studied[1-4] and reviewed recently by Ueda and Nagai.[5] However, to our knowledge, there is no systematic study on the molecular degradation characteristics of such polymers. In this paper thermodegradable polyurethanes (TDPU's) were synthesized from α,ω-dihydroxypolycaprolactone (PCL; M_n = 2000), 4,4′-methylenediphenylisocyanate (MDI), and 2,2′-azobis(2-cyanopropanol) (ACP) in a two-step polyaddition reaction. These polyurethanes are successfully utilized as thermodegradable films and adhesives.[6] The thermodecomposition characteristics and kinetics of ACP and the polyurethanes were investigated by thermogravimetric analysis (TG), Fourier transform infrared spectroscopy (FTIR), and UV-vis spectroscopy. The molecular degradation processes of the polyurethanes were pursued by gel permeation chromatography (GPC). A kinetic equation for degradation was proposed based on the disproportionation termination mechanism of radicals generated by thermal scission of azo groups.

Experimental Section

Materials. 4,4′-Methylenediphenylisocyanate (MDI), dimethylformamide (DMF), 1,4-dioxane, triethylenediamine (TEDA), and 1,1′-diphenyl-2-picrylhydrazyl (DPPH) were of reagent grade and used as received. 2,2′-Azobis(2-cyanopropanol) (ACP; a product of Wako Chemicals) was washed by swirling it in diethyl ether for 4 h at 30 °C, filtered, and dried in vacuo for 3 days. α,ω-Dihydroxypolycaprolactone (PCL; an Aldrich polycaprolactone diol, Mn = 2000) was dried in vacuo for 2 h at 110 °C.

General Polymerization Procedure. A two-step polymerization reaction was adopted. PCL (5 g) and MDI (1.25 g; in the molar ratio of PCL:MDI = 1:2) were stirred for 1 h at 70 °C in a nitrogen atmosphere to form an NCO-terminated prepolymer. The prepolymer was then cooled to room temperature and dissolved in 10 mL of DMF. TEDA (0.01 g) as catalyst was first dissolved in DMF (0.5 mL) and then added to the prepolymer solution. In the second step, the prepolymer was chain extended with ACP: ACP (0.49 g) was first dissolved in DMF (5 mL) and then added to the prepolymer solution and reacted for 2 h at room temperature in nitrogen with stirring. To terminate the polymerization, n-butylamine (ca. 10 mg) was added to control the pH of the polymer solution at 7. The polymer was precipitated in water, washed with demineralized water, and then dried in vacuum for several days at room temperature.

Preparation of Thermodegradable Polyurethanes Containing DPPH. Samples of thermodegradable polyurethanes (TDPU) containing 16 wt % (molar ratio of DPPH:ACP in TDPU = 1.1:1) and 30 wt % DPPH (molar ratio of DPPH:ACP in TDPU = 2:1) were prepared by mixing the two components in DMF and then freeze-drying them to obtain solid polymers.

Thermal Degradation. TDPU samples and the samples containing 16 wt % DPPH were heated at 135 °C for different times in a nitrogen atmosphere. Samples containing 30 wt % DPPH were first dissolved in 1,4-dioxane (0.25 g/dL) and then heated to its boiling point (ca. 100 °C) in a nitrogen atmosphere. A part of the solution was taken out for UV-vis measurement, and the remaining part was freeze-dried for GPC analysis.

Measurements. Viscosity. The inherent viscosities of the polymers were measured in DMF (0.25 g/dL) at 30 °C.

Molecular Weight. The molecular weight and molecular weight distribution of the polymers were obtained by GPC at 35 °C using a Shimadzu gel column and polystyrene standards (M_n = 2×10^3–6.6×10^5) and THF as eluent with a flow rate of 1.3 mL/min.

FTIR Spectroscopy. Thin films for FTIR measurements were cast on glass plates from a 2% THF solution of polymers, peeled, and dried in vacuo for several days before measurement. IR spectra were recorded on a Shimadzu FT-IR-4300 Fourier transform infrared spectrophotometer at room temperature. The signal was averaged by 100 scans at a resolution of 2 cm^{-1}. All films used for IR studies were sufficiently thin to obey the Beer-Lambert law.

UV-Vis Spectroscopy. A Shimadzu UV-1200 UV-vis spectrophotometer was used. The polymer concentration in 1,4-dioxane was 25 mg/dL.

Thermogravimetric Analysis. Thermogravimetric studies were performed from room temperature to 300 °C on a Shimadzu DT-40 thermal analyzer in a nitrogen atmosphere with a heating rate of 10 °C/min. Sample sizes ranged from 10 to 20 mg.

Results and Discussion

Synthesis and Characterization of Polymers. Thermodegradable polyurethanes (TDPU's) reported in this

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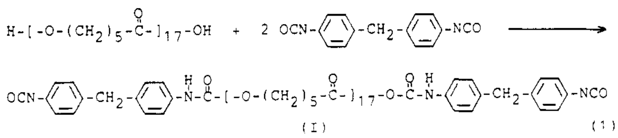
Scheme I



Scheme II

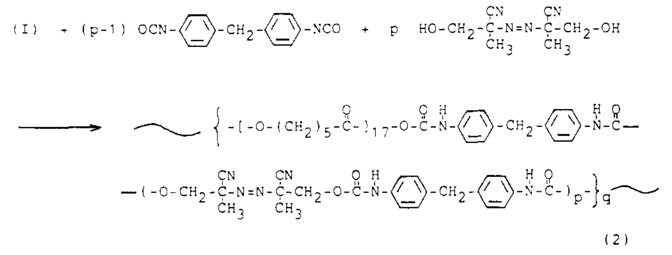


Table I. Viscosity and Molecular Weight of Thermodegradable Polyurethanes

sample	charged ratio (mol) PCL:MDI:ACP	η_{inh}	M_n (×10^{-4})	M_w (×10^{-4})	M_w/M_n
TDPU-1	1:2:1[a]	0.51	2.1	4.6	2.2
TDPU-2	1:3:2[b]	0.40	1.5	4.0	2.7
TDPU-3	1:4:3[c]	0.34	1.4	3.9	2.7

[a] Microanalytical values. Calcd for $PCL_1MDI_2ACP_1$: C, 63.3; H, 7.8; N, 4.2. Found: C, 63.3; H, 8.4; N, 5.1. [b] Microanalytical values. Calcd for $PCL_1MDI_3ACP_2$: C, 63.1; H, 7.3; N, 6.3. Found: C, 63.7; H, 8.3; N, 6.5. [c] Microanalytical values. Calcd for $PCL_1MDI_4ACP_3$: C, 63.0; H, 7.1; N, 7.9. Found: C, 63.3; H, 7.9; N, 8.2.

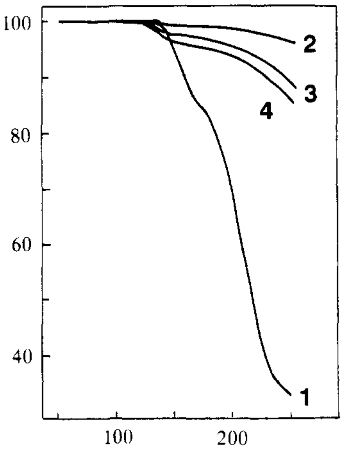


Figure 1. Thermogravimetric curves: (1) ACP, (2) TDPU-1, (3) TDPU-2, (4) TDPU-3. Abscissa: temperature (°C). Ordinate: weight retained (%).

work were synthesized in two steps. In the first step, PCL was reacted with MDI in a molar ratio of 1:2 to form a prepolymer as shown in eq 1 of Scheme I.

In the second step, the prepolymer was chain extended with ACP to form polyurethane macromolecules (Scheme II).

The results of molecular weight measurement for the TDPU samples are listed in Table I. Formation of the azo-containing polyurethanes was also examined by FTIR: typical IR absorption bands for TDPU's were NH (3340 cm^{-1}), CN (2222 cm^{-1}), C═O (1731 cm^{-1}), and HNC═O (1534 cm^{-1}).

Thermal Decomposition Properties of Azobis(2-cyanopropanol) and TDPU's. Thermogravimetric curves of ACP and TDPU's are shown in Figure 1. It can be seen from Figure 1 that the decomposition of ACP occurs in a multistage way. The initial weight loss starts at about 122 °C. The loss reaches 14.5% at about 155 °C. It is interesting that the amount of initial weight loss is fully consistent with the calculated weight percent (14.3%) of N═N groups in ACP. This result implies that the initial weight loss has come from the elimination of N═N groups in ACP.

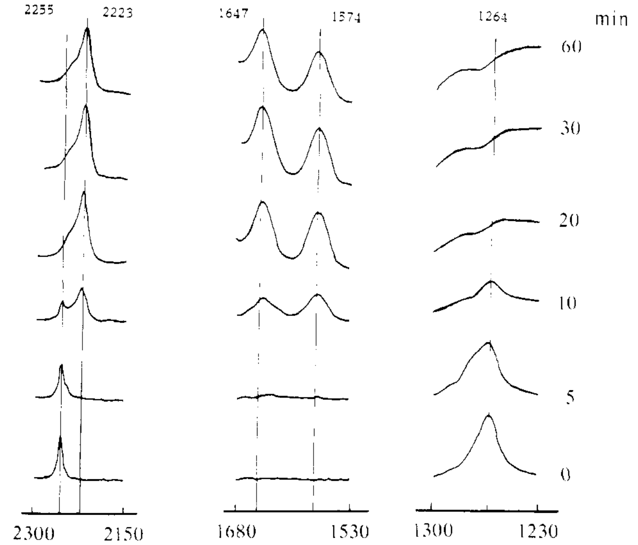


Figure 2. Change of IR absorptions of 2,2′-azobis(2-cyanopropanol).

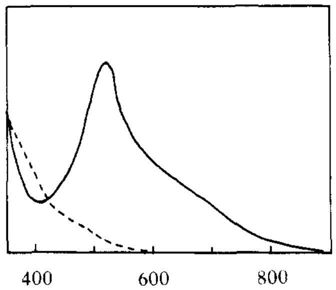


Figure 3. UV–vis spectra of 2,2′-azobis(2-cyanopropanol) before and after heating: (—) before heating; (---) after heating. Abscissa: wavelength (nm). Ordinate: absorbance.

Further information about the decomposition was obtained from the FTIR results. When ACP was heated at 80 °C for different times, no significant changes were observed in the IR spectra except for the OH stretching region. However, when ACP was heated at 110 °C for about 10 min, CN absorption split into two peaks at 2255 and 2223 cm^{-1} (Figure 2). This implies the structural change of CN from the CNCC type to CNC═C.[7] The peaks appearing in the 1570–1650-cm^{-1} region also reveal the formation of C═C bond. These results strongly suggest that the hydroxybutyronitrile radical $HOCH_2C^{\bullet}(CN)CH_3$ was generated and disproportionated to cyanoolefin compounds along with the formation of a dicyanodiol without the azo group.

The formation of radicals was indirectly checked by UV–vis spectroscopy. Bawn and Mellish have shown that stable free radical 1,1′-diphenyl-2-picrylhydrazyl (DPPH) is destroyed with the reaction of labile free radicals.[8] The hydroxybutyronitrile radicals generated by the scission of a molecule of ACP will consume two molecules of DPPH if the latter is an efficient radical scavenger. Because DPPH radical in 1,4-dioxane shows a strong absorption centered at 519 nm whereas ACP has no absorption in this region, consumption of DPPH was measured spectrophotometrically. As shown in Figure 3, a ACP/DPPH/1,4-dioxane solution before heating showed a strong absorption at 519 nm. The absorption disappeared when the solution was heated for 15 min at 100 °C. At this temperature the

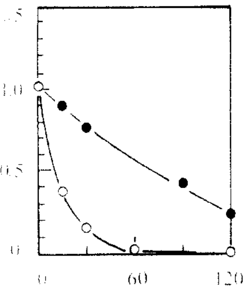


Figure 4. Normalized UV–vis absorption versus time: (●) blank test; (○) experimental data. Abscissa: time (min). Ordinate: $A(t)/A_0$.

Table II. Comparison of Initial Weight Loss with the Calculated Weight Percent of N=N in ACP and TDPU's

sample	ACP	TDPU-1	TDPU-2	TDPU-3
initial temp (°C)	122	133	110	105
initial weight loss (%)	14.5	0.6	2.8	4.2
weight percent of N=N in ACP and TDPU's (%)	14.3	1.04	1.78	2.34

self-combination of DPPH free radicals cannot be ignored and accordingly blank tests were carried out for comparison. The peak areas were normalized to the peak area at $t = 0$, and the results are shown in Figure 4.

In the thermograms of TDPU samples (Figure 1), the temperatures of initial weight loss were a little lower than that of ACP except for TDPU-1. The initial weight loss increased with an increase of the azo content in the TDPU. Comparison of the initial weight loss with the calculated weight percent of N=N groups in TDPU is listed in Table II. Although initial weight loss of TDPU samples differed somewhat from the calculated values of the azo content, we consider it to be of the same origin as ACP.

The radicals generated in TDPU samples were also checked by using the DPPH method. 1,4-Dioxane solutions of TDPU-2 having 30 wt % DPPH showed systematic changes in the absorption at 519 nm after heating at 100 °C for different times. As shown in Figure 4, the peak area of the absorption decreased with the heating time. Compared with the blank test, it was clear that some of the DPPH radicals were consumed by radicals of TDPU-2.

The kinetic parameters of thermal decomposition of ACP and TDPU, which will be published elsewhere, were estimated based on the following kinetic equation for thermal decomposition:

$$dx/dt = k(1-x)^n \tag{3}$$

where k is the rate constant, n is the order of reaction, and x is expressed as:

$$x = \frac{W_0 - W(t)}{W_0 - W_\infty} \tag{4}$$

where W_0, W(t), and W_∞ are the weights of the sample at $t = 0$, t, and ∞, respectively.

When the heating rate, $r = dT/dt$, is constant, the temperature scale can be easily converted to a time scale, that is, $dx/dt = r(dx/dT)$. Therefore, only one TG measurement is necessary to obtain the kinetic parameters. The temperature dependence of the rate constant k can be described by the Arrhenius equation, i.e., $k = A \exp(-E_d/RT)$, in which E_d is the activation energy of decomposition and R is the gas constant.

Therefore, eq 3 can be rewritten as:

$$dx/dT = r^{-1}A \exp(-E_d/RT)(1-x)^n \tag{5}$$

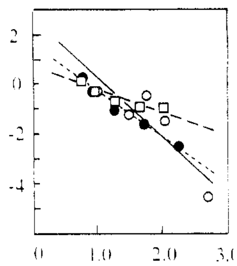


Figure 5. Relationship between X and Y in eq 8: (-○-) ACP; (-□-) TDPU-2; (---●---) TDPU-3. Abscissa: X (x10^{-4}). Ordinate: Y.

Table III. Values of E_d, n, r, and T_{max} for ACP and TDPU's

sample	ACP	TDPU-1	TDPU-2	TDPU-3
E_d (kJ/mol)	202		81	154
n	2.7		0.77	1.5
r	0.90		0.95	0.97
T_{max} (°C)	124		125	120

or

$$\frac{d\{\ln(dx/dT)\}}{d\{\ln(1-x)\}} = -\frac{E_d}{R}\frac{d(1/T)}{d\{\ln(1-x)\}} + n \tag{6}$$

Let

$$Y = \frac{d\{\ln(dx/dT)\}}{d\{\ln(1-x)\}} \quad \text{and} \quad X = \frac{d(1/T)}{d\{\ln(1-x)\}} \tag{7}$$

Equation 5 can be expressed as:

$$Y = -(E_d/R)X = n \tag{8}$$

Linear relationships between Y and X for ACP and TDPU samples were obtained by least-squares fits to the experimental data as shown in Figure 5. The values of E_d, n as well as the correlation coefficient (r), and T_{max} are listed in Table III.

The physical meaning of T_{max} is the temperature at which dx/dT reaches a maximum. It can be seen that the activation energy for the decomposition on ACP is about 200 kJ/mol, while the activation energies for the decomposition of TDPU are much lower than that of ACP. Similar results were reported by Nuyken et al. on their azo compound and related azo-containing polyurethanes.[1] It is also found that the activation energy increases with an increases of the azo content in the polyurethanes. This implies that a more temperature-sensitive TDPU be obtained by increasing the ACP content in the polyurethanes.

Degradation Behavior of TDPU's. The molecular degradation behavior of TDPU was investigated by measuring the molecular weight and molecular weight distribution of TDPU samples against the heating times at 135 °C. The results are shown in Figure 6. It can be seen that the molecular weight of TDPU's decreases initially with heating time and then increases. On the other hand, the molecular weight distribution index of TDPU's increases at first with heating time and then decreases. An explanation of these results has been proposed according to the decomposition mechanism of azo compounds. It is easily understood that the thermal degradation of TDPU is based on the thermal decomposition of N=N groups in the polymer chains (Scheme III).

When the N=N groups decompose, TDPU polymer chains are cut off and become segments with two radicals at both ends. The radicals formed in the above reaction can terminate in several ways: (a) disproportionation (b) recombination, and (c) transfer. This may result in a

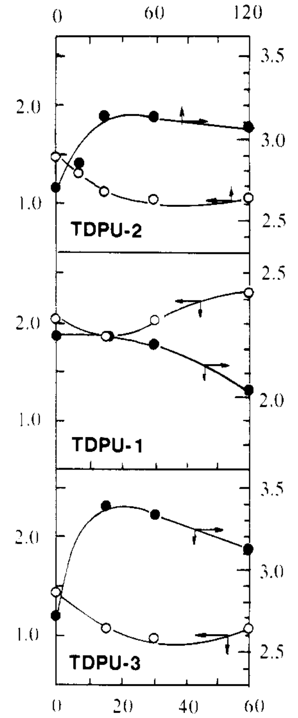
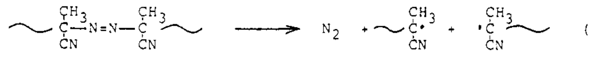


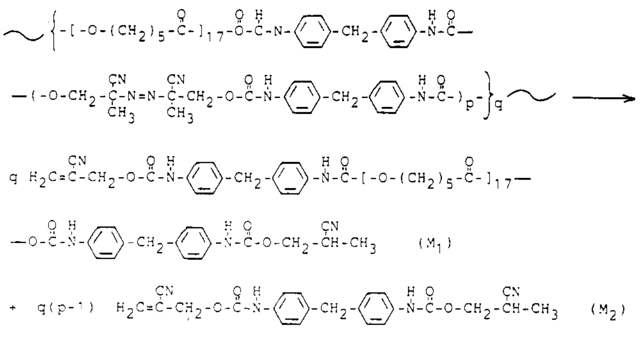
Figure 6. $M_n(t)$ and M_w/M_n values against heating time. Abscissa: time (min). Left ordinate: M_n (x10^{-4}). Right ordinate: M_w/M_n.

Scheme III



$$\sim\!\underset{CN}{\overset{CH_3}{C}}\!-N{=}N-\!\underset{CN}{\overset{CH_3}{C}}\!\sim \longrightarrow N_2 + \sim\!\underset{CN}{\overset{CH_3}{C}}\!\cdot + \cdot\underset{CN}{\overset{CH_3}{C}}\!\sim \qquad (9)$$

Scheme IV



(10)

Table IV. Limiting Average Molecular Weights for TDPU's

sample	TDPU-1	TDPU-2	TDPU-3
$M^d \times 10^{-1}$	267	154	117

complex degradation mechanism for TDPU. Only when the radicals terminate by a disproportionation mechanism does the real scission degradation of the polymers take place.

Let's consider an extreme case for the degradation. Suppose the radicals terminate by the mechanism of disporportionation (Scheme IV).

The limiting average molecular weight for the degradation of TDPU can be calculated as

$$M_\infty^{\ d} = \frac{M_1 + (p-1)M_2}{1 + (p-1)} \qquad (11)$$

The calculated limiting average molecular weight for the TDPU is listed in Table IV.

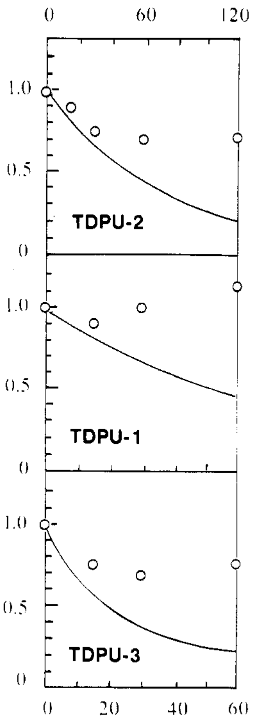


Figure 7. $M(t)/M_0$ versus time: (—) theoretical values; (○) experimental data. TDPU-1: $n_d = 0.77$, $K_d = 0.014$ min^{-1}. TDPU-2: $n_d = 0.77$, $K_d = 0.014$ min^{-1}. TDPU-3: $n_d = 1.5$, $K_d = 0.054$ min^{-1}. Abscissa: time (min). Ordinate: $M(t)/M_0$.

In such a case the thermal degradation kinetics of TDPU can be described by eq 3; however, in this case x should be expressed as:

$$x = \frac{M_0 - M(t)}{M_0 - M_\infty} \qquad (12)$$

where M_0, $M(t)$, and M_∞ are the molecular weights of TDPU at $t = 0$, t, and ∞, respectively.

By solving eq 3 under the condition of $M(0) = M_0$, the relationship between $M(t)$ and t can be established:

$$M^d(t) = M_\infty^{\ d} + (M_0 - M^d)\{1 + (n_d-1)k_d t\}^{1/(1-n_d)} \qquad (13)$$

when $n_d \gtrless 1$ and

$$M^d(t) = M_\infty^{\ d} + (M^0 - M_\infty^{\ d})\exp(-k_d t) \qquad (14)$$

when $n_d = 1$.

Theoretical curves and the experimental data are compared in Figure 7. It can be concluded from the figure that the thermal degradation of TDPU proceeds with more than a single disproportionation mechanism. Further investigation on the degradation mechanism will be reported in the next paper.

Conclusions

(a) Thermodegradable polyurethanes (TDPU's) were prepared in two-step reactions and characterized by viscosity, GPC, and FTIR.

(b) The thermal decomposition characteristics of N=N groups in polymer chains were examined by TG analysis, FTIR, and UV–vis spectroscopies. The initial weight loss in TG curves was ascribed to the thermal decomposition of azo groups. The activation energies for thermal decomposition increase with an increase of the azo content in TDPU, which implies that more temperature-sensitive TDPU be obtained by increasing the ACP content in the polyurethanes.

(c) The thermal degradation kinetics of TDPU was pursued by GPC and described by an assumed disproportionation mechanism. It was found that the real degradation proceeded in a complex mechanism ratherthan a single disproportionation. Treatments taking account of recombination and oxidation of radicals will be necessary.

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