

# Relationships between the Phase Structures and the Properties of Polycarbonatediol-based Polyurethanes

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## ABSTRACT

Polycarbonatediol (PCD) -based thermoplastic polyurethane (TPU) and Polyester (PES) -based TPU are prepared and tested for their water-resistance. The PCD-based TPU has excellent water-resistance compared to the PES-based TPU.

FT-IR spectra showed that the PCD molecules have highly hydrogen bonding property. Furthermore, the urethane-linkage of the PCD-based TPU has strong hydrogen bonding compared to the PES-based TPU. The nano-scale observation of phase-separated structures of the TPUs was performed using Dynamic-mode atomic force microscope (AFM). The PCD-based TPU has bi-continuous domains. Furthermore, the difference of stiffness between hard- and soft-domains is relatively small compared with PES-based TPU. The soft-domain of PES-based TPU represented the tendency to swell under the immersion in water; nevertheless the domain structure of PCD-based TPU was scarcely changed in the same condition. Molecular orbital calculations revealed that the hydrolysis property of the "lone" molecule of both of the polyols have no significant difference especially in the proton-catalyzed condition.

These results show that the water-resistance and the other superior properties like mechanical strength and heat-resistance of PCD-based TPU have been ascribed to the outstanding cohesive character of PCD molecules.

## INTRODUCTION

In general, polyurethane (PUR) has microphase-separated structure which constructed from hard- and soft-domain. The soft-domain is mainly consisted of long-chain polyol, as which polyether-polyol or polyester-polyol are generally used. Polyether-polyol brings about high water-resistant PUR. However, the mechanical strength of the PUR is less than that of polyester-polyol-based PUR. On the other hand, the biggest disadvantage of the polyester-polyol-based PUR is poor water-resistance, because ester-linkage is subject to hydrolysis under the humid circumstances.

That is to say, high water-resistance and high mechanical strength are incompatible with each other, so far as these conventional polyols are employed. Nevertheless, the PUR with both high water-resistance and high mechanical strength is strongly required in many applications. Polycarbonatediol (PCD) as the long-chain polyol is one of the solutions to the problem, and practically used in the fields like, thermoplastic elastomer (TPU), water-bone coatings and adhesives, synthetic leather, footwear, etc. The PCD-based PUR has high water-resistance, high mechanical strength, and also high heat-resistance compared to the conventional polyol-based PURs. The investigations into PCD-based PURs have recently increased [1,2].

In recent years, direct and easy observation of phase-separated structure of polymers is enabled by the development of atomic force microscope (AFM). Especially dynamic-mode observation of AFM is suitable for so called soft material. Dynamic-mode AFM becomes feasible not only the high-resolution observation of surface shape but also resolving by the difference of surface physical properties. Moreover, AFM have an advantage that it has been made possible to observe surface of samples under the controlled condition such as temperature, pressure and the surrounding gas or liquid. So many polymers including polyurethanes have been investigated by AFM [3,4]. Kojio et al revealed that the changes in phase-separated structure depend on the thickness of the polyurethane thin layers [5].

Furthermore, the development of computer hardware and software brings about a revolutionary change in the investigation of molecular structures, energy, reactivity, and many properties. Molecular orbital calculations can visualize the world in angstrom order. The accuracy of computer simulations is much improved by the development of hardware and software. As a result, the utilization of computer simulation for the investigation of polyurethanes is not the unusual method any more. However, there are few cases that the computer simulation method was utilized for the investigation into polyurethanes [6].

By means of the developed technologies described above, it has been made possible to investigate polymers from electron structure and reactivity of molecules to nano-scale structure of coagulated polymer assembly. In this paper, it has been investigated that the reason why the PCD is hardly hydrolyzed compared to polyester-polyols (PES), whereas its carbonate-linkage is a kind of ester-linkage by utilization of the innovative apparatus.

## EXPERIMENTAL

### Materials and Syntheses

A PCD-based and a PES-based thermoplastic polyurethane (PCD-TPU and PES-TPU) were synthesized and molded. The formulations of the TPUs are shown in **Table 1**. Both PCD and PES had ca. 1500 of molecular weight. The PCD was manufactured through ethanol elimination reaction of diethylcarbonate (DEC) and 3-methyl-1,5-pentanediol. The raw materials for PES were adipic acid, dimethylolheptane and 1,4-butanediol (1,4-BD). In order to prevent yellow discoloration of TPU, hexamethylene diisocyanate (HDI) was used as aliphatic diisocyanate monomer in both PCD-TPU and PES-TPU. PCD, PES and HDI are the products of Nippon Polyurethane Industry Co.,Ltd.

When preparation of TPUs, HDI and 1,4-BD react to make hard-segment, which will be constructed by repeating short alkyl chain and urethane linkage. Polyester or polycarbonate chain will directly become soft-segment.

The PCD or PES were controlled at 85 °C and mixed with 50 °C of 1,4-BD. Then HDI was added to the mixed-polyol. The reaction mixture was vigorously stirred at 120 °C and poured into a pan to cure spontaneously. The formed TPU was ground to particles and supplied to single-screw extruder, then the TPU was dispensed and cut into pellets. The 3 mm thickness sheets were molded from the TPU pellets by injection molding at 180 °C, and its properties were measured by the procedures as described below.

### Measurements

Mechanical properties like tensile strength at break (TB), elongation at break (EB) and tear strength at break (TR) were determined with A&D Company TENSILON static tensile testing machine. Water-resistance of the TPUs was evaluated as the retention of TB value of TPUs, which was immersed in a water bath whose temperature was controlled at 95 °C for periods up to 2 weeks. Differential Scanning Calorimetry was measured by SII Nanotechnologies DSC6200R in the range from -100 to 150 °C at the heating rate of 5 °C/min. The inflection point in the range below 0 °C of the DSC curve obtained was defined as Glass Transition Temperature ( $T_g$ ) of soft-segment.

The TPU samples were cut by a razor blade attached with a sample cutter in order to investigate the properties of inner region of TPU by FT-IR and AFM. FT-IR spectra were measured by Thermo Nicolet AVATER-360 attached with ATR apparatus, and peak resolution was performed in the range from 1600 to 1800  $\text{cm}^{-1}$ . Dynamic-mode AFM observation was performed by Shimadzu SPM-9600 attached with NANOSENSORS cantilever having 42 N/m of spring constant manufactured by NanoWorld AG. First the cut surface was observed in air, and then the sample was soaked in pure water for 3 hours. The *in situ* observation was performed under the wet condition by the AFM with Q-control system manufactured by nanoAnalytics.

### Computer Simulations

In order to compare the susceptibility of hydrolysis reaction of PCD and PES under non-catalyzed or proton-catalyzed condition, computer simulation was employed [7]. Molecular orbital calculations were carried out using Gaussian03 Revision D.02 [8]. Diethyl carbonate (DEC) and Ethyl propionate (EPA) were used as the model structures of PCD and PES respectively, because the too large models consume the computer resource unbearably. The overall reactions calculated are shown in **Scheme 1**. Calculations of Gaussian03 were performed by three nodal HPC-IA64 system equipped with two Intel Itanium2 processors and 16 GB memory in each node manufactured by HPC SYSTEMS Co.,Ltd.

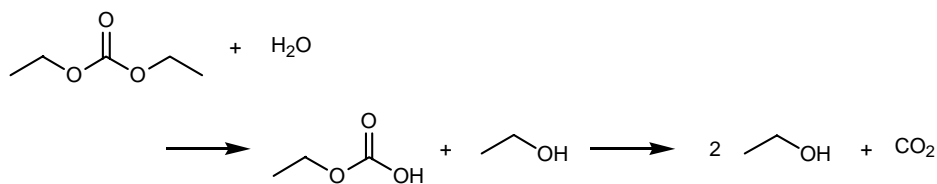
At first transition state (TS) structures were detected, and then the respective Intrinsic Reaction Coordinates were calculated in order to verify the transition state obtained connects the reactants and the products. Each energy value of reactants, TS, and products were detected. Furthermore, the enthalpy corrected energies were determined by force calculations at 298.15 °C and

**Table 1.** The formulations of the TPUs.

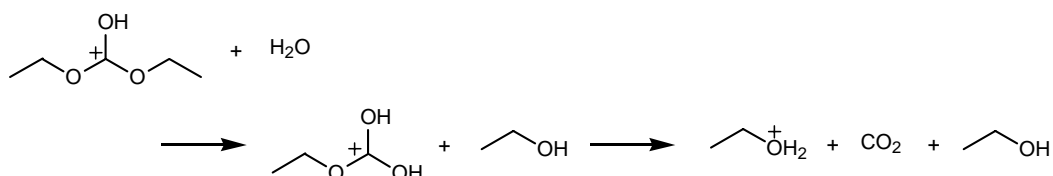
	PES-TPU	PCD-TPU
Polyester *	730.7 g	-
Polycarbonatediol **	-	724.2 g
1,4-butanediol	65.5 g	68.0 g
Hexamethylene diisocyanate	203.8 g	207.8 g

\* Polyester: adipic acid / dimethylolheptane / 1,4-butanediol, MW=ca.1500

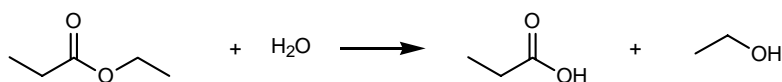
\*\* Polycarbonatediol: diethylcarbonate / 3-methyl-1,5-pentanediol, MW=ca.1500



(a) Hydrolysis of DEC



(b) Hydrolysis of DEC catalyzed with  $\text{H}^+$



(c) Hydrolysis of EPA



(d) Hydrolysis of EPA catalyzed with  $\text{H}^+$

**Scheme 1.** Overall hydrolysis reactions of PCD and PES models calculated by Gaussian03 Revision D.02

1.0 atm. Activation Energy ( $E_a$ ) and Heat of Formation ( $\Delta H$ ) was determined by using the corrected energies (Equation 1 and 2).

$$E_a = E_{\text{TS}} - E_{\text{reactants}} \quad (1)$$

$$\Delta H = E_{\text{products}} - E_{\text{reactants}} \quad (2)$$

All the optimization and the force were calculated using Density Functional Theory (DFT) [9]. The theory and the basis set were B3LYP/6-311+G(2d,p).

Coagulation energies were also estimated by same theory and basis set (B3LYP/6-311+G(2d,p)). The structure of Diethyl urethane (DEU) was optimized, and then the hydrogen-bonded molecules, DEC-DEU and EPA-DEU, were optimized with the same basis set. MP2 calculations was performed for the optimization calculation, however, the energies obtained were larger than that obtained by B3LYP/6-311+G(2d,p). Therefore the MP2 was not adopted. The energy difference between the hydrogen bonded molecule and the sum of single molecules was defined as the stabilization through the coagulation energy (Equation 3).

$$E_{\text{coagulation}} = E_{\text{A+B}} - (E_{\text{A}} + E_{\text{B}}) \quad (3)$$

A = DEC or EPA

B = DEU

A+B = supermolecules

**Table 2.** Physical properties at room temperature and  $T_g$  of PCD-TPU and PES-TPU.

	Hardness JIS A	TB MPa	EB MPa	TR %	$T_g$ °C
PCD-TPU	90	56	650	131	-34.9
PES-TPU	88	52	640	87	-50.5

## RESULTS AND DISCUSSION

### Physical Properties

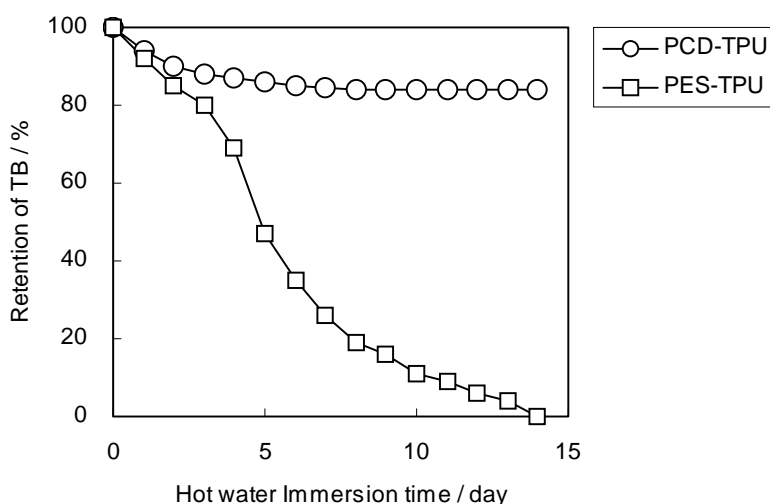
Physical properties of PCD-TPU and PES-TPU such as hardness and tensile strength at room temperature, shown in **Table 2**, were controlled to have the almost same value by the selection of source materials of PCD and PES (also see **Table 1**). In **Table 2**, only the  $T_g$ 's of soft-segment, which were read from the DSC chart, have different value, and namely the PCD-TPU indicates higher  $T_g$  compared with the PES-TPU.  $T_g$  should be defined as the temperature below which the Brownian motion of the main-chain of the soft-segment has frozen. Therefore, despite the physical properties of PCD-TPU and PES-TPU at the room temperature is almost the same, PCD-TPU retains the physical properties at the higher temperature compared with PES-TPU.

In general, PCD-based polyurethanes have a good heat-resistance. While the mechanical properties of the PCD-TPU and the PES-TPU at higher temperature have not been investigated in this work, it could be easily expected that the PCD-TPU can utilize in the wide temperature range compared with PES-TPU.

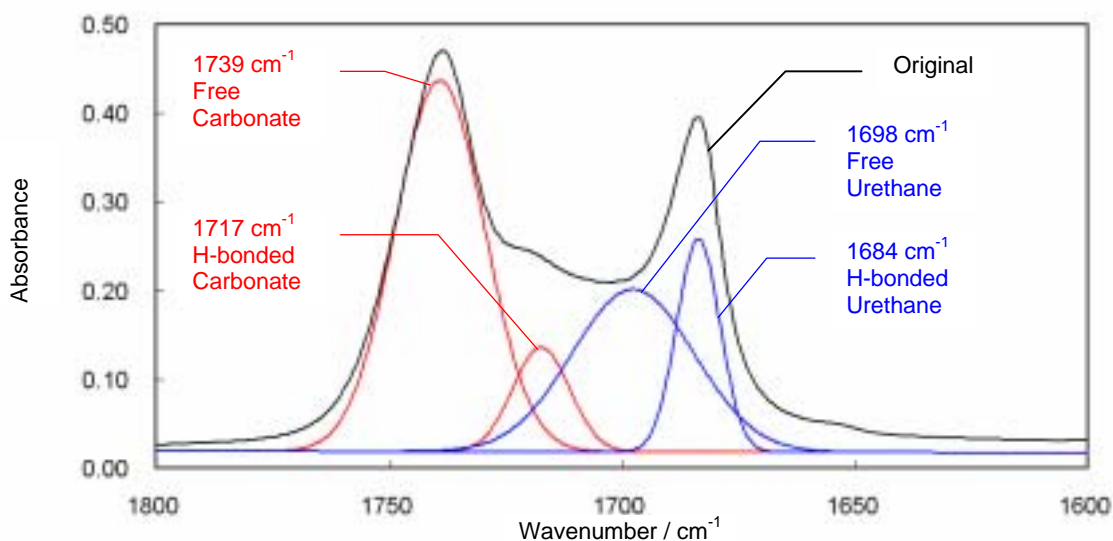
### Water-resistance

Generally polyester chain of TPU is subject to hydrolysis under the humid condition or of course in water. The chain scission necessarily leads to the degradation of the physical properties. The water-resistance of PCD-TPU and PES-TPU were evaluated though the retention of TB value, in case that the TPUs were immersed in 95 °C of water (See **Figure 1**).

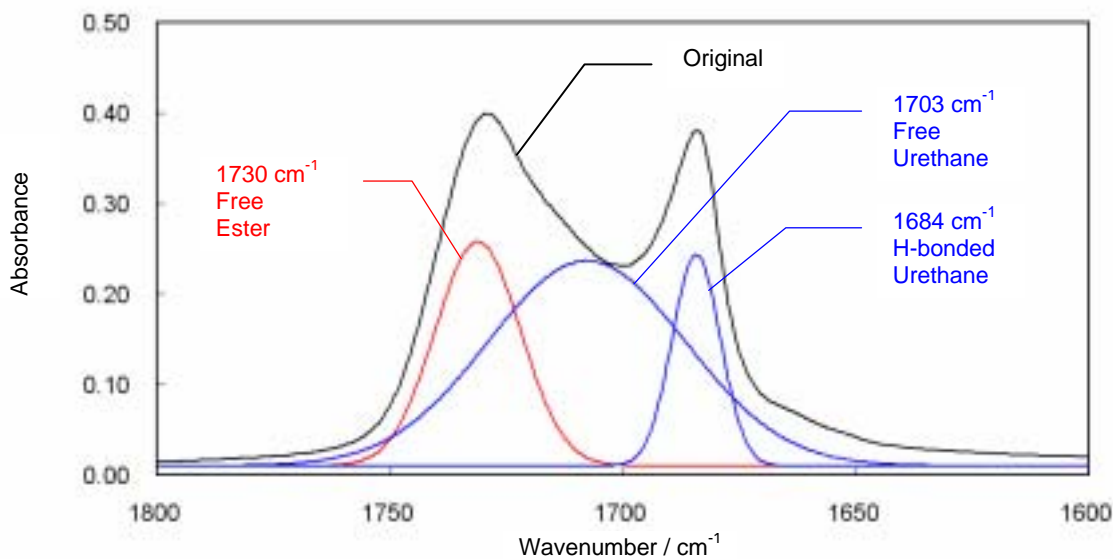
It is quite clear as shown in **Figure 1** that the TB retention of PCD-TPU was maintained above 84 % for 14 days and further degradation cannot be expected. In contrast to the PCD-TPU, PES-TPU showed a precipitous fall of TB retention in the same condition. These results show that the PCD molecule is hardly subject to hydrolysis even at the higher temperature compared with PES. As a result, general PCD-based polyurethanes have excellent water-resistance.



**Figure 1.** Retention of TB value of PCD-TPU and PES-TPU immersed in 95 °C of Water for 2 weeks.



**Figure 2(a).** FT-IR spectrum and the resolved peaks of PCD-TPU.



**Figure 2(b).** FT-IR spectrum and the resolved peaks of PES-TPU.

## FT-IR

**Figure 2 (a)** and **2 (b)** show the FT-IR spectra of the PCD-TPU and PES-TPU, respectively, in the range from 1600 to 1800  $\text{cm}^{-1}$  of wavenumber. The absorption peaks in this range were assigned to carbonyl (C=O) stretching vibration. In order to elucidate each of the absorption assigned to ester, carbonate and urethane, peak resolution method was performed.

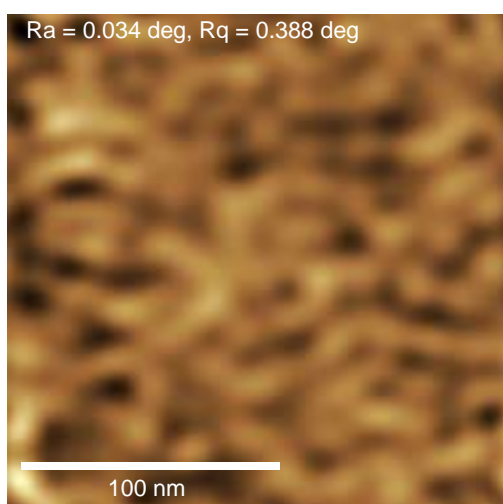
As shown in **Figure 2 (b)**, it was revealed that the PES-TPU has three absorption peaks of C=O stretching vibration, i.e. free ester, free urethane and hydrogen bonded urethane. Hydrogen bonded ester was not recognized in the PES-TPU. According to the observation, it can be understandable that urethane linkage has coagulated itself by hydrogen bond, and formed

hard-domain. The absorbance ratio of free and hydrogen bonded urethane (H-bond / free) is 1.02. The hard-segment connectivity through hydrogen bonds has been investigated by Wilkes et al [10-13].

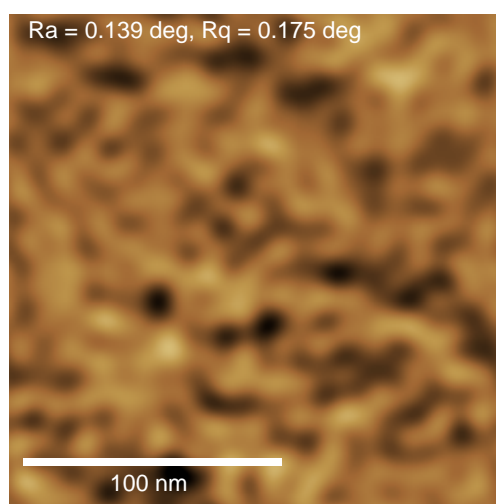
In the case of PCD-TPU as shown in **Figure 2 (a)**, four absorption peaks can be recognized through the peak resolution. The small peak at  $1717\text{ cm}^{-1}$  is assigned to hydrogen bonded carbonate. Free and hydrogen bonded urethane is also recognized in PCD-TPU. The absorbance ratio of free and hydrogen bonded urethane is 1.32, which value is relatively high compared to 1.02 of PES-TPU. These results indicate that the PCD-TPU has much higher hydrogen bonding property. Further, it is suggested that there is the hydrogen bond between urethane linkage and the carbonate linkage, while there is not the hydrogen bond between ester and urethane. Dimethylolheptane included in the PES has bulky side-chains which probably acts as inhibitor for hydrogen bonding because the side-chains present at close-neighboring urethane linkage. However, since half of the glycol component of the PES is straight-chain 1,4-BD, it could not be explain solely by bulky side-chain hypothesis that no hydrogen bond is detected in the PES-TPU.

### AFM Observations

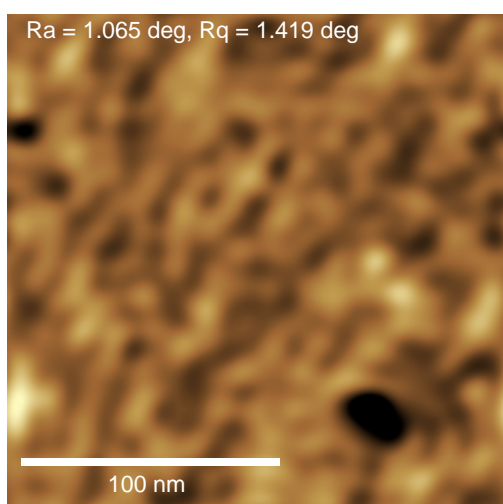
**Figures 3(a) to 3(d)** show the phase shift image of PCD-TPU and PES-TPU in air or water observed by dynamic-mode AFM. Generally the phase of oscillation shifts according to viscosity of surface, because the interaction between viscous surface and AFM probe dissipates the kinetic energy of the oscillated cantilever. In these Figures, bright area represents much more



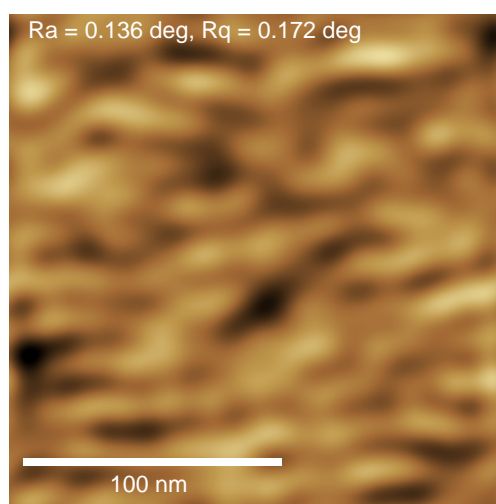
*Figure 3(a). AFM phase image of the PCD-TPU in air*



*Figure 3(b). AFM phase image of the PCD-TPU in water*



*Figure 3(c). AFM phase image of the PES-TPU in air*



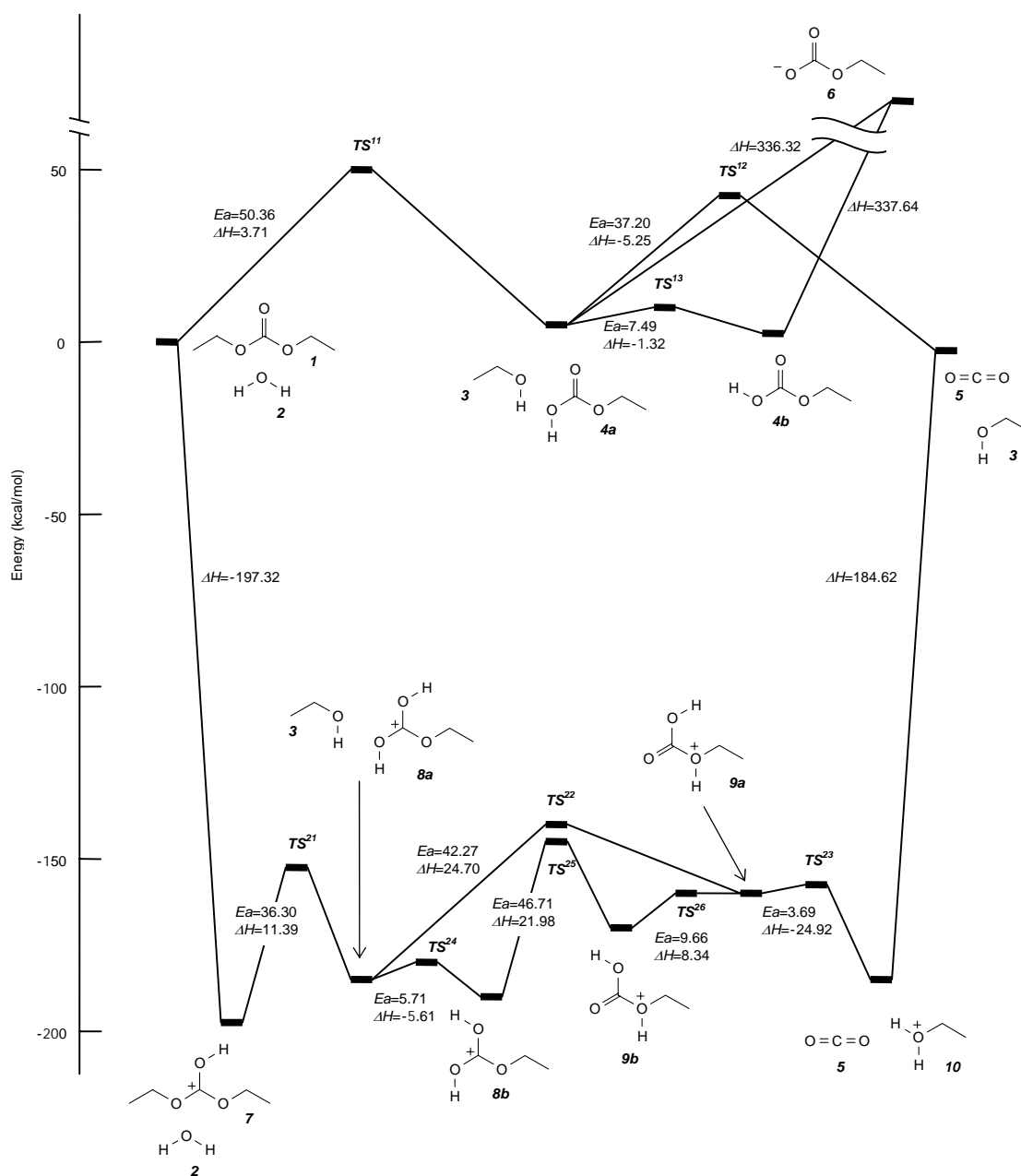
*Figure 3(d). AFM phase image of the PES-TPU in water*

shifted phase, i.e. the soft-domain mainly constructed by PCD or PES molecules. The values of  $R_a$  and  $R_q$  shown in the Figures represent “arithmetical mean deviation of the assessed profile” and “root mean square deviation of the assessed profile” respectively. These values imply the difference of hardness between the soft-domain (bright area) and the hard-domain (dark area).

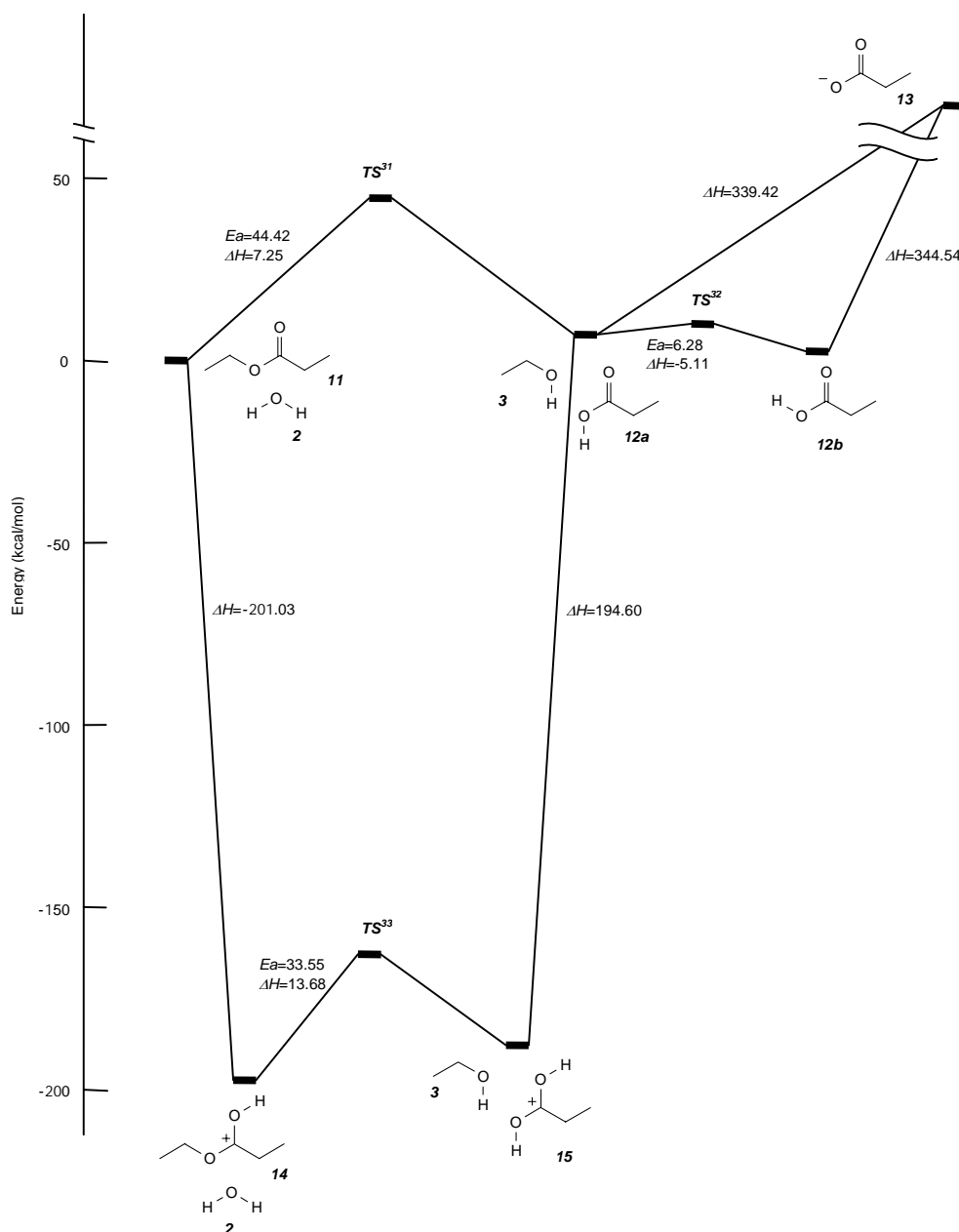
**Figure 3(a)** and **3(c)** are the phase images of PCD-TPU and PES-TPU respectively in air. The domain size of these TPUs is almost same, whereas the  $R_a$  and  $R_q$  values of PES-TPU are appreciably large. This result indicates that the difference of hardness (or viscosity) between the soft- and hard-domains is relatively large in PES-TPU. As implied in the results of FT-IR, PCD-TPU has higher hydrogen bonding property. Therefore, the soft-domain of PCD-TPU is comparatively hard.

PCD-TPU has bi-continuous domain structure as shown in **Figure 3(a)**. It is suggested that the domain structure had been constructed by spinodal decomposition during the cooling process after the injection molding. PES-TPU has also bi-continuous domain. However it has been somewhat inclined to make a lamellae domain.

Remarkable change of the phase structure of PCD-TPU by water immersion has not been recognized as shown in **Figures**



**Figure 4(a).** Energy balance of the calculated hydrolysis reactions of DEC.



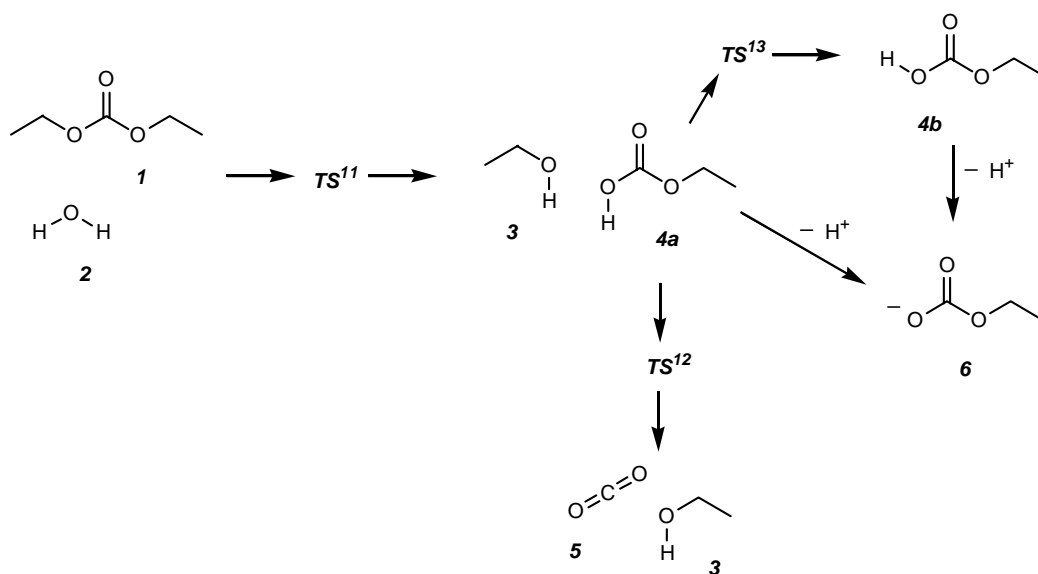
**Figure 4(b).** Energy balance of the calculated hydrolysis reactions of EPA.

**3(a)** and **3(b)**. On the other hand, as shown in **Figures 3(c)** and **3(d)**, the phase image of PES-TPU in water represents quite a change in domain size compared with that in air. The bright area, i.e. the soft-domain consisted mainly of PES segment, connects each other and grows. This phenomenon represents that the hydrophilic PES segment has been swollen with water. Therefore, PCD-TPU has a water-resistant property compared to PES-TPU.

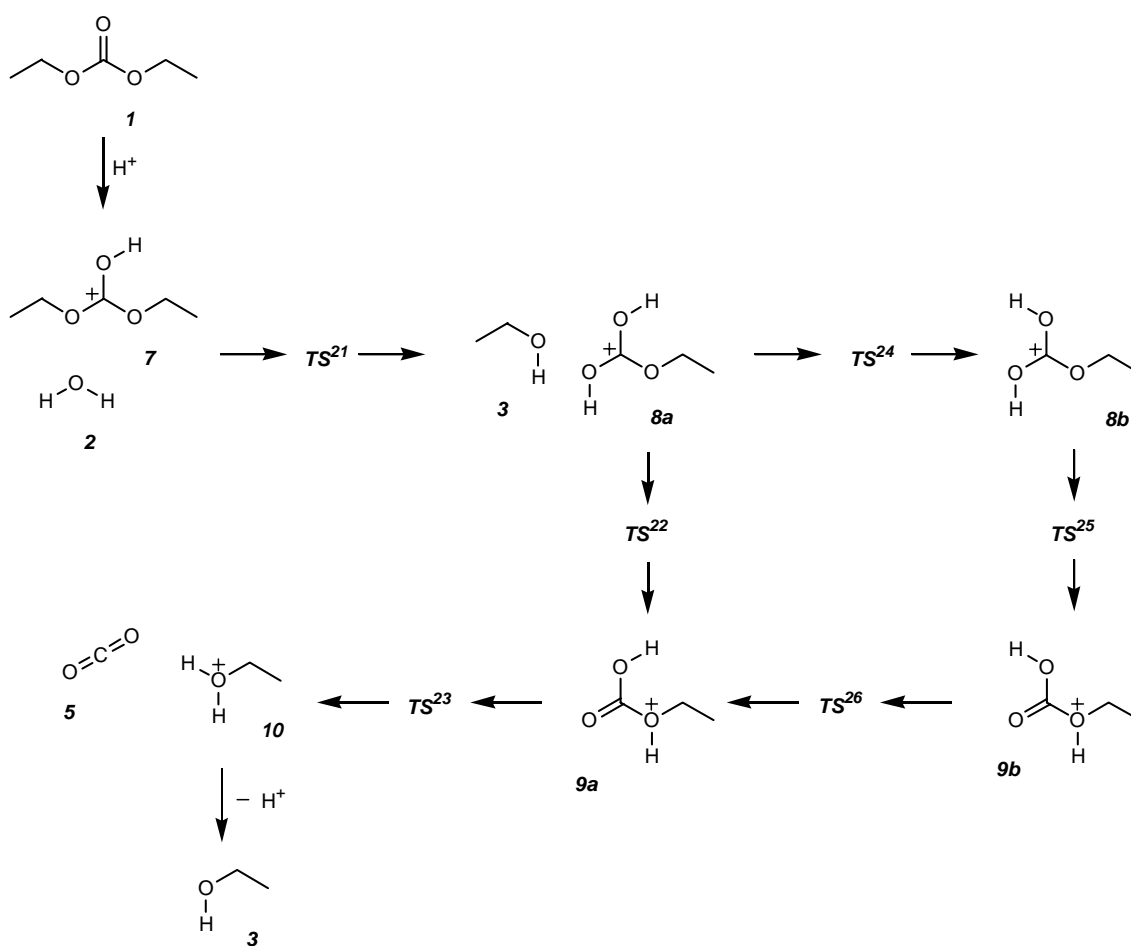
When the hydrolysis reaction and following chain scission occurs, it is required that water molecule attacks the PES or PCD molecule. If the hydrolysis property of lone molecules of PCD and PES assumed to be almost equivalent, swelling of soft-domain brings about the deterioration of physical properties of bulk TPU.

### Computer Simulation

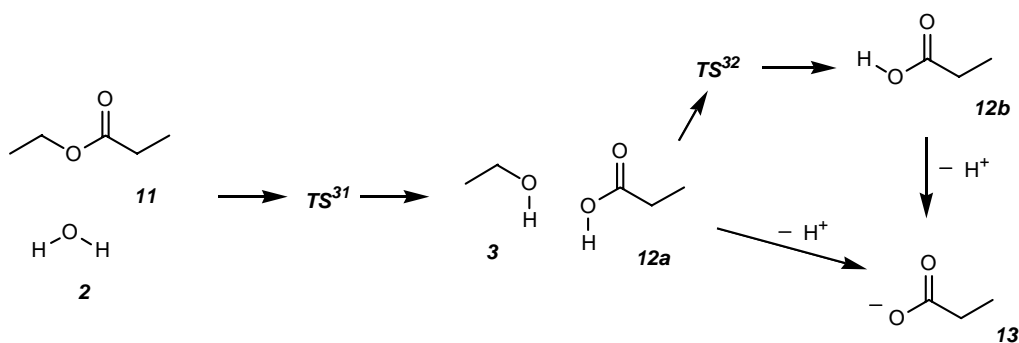
In order to evaluate the susceptibility of hydrolysis of PCD and PES molecules, molecular orbital calculation was performed on model structures. Diethyl carbonate (DEC) and ethyl propionate (EPA) were used as the models of PCD and PES.



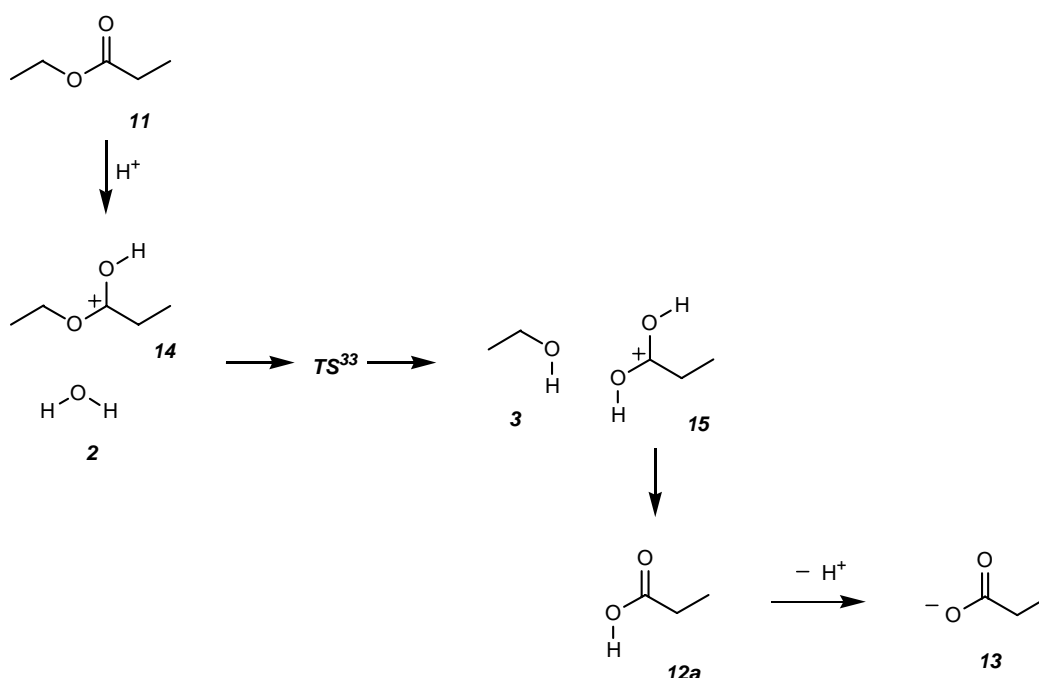
**Scheme 2(a).** Calculated hydrolysis reaction process of DEC.



**Scheme 2(b).** Calculated hydrolysis reaction process of DEC catalyzed with  $H^+$ .



**Scheme 2(c).** Calculated hydrolysis reaction process of EPA.



**Scheme 2(d).** Calculated hydrolysis reaction process of EPA catalyzed with  $H^+$ .

**Scheme 2(a)** and **2(b)** show the detailed reaction processes of DEC hydrolysis under the non-catalysis and the proton-catalysis respectively. Activation energies ( $E_a$ ) and heat of formation ( $\Delta H$ ) are summarized in **Table 3**, and the energy balance was explained in **Figure 4(a)** and **4(b)**. When non-catalyzed condition DEC (1) and water (2) react via  $TS^{11}$  producing ethanol (3) and monoethyl carbonate (4a). In this process of the reaction, the chain scission of PCD must be occurred. Monoethyl carbonate could be decomposed to carbon dioxide (5) and ethanol via  $TS^{12}$ . When the hydrolysis is undergone in acidic condition, proton bonds to the carbonyl oxygen (7), and the energy barrier of the reaction becomes a little lower shown in **Table 3**. The whole reaction process becomes somewhat complicate, namely a route with rotation of hydroxyl group might be traced (8b, 9b). Transform of proton from oxygen to the other oxygen is accompanied ( $TS^{22}$ ,  $TS^{26}$ ) in both of the routes.

The detailed processes of EPA (11) hydrolysis are shown in **Scheme 2(c)** and **2(d)**. The reaction process of proton-catalyzed hydrolysis of EPA is not complicate compared with the process of DEC.

As summarized in **Table 3** and **Figure 4**, the hydrolysis reactions of DEC and EPA becomes easier with proton. In both of the cases, even if it is in neutral condition, chain scission is first occurred, and carbonic acid or carboxylic acid should be produced. Therefore, complete neutral condition is not present in these cases. However, if the elimination of carbon dioxide is

**Table 3.** *E<sub>a</sub>* and *ΔH* values determined by molecular orbital calculation B3LYP/6-311+G(2d,p)

Whole reaction	Individual Reaction	<i>E<sub>a</sub></i> kcal / mol	<i>ΔH</i> kcal / mol
DEC hydrolysis under neutral condition	$1+2 \rightarrow TS^{11} \rightarrow 3+4a$	50.36	3.71
	$4a \rightarrow TS^{12} \rightarrow 3+5$	37.20	-5.25
	$4a \rightarrow TS^{13} \rightarrow 4b$	7.49	-1.32
	$4a \rightarrow 6$		336.32
	$4b \rightarrow 6$		337.64
DEC hydrolysis under proton-catalyzed condition	$1 \rightarrow 7$		-197.32
	$7+2 \rightarrow TS^{21} \rightarrow 3+8a$	36.30	11.39
	$8a \rightarrow TS^{22} \rightarrow 9a$	47.27	24.70
	$9a \rightarrow TS^{23} \rightarrow 5+10$	3.69	-24.92
	$8a \rightarrow TS^{24} \rightarrow 8b$	5.71	-5.61
	$8b \rightarrow TS^{25} \rightarrow 9b$	46.71	21.98
	$9b \rightarrow TS^{26} \rightarrow 9a$	9.66	8.34
	$10 \rightarrow 3$		184.62
EAP hydrolysis under neutral condition	$11+2 \rightarrow TS^{31} \rightarrow 3+12a$	44.42	7.25
	$12a \rightarrow TS^{32} \rightarrow 12b$	6.28	-5.11
	$12a \rightarrow 13$		339.42
	$12b \rightarrow 13$		344.54
EPA hydrolysis under proton-catalyzed condition	$11 \rightarrow 14$		-201.03
	$14+2 \rightarrow TS^{33} \rightarrow 3+15$	35.55	13.68
	$15 \rightarrow 12a$		194.60

readily occurred, the condition is kept neutral. *E<sub>a</sub>* value of carbon dioxide elimination through  $TS^{12}$  is 37.2 kcal/mol, which value represents the elimination may not be necessarily easy compared with the chain scission or the other reactions.

In conclusion from the simulated reaction processes, the susceptibility of hydrolysis of PCD is somewhat low compared to PES. Nevertheless, the difference of the hydrolytic susceptibility of the “lone” molecule could not explain the excellent water-resistance of PCD-based polyurethanes.

As implied by the results of FT-IR and AFM, the excellent water-resistance is brought by the strong cohesive property of PCD molecules that caused from the hydrogen bonding of carbonyl group and urethane linkage. In order to prove this assumption, stabilization energy by the hydrogen bond of urethane and PCD or PES were calculated by molecular orbital calculation. The stabilization energies of DEC+DEU and EPA+DEU calculated by B3LYP/6-311+G(2d,p) were -4.22 kcal/mol and -4.05 kcal/mol respectively. These values obtained seem to be reasonable to ascribe the hydrogen bond, because generally the stabilization energy by the hydrogen bond is 3 to 5 kcal/mol. As the result, PCD-TPU is more stabilized by hydrogen bond to urethane than PES-TPU.

## CONCLUSIONS

The susceptibility of hydrolysis of PCD is somewhat low compared to PES. However, only the susceptibility of hydrolysis could not explain the excellent water-resistance of PCD-based polyurethanes. All the results obtained by FT-IR measurement, AFM observation and computer simulations imply that PCD molecule have strong coagulation property to urethane *via* hydrogen bond. The conclusions of this investigation are as follows,

1. Susceptibility of hydrolysis of PCD molecule is somewhat low compared to PES molecule.
2. PCD molecule has higher hydrogen bonding property to urethane-linkage compared to PES molecule.
3. PCD-based TPU has excellent water-resistance because PCD molecule has strong cohesive property to urethane-linkage.

## ACKNOWLEDGEMENTS

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