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Reprocessable Aliphatic Polydithiourethanes based on Reversible Addition Reaction of Diisothiocyanates and Dithiols

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ABSTRACT:

Aliphatic polydithiourethanes (PDTU)s were successfully synthesized from diisothiocyanates and dithiols having a different value of carbon atom number. The thermal properties and hydrogen bonding behavior of PDTUs were studied in detail by using differential scanning calorimetry (DSC), thermal gravity analysis (TGA), temperature dependence nuclear magnetic resonance (NMR), Fourier transform infrared-attenuated total reflection (FTIR-ATR), and density functional theory (DFT) and semi-empirical molecular orbital (PM3) methods. In this

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3 work, we demonstrated that the thermal decomposition of PDTUs happened from the cleavage of
4 C-S bond of the dithiocarbamate moiety in the main-chain, and also the active isothiocyanate and
5 thiol groups were reprepared in the terminal of decomposed polymer (i.e. oligomer).
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7 Furthermore, we found that the thermal de-polymerization of PDTUs and the re-polymerization
8 of dithiourethane oligomers at room temperature proceeded repeatedly a few times.
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19 **1. Introduction**

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22 In the modern world supported by a variety of polymer materials, the reutilization and recycling
23 of degraded and damaged polymers are one of the important challenges. During the first decade
24 of this century, a lot of researchers have been interested in the self-healing and reprocessable
25 polymers,¹⁻² which are known as the intelligent materials such as response to external stimulus,³
26 molecular recognition,⁴ and shape memory,⁵ in not only academic but also industrial fields. The
27 self-healing polymers are classified broadly into the healing behavior of extrinsic and intrinsic
28 mechanisms.⁶ In the case of intrinsic self-healing process, the polymers exhibit the self-healing
29 behavior based on the reversible chemical bond systems, which are divided into the non-covalent
30 and covalent bonds.⁶ The self-healing based on the non-covalent bond system was provided with
31 the molecular interaction such as hydrogen bonds,⁷⁻⁸ electronic and ionic interactions,⁹⁻¹⁰ π - π
32 interactions.¹¹ In particular, polyurethanes and polyureas can be applied as the self-healing and
33 shape-memory materials, because the hydrogen bonding fashions can be tailored to the
34 requirement by designing the molecular structure.¹²⁻¹³ On the other hand, the Diels-Alder
35 reaction¹⁴ and bond exchange reaction of disulfide¹⁵ and ester moieties¹⁶⁻¹⁸ are applied as the
36 intrinsic self-healing materials based on the dynamic covalent bond chemistry¹⁹⁻²¹. Particularly,
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3 the Diels-Alder reaction between furan and maleimide components has been widely utilized to
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5 prepare the reversible cross-linked polymers.²² In the case of a covalent bond system,
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7 polyurethanes and polyureas have been also applied as the reprocessable polymers, which give
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9 rise to the bond exchange reaction of carbamate and carbamide moieties, respectively, by the
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11 external stimulus such as high temperature and an addition of catalysts.²³⁻²⁵ Several research
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13 groups have demonstrated that poly(urethane-urea) network derived from a hindered amine
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15 exhibited self-healing and shape-memory behaviors in a wide temperature range because the
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17 bond exchange reaction of the hindered urea derivatives happened under ambient temperature
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19 and catalyst-free conditions.²⁶⁻²⁹ Hence, polyurethanes and polyureas are attractive as the
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21 reprocessable materials from both perspectives of the molecular interaction due to hydrogen
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23 bonding and the dynamic covalent bonds due to bond exchange reaction. However, there are two
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25 requirements in this system.³⁰ First, the bulky substituents on the urea moieties are required to
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27 destabilize the urea bonds, which is one of the most stable chemical bonds **against further**
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29 **reactions**. Second, the reaction rate of isocyanates and hindered amines have to be more rapid
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31 than the degradation rate of isocyanates due to hydrolysis. Based on the previous research results,
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33 we hypothesized that the isothiocyanate-thiol system was suitable as the reprocessable materials,
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35 because the addition reaction of isothiocyanates and thiols, which are stable compounds in
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37 aqueous solution at room temperature,³¹⁻³² successfully proceeded with an amine catalyst at
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39 25 °C and the produced dithiocarbamate moiety was readily dissociated by the external
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41 stimulus.³³ Accordingly, we have demonstrated that polyaddition of various diisothiocyanates
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43 and dithiols was achieved with triethylamine in DMF at 25 °C to obtain the corresponding
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45 polydithiourethanes (PDTU)s in higher yield and molecular weight.³⁴ Recently, polythioureas are
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47 featured because the hydrogen bonding of their polymers is fairly weak and dynamic.
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3 Yanagisawa and coworkers have demonstrated that poly(ether-thiourea) exhibited self-healing
4 behavior at ambient temperature because of the less-ordered hydrogen bonding in the amorphous
5 polymer matrices.³⁵ Moreover, Wagner and Mioskowski et al. have reported the synthesis
6 procedure of *N,N'*-substituted thioureas by thermolytic cleavage of dithiocarbamate bonds in
7 solid-state.³⁶ Therefore, we have studied about the de-polymerization of aliphatic PDTUs based
8 on the thermal decomposition and the re-polymerization of the decomposed polymers at room
9 temperature to discover the reversible nature of addition and dissociation reaction of the aliphatic
10 diisothiocyanates and dithiols.
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26 **2. Experimental section**

27 **2.1 Materials.**

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30 1,3-propanedithiol, 1,6-hexanedithiol, 1,10-decanedithiol, 1,12-diaminododecane, 1,6-
31 hexanediol, hexyl mercaptan, and hexamethylene diisocyanate were purchased from Tokyo
32 Chemical Industry (Tokyo, Japan). 1,3-propane diisothiocyanate and hexamethylene
33 diisothiocyanate were supplied from Nippon Terpene Chemicals, Inc. (Tokyo, Japan).
34 Triethylamine (TEA), dibutyltin dilaurate (DBTL), and 1-[bis(dimethylamino)methylene]-1*H*-
35 benzotriazolium 3-oxide hexafluorophosphate (HBTU), *N,N'*-dicyclohexylcarbodiimide (DCC),
36 carbon disulfide (CS₂), and all solvents were purchased from Wako Pure Chemical Industries
37 (Osaka, Japan).
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50 **2.2 Measurements.**

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52 NMR spectra were obtained using a JEOL ECS-400 spectrometer operating at 400 MHz for ¹H
53 and 100 MHz for ¹³C in chloroform-*d* (CDCl₃) and *N,N*-dimethylformamide-*d*₇ (DMF-*d*₇) using
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3 a tetramethyl silane (TMS) as an internal reference. FTIR spectra were recorded on a Thermo
4 Scientific Nicolet iS10 spectrometer equipped with a Smart iTR diamond ATR sampling
5 accessory in the range of 4000–650 cm^{-1} . Gel permeation chromatography (GPC) was carried out
6 on TOSOH HLC-8320 system equipped with two consecutive polystyrene gel columns [TSKgel
7 guardcolumn SuperH-H (4.6 mmI.D. x 3.5 cm, 4 μm particle size) and TSKgel SuperHM-H (6.0
8 mmI.D. x 15 cm, 3 and 5 μm particle sizes)] and refractive index and ultraviolet (254 nm)
9 detectors at 40 °C. The system was operated in tetrahydrofuran (THF) as eluent at a flow rate of
10 0.6 mL/min. Polystyrene standards were employed for calibration. Thermogravimetric analysis
11 (TGA) was performed on a Seiko Instrument Inc. TG-DTA 6200 with 1.5 mg of samples in an
12 aluminum pan under a 100 mL/min N_2 flow at a heating rate of 10 °C/min. Differential scanning
13 calorimetry (DSC) analysis was conducted from 0 to 150 °C for the first heating scan and from -
14 50 to 180 °C for the second heating scan on a Seiko Instrument Inc. DSC-6200R with 1.5 mg of
15 samples in an aluminum pan under a 50 mL/min N_2 flow at a heating rate of 10 °C/min. The
16 second scan was selected to determine glass transition temperature (T_g) values. Geometry
17 optimized structures for the model compounds was estimated by using DFT calculation with
18 B3LYP/6-31G* and semi-empirical molecular orbital (PM3) methods (Wavefunction, Inc.,
19 Spartan'06 Windows version 1.1.0).³⁷ These model compounds were optimized by combination
20 of DFT and PM3 methods. First, the unit structures of model-1 and model-2 were optimized by
21 DFT (B3LYP/6-31G*) calculation. Second, The conformation between the units based on
22 molecular interaction estimated by semi-empirical molecular orbital calculation (PM3).
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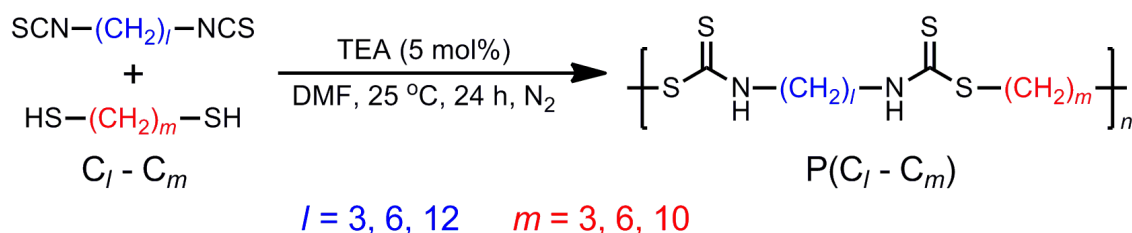
53 **2.3 Monomer synthesis.**

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Dodecamethylene diisothiocyanate³⁸ and hexyl diisothiocyanate³⁹ were synthesized according to the literatures. Procedures for monomer synthesis and characterizations of monomer were shown in supporting information.

2.4 Polymerization.

Polymerization of diisothiocyanates and dithiols were as shown in scheme 1.³⁴ The results of polymerization were summarized in Table 1. Synthesis of polyurethane and polythiourethane was also shown in scheme S2.³³ Typical procedures for polymerization, ¹H and ¹³C NMR spectra, and FTIR-ATR spectra of the obtained polymers were shown in supporting information.



Scheme 1. Synthesis of polydithiourethanes from aliphatic dithiocyanates and dithiols.

Table 1. Synthesis of polydithiourethanes from aliphatic diisothiocyanates and dithiols.

Entry	R ¹	R ²	Yield ^a (%)	M _n ^b (kg/mol)	M _w /M _n ^b
1	C3	C3	98	55	1.82
2	C3	C6	98	43	1.92
3	C3	C10	94	50	2.07
4	C6	C3	99	42	2.52
5	C6	C6	98	42	2.24
6	C6	C10	98	42	2.10
7	C12	C6	92	15	1.98

^a Insoluble fraction in hexane/ethanol mix solvent and methanol. ^b Determined by GPC analysis (PSt, THF).

2.5 Reversible reaction of model compound.

Hexyl isothiocyanate (287 mg) and hexyl mercaptan (237 mg) were mixed in bulk, and then triethylamine (21 mg) was added in the mixture. The mixture was held in an oven at 50 °C for 1 h. After cooling to room temperature, the crude product was held in an oven at 150 °C for 6 h. Before and after each step, the conversion of isothiocyanate group was estimated by FTIR-ATR method. The reversible reaction of model compound was repeated one more time.

2.6 De-polymerization and re-polymerization.

A solution of P(C6-C6) (M_n : 11,000 g/mol) in anhydrous DMF (1.0 mol/L) was stirred at 150 °C under a N₂ atmosphere for 1 h. After cooling to room temperature, the mixture was stirred in the presence of triethylamine (11 mg) at 25 °C under a N₂ atmosphere for 24 h. Before and after each step, M_n and M_w of polymer were estimated by GPC analysis. De-polymerization and re-polymerization of P(C6-C6) were carried out five times.

3. Results and discussion

The decomposition temperature for 5% weight loss (T_{d5}) observed by TGA, a glass transition (T_g), crystallization (T_c), and melting (T_m) temperatures observed by DSC, and chemical shift of the peak due to NH moiety (δ_{NH}) observed by NMR are summarized in Table 2.

Table 2. T_{d5} , T_g , T_c , T_m , and δ_{NH} of PDTUs

Polymer	T_{d5}^a (°C)	T_g^b (°C)	T_c^b (°C)	T_m^b (°C)	δ_{NH}^c (ppm)
C3-C3	200.0	36.7	-	-	9.95
C3-C6	220.9	17.2	-	-	9.87
C3-C10	222.2	8.8	-	-	9.86
C6-C3	182.0	26.6	-	-	9.91
C6-C6	206.9	16.8	-	-	9.85
C6-C10	213.8	4.8	-	-	9.83
C12-C6	190.3	-8.7	18.5	86.1	9.83

^a Measured by TGA under flowing N₂ gas. ^b Measured by DSC under flowing N₂ gas. ^c Observed at 25 °C in DMF-*d*₆ by NMR

3.1 Thermal property and hydrogen bonding behavior of aliphatic polydithiourethanes

Thermal properties of aliphatic PDTUs were observed by DSC analysis (Fig. 1). The T_g values of the polymers decreased with increasing value of the carbon atom number of diisothiocyanate and dithiol units in the main-chain (Table 2 and Fig. 1). Such behavior of T_g values suggests that the difference of the carbon atom number of diisothiocyanate and dithiol units in the main-chain affect the hydrogen bonding fashion between the polymer chains. In order to clarify the hydrogen bonding behavior of aliphatic PDTUs, ¹H NMR spectra observed in DMF-*d*₆. In the temperature dependence NMR spectra of P(C3-C3), the peak due to NH moiety of the polymers was shifted to a high magnetic field with increasing of temperature, although the other peaks

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3 never exhibited any chemical shift (Fig. S9a). In the case of P(C6-C6), the temperature
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5 dependence NMR spectra exhibited similar behavior of the chemical shift to that of P(C3-C3),
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7 whereas the NH peak of P(C6-C6) was observed at high magnetic field compared to that of
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9 P(C3-C3) without depending on a temperature (Fig. S9b). The temperature dependence NMR
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11 spectra of P(C3-C3) and P(C6-C6) indicate that the chemical shift of NH peak exhibits a strength
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13 of hydrogen bonding between the polymer chains. Accordingly, the hydrogen bonding of P(C3-
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15 C3) is stronger than that of P(C6-C6) because the NH peak due to a strong hydrogen bonding is
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17 observed at lower magnetic field.³³ Moreover, the hydrogen bonding of the polymers containing
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19 C3-dithiol unit was stronger than that of the polymers containing C6- or C10-dithiol units,
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21 because the peak due to NH moiety of the former polymers was observed at low magnetic field
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23 compared to that of the latter polymers (Table 2 and Fig. S10). Therefore, the T_g values of the
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25 polymers containing C3-dithiol unit was significantly higher than that of the polymers containing
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27 C6- or C10-dithiol units. On the other hand, the NH peaks of the polymers containing C6- or
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29 C10-dithiol units exhibited almost same chemical shift even though the T_g values of the polymers
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31 containing C6-dithiol units were higher than that of the polymers containing C10-dithiol units
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33 (Table 2 and Fig. S10). These results mean that the T_g values of the polymers containing C6- or
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35 C10-dithiol units depend on the alkyl chain length (i.e. flexibility) in not only dithiol but also
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37 diisothiocyanate units because the hydrogen bonding of those polymers is fairly weak. The
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39 degree of polymerization also affects the hydrogen bonding behavior of the polymers, because
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41 the number of hydrogen bonding moieties in the polymer chain depends on the degree of
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43 polymerization and alkyl length of the monomer units. Actually, P(C3-C3) has higher molecular
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45 weight and shorter alkyl units than the other polymers, meaning P(C3-C3) have a higher number
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47 of hydrogen bonding units (Table 1, Entry 1). On the other hand, a number of hydrogen bonding
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units of P(C12-C6) decreases compared to the other polymers because of the lowest molecular weight and the long alkyl chain in the monomer units (Table 1, Entry 7). Therefore, P(C3-C3) exhibited the highest T_g value and P(C12-C6) exhibited fairly lower T_g value. P(C12-C6) also exhibited the phase transition temperatures attributed to the crystallization and melting points due to the alkyl chain packing between the polymer chains.

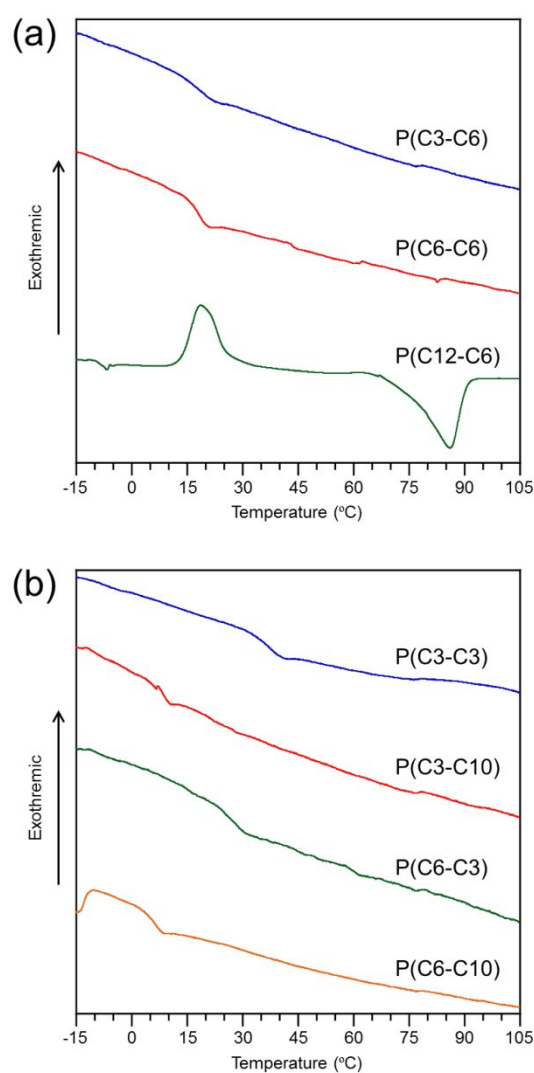


Figure 1. (a) DSC curves of P(C3-C6), P(C6-C6), and P(C12-C6). (b) DSC curves of P(C3-C3), P(C3-C10), P(C6-C3), and P(C6-C10).

3.2 Thermal decomposition behavior of aliphatic polydithiourethanes

Thermal decomposition behaviors of the aliphatic PDTUs were observed by TGA measurement (Fig. 2). The T_{d5} values of polymers decreased with increasing value of the carbon atom number in the diisothiocyanate unit, and also increased with increasing value of the carbon atom number in the dithiol unit (Table 2). In order to clarify the thermal decomposition behaviors of aliphatic PDTUs, that of polyurethane (PU) and polythiourethane (PTU) containing the alkyl chain units, which were the same as P(C6-C6), were also observed by TGA measurement (Fig. 3a). The T_{d5} values of PU and PTU, which were 281 °C and 244 °C, respectively, were higher than that of PDTU. The thermal stability of these polymers depends on strength of intermolecular hydrogen bonding.³³ In fact, PU and PTU were insoluble in any organic solvents because of the strong hydrogen bonding between the polymer chains, whereas PDTU was readily soluble in polar organic solvents such as THF and DMF. **More importantly, the bond energy can be directly related to thermal stability of these polymers.**⁴⁰ Fig. 3b and Fig. 3c show the FTIR-ATR spectra of polymers before and after annealing, respectively. The peaks due to carbonyl groups of carbamate moiety of PU and thiocarbamate moiety of PTU, and thiocarbonyl group of dithiocarbamate moiety of PDTU were observed at 1680 cm^{-1} , 1635 cm^{-1} , and 1495 cm^{-1} , respectively, in the FTIR-ATR spectra of polymers before annealing (Fig. 3b). After annealing in bulk at 150 °C for 12 h, the peaks due to diisothiocyanate group ($-\text{NCS}$) was observed around 2100 cm^{-1} in the FTIR-ATR spectra of PDTU, whereas the FTIR-ATR spectra of PU and PTU never changed before and after annealing (Fig. 3c). **These results indicate that the C-S bond of dithiocarbamate moiety is readily cleaved under a high-temperature condition because the bond energy of C-S bond is fairly lower than that of the C-O bond.**³³ Therefore, the thermal stability of

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3 PDTUs depends on not only the intermolecular hydrogen bonding but also the bond energy of
4 dithiocarbamate moiety. However, P(C3-C6) and P(C6-C3) exhibited the different T_{d5} values
5 even though the polymers was constructed with the aliphatic units of the same carbon atom
6 number in the main-chain. The model compounds of bisdithiocarbamate containing propane
7 diisothiocyanate and propane dithiol units (model-1 and model-2, respectively) were optimized
8 by combination of DFT and PM3 methods (Fig. 4). The optimized structures of model-1 and
9 model-2 showed the twisted and parallel conformations of the propane moieties, respectively.
10 The twisted conformation of model-1 can give rise to decreasing the bond energy of C-S bond
11 (Fig. 5a). In contrast, the C-S bond of model-2 is more stable than model-1 because of the
12 ordered structure of propane bisdithiocarbamate moiety (Fig. 5b). These results suggest that the
13 C-S bond energy decreases with increasing alkyl length of diisothiocyanate moiety and increases
14 with increasing alkyl length of dithiol moiety. Therefore, P(C3-C6) exhibited higher T_{d5} value
15 compared to P(C6-C3).
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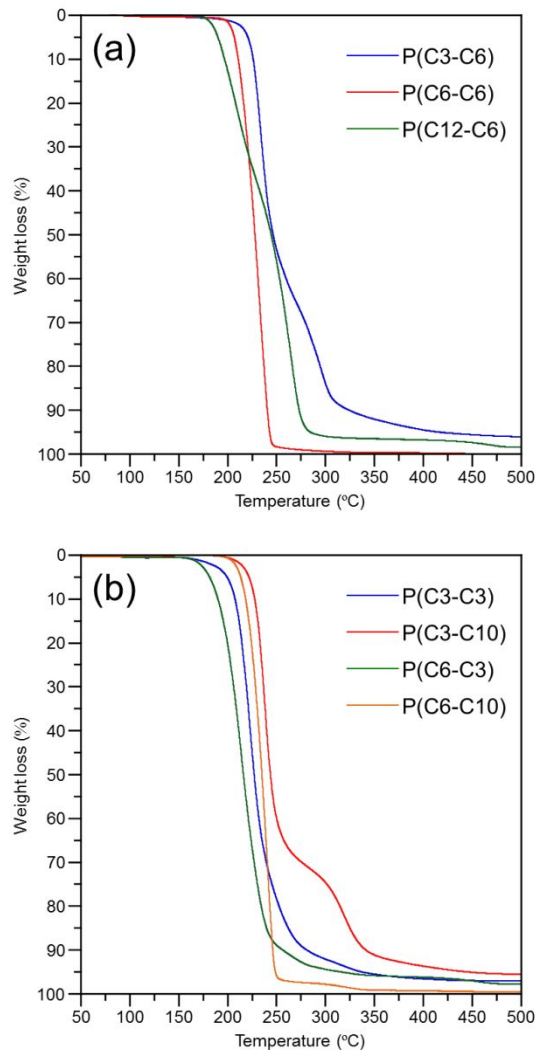
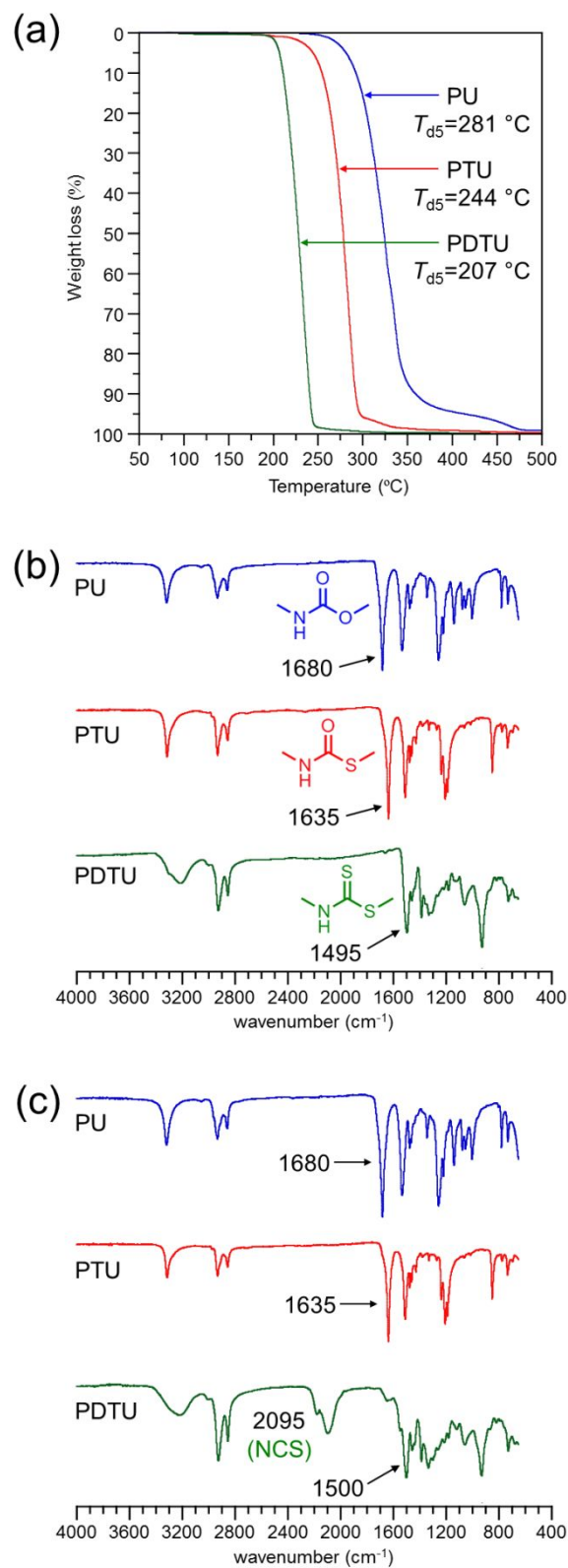


Figure 2. (a) TGA traces of P(C3-C6), P(C6-C6), and P(C12-C6). (b) TGA traces of P(C3-C3), P(C3-C10), P(C6-C3), and P(C6-C10).



55 **Figure 3.** (a) TGA traces, (b) FTIR-ATR spectra after purification, and (c) FTIR-ATR spectra after annealing in
56 bulk at 150 °C for 12 h of polyurethane (PU), polythiourethane (PTU), and polydithiourethane (PDTU).
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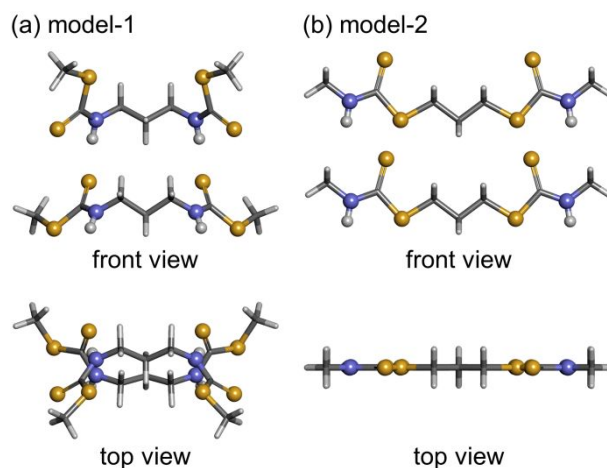


Figure 4. (a) The model compounds of bisdithiocarbamate containing propane diisothiocyanate unit. (b) The model compounds of bisdithiocarbamate containing propane dithiol units.

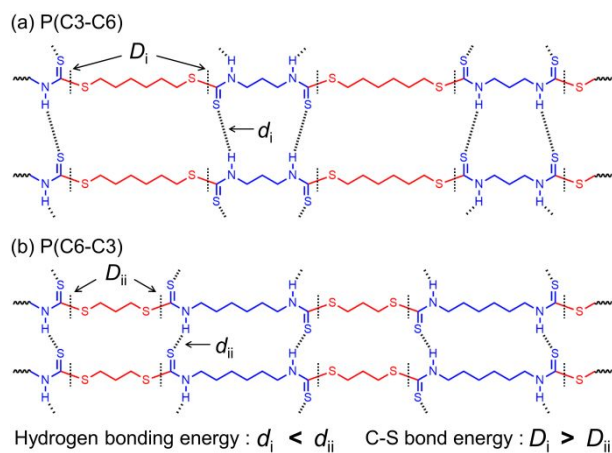


Figure 5. The presumed models of hydrogen bond (d_i and d_{ii}) and C-S bond (D_i and D_{ii}) attributed to alkyl length of diisothiocyanate and dithiol units.

3.3 Reversible reaction of aliphatic dithiocarbamate.

The isothiocyanate group dissociated after annealing of PDTU suggested a possibility of the thermal de-polymerization of PDTUs and the re-polymerization of the dissociated monomers.

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3 The reversible reaction was confirmed by using dihexyl dithiocarbamate as the model compound
4 (Fig. 6). First, hexyl isothiocyanate and hexyl mercaptan were reacted in the presence of TEA at
5 50 °C. The reaction was completely achieved for 1 h, because the peak due to –NCS was never
6 observed in FTIR-ATR spectra. Next, the retro-reaction of the obtained dihexyl dithiocarbamate
7 was carried out at 150 °C. The conversion ratio of retro-reaction was approximately 20% for 6 h,
8 although the peak due to –NCS was observed around 2100 cm⁻¹ in the FTIR-ATR spectra.
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10 Additionally, the conversion was almost the same ratio even after the reaction for 24 h. This
11 result suggests that the retro-reaction of dithiocarbamate derivatives and the reaction of a part of
12 dissociated residues proceed simultaneously during annealing at 150 °C. Furthermore, the
13 activity of dissociated isothiocyanate and thiol groups was also confirmed by the addition
14 reaction of them. The FTIR-ATR spectra showed that the reaction of dissociated isothiocyanate
15 and thiol was completely achieved in the presence of TEA at 50 °C for 1 h, because the peak due
16 to –NCS was never observed as well as the first reaction.
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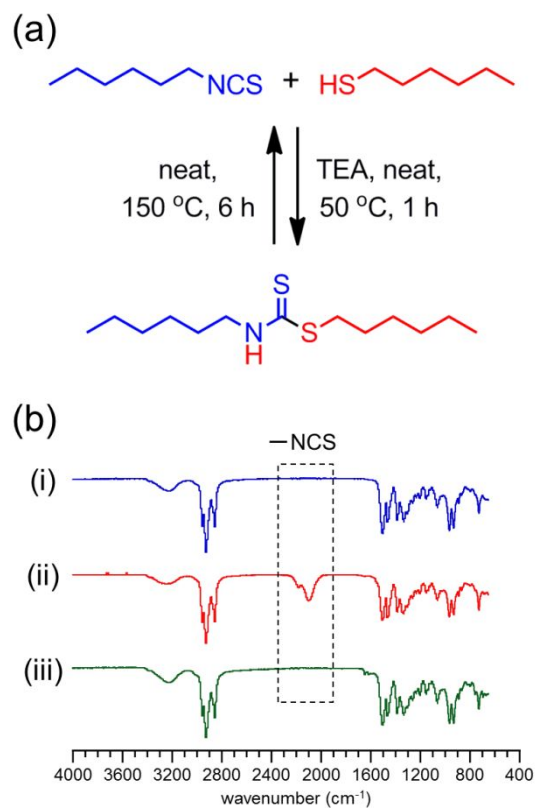


Figure 6. (i) The reaction of isothiocyanate and mercaptan derivatives at 50 °C for 1 h. (ii) The retro-reaction of aliphatic dithiocarbamate at 150 °C for 6 h. (iii) The reaction of dissociated isothiocyanate and mercaptan derivatives at 50 °C for 1 h

3.4 De-polymerization of PDTU and re-polymerization of dithiourethane oligmer.

Based on the reversible reaction of the model compound, the de-polymerization of PDTU was carried out in DMF at 150 °C for 1 h (Fig. 7a), and then GPC and FTIR-ATR of the de-polymerized PDTU were measured. After de-polymerization process, the M_n value estimated by GPC decreased from 11,000 g/mol to 1,400 g/mol and the peak due to -NCS was observed around 2100 cm^{-1} in the FTIR-ATR spectra (Fig. 7b-ii and 7c-ii). Accordingly, the residue ratio of -NCS group estimated by FTIR-ATR was 29.7% (Table 3). The re-polymerization was also carried out with TEA in DMF at 25 °C for 24 h (Fig. 7a). After re-polymerization process, the M_n value increased from 1,400 g/mol to 8,600 g/mol and the peak due to -NCS group was

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3 slightly observed around 2100 cm^{-1} in the FTIR-ATR spectra (Fig. 7b-iii and 7c-iii). These results
4 suggested that the dithiourethane oligomer was prepared via de-polymerization based on the
5 thermal cleavage of C-S bond of PDTU, and active isothiocyanate and thiol groups were
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slightly observed around 2100 cm^{-1} in the FTIR-ATR spectra (Fig. 7b-iii and 7c-iii). These results suggested that the dithiourethane oligomer was prepared via de-polymerization based on the thermal cleavage of C-S bond of PDTU, and active isothiocyanate and thiol groups were reprepared in the terminal of the obtained dithiourethane oligomer. The re-polymerization of the obtained oligomer was achieved incompletely because the M_n value of the resulting polymer was slightly less value compared to that of the original polymer and the -NCS moiety was not completely consumed via re-polymerization (Fig. 7 and Table 3). Furthermore, de-polymerization of PDTU and re-polymerization of the dithiourethane oligomers proceeded repeatedly, although the M_n value of the re-polymerized polymer decreased with increasing repeated cycle number (Table 4). Therefore, these results proved that the reversible reaction happened even in the case of the polymer as well as the aliphatic dithiocarbamate derivative of the model compound.

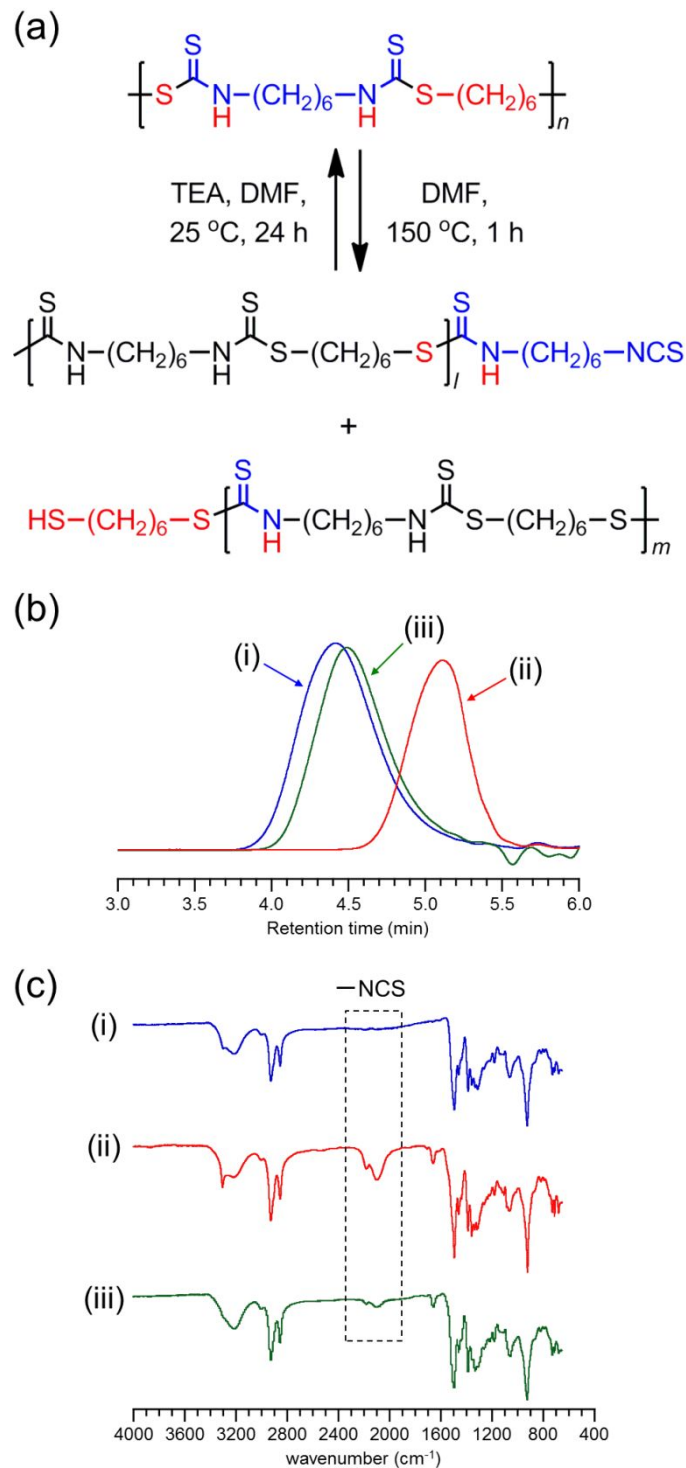


Figure 7. (a) De-polymerization of PDTU and re-polymerization dithiourethane oligomer. (b) GPC profiles and (c) FTIR-ATR spectra of (i) original PDTU, (ii) de-polymerized PDTU, and (iii) re-polymerized dithiourethane oligomer.

Table 3. M_n , M_w/M_n , and residue ratio of -NCS of (i) original PDTU, (ii) de-polymerized PDTU, and (iii) re-polymerized dithiourethane oligomer.

Polymer	M_n (g/mol) ^a	M_w/M_n ^a	-NCS (%) ^b
(i)	11,000	2.44	0
(ii)	1,400	1.48	29.7
(iii)	8,600	2.10	5.4

^a Determined by GPC analysis (PSt, THF). ^b Residue ratio of -NCS estimated by FTIR-ATR.

Table 4. M_n (M_w/M_n) values of de-polymerized PDTU and re-polymerized dithiourethane oligomer during five cycles.^a

	De-polymerization	Re-polymerization	-NCS
	M_n (g/mol) [M_w/M_n] ^b	M_n (g/mol) [M_w/M_n] ^b	(%) ^c
Run1	1,400 [1.48]	8,600 [2.10]	5.43
Run2	1,100 [1.30]	7,500 [1.68]	7.42
Run3	1,100 [1.32]	6,200 [1.61]	9.34
Run4	1,200 [1.35]	5,100 [1.55]	11.4
Run5	1,100 [1.30]	4,900 [1.75]	11.6

^a Initial M_n [M_w/M_n] value is 11,000 g/mol [2.44], ^b Determined by GPC analysis (PSt, THF). ^c Residue ratio of -NCS after re-polymerization estimated by FTIR-ATR.

4. Conclusion

Thermal properties of the aliphatic PDTUs synthesized from diisothiocyanates and dithiols were studied in detail by using DSC, TGA, temperature dependence NMR, FTIR-ATR, and computational methods. The DSC curves and ¹H NMR spectra indicated that the T_g values of PDTU s increased with decreasing value of the carbon atom number of diisothiocyanate and dithiol units, because the hydrogen bonding of polymers containing the diisothiocyanate and dithiol units of short alkyl chain was significantly strong compared to that of polymers containing the units of long alkyl chain. The TGA trace, FTIR-ATR, and DFT calculation also presumed that the thermal decomposition of PDTUs happened from the cleavage of C-S bond of dithiocarbamate moiety. Accordingly, the reversible reaction of isothiocyanate and thiol

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3 derivatives was confirmed by using the aliphatic dithiourethane carbamate as the model
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5 compound. Furthermore, the reversible reaction happened even in the case of the polymer as well
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7 as the low molecular compound. PDTU afforded the dithiourethane oligomer via de-
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9 polymerization based on the thermal cleavage of the C-S bond. The obtained dithiourethane
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11 oligomer also afforded PDTU via re-polymerization based on the addition reaction of the active
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13 isothiocyanate and thiol groups in the terminal, although the M_n value barely reached to the
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15 original polymer.
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