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Thermally stable Diels–Alder polymer using an azodicarbonyl compound as the dienophile

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HIGHLIGHTS

- Diels–Alder polymerization using an azodicarbonyl compound as the dienophile is effectively catalyzed by silver triflate.
- Diels–Alder polymer obtained from the azodicarbonyl monomer is thermally stable.
- C = C double bond in the Diels–Alder polymer can be cleaved without decrease of molecular weigh of the polymer.

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ABSTRACT

A novel Diels–Alder polymerization system was developed, using an azodicarbonyl compound as the dienophile. A bis(azodicarbonyl) monomer was prepared by quantitative oxidation of bis(diacylhydrazine) with ^{t}BuOCl in the presence of pyridine. Diels–Alder polymerization was carried out with a bisdiene monomer, using AgOTf as the catalyst. High thermal stability of the polymer is characteristic for the products of this Diels–Alder polymerization system, in which the Diels–Alder reaction is irreversible. The C = C bond in the Diels–Alder polymer can be cleaved by ozonolysis to give a polyketone.

1. Introduction

The Diels–Alder reaction is one of the most important addition reactions [1–6], and it is basically reversible. To shift the equilibrium in favor of the reaction progressing, the Diels–Alder reaction is generally carried out with an excess of either the diene or the dienophile. A decrease in the reaction temperature is also effective, although addition of a Lewis acid catalyst is essential in this case. Diels–Alder polymerization has also been studied [7–18]. However, as a result of the equilibrium nature of the Diels–Alder reaction, Diels–Alder polymerization has attracted less attention than other addition polymerizations, such as polyurethane formation and the curing of epoxide resin. To attain quantitative addition with stoichiometric amounts of the diene and dienophile, electron-donating and electron-withdrawing groups are introduced into the diene and dienophile, respectively, and the polymerization is carried out at a low temperature in the presence of a Lewis acid catalyst. Combination with an irreversible reaction, such as aromatization, is another method that has been effectively employed to shift the equilibrium to the product side [19–21]. Due to the retro-Diels–Alder reaction, Diels–Alder polymers without aromatization have been recognized as thermally unstable polymers. Various thermo-responsive polymers, in which the response is reversible, have been developed by using Diels–Alder polymerization [22–29]. A thermosetting polymer crosslinked by the Diels–Alder reaction can change its shape when heated [30]. Self-healing polymers can be obtained by using Diels–Alder crosslinking [31,32].

Recently, we developed a quantitative Diels–Alder reaction by using an azodicarbonyl compound as the dienophile (Scheme 1) [33]. Because the azodicarbonyl compound was an excellent dienophile, the Diels–Alder reaction with a stoichiometric amount of 2,3-dimethylbutadiene afforded the corresponding Diels–Alder product quantitatively, in the presence of $Hf(OTf)_4$ or AgOTf catalyst. Because of the high efficiency of this reaction, it is expected that this Diels–Alder reaction system can be applied to Diels–Alder polymerization without the introduction of any irreversible process. Furthermore, the N–N and C = C bonds in the Diels–Alder product could be cleaved by SmI_2 reduction and ozonolysis, respectively [33]. Thus, the polymer obtained from the Diels–Alder polymerization using an azodicarbonyl compound as the dienophile could be converted into another functionalized polymer.

In this paper, we report a novel Diels–Alder polymerization system using an azodicarbonyl compound as the dienophile moiety. It was found that the resulting polymers exhibited high thermal stability, even

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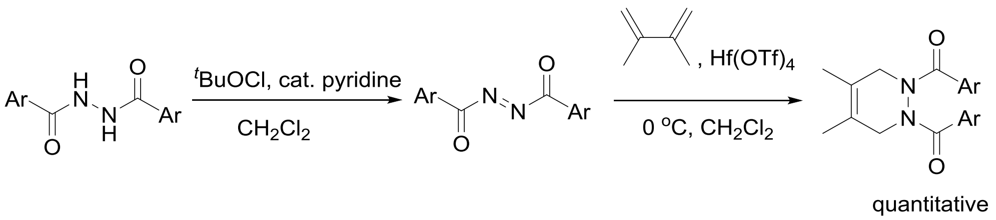


Scheme 1. Quantitative Diels–Alder reaction using an azodicarbonyl compound as the dienophile.

though they were obtained by a simple Diels–Alder polymerization. Furthermore, C = C bond-cleavage of the obtained polymer afforded a novel polymer that had carbonyl groups on the backbone.

2. Experimental

2.1. Preparation of the bis(diacylhydrazine)

2.1.1. Dihydrazide *4*

A solution of **3** (15.57 g, 55.9 mmol) and hydrazine monohydrate (15.0 mL, 300.0 mmol) in ethanol (100 mL) was stirred for 1 d. After removal of the volatiles in vacuo, the residue was recrystallized from ethanol to obtain **4** (8.78 g, 35.1 mmol, 64%) as colorless crystals.

2.1.2. Bis(diacylhydrazine) *2*

Compound **5** (7.1 mL, 39.1 mmol) was added dropwise to a solution of **4** (4.14 mL, 16.5 mmol) and pyridine (3.0 mL, 37.0 mmol) in *N*,*N*-dimethylformamide (DMF; 20 mL) at 0 °C. After being stirred for 1 d, the reaction mixture was poured into diethyl ether. The precipitate was collected by filtration, washed with diethyl ether, and dried in vacuo. The crude product was recrystallized from DMF–ethanol to obtain **2** (7.41 g, 13.0 mmol, 78%) as colorless crystals.

2.2. Preparation of the bisdiene

2.2.1. Monobrominated sulfolene *8*

A solution of **7** (2.8000 g, 19.15 mmol) and *N*-bromosuccinimide (3.4829 g, 19.56 mmol) in chloroform (60 mL) was heated to reflux under argon for 10 h. After evaporation of the volatiles, the residue was dissolved in diethyl ether and the insoluble materials were filtered out. The filtrate was concentrated in vacuo to give a brown oil (4.8827 g), which was subjected to chromatography over silica gel (eluent: ether-hexane-chloroform, 1/2/5) to furnish **8** (3.1540 g, 14.01 mmol, 74%) as a white solid.

2.2.2. Bis(sulfolene) *10*: typical procedure

A solution of **9a** (0.89 g, 4.00 mmol), potassium carbonate (1.19 g, 8.61 mmol), and **8** (1.81 g, 8.02 mmol) in DMF (5.0 mL) was stirred for 1 d. After addition of water, the reaction mixture was extracted three times with ethyl acetate. The organic layer was dried over magnesium sulfate, filtered, and evaporated in vacuo. The residue was subjected to chromatography over silica gel (eluent: ethyl acetate-hexane, 1/1) to obtain **10a** (1.40 g, 2.74 mmol, 68%) as a white solid.

2.2.3. Bis(diene) *6*: typical procedure

A solution of **10a** (0.32 g, 0.70 mmol) and hydroquinone (0.012 g, 0.11 mmol) in xylene (12.0 mL) was heated to reflux under argon for 15 h. After removal of the solvent, the residue was subjected to chromatography over silica gel (eluent: ether-hexane, 1/6) to obtain **6a** (0.21 g, 0.65 mmol, 93%) as a white solid.

2.3. Diels–Alder polymerization: general procedure

Tert-Butyl hypochlorite (1.5 equiv, 300 mol%) and pyridine (0.07 equiv, 0.14 mol%) were added to a suspension of **2** in dichloromethane at 0 °C. After the mixture had been stirred for 1 h, the volatiles were evaporated, and the atmosphere was replaced with argon. Dichloromethane was added to dissolve the azodicarbonyl compound **1**, and diene **6** (1.00 equiv) and AgOTf (0.20 equiv, 40 mol%) were added to the resultant red solution. After being stirred for 1 d, the reaction mixture was diluted with dichloromethane. The insoluble fraction was removed by filtration, and the filtrate was concentrated in vacuo. The residue was dissolved in tetrahydrofuran, and the solution was poured into methanol. The precipitate was collected by filtration, washed with methanol, and dried in vacuo to obtain polymer **11**.

2.4. Oxidative scission of C = C bonds by ozone: general procedure

An oxygen stream containing ozone was passed into a solution of **11** in dichloromethane-methanol (4:1, v/v) at −98 °C for 15 min. After the nitrogen stream had passed through for 5 min, tributylphosphane was added to reduce the ozonide. After the mixture had been stirred for 1 h, the solvent was evaporated; the residue was dissolved in tetrahydrofuran and poured into hexane. The precipitate was collected by filtration, washed with hexane, and dried in vacuo to obtain polymer **12**.

3. Results and discussion

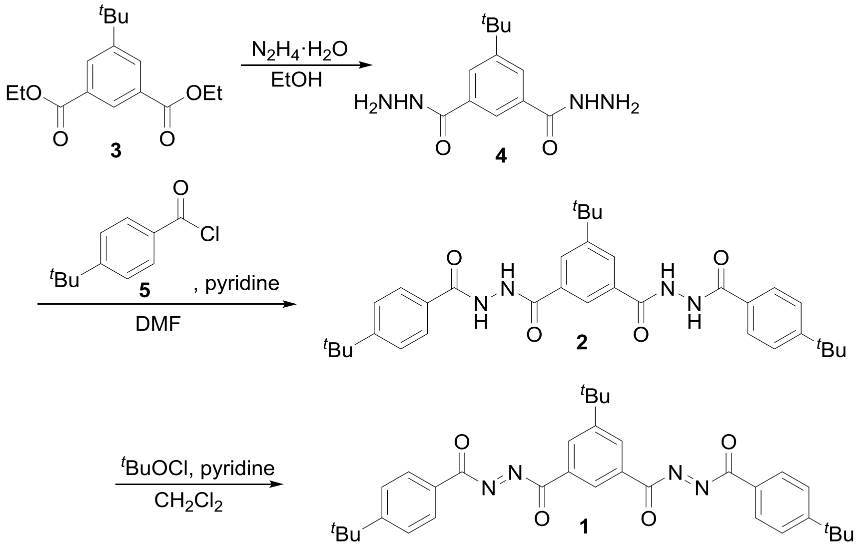
3.1. Monomers

Bis(azodicarbonyl) monomer **1** was synthesized by oxidation of the corresponding bis(diacylhydrazine) **2**, which was prepared by hydrazination of diester **3**, followed by acylation with acid chloride **5**, as shown in Scheme 2. The introduction of the three *tert*-butyl groups in the structures of **1** and **2** was necessary to make the monomer and precursor soluble in organic solvents. Azodicarbonyl compounds are not only thermally unstable but also highly reactive toward nucleophiles such as water. Therefore, bis(diacylhydrazine) **2** was oxidized with excess *tert*-butyl hypochlorite in the presence of a catalytic amount of pyridine, and bis(azodicarbonyl) **1** was used for polymerization, after evaporation of the volatiles, without further purification [33].

Bisdiene monomer **6** was synthesized by using sulfolene **7** as a protected butadiene, as shown in Scheme 3 [34,35]. Radical bromination of **7** afforded monobrominated sulfolene **8** in 82% yield. Alkylation of dicarboxylic acids **9** with **8**, followed by thermal decomposition of the sulfolene group, afforded the bisdiene monomers in good yields. Aromatic dicarboxylic acids, as well as an aliphatic one, were used as the dicarboxylic acids.

3.2. Diels–Alder polymerization

Diels–Alder polymerization was first examined with bis(azodicarbonyl) **1** and bisdiene **6a** as the monomers in dichloromethane. When 2,3-dimethylbutadiene was used as the diene for the Diels–Alder reaction with azodicarbonyl compounds, Hf(OTf)$_4$ showed the best catalytic activity, and the AgOTf catalyst also gave the Diels–Alder product almost quantitatively [33]. However, when Hf(OTf)$_4$ was used as the Lewis acid catalyst for the Diels–Alder polymerization, no methanol-insoluble part was obtained. It was supposed that the ester groups coordinated with Hf(OTf)$_4$ to deactivate it. Therefore, AgOTf was used as the Lewis acid catalyst, and the polymer was obtained as a



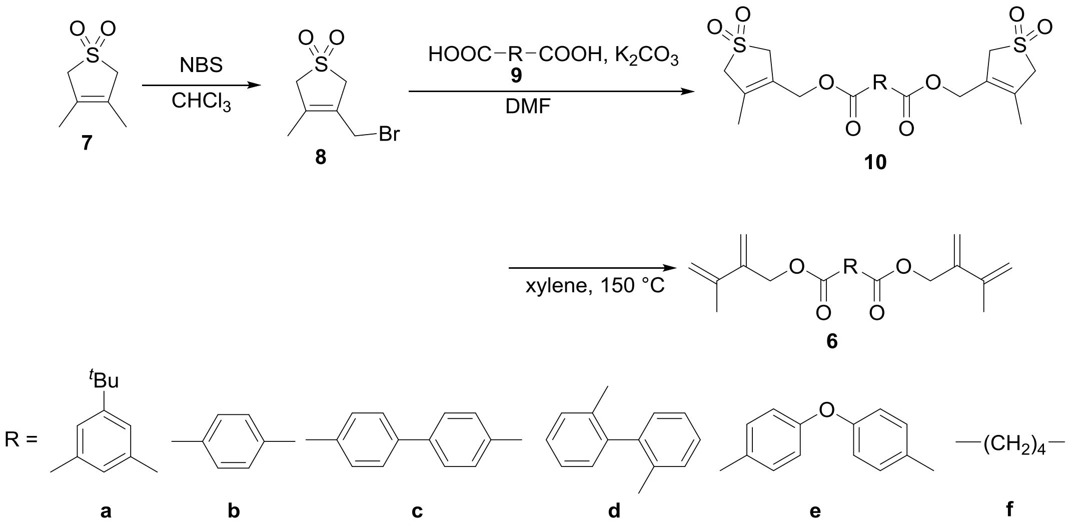
Scheme 2. Synthesis of the azodicarbonyl monomer.

methanol-insoluble part (Scheme 4). The polymerization conditions were examined. The results are summarized in Table 1.

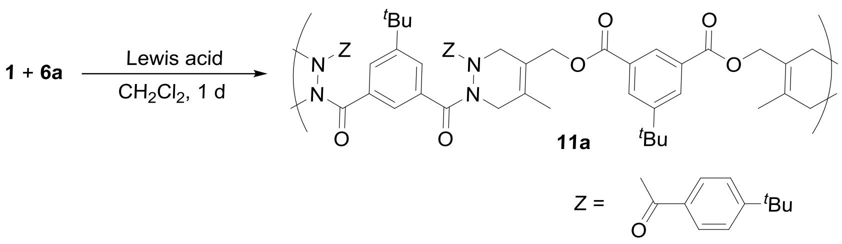
First, the Diels–Alder polymerization was carried out in dichloromethane in the presence of 40 mol% AgOTf. The characteristic red color of the azodicarbonyl group disappeared after 24 h. When the polymerization was carried out for 24 h or 48 h, no change was observed in the M_n value. Because of the low thermal stability of the azodicarbonyl group, decomposition of the azodicarbonyl group accompanies the polymerization, and the polymerization stopped within 24 h. Therefore, further polymerizations were carried out for 24 h, and the effect of the polymerization temperature was examined. In general, the yield and M_n value of the polymer increased when the reaction temperature was increased. However, when polymerization was carried out under reflux, the yield and M_n value decreased, probably because of thermal decomposition of azodicarbonyl monomer **1**. The best result was obtained when the polymerization was initiated at 0 °C and the flask was gradually warmed to room temperature. When the amount of AgOTf was reduced to 20 mol%, no methanol-insoluble part was obtained because of slow polymerization. However, an increase in the amount of AgOTf to 100% did not considerably affect the result. The concentration of the monomers also had little effect, which indicates that the equilibrium of the Diels–Alder reaction was completely shifted to the product side. When the polymerization was carried out from 0 °C to room temperature, the polydispersity index (PDI) of polymer **11a** ranged from 1.72 to 2.54, the expected values for polyaddition.

It was found that the signals in the ^{1}H NMR spectrum of **11a** were very broad (Fig. S19), and no structural information was obtained from them. It has been reported that the 1,2-diacyl-1,2,3,6-tetrahydropyridazine derivative exhibits very broad ^{1}H NMR signals [33]. The structure of **11** was therefore elucidated by using the ^{13}C NMR spectrum. Fig. 1 shows the ^{13}C NMR spectra of **2**, **6a**, and **11a**. Because the ^{13}C NMR spectrum of **11a** contained very broad peaks at room temperature, the spectrum measured at 80 °C is shown in Fig. 1.

The characteristic carbon signals (I, J, K, and L) of the butadiene moiety, observed in the spectrum of **6a**, disappeared in the spectrum of **11a**. Instead, very broad signals that can be assigned to methylene groups (J′ and L′) appeared at around 50 ppm. At the same time, the signals for the aliphatic carbon atoms in **6a**, attached to the butadiene system (H and M), shifted to the higher field (H′ and M′), and those for the carbonyl carbon atoms of the diacylhydrazine moiety shifted to the lower field (g′ and h′) in the spectrum of **11a**. These changes indicate the progress of the Diels–Alder reaction to form the 1,2-diacyl-1,2,3,6-tetrahydropyridazine moiety. The ^{13}C NMR spectra of 1,2-bis(4-*tert*-butylbenzoyl)-1,2,3,6-tetrahydropyridazine at different temperatures



Scheme 3. Synthesis of the bisdiene monomers.



Scheme 4. Diels–Alder polymerization.

Table 1
Diels–Alder polymerization of **1** and **6a**.

Entry	Lewis acid (mol%)	Conc. (M)	Temperature (°C)	Yield[a] (%)	M_n (P_n)[b]	M_w/M_n[b]
1	Hf(OTf)$_4$ (40)	0.3	0	0		
2	AgOTf (40)	0.3	−20	59	7700 (16.2)	1.43
3	AgOTf (40)	0.3	0	63	8000 (16.9)	1.46
4	AgOTf (40)	0.3	0 → r. t.	80	9900 (20.9)	2.54
5	AgOTf (40)	0.3	reflux	40	6600 (13.9)	1.30
6	AgOTf (100)	0.3	0 → r. t.	73	12000 (25.3)	1.72
7	AgOTf (20)	0.3	0 → r. t.	0		
8	AgOTf (40)	1	0 → r. t.	80	9800 (20.6)	2.20

[a] MeOH-insoluble part.
[b] Estimated by GPC (THF, PSt standards).

are shown in Figs. S1, S2, and S3. All signals were observed as a pair of peaks at room temperature. At higher temperature, the peaks became broad and coalesced. At 120 °C, most signals were observed as single peaks. However, the signal for J′ (L′) was still broad, even at 120 °C. Such characteristic behavior in the ^{13}C NMR spectrum can be explained by slow conversion between *s-cis/s-trans* conformations because the rotation of two vicinal acyl groups on a rigid cyclic structure requires high activation energy. The signals of J′ and L′ are observed as very broad separated peaks, even at 80 °C, which indicates the formation of the 1,2-diacyl-1,2,3,6-tetrahydropyridazine structure. Furthermore, some signals were observed as multiple peaks, indicating the presence of 1,3- and 1,4-addition structures.

The Diels–Alder polymerization of **1** with various diene monomers was examined using AgOTf as the catalyst (Scheme 5). The results are

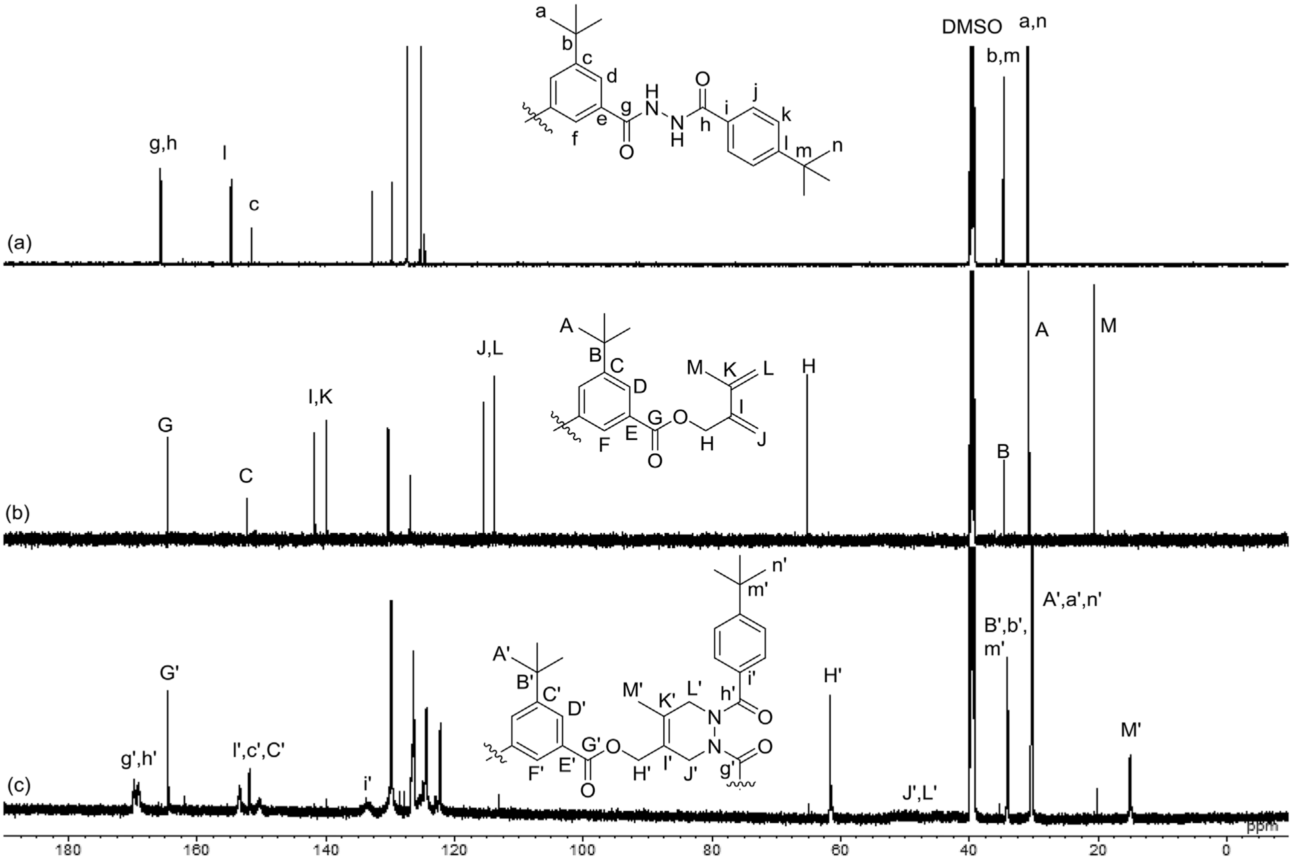
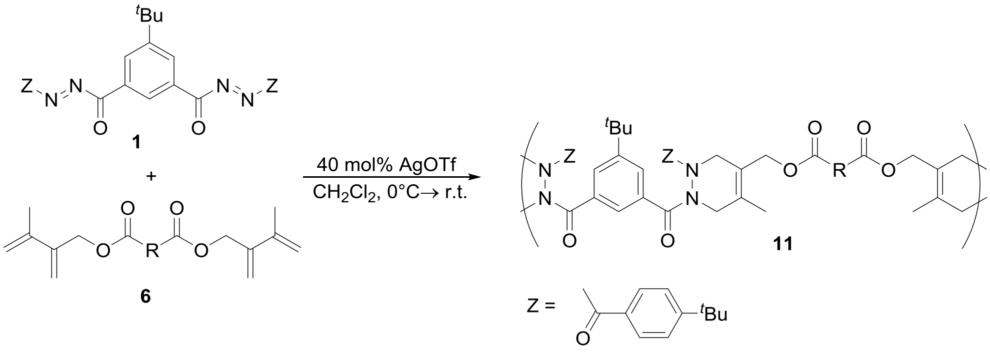


Fig. 1. ^{13}C NMR spectra of (a) **2** (150 MHz, DMSO-d_6), (b) **6a** (150 MHz, DMSO-d_6), and (c) **11a** (150 MHz, DMSO-d_6 at 80 °C).



Scheme 5. Diels–Alder polymerization using various bisdiene monomers.

Table 2
Diels–Alder polymerization of **1** and **6**.[a]

6	Yield[b] (%)	M_n (P_n)[c]	M_w/M_n[c]
A	80	9900 (20.9)	2.54
B	84	8300 (18.6)	1.75
C	86	10000 (20.6)	2.54
D	65	10000 (20.6)	1.80
E	78	5600 (11.4)	1.57
e[d]	82	8800 (17.9)	1.81
F	65	14000 (32.1)	1.67

[a] Polymerization was carried out in dichloromethane from 0 °C to r.t. for 24 h in the presence of 40 mol% AgOTf. Monomer **1** was prepared from **2** by oxidation with excess *tert*-butyl hypochlorite in the presence of pyridine and was used after evaporation of the volatiles, without further purification.
[b] MeOH-insoluble part.
[c] Estimated by GPC (THF, PSt standards).
[d] In the presence of 100 mol% AgOTf.

Table 3
5%-Weight-loss temperatures (T_{d5}) of Diels–Alder polymer **11**.[a]

11	T_{d5} (°C)		Residue at 500 °C	
	in N_2	in air	in N_2	in air
a	311	277	30	16
b	308	276	29	17
c	308	209	31	25
d	313	283	25	20
e	305	229	27	18
f	297	196	26	24

[a] Measurements were carried out by using TGA (10 °C/min).

summarized in Table 2. Polymer **11**, with M_n = 8000–10000 was obtained in 70–85% yields. The PDI ranged from 1.54 to 2.54, indicating that a typical polyaddition reaction had occurred. When **6e** was used as the monomer, the yield and M_n value increased when the amount of AgOTf was increased.

Table 4
Ozonolysis of polymer **11**.[a]

11	M_n of 11[b]	12		
		Yield (%)	M_n[b]	M_w/M_n[b]
a	9900	100	12000	1.77
b	8300	100	9000	1.65
c	10000	100	9900	2.23
d	10000	100	9800	1.71
e	8800	100	7500	1.82
f	14000	100	12000	1.56

[a] Ozonolysis was carried out in dichloromethane-methanol at −98 °C for 15 min. After a nitrogen stream had been passed through the mixture for 5 min, tributylphosphine was added.
[b] Estimated by GPC (THF, PSt standards).

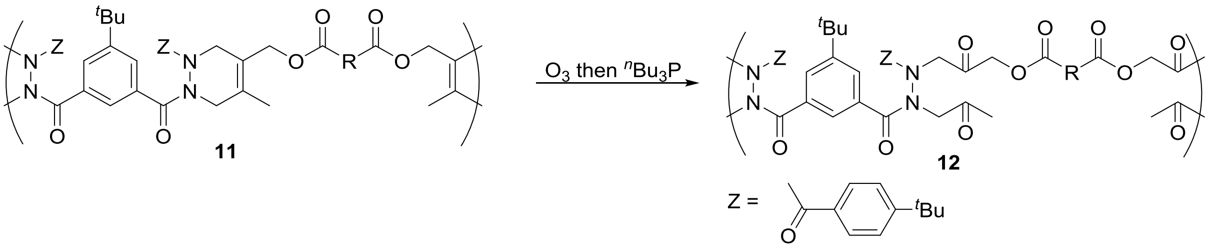
3.3. Thermal properties

Because the N=N double bond gives rise to high reactivity and thermal instability of the azodicarbonyl compound, the 4,5-diazacyclohexene moiety produced by the Diels–Alder reaction is expected to be stable enough for the thermal retro-Diels–Alder reaction to occur. When NMP solution of 1,2-bis(4-*tert*-butylbenzoyl)-1,2,3,6-tetrahydropyridazine (Figs. S1–S3) was allowed to stand at 200 °C for 5 h, no decomposition was observed. Therefore, the thermal properties of polymer **11** were studied using TGA and DSC. A clear glass-transition temperature was not observed in every case. The 5%-weight-loss temperatures (T_{d5}) of **11** are summarized in Table 3.

The T_{d5} values of polymer **11** were observed to be above 300 °C in a nitrogen atmosphere, and above 200 °C even in air. The thermal stability of **11** is much higher than that observed for other Diels–Alder polymers, which were characterized by thermal retro-Diels–Alder depolymerization. It was supposed that the retro-Diels–Alder reaction is negligible for **11** because of the instability of the azodicarbonyl moiety.

3.4. Polymer reaction

It has been reported that 4,5-diazacyclohexene can be easily converted into an α-aminoketone after cleavage of the N–N and C=C



Scheme 6. Ozonolysis of Diels–Alder polymer.

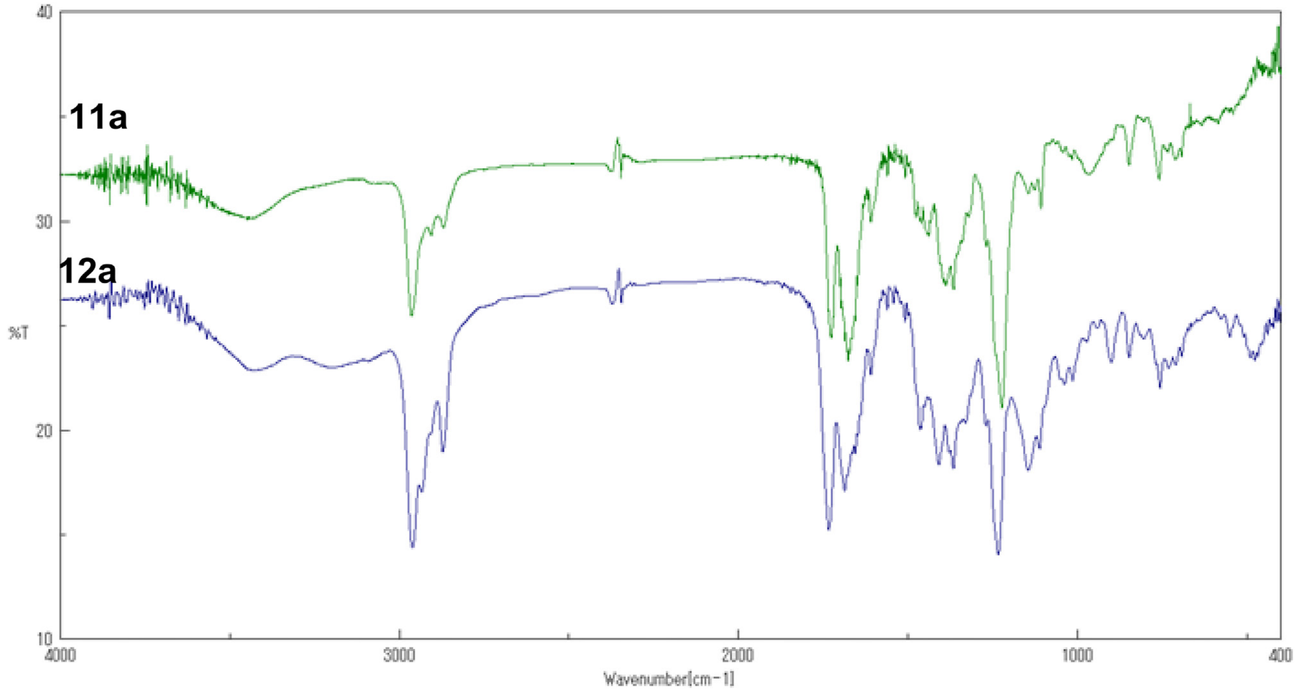


Fig. 2. IR spectra of **11a** and **12a**.

bonds by SmI_2 reduction and O_3 oxidation, respectively [33]. Because of the 4,5-diazacyclohexene moiety introduced during the Diels–Alder polymerization, polymer **11** can be converted into another functional polymer. Because SmI_2 reduction may cleave not only the N–N bond but also the allyl ester moiety [36], the ozonolysis of **11** was examined. Even though C=C bonds are present on the polymer backbone, it is expected that the polymer structure will remain after C=C bond cleavage, because the C=C bonds are included in the cyclic structure.

Polymer **11** was treated with O_3 at −98 °C in methanol-CH_2Cl_2; this was followed by addition of Me_2S to reduce the ozonide. No decrease in the M_n value was observed, and the polymer was recovered almost quantitatively in every case. These results proved that the C=C bond is installed in the cyclic structure and that the polymerization occurred by the Diels–Alder reaction. In the ^{13}C NMR spectrum of the product, a signal appeared at around 200 ppm, which is characteristic of a ketone carbonyl carbon atom. However, some increase in the M_n and M_w/M_n values was observed, indicating that a side reaction of the carbonyl group, such as an aldol reaction and/or acetalization, occurred to some extent during the reduction of the ozonide. A change of the reducing agent was examined to suppress the side reaction, and it was found that the increase in the M_n and M_w/M_n values could be suppressed when $^nBu_3P$ was used as the reducing agent. Therefore, ozonolysis of **11** was carried out with $^nBu_3P$ as the reducing agent (Scheme 6). The results are summarized in Table 4.

Fig. 2 shows the change in the IR spectrum caused by the ozonolysis of **11a**. In the IR spectrum of **11a**, the $\nu_{C=O}$ of the ester and amide group were observed at 1726 cm^{-1} and 1676 cm^{-1}, respectively. The $\nu_{C=C}$ of tetrasubstituted alkenes are generally very weak, and they were not clearly observed in the IR spectrum of **11a**. Ozonolysis induced no change in the $\nu_{C=O}$ of the ester group, but the $\nu_{C=O}$ of the ketone group appeared at 1686 cm^{-1}, and the $\nu_{C=O}$ of the amide group appeared on the lower wavenumber side as a shoulder. This change in the IR spectrum indicates the formation of a ketone carbonyl group.

4. Conclusions

Diels-–Alder polymerization was successfully carried out using bis(azodicarbonyl) **1** as the dienophile monomer. AgOTf was the best catalyst for the Diels–Alder polymerization. High thermal stability of the polymer is characteristic of this Diels–Alder polymerization system, in which the Diels–Alder reaction is actually irreversible. The C=C bond in the Diels–Alder polymer can be cleaved by ozonolysis to form a polyketone.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.polymer.2019.01.071.

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