Synthesis and Property of Polyoxazolidone Having Fluorene Moiety by Polyaddition of Diisocyanate and Diepoxide

Motohisa Azechi, Takeshi Endo

Molecular Engineering Institute, Kinki University, Kayanomori, Iizuka, Fukuoka 820–8555, Japan
Correspondence to: T. Endo (E-mail: tendo@moleng.fuk.kindai.ac.jp)

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ABSTRACT: Polyoxazolidones having fluorenyl group were synthesized by polyaddition of 9,9-diglycidyl fluorene with various diisocyanates. The polymer from 9,9-diglycidyl fluorene and methylenediphenyl 4,4′-diisocyanate was afforded in high yield although polydispersity of the polymer was found relatively broad. The IR spectrum of the obtained polymer showed two absorption in carbonyl region. One of them was assigned to the expected oxazolidone, while the other at 1710 cm^{-1} appeared due to a carbonyl group of the isocyanurate moieties produced by cyclotrimerization of isocyanate. It is assumed that the cyclotrimerization would cause the broad polydispersity caused by the branched structure formed by isocyanurate. The polymers obtained with three kinds of diisocyanates (methylenediphenyl 4,4′-diisocyanate, 1,6-hexamethylene diisocyanate, 1,4-phenylene diisocyanate) showed high thermal stability, as their T_{d10} was depended on the structure of diisocyanate. All polymers had high transparency in a visible region. © 2014 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2014**, *00*, 000–000

KEYWORDS: cyclopolymerization; fluorene; oxazolidone; polyaddition; thermal properties; transparency

INTRODUCTION Cycloaddition of the epoxide with isocyanate gives 3,5-disubstituted-oxazolidin-2-one, known as oxazolidone.[1–7] Oxazolidones were widely used in medicine as drugs and pharmaceutical preparations, intermediates in the paint and varnish industry, and lubricants. On the other hand, oxazolidone structure is well known that their high thermal stability is generally superior to those of carbodiimide, urea, and urethane.[8,9] Since 1960s, this reaction has ever been utilized for the synthesis of thermally stable polymers, poly(oxazolidone)s, derived from bifunctional epoxides and diisocyanates.[10–14] So far, it has been reported on the synthesis and thermal property of poly(oxazolidone)s obtained from the corresponding bifunctional epoxides and diisocyanates as monomer. Above all, Whitmore's group reported the synthesis and thermal stability of poly(oxazolidone)s prepared with as various diglycidyl ethers derivatives and diisocyanates.[13] According to this report, molecular weights of the poly(oxazolidone)s were 1340–4750 and the poly(oxazolidone)s were stable up to 260 °C by thermogravimetric analysis (TGA). However, further improvement of poly(oxazolidone) has not been studied in recent years. Thus, we focus on fluorene structure giving high thermal stability and optical property.

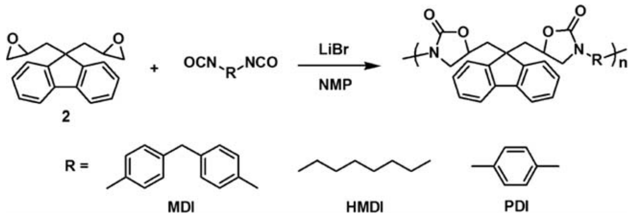
The fluorene group contains two benzene rings that are connected via a carbon–carbon bond and an adjacent methylene bridge. The methylene bridge forces the two phenyl rings to be planar, thereby providing high overlaps of π orbitals. Incorporating the rigid and bulky fluorene moiety to polymers leads to enhanced thermal properties, solubility, and optical properties. We expect that thermal property and optical property are improved further by introducing fluorene unit to poly(oxazolidone).

In this work, we carried out synthesis of poly(oxazolidone)s prepared from 9,9-diglycidyl fluorene and three diisocyanates [methylenediphenyl 4,4′-diisocyanate (MDI), hexamethylene diisocyanate (HMDI), 1,4-phenylene diisocyanate) (PDI); Scheme 1] and report the effects of reaction conditions (monomer concentration, catalysis amount, and temperature) on the polyaddition of 9,9-diglycidyl fluorene with diisocyanates. Further, we examined their thermal and optical properties.

EXPERIMENTAL

Materials

Fluorene was purchased from Sigma-Aldrich (St. Louis) and recrystallized from methanol before use. Allyl chloride was purchased from Wako Pure Chemical Industry (Osaka, Japan). Sodium methoxide was purchased from Kanto Kagaku (Tokyo, Japan). *m*-Chloroperbenzoic acid (*m*-CPBA) was purchased from Wako Pure Chemical Industry. *p*-Tolyl isocyanate, MDI, and HMDI were purchased from Tokyo Chemical Industry



SCHEME 1 Polyaddition of 9,9-diglycidyl fluorene and isocyanates.

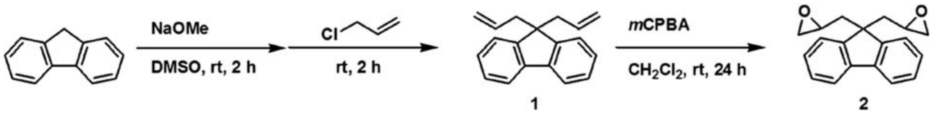
(Tokyo, Japan) and distilled under reduced pressure. PDI was purchased from Tokyo Chemical Industry and sublimated under reduced pressure. Lithium bromide was purchased from Kanto Kagaku dried under reduced pressure before use. *N*-Methylpyrrolidone (NMP) was distilled over calcium hydride (CaH_2) under reduced pressure. Other solvents were used without further purification.

Measurements

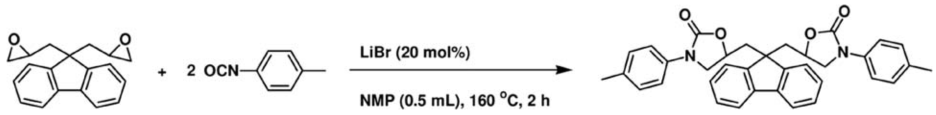
Nuclear magnetic resonance (NMR) measurements were recorded on JEOL JNM ECS 400 in $CDCl_3$ and DMSO-d_6 with tetramethylsilane as an internal standard. IR spectra were recorded on a Thermo Scientific NICOLET iS10 FTIR spectrometer equipped with a SMART iTR ATR sampling accessory. Number average molecular weight (M_n) and polydispersity (M_w/M_n) were estimated from size exclusion chromatography, performed on a Tosoh chromatograph model HLC-8220GPC equipped with Tosoh TSKgel Super AW 2500 columns (6.0 mmI.D. × 15 cm), TSKgel Super AW 3000 columns (6.0 mmI.D. × 15 cm), and TSKgel Super AW 4000 columns (6.0 mmI.D. × 15 cm), using *N*,*N*-dimethylformamide (DMF) containing 10 mM lithium bromide as an eluent at the flow rate of 0.5 mL min^{-1} at 40 °C. The molecular weight calibration curve was obtained with polystyrene standards. Differential scanning calorimetry (DSC) was carried out with DSC-6200 (Seiko Instrument) using aluminum pan under a 20 mL min^{-1} N_2 flow at the heating rate of 10 °C min^{-1}. TGA was performed with TG-DTA 6200 (Seiko Instrument) using aluminum pan under a 50 mL min^{-1} N_2 flow at a heating rate of 10 °C min^{-1}.

Monomer Synthesis

The synthetic route of the monomer is shown in Scheme 2.



SCHEME 2 Synthesis of 9,9-diglycidyl fluorene.



SCHEME 3 Model reaction of 9,9-diglycidyl fluorene and *p*-tolyl isocyanate.

TABLE 1 Polyaddition of 2 and MDI[a]

Run	Temperature (°C)	Time (h)	NMP (mL)	LiBr (mol %)	Yield[b] (%)	M_n[c]	M_w/M_n[c]
1	160	2	1.0	20	86	5,100	12.4
2	160	2	1.5	20	85	4,200	4.51
3	160	2	2.0	20	88	3,600	2.72
4	160	2	4.0	20	92	3,000	2.19
5	160	2	8.0	20	52	1,800	1.63
6	160	2	2.0	2	51	2,400	2.42
7	160	2	2.0	5	64	2,400	2.50
8	160	2	2.0	10	82	2,600	2.02
9	100	2	2.0	10	70	ND[d]	ND[d]
10	120	2	2.0	10	84	4,100	8.52
11	140	2	2.0	10	85	3,900	4.32
12	180	2	2.0	10	81	2,700	2.00

[a] Reaction conditions: 2 and MDI = 2 mmol, reaction time = 2 h.
[b] Methanol-insoluble part.
[c] Estimated by GPC analysis (eluent : DMF, polystyrene standards).
[d] ND, not determined.

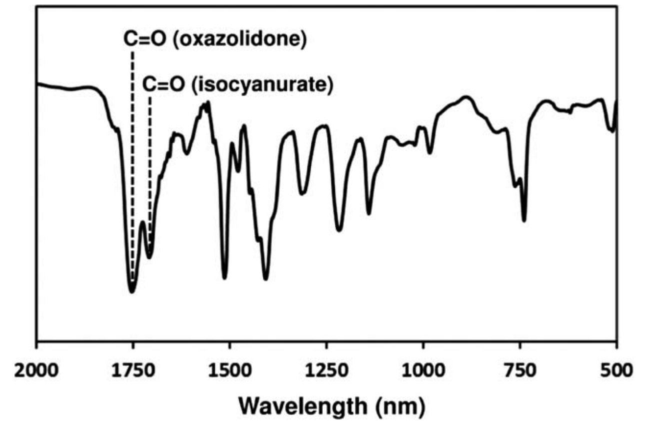


FIGURE 1 FTIR spectra of poly(oxazolidone) obtained at 160 °C for 2 h.

Synthesis of 9,9-Diallyl fluorene (1)

In a round-bottom flask, fluorene (20 g, 120mmol), sodium methoxide (19.5 g, 360 mmol), and DMSO (213 mL) were added and stirred at room temperature for 30 min under nitrogen. Then, allyl chloride (27.6 mL, 360 mmol) was added dropwise to the mixture at room temperature. The reaction mixture was stirred for 3 h, quenched with distilled water, and extracted with *n*-hexane three times. The combined organic layer was washed with distilled water and brine, dried over anhydrous $MgSO_4$, and filtered and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, eluted with *n*-hexane) and **1** was obtained as colorless oil (yield: 26.5 g, 108.8 mmol, 90%).

^{1}H NMR ($CDCl_3$): $\delta = 7.68$ (m, 2H), 7.39 (m, 2H), 7.29 (m, 4H), 5.24 (m, 2H), 4.77 (m, 4H), 2.69 (d, 4H), ^{13}C NMR ($CDCl_3$): $\delta = 149.4$, 140.9, 133.9, 127.3, 127.1, 123.8, 119.9, 117.7, 54.3, 43.7 ppm.

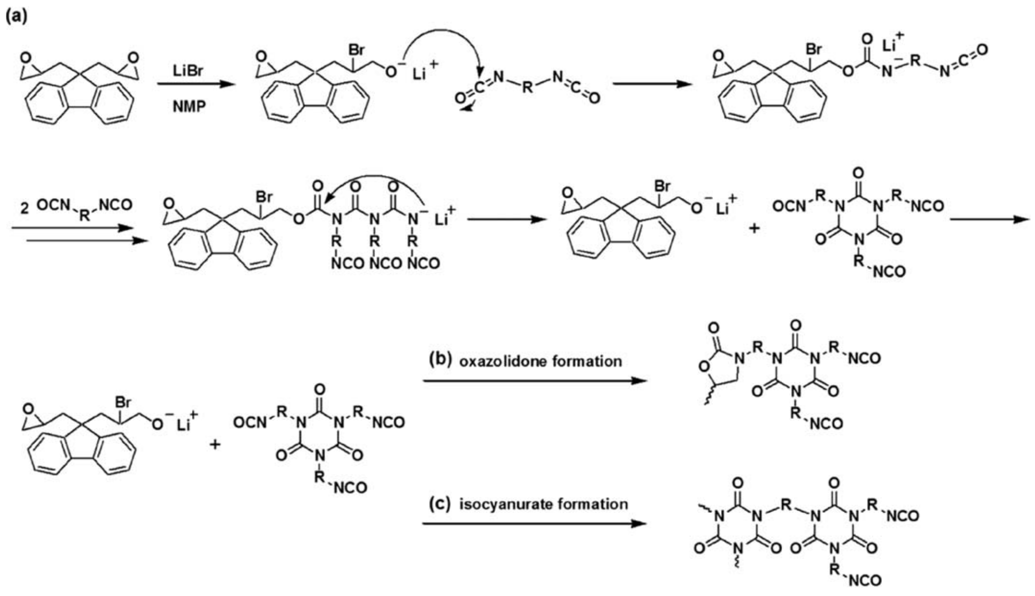
Synthesis of 9,9-Diglycidyl fluorene (2)

A solution of *m*-CPBA (22.0 g, 89.3 mmol, 70% purity) in dichloromethane (300 mL) was added dropwise a solution of **1** (10.0 g, 40.6 mmol) in dichloromethane (100 mL) at room temperature. The white suspension thus formed was stirred at room temperature for 24 h and then quenched by addition of a saturated solution of Na_2SO_3 in water. The product was extracted with dichloromethane. The combined extracts were washed successively with saturated $NaHCO_3$ solution and brine and dried with anhydrous Na_2SO_4, and filtered and concentrated under reduced pressure. The residue was purified by column chromatography with dichloromethane and then recrystallization with *n*-hexane twice and **2** was obtained as a white crystalline (yield: 7.6 g, 27.3 mmol, 67%).

^{1}H NMR ($CDCl_3$): $\delta = 7.77$ (m, 2H), 7.39–7.61 (m, 6H), 7.06 (s, 8H), 3.82 (m, 2H), 3.12 (dd, 1H), 2.91 (dd, 1H), 2.87 (m, 1H), 2.55 (m, 1H), 2.56 (s, 6H), ^{13}C NMR ($CDCl_3$): $\delta = 154.3$, 146.4, 140.4, 135.7, 133.7, 129.5, 129.0, 128.2, 123.6, 123.9, 120.9, 118.1, 70.3, 51.3, 50.9, 44.6, 20.8 ppm.

Synthesis of Model Compound (3)

The synthetic route of the model compound is shown in Scheme 3. **2** (279 mg, 1.0 mmol), *p*-tolyl isocyanate (266 mg, 2.0 mmol), and LiBr (18 mg, 0.2 mmol) were placed in a Schlenk reaction tube. The flask was evacuated and then filled with nitrogen gas. NMP (0.5 mL) was added to flask under nitrogen atmosphere. The mixture was stirred at 160 °C for 2 h. Then, the reaction mixture was cooled to room temperature, diluted with ethyl acetate, and washed with distilled water four times. The organic layer was dried over anhydrous $NaSO_4$, filtered, and concentrated under reduced pressure. The resulting residue was recrystallization with diethyl ether to isolate **3** as a slightly yellow solid (yield: 330 mg, 0.6 mmol, 60%).



SCHEME 4 Plausible mechanism of isocyanurate formation in polymerization.

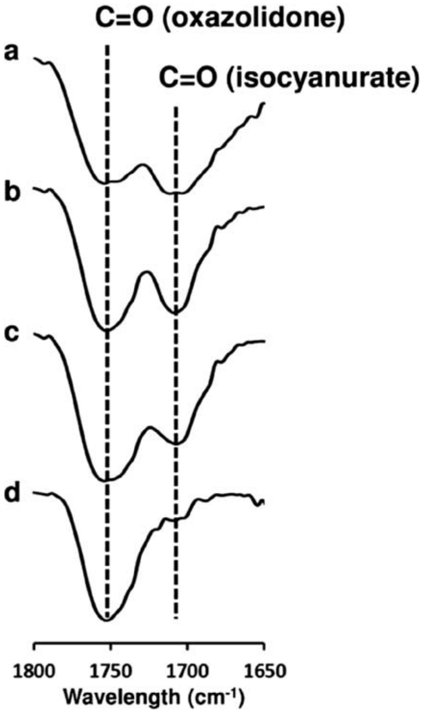


FIGURE 2 FTIR spectra of poly(oxazolidone) obtained at (a) 100 °C, (b) 120 °C, (c) 160 °C, and (d) 180 °C.

^{1}H NMR ($CDCl_3$): $\delta = 7.76$ (m, 2H), 7.36–7.62 (m, 6H), 7.05 (s, 8H), 3.81 (m, 2H), 3.11 (dd, 2H), 2.88 (m, 4H), 2.54 (m, 2H), 2.26 (s, 6H).

Polyaddition

A typical polyaddition procedure is described below. **2** (556 mg, 2.0 mmol), methylenediphenyl 4,4′-diisocyanate (500 mg, 2.0 mmol), and LiBr (18 mg, 0.2 mmol) were placed in a Schlenk reaction tube. The flask was evacuated and then filled with nitrogen gas. NMP (2.0 mL) was added to flask under nitrogen atmosphere. The mixture was stirred at 160 °C for 2 h. Then, the reaction mixture was cooled to room temperature and poured into 200 mL of methanol. The resulting precipitate was collected by centrifugation, and purified by reprecipitation from NMP–methanol systems two times. The obtained polymer was dried at 100 °C *in vacuo* to afford 82% yield. The M_n and M_w/M_n were 2600 g mol^{-1} and 2.02, respectively.

^{1}H NMR ($CDCl_3$): $\delta = 7.83$ (br, 2H), 7.65 (br, 2H), 7.16–7.50 (br, 6H), 6.92–7.15 (br, 6H), 3.88–3.60 (br, 4H), 3.29–3.03(br, 2H), 2.77–2.62 (m, 4H), 2.60–2.35 (m, 2H).

RESULTS AND DISCUSSION

Synthesis of Oxazolidone Compound from 2 and *p*-Tolyl isocyanate as a Model Reaction

Before studying polyaddition of **2** and diisocyanate, we investigated the oxazolidone ring formation of **2** and *p*-tolylisocyanate as a model reaction (Scheme 3). When **2** and *p*-tolylisocyanate was stirred with 20 mol % of LiBr at 160 °C for 2 h in NMP, the oxazolidone ring formation was confirmed from ^{1}H NMR spectrum of the crude compound. This reaction almost proceeded without side reaction and the corresponding oxazolidone compound was obtained in 95% NMR yield by ^{1}H NMR measurement. The oxazolidone compound was isolated by recrystallization with diethyl ether in 60% yield. These results suggest that the oxazolidone ring formation of **2** and *p*-tolylisocyanate which is monofunctional isocyanate might smoothly proceed without side reaction.

Polyaddition of 2 and Diisocyanate

Polyaddition of **2** and MDI carried out with 20 mol % of LiBr as a catalyst at 120 °C for 2 h in NMP on the basis of a model reaction of **2** and *p*-tolyl isocyanate. As a result, a white solid was obtained in 86% yield as a methanol insoluble part (Table 1, run 1). The polymer was soluble in many typical organic solvents such as chloroform, dichloromethane, NMP, and cyclohexanone. The number-averaged molecular weight (M_n) and the polydispersity (M_w/M_n) of the obtained polymer were 5100 and 12.4, respectively. M_w/M_n was broader than we expected. FTIR analysis of the polymer showed two strong absorptions at 1710 and 1750 cm^{-1} (Fig. 1). The latter absorption was attributed with carbonyl group of the desired oxazolidone structure. According to previous work on synthesis of poly(oxazolidone),[10–14] it was reported that isocyanurate was generated by cyclotrimerization of isocyanate as a side reaction. In the current system, the corresponding side reaction was presumed to form isocyanurate, which caused the presence of the other absorption at 1710 cm^{-1}. In this condition, as shown in Scheme 4(a), isocyanurate having three isocyanate groups might form by cyclotrimerization of diisocyanate. In addition, as shown in Scheme 4(b,c), the isocyanate group of isocyanurate reacted with epoxide or another isocyanate to form oxazolidone or isocyanurate, respectively. It could explain the broader dispersity may be due to a branched structure of isocyanurate formed in main chain.

To control the formation of isocyanurate, we examined the polyaddition with various conditions such as concentration,

TABLE 2 Polyaddition of **2** and Various Diisocyanates[a]

Run	Diisocyanate	Temperature (°C)	NMP (mL)	LiBr (mol %)	Yield[b] (%)	M_n[c]	M_w/M_n[c]
1	PDI	160	2.0	10	59	1,700	1.91
2	HMDI	160	2.0	10	81	ND[d]	ND[d]
3	HMDI	200	2.0	10	61	2,400	4.26

[a] Reaction conditions: reaction time = 2 h.
[b] Methanol-insoluble part.
[c] Estimated by GPC analysis (eluent : DMF, polystyrene standards).
[d] ND, not determined.

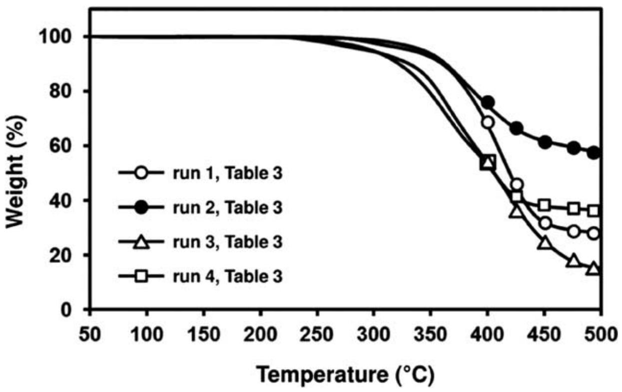


FIGURE 3 TGA curves of poly(oxazolidone)s obtained with MDI (open circle), HMDI (open triangle), and PDI (open square) and networked polymer obtained with MDI (filled circle).

catalyst amount, and temperature. The conditions and results are summarized in Table 1. As a result, the polymers were obtained in 52–92% yield. The M_n's and M_w/M_n's of the obtained polymers were 1800–4200 and 1.63–4.51, respectively (Table 1, runs 2–5). M_w/M_n was a narrow with decreasing concentration. As a result of FTIR spectra of these polymers, the polymers obtained in 2.0–8.0 mL of NMP showed weaker the absorptions of isocyanurate as compared with the polymers obtained in 1.0 or 1.5 mL of NMP. It might be necessary to polymerize in suitable concentration to control the formation of isocyanurate.

We examined the amount of LiBr on the polyaddition behavior (Table 1, runs 6–8). The polymers were obtained in 51–82% yield. The M_n's and M_w/M_n's of the obtained polymers were 2400–2600 and 2.02–2.50, respectively. As a result of FTIR analysis of the polymer, there was a tendency that the absorptions of the isocyanurate weaken as the amount of LiBr increases. In particular, it was hardly observed in the polymer obtained with 10 mol % of LiBr. However, absorption of isocyanurate appeared in the case of the polyaddition with 20 mol % of LiBr. Thus, using 10 mol % of LiBr, it was possible to prevent the formation of isocyanurate.

The polyadditions carried out in range from 100 to 180 °C (Table 1, runs 9–12). In the case of polyaddition at 100 °C, the mixture lost its fluidity after 2 h and obtained in 70% yield as a methanol insoluble part. The polymer was insoluble in many typical organic solvents such as chloroform, tetrahydrofuran, and DMSO. On the other hand, the polymers prepared at 120–180 °C were 81–85% yield, $M_n = 2700–4100$, and $M_w/M_n = 2.00–8.52$. Polydispersities of the polymers obtained at 120 and 140 °C were much broader, whereas those of the polymers obtained 160 and 180 °C were a narrow dispersity. Figure 2 shows FTIR spectra of the polymers obtained at 120–180 °C. In the IR spectrum of the polymers obtained 100 °C, the peak at 1710 cm^{-1}, assignable to isocyanurate moiety, was strongly appeared [Fig. 2(a)]. Increasing the reaction temperature, the absorption of isocyanurate for oxazolidone is reduced and hardly observed at 160–180 °C. Therefore, it was possible to prevent the formation of isocyanurate by the polyaddition at high reaction temperature (>160 °C).

The polyadditions with HMDI and PDI carried out as well as the polyaddition with MDI. The conditions and results were summarized in Table 2. The polymer obtained with PDI was 59% yield, $M_n = 1700$, and $M_w/M_n = 1.91$. On the other hand, in the polyaddition with HMDI, the polymerization solution was gelation and the insoluble polymer was formed. As a result of polyaddition carried out by raising to 200 °C, the soluble polymer was obtained with 61% yield, $M_n = 2400$, $M_w/M_n = 4.26$. This phenomenon was probably due to the reactivity of aliphatic isocyanate. It had been known that the reactivity of aliphatic isocyanate was lower than that of aromatic isocyanate. When using HMDI, isocyanurate structure might form preferentially because 160 °C was too low in the formation of oxazolidone.

Thermal and Optical Properties of Polyoxazolidones

The heat resistance of these oxazolidone polymers was evaluated by TG/DTA. Figure 3 shows typical TGA curves for the polymers obtained from **2** with various isocyanates. From TG/DTA curves, the corresponding T_{d5} and T_{d10} (5 and 10% weight loss temperature, respectively) and the char yield at 500 °C were determined and listed in Table 3. It is that, in all the cases, the resulting polymers exhibited high thermal stability. In particular, utilization of diisocyanate having aromatic group resulted in the higher thermal stability of the corresponding polymers than the polymer obtained with diisocyanate having only aliphatic group. The glass transition temperature (T_g) of the polymers was examined by DSC analysis. While T_g of the soluble polymer prepared with **2**

TABLE 3 Thermal Properties of Polymers Obtained from **2** and Various Diisocyanates[a]

Run	Diisocyanate	T_{d5}[a] (°C)	T_{d10}[a] (°C)	T_g[b] (°C)	Char[c] Yield (%)
1[d]	MDI	333	360	198	29
2[e]	MDI	343	363	ND[f]	57
3[g]	HMDI	300	322	ND[f]	15
4	PDI	295	331	ND[f]	36

[a] Determined by TGA under N_2.
[b] Determined by DSC under N_2.
[c] Char yield at 500 °C under N_2.
[d] Table 1, run 8.
[e] Table 1, run 9.
[f] Glass transition temperature was not detected (<250 °C).
[g] Table 2, run 3.

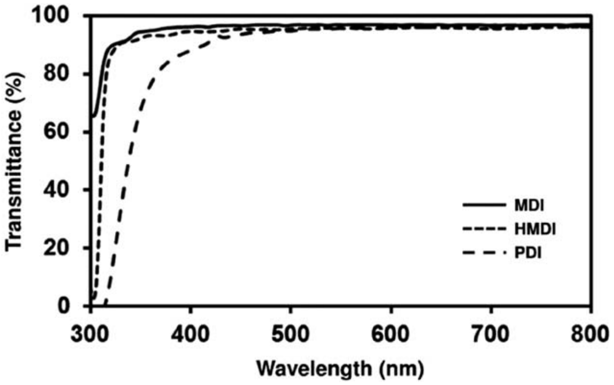


FIGURE 4 Transmittance of poly(oxazolidone) obtained with MDI (solid line), HMDI (dotted line), and PDI (dashed line).

and MDI was 198 °C, T_g of the networked polymer was not observed in range from 50 to 250 °C. Previously, we reported on the networked polymer consist of isocyanurate skeleton.[15–17] In previous report, T_g of the networked polymers was not observed in range from 50 to 300 °C similarly to the polymer obtained in this work. Therefore, isocyanurate formed in polymer is found to affect to T_g of poly(oxazolidone). T_g of the polymer prepared with **2** and MDI were compared with T_g of the polymer prepared with diglycidyl ether of bisphenol A and MDI.[13] While T_g of the latter was 134 °C, T_g of the former was 198 °C. Thus, the introduction of the fluorene skeleton is found to contribute to the thermal stability of poly(oxazolidone).

Figure 4 illustrated the UV–vis spectra of the prepared sample films in the wavelength region ranging from 200 to 800 nm. The polymers were dissolved in NMP to prepare 10 wt % solutions. The solution was filtered through membrane filter and casted on a glass plate. The plate was dried in a drying oven at 100 °C for 12 h and further dried at 120 °C for 12 h *in vacuo*. All polymers had good transparency in a visible region. The transmittances were higher than 80% at 450 nm.

SUMMARY

Poly(oxazolidone)s containing fluorene moiety were synthesized by polyaddition of 9,9-diglycidyl fluorene and various diisocyanates under various conditions. As a result of the polyaddition, it was found that isocyanurate formed by cyclotrimerization of isocyanate group. In particular, while isocyanurate formed preferentially at 100 °C, oxazolidone formed preferentially at 160 °C. In the thermal stability of the obtained polymers, T_{d5} and T_{d10} were 300–361 and 322–378 °C, respectively. The polymers possessed relatively high thermal stability. T_g of the polymer prepared with **2** and MDI was higher than T_g of the polymer prepared with bisphenol A diglycidyl ether and MDI. The introduction of the fluorene skeleton is found to contribute to the thermal stability of poly(oxazolidone). All polymers had good transparency in a visible region. The transmittances were higher than 80% at 450 nm.

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