Preparation of Novel Thermally Stable Polyurea by the Cationic Ring-Opening Isomerization Polymerization of Polycyclic Pseudourea

Masatoshi Miyamoto,* Yoshinori Takashima, and Yoshiharu Kimura

Department of Polymer Science and Engineering, Faculty of Textile Science, Kyoto Institute of Technology, Matsugasaki, Sakyo, Kyoto 606-8585, Japan

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ABSTRACT: The cationic ring-opening isomerization polymerization of 2,3-dihydro[4,5]benzimidazo[2,1-*b*]oxazole (DBO) was examined. The polymerization of DBO with methyl trifluoromethanesulfonate proceeded smoothly at 0 °C and gave poly(2,3-dihydro-1*H*-benzo[*d*]imidazol-2-one-1,3-diylethylene) (polyDBO) in high yield. The polymer was a crystalline solid whose T_g and T_m determined by DSC were 152 °C and 343 °C, respectively. TGA analysis showed that the polymer was stable up to 485 °C under air. Once it was isolated, it was soluble only in strongly acidic media. However, the solution polymerization of DBO could be carried out homogeneously under a high dilution at 0 °C in chloroform. A postpolymerization experiment revealed that the polymerization proceeded in a living fashion.

Introduction

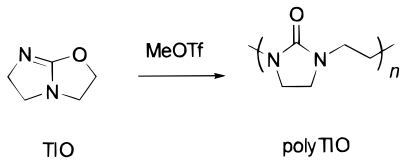
Recently, we have reported the cationic ring-opening polymerization of 2,3,5,6-tetrahydroimidazo[2,1-*b*][1,3]-oxazole (TIO) as a novel bicyclic monomer (Scheme 1).[1,2] The polymerization of TIO has some significant characteristics. (1) It has a much higher reactivity toward the ring-opening polymerization than its relatives, the 2-oxazolines, since its polymerization proceeds even at 0 °C in a nonpolar solvent. (2) The polymerization with MeOTf proceeds via a living mechanism. (3) The resulting polymer, poly(1,3-diazolidin-2-one-1,3-diylethylene) (polyTIO), is stable up to 425 °C under air and 436 °C under nitrogen.

Moreover, polyTIO has one more significant characteristic: it is water soluble. Another representative example of a water-soluble aprotic polymer is undoubtedly poly(ethylene oxide), which is soluble in almost all organic solvents except aliphatic hydrocarbons and diethyl ether. On the other hand, poly(TIO) is soluble only in chloroform and partly soluble in nitrobenzene and DMSO among common organic solvents.[1]

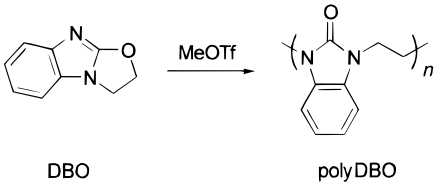
N,*N*,*N*′,*N*′-Tetramethylurea (TMU) is one of the representative aprotic polar solvents and is unique that it is miscible with either water or hexane. The amphiphilic nature of polyTIO is well understood when one considers poly(TIO) as a polymeric homologue of TMU or *N*,*N*-dimethylethyleneurea. Thus, the polymerization of TIO is interesting from the viewpoint of the preparation of a novel water-soluble polymer with limited solubility in organic solvents. This unique solubility, however, restricts the possibility of its use as a material; nevertheless, it has a high thermal stability.

The introduction of an aromatic ring into a polymer backbone has generally been known to increase its thermal stability. At the same time, it is expected to bring significant hydrophobicity into the polymer. Therefore, we extended our research on the polymerization of bicyclic pseudoureas to that of a polycyclic monomer having an aromatic ring. In the present paper, we describe the ring-opening polymerization of 2,3-dihydro-[4,5]benzo[2,1-*b*]oxazole (DBO) as a novel polycyclic pseudourea to afford the thermally stable polyurea, poly(2,3-dihydro-1*H*-benzo[*d*]imidazol-2-one-1,3-diylethylene) (polyDBO) (Scheme 2).

Scheme 1



Scheme 2



Experimental Section

Materials. Benzimidazole was prepared by the reaction of urea and *o*-phenylenediamine.[3,4] 2-Chlorobenzimidazole was prepared by the reaction of benzimidazole with phosphorus oxychloride and was purified by recrystallization from ethanol.[5] Ethylene oxide was prepared by the cyclization of ethylene chlorohydrin with NaOH.[6] Other reagents and solvents were commercially available and were dried by conventional methods and distilled under nitrogen. The solvents were stored over 3 Å molecular sieves after distillation.

Preparation of DBO. DBO was prepared according to a modified procedure reported before.[7] In a three-neck flask equipped with a thermometer, a three-way stopcock, and a stirrer bar were placed 10.0 g (65.5 mmol) of 2-chlorobenzimidazole and 100 mL of toluene. The suspension was cooled to 0 °C, and 10 mL of ethylene oxide was added in one portion with stirring. The mixture was kept at 0 °C overnight with stirring. Then, 100 mL of 3% aqueous NaOH was added to the suspension, and the mixture was kept at 0 °C with stirring until the emulsion separated into two clear layers. This required 96 h. The organic layer was separated and concentrated to yield crude DBO, which was purified further by recrystallization from toluene. Mp: 102.6 °C (DSC) (lit. 101 °C).[7] Yield: 4.95 g (47.2%). 300 MHz ^{1}H NMR ($CDCl_3$): δ 4.18 (t, CH_2O, 2H), 5.03 (t, CH_2N, 2H), 7.06−7.16 (m, Ar, 3H), 7.44 (d, HC^6, 1H). 75 MHz ^{13}C NMR ($CDCl_3$): δ 41.55 (CH_2N), 74.26 (CH_2O), 108.53 (C^5), 118.67 (C^8), 121.00 (C^7), 121.92 (C^6), 130.99 (C^{4a}), 146.80 (C^{8a}), 164.35(C═N). IR (KBr): 3056 (ν_{C-H}, aromatic), 2982, 2924 (ν_{CH}), 1634 ($\nu_{C=N}$), 1558, 1445, 1275, 982, 743 (ν_{C-H}, aromatic) cm^{-1}.

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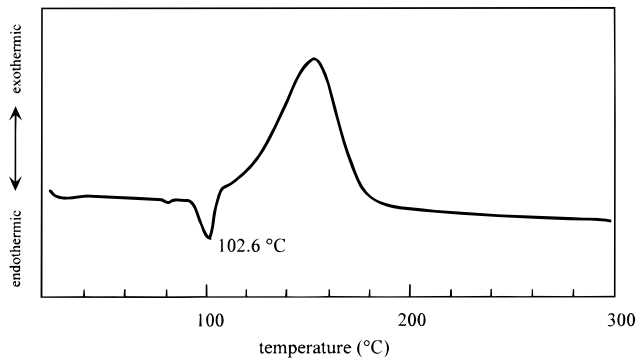


Figure 1. DSC thermogram of DBO.

Measurements. ^{1}H NMR spectra were recorded on a Varian Gemini-200, a GE QE−300 NMR, or a Bruker ARX-500 NMR spectrometer and ^{13}C NMR spectra were recorded on a GE QE−300 NMR spectrometer. IR spectra were obtained on a Jasco FT/IR-5300 infrared spectrometer. GPC analysis was performed on a Shimadzu LC-10A system using combined columns of Tosoh TSK gel G4000H8 and G2500H8 in chloroform containing 3 wt % of triethylamine at 35 °C. DSC measurements were performed on a Mac Science 3100 thermal analyzer under nitrogen with the heating rate of 5 °C/min. TGA analyses were carried out on a Shimadzu DT-30 apparatus under both nitrogen and air with a heating rate of 15 °C/min.

Polymerization of DBO. A typical procedure was as follows. In a test tube equipped with a three-way stopcock and a stirrer bar were placed 161 mg (1.01 mmol) of DBO and 10 mL of chloroform under nitrogen. The solution was chilled to −20 °C and 100 μL of MeOTf solution in chloroform (0.200 mol/L, 0.020 mmol) was added to the mixture. The tube was allowed to react at 0 °C for 24 h. After the reaction, 50 μL of triethylamine was introduced to the mixture to terminate the polymerization. The contents were poured into diethyl ether to obtain the product, which was isolated by decantation, dried in a vacuum, and weighed. The yield was 1.62 g (100%). ^{1}H NMR (CF_3SO_3H/TMS): δ 3.8−4.2 (4H, CH_2), 6.6−7.0 (4H, Ar). IR (KBr): 2863 (ν_{CH}), 1688 ($\nu_{C=O}$), 1497, 1441, 1260, 754(ν_{C-H}, aromatic), 586 cm^{-1}.

Results and Discussion

The preparation of DBO has been described in a few papers without any description concerning its polymerizability since the work focused on its biological activity.[7,8] The monomer was successfully prepared by the reaction of 2-chlorobenzimidazole with ethylene oxide in 47% yield according to the literature.[7]

The reason for the high reactivity of TIO toward the ring-opening polymerization is ascribed to both ring strain and isomerization of the functional group from pseudourea to give the more stable urea.[2] However, DBO contains a benzimidazole structure, a 10 π-electron heterocyclic aromatic system. Therefore, it can be considered that the aromatic stabilization inhibits the ring-opening ability of DBO. Figure 1 shows the DSC thermogram of DBO taken under nitrogen to clarify this problem. As temperature is increased, DBO melts at 102.6 °C and, thereafter, polymerizes spontaneously in the absence of initiator. This polymerization may be initiated by an acidic impurity incorporated in the monomer. A similar polymerization upon heating has already been observed for TIO.[1] The heat of polymerization of DBO can be estimated from the thermogram as −15.1 kcal/mol. From a comparison of this value to that of TIO (−15.8 kcal/mol), it can be concluded that the benzimidazole structure in DBO brings no obvious thermodynamic disadvantage when it polymerizes.

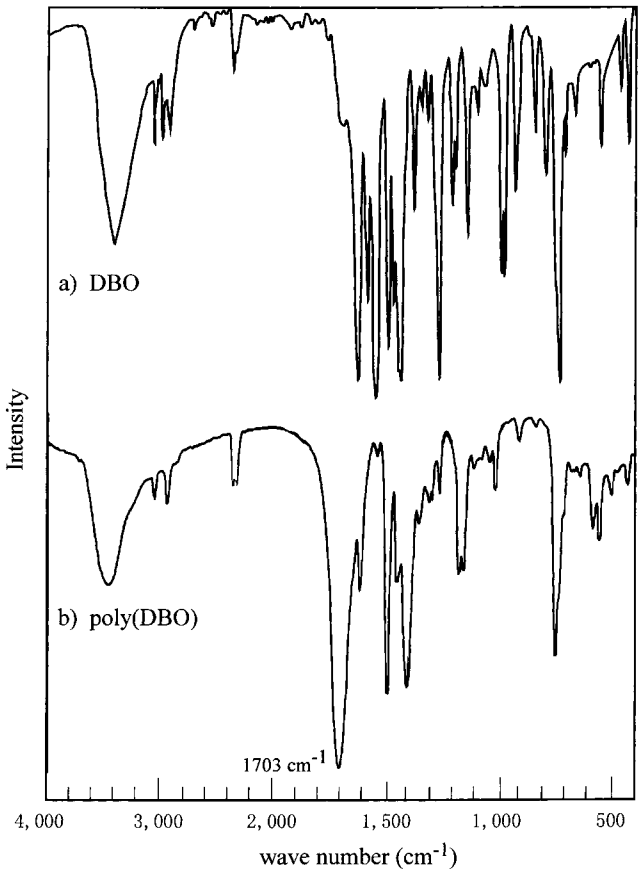


Figure 2. IR spectra of DBO (a) and polyDBO (b) (KBr).

Polymerization on Heating. As the DSC thermogram indicates, DBO polymerizes in the absence of cationic initiator above its melting point. When it was heated to 120 °C in bulk, the system became once transparent and, then, became turbid and solidified immediately. The resulting product was partly soluble in chloroform, and the yield and the M_n of the soluble part were 36% and 2400 (M_w/M_n = 1.71, determined from GPC with polystyrene calibration), respectively, while an additional chloroform insoluble product was obtained in 64% yield. Thus, the polymerization proceeded quantitatively. Although the product was partly soluble in chloroform, The solution became turbid as it stood, and the polymer once precipitated out was no longer soluble in chloroform. The comparison between IR spectra of both chloroform-soluble and -insoluble parts showed that they were essentially the same. The chloroform-insoluble part was only soluble in the strong acids, trifluoromethanesulfonic acid and concentrated sulfuric acid and was insoluble either in water or in common organic solvents including trifluoroacetic acid, *m*-cresol, DMF, DMSO, and NMP. Thus, we intended to design a polyurea of low affinity toward water, but obtained a polyurea of limited solubility.

The structure of the product was identified as polyDBO from ^{1}H NMR (measured in trifluoromethanesulfonic acid, see Experimental Section) and IR spectroscopies. In Figure 2 the IR spectrum of DBO (Figure 2a) is compared with that of polyDBO (Figure 2b). The absorption ascribed to the imino stretching observed at 1634 cm^{-1} in Figure 2a is replaced by the strong absorption due to the carbonyl stretching band in Figure 2b, indicating the formation of a five-membered urea carbonyl group. The frequency of this peak (1703 cm^{-1})

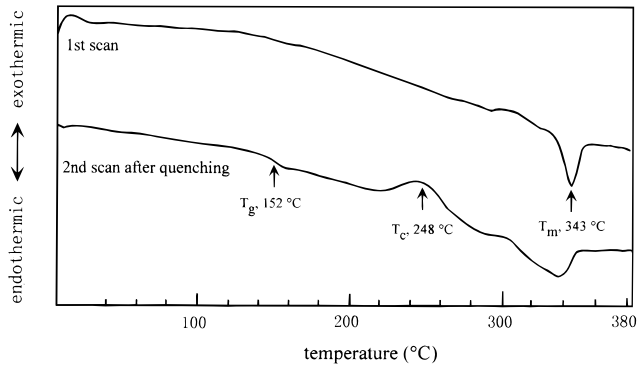


Figure 3. DSC thermograms of polyDBO prepared in bulk without initiator.

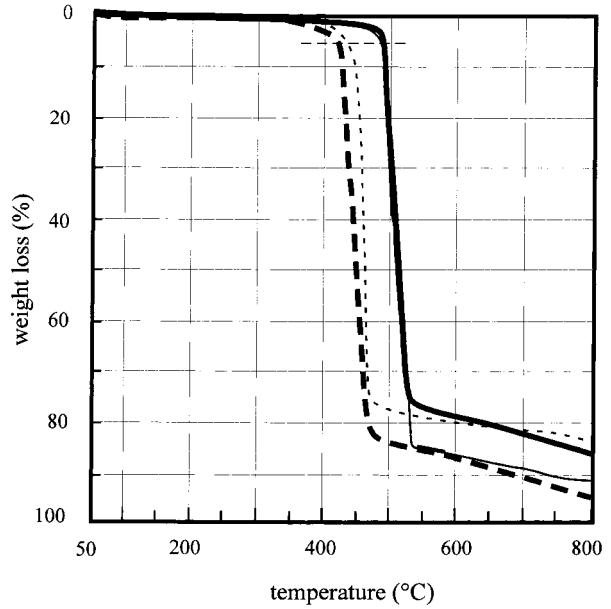


Figure 4. Comparison of TGA thermograms of polyDBO (—, under air; — under nitrogen) with those of polyTIO (- -, under air; - -, under nitrogen).

is higher than the corresponding carbonyl stretching of polyTIO (1687 cm^{-1}), indicating the conjugation of aromatic ring to the urea group. The presence of an ortho-disubstituted phenylene ring in the polymer as well as in DBO was confirmed from the absorptions at ~750 cm^{-1} (ν_{CH}, 744 cm^{-1} for DBO and 752 cm^{-1} for polyDBO).

PolyTIO can be prepared not only by the ring-opening polymerization of TIO, but also by the double isomerization polymerization of 1,4-bis(2-oxazolin-2-yl)piperazine.[9] However, the double isomerization polymerization cannot be applied to the preparation of polyDBO. Therefore, this is the first report on the preparation of polyDBO.

Thermal Properties. This polymer is crystalline. The DSC measurement of the sample (M_n = 47 500) under nitrogen showed that its melting point was 343 °C, which was significantly higher than that of polyTIO (296 °C). During the second heating of the once quenched sample, T_g and T_c were observed at 152 and 248 °C, respectively (Figure 3).

In Figure 4 the TGA thermograms of polyDBO taken under nitrogen and under air are compared with those of polyTIO. The temperature for 5% weight loss ($T_{5\%}$) of polyDBO is 485 °C regardless of the atmosphere. The introduction of benzene ring obviously improves the thermal stability since $T_{5\%}$ of polyTIO is 425 °C under air.

Polymerization in Chloroform. Chloroform is the only solvent available for the polymerization of TIO. Therefore, the polymerization of DBO was also examined in it. The results of the polymerization using methyl trifluoromethanesulfonate (MeOTf) as the initiator are summarized in Table 1. The polymerization proceeded smoothly at 0 °C and gave polyDBO in high yield, while no polymerization occurred in the absence of the initiator even at 60 °C. In these runs the initial monomer concentration was set to 0.5 mol/L. The polymerization system stayed homogeneous throughout the reaction when the initial feed ratio of the monomer to the initiator ($[M]_0/[I]_0$) was below 20. With a higher feed ratio, the polymerization system became heterogeneous along with the reaction. The product prepared with an initial feed ratio of 5 was soluble in chloroform after workup, but that prepared with a ratio of 20 was partly soluble in it, even though the polymerization proceeded homogeneously.

The ratio between chloroform-soluble and -insoluble parts was independent of the molecular weight of the sample, unless it was very low. The molecular weight distribution of the chloroform-soluble part was generally narrow and the molecular weight agreed with the calculated values on the basis of the polymer yield and the feed ratio, assuming that the polymer has the methyl group at the initiating end and the hydroxyl group at the terminating end. These observations suggested that the deposition of the product occurred after the completion of the polymerization.

In Table 2, the polymerization results with the initial monomer concentration varying from 0.05 to 1.0 mol/L are shown. The polymerization system stayed homogeneous when the initial concentration of DBO was set below 0.1 mol/L. In such a case, the molecular weight of polyDBO could be determined by the in situ GPC measurement using chloroform as the eluent. Even if the polymerization proceeded homogeneously, the product once isolated also contained a large amount of chloroform-insoluble part. The molecular weight of the chloroform-soluble product was, however, similar to that before workup. These results suggest that the difference in the solubility is not due to the difference in their molecular weight but is caused by the difference in the degree of crystallization.

This was proven to be true from the DSC measurements of both parts. In Figure 5 the DSC thermograms of chloroform soluble and insoluble parts (M_n = 8000) were compared with each other. The insoluble part is crystalline: neither T_g nor T_c is observed in Figure 5a, although two melting peaks are observed at 304 and 324 °C, lower temperatures than that observed in Figure 2. This will be due to its lower molecular weight. In the thermogram of the soluble part (Figure 5b), on the other hand, the broad exothermic absorption due to crystallization and the melting endothermal peak are observed. Since the exothermal peak compensates the melting peak, the sample is considered to be amorphous before the heating.

In Table 3, the results of the polymerization of DBO under the dilute condition, 0.1 mol/L, are summarized. The polymerization proceeded homogeneously as long as it was carried out at 0 °C. Since the polymerization was examined under high dilution, the rate of polymerization was considered to be low, and it decreased as

Table 1. Ring-Opening Polymerization of DBO in Chloroform with $[DBO]_0 = 0.5$ mol/L[a]

				$CHCl_3$-soluble part			$CHCl_3$-insoluble part
$[M]_0/[I]_0$	appearance[b]	total yield[c] (%)	calcd M_n[d]	yield (%)	M_n[e]	M_w/M_n[e]	yield (%)
5.0	homogeneous	100	830	100	1200	1.25	0
20	homogeneous	88	2800	20	2900	1.25	69
35	heterogeneous	99	5600	14	6400	1.12	85
50	heterogeneous	100	8000	33	8300	1.14	67
100	heterogeneous	98	15600	23	21500	1.03	75

[a] In $CHCl_3$ with MeOTf at 0 °C for 24 h. [b] Appearance of the polymerization system during the reaction. [c] The sum of the yields for the $CHCl_3$ soluble and insoluble parts. [d] Calculated values on the basis of the feed ratio combined with the polymer yield with assuming that the polymer has the methyl group at the initiating end and the hydroxy group at the terminating end; $M_n = 15 + (160.17 \times \text{feed ratio} \times 100/\text{yield}) + 17$. [e] Determined by GPC with polystyrene calibration.

Table 2. Effect of $[M]_0$ on the Polymerization of DBO[a]

				after workup				
		in situ		total	$CHCl_3$-soluble part			$CHCl_3$-insoluble part
$[DBO]_0$ (mol/L)	appearance[b]	M_n[c]	M_w/M_n[c]	yield[d] (%)	yield (%)	M_n[e]	M_w/M_n[e]	yield (%)
1.00	heterogeneous			79	26	8200	1.19	53
0.50	heterogeneous			100	33	8300	1.14	67
0.10	homogeneous	8200	1.13	100	27	7100	1.21	73
0.05	homogeneous	8100	1.18	90	16	7000	1.22	74

[a] In $CHCl_3$ with 2 mol % of MeOTf at 0 °C for 24 h. [b] Appearance of the polymerization system during the reaction. [c] Determined by the direct GPC measurement of the polymerization solution with polystyrene standard. [d] The sum of the yields for the $CHCl_3$-soluble and -insoluble parts. [e] Determined by GPC with polystyrene calibration.

Table 3. Polymerization of DBO in Chloroform with $[DBO]_0 = 0.1$ mol/L[a]

						after workup			
			in situ			total	$CHCl_3$-soluble part			$CHCl_3$-insoluble part
$[M]_0/[I]_0$	temp (°C)	appearance[b]	M_n[c]	M_w/M_n[c]	calcd M_n[d]	yield[e] (%)	yield (%)	M_n[f]	M_w/M_n[f]	yield (%)
20	0	homogeneous	3100	1.16	2900	91	17	2700	1.19	74
35	0	homogeneous	6400	1.12	5300	95	28	5900	1.16	67
50	0	homogeneous	8200	1.13	8000	100	27	7100	1.21	74
100	0	homogeneous	14000	1.27	12000	72	27	9500	1.59	45
500	0	homogeneous	39000	1.33	24000	30	4.8	32000	1.46	25
100	35	heterogeneous	7300	1.10	15000	91	21			70
500	35	heterogeneous	48000	1.24	50000	63	8.5			54

[a] In $CHCl_3$ with MeOTf at 0 °C for 24 h. [b] Appearance of the polymerization system during the reaction. [c] Determined by the direct GPC measurement of the polymerization solution with polystyrene standard. [d] Calculated values on the basis of the feed ratio combined with the polymer yield: see footnote *c* in Table 1. [e] The sum of the yields for the $CHCl_3$ soluble and insoluble parts. [f] Determined by GPC with polystyrene calibration.

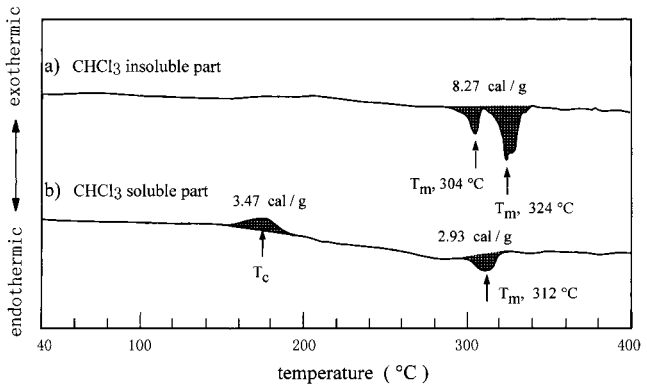


Figure 5. DSC thermograms of chloroform soluble (a) and insoluble parts of poly(DBO) (b).

the feed ratio was increased, which brought a decrease in the polymer yield. The experiments at 35 °C, aiming at the enhancement of the rate of polymerization, however, caused the deposition of the product, although the polymer yield was improved as expected. In these runs, the molecular weights of the polymer determined in situ agreed well with the corresponding calculated values.

Polymerization in Nitrobenzene. The polymerization of DBO proceeded also successfully in nitrobenzene at 0 °C, although the in situ GPC measurement could not be performed in this solvent. The polymerization with 20 mol % of MeOTf with 1.0 mol/L of the initial concentration of DBO proceeded homogeneously. This solvent was, however, proven to be not appropriate for the present polymerization. With a higher feed ratio, the system became turbid caused by the precipitation of the polymer, and then, the solvent (mp: 6 °C) froze as the system was kept further at this temperature. The dilution similarly caused the freezing of the solvent at 0 °C. Thus, no detailed examination could not be carried out in this solvent as well as in other solvents which have no solubilizing ability to poly(DBO): only one example using benzonitrile as the solvent is shown in Table 4.

Livingness of the Polymerization. The results of the cationic ring-opening polymerization described above show that DBO has a considerably higher reactivity than those of the 2-oxazolines, whose polymerization generally requires a higher temperature, at least 60 °C, even in polar solvents.[10] The agreement of the polymer molecular weight with the calculated one as well as the narrow molecular weight distribution of the polymer samples prepared in chloroform suggests that the present polymerization proceeds via a living mechanism as in the case of TIO.[2] Thus, the monomer addition

Table 4. Ring-Opening Polymerization of DBO in Nitrobenzene with $[DBO]_0 = 1.0$ mol/L[a]

solvent	$[M]_0/[I]_0$	appearance[b]	total yield[c] (%)	$CHCl_3$-soluble part yield (%)	M_n[d]	M_w/M_n[d]	$CHCl_3$-insoluble part yield (%)
nitrobenzene	5.0	homogeneous	97	97	1400	1.25	0
nitrobenzene	50	heterogeneous	84	20			64
nitrobenzene	100	heterogeneous	54	13	2300	1.85	41
benzonitrile	5.0	heterogeneous	45	0			45

[a] With MeOTf at 0 °C for 24 h. [b] Appearance of the polymerization system during the reaction. [c] The sum of the yields for the $CHCl_3$-soluble and -insoluble parts. [d] Determined by GPC with polystyrene calibration.

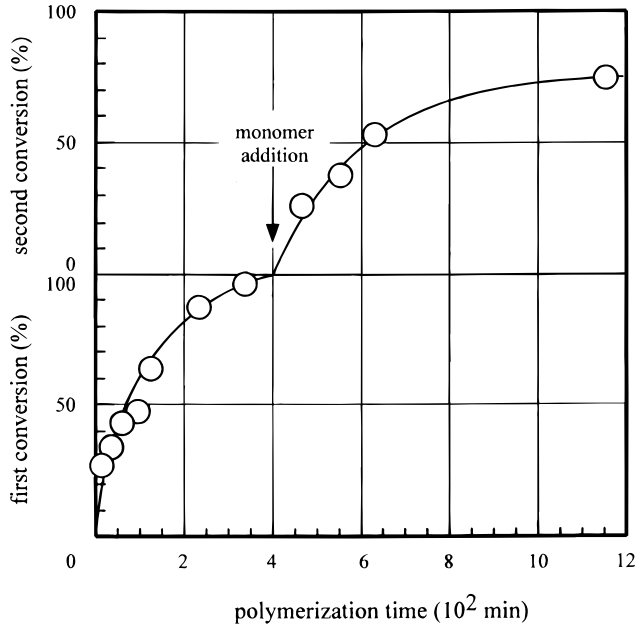


Figure 6. Time−conversion curve of DBO in the polymerization with MeOTf in chlororoform at 0 °C. $[DBO]_0 = 0.10$ mol/L; $[MeOTf]_0 = 1.5$ mmol/L.

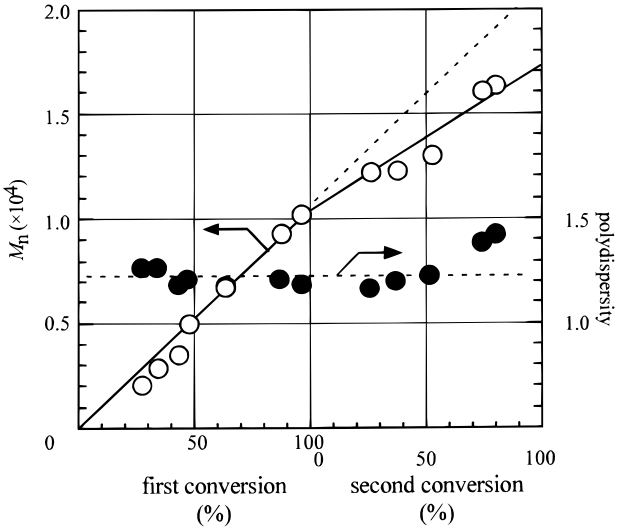


Figure 7. Plot of the polymer yield against M_n. The polymerization condition was the same as that in Figure 6.

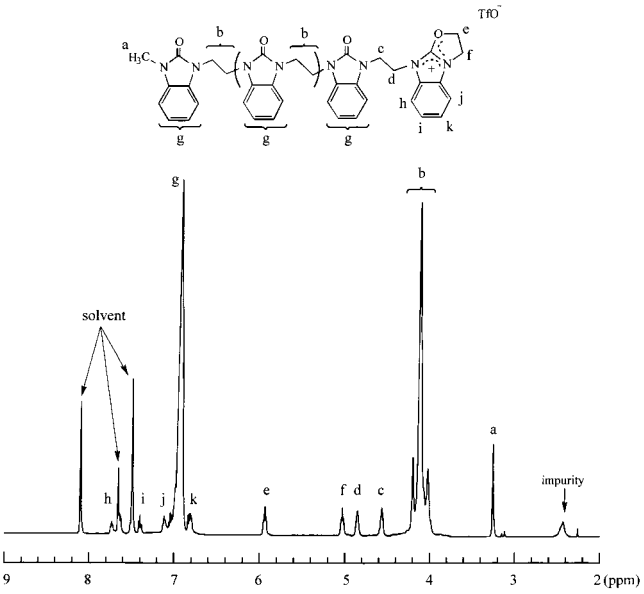


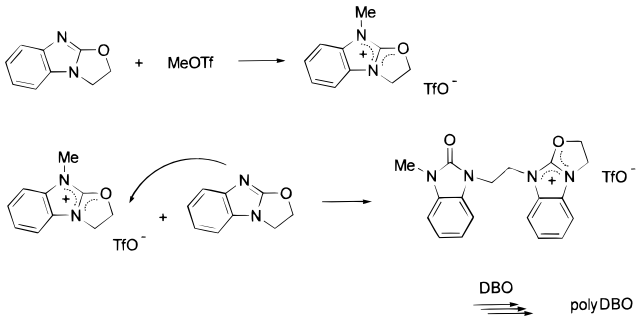
Figure 8. 500 MHz in situ ^{1}H NMR spectrum of the DBO/MeOTf system. $[DBO]_0 = 2$ mmol/L, and $[MeOTf]_0 = 0.4$ mmol/L, in nitrobenzene-d_5 at 35 °C after 775 s.

experiment was examined further to check the livingness.

The first stage of the polymerization was carried out in chloroform at 0 °C with $[M]_0 = 0.1$ mol/L and $[M]_0/[I]_0 = 67$. After the almost complete consumption of the monomer, an equimolar amount of DBO was added into the system to cause the second stage of the polymerization. The time conversion of DBO is plotted in Figure 6. The monomer consumption curve for the postpolymerization is not similar to that at the beginning, indicating not all of the propagating species survives after the first stage of the polymerization. It is more clearly shown when the monomer conversion is plotted against the molecular weight (Figure 6): the linear relationship between the M_n and the monomer conversion until the monomer addition suggests that the present polymerization proceeds substantially via a living mechanism. However, the molecular weight after the monomer addition is significantly lower than expected. Assumedly, the contamination of an impurity, supposedly the moisture, could not be avoidable since the polymerization was examined under high dilution. Thus, a part of propagating species was terminated by the moisture when the monomer solution was added to the living polymerization system.

Polymerization Mechanism. Figure 8 shows the in situ ^{1}H NMR spectrum of poly(DBO) with 20 mol % of MeOTf in nitrobenzene-d_5 at 35 °C after 775 s. At this point the monomer had already been consumed completely. In the spectrum, the signals ascribed to the main repeating unit are observed at δ 4.0−4.2 and 6.9−7.1, which are ascribed to ethylene and phenylene protons, respectively. In addition to them, weak signals ascribable to terminal groups are also observed. The signal due to the initiating methyl protons is observed at δ 3.25 (peak a). The other weak signals are derived from the propagating end as well as the penultimate unit. In particular, the presence of the two triplets located at δ 5.94 (peak e) and 5.03 (peak f) shows that the propagating end is an oxazolonium species.[11] From these observations, the mechanism of the present po-

Scheme 3



lymerization is considered as shown in Scheme 3. The high living character of the present polymerization is due to the lack of acidic proton, which will cause chain transfer, in the monomer, the polymer, and, in particular, the propagating end.

Conclusion

Thus, the thermoresistant polyurea was prepared by the ring-opening polymerization of DBO. Although, once isolated, the polymer is insoluble in most solvents, the molecular weight of the polymer can be controlled by changing the initial feed ratio since the polymerization proceeds in a living fashion and the propagation occurs much faster than the precipitation of the polymer.

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(11) The assignment for signals h−k were done in consideration of the assignment for *N*-methyl-3,4-dihydro-2*H*-benzo[4,5]-imidazo[2,1-*b*]oxazinium trifluoromethanesulfonate, which was prepared by the reaction of 3,4-dihydro-2*H*-benzo[4,5]-imidazo[2,1-*b*]oxazine, a homologue of DBO having a [4.3.0] bicyclic ring system, with MeOTf as a stable compound. The detailed data will be indicated in our forthcoming manuscript. Miyamoto, M.; Tomari, K.; Kimura, Y. *Macromol. Chem. Phys.*, in press.

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