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The Faculty of Textile Science and Technology,
Shinshu University, Ueda-shi, Nagano-ken, 386 Japan

Synthesis and Properties of Polyamideimides Containing a Bicyclooctene Ring

Akira Suzuki, Kesayoshi Kobayashi, Hirofusa Shirai, and Nobumasa Hojo

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SUMMARY:

A series of aliphatic and aromatic polyamideimides containing a bicyclooctene ring were synthesized. Low-temperature solution condensation polymerization involving various diamines and N,N'-dichloroformylmethyl-[bicyclo-(2.2.2)-oct-7-ene-2,3,5,6-tetracarboxylic acid 2,3,5,6-diimide] (**2**) were employed. Most of these polymers thus obtained were soluble in m-cresol, DMF, DMAc and DMSO etc. The inherent viscosities of the polymers ranged from 0.07 to 0.40 dl/g (in DMF at 25°C). The polymers obtained from **2** and aromatic diamines showed thermal stabilities above 380°C. The aliphatic polymers were more unstable than the aromatic polymers.

ZUSAMMENFASSUNG:

Eine Reihe aliphatischer und aromatischer Polyamidimide, die einen Bicyclooctenring enthielten, wurden synthetisiert. Die Polykondensation wurde bei niedriger Temperatur in Lösung durchgeführt, wobei eine Reihe von N,N'-Diaminen sowie N,N'-Dichlorformylmethyl-[bicyclo-(2.2.2)-oct-7-en-2,3,5,6-tetracarbonsäure-2,3,5,6-diimid] (**2**) eingesetzt wurden. Die meisten so erhaltenen Polymeren waren in m-Kresol, DMF, DMAc und DMSO löslich. Die Viskositätszahlen der Polymeren wurden in DMF bei 25°C bestimmt und lagen zwischen 0,07 und 0,40 dl/g. Die Polymeren aus **2** und aromatischen Diaminen zeigten thermische Stabilitäten bis über 380°C. Die aliphatischen Polymeren waren nicht so stabil wie die aromatischen.

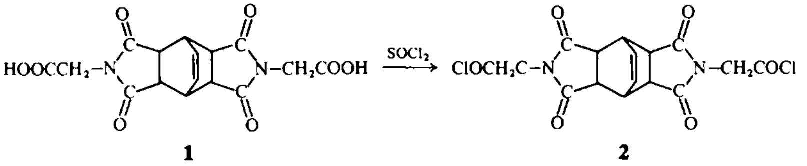
Introduction

It is generally recognized that polyimides, polyesterimides and polyamideimides with recurring aromatic units have high thermal stabilities[1–3]. However, this aromaticity causes also insolubility and intractability of them. One means to improve the solubility may be the introduction of an alicyclic ring[4] or of straight methylene groups[5] into the polymer chains. Therefore, the introduction of a bicyclooctene ring into the polymer chain may improve the solubility of the polymer, while still maintaining thermal stability. In a previous series of papers, we showed that polyimides and polyesterimides containing bicyclooctene rings have a high solubility and thermal stability[6-7]. The present paper is concerned with the synthesis and properties of new linear polyamideimides from N,N′-dicarboxymethyl-[bicyclo-(2.2.2)-oct-7-ene-2,3,5,6-tetracarboxylic acid-2,3,5,6-diimide] (**1**) and various aliphatic as well as aromatic diamines.

Results and Discussion

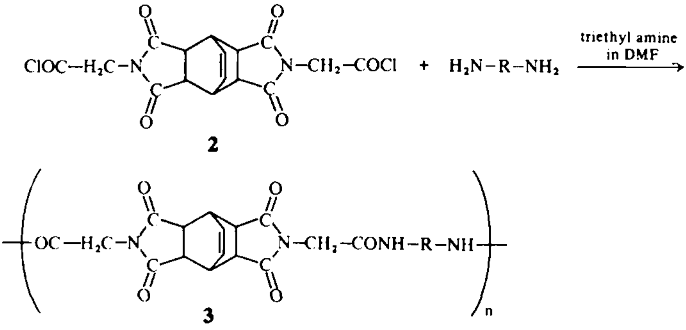
Polymer Synthesis

As already described **1** was synthesized from bicyclo-(2.2.2)-oct-7-ene-2,3,5,6-tetracarboxylic acid-2,3,5,6-dianhydride and glycine[7]. The diacid chloride **2** of **1** was synthesized in the following way:



(1)

Several aliphatic and aromatic diamines were reacted with **2** following the general scheme (2):



(2)

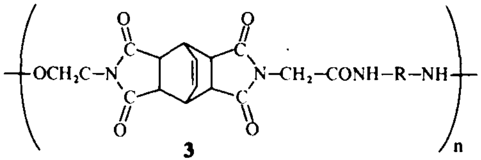
R = aliphatic or aromatic component

The polymerizations were carried out by the solution polymerization technique in N,N-dimethyl formamide (DMF). The polymerization in DMF proceeded very rapidly. Details of the preparation of polyamideimides are summarized in Tab. 1 and 2.

Tab. 1. Preparation and properties of polyamideimides.

Polyamideimides R=		Yield (%)	$[\eta]^a$ (dl/g)	MW of repeating unit	Elemental analysis (%) C	H	N	Precipitation method[c]
$+CH_2+_2$	**4**	80.1	—	(372.3)	54.74	4.48	14.17	A
					(55.96)	(4.69)	(14.17)[b]	
$+CH_2+_3$	**5**	88.8	0.33	(386.3)	56.69	5.23	13.21	A
					(57.00)	(5.03)	(13.99)	
$+CH_2+_4$	**6**	83.6	0.34	(400.4)	57.61	5.30	13.34	A
					(57.96)	(5.35)	(13.52)	
$+CH_2+_5$	**7**	79.4	0.31	(414.4)	57.92	6.37	13.12	B
					(58.87)	(5.65)	(13.08)	
$+CH_2+_6$	**8**	89.4	0.31	(428.4)	59.18	5.76	12.37	B
					(59.72)	(5.92)	(12.66)	
$+CH_2+_7$	**9**	70.4	0.37	(442.5)	59.43	6.08	11.92	B
					(60.51)	(6.18)	(12.27)	
$+CH_2+_8$	**10**	58.6	0.36	(456.5)	61.29	6.46	11.91	B
					(61.26)	(6.43)	(11.86)	
$+CH_2+_9$	**11**	78.0	0.35	(470.5)	61.37	6.94	11.42	B
					(61.97)	(6.66)	(11.56)	
$+CH_2+_{10}$	**12**	79.2	0.25	(484.5)	60.77	6.78	11.05	B
					(62.63)	(6.87)	(11.24)	

[a] In DMF at 25 °C. [b] Calc. [c] Precipitation method, A: in methanol, B: in ether-water.



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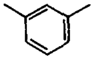
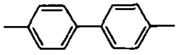
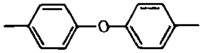
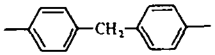
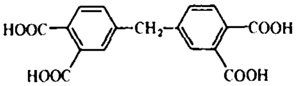
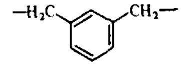
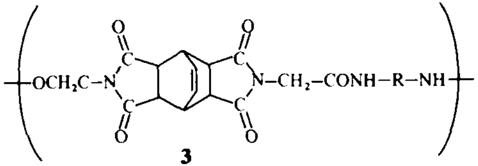
Tab. 2. Preparation and properties of polyamideimides.

Polyamideimides R=		Yield (%)	[η][a] (dl/g)	MW of repeating unit	Elemental analysis (%) C	H	N	Precipitation method
	**13**	81.3	0.29	(434.4)	59.86 (60.83)	4.27 (4.18)	13.45 (12.90)[b]	A[c]
	**14**	88.9	0.20	(434.4)	60.25 (60.83)	4.45 (4.18)	12.45 (12.90)	A
	**15**	80.7	0.29	(510.5)	64.86 (65.88)	4.43 (4.34)	10.56 (10.97)	A
	**16**	80.1	0.26	(526.5)	63.42 (63.87)	4.36 (4.21)	10.58 (10.64)	A
	**17**	82.0	0.26	(524.5)	65.71 (66.40)	4.75 (4.61)	10.68 (10.68)	A
	**18**	48.9	0.07	(612.5)	59.46 (60.78)	3.92 (3.95)	9.35 (9.35)	A
	**19**	67.5	0.15	(462.4)	62.02 (62.33)	4.76 (4.80)	11.96 (12.12)	A

[a] In DMF at 25°C. [b] Calc. [c] Precipitation in methanol A, precipitation in ether-water B.



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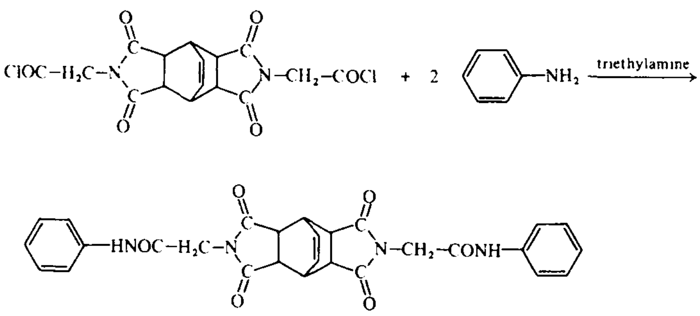
The intrinsic viscosities were determined in DMF at 25±0.05 °C in an Ubbelohde viscometer. The intrinsic viscosities of the polymers obtained from **2** and aliphatic diamines ranged from 0.30–0.40 dl/g, while in the case of polymers from **2** and aromatic diamines they ranged from 0.07–0.30 dl/g. The viscosities tended to increase with the number of methylene groups of the aliphatic diamine component in polymers **4–12**. The elemental analysis of the polymers agrees well with the calculated values as shown in Tab. 1 and 2. The methods of precipitation of polymers are also shown in Tab. 1 and 2. In order to identify the structures of the polymers a model compound, N,N′-diphenylcarbamoylmethyl-[bicyclo-(2.2.2)-oct-7-ene-2,3,5,6-tetracarboxylic acid-2,3,5,6-diimide] (**20**) was synthesized from the reaction of **2** with aniline:



20

The infrared spectra of the model compound **20** and the polyamideimides of **4**, **13** and **18** are shown in Fig. 1.

The spectrum of **20** exhibited imide carbonyl stretching bands at 1 780 cm^{-1} and 1 715 cm^{-1} and amide carbonyl bands at 1 690 cm^{-1} and 1 550 cm^{-1}. The structure of **20** was also supported by its NMR spectrum and elemental analysis. All polyamideimides showed similar absorption bands at 1 780, 1 690 and 1 550 cm^{-1}. The infrared spectra of the polyamideimides (**4–12**) show also the absorption band at 2880–2750 cm^{-1}, which tends to increase with increasing amount of methylene groups of diamine components. The NMR spectrum of a dilute DMSO–d$_6$ solution of the model compound **20** (TMS external standard) showed signals at $\delta = 6.10$ ppm for the vinyl protons based on double bond in a bicyclooctene ring. The fact implies that no side reactions to the double bond in a bicyclooctene ring occurred.

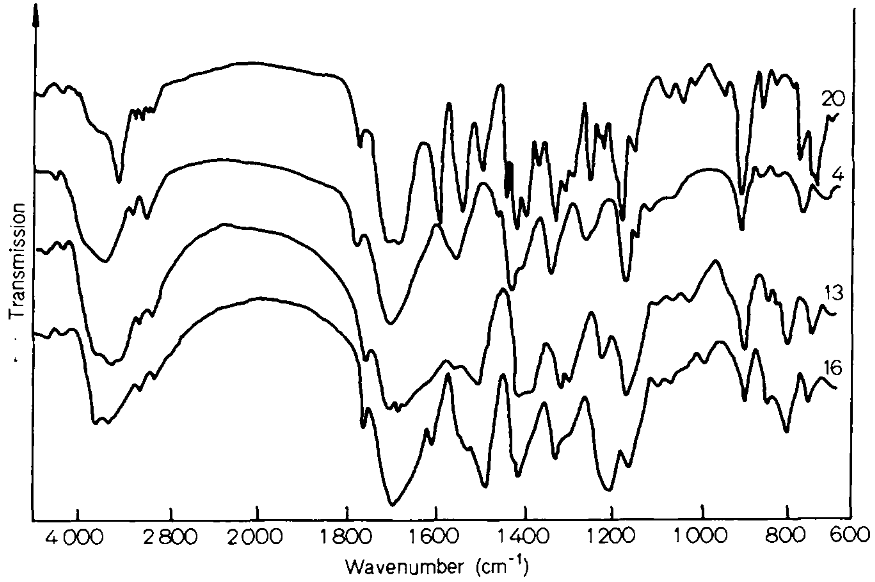


Fig. 1. Typical infrared spectra of polyamideimides (s. Tab. 1, 2).

Solubilities

The solubilities of the polyamideimides are summarized in Tab. 3.

All polyamideimides are easily soluble in conc. H_2SO_4 and DMSO, and most of the polymers are soluble in aprotic polar solvents such as DMF, DMAc as well as NMP, and m-cresol. They are insoluble in methanol, ethanol, acetone and dioxane. The polyamideimides obtained here exhibited higher solubilities than polyesterimides containing a bicyclooctene ring which has been previously reported by us.

Thermal Stability

Fig. 2 shows thermogravimetric analysis (TGA) and differential thermal analysis (DTA) curves of the polyamideimides obtained from **2** and p-phenylenediamine. The polymer showed an initial weight loss of about 2% up to 400°C, and extensive decomposition at 410–600°C, in which a rapid loss was observed between 410°C and 440°C.

Tab. 3. Solubility of polyamideimides[a].

Solvent	Polyamideimides					
	4	**12**	**13**	**14**	**16**	**17**
Methyl alcohol	–	–	–	–	–	–
Ethyl alcohol	–	–	–	–	–	–
Formic acid	+ +	+ +	–	±	+ +	+ +
DMF	–	+ +	+ +	+ +	+ +	+ +
DMAc	–	+ +	+	+ +	+ +	+ +
DMSO	+ +	+ +	+ +	+ +	+ +	+ +
m-cresol	+ +	+ +	±	±	+ +	+ +
NMP	–	+ +	+ +	+ +	–	–
Dioxan	–	–	–	–	–	–
Acetone	–	–	–	–	–	–
conc. H_2SO_4	+ +	+ +	+ +	+ +	+ +	+ +

[a] Solubility; + + : soluble at room temperature; + : soluble by heating, ± : swelling, – : insoluble.

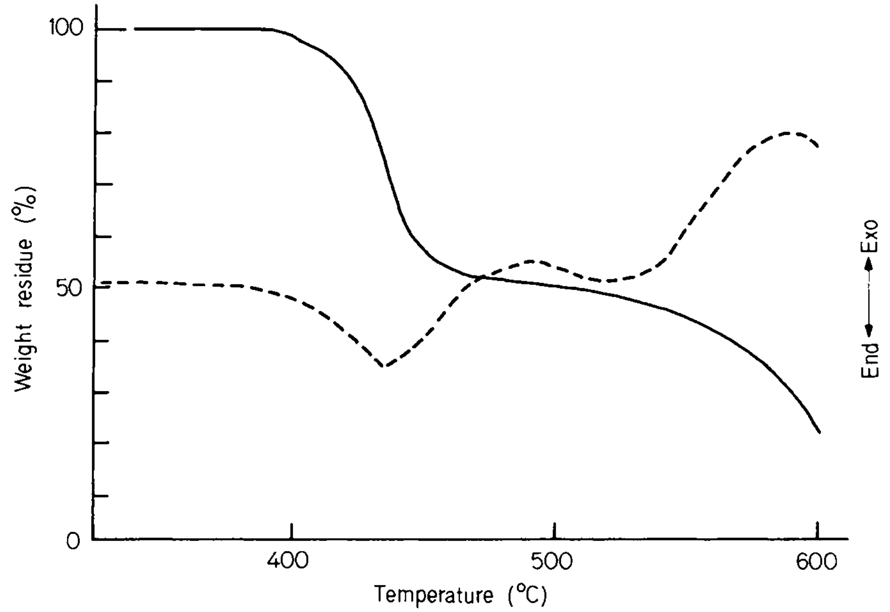


Fig. 2. TGA and DTA curves of the polyamideimides obtained from **2** and p-phenylenediamine, heating rate 10 °C/min, in air ---- = DTA, —— = TGA.

DTA thermograms exhibited exothermic changes in this region. The polyamideimides obtained from **2** and benzidine showed no endothermic change in DTA curves. The thermal stabilities of polyamideimides were evaluated by TGA curves with a heating rate of 10°C/min. Typical TGA curves are shown in Fig. 3.

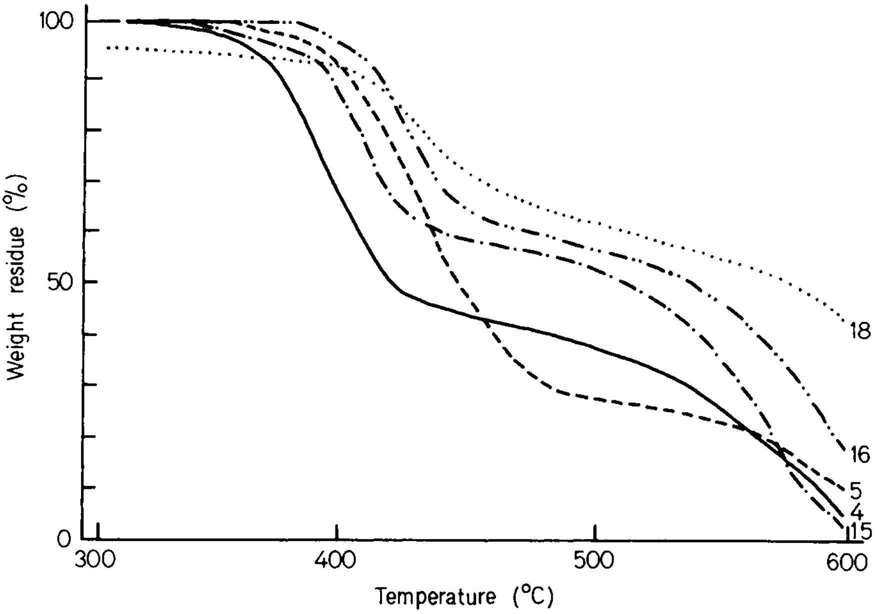
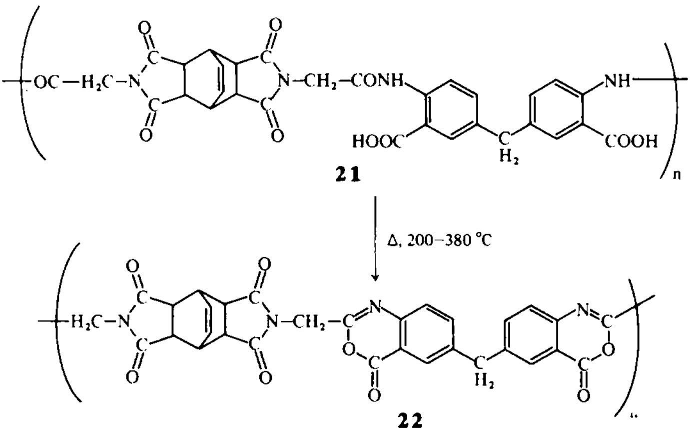


Fig. 3. Typical TGA curves of the polyamideimides; heating rate 10°C/min, in air.

Most of the polymers (**4–12**) showed the initial weight loss up to 350°C. The polyamideimides obtained from **2** and ethylenediamine showed a low thermal stability contrary to the expectation. This seems due to a low molecular weight of the polyamideimides because of the insolubility in DMF. According to Fig. 3, the polymer **18** shows a weight loss of 5.6% at 200–380°C. This value agrees fairly well with the calculated value of 5.8% based on the cyclodehydration of **21**.

Therefore, the polymer shows a good thermal stability on account of the oxadinone unit formed by the cyclodehydration[8]:



The thermal decomposition of polyamideimides is shown in Tab. 4. The activation energy was calculated from TGA curves by the method of Freeman-

Tab. 4. Thermal decomposition of polyesterimides, determined from TGA curves. 10 °C/min in air.

Polyamideimides	Initial decomp. temp. (°C)	Main decomp. temp. (°C)	Activation energy[a] (kcal/mol)
4	350	410	32.1
5	344	414	49.1
6	335	425	48.3
7	303	393	38.6
8	331	421	43.9
9	347	427	40.8
10	345	435	50.3
11	327	427	39.3
12	323	433	43.1
13	358	438	86.6
14	358	428	77.6
15	354	424	74.0
16	353	433	81.2
17	355	425	77.1
18	—[b]	441	—[c]
19	341	411	58.1

[a] Calculated by the method of Freeman-Carrol.

[b] About 200 °C.

[c] could not be determined.

Charoll[9]. Both the initial and the main decomposition temperature of the polymers (**13–19**) are higher than those of the polymers (**4–12**) except of that with m-xylylenediamine. This tendency is observed also in the activation energy for the main decomposition temperature. In conclusion, it became evident that the solubilities of the polyamideimides are improved by the introduction of a bicycloöctene ring into the polymer chain while still maintaining thermal stability.

Experimental

Reagents

BTA-diglycine (**1**) was purified by recrystallization from DMF. Aliphatic diamines and m-xylylenediamine were of analytical grade from commercial origin and used without further purification. Aromatic diamines used in this study are commercially available and were purified by recrystallization to constant melting points. DMF was purified by distillation under reduced pressure from calcium hydride. Methanol and triethylamine were distilled in a usual manner. Other reagents were of analytical grade from commercial origine and used without further purification.

Preparation of Monomer

N,N′-dichloroformylmethyl-[bicyclo-(2.2.2)-oct-7-ene-2,3,5,6-tetracarboxylic acid-2,3,5,6-diimide] (**2**). BTA-diglycine (30.3 g, 0.1 mol) was refluxed for 8 h with 75 ml (0.8 mol) of thionyl chloride and a few drops of pyridine.

The white product was filtrated, washed with cyclohexane, and dried at 70°C in vacuum.

Yield: 100%.

Elemental analysis

$C_{16}H_{12}N_2O_6Cl_2$ (399.16)	Calc.	C 48.14	H 3.03	N 7.02
	Found	C 47.83	H 3.05	N 7.00

IR (KBr): 1795 (s; C=O in acid chloride), 1780, 1715 cm^{-1} (s; C=O in imide ring).

Preparation of Model Compound

N,N′-diphenylcarbamoylmethyl-[bicyclo-(2.2.2)-oct-7-ene-2,3,5,6-tetracarboxylic acid-2,3,5,6-diimide] (**20**): To a solution of 0.380 g (0.042 mol) of aniline and 0.112 ml (0.08 mol) of triethylamine in 10 ml of DMF at room temperature, 0.798 g (0.040 mol) of the acid chloride **2** was added. After stirring at room temperature for 1 h, DMF was distilled off. The white product was recrystallized from acetic acid.

Yield 74.73%, m. p. 350 °C.

Elemental analysis

$C_{28}H_{24}N_4O_6$ (512.49)	Calc.	C 65.62	H 4.72	N 10.93
	Found	C 65.48	H 4.63	N 11.26

MS: m/e 512 (M^+), ^{1}H-NMR (DMSO-d_6): $\tau = 6.64$–6.48 (m; 6H), 5.84 (s; 4H), 3.90 (d; 10H), 2.85–2.32 (m; 10 H), −0.21 (s; 2H).

Preparation of Polymers

A 100 ml-three necked flask fitted with stirrer and thermometer was flushed with nitrogen and charged with diamine, triethylamine and DMF to obtain a 10–20% final solution of polymer. To the solution, diacid chloride **2** was added. A slightly viscous solution resulted containing dispersed crystals of triethylamine hydrochloride. After 1 h, the polymer solution was poured into methanol (method A) and ether (method B) respectively, and was fully washed with water and methanol. The product was dried at 60 °C in a vacuum oven for 40 h.

Procedure

Infrared spectra were recorded on Jasco-301 infrared spectrophotometer as KBr disks, and the mass spectrum was taken with a Hitachi RMU-6E spectrometer. NMR spectrum was measured on Jeol C-60 Hz (with trimethylsilan as internal standard). TGA and DTA were run on a Rigaku Denki differential thermo instrument 8001 type at 10 °C/min in air.

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