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Syntheses and Properties of New Aromatic-Aliphatic Copolyimides

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Dedicated to Professor Dr. ICHIRO SAKURADA on his 70th birthday

(Date of receipt: August 6, 1973)

SUMMARY:

Aromatic aliphatic copolyimides (**19a–m**) containing pyromellitdiimide and glutar- or succinimide rings in the main chain were synthesized by a two-step reaction of specified dianhydrides (**5a, b**) with primary diamines (**11a–h**). In the first step, poly(amic acid)s (**17/18**) having pyromellitdiimide rings were prepared by the reaction of 2,2′-pyromellitdiimido-diglutaric or disuccinic anhydride (**5b, 5a**) with **11a–h** in polar solvents. In the second step, the conversion of **17/18** to the copolyimides **19a–m** was carried out either thermally or by chemical means. **5b** and **5a** were synthesized by the reaction of pyromellitic anhydride with glutamic or aspartic acid, respectively. No gelation was observed during a long period of storage of the poly(imidoamic acid)s **17/18** in polar solvents at room temperature. For their conversion to copolyimides, a dehydrating agent such as acetic anhydride and a catalyst such as pyridine were applied successfully. The copolyimides gave clear, tough and flexible films from DMSO solution. They show excellent stabilities at high temperatures and against oxidative degradation. IR spectra, solubilities, TG analyses and the formation of the new copolyimides were studied and compared with those of corresponding model compounds.

ZUSAMMENFASSUNG:

Es wurden aromatisch-aliphatische Copolyimide (**19a–m**) dargestellt, die in der Hauptkette sowohl Pyromellithdiimid- als auch Glutarsäure- oder Bernsteinsäureimid-Ringe enthalten. Ausgangsprodukte waren 2,2′-Pyromellithdiimidodiglutarsäureanhydrid (**5b**), die durch Reaktion von Pyromellithsäureanhydrid mit Glutaminsäure bzw. mit Asparaginsäure erhalten wurden. Durch Umsetzung dieser speziellen Dianhydride **5a, b** mit Diaminen (**11a–h**) in polaren Lösungsmitteln wurden dann in einer ersten Reaktionsstufe polymere Aminosäuren mit Pyromellithimid-Bausteinen in der Hauptkette (**17/18**) erhalten. Diese Polyimidamidsäuren zeigen auch bei längerer Aufbewahrung bei Raumtemperatur und in polaren Lösungsmitteln keinerlei Gelbildung. Sie lassen sich jedoch rein thermisch oder durch Dehydratisierung mit Acetanhydrid in Gegenwart von Pyridin in die Copolyimide **19** überführen. Diese sind in DMSO löslich, lassen sich zu klaren zähen und flexiblen Filmen verarbeiten und zeigen ausgezeichnete Beständigkeit gegen hohe Temperaturen und gegen oxydativen Abbau. IR-Spektren, Löslichkeiten, thermogravimetrisches Verhalten sowie die Darstellung der neuen Copolyimide wurden mit den entsprechenden Daten von Modellverbindungen verglichen.

Introduction

During the last decade, the search for thermally stable polymers has resulted in the development of many new polymers containing aromatic or heterocyclic rings in the main chain. One of the most prominent examples are the polyimides. Aromatic polyimides[1-4] usually exhibit outstanding thermal stabilities. However, because of the high melting points and the absence of suitable solvents, it is very difficult to use them as matrix resins.

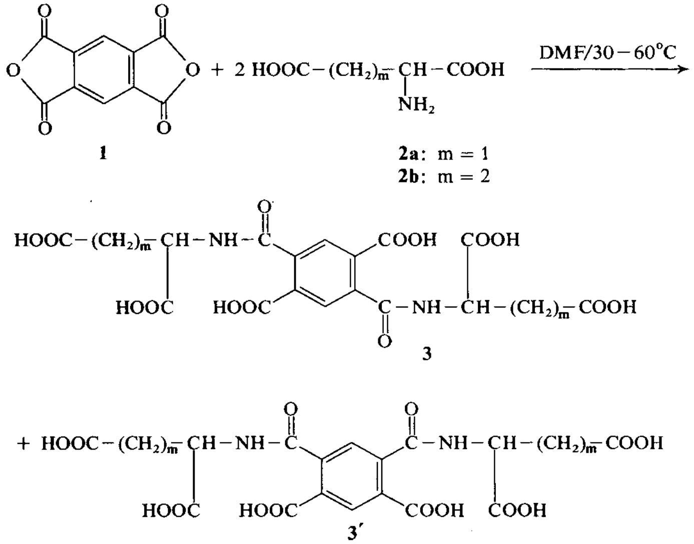
Aromatic poly(amic acid)s, precursors of aromatic polyimides are able to form films, to laminate and to vanish, but generally exhibit a poor storage stability. On the other hand, aliphatic polyimides[5,6] have better solubilites in organic solvents but lower resistance to high temperatures than aromatic ones.

In the present study, we prepared some new aromatic-aliphatic copolyimides containing pyromellitdiimide rings as aromatic units and glutarimide or succinimide rings as aliphatic units, for the purpose of producing soluble copolyimides. The starting dianhydrides, 2,2′-pyromellitdiimidodisuccinic anhydride (**5a**) and 2,2′-pyromellitdiimidodiglutaric anhydride (**5b**) were prepared from pyromellitic anhydride (**1**) and aspartic acid (**2a**) and from glutamic acid (**2b**), respectively, by the usual method.

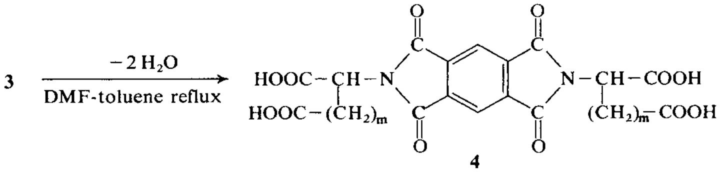
The ring opening reaction of phthalimido-2-glutaric anhydride (**6b**) and phthalimido-2-succinic anhydride (**6a**) with ammonia and amines have been reported by KING and KIDD[7] and TANENBAUM[8]. However, there has been no report on corresponding reactions of **5a** and **5b**.

Results and Discussion

Synthesis of the monomers



(i)



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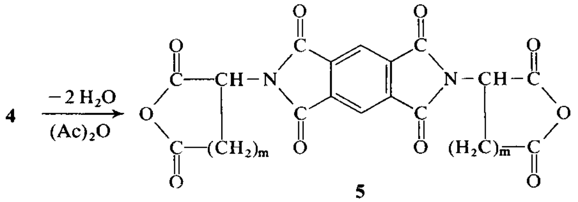
(ii)



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(iii)

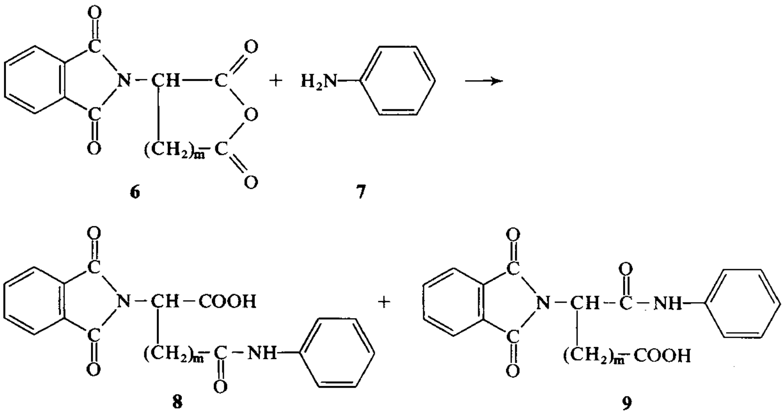
The reaction of **1** with **2a** or **2b** in DMF at 30–60 °C gave the corresponding products *N,N'*-(2,5-dicarboxyterephthaloyl)diaspartic acid (**3a**) and *N,N'*-(4,6-dicarboxyisophthaloyl)diaspartic acid (**3'a**) or *N,N'*-(2,5-dicarboxyterephthaloyl)diglutamic acid (**3b**), and *N,N'*-(4,6-dicarboxyisophthaloyl)diglutamic acid (**3'b**), tetracarboxylic acids, by azeotropic distillation of their DMF/toluene solution. Besides, the above reaction was performed in one step by refluxing the heterogeneous mixture of **1** and **2a** or **2b** with DMF and toluene (1:2 to 1:5). In the case of **5a**, some insoluble product was also formed, by which a lower yield was obtained.

4a, by recrystallization in boiling ethanol, became insoluble in usual organic solvents except in hot DMSO. Therefore, the cyclization reaction of **4a** was carried out by adding acetic anhydride to the solution of **4a**, resulting from reaction (ii). The cyclization reaction of **4b** was carried out analogously in pyridine solution with acetic anhydride. Yields, melting points and elemental analyses are described in the Exp. Part.

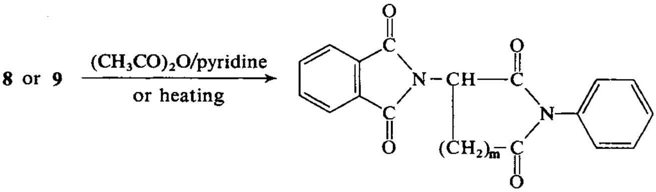
Model reaction

In contrast to the reactions with *aliphatic* amines[7, 8], little is known about the reaction of the anhydrides **6a, b** with *aromatic* amines. The reaction of **6a** and **6b** with aniline (**7**) gave the anilic acids, in good yields in THF at room temperature. The orientation of the ring opening was not elucidated, since both isomers **8** and **9** are expected to condense to the same succinimido or glutarimido derivative, respectively.

In the presence of acetic anhydride or by heating above their melting points *N*-phenyl-2-phthalimidosuccinimide (**10a**) and *N*-phenyl-2-phthalimidoglutar-



(iv)



(v)

10a: m = 1
10b: m = 2

imide (**10b**) were obtained. The dehydrating ring closure of **8a**, **9a** and **8b**, **9b** to the corresponding diimides **10a** and **10b** was investigated by means of thermal analyses. The result is shown in Fig. 1.

The DSC curve of **8a**, **9a** shows two endothermic peaks and one exothermic peak. The first endothermic peak is ascribed to the melting phenomenon, whereas the secondary one is ascribed to the melting phenomenon of **10a**, by comparison with the DSC curve of an authentic sample of **10a**. The exothermic peak following the first endothermic one may be reasonably attributed to the dehydrating ring closure process (imide formation) of the anilic acid. This was ascertained by a separate experiment using the apparatus of determination of melting point.

The DSC curve of compound **8b**, **9b** showed only one endothermic peak up to 300°C, and no obvious exothermic one. When the anilic acid **8b**, **9b** was heated above its melting point for some time, the IR spectra of the heated sample showed that the conversion proceeded very slowly. It took more than 18 h at 180°C and 200°C to accomplish the reaction as shown in Fig. 2, in contrast to the very fast ring closure of **8a**, **9a** at 200°C.

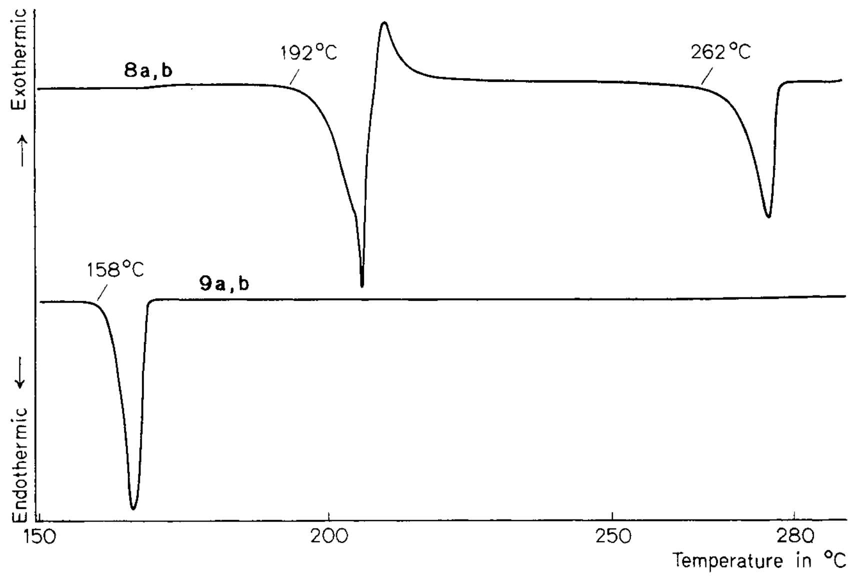


Fig. 1. DSC curves of **8a, b** and **9a, b**. Sample weight: 10 mg. Conditions: ±33,5 mJ s^{-1} (8 mcal s^{-1}); 5 °C min^{-1}; chart speed: 10 mm min^{-1}; pan: open

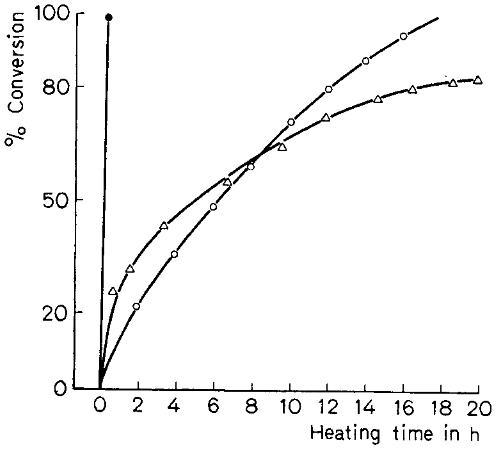
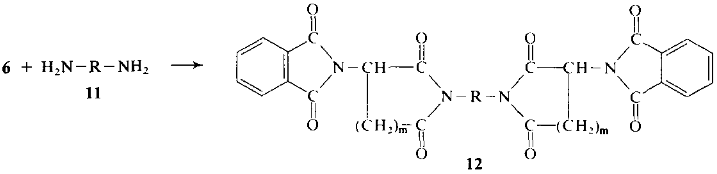
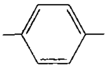
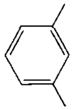
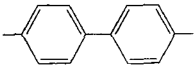
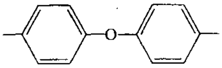
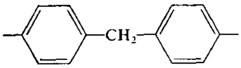
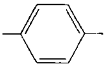
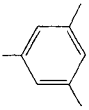
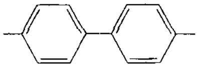
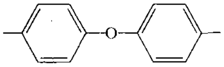
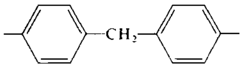
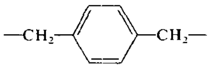


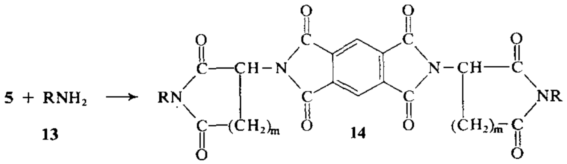
Fig. 2. Conversion of **8a, b** and **9a, b** to **10a** and **10b**, respectively, as af unction of the heating time. (•): **8a, b** at 200°C; (o): **9a, b** at 180°C; (△): **9a, b** at 200°C

Sixteen mixed tetraimides (**12a–m** and **14a–d**) were synthesized as model compounds of the polymeric products, described in the following chapter. The reaction conditions, yields and analytical data are summarized in Tab. 4 in the Exp. Part. A typical IR spectrum of a model compound (**14b**) and of its precursor 4,4′-pyromellitdiimidodiglutaranilic acid (**15**) or/and its 2,2′-isomer **16** are shown in Fig. 3.



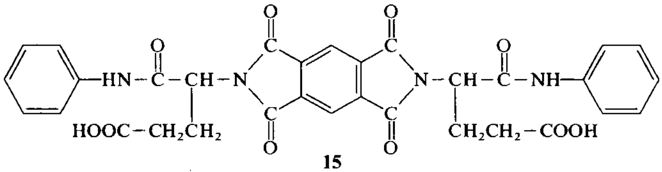
(vi)

	R		m
11a		**12a**	1
11b		**12b**	1
11c		**12c**	1
11d		**12d**	1
11e		**12e**	1
		**12f**	2
		**12g**	2
		**12h**	2
		**12i**	2
		**12k**	2
11f		**12l**	2
11g	$—[CH_2]_{10}—$	**12m**	2
11h	$—[CH_2]_6—$		2

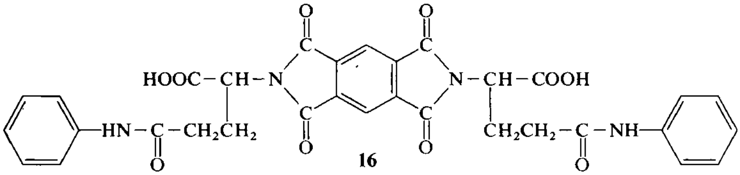


(vii)

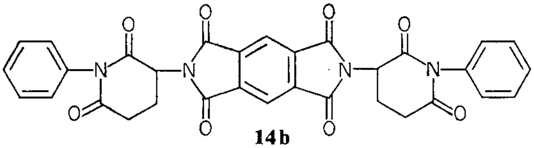
	R	m
14a	C_6H_5	1
14b	C_6H_5	2
14c	$CH_2C_6H_5$	2
14d	C_4H_9	2



15



16



14b

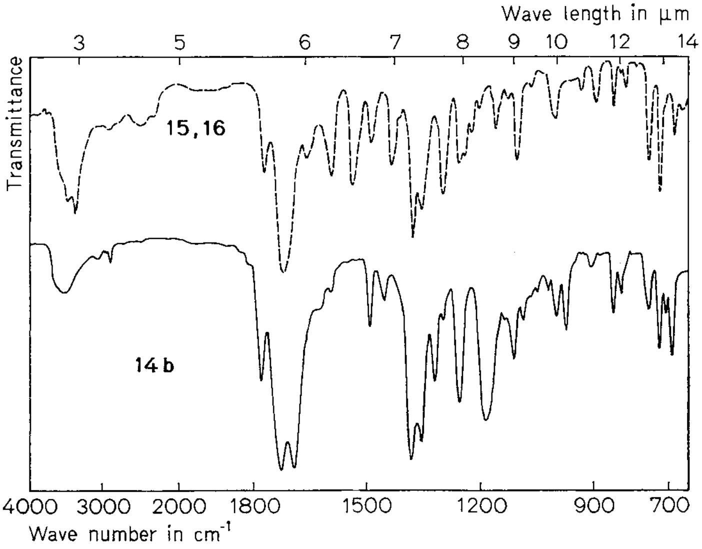
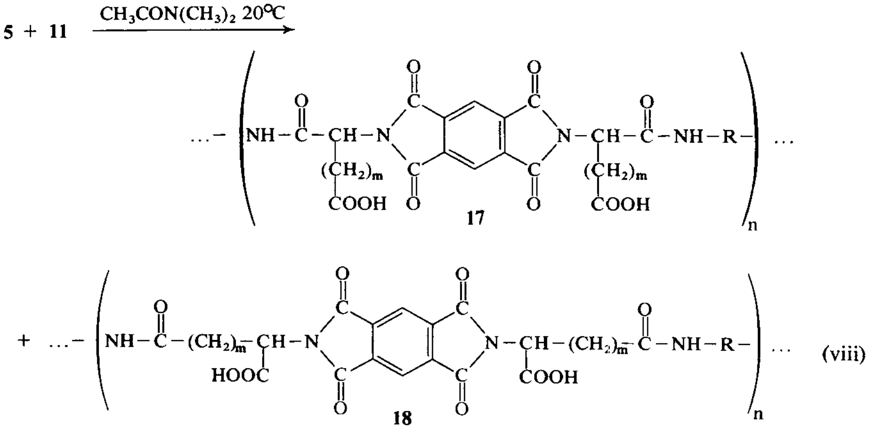


Fig. 3. IR spectra of the model compounds **14b** and **15** or/and **16** in KBr. (——): **14b**; (– – – –): **15, 16**

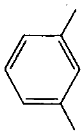
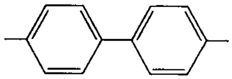
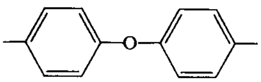
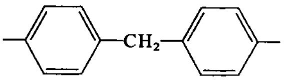
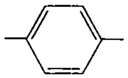
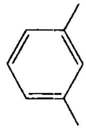
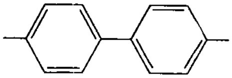
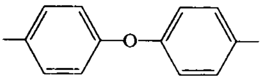
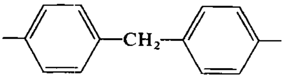
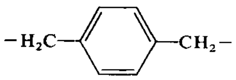
Polymer syntheses

Syntheses of poly(imidoamic acid)s

The values of η_{sp}/c and the analytical data of the poly(imidoamic acid)s are summarized in Tab. 5 in the Exp. Part.



(viii)

	R	m
17a, 18a		1
17b, 18b		1
17c, 18c		1
17d, 18d		1
17e, 18e		1
17f, 18f		2
17g, 18g		2
17h, 18h		2
17i, 18i		2
17k, 18k		2
17l, 18l		2
17m, 18m	$-[CH_2]_6-$	2

From the elemental analyses and the thermogravimetric analysis (TGA), shown in Fig. 10 and 11, it seems that these polymers contain small amounts of water at room temperature.

The polyaddition reaction was followed in terms of time-viscosity curves. The results are shown in Fig. 4 and 5.

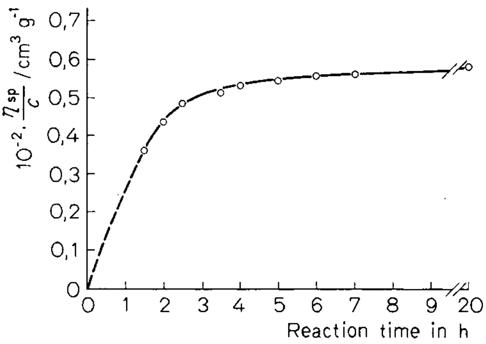


Fig. 4. Relationship between the viscosity of **17d/18d** and the polymerization time. Monomer concentration: $c = 10$ g in 100 cm^3 solvent

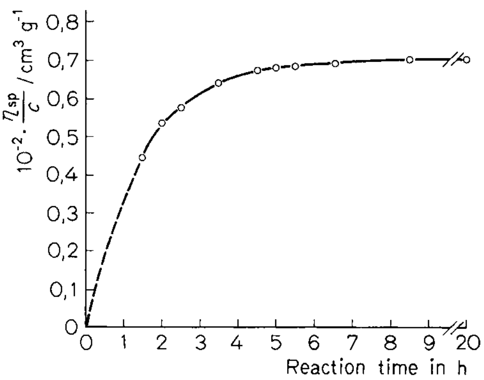
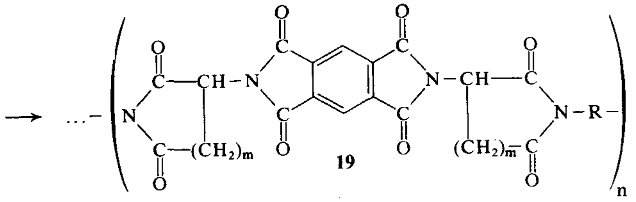


Fig. 5. Relationship between the viscosity of **17h/18h** and the polymerization time. Monomer concentration: $c = 10$ g in 100 cm^3 solvent

Conversion of poly(imidoamic acid)s

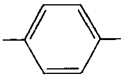
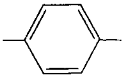
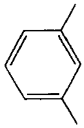
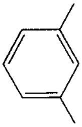
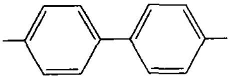
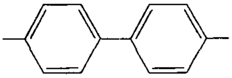
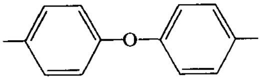
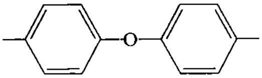
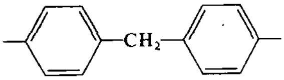
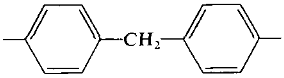
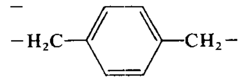
Chemical process: The poly(imidoamic acid)s **17/18** were converted to the corresponding copolyimides (**19a–m**) according to Eq. (ix), using acetic anhydride as dehydrating agent. After heating a mixture of **17/18**, acetic anhydride and pyridine in DMAC at 100 °C for 30 min or an hour, the resulting copolyimide **19** was precipitated and purified by reprecipitation from DMSO and acetonitrile. The values of η_{sp}/c and the analytical data of the polymers are shown in Tab. 6 in the Exp. Part.

17/18



19

(ix)

	R	m		R	m
19a		1	**19f**		2
19b		1	**19g**		2
19c		1	**19h**		2
19d		1	**19i**		2
19e		1	**19k**		2
			19l		2
			19m	$-[CH_2]_6-$	2

As shown in this Table the viscosity change in the polymers before and after the dehydration reaction was found to be greater in the case of the formation of a six-membered ring (**19f**–**m**) than in the case of the formation of a five-membered ring (**19a**–**e**).

In order to clarify the mechanism of the conversion of a poly(imidoamic acid) **17**/**18** a copolyimide of type **19f**–**m**, **19h** was subjected to the reaction with varying amounts of pyridine, changing the reaction temperature and time. The results are shown in Tab. 1.

When the conversion to copolyimides was carried out in the absence of pyridine or without heating, the percentage of yield was found to be > 100, and the IR spectra of these polymers showed strong absorption bands in the

Tab. 1. Preparation of **19h** from **17h**/**18h** under various conditions

	Conditions					Result		Presence (+) or absence (−) of IR-absorptions[d] (in cm^{-1}) at		
Exp. No.	**17h**/**18h**[a] $\frac{10^{-2}\cdot\eta_{sp}/c^{b)}}{cm^3\,g^{-1}}$	Volume of (CH_3CO_2) in cm^3	Volume of of pyridine in cm^3	Temp. in °C	Time in min	% Yield	$\frac{10^{-2}\cdot\eta_{sp}/c^{c)}}{cm^3\,g^{-1}}$	1820	1690	1530
1	0,8	5	0	95	90	(110)	0,48	++	+	+
2	0,8	5	0,5	98	90	(108)	0,29	+	++	+
3	0,8	5	1,0	98	90	93	0,29	−	++	−
4	0,8	5	2,0	96	85	97	0,29	−	++	−
5	0,8	5	2,0	98	115	85	0,28	−	++	−
6	0,8	5	2,0	99	160	83	0,27	−	++	−
7	0,8	5	2,0	≈20	20 h	(110)	0,51	++	+	+
8	0,48	5	1,0	98	200	98	0,22	−	++	−
9	0,48	5	1,0	120	140	84	0,19	−	++	−
10	0,48	5	0,2	140	70	73	0,18	−	++	−

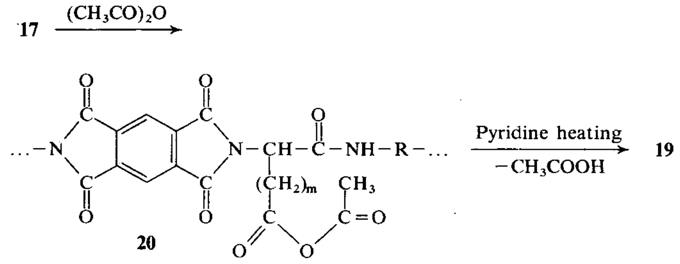
[a] 0,4 g of **17h**/**18h** in 5 cm^3 of DMAC.

[b] Measured in DMAC at 30°C ($c = 50$ mg/cm^3).

[c] Measured in DMSO at 30°C ($c = 50$ mg/cm^3).

[d] IR absorptions of the polymer film: anhydride at 1820 cm^{-1}, glutarimide ring at 1695 cm^{-1}, amic acid at 1530 cm^{-1}.

region of 1820 cm^{-1}, characteristic of carboxylic acid anhydrides, whereas increasing amounts of pyridine or a longer heating period resulted in a decrease of intensity of this absorptions. These results are interpreted as follows: The carboxylic acid groups at the side chain of the poly(imidoamic acid) react with acetic anhydride to produce first mixed anhydrides (**20**), which subsequently undergo intramolecular cyclization reactions leading to the corresponding imido derivatives **19**, as shown in the following scheme (x):



(x)

Pyridine catalyzes mainly the ring closure. The viscosity changes in the polymers before and after the dehydration, as shown in Tab. 1 and 6 (Exp. Part), may be attributed to a chain cleavage of the polymers. The mechanism of the chain cleavage remains unknown. It should, however, occur before ring closure because there is no change of viscosity during a prolonged reaction time as shown in Exp. No. 5 and 6 in Tab. 1.

Thermal process: The copolyimide formation was performed also by heating the poly(imidoamic acid) under reduced pressure in the form of a film or a precipitated powder. The conditions of heating, the yields and the solubilities of the copolyimides obtained are summarized in Tab. 2.

Tab. 2. Copolyimides prepared by the thermal process

Imidoamic acid	Heating condition[a] in °C/h	% Yield	Solubility DMSO	Solubility H_2SO_4
17, 18a	240/1–280/2–300/0,2	80	+	+
17, 18b	240/1–280/2–300/0,2	73	+	+
17, 18c	240/1–280/2–300/0,2	80	+	+
17, 18d	240/1–280/2–300/0,2	83	+	+
17, 18e	240/1–280/2–300/0,2	73	+	+
17, 18f	240/1–280/3–300/0,5	95	–	–
17, 18g	240/1–280/3–300/0,5	85	–	–
17, 18h	240/2–280/3–300/0,4	99	–	–
17, 18i	240/2–280/3–300/0,4	89	–	–
17, 18k	240/2–280/3–300/0,4	88	–	–
17, 18l	240/1–280/3–300/0,5	90	–	–
17, 18m	240/3–280/3–300/1,5	81	–	–

[a] The corresponding poly(imidoamic acid) was aged *i. vac.*

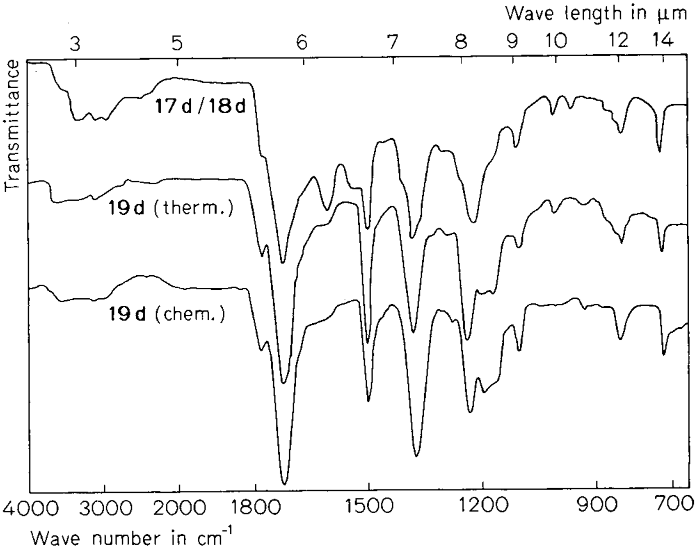


Fig. 6. IR spectra of films of **17d/18d** and of thermally and chemically prepared **19d**

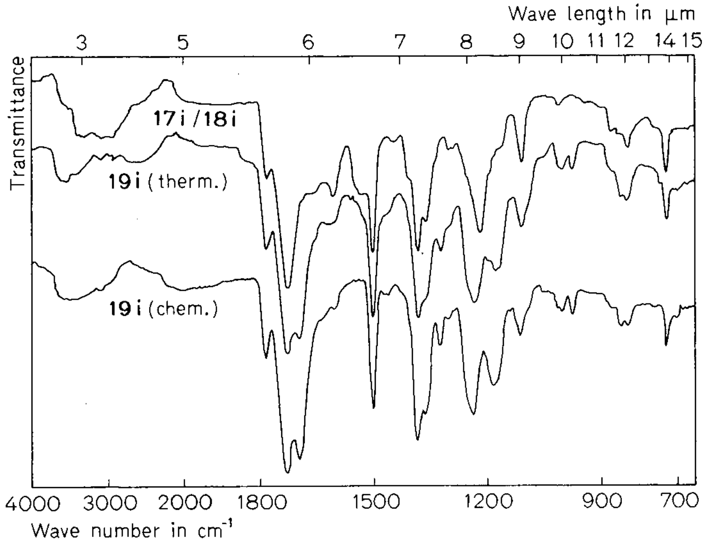


Fig. 7. IR spectra of films of **17i/18i** and of the thermally and chemically prepared **19i**

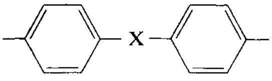
Copolyimides **19f–m** with six-membered rings are insoluble in organic solvents, whereas those with five-membered rings, **19a–d**, are soluble in DMSO. The IR spectrum of the thermally prepared copolyimide **19d**, containing a five-membered ring, shows similar patterns as that of the copolyimide **19d**, produced by a chemical process as shown in Fig. 6. On the other hand, the copolyimide **19i** with a six-membered ring, formed by a thermal process, shows a weak absorption of the remaining amide in the IR, even after a long period of heating (Fig. 7), indicating that the cyclization rate to the six-membered ring is much slower than that to the five-membered ring. Therefore, cross-linking reaction may be generated partially by intermolecular condensation reaction competing with the intramolecular cyclization.

Properties of the polymers

Solubility: The solubilities of the polymers are summarized in Tab. 3. Most of the poly(imidoamic acid)s are easily soluble in DMAC, DMF, DMSO, NMP, pyridine and dichloroacetic acid. All copolyimides prepared by a chemical process are partially soluble in polar solvents and easily soluble in DMSO except those derived from *p*-phenylenediamine. The poly(imidoamic acid)s have excellent storage stabilities either in solution or in solid state in contrast to the aromatic poly(amic acid)s prepared from pyromellitic anhydride.

Thermal stability: The thermal stability of the copolyimides was investigated by thermogravimetric analysis (TGA). The TGA curves are shown in Fig. 8, 9, 10, and 11. These indicate that the copolyimides have good thermal stabilities. The weight losses of copolyimides are less than 10 % after being heated up to 400 °C with a heating rate of 10 °C/min. However, the copolyimide containing a hexamethylene bridge, **19m**, appears to have a lower thermal stability.

Film flexibility: Most poly(imidoamic acid)s can easily be cast into films. Films of copolyimides prepared from diamines having the structure units



are flexible, where X is –O–, $-CH_2-$ or a single bond. The copolyimides **19a–e** with five-membered rings can also be cast into flexible films. However, it is comparatively difficult to form flexible films from the copolyimides **19f–m** with six-membered rings, because of their low molar mass.

Tab. 3. Solubility of poly(imidoamic acid)s and copolyimides[a)]

Solvent[c)]	17,18							17,18					19[b)]							19				
	f	**g**	**h**	**i**	**k**	**l**	**m**	**a**	**b**	**c**	**d**	**e**	**f**	**g**	**h**	**i**	**k**	**l**	**m**	**a**	**b**	**c**	**d**	**e**
DMF	+	+	+	+	+	+	+	+	+	+	+	+	+−	+−	+−	+−	+−	+−	+−	−	+−	+−	+−	+−
DMAC	+	+	+	+	+	+	+	+	+	+	+	+	+−	+−	+−	+−	+−	+−	+−	−	+−	+−	+−	+−
DMSO	+	+	+	+	+	+	+	+	+	+	+	+	+−	+−	+−	+−	+−	+−	+−	+−	+−	+−	+−	+−
NMP	+	+	+	+	+	+	+	+	+	+	+	+	+−	+−	+−	+−	+−	+−	+−	−	+−	+−	+−	+−
DCA	+	+	+	+	+	+	+	+	+	+	+	+	−	−	+−	+−	+−	+−	+−	−	+−	+−	+−	+−
PRD	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
10 % NaOH	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
conc. H_2SO_4	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
m-CRS	−	−	−	−	+−	+−	+−	−	−	−	−	+−	−	−	−	−	+−	−	+−	−	−	−	−	−
FA	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−
ACT	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−

[a)] +: soluble, +−: partially soluble, −: insoluble.

[b)] Polyimides prepared by thermal treatment were insoluble in any solvent.

[c)] Abbreviations: DCA: dichloroacetic acid, PRD: pyridine, *m*-CRS: *m*-cresol, FA: formic acid, and ACT: acetone.

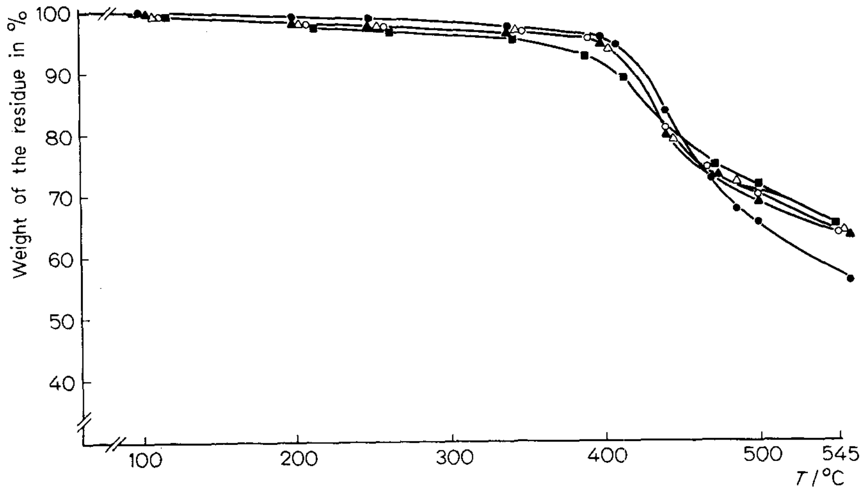


Fig. 8. Thermogravimetric analysis of **19**, chemically prepared. Heating rate: 10°C/min. (●): **19a**; (▲): **19b**; (△): **19c**; (○): **19d**; (■): **19e**

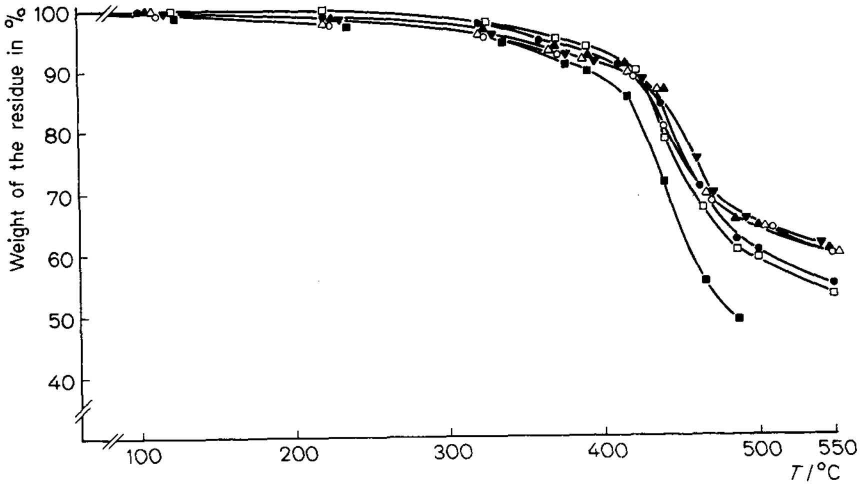


Fig. 9. Thermogravimetric analysis of **19**, chemically prepared. Heating rate: 10°C/min. (●): **19f**; (▲): **19g**; (△): **19h**; (○): **19i**; (▼): **19k**; (□): **19l**; (■): **19m**

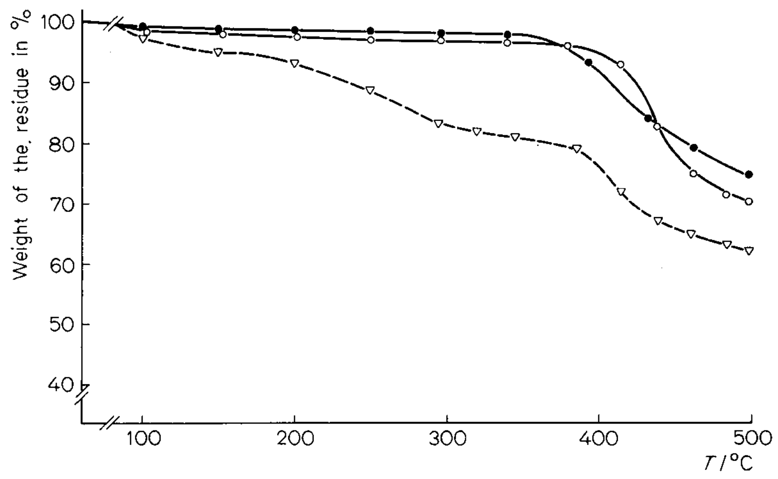


Fig. 10. Thermogravimetric analysis of **17d/18d** (●); **19d**, thermally prepared (●) and **19d**, chemically prepared (○). Heating rate: 10°C/min

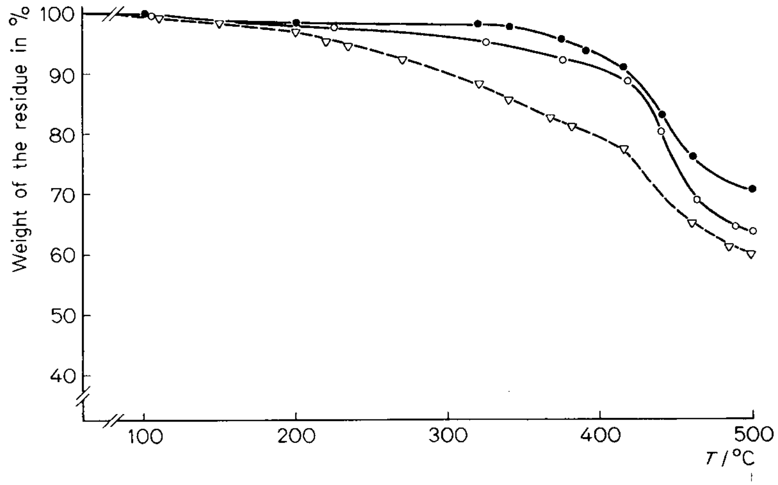


Fig. 11. Thermogravimetric analysis of **17i/18i** (▽); **19i**, thermally prepared (●) and **19i**, chemically prepared (○). Heating rate: 10°C/min

Experimental Part

Reagents: *N*,*N*-Dimethylacetamide and DMF were distilled on phosphorus pentoxide *i.vac.* DMSO was treated with calcium hydride and distilled at 20 mbar. Pyromellitic dianhydride was recrystallized from acetic anhydride. Bis(4-aminophenyl) ether and bis(4-aminophenyl)methane were recrystallized from ethyl methyl ketone under dry nitrogen with activated charcoal. 1,4-Phenylenediamine was recrystallized with activated charcoal under nitrogen from toluene. 1,3-Phenylenediamine and 1,6-hexamethylenediamine were purified by vacuum distillation. Benzidine (Tokyo Kasei GR grade) was used without further purification.

Monomers: 2,2'-Pyromellitdiimidodiglutaric anhydride (**5b**): A mixture of 21,8 g (0,1 mol) of pyromellitic dianhydride (**1**), 30,0 g (0,2 mol) of glutamic acid and 100 cm^3 of dry DMF was stirred at 40—50°C for *ca.* 1 h and then 400 cm^3 of dry toluene were added to the mixture. The mixture was heated at reflux in an oil bath until 3,6 cm^3 of water distilled off azeotropically and then it was cooled and filtered. The yellow clear filtrate was evaporated *i.vac.* to dryness. The residue was decolorized by treating with activated charcoal in methanol. The product thus obtained was dissolved in 150 cm^3 of pyridine and treated with 150 cm^3 of acetic anhydride. White crystals; mp > 390°C. Yield: 37,0 g (80 %).

$C_{20}H_{12}N_2O_{10}$ (440,3) Calc. C 54,55 H 2,75 N 6,36
Found C 54,54 H 3,04 N 6,30

2,2'-Pyromellitdiimidodisuccinic anhydride (**5a**): It was prepared by the same procedure as that described for **5b**. Dec.-p. 360°C; yield: 50 %.

$C_{18}H_8N_2O_{10}$ (412,3) Calc. C 52,45 H 1,94 N 6,80
Found C 52,15 H 2,10 N 6,83

Model compounds: 2-Phthalimidosuccinanilic acid (**8a**) and/or 3-phthalimidosuccinanilic acid (**9a**): A mixture of 2,45 g of 2-phthalimidosuccinic anhydride[8] (**6a**) in 30 cm^3 of dry THF and 2 cm^3 of aniline were stirred for 1 h at room temp. The reaction solution was then evaporated *i.vac.* to dryness. The residue was dissolved in a small amount of acetone, washed with hydrochloric acid ($c = 0,1$ mol/dm^3) to remove the excess aniline and then with water. After evaporation of acetone the residue was recrystallized from chloroform containing a small amount of acetone. Mp 192°C; yield: 3,08 g (92 %).

$C_{18}H_{14}N_2O_5$ (338,3) Calc. C 63,90 H 4,20 N 8,28
Found C 63,84 H 4,05 N 8,16

2-Phthalimidoglutaranilic acid (**8b**) and/or 4-phthalimidoglutaranilic acid (**9b**): **8b**/**9b** were prepared by the same procedure as **8a**/**9a** using 4-phthalimidoglutaric anhydride (**6b**)[9]. Mp 158°C; yield: 90 %.

$C_{18}H_{14}N_2O_5$ (338,3) Calc. C 63,90 H 4,20 N 8,28
Found C 63,84 H 4,05 N 8,16

$C_{19}H_{16}N_2O_5$ (352,3) Calc. C 64,75 H 4,55 N 7,96
Found C 64,13 H 4,53 N 7,82

Tab. 4. Model compounds

Compound	React. time in h[a] Step 1[b]	React. time in h[a] Step 2[c]	% Yield[d]	mp[e] in °C	Elemental analysis Brutto formula		C	H	N
N-Phenyl-2-phthalimidosuccinimide (**10a**)	2	1	79	262[f]	$C_{18}H_{12}N_2O_4$	Calc.	67,50	3,74	8,75
						Found	66,80	3,88	8,64
N-Phenyl-2-phthalimidoglutarimide (**10b**)	2	2	76	178[f]	$C_{19}H_{14}N_2O_4$	Calc.	68,26	4,23	8,38
						Found	68,32	4,18	8,44
N,*N'*-Bis(1-phenyl-2,5-dioxopyrrolidin-3-yl)pyromellitdiimide (**14a**)	1[g]	2	97	345	$C_{30}H_{18}N_4O_8$	Calc.	64,05	3,20	9,96
						Found	63,12	3,10	9,79
N,*N'*-Bis(1-phenyl-2,6-dioxo-5-piperidyl)-pyromellitdiimide (**14b**)	2,5	3	60	377	$C_{32}H_{22}N_4O_8$	Calc.	65,08	3,73	9,49
						Found	63,60	3,73	9,14
N,*N'*-Bis(1-benzyl-2,6-dioxo-5-piperidyl)-pyromellitdiimide (**14c**)	1[h]	3	82	267	$C_{34}H_{26}N_4O_8$	Calc.	66,02	4,21	9,06
						Found	65,75	4,21	8,89
N,*N'*-Bis(1-butyl-2,6-dioxo-5-piperidyl)-pyromellitdiimide (**14d**)	1,5[h]	3	32	279	$C_{28}H_{30}N_4O_8$	Calc.	61,09	5,45	10,18
						Found	61,01	5,42	10,15
2,2'-Phthalimido-*N*,*N'*-(1,4-phenylene)-disuccinimide (**12a**)	2	1[i]	85	400	$C_{30}H_{18}N_4O_8$	Calc.	64,05	3,20	9,96
						Found	64,05	3,17	10,03
2,2'-Phthalimido-*N*,*N'*-(1,3-phenylene)-disuccinimide (**12b**)	2	1	65	365	$C_{30}H_{18}N_4O_8$	Calc.	64,05	3,20	9,96
						Found	63,57	3,22	9,73
2,2'-Phthalimido-*N*,*N'*-(4,4'-biphenylylene)-disuccinimide (**12c**)	2	0,5	84	319	$C_{36}H_{22}N_4O_8$	Calc.	67,71	3,45	8,78
						Found	67,37	3,31	8,66
2,2'-Phthalimido-*N*,*N'*-[oxybis(1,4-phenylene)]disuccinimide (**12d**)	2	1	72	257[k]	$C_{36}H_{22}N_4O_9$	Calc.	66,05	3,37	8,56
						Found	65,76	3,27	8,31
2,2'-Phthalimido-*N*,*N'*-[methylene(1,4-phenylene)]disuccinimide (**12e**)	2	0,5	83	225–235[k]	$C_{37}H_{24}N_4O_8$	Calc.	68,09	3,68	8,59
						Found	67,30	3,52	8,36
2,2'-Phthalimido-*N*,*N'*-(1,4-phenylene)-diglutarimide (**12f**)	3	1	72	400	$C_{32}H_{22}N_4O_8$	Calc.	65,08	3,76	9,49
						Found	64,80	3,90	9,47

Tab. 4. (Continued)

Compound	React. time in h[a)] Step 1[b)]	React. time in h[a)] Step 2[c)]	% Yield[d)]	mp[e)] in °C	Brutto formula	Elemental analysis	C	H	N
2,2′-Phthalimido-*N*,*N*′-(1,3-phenylene)-diglutarimide (**12g**)	1	3	60	372	$C_{32}H_{22}N_4O_8$	Calc.	65,08	3,76	9,49
						Found	64,90	3,79	9,34
2,2′-Phthalimido-*N*,*N*′-(4,4′-biphenylylene)diglutarimide (**12h**)	2	2,5	75	345	$C_{38}H_{26}N_4O_8$	Calc.	68,46	3,90	8,40
						Found	68,13	3,79	8,28
2,2′-Phthalimido-*N*,*N*′-[oxybis(1,4-phenylene]diglutarimide (**12i**)	2	3	76	172–180[k)]	$C_{38}H_{26}N_4O_9$	Calc.	66,86	3,81	8,21
						Found	66,85	3,79	8,05
2,2′-Phthalimido-*N*,*N*′-[methylene(1,4-phenylene)]diglutarimide (**12k**)	3	3	62	308	$C_{39}H_{28}N_4O_8$	Calc.	68,83	4,15	8,23
						Found	68,70	4,23	8,02
2,2′-Phthalimido-*N*,*N*′-[methylene(1,4-phenylene)methylene]diglutarimide (**12l**)	3	3	71	339	$C_{34}H_{26}N_4O_8$	Calc.	66,02	4,24	9,06
						Found	65,37	4,30	8,93
2,2′-Phthalimido-*N*,*N*′-(decamethylene)-diglutarimide (**12m**)	1	3	34	170–185[k)]	$C_{36}H_{38}N_4O_8$	Calc.	66,05	5,86	8,56
						Found	65,50	5,83	8,20

[a)] Step 1 *cf.* Eq. (iv) and step 2 (Eq. (vi)).

[b)] Reaction was carried out at room temp. Solvent: THF in most cases.

[c)] Reaction solvent: pyridine, dehydrating agent: acetic anhydride, ratio = 1:1. Reaction temp.: 120°C.

[d)] Yields of compounds **10a**, **10b**, **14a–d** were calc. from the corresponding amic acid (yields of corresponding compounds from step 1 are: amic acid precursor of **10a**: 92 %, of **10b**: 90 %, of **14a**: 86 %, of **14b**: 80 %, of **14c**: 85 %, and of **14d**: 51 %).

[e)] Melting point are uncorrected, measured by DSC analysis.

[f)] Measured by the capillarly method.

[g)] DMAC was used instead of THF.

[h)] A small amount of pyridine was added to THF.

[i)] Reaction temp. × : 80°C.

[k)] Measured on a hot plate.

Tab. 5. Preparation of poly(imidoamic acid)s **17/18a–m**[a]

Polymer	Diimide dianhy-dride	Diamine	$10^{-2} \cdot \eta_{sp}/c$[b] cm³ g⁻¹	Formula	Elemental analysis					
					Calc.			Found		
					C	H	N	C	H	N
17a/18a	**5a**	**11a**	0,47	$C_{24}H_{16}N_4O_{10} \cdot 3/2\, H_2O$	52,60	3,47	9,88	52,60	3,68	10,18
17b/18b	**5a**	**11b**	0,31	$C_{24}H_{16}N_4O_{10} \cdot 3/2\, H_2O$	52,60	3,47	9,88	52,60	3,84	10,29
17c/18c	**5a**	**11c**	0,62	$C_{30}H_{20}N_4O_{10} \cdot 2H_2O$	57,01	3,80	8,85	56,50	3,79	9,13
17d/18d	**5a**	**11d**	0,64	$C_{30}H_{20}N_4O_{11} \cdot 2H_2O$	55,62	3,70	8,65	55,70	3,65	8,85
17e/18e	**5a**	**11e**	0,50	$C_{31}H_{22}N_4O_{10} \cdot 2H_2O$	57,60	4,03	8,67	57,80	4,10	9,01
17f/18f	**5b**	**11a**	0,53[c]	$C_{26}H_{20}N_4O_{10} \cdot 3/2\, H_2O$	54,35	4,00	9,73	54,60	4,02	9,50
17g/18g	**5b**	**11b**	0,39	$C_{26}H_{20}N_4O_{10} \cdot 1/2\, H_2O$	56,05	3,78	10,04	56,02	4,40	10,80
17h/18h	**5b**	**11c**	0,81	$C_{32}H_{24}N_4O_{10} \cdot 2H_2O$	58,40	4,27	8,53	58,39	4,06	8,77
17i/18i	**5b**	**11d**	0,69	$C_{32}H_{24}N_4O_{11} \cdot 3/2\, H_2O$	57,60	4,04	8,40	57,55	3,97	8,45
17k/18k	**5b**	**11e**	0,62	$C_{33}H_{26}N_4O_{10} \cdot 3/2\, H_2O$	59,55	4,36	8,44	59,08	4,49	8,48
17l/18l	**5b**	**11f**	0,39	$C_{28}H_{24}N_4O_{10} \cdot 1/2\, H_2O$	57,45	4,28	9,56	57,65	4,83	9,52
17m/18m	**5b**	**11h**	0,39	$C_{26}H_{28}N_4O_{10} \cdot 1/2\, H_2O$	55,20	5,13	9,91	55,01	5,35	9,89

[a] The polymerization was carried out in DMAC. Concentration: 0,1 g/cm³; temp.: room temp.; reaction time: 6–10 h. The yield of the polymer was almost quantitative in every case.

[b] Solvent: DMAC; concentration: 5 mg/cm³; temp.: 30°C.

[c] DMSO was used instead of DMAC.

Tab. 6. Copolyimides by chemical process

Polymer	% Yield	$10^{-2} \cdot \eta_{sp}/c$[a] $\text{cm}^3\,\text{g}^{-1}$		Brutto formula	Elemental analysis					
					Calc.			Found		
		17/18	**19**		C	H	N	C	H	N
19a	99	0,47		$C_{24}H_{12}N_4O_8 \cdot 3/2\,H_2O$	56,35	2,93	10,94	56,09	2,43	10,86
19b	97	0,31	0,28	$C_{24}H_{12}N_4O_8 \cdot 3/2\,H_2O$	56,35	2,93	10,94	56,18	2,33	10,78
19c	98	0,62	0,53	$C_{30}H_{16}N_4O_8 \cdot 3/2\,H_2O$	61,30	3,23	9,52	60,81	2,79	9,57
19d	93	0,64	0,57	$C_{30}H_{16}N_4O_8 \cdot H_2O$	60,65	3,03	9,44	60,19	2,61	9,39
19e	94	0,50	0,40	$C_{31}H_{18}N_4O_8 \cdot N_2O$	62,83	3,38	9,46	62,52	2,99	9,51
19f	90	0,54		$C_{26}H_{16}N_4O_8 \cdot 3/2\,H_2O$	58,00	3,53	10,39	58,13	3,42	10,33
19g	90	0,39	0,20	$C_{26}H_{16}N_4O_8 \cdot H_2O$	58,90	3,40	10,52	58,94	3,39	10,22
19h	97	0,81	0,29	$C_{32}H_{20}N_4O_8 \cdot 2H_2O$	61,55	3,84	8,99	61,65	3,67	8,98
19i	92	0,69	0,26	$C_{32}H_{20}N_4O_9 \cdot H_2O$	61,75	3,53	8,99	61,52	3,50	8,53
19k	98	0,62	0,24	$C_{33}H_{22}N_4O_8 \cdot 3/2\,H_2O$	63,10	3,98	8,91	63,12	3,83	8,75
19l	90	0,39	0,22	$C_{28}H_{20}N_4O_8 \cdot 1/2\,H_2O$	61,30	3,83	10,19	61,29	3,85	9,70
19m	85	0,39	0,20	$C_{26}H_{24}N_4O_8 \cdot H_2O$	58,00	4,83	10,38	58,08	4,64	10,03

[a] Viscosity was measured in DMSO at the concentration of 5 mg/cm^3 at 30°C for polyimides and in DMAC at the concentration of 5 mg/cm^3 at 30°C for poly(imidoamic acid)s.

N-Phenyl-2-phthalimidosuccinimide (**10a**): 1 g of **8a**/**9a** was heated under reflux with 5 cm^3 of pyridine and 5 cm^3 of acetic anhydride for 1 h and then the solution was cooled. The crude crystals were washed with methanol and then recrystallized from ethyl methyl ketone. Mp 262°C; yield: 0,76 g (80 %).

Reaction conditions, yields, mp and elemental analyses of the other model compounds are summarized in Tab. 4.

Poly(imidoamic acid)s:

General Procedure: The preparation of poly(imidoamic acid)s (**17**/**18a–m**) was carried out by adding crystalline **5a** or **5b** to a solution of an α,ω-diamine **11** in a polar solvent such as *N,N*-dimethylacetamide (DMAC), DMF, DMSO, or *N*-methylpyrrolidone (NMP). In all cases, **5a** or **5b** dissolved slowly and finely the reaction mixture became homogeneous and on stirring for several hours very viscous. The poly(imidoamic acid)s were isolated by pouring the reaction mixture in ether. The yields are almost quantitative in every case. In Tab. 5 viscosities and elemental analyses of the polymers are summarized.

Copolyimides: Viscosities, yields and elemental analyses of chemically prepared copolyimides are summarized in Tab. 6.

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