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Syntheses and Properties of *N*-(1,3-Diisocyanato-1-propyl)phthalimide and Its Polymers

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SUMMARY:

N-(1,3-Diisocyanato-1-propyl)phthalimide (**5**) was synthesized as a new monomer from glutamic acid (**1**) through *N*-phthaloylglutamic acid (**2**), *N*-phthaloylglutamoyl dichloride (**3**) and *N*-phthaloylglutamoyl diazide (**4**), followed by a Curtius rearrangement. In the Curtius rearrangement, the carbonylazido group with the phthalimido group in 4-position decomposes at 25 °C, whereas the other carbonylazido group with the phthalimido group in 2-position is stable up to 45 °C. The monomer is a viscous and transparent liquid which can be purified by molecular distillation without racemization. A series of polymers, including polyureas (**13a–i**), polyurethanes (**15a–d**) and a poly(urea-urethane) (**17**), were synthesized from monomer **5** and their thermal properties and solubilities were determined. It was found that all investigated polymers decompose readily between 200 °C and 250 °C.

ZUSAMMENFASSUNG:

N-(1,3-Diisocyanato-1-propyl)phthalimid (**5**) wurde hergestellt, ausgehend von Glutaminsäure (**1**) über *N*-(Phthaloylglutaminsäure (**2**), *N*-(Phthaloylglutaminsäure-dichlorid (**3**), *N*-(Phthaloylglutaminsäure-diazid (**4**) mit anschließender Curtius-Umlagerung. Bei dieser zerfallen die Carbonylazid-Gruppen in 4-Stellung zur Phthalimido-Gruppe ab etwa 25 °C während die anderen Carbonylazid-Gruppen in 2-Stellung zur Phthalimido-Gruppe bis etwa 45 °C beständig sind. Das Diisocyanat **5** ist eine viskose Flüssigkeit, die ohne Racemisierung zu erleiden durch Molekulardestillation gereinigt werden kann. Eine Reihe von Polyharnstoffen (**13a–i**), Polyurethanen (**15a–d**) und das Polyharnstoffurethan) (**17**) wurde hergestellt, und ihre thermischen und Lösungs-Eigenschaften wurden untersucht. Alle geprüften Polymeren zersetzen sich zwischen 200 und 250 °C.

Introduction

Recently, glutamic acid (**1**) is widely commercially available as raw material for organic syntheses. The three functional groups, two carboxylic groups and one amino group, make it suitable for polymer formation. By utilizing its amino and one of the carboxylic groups, poly(α-benzylglutamate)[1], poly(γ-methylglutamate)[2-4], and the copolymers of glutamate-NCA[5] have been obtained. Polyesters[6] and polyamides[7,8] were synthesized by reaction of *N*-phthaloylglutamic acid and *N*-phthaloylglutamoyl dichloride with diols and diamines, respectively. Also poly(acylsemicarbazide)s were synthesized via glutamodihydrazide[9,10]. *Iwakura* et al.[11] have synthesized a linear copolyglutarimide by utilizing the three functional groups of glutamic acid.

Syntheses of polyureas and polyurethanes derived from glutamic acid have not yet been attempted. The present paper describes the synthesis of the corresponding diisocyanate from glutamic acid via the Curtius reaction and the syntheses of a series of new polymers from the diisocyanate and diamines or diols. The properties of the new polymers were investigated.

Results and Discussion

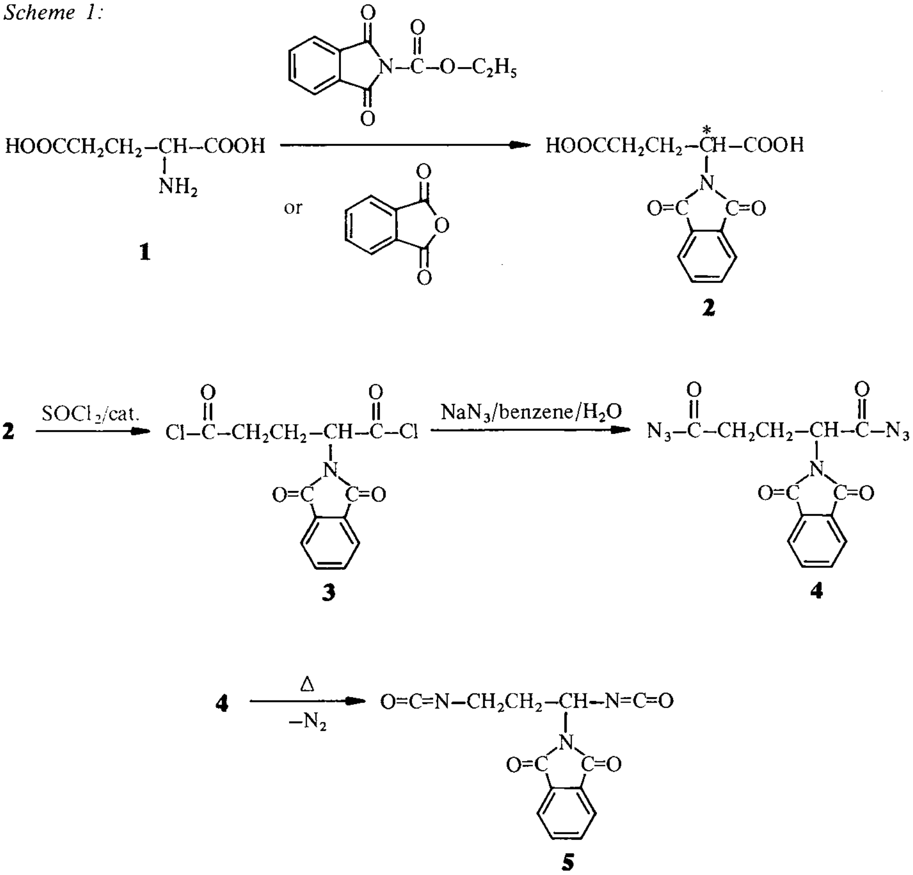
Synthesis of the monomer

The process of the synthesis of *N*-(1,3-diisocyanato-1-propyl) phthalimide (**5**) from **1** is shown in Scheme 1.

The optically pure *N*-phthaloylglutamic acid (2-phthalimidoglutaric acid) (**2**) was obtained by a process described by *Nefkens* et al.[12] using *N*-ethoxycarbonyl phthalimide. In case of the other methods[13,14], i.e. using phthalic anhydride, some racemization occurred as shown in Tab. 1.

In general acid chloride syntheses, it is possible to use PCl_5 or $SOCl_2$. The synthesis of *N*-phthaloyl-D-glutamoyl dichloride (**3**) by reaction of PCl_5 with **2** has been reported[10], and it has been found that PCl_5 is very difficult to remove. When $SOCl_2$ was used instead of PCl_5 *N*-phthaloylglutamic anhydride was obtained rather than the acid dichloride, although excessive $SOCl_2$ could be easily removed by distillation. Our experiment showed that a trace amount of a dialkylformamide, such as *N*,*N*-dimethyl- or *N*,*N*-diethylformamide prevents the formation of anhydride and gives the corresponding acid dichloride. The results are shown in Tab. 2.

Scheme 1:



From the results of Tab. 2, it can be seen that tertiary amines and tertiary amides promote the reaction, and that *N*,*N*-dialkylformamides can prevent the formation of the cyclic anhydride. This is due to the formylamino group which forms an intermediate complex with both $SOCl_2$ and carboxylic acid group leading to the formation of the acid dichloride rather than the anhydride. Details of the mechanism will be reported in a following paper[15)].

N-phthaloylglutamoyl diazide (**4**) was obtained by reacting the dichloride **3** with sodium azide. Aliphatic acid azides are generally less stable than aromatic ones. Thus, the solution of the aliphatic acid azide must be kept at low temperature (< 15 °C) before water is sufficiently removed, otherwise the yield will be lowered with increasing formation of urea derivatives.

Tab. 1. Data of the preparation of *N*-phthaloyl-L-glutamic acid (**2**)

Exp. No.	Reactants[a]	Solvent	Conditions		Yield in %	Results	
			temp. in °C	time in h		$[\alpha]_D^{20}$ [b]	mp in °C[c]
1	(L)**1** + NEP	H_2O[d]	0–5	1–2	70	−49	158
2	(L)**1** + PA	xylene	140	4	50	−43	159
3	(L)**1** + PA	toluene + DMF	135	8	40	−42	159–160
4	(L)**1** + PA	direct melt	150	0,3	52	−12	162–163

[a] NEP = *N*-ethoxycarbonyl phthalimide; PA = phthalic anhydride.

[b] 2 g dl^{-1}; in dioxane.

[c] Measured by the capillary method.

[d] Alkaline (pH 9,5).

Tab. 2. Effect of additives on the products of the reaction between $SOCl_2$ and *N*-phthaloylglutamic acid (**2**)

Additives[a] (amount[b] in %)	Reaction conditions temp. in °C	time in h	Product	Remark[c]
No	50–70	4	Anhydride[d]	S
Pyridine (1–5)	40–50	4	Anhydride	P
DMF (1)	25	4	Acid dichloride[e]	P
DMA (1–5)	40–50	3	Anhydride	P
DEF (1)	25	4	Acid dichloride	P

[a] DMF: *N*,*N*-dimethylformamide; DMA: *N*,*N*-dimethylacetamide; DEF: *N*,*N*-diethylformamide.

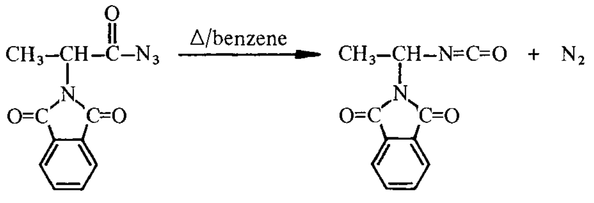
[b] The amounts of additives are given as relative weights to that of *N*-phthaloylglutamic acid (**2**).

[c] S: reaction is very slow at room temp.; P: reaction was promoted by the additives.

[d] *N*-phthaloylglutamic anhydride.

[e] *N*-phthaloylglutamoyl dichloride.

The properties of the two terminal azido groups in **4** are different from each other. In order to study the individual thermal stabilities, the reaction rates of the decomposition of 2-phthalimidopropionyl azide (**6**) and of **4** in benzene were compared.



6 **7** (i)

$$\mathbf{4} \xrightarrow{\Delta/\text{benzene}} \mathbf{5} + 2N_2 \qquad \text{(ii)}$$

The results are shown in Fig. 1.

From Fig. 1, it can be seen that reaction (i) does not occur below 45 °C. However, when the temperature was raised to 60 °C **6** decomposes quickly. On the other hand, the decomposition of **4** starts at 24 °C and 50% conversion

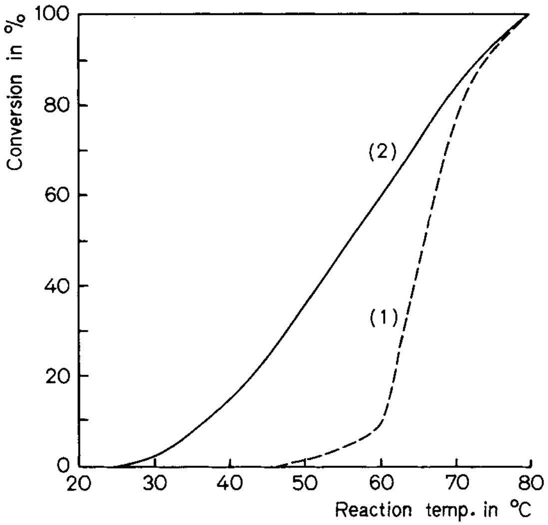


Fig. 1. Conversion of acid azides as function of temperature in benzene. Heating rate: 10°C/h. (1): Formation of isocyanate **7** (Eq. (i)); (2): formation of diisocyanate **5** (Eq. (ii))

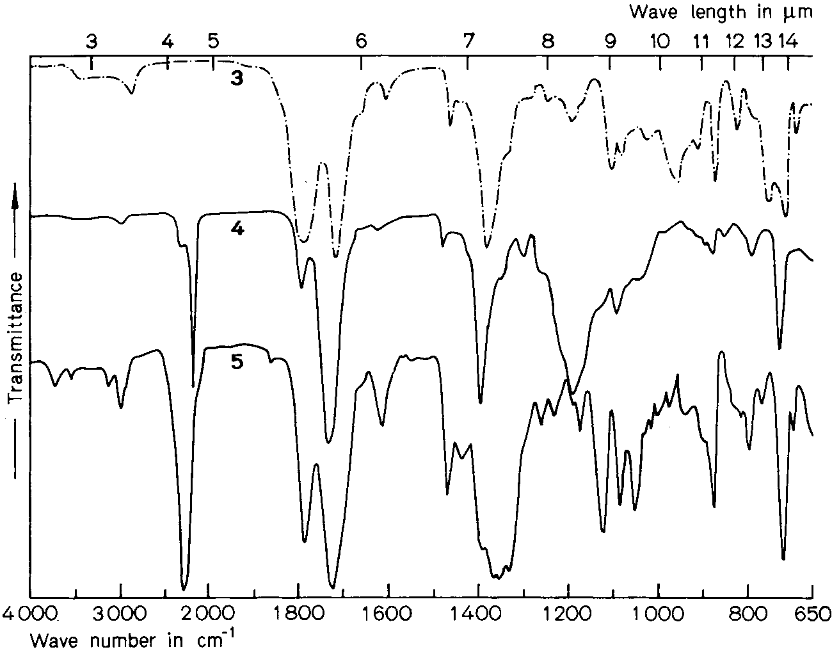


Fig. 2. IR spectra of N-phthaloyl-L-glutamoyl dichloride (**3**), N-phthaloylglutamic diazide (**4**), and N-(1,3-diisocyanato-1-propyl)phthalimide (**5**) (**3** in KBr, **4** and **5** in liq. film)

is achieved at about 56 °C. According to these results, it is evident that the azido group in **4** which has the phthalimido group in 2-position, is more stable than the other one with the phthalimido group in 4-position. The decomposition temperature of the former is between 45 and 80 °C, whereas that of the latter is between 24 and 56 °C. The difference in the stability of the two azido groups may be due to a negative inductive effect of the phthalimido group.

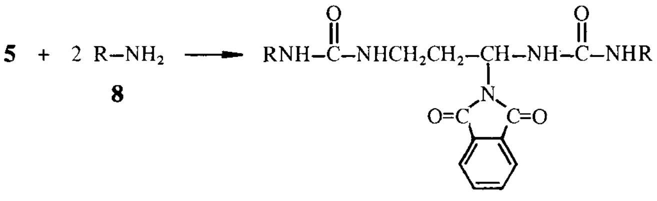
The IR spectra of **5**, of the diazide **4**, and the dichloride **3** are shown in Fig. 2. The characteristic absorption of the azido group appears at 2150 cm^{-1} and that of the isocyanato group at 2255 cm^{-1}.

5 is a viscous liquid with a specific gravity of 1,29 at room temperature. Its vapor pressure is too low to permit an ordinary distillation. However, it can be purified by molecular distillation at ≈0,2–0,6 mbar at an external temperature of 130–170 °C.

Because there was no racemization during the high temperature distillation, the optical properties of acid **2** were retained in the final product **5**.

Syntheses of the model compounds

Bisurea compounds are obtained by reaction of compound **5** with the primary amines **8a–c** in dioxane or benzene solution as shown by Eq. (iii). The products were recrystallized from ethanol to get needle-like crystals. Their properties are given in the Exptl. Part.



(iii)

9

	R
8, 9 a	C_6H_5
b	$C_6H_5CH_2$
c	$CH_3(CH_2)_3$

The optical properties change with the group R, and the melting points in the following order: phenyl > benzyl > butyl. Compound **5** with different optical properties gave a bisureido derivative **9a′** of different melting point and optical properties. The thermal stability of **9a** was studied by TG-DTA measurement as shown in Fig. 3.

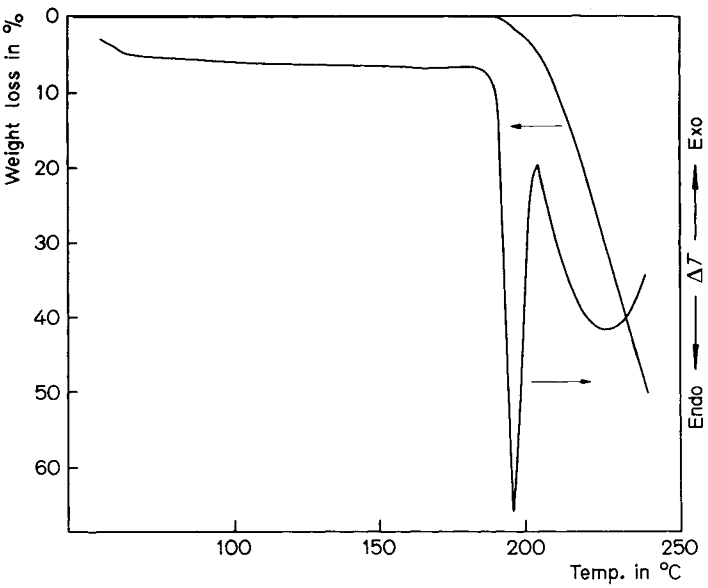


Fig. 3. TG-DTA curves of *N*-[1,3-bis(3-phenylureido)-1-propyl]phthalimide (**9a**). Heating rate: 10°C/min

When the temperature was just higher than that of the melting point, there was a weight loss with a simultaneous absorption of heat. The IR spectra (Fig. 4) revealed that decomposition takes place.

The corresponding dicarbamates **11a–c** are produced by reaction of compound **5** with phenol or alcohols in the presence of dibutyltin dilaurate, triethylamine, or pyridine, as catalysts as shown by Eq. (iv). The products are hygroscopic with the exception of the phenyl derivative **11a**. The properties of **11a–c** are given in the Exptl. Part.

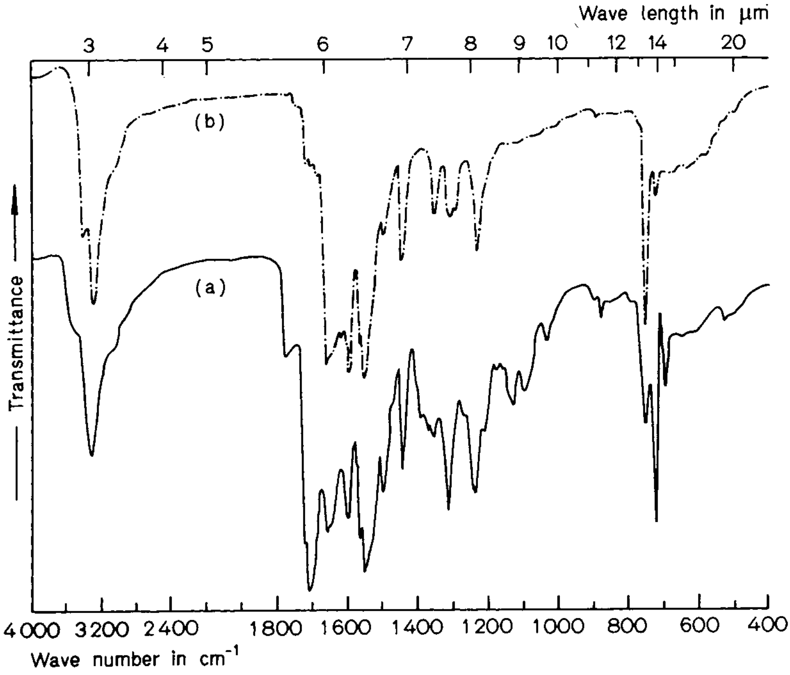
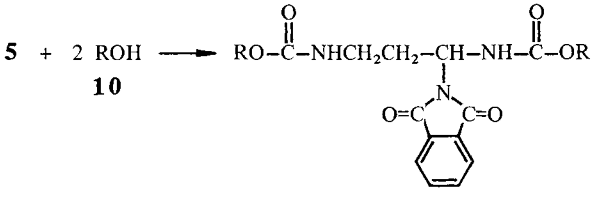


Fig. 4. IR spectra of *N*-[1,3-bis(3-phenylureido)-1-propyl]phthalimide (**9a**), (a), and of the volatile products formed by its thermal decomposition, (b)



10

11

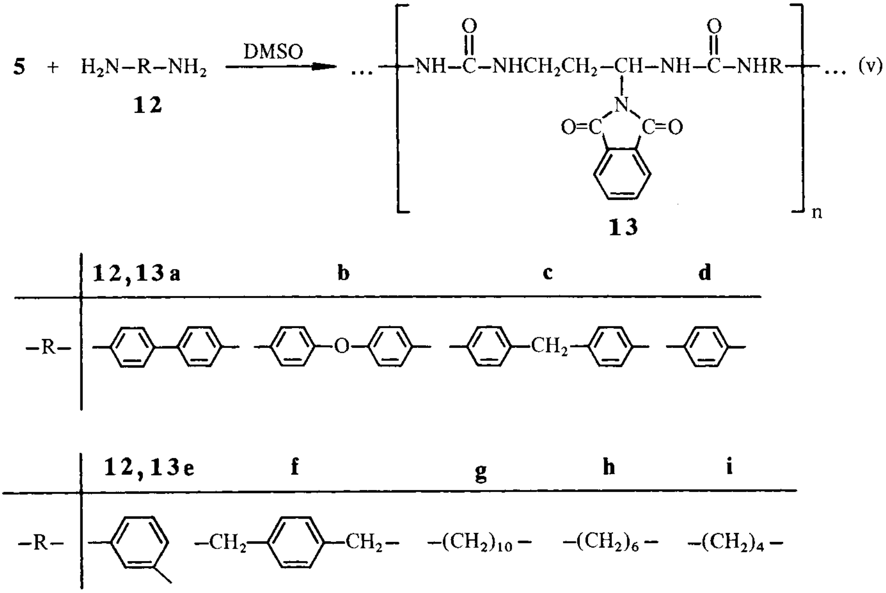
(iv)

	R
10,11 a	C_6H_5
b	$C_6H_5CH_2$
c	CH_3

Synthesis of polymers

Polyureas

The polyaddition reactions of diamines **12a–i** with **5** were carried out in polar aprotic solvents such as dimethyl sulfoxide (DMSO), *N*,*N*-dimethylacetamide (DMA), *N*-methylpyrrolidone (NMP), etc. The obtained solutions of polymers were poured into a nonsolvent, such as methanol to obtain the polymers as powders. The results are shown in Tab. 3.



Polyurethanes

Polyurethanes were produced by reaction of equivalent amounts of diols **14a–d** with the diisocyanate **5** in anisol or chloroform (Eq. (vi)). An organometal or amine catalyst was added to obtain polymers of higher molecular weights. The polymers were reprecipitated from hexane after the removal of the catalyst. The results are shown in Tab. 4.

Tab. 3. Data of the preparation of the polyureas **13a–i**[a]

Poly[ureylene-(1-phthalimidotrimethylene)ureylene-	Conditions		Results	
	solid Cont. in %	temp. in °C	yield[b] in %	$\frac{\eta_{sp}}{C} / (\mathrm{dl\ g^{-1}})$[c]
-4,4′-biphenylylene] (**13a**)	34	25	q[d]	0,31
13b[e]	26	25	q	0,23
-1,4-phenylenemethylene-1,4-phenylene] (**13c**)	25	25	q	0,22
-1,4-phenylene] (**13d**)	30	25	q	0,17
-1,3-phenylene] (**13e**)	25	25	q	0,18
-methylene-1,4-phenylene-methylene] (**13f**)	23	60	q	0,12
-decamethylene] (**13g**)	32	25	73	0,14
-hexamethylene] (**13h**)	42	80	91	0,14
-tetramethylene] (**13i**)	42	80	72	0,09

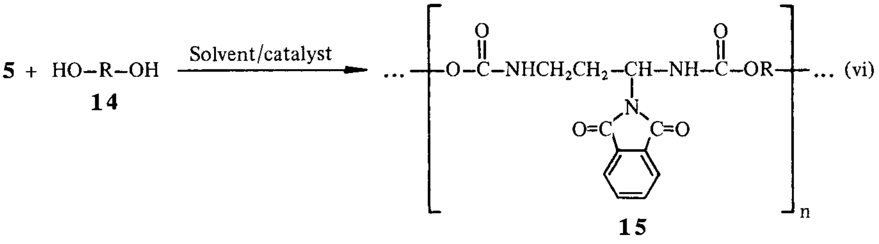
[a] Reaction solvent: DMSO.

[b] Polymers **13a–f** were precipitated from methanol, and polymers **13g–i** were precipitated from $CHCl_3$.

[c] 0,5 g dl^{-1}; in DMSO at 30°C.

[d] q = quantitative.

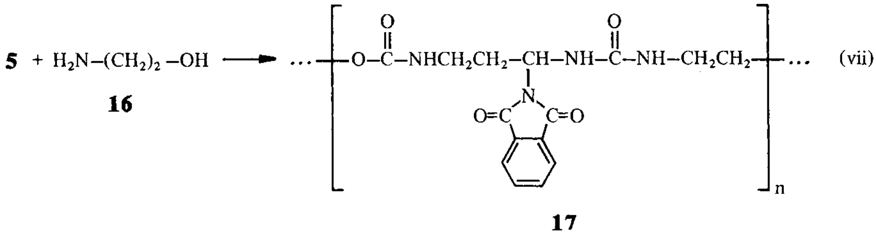
[e] Poly[oxy-1,4-phenyleneureylene-(1-phthalimidotrimethylene)ureylene-1,4-phenylene].



	–R–
14, 15 a	$-(CH_2)_{10}-$
b	$-(CH_2)_6-$
c	$-(CH_2)_4-$
d	$-(CH_2)_2-$

Poly(urea-urethane)s

The structure of the polymer, resulting from the reaction of compound **5** with 2-aminoethanol (**16**) is more complicated than the ordered structure **17**, shown in Eq. (vii), because the α-isocyanato group is more reactive than the other one due to the $-I$ effect of the phthalimido group, and also the amino group in **16** is more reactive towards the isocyanato group than the hydroxyl group.



Properties of the polymers

Solubility

The solubilities of the polymers are summarized in Tab. 5. Polyureas containing aromatic groups dissolve readily in polar solvents such as DMA, *N,N*-dimethylformamide (DMF), and DMSO. All the polyureas are insoluble in

Tab. 4. Data of the preparation of the polyurethanes **15a–d** and of poly(urea-urethane) **17**

-carbonylimino-(1-phthalimidotrimethylene)iminocarbonyl]	Solvent	Solid cont. in %	Cat.	Temp. in °C	Time in h	Yield in %	$\frac{\eta_{sp}}{C}\Big/(\mathrm{dl\ g^{-1}})$[a]
15a: Poly[1,12-dioxadodecamethylene-	Anisol	24	Sn-Cat.[b]	120	3	89	0,14
15b: Poly[1,8-dioxaoctamethylene-	Anisol	20	Sn-Cat.	120	3	94	0,22
15c: Poly[1,6-dioxahexamethylene-	Anisol	20	Sn-Cat.	120	2	q[c]	0,16
15d: Poly[1,4-dioxatetramethylene-	Anisol	19	Sn-Cat.	120	2	q[c]	0,09
15a	$CHCl_3$	24	PRD+TEA[d]	25–40	5	q[c]	0,12
15b	$CHCl_3$	20	PRD+TEA	25–40	5	q[c]	0,11
17[e]	DMSO	50	Sn-Cat.[f]	50	3	88	0,16

[a] 0,5 g dl^{-1}; in DMF at 30°C.

[b] Dibutyltin dilaurate, 1 drop.

[c] q = quantitative.

[d] Pyridine + triethylamine (1:1), 0,5 ml.

[e] Poly[oxycarbonylimino-(3-phthalimidotrimethylene)ureyleneethylene].

[f] Catalyst was added after 1 h reaction.

Tab. 5. Solubility[a)] of polyureas **13a–i**, of polyurethanes **15a–d**, and of poly(urea-urethane) **17**

Solvent[b)]	**13a**	**b**	**c**	**d**	**e**	**f**	**g**	**h**	**i**	**15a**	**b**	**c**	**d**	**17**
DMF	+	+	+	+	+	+	–	+	+	+	+	+	+	+
DMA	+	+	+	+	+	+	–	+	+ –	+	+	+	+	+
DMSO	+	+	+	+	+	+	–	+	+	+	+	+	+	+
FA	–	–	–	+ –	+ –	+	+ –	+	+	+ –	+	+ –	+	+
PRD	–	–	+	–	–	+ –	+ –	+ –	+ –	+	+	+	+	+ –
ACT	–	–	–	–	–	–	–	–	–	+ –	+ –	–	–	–
CH_3OH	–	–	–	–	–	–	+ –	+ –	+ –	+ –	+ –	+ –	–	–
C_2H_5OH	–	–	–	–	–	–	–	–	–	–	–	–	–	–
$CHCl_3$	–	–	–	–	–	–	–	–	–	+	+	+	+	–
$C_2H_2Cl_4$	–	–	–	–	–	–	–	–	–	–	–	–	–	–

[a)] + : soluble; + – : partially soluble; – : insoluble.

[b)] Abbreviations: PRD: pyridine; FA: formic acid; ACT: acetone.

acetone, ethanol, and chlorinated hydrocarbons. Methanol can swell polyureas when R is an aliphatic group. In general, the polyurethanes are more soluble than the polyureas. In addition to the ordinary polar solvents, polyurethanes can also dissolve in chloroform. However, they are insoluble in ethanol, tetrachloroethylene, and hexane.

Thermal stability

The thermal stability of the polymers was investigated by thermogravimetry (TG) and differential thermal analysis (DTA). The TG-DTA curves are shown in Figs. 5 and 6. Polyureas containing aromatic groups are comparatively thermally stable and do not change their weights at temperatures <190°C. Their decomposition temperatures are above 200°C. The rate of decomposition of polyureas with *p*-phenylene and 4,4′-biphenylylene groups is faster than that of polyureas with other aromatic groups, as shown by Fig. 5. Polyurethanes are more stable than polyureas. The decomposition temperature is about

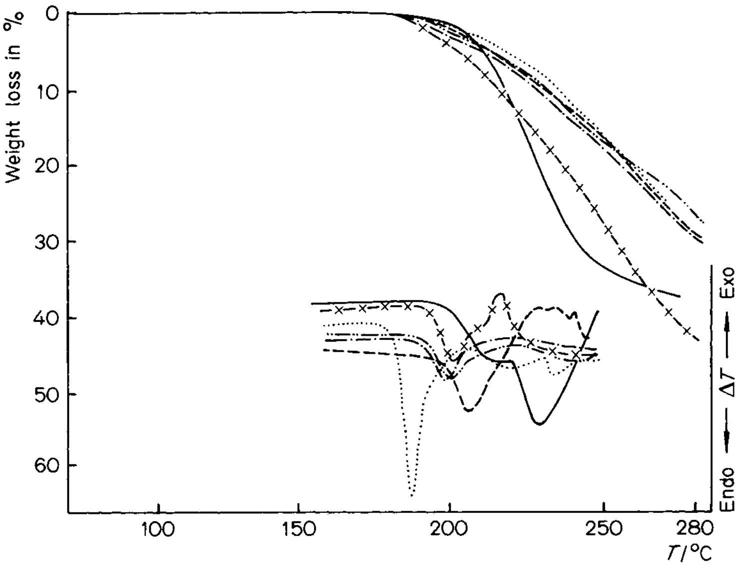


Fig. 5. TG-DTA curves of the polyureas **13a–f** (containing an aromatic system in the backbone). Heating rate: 10°C/min; (———): **13a**; (–··–··–): **13b**; (–·–·–): **13c**; (–×–×–): **13d**; (– – – –): **13e**; (·······): **13f**

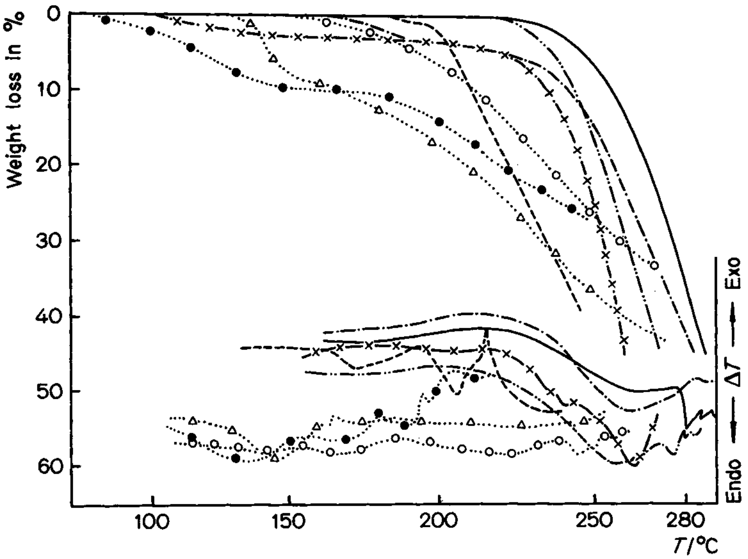


Fig. 6. TG-DTA curves of the polyureas **13g–i**, of the polyurethanes **15a–d**, and of the poly(urea-urethane) **17** (containing no aromatic system in the backbone). Heating rate: 10°C/min; (–·–·–): **15a**; (———): **15b**; (–·····–): **15c**; (–×–×–): **15d**; (–––): **17**; (··o··o··): **13g**; (··△··△··): **13h**; (··●··●··): **13i**

Tab. 6. Physical changes of the polymers during heating

Polymer	Temperature in °C of			
	softening	swelling	melting	10% weight loss
13a	197	203	300	213
13b	190	192	208	230
13c	188	192	206	240
13d	191	192	300	220
13e	200	203	225	234
13f	170	174	191	232
13g	145	155	170	210
13h	150	160	171	—
13i	142	147	190	—
15a	94	180	225	248
15b	—	115	215	251
15c	116	142	225	236
15d	132	145	223	242
17	177	184	197	210

230 °C or higher. The difference is more obvious when compared with polymers containing the same R groups as shown by Fig. 6.

In capillary melting point measurements, we observed that all polymers soften at a certain temperature, swell then, and finally melt, except the polymer containing the *p*-xylylene, (methylene-1,4-phenylenemethylene), group. The temperature change is shown in Tab. 6. Compared with the TG curve, it appears that most of the polymers decompose at the swelling temperature.

Optical activity

The optical properties of the polymers, synthesized from compound **5** of certain optical activity with diols or diamines which are not optically active, were examined. The difference, as shown in Tab. 7, seems to be related with the structure of the polyureas or polyurethanes.

Tab. 7. Optical activity of polymers

Polymer[a]	$[\alpha]_D^{20}$ [b]
13d	−36
15a	−12
15b	−12
15c	−25

[a] The optical activity of compound **5** used was $[\alpha]_D^{20} = -39,6$ ($C = 5$ g dl^{-1}; benzene).

[b] 1 g dl^{-1}; DMF.

Experimental Part

*N-Phthaloyl-*L*-glutamoyl dichloride (3):* 10 g of *N*-phthaloyl-L-glutamic acid[12], 0,10 g of DMF and an excess of freshly distilled $SOCl_2$ were allowed to react at room temp. After the solid was dissolved completely, the excess of $SOCl_2$ was distilled off i. vac. In order to remove $SOCl_2$ more thoroughly a small amount of dry toluene was added and distilled again. The residue was an oily colourless product, which was dissolved in a small amount of dry benzene, and a proper amount of dry non-solvent hexane was added to obtain a saturated solution. Then, the saturated solution, after having added a small amount of crystal seeds*), was put into a refrigerator for two days. A white needle-like crystalline precipitate was obtained and filtered under dry atmosphere. The yield was estimated to be 90%, mp 54–55 °C. $[\alpha]_D^{20} = -48$ ($c = 2$ g in 100 ml of dioxane).

N-(1,3-Diisocyanato-1-propyl)phthalimide (**5**): A 80 ml aqueous solution of 23 g of sodium azide was put into a 500 ml three-necked flask with a cooling and stirring equipment and cooled to 0–5 °C. While stirring, a 100 ml anhydrous benzene solution containing 44 g of *N*-phthaloyl-L-glutamoyl dichloride (**3**) (0,14 mol) was added in such a rate that the reaction temp. was kept below 6 °C. After the dropping was finished, the stirring was continued for 1 h before 250 ml of benzene were added. After stirring for another 3 h, the red aqueous lower layer was discarded by a separatory funnel and the benzene solution was transferred to a 600 ml Erlenmeyer flask. An excess of anhydrous Na_2SO_4 was added and left overnight at a temp. between 5 and 10 °C. After filtration, a benzene solution of *N*-phthaloyl-L-glutamoyl diazide (**4**) was obtained.

The above solution was poured into a dry 1 liter three-necked flask equipped with a $CaCl_2$ drying tube, thermometer, gas trap, and a refluxing system. With stirring, the temp. of the oil bath was raised at such a rate that the evolution of nitrogen could be controlled. The nitrogen gas was collected in a gas buret and the volume of nitrogen gas was measured. At the end of the reaction the mixture was refluxed for 1 h. After concentration i. vac. by distillation, 35,6 g of a viscous liquid of isocyanate **5** (80% purity, see last chapter) were obtained. The viscous liquid was purified by distillation in a molecular distillation apparatus at ≈0,35 mbar and 130–140 °C. A colourless transparent viscous liquid was obtained, specific gravity 1,29 and $[\alpha]_D^{20} = -53{,}6$ ($c = 0{,}8$ g in 100 ml benzene).

$C_{13}H_9N_3O_4$ (271,2)	Calc.	C 57,57	H 3,34	N 15,49
	Found	C 57,60	H 3,35	N 15,45

N-[1,3-Bis(3-phenylureido)-1-propyl]phthalimide (**9a**): About 30 ml benzene solution of 1,35 g (5 mmol) *N*-(1,3-diisocyanato-1-propyl)phthalimide (**5**) were added dropwise into a well stirred solution of 0,93 g (0,01 mol) aniline in 50 ml benzene. The mixture was stirred for 1 h at room temp. The product was filtered and dried to obtain 2,2 g of a white powder, which was recrystallized from ethanol to obtain needle-like crystals, mp 182 °C. Yield: 1,81 g (80%).

$[\alpha]_D^{20} = +35$ ($c = 1{,}0$ g in 100 ml CH_3OH).

$C_{25}H_{23}N_5O_4$ (457,5)	Calc.	C 65,63	H 5,07	N 15,31
	Found	C 65,29	H 5,18	N 15,08

From a diisocyanate **5** with different optical properties ($[\alpha]_D^{20} = -12$ ($c = 2{,}0$ g in 10 ml dioxane)) a compound **9a′** was obtained with mp 187 °C and $[\alpha]_D^{25} = +10$ ($c = 1{,}0$ g in 100 ml CH_3OH).

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*) *Preparation of crystal seed:* 1 g of freshly prepared oily *N*-phthaloyl-L-glutamoyl dichloride was dissolved in a small amount of dry benzene and saturated with dry petroleum ether. During evaporation in a rotary evaporator under reduced pressure without heating, a white solid crystallized out at a proper temperature.

The ureido derivatives **9b** and **9c** were prepared analogously.

N-[1,3-Bis(3-benzylureido)-1-propyl]phthalimide (**9b**): mp 171 °C, $[\alpha]_D^{20} = +16$ ($c = 1{,}0$ g in 100 ml CH_3OH).

N-[1,3-Bis(3-butylureido)-1-propyl]phthalimide (**9c**): mp 150 °C.

N-[1,3-Bis(3-phenylcarbamato)-1-propyl]phthalimide (**11a**): A mixture of 1,35 g of diisocyanate **5**, 0,94 g of phenol, 10 ml of tetrahydrofuran, and 1 drop of dibutyltin dilaurate was stirred for 1 h at 60 °C and then refluxed for 10 min. The resultant solution was concentrated under reduced pressure and the residue was refluxed with ethanol to remove the catalyst. After drying a white solid was obtained, mp 120 °C; yield: 2,1 g (91 %).

The carbamate derivatives **11b** and **11c** were prepared analogously.

N-[1,3-Bis(3-benzylcarbamato)-1-propyl]phthalimide (**11b**): mp 95 °C.

N-[1,3-Bis(3-methylcarbamato)-1-propyl]phthalimide (**11c**): mp 70 °C.

Preparation of the polyureas

A certain amount of the diamine was weighed in a 50 ml flask equipped with a magnetic stirrer and then a proper amount of dry DMSO was added leading to a reaction mixture with a conc. of 20–30% of solid content. Under nitrogen an equivalent amount of diisocyanate **5** or a 50% benzene solution of an equivalent amount of **5** was added into the flask. The mixture was stirred for 3 h at room temp., then it was heated to 60 °C, stirred for 20 min and poured into well-stirred methanol to precipitate the polymer. The product was washed with methanol and dried.

Poly[ureylene-(1-phthalimidotrimethylene)ureylene-4,4-biphenylylene] (**13a**): From 0,77 g of **5** and 0,523 g of benzidine in 4 ml DMSO and 1 ml benzene. Yield: 1,11 g (86%).

$(C_{25}H_{21}N_5O_4)_n$	$(455{,}5)_n$	Calc.	C 65,92	H 4,65	N 15,38
		Found	C 64,70	H 4,46	N 15,18

Poly[ureylene-(1-phthalimidotrimethylene)ureylene-1,4-phenylenemethylene-1,4-phenylene] (**13c**): From 0,72 g of **5** and 0,526 g of 4-(4-aminobenzyl)aniline in 4 ml of DMSO and 1 ml of benzene. Yield: 1,17 g (94 %).

$(C_{26}H_{23}N_5O_4)_n$	$(469{,}5)_n$	Calc.	C 66,51	H 4,94	N 14,92
		Found	C 65,10	H 4,78	N 14,72

Conditions of preparation, yields, and values of η_{sp}/C of the other polyureas prepared are given in Tab. 3.

Preparation of the polyurethanes

A certain amount of the diol was weighed in a 30 ml flask equipped with a magnetic stirrer and then 5 ml of dry anisol were added. The mixture was heated to melt at 100 °C and about 5 ml of a solution of an equivalent amount of diisocyanates **5** in toluene were added. The temp. was raised to 120°C and one drop of dibutyltin dilaurate was added. After stirring for 3 h the mixture was cooled, the desired polymer was separated and the remaining solution was discarded. The crude polymer was refluxed three times with 15 ml of ethanol to remove the catalyst and products of low molecular weight, and then it was dried.

Poly[1,6-dioxahexamethylenecarbonylimino-(1-phthalimidotrimethylene)iminocarbonyl] (**15c**): From 0,626 g of **5** and 0,273 g of 1,6-hexanediol. Yield: 0,836 g (94%).

$(C_{19}H_{23}N_3O_6)_n$	$(389,4)_n$	Calc.	C 58,60	H 5,95	N 10,80
		Found	C 58,87	H 5,96	N 10,80

Poly[1,4-dioxatetramethylenecarbonylimino-(1-phthalimidotrimethylene)iminocarbonyl] (**15d**): From 0,96 g of **5** and 0,318 g of 1,4-butanediol. Yield: 1,25 g (98%).

$(C_{17}H_{19}N_3O_6)_n$	$(361,3)_n$	Calc.	C 56,50	H 5,30	N 11,63
		Found	C 56,36	H 5,15	N 11,96

Conditions of preparation, yields, and values of η_{sp}/C of the other polyurethanes and of a poly(urea-urethane) (**17**) are given in Tab. 4.

Quantitative analysis of isocyanato groups

A standard solution of about 0,2 M dibutyl amine was prepared. An excessive amount of the standard amine solution was added to the benzene solution of the isocyanate. After stirring for 10 min, the mixture was titrated with a solution of 0,1 M $HClO_4$ in dioxane to determine the unreacted secondary amine. Methylred was used as indicater and a blank titration was made beforehand. The quantity of isocyanato groups was then calculated.

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