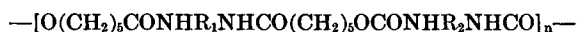


Synthesis of Alternating Polyamideurethans by Reacting Diisocyanates with N,N'-Di-(6-hydroxycaproyl)alkylenediamines and N-Hydroxyalkyl-6-hydroxycaproamide

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Synopsis

Polyamideurethans of structures I and II were prepared by reacting N,N'-di-(6-hydroxycaproyl)alkylenediamines and N-hydroxyalkyl-6-hydroxycaproamide with hexamethylene diisocyanate and 4,4'-diphenylmethane diisocyanate:



I

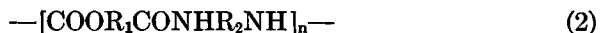
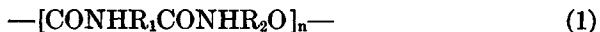


II

where R_1 is either a dimethylene or hexamethylene radical, and R_2 is a hexamethylene or 4,4'-diphenylmethane radical. Polymers I and II were of a high degree of polymerization and crystallinity, had high enough melting points for practical use, and gave colorless tough films both by dry and melt castings. The polymers from hexamethylene diisocyanate were much more crystalline and thermally more stable above the melting points than those from 4,4'-diphenylmethane diisocyanate. Polymerization conditions and characteristic properties of the resulting polymers were studied.

INTRODUCTION

There have been studies about regularly alternating copolyamideurethans like the structures (1),¹ (2)²⁻⁴ and (3)⁵⁻⁸:



Of interest in studying alternating polyamideurethan are the advantages which may be contributed by the combination of amide and urethan linkages and which may be quite different from those of block copolyamideurethans.⁹ On studying these contributions, three structural factors should be considered: (a) the direction of the linkages such as the difference of the

structures (1) and (2); (b) the number of amide and urethan linkages such as the difference between (1) or (2) and (3); and (c) the nature of R, i.e., whether alkylene or arylene, and whether even- or odd-numbered methylene.

The authors have prepared alternating polyamideurethans of structures (4) and (5) from the above point of view:



Polyamideurethan (4) has two amide linkages facing each other and two urethan linkages also facing each other in the repeating unit. Polyamideurethan (5) has one amide linkage and two facing urethan linkages. Polymer (4) may be provisionally named polydiamidediurethane and polymer (5), polyamidediurethan. The starting materials, i.e., ϵ -caprolactone, amines, and diisocyanates are all commercially available. Polymerizations were carried out by reacting either N,N'-di-(6-hydroxycaproyl)alkylenediamines or N-hydroxyalkyl-6-hydroxycaproamide with diisocyanates. Though there are some other methods, the diols were prepared by reacting ϵ -caprolactone with diamines and alkanolamine by the method of Rose and co-workers¹⁰ with additional modifications.

EXPERIMENTAL

Materials

ϵ -Caprolactone, bp 90°C/5 mm (supplied by Chisso Company, Limited), was fully dried over anhydrous sodium sulfate and distilled in a nitrogen atmosphere. Ethanolamine (bp 70°–73°C/3.5 mm), ethylenediamine (bp 116°–117°C), and hexamethylenediamine (bp 74°–75°C/4–5 mm) were treated with sodium hydroside and distilled in a nitrogen atmosphere. Hexamethylene diisocyanate (bp 114°C) and 4,4'-diphenylmethane diisocyanate (bp 155°–159°C/1.5–2 mm) (supplied by Nihon Polyurethane Company, Limited) were distilled in a nitrogen atmosphere. Acetonitrile (bp 81°–82°C) was dried over potassium carbonate and distilled in a nitrogen atmosphere. Distilled water was boiled again and cooled just before use. N,N'-Dimethylformamide (bp 74°–75°C/4–5 mm) with a small amount of 2,4-tolylene diisocyanate was distilled in a nitrogen atmosphere. Chlorobenzene (bp 130.5°–131.5°C) and *o*-dichlorobenzene (bp 34.5°–35.5°C/3 mm) were treated with calcium hydride and distilled in a nitrogen atmosphere. Di-*n*-butyltin dilaurate was fully dried.

N,N'-Di-(6-Hydroxycaproyl)alkylenediamines and N-Hydroxyalkyl-6-hydroxycaproamide

The preparations of the amide diols are based on the method by Rose and co-workers¹⁰ but with some modification. In the method the mixture of ϵ -caprolactone and a diamine or alkanolamine without solvent is heated at a rather high temperature for a rather long time, so that the resulting product becomes a bulky solid or viscous liquid, the latter of which also becomes a

bulky solid on cooling without agitation. Sometimes side products containing ester linkages are observed at higher temperatures. The authors tried a little modification by reaction in solution. Acetonitrile worked as a good solvent. Water was also used as solvent, based on the reaction of β -propiolactone with amines,^{11,12} but it was unsuccessful. A typical advantage using acetonitrile as solvent was that acetonitrile was itself a good recrystallization solvent. In some cases the resulting amide diol came out on cooling as a colorless powder which could be used for polymerization without further recrystallization with another solvent. In the other cases the amide diol remained in solution even after cooling. Acetonitrile was evaporated off from the solution to give a colorless powder, which was dissolved in hot acetonitrile for recrystallization to give the colorless amide diol powder. Another characteristic of the authors' method was that ϵ -caprolactone was added dropwise into the solution of an amine in acetonitrile during the whole reaction time. By this method side reactions like the formation of ester linkages by interchange reactions and a homopolymerization of ϵ -caprolactone were prevented, and acetonitrile and the unreacted ϵ -caprolactone could be recovered easily by fractional distillation without other volatile liquid.

In Table I are shown the results of the reactions of ϵ -caprolactone with ethanolamine, ethylenediamine, and hexamethylenediamine, which gave

TABLE I
Results of Reactions of ϵ -Caprolactone with Amines^a

Product	Amine, moles	CLn, moles	Solvent, ml	Reaction temp., °C	Reaction time	Yield, %
ECA	1.0	1.0	none ^b	100	16 hr	64.3
	0.5	0.5	AcCN 500	reflux	2 hr	50.8
	0.5	0.5	AcCN 500	0	2 hr	48.6
	0.3	0.3	H ₂ O	reflux	1 hr	0.0
CED	1.0	2.0	none ^b	100	30 min	70.0
	0.1	0.2	AcCN 100	reflux	30 min	54.0
	0.1	0.2	AcCN 100	0	2 hr	27.0
	0.2	0.2	AcCN 200	reflux	30 min	50.5
	0.2	0.2	AcCN 200	0	30 min	42.8
	0.5	0.5	H ₂ O 500	reflux	75 min	0.0
	0.2	0.2	H ₂ O 200	0	30 min	6.9
CHD	0.5	1.5	none ^b	100	18 hr	62.5
	0.1	0.2	AcCN 100	reflux	35 min	50.5
	0.1	0.2	AcCN 100	0	30 min	35.0
	0.2	0.2	AcCN 200	reflux	23 min	42.4
	0.2	0.2	AcCN 200	0	30 min	35.0
	0.2	0.2	H ₂ O 200	reflux	35 min	0.0
	0.1	0.1	H ₂ O 100	0	20 min	19.6

^a ECA = N-(2-Hydroxyethyl)-6-hydroxycaproamide; CED = N,N'-di-(6-hydroxycaproyl)ethylenediamine; CHD = N,N'-di-(6-hydroxycaproyl)hexamethylenediamine; CLn = ϵ -caprolactone; AcCN = acetonitrile.

^b By the method of Rose et al.¹⁰

TABLE II
Analytical Data of Amide Diols

Amide diol ^a	Elemental analysis, %						Melting point, °C		Molecular weight ^b	
	Calculated			Observed			Calcd.	Obsd.	Molecular weight ^b	
	C	H	N	C	H	N			Calcd.	Obsd.
ECA	54.84	9.78	7.99	55.16	9.97	8.12	73.5-75.1	175	176	
CED	58.31	9.79	9.71	58.33	9.90	9.90	156-157	288	292	
CHD	62.76	10.53	8.13	62.14	11.29	8.05	135-136	345	345	

^a ECA = N-(2-Hydroxyethyl)-6-hydroxycaproamide; CED = N,N'-di-(6-hydroxycaproyl)ethylenediamine; CHD = N,N'-di-(6-hydroxycaproyl)hexamethylenediamine.

^b Measured by freezing point depression in tertiary butanol.

N-(2-hydroxyethyl)-6-hydroxycaproamide (ECA), N,N'-di-(6-hydroxycaproyl)ethylenediamine (CED), and N,N'-di-(6-hydroxycaproyl)hexamethylenediamine (CHD), respectively. As an example, the synthetic procedure of N-(2-hydroxyethyl)-6-hydroxycaproamide is given as follows: In a 1-liter three-necked flask equipped with a stirrer, a dropping funnel with a nitrogen inlet, and a condenser with a nitrogen outlet was placed 30.6 g (0.5 mole) ethanolamine dissolved in 500 ml acetonitrile; 57.1 g (0.5 mole) ϵ -caprolactone was added dropwise from the dropping funnel in a nitrogen atmosphere into the amine solution, which was agitated and kept at refluxing temperature. In 2 hr all the ϵ -caprolactone was added, and acetonitrile was evaporated off under vacuum to give a colorless powder, which was recrystallized with acetonitrile. Yield, 58.0%, mp 73.5°–74.1°C. Typical analytical data of the resulting amide diols prepared by a similar method and used for polymerizations are given in Table II. The abbreviations ECA, CED, and CHD will be used hereafter. ECA may also be named CEA, for N-(6-hydroxycaproyl)ethanolamine, but ECA is better here to distinguish the amide diol (ECA) from the diamide diols (CED and CHD). The three amide diols showed typical IR absorptions in common at 3300–3350 cm^{-1} (νNH of amide + νOH of alcohol), 1640 cm^{-1} (amide I band), 1550 cm^{-1} (amide II band), and 1060–1065 cm^{-1} ($\nu\text{C—O}$ + δOH of alcohol) by the KBr tablet method.

Polymerization

All the polymerizations were carried out in a 200-ml three-necked flask equipped with a stirrer, a dropping funnel with a nitrogen inlet, and a condenser with a nitrogen outlet. Nitrogen was passed through the flask, which was then heated with a gas burner for complete drying. The flask was then cooled with passing nitrogen, and amide diol dissolved in solvent with or without catalyst was placed in the flask. The nitrogen stream was stopped, but the nitrogen pressure inside the flask was kept rather higher than the atmospheric pressure, using a mercury stopper. The content in the flask was stirred and heated at a constant temperature (25°–200°C). Diisocyanate was added to the flask by any one of three methods: (a) all diisocyanate was added directly at the beginning; (b) diisocyanate dissolved in solvent was added from the dropping funnel at the initial time; (c) after adding half the quantity of diisocyanate or its solution at the beginning, the remaining was added dropwise from the dropping funnel in x minutes.

After the polymerization, the resulting polymer was purified as follows: (i) when the polymer was dissolved in a solvent which was soluble in water, the solution was poured into the strongly agitated water in a high-speed mixer to give the polymer powder; (ii) when the polymer was dissolved in a solvent which was insoluble in water, the solution was poured into methanol for precipitation with strong agitation; and (iii) when the resultant polymer was a precipitate, the solvent was removed and the precipitate was dissolved in N,N'-dimethylformamide, the solution of which was poured into

strongly agitated water to give a precipitate. The resulting polyamide-urethan powder was dried under vacuum at 50°C for a few days until the weight of the polymer became constant.

Characterization of Polymers

Melting Point. A Yanagimoto (Japan) microscopic melting point apparatus Model MP-S2 equipped with a pair of crossed polaroids was used. The beginning and the end of the disappearing of the birefringence of the crystalline region of the polymers was observed in air.

Solution Viscosity. Inherent viscosity at 0.500 g/100 ml *m*-cresol was measured using a Ubbelohde viscometer at 30.00° ± 0.01°C.

Density. A density gradient tube with a carbon tetrachloride and benzene mixture was used for density measurement within ±0.0005 g/cm³ at 30.00° ± 0.01°C.

Infrared Analysis. A Shimadzu (Japan) IR spectrophotometer Model-27C was used with the KBr tablet method for polymer powder.

X-Ray Diffraction. Powder diagrams were obtained with a Cu-K α source using a Rigaku Denki (Japan) x-ray source Model D8, a goniometer Model SG7 and a recorder Model ECP-TS.

Thermal Gravimetric Analysis. Shimadzu automatic thermal gravimetric analyzer Model DT-2A was used to determine thermal decompositions of polymer powders in a nitrogen stream at a rate of temperature increase of 5°C/min.

Electrical Resistivity. A Toa Dempa (Japan) ohm meter Model SM-10 was used for the measurement of volume and surface inherent resistivities of films at 25°C and R.H. 65%.

RESULTS AND DISCUSSION

Polymerizability

Results of polymerizabilities and characteristic properties of the resulting polymers are shown in Tables III and IV. All polymers were soluble in *N,N'*-dimethylformamide (DMF) on polymerization, while insoluble in *o*-dichlorobenzene (DCB) and a mixture of *o*-dichlorobenzene and chlorobenzene (Mix), the former indicating homogeneous polymerization and the latter, heterogeneous polymerization. Hexamethylene diisocyanate (HMDI) reacted with any of the three amide diols, ECA, CED, and CHD, by both homogeneous and heterogeneous polymerizations to give polymers of high inherent viscosities. It may be concluded that generally high polymers were obtained from the initial monomer feeds having a 1:1.3 mole ratio of amide diol to diisocyanate on homogeneous polymerization and a 1:1.1 mole ratio on heterogeneous polymerization. From 4,4'-diphenylmethane diisocyanate (MDI) and amide diols, high polymers were obtained only by homogeneous polymerization, where the initial monomer feed was 1:1.3 mole ratio of amide diol to MDI. The reason why high polymers were not obtained by the heterogeneous polymerizations of amide diols with MDI

TABLE III
 Polymerizations of Amide Diols with Hexamethylene Diisocyanate (HMDI)^a

No.	Amide diol, mole/ml solvent	HMDI, mole/ml solvent	Method ^b	Bath temp. °C	Polym. time, min	Yield, %	mp, °C	η_{inh}
ECA								
1	0.010/15 DMF	0.010/none	A-N	110-120	75	59.8	128-137	0.22
2	0.010/15 DMF	0.010/10 DMF	B-T	110-120	90	64.3	140-148	0.31
3	0.010/25 DMF	0.010/none	A-N	160-165	90	64.5	135-144	0.14
4	0.010/20 DMF	0.013/none	A-T	110-120	75	98.8	136-147	0.49
5	0.020/70 Mix	0.020/30 Mix	C ₄₅ -T	140-145	60	83.7	139-148	0.41
6	0.010/35 Mix	0.011/20 Mix	C ₄₅ -T	150-155	60	77.8	140-148	0.73
7	0.020/70 Mix	0.021/30 Mix	C ₄₅ -T	155-160	60	75.4	142-153	0.78
8	0.010/35 Mix	0.011/20 Mix	C ₄₅ -N	155-160	60	51.6	140-157	0.25
CED								
9	0.010/10 DMF	0.010/10 DMF	B-N	130-140	60	72.4	192-195	0.18
10	0.010/10 DMF	0.010/10 DMF	B-T	130-140	60	74.8	182-189	0.27
11	0.010/25 DMF	0.013/5 DMF	B-T	145-155	60	99.1	192-204	0.73
12	0.010/35 DCB	0.010/20 DCB	C ₃₀ -T	175-180	90	60.0	208-212	0.34
13	0.010/35 DCB	0.011/20 DCB	C ₃₀ -T	185-190	90	80.6	200-214	0.46
CHD								
14	0.010/15 DMF	0.010/10 DMF	B-N	105-110	90	95.1	170-184	0.13
15	0.010/15 DMF	0.013/10 DMF	B-N	155-160	90	98.2	175-185	0.41
16	0.010/15 DMF	0.013/10 DMF	B-T	155-160	90	99.6	178-187	1.56
17	0.010/70 Mix	0.012/30 Mix	B-T	140-150	60	90.0	186-194	0.33
18	0.010/35 Mix	0.0115/20 Mix	C ₄₅ -T	155-165	90	83.8	178-190	0.31
19	0.010/40 DCB	0.0115/20 DCB	C ₄₅ -T	180-190	90	90.5	181-189	0.49
20	0.010/40 DCB	0.011/20 DCB	C ₃₀ -T	185-195	45	92.8	171-184	1.20

^a DCB = *o*-Dichlorobenzene; DMF = *N,N'*-dimethylformamide; Mix = mixture of *o*-dichlorobenzene and chlorobenzene 20:80.

^b N is without and T is with 0.011 g di-*n*-butyltin dilaurate per 0.01 mole amide diol.

TABLE IV
 Polymerizations of Amide Diol with 4,4'-Diphenylmethane Diisocyanate (MDI)^a

No.	Amide diol, mole/ml solvent	MDI, mole/ml solvent	Method ^b	Bath temp., °C	Polym. time, min	Yield, %	mp, °C	η_{inh}
ECA								
21	0.010/20 DMF	0.010/none	A-N	160-165	90	76.6	161-175	0.14
22	0.010/20 DMF	0.010/10 DMF	B-T	120-125	45	62.4	149-162	0.29
23	0.010/20 DMF	0.013/none	A-N	160-165	120	98.4	167-179	0.44
24	0.010/20 DMF	0.013/none	A-T	120-125	45	98.5	148-157	0.35
25	0.010/20 DMF	0.013/none	A-T	120-125	75	98.1	153-168	0.78
26	0.010/20 DMF	0.013/none	A-T	20-25	75	97.6	161-175	0.34
27	0.010/40 Mix	0.010/none	A-T	145-150	90	76.6	138-150	0.24
28	0.010/40 Mix	0.012/none	A-T	155-165	45	86.5	152-163	0.36
29	0.010/40 Mix	0.013/none	A-N	175-185	120	47.6	146-162	0.21
30	0.010/25 DCB	0.010/20 DCB	B-N	185-195	90	55.1	147-160	0.27
31	0.010/25 DCB	0.011/20 DCB	C ₈₀ -T	180-185	120	89.6	148-159	0.38
CED								
32	0.010/25 DMF	0.010/none	A-N	60-70	60	80.0	248-259	0.14
33	0.010/25 DMF	0.010/none	A-N	145-155	60	86.2	237-245	0.40
34	0.010/25 DMF	0.013/none	A-T	145-160	60	97.5	214-229	1.01
35	0.010/50 DCB	0.011/20 DCB	C ₈₀ -T	180-190	80	92.3	210-238	0.36
CHD								
36	0.010/10 DMF	0.010/10 DMF	B-N	130-135	30	87.9	215-224	0.30
37	0.010/10 DMF	0.011/10 DMF	B-N	130-140	30	89.0	220-230	0.31
38	0.010/50 DMF	0.010/none	A-N	125-130	120	71.3	195-205	0.22
39	0.010/10 DMF	0.010/10 DMF	B-T	135-140	90	84.0	213-227	0.29
40	0.010/25 DMF	0.013/none	A-N	110-120	30	98.2	200-213	0.65
41	0.010/25 DMF	0.013/none	A-T	125-135	30	98.3	197-215	1.13
42	0.010/50 DCB	0.011/none	A-T	185-195	60	93.4	200-214	0.34
43	0.010/50 DCB	0.013/none	A-T	185-195	60	95.1	201-213	0.32

^a Abbreviations are the same as those footnoted in Table III.

is that the resulting polymers undergo some thermal decompositions at higher temperatures on heterogeneous polymerization. Monomers were soluble in DMF at lower temperatures, but higher temperatures were necessary to dissolve monomers in DCB and the mixture of DCB and chlorobenzene. As will be described later, polymers from HMDI were thermally more stable than those from MDI, so that high polymers were obtained from HMDI both by homogeneous and heterogeneous polymerizations. No high polymers were obtained from the initial monomer feed of 1:1 mole ratio of amide diol to diisocyanate. Though not listed in the tables, polymerizations without solvent gave crosslinked polymers in most cases. Di-*n*-butyltin dilaurate worked as a good catalyst; 45 min to 2 hr were enough time for polymerization. Further polymerization time and addition of diisocyanate caused crosslinking of the resulting polymers in most cases. The preferred polymerization temperatures were 100°–160°C on homogeneous polymerization and 140°–200°C on heterogeneous polymerization.

Melting Point

The melting points of the resulting polymers on classifying them into those from MDI and those from HMDI, are of the following order:



In the case of either MDI or HMDI, the order becomes:



which is interestingly consistent with the order of the melting points of the amide diols. On evaluating the melting points of polymethylene heteropolymers, Korshak-Phrynze's equation¹³ useful:

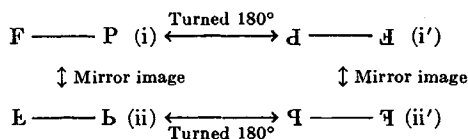
$$y = ax + 110 \quad (6)$$

wherein y is the melting point of the heteropolymer, x is the ratio multiplied by 100 of the number of heterolinkages over the number of methylene linkages, and a is a characteristic constant common to a heteropolymer series. We calculated Korshak-Phrynze's constants of polymers from amide diols and HMDI, newly calculating those of polyamides, polyurethanes and other polyamideurethans by further data, as Korshak-Phrynze's data do not offer enough detail for the present discussion. Korshak-Phrynze's constants of our polyamideurethans are in the order



It should be noted that poly(HMDI-CED) and poly(HMDI-CHD) have high constants almost equal to that of the poly- ω -aminoacid of odd-numbered methylenes and of the polyamide of odd-odd-numbered methylenes, while poly(HMDI-ECA) has the lowest constant of all, being lower than those of polyurethanes. The higher values of Korshak-Phrynze's constants of the polyamides are due to hydrogen bonding, and the lower values of

those of the polyurethanes are due to mobile oxa-linkages. Since the melting point is given as the ratio of enthalpy of fusion over entropy, though both polyamide and polyurethan have hydrogen bonding, polyamide has a higher melting point because of smaller entropy, while polyurethan has a lower melting point because of the bigger entropy due to the mobile oxa-linkages. When there are deficiencies of hydrogen bonding, enthalpy decreases and entropy increases to give a lower melting point. When a polymer of the repeat unit F—P forms sheets of hydrogen bonding networks, there should be four ways:



where (i)–(i), (ii'), (i)–(i)–(ii), and (i)–(ii'). There are four kinds of resulting hydrogen bonding networks: (A) in which the >C=O—HN< bondings are arranged in the same direction forming a planar zig-zag sheet without any deficiency of hydrogen bonding; (B) in which the >C=O—HN< bondings are arranged alternately up and down forming a planar zig-zag sheet without any deficiency of hydrogen bonding; (a) in which the >C=O—HN< bondings are arranged in the same direction to form either a planar zig-zag sheet with deficiencies of hydrogen bonding or a distorted sheet without deficiencies of hydrogen bonding; and (b) in which the >C=O—HN< bondings are arranged alternately up and down to form either a planar zig-zag sheet with deficiencies of hydrogen bonding or a distorted sheet without deficiencies of hydrogen bonding.

The thus far described types of hydrogen bondings and Korshak-Phrynze's constants are given in Table V. It should be noted that poly-(HMDI-ECA) cannot be expressed by a simple structure (5), for the starting monomer ECA is an asymmetric structure. Let us name one hydroxyl group H and the other, h, and each of the two isocyanate groups I; then the resulting poly(HMDI-ECA) contains either of the repeating units, HhII or HhIIhHII. As the reactivity of the each hydroxyl group of the two is not selective, both HhII and HhIIhHII linkages will be formed. According to Table VI, it may be concluded that Korshak-Phrynze's constants of polymers containing the same kinds of heterolinkages decrease their values in the following order related by the types of hydrogen bonding:

$$2A + 2B > 2A + 2(a + b) \quad (7)$$

$$4A + 4b > 4(a + b) \quad (8)$$

$$A + B > 2B + 2a \quad (9)$$

$$2A + 2b > 4(a + b) > 2(a + b) \quad (10)$$

Thus, $A > B > a$ and/or b .

TABLE V
Hydrogen Bonding Types and Korshak-Phrynze's Constants of Polyamideurethans Compared with Those of Polyamides and Polyurethans

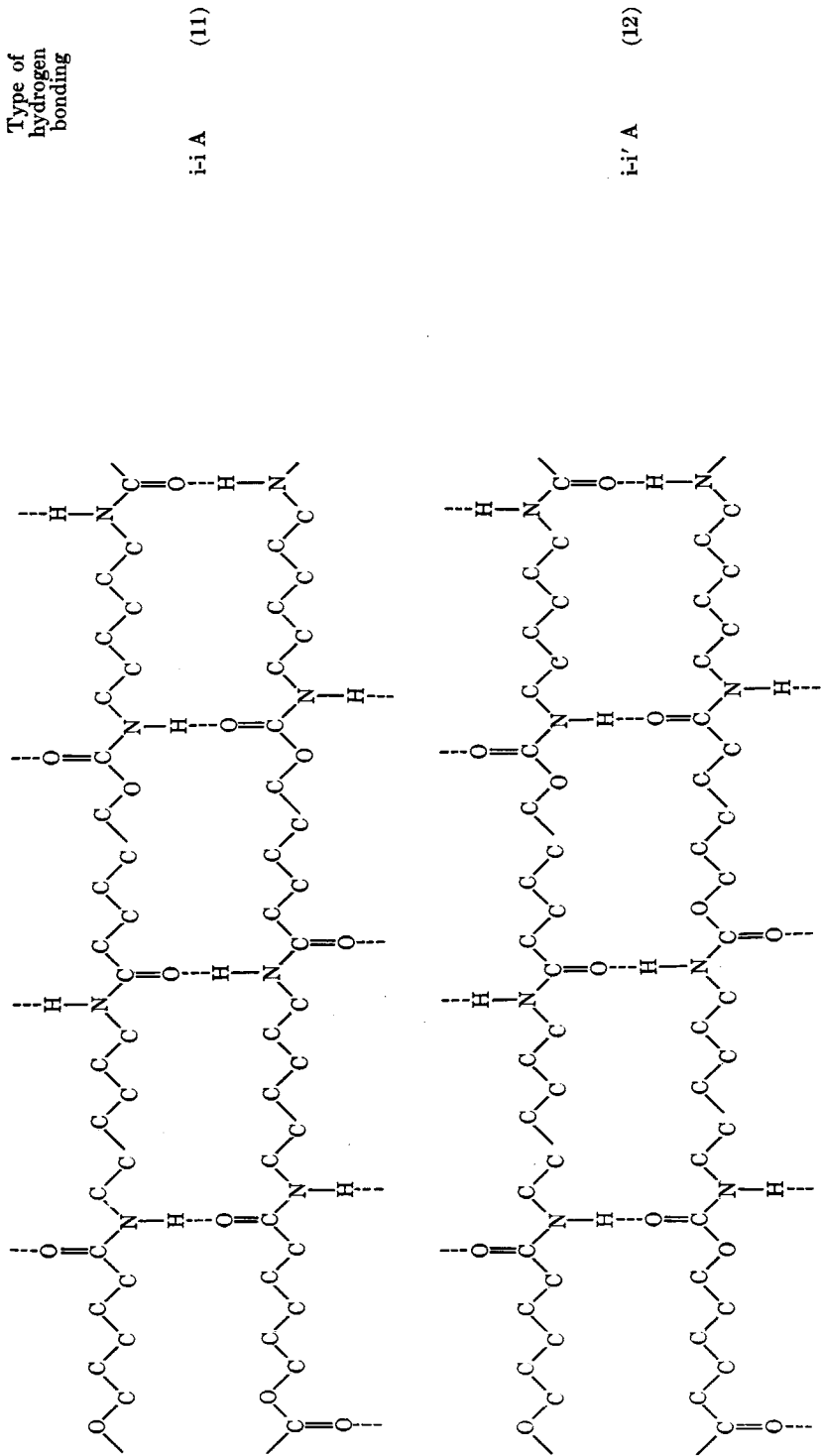
Polymers ^a	i-i	i-i'	i-ii	i-ii'	a ^b	Order of a	Crystal repeat- ing unit
HMDI-ECA	a + b	B + a + b	a + b	B + a + b	1.6 ± 0.5	1	2
HhII Type	a + b	a + b	a + b	a + b			1
HhIhII Type	A + a	A + a	B	B	4.2 ± 0.6	2	1
HMDI-CED	A	A	B	B	4.9 ± 0.4	1	1
HMDI-CHD							
—[COO(CH ₂) ₈ CONH(CH ₂) ₈ NH] _n — ⁴	a + b	a + b	a + b	a + b	2.7 ± 0.7	2	2
HhII Type	a + b	a + b	a + b	a + b			1
HhIhII Type	A	A	b	b	3.60	1	1
—[COO(CH ₂) ₆ CONH- (CH ₂) ₂ NH] _n — ^{2,3}	A	A	b	b			1
HhII Type	A	A	no	B	7.1 ± 0.2	1	1
HhIhI Type	A	A	a	B	5.1 ± 0.9	2	2
—[NH(CH ₂) ₆ CO] _n — ¹⁴	A	A	no	B			1
p = even	a	B	a	B			2
p = odd							
—[CO(CH ₂) ₆ CONH(CH ₂) ₄ NH] _n — ¹⁴	A	A	b(B)	b(B)	7 ± 1 (7)	1	1
p = even, q = even ^c	a + b	a + b	a + b	a + b	5.7 ± 0.7 (5.6)	2	2
p = even, q = odd	a + b	a + b	a + b	a + b	5.5 ± 0.7	2	2
p = odd, q = even	a + b(B + a)	no	no	a + b(B + a)	4.7 ± 0.6 (4.5)	3	1
p = odd, q = odd ^c							
—[CONH(CH ₂) ₆ NHCOO(CH ₂) ₄ O] _n —	A	A	b(B)	b(B)	3.2 ± 0.3	1	1
p = even, q = even ^d	a + b	a + b	a + b	a + b	2.5 ± 0.3	2	2
p = even, q = odd	a + b	a + b	a + b	a + b	2.4 ± 0.6	2	2
p = odd, q = even	a + b(B + a)	no	no	a + b(B + a)		(3)	1
p = odd, q = odd ^d							

^a Calculated from the data of the indicated references.

^b Data in parentheses are by Korshak-Phrynze.¹³

^c At p = q, the hydrogen bonding types become those in parentheses.

^d At q = p - 2, the hydrogen bonding types become those in parentheses.



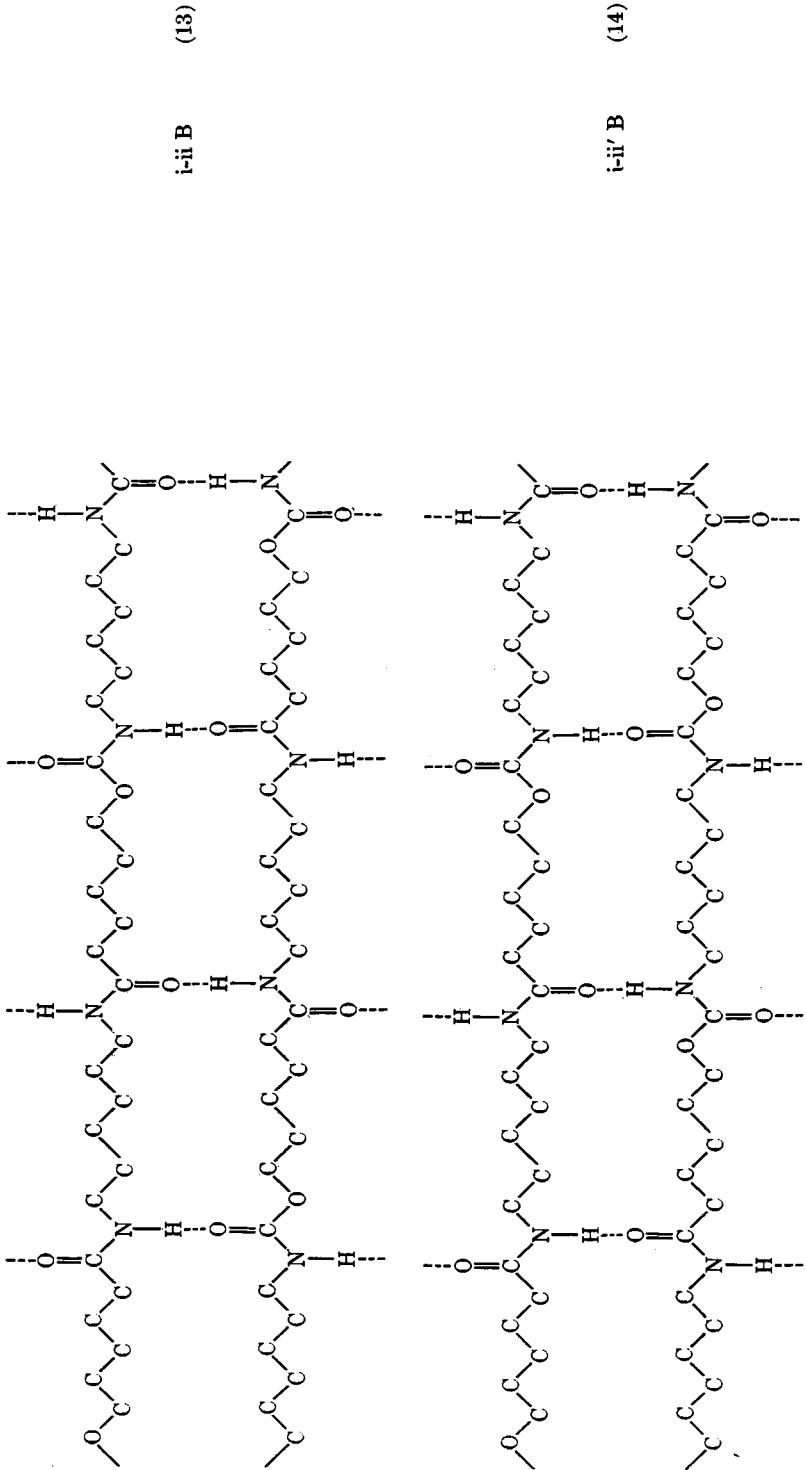


Fig. 1. Possible hydrogen bonding of poly(HMDI-CHD).

The highest a value of poly(HMDI-CHD) among polyamideurethans is due to the complete hydrogen bondings without any deficiency at any chances, as shown in Figure 1 in structures (11)–(14), which were formed by the high symmetry of the molecule that was quite rare of polymers in the past. The two A-type structures, (11) and (12), or the B-type structures, (13) and (14), each are mutually different in relation to the positions of the oxa-linkages. Poly(HMDI-CED) has the second-high a value because the A-type hydrogen bonding slightly lowered due to the a and b types.

The polyamideurethan of structure (2) wherein $R_1 = -(\text{CH}_2)_6-$ and $R_2 = -(\text{CH}_2)_2-$ has the middle a value. It has the same type of hydrogen bonding as that of polyurethan of even-even numbered methylenes. Though it has randomly configured HhII and HhIIhHII units, both are isomorphous, so that the value is a little higher than that of the corresponding polyurethan because of the contribution of the amide linkages. The polyamideurethan of the structure (2) wherein $R_1 = -(\text{CH}_2)_2-$ and $R_2 = -(\text{CH}_2)_6-$ has a lower a value. It has the same types of hydrogen bonding as those of the polyurethans of even-odd- and odd-even-numbered methylenes. Though it has randomly configured HhII and HhIIhHII units, both are isomorphous, so that the a value is a little higher than that of the corresponding polyurethans because of the contribution of the amide linkages. Poly(HMDI-ECA) has the lowest a value due to the random configurations of the HhII and HhIIhHII units which are mutually not isomorphous, and due to the smaller ratio of the number of amide linkages over the number of urethan linkages among the other polyamideurethans thus far discussed, though it may have B-type hydrogen bonding. Among the polyamideurethans of structures (2), (4), and (5), structure (4) has the highest melting point, structure (2) is next, and (5) is last.

Thermal Stability

As shown in Figures 2 and 3, and in Table VI, polyamideurethans from HMDI are thermally much more stable than those from MDI. The big differences over 100°C between the decomposition temperatures and melting points of the polymers from HMDI allowed melt castings of films to be made. It is notable that these polyamideurethans from HMDI have far

TABLE VI
Initiating Temperatures of Thermal Decomposition of
Polyamideurethans in a Nitrogen Stream

Polymer (sample no.) ^a	Decomp.		Polymer (sample no.)	Decomp.	
	temp. °C	temp. mp, °C		temp., °C	temp. mp, °C
HMDI-ECA (7)	275	122	MDI-ECA (25)	200	32
HMDI-CED (11)	305	101	MDI-CED (34)	230	1
HMDI-CHD (20)	305	121	MDI-CHD (41)	230	15

^a The sample number refers to the number in Tables III and IV.

higher decomposition temperatures than those of the usual polyurethans and also of some polyamideurethans; e.g., polyamideurethans of structure (3) decompose at 220°–40°C (from hydroxyethyl- or hydroxypropylamides of dibasic acids and 2,4-tolylene diisocyanate) and at 220° and 260°C (from HMDI or 2,4-tolylene diisocyanate and dipropylamides of dibasic acids),^{7,8}

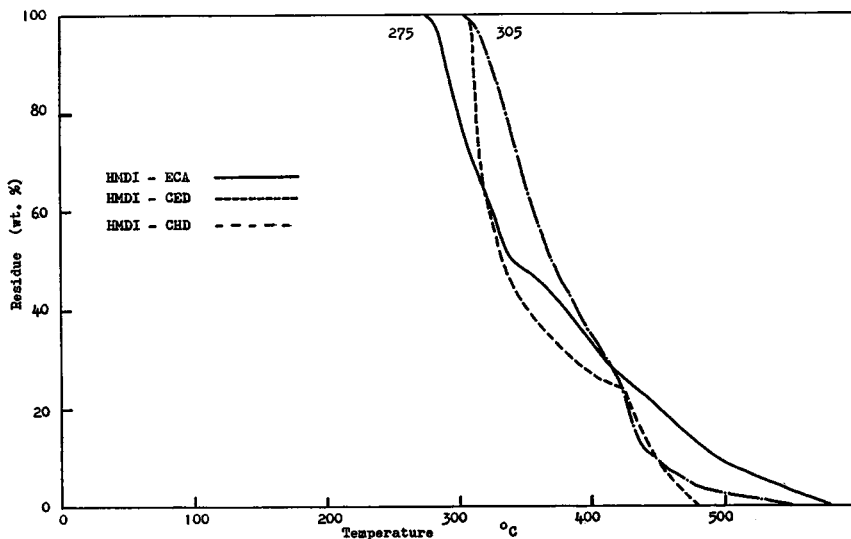


Fig. 2. Thermal decomposition curves of polyamideurethans from HMDI. Rate of temperature increase, 5°C/min.

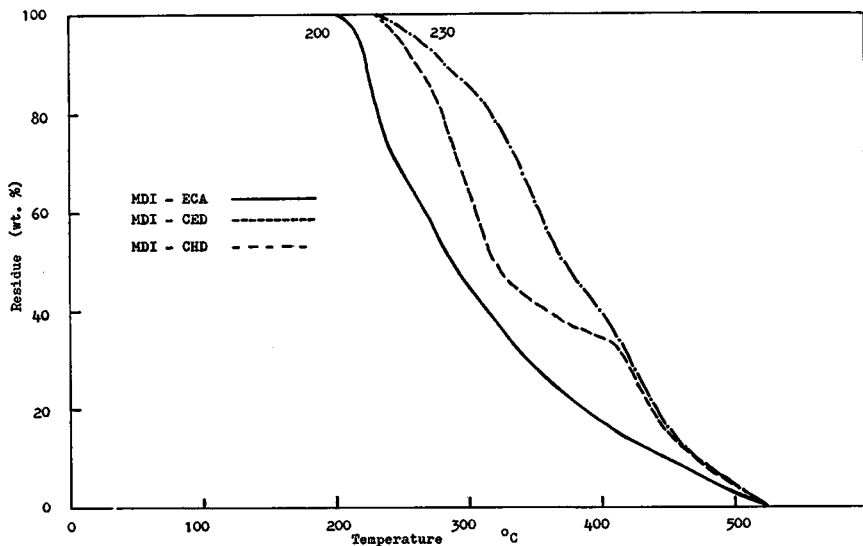


Fig. 3. Thermal decomposition curves of polyamideurethans from MDI. Rate of temperature increase, 5°C/min.

and the polyurethan from HMDI and 1,4-butanediol at 220°C.¹⁵ Polyamideurethans from MDI have decomposition temperatures just like those of most commercial polyurethans, so that castings of films from solution are preferred in this case. It was necessary to use aromatic diisocyanates to prepare polyurethans for practical use in order to obtain higher melting points, though the resulting polymers were thermally rather unstable, with few exceptions (the polyurethan from HMDI, for example, known as Igamid U).

The polyamideurethans are successfully utilizing aliphatic diisocyanate for practical use. It is also remarkable that the ethylenediamine and ethanolamine units in these polyamideurethans are very stable. Practical use of these monomers for polyamides, polyurethanureas, etc. has been mostly unsuccessful, mainly because high polymers were not obtained, coloration and decompositions took place, or the resulting polymers were thermally unstable.

Solubility

As shown in Table VII, polyamideurethans are soluble in formic acid, *m*-cresol, DMF, and DMSO, each of which is a solvent of either or both of polyamides and polyurethans. It is notable that these polyamideurethans, compared with random heterocopolymers, are very resistant to the usual common solvents and that glycols which can dissolve many polyamides and some polyurethans do not dissolve these polyamideurethans. The solubility of poly(HMDI-ECA) in methanol may be explained from its configuration discussed in the section on melting point. Films could be formed from solutions of *m*-cresol or formic acid of polymers by evaporation of the solvent. Tough films which could be drawn were obtained from polymers of inherent viscosity over 0.6. Films from polymers from HMDI were semi-transparent, while those from MDI were completely transparent. This is because of the higher crystallinities of the former and the lower crystallinities of the latter.

TABLE VII
Solubilities of Polyamideurethans^a

Polymer	HCOOH	<i>m</i> -Cresol	DMF	DMSO	Meth- anol	Ethylene glycol	Others ^b
HMDI-ECA	4	3	2	2	2	1	0
HMDI-CED	4	3	2	2	1	0	0
HMDI-CHD	4	3	2	2	1	0	0
MDI-ECA	2	3	2	2	0	0	0
MDI-CED	4	3	2	2	0	0	0
MDI-CHD	4	3	2	2	0	0	0

^a 0 = Insoluble; 1 = swells or partially soluble when hot; 2 = soluble when hot, but reprecipitates on cooling; 3 = soluble when hot, and keeps solution state even after cooling; 4 = soluble even when cold.

^b Acetone, ether, chloroform, benzene, chlorobenzene, dichlorobenzene, and water.

Density

As shown in Table VIII, densities of polyamideurethans are higher than those of polyamides, and some are near to or a little higher than those of polyurethans, e.g., nylons 6 and 66 are of density 1.14, polyurethan from HMDI and 1,4-butanediol (e.g., Igamid U or Perlon U) have densities of 1.20–1.21, etc.¹⁶ The smaller density of poly(HMDI-CHD) compared with those of poly(HMDI-ECA) and poly(HMDI-CED) may probably be due to the smaller ratio of the number of heteroatoms per number of methylenes of the former. This ratio has no effect on the densities of polymers from MDI since the bulky 4,4'-diphenylmethane radical plays a main role. The lower density of poly(MDI-ECA) compared with those of poly(MDI-CED) and poly(MDI-CHD) is probably due to the reason discussed in the section on melting point, i.e., random configuration and unstable hydrogen bonding.

TABLE VIII
Densities of Polyamideurethans

Polymer (sample no.) ^a	Density	Polymer (sample no.) ^a	Density
HMDI-ECA (7)	1.223	MDI-ECA (25)	1.163
HMDI-CED (11)	1.218	MDI-CED (34)	1.269
HMDI-CHD (20)	1.174	MDI-CHD (41)	1.219

^a The sample number refers to the number in Tables III and IV.

Electrical Resistivity

As shown in Table IX, resistivities of polyamideurethans from MDI are higher than those from HMDI. The volume-inherent resistivities (ρ) and surface-inherent resistivities (σ) of polyamides and polyurethans are, for examples, as follows:¹⁶ nylon 66, $\rho = 10^{12-15}$, $\sigma = 10^{-13}$; nylon 6, $\rho = 10^{10-12}$, $\sigma = 10^{12}$; polyurethans: Durethan U₀, $\rho = 10^{14-15}$, $\sigma = 8 \cdot 10^{13}$; Durethan U₂₀, $\rho = 10^{14}$, $\sigma = 2 \cdot 10^{13}$, in units of ohms/cm (ρ) and ohms(σ). In comparison with the resistivities of these polyamides and urethans, the resistivities of polyamideurethans are rather high. The higher surface resistivities of polyamideurethans and the almost equal values of the surface- and volume-inherent resistivities should be emphasized. The high resistivities point to the use of polyamideurethans as good insulators.

TABLE IX
Electrical Resistivities of Polyamideurethans^a

Polymers (sample no.) ^b			Polymers (sample no.) ^b		
	ohms/cm	σ , ohms		ρ , ohms/cm	σ , ohms
HMDI-ECA (7)	$4.7 \cdot 10^{13}$	$1.9 \cdot 10^{14}$	MDI-ECA (25)	$9.0 \cdot 10^{16}$	$1.1 \cdot 10^{16}$
HMDI-CED (11)	$5.2 \cdot 10^{14}$	$3.6 \cdot 10^{14}$	MDI-CED (34)	$1.1 \cdot 10^{15}$	$3.2 \cdot 10^{15}$
HMDI-CHD (20)	$1.6 \cdot 10^{15}$	$6.0 \cdot 10^{15}$	MDI-CHD (41)	$6.2 \cdot 10^{16}$	$4.1 \cdot 10^{16}$

^a Films prepared from *m*-cresol solutions at 100°C under vacuum, evaporating off *m*-cresol, and kept at 25°C, R.H. 65% for seven days.

^b The sample number refers to the number in Table III and IV.

Infrared and X-Ray Diffraction

As shown in Figure 4, polyamideurethans from HMDI have characteristic IR absorptions at 3300 cm^{-1} , $3050\text{--}3100\text{ cm}^{-1}$ (νNH of amide and urethan linkages which are hydrogen bonded), $1690\text{--}1695\text{ cm}^{-1}$ ($\nu\text{C=O}$ of urethan

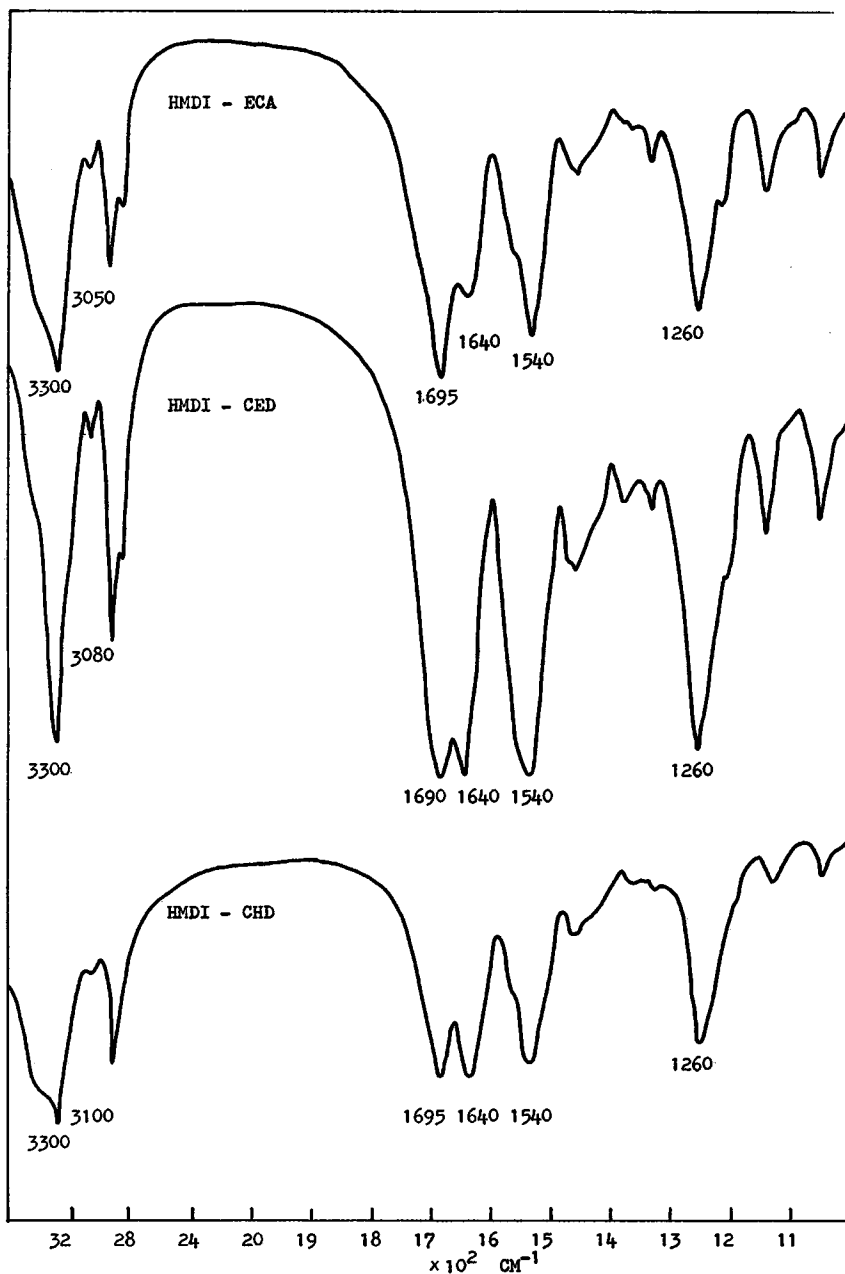


Fig. 4. IR spectra of polyamideurethans from HMDI.

linkage), 1640 cm^{-1} ($\nu\text{C}=\text{O}$ of amide linkage), 1540 cm^{-1} ($\delta\text{NH} + \nu\text{CN}$ of amide and urethan linkages), and 1260 cm^{-1} ($\nu\text{C}-\text{O}$ of urethan linkage).

Polyamideurethans from MDI (Fig. 5) have IR absorptions at 3280-

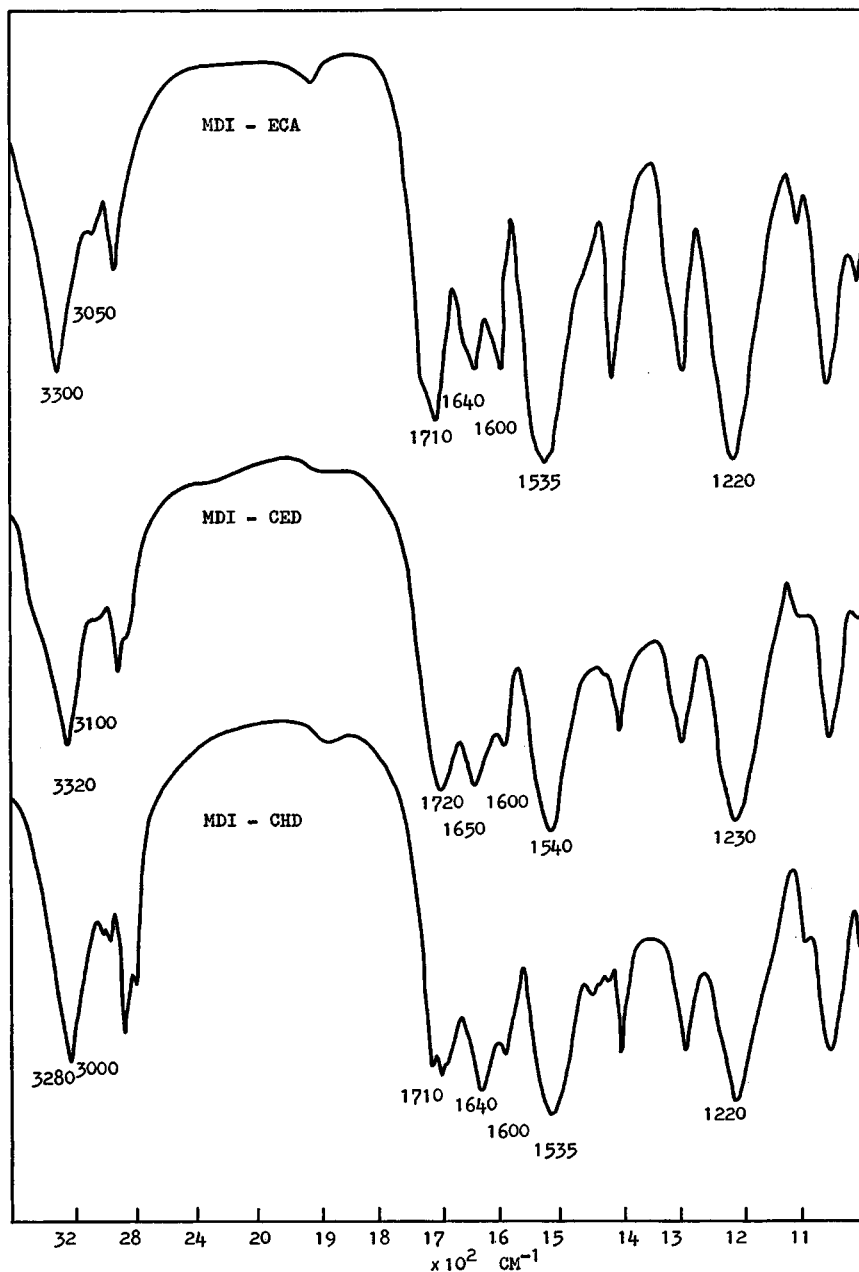


Fig. 5. IR spectra of polyamideurethans from MDI.

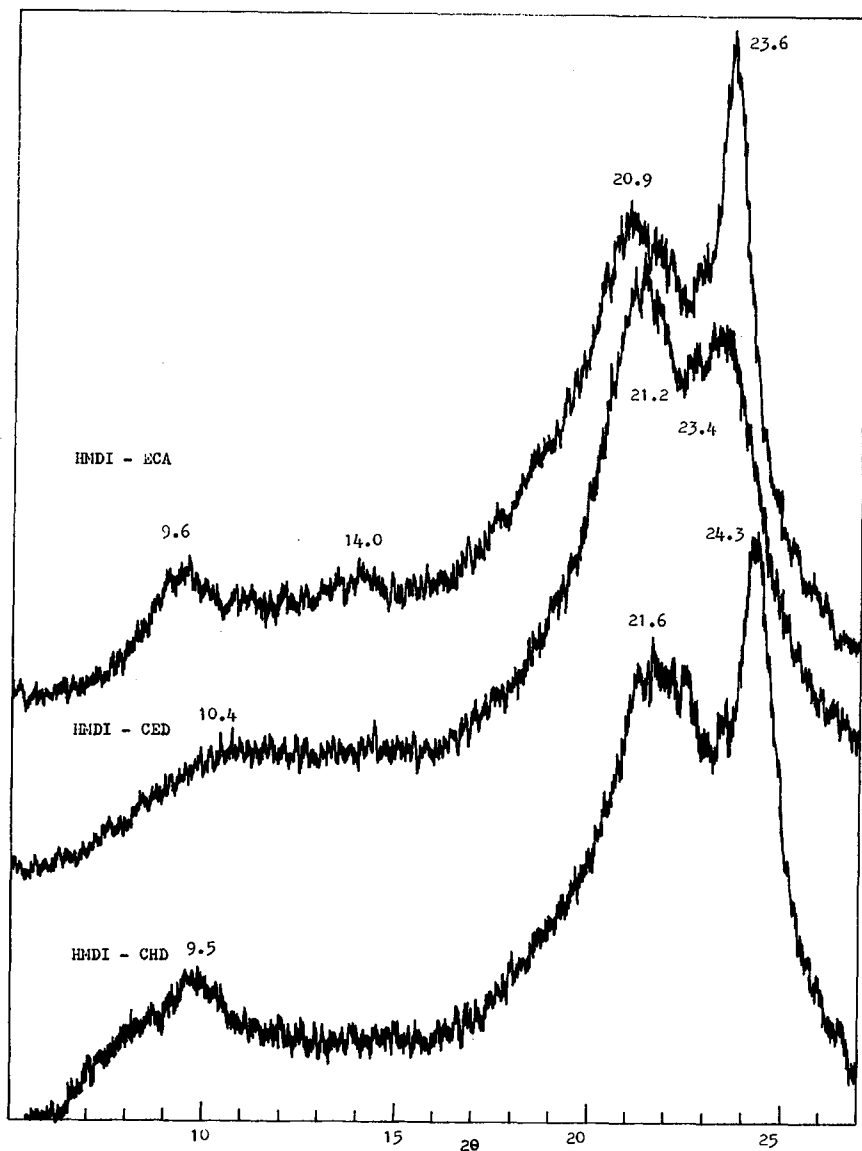


Fig. 6. X-Ray diffraction patterns of films of polyamideurethans from HMDI. The films listed are those in Table IX.

3320, 3000–3100 (νNH of amide and urethan linkages which are hydrogen bonded), 1710–1720 ($\nu\text{C}=\text{O}$ of urethan linkage), 1640–1650 ($\nu\text{C}=\text{O}$ of amide linkage), 1600 ($\nu\text{C}=\text{C}$ of phenyl group), 1535–1540 ($\delta\text{NH} + \nu\text{CN}$ of amide and urethan linkages), and 1220–1230 cm^{-1} ($\nu\text{C}-\text{O}$ of urethan linkage). The intensities of the amide I band ($\nu\text{C}=\text{O}$) of polyamideurethan from ECA are about half of those of the urethan I band ($\nu\text{C}=\text{O}$), while those of polyamideurethans from CED and CHD are of equal intensities.

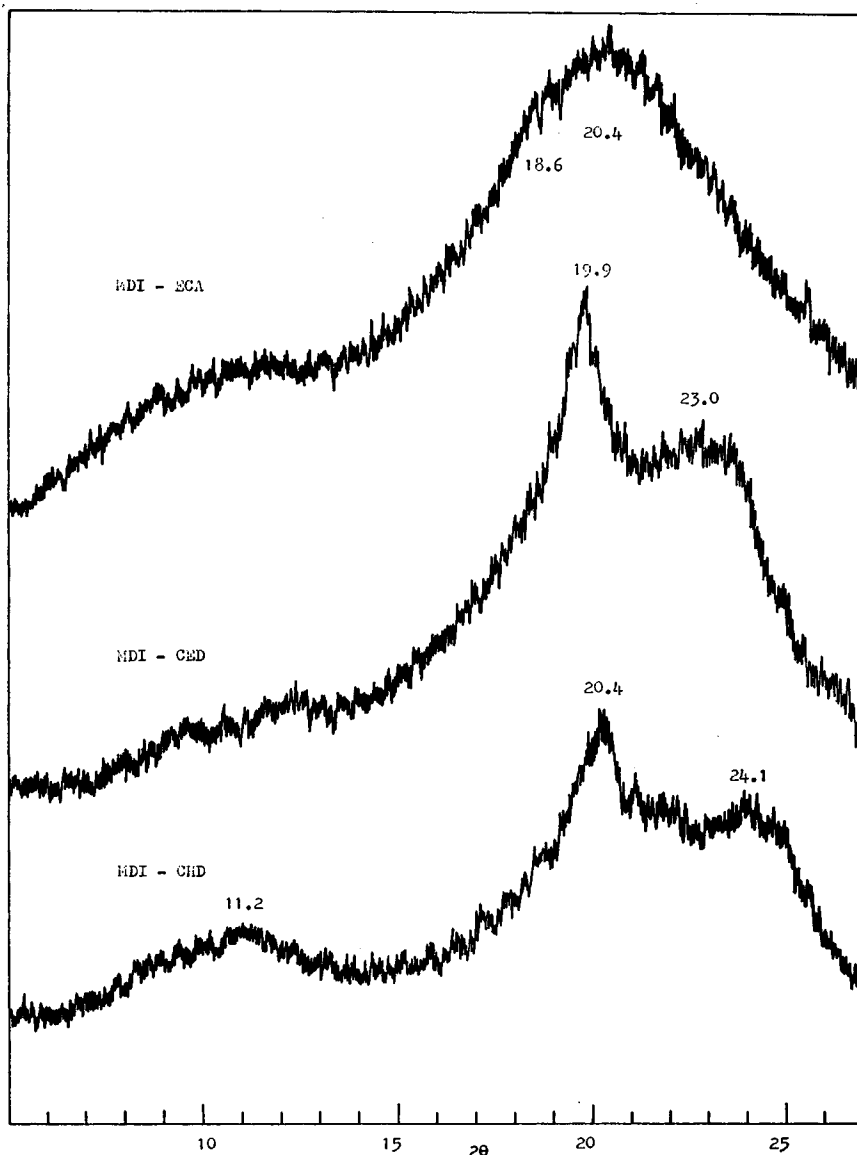


Fig. 7. X-Ray diffraction patterns of films of polyamideurethans from MDI. The films are those listed in Table IX.

This shows the ratios of the number of amide linkages over the number of urethan linkages, namely, 0.5 for the former polymer and 1 for the latter. The urethan I band of the aromatic urethan linkage is shifted to a higher wavenumber by a resonance, and so the C—O band is lowered. Amide II and urethan II bands are overlapping. As shown in Figures 6 and 7, polyamideurethans from HMDI are much more crystalline than those from MDI, which corresponds to the semitransparent films of the former and the

completely transparent films of the latter. The A and B types of hydrogen bonding can form both α and β forms^{17,18} of crystal structures, and a and b types of hydrogen bonding can form either α and β forms with deficiencies of hydrogen bonding or γ forms¹⁹ without deficiencies of hydrogen bonding. The stability of each form is in the order $\alpha > \beta > \gamma$ in polyamides, but Perlon U has a stable β form.²⁰ Poly(HMDI-ECA) is of the type of nylon 6, poly(HMDI-CED) is of the type of nylon 66, and poly(HMDI-CHD) may be either of the type of Perlon U or nylon 97 ($p = q = 7$). Based on these assumptions, the fiber axis identity distance of each polyamideurethan was calculated as follows: poly(HMDI-ECA), 50.6–51.0 Å; poly(HMDI-CED), 33.5–34.0 Å and 37.2 Å(?). The first two values are about equivalent to the fully extended planar zig-zag structures, but the last value is not realistic. Detailed x-ray studies will be reported in another paper.

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