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Interfacial Polycondensation. XI. Ordered Copolymers*

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INTRODUCTION

The term "order" as applied to copolymers refers to the arrangement of the components along the polymer chain. This arrangement may vary from an alternating structure, —ABABABABAB—, through a completely random distribution, —ABAAABBABBBAABAABBAAAB—, to that of a more or less ordered or block arrangement involving large sections of the two homopolymers, AAAAAAAAAAABBBBBBBB. The arrangement of these components in the polymer chain leads to differences in the physical properties of the copolymers. These differences have been demonstrated in block and graft copolymers.

In general, melt polymerization methods yield condensation copolymers with random distribution. Only by the use of special techniques such as melt blending,[1] or by using macrodifunctional intermediates containing noninterchangeable groups (such as the polyethylene glycols),[2] have condensation copolymers having essentially an ordered or block arrangement been prepared.

In contrast, the method of interfacial polycondensation[3] could yield condensation copolymers ranging in order from alternating to block arrangements, since no redistribution of groups would take place because of the low polymerization temperature. Thus, the interfacial polycondensation method should permit a more complete study of the effect or order on the properties of a condensation copolymer.

DISCUSSION

The development of interfacial polycondensation[3] has opened a new dimension in condensation copolymers by allowing a greater control over the arrangement of the components along the polymer chain. Interfacial polycondensation utilizes a fast, irreversible reaction of two fast-reacting intermediates in a two-phase system. By use of three intermediates, as shown below, copolymers can be prepared. The type

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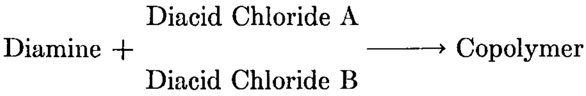
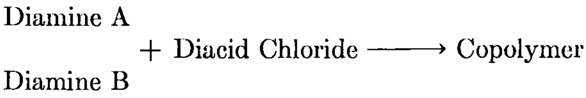
of order developed in the resulting condensation copolymers is determined by factors such as relative reaction rates, partition coefficients, and the manner in which the reactants are mixed.

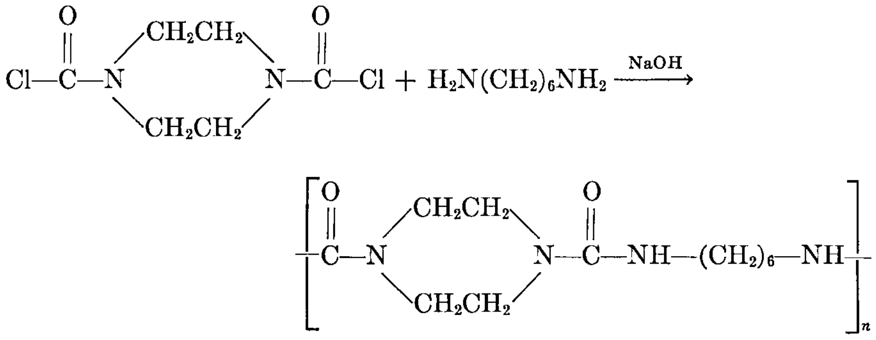


$$\text{Diamine} + \begin{matrix}\text{Diacid Chloride A}\\ \text{Diacid Chloride B}\end{matrix} \longrightarrow \text{Copolymer}$$

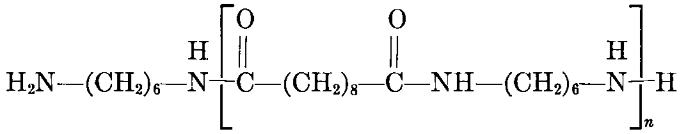


$$\begin{matrix}\text{Diamine A}\\ \text{Diamine B}\end{matrix} + \text{Diacid Chloride} \longrightarrow \text{Copolymer}$$

Since the interfacial polycondensation is carried out at low temperatures at which redistribution of groups does not occur, difunctional intermediates which contain preformed condensation linkage may be used. These intermediates would retain their configuration in the final copolymer. For example, the interfacial polycondensation of 1,4-piperazinedicarbonyl chloride with hexamethylenediamine would yield an alternating copolyurea.



Also, high molecular weight difunctional intermediates, such as an amine-ended poly(hexamethylene sebacamide), which contains many preformed condensation linkages, could be used.



$$H_2N-(CH_2)_6-\overset{H}{N}-\left[\overset{\overset{O}{\|}}{C}-(CH_2)_8-\overset{\overset{O}{\|}}{C}-NH-(CH_2)_6-\overset{H}{N}\right]_n-H$$

This latter type of copolymer preparation gives absolute control over the final order since there is just one diacid chloride and one diamine. However, this method will yield only copolymers with an alternating order.

The first type of copolymer preparation will yield copolymers possessing a distribution of components varying from random to ordered, involving large blocks of homopolymer, or even a physical mixture of the two homopolymers.

For example, in the interfacial polycondensation of two diacid chlorides with one diamine, the resulting copolymer would be essentially randomly arranged if the two diacid chlorides had similar reaction rates and were added together to the interfacial polycondensation. The same would apply to the interfacial polycondensation of one diacid chloride with two diamines possessing similar reaction rates, relative basicities, and partition coefficients. However, these factors are seldom equivalent, and the differences may be even further exaggerated. For example, the addition of one reactant prior to the other would allow the buildup of macrosegments of homopolymer. The addition of the second reactant would then give essentially block-type copolymers. However, if the reactants vary too much in reactivity, or one homopolymer is extremely insoluble and therefore precipitates from the reaction zone, a physical mixture of two homopolymers might result.

For such a copolymer system to be studied in detail, the copolymer must be such that one may determine (1) whether a mixture or a true copolymer exists, (2) the ratio of the two polymer units in the final copolymer, and (3) the arrangement of the components along the polymer chain. Where two diacid chlorides are used, their starting ratio would give only an approximate answer for their ratio in the final copolymer since yields are seldom 100%. The ratio of the two polymer units in the copolymer and whether a mixture or a true copolymer was formed must be determined from the product. There are two possible means of determining the arrangement of units along the polymer chain. One is to degrade the polymer selectively and study the resulting fragments. This is often not a desirable method, since selective cleavage of one type of linkage is not always possible. Also, separation of the resulting fragments could be difficult. A second method of determining the order of the copolymer is to study its mechanism of formation and the intermediates involved in the reaction. While the absolute order cannot be determined by this method, this information, combined with the directional "crystallinity"* (i.e., directional lattice order) as measured by x-ray diffraction patterns[4] can give an insight into the probable arrangement of groups along the polymer chain. This latter method was used in this study.

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* Polymeric crystals may show a normal three-dimensional lattice order, or crystallinity, or only a two-dimensional crystallinity which varies in its direction. Directional crystallinity in an unoriented polymer sample can be studied if an x-ray diffraction pattern of a crystalline, oriented fiber or film of this polymer is available. Each diffraction spot in this oriented pattern can be assigned a direction with respect to the molecular chain axis, assuming that the oriented molecules are aligned parallel to the fiber axis. Now, the rings in the unoriented polymer pattern can be related to these oriented diffraction spots; this provides an assignment of each ring to a molecular chain direction in the crystal.

The presence of lateral crystallinity or lateral lattice order is indicated by sharp diffraction in the pattern, due only to chain-to-chain regularity or lattice order; there is no sharp or discrete diffraction present to indicate regularity or lattice order in the chain direction. This means that the chains are regularly spaced apart but are not in registry along their lengths, as sketched in Figure 1A. (The circles are crystallographically equivalent diffraction centers.)

The reverse is found for longitudinal crystallinity or longitudinal lattice order. The chains are in registry along their lengths but are randomized in their placement apart, as sketched in Figure 1B.

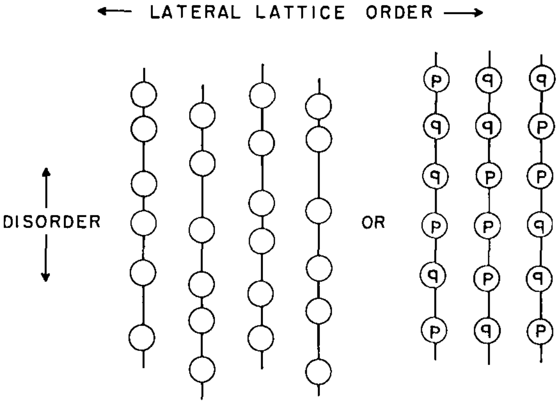


Fig. 1A. Schematic diagram of polymer system showing lateral lattice order. Produces equatorial diffraction.

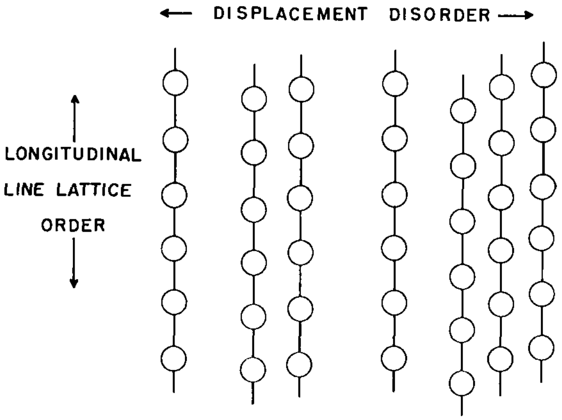


Fig. 1B. Schematic diagram of polymer system showing longitudinal lattice order. Produces meridional diffraction.

The intent of this paper is to introduce the general nature of interfacial polycondensation for the preparation of condensation copolymers, and to show the major variables and some of the effects which changes in polycondensation conditions may bring about.

RESULTS

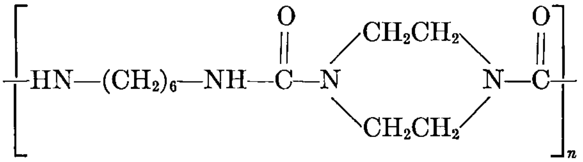
The alternating copolyurea prepared by the interfacial polycondensation of 1,4-piperazinedicarbonyl chloride with hexamethylenediamine was crystalline and had a polymer melt temperature of 265°C. In comparison, the random copolyurea prepared by melt polymerization was amorphous and had a polymer melt temperature of only 194°C. The random copolymer showed greater solubility than the alternating copolymer. A comparison of polymer properties is shown in Table I.

TABLE I
Effect of Degree of Order on Copolyurea Properties

Order	PMT, °C.	Solubility[c]	Crystallinity (estimated)	Films
Random[a]	194	very soluble	amorphous	moderately flexible
Alternating[b]	265	very slightly soluble	20%	brittle

[a] $\eta_{inh} = 0.66$ (*m*-cresol).
[b] $\eta_{inh} = 0.82$ (*m*-cresol).
[c] In hot *N*,*N*-dimethylformamide.

The alternating copolyurea could actually be considered a homopolymer by one definition, i.e., the chain has a simple, precise repeating unit:



This "homopolymer" would, therefore, be expected to possess greater crystallinity, a higher polymer melt temperature, and lower solubility than the random copolymer.

A series of copolyamide–urethanes prepared by the interfacial polycondensation of *trans*-2,5-dimethylpiperazine with terephthaloyl chloride (T) and ethylene bis(chloroformate) (EBCF) were examined to see what effect changes in the manner of diacid chloride addition had on the order of the resulting copolymers. The copolymers were extracted with ethanol to remove any urethane homopolymer formed from the condensation of ethylene bis(chloroformate) with *trans*-2,5-dimethylpiperazine. The insoluble amide homopolymer formed from the condensation of terephthaloyl chloride with *trans*-2,5-dimethylpiperazine was then removed by dissolving the soluble copolyamide–urethane in *sym*-tetrachloroethane and reprecipitating with ether. The properties of these copolyamide–urethanes are shown in Table II. The possible order of these copolymers was then postulated from consideration of the mechanism of interfacial polycondensation. Further, the directional crystallinity of the copolymers, as measured by their x-ray diffraction patterns, was obtained. These were consistent with the postulated orders. The copolymers are discussed individually below.

Simultaneous Addition of Diacid Chlorides (T + EBCF)

The greater rate of hydrolysis of benzoyl chloride as compared to ethyl chloroformate[5] would indicate that terephthaloyl chloride should be much more reactive than ethylene bis(chloroformate) toward amines. This greater reactivity of terephthaloyl chloride was shown by a competitive amidation of terephthaloyl chloride and ethylene bis(chloroformate) with cyclohexylamine. Therefore, in the initial stage of the interfacial copolycondensation, the terephthaloyl chloride should react preferentially

TABLE II
Properties of the Copolyamide-Urethanes

Method of diacid chloride addition[a]	Yield, %	Amount of homopolymer contamination, %		Amide/urethane ratio in copolymer[b]	η_{inh} (m-cresol)	Directional lattice order[c]	PMT, °C.	$\bar{M}_n$ (osmometry)[d]
		Urethane	Amide					
T + EBCF	95	2	2	50/50	1.04	lateral	350	38,000
T → EBCF	83	34	28	58/42	1.14	longitudinal	362	35,500
EBCF → T	91	14	6	55/45	1.32	longitudinal	338	44,500

[a] T + EBCF: Simultaneous addition of diacid chlorides (solutions combined); T → EBCF: prior addition of terephthaloyl chloride solution, ethylene bis(chloroformate) solution added 30 sec. later (see Experimental section); EBCF → T: prior addition of the ethylene bis(chloroformate) solution, terephthaloyl chloride solution added 30 sec. later.

[b] Determined from infrared spectra of copolymer. The ratio of urethane carbonyl intensity (5.87 μ) to the amide carbonyl intensity (6.09 μ) was plotted on semilogarithmic paper against the mole per cent urethane carbonyl in known homopolymer mixtures. Accuracy, ±5%.

[c] See footnote to Discussion.

[d] Determined in 90% formic acid.

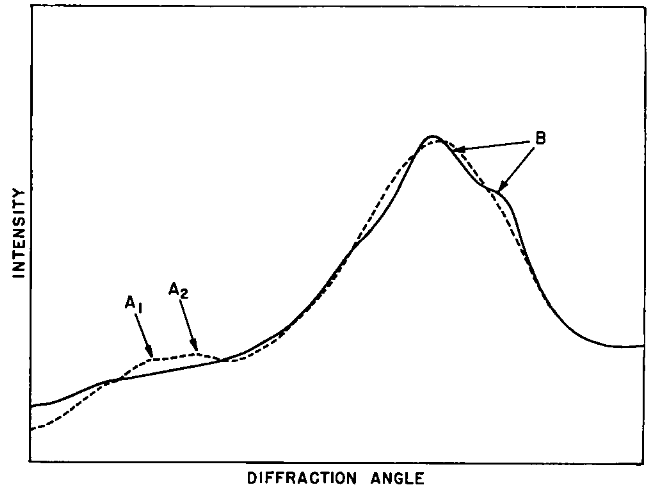


Fig. 2. Plot of wide-angle x-ray diffraction pattern. (——), copolymer from simultaneous addition of diacid chlorides. (--), copolymer from prior addition of ethylene bis-(chloroformate): (A) diffractions which occur on the first (A_1) and second (A_2) layer lines of oriented pattern; (B) diffractions which occur on equator of oriented pattern.

with the *trans*-2,5-dimethylpiperazine to form amide macrosegments. This was shown to be true, for when the polycondensation was stopped during this initial stage by quenching with aqueous hydrochloric acid, only amide homopolymer could be isolated. However, after the polycondensation had proceeded for times longer than five seconds, urethane linkages could be detected in the isolated product by infrared. As the reaction continued, the concentration of urethane linkages increased. The size of the amide macrosegments was limited by (1) the competing reaction of the ethylene bis(chloroformate), (2) the presence of excess *trans*-2,5-dimethylpiperazine, and (3) hydrolysis of the terephthaloyl chloride. However, it is believed that this latter factor is negligible because of the insolubility of the terephthaloyl chloride in water.

As the concentration of the terephthaloyl chloride decreases, its rate of reaction in relation to the ethylene bis(chloroformate) also decreases. Therefore, an intermediate stage in the polycondensation would be expected in which the two diacid chlorides are reacting equally to give random copolymer segments. The final stage of the polycondensation would begin when all of the terephthaloyl chloride was used up and only urethane macrosegments were being formed.

The structure of the resulting copolymer could be postulated as consisting of moderately long segments of amide homopolymer and urethane homopolymer interconnected by essentially random copolyamide–urethane segments. An ordered arrangement of this type would allow regular packing of the copolymer chains since the relatively short lengths of the flexible urethane segments and stiff amide segments would tend to minimize any disruption of chain packing. However, because the segments of amide polymer and urethane polymer are relatively short, the number of repeating units are small, and no longitudinal crystallinity would be developed. The copolyamide–urethane showed on examination by x-ray only lateral crystallinity (see Fig. 2), as is consistent with the proposed order.

Sequence Addition of Diacid Chlorides (T → EBCF)

The prior addition of terephthaloyl chloride to the stirred diamine solution allows high molecular weight amide macrosegments to be formed. The length of these amide segments would be limited only by the presence of excess diamine and by the hydrolysis of the acid chloride. When the polycondensation was stopped by quenching with aqueous hydrochloric acid just prior to the addition of the ethylene bis(chloroformate) it was found that the amide macrosegment had a molecular weight ($\bar{M}_n$) of about 20,000. Also, all of the terephthaloyl chloride had been used up in the reaction. Therefore, the ethylene bis(chloroformate) is added to a polycondensation consisting of swollen amide macrosegments (probably amine-ended) and *trans*-2,5-dimethylpiperazine. The ethylene bis(chloroformate) will react preferably with the *trans*-2,5-dimethylpiperazine to form urethane macrosegments. These segments eventually interlink with the amide macrosegments to give copolymer. A reaction of this type should produce the greatest amount of amide homopolymer and urethane homopolymer contamination.

This mechanism should give us a structure of the type AAAAAAAA-BBBBBBBBBBBBB or AAAAABBBBBBBBBBBBBBAAAAA. The long amide macrosegments would give rise to lattice repetition along the molecular chain axis since they are stiff and would be more extended. This type of structure would be expected to show longitudinal crystallinity. Both the long, stiff amide segments and the long, flexible urethane segments would be expected to prevent lateral packing of the chains. This structure is consistent with the observed x-ray diffraction pattern (see Table II).

Sequence Addition of Diacid Chlorides (EBCF→T)

The prior addition of ethylene bis(chloroformate) to the stirred diamine solution allows moderately high molecular weight urethane macrosegments to be formed. The length of these urethane segments would be limited by the presence of excess diamine, the slow rate of amidation, and hydrolysis of the ethylene bis(chloroformate). When the polycondensation was stopped by quenching with aqueous hydrochloric acid just prior to the addition of the terephthaloyl chloride it was found that the urethane macrosegment had a molecular weight ($\bar{M}_n$) of about 6,000. Also, only about 90% of the ethylene bis(chloroformate) was used up in forming the urethane segments. Therefore, the terephthaloyl chloride was added to a polycondensation consisting of soluble urethane macrosegments (probably amine-ended), *trans*-2,5-dimethylpiperazine, and residual ethylene bis(chloroformate). The terephthaloyl chloride would react preferentially with the *trans*-2,5-dimethylpiperazine to form amide macrosegments before any of the amide and urethane segments interlink to give copolymer.

The amount of urethane homopolymer and amide homopolymer contamination should be less than in the preceding reaction. The resulting structure could be postulated as consisting of two amide macrosegments and three urethane macrosegments as shown below:

AAAAABBBBBBBBBAAAAABBBBBBBBBAAAAA

This type of structure would be expected to show directional crystallinity similar to that shown when the terephthaloyl chloride was added first. This is consistent with the x-ray diffraction pattern (see Table II and Fig. 2).

Interfacial polycondensation has permitted the preparation of condensation copolymers with degrees of order different from those possible for copolymers prepared by melt polymerization methods. The order of these copolymers can be varied from an alternating structure through a random distribution to a block arrangement. Property differences resulting from these changes in order have been shown for alternating and random copolyurea. Directional crystallinity or lattice order determined from x-ray diffraction patterns has been used to support the order proposed for various copolyamide–urethanes. This indicates that different methods of interfacial polycondensation result in polymeric crystals having only two-dimensional instead of three-dimensional lattice order. This lattice order may be lateral or longitudinal, depending on the method used.

EXPERIMENTAL

1,4-Piperazinedicarbonyl Chloride

A solution of 86 g. (1.0 mole) of anhydrous piperazine and 203 g. (2.0 moles) of triethylamine in 250 ml. of chloroform was added dropwise with stirring to 450 g. of phosgene kept at 0 to −10°C. A heavy precipitate of triethylamine hydrochloride formed in the reaction. The cold bath was removed, and the reaction mixture was allowed to come to room temperature to evaporate the excess phosgene. The reaction mixture was filtered and the precipitate washed with 1000 ml. of dioxane. The combined filtrates were then concentrated to isolate the 1,4-piperazinedicarbonyl chloride. The yield was 97 g. (46% of theoretical). The material was recrystallized from chloroform–benzene, 153–155°C.

ANAL: Calc. for $C_6H_8N_2O_2Cl_2$: Cl 33.13%. Found: Cl 33.59, 33.15%.

Alternating Copolyurea

To a rapidly stirred solution of 2.91 g. (0.025 mole) of hexamethylenediamine, 5.30 g. (0.05 mole) of sodium carbonate, and 1.0 g. of sodium lauryl sulfate (Duponol ME detergent, trademark for Du Pont's surface active agent) in 100 ml. of water in a home blender was added a solution of 5.27 g. (0.025 mole) of 1,4-piperazinedicarbonyl chloride in 100 ml. of chloroform. A white precipitate formed. This was collected on a Büchner funnel, washed with water and acetone, then dried in a vacuum oven at

80°C. The polymer had an inherent viscosity ($\eta_{inh} = [\ln \eta_{rel}]/c$, where c is 0.5 g./100 ml.) of 0.82 in *m*-cresol at 30°C.

Random Copolyurea

A mixture of 4.32 g. (0.05 mole) of anhydrous piperazine, 5.81 g. (0.05 mole) of hexamethylenediamine, and 6.01 g. (0.1 mole) of urea were placed in a glass polymer tube. The mixture was then heated under a nitrogen atmosphere at 150–160°C. until the vigorous evolution of ammonia had subsided (approximately 1 hr). The resulting low molecular weight prepolymer was then heated under reduced pressure at 283°C. for one-half hour, then cooled. A hard solid plug of polymer was obtained. The inherent viscosity was 0.66 in *m*-cresol at 30°C.

Copolyamide–Urethane

A series of copolyamide–urethanes were prepared by the interfacial polycondensation of *trans*-2,5-dimethylpiperazine with terephthaloyl chloride and ethylene bis(chloroformate). Various modes of addition of the two diacid chlorides were used to determine the effect of the final order of the copolymer (see Table II). A typical interfacial polycondensation is described below:

To a rapidly stirred solution of 3.43 g. (0.03 mole) of *trans*-2,5-dimethylpiperazine and 2.40 g. (0.06 mole) of sodium hydroxide in 100 ml. of water in a home blender was added a solution of 3.05 g. (0.015 mole) of terephthaloyl chloride in 50 ml. of chloroform. Thirty seconds later a solution of 2.80 g. (0.015 mole) of ethylene bis(chloroformate) in 50 ml. of chloroform was added. The reaction was stirred for a total of 3 min., then 100 ml. of aqueous hydrochloric acid (10%) was added to quench the reaction. Ether was added to break up the emulsion. The reaction mixture was then filtered. The white powdery polymer was washed with water and dried in a vacuum oven at 100°C.

The two homopolymers were then prepared by quenching the interfacial polycondensation with aqueous hydrochloric acid instead of adding the second diacid chloride. This was done in order to determine (1) how much of the diacid chloride was used up in the interfacial polycondensation prior to the addition of the second diacid chloride, and (2) the size of the macrosegments formed by this reaction. A 100% yield of the polyamide was obtained, with an inherent viscosity of 0.92 in *m*-cresol at 30°C., and a molecular weight ($\bar{M}_n$) of about 20,000 (in 90% formic acid). A 90% yield of polyurethane was obtained, the inherent viscosity being 0.14 in *m*-cresol at 30°C. The molecular weight ($\bar{M}_n$) was about 6,000 (in 90% formic acid).

N,N′-Dicyclohexylterephthalamide

To a stirred solution of 3.97 g. (0.04 mole) of cyclohexylamine in 20 ml. of benzene was added 2.03 g. (0.01 mole) of terephthaloyl chloride in 25 ml. of benzene. A white precipitate formed at once. The reaction was stirred for ten minutes, then cooled. The precipitate was collected on a

Büchner funnel and washed with two 50-ml. portions of benzene. The white solid was then triturated with two 25-ml. portions of water, filtered, washed with water, and dried. The melting point was 344–344.5°C.

ANAL.: Calc. for $C_{20}H_{28}N_2O_2$: N 8.53%. Found: N 8.38, 8.48%.

The *N,N'*-dicyclohexylterephthalamide was insoluble in water, ethanol acetone, and benzene.

Ethylene *N*-Cyclohexylcarbamate

To a stirred solution of 3.97 g. (0.04 mole) of cyclohexylamine in 25 ml. of benzene was added 1.87 g. (0.01 mole) of ethylene bis(chloroformate) in 25 ml. of benzene. A swollen precipitate formed. The reaction was stirred for 15 min., then the benzene was removed under reduced pressure. The residue was triturated with two 25-ml. portions of water, then filtered, washed with water, and dried. The melting point was 138.5–139.5°C.

ANAL.: Calc. for $C_{16}H_{28}O_4N_2$: N 8.97%. Found: N 8.85, 8.80%.

The ethylene *N*-cyclohexylcarbamate was soluble in benzene, chloroform, and acetone. It was insoluble in water.

Competitive Amidation of Terephthaloyl Chloride and Ethylene bis(chloroformate)

A solution of 2.03 g. (0.01 mole) terephthaloyl chloride and 1.87 g. (0.01 mole) ethylene bis(chloroformate) in 50 ml. of benzene was rapidly added to a stirred solution of 3.97 g. (0.04 mole) cyclohexylamine in 40 ml. of benzene (the cyclohexylamine was also being used as the acid acceptor). A precipitate formed at once. The reaction mixture was stirred for ten minutes, then cooled. The precipitate was collected on a Büchner funnel and washed with two 50-ml. portions of benzene. The white solid was triturated with two 25-ml. portions of water, then filtered and dried, m. p. 343–344.5°C., weight 3.19 g. (98% of *N,N'*-dicyclohexylterephthalamide. This would indicate that the terephthaloyl chloride is much more reactive than the ethylene bis(chloroformate) and reacts preferentially with the amine.

Polymer Melt Temperature (PMT)

At the polymer melt temperature, a fresh polymer sample leaves a wet molten trail when stroked with moderate pressure across a clean metal surface. A temperature-gradient bar covering the range from 100–400°C. was used for this determination.

Directional Lattice Order Determinations

The directional lattice order of the copolyamide–urethanes was determined from wide angle x-ray diffraction patterns of the powdered material by the method of W. O. Statton.[4] A Leeds and Northrup microphotometer was used to obtain the intensity vs. diffracting angle. A typical plot is shown in Figure 2.

The authors are indebted to Dr. W. O. Statton for interpretation of the x-ray diffraction patterns and to Mary M. Schick for the infrared data.

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Synopsis

An alternating copolyurea was prepared by the interfacial polycondensation of 1,4-piperazinedicarbonyl chloride with hexamethylenediamine. Comparison of this alternating copolyurea with the corresponding copolyurea having a random distribution showed that the alternating copolymer had a higher melting point, greater crystallinity, and was somewhat less soluble than the random copolymer. A series of copolyamide–urethanes was prepared by the interfacial polycondensation of 2,5-dimethylpiperazine with terephthaloyl chloride and ethylene bis(chloroformate), various modes of addition of the two diacid chlorides being used. The degree of order developed in these copolyamide–urethanes was postulated from the probable mechanism of the reaction. The directional "crystallinity" or lattice order of the copolymers, as determined from x-ray diffraction patterns, was cited to support these postulated structures.

Résumé

Une copolyurée de structure alternante a été préparée par polycondensation interfaciale du chlorure de 1.4-pipérazinedicarbonyle avec l'hexaméthylènediamine. La comparison de cette copolyurée alternante avec la copolyurée correspondante de structure statistique a montré que le copolymère alternant a un point de fusion plus élevé, une cristallinité plus grande, et une solubilité moindre que le copolymère statistique. Une série de copolymamide-uréthannes a été préparée par polycondensation interfaciale de la 2.5 diméthylpipérazine avec le chlorure de phthaloyl et le bischloroformiate d'éthylène, en utilisant divers modes d'addition des chlorures acide. Le degré de régularité structurale au sein de ces copolyamides-uréthannes a été postulé sur la base du mécanisme probable de la réaction. La "cristallinité" ou l'ordre du réseau de ces copolyurés, comme l'indiquent les réseaux de diffraction au rayons-X, confirme les structures postulées.

Zusammenfassung

Ein alternierender Copolyharnstoff wurde durch Grenzflächenpolykondensation von 1,4-Piperazindicarbonylchlorid mit Hexamethylendiamin dargestellt. Ein Vergleich dieses alternierenden Copolyharnstoffs mit dem entsprechenden Copolyharnstoff mit statistischer Verteilung zeigte, dass das alternierende Copolymere einen höheren Schmelzpunkt und grössere Kristallinität besitzt und etwas weniger löslich als das statistische Copolymere ist. Eine Reihe von Copolyamid-urethanen wurden durch Grenzflächenpolykondensation von 2,5-Dimethylpiperazin mit Terephthaloylchlorid und Äthylenbischlorformiat dargestellt; wobei die Art und Weise des Zusatzes der beiden Dikarbonsäurechloride variiert wurde. Der Ordnungsgrad, der sich in diesem Copolyamidurethanen einstellen sollte, wurde aus dem wahrscheinlichen Reaktionsmechanismus postuliert. Zur Unterstützung dieser postulierten Strukturen wird die "Richtungskristallinität" oder Gitterordnung, wie sie sich aus den Röntgendiagrammen ergibt, angeführt.

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