[CONTRIBUTION FROM THE BELL TELEPHONE LABORATORIES]

Crystalline Behavior of Linear Polyamides. Effect of Heat Treatment

BY C. S. FULLER, W. O. BAKER AND N. R. PAPE

Because of the known chemical structure and comparatively high degree of crystallinity of linear polyesters and polyamides these substances offer excellent subjects for the study of the physical behavior of polymeric systems. Previous investigations[1,2] have shown that the crystallinity exhibited by these long-chain compounds has much in common with that of the simpler and more fully studied low molecular chain molecules. Thus, it has been shown that fully extended (zigzag) primary valence chains packed in parallel fashion are nearly always present. Further, analogous to the shorter homogeneous chain crystals, different modes of packing giving rise to different lattice-like arrangements often apparently exist in the same polymeric compound.

There are several respects, however, in which these synthetic linear polymers differ from the low molecular compounds. Most outstanding are the striking changes in physical properties which occur with sufficient increase in average chain length and the high degree of polycrystallinity exhibited by these substances. The changes in physical characteristics are chiefly pronounced increase in strength and flexibility.[3] Experiments have shown that the latter is probably related to amorphous portions present in these systems.[4] Furthermore, recent conceptions of the nature of natural high polymers have strengthened the view that both crystalline and amorphous matter exist in these substances.[5,6] It is of great importance, therefore, to investigate polymeric compounds of known constitution in order to learn more about the origin of the crystalline and amorphous components and the factors controlling their formation. It is for this reason that the present work was undertaken. The experiments reported relate to changes in the crystalline nature and in the elastic properties of linear polyamides as a result of quenching and annealing. Although the interpretation of the observed effects is in no way complete, the results imply a considerable rotational freedom of the chain molecules in the solid state and are in agreement with the conception of statistical units or segments of the long-chain molecules present in the solid in different states of organization.

Part I. X-Ray Examination

Experimental.—Two polyamide compounds were investigated, polyhexamethylene adipamide of intrinsic viscosity in cresol at 25° of 0.974 and polyhexamethylene sebacamide of intrinsic viscosity 1.021. The crystalline behavior of these compounds was studied under two types of heat treatments. One treatment consisted in quenching the materials from a fixed temperature above the melting point. The other consisted in an annealing of previously quenched samples. The latter treatment was applied to the polyamides both in the unoriented and in the oriented states.

In the quenching treatments the polyamides were first melted in a hydrogen atmosphere to prevent oxidation and then brought to temperatures of 260 and 280° for the hexamethylene sebacamide and adipamide, respectively. An automatically controlled electric furnace was employed for this purpose in which the total temperature variation was less than four degrees. A glass microscope slide previously heated to the temperature of the melt was then immersed in the molten material and withdrawn to a point above the liquid surface. This operation was performed within the furnace so that the temperature remained unchanged during the procedure. After thus forming a film on the glass slide, the entire tube containing the melted polyamide and the slide was removed to a second electric furnace maintained at the quenching temperature. Here it was allowed to remain until cooled to the temperature of the second oven. The time necessary for this cooling was generally forty minutes. In this way, by changing the temperature of the second cooling oven and repeating the procedure outlined, a series of samples cooled at different rates was obtained. The above procedure was varied only in the case of the sample quenched at 20°, in which case the melted film was cooled directly on a metal plate maintained at this tem-

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[1] Fuller and Frosch, *J. Phys. Chem.*, **43**, 323 (1939); THIS JOURNAL, **61**, 2573 (1939).

[2] Fuller, *Chem. Rev.*, **26**, 145 (1940).

[3] Carothers and Hill, THIS JOURNAL, **54**, 566 (1932).

[4] Fuller, *Ind. Eng. Chem.*, **30**, 472 (1938).

[5] Sisson, *Chem. Rev.*, **26**, 187 (1940).

[6] Mark, *J. Phys. Chem.*, **44**, 764 (1940).

perature. The quenching temperatures employed, *i. e.*, the temperatures of the oven in which the samples were cooled, were 20, 96, 180, 190 and 204° in the case of the polyhexamethylene sebacamide. In the case of polyhexamethylene adipamide, samples were quenched from the melt at 280 to 20° on a metal plate. X-Ray photographs using filtered copper X-radiation were taken of each of the quenched samples, care being employed to select sections of the polyamide films which had the same thickness in order to ensure comparable cooling rates and film intensity relations. This thickness was about 0.5 mm.

In the annealing treatments both oriented and unoriented samples were employed. In the case of the unoriented samples, specimens previously quenched at 20° as described above were annealed at various temperatures up to 200°. In the case of the oriented samples, fibers were first drawn from specimens quenched at 20° and these subsequently annealed as coarse fibers at various temperatures. X-Ray examination was carried out on all the specimens after the annealing treatments.

The equatorial sections of the Debye–Scherrer photographs obtained from the unoriented quenched specimens were micro-photometered in order to secure a quantitative measure of the various intensity changes. The degree of blackening was less than 1 in all cases and satisfactory proportionality between blackening and intensity was obtained with the apparatus used. The curves obtained were smoothed to eliminate variations caused by grain in the film emulsion.

X-Ray Results.—Figures 1A to 1E inclusive show the X-ray photographs secured on unoriented specimens of polyhexamethylene sebacamide quenched from the melt (260°) at 20, 96, 180, 190 and 204°, respectively. Figure 1F shows the result obtained after the sample of figure 1A was annealed at 200° in hydrogen for seventy-five hours. As is evident from a comparison of the photographs, a striking effect of the quenching and annealing treatments is noted. In the photograph of Fig. 1A there are apparently two intense rings present: a weaker inner ring which corresponds to planes of reflection related to the length of the hexamethylene sebacamide repeating unit and a broad intense outer ring which is related to planes associated with the interchain spacing. As the quenching temperature progressively increases from A to E (Fig. 1) the outer ring appears to split into two separate components, while the inner ring becomes progressively sharper. The situation is shown quantitatively by the curves of Fig. 2, which correspond in order to the photographs of Fig. 1. In each case the curves represent the intensity of the portion of the photographs of Fig. 1 extending from the central spot out along the equator line. The decrease in the line breadths at half intensity[7–11] as the temperature of quenching is increased is quite evident from these curves, particularly in the case of the inner circle, which is less complicated by superimposition effects.

Figure 1F is a photograph of the same specimen as in Fig. 1A taken after the latter had been subjected to an annealing treatment of seventy-five hours at 200° in hydrogen. As before, a splitting of the outer ring appears to take place, showing that considerable mobility of the chain molecules is present in the solid at this temperature. This agrees with the behavior of certain monomeric long-chain compounds below their melting points.[12] As expected, photograph 1F is more diffuse than 1E, although the samples they represent were finally treated at nearly the same temperature. However, as is evident from the thermal history, the molecules of the sample of 1F passed rapidly through the 200–215° region, under a 180–195° gradient, whereas those of 1E were held during the entire solidification in this region, where the relaxation-times were sufficiently short to permit extensive crystal order. Thus, the chains of sample 1E had a mobility during cooling never attained by those of 1F despite the latter's subsequent heating at a high temperature. Too, the lattice portions of 1F, originally rapidly quenched, are less perfect than those of 1E, and presumably interfere with the re-ordering in the annealing process.

Figure 3 shows in more detail the results of annealing both the unoriented and oriented polyamides. Figures 3B to 3E inclusive show the effect of various annealing temperatures on a specimen of unoriented polyhexamethylene sebacamide previously quenched at 20° (Fig. 3A). All of the samples were held at the temperatures indicated for ten minutes. Other tests for longer times than ten minutes showed that relatively little increased crystallinity occurs as a result of longer heating.

[7] Lorentz and Debye, *Ann. Physik*, **43**, 49 (1914).

[8] Scherrer, *Nachr. Ges. Wiss. Göttingen*, 96 (1918).

[9] Von Laue, *Z. Krist.*, **64**, 115 (1926).

[10] Thomson, *Proc. Roy. Soc.* (London), **125**, 352 (1929).

[11] Hosemann, *Z. Physik*, **113**, 751 (1939).

[12] Baker and Smyth, THIS JOURNAL, **60**, 1229 (1938).

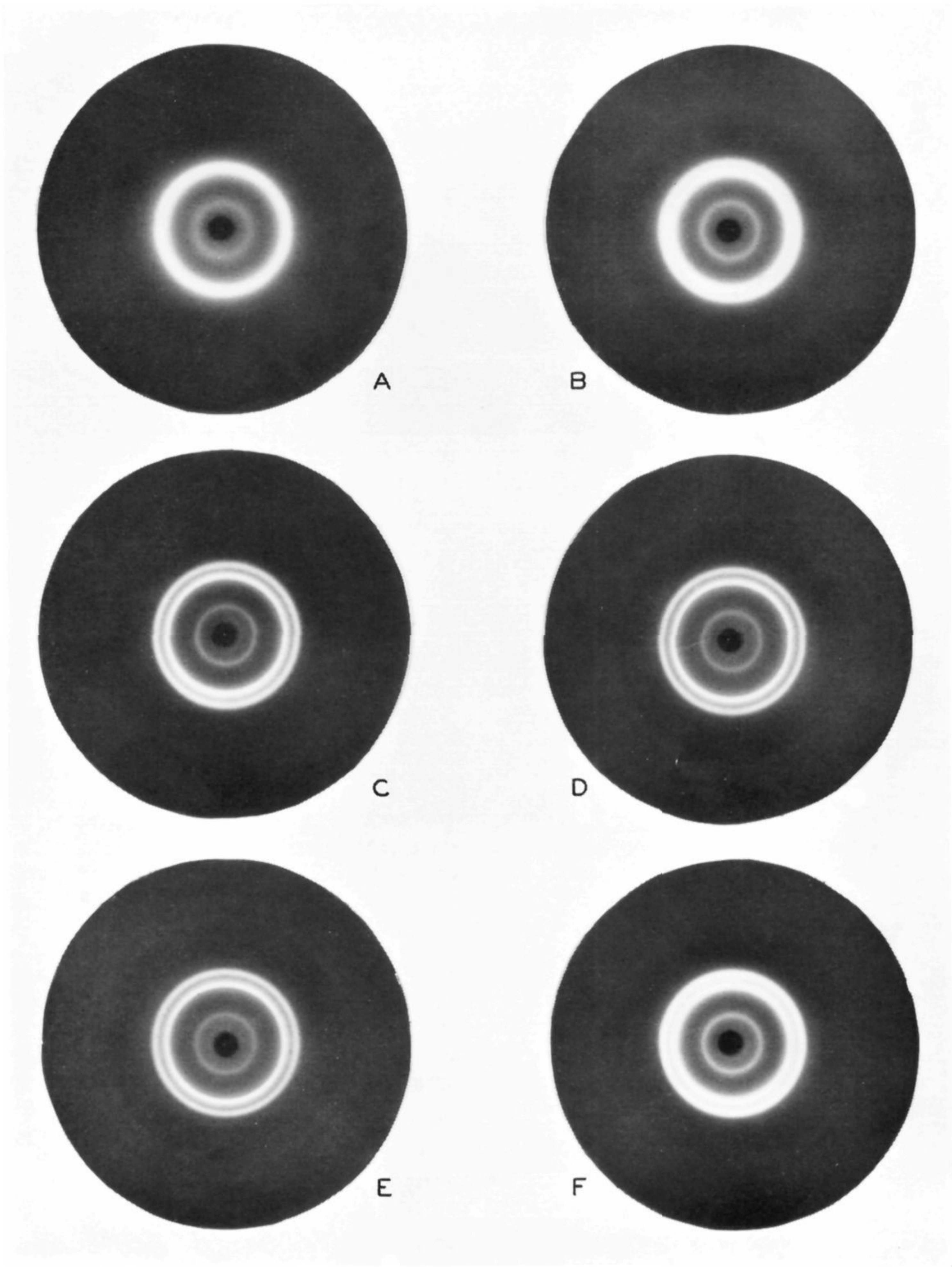

Fig. 1.—X-Ray patterns of unoriented samples of polyhexamethylene sebacamide subjected to various heat treatments: A, quenched at 20°; B, 96°; C, 180°; D, 190°; E, 204°; F, (A) annealed at 200°.

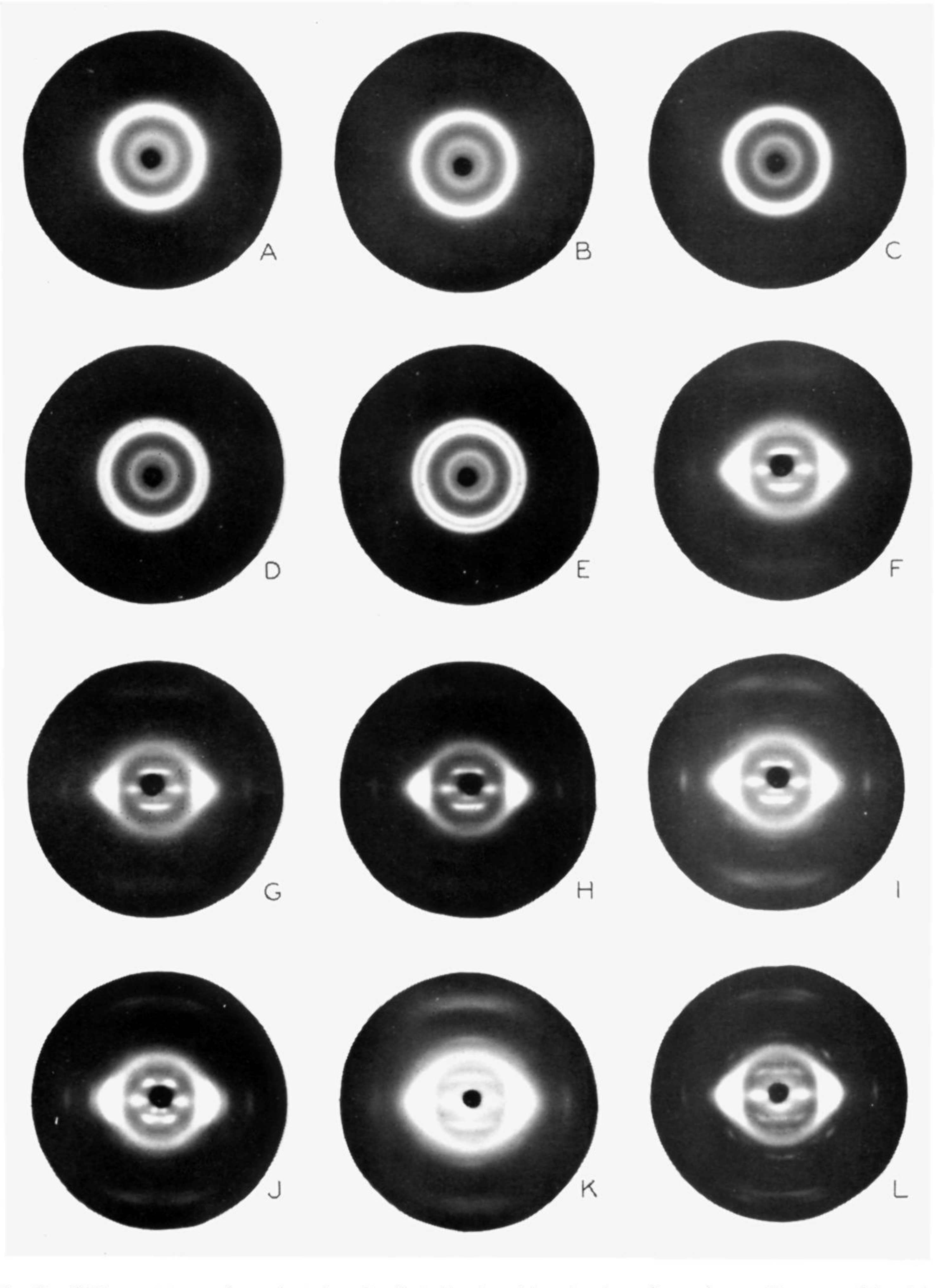

Fig. 3.—X-Ray patterns of unoriented and oriented polyamides showing effect of annealing material originally quenched at 20° (A, F, K) at various temperatures: A–E, unoriented polyhexamethylene sebacamide; F–J, oriented polyhexamethylene sebacamide; K–L, oriented polyhexamethylene adipamide; A, F, K, quenched at 20° from melt; B and G annealed for ten minutes at 120°; C and H at 160°; D and I at 190°; E and J at 200°; L at 230°. Fiber axes are vertical.

As the X-ray photographs show, a progressive sharpening of the rings occurs as the annealing temperature is increased.

The effect of annealing oriented samples of polyhexamethylene sebacamide previously quenched at 20° (Fig. 3F) at 100, 160, 190 and 200°, respectively, is shown in Figs. 3G to 3J inclusive. An analogous photograph of the adipamide annealed at 230° is shown in Fig. 3L. Figure 3K shows the adipamide quenched at 20°, prior to annealing. It is evident that in the case of the oriented specimens a splitting and progressive sharpening of the equatorial reflections is observed. In addition, the broad second-order meridian reflections present in the photographs of the quenched samples (Figs. 3F and 3K) are resolved by annealing into layer-line reflections. No further sharpening of the reflections with time of annealing more than ten minutes (five minutes at 200°) was observed.

Discussion of the X-Ray Results.—In the quenching experiments of Fig. 1 several processes appear to be occurring. As the rate of cooling increases the molecules appear to be "frozen" more nearly in the state in which they exist in the liquid. A considerable proportion of the chains form regions in which a number of chains lie parallel over a distance of their lengths corresponding to at least several chemical repeating units. This conclusion is necessary in order to explain the fine polycrystalline nature of the material quenched, for example, at 20° (Fig. 1A) and the existence of the two major spacings observed. The existence of a common spacing along the chain direction corresponding to the second order (Because of the small specimen-to-plate distance the photographs show only the second-order reflection corresponding to the repeating unit length. The first order is weaker because of the presence of an intermediate polar group) of the repeating unit length suggests also that the chains are arranged with the repeating units opposite, *i. e.*, that the polar groups in the chains fall approximately in planes perpendicular to the fiber axis. The pronounced broadening of this reflection further suggests that there is maladjustment of these units. With slower velocities of cooling, more chains are permitted to attain the preferred lattice-like arrangement. The result is that the single reflection (corresponding to the outer ring in Fig. 1A) gives way to the two reflections characteristic of the monoclinic or orthorhombic cells which have generally been found to apply to these chain compounds. The behavior is in effect the opposite of that observed by Müller[13] in which a coalescence of the 110 and 200 reflections was observed on heating crystalline paraffins containing 21 to 29 carbon atoms. Whereas Müller found a continuous change in spacing on heating, resulting ultimately in a single spacing, the results here support a progressive line narrowing with little or no change in the position of the lines. It can easily be shown, for example, that the curves of Fig. 2 can be obtained by the superimposition of two separate curves of varying line breadth whose maxima are held in fixed positions.

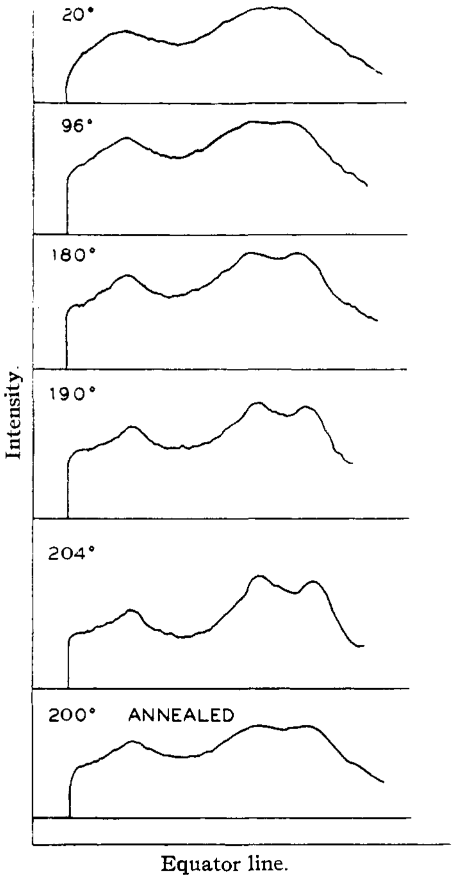

Fig. 2.—Photometer curves across semi-equators of photographs of Fig. 1.

It is conceivable that two processes are occurring simultaneously: a gradual increase in the size of the lattice-like regions as the quenching temperature is increased and a transformation of parallel, oppositely placed, but otherwise unordered repeating units (mesomorphic in the

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(13) Müller, *Proc. Roy. Soc.* (London), **136**, 514 (1932); **166A**, 316 (1938).

sense of Stewart[14,15]) into a more stable lattice-like arrangement. Both processes require a rotational movement of the chain molecules. Such a rotational motion accompanying devitrification far below the melting point has been demonstrated in detail for simple monomeric systems.[16] Furthermore, in the latter study the crystallization mechanism was found to be structurally associated with that of flow. Analogously, it is observed that linear polyamides which contain much amorphous or mesomorphic material cold draw more readily for a given temperature than those which are more fully crystallized. In addition, an amorphous content is essential for cold drawing, since it is found that very highly crystalline samples draw with great difficulty or not at all. The enhanced rotational freedom of the chains under stress, rather than largely chain "slippage," appears to be the cause of this behavior. It is conceivable that the amorphous regions in these chain polymers may act as energy propagation dampers.[17]

The fact that a continuous rather than abrupt transition of the mesomorphic into crystalline lattice arrangement occurs with an increase in the annealing temperature, as shown in Fig. 3, suggests that the successive steps themselves represent no true thermodynamic equilibria. The intermolecular forces (especially hydrogen bonds in the case of the polyamides) which oppose chain rotations are overcome in progressively larger segments or larger numbers of segments as the kinetic energy available for rotation increases. Thus, more and more units are permitted to achieve the crystalline state with a consequent sharpening of the X-ray diffraction lines.

The photographs of the oriented threads drawn from the samples quenched at 20° indicate that the mesomorphic groupings maintain their identity during the drawing process. Furthermore, the annealing effects observed with these samples (Fig. 3F—J) suggest that repeating units in these regions undergo a displacement in the chain direction with respect to one another on passing into the lattice. This conclusion appears necessary in order to explain satisfactorily the appearance of the strong layer-line reflections in place of the meridian reflection as a consequence of annealing.

The stability of the crystalline lattice arrangement is shown by the patterns of the oriented fibers annealed at the higher temperatures (Figs. 3I, 3J and 3L). These show that disorientation of the crystalline regions occurs before the lattice breaks down due to melting and that these regions determine the solid nature of the material as a whole. An analogous recrystallization followed by disorientation at still higher temperatures has been observed in gold alloys.[18] There are other similarities to metal behavior and further studies are planned to determine whether mechanical working like alternate extension and compression of a randomly-oriented sample will cause metal-like alteration of crystallites.[19]

In addition to the mesomorphic and crystalline lattice arrangements of the molecules or molecular segments suggested by the above results, it appears necessary also to postulate the existence of amorphous material in the long-chain polyamides and polyesters in order to explain certain other properties of these substances. As Mark[20] has pointed out, data on this type of matter in polymeric compounds can presumably be obtained from a study of the X-ray background scattering. Because of superimposition, however, this has not proven practicable in the present work. The elastic behavior of these compounds on the other hand provides an alternative way in which data on this point may be obtained. In the following, results on these elastic properties of the polyamides are considered.

Part II. Mechanical Properties

Experimental.—In order to secure a measure of changes in physical properties which occurred in the polyamide specimens as a result of the heat treatments employed, Young's modulus was determined on the unoriented samples. For this purpose the depth of impression made by a quartz hemisphere (0.35 cm. diameter) under a given load (1000 g.) was measured, care being exercised that the elastic limits of the materials were not exceeded, *i. e.*, there was never any detectable flow. The moduli were calculated according to the formula

$$E = 0.0849/d_1\sqrt{d_1}$$

where d_1 is the depth of impression in centimeters read after the load has been applied for five sec-

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[14] Stewart, *Proc. Nat. Acad. Sci.*, **13**, 787 (1927).

[15] Stewart, *Phys. Rev.*, **30**, 232 (1927).

[16] Baker and Smyth, This Journal, **61**, 2063 (1939).

[17] Fürth, *Nature*, **145**, 741 (1940).

[18] Trillat and Hirsch, *J. phys.*, **3**, 185 (1932).

[19] Wood and Thorpe, *Proc. Roy. Soc.* (London), **A174**, 310 (1940).

[20] Mark, *Chem. Rev.*, **25**, 121 (1939).

onds. Young's modulus was also determined on oriented fibers after various annealing treatments by stress–strain measurements. These values agreed with those determined on the unoriented samples using the ball method. The effect of temperature on the elongation of stressed fibers of polyhexamethylene sebacamide was also studied by passing the fibers through a tube heated electrically. Finally, the changes in length of oriented specimens as a consequence of annealing at various temperatures were measured by means of a traveling microscope.

Results and Discussion.—Figure 4 shows the results of measurements of Young's modulus on unoriented samples of polyhexamethylene sebacamide quenched at several temperatures as described in Part I. It is evident that for the lowest temperature of quenching (20°) the compound possesses considerable elasticity (*i. e.*, low modulus), which gradually decreases as the quenching temperature is increased. The value of the modulus for the most crystalline sample agrees satisfactorily with a fiber value quoted recently.[21] The explanation of these results appears to be that material present in the quenched samples as amorphous matter, is converted in part into crystalline matter by annealing. Evidence that the lower values of the modulus are in fact caused by rather freely moving chain elements (amorphous portions) is provided by the results obtained by heating loaded fibers. As is found in the case of rubber and other rubber-like substances, a negative temperature coefficient was observed. There is a contraction on heating the loaded fiber for all loads up to the breaking point. This is also true of the fiber after annealing provided too severe heating is avoided and shows that even after annealing some amorphous regions exist although apparently these are reduced in extent.

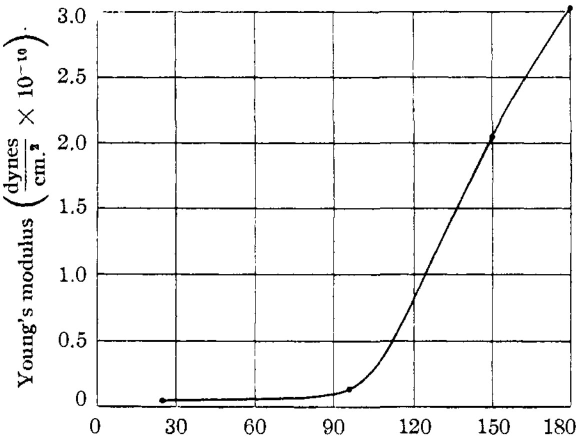

Fig. 4.—Change of Young's modulus of quenched polyamide with temperature.

It was observed also that a small but definite contraction occurred on heating coarse fibers drawn from material previously quenched at 20° even in the unloaded condition. Figure 5 shows the percentage change in length of such a fiber heated for ten minutes at successively increasing temperatures. A progressive shortening in length occurred which is approximately linear up to 180°. Above this temperature a sharp increase in the amount of shrinkage occurs. At the same time, as the photographs of Figs. 3I and 3J show, a slight disorientation of the crystalline regions takes place at this point. Amorphous chains that have been strained and abnormally extended by the drawing process can readily kink into arrangements of less order, and of lower free energy, as in rubber. The total shortening probably results not only from the rubber-like retraction into configurations of higher entropy of amorphous chains, but also from the settling down into regions of potential minima of crystallized molecules, *i. e.*, their active segments, strained from equilibrium by the drawing process. High orientation in fibers such as that induced by the severe mechanical stress of cold drawing has been con-

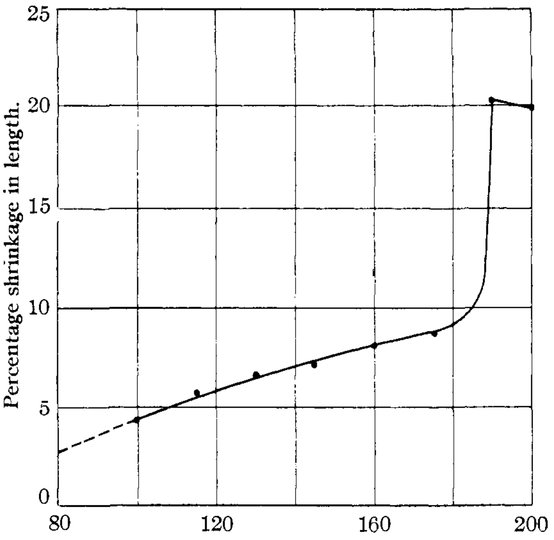

Fig. 5.—Change of length of oriented fiber drawn from quenched polyamide.

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[21] Wall, *Textile Mfr.*, **65**, 496 (1939).

sidered intrinsically unstable in some natural systems.[22] That the amorphous matter can crystallize into the unoriented state is indicated by the fact that the shrinkage on annealing is irreversible and characteristic for each temperature regardless of the time of heating. No X-ray evidence of such crystalline unoriented matter has as yet been observed, however, in the fibers.

Segment Theory of Chain Polymers.—There is increasing evidence that the kinetic unit in linear macromolecular assemblies is a chain segment. Its apparent size may vary with the phenomenon observed, *i. e.*, viscosity, colligative properties, elasticity, etc. The independence of the segments seems considerable, but the coupling in a given molecule precludes any direct gas-like treatment.

The segment concept in viscosity and plasticity is a consequence of Eyring's general theory, especially the portion relating the energetics of flow and vaporization.[23,24] Experimental support indicating an activation energy independent of molecular weight has been contributed by Flory.[25] Also, separate chain sections seem essential in explaining rubber-like elasticity.[20] Similar behavior may be implied from osmotic pressure studies of large molecules.[26] Vapor pressure studies,[27] although difficult to interpret at present, likewise favor the segment idea.

It appears that analogous ideas must be applied in order to explain the results reported in the present investigation. At the melting point a statistical unit consisting of a certain average number of chemical repeating units apparently behaves as the particle engaged in crystallizing. Given sufficient time to relax, these units form crystallites or regions of crystallinity of a certain average size. If the cooling is rapid, however, as in some of the quenching procedures above, the rate of loss of kinetic energy may exceed the time of relaxation of the given part of the unit and this part may become frozen, so to speak, in the instantaneous position it occupied at the melting point. In this manner a satisfactory explanation of the quenching and annealing results may be obtained. In annealing, the intermolecular forces are sufficiently weakened to allow rotations to occur in the molecule resulting in more complete lattice formation. The extent of these rotations and hence the amount of matter reaching the stable crystalline arrangement will depend on the distribution of energy along the molecular chain. The probability of any given segment rotating is simply determined by the concentration of energy in the segment and thus increases with the temperature. According to this view the molecule itself, as long as it is or sufficient length, loses its individuality and a new entity based on statistical considerations takes its place in explaining high molecular behavior. The origin of amorphous regions is explained by this assumption since there is no reason to expect that crystal nuclei which originate in different parts of a given chain molecule should grow into one continuous lattice.

The chain mobility in the solid state demonstrated by the present X-ray studies of the linear polyamides and in unpublished work on other chain polymers leads to the proposal that the melting properties, especially the independence of melting point and molecular weight in high polymers, of crystalline linear polymers likewise be regarded as the result of segment action. This concept will be considered in more detail separately. The chain segment or molecular freedom in solid polyamides, discussed above, probably also permits the solid state reactions, like further condensation, observed in these compounds.[28,29,30] The X-ray analysis shows that at the solid state reaction temperatures of the linear polyamides the chains can move freely enough for the requisite groups to inter-penetrate reaction zones and cause further condensation.

The present discussion is admittedly qualitative and is included simply to indicate what directions investigation may take in order to arrive finally at a more accurate explanation of the special physical properties exhibited by long-chain polymeric compounds. It is hoped to extend this investigation in the future in order to study more fully some problems from the present work.

Summary

1. X-Ray studies of unoriented polyhexamethylene sebacamide and adipamide which have

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[22] Kargin and Michailov, *Acta Physicochim. U. R. S. S.*, **11**, 343 (1939).

[23] Eyring, *J. Chem. Phys.*, **4**, 283 (1936).

[24] Eyring and Ewell, *ibid.*, **5**, 726 (1937). For a precise application of the segment theory, see Eyring and Kauzmann, THIS JOURNAL, **62**, 3113 (1940).

[25] Flory, *ibid.*, **62**, 1057 (1940).

[26] Klages, Kucher and Fessler, *Ann.*, **541**, 17 (1939); see also *ibid.*, **520**, 71 (1935).

[27] Meyer, Wolff and Boissonnas, *Helv. Chim. Acta*, **23**, 430 (1940).

[28] Frenkel and Katschelski, *Nature*, **144**, 330 (1939).

[29] Pacsu, *ibid.*, **144**, 551 (1939).

[30] Flory, United States Patent 2,172,374 (1939).

been solidified from melts at different rates demonstrate that the degree of polycrystallinity as well as the perfection of the crystal lattice is dependent on the rate of cooling. Annealing completely quenched specimens (both oriented and unoriented) restores the crystalline lattice arrangement in an amount which increases with the annealing temperature. The macromolecular behavior has been related to that of ordinary monomeric systems.

2. Parallel with the X-ray results a continuous increase in Young's modulus with decreasing rate of cooling from the melt is observed, indicating an increased degree of crystallinity.

3. Both the X-ray and mechanical data are considered in terms of the segment theory of chain polymers.

4. The results obtained support the view that segments of the chain molecules may exist as crystalline, mesomorphic or as non-crystalline (amorphous) regions in the solid polymers.

SUMMIT, N. J. RECEIVED SEPTEMBER 19, 1940

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

The Effect of Solvation upon the Dissociation of Acetone Cyanohydrin

BY T. D. STEWART AND B. J. FONTANA

Following Lapworth's[1] study of the alkali catalysis of cyanohydrin formation, Ultée[2] determined the degrees of dissociation of a number of cyanohydrins, in the absence of solvent and with a trace of aqueous potassium hydroxide as catalyst. The pure substances, mostly aliphatic aldehyde and ketone derivatives, were dissociated to the extent of 10% or less. W. J. Jones[3] established the nature of the equilibrium as

$$\mathrm{R_2C(OH)CN} \overset{K_{\mathrm{I}}}{\rightleftarrows} \mathrm{R_2C{=}O + HCN} \qquad \mathrm{(I)}$$

in both water and 98% ethanol through large variations in the initial concentrations of the reactants. Lapworth and Manske[4] made an extensive investigation of a number of cyanohydrins in 96% ethanol, using a trace of tripropylamine as catalyst. In seven compounds investigated by both Ultée and Lapworth, including one cyclic and one aromatic derivative, the same order for the degree of dissociation is observed (except for one minor reversal); hence it would appear that specific solvent effects are absent except as the pure cyanohydrins, being themselves alcohols, constitute a solvent medium comparable to ethanol. The possible effects of solvents as dipoles have been discussed by Moelwyn-Hughes and Sherman,[5] who conclude that dipolar interaction may involve from 200 to 15,000 calories. C. H. Li and T. D. Stewart[6] reported the dissociation of acetone cyanohydrin in a number of solvents, using in each case both secondary and tertiary amines. They assumed the equilibrium

$$\mathrm{R_2C(OH)CN + R_3N} \rightleftarrows \mathrm{R_2C{=}O + R_3NH^+ + CN^-} \qquad \mathrm{(II)}$$

to account for the variation in titratable cyanide which accompanied variation in the character of the amine. Through this they obtained correct values for the relative basicities of the amines in water and the lower alcohols. On the basis of the present work their conclusions must be corrected. Although their data in water solution can be duplicated, in the alcohols it is found that amines exert a catalytic influence only and do not shift any equilibrium.[7]

The following experiments were performed to gain further information upon the nature of cyanohydrin dissociation.

Experimental Results

The Dissociation in Water.—In water alone acetone cyanohydrin dissociation reaches equilibrium in eighteen hours; with amine present attainment of equilibrium is instantaneous. Table I includes data of Li and Stewart and of Jones. K_{I} and K_{II} refer to equilibrium constants based

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[1] A. Lapworth, *Trans. Chem. Soc.*, **79**, 1268 (1901); **83**, 1001 (1903).

[2] A. J. Ultée, *Rec. trav. chim.*, **28**, 1, 248, 257 (1909).

[3] W. J. Jones, *J. Chem. Soc.*, **105**, 1560 (1914).

[4] A. Lapworth and R. H. F. Manske, *ibid.*, 2533 (1928); 1976 (1930).

[5] Moelwyn-Hughes and A. Sherman, *ibid.*, 101 (1936).

[6] C. H. Li and T. D. Stewart, THIS JOURNAL, **59**, 2596 (1937).

[7] In non-polar solvents the situation is more complicated. The source of Li and Stewart's difficulty was probably experimental, in not attaining true equilibrium in the absence of amine and in the case of secondary amines allowing too much time, thereby permitting some aminonitrile formation.