

[CONTRIBUTION FROM BELL TELEPHONE LABORATORIES]

## Macromolecular Disorder in Linear Polyamides. Relation of Structure to Physical Properties of Copolyamides

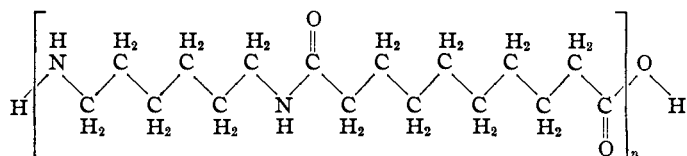
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Macromolecular solids are supposed to gain especial strength and continuity because the primary valence bonds of a single chain extend for hundreds of Ångström units and it thus reacts with the force fields of numerous other polymer molecules. Also, the ends of adjacent chain molecules in a given cell are presumed not to be coplanar. Rather, the chains overlap,<sup>1</sup> and thus planes along which ordinary molecular solids are easily sheared and ruptured are actually absent in the polymers. It is desirable to investigate what general chain arrangements (such as dipole association) are characteristic of these especial physical properties of polymer solids.

The present report includes the results of X-ray diffraction and elastic modulus measurements on several linear polyamides.<sup>2</sup> Simple relations between the mechanical properties of the molecular solids, and the atomic constitution and relative positions of the long chains have been found.

### Experimental

**Materials.**—The linear polyamides studied are obtained from the controlled reaction of dibasic acids and diamines.<sup>3</sup> For the aliphatic series, a single dibasic acid and a single diamine yield a simple linear polyamide which is described by two numbers: the first, the number of C atoms in the diamine chain; the second, the number in the acid chain. Thus, polyhexamethylene adipamide, from hexamethylenediamine (1,6-diamino-hexane) and adipic acid, is a 6-6 polyamide, polyhexamethylene sebacamide is a 6-10 of the typical formula



Various diamines and various dibasic acids may react together to form copolyamides, as shown by Carothers' work.<sup>4</sup> These contain the base units presumably randomly distributed (see a later discussion) along the chain, but always in the sequence dibasic acid-diamine-dibasic acid-, etc. The randomness varies with the relative amounts of different diamines and/or different acids.

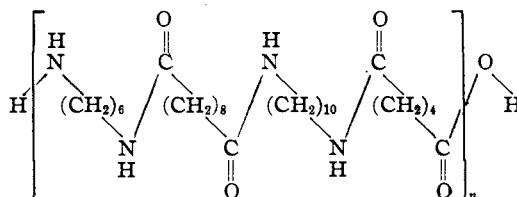
(1) This was suggested by H. Staudinger, see Staudinger and Signer, *Z. Krist.*, **70**, 193, 202 (1929).

(2) "The Collected Papers of W. H. Carothers," Interscience Publishing Company, New York, N. Y., 1940.

(3) Carothers, U. S. Patent 2,071,250.

(4) U. S. Patents 2,130,948 and 2,191,367.

A representative copolyamide chain containing 50-50 proportions of the 6-6 and 10-10 base units is



For convenience in describing the copolyamide series studied here, each composition has been considered to arise from the random mixture of the components of simple polyamides which have also been studied. No polymers containing more than two different diamines and two different dibasic acids are discussed below, so that the compositions of the series are recorded as the molar percentage of one pair (giving one simple polyamide), say 6-6, in another, say 6-10. Such grouping of constituents does not, of course, imply that order in the reaction products.

The polymers were obtained either commercially or according to the published procedures. The intermediates were carefully purified and each polymer represents a well-characterized compound containing a statistical distribution of chain lengths. All polymers were of weight average molecular weight,  $M_w$ , greater than 10,000, as estimated from viscosities.

X-Ray diffraction patterns were obtained for both unoriented and cold drawn<sup>2</sup> polyamides. The latter were highly oriented fibers; both types of samples were first studied quenched from the melt, and then annealed to states of maximum crystallinity.<sup>5,6</sup> The determinations of Young's modulus and moisture sorption were made on sheets molded in a nitrogen atmosphere between plane plates and uniformly annealed. Each was  $3 \times 2$  cm. and 0.051 cm. thick. These specimens were conditioned or dried over phosphorus pentoxide before measurement.

**X-Ray Methods.**—Copper characteristic radiation, nickel filtered and carefully collimated, was directed through rigidly mounted samples onto a cassette containing the film. Each oriented sample employed for estimation of the repeating distance,  $I$ , along the fiber axis was dusted with finely ground and screened sodium chloride, whose Debye-Scherrer rings superposed on the fiber pattern served as a primary standard for the distance determinations on each photograph. The fibers were flat, and of approximately 18-mil thickness; the salt was always dusted on both sides. Repeated exposures of each composition facilitated selection of an exposure time giving the optimum intensity of the features measured. This was essential for the copolyamides possessing the middle concen-

(5) Fuller, Baker and Pape, *THIS JOURNAL*, **62**, 3275 (1940).

(6) Baker, Fuller and Pape, *ibid.*, **64**, 776 (1942).

trations of components, since their "identity period" spots were relatively diffuse. The X-ray negatives were measured on an improved light box of the type described by Klug.<sup>7</sup>

All of the I, Å. values reported were obtained on separately repeated photographs with a precision of  $\approx 0.3$  Å.

**Elastic Modulus.**—Young's modulus was computed from the elastic indentation of a spherical quartz segment in a plane panel of the polymer. For such a penetration

$$E = c \frac{L}{d^3 D^2} \quad (1)$$

where  $E$  is Young's modulus in dynes per sq. cm.,  $c$  is a constant,  $L$  is the load on the sphere, in grams,  $D$  is its diameter, in cm., and  $d$  is the depth (cm.) to which the sphere sinks below the surface under the weight.<sup>8,9</sup> This depth was read five seconds after application of the load. The latter was chosen so that only elastic and no permanent deformation occurred, except for a few of the softest compositions. For the latter,  $E$  is modified by a plasticity factor (yield point), but it still characterizes the polymer.

The measuring apparatus is essentially a Pfund hardness tester. A heavy steel lever with the fulcrum at one end contains the quartz spherical segment in the center and a platform for the load weights on the other end. The quartz segment is ground on the end of a quartz cylinder. Coaxially with this cylinder and above the lever is mounted a microscope fitted with a Leitz ocular micrometer. Since the refractive index of the quartz-polymer interface differs from that of the quartz-air interface, the intersection of the plane of the surface of the test material with the periphery of the quartz segment produces a dark disc in the microscope field. The diameter of this highly magnified disc is measured with the micrometer. The radius of the sphere corresponding to the quartz section,  $D/2$ , is 3.24 mm. When  $r$  is the radius of the dark disc, the depth of impression,  $d$ , is given by

$$d = 0.324 - \sqrt{(0.324)^2 - r^2} \quad (2)$$

Numerous readings were obtained and averaged for each dried sample, at  $25 \pm 2^\circ$ .

**Moisture Sorption.**—Samples of equal dimensions were dried to equilibrium over phosphorus pentoxide, in glass-stoppered weighing bottles, weighed and reweighed after equilibration at 100% R. H. in water at  $25.0 \pm 0.5^\circ$ .

## Results and Discussion

**Crystalline Nature of Linear Polymers.**—The molecules of  $n$ -paraffins and their derivatives have been shown to lie in the crystal as extended chains whose terminal groups formed planes in some cases perpendicular and in others oblique to the long chain axes.<sup>10,11,12</sup> Linear polymers such as polyoxymethylenes, polyesters and polyamides likewise possess chains, and a series of studies has indicated analogous structures

except that the repeating polar groups of the polymers replace the terminal groups of the monomers in generating the characteristic planes recurring along the chain axes.<sup>1,13,14,15</sup> However, other investigations<sup>5,6</sup> have emphasized sharp differences, and especially imperfections, in the crystalline state of macromolecules compared to ordinary molecular crystals. The molecules are of non-uniform size; the chains comprise a distribution of lengths clustering about an average value.<sup>16</sup> Also, they presumably do not lie like extended rods for their whole length in the polycrystalline solid but are highly kinked.<sup>17,18</sup> The crystalline content profoundly affects the physical properties of the solid polymers and can be readily varied by thermal treatment: quenching produces minimum and annealing maximum crystallinity.

Amid the complexity, striking generalities about these polymer solids appear. The polar groups which repeat along the chains always associate strongly to form dipole layers. The interaction in these layers and their concentration per unit volume govern the internal energy, melting point and strength of the solids. Such interaction is especially significant in the polyamides, where, as in the proteins, both ordinary dipole attraction and also hydrogen bonding obtain. Laterally, the chains pack somewhat similarly in all of the compounds, although even the lateral packing is a function of the structure of the polar layers. (Also, the chains do not necessarily assume planar zigzag configurations.) We shall thus regard the dipole layers, distributed through the polycrystalline mass as though imbedded in a paraffin chain matrix, as the critical factors in the solid structure. In the studies below, (1) the separation of these planes has been varied by varying the number of methylene group "spacers" in the base units of the simple polyamides. The (2) population of polar groups in the average planes has been varied by copolymerization, for, in adjacent chain sections containing mixed base units, if the polar groups coincide at one point, they will often fail to do so further along the same chains, because of unequal methylene group spacing. This factor is represented to scale in Fig. 1, for the 50% composition of the 6-6:6-10 copolyamide. The circles indicate the polar groups

(7) Klug, *Ind. Eng. Chem., Anal. Ed.*, **12**, 753 (1940).

(8) Larrick, *Bull. Am. Phys. Soc.*, **14**, 17 (67) (1937).

(9) Davies, Miller and Busse, *THIS JOURNAL*, **63**, 361 (1941).

(10) Müller, *J. Chem. Soc.*, **123**, 2043 (1923).

(11) Müller, *Proc. Roy. Soc. (London)*, **A120**, 437 (1928).

(12) Malkin, *J. Chem. Soc.*, 2796 (1931).

(13) Hengstenberg, *Ann. Physik*, **84**, 245 (1927).

(14) Fuller, *Chem. Rev.*, **26**, 143 (1940).

(15) Fuller, Frosch and Pape, *THIS JOURNAL*, **64**, 154 (1942).

(16) Schulz, *Z. physik. Chem.*, **B32**, 27 (1936).

(17) Kuhn, *ibid.*, **A161**, 1, 247 (1932).

(18) Meyer, *Z. Elektrochem.*, **45**, 225 (1939).

along the chains. Thus, fewer of them can inhabit the average planes, and, also, the displaced polar units are, in general, surrounded by hydrocarbon groups. They are effectively sheathed from contributing to the dipole interaction. The copolymerization also alters the apparent average plane separation (in addition to the plane population) in striking and still unexplained fashion. Finally, (3) the order in the dipole planes has been modified by both changes in population (whereby hydrocarbon chains occupy defect sites in the layers) and by quenching (whereby the groups are turned out of the most stable positions in the layers<sup>5</sup>).

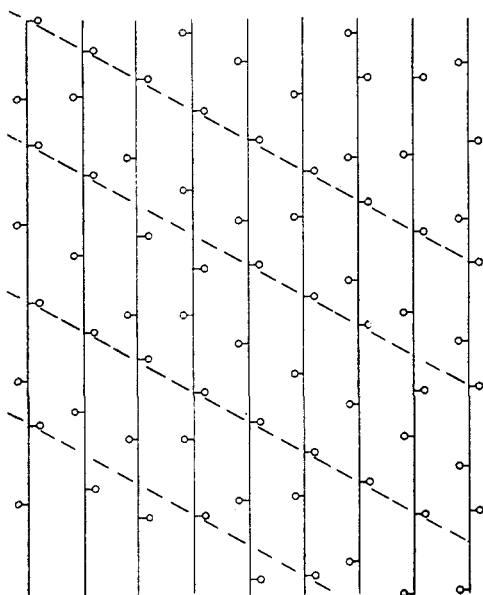


Fig. 1.—Formation of polar layers in 50% 6-6 and 50% 6-10 copolyamide (schematic).

**Spacing of Dipole Layers.**—Either layer-line or meridian reflections<sup>19,20</sup> on the fiber diagrams yielded several orders of the identity period,  $I$ . This we associate with the separation of successive planes of polar groups tilted or normal, as the case may be, to the chain axes. Less directly,  $I$  represents the identity period within the molecules. A possible formation of these layers in the 6-6 polyamide is represented schematically in Fig. 2. Actually, disorder may occur in this idealized arrangement. For instance, a polar linkage in a given chain is formed by an A-D (acid-diamine) union. The associated linkage in an adjacent chain may result (in the same direction along the

(19) Polanyi, *Z. Physik*, **7**, 149 (1921).

(20) Katz, "Die Röntgenspektrographie als Untersuchungsmethode," Urban and Schwarzenberg, Berlin, 1934.

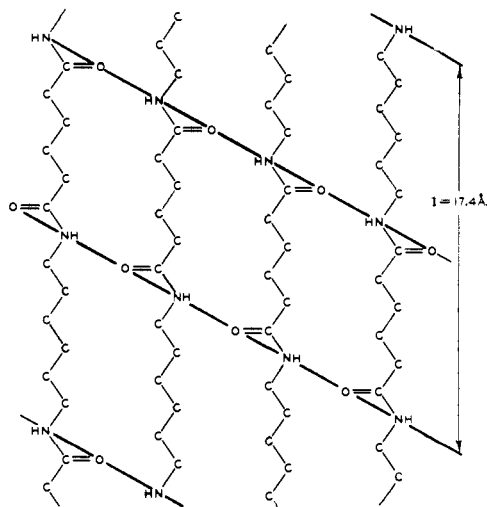


Fig. 2.—Layer structure resulting from association of polar groups in polyhexamethylene adipamide (schematic).

chain axis as above) from a D-A union. This phenomenon leads to a displacement of certain succeeding polar groups along the chains, and thus causes disorder in the system. This condition can be seen by turning one of the chains in Fig. 2 end-for-end about a C=O axis. Such "chain inversion" in adjacent segments in the solid must be considered in the structures of all polymers of the types considered here.

Figure 3 relates the structural property,  $I$ , to a thermodynamic quality, the melting point, of simple polyamides. The triangles are the spacings calculated for a plane, zigzag chain containing no kinks or bends between the diffracting planes. The best interatomic distances were used.<sup>21</sup>

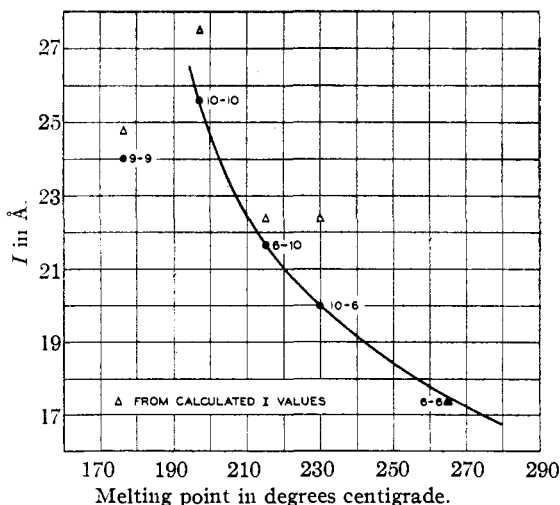


Fig. 3.—Relation of interplanar spacing,  $I$ , to melting points of linear polyamides.

(21) Astbury, *Chem. and Ind.*, **60**, 491 (1941).

Only for polyhexamethylene adipamide (6-6) do the calculated agree with the observed values. The observed spacings in the other polyamides are, although carefully checked, always short. It appears that chain tilting or twisting *between* the planes defining the period I may occur. Figure 3 gives independent evidence of diminished plane separation and attendant closer packing. The observed points, except those of polynonamethylene azelamide (9-9), lie on a smooth curve; the calculated points cannot be thus connected. The greater the I, the lower the melting point, because the fewer the polar groups per unit volume to contribute to the mol cohesion. But, the comparison of polyhexamethylene sebacamide (6-10) with polydecamethylene adipamide (10-6) and of 9-9 with the rest of the series emphasizes further significance of the separation. When the dipole planes are oblique to the chain axes, the chains are "tilted" and pack more closely than when the chains are vertical and the planes perpendicular; the lattice energy is higher. This was strikingly demonstrated for the paraffin derivatives.<sup>12,22,23,24</sup> From the X-ray results for 9-9, its chain sections are essentially in the perpendicular form; a low melting point is implied. If its chains were in the form of the other polyamides, it should melt at 202°; a 27° lower value is found, 175°. Further, 6-10 and 10-6 have the same calculated I, their chains are in the tilted form, and if they had the same sort of interplanar modification to explain the shortened observed I, they should melt at the same temperature. However, 10-6 exhibits a markedly reduced I, closer packing is expected, and the observed melting point is 15° higher than for 6-10. The association

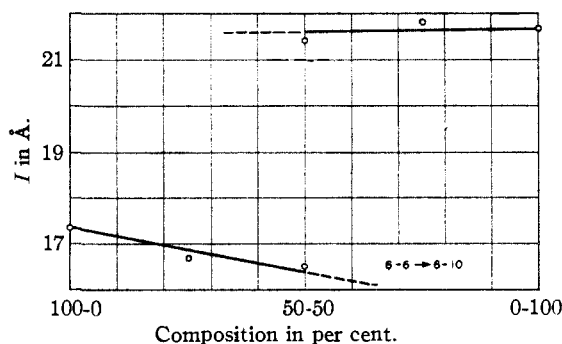


Fig. 4.—Variation of the spacing I with composition of a mechanical mixture of the polyamides 6-6 and 6-10.

(22) Müller and Saville, *J. Chem. Soc.*, 127, 599 (1925).

(23) Garner, van Bibber and King, *ibid.*, 1533 (1931).

(24) King and Garner, *ibid.*, 1449 (1934).

of the lattice energy with the spacing between dipole layers and their concentration per unit volume is thus established. The vertical form of the odd-membered (9-9) polyamide chains has been proposed to result from the alternating directions of the interchain dipole association, as generally found for polymers formed from odd-membered base units,<sup>25</sup> in addition to the favorable hydrogen bonding of the vertical form.

**Mechanical Mixture Patterns.**—We proceed next to consider the effect on I and on the solid state properties of mechanical mixtures of two simple polyamides. Can the effective spacings in the lattice be thus altered? The molar proportions indicated in Fig. 4 of 6-6 and 6-10 were fused and thoroughly mixed under hydrogen at 280°. Fibers were drawn, and the patterns of both polymers appeared on each photograph obtained. These are illustrated in Fig. 5C. However, the component present in 25% amount gave features too weak to measure well, and these points have been omitted from the graph. While there appears to be some systematic decrease of I with increase in added polymer, the respective contributions to the structure are relatively independent. Similarly, the crystallization appears to be separate, although the melting points of the mixtures lie surprisingly near the figures for the higher melting component, 6-6. The mechanical and structural effects of mechanical mixture are slight. Interestingly, although the two polymers differ by only four carbon atoms in the acid chains, mixed crystal formation was undetected. The same result arose for mixtures of polyesters<sup>26</sup> and also of ten- and twelve-membered polyoxymethylenes<sup>13</sup>; the individual patterns (from the end-group planes) persisted. When, however, the polyoxymethylene chains were very long and of a distribution of lengths, a single pattern was found, involving repeating distances within the chains. We show below that when a mixture of base units in the solid is effected by co-reaction rather than mechanical mixture of chains, a single pattern with an "identity period" depending on composition is obtained.

**Copolyamide Patterns.**—The curve for the copolyamide 6-6:6-10 in Fig. 6 (the data for all of the series are in Table I) resembles Fig. 4 but the diagrams of the former showed always but one set of I spacings, in contrast to the mechanical mix-

(25) Yager and Baker, *THIS JOURNAL*, 64, 2164 (1942).

(26) Fuller, *Ind. Eng. Chem.*, 30, 472 (1938).

tures. The copolyamide structure exhibits a rapid change in the neighborhood of 50%, and here, also, the diffuse scattering is greatest and the population of the scattering planes least. The melting point is near the minimum and the polymer is softest, with greatest molecular disorder. The concentration variation of *I* in the similar system containing the components of 6-6:10-6

TABLE I

Composition, mole per cent.		<i>I</i> , Å. calcd.	<i>I</i> , Å. obs.	$E \times 10^{-9}$ (dynes, sq. cm.)	Per cent. water sorption 100% R. H.
6-6	9-9				
100	0	17.4	17.4		
80	20		16.6		
66	33		16.2		
60	40		16.8		
50	50		20.2		
33	66		20.9		
0	100	24.9	24.0		
6-6	6-10				
100	0	17.4	17.4	3.6	10.1
66	33		16.8	2.2	5.6
59	41		17.0		
30	50		20.9	1.1	4.3
33	66		21.1	1.6	5.0
0	100	22.4	21.7	2.2	3.0
6-6	10-6				
100	0	17.4	17.4		
60	40		20.9		
40	60		20.9		
20	60		20.7		
0	100	22.4	20.0		
6-6	10-10				
100	0	17.4	17.4	3.6	10.1
80	20		16.5	1.9	5.7
66	33		16.1	1.2	4.5
50	50		22.3	0.8	4.7
33	66		24.1	1.1	3.7
20	80		26.3	1.3	3.5
0	100	27.5	25.6	1.3	2.0
6-10	10-6				
100	0	22.4	21.7		
66	33		21.7		
50	50		22.6		
33	66		21.2		
0	100	22.4	20.0		
6-10	10-10				
100	0	22.4	21.7		
60	40		20.5		
45	55		21.5		
30	70		24.4		
0	100	27.5	25.6		
10-6	10-10				
100	0	22.4	20.0		
60	40		23.7		
45	55		25.9		
30	70		26.6		
0	100	27.5	25.6		

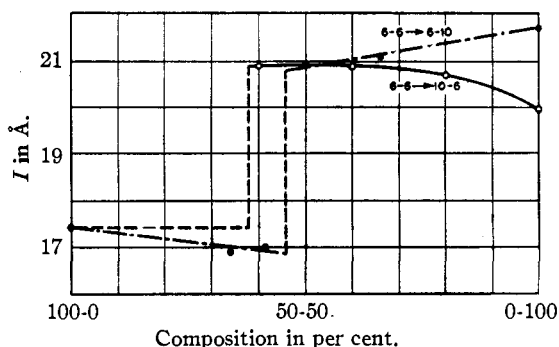


Fig. 6.—Variation of the spacing *I* with composition of copolyamides: hollow circles, 6-6:10-6; filled circles, 6-6:6-10.

also has a rapid change in the 50% region, but here the altered structure of the 10-6, remarked above, is evident as a down slope of the *I* curve on the 10-6 side. In both the 6-6:6-10 and 6-6:10-6 series, and the 6-10:10-10 and 10-6:10-10 subsequently discussed, the introduction of a single new acid or single new diamine so that it just exceeds in molar concentration the other acid or other diamine, respectively, causes the sharp change in spacing. That is, keeping the diamine constant and changing the relative concentration of the dibasic acids, or keeping the acid constant and changing the diamines, causes this characteristic sharp shift of *I* around 50%.

When the constituent units are made longer, but when still only an acid or a diamine, not both, is varied, the phenomena of Fig. 7 result. For the system 6-10:10-10, the "transition" range is broadened. The concentration of the dipole layers per unit volume is decreased, compared to the earlier series, and there is enhanced opportunity for defects in their population, *i. e.*, there is more hydrocarbon matter in which a polar linkage may become isolated. Some illustrative patterns from this series are shown in Fig. 8. The 55-45 (8C) copolymer exhibits the characteristically diffuse reflections corresponding to the layer line spots of the ordered structures. Throughout the series, normal equatorial features can be obtained, in support of the concept that the lateral packing is essentially constant despite changes in the dipole layer spacing. The data for 10-6:10-10 really only define the 10-10 side of the curve in Fig. 7, but have a pronounced maximum in *I* when about 70% 10-10 is introduced. This may occur partly because the peculiar 10-6 structure perturbs and lessens the factors causing the generally shortened *I*.

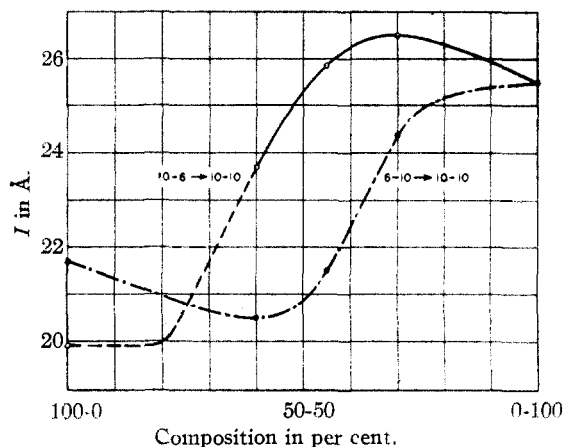


Fig. 7.—Variation of the spacing  $I$  with composition of copolyamides: hollow circles, 10-6:10-10, filled circles, 6-10:10-10.

Figure 9 represents the behavior of series in which two dibasic acids and two diamines occur as variables. All of the base units are of different lengths; there is increased scrambling, and the change in  $I$  occurs over a very broad concentration range. For 6-6:10-10, addition of the longer components first depresses the  $I$  values, then a steep and broad increase leads to a maximum from which still further addition of longer units again decreases  $I$  to the figure for pure 10-10. The crystallinity, melting point and elastic modulus are persistently low through the 20 to 80% range. The large and rapid change in the average inter-

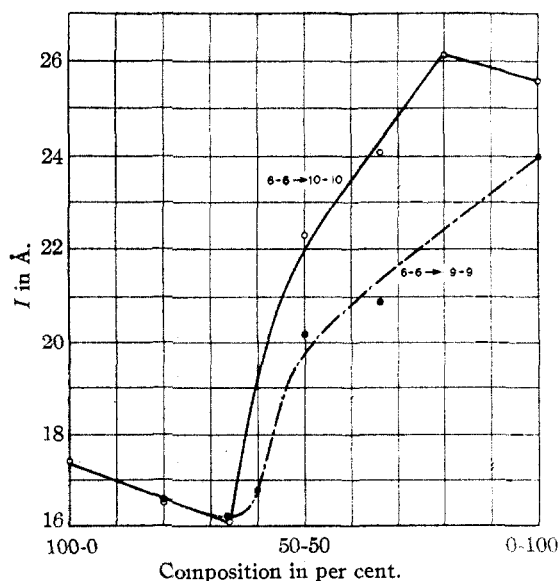


Fig. 9.—Variation of the spacing  $I$  with composition of copolyamides: hollow circles, 6-6:10-10; filled circles, 6-6:9-9.

planar spacing is accompanied by much defection in the layers.

The 6-6:9-9 data reflect a new variable of structure. As noted before, the dipole planes of polynonylamethylene azelamide (9-9) are essentially vertical to the chain axes, whereas those of 6-6 are tilted. Thus, different features as well as different distances appear on the photographs. At high concentrations of either (arbitrary) pair of components, the patterns of the other are invisible, but at intermediate proportions, features suggestive of both patterns appear and yield the same  $d$  values. Thus, each structure is modified quantitatively by components leading to the presence of the other. Figures 10A and 10D illustrate the different structures of 6-6 and 9-9 whereas 10B represents qualitatively the 6-6 structure. However, the 50% composition is dominated by the 9-9 form. The contrast in sharpness of the 50% and 100% 9-9 meridian spots again emphasizes the disorder in the copolyamides.

Figure 11 provides independent evidence for previous interpretations. The components plotted there, 6-10 and 10-6, have the same calculated  $I$ . Thus, various molar percentages of the pairs should result in constant identity periods. Of course, this is affected by the shortening found in pure 10-6, but, further, a maximum in  $I$  occurs near the usual 50% transition region. It is again as though in the region of maximum scrambling of polar groups, where there are most defects in plane population, the additive scattering produces a concentration on the film corresponding to an increased average plane separation. That is, planes capable of producing the  $I$  features occur with diminished frequency throughout the crystals because beginning with one plane, additional progression (than normal) is needed to find enough polar groups organized together to form another.

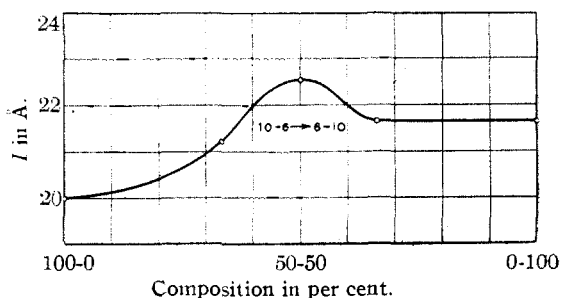


Fig. 11.—Variation of the spacing  $I$  with composition of the copolyamide 10-6:6-10.

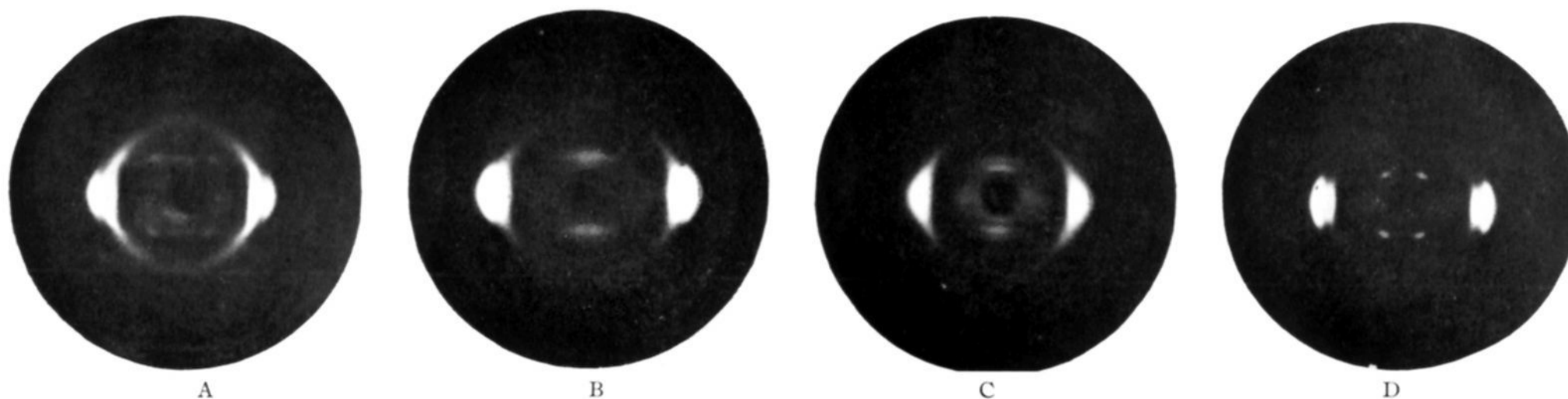


Fig. 5.—Effects of copolymerization and mechanical admixture on X-ray patterns of oriented polyamides (fiber axis vertical): A, 100% 6-6; B, 50% 6-6:6-10 copolymer; C, 50% 6-6:6-10 mechanical mixture (quenched); D, 100% 6-10.

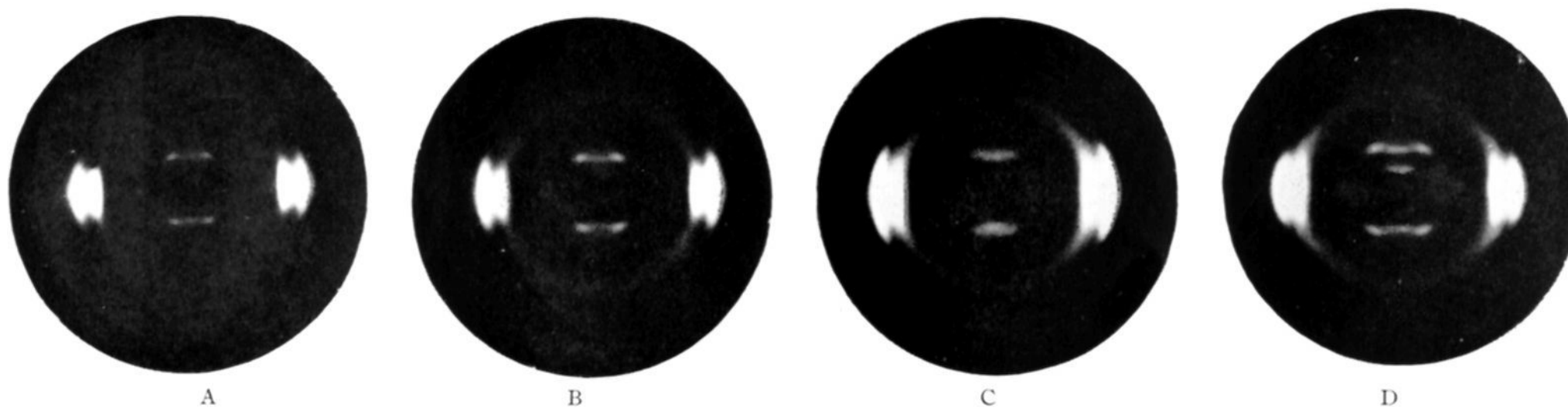


Fig. 8.—X-Ray patterns of oriented polyamides and copolyamides of the 10-10:6-10 series: A, 100% 10-10; B, 70% 10-10 and 30% 6-10; C, 55% 10-10 and 45% 6-10; D, 100% 6-10.

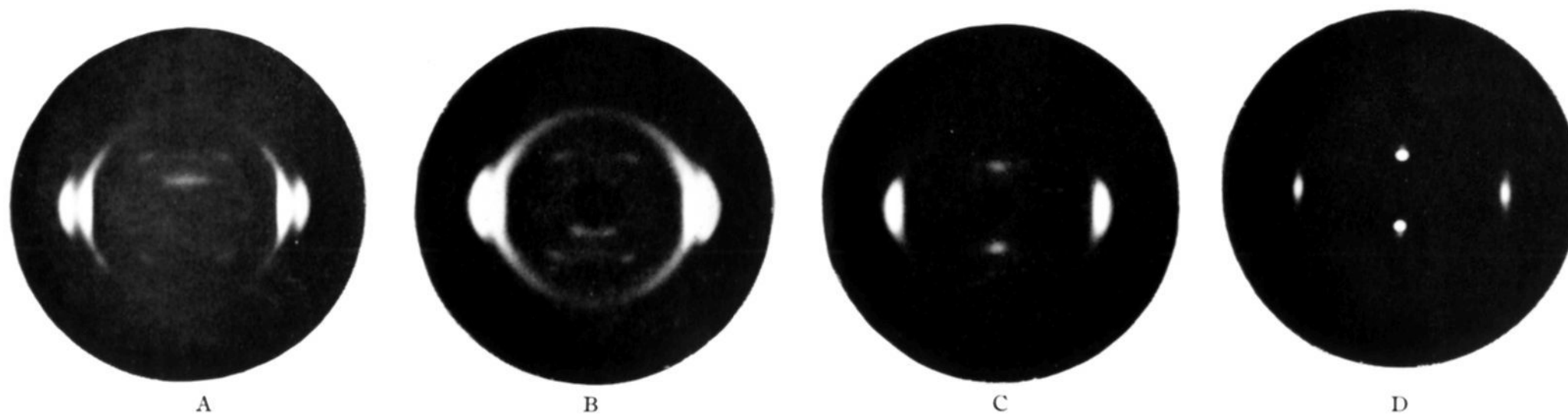


Fig. 10.—X-Ray patterns of oriented polyamides and copolyamides of the 6-6:9-9 series: A, 100% 6-6; B, 80% 6-6 and 20% 9-9; C, 50% 6-6 and 50% 9-9; D, 100% 9-9.

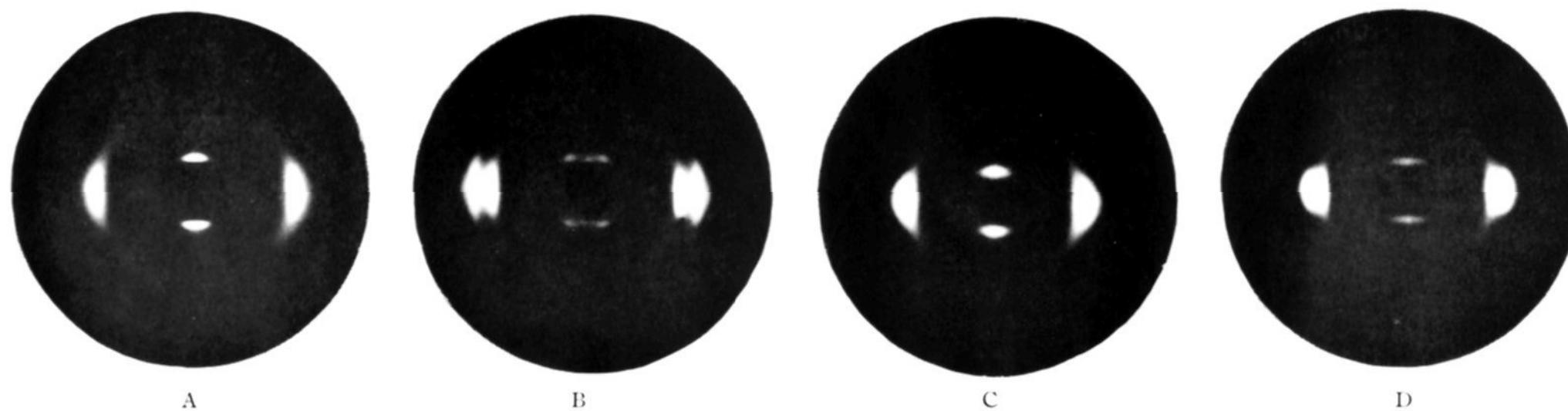


Fig. 12.—Effect of heat treatment on X-ray fiber patterns of typical polyamide and copolyamide: A, 100% 10-10, quenched; B, 100% 10-10 annealed; C, 80% 10-10 and 20% 6-6 quenched; D, 80% 10-10 and 20% 6-6, annealed.



Equivalently, a large  $I$  may result from irregularities in a given long molecule, such as periodic twisting. This is adjunctive to the decreased plane population and enhanced amorphous content already noted for the middle concentrations. A statistical analysis would be required for proof of the preceding hypothesis.

Salt pairs reacted in the formation of the present polyamides,<sup>3</sup> *i. e.*, the salt of the organic base (diamine) and acid was used for a given polymer. If the components react randomly, independent of this salt grouping (which is reflected in the symbols 6-10:10-6, etc.), the 50% concentration in the 6-6:10-10 and 6-10:10-6 series should be the same. Accordingly, equal melting points are found and the  $I$  values agree, as seen from Table I.

None of the copolyamide series follows the linear change of  $I$  with composition calculated by simple weighted averaging of the constituent units. Thus, they do not follow Vegard's rule for ordinary mixed crystal formation. This rule was approximately observed for the single spacings from mixtures of  $n$ -fatty acids, by Ott and Slagle.<sup>27</sup> The intrachain nature of the polyamide mixture causes the new behavior.

Quenching of all the copolyamides caused extensive lateral disorder of the chains, including the groups in the dipole layers. This was inferred from the large background scattering and blurring of features, and especially from the characteristic<sup>6</sup> replacement of the two side spacings (4.40 and 3.70 Å.) occurring in the highly crystalline state by a single spacing (4.18 Å.). This indicates that the chains are turned in all directions about their long axes. Annealing (at 20 to 50° below the melting points, in general) was found in all cases to cause rotation of segments in the solid state into the ordered, crystalline array, and a marked hardening of all samples. The temperature (thermal energy) necessary for annealing was in all cases, however, less the greater the dipole layer separation, and the larger the number of defects introduced into the layers by copolymerization. Annealing of the fiber samples always effected a sharpening of the  $I$  features as well as resolution of the equatorial spots. Typical examples of these changes appear in Fig. 12, where quenched fiber patterns are compared with those produced by annealing in the solid state. This annealing was evidently effected without loss of orientation since the drawn fibers were annealed and not redrawn.

(27) Ott and Slagle, *J. Phys. Chem.*, **37**, 257 (1933).

Incidentally, when certain of the oriented copolyamides were annealed, especially near the 50% compositions, spontaneous elongation, as observed on cooling stretched rubber, occurred on cooling. This indicates again a partial content of amorphous, kinked chains<sup>6</sup> which straighten as they crystallize.

**Elastic Properties.**—The graph of Young's modulus in Fig. 13 shows the composition dependence and the abrupt change at 50% of the 6-6:6-10 copolyamide. The diffraction results predict such behavior in support of the concept that the separation, order and population of the dipole layers dominate the internal energy. If the  $E$  values reflect the force necessary to displace the chain sections from their equilibrium positions, such motion is markedly easiest when disorder is greatest. We regard the 50% composition as representing the minimum of both crystalline content and order in the crystallites. The elastic modulus can thus be interpreted by structural knowledge of the dipole layers.

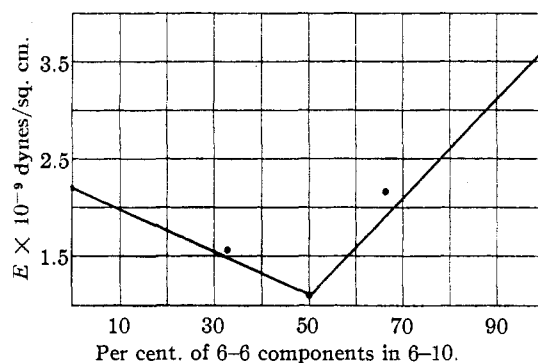


Fig. 13.—Dependence of Young's modulus,  $E$ , on composition of the copolyamide 6-6:6-10.

The dependence of  $E$  on composition in the 6-6:10-10 series of Fig. 14 differs from Fig. 13, again in agreement with the X-ray results. The minimum for  $E$  is shallow and broad, corresponding to the relatively continuous  $I$  variation through the system. Traced from the 6-6 side,  $E$  in Fig. 14 falls off on addition of 10-10 components considerably more steeply than in Fig. 13, from addition of 6-10 components, in which only one new unit, the 10 acid, is introduced. The  $I$  values follow, respectively, a similar course. The triangle in Fig. 14 was obtained for a sample of relatively short chain-length in which crystallization was more complete than in the high polymers. The higher  $E$  shows the importance of crystallite formation as well as copolymeriza-

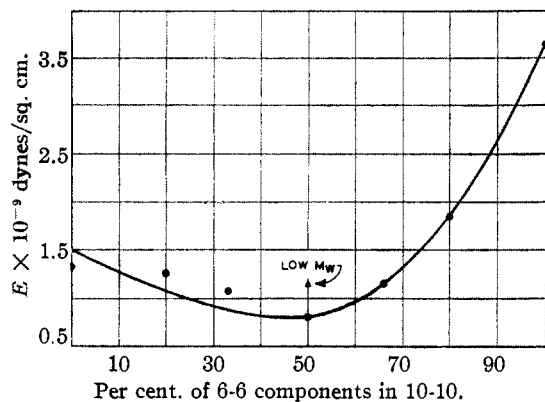


Fig. 14.—Dependence of Young's modulus,  $E$ , on composition of the copolyamide 6-6:10-10.

tion in the solids' properties. On the other hand, the significance of the latter factor is repeatedly evident; a new example appears from comparison of the pure 6-10 and the 33% 6-10 polymers of the 6-6:6-10 series in the plot of Fig. 15. These have the same  $E$  and virtually the same melting points. Although the disorder is greater in the 33% compound than in the 100%, the former's crystallites contain so many more polar groups because of the 6-6 content that the lattice energies of the two are nearly equal. The maximum disorder in the 50% composition causes it to fall off the line in Fig. 15. Its crystallite content is so sharply reduced compared to the rest of the series that  $E$  is reduced beyond the value proportional to the melting point of the remaining crystalline regions.

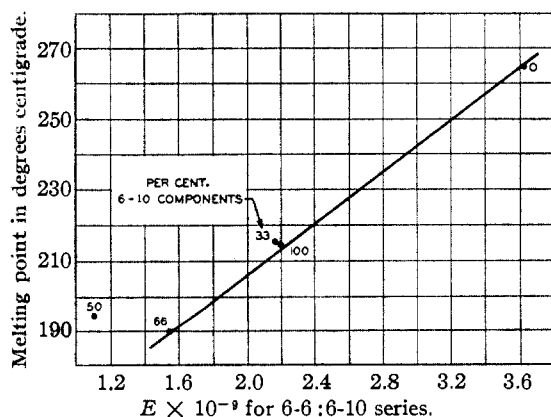


Fig. 15.—Relation of Young's modulus,  $E$ , to melting point in 6-6:6-10 series.

**Moisture Sorption.**—The polar groups in polymers provide loci of water sorption; only minute amounts of moisture are taken up by non-polar solids like polystyrene or polyethylene.

Hence, the preceding ideas of dipole layer population may be further tested by sorption measurements. The greater the concentration of polar groups in the simple polyamides, the higher their sorption; this is the chief factor also in the copolyamides and appears for both types in Figs. 16 and 17. Both series show inflection of the sorption

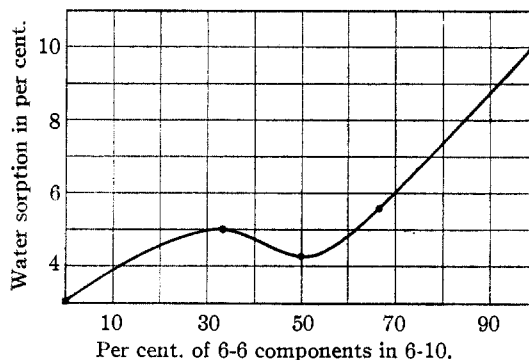


Fig. 16.—Relation of water sorption at 100% R. H. and 25° to composition of the copolyamide 6-6:6-10.

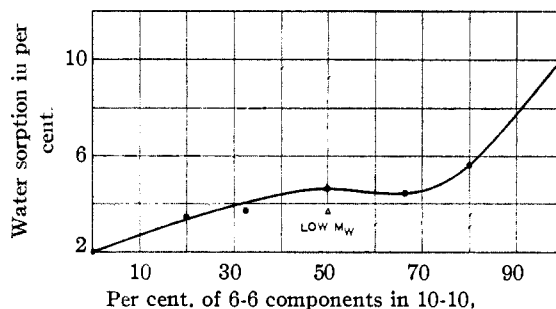


Fig. 17.—Relation of water sorption at 100% R. H. and 25° to composition of the copolyamide 6-6:10-10.

curves in the middle regions of concentration, in accord with the X-ray and elastic modulus determinations. When defects are introduced in the layers by copolymerization, the displaced polar groups are uncompensated by association with other dipoles and can bond with water. This presumably causes the maxima in Figs. 16 and 17. However, the exact significance of the maxima's positions is obscured because the "freed" polar linkages occur immersed in paraffin surroundings (from the methylene portions of the chains). This is a hydrophobic environment, so the water content is not affected as sensitively by disorder as the other properties studied. However, such qualities of technical importance as moisture sorption have not previously shown this direct connection with molecular structure in polymer materials.

A large portion of the water sorption is sup-

posed to be in non-crystalline regions of the polymers. Furthermore, the total polar group concentration changes gradually and continuously in a given series. Hence, the percentage taken up should not be so sensitive a function of composition as I, the spacing in the crystallites. This is confirmed by the data of Table I or by comparison of Figs. 16 and 17.

**Acknowledgment.**—We are grateful to Dr. B. S. Biggs and Mr. R. H. Erickson, who prepared many of the polymers, especially to Mr. N. R. Pape, who gave valuable assistance in the X-ray studies, and to Mr. J. H. Heiss, Jr., for the determinations of Young's modulus and moisture sorption.

### Summary

Thirty-one linear polyamides and copolyamides of varying crystal structures and concentrations of polar linkages along the chains have been studied as fibers and as polycrystalline sections by X-ray diffraction. Also, the elastic modulus and moisture sorption were determined on typical samples of the polymers.

The series represents a range of solid polymers from soft to porcelain-like in properties, with several-fold variation in Young's modulus. The polar linkages which join the paraffin sections of the

base units together in the long chains associate in adjacent macromolecules to form hydrogen-bonded dipole layers. This interaction is supposed to govern the physical properties of the solids. By this concept it was possible to interpret systematically the melting points, hardness, elastic modulus and moisture sorption of the solids in terms of the concentration, separation, population and perfection of the dipole layers. Disorder introduced by copolymerization in which dipoles were shifted randomly along the chains altered the average dipole layer separations and also replaced polar groups in the layers by hydrocarbon chain sections. Such disorder caused marked softening of the solids. It likewise caused the X-ray identity periods along the chains to vary with composition of the copolyamides in a novel fashion. Periods were found in the copolymers both larger and smaller than those which arise from any simple polyamides made from the same base units.

Macromolecular solids containing some crystalline regularity may apparently be treated as defect systems in which, nevertheless, relatively simple factors such as the position and organization of interacting polar groups govern physical properties.

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## Crystalline Aliphatic Esters of Vitamin A<sup>1</sup>

BY JAMES G. BAXTER AND CHARLES D. ROBESON

This Laboratory is engaged in the preparation of the pure growth promoting factors in fish liver oils. As part of this program three crystalline aliphatic esters of vitamin A have been prepared: vitamin A acetate, vitamin A palmitate, and divitamin A succinate. Since in fish liver oils vitamin A is esterified with aliphatic acids, such as palmitic,<sup>2</sup> these crystalline esters are suitable for the study of vitamin A as it occurs naturally. Vitamin A  $\beta$ -naphthoate, a previously prepared crystalline ester,<sup>3</sup> was also made to compare it with the aliphatic esters. It had the undesirable

property that the aromatic nucleus contributed extraneous absorption at 328  $m\mu$ .

This paper is concerned with these properties of the esters: (a) their resistance to atmospheric oxidation, (b) their extinction coefficients at 328  $m\mu$  and of their antimony trichloride blue colors at 620  $m\mu$ , (c) their biological potency compared with that of crystalline vitamin A. Part (c) is a preliminary report of bioassays made by Dr. P. L. Harris of this Laboratory.

The esters were made by esterifying crystalline vitamin A<sup>4</sup> with the appropriate acid halide. The yields of ester were sharply reduced when potent vitamin A concentrates ( $E_{1\text{ cm}}^{1\%}$ , 328  $m\mu$  = 1200 or greater) were esterified instead of crystalline vitamin A.

(1) Presented in part before the Division of Biological Chemistry of the American Chemical Society, Atlantic City meeting, Sept., 1941.

(2) Tischer, *J. Biol. Chem.*, **125**, 475 (1938).

(3) Hamano, *Sci. Pap. Inst. phys. chem. Res.*, Tokyo, **23**, 69 (1935); Mead, *Biochem. J.*, **33**, 589 (1939).

(4) Baxter and Robeson, *THIS JOURNAL*, **69**, 2411 (1942).