[CONTRIBUTION FROM THE BELL TELEPHONE LABORATORIES]

Intermolecular Forces and Chain Configuration in Linear Polymers—The Effect of N-Methylation on the X-Ray Structures and Properties of Linear Polyamides

BY W. O. BAKER AND C. S. FULLER

If linear polymer molecules are assumed to have a relatively high, fixed, average molecular weight, the properties of their solids depend primarily on two factors: The kind and extent of the molecular order or arrangement present, and the intermolecular forces. The linear polyamides have been chosen as models to investigate these relations, and the general results apply to all chain polymers.

The molecular order may approach that of crystalline perfection as it does in ramie and certain synthetic polyesters,[1] or it may reach maximum disorder as in unstretched, unfrozen natural rubber. In general, real polymeric compounds, unless they are completely disordered molecularly, consist of a dispersion of two or more kinds or degrees of order,[2] and these are associated with various chain configurations.[3,5] With X-ray patterns as a criterion, it is convenient to distinguish regions which show (1) crystalline order in which the repeating units are arranged according to a lattice in three dimensions, (2) mesomorphic order in which the units are arranged parallel to the chain direction with corresponding groups opposite but are otherwise random or in which the units are simply arranged parallel to the chain direction, and (3) no molecular order. In this case the repeating unit loses its significance and the order becomes atomic. These regions may be termed amorphous.

Certain subclasses of mesomorphic order exist for essentially linear polymers. One possible description of these follows:

(I) Lateral disorder of chains of uniform composition (homo-chains). That is, the chains are composed of a single repeating unit. Their lateral disorder means that they are randomly rotated about their long axes, in the polymer solid. In addition, of course, they are presumably kinked, but we are considering more local order, less affected by gross orientation, than that of the meandering paths of long chains. Examples of this class include polyamides,[5] cellulose triesters,[3] polyvinylidene chloride, polyethylene, etc., in the quenched state.

(II) Longitudinal disorder in chains of nonuniform composition (hetero-chains). Here the chains may include repeating units of various lengths, so that equivalent chain sections, such as polar linkages, do not come together in adjacent, parallel chains. Evidently this order may also have superimposed on it (I) above[4] or (III) below. Examples are copolyamides, copolyesters, copolysulfides and indeed most copolymers. However, many vinyl and diene copolymers have such large side groups that the effect of the type (II) disorder is obscured by extensive type (III) steric disorder. Also, chain inversion,[4] in which adjacent chain segments do not have the repeating units running in the same direction along the chains, might cause special longitudinal disorder.

(III) Steric disorder from side groups in either homo- or hetero- chains. Chains made irregular in packing by side groups include most vinyl polymers, such as polyvinyl chloride, polystyrene, etc. Here the side groups do not occur regularly or frequently enough (as contrasted to polyisobutylene, which is quite highly ordered when stretched) so that the combined main-chain and side-group packing is orderly. Also, vinyl copolymers as polyvinyl chloride acetate, synthetic rubbers such as Bunas, cellulose partial esters and mixed esters, natural proteins and many other chain polymers show this disorder.

It is assumed always that the given order refers to the properties of the solid polymer under definite conditions, *i. e.*, stretched rubbers or quenched polymers[3,4,5] may have temporary degrees of order.

The preceding three classes of order are not proposed to classify uniquely the organization in a given polymer solid. Rather, they are hoped to show the varieties of chain configurations and packing which must be considered in investigating a definite chemical composition.

The N-methyl substituted polyamides discussed

---

[1] "The Collected Papers of W. H. Carothers," Interscience Publishers, New York, N. Y., 1940; Fuller, *Chem. Rev.*, **26**, 143 (1940).

[2] Gerngross, Herrmann and Abitz, *Z. physik. Chem.*, **B10**, 371 (1930).

[3] Baker, Fuller and Pape, THIS JOURNAL, **64**, 776 (1942).

[4] Baker and Fuller, *ibid.*, **64**, 2399 (1942). "Conference on Physics of the Solid State," N. Y. Academy of Sciences, 1942.

in this report possess chiefly Type III disorder, which leads also to Type I disorder. The methyl groups occur in the dipole layers of the solids and disorganize the forces in these regions. Other disorganization of these dipole layers has been found in the copolyamides.[4] In both cases hydrogen bonding is greatly reduced, in analogy to the substitution of cellulose to give esters, ethers, etc. Further, significant differences in configuration along the chains, apparently involving a twisting or bending, seem to occur as a result of this force weakening and disordering.[4] Since such twisting is suspected in the mechanism of high elasticity, direct evidence for it bears on the properties of rubbers. The highly substituted N-methyl polyamides indeed show rubberiness. X-ray diffraction has shown that various chain configurations in these compounds do exist as functions of external stress and degree of methylation (force weakening). Other physical properties, such as elastic modulus and moisture sorption have also been measured and related to the molecular structure.

Experimental

Materials.—Polydecamethylene sebacamides in which the degree of N-methylation was varied from 0 to 55 mole per cent. of the amide groups were employed. They were prepared from purified intermediates and were all of sufficiently high average molecular weight to allow ready drawing of fibers for X-ray examination. In the range up to 50% methylation, usually the mono-secondary diamine was employed to supply the methyl components. Above 50% a random mixture of di-secondary and mono-secondary diamines was employed. No effect of the distribution of methyls among the primary amide groups was evident from these experiments.

Samples were oriented from quenched[5] or partially quenched polymers, and were then annealed in an inert atmosphere for two hours at 20 to 25 ± 0.5° below their melting points. This caused no discernible disorientation, but in all cases the expected improved crystallization. The samples were 23 to 25 mils thick when exposed, unless they were further stretched. In most cases they were annealed in a clamp to prevent shrinkage, and where noted they were further elongated after annealing, and thus exposed in a small clamp which was rigidly fastened on the X-ray collimator. The jaws of this clamp were movable so that the samples could be slowly and uniformly stretched.

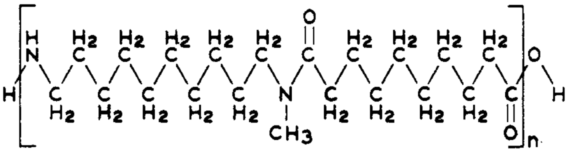
X-Ray Diagrams.—X-ray photographs of the fibers and unoriented sections were obtained as described previously.[4] A CA-6 G. E. tube supplied Cu K radiation through beryllium windows. The K_α was filtered with Ni foil to remove the K_β. Salt dusted on the mono-filaments gave direct distance calibration. The specimen-to-plate distance was commonly 6 cm. and critical features were repeatedly checked. Fibers were frequently irradiated in positions 90° apart about the fiber axis, to establish uniaxial orientation. The doubly-oriented (biaxial) samples were produced by drawing and rolling of filaments.

Elastic Modulus.—Methods previously discussed[4] were used to obtain Young's modulus, E, from the penetration of a quartz spherical section into a plane panel of the polymer. However, some of the 10-10 (the numbers refer to the carbon atoms in the acid and diamine chains) N-CH_3 polyamides were so soft that even light loads caused a slight permanent deformation; hence, some of the values quoted reflect a plastic as well as elastic behavior. The polymer panels were dried before test, and average values from triplicate readings are reported.

Moisture Sorption.—The water sorption was determined on flat sections 3 × 2 × 0.051 cm. Equilibrium was checked by repeated weighings after exposure at 25.0° to saturated ammonium sulfate (81% RH) and immersion in water (100% RH). The sorption is reported as weight per cent. of the dried (phosphorus pentoxide) sample. Humidified samples were dried and re-equilibrated, and only a very small hysteresis was found.

Results and Discussion

The effects of polar coördination and disorder on mechanical properties of solid polymers already have been examined.[4] Figure 2 illustrates the sevenfold change in stiffness which was introduced in the polydecamethylene sebacamide series by substitution of various (molar) proportions of methyl groups for hydrogen atoms in the diamine. The structure for a typical composition is shown in Fig. 1. This wide range in properties is, in this case, apparently chiefly the result of a sharp reduction in intermolecular forces. Methylation removes hydrogen bonding and reduces dipole attraction sterically, much as do larger acyl radicals in cellulose esters.[3] Thus, while the unmethylated polyamide is hard, high melting and somewhat brittle, the higher ranges of methylation are soft and rubbery. If reduced molecular interaction causes this transition in mechanical properties, the melting points should follow the decline of elastic modulus in the series. This is shown in Fig. 3, where the relation is approximately linear.



Average unit of 50% N-methylated 10·10 polyamide.

Fig. 1.—Structural formula of an average unit of polydecamethylene sebacamide with 50 mole per cent. of N-methylation.

---

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

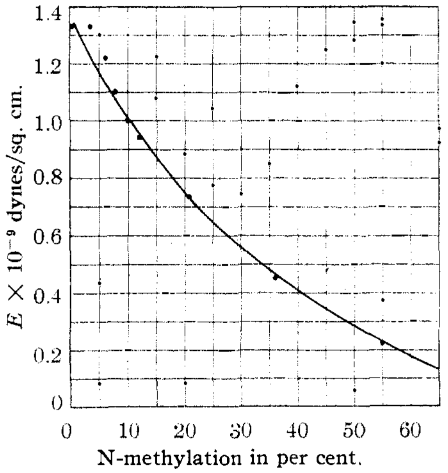


Fig. 2.—Dependence of Young's modulus, E, on the molar proportion of N-methylation for polydecamethylene sebacamides.

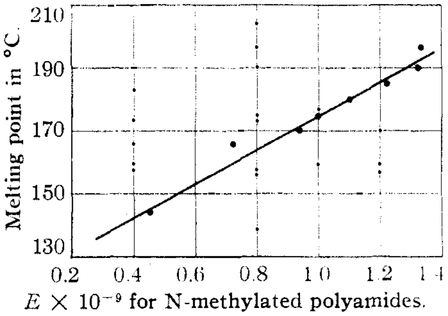


Fig. 3.—Relation of the elastic modulus to the melting point of N-methylated polydecamethylene sebacamides.

The elastic modulus, whose values appear in Table I, approximates an exponential function of composition, of the form $E = Ae^{-Bc}$, where A and B are constants, and c is the mole fraction of N-methylated groups.

TABLE I

10-10 Polyamide N-Methylation, %[a]	$E \times 10^{-9}$ (dynes/sq. cm.)	Water sorption 81% RH	Water sorption 100% RH
0	1.33	1.6	2.0
3.5	1.30	1.6	2.2
6	1.22	1.6	2.1
8	1.10	1.6	2.1
10	1.00	1.6	2.1
12	0.94	1.7	2.3
21	.73	1.7	
36	.45	2.0	2.6
55	.22	2.4	3.1

[a] Van Slyke.

Small polar molecules can be sorbed on polar linkages which are not strongly associated. Thus, the moisture sorption of the polyamides would be expected to rise with increasing methylation, as shown in Fig. 4 and Table I. This is another indication of reduced intermolecular forces in the solids. It is interesting that the moisture sorption increases by about 50% of its original value when about half of the —NH— groups are methylated. Unlike the copolyamides,[4] water take-up is here uncomplicated by changes in polar group concentration. In all cases, however, it can serve as a measure of the organization in the dipole layers. The hydrogen bonds of perfectly ordered, associated —CONH— groups are apparently seldom split by water at 25°; for example, in films, the self-bonded linkages are about 640 cal./mole more stable than those bonded to water.[6] While moisture may be sorbed in the dipole fields of self-bonded linkages, it will be expected chiefly to seek amido groups uncoördinated because of chain disorder or of N-methylation. Similar effects occur in partially substituted cellulose and proteins. There remains, of course, the further factor that among comparably hydrophilic materials, softer substances always absorb more water than harder ones; this must be considered in interpreting sorption results.

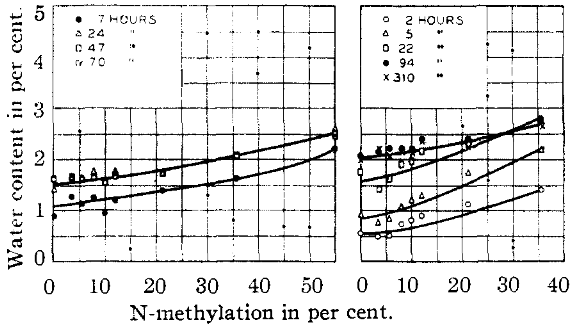


Fig. 4.—The water sorption at 81 and 100% relative humidity, respectively, of N-methyl substituted polydecamethylene sebacamides.

Although unsubstituted, hydrocarbon-chain, polyamides are soluble only in strong hydrogen-bonding solvents such as cresol, the reduction in interchain forces discussed above should increase the solubility in a given series. Thus, while 40% ethanol–60% chloroform (by volume) only penetrates the usual polyamides, such a mixture swells the lower ranges of methylation, and dissolves the higher. Figure 5 illustrates this solvation, since it indicates the amount of extraction (of low species) from comparable samples in contact with this solvent at 25°.

The chemical measurements therefore agree with the mechanical studies in implying intermolecular forces weakened by substitution. The

(6) Alexander, *Proc. Roy. Soc.* (London), **A179**, 470 (1942).

elastic modulus values show, for example, that the polymer chains (in segments) may be displaced from potential minima more easily the higher the substitution, or lower the effective polar group association.[4] The question occurs of whether such displacements can cause significant variation in inter- or intra-chain configurations. This is one of the primary problems in the theories of rubberiness. Since, as noted above, much rubberiness appears in the disordered polyamides, their structures yield information from X-ray diffraction of the behavior of chain molecules under stress.

Inter-Chain Spacings.—The equatorial or near-equatorial fiber features yielded in all cases of annealed fibers the characteristic[4,5] polyamide spacings of 3.76 and 4.40 Å. These are taken to represent lateral chain separations in the stable, crystalline chain configurations of polyamides whose dipole layers are oblique to the chain axes. When these same polyamides are quenched, there is metastable dipole association into planes which are perpendicular to the chain axes. Here, the single equatorial spacing is about 4.18 Å., suggestive of hydrocarbon chain packing. This same spacing is found in certain polyamides (as from base units containing odd numbered chains, such as 9–9) whose chains assemble perpendicular to the dipole layers even in the most crystallized state. These variations are found throughout the N-methyl polyamides, but the methyl side groups do not appear to alter directly the lateral separation of the chains. They do diffuse some of the equatorial features at the higher degrees of methylation. Since main chain axes do not approach much closer than 4.7 Å., there is evidently room for a methyl group of bond radius 1.47/2 Å. and kinetic theory radius 2 Å. Thus, while the amido hydrogen projects from the N for a bond distance of 1.0 and a probable kinetic theory distance of 1.1 Å. beyond that, for a total of 2.1 Å., the methyl group probably projects 3.5 Å. from the N. To its lack of a bonding hydrogen there is thus added, for the N-methylated linkage, a steric hindrance which may lead to chain repulsion. Hence, it is interesting that in the present series the prime effect of a lateral substituent is to change not the side spacings but the long spacings of the chains. These long spacings have previously been found for many of the simple polyamides[4] to be less than the calculated values. For instance, polydecamethylene sebacamide generally exhibits an identity period, I, of 25.6 Å.; the expected value for an extended zigzag chain is 27.5 Å. Further, for the following methylated polyamides, and various others not discussed, I values can be reduced by 26.5% of the calculated values.

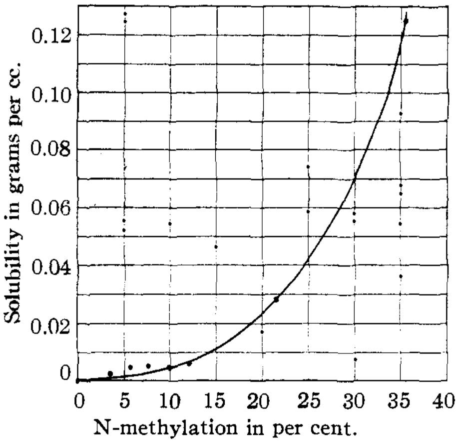


Fig. 5.—The relative solubilities in ethanol–chloroform mixture of polydisperse samples of N-methylated polydecamethylene sebacamides of comparable molecular weights.

Suggested Packing of Polar Hydrocarbon Chains.—A possible explanation for these varying chain structures may be considered now so that it can be related to further experimental results. It may be assumed that the methylene group sections of the polyamides tend always to pack like the chains in pure hydrocarbons, whose structures have been previously described.[7] Each hydrocarbon chain section has a polar group, the polymer linkage, at either end. Polar coördination of these groups (association of dipoles and formation of hydrogen bonds) apparently does not favor the paraffin packing This is reasonable when one imagines the changes in the "setting angle,"[7,8,9] φ, which would occur if attracting polar groups were inserted in the chains shown end-on in Fig. 10. The chains in the cell drawn would tend to twist at the polar *groups*. Some of the twisting tendency in the dipole layers could occur in the direction of the dotted arrows. There is thus a competition between the preferred positions of the paraffin portions and of the associated polar portions of the chains. Consequently, at each of the dipole layers there is a torque tending to skew portions of the chains from the preceding paraffin arrangements into the polar arrangements

---

(7) Müller, *Proc. Roy. Soc.* (London), **120**, 437 (1928).

(8) Kohlhaas and Soremba, *Z. Krist.*, **100**, 47 (1938).

(9) Bunn, *Trans. Faraday Soc.*, **35**, 482 (1939).

and the result is a rotation about the freer bonds near the polar linkages so that, as seen normal to the fiber axis, the chains progress as illustrated in Fig. 11a. Of course, there is doubtless less regularity and uniformity, and certainly less planarity than appear in the scheme of Fig. 11a. We may consider briefly the relative energies of the packing competition.

Müller[10,11] has calculated from polarizability and susceptibility values the van der Waals attraction of paraffin chains, which leads to φ values of 0 to 90° for the minimum potential. However, when the repulsion terms are also accounted for, the total potential follows the curve of Fig. 12, and the minimum is near the experimentally observed angle of $\varphi = 30°$. Further, the average energy difference per mole of methylene groups between the 30° and, say, 0° position, can be estimated as 520 calories. This value may be multiplied by the number of methylene groups in a paraffin segment in so far as these segments can be regarded as relatively rigid. The energy of rotation around the CH_2–CH_2 bond is apparently high[12] compared to that about a C–C bond in CH_2–C=O,[13] which occurs in the polymers. We may thus approximate the energy of position of the paraffin sections restraining them from occupying the orientation accompanying closest coördination of their polar ends. On the other hand, the coördination energy must be about 6–8000 calories per hydrogen bond[14,15] (two chains). Therefore, a sufficiently high concentration of polar linkages along the chain should yield a structure well dominated by the polar coördination. This results in extended chain configurations as in Fig. 11b. These have the calculated length per repeating unit, and well resolved side spacings of 3.70 and 4.40 Å. Such alternatives seem significant in the succeeding results.

Relation of Mechanical Treatment to Fine Structure.—Figure 6A is for the lowest per cent. of N-methylation, 3.5. This pattern is typical of polyamide fibers. The quenched polymer was cold-drawn, fixed in a clamp, and annealed for two hours at 170° in an inert atmosphere. Figure 6B is the strikingly altered diagram obtained from a portion of the same fiber annealed under like conditions without a clamp. The normal shrinkage[5] of the fiber has been attended by a change in structure. The identity period spacing has decreased from 25.8 Å. for the clamped specimen to about 20.2 Å. for the retracted form. The outer equatorial spots of 6A have split in 6B, and the resolved layer line features have coalesced into intense meridian reflections. The phenomenon is the same in all of the substituted polyamides and related substances in which it is observed. Table II compares typical observed features of the patterns for the 3.5% methylated fibers.

TABLE II

Specimen	Reflection	Inter-planar spacing, Å.
3.5% methylation fiber clamped during annealing	A_1	4.4
	A_2	3.8
	II_0	25.8
	II_1	25.9
3.5% methylation fiber free during annealing	A_1	4.5
	I_0	20.2
	II_0	20.3
	III_0	19.8
	IV_0	19.8
	III_1	20.1

Since the final crystalline forms of Figs. 6A (extended) and 6B (retracted) resulted from different mechanical treatments of the original oriented but highly disordered (quenched) fiber, the latter must contain molecular configurations capable of crystallizing in the solid state in different forms. Figure 6C is a typical quenched fiber pattern,[5] in this case for 9.9 mole per cent. N-methylation. The long chains are approximately parallel to the fiber axis and are randomly rotated about their long axes; their dipole planes are nearly normal to the axis and in these planes the polar linkages are strongly associated. The single equatorial spot of Fig. 6C corresponds to about 4.18 Å.; the principal meridian feature, II_0, to 24.8 Å. This distance is thus between the extended and retracted values. The usual behavior on annealing polyamides with relatively high polar group concentration and thus high interaction, such as polyhexamethylene adipamide and polyhexamethylene sebacamide, is like the clamped behavior of the less strongly associated polymers. Thus, Fig. 6C would be transformed to Fig. 6A. It now appears that this transformation of the substituted polyamides *unclamped* can be effected by annealing at low temperatures. The freedom of the molecules in the solid is then

---

(10) Müller, *Proc. Roy. Soc.* (London), **154A**, 624 (1936).

(11) Müller, *ibid.*, **178A**, 227 (1941).

(12) Kistiakowsky and Nazmi, *J. Chem. Phys.*, **6**, 18 (1938); Kistiakowsky and Rice, *ibid.*, **8**, 618 (1940).

(13) Schumann and Aston, *ibid.*, **6**, 485 (1938).

(14) Unpublished studies.

(15) Baker and Yager, THIS JOURNAL, **64**, 2171 (1942).

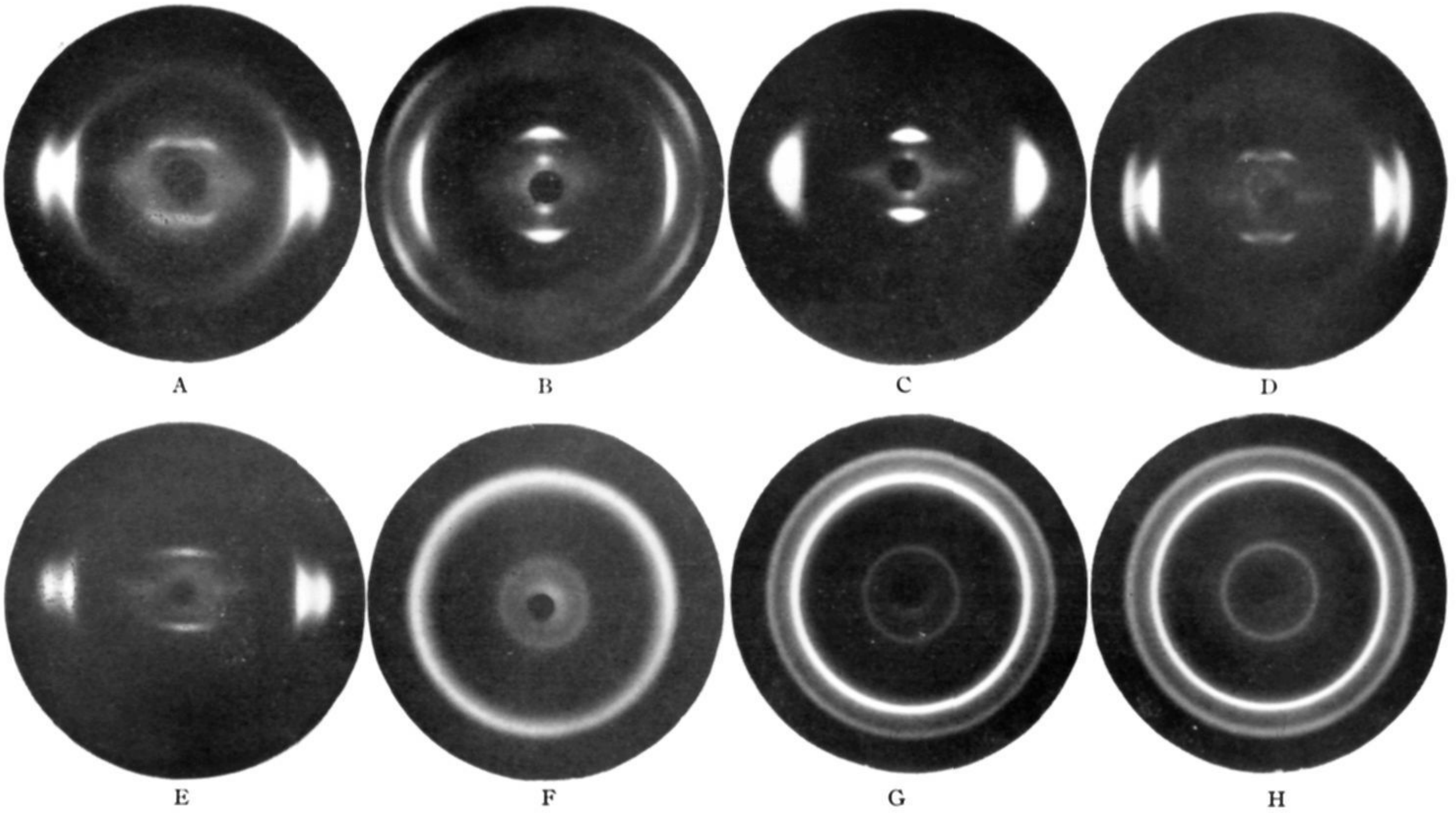


Fig. 6.—X-Ray patterns (where oriented, with fiber axis vertical) of N-methylated polydecamethylene sebacamides (the numbers refer to the mole per cent. of N-CH$_3$ groups): A, extended form, 3.5%; B, retracted form, 3.5%; C, quenched fiber, 9.9%; D, low temperature annealing, 5.7%; E, sample of (D) stretched; F, quenched, unoriented, 9.9%; G, (F) annealed in solid state; H, cooled slowly from melt, unoriented, 9.9%.

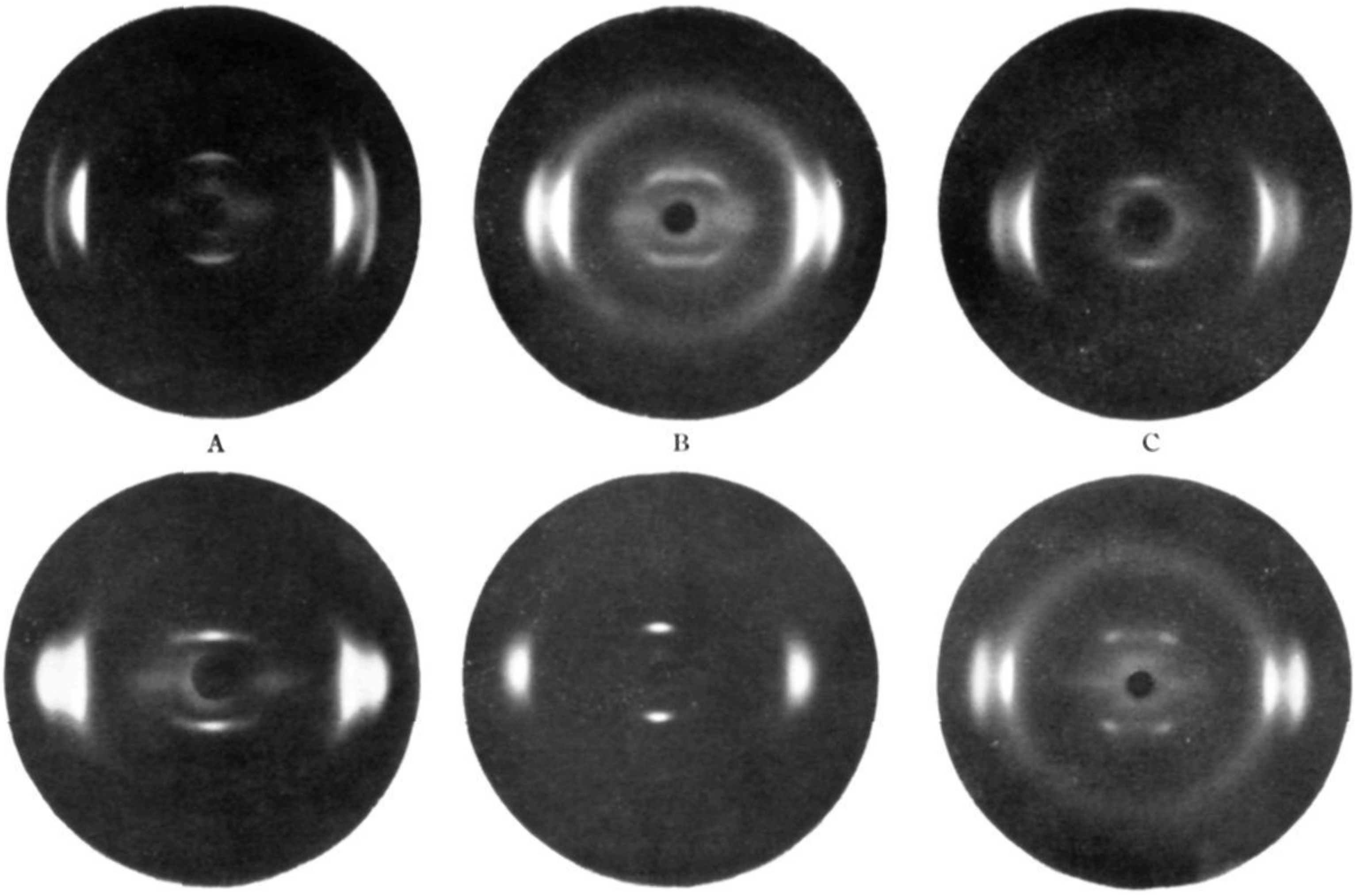


Fig. 8.—X-Ray fiber patterns (axis vertical) of N-methylated polydecamethylene sebacamides showing effects of tension: A, 9.9% N–CH$_3$, annealed two hours at 162°, unclamped; B, sample of (A) stretched 25%; C, sample of (A) stretched 75%; D, 22.5% N–CH$_3$, stretched to maximum; E, 35.6% N–CH$_3$ annealed, unclamped; F, 35.6% N–CH$_3$ annealed in clamp, exposed unclamped; G, 54.7% N–CH$_3$ annealed in clamp, exposed unclamped; H, sample of (G) stretched 200% exposed clamped; I, sample of (H), exposed unclamped. (G, H and I, see over.)

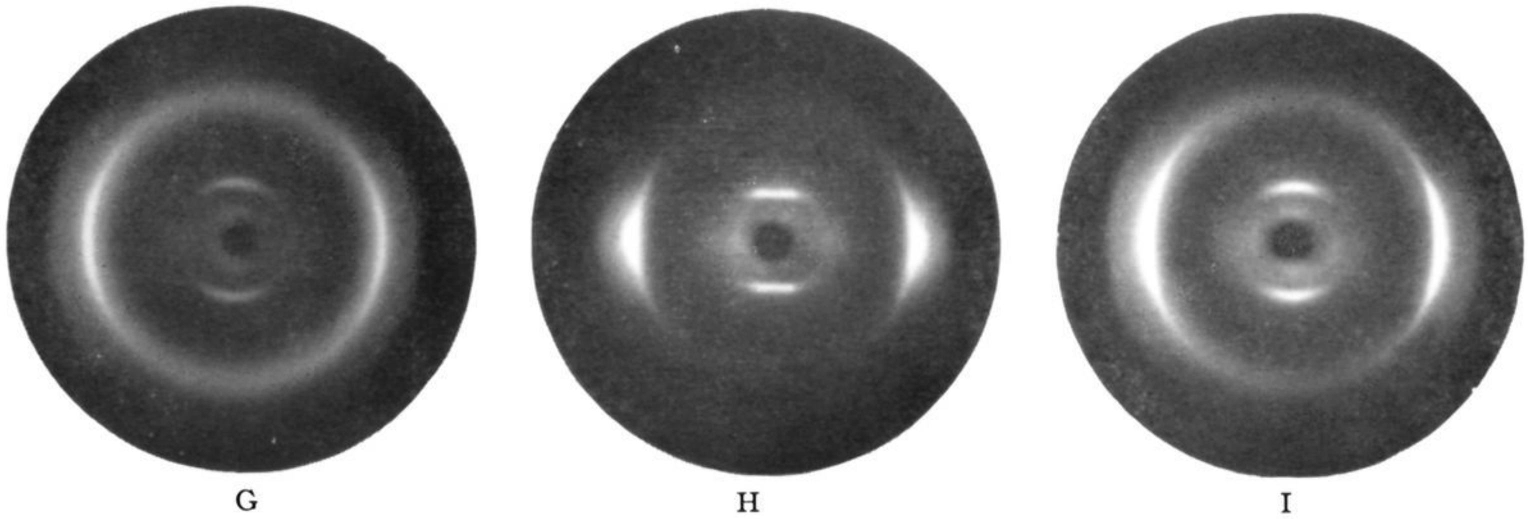


Fig. 8.—(Continued.)

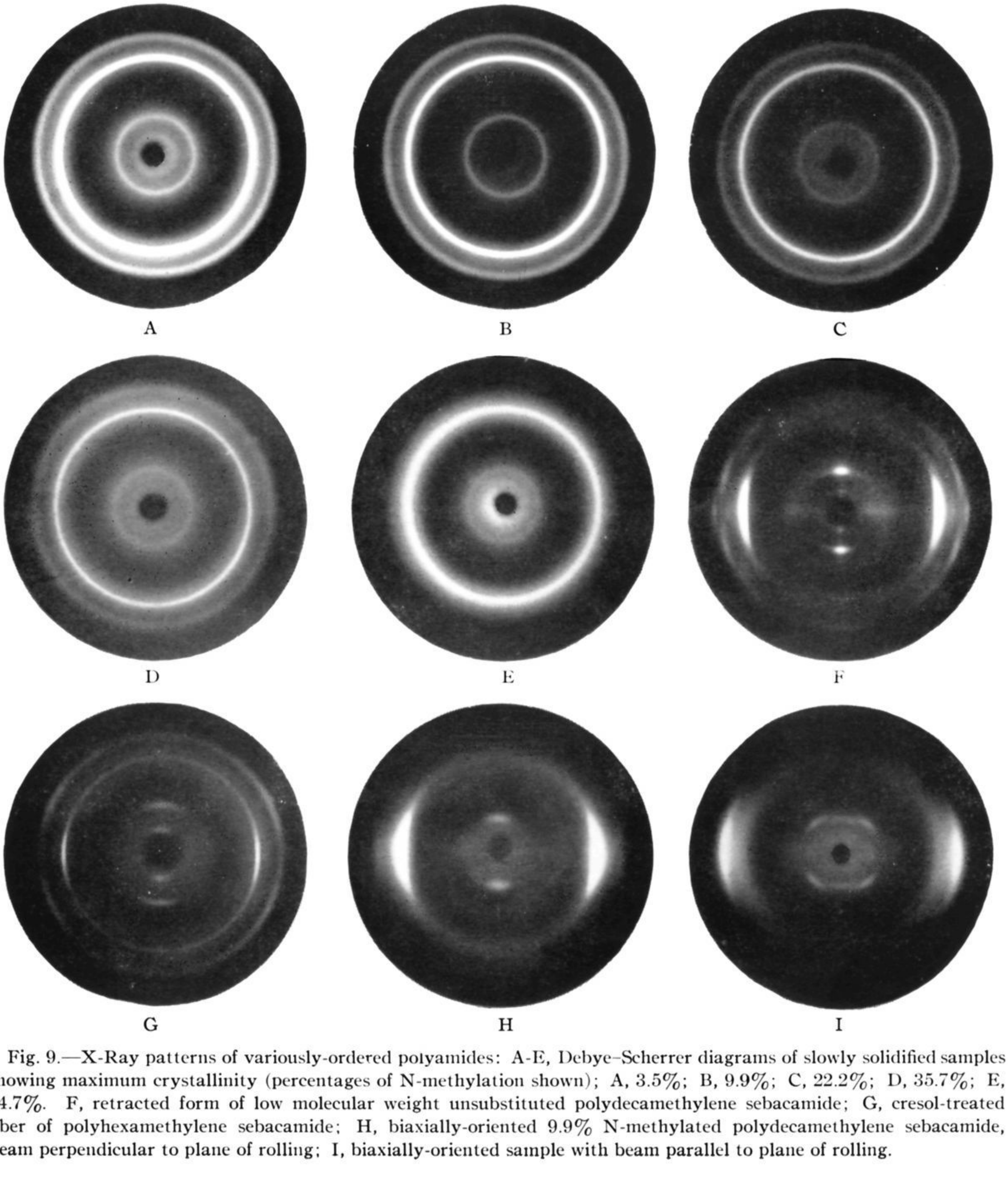


Fig. 9.—X-Ray patterns of variously-ordered polyamides: A-E, Debye–Scherrer diagrams of slowly solidified samples showing maximum crystallinity (percentages of N-methylation shown); A, 3.5%; B, 9.9%; C, 22.2%; D, 35.7%; E, 54.7%. F, retracted form of low molecular weight unsubstituted polydecamethylene sebacamide; G, cresol-treated fiber of polyhexamethylene sebacamide; H, biaxially-oriented 9.9% N-methylated polydecamethylene sebacamide, beam perpendicular to plane of rolling; I, biaxially-oriented sample with beam parallel to plane of rolling.

insufficient for formation of the retracted state. Figure 6D is from annealing at 150° for two hours a 5.7% methylated sample, *unclamped*. While the outer equatorial spots show a definite elongation tending toward the retracted forms the identity period from II_1 layer lines is 23.6 and from the II_0 meridian spots, 25.8. Both are well above the retracted value of 20.2, but mixed forms are also indicated. However, a form of molecular clamping has been seemingly introduced by the lower temperature crystallization.

It will be shown below that the retracted spacings can always be transformed into extended ones by some sort of stretching. In the experiment above, can the apparently stable "intermediate" form represented by Fig. 6D be similarly influenced? Figure 6E is the sample of 6D stretched 130% at room temperature. The II_0 features now represent an *I* value of 26.4 Å.; the equatorial spacings are unchanged and the arcing of the outer spots has been narrowed. It now appears that the process of apparent chain elongation (to give a value only 4% rather than 26.5% shorter than the calculated) has drawn the formerly tilted (Fig. 6D) dipole layers into a position approximately normal to the chain axes. This is not a low energy arrangement,[15] and therefore the fiber has to be photographed under stress. But this experiment emphasizes further[4] that extended forms having the calculated planar chain spacing value are not stable, for these compounds.

Although the oriented state has so far been considered, the occurrence of the retraction phenomenon is not limited by this condition. Figure 6F is a typical diagram from an unoriented quenched section. The ring corresponding to the identity period has a *d* value of 24.3 Å. When such a sample is annealed, for instance a 9.9% N-methylated specimen, the pattern of 6G results, and here the spacing along the chain from ring *d* values is 21.3 Å. The same figures were obtained from the Debye-Scherrer rings of samples allowed to crystallize very slowly from the melt as illustrated by Fig. 6H. Such spacings correspond to a 22.5% shortening of the calculated period. Thus, retracted chain forms[15a] occur spontaneously in the formation of a random mass of crystallites. These forms presumably represent the lowest free energy and resemble the conditions assumed for unstretched rubber.

Effect of Stretching.—Since the crystallization of disordered polyamide chains may be diverted into the extended form by clamping or low temperature annealing, the question occurs of whether the retracted form can be converted by stress alone. Certain effects of stretching polyester fibers have been noted[16] which resemble those found here, and probably have similar causes. Figure 7 illustrates the change in fiber period caused by stretching and exposing in a clamp an annealed, essentially retracted, fiber of 9.9% N-methylation. The sample exhibited rubbery behavior throughout this range, and in so far as identity periods reflect distances along a given molecule, Fig. 7 offers direct evidence of chain lengthening with sample stretch. If rubbers had polar groups which would associate strongly enough to form similarly ordered layers in the retracted state, such changes should likewise be evident in their diagrams.

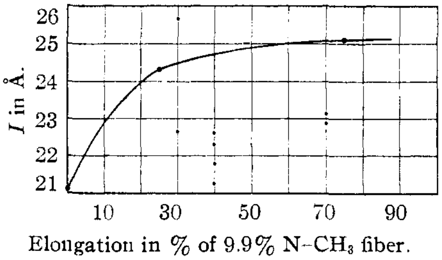


Fig. 7.—Change in identity period, I, caused by stretching fiber of 9.9% N-CH_3 polydecamethylene sebacamide.

Figures 8A, 8B and 8C show the X-ray patterns of the retracted, 25% and 75% stretched fibers, respectively, of 9.9% methylated polymer. The sample for Fig. 8A was not annealed to the complete retraction, hence the equatorial splitting is not well resolved. In Fig 8B the II_1 layer lines are evident, while in 8C, they have been coalesced again into the meridian. The extended value of I = 25.1 Å. from 8C is, of course, considerably less than the theoretical. However, Fig. 8D represents the effect of severe stress on even more weakly interacting chains—those with 22.5% methylation. In this pattern, the II_0 features have *d* values of 26.4 Å., and the vestiges of the II_1, of 27.1. These approach the fully extended value of 27.5, which might even be attained with further stretching, but which is, we emphasize again, an unstable configuration. For instance, the unstretched period of this sample was 20.5 Å.

So far, any explanation of the retraction phe-

(15a) Some evidence for chain retraction also occurs in patterns from dried muscle fibers; see Lotmar and Picken, *Helv. Chim. Acta*, **25**, 538 (1942).

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

nomenon would appear related to two factors: (1) the relative proportion of polar to paraffinic matter in the chains, (2) the strength of interaction in the polar planes. If the chain identity period shortening is from twisting of chain sections about bonds near the polar links, and if such twisting is induced by differences in the preferred packing of the polar and paraffin portions, then weakening of the polar interaction should eventually reduce the observed retraction. This condition apparently occurs when about a third of the amide hydrogens are substituted, in the series studied. For while 22.5% N-methylation readily yields retracted forms of *I* = 20.5 Å., the 35.6% substituted members give I values of 25.3 Å. or more after the usual treatment for retraction. The extensive amorphous portions of the 35.6% polymers confer considerable rubberiness on the samples; the pronounced chain retraction is simply absent from the more ordered regions. Figure 8E is the pattern resulting when an oriented filament of 35.6% N-methylation is annealed without tension. For this, and several check samples, *I* = 25.3 Å. The appearance of meridian spots is partly because of double orientation introduced by stretching ribbons of these soft polymers. Thus, the 8E pattern is not uniaxial, whereas that of 8F was established to be so. Figure 8F is the pattern obtained after annealing in a clamp, even when the fiber is unstressed during exposure. Again, *I* approaches 25.0 Å., and this pattern further illustrates a stable, extended form.

The 54.7% N-methylated polymers show most plainly in this series the rubbery properties of the solids, both mechanically and in diffraction effects. The patterns likewise emphasize the extensive lateral disorder caused when about half of the polar linkages in the dipole layers contain methyl groups. Figure 8G was from a sample annealed while clamped, which showed a comparatively high degree of orientation in the stretched condition, but the arcing of 8G when it was allowed to relax. Accompanying this relaxation is a certain retraction of the identity period, since *I* = 23.2 Å. from the II_0 feature of 8G. This retraction is, however, not to be considered an equilibrium figure, unlike the retracted values of 20.5 Å. Then, when the sample was stretched 200% and clamped during exposure, the sharpening of Fig. 8H occurred, and the poorly resolved layer-lines correspond to *I* = 25.2 Å. Subsequent removal of tension (at room temperature) caused the disorientation of Fig. 8I. *I* has returned to 23.2 for the II_0 features, and, of course, the whole sample shortened. Apparently here more than in any previous member of the series, crystallites or ordered regions are orienting and disorienting during the easily reversible rubbery manipulation of the polymer. Correspondingly, and similarly to the phenomenon illustrated in Figs. 8A, 8B and 8C, the sample of 8G was photographed (not shown) after 100% elongation, and here *I* = 24.6 Å., intermediate between the 0 and 200% values. The system thus shows a revealing sensitivity to stress: the ordered regions orient and spacings within these regions are expanded, presumably by molecular elongation.

The lateral disorder in the dipole layers which has been predominant in all of the effects thus far discussed may be reviewed in the patterns of Figs. 9A, B, C, D and E. These are strictly comparable exposures of unoriented sections of compositions 3.5, 9.9, 22.2, 35.6 and 54.7% N-methylation, respectively. Each sample was solidified near its melting point, and represents the highest order characteristic of the compound. The striking effect of the lateral disorder is deterioration of the 3.76 Å. reflection, which apparently contributes only diffuse scattering in the 54.7% substituted polymer. The 4.40 Å. spacing features remain relatively sharp with increasing N-methylation. So do the inner rings on Fig. 9 which correspond to dipole layer separations along the chains; this is expected since primarily the imperfections are in these layers, and not between them. However, the dissimilar behavior of the two principal side spacings leads to brief consideration of possible causes of the retraction phenomenon itself.

Retraction Mechanism.—Since disorder and intermolecular force weakening in the dipole layers operate in the retraction, we look first for unusual behavior of side spacing features on the X-ray diagrams. First, the 3.7 Å. spacing characteristically splits on the equator and forms layer-line arcs in the retracted forms, as seen in previous figures. Second, this same feature deteriorates into diffuse scattering at high degrees of methylation. The other principal side spacing, 4.4 Å., remains intense and virtually unchanged in position through all phases of the extension and retraction. It is, indeed, well resolved in the rubbery sample of 54.7% N-methyla-

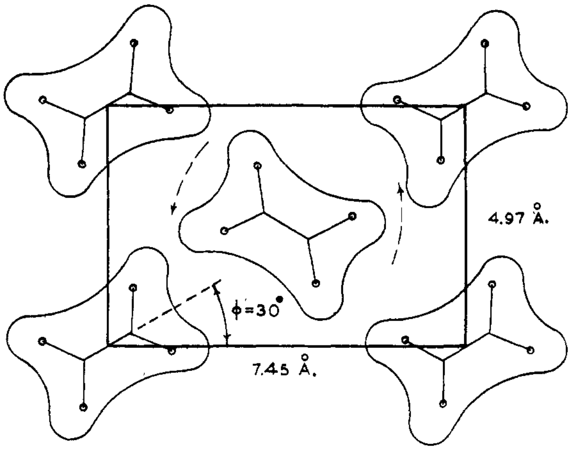
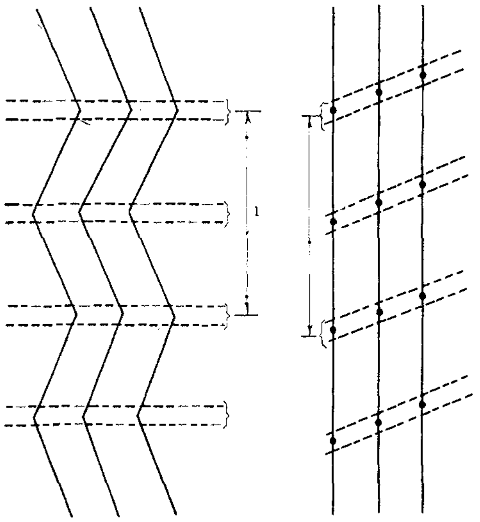


Fig. 10.—Schematic diagram of paraffin chain packing in a plane normal to the chain axes, after Müller. The enclosed areas represent the contours of the force fields.

tion (Fig. 9E). Such sharpness differs from the scattering found when the entire chains are assumed to be randomly disposed about their long axes.[3,5] The 4.4 Å. spacing seems therefore to result from planes whose scattering components are relatively unaffected by disorder in the dipole layers and by the retraction phenomenon. This condition may be attributed to the hydrocarbon sections of the polyamide chains. They are apparently dominating the arrangement in the 54.7% N-methyl compound, as discussed in the paragraph on chain packing. On the other hand, polyhexamethylene adipamide is an example of a highly polar structure, with an average of five methylene groups per linkage, and seems to give the expected extended structure predominated by the polar groups. When, however, nine methylene groups per linkage obtain, as in polydecamethylene sebacamide, the tendency for a compromise structure is strong, since the energy of position of the hydrocarbon segments is about 4700 calories per mole. The "normal" pattern for high molecular weight or extended 10–10 is like that of Fig. 6A, but Fig. 9F is the "compromise," further retracted, form obtained by annealing unclamped a medium molecular weight sample. (The influence of molecular weight in these phenomena is apparently its effect on the internal viscosity, which controls the ease of chain rearrangement.) Likewise, instead of increasing methylene group concentration, or in addition to it, the effect of polar coördination may be lessened by substitution, and then the same results occur. In this case, however, apparently an extreme can be reached at which the compromise structure satisfies the preferred hydrocarbon packing sufficiently so that relatively little twisting and shortening occur, as noted in a previous section. In this condition, only one side spacing remains well defined, however, the 4.4 Å.; the 3.7 Å. planes have apparently been disordered. Therefore, the chain configurations are actually different from the initial case where extended chains resulted from dipole domination. This disordering is consistent with other behavior of poorly organized systems; for example, only one side spacing (4.18 Å.) appears when quenched samples of any polyamide chains are studied. Further, the 3.7 Å. planes are those shifted off the equator when the retraction enters. The remaining 4.4 Å. planes must be from layers in the plane of Fig. 11a, while the 3.8 Å. planes are at one or various angles to the plane of the paper. Hence, the whole behavior of the 3.7 Å. planes traces the course of the proposed compromise structure.



(*a*) Retracted form (*b*) Extended form

Fig. 11.—Schematic representation of identity period shortening, a, and of the chains in the fully extended form, (b). The dotted lines represent the boundaries of polar group zones in which the principal interaction and twisting tendency occur.

Thus, the variations in the side spacing features on the model polymer X-ray diagrams can be related to a general mechanism for chain retraction and extension.

Force Reduction by Solvation.—The preceding ideas of chain packing suggest that weakening of polar interaction by solvation should produce similar configuration changes to those caused by substitution or dilution by methylene groups.

The solvating agent cannot, of course, be allowed too greatly to disorder the fiber studied. Polyhexamethylene sebacamide, with seven methylene groups per polar linkage, ordinarily shows no trace of a retracted form. When, however, an annealed fiber was exposed to cresol vapor in equilibrium with the liquid at 120° for twelve minutes, the equatorial splitting of the 3.7 Å. spacing features and the deterioration of these planes appeared strikingly as in Fig. 9G. (The untreated pattern closely resembles that of Fig. 6A.) The changes throughout the pattern are just like those introduced by N-methylation, and are dependent on the actual presence of the cresol. The identity period features from the solvated diagram give I = 17.0 Å.; a 24.1% shortening of the theoretical period. A wide variety of hydrogen-bonding agents may be used to cause similar effects, in extent varying with the degree of solvation. Such behavior, incidentally, agrees with the view that specific polar groups in polymers can frequently be solvated without development of extensive disorder in other parts of the same chains. The cresol, like water, bonds at the polar linkages, and small molar amounts of it would, because of its molecular volume, disorder the polar planes. The mechanism of polar plasticizer action is thus illustrated in detail. The fact that such plasticizers can weaken the polar forces without disrupting seriously the paraffin chain packing seems to result in desirable physical properties. One reason is that the paraffin sections of the chain are already plastic enough in the original polymer; the forces between them should not be weakened further. Rather, the polar group forces need modification, and this the polar plasticizier does.

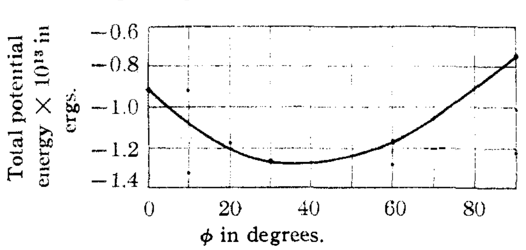


Fig. 12.—Potential energy of interaction of paraffin chains as a function of their "setting angle," ϕ.

The changes in chain configuration resulting from substitution or solvation represent clear evidence for the importance of *inter*molecular force reduction in permitting chain retraction associated with rubbery elasticity.

Double Orientation.—In addition to the influence of lengthwise fiber stress on chain configurations and crystallite structure, the effect of rolling or otherwise compressing uniaxially oriented fibers can be studied. Such treatment results in double orientation, at least of the crystalline regions. The crystallite arrangement in this condition appears to be very similar among all of the even-membered polyamides. From specimens photographed perpendicular to the plane of rolling, meridian spots and equatorial features from the 4.40 Å. spacing appear. Sections photographed with the beam in the plane of rolling give only sharply resolved layer-lines and the strong equatorial spots correspond to the 3.70 Å. spacings At about 44 degrees incidence of the beam to the plane of rolling, the intensities of the two equatorial reflections are approximately equal.

Figure 9H shows a typical biaxially oriented fiber diagram taken with the beam perpendicular to the plane of rolling, whereas Fig. 9I is with the beam parallel. The sample of these patterns was in the extended form. The crystallites are apparently forced down by the rolling so that the identity period planes (basal planes of the cells) give only meridian reflections when the 3.70 Å. planes lie in the plane of rolling (or at non-reflecting angles thereto) and the beam is normal to this plane. In this direction the beam may be imagined to travel along the Z axis and strike $(0YZ)$ planes, whereas when the beam is parallel to the plane of rolling, it travels along the Y axis to strike, figuratively speaking, planes just displaced by the glancing angle from the $(X0Z)$ plane, and layer-line reflections are thereby produced.

Higher orientation of the retracted forms of the fibers would have yielded desirable information on their crystallite order. However, repeated experiments always indicated that the retracted form was largely transformed to the extended form by the cold working accompanying rolling or other necessary types of compression. It may be noted the physical properties such as elastic modulus discussed previously represent chiefly the retracted form, and somewhat different values might be expected from the extended state. A comparison of the melting points of the two forms would be especially interesting, since the unstable extended form is presumably retained at melting temperatures only by tension. This is reminiscent of the melting range in stretched rubber, for which varying local tensions are sometimes held responsible.

Chain Packing in Copolyamides.—The extensive interchain force reduction attending the dipole layer disorder in copolyamides[4] might be expected to provide conditions for retracted chain forms. These were always found to some extent although incipient retracted type patterns occurred only in a few instances such as for the fifty per cent. copolymer polyhexamethylene sebacamide-polydecamethylene adipamide (6–10: 10–6), and others containing the often retracted 10–6 units. This poor definition of the retracted form in the copolyamides as contrasted to the N-substituted series agrees with the idea that not only polar force weakening but also the strong interaction of the hydrocarbon portions is required for extensive retraction. In order words, the copolyamides do not contain sufficient competition of the hydrocarbon chain and dipole packing forces. For in the copolyamides (especially in the middle percentages) a great proportion of the polar linkages are so displaced that they interfere with the orderly packing tendencies of the methylene chains, which might otherwise tend to twist into the shortened form. Copolymerization may thus be regarded as more complex than substitution. In copolymers, not only are the polar layers disorganized, but also the packing of the chain sections between them is disrupted by occasional occurrence of groups and linkages which belong in the dipole regions. This difference is useful in analyzing the behavior of many polymers, including numerous vinyl derivatives. Cellulose derivatives, on the other hand, are evidently capable in general of showing only the behavior characteristic of substituted polymers.

The chain disruption noted above, caused by the displaced linkages in copolyamides, may be illustrated in another way. The systematic relation of elastic modulus to melting point has been shown for the substituted series, and a similar comparison has been discussed for the copolymers. Comparison of the two general types shows a different result. For example, the copolyamide from 66% of 6–6 (polyhexamethylene adipamide) and 33% of 10–10 (polydecamethylene sebacamide) base components (reacted at random) melts at 174°, 9.9% N-methylated 10–10 melts at 175°. These values may be considered the same, and are at about the limiting values (convergence temperatures) for increase of melting point with chain length. The Young's modulus of the copolyamide (1.2×10^9 dynes/sq. cm.) is 20% higher than that of the N-substituted polymer (1.0×10^9) of the same melting point. This is to be expected, since the copolyamide actually contains a greater concentration of interacting polar groups, despite its disorder, than the substituted one and is thus harder. The significant factor seems to be that the displacement of the polar groups so disturbs the chain packing, that the copolymer in spite of its higher polar group concentration shows the same melting point as the substituted compound.

The authors wish to thank Dr. B. S. Biggs and Mr. W. S. Bishop for supplying the polyamides, and Messrs. N. R. Pape and J. H. Heiss, Jr., for considerable help in connection with the experimental work.

Summary

A series of nine N-methylated polyamides, with methyl substitution varying in polydecamethylene sebacamide from 0 to 55 mole per cent., has been studied as a representative group of linear polymers showing physical properties ranging from hard brittleness to rubberiness. Young's modulus, moisture sorption and relative solubility were chosen as properties representing the gross solids, while the corresponding fine structure was studied by X-ray diffraction from oriented and unoriented sections.

The elastic modulus and hardness decrease rapidly with increasing N-methylation, as the hydrogen bonding and other polar forces decline. Relative solubility increases. Moisture sorption also increases, since the disorder introduced by the N-methylation leaves polar groups uncoordinated, and hence free to sorb water. This is in spite of the somewhat hydrophobic character of the methyl group, which replaces bonding hydrogen.

The interchain spacings are not appreciably changed by the methyl substitution, but at higher amounts of substitution one of the principal spacings (3.76 Å.) becomes diffuse. However, the spacings between the dipole layers, related to the identity period along the chain, are more than 25% shorter in the crystal form characteristic of the lower ranges of N-methylation than in the normal extended form. The chains appear to be retracted by partial folding along the fiber axis. This retracted form can be converted to an ex-

tended one by stretching in which the fiber period lengthens (as from 20.5 to 26.5 Å.) and the structure changes also. This behavior is reminiscent of fibrous proteins, as are many other properties of these polymers.

Similar retraction phenomena have been introduced in normally extended, unsubstituted polyamides by allowing plasticizers, such as cresol, to penetrate into the polar layers. The resulting structural changes demonstrate polar association of the plasticizer, often considered as a mechanism for plasticizer action.

A possible explanation of chain twisting is that it results from a compromise of the packing tendencies of the paraffin sections and polar sections of the chain. In general, it may reflect competing packing tendencies.

The chain retraction and extension observed may be the first stages of rubbery elasticity.

463 WEST STREET
NEW YORK, N. Y.

RECEIVED JANUARY 28, 1943

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND PHYSICS, ILLINOIS INSTITUTE OF TECHNOLOGY]

Raman Spectra of Four Pairs of *meso* and *dl* Disubstituted Butanes

BY HARVEY J. TAUFEN, M. J. MURRAY AND FORREST F. CLEVELAND

Weissberger[1] has pointed out that since *meso* and *dl* compounds possess different dipole moments, they do not have free rotation about the carbon–carbon single bond. The use of these differences for assignment of structure has been shown by Winstein and Wood[2] to be of no general application. However, of the diastereomers examined[1,2] which possess no angular polar groups, the *dl* isomer has the larger dipole moment with the exception of the 2,3-dibromobutanes. Electron diffraction measurements[3] of this pair have shown that in the equilibrium position both these compounds have the bromine atoms *trans* to each other. It has been pointed out[2,3] that this would lead to a small dipole moment and that the observed moment must, therefore, arise not only from the equilibrium configuration but also from the vibrations and rotations (librations) about the carbon–carbon bond. This also suggests the presence of rotational isomers (in amounts undetectable by electron diffraction), whose presence could aid in correlating the dipole moment data (see Fig. 1). The detection of rotational isomers by the Raman effect has been the subject of lengthy investigations by Kohlrausch and co-workers,[4] Glockler and co-workers,[5] Mizushima and Morino,[6] and others with quite satisfactory results in many cases.

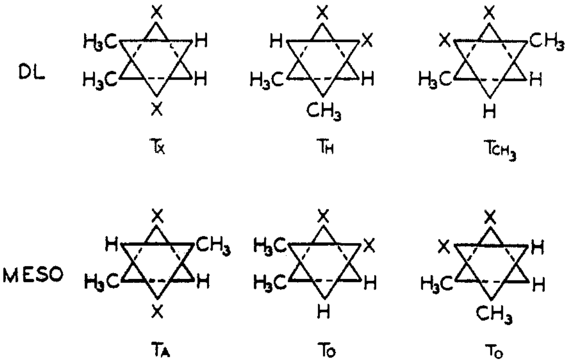


Fig. 1.—Possible rotational isomers for diastereomeric 2,3-disubstituted butanes.

In the present investigation the Raman spectra of *meso*- and *dl*-2,3-dibromobutane, *meso*- and *dl*-2,3-dichlorobutane, *meso*- and *dl*-2,3-diacetoxybutane, and *meso*- and *dl*-2,3-butanediol have been obtained and studied. Kohlrausch and his co-workers[7] have previously examined 2,3-dibromobutane and 2,3-dichlorobutane and reported in the former case that only the *trans* configuration was present. A mixture of isomers was employed in both these investigations, however, and weaker lines due to one or the other structural isomer could therefore have been easily overlooked.

Trieschmann[8] has obtained the Raman spectra of *dl*- and *meso*-2,3-dibromobutane, but the compounds which he used were of doubtful purity[2] and the data which he reported were incomplete.

Diastereomeric pairs often show no large differences in physical properties, which makes de-

---

(1) Weissberger, *J. Org. Chem.*, **2**, 245 (1937).

(2) Winstein and Wood, THIS JOURNAL, **62**, 548 (1940).

(3) Stevenson and Schomaker, *ibid.*, **61**, 3173 (1939).

(4) Kohlrausch, "Der Smekal-Raman-Effekt, Ergänzungsband," Julius Springer, Berlin, 1938, p. 169.

(5) Edgell and Glockler, *J. Chem. Phys.*, **9**, 375 (1941).

(6) Mizushima and Morino, "Raman Jubilee Volume," 1938, p. 315.

(7) Kohlrausch and Ypsilanti, *Z. physik. Chem.*, **B32**, 407 (1936); Kahovec and Kohlrausch, *ibid.*, **B48**, 7 (1940).

(8) Trieschmann, *ibid.*, **B33**, 283 (1936).