made that, though the pure acids separately follow Freundlich isotherms, they do not, as binary mixtures, obey the binary Freundlich isotherm equation proposed by Glueckauf. If, however, it is modified as previously described (that is, use separate β-ratio values determined from the observed results, for each component of a mixture) it gives reasonable agreement with the experimental data and appears to smooth out inconsistencies in the experimental points. But the agreement results only by virtue of the introduction of an empirical factor for one which previously bore a physical interpretation.

The authors wish to express appreciation to the Nutrition Foundation, Inc., for their generous support of this work.

Summary

1. Measurement of the adsorption isotherms of the aliphatic fatty acids acetic, propionic and butyric from aqueous solution and on a commercial activated charcoal, showed each acid to be preferentially adsorbed throughout the concentration range of 0–100% of acid by weight.

2. The experimental data could be fitted by the Freundlich isotherm equation over only a narrow concentration range of approximately 0.005 to 0.5%.

3. The technique of frontal analysis has been utilized in order to obtain data relating to the adsorption of binary mixtures of low molecular weight aliphatic fatty acids, with a view to an analytical method. By this means, the adsorption isotherms for each component of the binary acid mixtures, acetic plus propionic, and propionic plus butyric, have been determined for the equilibrium concentration range of approximately 0.3 to 1.5%. These data could be fitted also by the Freundlich equation.

4. The adsorption data for each acid obtained by static adsorption and from frontal analysis of mixtures, when plotted according to the linear form of the Freundlich equation, gave straight lines, corresponding ones of which appeared to be approximately parallel to each other.

5. Using the binary isotherm equation proposed by Glueckauf to express the adsorption data of mixtures, where the individual components follow the Freundlich equation, it was possible to obtain fair agreement between the observed data, and that calculated from his equation, but only when a modification was made in the interpretation attached to one of the constants in the equation.

6. The effect, upon the static adsorption isotherms, of moisture adsorbed in the charcoal, appeared to be one of dilution only.

7. Changes in adsorption, as evidenced by alterations in frontal analysis diagrams, were not observed when various experimental factors were varied. Thus, columns were packed differently, flow rate was increased by doubling the external pressure, a solid diluent was added to the charcoal in order to increase the rate of liquid flow and several columns were operated either initially dry, or prewetted with solvent before addition of the acid solutions.

8. The threshold values for each of the components of a binary mixture analyzed by frontal analysis are related exponentially to the respective initial or equilibrium concentrations.

9. The specific adsorption values in the static adsorption experiments were found to be dependent upon the quantity of adsorbent used, contrary to the findings of Burgers.[29]

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Multilinked Polyamides[1a]

BY JOHN R. SCHAEFGEN AND PAUL J. FLORY[1b]

The synthesis of multichain polyamides having the general structure

$$R\{\text{—CO}[\text{—NH}(CH_2)_5CO\text{—}]_{\bar{y}}\ OH\}_b$$

by reaction of ϵ-caprolactam with cyclohexanonetetrapropionic acid ($b = 4$) or with dicyclohexanoneoctapropionic acid ($b = 8$) has been described in a previous paper.[2] In the present investigation a technique has been developed for interlinking carboxyl end-groups of these multichain polymers by treating them with a reactive diamine under proper conditions. Using a quantity of the diamine which is stoichiometrically equivalent to the free carboxyl end-group content of the polymer, the interlinking of the carboxyl groups can be made nearly quantitative. Polymeric networks of definite structure may be prepared in this manner.

These interlinked multichain polyamides, which will be called "multilinked polyamides," exhibit an interesting combination of properties. At ordinary temperatures they behave like linear polyamides. Thus they are highly crystalline solids which, in the form of fibers, may be oriented by drafting to several times their initial lengths, resulting in an increase in strength and stiffness.

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[2] J. R. Schaefgen and P. J. Flory, THIS JOURNAL, **70**, 2709 (1948).

When heated, the multilinked polyamides lose crystallinity in the same temperature range in which the corresponding multichain polymers melt. However, unlike either linear or multichain polyamides, they do not liquefy, but instead become rubber-like as crystallinity disappears. They may then be stretched to many times their initial lengths, and on removal of the applied stress, they quickly recover. Crystallinity reappears on cooling. If a multilinked poly-ε-caproamide is drafted and then warmed above its "melting point,"[3] it immediately retracts to its approximate initial dimensions. It recrystallizes when cooled and may again be drafted and the process repeated. In the presence of sulfuric acid or *m*-cresol, either of which dissolves crystalline linear polyamides, the multilinked polyamides undergo manifold swelling without passing into solution, thus exhibiting another characteristic property of network structures.

These latter properties demonstrate a close similarity between the multilinked polyamides above their "melting points" and other known network structures, namely, vulcanized rubber or certain previously described cross-linked polyester systems.[4] The *methods* by which the networks are constructed differ significantly, however. In the preparation of a vulcanized rubber, for example, linear molecules of high molecular weight are converted to a network structure by random introduction of cross-linkages between structural units. It is important that the molecular weight of the polymer subjected to cross-linking (called the "primary" molecular weight) be high, inasmuch as each portion of the structure extending from the end of a "primary" molecule to the first cross-linkage along its length contributes a "flaw" to the network structure,[5,6] thus the higher the molecular weight, the fewer the ends of molecules and hence the fewer number of network imperfections. Deviations from linearity in the initial polymer molecules are undesirable for the same reason. *In the procedure followed here*, the "cross-linkages" are introduced at the start, and the development of the linear chains is limited in the synthesis of the primary structure. The network then is created by completing, insofar as possible, the linear combination of terminal units.

The structure of the multilinked polyamides may be expressed in quantitative terms through reasoning similar to that previously applied to cross-linked systems.[5] The effective number of network elements ν in the interlinked polymer can be calculated as a function of ν_0, the number of network elements which would be present if interlinking were complete (a network element, or chain, being defined as the portion of the structure extending from one multifunctional linkage to the next), and α, the fraction of the initially present free carboxyl end-groups which are interlinked with one another through reaction with diamine molecules. The number of multichain molecules present initially will be $2\nu_0/b$ where b is the functionality of the multifunctional unit. Let N represent the number of primary linear molecules which would be present if all multifunctional units were replaced by an equivalent number of bifunctional units (*i. e.*, if each of the former were replaced by $b/2$ dibasic acid radicals). According to the theory of network structure previously set forth,[5] the effective number $2\nu/b$ of multifunctional units should be given approximately by the actual number, $2\nu_0/b$, minus the minimum number required for the combination of all of the primary linear molecules (as defined above) into a continuous structure devoid of circuitous connections. Replacement of $b/2$ of the above-mentioned dibasic acid radicals by one b-functional radical decreases the number of molecules by $(b - 2)/2$; hence the number of such replacements required for combination of all primary molecules into one species is $2N/(b - 2)$, and the effective number of multifunctional units is therefore

$$2\nu/b = 2\nu_0/b - 2N/(b - 2)$$

The total number of free carboxyl end-groups in the network is $2\nu_0(1 - \alpha)$ and $N = \nu_0(1 - \alpha)$. Hence, the effective number of network elements becomes

$$\nu = \nu_0(\alpha b - 2)/(b - 2) \qquad (1)$$

For the tetrafunctionally linked polyamides

$$\nu = \nu_0(2\alpha - 1) \qquad (2)$$

and for the octafunctionally connected networks

$$\nu = \nu_0(4\alpha - 1)/3 \qquad (3)$$

If ν/ν_0 is taken as an index of the degree of perfection of the network, the molecular weight at the intermediate, or thermoplastic, stage is seen to be unimportant, the perfection of the structure being solely dependent on the degree of interlinking, α. It is also evident by comparison of equations (2) and (3) that approach to the maximum effective number of chains with increase in α is somewhat more rapid in the case of the octafunctionally connected network. If diamine is introduced in exact equivalence to the unreacted carboxyl groups, α will equal p'^2, where p' is the fraction of the terminal carboxyl groups amidated. If an excess (or deficiency) of diamine is used and the reaction is carried to completion so that all carboxyl (or all amine) groups have reacted, α will equal $1/r$ (or r) where r is the ratio of added amine groups to unreacted carboxyl end-groups prior to interlinking.

In order to achieve as nearly complete interlinking as possible, it is important that the sample

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[3] "Melting point" as used here refers to the temperature range in which crystallinity disappears on heating measured as outlined in ref. 2 and recorded in Table VII.

[4] W. O. Baker, THIS JOURNAL, **69**, 1125 (1947); B. S. Biggs, R. H. Erickson and C. S. Fuller, *Ind. Eng. Chem.*, **39**, 1090 (1947).

[5] P. J. Flory, *Chem. Rev.*, **35**, 51 (1944).

[6] P. J. Flory, *Ind. Eng. Chem.*, **38**, 417 (1946).

of multichain polymer be sufficiently thin to permit uniform penetration of diamine. Moreover, for the purposes of this investigation, specimens of the *interlinked* polymer were required in a form suitable for measurement of its elastic properties above the "melting point." A physical form that satisfies both of these requirements is that of fibers, of a diameter (*ca.* 0.01 inch) so chosen that diamine can penetrate uniformly and that physical measurements may be conveniently made. The problem then becomes one of preserving the fiber structure (formed by melt extrusion of the multichain polymer) through the interlinking process. This has been accomplished by carrying out the initial phase of the reaction with diamine in the solid state some 20° below the melting point of the polymer.[7] After the establishment of a network structure in this manner, the process was completed at a temperature above the "melting point" without destruction of the fibers.

Methods for interlinking multichain polyamides terminated by carboxyl groups are described in the present paper, and measurements of their elastic properties, including swelling behavior in solvents, are presented. The results of these measurements are compared with the predictions of the theory of rubber elasticity.

Experimental

Materials.—Commercial ε-caprolactam was distilled at reduced pressure, recrystallized twice from acetone and redistilled. The final product had a purity of 99.9% or better as determined by freezing curves.

2,2,6,6-Tetra-(β-carboxyethyl)-cyclohexanone (cyclohexanonetetrapropionic acid), prepared by the method of Bruson and Riener,[8] was recrystallized from water and dried; neutral equivalent 96.96, calcd. 96.60. Bis-[3,3,5,5-tetra-(β-carboxyethyl)-4-ketocyclohexyl] (dicyclohexanoneoctapropionic acid), prepared by the method previously described,[9] was also recrystallized from water and thoroughly dried; neutral equivalent 96.76, calcd. 96.34.

Hexamethylenediamine was purified by fractional distillation at reduced pressure; b. p. 92° at 18 mm. The diamine was used as a dilute solution in methanol (*ca.* 7% by weight).

Preparation of Multichain Polymers.—(See Table I) The polycarboxylic acid was dissolved in the molten ε-caprolactam by heating the mixture with shaking to 80–90° in a "Pyrex" glass tube in a nitrogen atmosphere. (It was necessary to heat polymer 8–1 to 160° with shaking in a sealed tube to obtain complete solution. The tube was cooled and opened before proceeding.) After cooling, the distilled water was added. The open tubes were then placed in an autoclave containing an additional 25 cc. of water and heated in a nitrogen atmosphere successively for one hour at 180°, one hour at 180–245°, and three hours at 245°. At the end of the first hour of heating at 245°, the pressure was slowly decreased to atmospheric. The polymer thus produced was transferred to a glass apparatus and heated at a temperature above the melting point alternately at atmospheric pressure and at 20 mm. pressure (columns 5 and 6, Table I) until the reaction was very nearly complete. The last four polymers listed in Table I were heated at 229°, rather than 253° as previously,[2] to minimize decomposition. The polymer was cooled, removed from the glass tube and weighed. In two cases, 4–3 and 4–5, some polymer was accidentally lost and it was therefore necessary to make an estimate of the amount of polymer produced. From the weight of polymer and that of polycarboxylic acid one can calculate Q, the equivalents of multifunctional unit per caproamide unit, or T_c, the equivalents of free carboxyl end-groups per gram of polymer (see Table II), assuming complete reaction in each case.

The major portion of each polymer was spun into fibers by extruding the molten material (heated at 220 to 250°) through an orifice in conventional fashion. The orifices were 0.015 to 0.030 in. in diameter and 0.25 to 0.41 in length. On leaving the orifice the fiber passed through a carbon tetrachloride quenching bath and then to a reel on which it was wound at a rate (60 to 250 ft. per min.) so adjusted as to give fiber diameters in the vicinity of 0.01 in. Small samples of each polymer in the form of thin shavings (prepared by turning down cylindrical slugs of polymer on a lathe) were saved for viscosity and end-group titration measurements. Both shavings and fibers were heated an additional four hours at either 202° (16 mm.) or at 184° (1 mm.) in order to complete[7] the amidation and to remove the last traces of monomeric ε-caprolactam before use.

TABLE I

MULTICHAIN POLYMERS

Polymer designation[a]	Polycarboxylic acid, g.	ε-Caprolactam, g.	Water, cc.	Heated		Wt. of polymer, g.	Q[b]	M. p., °C.[d]
				At temp., °C.	For hr.			
4–1	1.083	30.78	0.95	253	2.5	29.2	0.0450	218–221
4–2	1.199	50.00	1.6	245	2	48.0	.0298	222–224
4–3	0.589	30.05	0.95	229	5.2	28.5[c]	.0246	219–226
4–4	.549	30.37	.95	253	2	28.8	.0226	218–226
4–5	.278	30.32	.95	229	5.3	28.5[c]	.0115	226–229
8–1	1.179	20.22	.95	229	2.4	20.3	.0720	216–219
8–2	0.811	30.05	.95	229	4	27.9	.0350	219–225

[a] The 4 refers to tetrachain, the 8 to octachain, polymers. [b] Equivalents of multifunctional unit per ε-caproamide unit. [c] Estimated. [d] Measured as described in ref. 2.

Viscosities.—Melt viscosities were determined by the capillary tube method previously described.[2,10,11] Dilute solution viscosities were measured at various concentrations in *m*-cresol and in concentrated sulfuric acid using a Ubbelohde no. 2 viscometer. Intrinsic viscosities, expressed in (g./100 cc.)$^{-1}$, were obtained by extrapolation to infinite dilution.

End-Group Titrations.—The concentrations of amino end-groups, T_n, in the polymers were determined by titration with *p*-toluenesulfonic acid in *m*-cresol as described in the preceding paper.[2] The free carboxyl group concentrations, T_c, were determined by the method of Waltz and Taylor,[12] involving titration with potassium hydroxide in benzyl alcohol solution at 155° using phenolphthalein as indicator. The end-group concentrations, T_n and T_c, were expressed in equivalents per gram of polymer. Blank corrections, where necessary, were made for the solvent used. The methods were applied to the interlinked fibers after allowing them to swell in the titration medium, *i.e.*, *m*-cresol or hot benzyl alcohol (155°). End-points appeared to be reasonably sharp and permanent in spite of the insolubility of the interlinked fibers.

Interlinking Procedures.—Individual interlinking experiments were carried out on samples consisting of about 0.7 g. of fiber wound in a single uniform layer on a 13 mm.

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(7) The facility with which polymerization processes proceed in highly crystalline polyamides below their melting points (U. S. Patent 2,172,374 (1939)) is consistent with recent investigations on the nature of the crystalline state in polymers, which indicates that the ends of the polymer chains are concentrated in the amorphous regions where mobility is comparatively high. See P. J. Flory, *J. Chem. Phys.*, **17**, 223 (1949); THIS JOURNAL, unpublished.

(8) H. A. Bruson and T. W. Riener, *ibid.*, **64**, 2850 (1942).

(9) J. R. Schaefgen and P. J. Flory, *ibid.*, **70**, 2823 (1948).

(10) P. J. Flory, THIS JOURNAL, **62**, 1057 (1940).

(11) T. G. Fox, Jr., and P. J. Flory, *ibid.*, **70**, 2384 (1948).

(12) J. E. Waltz and G. B. Taylor, *Anal. Chem.*, **19**, 448 (1947).

(o. d.) "Pyrex" glass tube about 10 cm. in length. In some cases this tube was closed at its lower end ("closed tube" experiments); in others it was left open ("open tube" experiments). The desired amount of the diamine dissolved in methanol (*ca.* 7% solution) was placed within the closed tube, or, in open tube experiments, it was added to a smaller tube (10 mm. o. d. and 4 cm. long) sealed at one end and inserted within the open tube. The tube wound with fiber and its contents were placed in an outer tube (19 mm. o. d.). After evaporation of the methanol, the outer tube was flushed with pure nitrogen, evacuated to the desired reduced pressure and sealed. The interlinking process was carried out in two stages. In the first stage the sealed tube and contents were heated for several hours at a temperature (184 to 209°) somewhat below the melting point of the polymer. The tube was then opened and the second stage, involving heating of the fiber for several hours at reduced pressure in a nitrogen atmosphere successively at temperatures of 202° and 241°, was carried out. The latter temperature is some 20° above the melting point of the fiber. *In the preferred procedure* finally adopted the first stage was carried out at 202° for two hours in pure nitrogen at about 20-mm. pressure (measured at room temperature). The interlinking process was then completed by heating the fiber for two hours at 202° (20 mm.) followed by three hours at 241° (1 mm.) in the presence of nitrogen. Fibers from polymer 4–5 (see Table VII), which tended to stick together during the heating at 241°, were rewound before this final heating in such a way that contact between adjacent turns was avoided. This was accomplished most easily by rewinding the fiber on a threaded (30 per inch) stainless steel rod, 12 in. long and 0.5 in. in diameter.

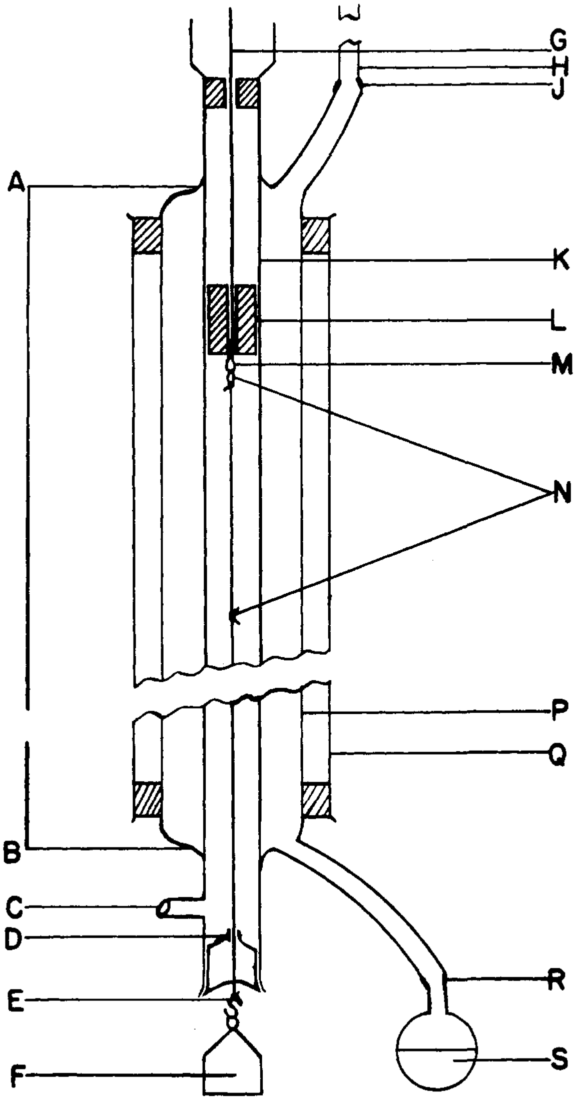

Fig. 1.—Apparatus for measuring stress–strain curves: A to B, heated zone; C, nitrogen inlet; D, bottom guide (held in by friction); E, bottom hook; F, load; G, nichrome wire, B. and S. no. 24; H, air condenser; J, 15/35 standard taper joint; K, inner tube, 11 mm. (o. d.); L, capillary glass movable guide; M, end of nichrome wire bent to form long hook; N, fiber sample; P, heating jacket, 52 cm. × 22 mm. (o. d.); Q, insulating jacket, 35 mm. (o. d.); R, 24/40 standard taper joint; S, boiling liquid in 200-ml. round-bottom flask.

Swelling Volume.—Equilibrium swelling volume ratios (*SV*) in *m*-cresol were determined by either of two methods. In some of the preliminary studies fiber samples of measured length L_0 were placed in pure *m*-cresol and their lengths measured on successive days until an equilibrium length L was reached. The cube of the ratio of the final to the initial length, *i.e.*, $(L/L_0)^3$, was taken equal to the swelling volume (*SV*). More accurate values were obtained by the "weight" method, wherein swelling volume was related to the relative weights of the swollen and the original fiber. A 5 to 10-mg. sample of the interlinked fiber, weighed to 0.01 mg. on a torsion balance, was placed in pure neutral *m*-cresol. At intervals the fiber was removed from the swelling agent, blotted on filter paper and weighed to 0.1 mg. Weighings were repeated daily until the weight became constant, which usually required two or three days. (Difficulty was encountered only with certain of the less highly interlinked fibers from polymer 4–5 [in which the proportion of multifunctional units was lowest], the swollen weight of which decreased with time. This may have been due to gradual extraction of a sizeable sol fraction in this case.) Assuming that volumes are additive in the swollen phase, the swelling volume ratio was computed from the equation

$$SV = [w/d_1 + w_0\,(1/d_2 - 1/d_1)]/(w_0\,/d_2)$$

where w_0 and w represent, respectively, the weights of dry polymer and of swollen polymer, and the densities of the solvent and polymer are given by d_1 and d_2, respectively. Swelling measurements were carried out at 30°.[13] The density d_1 of the *m*-cresol ($d^{30}{}_4$) was 1.026. That of the polymers was determined at the same temperature by measuring the density of the nitrobenzene–chlorobenzene mixture in which the fiber (prior to interlinking) remained suspended. Freshly added fibers remained suspended along with those which had been in the medium for some time, indicating that the apparent density was not vitiated by solvent absorption. Density values (30°) were 1.131 ± 0.003 for all polymers except 4–1 and 8–1 for which the densities were 1.136 and 1.141, respectively. Values of *SV* determined by the "linear" method were somewhat lower than those based on the swollen weight.

Stress-Strain Measurements.—The apparatus used is shown in Fig. 1. The inner tube was thermostated by refluxing a pure liquid in the outer jacket. Liquids used for this purpose were *n*-propyl benzoate (229°), α-methylnaphthalene (241°), diphenyl (253°), and dimethyl phthalate (281°). A slow stream of oxygen-free nitrogen was passed through the inner tube during use to prevent oxidation of the fiber. In making the actual measurements, a sample of fiber about 12 cm. long was cold drafted at each end for a distance of 2 cm., leaving an 8-cm. undrawn mid-portion. One end was knotted to form a loop and the other end was tied to another piece of interlinked fiber (not necessarily from the same polymer). The fiber

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[13] Swelling measurements at 40° in comparison to those at 30° indicated a 2% decrease in *SV* with a 10° rise in temperature.

TABLE II

END-GROUP, MOLECULAR WEIGHT AND VISCOSITY DATA ON THE MULTICHAIN POLYMERS

Polymer	End-group concn. detd. by titration, equiv./g. $T_n \times 10^6$	$T_c \times 10^4$	$T_c \times 10^4$ calcd.	$\bar{y}_n$	$\bar{M}_n$	$\bar{M}_w$	Intrinsic visc. at 30° In m-cresol	In H_2SO_4	Melt visc. in poises at 253°
4–1	5.2	3.84	3.88	22.2	10,000	13,000	0.562	0.473	41.5
4–2	5[a]	2.75	2.64	31.4	13,800	18,100	...	.526[b]	....
4–3	3.8	2.35	2.17	36.8	16,300	21,100	.752	.712	167
4–4	5.1	2.12	2.02	41.0	17,600	23,300	.842	....	276
4–5	7.2	1.13	1.08	77.4	29,700	42,600	1.213	1.127	2770
8–1	1.5	6.28	6.02	13.3	12,500	14,400	0.458	0.408	15.3
8–2	1.7	3.20	3.03	26.9	24,100	28,000	.726	.702	126

[a] Estimated value. [b] At 25°.

was marked with black lacquer at either end of the undrafted portion, the pair of marks being placed just within the drafted sections. Retraction of the drafted fiber on "melting" narrowed the marks to sharp lines. The loop was attached to the hook M at the end of a piece of nichrome wire (see Fig. 1) and the fiber was drawn into the heated zone (A to B). A small weight (0.13 g.) was suspended from the lower end E of the fiber during this operation to prevent it from oscillating and adhering to the glass. The weight was then decreased to 0.03 g., and, after the elapse of three to four minutes, the zero length, L_0, between marks was measured to 0.01 cm. by means of a cathetometer. The load was attached to the lower end of the fiber, and the distance, L, between marks again measured. An irreversible "creep" occurred; therefore the variation of L with time for each sample was recorded. This also made it necessary to use a fresh section of fiber for each load, except where stated otherwise. The cross-section of the fiber was determined from its length and weight. The latter was measured on a torsion fiber balance accurate to ±0.01 mg.

The density of the interlinked fibers at elevated temperatures was assumed to be equal to that of the original multichain polymer at the same temperature. To determine the density of the latter, a known volume of molten polymer at the temperature in question was drawn up into a calibrated pipet, cooled and weighed.[10] Values obtained for the density in g./cc. at the stated temperatures are: 229°, 0.999; 241°, 0.992; 253°, 0.985; 281°, 0.970 (extrapolated value). Polymer 4–2 was used for these measurements. Densities of the other polymers should not differ significantly from these values.

Results and Discussion

Multichain Polymers.—The results of amine (T_n) and carboxyl (T_c) end-group titrations on the multichain polymers prior to interlinking are given in the second and third columns of Table II. The carboxyl group concentration calculated from the proportion (Q in Table I) of multifunctional units present and the extent of incompletion of the amidation as indicated by the amino titer (T_n) is given for comparison in the fourth column. The close agreement between the observed and calculated carboxyl group concentrations, as well as the fact that it was possible to recover the octabasic acid nearly quantitatively from polymer 8–1 by hydrolysis, substantiates the structure assumed for these polymers on the basis of the normal reactions to be expected of the molecules involved. (Actually the agreement is even closer than is indicated if account is taken of the small amount of ϵ-caprolactam evolved in in the final four-hour heating period in the solid state.)

The average number $\bar{y}$ of ϵ-caproamide units per chain given in the fifth column of Table II has been calculated from the relationship (equivalent to equation (1) of ref. 2)

$$\bar{y} = [(c/m) - T_n]/T_c \tag{4}$$

where T_c and T_n are the experimentally determined concentrations of carboxyl and amino end-groups per gram, respectively, c is the weight concentration of the ϵ-caproamide units in the polymer, and m (= 113) is the molecular weight of the unit. Similarly, the number average molecular weights have been calculated from the relationship (equivalent to equation (5) of ref. 2)

$$\bar{M}_n = b/[T_c + T_n(b - 1)] \tag{5}$$

The weight average molecular weights have been calculated from relationships involving T_c and T_n similar to those previously derived.[2] Values found for the intrinsic viscosities as a function of molecular weight are in good agreement with the relationships established in the preceding paper. The melt viscosities (η) for the octachain polymers fall somewhat below the previous log η *vs.* $\bar{M}_w^{1/2}$ plot,[2] but the data for the tetrachain polymers show good agreement. The milder polymerization conditions employed here, involving completion of the reaction at lower temperatures than heretofore used, may diminish appreciably the occurrence of side reactions. The results reported in Table II are therefore believed to be more reliable, insofar as they differ from those reported earlier. The intrinsic viscosities and the carboxyl and amine titers remained unchanged, within experimental error, after extrusion of the polymers in the form of fibers, indicating that no appreciable change in structure took place during the spinning operation.

Interlinking Experiments. A. Effect of Different Diamines on Extent of Interlinking.—The results of preliminary experiments, carried out on fibers from a tetrachain polymer (not included in Tables I and II) for which T_c = 2.84 × 10^{-4} for the purpose of comparing the action of various diamines, are reported in Table III. The proportions of the various diamines used in these experiments are given in the second column. The closed tube technique described in the Experimental section was employed.

Heating was confined to temperatures below the melting point, *i. e.*, from 190 to 209° at atmospheric pressure within the sealed outer tube, followed by an additional hour at 209° in a slow stream of nitrogen at 11 to 13 mm. pressure. Measured swelling volumes and the extents of reaction of the carboxyl groups ($p' \times 100$) lead to the following conclusions: hydrazine is ineffectual, ethylenediamine is poor and the two higher diamines are of comparable merit. Hexamethylenediamine was chosen for all subsequent experiments because of its greater volatility.

TABLE III

EFFICACY OF VARIOUS DIAMINES AS INTERLINKING AGENTS

Diamine	NH_2/COOH ratio[a]	*SV* in *m*-cresol[b]	% COOH reacted[c]
Hydrazine	1.04	Partly soluble	37
Ethylene	0.93	55	48
Hexamethylene	1.07	16	76
Decamethylene	1.11	19	80

[a] Based on the experimentally determined T_c. [b] By the "linear" method. [c] Residual carboxyl group content determined by titration of the swollen fiber in benzyl alcohol at 155°.

B. Effect of Temperature and Duration of Heating on Extent of Interlinking.—A sample of the same fiber (as in A), similarly treated with 1.25 equivalents of hexamethylenediamine per carboxyl end-group, failed to volatilize any diamine when heated in the second (open tube) stage of the interlinking procedure, indicating that the diamine was completely used up by reaction of at least one amino group of each molecule. However, the interlinking was by no means complete as shown by residual carboxyl group titrations. Further heating under reduced pressure at temperatures *above the "melting point"* (237 to 253°) as described in the Experimental section reduced the swelling volume of the fibers from 18.0 to a substantially constant limiting value of 10.0. This treatment also decreased the residual carboxyl titer to a small value. Evidently the interlinking reaction is restricted to some extent by the presence of crystalline regions, a result which is by no means surprising.

The effect of duration of heating on swelling volume (and hence on extent of interlinking, see E below) is demonstrated by the results shown in Table IV. The swelling volume (*SV*) approaches a minimum after heating for three hours.

TABLE IV

SWELLING VOLUMES[a] FOR FIBERS HEATED VARYING PERIODS AT 241° (1 MM.). (FIBERS FROM POLYMER 8-2)

Comments[b]	Duration of heating 3 hr.	6.5 hr.	10 hr.
High amine content	11.00	10.96	11.03
High amine content	10.27	10.12	10.06
Equivalent amounts	9.74	9.66	9.59
High carboxyl content	10.54	10.37	10.36
High carboxyl content	11.70	11.34	11.30

[a] By weight method. [b] Fibers are high in diamine if $NH_2/COOH > 1$ etc. Position of fiber along tube, see C, determines this.

C. Uniformity of Interlinking.—It was ascertained that samples selected from various locations along the glass tube on which the fiber was wound during the interlinking process exhibited different swelling volumes. Thus in a particular experiment for a series of interlinked fiber samples selected at equal intervals from bottom (1) to top (6) along the "closed" tube, the swelling volume (by the linear method) varied as follows:

No.	1	2	3	4	5	6
SV	16.6	13.6	10.8	10.0	10.5	11.1

It is indicated that the top material (nearest the diamine vapors) got too much diamine and $-CONH(CH_2)_6NH_2$ groups were formed, while the material close to the bottom did not get enough diamine leaving unreacted carboxyl groups. Either result lowers the degree of interlinking and is reflected in a relatively higher swelling volume. By plotting *SV vs.* running numbers, a curve is obtained, the minimum of which occurs at $SV =$ 9.7 corresponding presumably to the optimum proportion of diamine. Use of an "open" glass tube instead of a "closed" tube during the initial stage of the process should enable the diamine vapors to attack from either end. A reduction in pressure raises the diffusion rate of the diamine at the temperature (202°) used to initiate the interlinking reaction, and hence should facilitate its distribution over the fiber. The effect of these changes on the uniformity of interlinking as indicated by swelling volumes is shown in Table V for fibers from polymers 4-3 and 4-5 interlinked by the preferred procedure given in the Experimental section. Graphs of selected experiments from Table V appear in Fig. 2. Either the "open" or "closed" tube technique at sealing

TABLE V

EFFECT OF SEALING UNDER VARIOUS PRESSURES AND OF USING "OPEN" AND "CLOSED" TUBES ON UNIFORMITY OF INTERLINKING

		Interlinking conditions[a]			Swelling volume at 30° (wt. method)		
Polymer	No.[b]	Pressure, mm.	Tube	n[c]	High	Low	Average[d]
4-3	1	730	Open	15	25.50	13.46	17.52
4-3	2	300	Open	10	16.11	13.58	14.55
4-3	3	20	Open	15	14.46	13.66	14.03 ± 0.24
4-3	4	2	Open	13	17.77	13.56	14.69
4-3	5	300	Closed	11	47.29	13.33	22.19
4-3	6	20	Closed	13	14.14	13.34	13.68 ± 0.28
4-5	..	14	Open	10	24.74	23.02	24.48
4-5	..	14	Closed	10	28.22	22.57	25.40
4-5	..	1	Closed	9	58.2	26.3	42.4

[a] Heated for two hours at 202° in sealed tube. Opened tube and heated fiber successively for two hours at 202° (20 mm.) and three hours at 241° (1 mm.). [b] Numbers refer to curves in Fig. 2. [c] Number of samples taken. [d] $\Sigma(SV/n) \pm \sqrt{\Sigma(\Delta SV)^2/n}$ where $\Delta SV = SV - (\Sigma SV/n)$.

pressures near 20 mm. gives fairly uniformly interlinked fibers, and even at higher pressures a small portion of the fiber reaches optimum interlinking as is to be expected. The "open" tube experiments show less variation in uniformity with change in pressure within the sealed tube, but the "closed" tube technique gives the lower minimum swelling volume. Both methods were used (see Table VII) to secure adequate samples of optimally interlinked material.

The results given in Table VI show the influence of variations in the ratio of equivalents of added diamine to carboxyl end-group content of the polymer on the uniformity of interlinking. These experiments were conducted in "open" or "closed" tubes according to the preferred procedure. In each case at the end of the heating periods n samples were taken at intervals along the tube and swelling volumes were determined on each sample. High, low and average swelling volumes are given in the Table. Ratios of 1.00 to 1.10 seem preferable, but even with ratios as high as 1.25 a portion of the material is highly interlinked.

TABLE VI

EFFECT OF VARYING THE RATIO OF DIAMINE TO CARBOXYL END-GROUP CONTENT ON THE UNIFORMITY OF INTERLINKING

Polymer	NH_2/COOH[a]	n	Swelling volume[b] High	Low	Average[c]
4–2	0.90	8	13.0	11.2	12.2 ± 0.6
4–2	0.95	8	11.5	10.4	11.0 ± .4
4–2	1.01	10	10.7	10.1	10.47 ± .16
4–2	1.07	10	10.9	10.5	10.76 ± .13
4–2	1.20	10	11.6	10.6	11.1 ± .3
8-2	1.00	12	11.03	9.85	10.30 ± .43
8–2	1.25	11	11.70	9.74	10.75 ± .69

[a] Based on experimental T_c. [b] SV's on polymer 4–2 determined by the linear method, on polymer 8–2 by the weight method. [c] See note d to Table V.

D. Samples of Interlinked Fiber for Elastic Measurements.—On the basis of the preliminary experiments described in A, B and C, above, the preferred procedure given in the Experimental section was adopted as the most effective means of achieving maximum degrees of interlinking, and the ratio of amine to free carboxyl groups in the polymer prior to interlinking was held within the range 1.00 to 1.10.[14] Further details of the procedure by means of which samples for elastic measurements were prepared are summarized in Table VII. Swelling volumes were measured on samples selected at intervals along the tube, and samples for elastic measurements were chosen from the region of minimum swelling. The range in SV for the portion of the fiber from which specimens were selected for elastic measurements is given in the last column of Table VII.

TABLE VII

INTERLINKING PROCEDURES FOR THE PREPARATION OF MULTILINKED POLYAMIDES FOR STRESS–STRAIN MEASUREMENTS[a]

Polymer	$(T_c - T_n) \times 10^4$	NH_2/COOH	Open (o) or closed (c) tube method	SV (30°) for samples selected for stress-strain measurements	M. p., °C.[b]
4–1	3.79	1.10	c	10.07 ± 0.02	200–215
4–2	2.70	1.10	c	11.50 ± .03	216-227
4–3	2.31	1.07	c	13.26 ± .02	218-226
4–4	2.07	1.10	c	13.40 ± .02	219–229
4–5	1.06	1.02	o	21.95 ± .05	222–238
8–1	6.26	1.00	o	7.33 ± .08	199–208
8–2	3.18	1.25	c	9.64 ± .02	214–224

[a] Standard procedure used except for 4–1 which was sealed at 100 mm. pressure. [b] Designates the range of temperature in which crystallinity disappears, measured as described in ref. 2.

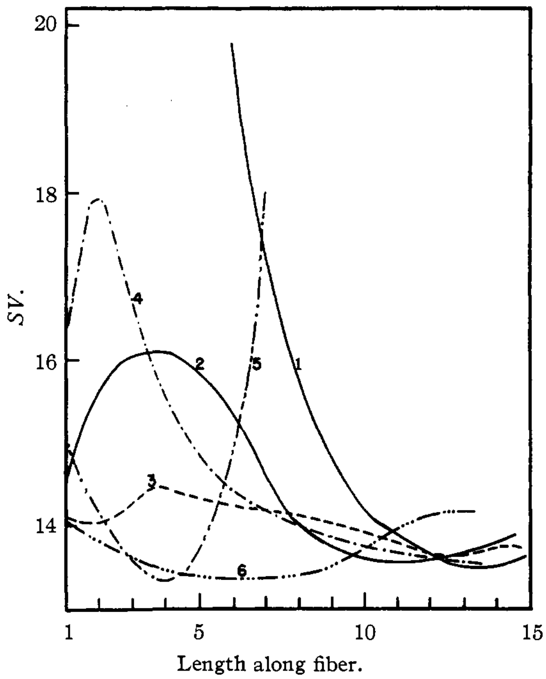

Fig. 2.—The variation of swelling volume (SV) with length along fiber in interlinking experiments. The numbers refer to the experiments listed in Table V.

E. Completeness of Interlinking.—Various samples of interlinked fibers were titrated to determine free amine (T_n') and free carboxyl groups (T_c') in an effort to establish the degree of completion of the interlinking process. The reliability of these determinations is questionable because (1) the fiber is swollen, not dissolved, (2) the fiber sample has to be large to get precise results and cannot therefore be uniformly interlinked throughout its length (see C), (3) blank corrections and fading end-points cause difficulty especially inasmuch as the end-group concentrations are very small. The values found for T_n' seldom differed significantly from zero, but T_c' usually was ap-

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(14) Except for polymer 8-2, see Table VII, in which a ratio of 1.25 was used. This resulted in a lower yield of usable fiber interlinked to a maximum degree.

preciable though small. This disparity between T_c' and T_n' casts doubt on the validity of these (small) titration values, for they should be nearly equal at optimum diamine concentration. Even if $T_n' \cong 0$ is rejected and calculations of the extent of interlinking are based on T_c', results on fibers from polymer 4–1, for example, give $p' \cong 0.9$, or $\alpha \cong 0.8$. The actual extent of interlinking, however, doubtless is greater than this minimum figure.

The exploratory experiments which have been described show that the swelling volume reaches a limiting minimum value beyond which it changes imperceptibly with further heating. This fact, in conjunction with the seemingly unavoidable conclusion that the portion of fiber in a given interlinking experiment which is optimally exposed to diamine must acquire diamine in very nearly the stoichiometric ratio to the free carboxyl groups, indicates in a fairly conclusive manner that interlinking in fibers exhibiting the minimum swelling volume must be nearly complete, *i. e.*, $\alpha \geqq 0.9$. In further substantiation of this conclusion, interlinking experiments carried out under different conditions lead to about the same minimum SV. In the following discussion α will be assumed equal to unity. Thus, ν will be taken equal to ν_0, where ν_0 per gram is given by $(T_c - T_n)/2$ for the multichain fibers prior to interlinking (Table II).

Elastic Properties of Multilinked Polyamides at High Temperatures.—At room temperature the multilinked polyamide fibers differ little in appearance or properties (apart from solubility relationships) from the multichain fibers from which they are derived. Some slight differences noted were (1) that those multichain fibers in which the average chain length $\bar{y}$ is low are somewhat brittle and cold draw with difficulty[2] or not at all (as in the case of 8–1), whereas the corresponding interlinked fibers cold draw with ease, and (2) that interlinking noticeably increases the stiffness. The elastic character of the multilinked fibers at temperatures above their melting points has been remarked upon earlier, and in this respect they differ entirely from their thermoplastic antecedents.

In attempting to establish the stress–strain curves for the multilinked polyamides in the "rubbery" state, a marked irreversible creep was observed to occur. When fibers were subjected to fixed loads giving *low elongations*, the stretched length L increased steadily with time. The change in length became linear with time after an initial period of decreasing rate of creep, as shown in Fig. 3 where typical creep curves appear for several polymers at 241°. The initial non-linear portion of the curve is attributed to delayed elastic effects, that is, to the slow rate of the configurational rearrangements within the given valence structure which are required to bring it to a state of equilibrium with the applied load. In general this effect becomes greater as the load increases (see Fig. 4) or as the number of cross-links decreases (Fig. 3). In the latter case the greater average length of the chain elements between cross-linkages as the

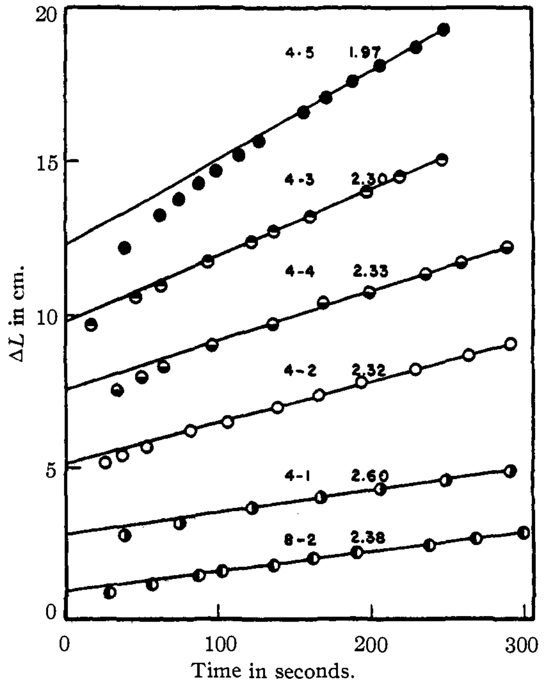

Fig. 3.—Creep curves for the various interlinked multichain polyamides at 241° at the similar relative lengths (α_e) indicated following the code number along each curve.

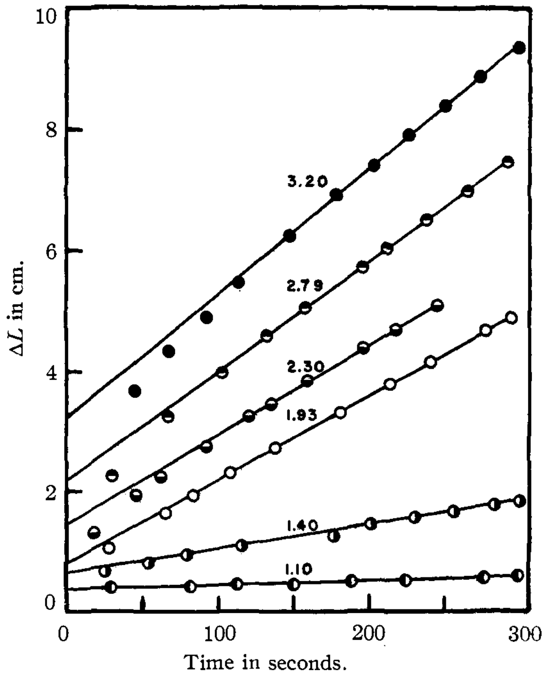

Fig. 4.—Creep curves for polymer 4–3 at 241°. The numerical values are those of the relative lengths (α_e).

number of cross-linkages per unit volume diminishes leads to longer relaxation times and hence to slower attainment of elastic equilibrium. In any event, the asymptotic creep due to delayed elastic effects invariably proceeds at a rapidly diminishing rate and becomes negligible after the elapse of one hundred to two hundred seconds. The irreversible creep observed thereafter, which is reflected in the linear portions of the graphs in Figs. 3 and 4, continues unceasingly until failure eventually occurs. On releasing the load, the fiber fails to return to its initial length, the residual elongation being somewhat less than the amount of irreversible creep which occurred under stress. This irreversible creep is more pronounced the lower the degree of interlinking, the higher the temperature and the higher the elongation (or load), except at very high elongations as will be explained later. It is doubtless caused by amide–amide interchange, which other evidence[15] has indicated takes place in polyamides heated to high temperatures. Tobolsky[16] has demonstrated the occurrence of an analogous stress relaxation in other deformed polymers which are susceptible to interchange processes. Although the stress should not alter appreciably the rate of interchange, it does introduce a preference for the reformation of bonds in such a way as to relieve the strain, thus leading to continual creep under the conditions of our experiments. The effect of both delayed elastic effects and irreversible creep on the measurement of the stressed length was eliminated by extrapolating the length–time curves to zero time. Such extrapolations offered no difficulty for loads up to those giving an initial elongation of about 250%, corresponding to initial relative lengths $\alpha_e \equiv L_s/L_0 = 3.5$, where L_s is the extrapolated stressed length at zero time and L_0 is the unstressed length measured between marks on the fiber.[17]

At *higher elongations*, *i. e.*, when $\alpha_e > 3.5$, the situation is further complicated by the occurrence of crystallization; crystallinity may increase with time (or with creep) with consequent distortion of the creep curves. At high elongations, ($\alpha_e > 5.5$ in the case of 4–3 for example) the fiber is believed to become highly crystalline and creep is greatly suppressed. This leads again to linear plots which may be extrapolated to zero time to obtain L_s. Since creep is nearly independent of load (or elongation) in this region of high crystallinity, one fiber can be used for several measurements. No measurements were made in the intermediate range of elongations where incipient crystallization occurs, because of the difficulty of estimating L_s from the non-linear creep curves obtained.

The stress–strain relationship for fibers from polymer 4–2 of *SV* 12.4 ± 0.1 (not quite as well interlinked as those reported in Table VII) up to relative lengths of 2.3 at four temperatures above the melting point is shown in Fig. 5. A similar graph of the stress–strain curve for polymer 4–3 of *SV* 13.26 ± 0.02 over a larger range of elongations at three temperatures is shown in Fig. 6. Each value of α_e was obtained by extrapolating creep–time data on separate fibers except where $\alpha_e > 5$ as set forth above. The loads τ are expressed in g. per sq. cm. of cross-section of the unstretched fiber (as calculated from the weight of the fiber per unit length and the density; see the Experimental section). At low elongations a single curve is drawn through the points representing measurements at the several temperatures.[18] Errors introduced by the small variations in the degree of interlinking in different samples from the same preparation, as indicated by the range of swelling volumes, should not be significant. At higher elongations, $\alpha_e > 5.5$ (Fig. 6), a definite effect of temperature is observed.

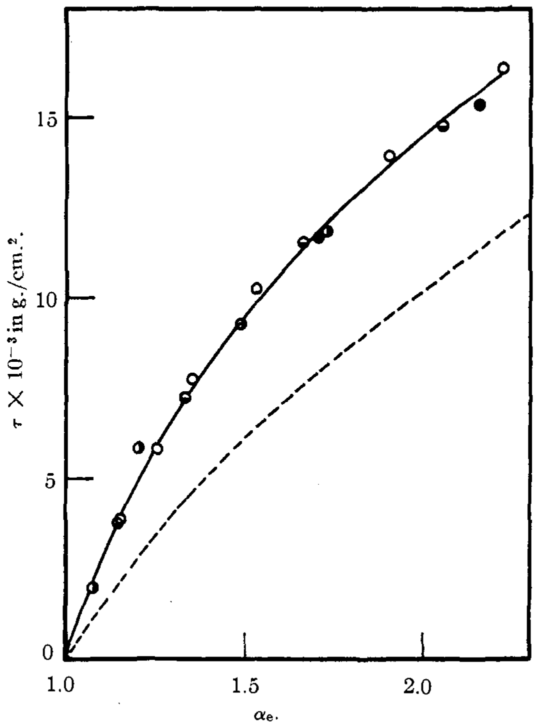

Fig. 5.—Experimental and theoretical (dashed line) stress–strain curves for interlinked polymer 4–2 at low elongations. Temperatures used were: 229°, ●; 241°. ○; 253°, ◒; 281°, ◑.

The theoretical curves in Figs. 5 and 6 have been calculated from the relationship

$$\tau = RT\,(\nu/V)\,(\alpha_e - 1/\alpha_e^2) \qquad (6)$$

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[15] P. J. Flory, *Chem. Rev.*, **39**, 137 (1946).

[16] M. D. Stern and A. V. Tobolsky, *J. Chem. Phys.*, **14**, 93 (1946).

[17] The subscript in the symbol α_e for the relative length has been included here in order to differentiate it from the α used earlier to express the degree of interlinking.

[18] Additional points which could not be shown in Fig. 6 were: 252°, α_e = 2.46, τ = 16,500 g./cm.^{2}; 281°, α_e = 2.44, τ = 16,500 g./cm.^{2}.

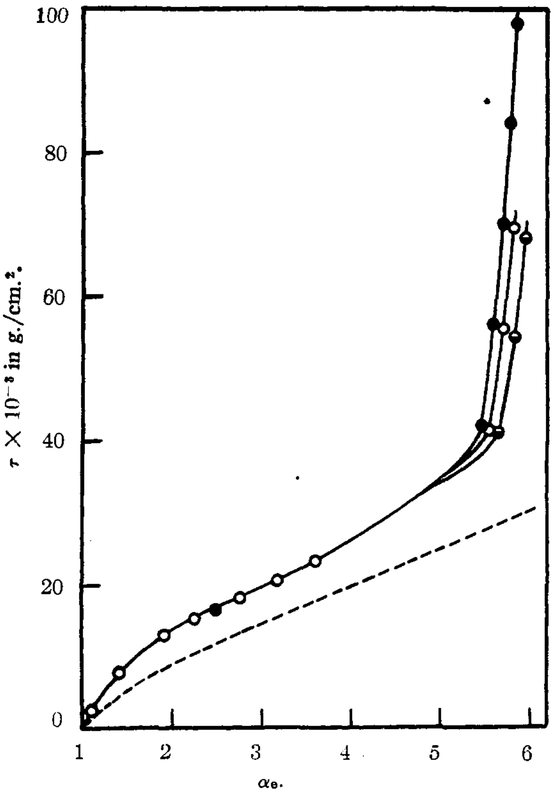

Fig. 6.—Experimental and theoretical (dashed line) stress–strain curves for interlinked polymer 4–3. Temperatures used were: 229°, ●; 241°, ○; 252°, ◒.

derived from the theory of rubber elasticity,[5,19] where ν/V represents the effective number of chain elements per unit volume in the network as expressed by equations (2) or (3), T is the absolute temperature (taken as 514° in calculating the curve), and R is the gas constant. It has been assumed that interlinking is complete, *i. e.*, that $\alpha = 1$ in equation (2) so that $\nu = \nu_0 = (T_c - T_n)/2$ per gram (Table II). To the extent that this assumption is in error, the theoretical curve should be lowered by the factor $2\alpha - 1$. The experimentally observed forces of retraction are somewhat higher than predicted by equation (6). The discrepancy is similar to that observed for vulcanizates of butyl rubber,[6] of GR-S[20] and of natural rubber[21] for which the value of ν has been established by independent means in each case. The present results are not sufficiently precise to establish the dependence of τ on temperature at low elongations (Fig. 5). In drawing the comparison with equation (6), which is derived on the assumption that the change in internal energy with relative length (α_e) is zero, it is implied that only the entropy changes on stretching, and this is equivalent to the assumption of proportionality between τ and T. If a considerable change in internal energy E also is involved (which seems altogether unlikely), a term expressing the contribution due to $(\partial E/\partial L)_T$ should be included in equation (6).

The complete stress–strain curves for polymer 4–3 shown in Fig. 6 exhibit the abrupt rise in slope at higher elongations which is characteristic of rubber-like polymers that crystallize on stretching. The occurrence of crystallization when the "liquid" multilinked polyamides are stretched to sufficiently high elongations seems to be clearly indicated. Crystallization occurs at a greater elongation the higher the temperature. This is in harmony with expectation and with the theoretical treatment of crystallization in elongated polymers published a few years ago.[22] In other words, elongation raises the melting point, *i. e.*, the greater the elongation the higher the melting point.

Stress–strain curves over the low elongation range at 241° are shown in Fig. 7 for each of the seven multilinked polymers listed in Table VII. Fibers from polymer 8–1 broke at very low elongations, making further extension of the curve impossible. The shape of the curves for polymers 8–2 and 4–1 appears to differ somewhat from those of the other polymers, but this difference may be due to the onset of crystallization at lower elongations in these cases.

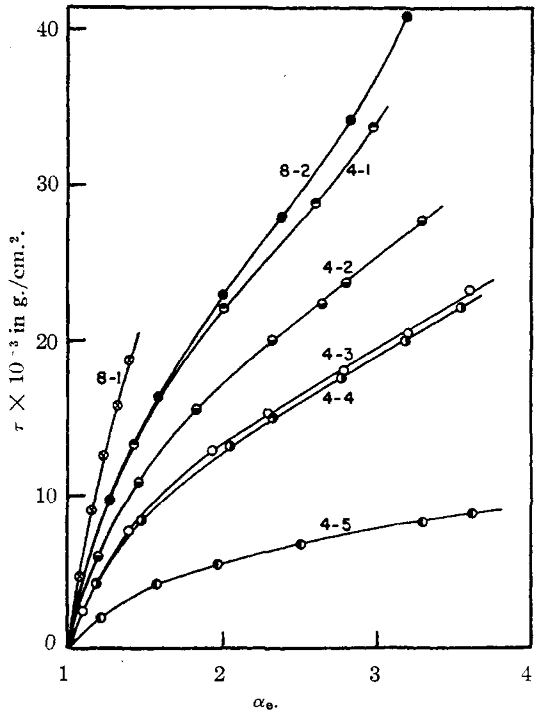

Fig. 7.—Stress–strain curves at low elongations. Numbers refer to polymer used (see Table VII).

Values of τ interpolated from these curves at relative lengths α_e of 1.4, 2.0 and 3.0 are given

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(19) F. T. Wall, *J. Chem. Phys.*, **10**, 485 (1942).

(20) J. Bardwell and C. A. Winkler, *India Rubber World*, **118**, 509 (1948).

(21) P. J. Flory, N. Rabjohn and M. C. Shaffer, *J. Polymer Sci.*, **4**, 225 (1949).

(22) P. J. Flory, *J. Chem. Phys.*, **15**, 397 (1947).

in Table VIII along with the values of ν/V computed from the end-group titers of the respective multichain polymers, assuming $\alpha = 1$. These results are plotted in Fig. 8, where the theoretical line based on equation (6) with $\alpha_e = 1.4$ also is shown for comparison. Again an average degree of interlinking α less than unity would require a theoretical line of lower slope. The divergence between observed and theoretical values for the force of retraction probably is due to network entanglements, as has been suggested for the corresponding discrepancy in vulcanizates of conventional rubbers.[6,21] In contrast to the results recently published[21] on natural rubbers vulcanized with disazodicarboxylates, however, τ at fixed α_e appears to be proportional to ν/V throughout the range investigated. It is possible that the values of ν/V for the azo vulcanized rubbers may have been in error at higher degrees of cross-linking owing to the limited compatibility of these vulcanizing agents with rubber. The τ's for interlinked octachain polymer 8–2 are somewhat higher than the values obtained by interpolation of the results for the interlinked tetrachain polymers at the same ν/V. (The result at $\alpha_e = 1.4$ for polymer 8–1 is not sufficiently accurate to be considered significant in this connection.) The fact that entanglement may be more severe in octafunctionally connected networks would account for this discrepancy.

TABLE VIII

FORCES OF REFRACTION AT FIXED ELONGATION FOR VARIOUS POLYMERS

Polymer	$\nu/V \times 10^{4}$ [a]	τ in (g./cm.^{2}) $\times 10^{-3}$ α_e = 1.4	α_e = 2.0	α_e = 3.0	SV, 30°, m-cresol	$-\mu$ at α_e = 2.0
4–5	0.53	3280	5630	7750	21.95 ± 0.05	0.73
4–4	1.03	7520	12830	18960	13.40 ± .02	.69
4–3	1.15	7750	13360	19300	13.26 ± .02	.72
4–2	1.34	10440	17250	25360	11.50 ± .03	.73
4–1	1.88	12700	21950	34270	10.07 ± .02	.73
8–2	1.58	12700	23000	37200	9.64 ± .02	.77
8–1	3.10	18800	...	...	7.33 ± .08	..

[a] Number of chain elements per cc. at 241° ($d = 0.992$ g./cc.) calculated assuming $\nu = (T_c - T_n)/2$ per g. (see Table II).

Some of the stress–strain measurements were extended to the point of rupture. Frequently, in applying progressively larger loads to a fiber sample, rupture occurred at a comparatively low stress, *e. g.*, at less than 40,000 g./sq. cm. If, however, the fiber withstood a load of this magnitude, the load could then be increased to a roughly reproducible ultimate tensile stress. It would appear, therefore, that the fibers are quite fragile until crystallization sets in, whereupon substantial strength is acquired, in close analogy with natural rubber[23,24] and vulcanized synthetic rubbers that crystallize on stretching.[6] The magnitudes of the tensile strengths observed are therefore of some significance. Thus, tensile strengths of interlinked fibers from polymer 4–3 at 229° were 100,000 g./sq. cm. (1,400 p. s. i.), from polymer 4–2 at 240° to 250°, 175,000 g./sq. cm. (2,500 p. s. i.), and from a similar tetrachain polymer of SV 11, 250,000 g./sq. cm. (3,500 p. s. i.) at 237°. These values are very nearly the same as those found for natural rubber cross-linked to a corresponding extent.[24] At the highest temperature used for stress–strain measurements, 281°, all fibers examined broke at tensions below 15,000 g./sq. cm. Apparently rupture invariably occurred before the development of crystallinity.

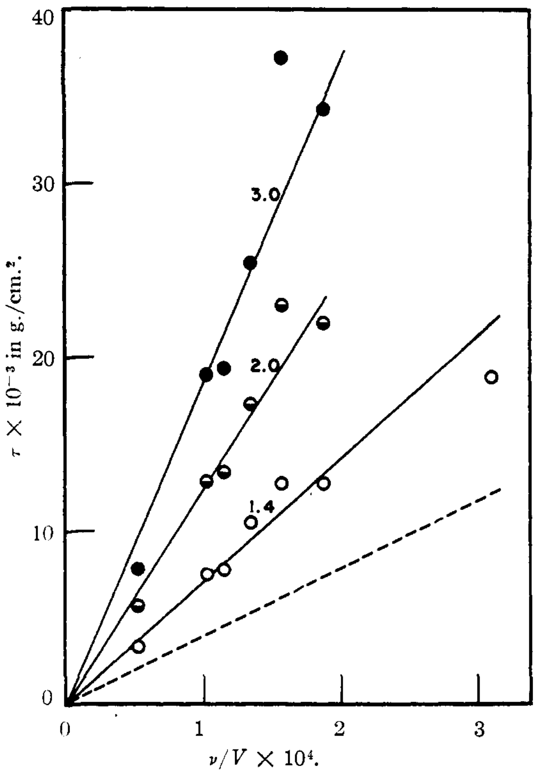

Fig. 8.—The relationship between τ and ν/V at relative lengths (α_e) of 1.4, 2.0 and 3.0. The theoretical relationship at $\alpha_e = 1.4$ is shown by the dashed line.

Equilibrium Swelling Volume and Network Structure.—The equilibrium swelling volume has been used here primarily as a criterion for the degree of completion of the interlinking process. It remains to point out the quantitative dependence of SV on the network structure as embodied in the parameter ν/V. Instead of comparing the observed swelling volumes with the theoretical equation derived to express this relationship,[25] we shall employ the following expression obtained by eliminating the network structure parameter ν/V from this equation and equation (6). The resulting expression relating the swelling volume to τ at a given α_e can be written

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(23) G. Gee, *J. Polymer Sci.*, **2**, 451 (1947).

(24) P. J. Flory, N. Rabjohn and M. C. Shaffer, *ibid.*, **4**, 435 (1949).

(25) P. J. Flory, *J. Chem. Phys.*, forthcoming publication.

$$\mu v_2^2 = -[\tau V_1/RT(\alpha_e - 1/\alpha_e^2)](v_2^{1/3} - 2v_2/b) - \ln(1 - v_2) - v_2 \quad (7)^{25}$$

where V_1 is the molal volume of the swelling agent, $v_2 = 1/SV$ is the volume fraction of polymer in the swollen sample, b is the functionality of the multifunctional unit and μ is the widely used energy of mixing parameter generally assumed to be characteristic of a given solvent–polymer pair at a given temperature. Equation (7), relating τ at a given temperature and elongation α_e to the swelling volume $SV = 1/v_2$, contains the single parameter μ.

In the last column of Table VIII are given the values of μ calculated from SV and τ at $\alpha_e = 2.00$ using equation (7). Variations about the average (−0.73) are no greater than the experimental errors involved, and no trend with ν/V is evident. Since the shape of the stress–strain curve is not truly represented by the factor $(\alpha_e - 1/\alpha_e^2)$ predicted by the theory of rubber elasticity, the value calculated for μ in this manner will depend on the value of α_e chosen for making the calculation. Thus, the values of τ at $\alpha_e = 1.40$ and 3.00 lead to average values of −0.90 and −0.56, respectively, for μ. The curves in Fig. 9, which deviate almost imperceptibly from straight lines,[6] have been computed from equation (7) using the respective average values of μ at the three elongations. Equation (7) is well verified, and the slight displacement predicted for the octalinked compared with the tetralinked polymers seems to be borne out.

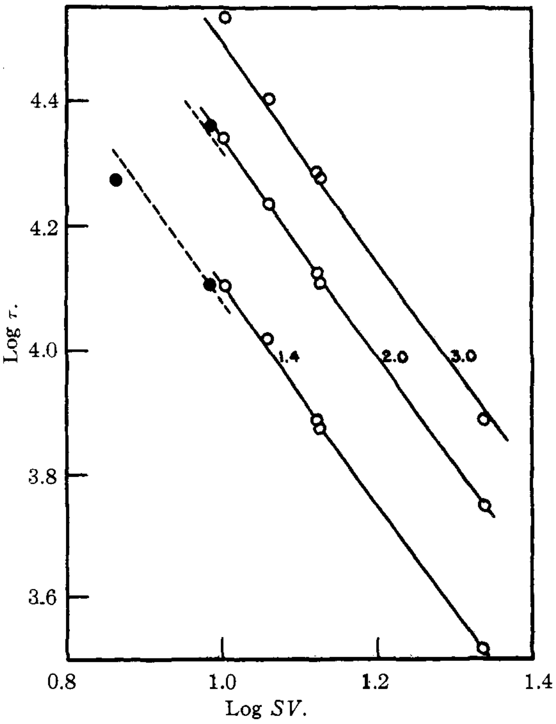

Fig. 9.—The relationship between τ and log SV at relative lengths of 1.4, 2.0 and 3.0: ○, tetralinked polymers; ●, octalinked polymers.

The conclusion may be drawn that deviations from the theoretical relationship[26] between SV and ν/V correspond very closely to those found in the observed dependence of τ on ν/V at fixed α_e. The entanglements or other factors responsible for the latter deviation must be operative also in the swollen network.[5,6,21]

Summary and Conclusions

Tetrachain and octachain polyamides in the form of fibers have been converted to network structures by reaction of their terminal carboxyl groups with stoichiometric proportions of hexamethylenediamine. The interlinking reaction appears to be nearly quantitative, and the procedure therefore lends itself to the preparation of networks of known structure determined by the type and proportion of multifunctional reactant used in the initial preparation of the thermoplastic multichain polymer. The network polymers prepared in this manner and called "multilinked" polyamides possess at room temperature many of the properties characteristic of linear and multichain polyamides, such as high crystallinity, ability to be oriented to form strong fibers, and high melting points. In addition they possess the properties characteristic of network structures such as insolubility in common polyamide solvents and rubber-like elasticity at temperatures above the melting point of the crystallites. In the latter property they are remarkably similar to natural rubber. The stress–strain curve at 229 to 280° is of the same shape as that for vulcanized rubber at room temperature, including a steep rise at high elongations due to crystallization on stretching. Even the ultimate tensile strength and elongation are very nearly the same as those observed for crystallizing rubbers vulcanized to a similar degree of cross-linking.

The forces of retraction τ exhibited by the multilinked fibers at a given relative length α_e have been compared with those calculated according to the theory of rubber elasticity from the number ν/V of network elements in the structure per unit volume. τ is approximately proportional to ν/V, but the constant of proportionality is somewhat greater than theory predicts. This discrepancy is similar in magnitude to those observed for conventional rubbers, and like the latter is attributed to restraints imposed by entanglements of the network elements. An octalinked polyamide, the chains of which presumably are more entangled, exhibited slightly higher forces of retraction at given elongations than were found for the tetralinked (*i. e.*, crosslinked) polyamides at the same concentration ν/V of network elements.

The multilinked polyamides swell extensively but do not dissolve in solvents such as *m*-cresol in which polyamides dissolve readily. The equilibrium swelling volumes at 30° of various multilinked polymers differing in extent of multilinking

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[26] See equation (12) of ref. (25).

can be correlated with their τ's at selected relative lengths α_e in accordance with the theoretical relationship between these two quantities.

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[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY AND NUTRITION, A. AND M. COLLEGE OF TEXAS, AND THE TEXAS AGRICULTURAL EXPERIMENT STATION]

Displacement Analysis of Lipids. II. Increased Separability of Fatty Acids by Depressed Solubility[1]

BY LENNART HAGDAHL[2] AND RALPH T. HOLMAN

Introduction

Displacement analysis, developed by Tiselius,[3] has been shown to be an effective technique in chromatographic investigations. The displacement development of a chromatogram by a substance which is adsorbed more strongly than any constituent of the sample, separates the constituents into zones, the least adsorbed constituent migrating first. Theoretically, with significant differences in adsorption, the separated constituents should be virtually quantitatively recoverable. Displacement development has been used successfully for the separation of sugars,[3,4] peptides[5] and amino acids.[5]

Considerable work has been done on the chromatographic separation of fatty acids by elution techniques,[6,7,8] but displacement separation of fatty acids has received little attention. Unfortunately, attempts by Claesson[9] to displace saturated fatty acids on charcoal by their higher homologs were unsuccessful, and he concluded that displacement analysis could not be applied to this homologous series with the adsorbents tried. He did, however, report group separation of saturated, unsaturated and branched fatty acids on silica gel by displacement.[10] After coupled filters and a mixer[11] were developed and added to the Tiselius–Claesson apparatus,[12] the improved performance of the instrument allowed the displacement separation of saturated fatty acids to be observed under conditions similar to those of Claesson's experiments. Thus, for example, the present authors[13] were able to separate lauric, myristic, palmitic and stearic acids by development using picric acid as displacer on Carbo Activ charcoal. The present report is a continuation of these investigations, extending the usefulness of displacement separation to the lower and higher fatty acids.

Methods

The fatty acids used in this investigation were Eastman Kodak Co. Organic Chemicals. Adsorption isotherms were made at 25° using 1-g. samples of adsorbent shaken ten minutes with 25 ml. of solutions of differing concentrations of fatty acid. After equilibration, the adsorbent was removed by filtration and aliquots of the filtrate were titrated.

The instrument used for the chromatographic experiments was a modified copy of the Tiselius–Claesson interferometric adsorption analysis apparatus[12] built by D. Milton Kvanbeck of Minneapolis. In all experiments the mixer and coupled filters developed by Hagdahl[11] were used. All frontal and displacement analyses were made using 1 part Darco G 60 charcoal and 2 parts Hyflo Supercel as adsorbent.

Experimental and Results

In order to continue in this country the studies begun at Uppsala[13] it was realized that a locally-available adsorbent was necessary. Therefore, investigations on the European charcoals were discontinued, and a search for an adsorbent available on the American market was begun. Adsorption isotherms were measured for a variety of representative adsorbents using 95% alcohol solutions of lauric and myristic acids. The adsorbents were evaluated as regards the shape of the isotherms and the difference between adsorption isotherms for myristic and lauric acids on a given adsorbent. The data thus gained are summarized briefly in Table I. According to the theory of displacement analysis put forth by Tiselius, the separability of substances can be predicted from an inspection of the respective isotherms.

Judging from the isotherms it appears that several of the adsorbents could be used for separation of fatty acids and are superior to Carbo Activ and Carboraffin Supra which were used in the preliminary studies.[13] From these, Darco G60 was chosen as a suitable adsorbent for separation of

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