

Acid-Base Properties of Fibers. Part I. Nylon

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Synopsis

The acid-base titration curves of solid nylon 6 resins and nylon 66 fibers have been measured, and isoionic points and endgroups determined. Five nylon 6 polymers of different molecular weights and two commercial nylon 66 yarns have been studied. Titration curves of these materials with hydrochloric acid and sodium hydroxide in the absence of added salt, and of nylon 66 in the presence of added salt, at three different temperatures, and with benzenesulfonic, trichloroacetic, and naphthalene-2-sulfonic acid, allowed the effect of polymer molecular weight, salt, temperature, and anion affinity on the titration curves to be determined. All the results are consistent with the view that nylon possesses a zwitterion structure at neutral pH, carboxyl groups being protonated on acid titration. A proportion of the endgroups is not available to titration in the solid polymers. Existing theories of the acid-base combination of solid polymers fail to explain all the results. The titration curves and elastic properties of the following modified nylon 66 yarns have also been determined and interpreted: nylon deaminated by nitrous acid, dinitrophenylated, acetylated, carboxymethylated, hydrolyzed, and dihydrophenylated nylons, and nylon treated with alkaline hypochlorite, boiling water, and boiling benzene. In all cases the increase in the work to stretch the filament is independent of pH.

INTRODUCTION

Studies of the acid-base properties of fibers have been concerned particularly with wool, for which much accurate information is available.¹⁻³ For polyamides, few precise data exist. Wall and his co-workers⁴⁻⁶ have published titration curves for nylon 66 fibers with sodium hydroxide and hydrochloric acid, including commercial fibers and fibers having an excess of amino over carboxyl endgroups. Their interpretation of the results was based on the theory of Gilbert and Rideal,⁷ developed for wool, but the agreement between the results and the theory was not complete. Myagkov and Pakshver⁸ have presented titration curves for nylon 6 fibers and resins (Kapron) with hydrochloric acid, naphthalene-2-sulfonic acid, methyl orange, methylene blue hydrochloride, potassium hydroxide, and triethylbenzeneammonium hydroxide. They used an ion-exchange model to interpret their results, but obtained only limited agreement with experiment. This paper describes the isoionic points and titration curves of nylons 6 and 66, and the effects of salt, temperature, polymer molecular weight, and different acids on the titration curves. Several chemically modified nylons have also been studied. Theoretical interpretation is

made in the following paper,⁹ where a polyelectrolyte theory for the acid-base properties of fibers is described and applied to wool, nylon, and collagen.

EXPERIMENTAL

Nylon 66 Fibers

Two types of commercial nylon 66 yarn were used. Nylon I was 35 filament 210 den. bright nylon, and nylon II was 10 filament 35 den. semi-bright nylon, selected from one delivery batch from British Nylon Spinners Ltd. The fibers were extracted with ether and alcohol and subjected to prolonged washing in distilled water. They were stored at 20°C. and 65% R.H. and their moisture regain determined so that conditioned fibers could be used directly.

Nylon 6 Resin

Aqueous solutions of ϵ -caprolactam were sealed in Carius tubes and heated for 24 hr. at 220–230°C. Five polymers were prepared, labeled A to E, for the various mole ratios of water to ϵ -caprolactam shown in Table I. Soft polymers were twice shaken with hot water and centrifuged, after which the clear supernate contained no dissolved residues. Hard polymers were ground and dissolved by refluxing in methanol saturated with calcium chloride. The polymers were precipitated in water as fine suspensions, washed in hot water, centrifuged, washed in methanol and centrifuged, these processes being repeated until the supernate was free of chloride. They were dried to constant weight over calcium chloride *in vacuo*.

TABLE I
Properties of the Polymers

Polymer	Water/ caprolactam mole ratio	Carboxyl endgroup content, meq./g.	Maximum endgroup combination of acid by solid ^a	\bar{M}_n	Isoionic point
Nylon 66, I	—	—	—	—	6.20
Nylon 66, II	—	0.0852	0.440	11,700	—
Nylon 6, A	18.85	—	—	—	7.55
Nylon 6, B	0.75	0.177	0.847	5,650	7.60
Nylon 6, C	2.10	0.390	0.769	2,600	—
Nylon 6, D	3.92	0.589	0.747	1,700	—
Nylon 6, E	6.28	0.726	0.730	1,380	—

^a As fraction of the carboxyl endgroup content.

Endgroup Determinations

The method of Waltz and Taylor¹⁰ was used, and the results are shown in Table I. To check that no degradation was induced by dissolution of the

polymer in benzyl alcohol at 170–180°C., a second determination was made on a sample of polymer II which had already once been subjected to the treatment required. A value of $\bar{M}_n = 11,900$ was found for this polymer, in substantial agreement with the original determination (Table I). The second treatment evidently caused no degradation, and it seems reasonable to conclude that this is true of the first also. The point is important in connection with the lower values found for the maximum end-group uptake of acid by the solid polymers in the titration experiments (q.v.).

Isoionic Points

The method of Lemin and Vickerstaff¹¹ as modified by da Silva¹² was used, the isoionic point being that pH where the effect of the addition of neutral salt is zero, found by interpolation from a set of results on the shift of pH produced by the addition of neutral salt to solutions in equilibrium with the polymer. Duplicate polymer samples, previously adjusted to an equilibrium solution pH between 5.5 and 6.5 by washing with distilled water, were placed in identical solutions of hydrochloric acid or sodium hydroxide of pH between 4.00 and 10.00. To one set of solutions sodium chloride was added to make them 0.068*M*. The solutions were allowed to attain equilibrium at 22.2°C. and their pH's measured.

Acid-Base Combining Capacity

A discontinuous method was used. A series of solutions of pH values within the ranges 2.00–4.50 and 9.50–12.50, were made by diluting an appropriate acid or sodium hydroxide solution, carbon dioxide being carefully excluded. Determination of pH was made by use of a Cambridge pH meter with a standard or Alki glass electrode, a calomel electrode, and phthalate and borate buffers. The solutions (50 ml.) were contained in closed vessels containing the glass electrode, a calomel electrode, a stirrer, and an inlet and outlet for oxygen-free nitrogen. The pH was measured before polymer addition (0.2–2.0 g.) and after equilibrium had been established at the appropriate temperature. For all solutions containing the nylon 6 polymers, 24 hr. was sufficient for equilibrium to be attained, but for solutions containing nylon 66 fibers, 48 hr. was needed for equilibrium with the acid solutions, and up to 96 hr. with the alkaline solutions. Determinations were made in duplicate or triplicate, and control experiments were carried out. Individual pH measurements were accurate to ± 0.005 pH unit, and were used to calculate the uptake of acid or base by the nylon.

Preparation of Chemically Modified Nylons

Nylons I and II (nylon 66 fibers) were used throughout.

Deamination. A 5-g. portion of nylon I was agitated with a solution of 8.69 g. sodium nitrite and 7.2 ml. glacial acetic acid in 74 ml. water for

46 hr. at room temperature. The nylon was removed and washed until the pH of the washings was unchanged. The nylon was slightly yellowed by the treatment. Measurements of the acid combining capacity of this nylon showed that only about 50% of the amino groups had reacted, so a more vigorous treatment was adopted. In this treatment, 10 g. of nylon I was immersed in 95.6 g. sodium nitrite, 79.2 ml. glacial acetic acid, and 374 ml. water for 24 hr. at room temperature. The nylon was then treated with a fresh solution for a further 24 hr. and the process repeated a third time. The nylon was washed as already described and conditioned at 20°C. and 65% R.H. Its regain was determined. This material was used for subsequent experiments.

Dinitrophenylation. Nylon II (65 g.) was treated with 25 g. dinitrofluorobenzene in 1500 ml. of an ethanol-water mixture (2:1 by volume) made 1.3% in sodium bicarbonate for 48 hr. at room temperature. It was washed until no more dinitrofluorobenzene could be detected colorimetrically in the washings and dried at 20°C. and 65% R.H.

Acetylation. A 50-g. portion of nylon II was refluxed with 50 ml. acetic anhydride and 300 ml. benzene for 48 hr. with agitation. The nylon was given three 24-hr. soakings in ethanol, washed in water, and dried at 20°C. and 65% R.H.

Dihydroxyphenylation. Here, 5 g. nylon I was boiled in 100 ml. of 2% aqueous benzoquinone (pH 5-6) for 1.5 hr., washed, and dried at 20°C. and 65% R.H. The treated nylon was dark brown.

Treatment with Alkaline Hypochlorite. In this treatment,¹³⁻¹⁶ 8 g. nylon I was immersed in 800 ml. of a borate buffer at pH 9.25 and 4 ml. of sodium hypochlorite solution containing 15 g. available chlorine/100 ml. was added slowly with stirring. After standing for 75 min. at room temperature with occasional stirring, the nylon was washed for 15 min. in water, then stirred in a 1.5% solution of sodium bisulfite for 15 min. to remove uncombined chlorine. It was washed and dried at 20°C. and 65% R.H.

Alkaline Hydrolysis. Nylon II (55 g.) was refluxed in 400 ml. of 0.1M sodium hydroxide for 1 hr., washed until the pH of the washings was unchanged on 48 hr. soaking, and dried at 20°C. and 65% R.H.

Carboxymethylation. Carboxymethylation¹⁷ was accomplished by refluxing 100 g. nylon II in 1 liter of 5% aqueous magnesium bromoacetate containing excess magnesium oxide for 2 hr. The nylon was washed until the pH of the washings was unchanged on 24 hr. soaking and dried at 20°C. and 65% R.H.

Elastic Properties of Fibers

Load-extension curves were determined at 22.2°C. by means of a Cambridge Fibre Extensometer. The filaments were stretched at a constant rate of loading, and extension was limited to 10%. Each filament was mounted on glass hooks as described by Bentham,¹⁹ after having been equilibrated for 48 hr. with one of the following solutions: (1) 0.1M hydro-

chloric acid; pH \approx 1.0, (2) distilled water pH 5.5-6.0; (3) Cambridge buffer solution, pH 7.00; (4) 0.05*M* sodium borate, pH 9.20. The filaments were extended while immersed in the same solution. Filaments for extension were selected as far as possible at random, and the variability between filaments was studied by using untreated nylon II in the four media. With the use of nine filaments, standard deviations of 14.8, 11.7, 4.1, and 8.6 were found for the four media, respectively, with corresponding coefficients of variation of 4.5, 3.56, 1.24, and 2.59%. It was judged that at least seven filaments needed to be examined. This procedure was necessary as a filament cannot be calibrated by a preliminary stretch in water, since this initial stretch modifies the properties of the filament.²⁰

Viscosity

An Ostwald viscometer was used, calibrated by the method given in British Standard 188 (1937). Nylons and chemically modified nylons were dissolved in formic acid at a concentration of 1 g. in 65 ml. and viscosities determined at 25°C. This was used as a simple empirical criterion of degradation.

X-Ray Diffraction

Wide-angle x-ray diffraction patterns were taken at room temperature by means of a conventional camera with nickel-filtered copper K_{α} radiation, the x-ray beam being normal to the fiber axis. Fiber bundles, 1 mm. thick, were held in stainless steel stretching frames 4 cm. from the film and exposed for about 1 hr.

RESULTS AND DISCUSSION

Isoionic Points

The results of the experiments on polymer B are shown in Figure 1, and the isoionic points of the nylon 6 and 66 polymers are given in Table I. The monomer corresponding to nylon 6, ϵ -aminocaproic acid, has *pK* values²¹ of 4.43 and 10.75.

Titration Curves of Nylon 6 Resins

Figure 2 shows the titration curves of polymers A, B, C, D, and E with hydrochloric acid and sodium hydroxide at 21.5°C. in the absence of added salt. All the acid titration curves show a small inflection at the level of maximum endgroup combination of the solid between pH 2.3 and 2.5, and further sorption of acid at lower pH, presumably by interaction with the CONH groups. No inflexion occurs in the base titration curves, although Myagkov and Pakshver⁸ claimed a plateau of maximum base combination at pH 12.3-12.4 for Kapron. This maximum endgroup combination of acid falls as the degree of polymerization (\overline{DP}_n) rises, and Figure 3 shows that it is linearly related to $1/\overline{DP}_n$, as expected.

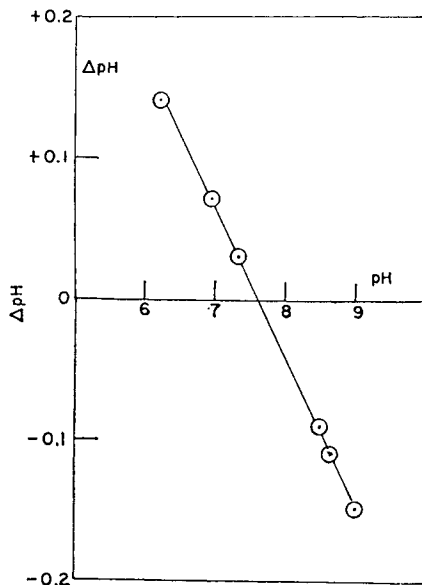


Fig. 1. Determination of the isoelectric point for polymer B.

Values of the maximum endgroup combination of acid by the solid polymer, obtained from the titration curves, are lower than the values of the carboxyl endgroup content measured by the Waltz and Taylor method, and are expressed as fractions of these in column four of Table I. These fractions rise with increasing degree of polymerization, roughly linearly. This discrepancy could be due to the inaccessibility of some endgroups to acid in the solid polymer, to degradation of the polymer by the Waltz and Taylor treatment or to some carboxyl groups being undissociated even at pH 7. Degradation has been shown to be unlikely for nylon 66. Dawydoff²² found for nylon 6 that treatment for 30 min. at 200°C. in benzyl alcohol solution reduced the intrinsic viscosity by 8.7%, but at 170°C. by only 0.25%. In the present work the temperature used was 175°C. and the time less than 20 min., and so it seems likely that for the nylon 6, as well as the nylon 66, there was negligible degradation during the endgroup determinations by the Waltz and Taylor method. No conclusion can be drawn from the increase of the maximum endgroup combination of acid by the solid polymers with their molecular weight as the degrees of crystallinity are not known. Inaccessibility to acid of some endgroups in the solid polymer remains as the more probable explanation, since undissociated carboxyl endgroups at neutral pH could titrate in the alkaline region, and corresponding unchanged amino groups in the acid region. The titration curves show no evidence of this.

The apparent pK values of nylon 6 are shifted toward the extremes of the pH scale from the values of 4.43 and 10.75 for ϵ -amino-*n*-caproic acid. This is the same electrostatic effect as observed for wool.

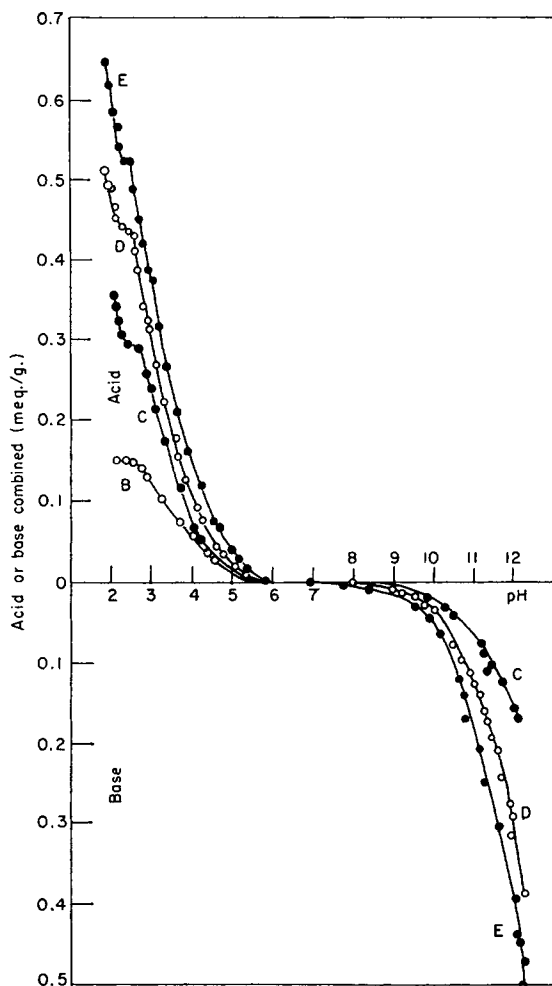


Fig. 2. Titration curves of nylon 6 resins with HCl and NaOH at 21.5°C. (Polymers B, C, D, E).

Titration Curves of Nylon 66 Fibers

The titration curve of nylon II with hydrochloric acid and sodium hydroxide is shown in Figure 4. It possesses an inflection at maximum endgroup acid combination of the solid, as for nylon 6. Although this nylon has an excess of carboxyl over amino endgroups, this maximum endgroup combination will correspond to the number of amino endgroups present, even though the carboxyl groups are titrated over the acid region, since in a zwitterion system at the isoionic point only the same number of carboxyl groups can be charged as there are charged amino groups present, the remainder being undissociated. These undissociated carboxyl groups should titrate in the alkaline region, and, indeed, nylon II is seen to take up much

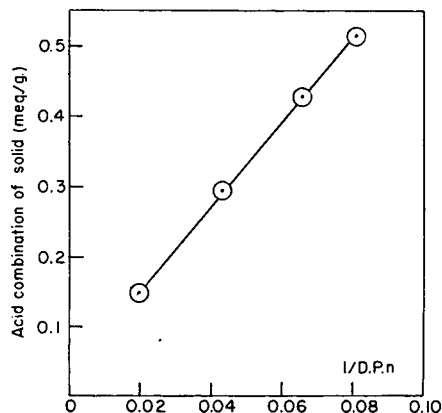


Fig. 3. Maximum endgroup acid combination of solid nylon 6 resins.

more alkali between pH 7 and 9 than do the nylon 6 polymers which have equal numbers of carboxyl and amino endgroups. Again the maximum endgroup acid combination of the solid is less than that of dissolved nylon determined by the Waltz and Taylor method (Table I), part of the very large discrepancy for nylon 66 being due to the presence of uncharged carboxyl groups at neutral pH, and part probably to inaccessibility as for nylon 6.

Effect of Temperature on the Acid Titration Curve of Nylon 66

Figures 4 and 5 show the titration curves of nylon II with hydrochloric acid at 1.5, 21.5, and 47.0°C. The apparent pK is evidently decreased by increase in temperature, but only to a small extent. Although apparent pK values cannot readily be obtained from titration curves in the absence of added salt (see Part II),⁹ a rough calculation with the use of the pH of half titration is worth making to decide whether the heat of ionization ($-\Delta H_1$) has the magnitude expected for the dissociation of carboxyl or amino groups, roughly -500 to 2000 and $10,000$ to $13,000$ cal./mole, respectively. A value of $-\Delta H_1$ of 1700 cal./mole was found, confirming that carboxyl groups are titrated from a zwitterion structure on addition of acid.

Titration of Nylon 66 with Various Strong Acids

Titration curves of nylon II with benzenesulfonic acid, trichloroacetic acid, and naphthalene-2-sulfonic acid at 20°C. are shown in Figure 6. The curves are displaced toward the neutral region when compared with that for hydrochloric acid, due to the affinity of the anions for nylon. The affinities ($-\Delta\mu^\circ$) calculated from the pH of half titration by the method given in Part II are as follows, that for hydrochloric acid being taken arbitrarily as zero; benzenesulfonic acid, 2300; trichloroacetic acid, 3400; naphthalene-2-sulfonic acid, 4300 cal./mole. The corresponding values

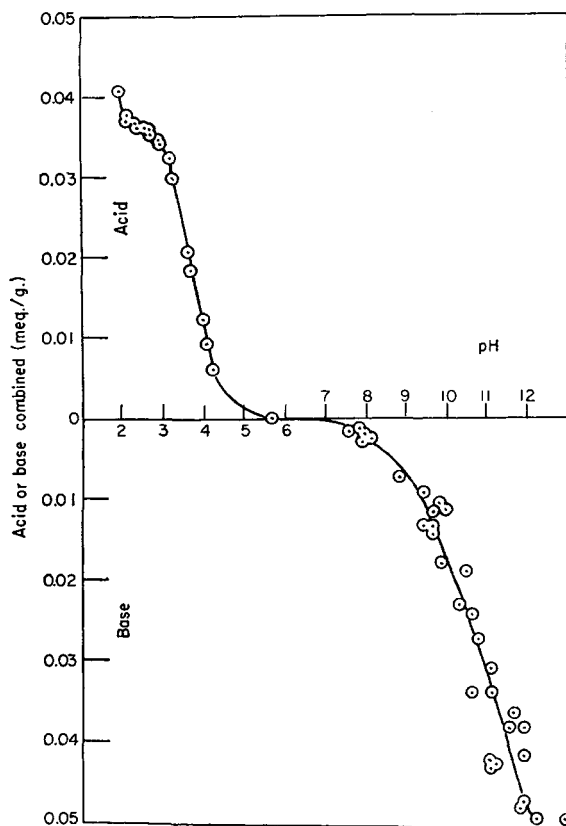


Fig. 4. Titration curve of nylon 66 (nylon II) with HCl and NaOH at 21.5°C.

for the three acids for wool are 810, 1210, and 2450 cal./mole, respectively. Thus, nylon has a greater affinity for the anions than has wool.

The plateau of maximum endgroup acid combination has been partly lost for trichloroacetic acid. X-ray photographs of nylon II equilibrated with this acid at pH 2.0 showed no difference from those of untreated nylon II, so penetration of crystallites can be discounted. The same result has been found for methacrylic acid.²³ The explanation may be that this acid has a high affinity for the CONH groups, causing the adsorption curve for these groups to merge with the titration curve of the endgroups.

Effect of Salt on the Acid Titration Curve of Nylon 66

Titration curves for nylon II with hydrochloric acid in the presence of various concentrations of potassium chloride at 20°C. are shown in Figure 7. The presence of the salt moves the titration curve towards the neutral region, the salt ions suppressing the electrostatic effect by screening the fixed charges on the endgroups.

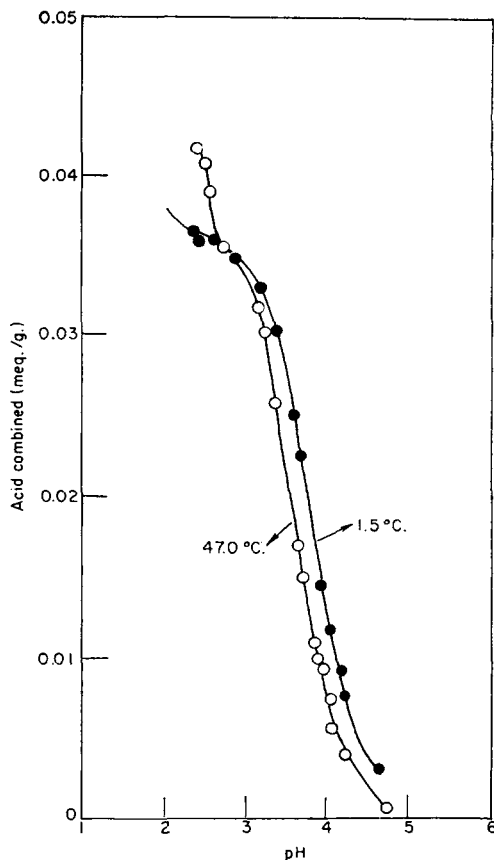


Fig. 5. Titration curves of nylon 66 (nylon II) with HCl (●) at 1.5°C.; (○) at 47.0°C

Theoretical Interpretations of the Acid Titration Curves

The above data were examined in the light of four existing theories on the acid-base properties of fibers, viz., the theories of Myagkov and Pakshver,⁵ of Wall et al.,⁴⁻⁶ and the theories of Gilbert and Rideal⁷ and of Peters and Speakman,²⁴ for wool. The theory of Myagkov and Pakshver predicts that in the presence of added salt,

$$\log x/(x_0 - x) = \log K - 2 \text{ pH} \quad (1)$$

where x_0 is the total number of sorption sites, x the number occupied, and K the equilibrium constant for the sorption. Thus $\log x/(x_0 - x)$ should be linear in pH with a slope of -2 . The results for nylon II were pronouncedly sigmoid about a line having the theoretical slope. A more stringent test requires that x should be linear in $x/[\text{H}^+]^2$, but the results fall on a pronounced curve approximating to a hyperbola. Evidently this theory is not satisfactory.

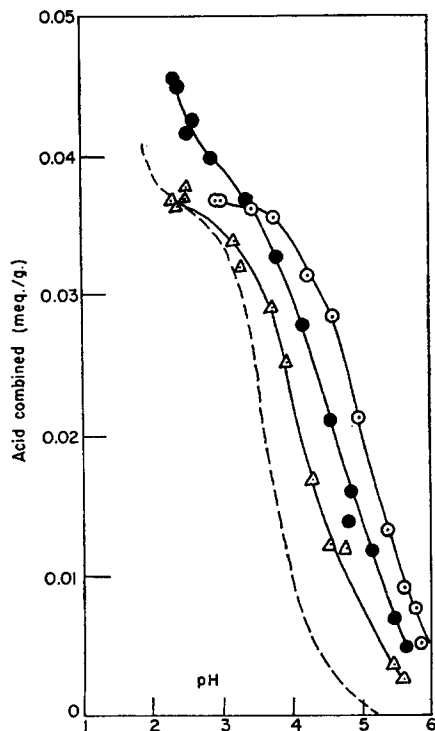


Fig. 6. Titration curves of nylon 66 (nylon II) with various strong acids at 21.5°C.: (○) naphthalene-2-sulfonic acid; (●) trichloroacetic acid; (△) benzenesulfonic acid; (---) hydrochloric acid.

Wall's theory requires that

$$K^{1/2}(B_0 - c) = \{c[c + (A_0 - B_0)]/[H^+]^2\}^{1/2} \quad (2)$$

where A_0 and B_0 are the total concentrations, respectively, of carboxyl and amino endgroups ($A_0 > B_0$), and c is the concentration of groups which have reacted. A plot of values of the right-hand side of the equation for various c should be a straight line, but again the results for nylon II lie in a sigmoid curve around the straight line, though they are closer to it than in the test of eq. (1). Equation (2) gives the correct values for A_0 . The theory of Gilbert and Rideal corresponds to Wall's theory when $A_0 = B_0$, and its direct application to the acid titration of nylon II involves ignoring the carboxyl groups which are in excess of the amino groups. In this theory for the absence of salt,

$$\log \theta/(1 - \theta) = 1/2 \log K - \text{pH} \quad (3)$$

where θ is the fraction of the carboxyl groups, originally charged, which are uncharged at the given pH. A plot of $\log [\theta/(1 - \theta)]$ against pH should be linear with a slope of -1 , and a plot of $\theta/[H^+]$ against θ should be linear

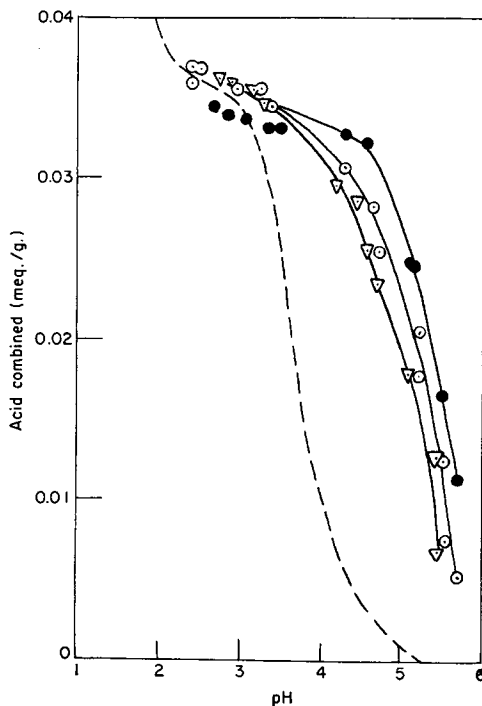


Fig. 7. Titration curves of nylon 66 (nylon II) with hydrochloric acid at 21.5°C. in the presence of potassium chloride: (●) 0.10M KCl; (○) 0.04M KCl; (△) 0.02M KCl; (---) no salt added.

with an intercept equal to the maximum endgroup acid combination of the solid. The results for nylon II and polymer C fall well on the straight lines as required, but the intercepts give values of the maximum acid combination too high by a factor of about 1.2.

These theories give approximate agreement with experiment in the absence of salt. Predictions of the effects of salt on the titration curves are less satisfactory. It would be expected that the pH of half titration should be linear in $\log [X^-]$, where X^- is the salt anion, common to that of the acid. Figure 8 shows that for the acid titration of nylon II the experimental findings do not conform to this pattern.

The theory of Peters and Speakman relates the pH inside the fiber ($\text{pH}_{\text{int.}}$) to that of the solution ($\text{pH}_{\text{ext.}}$) by use of the Donnan equations. For nylon with hydrochloric acid, it gives:

$$\text{pH}_{\text{int.}} \approx \text{pH}_{\text{ext.}} - \log [X^-] + \log (a/v)\gamma \quad (4)$$

where a is the acid combined at $\text{pH}_{\text{ext.}}$, v is the internal volume of the fiber phase available to the solution, and γ is the activity coefficient of the anion, assumed to be unity. The same curve of $\text{pH}_{\text{int.}}$ against acid combined should be obtained for all salt concentrations, and was so obtained for wool.

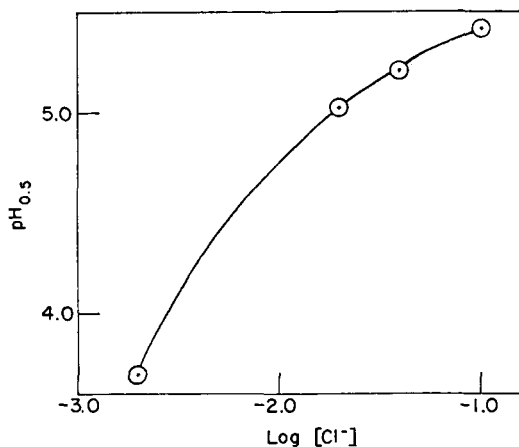


Fig. 8. Effect of ionic concentration on the pH of half titration of nylon 66 (nylon II) with HCl in the presence of KCl at 21.5°C.

However, for nylon II different curves were obtained: for example the $\text{pH}_{\text{int.}}$ values corresponding to half titration were 4.5, 3.8, and 3.5 for no salt added, 0.02M, and 0.10M salt, respectively, when ν was taken as²⁴ 0.016 cc./g. The values are very dependent on ν which is very uncertain; for instance, if the maximum possible value of ν of 0.88 cc./g. is taken, $\text{pH}_{\text{int.}}$ values, corresponding to those already given, of 6.6, 6.0, and 5.6 are obtained. None of the existing theories can therefore be regarded as completely satisfactory. A new theory of the acid-base properties of fibers has been developed and is presented in Part II.⁹

Titration Curves of Chemically Modified Nylons

Titration curves for nylon 66 fibers, with hydrochloric acid at 21.5°C., (a) deaminated by nitrous acid, and (b) dinitrophenylated with dinitrofluorobenzene, are shown in Figure 9. In both cases a great reduction in acid-combining power has occurred, indicating that most of the available amino groups have reacted with the reagents. The removal of amino groups should cause charged carboxyl groups to be protonated, making them available for titration with base. This is observed, the base combined by deaminated nylon at pH values of 9.30, 10.34, and 10.86 being 0.045, 0.082, and 0.090 meq./g., respectively, untreated nylon combining with only 0.020, 0.027, and 0.030 at the same pH values. Some degradation of the nylon occurred on deamination by nitrous acid, but not on dinitrophenylation (see Table II).

Titration curves of nylon 66 fibers which have been acetylated, hydrolyzed with alkali, or carboxymethylated, are shown in Figures 10, 11, and 12, respectively. The first is to be compared with that for nylon treated with boiling benzene for 48 hr., and the other two with that for nylon treated with boiling water for 1 hr., since both these treatments

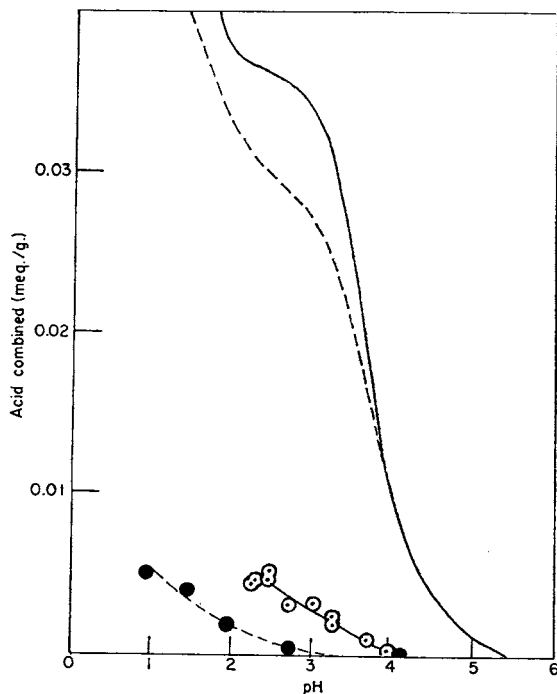


Fig. 9. Titration curves with HCl of nylon 66 (treated with (●) nitrous acid and (○) dinitrofluorobenzene. Titration curves for (---) untreated nylon I and (—) untreated nylon II are shown for comparison.

cause a reduction in the acid- and base-combining capacities, due presumably to a decrease in the degree of accessibility of the endgroups brought about by some relaxation in the fiber structure. This is further evidence that inaccessibility of some endgroups in the solid polymers to acid is indeed the cause of the maximum endgroup acid combination of the fibers and resins being less than the endgroup content determined by the Waltz and Taylor method. R. T. Shet, working in this laboratory, has recently

TABLE II
Fluidity of Nylons ($100/\eta$) in Formic Acid at 25°C. and 15.4 g./l.

Treatment	Fluidity	
	Nylon I	Nylon II
Untreated	22.05	22.80
Nitrous acid	27.52	—
Dinitrophenylated	21.81	22.20
Acetylated	22.29	22.82
Dihydroxyphenylated	21.72	—
Hypochlorite	22.57	—
Hydrolyzed	—	23.12
Carboxymethylated	—	23.09

found a similar result for crosslinked poly(methacrylic acid) resins, the effect becoming more pronounced the greater the extent of crosslinking.

The titration curve of acetylated nylon shows that most of the amino groups have been acetylated and this has resulted in a reduced acid-combining capacity. The base titration curve shows an increase in the number of groups titrating between pH 7 and 10, due to uncharged carboxyl groups, and a decrease between pH 10 and 13 due to acetylation of amino groups, when compared with the curve for nylon treated in boiling benzene.

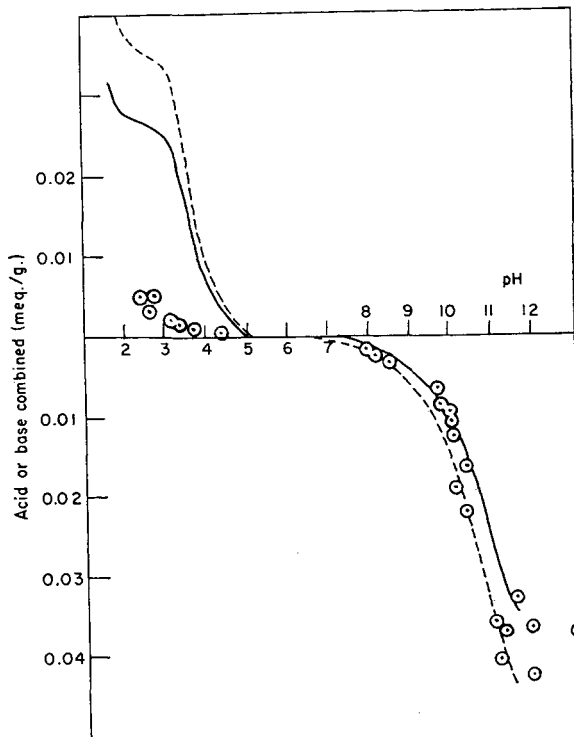


Fig. 10. Titration curves of: (O) acetylated nylon II; (—) untreated nylon II; (- - -) nylon II treated with boiling benzene.

No significant degradation took place. Alkaline hydrolysis brought about an increase in the number of available acid-combining groups and little change in the base combination compared with nylon treated in boiling water. The increase in the acid combination will be due to hydrolysis of acetylated amino endgroups, allowing further carboxyl groups to ionize. Carboxymethylation produced a large increase in the acid combination, presumably due to the carboxymethyl groups which titrate in the region pH 4-7 because they are ionized in conjunction with magnesium ions present from the treatment. The base combination is increased between pH 7 and 9, perhaps by some unionized carboxymethyl groups, and decreased at

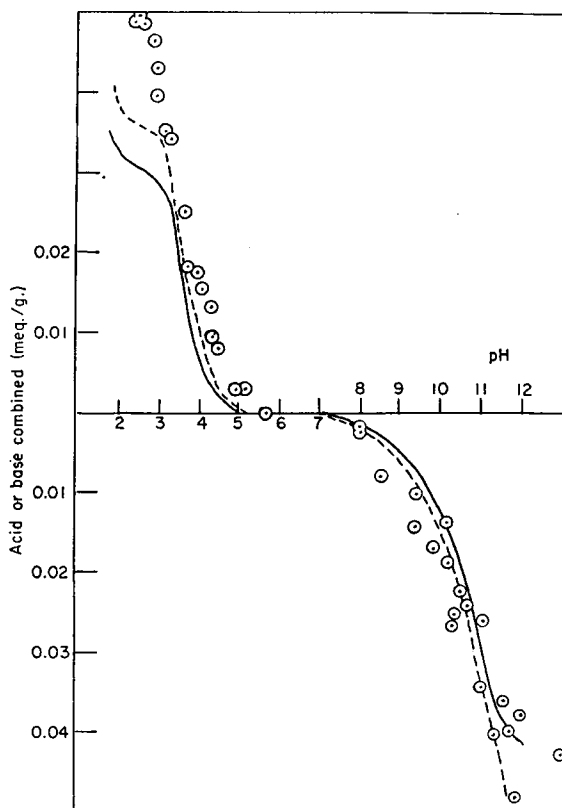


Fig. 11. Titration curves of: (O) alkali-treated nylon II; (---) nylon untreated II; (—) nylon II treated with boiling water.

higher pH due to loss of amino groups. The material was not significantly degraded.

The acid combination of nylon 66 fibers treated with alkaline hypochlorite was reduced almost to zero, presumably by almost complete deamination, but the exact mechanism is not clear. There was no significant degradation. Nylon treated with benzoquinone also showed almost no acid combination, dihydroxyphenylation of the available amino groups being almost complete, with some degradation.

Elastic Properties of Modified Nylons

Mean values of the percentage increase in the work to stretch 10% over corresponding untreated filaments in distilled water, calculated from the load-extension curves of the filaments in the four media studied, are shown in Table III.

There is no evidence, for any of the filaments, of an effect of pH on the increase in the work to stretch. Thus, if any pairing of positively and negatively charged endgroups does occur, it has no influence on the elastic

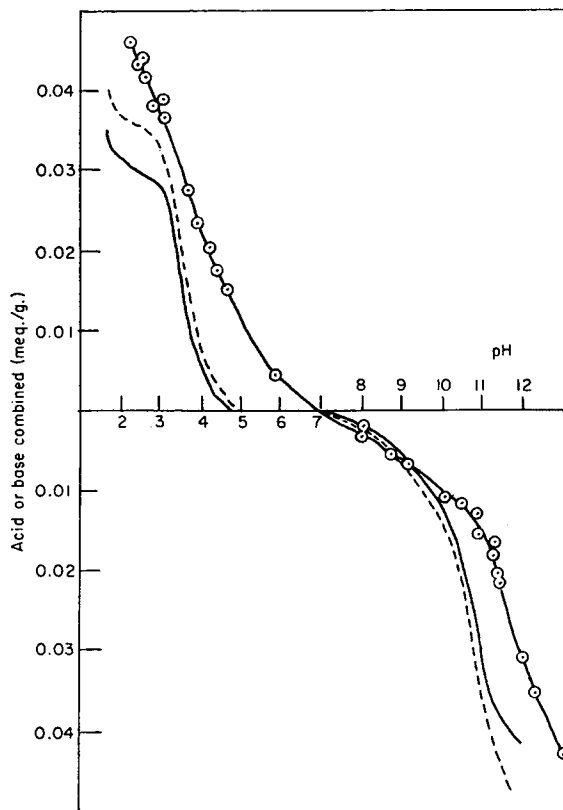


Fig. 12. Titration curves of: (○) carboxymethylated nylon II; (---) untreated nylon II; (—) nylon II treated with boiling water.

TABLE III
Percentage Increase in Work to Stretch 10% for Nylon 66 and Modified Nylon
Filaments at 22.2°C.

Nylon	Treatment	Increase in work to stretch, %			
		pH 1.0	pH 5.6	pH 7.0	pH 9.2
I	Untreated	-2.9	0	-0.6	0.6
II	Untreated	0	0	0.9	0.9
I	Nitrous acid	Samples broke at about 7% extension			
I	Dinitrophenylated	5.8	6.1	7.3	1.9
II	Dinitrophenylated	10.3	10.0	10.9	9.4
I	Acetylated	-6.4	-8.3	-7.7	-7.7
II	Acetylated	8.8	8.8	8.5	10.0
I	Benzene, 24 hr., 50°C.	-8.3	-7.0	-4.5	-5.1
II	Benzene, 24 hr., 50°C.	—	4.9	—	4.6
I	Dihydroxyphenylated	6.4	5.8	4.8	7.0
II	Alkaline hydrolysis	—	2.4	—	1.5
II	Boiling water, 1 hr.	—	—	3.4	3.1
II	Boiling water, 2 hr.	3.1	—	3.6	—
II	Carboxymethylated	9.7	8.5	9.1	10.0

properties. Treatment in hot benzene causes a reduction in the strength of nylon I but an increase for nylon II, the same result as for acetylation. The reason for this difference is not known, but evidently the actual introduction of the acetyl groups has little effect. Boiling water and alkaline hydrolysis bring about a small increase in strength, but dinitrophenylation, dihydroxyphenylation, and carboxymethylation all cause larger increases, perhaps due to the steric effect of the bulky substituent groups. Treatment with nitrous acid caused a marked reduction in both breaking load and breaking extension, probably caused by the chain degradation.

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Résumé

Les courbes de titration acide base de résines solides de nylon 6 et de fibres nylon 66 ont été mesurées; leurs points isoioniques et leurs groupes terminaux ont été déterminés. Cinq polymères nylon-6 de poids moléculaires différents et deux fils commerciaux de nylon 66 ont été étudiés. Les courbes de titration de ces matériaux avec l'acide chlorhydrique et la soude caustique en absence de sel, et du nylon-66 en présence de

sels, à trois températures différentes, de même qu'avec l'acide benzènesulfonique, l'acide trichloracétique et l'acide naphthalène-2-sulfonique, ont permis de déterminer l'effet du poids moléculaire du polymère, du sel, de la température et de l'affinité à l'égard de l'anion dans ces courbes de titration. Tous les résultats s'accordent avec la vue que le nylon possède une structure ion-hybride à pH neutre, les groupes carboxyliques étant protonés au cours de la titration acide. Une certaine proportion des groupes terminaux ne peut être titrée sur les polymères solides. Les théories existantes sur la combinaison acide-base de polymères solides ne peuvent pas expliquer tous les résultats. Les courbes de titration et les propriétés élastiques des fils de nylon-66 modifiés suivants ont été également déterminées et interprétées: les nylons désaminé par l'acide nitreux, dinitrophénylé, acétylé, carboxyméthylé, hydrolysé et dihydrophénylé, et les nylons traités par les hypochlorites alcalins, l'eau bouillante, et le benzène bouillant. Dans tous les cas, l'accroissement de travail nécessaire à étirer le filament est indépendant du pH.

Zusammenfassung

Die Säure-Basentitrationskurve von festen Nylon-6-harzen und Nylon-66-fasern wurden gemessen und isoelektrischer Punkt sowie Endgruppen bestimmt. Fünf Nylon-6-polymere von verschiedenem Molekulargewicht und zwei handelsübliche Nylon-66-garne wurden untersucht. Titrationskurven dieser Stoffe mit Salzsäure und Natronlauge ohne Salzzusatz bei drei verschiedenen Temperaturen sowie mit Benzolsulfosäure, Trichloressigsäure und Naphthalin-2-sulfosäure erlaubten eine Bestimmung des Einflusses des Molekulargewichts des Polymeren, von Salz, Temperatur und Anionenaffinität auf die Titrationskurven. Alle Ergebnisse sind mit der Annahme verträglich, dass Nylon bei neutralem pH eine Zwitterionstruktur besitzt und die Karboxylgruppen bei der Säuretitration protoniert werden. Ein Teil der Endgruppen wird im festen Polymeren durch die Titration nicht erfasst. Die bekannten Theorien der Säure-Basenkombination von festen Polymeren können nicht alle Ergebnisse erklären. Titrationskurven und elastische Eigenschaften folgender modifizierter Nylon-66-garne wurden ebenfalls bestimmt und interpretiert: durch salpetrige Säure desaminiertes Nylon; dinitrophenyliertes, acetyliertes, carboxymethyliertes hydrolysiertes und dihydrophenyliertes Nylon; sowie mit Alkalihypochlorit, siedendem Wasser und siedendem Benzol behandeltes Nylon. In allen Fällen ist die Zunahme der Dehnungsarbeit der Fäden unabhängig vom pH.

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