Kinetics of Contraction of Drawn Nylon 66 in Aqueous Phenol

MARTIN I. JACOBS, LUDWIG REBENFELD, and
HUGH S. TAYLOR, *Textile Research Institute, and Department of
Chemistry, Princeton University, Princeton, New Jersey 08540*

Synopsis

The rate of contraction of drawn nylon 66 in aqueous phenol was investigated, and a method is described for correlating this contraction with a series of elementary rate processes.   The rate constants so obtained were analyzed by absolute rate theory, and the variations of $\Delta H\ddagger$ and $\Delta S\ddagger$ with phenol concentration gave evidence of the nature of the reaction steps.

INTRODUCTION

Nylon 66 fibers are dimensionally unstable in the presence of either heat or certain chemical agents (those capable of disrupting the nylon's intermolecular bonding).   In undrawn and slightly drawn fibers the tendency is to a length increase (along the fiber axis), while highly drawn filaments contract.

In our experiments the rate of longitudinal contraction of a drawn yarn has been used as a probe for following the kinetics of the interaction of nylon 66 with aqueous phenol.   This interaction has previously been studied by several authors,[1-3] and the contraction (both thermal and chemical) has been ascribed to breakage of interchain hydrogen bonds,[1,2,4] followed by conversion of the polymer chains from the extended to the folded conformation[4] and formation of new, stronger bonds.[2,4,5]

The intention of this work is to calculate the rate constants and activation energies of these elementary processes and to relate them to fiber structure.

EXPERIMENTAL

Samples

The samples used in these experiments were from an experimental nylon 66 yarn prepared by Chemstrand Research Center, Inc.   The draw ratio was 4, and the yarn had 17 filaments with a total denier of 50 and a 0.5 twist per inch.   The samples contained 0.025 ± 0.015% TiO_2 and no other additives.

Apparatus

The apparatus consisted of a 500 ml, graduated cylinder surrounded by a glass jacket, through which water, held at constant temperature ($\pm 0.05°C$), was circulated. The yarn (≈ 40 cm long) was looped through a wire ring (≈ 50 mg in weight), which made immersion possible; otherwise the fiber would float until completely soaked by the solution. The yarn ends were held by a small clamp, which was suspended above the apparatus.

The shrinkage of the fiber was measured in solution by means of the graduations on the cylinder. The length at any given time could be determined to within 1 part in 350 while the fiber contracted. Phenol concentration and temperature were varied, and at least five determinations were made for each set of conditions. Reproducibility was approximately ●3% (coefficient of variation) of the average length change at a given time.

Reagents

Crystalline phenol (Baker reagent-grade, containing 0.15% H_3PO_2 as preservative) was dissolved in distilled water to form solutions of 1, 2, 3, and 4% phenol by weight. Since no correction was made for the water content of the phenol (perhaps as high as 10%), these concentrations are only approximate, though their relative values are accurate.
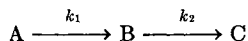
KINETIC ANALYSIS

As noted in the introduction, it has been proposed by several authors that the longitudinal contraction (both thermally and chemically induced) of drawn nylon consists of the following steps: (*1*) bond breaking, (*2*) motion of polymer segments, and (*3*) bond re-formation (the effects of diffusion will be considered separately).

If the folding of polymer chains is fast compared to the other steps (this is reasonable, considering that bond formation, usually an extremely rapid process, is hindered by the presence of bound phenol), the mechanism may be pictured as follows:

$$A \xrightarrow{k_1} B' \xrightarrow{\text{fast}} B \xrightarrow{k_2} C$$
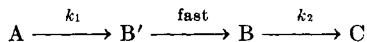
where A is extended chains with hydrogen bonds intact, B' is segments where these bonds have been broken, B is contracted segments, and C is contracted segments whose hydrogen bonds have re-formed. Representing the above sequence as

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

would not alter the kinetic analysis.

Dismore and Statton[4] have proposed that shrinkage is equal to the fraction of molecules converted from the extended to the folded conformation. This relation may be expressed as follows:

$$100[([C] - [C]_0)/[A]_0] = S = (l_0 - l)/l_0 \times 100 \qquad (1)$$

where S is the percent shrinkage, l_0 the initial length, and l the length at time t. If both steps in the preceding kinetic scheme are first-order (evidence of this will be given later), it can be shown[6] that

$$[C] - [C]_0 = \{ [A]_0/(k_2 - k_1) \} [k_2(1 - \exp\{ - k_1 t \})$$
$$- k_1(1 - \exp\{ - k_2 t \})] \quad (2)$$

Combining eqs. (1) and (2) gives

$$S_t = [100/(k_2 - k_1)] [k_2(1 - \exp\{ - k_1 t \}) - k_1(1 - \exp\{ - k_2 t \})] \quad (3)$$

At large times eq. (3) reduces to $S_\infty = 100\%$, which is true only if there is complete dissolution of the fiber. Dismore and Statton,[4] however, suggested that only the weakest bonds break under a given set of experimental conditions. Thus, $[A]_0$ in eq. (2) would be replaced by $[A']_0$, which represents the number of segments whose hydrogen bonds are "breakable." Therefore,

$$S_t = 100 ([A']_0/[A]_0) [k_2(1 - \exp\{ - k_1 t \}) - k_1(1 -$$
$$\exp\{ - k_2 t \})]/(k_2 - k_1) \quad (4)$$

Now the final shrinkage S_∞ can be expressed as

$$S_\infty = \lim_{t \to \infty} S_t = 100 ([A']_0/[A]_0) \quad (5)$$

Therefore,

$$S_t/S_\infty = \text{relative contraction} = [k_2(1 - \exp\{ - k_1 t \})$$
$$- k_1(1 - \exp\{ - k_2 t \})]/(k_2 - k_1) \quad (6)$$

Since bond formation is nearly always faster than bond breaking, it can be assumed that $k_2 > k_1$. Equation (6) then simplifies to

$$S_t/S_\infty = [k_2(1 - \exp\{-k_1 t\}) - k_1]/(k_2 - k_1) \quad (7)$$

or

$$k_1 = -\ln[(k_2 - k_1)/k_2] (1 - S_t/S_\infty)]/t \quad (8)$$

If $k_2 \gg k_1$ (not always true), then

$$k_1 \approx -\ln (1 - S_t/S_\infty)/t \quad (9)$$

Equation (9) permits the calculation of an approximate k_1 for each measurement of S_t. However, solving eq. (7) for k_2 gives

$$k_2 = k_1(1 - S_t/S_\infty)/[(1 - S_t/S_\infty) - \exp\{-k_1 t\}] \quad (10)$$

Inspection of eq. (9), however, reveals that the denominator of eq. (10) represents the difference of two nearly equal quantities, making it impossible to determine k_2 accurately. This difficulty can be resolved by making a further assumption about the nature of the shrinkage process: when the rate of shrinkage is large, then the concentration of contracted segments B

must be large, but as B reacts to form C (i.e., re-formation of hydrogen bonds) the rate of shrinkage should decrease. This suggests the following expression:

$$[B] \propto dS/dt \tag{11}$$

The factor that directly affects the length change, though, is, not the concentration of B, but the fraction of segments in state B (i.e., $[B]/[A]_0$). Therefore,

$$[B]/[A]_0 = -(1/l_0) \, (dl/dt) = (1/100) \, (dS/dt) \tag{12}$$

However, the rate of formation of C is

$$d[C]/dt = k_2[B] \tag{13}$$

Combining eqs. (12) and (13) and integrating gives

$$100([C] - [C]_0)/[A]_0 = k_2 S \tag{14}$$

This equation is nearly identical with eq. (1), the only difference being the rate constant k_2. Substituting eq. (14) into eq. (2) gives

$$S_t = [100/k_2 \, (k_2 - k_1)] \, [k_2(1 - \exp\{-k_1 t\}) - k_1(1 - \exp\{-k_2 t\})] \tag{15}$$

and, therefore,

$$S_\infty = 100/k_2 \tag{16}$$

This removes the necessity of assuming that some bonds can break and others cannot, since S_∞ does not reduce to 100%.

As a result, the expressions for the relative contraction [eqs. (6), (7), (8), and (9)] are unchanged, but the final shrinkage is only dependent on the rate of bond re-formation. Thus, equilibrium measurements (S_∞) will give a reasonably accurate value of k_2, and k_1 can be approximated from eq. (9); substitution of k_2 and this approximate k_1 into eq. (8) should give an accurate value of k_1.

It was found that the k_1's increased with time, until a nearly constant value was obtained, and then decreased as equilibrium was approached. An average (neglecting the k_1's at both extremes of the time scale) was taken, and curves of S_t versus time were calculated from eq. (7). Comparison of these curves with experimental results showed good fit at all but the first few points.

The agreement between the calculated and experimental results improved with increasing temperature, however, suggesting that the discrepancy is related to diffusion of the reagent into the fiber. This diffusion effect can be accounted for by assuming that the rate of diffusion is constant (on a macroscopic scale) along any fiber radius:

$$t \propto r/R, \quad 0 < r < R \tag{17}$$

where R = fiber radius and r = distance penetrated by diffusion species. But $t = t_D$ at $r = R$, where t_D = time for diffusing to the fiber's center. Therefore,

$$t = t_D (r/R) \quad \text{and} \quad r = R(t/t_D) \tag{18}$$

Because of diffusion the effective concentration of A is proportional to the area penetrated at time t (if $t < t_D$):

$$[A]_{eff} = K'\pi r(2R - r) = K(t/t_D) (2 - t/t_D) \tag{19}$$

where $K = K'\pi R^2 \approx [A]$; $K = [A]$ only if the rate of reaction of A is much slower than diffusion. Thus, the actual rate in the interval 0 to t_D is $k_1[A]_{eff}$ and not $k_1[A]$. Therefore,

$$\text{rate} = k_1[A]_{eff} = k_{eff} [A] \tag{20}$$

where k_{eff} is the rate constant calculated from eq. (8). Rearranging eq. (19) gives

$$[A]_{eff}/K = [A]_{eff}/[A] = (t/t_D) (2 - t/t_D) \tag{21}$$

Combining eqs. (20) and (21) gives

$$k_{eff} = k_1 (t/t_D) (2 - t/t_D) \tag{22}$$

By substituting values of k_{eff} into eq. (22) a value of t_D can be calculated for each $t < t_D$. An average value of t_D can then be substituted into eq. (22) and a theoretical k_{eff} found for each t. By using these k_{eff}'s the S_t's corrected for diffusion can be calculated from eq. (7).

For example, in 3% phenol at 35°C the k_{eff}'s calculated were 0.0083, 0.0234, and 0.0296 for 10, 20, and 30 sec, respectively. When substituted into eq. (22) they yield 80, 39.6, and 38.1 as values of t_D. By choosing $t_D = 39$ and calculating new k_{eff}'s from eq. (22) it can be seen, in Table I, that the agreement with the observed S_t's is greatly improved.

TABLE I

t, sec	S_t (obsd.)	S_t (calcd., for $k_1 = 0.0309$)	k_{eff} (theor.)	S_t (corrd. for diffusion)
10	1.0	3.3	0.014	1.6
20	4.7	5.8	0.024	4.8
30	7.4	7.6	0.029	7.3

Figure 1 shows a set of curves calculated from eq. (7) with the correction for diffusion.

The preceding analysis shows that the shrinkage rate of nylon filaments may be approximately fitted to a two-parameter equation, in which the parameters may be represented as rate constants for two consecutive reactions (additional steps with rate constants much larger than k_1 and k_2 will not affect the kinetics). It has also been shown that if the number of
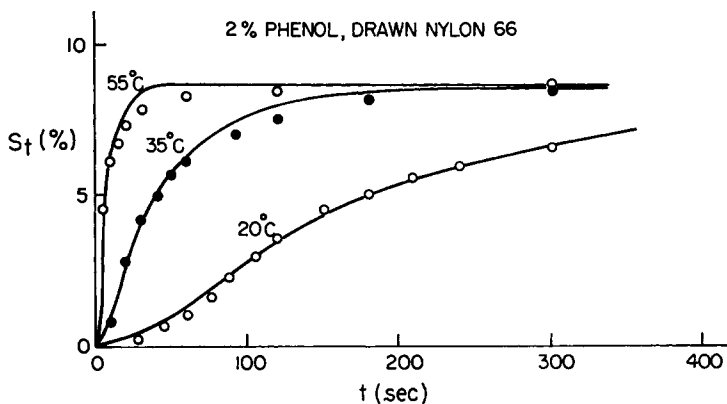
Fig. 1. Shrinkage as a function of time for drawn nylon 66 filaments in 2% aqueous phenol solution. Lines are calculated from eq. (7); points represent experimental measurements.

chain folds is proportional to shrinkage, k_2 must be a first-order rate constant. The choice of k_1 as first-order was purely empirical. In addition, the introduction of a parameter (t_D), which can be related to diffusion rate, greatly improves the correlation between experimental and calculated behavior.

RESULTS

Shrinkage measurements as a function of time were made with nylon 66 filaments in water and 1, 2, 3, and 4% aqueous phenol solutions at several temperatures. The data were analyzed as outlined in the preceding section, and the results are shown in Table II.
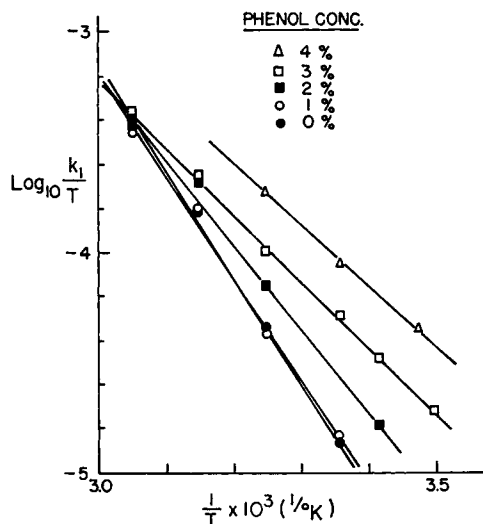

Fig. 2. Temperature dependences of k_1 according to eq. (24).

TABLE II
Rate Constants

Phenol concn., %	Temp., °C	S_∞, %	k_1, sec^{-1}	k_2, sec^{-1}	t_D, sec
4	15	17.2	0.0130	5.81	160
	25	17.2	0.0267	5.81	80
	35	17.1	0.0589	5.85	32
3	13	12.4	0.00554	8.06	456
	20	12.6	0.00945	7.94	194
	25	12.4	0.0154	8.06	130
	35	12.6	0.0309	7.94	38
	45	12.2	0.0703	8.20	11.5
	55	12.1	0.14	8.26	0
2	20	8.8	0.00474	11.36	175
	35	8.7	0.0216	11.49	33
	45	9.0	0.067	11.11	5.5
	55	8.7	0.12	11.49	0
1	25	5.5	0.00434	18.18	98
	35	5.8	0.0131	17.39	39
	45	6.4	0.0506	15.63	11.5
	55	6.5	0.115	15.38	0
0	25	3.5	0.00404	28.57	140
	35	4.3	0.0136	23.26	43
	45	4.3	0.05	23.26	11
	55	4.8	0.13	20.83	0

According to transition state theory,[7] a rate constant (k) can be expressed as:

$$k = (k_B T/h) \exp\{-\Delta H\ddagger/RT\} \exp\{\Delta S\ddagger/R\} \tag{23}$$

where k_B is Boltzmann's constant, h is Planck's constant, T is the absolute temperature, R is the gas constant, $\Delta H\ddagger$ is the enthalpy of activation, and $\Delta S\ddagger$ is the entropy of activation. This equation can also be expressed as:

$$\ln(k/T) = -(\Delta H\ddagger/R)(1/T) + (\Delta S\ddagger/R) + \ln(k_B/h) \tag{24}$$

Thus, the slope of a plot of $\ln k/T$ versus $1/T$ should be $-\Delta H\ddagger/R$ and the intercept $\Delta S\ddagger/R + \ln k_B/h$. Figures 2 and 3 show such plots for k_1 and k_2, and Table III summarizes the results.

TABLE III
Thermodynamic Behavior of Rate Constants[a]

Phenol concn., %	k_1			k_2		
	$\Delta H\ddagger$	$\Delta S\ddagger$	$\Delta F\ddagger$	$\Delta H\ddagger$	$\Delta S\ddagger$	$\Delta F\ddagger$
4	12.7 ± 0.8	-22.9	19.5	-0.3 ± 0.1	-56.8	16.6
3	13.8 ± 0.3	-20.5	19.9	-0.5 ± 0.1	-56.0	16.2
2	17.4 ± 0.7	-9.5	20.2	-0.6 ± 0.3	-55.7	16.0
1	21.1 ± 2.2	1.6	20.6	-1.8 ± 0.5	-58.8	15.7
0	22.2 ± 1.0	4.9	20.7	-2.5 ± 1.1	-60.2	15.4

[a] $\Delta H\ddagger$ and $\Delta F\ddagger$ are in kcal/mole, $\Delta S\ddagger$ in cal/deg-mol; estimates of error are 95% confidence intervals.
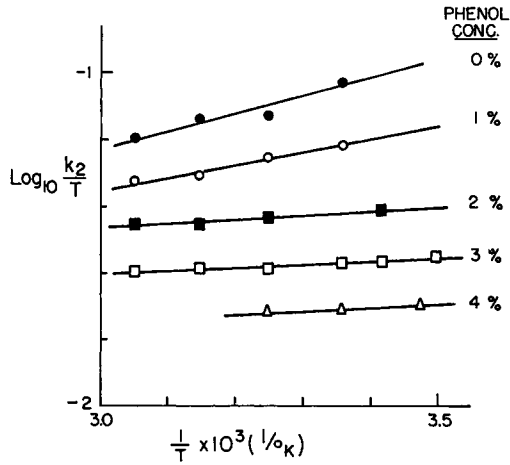
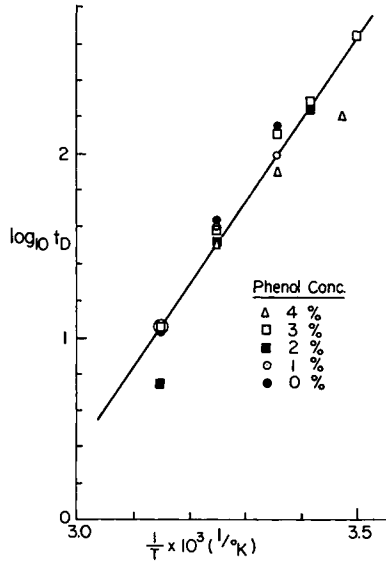Fig. 3. Temperature dependences of k_2 according to eq. (24).

Fig. 4. Temperature dependences of t_D according to eq. (26).

Further, t_D can be considered inversely proportional to the diffusion coefficient D. The diffusion coefficient can be expressed as:[8]

$$D = D_0 \exp \left\{ -E_D/RT \right\} \qquad (25)$$

where E_D is the activation energy for diffusion. If $t_D \propto 1/D$, then

$$t_D = (K/D_0) \exp \left\{ E_D/RT \right\} \qquad (26)$$

where K is a proportionality constant whose value is unknown. A plot of $\ln t_D$ versus $1/T$ should be a straight line with a slope of E_D/R, provided

that K/D_0 is approximately temperature-dependent. This is confirmed in Figure 4. Since there is no apparent concentration dependence, the t_D's were considered concentration-independent.

The slope of the line in Figure 4 results in an apparent activation energy of 20.5 ± 2.5 kcal/mol for E_D, which is not unreasonable for diffusion into a hydrogen-bonded system.

DISCUSSION

The reaction of nylon with phenol has been reported by Cannon[9] to consist of attack by the phenolic proton on a nylon carbonyl oxygen, leading to dissociation of an intermolecular hydrogen bond. Similarly, Dismore and Statton[4] have theorized that intermolecular bond-breaking is the rate-controlling step for thermal shrinkage of nylon.

If k_1 is actually the rate constant for bond-breaking, positive values of $\Delta S\ddagger$ would be expected. This is observed in water and 1% phenol, but the increasingly negative values of $\Delta S\ddagger$ at larger concentrations imply increasing participation of phenol in the activated state. This is in agreement with measurements of phenol uptake in nylon yarns,[5] which show a linear increase in uptake with the concentration of phenol in solution.

The fact that the values of k_1 for water and 1% phenol are nearly equal suggests that these solutions break the same percentage of hydrogen bonds, even though the latter produces a slightly larger contraction. This phenomenon has also been observed by Forward and Palmer,[5] who reported that the irreversible portion of the length change of drawn nylon is unaltered up to a concentration of 1% phenol.

If enough intermolecular bonds are broken, the polymer chains would be free to assume a more random configuration, resulting in a decrease in length along the fiber axis. Such a step would appear to be much faster than the other reactions considered, and it could thus be eliminated from the kinetic analysis.

The large negative values for the activation entropy of k_2 indicate that the final reaction step is indeed preceded by a random conformation, while the small activation energies are evidence that this step represents bond formation.

The negative values for $\Delta H\ddagger$ are not unreasonable, considering that thermal shrinkage of nylon increases with temperature.[4,5] This implies that k_2 [see eq. (16)] for thermal contraction has a negative temperature coefficient.

Since $\Delta H\ddagger$ is nearly equal to the Arrhenius activation energy, ($\Delta H\ddagger = E_{act} - RT$), the supposition of a negative value for this quantity may seem meaningless. However, according to Glasstone et al.,[7] it is "the free energy of activation, and not necessarily the heat of activation, which determines the rate of a chemical reaction." Thus, the behavior of k_2 suggests that the activated state for the final step is slightly favored energetically (possibly owing to partial bond formation) and that the free-energy barrier to

reaction is almost entirely entropic.   The energy of activation often seems to be the controlling factor in a reaction only because entropy changes are usually small.   The reaction under consideration, though, may be compared to vapor condensation, where the heat of activation is nearly zero but the rate of condensation is slow owing to a large decrease in entropy.[7]

In conclusion: it has been shown that the rate of contraction of a drawn nylon yarn in aqueous phenol can be analyzed on the basis of a consecutive reaction scheme with two first-order steps (and appropriate corrections for diffusion).   Evidence has been presented that indicates the nature of these steps and that yields information about the yarn structure.

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