JOURNAL OF APPLIED POLYMER SCIENCE VOL. 13, PP. 1191–1199 (1969)

Role of Hydrophobic Bonding in the Contraction of Nylon 66 in Phenolic Solutions

MARTIN I. JACOBS,* *Textile Research Institute and Princeton University, Princeton, New Jersey 08540*

Synopsis

Rate constants for intermolecular bond breaking (k_1) and bond re-formation (k_2) were calculated from contraction measurements. Variation of $\Delta H\ddagger$ and $\Delta S\ddagger$ for k_1 with phenol substituents and concentration suggests the existence of hydrophobic bonding between the solution and the polymer activated complex. This behavior has been substantiated by correlating $\Delta H\ddagger$ and $\Delta S\ddagger$ for k_1 with a parameter related to hydrophobicity.

INTRODUCTION

It has been shown in an earlier paper[1] that the rate at which drawn fibers of nylon 66 contract in aqueous phenol solutions can be related to a series of elementary molecular processes. Rate constants for intermolecular bond breaking (k_1) and bond re-formation (k_2) were calculated, as well as a parameter (t_D) related to the diffusion of phenol into the fiber. In addition, $\Delta H\ddagger$ and $\Delta S\ddagger$ were calculated for k_1 and k_2 according to the usual procedure.

A decrease in $\Delta H\ddagger$ for bond breaking was observed at higher phenol concentrations, even though it has been proposed[2] that concentrated phenol solutions are better able to penetrate regions of higher order in the nylon than dilute solutions. Since highly ordered regions would be most likely to contain the strongest hydrogen bonds, there appears to be no reason to expect any change in activation energy with phenol concentration other than a slight increase. The observed decrease in $\Delta H\ddagger$, however, covers a range of nearly 10 kcal/mole.

An explanation for these observations has been proposed by Eyring,[3] who emphasized the need for considering hydrophobic interactions, as well as hydrogen bonding. According to Eyring, both the hydrophilic and hydrophobic (methylene) groups of nylon have their bonding needs satisfied in the initial and final states by juxtaposition with similar groups on adjacent chains. However, in the transition state some of these bonds are broken, increasing the need for the activated complex to make bonds with the solvent. Water can hydrogen bond well with the activated complex, but the hydrophobic groups would be poorly bonded.

The use of a mixed solvent (e.g., aqueous phenol) capable of both hy-

* Present address: Allied Chemical Corp., Morristown, N. J. 07960.

drogen bonding and hydrophobic bonding enables the activated complex to make more suitable bonds with the solvent for both its exposed hydrophobic groups as well as hydrophilic groups. The result is a slight decrease in the free energy of activation in the mixed solvent as phenol is added, because the bonds formed lower $\Delta H\ddagger$ only slightly more than enough to compensate for the decrease in $\Delta S\ddagger$. The negative entropy of activation is due, in this case, not to increased order in the nylon (cf. $\Delta S\ddagger$ for k_2), but to inclusion of phenol in the activated complex (association reactions are commonly accompanied by decreased entropy).

In order to investigate Eyring's hypothesis[3] that hydrophobic interactions are responsible for the decreased activation energy of bond breaking, contraction measurements were made in a series of substituted phenols of varying hydrophobicity:resorcinol (1,3-benzenediol), hydroquinone (1,4-benzenediol), *o*-cresol (*o*-methylphenol), and *m*-cresol. The results of these rate measurements are discussed in this paper and compared to those previously obtained in aqueous phenol solutions.

Experimental

The yarn samples, apparatus, and experimental procedure for measuring length changes in solution have been described previously.[1] Phenol absorption by nylon was measured by analyzing 100 ml of solution after several hours contact with a 3-g sample of nylon. The phenol concentration in solution was measured spectrophotometrically by using the ultraviolet absorption at 270 mμ.

Results and Discussion

The rate constants for aqueous phenol have been tabulated previously,[1] while those for the phenol derivatives are listed elsewhere.[4] What is of importance here, though, are the values of $\Delta H\ddagger$ and $\Delta S\ddagger$ for k_1 and k_2, and these are shown in Table I.

TABLE I
Activation Parameters

		$\Delta H\ddagger_{k_1}$ kcal/mole	$\Delta S\ddagger_{k_1}$ e.u.	$\Delta H\ddagger_{k_2}$ kcal/mole	$\Delta S\ddagger_{k_2}$ e.u.
$C_6H_5(OH)_2$	3.5% Resorcinol	23.6	8.1	−1.2	−57.2
	1.75% Hydroquinone	18.6	−7.8	−1.0	−55.8
	3.5% Hydroquinone	21.5	1.7	−1.3	−57.3
Water		20.1	−2.0	−3.3	−62.7
C_6H_5OH	1% Phenol	21.2	1.8	−1.7	−58.4
	2% Phenol	17.2	−10.4	−0.6	−55.7
	3% Phenol	13.9	−20.3	−0.5	−56.0
	4% Phenol	12.7	−22.9	−0.3	−56.8
MeC_6H_4OH	1.7% *o*-Cresol	14.6	−19.2	0.0	−54.7
	1.7% *m*-Cresol	13.7	−22.1	0.9	−52.3

TABLE II
Acidity of Substituted Phenols

	Water solubility, g/100 ml	pK_a
Resorcinol	200	9.8
Hydroquinone	6.7	10.35
Phenol	8.7	9.9
o-Cresol	2.4	10.2
m-Cresol	2.5	10.0

The phenol derivatives used in these experiments were chosen not only for their varying hydrophobicities—a rough measure of which is solubility in water—but also because they all have nearly the same acidity (Table II). Thus, any change in activation energy should be due to hydrophobic interactions, since the extent of hydrogen bond formation with the solvent, as evidenced by acidity, is nearly invariant.

The important role of hydrophobicity is obvious from the variation of the activation enthalpies and entropies with the nature of the substituent (Table I). The benzenediols have the largest activation energies for bond-breaking, while the cresols are on the low end of the scale, comparable to 3 and 4% phenol. The other quantities show a similar dependence on the type of substituent, though the trend is inconclusive for $\Delta S\ddagger_{k_2}$.

The concept of hydrophobic bonding is well established in protein chemistry, and since nylon and proteins have similar structures (both contain amide linkages separated by hydrophobic segments), some of the principles which have evolved from protein chemistry may be helpful in understanding the present case. Nemethy and Scheraga[5] have noted that hydrophobic bonds, individually, are weaker than other interactions, but they become important because of their number. They also exhibit less specificity than hydrogen bonds, both with respect to steric requirements and the types of molecules which can participate in their formation. Scheraga also proposed[6] that, if formation of activated complexes in a native protein is accompanied by making or breaking of hydrophobic bonds, then these bonds will contribute to the standard free energy of activation.

In order to establish a relationship between hydrophobic bonding in nylon and the nature of the solvent, it would be desirable to have a quantitative measure of hydrophobicity. Tanford[7] has proposed such a quantity for proteins, based on solubilities of amino acids in ethanol and water. This relationship arises from the fact that relative solubilities (N) in these solvents are a measure of the free energy change (ΔG_t) for transfer of one mole of amino acid from ethanol to water:

$$\Delta G_t = RT \ln(N_{EtOH}/N_{H_2O}) \quad (1)$$

Ethanol was chosen because more solubility data are available in it than any other organic solvent.[8] Tanford also showed that the use of other solvents does not change the transfer free energies much (more precisely,

the difference in free energy between two amino acids does not change appreciably from solvent to solvent). This is expected from the nature of hydrophobic forces, which originate in "iceberg" structures in water, not in structures peculiar to the organic phase.[9]

By using Tanford's concept, a similar definition of hydrophobicity ($H\phi$) can be proposed in relation to nylon:

$$H\phi = RT \ln(N_{H_2O}/N_{np}) \quad (2)$$

where N_{np} refers to the solubility of a given phenol in one of various nonpolar solvents (solubility data for all the phenols used were not available in any one organic solvent). Hydrophobicity values for the phenols under consideration are listed in Table III, based on tabulated values of solubilities in a number of solvents.

TABLE III
Hydrophobicity of Phenols in Various Solvents

	Hydrophobicity $H\phi$, cal/mole[a]				
	Resorcinol	Hydroquinone	Phenol	*o*-Cresol	*m*-Cresol
Benzene	1400[b]	—	−1550[b]	—	—
m-Xylene	1350[c]	—	−1750	—	—
Aniline	—	—	−1800	−3250	−3300
p-Toluidine	−300	—	−1900	—	—
Dimethylpyrone	—	—	−2150	−3250	−3300
Ethanol	100	−1500	−2300	—	—
Acetamide	−200	—	−2350	—	—
Acetone	−400	—	−2350	—	—
Pyridine	—	—	−2350	−3250	−3300

[a] Except as otherwise noted, data are taken from *International Critical Tables*, Vol. 4.[10a]
[b] Data taken from Landolt-Bornstein *Physikalisch-Chemische Tabbellen*.[11]
[c] Data from *International Critical Tables*, Vol. 3.[10b]

The differences between the various phenols are fairly constant, similar to Tanford's observation, but a reference point is necessary in order to set up an absolute scale of hydrophobicities.

Tanford solved the problem by subtracting ΔG_t for glycine (the amino acid with no side chain) to obtain a side-chain hydrophobicity which was approximately invariant with solvent. No such correction is available for phenol, so it was necessary to choose a solvent which approximated the behavior of nylon in relation to phenol.

In this regard, a series of measurements of phenol uptake by nylon had been made (see experimental section) and the partition coefficient for phenol (on a mole fraction basis) between water and nylon was calculated to be 0.0855. The partition coefficient of phenol between water and benzene has a remarkably similar value of 0.0817, so the hydrophobicity of phenol in benzene (−1550 cal/mole) was chosen as a reference point. The difference between resorcinol and phenol, averaged over six solvents, was 2550 cal/mole, indicating a value of 1000 cal/mole for resorcinol. Hydroquinone

could only be estimated, but its solubility in water and ethanol indicated that it is closer to phenol than resorcinol in nature, so −1250 cal/mole seemed to be a reasonable approximation.

The hydrophobicity of the two cresol isomers was constant, regardless of the solvent, because they are so hydrophobic as to be miscible with most organic solvents. This miscibility makes a meaningful calculation of the cresols' hydrophobicity difficult, but Tanford[7] has noted that a CH_2 group always changes ΔG_t by about 750 cal/mole. Thus, *o*-cresol was estimated to have a value of −2300 cal/mole and *m*-cresol, −2350 cal/mole.

However, the hydrophobicities determined by this method are independent of concentration to the extent that the partition coefficient does not vary with concentration, since

$$K = N_{np}/N_{H_2O} = \exp\{-H\phi/RT\} \tag{3}$$

where K is the partition coefficient for saturated solutions. Increasing phenol concentration will, then, not change the solvent's hydrophobicity, but will cause an increase in phenol uptake, as seen from eq. (4),

$$n_{nylon} = n_{H_2O} \exp\{-H\phi/RT\} \tag{4}$$

where the n's represent concentrations, as opposed to N which is the saturation concentration. Thus, doubling the concentration of phenol in the aqueous phase (n_{H_2O}) should double the nylon's uptake of phenol (n_{nylon}). Increased hydrophobicity (i.e. more negative $H\phi$) would also increase uptake of a phenol derivative by the nylon, so one would expect n_{nylon} to be proportional to the number of hydrophobic bonds formed between a given solvent and the activated complex in nylon. In other words, it is assumed that the activated complex has the same attraction for phenol as nylon does, so that the number of hydrophobic bonds formed with an activated complex is a constant fraction of the total amount of phenol bound to the nylon. Calculated values of n_{nylon} are listed in Table IV, and correlations between this parameter and various quantities related to shrinkage behavior are shown in Figures 1–5.

TABLE IV
Relative Number of Hydrophobic Bonds

	$H\phi$, cal/mole	n_{H_2O}, mole fraction	$n_{nylon} \times 10^3$
Water	6000	—	0
3.5% Resorcinol	1000	0.006	1
1.75% Hydroquinone	−1250	0.003	25
3.5% Hydroquinone	"	0.006	50
1% Phenol	−1550	0.002	27
2% Phenol	"	0.004	55
3% Phenol	"	0.006	82
4% Phenol	"	0.008	110
1.7% *o*-Cresol	−2300	0.003	147
1.7% *m*-Cresol	−2350	0.003	159

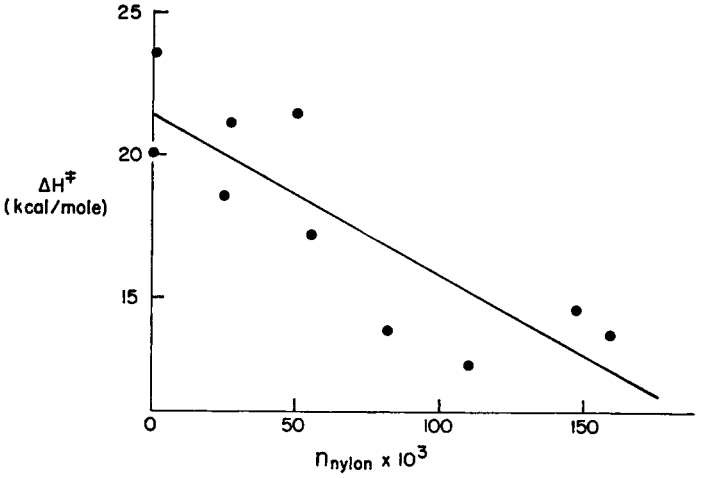

Fig. 1. Activation energy for bond breaking.

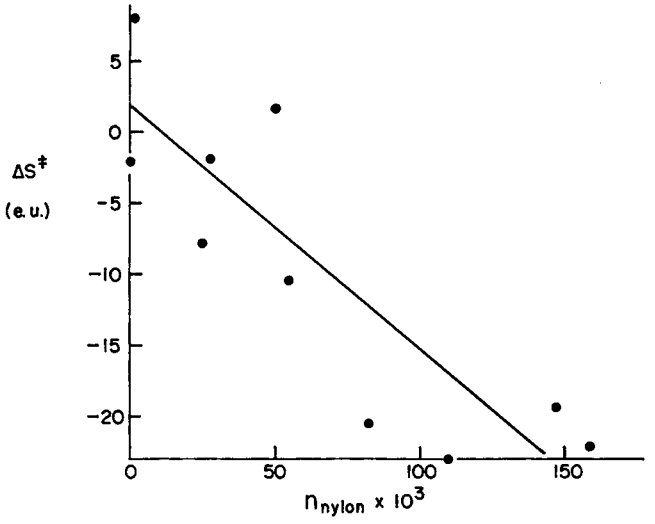

Fig. 2. Entropy of activation for k_1.

Figure 1 provides convincing evidence for the hypothesis that hydrophobic bonding with the activated complex is responsible for decreased activation energy in the more concentrated phenol solutions. Figure 2 indicates that increased phenol uptake by the activated complex causes a reduction in entropy, while $\Delta S\ddagger$ for k_2 (Fig. 4) is nearly constant. The enthalpy of activation for k_2 (Fig. 3), however, has a small but definite trend in the opposite direction as $\Delta H\ddagger$ for k_1. This is to be expected, since the reformation of intermolecular bonds would result in the breaking of hydrophobic bonds with the solvent and increased activation energies.

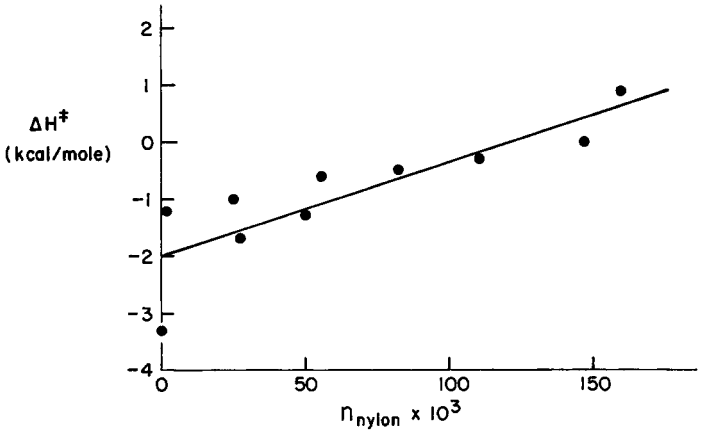

Fig. 3. Activation energy for k_2.

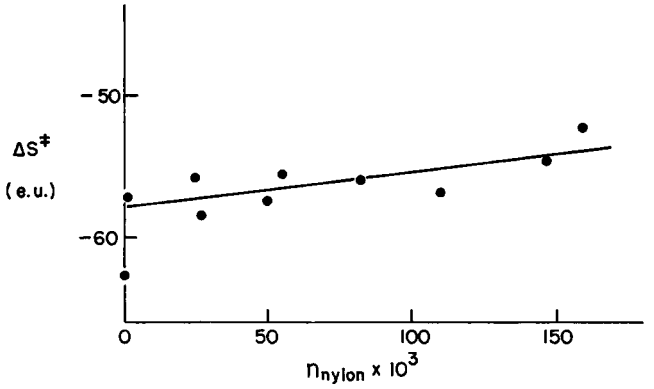

Fig. 4. Entropy of activation for bond re-formation.

The net result is that k_1 cannot be simply related to changes in hydrophobicity, since $\Delta H\ddagger$ and $\Delta S\ddagger$ vary in such a manner as to leave the free energy of activation virtually unchanged (Table V). On the other hand, k_2 is more sensitive to changes in hydrophobicity, because $\Delta S\ddagger$ is nearly constant. Thus, the free energy of activation varies in a manner similar to $\Delta H\ddagger$. Since shrinkage is inversely proportional to k_2,[1] this accounts for its correlation with hydrophobicity (Fig. 5).

In general, the hydrophobic solvents produce the largest shrinkages, but do not necessarily produce the greatest shrinkage rate (k_1). That k_1 is a measure of the rate of length change can be seen from eq. (5):[1]

$$k_1 \cong \ln(1 - S_t/S_\infty)/t \tag{5}$$

where increasing the shrinkage (S_t) produced at a given time t, i.e., increasing the shrinkage rate, will result in a larger value of k_1, and vice versa.

TABLE V
Shrinkage and Free Energy versus Hydrophobicity

	n_{nylon}	$\Delta G^{\ddagger}_{k_1}$, kcal/mole	$\Delta G^{\ddagger}_{k_2}$, kcal/mole	S_∞, %
Water	0	20.7	15.4	3.2
3.5% Resorcinol	1	21.2	15.8	7.0
1.75% Hydroquinone	25	20.9	15.6	4.7
1% Phenol	27	20.7	15.7	5.6
3.5% Hydroquinone	50	21.0	15.8	6.2
2% Phenol	55	20.3	16.0	8.8
3% Phenol	82	19.9	16.2	12.4
4% Phenol	110	19.5	16.6	17.2
1.7% *o*-Cresol	147	20.3	16.3	14.0
1.7% *m*-Cresol	159	20.3	16.5	18.6

The chief implication of these results is that the activation energy of the rate-determining step for nylon shrinkage must include a significant contribution from the disruption of intermolecular methylene–methylene

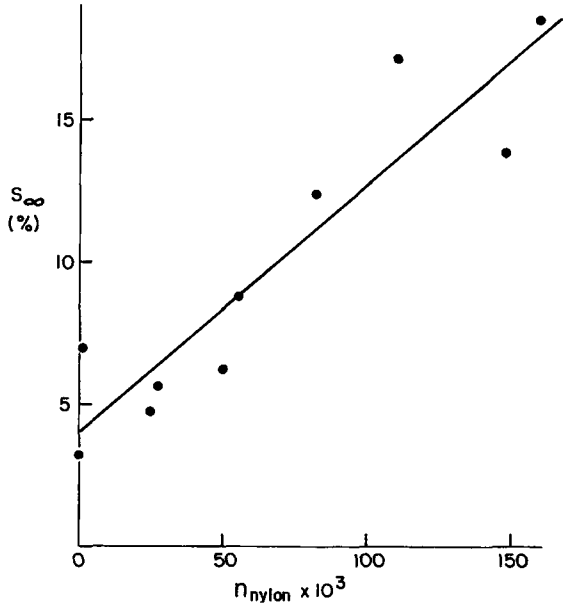

Fig. 5. Shrinkage as a function of solvent hydrophobicity.

interactions. This conclusion follows from the fact that activated nylon methylene groups can form hydrophobic bonds in solution, thus reflecting the importance of intermolecular hydrophobic bonding in the original structure.

The author wishes to thank Professor Hugh S. Taylor and Dr. Ludwig Rebenfeld for their comments and discussions concerning this work. He is also indebted to Professor Henry Eyring of the University of Utah for indicating the importance of hydrophobic bonding in these studies.

References

1. M. I. Jacobs, L. Rebenfeld, and H. S. Taylor, *J. Appl. Polym. Sci.*, **13**, 427 (1969).
2. M. V. Forward and H. J. Palmer, *J. Text. Inst.*, **45**, T510 (1954).
3. H. Eyring, private communication.
4. M. I. Jacobs, Ph.D. Thesis, Princeton Univ., 1968.
5. G. Nemethy and H. A. Scheraga, *J. Phys. Chem.*, **66**, 1773 (1962).
6. H. A. Scheraga, *J. Phys. Chem.*, **65**, 1071 (1961).
7. C. Tanford, *J. Amer. Chem. Soc.*, **84**, 4240 (1962).
8. C. C. Bigelow, *J. Theoret. Biol.*, **16**, 187 (1967).
9. W. Kauzmann, *Advan. Protein Chem.*, **14**, 1 (1959).
10. *International Critical Tables*, (a) Vol. 4; (b) Vol. 3, McGraw-Hill, New York, 1928.
11. Landolt and Bornstein, Eds., *Physikalisch-Chemische Tabbellen*.

Received November 6, 1968