

A Direct Infrared Estimation of Cyclic Oligomers in Water Extract of Nylon 6

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Introduction

Methods described in the literature for the estimation of the cyclic oligomer content (which includes cyclic dimer, trimer, etc.) of nylon 6 are indirect determinations, generally based on weight differences, requiring the complete extraction of ϵ -caprolactam (monomer) from the sample. For example, Van Velden and co-workers⁷ use extraction of the monomer and oligomers with hot methanol for 36 hrs. followed by sublimation to remove the monomer. According to Schenker and co-workers,⁶ the oligomer content can be estimated from the difference in results between per cent water extractables and per cent monomer obtained by a special vacuum extraction technique. In addition, recent methods with ϵ -caprolactam, which involve a colorimetric determination based on conversion to the red-violet ferric complex of the hydroxamate³ and a titration method requiring acid hydrolysis of the ϵ -caprolactam and then potentiometric titration with NaOH to two neutralization points,⁴ cannot differentiate monomer from the cyclic oligomer content in a sample because heating with a concentrated mineral acid will quantitatively convert the cyclic oligomers to ϵ -aminocaproic acid.² Infrared spectra given by Ogata⁵ show that all of the cyclic oligomers give a strong band at 6.4μ due to NH deformation, whereas ϵ -caprolactam monomer does not exhibit such a band. In general, lactams with less than nine members in the ring do not exhibit the NH deformation band.¹ This difference in the infrared is the basis of the direct determination of the cyclic oligomer content, in the presence of monomer, described in this paper. In the method, the residue obtained after evaporation of the water extract of nylon 6 is dissolved in tetrafluoropropanol, and the absorbance at 6.4μ is determined by the base line method. This method has a precision of about $\pm 5.0\%$ relative in determining the per cent oligomers in the water extractables.

By knowing the per cent moisture in the original nylon 6 the per cent water extractables, and the per cent oligomers in the water extract, one can also estimate the monomer content of the sample.

Experimental

Instrument

Infrared spectra were recorded with a Perkin-Elmer Model 21A double-beam infrared spectrophotometer equipped with NaCl optics. Two matched sodium chloride scaled cells with a spacing of 85 μ were used in the analysis. Quantitative measurements were taken at the following instrument settings: slit width 57, resolution 927, response 1:1, gain 4.8, speed 5 cm./ μ .

Material

The cyclic oligomer standard was obtained by evaporating the water extract of nylon 6, collecting the residue, extracting three times with a few milliliters of cold water to remove ϵ -caprolactam, and then drying the residue at 60°C. under vacuum for 1 hr. An alternative way of obtaining the pure cyclic dimer is to heat the initial residue in a capillary melting-point tube and collect the sublimate setting on the cooler portion of the tube.²

Tetrafluoropropanol (obtained from the Organic Chemicals Department, Du Pont) was redistilled (b.p. 109°C.).

Procedure

A calibration curve is constructed by dissolving a series of samples of the cyclic oligomer standard, ranging up to 50 mg., in 1 ml. of tetrafluoropropanol in 10 ml. glass-stoppered Erlenmeyer flasks. The flasks are placed in 70°C. water and shaken to facilitate solution. The solution is injected into the sealed NaCl cell and the infrared curve recorded between 6.0 and 7.0 μ with tetrafluoropropanol in the matched reference cell. The absorbance at 6.4 μ is then determined by the base line drawn through 6.3 and 6.7 μ .

For analyzing an unknown, a dried weighed sample of the nylon 6 is Soxhlet-extracted with water for 24 hrs., and the per cent water extractables are determined. The solution is then evaporated to dryness and the residue is collected and dried in a vacuum oven at 60°C. for 1 hr. A 50-g. quantity of the residue is carefully weighed into a 10 ml. glass-stoppered Erlenmeyer flask, 1 ml. of tetrafluoropropanol added, the mixture heated and shaken, and the infrared spectrum recorded according to the previous instructions. The per cent of cyclic oligomers in the sample is then determined by:

% cyclic oligomers in water extract

$$= \% \text{ H}_2\text{O extractables} \times \frac{\text{mg. oligomers found}}{\text{wt. residue (mg.)}}$$

Discussion

The use of tetrafluoropropanol as a solvent has a twofold advantage: it will dissolve nylon 6, nylon 66, and nylon 6 oligomers, and it is trans-

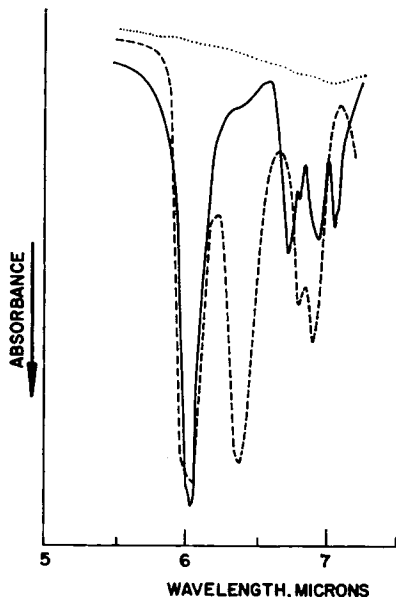
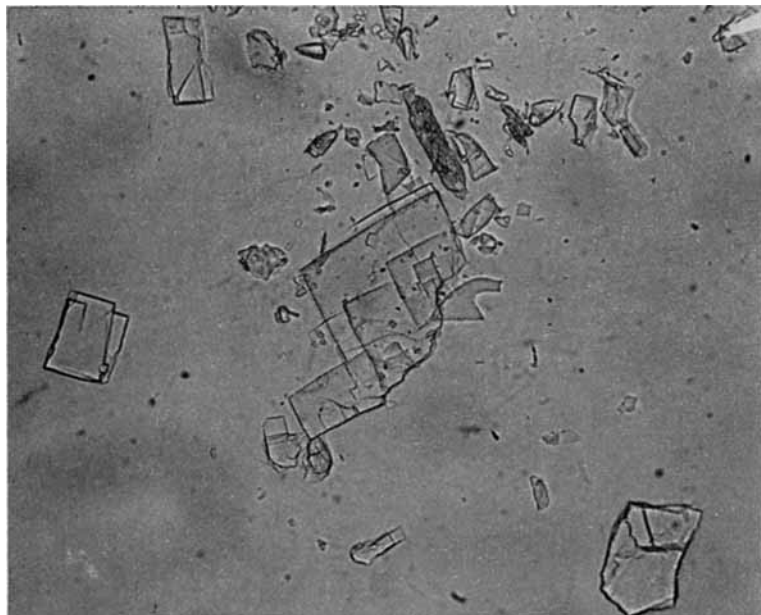


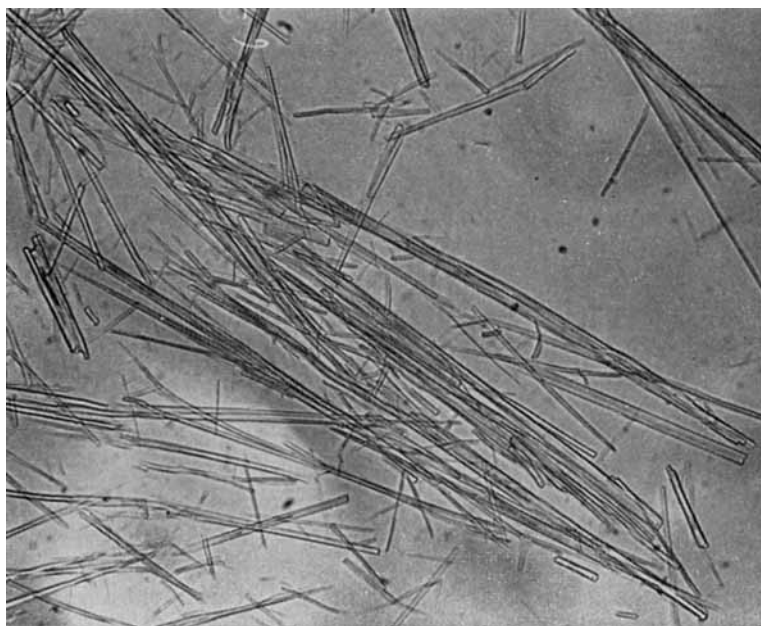
Fig. 1. Infrared spectra of ϵ -Caprolactam and cyclic dimer in tetrafluoropropanol, Concentration 5% (\cdots) tetrafluoropropanol compensated; (—) ϵ -caprolactam; (---) cyclic dimer.

parent at 4–6.5 μ (Fig. 1). In the preparation of the cyclic oligomer standard, the residue collected after the water extraction is the β cyclic dimer (m.p. 250°C.), while the sublimate is the α form (m.p. 350°C.). The β form has a platelike appearance, while the α form exists in needle-like crystals (Fig. 2). According to Hermans,² the two forms of cyclic oligomers are due to the hydrogen bonding between the CONH groups. When the CONH groups are in the *cis* position in the cyclic dimer there are two intramolecular hydrogen bonds rather than the one existing when these groups are in the *trans* position. The latter structure, which would be more water-soluble because of less hydrogen bonding, corresponds to the β form. No variation in absorptivity in the infrared at 6.4 μ was detected between the two crystalline dimer forms. The nylon 6 water-soluble linear molecules, which have an amide NH peak at 6.4 μ , are present to a negligible extent, as indicated by the high melting point of the residue.

The accuracy of the method was determined by analyzing known weights of dimer mixed with known weights of ϵ -caprolactam monomer. The relative precision and accuracy of the method, as indicated in Table I, is about $\pm 5\%$. Table II is a compilation of data obtained on actual samples of both infrared and vacuum extraction³ methods. In the infrared method, the per cent monomer is obtained from the difference between the per cent water extractables and the per cent oligomers found. The per cent oligomer, determined by the vacuum extraction technique,³ is obtained by taking the difference between the per cent water extractables



(a)



(b)

Fig. 2. Isomers of caprolactam dimer: (a) β cyclic dimer (m.p. 250°C.); (b) α cyclic dimer (m.p. 350°C.).

TABLE I
Infrared Determination of Cyclic Oligomer in the Presence of ϵ -Caprolactam

Sample no.	Cyclic oligomer concn., mg.		Relative error, %
	Present	Found	
1	35.5	35.0	-1.4
2	11.3	11.9	+5.5
3	6.4	6.3	-1.6
4	5.3	5.5	+3.8

Estimated precision = $\pm 5.0\%$ (relative).

TABLE II
Comparison of the Vacuum Extraction and Infrared Methods of Determining Cyclic Oligomers in Nylon 6 Water Extract

Sample	% H ₂ O extractables	Vacuum extraction ^a		Infrared method	
		Monomer, %	Oligomer, %	Oligomer, %	Monomer, %
A	1.27	0.65	0.62	0.61	0.66
B	1.47	0.62	0.85	0.81	0.66
C	0.92	0.21	0.71	0.71	0.21
D	2.72	1.38	1.34	1.41	1.31

and the per cent monomer found. Data from both methods compare quite favorably.

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References

1. Bellamy, L. J., *Infrared Spectra of Complex Molecules*, 2nd ed., Methuen, London, 1958, p. 217.
2. Hermans, P. H., *Rec. Trav. Chim.*, **72**, 798 (1953).
3. Horacek, J., and A. Malkus, *Z. Anal. Chem.*, **175**, 415.
4. Markus, L., and A. Kayser, *Mazyar Ken Lapja*, **15**, 86 (1960).
5. Ogata, N., *Bull. Chem. Soc. Japan*, **32**, 813 (1959).
6. Schenker, H. H., C. C. Casto, P. W. Mullen, *Anal. Chem.*, **29**, 825 (1957).
7. Van Velden, P. F., G. M. Want, D. Van Des Heikens, Ch. A. Krussink, P. H. Hermans, A. J. Staverman, *Rec. Trav. Chim.*, **74**, 1366 (1955).

Synopsis

Methods described in the literature for the estimation of the cyclic oligomer content (which includes cyclic dimer, trimer, etc.) of nylon 6 are indirect determinations, generally based on weight differences, and require the prior extraction of ϵ -caprolactam (monomer) from the sample. Infrared studies show that all of the cyclic oligomers have a strong NH deformation band at 6.45μ , whereas the monomer does not exhibit such a band. This difference in the infrared is the basis of a direct determination of the cyclic oligomer content in the presence of monomer. In the method, the residue obtained after evaporation of the water extract of nylon 6 is dissolved in tetrafluoropropanol, and the absorbance at 6.45μ is determined by the base line method. If the per cent moisture in the original nylon 6, the per cent water extractables, and the per cent oligo-

mers in the water extract are known, one can also estimate the monomer content of the sample.

Résumé

Les méthodes décrites dans la littérature permettant d'estimer le taux en oligomère cyclique (ce qui inclut dimère cyclique, trimère, etc.) du nylon 6 sont des déterminations indirectes généralement basées sur des différences en poids et exigent au préalable l'extraction de l' ϵ -caprolactame (monomère) de l'échantillon. Des études infra-rouges révèlent que tous les oligomères cycliques sont caractérisés par une bande à 6.45μ due à la déformation NH alors que cette bande est absente dans les spectres du monomère. Cette différence entre les spectres infra-rouges est la base de la détermination directe du taux en oligomère cyclique en présence du monomère. Dans cette méthode le résidu d'évaporation de l'extrait aqueux de nylon 6 est dissous dans le tétrafluoropropanol et l'absorbance à 6.45μ est déterminée par la méthode de la ligne de base. Si l'on connaît le taux d'humidité dans le nylon original ainsi que le taux de matières extractibles par l'eau et le taux d'oligomères dans l'extrait aqueux, on peut aussi estimer le contenu en monomère de l'échantillon.

Zusammenfassung

Die in der Literatur beschriebenen Methoden zur Bestimmung des Gehalts von 6-Nylon an cyclischen Oligomeren (einschliesslich des cyclischen Dimeren, Trimeren usw.) sind indirekt, beruhen im allgemeinen auf Gewichtsunterschieden und erfordern die vorherige Extraktion von ϵ -Caprolactam aus der Probe. Infrarotuntersuchungen zeigen, dass alle cyclischen Oligomeren eine starke NH-Deformationsbande bei $6,45 \mu$ besitzen die das Monomere nicht aufweist. Dieser Unterschied in der Infrarotabsorption bildet die Grundlage für eine direkte Bestimmung des Gehalts an cyclischen Oligomeren in Gegenwart des Monomeren. Der nach Eindampfen des Wasserextrakts von 6-Nylon erhaltene Rückstand wird in Tetrafluoropropanol gelöst und die Absorption bei $6,45 \mu$ nach der Grundlinienmethode bestimmt. Bei Kenntnis des Feuchtigkeitsgehaltes der ursprünglichen 6-Nylonprobe, des Prozentgehaltes an Wasserextrahierbarem und des Prozentgehaltes an Oligomeren im Wasserextrakt, kann auch der Monomergehalt der Probe bestimmt werden.

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