Equilibrium Ring Concentrations and the Statistical Conformations of Polymer Chains II—Macrocyclics in Nylon 6

J. A. SEMLYEN and G. R. WALKER

The Jacobson and Stockmayer equilibrium theory of macrocyclization is used to calculate the concentrations of large ring molecules in commercial nylon 6. Chains in equilibrated melts of nylon 6 are assumed to be unperturbed by excluded volume effects, and their average dimensions at 500° to 550°K are computed using the Flory and Williams rotational isomeric state model of the linear polymer. The calculated concentrations of the tetramer $\{\overline{NH(CH_2)_5CO}\}_4$ *and pentamer* $\{\overline{NH(CH_2)_5CO}\}_5$ *are in accord with published experimental values. Larger cyclics* $\{\overline{NH(CH_2)_5CO}\}_x (x \geqslant 6)$ *are predicted to be present in nylon 6 as five per cent to eight per cent by weight depending upon the molecular weight of the polymer and the temperature of equilibration.*

THE important fibre-forming polymer nylon 6 is manufactured by the polymerization of ϵ-caprolactam using water as the initiating agent[1]. Equilibrium melts at 500° to 550°K contain linear polymer and cyclics including ϵ-caprolactam. The number average molecular weights of polymers which are suitable for the production of textile fibres are typically in the range 15 000 to 20 000.

Numerous investigations have been directed at the elucidation of the mechanism of polymerization, and it is now well established that polymerization proceeds principally by the reversible addition of linear chains to ϵ-caprolactam rings[2-7]. At equilibrium, nylon 6 has the molecular weight distribution of a random condensation polymer[8], and the aminocaproic acid content is in agreement with that predicted theoretically[9,10]. The equilibrium concentration of ϵ-caprolactam has been the subject of several thorough experimental and theoretical studies[11-14]. It is present in the equilibrated melt in appreciable amounts and must be removed prior to the industrial melt-spinning process. In addition to linear polymer and ϵ-caprolactam, cyclic oligomers have been shown to be present in nylon 6. The lower cyclic oligomers may be readily extracted with hot water or with boiling aqueous methanol, and their equilibrium concentrations have been determined by Zahn and his co-workers[15,16], and by Rothe and Rothe[17,18].

Although the cyclics $\{\overline{NH(CH_2)_5CO}\}_x (x \geqslant 2)$ are present in relatively small amounts, a knowledge of their equilibrium concentrations is of considerable theoretical interest because these concentrations may be related directly to the statistical conformations of the corresponding linear chains by the Jacobson and Stockmayer[19] equilibrium theory of macrocyclization. As originally formulated, the theory is applicable to the cyclization of chains of sufficient length to obey Gaussian statistics. It has been used recently to calculate the experimental macrocyclic concentrations of dimethylsiloxanes $\{\overline{(CH_3)_2SiO}\}_x$[20,21].

Application of the Jacobson–Stockmayer theory to the calculation of macrocyclic concentrations in nylon 6 has been made possible by the publication of a rotational isomeric state model of the linear polymer by Flory and Williams[22]. Their model is based on experimental and structural data for nylon 66 and related polymers, and takes into account the interdependence of bond rotational states arising from short-range intramolecular interactions. Rotational isomeric state models have been successfully used to interpret the statistical conformations of a large number of linear macromolecules[23], and the Flory and Williams model is used in this paper without further discussion.

THEORETICAL MACROCYCLIC CONCENTRATIONS

The equilibrium between x-meric cyclics and polymeric chains in nylon 6 may be described as follows

$$H\{NH(CH_2)_5CO\}_yOH \rightleftharpoons H\{NH(CH_2)_5CO\}_{y-x}OH + \overline{\{NH(CH_2)_5CO\}}_x \qquad (1)$$

Termini of acyclic molecules are specified as amino and carboxylic acid groups for convenience, but their nature in no way affects the discussion to follow.

Fibre-forming equilibrates of nylon 6 have a most probable distribution of chain lengths characterized by a weight average to number average molecular weight ratio[1] $\overline{M}_w/\overline{M}_n=2$. It follows that the equilibrium constant K_x of the above reaction is given[19] by

$$K_x=[\overline{\{NH(CH_2)_5CO\}}_x]/p^x \qquad (2)$$

where p, the extent of reaction of functional groups for the chain molecules, equals the ratio of the concentrations of acyclic species containing y and $y-1$ monomeric units. The factor p is related to the number average degree of polymerization of the linear polymer $\bar{x}$ by

$$\bar{x}=1/(1-p) \qquad (3)$$

The Jacobson and Stockmayer[19] theory provides a theoretical expression for the concentrations of large ring molecules in equilibrated condensation polymers. The theory is applicable to cyclics formed by the forward reaction of equation (1) with zero enthalpy change, provided the corresponding linear molecules are of sufficient length to obey Gaussian statistics. If the Gaussian condition is fulfilled, then the cyclization equilibrium constant K_x is related to the mean-square end-to-end distance $\langle r_x^2\rangle$ of the x-meric chains thus

$$K_x=(3/2\pi\langle r_x^2\rangle)^{3/2}(1/xN) \qquad (4)$$

where N is the Avogadro's number. If the units of K_x are mole l^{-1}, the percentage by weight w_x of a macrocyclic $\overline{\{NH(CH_2)_5CO\}}_x$ is given by

$$w_x=K_xM_xp^x/10\rho \qquad (5)$$

where M_x is the molecular weight of the cyclic, and ρ is the density of the melt at the equilibration temperature (i.e. 0·935 g ml^{-1} at 500°K, and 0·925 g ml^{-1} at 550°K[11,24]).

COMPARISON OF THEORY WITH EXPERIMENT

In order to calculate the individual concentrations of macrocyclics in nylon 6, a knowledge of the spatial dimensions of the polymer chains is required. There is convincing experimental evidence in support of the theoretical prediction that excluded volume effects should be negligible in undiluted liquid polymers[25-27], and it is legitimate to identify the mean-square end-to-end distances $\langle r_x^2 \rangle$ of x-meric chains in nylon 6 melts with the corresponding unperturbed dimensions $\langle r_x^2 \rangle_0$. In this connection we note that poly(dimethylsiloxane) chains of intermediate length (30–80 chemical bonds) are not appreciably expanded by excluded volume effects either in the undiluted polymer[21] or in toluene solution[20].

We have used the Flory and Williams[22] rotational isomeric state model of nylon 6 in order to compute the unperturbed dimensions of finite chains in the equilibrated melt. Values of the ratio $\langle r_x^2 \rangle_0/M_x$ are plotted against the number of monomer units x for chains of molecular weight M_x at 298°, 500° and 550°K in *Figure 1*. The dimensions of the chains are calculated to decrease with increase in temperature.

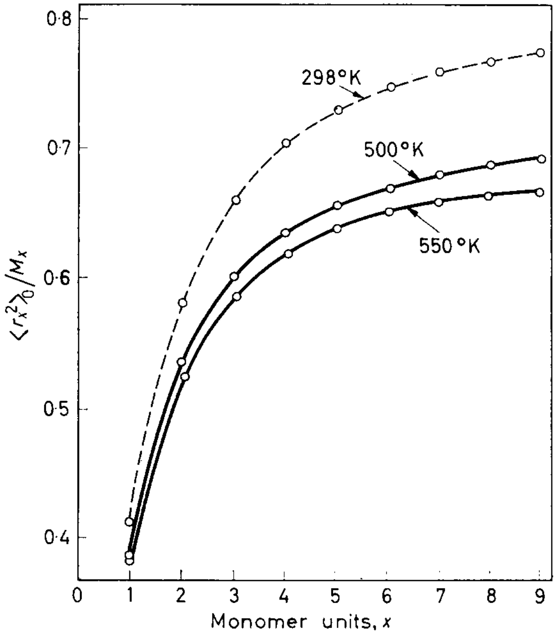

Figure 1—Mean-square end-to-end distances of unperturbed nylon 6 chains at 298°, 500° and 550°K

Theoretical molar cyclization equilibrium constants for cyclics in nylon 6 at 550°K were calculated by substitution of the unperturbed dimensions of the linear chains into equation (4). They are compared with Zahn's[15,16] experimental values in *Figure 2*. The corresponding plots for oligomeric dimethylsiloxanes[20,21] are reproduced for purposes of comparison. For both systems, there is satisfactory agreement between theory and experiment for

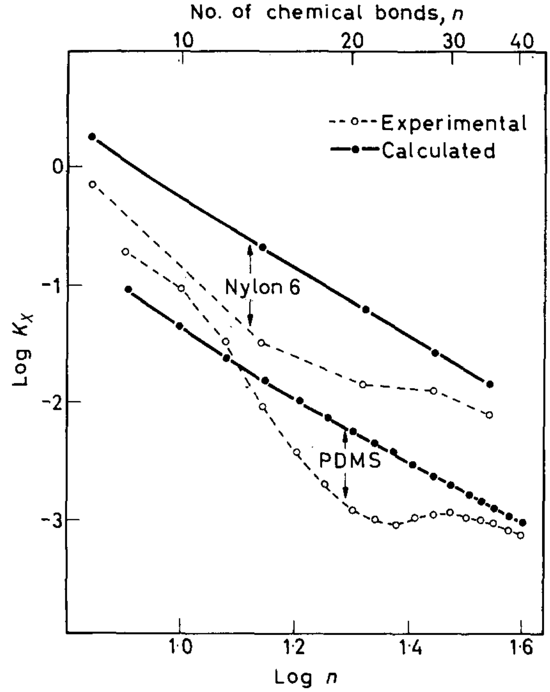

Figure 2—Cyclization equilibrium constants K_x for high molecular weight bulk equilibrates of nylon 6 at 550°K and poly(dimethylsiloxane) (PDMS) at 383°K

the larger rings. Such rings correspond to chains that are evidently of sufficient length to validate the Gaussian assumption of the Jacobson–Stockmayer theory.

The percentages by weight of the cyclics in nylon 6 have been calculated as functions of the molecular weight of the polymer and the temperature of equilibration. Values corresponding to various extents of reaction of func-

Table 1. Cyclic concentrations in nylon 6 (per cent by weight)

Monomer units x	*Exptl values (see refs. 15–18, 28–30)*	*Calculated by equation (5) with the enthalpy change for reaction (1) $\Delta H^0=0$*					
		at 500°K			*at 550°K*		
		$p=0{\cdot}99$	$p=0{\cdot}995$	$p=1$	$p=0{\cdot}99$	$p=0{\cdot}995$	$p=1$
1	8·4*						
2	0·78†	4·86	4·91	4·96	5·07	5·12	5·18
3	0·52†	2·21	2·24	2·27	2·31	2·35	2·39
4	0·56	1·30	1·33	1·35	1·37	1·39	1·42
5	0·48	0·88	0·90	0·92	0·93	0·95	0·97
6 and higher‡	0·76	4·90	5·59	7·57	5·19	5·92	8·02

*Monomeric ε-caprolactam is strained relative to the open chain ($\Delta H^0 \simeq 4$ kcal mole^{-1})[13, 14]. Its concentration is markedly temperature dependent, and values calculated with $\Delta H^0=0$ (as in *Figure 2*) are omitted from this table.

†Zahn[15, 16] reported the concentration of dimer plus trimer together as 1·3 per cent by weight. The results of other authors[1, 17, 18] suggest a dimer:trimer ratio of 3:2

‡Total macrocyclic concentrations were calculated by summing equation (5) from $x=6$ to $x=\infty$. When $p=1$, w_x is predicted to fall off as $x^{-1{\cdot}65}$ over the range $x=6$–9 and as $x^{-1{\cdot}5}$ in the limit $x \to \infty$.

tional groups in the chain fraction are listed in *Table 1*. A change in the temperature of equilibration from 500°K to 550°K is estimated to have a relatively small effect on the macrocyclic concentrations, and commercial samples of nylon 6 are predicted to contain from five per cent to eight per cent by weight of cyclics with more than six monomer units, depending upon the molecular weight of the equilibrated polymer. Zahn's[15,16] value for the concentration of cyclics with $x \geqslant 6$ is only 0·76 per cent by weight, and we conclude that the larger ring molecules were not extracted by his method. It will be possible to obtain more detailed information relating to the spatial dimensions and statistical properties of chains in equilibrated nylon 6 melts when precise values of the macrocyclic concentrations become available.

One of us (G.R.W.) is indebted to the Salters' Company for a Research Scholarship. We gratefully acknowledge computational facilities at the University of York.

Department of Chemistry,
University of York

(*Received January 1969*)

REFERENCES

[1] SBROLLI, W. in *Man-Made Fibres: Science and Technology*, Vol. II, edited by MARK, H. F., ATLAS, S. M. and CERNIA, E. Interscience: New York, 1968
[2] MATTHES, A. *Makromol. Chem.* 1951, **5**, 197
[3] HERMANS, P. H. *Rec. Trav. chim. Pays-Bas*, 1953, **72**, 792
[4] WILOTH, F. *Kolloidzschr.* 1955, **143**, 129
[5] HERMANS, P. H., HEIKENS, D. and VAN VELDEN, P. F. *J. Polym. Sci.* 1958, **30**, 81
[6] WILOTH, F. *Z. phys. Chem. (Frankfurt)*, 1957, **11**, 78
[7] WILOTH, F. *Makromol. Chem.* 1959, **30**, 189
[8] WILOTH, F. *Makromol. Chem.* 1954, **14**, 156
[9] HERMANS, P. H., HEIKENS, D. and VAN VELDEN, P. F. *J. Polym. Sci.* 1955, **16**, 451
[10] HEIKENS, D. and HERMANS, P. H. *Makromol. Chem.* 1958, **28**, 246
[11] VAN VELDEN, P. F., VAN DER WANT, G. M., HEIKENS, D., KRUISSINK, CH. A., HERMANS, P. H. and STAVERMAN, A. J. *Rec. Trav. chim. Pays-Bas*, 1955, **74**, 1376
[12] WILOTH, F. *Z. phys. Chem. (Frankfurt)*, 1955, **5**, 66
[13] TOBOLSKY, A. V. and EISENBERG, A. *J. Amer. chem. Soc.* 1959, **81**, 2302
[14] TOBOLSKY, A. V. and EISENBERG, A. *J. Amer. chem. Soc.* 1960, **82**, 289
[15] SPOOR, H. and ZAHN, H. *Z. analyt. Chem.* 1959, **168**, 190
[16] ZAHN, H., KUNDE, J. and HEIDEMANN, G. *Makromol. Chem.* 1961, **43**, 220
[17] ROTHE, I. and ROTHE, M. *Chem. Ber.* 1955, **88**, 284
[18] ROTHE, M. *J. Polym. Sci.* 1958, **30**, 227
[19] JACOBSON, H. and STOCKMAYER, W. H. *J. chem. Phys.* 1950, **18**, 1600
[20] FLORY, P. J. and SEMLYEN, J. A. *J. Amer. chem. Soc.* 1966, **88**, 3209
[21] SEMLYEN, J. A. and WRIGHT, P. V. *Polymer, Lond.* 1969, **10**, 543
[22] FLORY, P. J. and WILLIAMS, A. D. *J. Polym. Sci.* 1967, **A2**, **5**, 399
[23] FLORY, P. J. *Statistical Mechanics of Chain Molecules.* Interscience: New York, 1969
[24] BRANDRUP, J. and IMMERGUT, E. H. *Polymer Handbook.* Interscience· New York, 1966
[25] FLORY, P. J. *Principles of Polymer Chemistry.* Cornell University Press: New York, 1953
[26] FLORY, P. J. in *Lectures in Materials Science.* W. A. Benjamin: New York, 1963
[27] MORAWETZ, H. *Macromolecules in Solution.* Interscience: New York, 1965
[28] ZAHN, H. and GLEITSMAN, G. B. *Angew. Chem.* 1963, **75**, 772
[29] ZAHN, H. *Z. ges. Textil. Ind.* 1964, **66**, 928
[30] KATORZHNOV, N. D. *Khim. Volokna.* 1966, **1**, 3