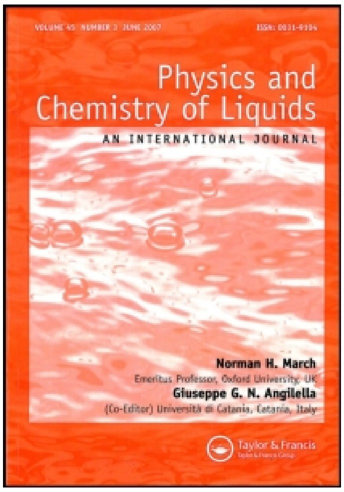

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Shear Viscosity of Dilute Polymer Solutions Compared and Contrasted with Mechanical Properties of Nylon Plus Plasticizer

M. L. Zhang[a]; N. H. March[ab]; V. E. Van Doren[a]
[a] Department of Physics, University o Antwerp (RUCA), Antwerp, Belgium [b] Oxford University, Oxford, England

To cite this Article Zhang, M. L. , March, N. H. and Van Doren, V. E.(2002) 'Shear Viscosity of Dilute Polymer Solutions Compared and Contrasted with Mechanical Properties of Nylon Plus Plasticizer', Physics and Chemistry of Liquids, 40: 1, 101 — 113

To link to this Article: DOI: 10.1080/00319100208086652

URL: http://dx.doi.org/10.1080/00319100208086652

Phys. Chem. Liq., 2002, Vol. 40(1), pp. 101 – 113

Taylor & Francis
Taylor & Francis Group

SHEAR VISCOSITY OF DILUTE POLYMER SOLUTIONS COMPARED AND CONTRASTED WITH MECHANICAL PROPERTIES OF NYLON PLUS PLASTICIZER

M. L. ZHANG[a], N. H. MARCH[a,b,*] and V. E. VAN DOREN[a]

[a]*Department of Physics, University of Antwerp (RUCA), Groenenborgerlaan 171, B-2020, Antwerp, Belgium;* [b]*Oxford University, Oxford, England*

(Received 10 November 2000)

Both the shear viscosity $\eta(c)$ of dilute polymer solutions and Young's modulus $Y(c)$ of nylon plus plasticizer with concentration c are assumed to be expressible as a power series in concentration. Scaling arguments are then presented which reveal an intimate relation between the coefficients of $O(c)$ and $O(c^2)$ terms in both $\eta(c)$ and $Y(c)$. The coefficient of the $O(c^2)$ term is predicted always to be positive, while that of the $O(c)$ term can in principle have either sign. Comparison with experiment is made for $\eta(c)$ and $Y(c)$. Some further experiments are proposed for both $Y(c)$ and $\eta(c)$.

Keywords: Viscosity; Young's modulus; Shear modulus; Polymer solutions

1. BACKGROUND AND OUTLINE

Plasticization, as an effective method to increase flexibility and impact strength and to reduce tensile and flexural strengths of nylon, is widely used to improve mechanical properties of various polyamides (PA) [1,2]. Therefore the dependence of the mechanical properties of a nylon+plasticizer system on the concentration of plasticizer is interesting for both science and technology. In a previous study [3], we have suggested a model based on the cutting of hydrogen bonds to

---

*Corresponding author.

ISSN 0031-9104 DOI: 10.1080/00319100290005703

explain the decrease of both Young's modulus and the shear modulus in the small plasticizer concentration limit. A connection between $(1/L)(dL/dc)|_{c=0}$ (the relative change of characteristic length L with plasticizer concentration c of the phenomenology of Bhatia-March [4] concerning surface segregation in binary alloys) and pure nylon properties was also exhibited. However the properties of nylon + plasticizer at larger concentration c have received scant attention to date.

Independently of the above work on the mechanical properties of solid nylon plus plasticizer, much attention has been given to the shear viscosity of a solution of a polymer in a variety of solvents. A recent example has appeared in this Journal [5] in which the viscosity of solutions of the polymer 'dextran' in various solvents has been measured. In their work, Mahapatra *et al.* [5] start from the assumption that the concentration c dependence of the viscosity of a dilute polymer solution can be expressed as a power series in c. This is precisely the assumption underlying the present studies of Young's modulus of various solid nylons as a function of plasticizer concentration.

With this as general background, the outline of the present paper is as follows. In Section 2 we compare and contrast such series expansions referred to above for the dilute solutions of polymer in different solvents with the problem of plasticizer at concentration c in solid nylons. Immediately, a qualitative difference is evident at low concentrations, the sign of the linear term in c being different in the two examples chosen. This has prompted the discussion of the $O(c^2)$ term in both $\eta(c)$ and Young's modulus $Y(c)$. For both these 'mechanical' properties it is argued that there is an intimate relation between the coefficients of the $O(c)$ and the $O(c^2)$ terms. Section 3 constitutes a summary, plus some proposals for future work, both theoretical and experimental. Some details of the general scaling arguments invoked in Section 2 are set out in an Appendix.

2. SHEAR VISCOSITY OF DILUTE POLYMER SOLUTION AND YOUNG'S MODULUS OF NYLON + PLASTICIZER SYSTEM

The structure of the Taylor expansion of the viscosity $\eta(c)$ of a dilute polymer solution is similar to that of Young's modulus $Y(c)$ of a nylon + plasticizer system. It will be convenient to define the concentration c as the ratio $(n_{\text{polymer}}/(n_{\text{polymer}}+n_{\text{solvent}}))$, where n_{polymer} is the number of the polymer coils in solution while n_{solvent} is the number of solvent molecules. The concentration c dependence of the viscosity $\eta(c)$ of a dilute polymer solution can then be expressed as a power series in the concentration [5], namely

$$\eta(c) = \eta_0(1 + H_1 c + H_2 c^2 + H_3 c^3 + \cdots), \quad H_1 = \lim_{c\to 0}\frac{\eta(c) - \eta_0}{c\eta_0}. \tag{1}$$

The intrinsic viscosity H_1 is independent of the concentration of the solution but is a function of the solvent used [5]. For polymer solutions $H_1 > 0$: this can be argued hydrodynamically from the presence of polymer coils in the solvent or alternatively from the stress exerted by the elasticity of such coils [6]. Huggins found an interesting relation between the coefficient H_2 of the second order term and the coefficient H_1 of the first order term [7, 8]

$$H_2 = k_1 H_1^2, \quad k_1 > 0. \tag{2}$$

$H_1 > 0$ and the Huggins relation $H_2 > 0$ have a simple physical meaning, *i.e.*, $\eta(c)$ is a monotonic increasing function of the polymeric concentration c and $(\partial^2\eta(c)/\partial c^2) > 0$. The minimum of $\eta(c)$ is at $c = 0$ for pure solvent and $\eta(c)$ monotonically increases with c. This is different from the viscosity of the surfactant-small molecule solvent system, for example dimethylsulfoxide + 1-alkanols where the viscosity $\eta(c)$ first decreases from its pure small molecule solvent value and gradually reaches a minimum [9]. Then the interaction between surfactant molecules comes into play. The viscosity will then gradually increase to the value of the pure surfactant at $c = 1$. With increasing surfactant concentration c, the interaction between solvent molecules and therefore the surface tension decreases. Then the bulk modulus $B(c)$ or surface tension $\gamma(c)$ have the general shape of upward parabolas. The similarity in behavior of viscosity and elastic modulus illustrated above may also be obtained from the following macroscopic arguments. The viscosity $\eta(\omega, c)$ and shear modulus $\mu(\omega, c)$ are the imaginary part and real part respectively of the response function due to a frequency (ω) dependent external shear stress. These are linked by a Kramers-Krönig relation. If we make the further simplifying assumption that the viscosity has the separable form $\eta(\omega, c) \approx g(\omega)f(c)$ both for the highly viscous fluid [10] and, more drastically for the low viscosity system, then the shear modulus would plainly have the same concentration dependence as the viscosity. Further, by means of $\gamma(c) \sim B(c)L$ with B the bulk modulus and L a characteristic microscopic length [11], the surface tension $\gamma(c)$ can be expected to have the same concentration dependence as $\eta(c)$.

Mahapatra *et al.* [5] speculated that, one could write generalized Huggins relations for the coefficients $H_n (n \succeq 2)$ of higher order terms: that is

$$H_n = k_{n-1} H_1^n, \quad k_{n-1} > 0 \quad (n \succeq 2) \tag{3}$$

We propose here analogous relations to Eq. (3) for the Taylor expansion coefficients of Young's modulus $Y(c)$ of the nylon+plasticizer systems. In the Appendix we argue, following the scaling law proposed by De Gennes, that the Young's modulus of the nylon+plasticizer system can be approximately represented by

$$Y(c) = \frac{V_0(1 + (L_0/a)c)^{-2/5} + S^H(1 - c)}{L_0(1 + (L_0/a)c)^{-2/5}[a(1 + (L_0/a)c)^{3/5}]^2}. \tag{4}$$

Here $c = (n_{\text{plasticizer}}/n_{\text{nylon}})$ is the concentration of plasticizer, the ratio of the number of plasticizer molecules $n_{\text{plasticizer}}$ to the number of polyamide units n_{nylon} while S^H is the original hydrogen bond energy in nylon, and V_0 measures the average van der Waals interaction per polyamide unit. a is the linear dimension of a monomer while L_0 denotes the length of one polyamide unit in a completely stretched chain. Figure 1 shows that Eq. (4) is in general accord with available experimental data. Making use of Eq. (4), a simple calculation gives the relative change of Young's modulus in the small c limit as

$$\begin{aligned}\frac{Y(c) - Y(0)}{Y(0)} = &-\frac{[(4/5)(V_0 + S^H) + ((2/5)V_0 + S^H(a/L_0))]}{(V_0 + S^H)} \frac{L_0}{a} c \\ &+ \frac{[(18/25)(V_0 + S^H) + (7V_0/25) + (4/5)((2/5)V_0 + S^H(a/L_0))]}{(V_0 + S^H)} \left(\frac{L_0}{a}\right)^2 c^2 \\ &+ \frac{[(84/125)(V_0 + S^H) + (56V_0/125) + (18/25)((2/5)V_0 + S^H(a/L_0))]}{(V_0 + S^H)} \left(\frac{L_0}{a}\right)^3 c^3 \\ &+ \frac{[(399/625)(V_0 + S^H) + (357V_0/625) + (84/125)((2/5)V_0 + S^H(a/L_0))]}{(V_0 + S^H)} \left(\frac{L_0}{a}\right)^4 c^4 - \cdots\end{aligned} \tag{5}$$

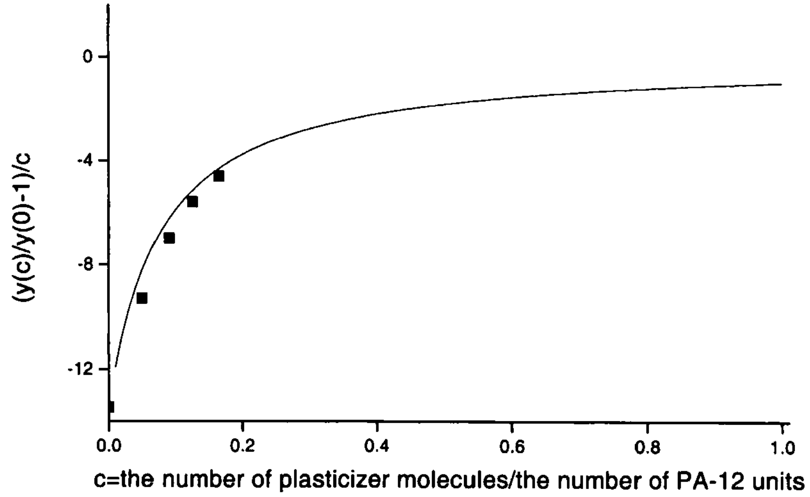

FIGURE 1 Comparison of available experimental data (taken from Ref. [1, 2], solid square) with the curve predicted by Eq. (A8) for PA-12, $V_0 = 2.5 \times 12 = 30$ Kcal/mole, $(L_0/a) = 12$, $S^H = 10$ Kcal/mole.

If we define Y_1 as

$$Y_1 = \lim_{c \to 0} \frac{Y(c) - Y(0)}{Y(0)c} = -\frac{[(4/5)(V_0 + S^H) + ((2/5)V_0 + S^H(a/L_0))]}{(V_0 + S^H)} \frac{L_0}{a} < 0, \qquad (6)$$

then Y_1 depends only on the properties of the solvent (nylon): this is similar to H_1 which depends only on the solvent. The coefficients Y_n of the Taylor expansion of Young's modulus $Y(c)$

$$Y(c) = Y(0)[1 + Y_1 c + Y_2 c^2 + Y_3 c^3 + \cdots] \qquad (7)$$

also obey the generalized-Huggins relations

$$Y_n = y_{n-1} Y_1^n, \quad y_{n-1} > 0, \quad n \geq 2 \qquad (8)$$

They resemble the form of Eq. (3) for the Taylor expansion of $\eta(c)$ in a dilute polymeric solution. The first three dimensionless constants y_1, y_2

and y_3 can easily be extracted from Eq. (5) as

$$\begin{aligned} y_1 &= \frac{(V_0+S^H)[(18/25)(V_0+S^H)+(7V_0/25)+(4/5)((2/5)V_0+S^H(a/L_0))]}{[(4/5)(V_0+S^H)+((2/5)V_0+S^H(a/L_0))]^2} \\ y_2 &= \frac{(V_0+S^H)^2[(84/125)(V_0+S^H)+(56V_0/125)+(18/25)((2/5)V_0+S^H(a/L_0))]}{[(4/5)(V_0+S^H)+((2/5)V_0+S^H(a/L_0))]^3}, \\ y_3 &= \frac{(V_0+S^H)^3[(399/625)(V_0+S^H)+(357V_0/625)+(84/125)((2/5)V_0+S^H(a/L_0))]}{[(4/5)(V_0+S^H)+((2/5)V_0+S^H(a/L_0))]^4} \end{aligned} \tag{9}$$

and, should it be eventually useful, higher order coefficients can be directly calculated from the general Eq. (4). It should be pointed out that the generalized Huggins relations (8) automatically account for the sign change in the Taylor expansion (5). $Y_2 > 0$ indicates that Young's modulus always exceeds the linear contribution [3]: this is consistent with the experimental observation of $Y(c)$ [1,2].

Young's modulus is a monotonically decreasing function of c for nylon + plasticizer systems, whereas the viscosity of a dilute solution of dextran in the solvents chosen in Ref. [5] is a monotonically increasing function of c. If we take the same polymer and the same solvent to form two extremes of a composite system, then $Y(c)$ and $\eta(c)$ will both be monotonically increasing functions of c. The dilute solution of dextran discussed in [5] corresponds to $c \to 0$, whereas the nylon + plasticizer system corresponds to $c \to 1$. If there exists a continuous transition (no phase separation) from $c = 0$ to $c = 1$ for some polymer + small molecule system, we may expect a continuously and smoothly monotonically increasing form from $c = 0$ to $c = 1$ for $\eta(\omega, c)$, $\mu(\omega, c)$ and $Y(\omega, c)$. Therefore $H_1 > 0$ in Eq. (1) in the dilute limit and $Y_1 < 0$ in Eq. (7) of the pure nylon limit are consequences of the same monotonically increasing $\eta(\omega, c)$ and $Y(\omega, c)$ from $c = 0$ to $c = 1$. In other words we may anticipate that $Y(c)$ and $\eta(c)$ will satisfy similar laws yielding a monotonically increasing behavior through a scaling relation of the form

$$Y(c) = Y(c^*)F(c), \quad \eta(c) = \eta(c^*)F(c),$$

where c^* is some characteristic concentration. Because the Taylor expansion of $F(c)$ converges in the range c from 0 to 1, we can write $F(c) = F(0)(1 + F_1c + F_2c^2 + F_3c^3 + \cdots)$, the coefficients F_1, F_2, $F_3, \ldots$ being independent of c.

We may also obtain the Huggins relation by following dimensional analysis and analytic arguments. In the hydrodynamic model for the viscosity of a dilute solution, the dimensionless small expansion parameter ϕ is the ratio of the volume of the polymer coil and the volume occupied by one coil. If we approximate the polymer coil as a sphere, $\phi=(4\pi R^3/3)\cdot n$, where R is the radius of coil while n is the number of the coils per unit volume. Since the viscosity η as a function of polymer concentration is a single-valued function, its expansion in n will not include fractional powers. Furthermore η does not have any singular points near $n=0$. Therefore η is an analytic function near to $n=0$. It has therefore the Taylor expansion, $\eta(n)=\eta_0(1+k_1\phi+k_2\phi^2+\cdots)$, with $k_1=(5/2)$ according to Einstein's result. Substituting the expression for ϕ into η we have

$$\eta(n)=\eta_0\left(1+k_1\frac{4\pi R^3}{3}\cdot n+k_2\left(\frac{4\pi R^3}{3}\right)^2\cdot n^2+\cdots\right).$$

The Huggins relation between the coefficient of n^m and the coefficient of n is then obviously

$$k_m\left(\frac{4\pi R^3}{3}\right)^m=\text{constant}\cdot\left(k_1\frac{4\pi R^3}{3}\right)^m,$$

where the constant is (k_m/k_1^m): it does not relate to any properties of the solute. The same reasoning can be used to establish the existence of the Huggins relation among the Taylor expansion coefficients of Young's modulus, where the dimensionless small expansion parameter is $(L_0/a)(N_{\text{plasticizer}}/N_{\text{nylon unit}})$.

We stress that the Taylor expansion of $Y(c)$ for nylon + plasticizer system in the $c\rightarrow 0$ limit and the Taylor expansion of $\eta(c)$ of dilute polymer solution in the same limit have similar structure and in particular obey the generalized Huggins relations of the expansion coefficients. Scaling arguments and the Kramers-Krönig relation lead us to anticipate this structure of the Taylor expansion of Young's modulus and viscosity. If we can prove the existence of generalized Huggins relations in any one of the two situations then we may in fact obtain such relations in the other. Since we have obtained the generalized Huggins' relations from the analysis of Young's modulus, the existence of such relations may be widespread. An attempt based on the systematic solution of a Navier-Stokes equation together with the elasticity of the polymer coils will be developed elsewhere to study viscosity.

3. SUMMARY AND FUTURE DIRECTIONS

We have compared and contrasted models of the concentration dependence of the shear viscosity $\eta(c)$ of polymer solution with a mechanical property, Young's modulus $Y(c)$, of nylon with a concentration c of plasticizer. Denoting either property by $P(c)$, we have focussed in the main text on the low concentration form

$$\frac{P(c)-P(0)}{P(0)c} = [P] + p_1[P^2]c + p_2[P]^3c^2 + \cdots, \ [P] = \lim_{c\to 0}\frac{P(c)-P(0)}{P(0)c}. \tag{10}$$

Such a low concentration form has been known for a long time, going back at least to the work of Huggins [8], for the viscosity $\eta(c)$ of dilute polymer solutions and as stressed in the Appendix, this might suggest an approximate scaling property of the form

$$\frac{(P(c)-P(0))/(P(0))}{[P]c} = S(c) \tag{11}$$

where $S(0)=1$. In a recent issue of this Journal two experimental studies of solutions have been made which we may cite for comparison [5, 9] with the theoretical proposals made here.

Turning to the case of nylons + plasticizer the breaking of hydrogen bonds is again invoked in arriving at a model for $Y(c)$ having the form of Eq. (3) at low concentrations. Using De Gennes scaling, the Appendix suggests a form $Y(c)$ which we expect to be valid at least semi-quantitatively over a wide range of the concentration c of the plasticizer. When this expression for $Y(c)$ is expanded for low concentration c, we recover a form analogous to Eq. (3), namely Eq. (8). The Huggins relation therefore results from the model in the Appendix, as for the shear viscosity of dilute polymer solutions. Though data is sparse for comparison with the predictions of the present model for nylons + plasticizer, there is at least semi-quantitative agreement between the model and currently available data.

It seems now a matter of considerable interest to have systematic experiments not only for $\eta(c)$ on further polymer solutions, designed such that addition of solute is known to break hydrogen bonds in the solvent, but also on $Y(c)$ for a wider range of nylons plus a variety of plasticizers. These measurements should then allow a test of the validity of the model of disruption of hydrogen bonding in the nylons by the different plasticizers, and if it proves necessary, should point the way to refinements of the model proposed here.

Acknowledgements

We are indebted to the Flemish Science Foundation (Grant No. G2131,94) and to the Concerted Action of the University of Antwerp (Grant No. GOA-BOF-UA 23) for research support. NHM wishes to acknowledge partial financial support for work on mechanical properties of materials from the Office of Naval Research, USA. Especial thanks are due to Dr. P. Schmidt of that Office for his continuing motivation and stimulation.

References

[1] Welgos, R. J., "Polyamides, Plastics", In: "*Encyclopedia of Polymer Science and Engineering*" Vol. 10, Ed. Mark, H. F. 2nd edition, Wiley-Interscience (1985); De Groote, P., Plasticization of Polydodecamide by Benzenesulfonamides, *Ph.D. Thesis of Université Catholique de Louvain* (Belgium), 1998.
[2] Billmeyer, F. W. Jr., "*Textbook of Polymer Science*", 2nd edition, Wiley-Interscience, New York, 1971.
[3] Zhang, M. L., March, N. H., Peeters, A., Van Alsenoy, C. and Van Doren, V. E., *Journal of Applied Physics* (in the press).
[4] Bhatia, A. B. and March, N. H. (1978). *J. Chem. Phys.*, **68**, 4651; Freeman G. R. and March, N. H. (1998). *J. Chem. Phys.*, **109**, 10521.
[5] Mahapatra, A. P., Samal, R. K., Samal, R. N. and Roy, G. S. (2000). *Phys. Chem. Liquids*, **38**, 405.
[6] de Gennes, P. G., *Scaling Concepts in Polymer Physics*, Ithaca, N.Y., 1979.
[7] Kraemer, E. O. (1938). *Ind. Eng. Chem.*, **30**, 1200.
[8] Huggins, M. L. (1942). *J. Am. Chem. Soc.*, **64**, 2716.
[9] Ali, A., Tewari, K., Nain, A. K. and Chakravotty, V. (2000). *Phys. Chem. Liquids*, **38**, 459.
[10] Landau, L. D. and Lifshitz, E. M. (1970). Theory of elasticity, 2nd edition, Pergamon Press, Oxford.
[11] Alonso, J. A. and March, N. H., *Electrons in Metals and Alloys*, Academic Press, NewYork, 1989.
[12] Dasgupta, S., Hammond, W. B. and Goddard III, W. A. (1996). *J. Am. Chem. Soc.*, **118**, 12291; Peeters, A., Van Alsenoy, C. and Van Doren, V. E., *Young's modulus of PA-6, PA-11 and PA-12*, in preparation.

[13] De Gennes, P. G. (1980). *Macromolecules*, **13**, 1069.
[14] De Gennes, P. G. (1974). *J. Chem. Phys.*, **60**, 5030.
[15] Day, M. C. and Selbin, J., *Theoretical Inorganic Chemistry*, 2nd edition, Reinhold Corporation, NewYork, 1969.

APPENDIX: YOUNG'S MODULUS *Y*(*c*) FOR NYLON+PLASTICIZER AS A FUNCTION OF PLASTICIZER CONCENTRATION *c*

The Young's modulus of infinite nylon chains or crystal is about 180–300 GPa [12], whereas the Young's modulus of pure commercial nylons is in range 1400–3000 MPa [1,2]. This is due to the finite length of nylon chains in these commercial materials, for example in PA-12 the average length is about 180–200 units. The Young's modulus of practical nylon material is not determined by the chemical bonds of the single polyamide chain, but is determined by the hydrogen bonds and van der Waals interaction between the nylon chains. In a pure nylon, the chains are stretched until they are rather straight and the whole structure is still very rigid. To soften a nylon and increase its elasticity range, plasticizer must be used to cut hydrogen bonds between its polyamide chains. After some hydrogen bonds are cut, the original stretched chains are slackened. These loosened parts of a chain will coil. This will decrease the length of chain and the face-to-face contact between chains. The latter will weaken the van der Waals interaction between the chains. In addition the coiled chain corresponds to an increase in its effective cross section.

We now approximate the problem of a bundle of nylon chains by that of a single chain in the mean field of surrounding chains. The essence of the argument below is to write

$$Y(c) = \frac{L(c)k(c)}{A(c)}. \tag{A1}$$

Here $L(c)$ measures the effective length of the nylon chain in the presence of plasticizer, $A(c)$ is the cross-section incorporating again the effect of plasticizer molecules. Finally, in Eq. (A1), $k(c)$ denotes the spring constant in the presence of a concentration c of plasticizer.

First of all let us consider the change in effective cross Section A of the single nylon chain with plasticizer concentration c. We define c as

$c = (n/N)$, where n is the number of plasticizer molecules while N is the number of polyamide units in the whole system. When c gradually increases from 0 to 1, the nylon chain gradually changes from its stretched state to a coil conformation. The effective cross section $A(c)$ is determined by the linear size of the blob $D(c)$ formed by the coiled chain, where $A(c) = D^2(c)$. The linear size D of the blob is given by

$$D = a g_D^{3/5}, \tag{A2}$$

where a is the linear size of a monomer and g_D is the number of monomers in a blob [13, 14]. If all the hydrogen bonds among nylon chains are broken by plasticizer molecules, the whole chain is released and forms a coil. When the plasticizer concentration is c, the monomer number g_D in the released part for one polyamide unit is $(L_0/a)c$, where L_0 denotes the length of one polyamide unit in a completely stretched chain. In a completely stretched nylon chain, the monomer number in a blob is 1. Therefore for a qualitative estimate we shall approximate $g_D(c)$ by

$$g_D(c) = 1 + \frac{L_0}{a}c. \tag{A3}$$

Substituting Eq. (A3) into Eq. (A2), one finds the linear size of a blob

$$D(c) = a\left(1 + \frac{L_0}{a}c\right)^{3/5}. \tag{A4}$$

The length of a coiled chain is $L = L_0 g_D^{-2/5}$. Making use of Eq. (A3), $L(c)$ takes the form

$$L(c) = L_0\left(1 + \frac{L_0}{a}c\right)^{-2/5}. \tag{A5}$$

We turn next to the dependence of the spring constant k of a nylon chain on the plasticizer concentration c. The force constant can be separated into two parts $k = k_{\text{hydrogen bond}} + k_{\text{van der Waals}}$, where $k_{\text{hydrogen bond}}$ is the contribution from the hydrogen bonds between nylon chains and $k_{\text{van der Waals}}$ comes from the van der Waals interaction between nylon chains. Because the characteristic length of an obvious change of the energy of the chain is about the distance between two hydrogen bonds along the chain, *i.e.*, the length of one polyamide unit $L(c)$, the order of magnitude of the spring constant is

$$k(c) \sim \frac{V(c) + E^H(c)}{[L(c)]^2}. \tag{A6}$$

Here $E^H(c)$ is the average hydrogen bond energy E^H at concentration c. Since each plasticizer molecule cuts one hydrogen bond, $E^H(c) = S^H - S^H c$, where S^H is the original hydrogen bond energy in nylon, and is about 5–10 Kcal/mole [15]. $V(c)$ is the average van der Waals interaction per polyamide unit at concentration c. The van der Waals interaction rapidly decays with distance. Therefore for two coiled chains only the face-to-face parts play a role and the interaction between the far separated parts of two coiled chains may be neglected. Thus one finds

$$V(c) = V_0 \frac{L(c)}{L(c=0)} = V_0\left(1 + \frac{L_0}{a}c\right)^{-2/5}, \tag{A7}$$

where V_0 is the van der Waals interaction between two nylon chains per unit polyamide(for PA-12, $V_0 \sim 12 \times$ van der Waals interaction per CH_2).

Substituting the expressions of $L(c)$, $A(c)$ and $k(c)$ into Eq. (A1), we obtain the Young's modulus $Y(c)$ of a nylon+plasticizer system at plasticizer concentration c as

$$Y(c) = \frac{V_0(1 + (L_0/a)c)^{-2/5} + S^H(1 - c)}{L_0(1 + (L_0/a)c)^{-2/5}[a(1 + (L_0/a)c)^{3/5}]^2}. \tag{A8}$$

It should be pointed out at this stage that in the derivation of formula Eq. (A8), there are some other physical effects which are not presently incorporated. We have only considered the universal properties of plasticizer; namely the cutting of hydrogen bonds. The details of the plasticizer, for example, the miscibility with nylon and the self-assemble properties are neglected. Furthermore the entanglement among the nylon chains is beyond the scope of the present approximation, which allows a single chain to interact with an effective environment.

If we take the van der Waals interaction as 2.5 Kcal/[mole$\cdot$CH$_2$], then $V_0 \sim 2.5 \times (L_0/a)$ Kcal/mole for PA-x, $x = (L_0/a)$. $S^H \sim 10$ Kcal/mole [15]. For PA-12, $a \sim 2.5$ Å $Y(c = 1) = (V_0/L_0a^2)(L_0/a)^{-6/5} \sim$ 50 Mpa, $Y(c = 0) = (V_0 + S^H/L_0a_0^2) \sim 1460$ MPa. The above estimate of $Y(0)$ is in general accord with experimental values in the range 1300–1400 MPa for pure PA-12 [1, 2].