indicating a macroscopically discontinuous second phase. However, at a microscopic level some of the spheres were still interconnected. It is only when polymer II is around 10% that the discontinuity is evident and only a few individual particles are connected.

The major conclusion from this paper relates to the dual phase continuity of PnBA/PS in sequential IPN's:

(1) Above 20% of polymer network II, its phase domain structure was continuous.

(2) Throughout the composition range studied, polymer network I was continuous.

In a forthcoming paper,[27] a further analysis of the domain sizes will be given, especially with regard to the theory by Yeo et al.,[6] and data on semi-IPN's containing AA will be presented.

**Acknowledgment.** We thank the National Science Foundation for financial support through Grant No. DMR-8015802, Polymers Program.

### References and Notes

(1) Klempner, D.; Frisch, K. C., Eds. "Polymer Alloys"; Plenum Press: New York, 1980; Vol. II.
(2) Manson, J. A.; Sperling, L. H. "Polymer Blends and Composites"; Plenum Press: New York, 1976.
(3) Lipatov, Yu. S.; Sergeeva, L. M. "Interpenetrating Polymeric Networks"; Naukova Dumka: Kiev, 1979.
(4) Sperling, L. H. "Interpenetrating Polymer Networks and Related Materials"; Plenum Press: New York, 1981.
(5) Donatelli, A. A.; Sperling, L. H.; Thomas, D. A. *J. Appl. Polym. Sci.* **1977**, *21*, 1189.
(6) Yeo, J. K.; Sperling, L. H.; Thomas, D. A. *Polymer*, submitted.
(7) Yeo, J. K.; Sperling, L. H.; Thomas, D. A. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1980**, *21* (2), 53.
(8) Yeo, J. K.; Sperling, L. H.; Thomas, D. A. *Polym. Eng. Sci.* **1982**, *22*, 190.
(9) Neubauer, E. A.; Thomas, D. A.; Sperling, L. H. *Polymer* **1978**, *19*, 188.
(10) Kresge, N. E. In "Polymer Blends"; Paul, D. R., Newman, S., Eds.; Academic Press: New York, 1978; Vol. 2.
(11) Sperling, L. H.; Friedman, D. W. *J. Polym. Sci., Part A-2* **1969**, *7*, 425.
(12) Yomoda, S.; Sperling, L. H. *J. Appl. Polym. Sci.* **1977**, *21*, 2609.
(13) Heine, H. G.; Rudolph, H.; Rosenkranz, H. *J. Appl. Polym. Symp.* **1975**, *26*, 157.
(14) Widmaier, J. M. *Makromol. Chem.* **1978**, *173*, 1743.
(15) Gehman, S. D.; Woodford, D. E.; Wilkinson, C. S. *Ind. Eng. Chem.* **1947**, *39*, 1108.
(16) American Society for Testing and Materials, ASTM D 1052-73T, 1974.
(17) Flory, P. J.; Rehner, J. *J. Chem. Phys.* **1943**, *11*, 512, 521.
(18) Frank, H. P.; Mark, H. *J. Polym. Sci.* **1951**, *6*, 243.
(19) Walsh, D. J.; McKeown, J. G. *Polymer* **1980**, *21*, 1335.
(20) Hildebrand, J. H.; Scott, R. L. "The Solubility of Nonelectrolytes", 3rd ed.; Reinhold: New York, 1950.
(21) Flory, P. J. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, N.Y., 1953.
(22) Tobolsky, A. V.; Katz, D.; Takahashi, M.; Schaffhauser, R. *J. Polym. Sci., Part A* **1964**, *2*, 2749.
(23) Sperling, L. H.; Ferguson, K. B.; Manson, J. A.; Corwin, E. M.; Siegfried, D. L. *Macromolecules* **1976**, *9*, 743.
(24) Yeo, J. K.; Sperling, L. H.; Thomas, D. A. *Polym. Eng. Sci.* **1981**, *21*, 696.
(25) Yeo, J. K.; Sperling, L. H.; Thomas, D. A. *J. Appl. Polym. Sci.* **1981**, *26*, 3283.
(26) Michel, J.; Hargest, S. C.; Sperling, L. H. *J. Appl. Polym. Sci.* **1981**, *26*, 743.
(27) Widmaier, J. M.; Sperling, L. H. *J. Appl. Polym. Sci.*, submitted.

---

# Stress Relaxation of a Polyelectrolyte Network As Affected by Ionic Strength

**Carlos A. Kienzle-Sterzer, Dolores Rodriguez-Sanchez, Diane Karalekas, and ChoKyun Rha***

*Biomaterials Science and Engineering Laboratory, Department of Nutrition and Food Science, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.*
*Received November 10, 1981*

ABSTRACT: Stress relaxation behavior of polyelectrolyte films under simple tension is affected by the ionic strength (NaCl) of the swelling medium. In this study, the cationic polyelectrolyte chitosan [(1→4)-2-amino-2-deoxy-$\beta$-D-glucan] was used to prepare films. Swelling at 24 °C showed a salting-in effect up to ionic strength 0.4, reaching an equilibrium volume of approximately 180% (w/w). Linear stress relaxation behavior indicated a predominant first elastic component in a two-component Maxwell model, with a first relaxation time of approximately $10^{-4}$ s. The apparent Young's modulus increased, with an inflection point at ionic strength between 0.4 and 1.0. Internal stress of the polycationic films, calculated from linear stress relaxation experiments, decreased as the ionic strength increased. The internal stress changed from positive to negative at ionic strengths between 0.4 and 1.0. Nonlinear stress relaxation measurements at extension ratios between 10 and 40% showed that the instantaneous stress–strain relationships can be represented by the Mooney–Rivlin equation, where both $C_1$ and $|C_2|$ decrease with time, showing a marked dependence on ionic strength. The results indicate a rearrangement of the molecular chains in the network under tensile stress and also the electrostatic nature of the interactions responsible for the network integrity in the polyelectrolyte films.

## Introduction

Interchain interaction in random coil polyelectrolytes is largely electrostatic and thus is strongly affected by ionic strength. Consequently, the mechanical properties of any polyelectrolyte network is affected by ionic strength. In order to evaluate the effect of ionic strength on interchain interactions, a cationic polyelectrolyte, chitosan [(1→4)-2-amino-2-deoxy-$\beta$-D-glucan], deacetylated chitin, was selected for this study. The removal of some or all acetyl groups from chitin imparts the polycationic nature to chitosan.[1] We selected chitosan since it is the only known available high molecular weight cationic polysaccharide.

The film-forming qualities of chitosan, methods of film preparation, and some mechanical properties such as breaking stress and tensile elongation have been reported.[1]

Previously, we examined the network-forming mechanism of polyelectrolytes using films cast by the evaporation of solvent from chitosan solutions.[2-4] The results revealed the electrostatic mechanism of interaction and nonideal rubber-like elasticity of the films. The non-Guassian be-

0024-9297/82/2215-0631$01.25/0 © 1982 American Chemical Society

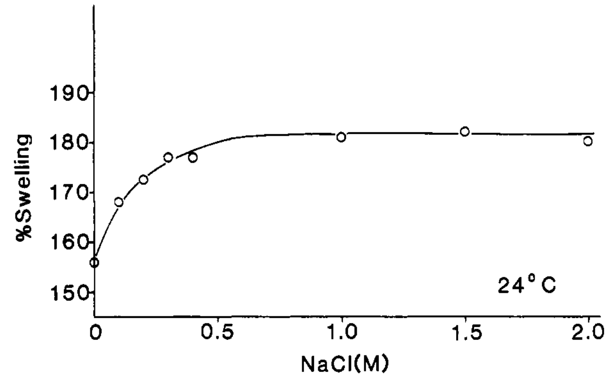

**Figure 1.** Effect of ionic strength on swelling of chitosan film.

havior was attributed to the increase in cross-linking density or the increase in electrostatic or hydrogen bonding upon elongation between the chains as they became more aligned during deformation.

This study was carried out in order to evaluate the influence of ionic strength on both the linear and nonlinear mechanical stress relaxation in simple extension and on the internal stress of polyelectrolyte films. The films were tested in a swelling medium containing different concentrations of NaCl to determine the effect of ionic strength on the chitosan molecules in the network and its repercussions on the relaxation process.

## Experimental Methods

**Sample Preparation.** Chitosan (Flonac-N, Velsicol) was dissolved in dilute acetic acid (0.1665 N) to make a 1.5% (w/w) solution. The chitosan solution was allowed to stand overnight and was then filtered. Films were prepared by drying the chitosan solution in an oven at 80 °C for approximately 24 h. Dried chitosan films were then neutralized by immersion in NaOH solution (1.0 N) for 20 min and immediately washed several times with deionized water until the pH of the wash water remained constant near neutral. The films were cut and stored in deionized water until used.

**Determination of the Degree of Swelling.** Chitosan film samples were immersed in deionized water and in NaCl solutions (0.2, 0.4, 1.0, and 2.0 N) at 24 °C. The weights of the swollen films were determined at 12-h intervals until they remained constant. After the weights of the swollen samples were determined, the films were dried and weighed and their densities were determined with a pycnometer to obtain the volume fraction of swollen chitosan films.[4,5]

**Mechanical Tests.** Tensile tests were carried out on strips (thickness = 2.0 mm; width = 5.5 mm; length = 10 mm) of chitosan film with an Instron universal testing machine Model 1122 (Instron Corp.). Stress relaxation of the chitosan films was determined while the films were immersed in the swelling medium at room temperature (24 °C) and at a deformation rate of 500 mm/min. For the internal stress experiment, the maximum strain was 5%. The strain imposed was between 5 and 40% for the stress relaxation experiments. After the deformation, 5–10 min was allowed for relaxation to calculate the maximum time at which there was no change in the degree of swelling.[3,4]

## Results and Discussion

The volume fraction of the polymer in the swollen film was calculated assuming isotropic swelling (Table I). The plot of the uptake of the swelling medium by the chitosan film vs. NaCl concentration (Figure 1) clearly indicated an increase in swelling, salting-in effect, up to values of 0.4 N NaCl concentration, above which an equilibrium value of 180% (w/w) swelling was established.

Stress relaxation curves of swollen chitosan films at different elongations up to 5% were used to assess the internal stresses due to the condition of the film casting. The Kubat–Rigdhal method was used to determine the internal stresses.[6,7] The steepest slope from each curve of stress vs. log time for a series of specimens tested at different elongations up to 5% was taken. The slopes were then plotted against the initial stress, i.e., the stress from which relaxation was initiated (Figure 2). The intercepts obtained by extrapolation of the straight lines and their slopes are given in columns 3 and 4 of Table I, respectively. The internal stresses decreased with increasing NaCl concentration and changed from positive to negative at ionic strengths between 0.4 and 1.0, which corresponds roughly to the plateau zone observed in the swelling experiments (Figure 1). The decrease in the internal stress, resulting from an increase in the internal resistance of the molecules in the network to the applied stress,[6,9] can be due to an increase in counterions bound onto the polyion chains with increased salt concentration.[10] This effect increases friction by decreasing the electrostatic repulsive forces sufficiently to allow interchain hydrogen bonding. The increase in hydrogen bonding also causes an increase in the relaxation time at higher salt concentrations (Table II).

Table I
Volume Fraction of Chitosan and Internal Stress Parameter in Swollen Film

| NaCl concn, N | vol fraction of chitosan | internal stress, g/mm$^2$ | [d$\sigma$/d ln $t$]/init stress |
|---|---|---|---|
| 0.0 | 0.6316 | 5.6 | 0.700 |
| 0.2 | 0.6109 | 2.4 | 0.594 |
| 0.4 | 0.6061 | 0.2 | 0.375 |
| 1.0 | 0.6051 | −1.2 | 0.206 |
| 2.0 | 0.6049 | −2.6 | 0.014 |

Table II
Maxwell Model Components for Swollen Chitosan Films as a Function of the Ionic Strength in the Swelling Solution[a]

| NaCl concn, N | $E_1$, g/mm$^2$ | $\tau_1 \times 10^{-4}$, s | $E_2$, g/mm$^2$ | $\tau_2 \times 10^{-4}$, s |
|---|---|---|---|---|
| 0.0 | 252 | 1.89 | 1.02 | 0.85 |
| 0.2 | 380 | 1.94 | 1.02 | 0.86 |
| 0.4 | 435 | 2.10 | 1.02 | 0.90 |
| 1.0 | 460 | 2.21 | 1.02 | 0.93 |
| 1.5 | 593 | 2.40 | 1.02 | 0.95 |
| 2.0 | 757 | 2.70 | 1.02 | 0.98 |

[a] 5% deformation.

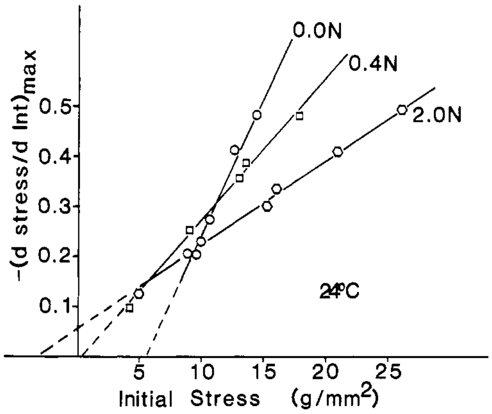

**Figure 2.** Internal stress Kubat–Rigdhal analysis in swollen chitosan films at different NaCl concentrations.

The apparent Young's modulus was calculated from the stress relaxation data by using the expression[11,12]

$$E_a(t,\lambda) = \frac{3f(t)V^{1/3}}{A(\lambda - \lambda^{-2})}$$

Table III
Relaxation Times for Some Biopolymer Networks

| compound | concn, % (w/w) | first relaxation time, s | type of bond |
|---|---|---|---|
| agar-agar gel[a] | 2.6 | $1.5 \times 10^5$ | hydrogen |
| agar-agar gel[b] | 2.0 | $1.0 \times 10^5$ | hydrogen |
| agarosa gel[b] | 2.0 | $9.8 \times 10^4$ | hydrogen |
| agarosa gel[b] | 1.6 | $5.9 \times 10^4$ | hydrogen |
| agarosa gel[b] | 1.4 | $4.9 \times 10^4$ | hydrogen |
| agarosa gel[b] | 1.25 | $3.8 \times 10^4$ | hydrogen |
| curdlan gel[c] | 2.0 | $6.0 \times 10^2$ | electrostatic |

[a] Reference 17. [b] Reference 19. [c] Reference 18.

where $E_a(t,\lambda)$ is the apparent relaxation Young's modulus (g/mm$^2$), $f(t)$ is the time-dependent force (g), $V$ is the volume fraction of the polymer in the swollen film, $A$ is the cross-sectional area of the network in the unrestricted state (mm$^2$), and $\lambda$ is the extension ratio.

Young's moduli at a standard time (7 min) from linear stress relaxation obtained at 5% elongation were plotted vs. the ionic strength of the swelling media (Figure 3). The elastic modulus increases with increasing ionic strength, showing a plateau at ionic strength between 0.4 and 1.0. This ionic strength region corresponds to the leveling-off zone in the swelling experiment and also to the point where the change from positive to negative values occurs for the internal stresses.

Linear stress relaxation curves were fitted into a generalized Maxwell model using the method of successive residuals.[13] The first components of the model, Young's modulus and relaxation time, for each ionic strength are shown in Table II, where both values increase with increasing ionic strength.

The relaxation times of chitosan film determined in this experiment are of the order of $10^4$ s. In cross-linked rubber-like materials, the stress relaxation behavior is associated with three main processes,[14-16] one with the orientation of the free molecular chain segments, with relaxation times between $10^{-4}$ and $10^{-6}$ s, another with the rearrangement and friction of segments making the network structure, with relaxation times of $10^2$–$10^5$ s, and the last with the rearrangement of interchain chemical bonds, with relaxation times between $10^7$ and $10^9$ s. The relaxation times determined in this experiment are on the order of magnitude corresponding to the rearrangement of the chitosan chains in the network. The relaxation time of chitosan film, $10^4$ s, can also be compared with those of other biopolymers (Table III). Relaxation times on the order of $10^3$–$10^5$ s have been related to the electrostatic interactions and hydrogen bonds,[17-19] which is in accord with our previous results.[2,4]

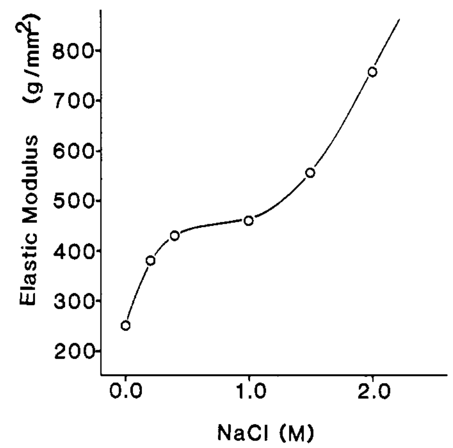

**Figure 3.** Effect of ionic strength on the Young's modulus $E_a(t_1\lambda)$ (g/mm$^2$) at 5% deformation.

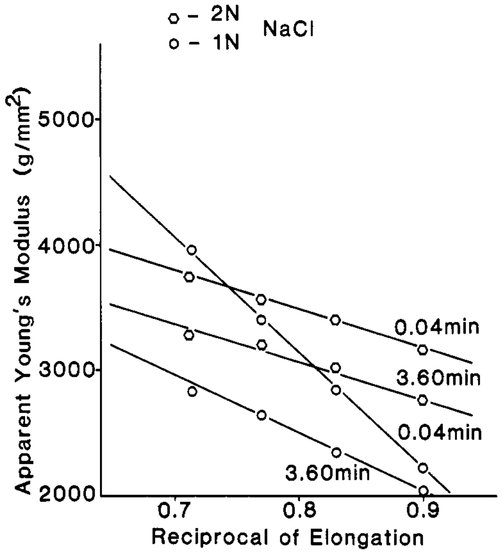

**Figure 4.** Apparent Young's modulus $E_a(t_1\lambda)$ (g/mm$^2$) vs. inverse of elongation ratio ($\lambda^{-1}$).

The experimental values of the apparent Young's modulus for deformation between 5 and 40% were interpreted by using the Mooney–Rivlin equation[20-23]

$$E_a(t,\lambda) = 6C_1 + 6C_2\lambda^{-1}$$

Thus a plot of $E_a(t,\lambda)$ vs. $\lambda^{-1}$ at various times gave a straight line with an intercept $6C_1$ and slope $6C_2$. Selected values are shown in Figure 4 and for all the samples in Table IV. Figure 5 shows $C_1$ decreasing with increasing NaCl concentration in the swelling media. This phenomenon is caused by a decrease in the electrostatic repulsive

Table IV
Mooney–Rivlin Equation Constants for Chitosan Film as a Function of Time and Sodium Chloride Concentration in the Swelling Solution[a]

| NaCl concn, N | constants, g/mm$^2$ | time, s | | | | | |
|---|---|---|---|---|---|---|---|
| | | 3.0 | 8.0 | 17.0 | 41 | 110 | 220 |
| 0.0 | $6C_1$ | 10452 | 10204 | 10205 | 9922 | 9799 | 9413 |
| | $6C_2$ | -9818 | -9576 | -9482 | -9316 | -8962 | -8800 |
| 0.2 | $6C_1$ | 8523 | 8310 | 8119 | 7914 | 7637 | 7491 |
| | $6C_2$ | -7444 | -7245 | -7059 | -6858 | -6583 | -6453 |
| 0.4 | $6C_1$ | 7344 | 7238 | 7160 | 7005 | 6794 | 6682 |
| | $6C_2$ | -5584 | -5526 | -5482 | -5351 | -5154 | -5017 |
| 1.0 | $6C_1$ | 6612 | 6446 | 6290 | 6128 | 5962 | 5626 |
| | $6C_2$ | -4832 | -4709 | -4588 | -4438 | -4293 | -3937 |
| 2.0 | $6C_1$ | 5883 | 5705 | 5664 | 5571 | 5453 | 5272 |
| | $6C_2$ | -2987 | -2895 | -2764 | -2749 | -2749 | -2749 |

[a] 10–40% deformation.

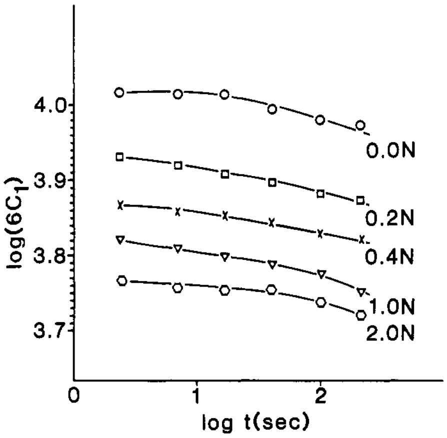

**Figure 5.** log $(6C_1)$ vs. log $t$ at different NaCl concentrations.

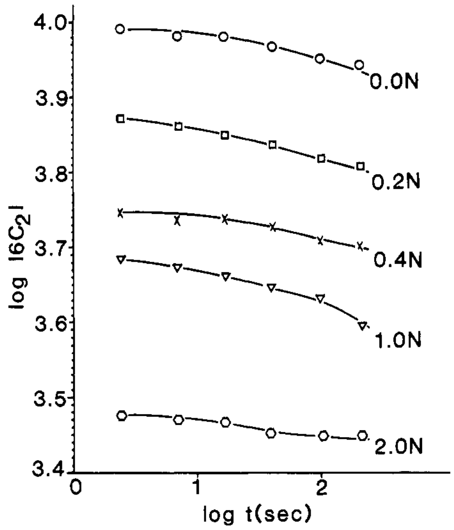

**Figure 6.** log $|6C_2|$ vs. log $t$ at different NaCl concentrations.

forces as a result of the neutralization of the fixed charges on chitosan by counterion bonding. This is in accord with the decrease in the internal stress observed with increasing ionic strength. The counterion bonding decreases with chain stiffness, making the chitosan molecular conformation more ideal[8] since electrostatic interaction can impair the validity of single-chain statistics.[24] Accordingly, Table IV shows the tendency of $6C_2$ to approach the ideal behavior ($6C_2 = 0$) with an increase in NaCl concentration.

Figures 5 and 6 show the log of $6C_1$ and the log of $|6C_2|$ against the log of time. Figure 5 shows that in all cases $6C_1$ decreases. The decrease can be associated with the readjustment of entanglements in the network,[2] a phenomenon that is also supported by relaxation time from the linear stress relaxation experiments as discussed previously. Figure 6 also indicates an increase of $6C_2$ with time, which can be related to the renewal of the random configuration of the polyelectrolyte molecules in the network.[23]

## Conclusions

The results of this study on mechanical properties of polyelectrolyte film indicated the following:

(1) The polyelectrolyte network in films showed a salting-in effect. The chitosan film swelled up to ionic strength 0.4, above which an equilibrium value of 180% (w/w) was established.

(2) Internal stresses decreased with an increase in ionic strength and became negative at ionic strength between 0.4 and 1.0. This decrease may be due to an increase in the internal resistance of chitosan chains due to an increase in ion condensation onto the polyelectrolyte chains.

(3) Linear stress relaxation was described by a two-element Maxwell model, where the elastic modulus increased with increasing NaCl concentration, with an inflection point at ionic strength between 0.4 and 1.0 and relaxation times of the order of $10^4$ s. These results suggest a rearrangement of the chitosan chains within the network and the electrostatic nature of the bonds responsible for the film structure.

(4) Nonlinear stress relaxation described by the Mooney–Rivlin equation showed a decrease in $C_1$ and an increase in $C_2$ with time. This was associated with the readjustment of entanglements and renewal of the random configuration of the chitosan molecules in the network.

## Nomenclature

| | |
|---|---|
| $A$ | cross-sectional area of the network in the unrestricted state |
| $C_1$ and $C_2$ | constants in Mooney–Rivlin equation |
| $E_a(t_1\lambda)$ | apparent relaxation Young's modulus |
| $E_1$ and $E_2$ | first and second elastic component in the generalized Maxwell model |
| $f(t)$ | time-dependent force |
| $t$ | time |
| $\lambda$ | extension ratio |
| $\sigma$ | stress |
| $\tau_1$ and $\tau_2$ | first and second relaxation time from the generalized Maxwell model |

**Acknowledgment.** This study was partially supported by MIT Sea Grant No. 88133 from NOAA, Department of Commerce, Office of Sea Grant, Na79AA-D-00-101, and by CONICIT, Venezuela, and the Instituto Tecnologico para Postgraduados (ITP) Foundation, Spain. We thank Dr. Dean Horn and Professor J. Connor of the MIT Sea Grant Office and Professor Frederick J. McGarry of the Department of Materials Science and Engineering, MIT, for their support and Mr. Peter Perceval and Mr. R. Pariser for providing Flonac-N. We also thank Elizabeth Robinson Lang for helpful criticism.

## References and Notes

(1) Muzzarelli, R. A. A. "Chitin"; Pergamon Press: Oxford, 1977; p 1.
(2) Kienzle-Sterzer, C. A.; Rodriguez-Sanchez, D.; Rha, C. K. "Rheology"; Plenum Press: New York, 1980; Vol. 3, p 621.
(3) Kienzle-Sterzer, C. A.; Rodriguez-Sanchez, D.; Rha, C. K., accepted for publication in *Makromol. Chem.*
(4) Kienzle-Sterzer, C. A. Master of Science Thesis, Massachusetts Institute of Technology, Cambridge, Mass., 1980.
(5) Hasa, J.; Ilavsky, M. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 263.
(6) Kubat, J.; Rigdhal, M. *Mater. Sci. Eng.* **1975**, *21*, 63.
(7) Kubat, J.; Rigdhal, M. *Int. J. Polym. Mater.* **1975**, *3*, 287.
(8) Adler, R. S.; Freed, K. F. *J. Chem. Phys.* **1980**, *72*, 4186.
(9) Coxon, L. D.; White, J. R. *J. Mater. Sci.* **1979**, *14*, 1114.
(10) Chien, H. W.; Isihara, C. H.; Isihara, A. *Polym. J.* **1976**, *8*, 288.
(11) Kramer, O.; Greco, R.; Ferry, J. D.; McDonel, E. T. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 1675.
(12) Mark, J. E. *Rubber Chem. Technol.* **1975**, *51*, 731.
(13) Lipka, J. L. "Graphical and Mechanical Computation"; Wiley: New York, 1918.
(14) Bartenev, G. M.; Lyalina, N. M. *Vysokomol. Soedin., Ser. A* **1970**, *12*, 922.
(15) Bartenev, G. M.; Lyalina, N. M. *Vysokomol. Soedin., Ser. A* **1970**, *12*, 922.
(16) Bartenev, G. M.; Zelener, Y. V. *Polym. Mech.* **1975**, *11*, 94.
(17) Arakawa, K. *Bull. Chem. Soc. Jpn.* **1961**, *34*, 1233.
(18) Konno, A.; Azechi, Y.; Kimura, H. *Agric. Chem.* **1979**, *43*, 101.
(19) Watase, M.; Arakawa, K. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 1830.
(20) Mooney, M. *J. Appl. Phys.* **1948**, *19*, 434.
(21) Rivlin, R. S. *Philos. Trans. R. Soc. London, Ser. A* **1948**, *241*, 379.
(22) Taylor, C. R.; Greco, R.; Kramer, O.; Ferry, J. D. *J. Soc. Rheol.* **1976**, *20*, 141.
(23) Greco, R. *Eur. Polym. J.* **1978**, *14*, 233.
(24) Dusek, K.; Prins, W. *Adv. Polym. Sci.* **1969**, *6*, 1.