Table I
Values of $\partial(K_2 - K_1)/\partial C_s \times 10^3$ in (S·L)/(cm·mol) for Various Polyions and Various Quaternary Ammonium Ions[a]

	Me_4N^+	Et_4N^+	Pr_4N^+	Bu_4N^+
p(Et-co-MA)	8	12	5	7
	2	0	0.7	0.5
p(MVE-co-MA)	22	22	29	32
	12	6.5	7	12
p(EVE-co-MA)	30	32	34	38
	6	10	13	16
p(iBVE-co-MA)	36	38	38	42
	16	12	16	11
p(nBVE-co-MA)	56	48	48	46
	11	10	12	15

[a] For each copolymer, the first row of values is for the low salt region ($C_s < 0.0008$ mol/L) and second row is for the saturated region.

$Et_4NBr > Me_4NBr$ and the strength of hydrophobic interaction per alkyl side chain follows the order n-$C_4H_9 \sim i$-$C_4H_9 > C_2H_5 > CH_3$. Accordingly, it can be concluded that tetraalkylammonium ions must be bound to the polyion due to hydrophobic interactions.

References and Notes

(1) Tanford, C. "The Hydrophobic Effect: Formation of Micelles and Biological Membrane"; Wiley-Interscience: New York, 1973.
(2) Chen, Chang-Hwei; Berns, D. S. *J. Phys. Chem.* **1977**, *81* (2), 125.
(3) Gregor, H. P. "Charged and Reactive Polymers"; Sélégny, Ed.; D. Reidel Publishing Co.: Dordrecht, The Netherlands, 1974; Vol. 1, p 87.
(4) Chen, Chang-Hwei; Berns, D. S. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 3407.
(5) Martin, P. J.; Morss, L. R.; Strauss, U. P. *J. Phys. Chem.* **1980**, *84*, 577. Martin, P. J.; Strauss, U. P. *Biophys. Chem.* **1980**, *11*, 397.
(6) Miyamoto, S.; Ishii, Y.; Ohnuma, H. *Makromol. Chem.* **1981**, *182*, 483.
(7) Miyamoto, S. *Biophys. Chem.* **1979**, *9*, 79.
(8) Leyte, J. C.; Mandel, M. *J. Polym. Sci., Part A* **1964**, *2*, 1879.
(9) Dubin, P. L.; Strauss, U. P. *J. Phys. Chem.* **1970**, *74*, 2842.
(10) Sasaki, S.; Minakata, A. *Biophys. Chem.* **1980**, *11*, 199.
(11) Miyamoto, S.; Imai, N. *Biophys. Chem.* **1980**, *11*, 91.
(12) Ikegami, A. *J. Polym. Sci., Part A* **1964**, *2*, 907.
(13) Wen, Wen-Yang "Water and Aqueous Solutions"; Horne, R. A., Ed.; Wiley-Interscience: New York, 1971.
(14) Begala, A. J.; Strauss, U. P. *J. Phys. Chem.* **1972**, *76*, 254.

Sodium Ion Diffusion in Aqueous Salt-Free Heparin Solutions

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Received November 14, 1980

ABSTRACT: Sodium ion tracer diffusion coefficients have been determined in aqueous salt-free heparin solutions at 25 °C over a concentration range of 4×10^{-5} to 8×10^{-2} N. With increasing dilution, the Na^+ diffusion coefficients decreased, reached a shallow minimum, and then increased. The data are discussed in light of the Manning and Yoshida theories. Condensation of multivalent ions onto heparin is demonstrated in aqueous salt solutions of excess polyelectrolyte to salt concentration.

It has been demonstrated[1,2] that the charge fraction of polyelectrolyes, i.e., the fraction of stoichiometric charge on the polyelectrolyte uncompensated by bound counterions, of high charge density can be determined by using the Manning theory[3-5] together with the experimentally determined counterion and coion tracer diffusion coefficients in aqueous solution containing simple salt. With Na^+ as the counterion, rN_p equivalents of Na^+ of the total $N_p + N_s$ equivalents are condensed on the polyion and the fraction of Na^+ in the solution which is condensed, $f^c{}_{Na^+}$, is[1,2]

$$f^c{}_{Na^+} = rN_p/(N_p + N_s) = rX/(X + 1) \qquad (1)$$

where $X = N_p/N_s$, N_p and N_s are the equivalent concentrations of polyelectrolyte and salt, respectively, and r is the fraction of condensed or bound Na^+ ions originally on the polyelectrolyte and $1 - r$ is the charge fraction of the polyelectrolyte. From the Manning theory we have shown[1,2] that

$$f^c{}_{Na^+} = 1 - (D_{Na^+}/D_{Na^+}{}^\circ)(D_{Cl^-}/D_{Cl^-}{}^\circ)^{-1} \qquad (2)$$

where D_i and $D_i{}^\circ$ are the small-ion i diffusion coefficients in the presence of polyelectrolyte and at infinite dilution of salt in the absence of polyelectrolyte, respectively. Plots of eq 1 as $f^c{}_{Na^+}(X + 1)$ vs. X for several polyelectrolytes were found to be linear over the range of X studied.[1,2] The agreement for the experimental r values with the Manning theory predictions for monovalent counterions, $r = 1 - \xi^{-1}$, was excellent for the sodium salts of dextran sulfate, alginate, and poly(styrenesulfonate) and was good for DNA and heparin.[1,2] The fraction of Ca^{2+} ions condensed on heparin[1] and on DNA[2] determined from calcium and coion diffusion coefficients was found to be in excellent agreement with that predicted for divalent counterions from the Manning theory, $r = 1 - (2\xi)^{-1}$. Thus, the general experimental accord with the Manning theory for highly charged polyelectrolytes showed that the charge fraction in salt solutions was found to be constant, independent of ionic strength, independent of the ionic group of the polyelectrolyte, and dependent only on the charge density parameter ξ

$$\xi = e^2/\epsilon kTb \qquad (3)$$

where e is the protonic charge, ϵ is the dielectric constant of the solvent, T is the temperature, b is the average distance between charge groups on the polyelectrolyte, and k is the Boltzmann constant.

The salt-free limit of eq 1 gives $f^c{}_{Na^+} = r$, which according to the Manning theory is $r = 1 - (Z_1\xi)^{-1}$, indicating that the fraction of counterions dissociated from a polyion is constant and dependent only on its charge density[6] and Z_1, the valence of the counterion. Since this is inherent in the Manning theory, the salt-free limiting laws for the counterion diffusion coefficient D_{Na^+}, the counterion activity coefficient γ_{Na^+}, and the activity osmotic coefficient

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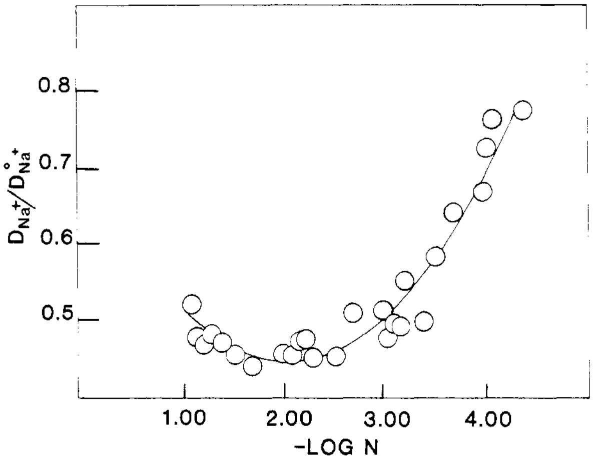

Figure 1. Sodium ion diffusion ratios in aqueous salt-free heparin solutions of concentration N. The values are uncorrected for the diffusion of heparin.

ϕ depend *only* on the nature of the polyelectrolyte through ξ^{3-5}

$$D_{Na^+}/D_{Na^+}^\circ = 0.87\xi^{-1} \qquad (4)$$

and

$$\gamma_{Na^+} = 0.61\xi^{-1} \qquad (5)$$

where $D_{Na^+}^\circ$ is the Na^+ ion diffusion coefficient in the absence of polyelectrolyte at infinite dilution. It is of interest to explore salt-free polyelectrolyte solutions to examine if the above expressions are valid.

Here we report Na^+ ion diffusion results obtained for aqueous solutions of the sodium salt of heparin and compare these results with pertinent ones reported.[7-9] Also, the condensation of multivalent ions on heparin is demonstrated from diffusion studies. Heparin is an interesting polyelectrolyte because of its high charge density ($\xi = 3.0$) and because it contains three different ionic groups, carboxyl, N-sulfate, and O-sulfate groups. Counterion and coion diffusion coefficients for heparin solutions containing Na_2SO_4 and $CaCl_2$ indicate constant charge fractions of sodium heparin and calcium heparin of 0.43 and 0.14, respectively, over a large X range. These values are in good agreement with their respective $(Z_1\xi)^{-1}$ values of 0.33 and 0.17 predicted by the Manning theory. Sodium-23 NMR studies indicate condensation of Na^+ ions on heparin.[10]

Experimental Section

The capillary diffusion technique has been described previously.[2,11] The sodium heparin sample is the same sample used in a previous study.[11] The radioactive salts $^{22}NaCl$ and $^{154}EuCl_3$ were supplied by ICN Pharmaceuticals, Inc., and radioactive sodium heparin with ^{35}S on the sulfonate group was supplied by Amsham, Inc.

Results and Discussion

Table I
Sodium Ion Diffusion Coefficients in Aqueous Sodium Heparin Solutions at 25 °C

$N \times 10^3$, equiv/L	$D_{Na^+} \times 10^5$,[a] $cm^2\ s^{-1}$	$N \times 10^3$, equiv/L	$D_{Na^+} \times 10^5$,[a] $cm^2\ s^{-1}$
0.040	1.03 ± 0.04	5.00	0.60 ± 0.04
0.080	1.02 ± 0.03	6.00	0.63 ± 0.05
0.090	0.97 ± 0.09	7.00	0.63 ± 0.04
0.100	0.89 ± 0.05	8.00	0.61 ± 0.01
0.200	0.86 ± 0.03	10.0	0.61 ± 0.05
0.300	0.78 ± 0.02	20.0	0.59 ± 0.05
0.400	0.66 ± 0.05	30.0	0.61 ± 0.03
0.600	0.74 ± 0.06	40.0	0.63 ± 0.05
0.700	0.65 ± 0.06	50.0	0.64 ± 0.03
0.800	0.66 ± 0.05	60.0	0.62 ± 0.04
0.900	0.63 ± 0.02	70.0	0.64 ± 0.04
1.00	0.68 ± 0.05	80.0	0.69 ± 0.05
2.00	0.68 ± 0.06		
3.00	0.60 ± 0.02		
4.00	0.60 ± 0.07		

[a] Uncorrected for heparin diffusion.

Figure 1 and Table I contain the experimental diffusion data for aqueous sodium heparin over a polyelectrolyte concentration range of 4.0×10^{-5} to 8.0×10^{-2} N, where at infinite dilution the $D_{Na^+}^\circ$ value is 1.33×10^{-5} cm^2/s. The points were not corrected for the diffusion of heparin. The last portion of this paper reports that in salt-free and salt-containing heparin solutions, the heparin molecule diffusion coefficient is fairly constant at 0.16×10^{-5} cm^2 s^{-1} and thus, one need only subtract this value from those values in Figure 1 and Table I to obtain the counterion diffusion coefficient. Since the points in Figure 1 appear to be parabolic, the solid line is the computer fit for a quadratic equation. Figure 1 shows that the ratio $D_{Na^+}/D_{Na^+}^\circ$ decreases with increasing dilution, forming a fairly shallow minimum, and increases with further dilution. Similar dependencies of $D_{Na^+}/D_{Na^+}^\circ$ on the equivalent concentration N has been reported for other polyelectrolytes in salt-free solutions.[7-9] The dependency observed is not in agreement with that predicted from eq 4 nor from the Yoshida equation[14]

$$D_{Na^+}/D_{Na^+}^\circ = (1 + 1.300/\xi)/3 \qquad \text{for } \xi > 1 \qquad (6)$$

which was derived by assuming that condensed ions can move parallel to the axis of the polyion. Equations 4 and 6 have a phenomenological basis.[15] The experimental results are not in accord with eq 4 and 6 since both equations predict the diffusion coefficients to be independent of the polyelectrolyte concentration. Since the values of $D_{Na^+}/D_{Na^+}^\circ$ are most constant near the shallow minimum, the theoretical predictions might be compared with the experimental results at the minimum $D_{Na^+}/D_{Na^+}^\circ$ values. It is of interest that the minimum $D_{Na^+}/D_{Na^+}^\circ$ value of 0.33 for heparin ($\xi = 3.0$) in Figure 1 is in good agreement with the value of 0.29 predicted from eq 4 but in poor agreement with the value of 0.48 predicted from eq 6. It should be pointed out that this minimum $D_{Na^+}/D_{Na^+}^\circ$ value for sodium heparin in Table II was corrected for the diffusion of heparin because of its low molecular weight. A comparison of the minimum $D_{Na^+}/D_{Na^+}^\circ$ values obtained for other polyelectrolytes[7-9] in salt-free solutions is shown in Table II. An examination of eq 4 and 6 indicates that $D_{Na^+}/D_{Na^+}^\circ$ is linear in ξ^{-1} for both equations, with close agreement between them for low ξ values (approximately $\xi < 1.4$) and increasing disagreement as ξ increases. The least-squares slope of the minimum $D_{Na^+}/D_{Na^+}^\circ$ values vs. ξ^{-1}, shown in Figure 2, for the polyelectrolytes listed in Table II is 0.90 ± 0.21, which compares more favorably with the value of 0.87 predicted by Manning than with the value of 0.43 predicted by Yoshida.[12] At the value of N which gives the minimum $D_{Na^+}/D_{Na^+}^\circ$ and at nearby values of N, the experimental diffusion ratios are in good agreement with both the Manning and Yoshida values at low ξ values ($\xi = 1.66$ and 1.43), while at higher ξ values ($\xi = 2.85$ and 3.0) better agreement is observed with the Manning line. More intermediate ξ values are needed to verify this and to verify if the minimum $D_{Na^+}/D_{Na^+}^\circ$ values are linear with respect to ξ^{-1}, as predicted. It is evident from the data, however, that for high ξ values, Yoshida's assumption that the mobility of the condensed ions on the polyion is equal to one-third that of the free ions in solutions substantially overestimates their actual mobility.

Table II
Comparison of the Minimum $D_{Na^+}/D_{Na^+}{}^{\circ}$ Experimental Values with Those Predicted Theoretically for Several Polyelectrolytes in Salt-Free Solutions

polyelectrolyte	ionic group on polyelectrolyte	ξ	exptl[c]	theor eq 4	theor eq 6
heparin	COO^-, OSO_3^-, $NHSO_3^-$	3.0	0.33	0.29	0.48
dextran sulfate[a]	OSO_3^-	2.85	0.27	0.30	0.49
poly(styrenesulfonate)[b]	SO_3^-	2.85	0.39	0.30	0.49
ι-carrageenan[a]	OSO_3^-	1.66	0.65	0.52	0.59
alginate[a]	COO^-	1.43	0.62	0.61	0.64

[a] Reference 7. [b] References 8 and 9. [c] $D_{Na^+}{}^{\circ} = 1.33 \times 10^{-5}$ cm² s⁻¹.

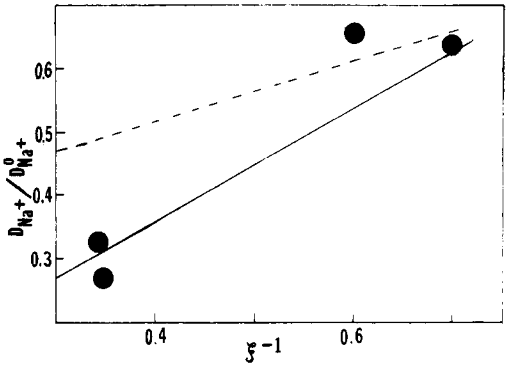

Figure 2. Minimum $D_{Na^+}/D_{Na^+}{}^{\circ}$ values vs. ξ^{-1} for the polysaccharides in Table II. The solid line is predicted by Manning and the dashed line by Yoshida.

The experimental results suggest that the ability of the counterions to bind to polyelectrolytes depends strongly on the linear charge density of the polyion and not on the mobility of condensed counterions.

Manning and Yoshida predict that the charge fraction and $D_{Na^+}/D_{Na^+}{}^{\circ}$ depend only on ξ and are independent of N for salt-free solutions. Since this is not in accord with the experimental data, it is tempting to attribute the increase in $D_{Na^+}/D_{Na^+}{}^{\circ}$ with increasing dilution below the minimum (at approximately 10^{-3} N) to an increase in the charge fraction of the polyelectrolyte because of decreased screening of the polyelectrolyte charges as it is diluted. An increase in the charge fraction may be the reason for the observed increase in the sodium ion activity coefficients *below* 10^{-3} N in salt-free solutions of sodium poly(styrenesulfonate),[14] sodium carrageenan,[15,16] sodium dextran sulfate,[17] sodium (carboxymethyl)cellulose,[17] sodium alginate,[19] sodium poly(vinyl sulfate),[18] and sodium poly(methylstyrenesulfonate).[20] No such minimum has been noted for the sodium ion activity coefficient in aqueous sodium heparin solutions down to 1×10^{-4} N.[21,22] Having covered a wide poly(methylstyrenesulfonate) concentration range, Oman and Dolar[20] observed a minimum in counterion activity coefficients in the concentration range 10^{-3}–10^{-2} N for salt-free solutions for both monovalent and divalent counterions. In the region of the minimum, the experimental counterion activity coefficients agreed best with Manning predictions. This suggests that at the minimum, when the counterion–polyion interactions are at a maximum, the charge fraction of the polyelectrolyte is at a minimum, and the Manning theory gives this effective value in salt-free solutions.

For heparin concentrations above 5×10^{-2} N, Figure 1 shows that $D_{Na^+}/D_{Na^+}{}^{\circ}$ increases an N increases. Similar results have been obtained for sodium dextran sulfate, sodium carrageenan, and sodium alginate.[7] Dolar et al.[20] reported an increase in the Na^+ and Tl^+ counterion activity coefficients in the polyelectrolyte concentration range 10^{-2} to 5×10^{-1} N for the sodium salts of poly(methylstyrenesulfonic acid) and an increase in the osmotic coefficient for only the monovalent salts in the same concentration range.[23] Agreement with the Manning theory was best for the minimum values of the osmotic coefficients. Dolar et al.[23] attribute the increase in the osmotic coefficients to an increase in the charge fraction of the polyelectrolyte as the polyelectrolyte concentration increases. It appears unlikely that this should occur in this concentration range because of greater polyelectrolyte overlap. If the counterion–polyion interaction is a maximum at the minimum $D_{Na^+}/D_{Na^+}{}^{\circ}$ value, it would be expected that this maximum interaction would at least persist and *not* decrease as the concentration increases. Possibly, the trend observed after the minimum is due to competition for water molecules between the counterion and the polyion. As their concentration is increased, the polyions attract more and more water molecules, which decreases their availability for the counterions, thereby making the counterions more mobile. The Zn^{2+} and Ca^{2+} ion activity coefficient data for the poly(styrenesulfonates)[24] and the osmotic coefficients for the Mg^{2+} and Ca^{2+} poly(styrenesulfonate) solutions[25] show much more shallow minima and a very small rise with increasing concentration, when compared to the Na^+ ion data. The more hydrated divalent ions can retain their hydration spheres more effectively than can Na^+ ions as the polyion concentration increases.

Generally, good agreement was found between the experimental counterion diffusion results and the Manning prediction for salt-containing polyelectrolyte solutions at X values greater than 3 for polyelectrolytes of $\xi > 1$. This agreement suggests that counterion condensation does take place, even though counterion diffusion monitors counterions in the ionic atmosphere. According to the Manning theory, the addition of the multivalent ions to a solution containing the salt-free monovalent salt of a polyelectrolyte whose ξ is greater than its critical value results in the replacement of a condensed monovalent counterion by the multivalent one. Then, the addition of tracer amounts of radioactive multivalent ions to solutions with an excess of polyelectrolyte to simple salt, i.e., high X values, should reveal the self-diffusion coefficient of the polyelectrolyte. For sodium heparin solutions in 0.000 50 N $CaCl_2$, the Ca^{2+} diffusion coefficient[11] was found to be $(0.147 \pm 0.014) \times 10^{-5}$ cm²/s and in 0.000 50 N NaCl the Eu^{3+} diffusion coefficient[26] was found to be $(0.157 \pm 0.020) \times 10^{-5}$ cm²/s, both values being constant for $X > 2$ and much lower than their values in polyelectrolyte-free simple salt solution. The proximity of the above diffusion coefficients for Ca^{2+} and Eu^{3+} suggests both are condensed on heparin and the diffusion coefficients are those for the heparain molecule. This is also borne out by recent results[27] which gave tracer Ca^{2+} ion diffusion coefficients of $(0.150 \pm 0.013) \times 10^{-5}$ and $(0.160 \pm 0.007) \times 10^{-5}$ cm²/s for salt-free sodium haparin solutions of 1.00×10^{-3} and 9.00×10^{-3} N, respectively. A slightly larger constant value of $(0.21 \pm 0.029) \times 10^{-5}$ cm²/s

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was observed for radioactively tagged heparin in 0.010 N Na_2SO_4 with X between 0.10 and 10.0.[26] Certainly, these data indicate that counterion condensation does take place and that the diffusion coefficient of the polyelectrolyte could be obtained from tracer diffusion studies of condensed or bound counterions. A recent review of counterion binding to polyelectrolytes summarizes the experimental evidence for this phenomena.[6]

Acknowledgment. This project was supported by Grant No. GM 21234, awarded by the Public Health Service, DHEW.

References and Notes

(1) Ander, P. *ACS Symp. Ser.* **1981**, *No. 150*, Chapter 28.
(2) Trifiletti, R.; Ander, P. *Macromolecules* **1979**, *12*, 1197.
(3) Manning, G. S. *J. Chem. Phys.* **1969**, *51*, 924.
(4) Manning, G. S. *J. Chem. Phys.* **1969**, *51*, 934.
(5) Manning, G. S. *J. Chem. Phys.* **1969**, *51*, 3249.
(6) Manning, G. S. *Acc. Chem. Res.* **1979**, *12*, 443.
(7) Lubas, W.; Ander, P. *Macromolecules* **1980**, *13*, 318.
(8) Fernandez-Prini, R.; Lagos, A. E. *J. Polym. Sci.* **1964**, *2*, 2917.
(9) Fernandez-Prini, R.; Baumgartner, E.; Liberman, S.; Lagos, A. E. *J. Phys. Chem.* **1969**, *73*, 1420.
(10) Herwat, L.; Laszlo, P.; Genard, P. *Nouv. J. Chim.* **1977**, *1*, 173.
(11) Ander, P.; Gangi, G.; Kowblansky, A. *Macromolecules* **1978**, *11*, 904.
(12) Yoshida, N. *J. Chem. Phys.* **1978**, *69*, 1978.
(13) Schmitt, A.; Varoqui, R. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 1087.
(14) Ueda, T.; Kobatake, Y. *J. Phys. Chem.* **1973**, *77*, 2995.
(15) Podlas, T.; Ander, P. *Macromolecules* **1969**, *2*, 433.
(16) Pass, G.; Phillips, G. O.; Wedlock, D. *Macromolecules* **1977**, *10*, 197.
(17) Satake, I., et al. *J. Polym. Sci.* **1959**, *60*, 169.
(18) Liquori, A. M., et al. *J. Polym. Sci.* **1959**, *60*, 169.
(19) Podlas, T.; Ander, P. *Macromolecules* **1970**, *3*, 154.
(20) Oman, S.; Dolar, D. *Z. Phys. Chem. (Frankfurt am Main)* **1967**, *56*, 1.
(21) Ascoli, F.; Botre, C.; Liquori, A. M. *J. Phys. Chem.* **1961**, *65*, 1991.
(22) Diakun, G. P., et al. *Macromolecules* **1978**, *11*, 1110.
(23) Kozak, D.; Kristan, J.; Dolar, D. *Z. Phys. Chem. (Frankfurt am Main)* **1971**, *76*, 85.
(24) Kozak, D.; Dolar, D. *Z. Phys. Chem. (Frankfurt am Main)* **1967**, *56*, 13.
(25) Omar, S.; Dolar, D. *Z. Phys. Chem. (Frankfurt am Main)* **1971**, *76*, 93.
(26) Ander, P.; Kowblansky, A. B.S. Thesis, Seton Hall University, 1978.
(27) Ander, P.; Lazaro, D., to be submitted for publication.

Effect of Chain Alignment on the Brillouin Scattering Spectra of Hydrostatically Extruded Polypropylene

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ABSTRACT: A detailed Brillouin scattering study of hydrostatically extruded polypropylene at room temperature is carried out. The spectra obtained in various scattering configurations are used to determine the hypersonic velocity and elastic constants of the uniaxially deformed polycrystalline polymer. As polypropylene is extruded, C_{33} increases rapidly with increasing extrusion, whereas C_{11} decreases slightly. This result reflects the increasing alignment of the polymer chain segment along the direction of extrusion. The elastic constant C_{13} decreases slightly, but C_{44} does not undergo significant change as the sample is extruded, thus indicating that the shear modulus is insensitive to the orientation of chain segments in semicrystalline polypropylene. Comparison of the Brillouin scattering results with the ultrasonic values indicates that considerable frequency dispersion in the elastic constants is present. Calculation of the orientation parameter using Mosely's theory does not yield correct results. Reasons for the discrepancy are discussed.

Introduction

When a high polymer sample is uniaxially deformed by extrusion it exhibits anisotropic mechanical properties. It has been known for some time that the sound velocity along the draw direction increases progressively with increasing orientation, whereas the sound velocity transverse to the draw direction may decrease or remain unchanged. It is the purpose of this paper to investigate the effect of extrusion on the elastic constants in hydrostatically extruded polypropylene using the Brillouin scattering technique.

Brillouin scattering is very useful in characterizing both the equilibrium and dynamic states of polymeric materials.[1] In Brillouin scattering, light is inelastically scattered from thermal phonons to produce side bands which are shifted from the incident frequency by an amount ν given by

$$\nu = \pm(V/\lambda_0)\{n_i^2 + n_s^2 - 2n_i n_s \cos\theta\}^{1/2} \qquad (1)$$

where θ is the scattering angle, λ_0 is the wavelength of the incident light in vacuo, V is the acoustic phonon velocity, and n_i and n_s are, respectively, indices of refraction of the incident and scattering light waves in their respective directions of propagation.

Most previous Brillouin scattering studies of polymers deal with liquid or clear solid amorphous samples, due to the experimental difficulty associated with a very strong central elastic peak which covers up the much weaker Brillouin side bands.[1,2] As a result, Brillouin scattering has not been used extensively in the study of semicrystalline polymers. However, recent development of high-contrast interferometry has alleviated the experimental difficulty and allows opaque samples to be studied.

In this paper, we report the Brillouin scattering study of hydrostatically extruded isotactic polypropylene using a five-pass Fabry-Perot interferometer system. We have examined the effect of extrusion on the elastic constants of polycrystalline polypropylene in various deformation states. This study should complement the results of polarized Raman scattering studies which we have reported previously.[3]

Experimental Section

The extruded polypropylene samples were kindly provided by Dr. H. Kanetsuna. The technique of preparation has been described previously.[4] An unextruded sample and samples with extrusion ratios (R_e) equal to 2.7, 3.0, 4.5, and 6.3 are used for the Brillouin scattering experiment. The extrusion ratio is defined as the ratio of the cross-sectional area of the original billet to that

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