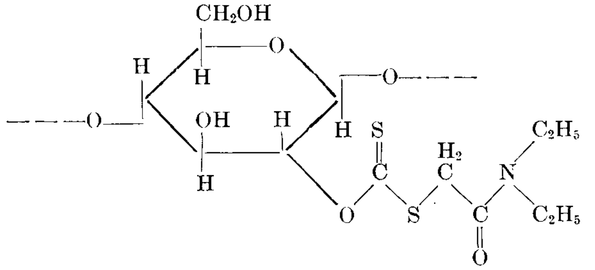
JOURNAL OF APPLIED POLYMER SCIENCE VOL. V, ISSUE NO. 18, PAGES 641-646 (1961)

Solution Properties of Diethylacetamide Cellulose Xanthate in Dimethyl Sulfoxide*

R. H. Cornell† and H. A. Swenson

The Institute of Paper Chemistry, Appleton, Wisconsin

Quite commonly the stable diethylacetamide derivative of cellulose xanthate is prepared in investigations concerned with the xanthation of cellulose. The side group is comparable in length with the parent glucose monomer unit,[1] which presumably will influence its properties in solution:



Although use of the light-scattering technique on solutions of common synthetic polymers has been extensive, its application to cellulose derivatives has been limited to investigations of the nitrate,[2-11] acetate,[12] carboxymethyl ether,[7,9,13] xanthate,[14,15] and caproate.[16]

The present study deals with the solution properties of diethylacetamide cellulose xanthate (hereafter referred to as DAX). Light-scattering and viscosity measurements are reported for a series of samples ranging in degree of substitution (D.S.) from 0.4 to 1.22.

EXPERIMENTAL

Samples

In each case the samples were fractions isolated by precipitation with water from a 1% solution of the derivative in 70% 2-chloroethanol at 25°C. The samples were chosen from different fractionations to obtain the desired range of substitution.

DAX Solutions

All light-scattering and viscosity determinations were obtained for solutions of the DAX derivative in a solvent composed of 90% dimethyl sulfoxide–10% water (90 DMSO). The dimethyl sulfoxide (Stepan Chemical Co., Chicago, Illinois) was purified by vacuum distillation from calcium hydroxide and stored in the frozen state. The solvent was prepared by adding 10% water by weight. The density of the solvent at 25°C. was 1.099 g./ml.

Complete solution of all of the DAX fractions was accomplished in less than 24 hr. The solutions were filtered through a sintered-glass filter (maximum pore size 2.0–2.5 microns). Two fractions (Samples 3 and 7) that filtered with unusual difficulty were centrifuged in specially designed cells at 19,000 r.p.m. in a helium atmosphere for 1.5 hr. Both techniques adequately removed extraneous dust from the solutions, without altering the solution concentration. Where possible, the solutions were transferred directly by filtering into a semioctagonal light-scattering cell (Brice-Phoenix D-104). Dilution was accomplished by adding filtered solvent directly to the light-scattering cell until data were obtained for four or five concentrations.

Light-Scattering Measurements

The light-scattering measurements were made using a Brice-Phoenix Photometer (Series 1937).[17] A wavelength of 5461 A. was used, since no significant fluorescence was detected for the DAX solutions at this wavelength, whereas, at a wavelength of 4358 A., fluorescence led to scattering ratios approximately 15% too high. The calibration was checked by measuring the excess turbidity of a 0.5% solution of Cornell University standard

---

* This paper is a portion of a thesis submitted in partial fulfillment of the requirements of The Institute of Paper Chemistry for the degree of Doctor of Philosophy from Lawrence College, Appleton, Wis., June, 1960. The work was carried out under the direction of Kyle Ward, Jr.

† Present address: Riegel Paper Corporation, Milford, New Jersey.

polystyrene in toluene. The value of 3.49×10^{-3} cm.$^{-1}$ was in good agreement with the value of 3.51×10^{-3} cm.$^{-1}$ reported by Maron and Lou.[18]

Scattering intensities were measured at angles of 45, 90, and 135°. All measurements were made at a temperature of 24 ± 1°C. Scattering ratios were obtained for the solvent and subtracted from the observed ratios for the solutions in the usual manner. The molecular weight (M_w) was obtained by the extrapolation of $Hc/\tau(90°, c)$ to zero concentration, according to the following relation:

$$Hc/\tau(90°, c) = 1/M_wP(90°) + 2A_2c \qquad (1)$$

where $H = [(32\pi^3n_0^2)/3N\lambda^4]\ (dn/dc)^2$, n_0 = refractive index of the pure solvent, N = Avogadro's number, λ = wavelength of the unpolarized incident light, and dn/dc = refractive index increment, c is the solution concentration (g./ml.), and A_2 is the second virial coefficient (ml. mole/g.^{2}). The correction for dissymmetry, $P(90°)$, was obtained from the tables of Doty and Steiner.[19] The correction for depolarization was determined and applied in the usual manner.[20] In spite of the fact that some of the solutions were colored, correction for selective adsorption was found to be unnecessary.

Refractive Index Measurements

The refractive index increment, *dn/dc*, for the DAX solutions was measured with a Rayleigh interferometer (Baird Associates, Cambridge, Mass.). The instrument was calibrated with aqueous solutions of sucrose.

Two preparations of 90% dimethyl sulfoxide were made. Samples 1, 3, and 4 were run with the first and Samples 2, 5, 6, and 7 with the other. As can be seen from Table I, the *dn/dc* values are quite different for the two series of runs. The consistent light-scattering results, however, indicate that the values are real.

It is possible that a small variation in the proportion of the two solvent components (which vary widely in refractive index) may have resulted in selective adsorption by the solute of the one component in preference to the other. A decrease in the refractive index increment with increasing substitution is seen in the samples with highest substitution. Both Jullander,[3] and Badger and Blaker[4] have reported a decrease in *dn/dc* with increasing D.S. for cellulose nitrate.

Viscosity Measurements

The reduced viscosities were determined at 25 ± 0.02°C. with an Ubbelohde dilution viscometer. Corrections for shear and kinetic energy were found to be negligible. The shear rates for all measurements were 550 ± 25 sec.$^{-1}$. The intrinsic viscosities, $[\eta]$, were determined by extrapolation of the logarithm of the reduced viscosity to zero concentration, according to the Martin relation:

$$\log(\eta_{sp}/c) = \log[\eta] + k[\eta]c \qquad (2)$$

RESULTS AND DISCUSSION

The summarized light-scattering and viscosity data are shown in Table I. The $Hc/\tau(90°, c)$ plots for the samples are shown in Figure 1 and the viscosity plots in Figure 2. The Martin constant, k, was calculated from eq. (2). The k_m constant

TABLE I
Summarized Light-Scattering and Viscosity Data

Sample	D.S.	Monomer mol. wt.	dn/dc [a]	Hc/τ (90°, c) $\times 10^6$	$[Z]$ [b]	ρ_u [c]	$M_w \times 10^{-5}$	D.P.$_w$	$[\eta]_{90\text{ DMSO}}$, dl./g.	Martin const.,[d] k	$k_m \times 10^4$ [e]
1	0.40	238	0.144	9.62	1.35	0.067	1.12	473	1.79	0.12	37.9
2	0.49	255	0.098	9.21	1.51	0.064	1.29	506	2.31	0.15	45.6
3	0.60	275	0.144	5.89	2.29	0.039	3.16	1150	4.40	0.18	38.0
4	0.80	313	0.144	5.48	1.72	0.067	2.45	781	2.44	0.21	31.6
5	0.92	336	0.098	2.88	1.43	0.058	4.01	1190	2.67	0.15	22.5
6	1.00	351	0.096	3.50	1.45	0.048	3.40	969	1.89	0.16	19.6
7	1.22	393	0.079	3.26	1.45	$\backsim$0.01	4.46	1130	2.04	0.19	18.0

[a] Refractive index increment.

[b] Limiting dissymmetry (at zero concentration).

[c] Depolarization factor for unpolarized incident light (at zero concentration).

[d] Martin constant calculated from eq. (2).

[e] $k_m = [\eta]/\text{D.P.}_w$.

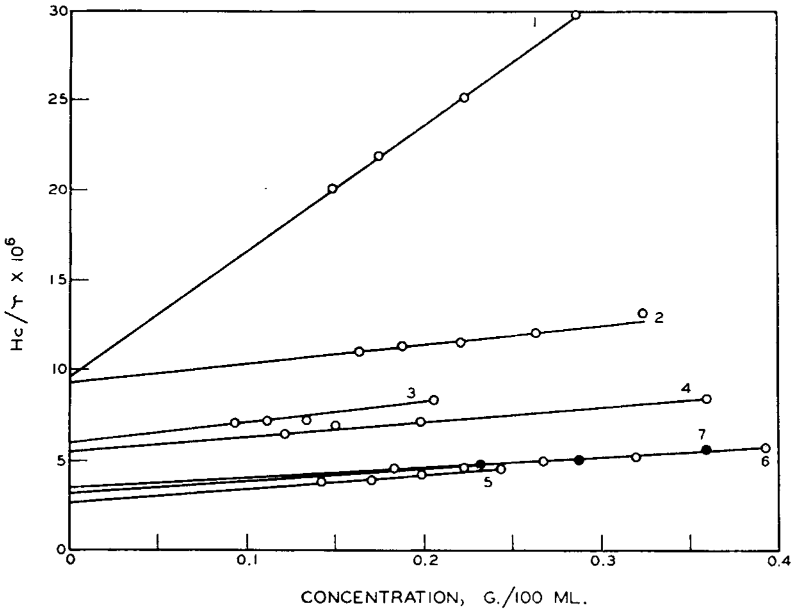


Fig. 1. Hc/τ (90°C., c) plots for DAX samples in 90% dimethyl sulfoxide.

was obtained from the modified Staudinger equation:

$$[\eta] = k_m \mathrm{D.P.}^a \quad (3)$$

The constant a has been assumed to be unity as has been found to be the case with other derivatives of cellulose.[8,10,21] The assumption was necessary since determination of the constant for each D.S. level was not possible in the present study.

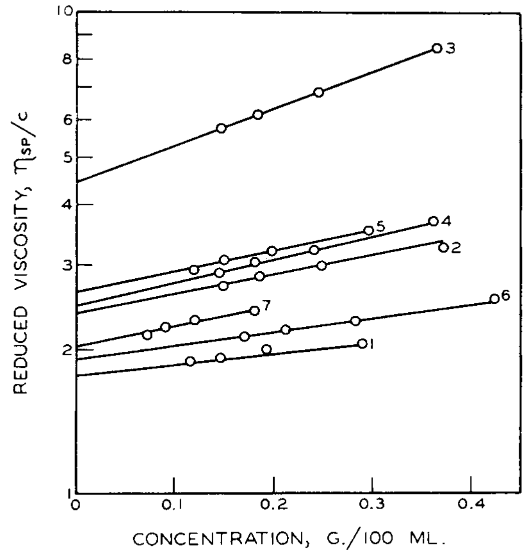


Fig. 2. Viscosity plots for DAX samples in 90% dimethyl sulfoxide.

RELATIONSHIP BETWEEN k_m AND D.S.

It has been well established that k_m is a function of the solvent and the D.S. of cellulose derivatives. Figure 3 shows the relationship between k_m and D.S. for the DAX derivative in 90% dimethyl sulfoxide. Statistically, the points are adequately represented by the following linear regression (correlation coefficient = −0.93):

$$k_m = (5.63 - 3.35\ \mathrm{D.S.}) \times 10^{-3} \quad (4)$$

The Staudinger equation for the DAX derivative at a temperature of 25°C. may be written in the following form:

$$[\eta] = (5.63 - 3.35\ \mathrm{D.S.}) \times 10^{-3}\ \mathrm{D.P.}_w \quad (5)$$

Configuration Parameters

The expansion factor, α, which accounts for the density of the polymer elements within the effective volume of the molecule and the interaction of these elements with the solvent, was calculated according to the method of Orofino and Flory.[22] The calculated values of α, shown in Table II, range from 1.01 to 1.12. These values are similar to those reported for cellulose nitrate[10,11] and cellulose caproate.[16]

The root mean square end-to-end length, $(\bar{r}^2)_z^{1/2}$, was calculated from the experimentally determined limiting dissymmetry, assuming a random-coil con-

TABLE II
Configuration Parameters for Diethylacetamide Cellulose Xanthate in 90% Dimethyl Sulfoxide

Sample	D.S.	D.P.$_w$	Expansion factor, α	$(\bar{r}^2)_z^{1/2}$, A.	$(\bar{r}_0^2)_z^{1/2}$, A.	$(\bar{s}^2)_z^{1/2}$, A.	$(\bar{s}_0^2)_z^{1/2}$, A.	$(\bar{r}^2/\text{D.P.}_w)^{1/2}$, A.	$(\bar{r}_{0f}^2)^{1/2}$, A.	$(\bar{r}_0^2/\bar{r}_{0f}^2)^{1/2}$, A.
1	0.40	473	1.10	864	786	352	319	39.6	171	4.60
2	0.49	506	1.02	1030	1010	420	412	45.6	179	5.63
3	0.60	1150	1.02	1555	1520	634	631	45.8	268	5.68
4	0.80	781	1.01	1245	1230	510	504	44.5	221	5.56
5	0.92	1190	1.12	934	834	380	339	27.1	272	3.06
6	1.00	969	1.07	980	915	400	374	31.2	246	3.71
7	1.22	1130	1.10	980	890	400	363	29.1	266	3.34

figuration. The unperturbed end-to-end length, $(\bar{r}_0^2)_z^{1/2}$, was determined from the relationship:

$$(\bar{r}^2)_z^{1/2} = \alpha(\bar{r}_0^2)_z^{1/2} \qquad (6)$$

The perturbed and unperturbed root mean square radii of gyration were calculated from the end-to-end lengths.

For cellulose derivatives, free rotation is possible only about the ether linkages; however, at these points rotation is restricted by both valence angle and steric hindrance. If these were the sole factors influencing the freedom of rotation, samples with a high D.S. would be expected to be more highly extended in solution than low D.S. samples. Subsequent discussion will point out that this does not appear to be the case, and that the affinity of the solvent for the polymer molecule plays an important role in determining its extension in solution.

The effective bond length, $(\bar{r}_z^2/\text{D.P.}_w)^{1/2}$, is defined by Doty, et al.[7,8] as the bond length of a hypothetical freely jointed analog possessing no restrictions to coiling. A value of 35 A. has been reported for cellulose nitrate in solution.[8,10] The effective bond lengths for cellulose tricaproate in dimethylformamide and 1-chloronaphthalene decrease from a value of approximately 50 A. to a value of 35 A. with increasing molecular weight (calculated from the data of Sperling[16]). The average value for the DAX derivative, which decreases with increasing substitution, is 37 A. (see Table II), corresponding to somewhat over seven glucose units. The freedom of rotation of the DAX derivative is, therefore, comparable to that of the trinitrate and tricaproate.

Effects on the configuration other than those due to valence and bond angle may be obtained from the ratio $(\bar{r}_0^2/\bar{r}_{0f}^2)^{1/2}$, where $\bar{r}_{0f}^2$, calculated from the relationship:[21]

$$\bar{r}_{0f}^2 = 62.4\ \text{D.P.} \qquad (7)$$

is the mean square end-to-end distance when rotation about the ether linkages is unhindered by

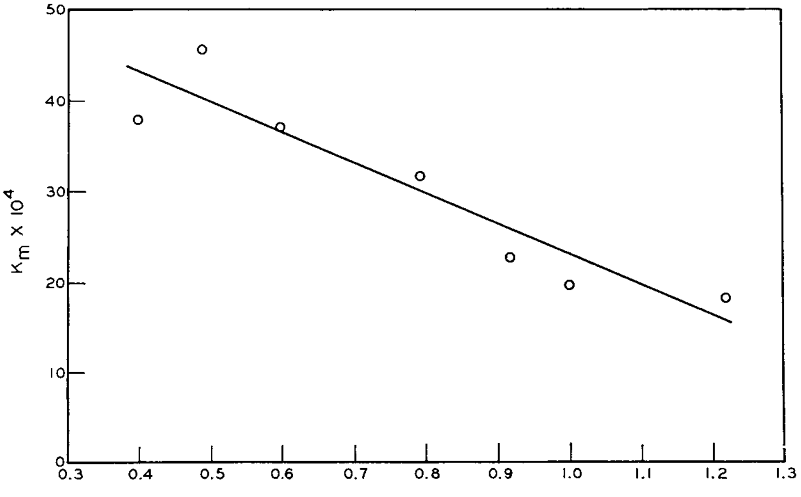


Fig. 3. k_m as a function of D.S. for DAX samples in 90% dimethyl sulfoxide.

steric and solvent–polymer interaction effects. $\bar{r}_0^2$ is the unperturbed mean square end-to-end length.

As shown in Table II, this ratio varies from 3.06 to 5.68 for the DAX derivative in 90% dimethyl sulfoxide. Decreasing solubility with increasing D.S. appears to lower the ratio as much as does the increase in molecular weight. The ratios calculated from the data of Sperling[16] for the tricaproate (4.3 to 6.5) decrease steadily with increase in molecular weight, as is the case for cellulose nitrate,[10] in which the ratios have a narrower compass (3.4 to 4.3). The values for cellulose derivatives are significantly higher than the usual range reported for common synthetic polymers (1.4 to 2.4).[23]

Hydrodynamic Considerations

According to the Fox–Flory theory,[24] the intrinsic viscosity, radius of gyration, and molecular weight are related as follows:

$$[\eta] = \Phi' \, (\bar{s}^2)^{3/2}/M \qquad (8)$$

where Φ' for many flexible polymers is equal to 3.2×10^{22}. In the case of more extended polymer molecules, such as the cellulose derivatives, Φ' has been found to vary with molecular weight. Here Φ is more properly designated as $\{\Phi'\}$. Only at high molecular weights does $\{\Phi'\}$ approach the asymptotic value of 3.2×10^{22}. Introducing the factor q_Φ, as suggested by Flory, et al.,[10] to account for the effects of molecular weight heterogeneity eq. (8) may be written in the following form:

$$\{\Phi'\} = q_\Phi \, [\eta] \, M_w/(\bar{s}^2)_z^{3/2} \qquad (9)$$

where q_Φ may be estimated from the following relationship:

$$\begin{aligned} q_\Phi = {} & [\Gamma(y + 3 + 2a_1 + a_2)]^{3/2} \, (y + 1)^{-2} \\ & [\Gamma(y + 2)]^{-1/2} \\ & [\Gamma(y + 3/2 + 3a_1 + 3a_{2/2})]^{-1} \end{aligned} \qquad (10)$$

The values of a_1 and a_2 were determined in the manner suggested by Flory, et al.,[10] while y was calculated from the molecular weight heterogeneity according to the following relation:

$$M_z{:}M_w{:}M_n = (y + 2){:}(y + 1){:}y \qquad (11)$$

The values of q_Φ have been calculated for $y = 1$ and $y = 2$, corresponding to M_w/M_n ratios of 1.5 and 2.0, respectively. These values, along with the calculated hydrodynamic parameters are shown in Table III. It is apparent from the samples considered in this study that $\{\Phi'\}$ approaches the theoretical asymptotic value only for high degrees of substitution (D.S. >0.9) and molecular weights above 400,000.

The data presented here are insufficient to provide a complete interpretation of the hydrodynamic effects, but even in the case of more extensive studies[10] with cellulose nitrate it has been concluded that "existing theories fail to offer a self-consistent interpretation of the observed decreases in $\{\Phi'\}$ with decreasing molecular weight."

CONCLUSIONS

For cellulose derivatives, where the side groups are of significant length as compared to the glucose unit, one would expect the configuration in solution to be significantly influenced by the added steric restrictions upon free rotation. As shown with the tricaproate in a theta solvent[16] and in the present study, the effect is not as great as might be anticipated. This is particularly evident from the persistence length of the DAX derivative which is less than that of cellulose trinitrate at degrees of substitution above 0.8.

The configuration of the DAX derivative appears to be influenced as much by decreasing affinity for the solvent as substitution is increased, as it is by increase in molecular weight. This is shown also by

TABLE III
Hydrodynamic Parameters for Diethylacetamide Cellulose Xanthate in 90% Dimethyl Sulfoxide

Sample	$[\eta]M_w/(\bar{s}^2)_z^{3/2} \times 10^{-22}$	a_2	q_Φ ($y = 1$)	q_Φ ($y = 2$)	$\{\Phi'\} \times 10^{-22}$ ($y = 1$)	$\{\Phi'\} \times 10^{-22}$ ($y = 2$)
1	0.46	0.10	2.12	1.70	0.98	0.79
2	0.40	0.14	2.10	1.64	0.85	0.66
3	0.55	0.07	2.06	1.63	1.12	0.89
4	0.45	0.11	2.13	1.70	0.96	0.77
5	1.95	0.02	2.00	1.63	3.90	3.18
6	1.00	0.03	2.00	1.62	2.00	1.62
7	1.42	0.02	2.00	1.63	2.84	2.32

the effect of degree of substitution on the viscosity, i.e., the k_m constant doubles as the substitution is reduced from 1.22 to 0.4.

References

1. Schurz, J., *Z. physik. Chem.*, **5**, 261 (1955).
2. Blaker, R. H., R. M. Badger, and T. S. Gilman, *J. Phys. & Colloid Chem.*, **53**, 794 (1949).
3. Jullander, I., *Arkiv Kemi Mineral. Geol.*, **A21**, 1 (1945).
4. Badger, R. M., and R. H. Blaker, *J. Phys. & Colloid Chem.*, **53**, 1056 (1949).
5. Badger, R. M., and R. H. Blaker, *J. Am. Chem. Soc.*, **72**, 3129 (1950).
6. Newman, S., and P. J. Flory, *J. Polymer Sci.*, **10**, 121 (1953).
7. Doty, P., N. S. Schneider, and A. Holtzer, *J. Am. Chem. Soc.*, **75**, 754 (1953).
8. Holtzer, A., H. Benoit, and P. Doty, *J. Phys. Chem.*, **58**, 624 (1954); **58**, 635 (1954).
9. Schneider, N. S., and P. Doty, *J. Phys. Chem.*, **58**, 762 (1954).
10. Hunt, M. L., S. Newman, H. A. Scheraga, and P. J. Flory, *J. Phys. Chem.*, **60**, 1278 (1956).
11. Huque, M. M., D. A. I. Goring, and S. G. Mason, *Can. J. Chem.*, **36**, 952 (1958).
12. Stein, R. S., and P. Doty, *J. Am. Chem. Soc.*, **68**, 159 (1946).
13. Trap, H., and J. J. Hermans, *J. Phys. Chem.*, **58**, 757 (1954).
14. Tait, C. W., R. J. Vetter, J. M. Swanson, and P. Debye, *J. Polymer Sci.*, **7**, 261 (1951).
15. Onyon, P. F., *J. Polymer Sci.*, **37**, 295 (1959).
16. Sperling, L. H., Ph.D. Thesis, Duke University, 1958.
17. Brice, B. A., M. Halwer, and R. Speiser, *J. Opt. Soc. Amer.*, **40**, 768 (1950).
18. Maron, S. H., and R. L. H. Lou, *J. Polymer Sci.*, **14**, 29 (1954).
19. Doty, P., and R. F. Steiner, *J. Chem. Phys.*, **18**, 1211 (1950).
20. Cabannes, J., and Y. Rocard, *La Diffusion Moléculaire de la Lumière*, Les Presses Universitaires de Paris, 1929.
21. Mandelkern, L., and P. J. Flory, *J. Am. Chem. Soc.*, **74**, 2517 (1952).
22. Orofino, T. A., and P. J. Flory, *J. Chem. Phys.*, **26**, 1067 (1957).
23. Flory, P. J., *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca, New York, 1953, p. 618.
24. Flory, P. J., and T. G. Fox, *J. Am. Chem. Soc.*, **73**, 1904 (1951).

Synopsis

Light-scattering and viscosity measurements were obtained for seven fractions of the diethylacetamide derivative of cellulose xanthate (DAX) in 90% dimethyl sulfoxide. The degree of substitution (D.S.) range represented by the samples was 0.4 to 1.22; the molecular weight range was 112,000 to 446,000. The following empirical equation between the intrinsic viscosity and D.P.$_w$ was found: $[\eta] = (5.63 - 3.35 \text{ D.S.}) \times 10^{-3}$ D.P.$_w$. As reflected by the k_m–D.S. plot, the Martin constants, and the configuration parameters, it was apparent that the low D.S. derivatives are considerably more extended in solution than high D.S. derivatives of the same chain length. Under such conditions, it is apparent that solvent–polymer interaction has assumed an important role in determining the polymer configuration. The behavior of the DAX molecule in solution was found to be strikingly similar to that of other cellulose derivatives. Hydrodynamic considerations revealed that the behavior in solution appears to approach that of the more flexible synthetic polymers at D.S. levels above 0.9 and molecular weights above 400,000.

Résumé

On a effectué des mesures de diffusion lumineuse et de viscosité sur sept fractions du dérivé diéthylacétamidé du xanthate de cellulose (DAX) dans 90% de diméthylsulfoxyde. Le DS des échantillons était de 0.4 à 1.22; le poids moléculaire, 112.000 à 446.000. On a pu établir entre la viscosité et le DP_w l'équation empirique suivante: $(\eta) = (5.63 - 3.55 \text{ DS}) 10^{-3} DP_w$. Comme on peut le voir d'après le diagramme k_m–DS, les constantes de Martin et les paramètres configurationnels, les dérivés à DS élevé ayant la même longueur de chaîne. Il est donc clair que l'interaction polymère–solvant joue un rôle important dans la détermination de la configuration du polymère. Le comportement de la molécule de DAX en solution a été trouvé tout à fait semblable à celui des autres dérivés de la cellulose. Des considérations hydrodynamiques montrent que le comportement en solution semble s'approcher de celui des polymères synthétiques plus flexibles à des degrés de substitution supérieurs à 0.9 et pour des poids moléculaires supérieurs à 400.000.

Zusammenfassung

Es wurden Lichtstreuungs- und Viskositätsmessungen an sieben Fraktionen des Diäthylacetamidderivates von Cellulosexanthat (DAX) in 90% Dimethylsulfoxyd durchgeführt. Der D.S.-Bereich der Proben erstreckte sich von 0,4 bis 1,22, der Molekulargewichtsbereich von 112.000 bis 446.000. Es wurde folgende empirische Beziehung zwischen der Viskositätszahl und dem DP$_w$ gefunden: $[\eta] = (5{,}63 - 3{,}35 \text{ DS}) \times 10^{-3}$ DP$_w$. Das k_m–D.S.-Diagramm, die Konstanten nach Martin und die Konfigurationsparameter zeigen, dass bei gleicher Kettenlänge die Derivate mit niedrigem D.S. in Lösung beträchtlich stärker aufgeweitet sind als die Derivate mit höherem D.S. Offenbar spielt hier die Wechselwirkung zwischen Lösungsmittel und Polymeren eine wichtige Rolle bei der Festlegung der Polymerkonfiguration. Es wurde gefunden, dass das Verhalten des DAX-Moleküls in Lösung dem Verhalten anderer Cellulosederivate auffallend ähnlich ist. Hydrodynamische Erwägungen zeigen, dass das Verhalten in Lösung sich dem der flexibleren synthetischen Polymeren bei einem D.S. oberhalb 0,9 und einem Molekulargewicht oberhalb 400.000 zu nähern scheint.