

Optical Properties of Polyacrylonitrile Molecules in *N,N*-Dimethylacetamide

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ABSTRACT

The present paper deals with the investigations of hydrodynamic properties of PAN, as an engineering material with increasing technological interest. The methods of translational diffusion, velocity sedimentation and viscometry are employed. At first time, optical anisotropy of the PAN molecule was determined with flow birefringence technique which is very sensitive to intramolecular structure. The PAN sample with molecular weight of 9×10^5 and low stereoregularity was studied in dilute solution in *N,N*-dimethylacetamide. Intrinsic viscosity was calculated according to Huggins equation from the dependence of reduced viscosity on concentration of solution. Molecular mass was determined with Svedberg's equation. The heterogeneity parameter was evaluated by the absolute method of analytical ultracentrifugation. Translation diffusion was investigated using a gradient method in a cell Teflon in the Tsvetkov's interferometric diffusometer. The flow birefringence measurements were made in titanium dynamometer and the Hg-lamp was used as a light source. The sign of the effect and the stress optical coefficient were determined. The role of the micro and macro form effects in flow birefringence is discussed. The intrinsic optical anisotropy (-3.3×10^{-25}) cm^3 of the chain unit of the PAN molecule is attributed to structural features of the polymer molecule and anisotropy of the cyano-groups.

Key Words: polyacrylonitrile, flow birefringence, hydrodynamic properties, macromolecule, optical anisotropy

INTRODUCTION

Polyacrylonitrile (PAN) is a widely used and commercially important polymer because of its unique properties and chemical resistance [1, 2]. Polymeriz-

ation of PAN is described in detail [1, 3] as well as the PAN molecular characterization.

Classical light scattering [4-9], diffusion-sedimentation [10], equilibrium ultracentrifugation (and Archibald method) [11, 12], sedimentation-

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viscometry [13] and translational diffusion [7] methods have been successfully employed. As a result, the molecular-weight dependence of hydrodynamic properties is already determined, and the coiling of the PAN macromolecules in dilute solution is characterized. The stereoregularity effects on solubility and molecular parameters of PAN are also studied [5, 6, 14].

Experimental results of these works show clearly that insertion of a cyano-group as a side substituent to a vinyl molecule brings about, unexpectedly, large stiffness in the polymer chain (the steric factor σ from 2.2 to 2.8 [6]) which cannot be explained by a simple steric hindrance due to the molar volume of the side cyano-groups.

The intramolecular electronic interactions of the CN-groups are supposed to be mainly responsible for the chain stiffness observed for PAN. The similar effect was observed for cyano-derivatives of other polymers, for example, for cyanoethylated cellulose ethers [15].

The cyanoethylation of cellulose ethers leads also to higher optical anisotropy of the macromolecule [16].

To study origins of the effect, in the present work, dynamo-optical (the Maxwell effect) and hydrodynamic properties of PAN in dilute solution in *N,N*-dimethylacetamide (DMAA) have been investigated, and optical anisotropy of the PAN molecule is estimated.

EXPERIMENTAL

Sample and Solutions

Sample of PAN with low stereoregularity of the molecules was synthesized by anionic polymerization and purified as early described [17]. DMAA of chemically pure grade with density $\rho_0^{21}=0.943 \text{ g/cm}^3$, viscosity $\eta_0^{21}=1.04 \times 10^{-2} \text{ gcm}^{-1}\text{s}^{-1}$, and a refractive index of $n_D=1.4365$ was used as a solvent. Solutions were prepared with magnetic stirring at ambient temperature. They were stable during, at least, two weeks. Intrinsic viscosity, sedimentation velocity and free diffusion measurements were made at 26 °C.

Methods

Solution viscosity, η , was measured by using an ordinary capillary viscometer of the Ostwald type with average shear rate $\leq 100 \text{ s}^{-1}$. The kinetic energy correction was negligible.

Sedimentation velocity measurements were made on a MOM model 3180 analytical ultracentrifuge (Hungary) in a double-sector polyamide cell 1.2 cm in height, h , with a synthetic boundary at a rotation frequency of $n=50.10^3 \text{ rpm}$. The accuracy in n was not lower than 0.2%.

Fluctuations in temperature did not exceed $\pm 0.05 \text{ K}$. A high sensitive polarizing-interferometric recording system [18] with spar twinning of $\alpha=0.020 \text{ cm}$ and interferometric fringes period of $b=0.094 \text{ cm}$ was used.

Free diffusion of the polymer molecules in solution was investigated using a gradient method in which a sharp boundary was formed between solvent and solution in a Teflon cell [19] of 2.0 cm in height in the Tsvetkov's interferometric diffusometer [18].

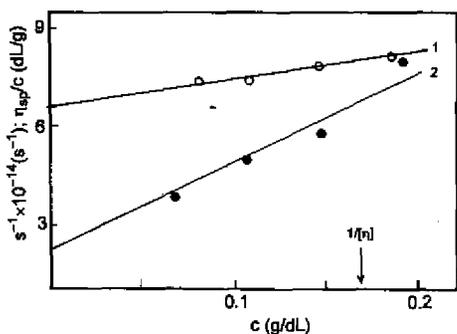
The flow birefringence (FB) measurements were made at 21 °C in temperature controlled titanium dynamooptimeter with an internal rotor 8.08 cm in height and a rotor-stator gap of 0.059 cm. The double refraction (birefringence), Δn , induced in the polymer solution by shear flow (the Maxwell effect) was measured by the visual compensation technique [18]. Two mica plates with the optical retardation of 0.019 λ and 0.0389 λ at wavelength λ were used as the elliptic compensatories. The Hg-lamp ($\lambda=546.1 \text{ nm}$) was used as a light source.

All data were evaluated via non-weighted linear regression analysis.

RESULTS AND DISCUSSION

Hydrodynamic Properties

Intrinsic viscosity, $[\eta]$, was obtained from extrapolation of relative viscosity increment, $\eta_{sp}/c = \eta - \eta_0/\eta_0 c$, to vanishing solute concentration $[\eta] = \lim_{c \rightarrow 0} (\eta_{sp}/c)$ made according to Huggins' equation $\eta_{sp}/c = [\eta] + [\eta]^2 k_{HC}$, where c is the solute concentration (g/cm^3) and k_H the Huggins' constant. Figure 1 shows



The solid lines represent linear approximation in the range $c \leq 1/\eta$.

Figure 1. Concentration dependence of (1) relative viscosity increment and (2) reciprocal sedimentation coefficient for PAN in DMAA at 26 °C (points).

η_{sp}/c versus c (points on curve 1). Experimental data are well approximated by a linear function with the intercept $[\eta]$ equal 6.4 g/dL and the slope which yields $k_H=0.3$.

A series of experiments with a freely sedimenting boundary between the solvent and the solution was performed at several different dilutions (with decreasing value of c down to the minimum possible value) and under identical experimental conditions (frequency, temperature and cell). The first moment of the sedimentation curve was used as the boundary

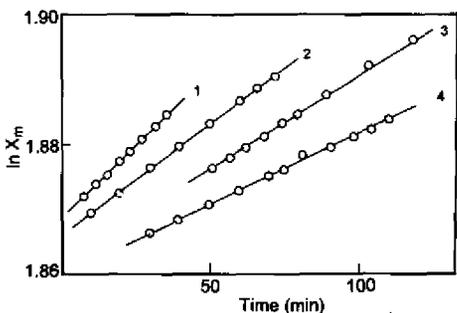


Figure 2. Semi-logarithmic plot of the sedimentation boundary position X_m versus time at a rotor rotation frequency of $n=50 \times 10^3$ rpm. Solute concentration is $c(\times 10^2)=(1) 0.0687$, (2) 0.107, (3) 0.148, and (4) 0.193 g/cm³.

position, x_m , counted from the axis of rotation of the rotor. Sedimentation coefficient, s , was determined from the time dependence of x_m (shown in Figure 2) by $s=\omega^{-2}(dx_m/dt)$. Here, ω is the angular rotor rate, $\omega=2\pi n/60$, and n is the frequency of the rotor rotation. Pressure (P) effect was evaluated by $s_1=s_0(1+\mu P)$ with μ the DMAA compressibility parameter (0.8×10^{-9} cm s²/g) and s_0 sedimentation coefficient determined at pressure P , where:

$$P \approx (\omega^2 x_0^2 \rho_0 / 2) [(x_m / x_0)^2 - 1]$$

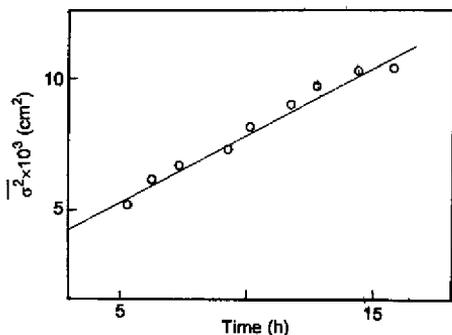
The effect does not exceed the experimental uncertainty (3%) and it is, therefore, ignored.

Points on curve to 2 in Figure 1 represent the s values, thus obtained at various concentrations, as $1/s$ versus c . At $c \leq 1/[\eta]$, this dependence was approximated by a linear function (solid curve 2) described by expression $s_0 = s(1 + k_c c)$ where $s_0 = \lim_{c \rightarrow 0} s$ and k_c is the concentration parameter. The result is $s_0 = 5.0 \times 10^{-13}$ s, $k_c = 13$ dL/g, and $k_c/[\eta] \approx 2$. The last value is typical for the coiled molecules of many flexible polymers [20].

The sedimentation curve area, Q , was used to estimate the specific refractive index increment by $dn/dc = (Q/c)(\lambda/abh)$. The result is $(dn/dc)_{446} = 0.07$ cm³/g. This value agrees well with those known for PAN in other solvents [8] if we take into account the difference in solvent refractive indices. Hence, we may conclude that the PAN molecules dissolve molecularly in DMAA.

Figure 3 shows time dependence of the diffusion curve dispersion, $\bar{\sigma}^2$, which was calculated by the height-area method. Diffusion coefficient, D , was evaluated from the slope of this dependence by $D = (1/2) \partial \bar{\sigma}^2 / \partial t$. A correction to the concentration effect (14%) was made using expression $D = D_0(1 + k_D c)$ with $k_D = 3.9$ dL/g [7]. Here, $D_0 = \lim_{c \rightarrow 0} D$. The result is $D_0 = 0.6 \times 10^{-7}$ cm²/s.

The experimental $[\eta]$, D , and s_0 values were used to evaluate the hydrodynamic parameter A_0 defined by [21]: $A_0 = (D\eta_0/T)^{2/3}([\eta]s/R/100)^{1/3}$. Here, $[s] = s_0\eta_0/(1 - \bar{v}\rho_0)$, R is the gas constant, T is the Kelvin temperature, \bar{v} is the partial specific volume of PAN in solution ($\bar{v} = 0.83$ cm³/g [8, 10]), and other



The solid line represents linear approximation.

Figure 3. Time dependence of dispersion $\bar{\sigma}^2$ (second central moment) of the x -spectrum of the macromolecules in the region of diffusion boundary in DMAA solution of PAN at solute concentration $c=0.07 \times 10^{-2}$ g/cm³ (points).

quantities as defined above. The result is $A_0=3.4 \times 10^{-10}$ erg.K⁻¹.mol^{-1/3} which coincides with those of many vinyl polymers [21].

Molecular mass was determined with the Svedberg's equation $M_{sD}=RT(s_0/D_0)/(1-\bar{v}\rho_0)$. The application of the experimental s_0 and D_0 values yields $M_{sD}=9 \times 10^5$. For the PAN molecule in solution, the length, A , of the random link is close to 30 Å [6, 8, 10] with mass per this link is being 636 Dalton [6].

Hence, the chain of the investigated PAN sample consists of near 10^3 random links, and the coil conformation may be obviously accepted as a good model in a treatment of the polymer solution properties.

The M_{sD} and $[\eta]$ values obtained are in agreement with Mark-Kuhn equation $[\eta] \sim M^a$ found in refs. [5, 6 and 11] for PAN in solution with average $a=0.67 \pm 0.07$. We may assume, therefore, that scaling exponent b in equation $s_0 \sim M^{1-b}$ is close to 0.56 ± 0.02 as evaluated by $b=(1+a)/3$ valid for the coiled chains.

Polydispersity

Heterogeneity was evaluated by the absolute method of analytical ultracentrifugation. Dispersion $\bar{\sigma}^2$ (the second central moment) of the x -spectrum was calculated at different time t using the boundary

profile as described previously [18]. Figure 4 shows the change in $\bar{\sigma}^2$ with t . This dependence is obviously not linear, the rate of change being profoundly affected by solute concentration.

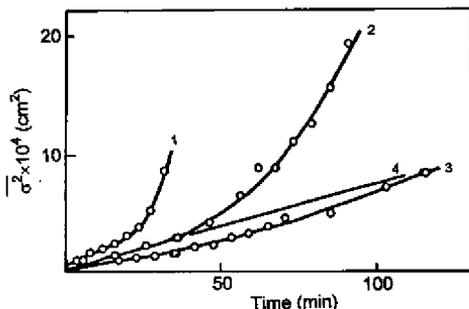
The concentration effect as well as the diffusion effect were, therefore, taken into account with the aid of a recently proposed method [22]. In this way, the standard deviation, σ , of the x -spectrum is plotted in Figure 5 against the boundary position, x_m .

The slope at the origin, $\partial\sigma/\partial x_m$, was determined and then extrapolated to vanishing concentration in coordinate axes $\partial\sigma/\partial x_m - \Delta s$, where $\Delta s = s_0 - s$. The result is $(\partial\sigma/\partial x_m)_0 = \lim_{\Delta s \rightarrow 0} (\partial\sigma/\partial x_m)_{\Delta s} = 0.33$. Time dependence of $\bar{\sigma}_{c \rightarrow 0}^2$ was, first, approximated in terms of displacements x by:

$$\bar{\sigma}_{c \rightarrow 0}^2 = (\partial\sigma/\partial x_m)_0^2 (x_m - x_0)^2 \quad (1)$$

where x_0 is equal to x_m at the initial time, $t=0$. By using definition of sedimentation coefficient, s , given by $x_m = x_0 \exp(\omega^2 s t)$ with $s=5 \times 10^{-13}$, s function (1) was, rewritten in terms of the sedimentation time (in s) as:

$$\bar{\sigma}_{c \rightarrow 0}^2 = 4.46 [\exp(1.37 \times 10^{-5} t) - 1]^2 \quad (2)$$



Solid curves 1-3 connect smoothly the data points. Curve 4 represents diffusion spreading as calculated by $\bar{\sigma}^2=2Dt$.

Figure 4. Time dependence of sedimentation curve dispersion $\bar{\sigma}^2$ in DMAA solution of PAN at a rotor rotation frequency of $n=50 \times 10^3$ rpm and solute concentration $c(\times 10^2)=(1) 0.0687$, (2) 0.107, (3) 0.148, and (4) 0.193 g/cm³ (points).

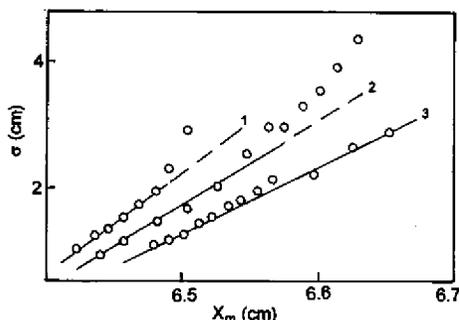


Figure 5. Standard deviation σ of the sedimentation curve versus the boundary abscissa x_m in DMAA solution of PAN at $c(\times 10^2)=(1)$ 0.148, (2) 0.107, (3) 0.0687 g/cm³.

On the other hand, during concentration-independent sedimentation, the dispersion of the x -spectrum is known [23] to satisfy equation:

$$\bar{\sigma}^2 = 2Dt + x_m^2 \omega^4 \bar{\sigma}_s^2 \quad (3)$$

where $\bar{\sigma}_s^2$ is the dispersion of the s -spectrum (distribution of the macromolecules with respect to sedimentation coefficients). Hence, we have to find a power series which approaches to eqn (3) at starting time (mainly, diffusion spreading) and, in turn, to eqn (2) at large time when the boundary spreading is mainly provided by heterogeneity of the sample. The least mean-square treatment of sedimentation data yields:

$$\bar{\sigma}_{c \rightarrow 0}^2 = 1.8 \times 10^{-7} t + 13.5 \times 10^{-12} x_m^2 t^2 \quad (4)$$

Comparison of eqns (3) and (4) leads to the sedimentation heterogeneity parameter $(\bar{\sigma}_s^2)^{1/2}/s_0 = 0.27$. Further, the polydispersity parameter \bar{M}_z/\bar{M}_w was evaluated by $\bar{M}_z/\bar{M}_w = [(\sigma_s/s_0)/(1-b)]^2 + 1$ with $(1-b) = 0.44$ as estimated above. The result is $\bar{M}_z/\bar{M}_w = 1.4 \pm 0.3$.

Flow Birefringence

Figure 6 shows the dependence of the FB, Δn , on the shear rate, g , for PAN sample in DMAA. Experimental points are well approximated by a linear function with the slope giving the dynamo-optical

constant $[n]$. It is defined by $[n] = \lim_{\Delta n \rightarrow 0} (\Delta n / g c \eta_0)_{c \rightarrow 0}$ with Δn being the excess FB of the solution. The intrinsic FB $[n]/[\eta]$ was thus obtained to be $-(1.7 \pm 0.3) 10^{-10} \text{ cm} \cdot \text{s}^2 \cdot \text{g}^{-1}$.

For PAN in DMAA, $dn/dc \neq 0$, and intrinsic FB is provided by proper optical anisotropy of the macromolecule (i) as well as by the macroform (f) and microform (fs) effects [18]:

$$[n]/[\eta] = [n]/[\eta] + [n]_f/[\eta] + [n]_{fs}/[\eta]$$

The form effects are caused by the form asymmetry of the macromolecule and the Kuhn segment, respectively, and the difference in refractive indices of PAN and DMAA. The macroform effect was estimated by:

$$[n]_f = (0.23 \Phi / \pi N_A R T) [(n_0^2 + 2)^2 / n_0] (dn/dc)^2 M / [\eta]$$

where Φ is Flory coefficient, N_A is Avogadro's number, R is the gas constant, and n_0 is refractive index of the solvent. The application of $\Phi = 2.1 \times 10^{23} \text{ mol}^{-1}$, $T = 294 \text{ K}$ and the experimental dn/dc value ($0.07 \text{ cm}^3/\text{g}$) yields $[n]_f/[\eta] = 0.6 \times 10^{-10} \text{ cm} \cdot \text{s}^2 \cdot \text{g}^{-1}$.

In the random coil limit (in the Gaussian approximation), intrinsic FB does not depend on M and may be related to optical anisotropy $\Delta \alpha_s$ of the random link by $[n]/[\eta] - [n]_f/[\eta] = B \Delta \alpha_s$, where B is the optical constant, $B = (4\pi/45 k_B T) (n_0^2 + 2)^2 / n_0$, and k_B is

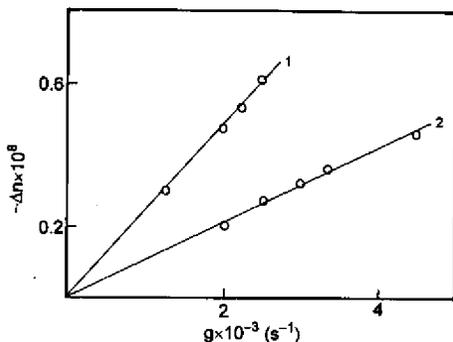


Figure 6. Shear rate (g) dependence of flow birefringence Δn observed in DMAA solution of PAN at $c(\times 10^2)=(1)$ 0.175, and (2) 0.109 g/cm³.

the Boltzmann constant.

The application of $B=7.8 \times 10^{13}$ yields $\Delta\alpha_s = -(30 \pm 5) \times 10^{-25} \text{ cm}^3$. The microform effect caused by the form asymmetry of the segment was evaluated from:

$$\Delta\alpha_{fs} = ([\eta]_{fs}/[\eta])/B = (dn/dc)^2(M_0s/\pi N_A \bar{v})\epsilon$$

with mass per segment length, M_0s , number s of the monomer units in the segment, and the form factor ϵ .

The application of $M_0s=636[6]$, $\bar{v}=0.83 \text{ cm}^3/\text{g}$ [8], and $\epsilon=1/2$ yields $\Delta\alpha_{fs}=10 \times 10^{-25} \text{ cm}^3$. Thus, the proper optical anisotropy of the PAN random link is $-(40 \pm 10) \times 10^{-25} \text{ cm}^3$ as evaluated by $\Delta\alpha_s = \Delta\alpha_{fs} - \Delta\alpha_{fs}$.

This quantity per monomer unit we obtain by $a_{\parallel} - a_{\perp} = \Delta\alpha/s$ with a_{\parallel} and a_{\perp} being, respectively, the longitudinal and transvers (in relation to the main chain axis) polarizabilities of the PAN monomer unit, and it is equal $-3.3 \times 10^{-25} \text{ cm}^3$. Part of the skeleton chain anisotropy may be assumed to be equal to anisotropy of the polyethylene chain unit, $(a_{\parallel} - a_{\perp})_{PE} = 7 \times 10^{-25} \text{ cm}^3$ [24].

Hence, the contribution of the CN-group to the optical anisotropy of the PAN monomer unit may be estimated by $(a_{\parallel} - a_{\perp})_{CN} = (a_{\parallel} - a_{\perp})_{PAN} - (a_{\parallel} - a_{\perp})_{PE}$ to be $-10.3 \times 10^{-25} \text{ cm}^3$.

CONCLUSION

Negative in sign the Maxwell effect was observed in DMAA dilute solution of PAN sample with low stereoregularity. The effect is referred to negative optical anisotropy of the PAN monomer unit which is estimated by the value $-3.3 \times 10^{-25} \text{ cm}^3$.

Negative sign of this quantity agrees well with the fact that, in the PAN monomer unit structure, the main axis of the $-C \equiv N$ group is oriented in the direction normal to the contour axis of the macromolecule.

The different orientation of the cyano-group is predicted for PAN with higher stereoregularity of the chain [6]. We may expect, therefore, that the FB method may be used as the instrument sensitive to the PAN chain tacticity as well as to other changes in internal structure of the PAN macromolecule [25].

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