Polymer Bulletin 5, 627-633 (1981)

Polymer Bulletin

Small Angle Neutron Scattering on Polyacrylonitrile Polymerized by Gamma-Ray Irradiation

A. Czuppon[1], N. Kroó[2], I. Vizi[2], L. Rosta[2] and L. Kiss[3]

[1] Central Research Institute of Chemistry of the Hungarian Academy of Sciences, 1088 Budapest, Hungary

[2] Central Research Institute for Physics of the Hungarian Academy of Sciences, 1121 Budapest, Hungary

[3] Research Institute for Plastics, 1950 Budapest, Hungary

SUMMARY

Small angle neutron scattering experiments were carried out on unfractionated polyacrylonitrile (PAN) - dimethylsulfoxide system. The PAN sample was polymerized at - 78°C by gamma - ray irradiation in urea - canal complex. The yield of the polymerization was 30 %. Deuterated dimethylsulfoxide served as solvent.

The neutron intensities scattered from the polymer solutions, concentrations ranging from 1,8 to 19×10^{-3} $g \cdot cm^{-3}$, were measured with a triple-axes spectrometer in a range of scattering angle between 0,5° - 2,0° (8-35 mrad).

The data were taken in the vicinity of critical concentration c^*. We have measured the screening length $\xi(c)$ (introduced by Edwards) in the dilute and in the semi-dilute concentration regimes. The ratio between $\xi_d \cdot c^{\frac{1}{2}}$ and $\xi_{sd} \cdot c^{\frac{1}{2}}$ yields a value of 2.

INTRODUCTION

Several papers have been published dealing with the solution behaviour of polyacrylonitrile (PAN) prepared by conventional free-radical polymerization technique. The review of R.B.Beevers gives an excellent survey of these works (1968). The experimental results give evidence of (i) extensive association of PAN polymers in different solvents, (ii) a relative high stiffness of PAN molecules, and (iii) that the highly polar nature of the CN groups render more difficult to calculate the configuration of PAN chain.

Recently, WHITE (1960), KISS (1968), and KAMIDE (1972) published data for polyacrylonitrile prepared by gamma-ray irradiation of urea-canal complex of acrylonitrile. YAMADERA (1967), and MATSUZAKI (1968) carried out NMR experiments and pointed that the configuration of acrylonitrile may play an important role for constructing the comparatively stereoregular chain when the polymerization proceeds. Furthermore, these authors came to

0170-0839/81/0005/0627/$01.40

the conclusion that PAN polymerized in urea-canal contains 75 % of isotactic dyads. While conventionally prepared PAN contains 50% of isotactic and 50% syndiotactic dyads.

It is well known that the properties of macromolecules in solution depend considerably on the stereoregularity of the polymer chains. So the solution behaviour of PAN produced in urea-canal complex deserves special attention.

In our previous works (1972, 1973) we reported viscosity and light scattering measurements on urea-complex PAN. The present paper is to show our experimental results on small angle neutron scattering of solutions of unfractionated PAN polymerized by gamma-ray irradiation. This is followed by a brief discussion of the correlations between the conclusions and theoretical predictions.

EXPERIMENTAL

Polymerization

The polymer used in these neutron scattering experiments was PAN polymerized by gamma-ray irradiation.

The acrylonitrile monomer was agitated with a 2% aqueous solution of $NaHCO_3$, separated the aqueous phase, dried with $CaCl_2$ and distilled three times from $CaCl_2$ in a rectification column. The fraction from the third destillation, temperature range 77,2-77,3 °C was used in the experiment. The melting point of the monomer was - 83 °C, its refractive index $n_D^{20} = 1{,}3911$.

Analytical grade urea was recrystallized three times from methanol in a vacuum oven.

Polymerization was carried out at - 78°C. A 500 curie ^{60}Co source was used for irradiation. All other polymerization conditions were reported earlier.

Preparation of solutions

Deuterated dimethylsulfoxide ($CD_3\ SOCD_3$) was used as solvent. Isotopic purity 99% D. (product of Zentralinstitut für Isotopen - und Strahlenforshung, Leipzig, GDR)

The concentration of polymer solution range from 1,8 to $19{,}0 \times 10^{-3}\ g \cdot cm^{-3}$ for polyacrylonitrile sample of 30% conversion. The concentration range was restricted on the one hand by the contrast and by the poor solubilization tendency of the polymer on the other.

The weight average molecular weight determined by light scattering was $M_w = 1.2 \times 10^6\ g \cdot mol^{-1}$. We could infer a relatively narrow molecular weight distribution from sedimentation velocity measurements. This conclusion was confirmed by light scattering analysis too.

The procedure of preparation of polymer was previously given by KAMIDE and TERAKAWA (1972).

Apparatus

The neutron scattering experiments were made with a triple axes spectrometer in a range of scattering angle between 0,5°-2,0° (8 - 35 mrad). A reactor Typ. VVRM (KFKI) served as neutron source.

The monochromatization was performed by a tryolitic graphite single crystal monochromator. The scattering intensities were measured with a BF_3 counter of 100% efficiency at 4 Å wavelength.

The volume of the cylindrical, aluminium sample holder was 10 cm^3. The beam area was 1x8 cm^2.

The required numerical computations were performed on CDC 3300 computer using FORTRAN language.

RESULTS AND DISCUSSION

The angular dependence of neutron intensities scattered from the solvent and from the two solutions of limiting concentrations are shown in Figure 1.

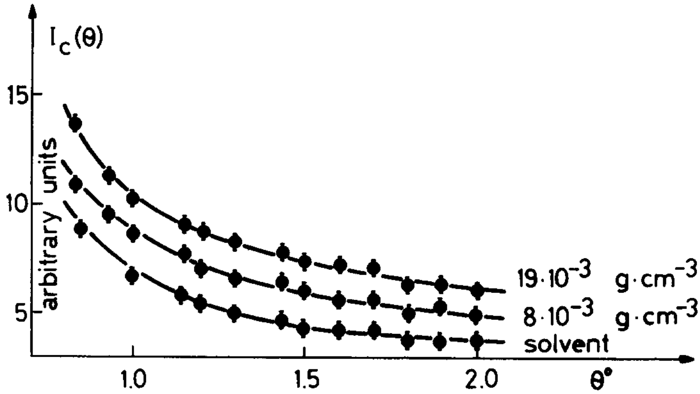

Figure 1. Scattered neutron intensities versus scattering angle Θ for two concentrations and for solvent. The concentration corresponding to each is written on right side. Full lines are calculated curves (Eq.1.). Experimental data are open circles for solutions.

According to COTTON et al. (1972) the intensities scattered from dilute solutions of different concentrations at different scattering angles can be described as follows:

$$I_c(\Theta) = A_c\int_0^\infty d\lambda\ [\frac{f(\lambda)}{(\frac{2\pi\Theta}{\lambda})^2 + \xi^{-2}}] + Tr(c)S(\Theta) + B_c \qquad (1)$$

The parameters A, and B, are unknown and have to be fitted together with ξ. The function $S(\Theta)$ is the interpolation of the empirical formula accounting for the scattering by solvent and container. Tr(c) is the transmission factor with respect to pure solvent, for a given concentration c. The third term in Eq.1. is the back ground due essentially to the protons of the solute molecules. ξ depends on mass, mean squared length and exluded volume of statistical segments.

The best fit was obtained with the values of shown in Table I.

Table I.

The values of screening length ξ as a function of concentration

concentration 10^{-3} g·cm^{-3}	ξ (Å)
1,8	789
4,2	811
8,0	874
11,8	875
14,7	557
19,0	507

The radius of gyration of the polymer sample used in our experiments was $R_g = 530$ Å. This value was determined from a Zimm-diagram by light scattering at 25°C and $\lambda = 5460$ Å in dimethylsulfoxide.

One can estimate the volume taken up by a polymer molecule in solution to be $R_g{}^3$. This would be roughly the volume required to enclose the polymer. Since the polymer is quite extended, this volume is still occupied mostly by solvent. At a concentration

$$c^* = \frac{M}{N\ R_g{}^3} \qquad (2)$$

where M is the molecular mass, N is the Avogadro's number, R_g is the radius of gyration, we would expect to observe the first strong effects of polymer - polymer interactions. At c^* the coils begin to overlap. So we are supposed to have tightly coiled separeted chains below c^* (dilute regime) and extended interpenetrating chains above c^* (semi-dilute regime).

The estimation of so called critical concentration c^* our data gives in our case $c^* \sim 13 \cdot x10^{-3}$ g·cm^{-3}.

The concentration dependence of the experimental characteristic length ξ determined from the Lorentzian broadening of scattering intensity is supposed to describe the changes of solution structure in the vicinity of c^*. According to COTTON'S report, cited above (1972), $\xi_d \cdot c^{\frac{1}{2}}$ and $\xi_{sd} \cdot c^{\frac{1}{2}}$ are linear functions of the concentration c in both regimes. The ratio of these quantites

$$\frac{\xi_d \cdot c^{\frac{1}{2}}}{\xi_{sd} \cdot c^{\frac{1}{2}}}$$

gives the expansion of the polymer molecules. The function of $\xi \cdot c^{\frac{1}{2}}$ versus c can be seen in Figure 2.

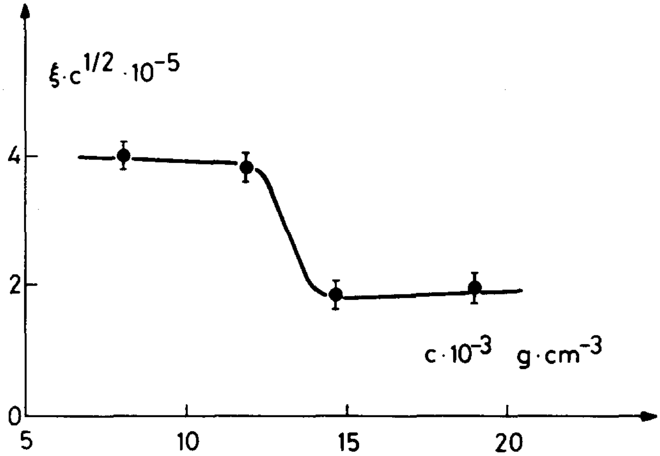

Figure 2. The function of $\xi \cdot c^{\frac{1}{2}}$ versus c.

The ratio between the heights of the two plateaus is about 2. This value seems to be more realistic then was published by COTTON et al.. The estimated critical concentration c^* almost coincides with the point of inflexion of the curve.

The values ξ obtained from the intercept of the $I(q)^{-1}$ versus $q^2/q = 4\pi/\lambda \cdot \sin \Theta(2)$ function show the same concentration dependence as was determined from the Lorentzian broadening.

DAOUD et al. (1975) recently refined EDWARD'S theory (1966) on the basis of the work of Des CLOIZEAUX (1975). They reported several observations to support the conclusion that in case of $c > c^*$ the experimental length ξ determined from the Lorentzian broadening of the scattered intensity is clearly not proportional to $c^{-\frac{1}{2}}$, but rather to c^{-z}, where $z = o, 72$. The function of the relation $\log \xi = F(\log c)$, calculated for solutions of concentrations higher, than $c = 8{,}0 \times 10^{-3}$ is shown in Figure 3.

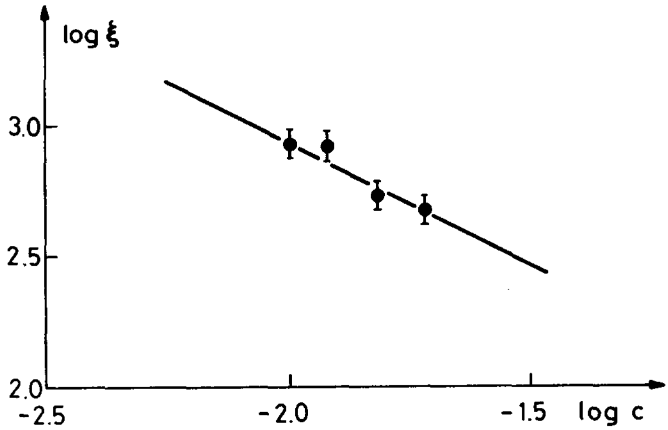

Figure 3. The log - log plot of ξ as a function of concentration for the semi-dilute regime. ξ is determined from the Lorentzian broadening ξ^{-2} of the scattered intensity curves. The exponent z calculated by least squares method, is fairly close to the value expected from the refined theory.

,CONCLUSIONS

(i) The Lorentzian form fits the neutron scattering data for all concentrations up to $c = 19 \times 10^{-3}$ $g \cdot cm^{-3}$.
(ii) The ratio between the heights of the two plateaus in the functions of $\xi\, c^{-\frac{1}{2}}$ versus c yields about 2.
(iii) The characteristic length ξ is proportional to c^{-z} in the $c > c^*$ concentration regime. The value of z is about 0,70 for PAN polymerized in urea-canal complex.

REFERENCES

BEEVERS,R.B. Macromolecular Reviews Vol.3. Interscience Publishers, New York - London 141 p. (1968)

DES CLOIZEAUX,J. J.Phys. (paris), 36, 281 (1975)

COTTON,J.P., FARNOUX,B. and JANNINK,G. J.Chem., 57, 290 (1972)

CZUPPON,A., KISS,L. and POLGÁR,S. paper presented at the IUPAC International Symposium on Macromolecules, Helsinki, Abstract, preprint Supplement 27 p. (1972)

CZUPPON,A., KOVÁCS,P. and KISS,L. paper presented at the IUPAC 12th Microsymposium on Makromolecules, Prague, Abstract (1973)

DAUOD,M., COTTON,J.P., FARNOUX,B., JANNINK,G., SARMA,G., BENOIT,H., DUPLESSIX,R., PICOT,C., and DE GENNES,P.G. Macromolecules, 8, 804 (1975)

EDWARDS,S.F. Proc.Phys.Soc., London, 88, 265 (1966)

KAMIDE,K. and TERAKAWA,T. Makromol. Chem., 155, 25 (1972)

KISS,L. Magy.Kém. Folyóirat, 74, 125 (1968)

MATZUSAKI,K., URYU,T., OKADA,M. and SHIROKI,H. J.Polymer Sci. Part A-1, 6, 1475 (1968)

YAMADERA,R. and MURANO,M. J.Polymer Sci. Part A-1, 5, 1059 (1967)

WHITE,D.M. J.Am. Chem. Soc., 82, 5678 (1960)

Received September 28, accepted October 6, 1981

C