

Rigid Backbone Polymers

19. Apparent Minimal Viscosity – Molecular Weight Dependence of Anisotropic Poly(n-hexylisocyanate) Solutions

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SUMMARY

It is shown that the inverse velocity of a falling-ball in, or η'_m the apparent minimum viscosity of, anisotropic solutions of poly(n-hexylisocyanate) in toluene, are molecular weight dependent. The molecular weight dependence follows two linear branches. Below $M_w=42600$ the apparent minimum viscosity is very weakly dependent on M_w . Above $M_w=42600$ the apparent minimum viscosity of the anisotropic solution is strongly dependent on the molecular weight.

INTRODUCTION

In a paper recently published (MATHESON 1980) it is indicated that the viscosity of a fully anisotropic solution of monodisperse rigid rodlike macromolecules, passes through a minimum, η'_m , which is of the order of one hundredth the viscosity of the isotropic solution at the point of appearance of the first anisotropic inclusions, η^* . Experimental data in the literature on solutions of polyisocyanates (AHARONI 1979, AHARONI & WALSH 1979, AHARONI 1980a) and poly (γ -benzyl-L-glutamate) (PBLG)(HERMANS 1962, IIZUKA 1974, WEE & MILLER 1971, MILLER et al. 1974, KISS & PORTER 1978, 1980), indicate that η'_m is far larger than predicted by Matheson, η'_m being usually of the order of 10-20% of the corresponding value of η^* . It should be noted that both systems above produce well-defined spherical

entities of anisotropic phase in isotropic matrix, making them most amenable to theoretical treatment. Using the observed experimental data as boundary conditions, equations relating the viscosity and concentration of polydisperse polymers were recently developed (AHARONI 1980b) which give numerical values in reasonable agreement with experiment throughout the regions of isotropic, biphasic and anisotropic solution. In both treatments the anisotropic solution viscosity is dependent directly on the molecular weight M or the associated average axial ratio \bar{x} . The literature data are, however, too few to draw conclusions with respect to the dependence of the minimal viscosity in the anisotropic region, η'_m , on the molecular weight of the polymer in question. Thus, the purpose of this work is to obtain η'_m values from a sufficient number of samples covering a sufficiently broad molecular weight interval, in order to relate η'_m with M . The system chosen for this study was a series of different M samples of poly(*n*-hexylisocyanate)(PHIC) dissolved in toluene and studied at 23°C.

EXPERIMENTAL

The polymer was synthesized following the procedure of SHASHOUA et al. (1960) but using a 1:1 DMF and toluene mixture as the polymerization medium. The higher M samples were obtained by changing polymerization conditions, while the three lowest molecular weight samples were obtained by hydrolysis of PHIC in toluene/trifluoroacetic acid mixture at 75°C. The molecular weights of the samples were obtained from intrinsic viscosity values measured in toluene using the relationship of BERGER & TIDSWELL (1973). Concentrated solution viscosity measurements were carried out by the falling-ball method, using lead balls in glass tubes. From the measured time and falling distance, the velocity of the falling balls was calculated, and

the viscosity was calculated as described by FERRY et al. (1950). In isotropic solutions the measurement of viscosity by the falling-ball procedure is straightforward. In anisotropic solutions the situation may be somewhat altered, at least conceptually. However, because the anisotropic swarms are randomly distributed in space and each is several orders of magnitude smaller than the falling ball, the anisotropic solution can be visualized as an isotropic one on the scale of the size of the falling ball. Furthermore, experimental results in the literature (CHANDRASEKHAR 1977) indicate that in order to measure the three anisotropic viscosity coefficients, the liquid crystalline phase must be subjected to a strong external force field. In its absence, separation of the coefficients is impossible. Hence, it was felt that an apparent viscosity η can be estimated by the falling-ball procedure.

At each concentration the phase relationship was observed by means of a Reichert cross-polarized light microscope operating at 100x magnification.

RESULTS AND DISCUSSION

The curves of apparent viscosity vs. concentration of the seven PHIC samples studied in this work were all similar (except for the one for the lowest M sample) in shape to viscosity η' vs. concentration curves shown before (AHARONI 1979, AHARONI & WALSH 1979, AHARONI 1980a). A typical curve, plotted in terms of the inverse velocity of the falling ball, as well as in terms of the apparent viscosity calculated according to FERRY et al. (1950), is shown in Fig. 1. It should be noted that because the falling-ball method operates at shear rates different from those previously used, the numerical values of η are expected to differ somewhat from those of η' . The inverse velocities and the corresponding values of η_m of the

investigated PHIC solutions are plotted in Fig. 2 against the M_w values of the corresponding polymers.

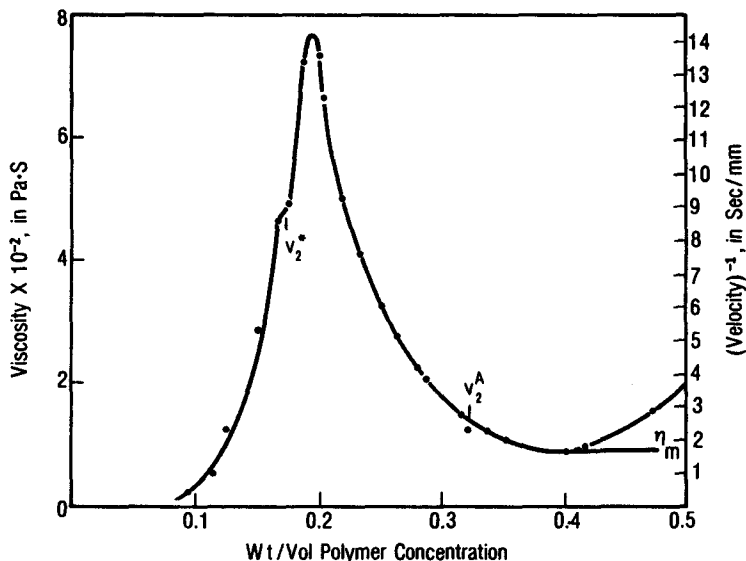


Figure 1. Plot of the apparent viscosity, and inverse velocity of the falling ball, as a function of PHIC concentration in toluene. The points v_2^* where anisotropy appears and v_2^A where isotropy vanishes, are indicated. The point η_m is defined.

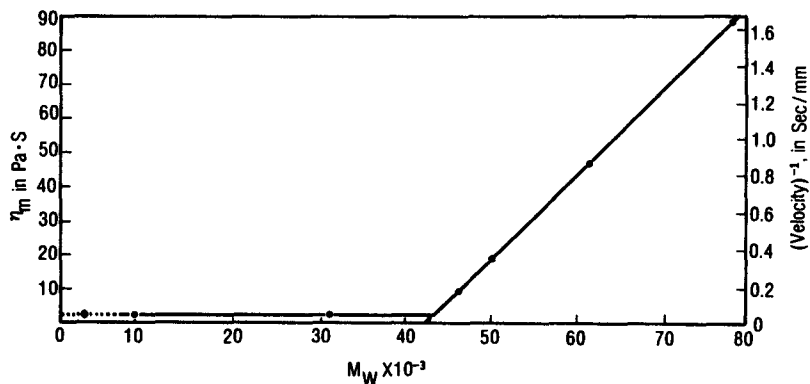


Figure 2. Plot of η_m , the minimal viscosity in the anisotropic range, and the corresponding inverse velocity as a function of M_w of PHIC.

The inverse velocity - M_w or the $\eta_m - M_w$ dependence clearly follows two linear relationships, one for M_w higher than 42 600 and the other for lower molecular weights. The slope of the high molecular weight branch of the curve is represented by the relationship

$$\eta_m (\text{in Pa}\cdot\text{s}) = 2.5 \times 10^{-3} (M_w - 42\,600) .$$

The reason for the linearity of the curve, as well as for the abrupt break in it, is not ascertained yet, but we assume that the latter may be associated with the point at which the PHIC macromolecules start deviating from rodlike behavior and gradually adopt a worm-like conformation (KRATKY & POROD 1949).

In five of the seven samples, the values of η_m were 15% or higher of the corresponding values of η^* . In one sample, of $M_w = 31\,200$, η_m amounted to only 0.09 of its η^* , and in a sample of $M_w = 46\,600$, η_m was only 0.07 of η^* . All these values are higher than anticipated by MATHESON (1980) for the minimum viscosity of anisotropic solutions. A deviation of the ratios η_m/η^* from prediction may be expected for macromolecules deviating from rodlike behavior, but it is surprising for the samples of low M polymer, assumed to be rodlike. It should be recognized that, allowing 0.2 nm chain length per repeat unit (BERGER & TIDSWELL 1973) and about 1.0 nm for the chain diameter, the average axial ratio at the break in the curve in Fig. 2 corresponds to $\bar{x} = 67$. Samples of lower molecular weight are in the \bar{x} range discussed by Matheson and were expected to conform with his estimates. The fact that for these samples η_m/η^* is significantly larger than predicted, is not understood by us.

With respect to the high M branch of the curve in Fig. 2, it was gratifying to find that the numerical values of η_m measured in this work were in a modest agreement with calculations according to AHARONI (1980b). The lowest molecular weight sample ($M_w < 4000$) failed to

show lyotropic mesomorphism, as expected from a polymer with very small axial ratio.

One final point: the apparent viscosities measured in this study are several orders of magnitude larger than those encountered in studies of low molecular weight liquid crystals (CHANDRASEKHAR 1977, DeGENNES 1975). Under our experimental conditions, one can not separate the three anisotropic viscosity coefficients and measures an average apparent viscosity. Furthermore, values of η and η_m obtained in this work were very close to the values of η' and η'_m obtained by other techniques, for isotropic as well as anisotropic solutions, leading us to believe that the corresponding values are essentially the same. Because of all these, it is felt that the use of the falling-ball method was justified. Alternatively, one can plot the molecular weights in Fig. 2 against time or inverse velocity and reach the same conclusions as above, altogether avoiding the need to determine numerical values for the apparent viscosity.

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