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Concentration Dependence of Solution Viscosities of Rigid Rod Polymers

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Considerable theoretical and semiempirical efforts have been devoted to the study of the concentration dependence of the viscosities of polymer solutions.[1] Equation 1 is a general expression of specific viscosity, η_{sp}, in the form of a power series of concentration, C, and intrinsic viscosity, $[\eta]$.

$$\eta_{sp} = C[\eta]\{1 + k_1C[\eta] + k_2(C[\eta])^2 + k_3(C[\eta])^3 + ...\} \tag{1}$$

In eq 1, $C[\eta]$ is a measure of the hydrodynamic volume fraction of the polymer in solution and is a dimensionless parameter used to obtain the scaling quantity $\eta_{sp}/C[\eta]$ used by Simha and Utracki;[2] the k_i's are the coefficients of the power series with the k_1 commonly known as the Huggins constant. For flexible polymers, the majority of experimental k_1 values fall in the range 0.3−0.5, as can be seen in the extensive compilation by Stickler and Sutterlin.[3] The higher order k terms embody the modification of the flow pattern around each polymer as a result of overlap which is alternatively referred to long-range hydrodynamic interaction.

However, a consensus has yet to be reached about the magnitudes of the higher order coefficients. Recently, Matsuoka and Cowman[4] have found that the specific viscosities of the two diversely different polymers, hyaluronan (a polysaccharide) in aqueous salt solutions[5] and polyisoprene in Isopar G (a hydrocarbon),[6] can be represented by the first four terms of eq 1 with a common set of k_i values, namely, $k_1 = 0.4$, $k_2 = (k_1)^2/2!$, and $k_3 = (k_1)^3/3!$. These coefficients provide an excellent fit of the experimental data which cover 6 decades of η_{sp} and more than 2 decades of $C[\eta]$ values (Figure 1). Note that the k_i values obtained by Matsuoka and Cowman constitute the terms in the series expansion of the function $C[\eta]\ \exp(kC[\eta])$, which was proposed earlier by Martin[7] and was shown to be obeyed reasonably well by several investigators.[12] But the full exponential function overestimates η_{sp} at $C[\eta]$ values larger than about 3, and three k terms seem to suffice.

There are only fragmentary data in the literature on the solution viscosities of rigid polymers, primarily because rodlike polymers generally have limited solubilities. The situation is further complicated by the fact that strong acids are sometimes used as solvents that may protonate the polymer chain, leading to intermolecular electrostatic repulsion. A rigid polymer that is soluble in common organic solvents would alleviate some of the complexities in viscosity behaviors and would be an attractive candidate to see whether an expression similar to eq 1 is applicable. We have therefore synthesized a series of poly(benzoyl-1,4-phenylene)s (PBP) having different molecular weights and microstructures that are soluble in organic solvents such as *N*-methylpyrrolidone (NMP), dimethylacetamide (DMAc), tetrahydrofuran, and chloroform. The synthetic procedures have been described in the literature.[8,9] By using different catalysts, we have synthesized PBP-II which contains both head-to-tail and head-to-head linkages and PBP-I in which the repeating units are arranged predominantly in a head-to-tail fashion (Figure 2). PBP-II has an intrinsic viscosity of 2.90 dL/g in DMAc. The GPC (gel permeation chromatagraphy) molecular weight (M_w) is 1.68 × 10^5 (polystyrene equivalent). Although GPC molecular weights of rigid polymers often show larger discrepancies with light scattering M_w's, the value nevertheless provides an estimate of the length of the rod. (For a MW of 1.68 × 10^5, the contour length of the rod is about 410 nm; the diameter of the rod is about 1.2 nm if it is assumed that the benzoyl group can be placed on either side of the main chain.) The intrinsic viscosity of PBP-I in DMAc is 0.57dL/g, and the GPC molecular weight (M_w) is 2.65 × 10^4. The ratio of M_w/M_n, from GPC data, is 1.7 for PBP-II and 2.5 for PBP-I.

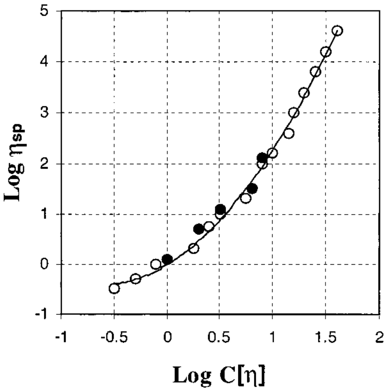

Figure 1. Plot of specific viscosity vs $C[\eta]$ for hyaluronan and polyisoprene solutions (solid line calculated with k_1 = 0.4) (●, polyisoprene;[6] ○, hyaluronen;[5] —, eq 1) with four terms.

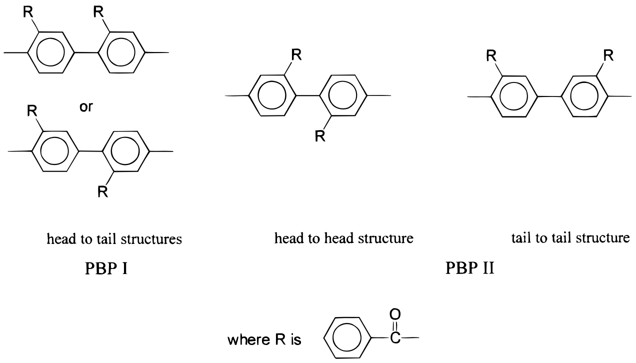

Figure 2. Structures of poly(benzoyl-1,4-phenylenes).

The viscosities of PBP-I and -II solutions were determined with the use of an Ubbelohde viscometer, which has a flow time of 120 s at 25 °C for DMAc.

In the concentration ranges of our study, up to 1.58 g/dL for PBP-II and 10.13 g/dL for PBP-I, the solutions are clear and show no birefringence when examined by a microscope with cross polars. The PBP-II data can be fitted by eq 1 with a k_1 value of 0.4 with $k_2 = (k_1)^2/2!$ and $k_3 = (k_1)^3/3!$. In Figure 3, the specific viscosities are plotted against $C[\eta]$, and for the purpose of illustration,

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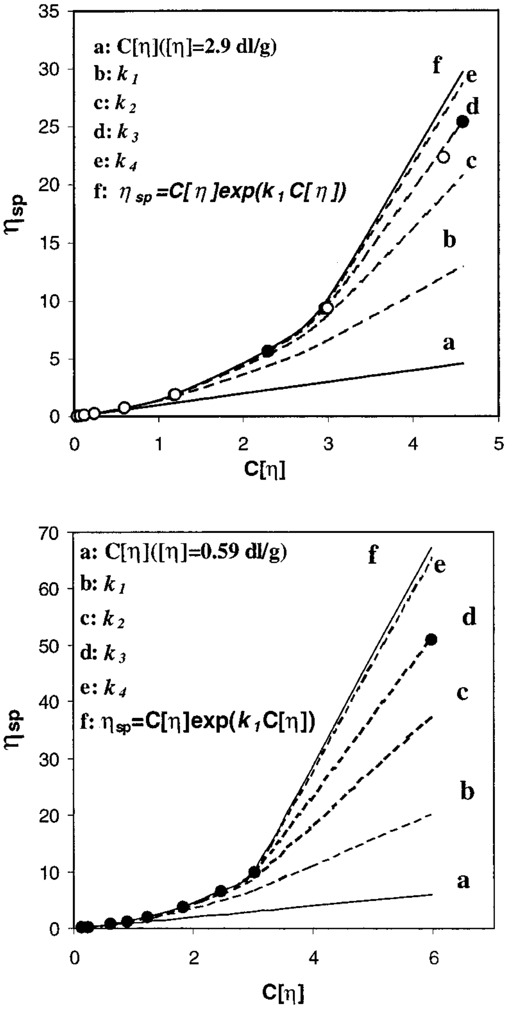

Figure 3. Plots of specific viscosity vs $C[\eta]$ for PBP-II (top) (●, PBP-II (DMAc); ○, PBP-II (NMP)) and PBP-I (bottom) (●, PBP-I (DMAc)).

the right-hand side of eq 1 is calculated to contain one, two, three, and four terms, respectively. The viscosity data for PBP-II in NMP ($[\eta] = 2.85$ dL/g) fall on the same curve. If a k_4 term is added to eq 1, the calculated η_{sp} values are too large when $C[\eta]$ exceed about 2.8. The exponential function $\exp(k_1(C[\eta]))$ overestimates η_{sp} by an even greater margin; the exponential function, however, gives a good fit of the experimental data for $C[\eta]$ less than 2.8. In the case of PBP-I in DMAc, a k_1 value of 0.5 gives an excellent fit of the experimental results when the same relation among the k's is used. We note that the theoretical k_1 value for a rigid rod is 0.73−0.77,[10,11] higher than our experimental values. The reasons for the higher theoretical estimate derived from long-range hydrodynamic interaction can be found in ref 11. Although the ranges of η_{sp} and $C[\eta]$ values in this investigation are limited in comparison to the data in Figure 1, the interrelationship among the k values appears not to have been reported previously for rigid polymers. That the same viscosity−concentration relationship seems to be applicable to both flexible and rigid polymer provides materials for thought. We are currently engaged in additional studies using other rodlike polymers to see whether the relation has a wider applicability.

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