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# Molecular Weight Characterization of Wholly Para-Oriented, Aromatic Polyamide-Hydrazides and Wholly Aromatic Polyamides

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# Molecular Weight Characterization of Wholly Para-Oriented, Aromatic Polyamide-Hydrazides and Wholly Aromatic Polyamides*

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## ABSTRACT

A series of Monsanto Co.'s X-500 class, wholly para-oriented, aromatic amide-hydrazide polymers having molecular weights between 25,000 and 65,000 has been characterized by viscometry and light scattering in DMSO solution. Viscosity measurements are not complicated by degradation, polyelectrolyte effect, or shear corrections in this molecular weight range where intrinsic viscosities ([$\eta$]) are 3-8 dl/g. The viscosity-molecular weight relationship is

$$[\eta] = 6.15 \times 10^{-5} M_v^{1.06}$$

Relationships among specific, inherent, and intrinsic viscosities, viscosity-average molecular weight ($M_v$), and weight-average molecular weight are derived.

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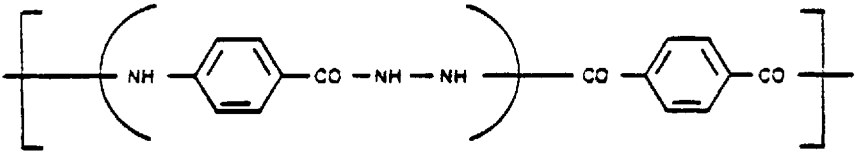
The polymer coil of the X-500 class, completely aromatic polyamide-hydrazide has a highly extended chain conformation in solution owing to its wholly para-orientation. Individual polymer coils occupy large "effective volumes" in solution, and moderate molecular weights lead to extremely high intrinsic viscosities. Estimates of unperturbed polymer coil dimensions indicate abnormally low chain flexibility. Mean square displacement length of the polyamide-hydrazide chain is extremely large. Intrinsic viscosity-molecular weight relationships for M3P, a wholly aromatic polyamide prepared from a meta-oriented diamine containing preformed amide linkages and terephthaloyl chloride, in two different solvents are reported. In addition, recipes are given for estimating molecular weights of other aromatic polyamides.

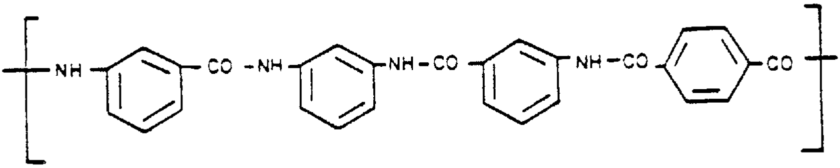
## INTRODUCTION

A reliable and meaningful procedure for viscometric characterization of wholly aromatic polymers is required for routine quality control analysis and fundamental molecular weight determination. A knowledge of polymer molecular weight, preferably expressed by one or more averages, is indispensable in even the cursory characterization of a given sample. Information gained from polymer solution property studies can be indispensable in understanding wholly aromatic polymer systems, since polymerizations are conducted in solution and fibers, films, etc., are formed from these solutions.

Polymers characterized in this work are one member of Monsanto Co's X-500 class of high-modulus, fiber-forming polymers, an all-para polyamide-hydrazide, with the structure [1, 2]



and a thermally stable aromatic polyamide M3P, or MMM-P as originally described by Preston [3], prepared from a meta-oriented diamine containing preformed amide linkages and teraphthaloyl chloride with the structure



## EXPERIMENTAL RESULTS

### Solvents

The following solvents were employed in characterization: dimethyl sulfoxide (DMSO), dimethyl acetamide (DMAc)/5% LiCl, and 96% $H_2SO_4$. Analytical reagent grade $H_2SO_4$; pure, dry DMAc; and reagent grade LiCl were used without further purification. DMSO was vacuum distilled for light-scattering studies and used as received for viscometry.

### Polymers

Series of each three M3P and four X-500 class polyamide-hydrazide samples having a broad range of molecular weights were characterized in this work. All polymers were prepared at Monsanto Co's Chemstrand Research Center, Inc. under the guidance of Preston and Black [1-3]. Samples of the polyamide-hydrazide had inherent viscosities of 3-7 dl/g at 0.1% concentration in DMSO at 25°C. The M3P inherent viscosities were 1-3 dl/g at 0.1% concentration in DMAc/5% LiCl at 25°C.

### Viscometry

Viscosity measurements were carried out in the normal fashion [4]. Sulfuric acid (96%) and DMAc/5% LiCl were the solvents for

M3P, and DMSO was solvent for the polyamide-hydrazide. Solutions were prepared at room temperature in all cases. Viscosities were determined at four or five different concentrations at 25°C. Cannon-Fenske viscometers were employed, and these were selected to give solvent flow times in excess of 100 sec. All flow times encountered were sufficiently long to justify neglect of kinetic energy corrections.

The specific viscosity $\eta_{sp}$ is defined by the expression

$$\eta_{sp} = \rho t/\rho_0 t_0 - 1 \simeq (t - t_0)/t_0 \tag{1}$$

where t and $t_0$ are the observed flow times for solution and solvent, respectively, and $\rho$ and $\rho_0$ are the corresponding densities. For dilute solutions, $\rho/\rho_0$ may be taken as unity. The intrinsic viscosity was determined by measuring $\eta_{sp}$ at several concentrations selected to yield $0.2 \leq \eta_{sp} \leq 0.8$ and co-plotting the reduced specific viscosity $\eta_{sp}/c$ and the reduced natural logarithm of relative viscosity $(\ln \eta_{rel})/c = [\ln(\eta_{sp} + 1)]/c$ vs polymer concentration c. Coincidence of intercepts and correlation of limiting slopes were imposed in accordance with the requirements of the functional relationships assumed, viz., the Huggins [5] and Kraemer [6] equations

$$\begin{aligned} \eta_{sp}/c &= [\eta] + k'[\eta]^2 c + 0(c^2) \\ (\ln \eta_{rel})/c &= [\eta] - k''[\eta]^2 c + 0(c^2) \end{aligned} \tag{2}$$

in which k' and k'' are constants with k' + k'' = 1/2.

The double extrapolations of $\eta_{sp}/c$ and $(\ln \eta_{rel})/c$ to zero concentration were linear for all solvents. Values of $[\eta]$, k', and k'' for M3P and polyamide-hydrazides in the three solvents employed are shown in Table 1.

Theoretically, the sum k' + k'' should equal 1/2. Experimentally (cf. Table 1) we found k' + k'' = 0.50 ± 0.04, which we consider in excellent agreement with theory.

To ascertain whether or not the polymers are degraded in solution, viscosities were measured as a function of time. In no

TABLE 1. Solution Viscosity Parameters at 25°C

| Polymer | Solvent | $\eta_{inh}$[a] | $[\eta]$ | k' | k'' |
|---|---|---|---|---|---|
| Amide-hydrazide-1 | DMSO | 3.25 | 3.33 | 0.50 | 0.02 |
| Amide-hydrazide-2 | DMSO | 3.84 | 4.05 | 0.40 | 0.12 |
| Amide-hydrazide-3 | DMSO | 5.11 | 5.50 | 0.39 | 0.13 |
| Amide-hydrazide-4 | DMSO | 7.02 | 7.29 | 0.51 | 0.05 |
| M3P-1 | DMAc/5% LiCl | 1.23 | 1.27 | 0.25 | 0.21 |
| M3P-2 | DMAc/5% LiCl | 1.89 | 1.94 | 0.37 | 0.12 |
| M3P-3 | DMAc/5% LiCl | 2.94 | 3.03 | 0.44 | 0.09 |
| M3P-1 | $H_2SO_4$ (96%) | 1.05 | 1.07 | 0.27 | 0.19 |
| M3P-2 | $H_2SO_4$ (96%) | 1.70 | 1.74 | 0.35 | 0.15 |
| M3P-3 | $H_2SO_4$ (96%) | 2.77 | 2.95 | 0.27 | 0.20 |

[a] $\eta_{inh} = (\ln \eta_{rel})/c$ at 0.1% concentration.

case was any decrease in viscosity observed over times much longer than those encountered in solution characterization measurements. The viscosity of the polyamide-hydrazide in DMSO solution at room temperature remained unchanged over a 5-day period, for example.

If the intrinsic viscosity is high (i.e., > ~5 dl/g), it is often dependent on the rate of shear in the capillary viscometer. It should be noted in passing that extrapolation to zero polymer concentration does not eliminate effect of shear. The two highest molecular weight polyamide-hydrazide polymers were characterized as a function of shear in DMSO solution at 25°C. A range of shear rates was achieved by varying the capillary radius of the viscometers. Viscometers having capillaries larger and smaller than the series 75 viscometers normally employed in X-500 characterization were used. Kinetic energy corrections were applied when necessary. The results are given in Table 2.

The amide-hydrazide Polymer 3 shows no detectable dependence on shear rate, while polyamide-hydrazide 4, a higher molecular weight sample, indicates a slight dependence in the expected direction. The rate of decrease of viscosity with shear rate, $-d\eta_{sp}/d\dot{\gamma}$, is 0.005 for Polymer 4. Since the difference between

TABLE 2. Effect of Shear Rate on Polyamide-Hydrazide Solution Viscosity

| Polymer | Concn (g/dl) | Viscometer[a] | $\dot{\gamma}$[b] | $\eta_{sp}$ |
|---|---|---|---|---|
| Amide-hydrazide-3 | 0.10 | 50 | 1.35 | 0.640 |
| | 0.10 | 75 | 2.54 | 0.650 |
| | 0.10 | 100 | 4.84 | 0.640 |
| | 0.10 | 150 | 12.9 | 0.645 |
| Amide-hydrazide-4 | 0.05 | 50 | 1.92 | 0.426 |
| | 0.05 | 75 | 3.06 | 0.416 |
| | 0.05 | 100 | 6.33 | 0.404 |

[a] Cannon-Fenske viscometer series.
[b] Shear rate in arbitrary units.

$\eta_{sp}$ at shear rates encountered with 75 series viscometers and at extrapolated zero shear rate are within experimental error, shear corrections were not applied. Unless there is a considerable increase in polymer molecular weight over that studied herein, shear corrections can be neglected in routine viscometric characterization of wholly aromatic polymers.

Linearity of the plots of $\eta_{sp}/c$ and $(\ln \eta_{rel})/c$ and lack of shear dependence enables one to calculate $[\eta]$ from a one point $\eta_{sp}$ measurement at concentration c using the expression [4]

$$[\eta] = (2^{1/2}/c)(\eta_{sp} - \ln \eta_{rel})^{1/2} \quad (3)$$

The inherent viscosity $\eta_{inh}$ is defined by

$$\eta_{inh} = (\ln \eta_{rel})/c \quad (4)$$

For the wholly para polyamide-hydrazides a concentration of 0.1 g/100 ml of solution in DMSO is often employed. Rearranging Eq. (3) and recalling that $\eta_{sp} = \eta_{rel} - 1$, one obtains, for X-500 at $c = 0.1$ g/dl

$$[\eta] = 14.14[\exp(0.1\,\eta_{inh}) - 1 - 0.1\eta_{inh}]^{1/2} \quad (5)$$

Thus $\eta_{sp}$, $\eta_{rel}$, $\eta_{inh}$, and $[\eta]$ are simply interrelated. In most instances, using Eq. (3) or (5), one can obtain $[\eta]$ within a few per cent of the value gotten by running a full concentration dependence when the specific viscosity of the solution is low (i.e., $\eta_{sp} < 0.8$).

Attempts were made to determine $[\eta]$ of the polyamide-hydrazide polymers in DMAc/5% LiCl and $H_2SO_4$. The former was not a good solvent for the polyamide-hydrazide. The latter appeared to degrade the polymer to monomeric type species, probably by hydrolyzing the hydrazide linkages. No further work was performed with these solvents. A study to find a suitable solvent for osmometry was unsuccessful because all polyamide-hydrazide solvents found either degraded the polymer or the membrane or both.

For two M3P samples $[\eta]$ was measured as a function of LiCl concentration in DMAc and of temperature. The LiCl concentration was varied between 2.0 and 5.0% in 0.5% increments. There was a maximum in $[\eta]$ at ~3% LiCl concentration, indicating that this composition was the best M3P solvent. All $[\eta]$'s decreased smoothly with increasing temperature over the range 25 to 65°C. This decrease in $[\eta]$ with T has been observed with other polyamides [4]. Similarly, a smooth decrease in $[\eta]$ with increasing T between 25 and 75°C was observed for the wholly para-oriented polyamide-hydrazide in DMSO solution.

## Light Scattering

The light-scattering procedure employed has been described previously [4] in great detail; therefore, only a brief description is presented herein. Light-scattering measurements required for evaluation of weight-average molecular weight $\overline{M}_w$ were carried out with a Brice Phoenix Light Scattering Photometer, Series 1999-108, employing unpolarized blue and green light. The solvents were DMSO and $H_2SO_4$ (96%) for the X-500 class polyamide-hydrazide and M3P, respectively. The temperature of the sample cell was maintained at approximately 25°C by circulation of water from an external source through the hollow cell table. For each sample, scattering intensities for four or more polymer concentrations were determined at angles between 30 and 135°. Solutions spanning an appropriate concentration range (0.1-0.4% at $\overline{M}_w = 60{,}000$ for the polyamide-hydrazide) were individually prepared and clarified by filtration through ultrafine glass frits under 4-10 lb nitrogen pressure directly into the cell, previously rendered dust-free with freshly distilled acetone condensate.

All of the samples investigated exhibited fluorescence under blue light, increasing with polymer concentration and contributing up to 20% of the total radiation scattered at 90°. For this reason all $\overline{M}_w$ values were obtained with green light where fluorescence was negligible. The measured values of the refractive index increment (dn/dc) at 25°C for the polyamide-hydrazide and M3P are given in Table 3.

In the treatment of data, reciprocal excess scattering intensities $I_\theta^{-1}$ were plotted vs $\sin^2(\theta/2)$ and extrapolated to zero

TABLE 3. Refractive Index Increments for Polymers in Solution

| | | (dn/dc) (cm$^3$/g) | |
|---|---|---|---|
| Polymer | Solvent | Blue (4358 Å) | Green (5461 Å) |
| Amide-hydrazide | DMSO | 0.195 | 0.166 |
| M3P | $H_2SO_4$ (96%) | - | 0.305 |
| M3P | DMAc/5% LiCl | 0.292 | 0.254 |

angle for each polymer concentration. The dissymmetry ratio $I_{45}/I_{135}$ observed for solvent was 1.04 and less than 1.4 for all solutions studied. Extrapolation to zero polymer concentration was best effected by plotting $(c/I_0)^{1/2}$ vs c, in accordance with the relationship

$$(Kc/R_0)^{1/2} = (1/\overline{M}_w)^{1/2}(1 + A_2\overline{M}_w c) \qquad (6)$$

where $R_0$ is the Rayleigh ratio at zero angle, K is the optical constant, and $A_2$ is the second virial coefficient. Values of $\overline{M}_w$ determined in this manner are listed in Table 4. Virial coefficients were $\sim 10^{-3}$ cm$^3$ mole g$^{-2}$ for the polyamide-hydrazide in DMSO at 25°C.

## DISCUSSION

Viscosity-molecular weight relationships were established in accordance with procedures and recipes previously described [4]. A preliminary plot of log $[\eta]$ vs log $\overline{M}_w$ was constructed. By calculating the slope "a" of this line and assuming a molecular weight distribution, one can calculate the viscosity-average molecular weight $M_v$ from $\overline{M}_w$. The "most probable" distribution is a reasonable choice for condensation polymers of this type [7]. In this case

TABLE 4. Weight-Average Molecular Weights

| Polymer | Solvent | $[\eta]$ | $\overline{M}_w$ |
|---|---|---|---|
| M3P-2 | $H_2SO_4$ | 1.74 | 110,000 |
| M3P-7 | $H_2SO_4$ | 2.95 | 195,000 |
| Amide-hydrazide-1 | DMSO | 3.33 | 29,700 |
| Amide-hydrazide-3 | DMSO | 5.50 | 44,000 |
| Amide-hydrazide-4 | DMSO | 7.29 | 62,300 |

$$M_v = [(1 + a)\Gamma(1 + a)]^{1/a}\overline{M}_w/2 \tag{7}$$

in which Γ denotes the gamma function.

After calculating $M_v$ from $\overline{M}_w$ and plotting log $[\eta]$ vs log $M_v$, one arrives at the desired viscosity-molecular weight relationship

$$[\eta] = K'M_v{}^a \tag{8}$$

In the applications following, K' and "a" were determined by least squares analysis. The $[\eta]$-M relationship for the wholly para-oriented polyamide-hydrazide in DMSO at 25°C was

$$[\eta] = 6.15 \times 10^{-5} M_v{}^{1.08} \tag{9}$$

where $\overline{M}_w = 0.99\ M_v$ for the "most probable" distribution. It should be noted in passing that

$$M_v < \overline{M}_w \text{ for } a < 1$$

$$M_v = \overline{M}_w \text{ for } a = 1$$

$$M_v > \overline{M}_w \text{ for } a > 1$$

Two relationships were established for M3P at 25°C. They were

$$[\eta] = 2.6 \times 10^{-4} M_v^{0.77} \tag{10}$$

in DMAc/5% LiCl where $\overline{M}_w = 1.05 M_v$, and

$$[\eta] = 4.2 \times 10^{-5} M_v^{0.92} \tag{11}$$

in 96% $H_2SO_4$ where $\overline{M}_w = 1.02 M_v$.

At a given molecular weight the wholly aromatic amide-hydrazide polymer sample will have a much higher intrinsic viscosity than most random coiling polymers owing to its all-para orientation. For example, an intrinsic viscosity of 9 dl/g on the polyamide-hydrazide corresponds to a viscosity-average molecular weight of only 73,000. Most polymers would have viscosities an order of magnitude lower at this molecular weight.

It is interesting to compare the polymer chain dimensions in solution for M3P and the polyamide-hydrazide. A priori one would predict a more extended conformation for the all-para X-500 class polymer. This is already partially indicated by the high exponent in the $[\eta]$-M relationship. According to Flory [8], the root-mean-square end-to-end length $\langle r^2 \rangle^{1/2}$ of a polymer chain in solution can be expressed approximately by

$$\langle r^2 \rangle^{1/2} = 8(M_v[\eta])^{1/3} \tag{12}$$

where r is in Angstrom units.

At a common molecular weight of 60,000, $\langle r^2 \rangle^{1/2}$ for the all-para X-500 class polymer in DMSO is twice that for M3P in DMAc/5% LiCl. Neglecting specific solvent effects, one would estimate that a polyamide-hydrazide polymer coil occupies eight times more "effective volume" in solution than an M3P coil. One would expect behavior similar to that of the all-para polyamide-hydrazide for other all-para systems.

Recently, a series of papers which give semi-empirical recipes for estimating $[\eta]$-M relationships from chemical compositions has appeared [9]. It has been demonstrated that these procedures can be employed to estimate unperturbed dimensions and $[\eta]$-M relationships in certain instances. Essentially the procedure allows one to determine K' in terms of "a" (cf. Eq. 8). For the polyamide-hydrazide, the result is

$$[\eta] = 86.4 \times 10^{-3(1+a)} M_v{}^{a} \tag{13}$$

Immediately the number of unknowns is reduced from two to one. Thus one needs only to perform a single light-scattering and viscosity experiment or make an educated guess at "a" based on other known relationships to arrive at the $[\eta]$-M relationship. Substituting the known value for "a" into Eq. (13), one obtains

$$[\eta] = 5.72 \times 10^{-5} M_v{}^{1.06} \tag{14}$$

which is within ~7% of Eq. (9) over the molecular weight range encountered in this work.

This method could circumvent the need for tedious establishment of $[\eta]$-M relationships for every new polymer that comes along, especially for those of only transient interest. Such techniques would be appropriate for estimating $[\eta]$-M relationships for other wholly aromatic polyamides should the need arise. Additional $[\eta]$-M approximation techniques are discussed in Ref. 4.

The value of K' in Eq. (8) for a Θ-solvent, i.e., a = 0.50, according to the method of van Krevelen and Hoftyzer is $K = 273 \times 10^{-5}$. This value represents a fairly reasonable ordinate intercept in a plot of $[\eta]/M^{1/2}$ vs $M^{1/2}$ as recommended by Stockmayer and Fixman [10].

In a Θ-solvent

$$[\eta]_{\Theta} = KM^{1/2} \tag{15}$$

and

$$K = \Phi(\langle r^2\rangle_0/M)^{3/2} \tag{16}$$

where Φ is the viscosity constant and $\langle r^2\rangle_0$ is the mean square displacement length of the polymer chain in its unperturbed state.

The procedure of Kurata and Stockmayer [11] was employed to correct $\Phi$ for molecular weight heterogeneity according to the "most probable" distribution. A value of $2.70 \times 10^{21}$ dl mole$^{-1}$ cm$^{-3}$ was obtained and used to calculate unperturbed chain dimensions of the polyamide-hydrazide given by

$$(\langle r^2 \rangle_0 / M)^{1/2} = 1000 \times 10^{-11}$$

The unperturbed dimensions of polymer molecules are practically independent of the choice of $\Theta$-solvent and, therefore, are characteristic of the particular macromolecule chain. The estimated values for unperturbed dimensions of the polyamide-hydrazide polymer coil indicate abnormally low chain flexibility. The polyamide-hydrazide polymer chain assumes a highly extended chain conformation in solution in comparison with most random coiling synthetic polymers.

The highly extended chain conformation for the polyamide-hydrazide in solution prevails also in the solid state where the degree of order is much greater, as expected, and the polymer chain can be virtually completely extended [12].

## CONCLUSIONS

Viscosity-molecular weight relationships have been established in DMSO for a wholly para-oriented, aromatic polyamide hydrazide useful for very high-modulus fibers and in DMAc/5% LiCl and 96% $H_2SO_4$ for the largely meta-oriented, wholly aromatic polyamide, M3P. Interrelationships among $\eta_{sp}$, $\eta_{inh}$, $[\eta]$, $M_v$, and $\overline{M}_w$ have been derived for both polymers.

Recipes for estimating $[\eta]$-M relationships for wholly aromatic polymers were considered and found to be appropriate approximations.

The polymer coil of the X-500 class, wholly para-oriented polyamide-hydrazide has a highly extended chain conformation in solution owing to its all-para orientation. Individual polymer coils occupy large "effective volumes" in solution, and moderate molecular weights lead to extremely high intrinsic viscosities. Estimates of unperturbed polymer coil dimensions indicate abnormally low chain flexibility. Mean square displacement length of the polyamide-hydrazide chain is extremely large.

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