

# The Effect of Additives, Solvent Type, and Polymer Concentration on Macromolecule Dimensions

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## SYNOPSIS

An equation is derived to estimate the hydrodynamic volume occupied by a typical linear polymer molecule, knowing only the polymer molecular weight and concentration of polymer in the solution. This equation may be applied to solutions above a minimum polymer concentration. Accuracy of the equation is determined by comparing it to an established method of calculating macromolecule dimensions.

Above dilute solution conditions, the volume pervaded by a macromolecule is affected mainly by the polymer molecular weight and concentration of polymer in the solution. Chain dimensions are generally unaffected by the type of polymer, solvent, or additive in the solution.

## INTRODUCTION

The hydrodynamic structure of nonentangled linear polymer solutions can be determined by the following equation<sup>1-5</sup>:

$$v\epsilon = 4\pi R^3/3 \quad (1)$$

where  $v$  is the bulk (crystalline) polymer volume ( $\text{cm}^3/\text{molecule}$ ),  $\epsilon$  is a swelling factor to account for the increase in volume pervaded by a polymer molecule when in a solvent, and  $R$  is the hydrodynamic radius of the volume occupied by each polymer molecule (cm). In dilute solutions, the above equation is reduced to the following<sup>6</sup>:

$$4\pi R_0^3/3 = [\eta]M/2.5N_0 \quad (2)$$

where  $R_0$  is the dilute solution macromolecule radius;  $[\eta]$  is the solution intrinsic viscosity ( $\text{cm}^3/\text{g}$ ), a thermodynamic parameter to characterize dilute polymer solutions;  $M$  is the number-averaged polymer molecular weight ( $\text{g}/\text{gmol}$ ); and  $N_0$  is Avogadro's number ( $6.023 \times 10^{23}$  molecules/ $\text{gmol}$ ).

The solution intrinsic viscosity is also related to the polymer molecular weight by the Mark-Houwink equation:

$$[\eta] = KM^\alpha \quad (3)$$

where  $K$  ( $\text{g}/\text{cm}^3$ ) and  $\alpha$  are constants that change with the solution temperature and choice of solvent used to dissolve the polymer. By comparing eq. (3) to eq. (2), the hydrodynamic volume occupied by a polymer molecule in a dilute solution is dependent on the type or strength of solvent. Additives (inorganic salts, different solvents, or different polymers) used in polymer solutions can influence  $[\eta]$ ,  $K$ , and  $\alpha$ , thereby affecting the dilute macromolecule radius.

Equation (2) may be applied to dilute polymer solutions only. As polymer is added to the solution, a critical polymer concentration  $g_0$  ( $\text{g}/\text{mL}$  solvent) is reached that separates the dilute from the semi-dilute regions.  $g_0$  is considered to be the point where adjacent macromolecules can interact, i.e., when the volume occupied by a macromolecule becomes dependent on the number of polymer molecules in a given volume of solution.<sup>7-9</sup> Approximations of  $g_0$  can be made by the following equation:

$$g_0 \approx A/[\eta] \quad (4)$$

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where  $A$  is a constant that is dependent on the assumed size, shape, structure, volume fraction, and packing arrangements of the macromolecules in the solution.<sup>7-13</sup>  $A$  may be calculated to be between 0.48 and 2.5, but is experimentally determined to be about 5.<sup>13</sup> Equation (1) is used to determine polymer solution structure when above the critical polymer concentration.

### THE VOLUME OF A MACROMOLECULE ABOVE DILUTE SOLUTION CONDITIONS

Each macromolecule shrinks as an increasing number of them are put into the solution.  $R$  decreases with increasing polymer concentration  $g$  ( $g/\text{mL}$  solvent) until an upper critical polymer concentration  $g_x$  is reached.  $g_x$  occurs when the volume fraction occupied by the macromolecules in the solution approximately equals 0.507,<sup>3</sup> about the volume fraction in space occupied by randomly packed spheres. The macromolecule radius at or above  $g_x$  is approximately the unperturbed macromolecule radius,  $R_x$ , the radius of the polymer molecules when at the point of precipitation from the solution.<sup>8,10,14-19</sup> Individual polymer molecules are generally separate, distinct entities in solutions when the concentration is below  $g_x$ . Above  $g_x$ , due to intermolecular contacts or entanglements, a small increase in the polymer concentration will cause a large increase in the solution viscosity. A general curve illustrating the variation in polymer coil dimensions with polymer concentration is found in Ref. 10.  $R$  does not change until  $g$  is above  $g_0$  and then decreases to a minimum value when  $g_x$  is reached.

$R$  may be calculated from eq. (1) by determining  $\epsilon$  from the following equation<sup>1-5</sup>:

$$1/\epsilon = 1/\epsilon_0 + g[(\epsilon_0 - \epsilon_x)/\epsilon_0\epsilon_x]/g_x \quad (5)$$

where  $\epsilon_0$  and  $\epsilon_x$  are the swelling factors in dilute and concentrated solutions, respectively. By comparing eqs. (1) and (2),<sup>1-5</sup>

$$\epsilon_0 = [\eta]d/2.5 \quad (6)$$

where  $d$  is the density of the bulk polymer ( $g/\text{cm}^3$ ). It was experimentally determined that<sup>1,2</sup>

$$\epsilon_x = 2.60 + 1.70 \times 10^{-4}Z \quad (7)$$

where  $Z$  is the number of main chain atoms per polymer strand. Since  $g_x$  occurs when the macro-

molecule volume-solvent volume fraction is 0.507,<sup>1-5</sup> then

$$g_x = 0.507d/\epsilon_x \quad (8)$$

and by substituting eqs. (2), (5), (6), and (8) into eq. (1) and rearranging,

$$4\pi R^3/3 = ([\eta]M/2.5N_0) / \{[(\epsilon_0 - \epsilon_x)/0.507d]g + 1\} \quad (9)$$

From eq. (9),  $R$  is related to  $g$  in the following way:

$$R^3 = A_1/(A_2g + 1) \quad (10)$$

where  $A_1$  and  $A_2$  are constants for a particular molecular weight polymer-solvent combination. Therefore, at any polymer concentration,  $R$  can be determined from eq. (1) if  $M$ ,  $[\eta]$ ,  $d$ , and the repeat unit structure are known.

### THE GENERAL MACROMOLECULE VOLUME-POLYMER CONCENTRATION RELATIONSHIP

By comparing eq. (6) to eq. (7), if  $\epsilon_0$  is significantly larger than  $\epsilon_x$ ,

$$4\pi R^3/3 \approx ([\eta]M/2.5N_0)/[(\epsilon_0g/0.507d) + 1] \quad (11)$$

and as long as  $[\eta]$  or the polymer concentration is high enough so that  $\epsilon_0g/0.507d$  is much greater than 1,

$$v\epsilon = 4\pi R^3/3 \approx 0.507M/gN_0 \quad (12)$$

From eq. (12), the hydrodynamic volume occupied by a certain molecular weight polymer can be estimated knowing only the solution polymer concentration. From eq. (12), neglecting bulk polymer density differences,  $R$  above dilute solution conditions is relatively independent of the type of polymer and solvent. This is consistent with the observation that  $\epsilon$  for a certain molecular weight polymer above dilute solution conditions is dependent only on the polymer concentration.<sup>1</sup>

Another method of deriving eq. (12) is by assuming that the volume fraction occupied by the macromolecules is equal to 0.507 at any polymer concentration. This is in agreement with the assumption that the macromolecule volume fraction is quite high

when the critical polymer concentration  $g_0$  is reached.<sup>7-13</sup> Therefore, at any polymer concentration, the volume fraction occupied by macromolecules may be dependent on the type of polymer or solvent used in the solution.

## VERIFICATION AND APPLICATIONS OF THE GENERAL EQUATION

Let  $R$  that is calculated from eq. (1) be designated as  $R_c$ , and  $R$  estimated from eq. (12) be  $R_e$ . Then, for any  $g$  between  $g_0$  and  $g_x$ ,

$$\Delta R = R_e - R_c \quad (13)$$

where  $\Delta R$  is a measure of the effect of the solvent type on macromolecule swelling. The magnitude of  $\Delta R$  also reveals the accuracy of eq. (12) at any  $g$  above  $g_0$ .

Table I lists  $R_c$ ,  $R_e$ , and  $\Delta R$  at various values of  $g$  for a typical phase inversion membrane aromatic polyamide polymer (PA) in dimethyl acetamide (DMA). From Ref. 20,  $d$  equals 1.3 g/cm<sup>3</sup>,  $M$  equals 31,300 g/gmol, and  $[\eta]$  at 20°C equals 147.22 cm<sup>3</sup>/g. In order to calculate  $g_x$  from eqs. (7) and (8), the molecular weight of each PA repeat unit, composed of 16 main chain atoms, is 238 g/gmol. For illustrative purposes, from eq. (10),

$$R_c^3 = 7.306 \times 10^{-19} / (111.66g + 1) \quad (14)$$

and from eq. (12),

$$R_e^3 \approx 6.290 \times 10^{-21} / g \quad (15)$$

**Table I** Calculated and Approximated Macromolecule Radius Data for Solutions of an Aromatic Polyamide Phase Inversion Membrane Polymer<sup>a</sup>

Polymer Conc (g) (g/ml)	$R_e$ eq. (12) (Å)	$R_c$ eq. (1) (Å)	$\Delta R$ ( $R_e - R_c$ ) (Å)
0.01	85.68	70.15	15.53
0.04	53.98	51.13	2.85
0.05	50.11	48.06	2.05
0.10	39.77	39.16	0.61
0.15	34.74	34.53	0.21
0.20	31.57	31.52	0.05
0.22284 <sup>+</sup>	30.45	30.45	0

<sup>a</sup> Solvent: dimethyl acetamide; solution temperature: 20°C; polymer molecular weight: 31,300 g/gmol.

where the units of  $R$  and  $g$  are cm and g/mL, respectively.

From Table I,  $R_c$  values calculated from eq. (1) exponentially decrease as  $g$  increases. Note by the form of eq. (1) that  $R_c$  does not quite asymptotically approach the unperturbed or Gaussian radius  $R_x$  as  $g$  approaches  $g_x$  (0.22284 g/mL).  $R_c$  calculated above  $g_x$  is less than  $R_x$ . The difference between  $R_c$  and  $R_x$  when  $g$  is greater than  $g_x$  is small, however, due to the inverse exponential relationship between  $g$  and  $R_c$  in eq. (1). Therefore,  $g_x$  is determined from eq. (8) and  $R_c$  is assumed equal to  $R_x$  at or above  $g_x$ .

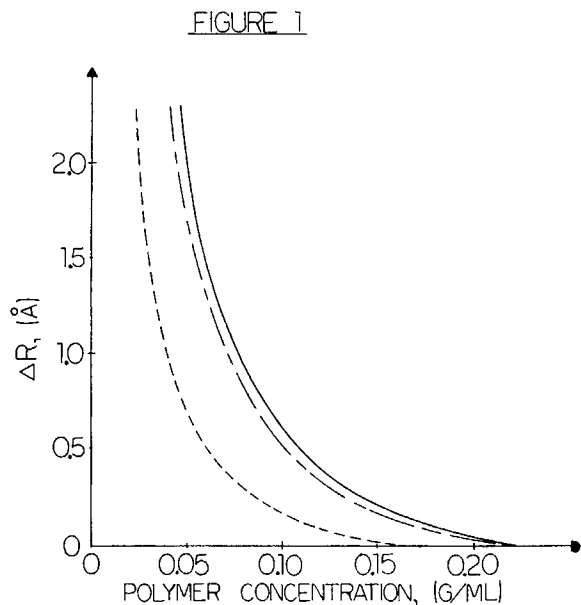
Table I shows that a similar trend exists between  $R_e$  and  $g$ .  $\Delta R$  quickly decreases as  $g$  increases due to the assumption that  $g$  be sufficiently large in order to derive the general equation (12).  $\Delta R$  equals 0 when  $g$  equals  $g_x$ . This is because eq. (12) may be derived by assuming  $\phi$  equals 0.507 at any concentration of polymer.  $\Delta R$  remains close to 0 at polymer concentrations above  $g_x$ . Therefore,  $R_e$  for the concentrated solution region is also determined with eq. (8). It is also observed in Table I that the general equation provides accurate estimates of  $R$  when  $g$  is above 0.05 g/mL.

Because of an assumption used to derive eq. (12), at any  $g$ ,  $\Delta R$  increases as  $[\eta]$  increases. The effect of the solvent type on macromolecule dimensions at any  $g$  can then be related to the magnitude of  $\Delta R$ . In Figure 1, there is a graph of  $\Delta R$  versus  $g$  for the PA in DMA and for the PA in H<sub>2</sub>SO<sub>4</sub> at 20°C. To calculate  $R_c$ , from Ref. 20, the PA—H<sub>2</sub>SO<sub>4</sub> intrinsic viscosity is 179.72 cm<sup>3</sup>/g. From Figure 1, in either solvent,  $\Delta R$  decreases as  $g$  increases and becomes 0 when  $g$  equals  $g_x$ . This means that the effect of the solvent type on  $R$  increases as  $g$  decreases. Variations in  $\Delta R$  with solvent type is less than  $\frac{1}{2}$  Å when  $g$  is above about 0.05 g/mL. Therefore, Figure 1 illustrates that the choice of solvent has little to no effect on  $R$  when above dilute solution conditions.

Comparisons of  $\Delta R$  at any  $g$  can be made for different polymers as long as their molecular weights are equal. Note that for any certain  $M$ , estimates of  $R$  from eq. (12) are independent of the type of polymer used in the solution. However,  $R$  calculated from eq. (1) can be influenced by the bulk polymer density, number of main chain atoms, molecular weight of the polymer repeat unit [eqs. (7) and (8)], and solution intrinsic viscosity [eq. (6)].

## THE EFFECT OF ADDITIVES ON MACROMOLECULE DIMENSIONS

When additives are in a polymer solution,  $R$  is calculated in relation to the polymer-solvent-additive



**Figure 1.** The influence of solvents and additives on macromolecule dimensions: (—) PA in DMA; (---) PA in  $H_2SO_4$ ; (- - -) PA in DMA + 0.3 g  $CaCl_2/g$  PA.

solution intrinsic viscosity. Additives also affect  $R$  at any  $g$  in the following way<sup>20-22</sup>:

$$\epsilon_x = 2.60 + 1.70 \times 10^{-4} Z_{app} \quad (16)$$

where  $Z_{app}$  is the apparent number of main chain atoms per polymer strand.  $Z_{app}$  can be determined if  $M_{app}$ , the apparent polymer molecular weight, is known:

$$[\eta]' = KM_{app}^\alpha \quad (17)$$

where  $[\eta]'$  is the polymer-solvent-additive solution intrinsic viscosity and  $K$  and  $\alpha$  are the Mark-Houwink constants for the polymer in pure solvent. Therefore, polymers in solutions containing additives that cause a large intrinsic viscosity increase have a large  $M_{app}$  value.

Equation (16) combined with eq. (8) can be used to approximate the boundary curve of polymer-solvent-additive solutions that separates the concentrated from nonentangled regions. An example of an aromatic polyamide phase separation curve on a triangular diagram, which is estimated from these equations, is found in Ref. 21.  $g_x$  decreases if an additive causes an intrinsic viscosity increase. Therefore, the concentrated solution boundary occurs at a much lower polymer concentration when strongly swelling additives are in the solution.

From eq. (12), macromolecule dimensions are not

influenced by the presence of additives in the solution. Then,  $\Delta R$  may be calculated at any  $g$  to measure the effect of the additive on macromolecule volume. In Figure 1,  $\Delta R$  is plotted versus  $g$  for the PA in DMA when 0.3 g of  $CaCl_2$  are added per gram of PA. This additive causes a relatively large intrinsic viscosity increase; at 20°C,  $[\eta]'$  equals 418.96  $cm^3/g$ .<sup>20</sup> The Mark-Houwink constants for PA in pure DMA are  $K = 3.13 \times 10^{-2} cm^3/g$  and  $\alpha = 0.81$ .<sup>20</sup> Then, from eq. (9),

$$R_c^3 = 2.079 \times 10^{-18} / (324.440g + 1) \quad (18)$$

and  $R_c$  is determined from eq. (15). Comparisons between eq. (18) and eq. (14) illustrate the effect of additives on the constants  $A_1$  and  $A_2$ .

From Figure 1,  $\Delta R$  for the PA-DMA- $CaCl_2$  solution decreases as  $g$  increases and becomes 0 at or above  $g_x$ . When  $g$  is above about 0.04 g/mL,  $\Delta R$  is less than 1 Å. This indicates that the general equation may be used to make accurate estimates of  $R$  in polymer-solvent-additive solutions, especially if additive use causes a large intrinsic viscosity increase. As well, since the  $\Delta R$  values are very small, then  $R$  is relatively unaffected by additives in semidilute-to-concentrated solutions.

Typical phase inversion membrane polymer solution additives increase the solution intrinsic viscosity. Aggregation, gelation, or supermolecular particle formation may occur in solutions if additives are used that decrease the solution intrinsic viscosity. It may be difficult to apply eq. (1) or eq. (12) to these solutions.

## CONCLUSIONS

The general equation  $4\pi R^3/3 \approx 0.507M/gN_0$  is derived by assuming that macromolecule dimensions are independent of the type of polymer, solvent, or additive used in the solution. Estimates of  $R$  from the general equation agree well with calculated values. Accuracy of the general equation increases as the polymer concentration increases. Therefore, the volume occupied by a polymer molecule is primarily dependent on the polymer molecular weight and concentration of polymer in the solution.

Care should be taken when applying the general equation to high-polymer concentration solutions.  $R$  is independent of the polymer concentration in the concentrated solution region; therefore, the minimum macromolecule radius should be checked before applying the general equation to these solutions. If additives are used in the solution, the min-

imum macromolecule radius can be determined only if the Mark-Houwink constants for the polymer in pure solvent and the intrinsic viscosity of the polymer-solvent-additive solution are known.

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