

## **The effect of polydispersity on the analysis of optical tracer diffusion experiments**

### **II. Intramolecular interference**

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#### **Summary**

The effect of intramolecular interference on the wave vector dependence of the average tracer diffusion coefficient in a dynamic light scattering experiment from an optically matched ternary system in which the tracer polymer reptates is examined using a Schulz molecular weight distribution and the Debye interference function for random coils. The average tracer diffusion coefficient in a system in which the tracer is polydisperse is shown to vary continually with  $q$ . This variation can be quite substantial for moderate polydispersities even in the regime  $q\bar{R}_g^{(n)} < 1$ . It is shown that a two parameter linear fit of  $\langle \Gamma \rangle$  versus  $q^2$  data will have a negative intercept and that the apparent  $q$  power law dependence of the average decay rate will be greater than 2.

#### **Introduction**

In a previous paper it was shown that tracer polydispersity can have a significant effect upon the shape of the autocorrelation function,  $g(t)$ , and upon the extraction of the average decay rate,  $\langle \Gamma \rangle$ , in a ternary isorefractive tracer diffusion experiment at higher concentrations of the "invisible" matrix polymer (1). A number of investigators have observed this marked deviation from single exponential behavior at higher "invisible" polymer concentrations (1, 2, 3). The analysis in this earlier paper was carried out assuming that the particle form factor,  $P(q, M)$ , for an individual chain was unity. We examine here the effect of intraparticle interference on the average decay rate for a Schulz distribution of random coil tracer polymers diffusing via reptation.

#### **Results and Discussion**

In principle, the intensity of light scattered from ternary systems composed of two

compatible polymers and a solvent chosen to have the same refractive index as one of the two polymers, with the other "visible" polymer present in only small amounts, should be analogous to light scattering from a dilute binary solution. In particular, if the tracer species is sufficiently dilute, then the intensity of scattering from tracer species "i" at wave vector  $q$  should be proportional to the product  $c_i M_i P(q, M_i)$ , where  $c_i$  is the concentration of species "i",  $M_i$  is its molecular weight, and  $P(q, M_i)$  is the intraparticle interference factor (form factor) associated with a chain of molecular weight  $M_i$ . Although the intensity of scattering from an isorefractive ternary solution follows directly from the infinitely dilute binary solution analog, the dynamics of the decay of the autocorrelation function can be substantially altered by the fact that the molecular weight dependence of the tracer diffusion coefficient becomes stronger as the concentration of the "invisible" matrix polymer is increased. For the ternary solution light scattering experiment, where the "visible" tracer is present only in small quantity, we may write the expression for the autocorrelation function,  $g(q, t)$ , as (assuming that the Schulz distribution adequately describes the molecular weight distribution of the tracer):

$$g(q, t) = \frac{\int_0^{\infty} M^{2+1} \exp[-yM] \exp[-\alpha q^2 t / M^v] P(q, M) dM}{\int_0^{\infty} M^{2+1} \exp[-yM] P(q, M) dM} \quad (1)$$

where we have assumed that, for a monodisperse sample,  $\Gamma = \alpha q^2 / M^v$ . In the following discussion, only the reptation case will be considered, i.e.  $v = 2$ .

The average decay rate of the autocorrelation function can be found by differentiating equation (1) with respect to time, and then setting  $t=0$ :

$$\langle \Gamma \rangle(q) = \frac{\alpha q^2 \int_0^{\infty} M^{2-1} \exp[-yM] P(q, M) dM}{\int_0^{\infty} M^{2+1} \exp[-yM] P(q, M) dM} \quad (2)$$

If we assume that the tracer molecules adopt their random flight configurations, then the form factor,  $P(q, M)$ , is given by the Debye relationship (4):

$$P(q, M) = \{2/(q\langle R_g \rangle)^4\} \{ \exp[-(q\langle R_g \rangle)^2] + (q\langle R_g \rangle)^2 - 1 \} \quad (3)$$

where  $\langle R_g \rangle = aM^{1/2}$  is the power law relationship for the root mean square radius of gyration for *monodisperse* random coils. The integrals of equation (2) are easy to perform with this form factor and the final result is:

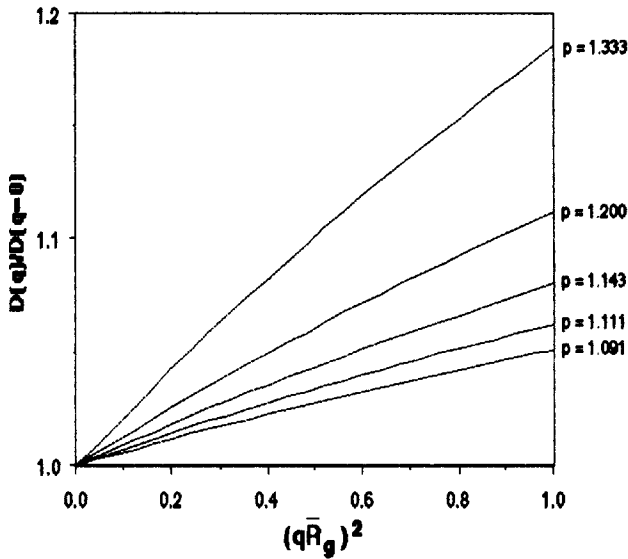
$$D(q)/D(q=0) = \frac{(z+1)\{z + (q\bar{R}_g^{(n)})^2\}^2}{(z-1)(z-2)} \left[ \frac{z^{z-1} + \{(q\bar{R}_g^{(n)})^2(z-2) - z\}\{z + (q\bar{R}_g^{(n)})^2\}z^{-2}}{z^z + \{(q\bar{R}_g^{(n)})^2 - 1\}\{z + (q\bar{R}_g^{(n)})^2\}z} \right] \quad (4)$$

where we have defined  $D(q) = \langle \Gamma \rangle(q)/q^2$  and  $\bar{R}_g^{(n)} = \langle R_g \rangle(\bar{M}_n) = a\bar{M}_n^{1/2}$  (by this, we do not mean the molecular weight power law expression derived through a power law fit using the number average molecular weight of a distributed polymer, but rather the power law expression valid for absolutely monodisperse polymers evaluated at the number average molecular weight of the distributed polymer). Note that if  $\langle \Gamma \rangle(q) \sim q^2$  then  $\langle \Gamma \rangle/q^2$  should be independent of  $q$ . The variation of the average tracer diffusion coefficient with  $q$  for various polydispersities is shown in Figure 1.

Often it is implicitly assumed that there is a  $q^2$  dependence to the average decay rate in a tracer experiment; "the" tracer diffusion coefficient is taken to be the slope calculated from a linear fit of available  $\langle \Gamma \rangle$  versus  $q^2$  data. It is clear from equation (4) and from Figure 1 that there is no simple power law relationship between the wave vector,  $q$ , and the average decay rate,  $\langle \Gamma \rangle(q)$ . However, for reasonably monodisperse tracer samples over a restricted range of  $q\bar{R}_g^{(n)}$  ( $0 < q\bar{R}_g^{(n)} < 0.7$ ) the variation of the tracer diffusivity with  $q$  is rather mild so that one might be justified in assuming that  $\langle \Gamma \rangle \sim q^2$ . The assumption is more questionable for somewhat higher polydispersities since there is a strong residual  $q$  dependence to the average tracer diffusivity.

The upward curvature in the  $\langle \Gamma \rangle$  versus  $q^2$  data results in a negative intercept, rather than the expected intercept of zero, when this data is fit to a two parameter linear form, as demonstrated in Figure 2. Certainly, the magnitudes of the intercept and the slope depend upon the range of  $q\bar{R}_g^{(n)}$  as well as upon the number of data points

FIGURE 1

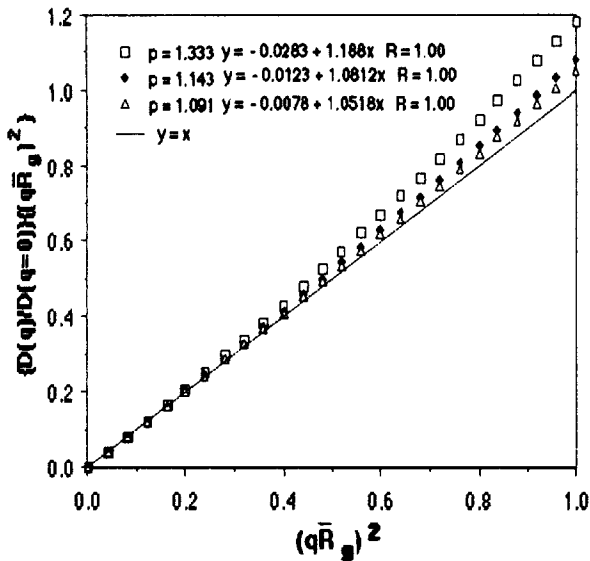


The ratio of the average diffusion coefficient at wave vector  $q$  to the average diffusion coefficient in the limit  $P(q, M) \rightarrow 1$  ( $q \rightarrow 0$ ) for different polydispersities as calculated from equation (4).  $\bar{R}_g$  means, in this case, the radius of gyration calculated from the equation for monodisperse polymers,  $(R_g) = aM^{1/2}$ , evaluated for the number average molecular weight  $\bar{M}_n$ .

included in the fit, so that the values for the slope and intercept calculated here represent perhaps the largest deviations to be expected. Figure 2 also shows that the deviation from the simple  $q^2$  power law dependence is not very evident to the eye with this type of plot if  $(q\bar{R}_g^{(n)}) < 0.7$ .

The implications for this type of  $q$  dependence to the average decay rate due to the coupling between intramolecular interference and polydispersity might be important in other types of tracer diffusion experiments performed at higher matrix polymer concentrations. For tracer light scattering experiments carried out in the high  $qR_g$  regime in the presence of high concentrations of matrix polymer, hydrodynamic

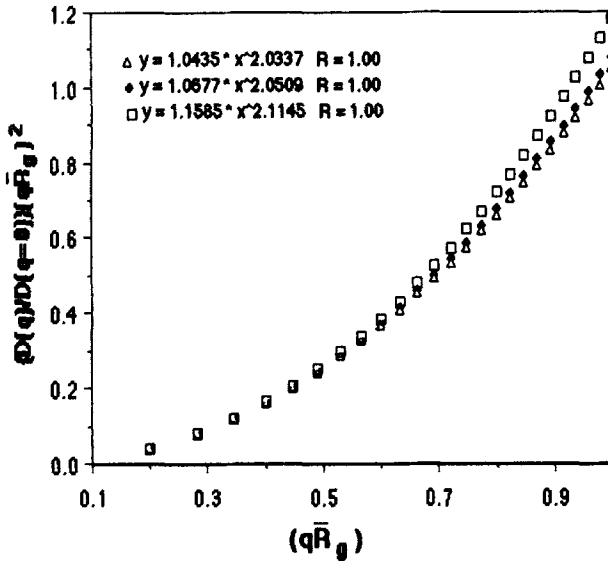
FIGURE 2



Data of Figure 1 plotted as  $\Gamma$  versus  $q^2$ , normalized such that  $\Gamma(q=0) = 1$ . 25 data points were used in each fit with  $q\bar{R}_g^{(h)}$  extending from 0 to 1. The fitting parameters probably represent a good estimate of the magnitudes of the slope and intercept to be expected for a given polydispersity.

screening might change the predicted  $q$  dependence of the average decay rate from  $q^2$  to  $q^3$  or  $q^4$  for monodisperse tracers (5, 6). The absolute value of the higher  $q$  power law exponent might be masked by effects such as those discussed above, giving rise to some nonintegral value of the power law exponent which falls between 3 and 5 (see Figure 3).

FIGURE 3



Data of Figure 2 plotted versus  $q\bar{R}_g^{(n)}$ . No assumption has been made about the  $q$  dependence of the data. Note that the "apparent"  $q$  power law exponent is non - integral, greater than 2 and varies with polydispersity.

### References

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