takes place within a fibre can be effectively eliminated by immersing the fibre in a liquid which has a similar refractive index to that of the fibre.

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A second comment on the histogram method in photon correlation spectroscopy applied in dilute polymer solutions

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The histogram method approximates the linewidth distribution function and permits us to obtain an estimate of the molecular weight distribution function by making only one measurement of the time correlation function of a polymer solution of known molecular weight at one concentration and one scattering angle. Caroline has corrected a conceptual error on the collective coefficient $\bar{k}_D$. However, it is incorrect to assume that an incorrect estimate of k_D invalidates all our conclusions because the changes introduced by our erroneous computation of k_D is smaller than the difference predicted by the theoretical descriptions of Yamakawa, Imai and of Pyun and Fixman.

Keywords Analysis; histogram; photon correlation; polymer dispersity; molecular weight distribution

In a recent comment by Caroline[1] on our histogram method of data analysis for polystyrene in cyclohexane[2], he has correctly pointed out that for a polydisperse polymer in solution,

$$D(M)=D^0(M)(1+\bar{k}_D{}^\theta C) \tag{1}$$

where $\bar{k}_D{}^\theta=-p\bar{v}_h-v$. p is unity in the theories of Yamakawa[3] and Imai[4] and 2.23 according to the 'soft-sphere' model of Pyun and Fixman[5]. v is the specific volume of the bulk polymer and $\bar{v}_h$ is the weight-average specific hydrodynamic volume as defined by

$$\bar{v}_h=\int f(M)Mv_h\mathrm{d}M\Big/\int f(M)M\mathrm{d}M \tag{2}$$

where $f(M)$ is the molecular weight distribution function. Since $D(M)=\Gamma/K^2$ and $D^0(M)=k_TM^{-1/2}$, we have

$$\Gamma/K^2=k_TM^{-1/2}(1+\bar{k}_D{}^\theta C) \tag{3}$$

As $\bar{k}_D{}^\theta$ varies with polymer polydispersity, it becomes necessary to determine $\bar{k}_D{}^\theta$ in order to transform $G(\Gamma)$ to $f(M)$ at finite concentrations. However, his statement that 'their conclusions may need revising' is not appropriate because we have actually used a fairly narrow molecular weight distribution polymer with maximum variation in molecular weight by a factor of about 2. The corresponding variation in $k_D{}^\theta$ is shown in *Table 1*. We see that the maximum deviation from the mean is ±15% with a standard deviation of ~8%. Thus, irrespective of the exact $k_D{}^\theta$ values, our conclusions remain the same.

Caroline states that 'the best that could be achieved with the histogram method is to obtain a measure of $\bar{k}_D{}^\theta$ from a shift in the maximum of the histogram, but its

Table 1 $k^\theta_{D,i}$ values at C_1

$f(M)\times10^5$ (arbitrary units)	$\Delta M_i\times10^{-5}$	$M_i\times10^{-5}$	$k^\theta_{D,i}$ (cm^3)
0.02	0.11	1.273	−23.6
0.87	0.11	1.385	−24.6
1.48	0.12	1.49	−25.6
1.51	0.15	1.63	−26.6
1.25	0.17	1.78	−27.9
0.79	0.21	1.98	−29.3
0.39	0.25	2.20	−30.9
0.01	0.30	2.48	−32.7

$\overline{k^\theta_D}=-27.7$ cm^3

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location is subject to considerable uncertainty'. Unfortunately, he is missing the important point we are making, i.e., we can determine an approximate distribution function, and consequently, compute not only the mean but also other moments from the distribution function as shown in our Tables 2 and 4 of ref. 2. A simple comparison of the numbers given in Tables 2 and 4 (histograms vs. cumulants) will show that the histogram method and the cumulants method are in excellent agreement.

The statement 'Despite the considerable and complex calculations required by the method and its demands on high quality data it offers no advantages over simpler fitting procedures for investigations of the concentration dependence and indeed turn out to be not as accurate', is incorrect because for a polydisperse polymer solution, it is very difficult to determine the mean linewidth using the standard cumulants method. The force fitting of single exponentials with unjustifiable floating baselines, as Caroline[6] has done, is likely to introduce systematic errors for polydisperse polymer solutions.

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A study of micelles in a base lubricating oil by gel permeation chromatography

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Micellar solutions of two polystyrene–poly(ethylene/propylene) block copolymers in a base HVI lubricating oil were studied by gel permeation chromatography (g.p.c.). The Styragel columns employed in the work were calibrated using polyisobutylene fractions. At 50°C each copolymer solution gave a single sharp peak which was well within the resolution of the columns, indicating that the micelles were able to enter the pores of the Styragel and elute through the columns as stable particles. Analysis of the chromatograms showed that the micelles had narrow size distributions. Light scattering provided a method of determining the weight-average molecular weights and apparent mean-square radii of gyration of the micelles. Molecular weights determined from g.p.c. using the universal calibration procedure were in fair agreement with the light scattering values. Unfortunately g.p.c. experiments attempted over the range 75°–150°C were unsuccessful because the Styragel strongly absorbed the copolymer at these higher temperatures.

Keywords Micelles; lubricating oil; gel permeation chromatography; block copolymers

Introduction

Since the early 1920s investigations have been made of the reversible aggregation of amphiphiles dissolved in water, the colloidal products of aggregation being termed micelles[1,2]. More recently studies have shown that certain block[3–7] and graft[8,9] copolymers in hydrocarbon solvents that are selectively bad for one of the polymer components can also interact reversibly to form large aggregates. The aggregates are usually globular in shape and consist of a compact swollen core of insoluble polymer blocks surrounded by a protective flexible fringe of soluble blocks. These investigations indicate that association colloids can be formed in the absence of water (or other hydrogen-bonding solvents) and the hydrophobic effect. Consequently the term micelle has been extended to cover any aggregate formed under reversible conditions regardless of the nature of the solvent.

Block copolymers of the type polystyrene–poly(ethylene/propylene), designated SEP, have been found to possess good viscosity index improver properties for lubricating oils. The mechanism by which the viscometric properties are modfied in such systems is believed to involve the formation of micelles by the block copolymers[10]. In the present work we have investigated the use of gel permeation chromatography (g.p.c.) for characterizing the micellar aggregates formed by two SEP copolymers in a base lubricating oil. The oil is a selectively bad solvent for the polystyrene blocks which form the cores of the micelles. Light scattering and dilute solution viscometry have been used to provide additional characterization data.

Experimental

Materials. The two block copolymers, SEP 1 and SEP 2, were provided by Shell Research Ltd. They had been prepared by hydrogenating the polyisoprene blocks of anionically synthesized polystyrene–polyisoprene block copolymers. Molecular characteristics of the copolymers determined by light scattering and g.p.c. (via the universal calibration procedure) in toluene are given in *Table 1*. Also listed are the percentages by weight of polystyrene in the copolymers as determined by ultra-violet spectroscopy of

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