Quasi-elastic light scattering from dilute solutions of a semi-rigid macromolecule: cellulose tricarbanilate

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(*Received* 18 *January* 1982*; revised* 4 *March* 1982)

First measurements are presented for quasi-elastic light scattering from dilute solutions of cellulose tricarbanilate in dioxane. The results are discussed principally in the light of the Yamakawa's model for semi-rigid macromolecules. It is shown that this theory provides a good description of the spectra as a function of molecular weight. We find a mean persistence length of 170 Å and a hydrodynamic chain diameter of 15 Å. We also report the existence of a slowly decaying component in the time correlation function which is associated with the existence of large aggregates in dynamic equilibrium with the isolated macromolecules.

Keywords Cellulose tircarbanilate; macromolecule; persistence length; quasi-elastic light scattering; temporal spectrum; dynamic spectrum; translational diffusion; translational coefficient

INTRODUCTION

Quasi-elastic light scattering is a powerful tool in studying molecular motions in liquids. It has been applied here to the study of the translational motion of semi-rigid macromolecules in a dilute solution.

The translational diffusion of flexible polymer in dilute solution has been the subject of a number of studies, both theoretical[1,2] and experimental[3-6]. Other works (see for example ref 7) have dealt with semi-dilute solutions and have given information either on the local dynamics of sections of polymer between the entanglement points, or on the macroscopic behaviour of the pseudo-gel. These previous studies have been concerned only with flexible polymers. Very few studies investigating light scattering exist for the more complicated case of semi-rigid polymers (see for example ref 8). Cellulose tricarbanilate was studied here. A semi-rigid chain can be characterized by the correlation length for the orientation of the monomer units, called the persistence length q. Various models can then be used to calculate physical parameters in terms of q. For instance, the very simple Kratky and Porod[9] model of a worm-like chain establishes relationships between the mean radius of gyration $\bar{R}_G$ or the mean square end-to-end distance $\bar{r}$ and the parameter x, the ratio of the contour length l of the chain* to the persistence length q[10]:

$$\bar{R}_G^2 = q^2\left[\frac{x}{3} - 1 + \frac{2}{x} - \frac{2}{x^2}(1 - e^{-x})\right] \tag{1}$$

$$\bar{r}^2 = q^2[2x - 2(1 - e^{-x})] \tag{2}$$

Figure 1 shows the ratio $\bar{R}_G^2/(\bar{r}^2/6)$ as a function of x for this model. When the contour length is much greater than the persistence length, this ratio tends to unity and the chain acquires the Gaussian statistics of a flexible chain, but where the statistical length is equal to the persistence length instead of the monomer length. At the opposite limit when the persistence length is much greater than the contour length, the chain acquires the properties of a stiff rod. In *Figure 1* we also show a number of points calculated for the polymers used here. The points were calculated for a persistence length $q = 170$ Å. This value will be justified later. It can be seen that the points lie in the intermediate zone corresponding to semi-rigid polymers. The purpose of this paper is to confront experimentally measured values of the translational diffusion coefficients with the predictions of theoretical models. As mentioned above, the Kratky and Porod model provides an expression for the radius of gyration. However our light scattering measurements yield the translational diffusion coefficient D_T. The Stokes–Einstein equation can be used to define an experimental hydrodynamic radius R_H, (the radius of an equivalent sphere for the hydrodynamical properties) which in general is quite different from R_G. The problem of the relationship between the R_H and R_G of a polymer in solution has been recently reviewed by Kok

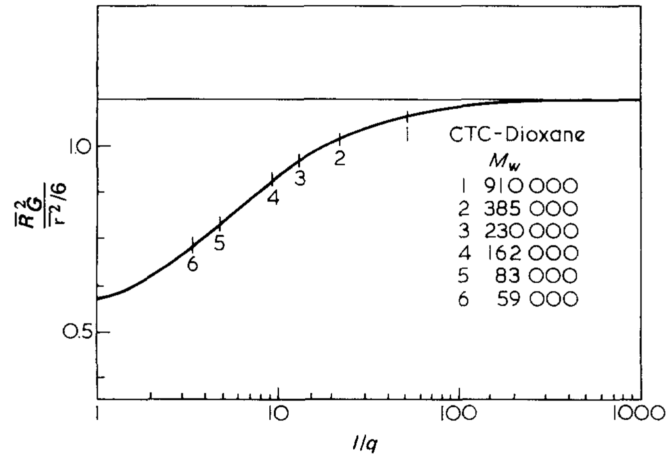

Figure 1 Application of the Kratky—Porod theory of worm-like chains. R_G is the gyration radius, $\bar{r}$ is the end-to-end distance, l the contour length and q the persistence length

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* The contour length of the chain is defined as: $1 = D_p \times l_0$, where D_p is the degree of polymerization and l_0 is the projection of the monomer bond.

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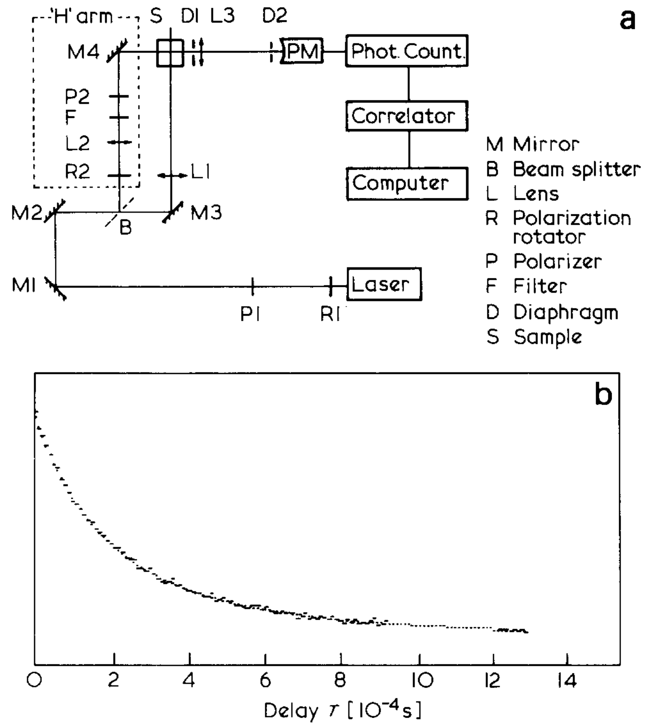

Figure 2 (a) Block diagram of the light scattering experiment (Laser Spectra Physics 165 Argon Ion; pM Hammamatsu; Photon Counting Ortec; Digital Correlator Langley Ford LIF 128; Computer ITT 2020), (b) a typical spectrum (— — — —) experimental points, (·····) fitted points. The curve is fitted with a sum of a distributed exponential of short relaxation time and an exponential of characteristic long time (CTC-Dioxan 385 000 1.68E-4G/G 21.5C 90D 4765A HET. Long decay constant: 1.3990E-03 sec. ampl: 123444.556. Short decay constant: 1.9502E-04 sec. ampl: 90492.360 var: 0.19. CHI2: 0.996376. Hydrodynamic radius: 236.6 Å)

and Rudin[11]. R_H is, in all cases, substantially smaller than R_G[12]. The relationship is not, in general, so obvious and thus a direct comparison of R_H and R_G is impossible. For this reason, our results will be discussed essentially in the light of a more recent theory, from Yamakawa[13–15]. This model, which calculates the viscous drag on a wormlike chain, taking into account the non-zero hydrodynamic diameter of the chain and the statistical properties of a semi-rigid chain, yields direct expressions for the intrinsic viscosity and the translational diffusion coefficient.

EXPERIMENTAL

A block diagram of the apparatus is shown in *Figure 2a*. It is an optical beating spectrometer which can function either in the homodyne mode or in the heterodyne mode with the help of the 'H' arm. The incident beam is focused by L1 into a square sample cell housed in a cryostat. The light scattered at 90° is limited in a solid angle and collected on a photomultiplier. In the heterodyne experiments a small fraction of the laser beam, suitably attenuated and focused, is mixed with the scattered light. The photo-pulses from the photo-multiplier are standardized and then analysed by a digital correlator which calculates the average time correlation function or time 'spectrum'. A typical spectrum is shown in *Figure 2b*. These spectra were analysed on a micro-computer using a conjugated gradient fitting procedure.

For each sample and at a given temperature a series of spectra was recorded for different ranges of delay times so as to determine the full decay of the spectrum. In general the decay was not a simple exponential. This point will be discussed later. The time spectrum of light scattered by the translation motions of a monodisperse solution of macromolecules is given by

$$C(\tau) = A + B\exp[-h\,D_T\mu^2] \qquad (3)$$

where μ is the magnitude of the scattering vector $\mu = 4\pi/\lambda\,\sin\theta/2$ (θ = scattering angle, λ = wavelength of the incident light in the solution) and h is equal to 1 or 2 respectively for heterodyne or homodyne spectra.

The semi-rigid polymer used in these experiments was cellulose tricarbanilate (CTC). The samples were kindly supplied by E. Marchal* and prepared and fractionated by W. Burchard and B. Pfannemüller*. They are well characterized, the polydispersity ratio M_w/M_n is weak, from 1.1 to 1.4 according to the samples. The molecular weights and solution concentrations C are quoted in *Table 1*. This work is concerned only with very dilute solutions; i.e. with solutions whose concentrations are, in all cases, less than the critical concentration C^* for overlapping of the chains[6,28]: $C^* = M_w/R_G^3 N_A \rho$ (M_w is the mass of the polymer, ρ: the density of the solution and N_A is the Avogadro's number). The solvent was Uvasol quality Dioxane (Merck) filtered prior to use. The refractive index of dioxane at 20°C is 1.4280 at 4880 Å and 1.4264 at 5145 Å, the temperature coefficient is $dn/dt = -4.75 \times 10^{-4}$ deg^{-1} [16]. The viscosity is given by the following expression[17]:

$$\eta(\mathrm{cP}) = 8.5449 \times 10^{-3} \exp\{1.4741 \times 10^3/T(\mathrm{K})\}$$

This cellulose derivative is particularly interesting. Burchard *et al.*[18,19] have studied its intrinsic viscosity in dioxane at 20°C for a large number of molar masses. Some optical studies, flow birefringence[20] and Kerr effect[21] have been performed in the same solvent, or in a different solvent[22]. Lastly a detailed study by dielectric relaxation[24] and small-angle neutron scattering[25] has been performed on very dilute solutions of CTC in dioxane. The persistence length at 20°C was found to be 108 Å for the dielectric relaxation and 136 Å for the small-angle neutron scattering. Gupta *et al.*[24] have shown the existence of a cooperative thermally induced conformation change, similar to a helix-coil transition.

RESULTS AND DISCUSSION

Determination of the persistence length

In previous studies, the persistence length has been obtained using the Kratky–Porod model[9] or Hearst's theory[26]. Here, we will apply Yamakawa's model of a wormlike cylinder to our results. In dilute solution, the friction coefficient ξ_T (and thus the translation diffusion coefficient $D_T = kT\xi_T$) is evaluated by a procedure similar to that of Kirkwood and Riseman[27]. Yamakawa showed that the results can be written in terms of the contour length l, the persistence length q and the hydrodynamic diameter d, or more precisely in terms of the reduced quantities $L = l/2q$ and $D = d/2q$. The results

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Table 1 Experimental and theoretical parameters as function of molecular weight of CTC

M_w	59 700	83 000	230 000	385 000	910 000
D_p	115	160	443	742	1753
l/q	3.48	4.85	13.42	22.50	53.10
C	$9.60\ 10^{-4}$	$6.00\ 10^{-4}$	$4.60\ 10^{-3}$	$1.68\ 10^{-4}$	$1.60\ 10^{-3}$
C/C^*	$2.14\ 10^{-2}$	$2.02\ 10^{-2}$	$4.2\ 10^{-1}$	$2.25\ 10^{-2}$	$3.7\ 10^{-1}$
R_G Kratky–Porod	129.0	165.2	323.0	436.0	695.0
R_G Flexible ($\nu = 0.6$)	36.2	44.2	81.4	110.9	185.8
R_G Flexible ($\nu = 0.5$)	22.6	26.6	44.3	57.3	88.0
R_G Exp	159	195	364	498	850
R_H Yamakawa worm-like	67.2	84.4	166.9	231.7	390.2
R_H Yamakawa coil limit	123.1	147.0	242.3	312.6	478.7
R_H Yamakawa rod-like limit	72.9	93.8	210.8	322.4	665.2
R_H exp	68.5	85.0	167.5	235.0	–

All lengths are expressed in Angstroms

The concentrations are expressed in gm of CTC/gm of dioxane. C^* is the critical concentration ($C^* = M_w/R_G^3 N_A \rho$) calculated with R_G deduced from the Kratky–Porod theory (with $q = 170$ Å)

All theoretical radii presented in this table are calculated using the following parameters: $q = 170$ Å and $d = 15$ Å (see text)

The gyration radii R_G in the case of flexible chains is obtained by using the relation $R_G = (l_0^2/6)^{1/2} D_p^{\nu}$ with $\nu = 0.6$ or 0.5 when the excluded volume behaviour is or is not taken into account[29]. R_G exp are the values extrapolated from Ref. 33

R_H exp are the values obtained in the present study. Due to the very high concentration of aggregates in the solution of CTC of mass 910 000, the radius could not be reliably obtained

D_p is the degree of polymerization l is the polymer contour length and l_0 the monomeric unit length

appear in a different form according to the numerical value of L:

for $L > 2.278$:

$$\xi_T = 3\pi\eta L/[A_1 L^{1/2} + A_2 + A_3 L^{-1/2} + A_4 L^{-1} + A_5 L^{-3/2}] \tag{4a}$$

and for $L \leqslant 2.278$:

$$\begin{aligned}\xi_T = 3\pi\eta L/[C_1 Ln(L/D) + C_2 + C_3 L + L^2 \\ + C_5 L^3 + C_6 (D/L) Ln) L/D) + C_7 (D/L) \\ + C_8 (D/L)^2 + C_9 (D/L)^3 + C_{10} (D/L)^4 + 0(D/L)^5]\end{aligned} \tag{4b}$$

The A_i and C_i are functions of D and are given explicitly in ref 13. For ease of comparison with other theories, and in order to provide a physical image we will continue the discussion in terms of the hydrodynamic radius of an 'equivalent' solid sphere, given by Stokes's formula:

$$R_H = kT/6\pi\eta D_T = \xi_T/6\pi\eta \tag{5}$$

(where η is the macroscopic viscosity of the solvent), D_T is measured experimentally and ξ_T is calculated from equations (4a) or (4b). We thus can determine the molecular quantities q and d for which Yamakawa's model gives the best agreement with the experimentally determined hydrodynamic radius. We should emphasize that in doing this, we suppose that the conformational state of the macromolecules does not change with the molecular weight, and neither do the quantities q and d. Thus, we can effectively determine the mean values of $\bar{q}$ and $\bar{d}$ for the range of weights investigated. The contour length of the polymer is calculated from the degree of polymerization and the known length of the monomer unit $l_0 = 5.15$ Å[23,24].

As mentioned above, the experimental spectra were not simple exponentials as indicated in ref 3. There are two principal sources of complication. Firstly the mass polydispersity of the samples gives rise to a distribution of decay times for the exponentials. The polydispersity index for our samples was quite low, giving rise to a fairly narrow distribution of decay times which could be introduced into the fitting procedure *via* a moments expansion. The second source of complication was the existence of a second exponential with a longer decay time, typically 10 to 20 times longer than the time associated with the translational motion of the macromolecules.

This second exponential was taken into account using the information from the long time tail of the time spectra. The origin of this second exponential will be discussed later. In *Figure 3* and *Table 1*, the values of $\mathbf{R}_H$ measured at 20°C as a function of molecular weight are given.

The diffusion coefficient and thus the radius have been found to be independent for each mass of the concentration of the solution when $C \ll C^*$. We then searched graphically and numerically the pairs of values of $\bar{q}$ and d which satisfy equations (4a) and (4b) for the masses measured. It should be stated that R_H depends simultaneously on both $\bar{q}$ and $\bar{d}$ but with opposite sign. That is the reason why a very great number of masses have to be studied to get a precise value for these quantities and why measurements concerning other samples are presently in progress. The values which best fit our experimental values of $\mathbf{R}_H$ are:

$$\bar{q} = 170\,\text{Å} \pm 40\,\text{Å} \qquad \bar{d} = 15\,\text{Å} \pm 3\,\text{Å}$$

The values correspond to the solid line 'worm-like' Yamakawa 1 in *Figure 3* where we also show the curves corresponding to the values $\bar{q} = 215$ Å, $\bar{d} = 12$ Å (Yamakawa 2) and $\bar{q} = 135$ Å, $\bar{d} = 18$ Å (Yamakawa 3).

It should be noted, by plotting the curves $R(q)$ at constant d for the different masses, that the friction coefficients are more sensitive to the diameter than to the persistence length of the polymer in the case of the low molecular weight limit, while the opposite is observed with the high molecular weight limit. These cases tend to the two extreme limits defined by Yamakawa: i.e. the long-rod limit where D and L approach zero ($q \to \infty$, $D \to 0$) at constant $L/D \gg 1$ and the coil limit where $L \to \infty$. The curves corresponding to these limiting cases are also shown in *Figure 3*. They are nearly the same as those

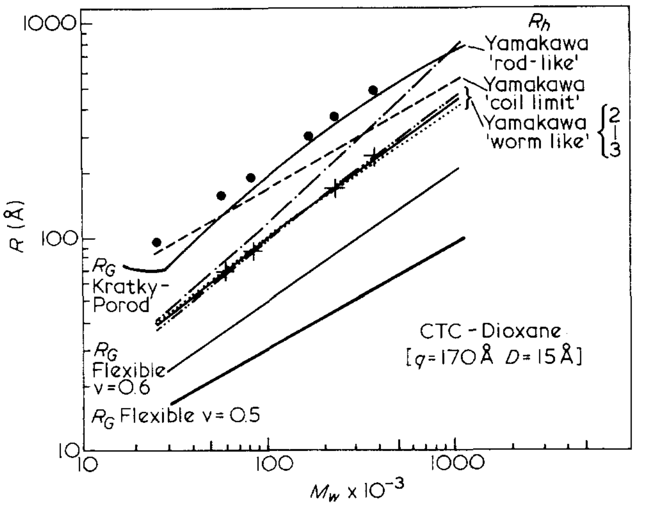

Figure 3 Calculated and experimental radii of CTC chains of various molecular weight M_W. All theoretical lengths are calculated by using the parameters q = 170 Å and d = 15 Å except in the case of worm like theory of Yamakawa, where curves 2 and 3 are drawn by using q = 215 Å, d = 12 Å and q = 135 Å, d = 18 Å respectively. (●●): experimental gyration radii[33], (+ +): experimental hydrodynamic radii [present work]

which would be obtained by using the very simple rod-like chain[31] or flexible chain[32] theories but in the case where the persistence length q is taken as basic unit length and the number of units is then $N^* = l/n$ (q = contour length) instead of the degree of polymerization. It can be seen that the hydrodynamic behaviour of CTC is intermediate between these two limits and is described well by Yamakawa's theory. It certainly constitutes a better description for semi-rigid molecules than that of a Gaussian coil or the Kratky–Porod model (even with an arbitrary corrective factor to take into account the difference between the radius of gyration and the hydrodynamic radius).

The applicability of the worm-like chain model of Yamakawa can also be tested by studying the intrinsic viscosity $[\eta]$ of the same solutions. The hydrodynamic diameter and the persistence length have been calculated from various experimental determinations[30]. Their mean values are $\bar{q} = 154$ Å and $\bar{d} = 14$ Å. The agreement between the molecular quantities deduced from the two independent experimental measurements is quite satisfactory.

A thermally induced conformational change of the CTC macromolecules has been observed by dielectric measurements[24]. These authors also show that the transition temperature observed with CTC is chain length dependent. Preliminary measurements of the diffusion coefficients by light scattering seem to confirm these observations. A variation of the hydrodynamic radius with temperature is observed, corresponding to the conformational change of the macromolecules. For example, in the case of CTC ($M_w = 385\,000$), R_H is equal to 235 ± 10 Å at 20°C and 205 ± 10 Å at 90°C. Measurements are in progress and will be reported in a further publication.

Form of the photon-correlation spectra. Problem of aggregation in solution

We can recall that at 20°C the light spectrum of solutions of CTC macromolecules in dioxane could not generally be fitted by a simple exponential. We observe two decays with well separated time scales. The shortest one, which is represented by a distributed exponential has been attributed to the translational diffusion of the individual chains. The slow decay may be due to the presence of aggregates in solution. They are not physical or chemical impurities since if they disappear either by heating or by centrifugation, they reappear with a slow rate of formation. We have also observed that the relative amplitude of the slow mode increases rapidly with the solution concentration. It does not seem that a significant trend of variation of the characteristic time with the mass exists, but we must note that for the lowest mass investigated, this phenomenon was too weak to be observed. However, on heating, we observe a decrease in relaxation time and a decrease in relative amplitude of the slow decay. We propose that this second relaxation could be due to the diffusion of aggregates in the solution. The equivalent hydrodynamic radius R_H of these entities is rather large: 2500 to 4500 Å. They could constitute the first precursors of an anisotropic phase which should exist at a much higher concentration.

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