

## Another way to view the chain conformation broadening of the line-width distribution measured in dynamic light scattering\*

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**Abstract** In dynamic laser light scattering (LLS), for a given polydisperse sample, a line-width distribution  $G(\Gamma)$  or the translational diffusion coefficient distribution  $G(D)$  can be obtained from the measured time correlation function. For rigid colloid particles,  $G(\Gamma)$  can be directly related to the hydrodynamic size distribution. However, for flexible polymer chains,  $G(\Gamma)$  depends not only on the chain length distribution, but also on the relaxation of the chain conformation; that is, even for a monodisperse polymer sample there still exists a chain conformation distribution. If the time scale of the chain conformation relaxation is comparable to that of the translational diffusion, such as in the case of a very long polymer chain, the conformation relaxation might lead to an additional broadening in  $G(\Gamma)$ . This "conformation broadening" has been directly observed for the first time by comparing two  $G(\Gamma)$ s obtained from a poly(N-isopropyl-acrylamide) solution at  $\sim 25^\circ\text{C}$  and  $\sim 32^\circ\text{C}$  at which the solution is thermodynamically stable, where the fact is utilized that the PNIPAM chain can change from an extended and flexible coil at  $\sim 25^\circ\text{C}$  into a highly collapsed and compact globule at  $\sim 32^\circ\text{C}$  at which point the polymer chain conformation distribution has diminished.

**Keywords:** dynamic laser light scattering, line-width distribution, polymer chain conformation distribution.

During the past twenty years, due to advancements in computer, detector and laser technology, laser light scattering (LLS), especially dynamic LLS, has gradually become a fast and convenient routine analytical tool of polymer and colloid science<sup>[1, 2]</sup>. A classic example would be the characterization of the molecular weight distribution of poly(tetrafluoroethylene) (also known as Teflon) in perfluorotetracosane at  $\sim 330^\circ\text{C}$ <sup>[3]</sup>. In dynamic LLS, a precise intensity-intensity time correlation function  $G^{(2)}(t, q)$  in the self-beating mode can be measured, which has the following form<sup>[4, 5]</sup>:

$$G^{(2)}(t, q) = \langle I(t, q)I(0, q) \rangle = A[1 + \beta |g^{(1)}(q, t)|^2], \quad (1)$$

where  $A$  is the measured baseline;  $\beta$ , a parameter depending on the detection optics;  $t$ , the delay time;  $q = (4\pi n/\lambda_0)\theta$  with  $n$ ,  $\lambda_0$  and  $\theta$  being the solvent refractive index, the wavelength of the laser light in vacuum and the scattering angle, respectively; and  $g^{(1)}(t, q)$ , the normalized first-order electric field time correlation function. For a polydisperse sample,  $g^{(1)}(t, q)$  is related to the line-width distribution  $G(\Gamma)$  by<sup>[4, 5]</sup>

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$$g^{(1)}(q, t) = \langle E(t, q)E(0, q) \rangle = \int_0^\infty G(\Gamma)e^{-\Gamma t}d\Gamma. \quad (2)$$

$\Gamma^{-1}$  corresponds to the characteristic relaxation time  $\tau$ . If the solution is infinitely dilute and  $\theta \rightarrow 0$ ,  $\tau$  becomes the diffusion related relaxation time (denoted by  $\tau_D$ ) and  $\Gamma$  is related to the translational diffusion coefficient  $D$  by  $\Gamma = Dq^2$ . Practically, we try to measure a solution as dilute as possible and use a scattering angle as small as possible to ensure that  $qR_g \ll 1$ , where  $R_g$  is the average radius of gyration of polymer chains.  $G(\Gamma)$  can be calculated from the Laplace inversion of eq. (2) and the well-accepted Laplace inversion CONTIN algorithm was used in this study<sup>[6]</sup>. It should be noted that  $D$  can be further converted to the hydrodynamic radius  $R_h$  using the Stokes-Einstein equation,  $R_h = k_B T / (6\pi\eta D)$ , where  $k_B$  and  $\eta$  are the Boltzmann constant and solvent viscosity, respectively.

## 1 Experimental

A commercial LLS spectrometer (ALV/SP-150 equipped with an ALV-5000 digital time correlator and an ADLAS DPY425II solid-state laser as the light source, output power = 400 mW at  $\lambda_0 = 532$  nm) was used. The incident light beam with a divergence of  $\sim 1$  mrad was vertically polarized with respect to the scattering plane and the light intensity was regulated with a beam attenuator, (Newport M-925B) so that the possible localized heating in the light scattering covette can be avoided. With some proper modifications<sup>[7]</sup>, the LLS spectrometer has an accessible scattering angle range of  $6^\circ$ — $154^\circ$ . The small scattering angle of  $\theta = 10^\circ$  used in this study increases the reciprocal of the scattering vector length, which had minimized the "additional conformation broadening" as much as possible. It should be noted that  $(qR_g)^2 \sim 0.15$ . The uncertainty of the scattering angle is  $\sim 0.01^\circ$ . All solutions used in this study are so dilute ( $\sim 10^{-6}$  g/mL) that the concentration correction is not necessary. The resistivity of the deionized water used was 18.3 M $\Omega$ cm.

## 2 Results and discussion

In a colloidal dispersion, rigid particles with different hydrodynamic sizes will have different  $D$ . The width of the line-width distribution reflects the hydrodynamic size distribution of the particles. On the other hand, for linear and flexible polymer chains in a good solvent, not only can different chain lengths lead to different values of  $\tau$ , but also the incomplete relaxation of different chain conformations can lead to different  $\tau_0$ , i. e. even for absolutely monodisperse polymer chains,  $G(\Gamma)$  might still have a finite distribution width especially when the chains are very long, where the long chain might stay in a given configuration. For a long time compared to the time it takes the chain to diffuse a length comparable to the reciprocal of the scattering vector length. In such a case, the concentration fluctuations observed by light scattering at a given scattering vector would effectively relax with a distribution of relaxation times; that is, the relaxation of the chain conformations introduces an additional broadening and this additional broadening cannot be averaged out in the time scale of the concentration fluctuation. Therefore, for a polydisperse polymer,  $G(\Gamma)$  might be a convolution of the two relaxation processes related to both the translational diffusion and chain conformation fluctuation. This "additional conformation broadening" can be viewed by 1) increasing  $q$ , i. e. decreasing  $\tau_D$ , for a given polymer chain; or 2) increasing the chain length, i. e. increasing the characteristic times ( $\tau_n$ )

associated with the relaxation of the chain conformations. In the first case,  $q$  is limited by the maximum scattering angle ( $180^\circ$ ); while in the second case, it is difficult to prepare long and flexible polymer chains with a uniform chain length.

In a recent study of poly (N-isopropylacrylamide) (PNIPAM) in water, we found that a linear and flexible PNIPAM chain can change from an expanded and flexible coil at  $\sim 25^\circ\text{C}$  to a highly collapsed and compact globule at  $\sim 32^\circ\text{C}$ . This provides us the first chance to study the "additional conformation broadening" in  $G(\Gamma)$  since at  $\sim 25^\circ\text{C}$  the flexible PNIPAM chain has a conformation relaxation, while at  $\sim 32^\circ\text{C}$  the collapsed PNIPAM globule has lost its conformation relaxation (strictly speaking, the relaxation of the chain conformation has diminished). The width difference between the two line width distributions respectively measured at  $25^\circ\text{C}$  and  $32^\circ\text{C}$  should reflect the additional "chain conformation broadening".

For comparison, we also synthesized very narrowly distributed spherical microgels made of crosslinked PNIPAM chains. The PNIPAM microgels and linear chains have a similar hydrodynamic size. Due to the crosslinking, it is expected that whether in the swollen or collapsed state the measured line width distribution of the microgels should contain no "additional conformation broadening" induced by the relaxation of the chain conformations. The details of both the PNIPAM linear chains ( $M_w = 1.08 \times 10^7 \text{ g/mol}$ ) and microgel particles can be found elsewhere<sup>[8, 9]</sup>.

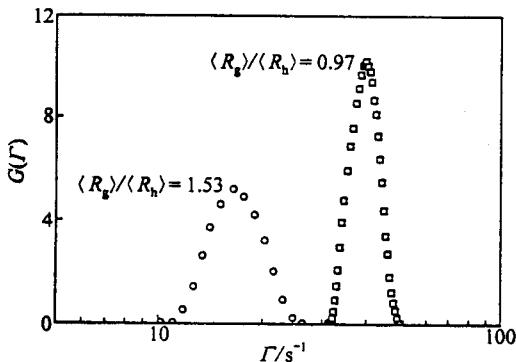


Fig. 1. The apparent line-width distribution  $G(\Gamma)$  of the PNIPAM solution at two different temperatures. ("o",  $T = 25.02^\circ\text{C}$ ; "□",  $T = 31.82^\circ\text{C}$ )

Figure 1 shows the line-width distributions at two different temperatures. The apparent average line-width  $\langle \Gamma \rangle$  and the relative distribution width  $\mu_2/\langle \Gamma \rangle^2$  for the PNIPAM linear chains are  $17.08 \pm 0.02 \text{ s}^{-1}$  and  $0.030 \pm 0.005$  in the swollen state and  $40.33 \pm 0.05 \text{ s}^{-1}$  and  $0.010 \pm 0.005$  in the collapsed state, respectively, where  $\langle D \rangle = \int_0^\infty G(D) D dD$  and  $\mu_2 = \int_0^\infty G(D) (D - \langle D \rangle)^2 dD$ . It should be stated that in the angular range of  $qR_g < 1$  there is no angular dependence of  $\langle \Gamma \rangle$ , but  $\mu_2/\langle \Gamma \rangle^2$  slightly increases as  $q$  increases. The values of  $\langle \Gamma \rangle$  and  $\mu_2/\langle \Gamma \rangle^2$  show a clear shrinking of the PNIPAM chains in water and the narrowing of  $G(\Gamma)$  when temperature increases from  $25.02$  to  $31.82^\circ\text{C}$  at which point the solution is thermodynamically stable and there is no change in the observed  $G(\Gamma)$  for more than 100 h. Moreover, the change of  $\langle R_g \rangle/\langle R_h \rangle$  from 1.53 to 0.97 indicates that the PNIPAM chain collapsed from an extended random coil into a much more compact globule since the theoretically predicted values for a flexible coil and a uniform hard sphere are  $\sim 1.5$  and  $\sim 0.78$ , respectively. It should be noted that this shrinking and narrowing can also be viewed directly from the relaxation time and the curvature change of  $\log[g^{(1)}(t)]$  versus  $t$ . Using the CONTIN analysis is only for a better view of the broadening. Actually, we can use the cumulants analysis or a simple ruler to show what we intend to address here. It also should be mentioned that Meewes et al.<sup>[10]</sup> have examined this "additional conformation broadening".

Figure 2 shows an even better view of the broadening of  $G(\Gamma)$  in the swollen state after normal-

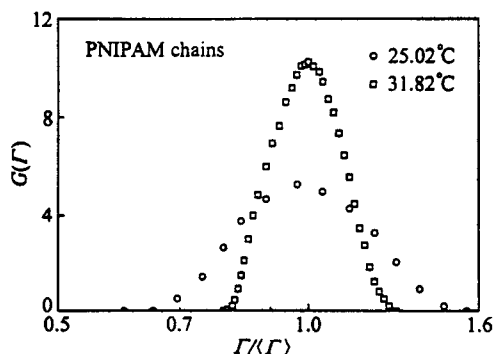


Fig. 2. Reduced apparent line-width distribution  $G(\Gamma/\langle\Gamma\rangle)$  of linear PNIPAM chains in the swollen (25.02°C) and collapsed (31.82°C) states.

izing each  $G(\Gamma)$  in fig. 1 with its own  $\langle\Gamma\rangle$ . The finite width of  $G(\Gamma)$  in the collapsed state reflects the chain length distribution, while the relatively broader width of  $G(\Gamma)$  in the swollen state shows the "additional conformation broadening" induced by the chain relaxation, which is on top of the chain length distribution. In principle, from these two  $G(\Gamma)$  distributions, we are able to calculate the "additional chain conformation broadening". However, this is not what we intend to address in this paper. As stated before, in order to have a comparison and to have a better controlled experiment, we also measured the line-width distributions of very narrowly distributed

PNIPAM microgel particles in both the swollen and collapsed states.

Figure 3 shows that there is no change in the width of  $G(\Gamma)$  when the PNIPAM microgels change from a swollen state to a collapsed one. This is exactly what we had expected since the crosslinking inside the microgels greatly suppresses the relaxation of the chain conformation. The ratio of  $R_g/R_h$  for the microgels in both the swollen and collapsed states are  $\sim 0.78$ , which confirms that the particles are spheres with a uniform chain density.

A comparison of figs. 2 and 3 shows that even with the scattering angle as small as  $10^\circ$  the line-width distribution of flexible polymer chains in solution still contains the "additional conformation broadening" induced by the relaxation of the chain conformations, which can be viewed as follows: Just considering an assembly of uniform polymer chains, the conformation of each chain fluctuates. If averaged over a sufficient time, the average conformation of every chain will be identical. However, if the average time is not sufficient, each chain will have a slightly different average conformation, leading to an additional broadening in the measured line width distribution. On the basis of the Rouse-Zimm model<sup>[11,12]</sup>, the relaxation times ( $\tau_n$ ) associated with the chain conformations is proportional to the molar mass ( $M$ ) of the polymer chain, i. e.  $\tau_n = M\eta_0[\eta]/0.293RT\lambda_n$  with  $\eta_0$ ,  $[\eta]$ ,  $R$ ,  $T$  and  $\lambda_n$  being the solvent viscosity, the intrinsic viscosity, the gas constant, the absolute temperature and the eigenvalues in the Zimm model<sup>[13]</sup>. The shortest relaxation time  $\tau_1$  is of the same order of  $\sim 10^{-3}$  s as  $\tau_D$ . Therefore, after the relaxation of the translational diffusion, the conformations of each chain have not completely relaxed, or say, averaged out. This is why the "additional conformation broadening" have been observed in fig. 2. It should be noted that for a given scattering vector  $\tau_D$  is proportional to  $R_h$ , or roughly, to  $M^{0.5-0.6}$  for flexible chain in a normal solvent, so that  $\tau_n$  decreases much faster than  $\tau_D$ . For a typical polymer chain ( $M_w \sim 10^5$  g/mol),  $\tau_D$  is  $\sim 10$  times longer

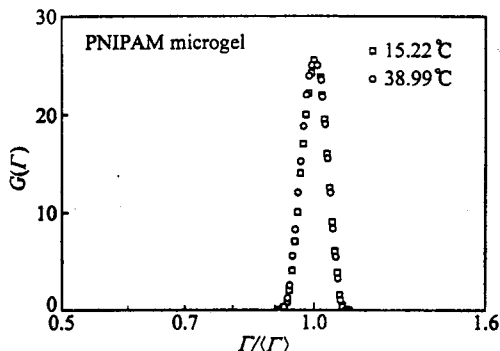


Fig. 3. Reduced apparent line-width distribution  $G(\Gamma/\langle\Gamma\rangle)$  of spherical PNIPAM microgels in the swollen (15.22°C) and collapsed (38.99°C) states.

than  $\tau_n$ , so that the "additional conformation broadening" is not a problem. On the other hand, if  $\theta$  increases,  $q^{-1}$  will decrease and the diffusion related relaxation will be faster, i.e.  $\tau_D < \tau_n$  so that the "additional conformation broadening" can be seen<sup>[7,14]</sup>. For a sample with a broad chain length distribution, this small "additional conformation broadening" actually has little effect on the measured line-width distribution as long as  $qR_g < 1$ . However, for a very narrowly distributed sample, it might be necessary for us to consider this additional chain conformation broadening because, practically,  $q$  has a low limit. In principle, this additional chain conformation distribution has to be considered in other experimental methods as long as the measurement time is longer or comparable to the chain conformation relaxation times  $\tau_n$ .

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