Available online at www.sciencedirect.com
SCIENCE DIRECT®

Polymer 45 (2004) 1739–1742

polymer

www.elsevier.com/locate/polymer

Polymer Communication

Reexamination of slow relaxation of polymer chains in sol–gel transition

Chi Wu[a,b,*], To Ngai[a]

[a] Department of Chemistry, The Chinese University of Hong Kong, Shatin, NT, Hong Kong, China
[b] The Open Laboratory of Bond Selective Chemistry, Department of Chemical Physics, University of Science and Technology of China, Hefei, Anhui, China

Received 2 September 2003; received in revised form 10 November 2003; accepted 18 November 2003

Abstract

Using $[2+2]$ photocycloaddition of coumarin groups attached to the PMMA chain backbone, we can gradually transfer a semidilute copolymer solution to a uniform speckle-free gel. We reexamined the effects of concentration, crosslinking density, solvent quality on the controversial scaling exponent (α_s) between the linewidth (Γ_s) of the slow mode and the scattering vector (q) during the sol–gel transition. Our results suggest that the slow mode is attributed to large thermally agitated density fluctuation and revealed that the variation of α_s is due to the relative length of $1/q$ to the correlation length (ξ) of the density fluctuation; namely, if $\xi > 1/q$, $\alpha_s \to 3$, while when $\xi < 1/q$, $\alpha_s \to 2$.

Keywords: Sol–gel transition; Slow relaxation; Laser light scattering

The dynamics of polymer chains in semidilute solutions as well as in gels is an old problem. The dynamic laser light scattering (LLS) has revealed that there coexist two relaxation (fast and slow) modes in semidilute solution [1,2]. At different scattering vectors ($q = 4\pi \sin(\theta)/\lambda$ with θ and λ being the scattering angle and the wavelength of laser light in solution), the linewidth (Γ_f) of the fast mode is normally q^2-dependent [3], which has been satisfactorily attributed to the cooperative diffusion of the chain segment (blob) between two entangled points in 70′ [4]. As for the slow mode, there has been no clear and well-accepted explanation so far, to our knowledge. The scaling exponent (α_s) between Γ_s and q ranges between 2 and 3, extremely controversial [5,6]. In the past, it was sometimes wrongly attributed to the slow diffusion of individual chains in the maze of other entangled chains. However, dynamic LLS cannot detect the motions of individual chains in semidilute solution, except in that case that a polymeric trace with a very different refractive index is used inside an iso-refractive polymer matrix [7]. Therefore, it is helpful to note that the slow relaxation observed cannot be directly linked to the well-known tube model and reptation theory [8]. There were evidences to relate it to the slow density fluctuation of entangled chains, but there was no clear explanation on different values of α_s [3,9]. As the polymer concentration increases, the slow relaxation persists (sometimes apparently disappears at lower scattering angles) in concentrated solutions, melts as well as gels in which polymer chains are crosslinked instead of entangled. As a general phenomenon, it certainly deserves a careful reexamination so that we can find its physical nature and explain why it cannot be scaled to the observation length ($1/q$) in LLS by a constant scaling exponent α_s.

Recently, we found that the $[2+2]$ photocycloaddition of two coumarin groups under the UV irradiation of ~310 nm could convert a poly(methyl methacrylate-*co*-7-acryloyloxy-4-methylcoumarin) [P(MMA-*co*-AMC)] semidilute solution to a chemical gel which is uniform, speckle-free, and ergodic; namely, the time- and assembly-average scattered light intensities ($\langle I\rangle_T$ and $\langle I\rangle_E$) are equal, as shown in Fig. 1. It is helpful to note that the photocyclo-addition is different from conventional UV-induced crosslinking of vinyl monomers because there is no propagation in reaction. Such a gelling system enables us to use LLS to study the effect of polymer concentration, crosslinking density and solvent quality (temperature) on the chain dynamics during the entire sol–gel transition without any fatal interference of frozen-in inhomogeneous static components. In this letter, we like to report that the slow relaxation in semidilute solution and gels is indeed related to thermally agitated density fluctuation and the value of α_s is determined by the ratio of the observation length ($1/q$) to the static correlation

---

[*] Corresponding author. Address: Department of Chemistry, The Chinese University of Hong Kong, Shatin, NT, Hong Kong, China. Tel./fax: +852-2603-5057.

E-mail address: chiwu@cuhk.edu.hk (C. Wu).

0032-3861/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2003.11.045

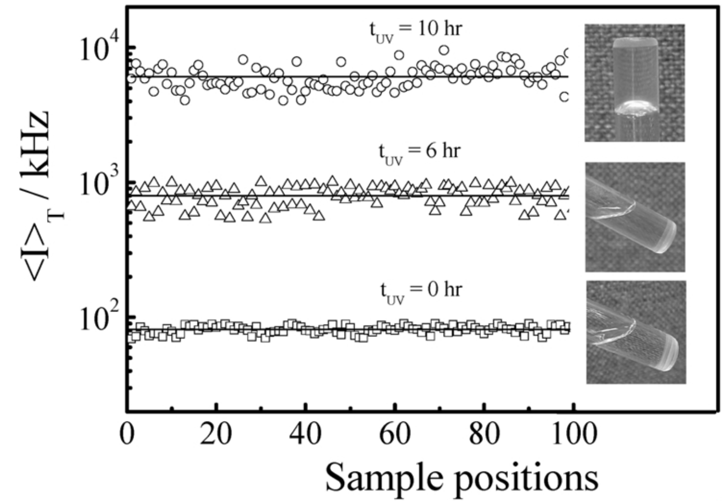

Fig. 1. Sample position dependence of time-average scattered light intensity $\langle I \rangle_T$ during the sol–gel transition, where the scattering angle $\theta = 30°$, and each solid line represents an ensemble-average scattered light intensity $\langle I \rangle_E$ defined as $(\sum_i \langle I \rangle_{T,i})/N$ with N being the total number of randomly chosen sample positions.

length (ξ_S) of the density fluctuation. The copolymer preparation and the LLS and theory instrumentation can be found elsewhere [10–12].

Fig. 2 shows that as the crosslinking proceeds, the slow relaxation becomes even slower, and at the same time, contributes more in the normalized intermediate scattering function $f(q,\tau)$, calculated from the measured normalized intensity–intensity time correlation function $[g^{(2)}(q,\tau) = \langle I(q,0)I(q,\tau)\rangle / \langle I(q,0)\rangle^2 - 1]$ as [13–15]

$$f(q,\tau) = 1 + \frac{\langle I \rangle_T}{\langle I \rangle_E} \times \left[\sqrt{1 - \left[\frac{g^{(2)}(q,0) - g^{(2)}(q,\tau)}{\beta} \right]} - 1 \right] \qquad (1)$$

where $0 < \beta < 1$, a constant related to the coherence of the detection optics. Note that $f(q,\tau)$ can completely relax to zero within the delay time window of a few seconds used in dynamic LLS, similar to an ergodic polymer solution, but much slower. This indicates that there is indeed no frozen-in static component. To our knowledge, this is the first observation of fully relaxable $f(q,\tau)$ in a chemical gel because $f(q,\tau)$ in previous studies of different gels always decays to a non-zero plateau [14,16]. In order to qualitatively extract the data related to the two relaxation, we used a combination of an exponential decay for the fast mode and a stretched exponential decay for the slow mode, which is normally used for semidilute solution [17–19]

$$f(q,\tau) = \beta\{A_f \exp(-\Gamma_f \tau) + A_s \exp[-(\Gamma_s \tau)^b]\} \qquad (2)$$

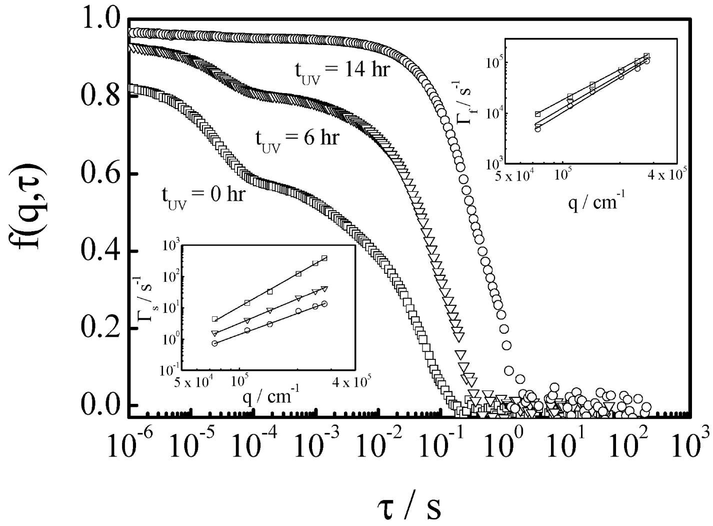

Fig. 2. UV irradiation time dependence of the normalized intermediate scattering function $f(q,\tau)$ during the sol–gel transition where $\theta = 60°$ and $T = 25$ °C. The inset shows that both Γ_f and Γ_s can be scaled to q as $\Gamma_f \sim q^{\alpha_f}$ and $\Gamma_f \sim q^{\alpha_s}$ for the fast and slow relaxation modes, where $\alpha_f = 2.0 \pm 0.1$, 2.2 ± 0.1, 2.4 ± 0.1 and $\alpha_s = 3.0 \pm 0.1$, 2.5 ± 0.1, 2.3 ± 0.1 at the $t_{UV} = 0$, 6, 14 h, respectively.

where A and Γ are the intensity weighting and the linewidth of the fast and slow relaxation, respectively; $A_f + A_s = 1$; and $0 < b < 1$, a constant related to the distribution width of the slow relaxation. The solid lines demonstrate that Eq. (2) provides an adequate regression of $f(q, \tau)$. The fitting results four parameters A_f, Γ_f, Γ_s and b. The insets shows that both Γ_f and Γ_s can be scaled to q as $\Gamma_f = q^{\alpha_f}$ and $\Gamma_s = q^{\alpha_s}$. Note that b changes from ~0.5 in the semidilute solution to ~1 in the gel during the sol–gel transition.

Fig. 3 shows that the crosslinking has nearly no effect on the dynamic correlation length ($\xi_D = k_B T q^2 / 6\pi\eta\Gamma_f$). It is helpful to note that ξ_D is related to the average size of the blobs (sub-chains) between two entangled points in semidilute solution [4,12]. The fact that ξ_D has a similar value during the sol–gel transition implies that the crosslinking reaction mostly occurs at the entanglement points. This is reasonable because the photocycloaddition only occurs when two coumarins are very close in space, which also explains why the chemical gel resulted from the semidilute solution is homogeneous. On the other hand, the static correlation length (ξ_S) decreases from 165 to 118 nm during the sol–gel transition, where ξ_S was calculated from the slope-to-intercept ratio of $1/\langle I(q)\rangle_T$ versus q^2 (the Ornstein–Zernike plot) [20,21]. This is also reasonable because the crosslinking reduces the dimension of the density fluctuation of the entangled (crosslinking) chains.

It is important to note that in the semidilute solution, $\alpha_f = 2.0 \pm 0.1$, which is expected for the cooperated diffusion of the blobs [3,4], and $\alpha_s = 3.0 \pm 0.1$, indicating that the slow mode is not diffusive. As the crosslinking proceeds, α_f increases, but α_s decreases, indicating that the fast relaxation also becomes non-diffusive. What is the nature of the slow mode and how can we explain such changes in both α_f and α_s? To answer these questions, let us examine how the light is scattered in semidilute solution. First, the refractive index contrast between chains and solvent leads to the scattering. Second, thermal agitation causes the fluctuation of chain density in space so that the refractive index contrast between the denser and sparser parts also results in the scattering. The motion of the sub-chains (blobs) has been assigned to the fast mode. Therefore, it is reasonable to attribute the slow mode to the density fluctuation. If it is the case, the thermally agitated density fluctuation should be a random process, just like the diffusion of 'particles' in dispersion, and Γ_s should not be q^3-dependent.

However, it has been known in the LLS theory that for a flexible scattering subject with a radius of gyration (R_g), when $1/q > R_g$, $\Gamma \propto q^2$ (pure diffusive relaxation), while at $1/q \ll R_g$, Γ becomes q^3-dependence (internal motions) [12,22]. The scaling exponent (α) should gradually increase from 2 to 3 as q increases. In the present study ($25° < \theta < 154°$), $1/q$ ranges from ~35 to 135 nm. Therefore, $q\xi_S > 1$ in the semidilute solution, while $q\xi_S \sim 1$ in the gel, which satisfactorily explains the decrease in α_s from 3.0 ± 0.1 to 2.3 ± 0.1. On the other hand, the increase in α_f probably shows that the motions of different 'blobs' become less independent or more correlated when the chains are gradually cross-linked together.

Further, we found that the crosslinking has nearly no effect on the time-average scattered light intensity related to the fast modes ($\langle I\rangle_f$) (Fig. 4) even though its relative contribution to the total time-average scattered light intensity (A_f) dramatically decreases during the sol–gel transition. This is consistent with the invariant of ξ_D in Fig. 3 and expected because the fast relaxation is related to the motions of the sub-chains between two entangled (or crosslinking) points. On the other hand, considering that the dimension of the density fluctuation (ξ_S) decreases as the crosslinking proceeds, we can only attribute the increase in $\langle I\rangle_s$ to the increase in the density contrast between the dense and sparser parts. To support our proposed linkage between the variation of α_s and the dimension of the density fluctuation, we varied the solvent quality by temperature.

The results in Fig. 5 are indeed what we expected. The partially crosslinked chains at higher temperatures have a higher thermal energy and swell more so that the motions of

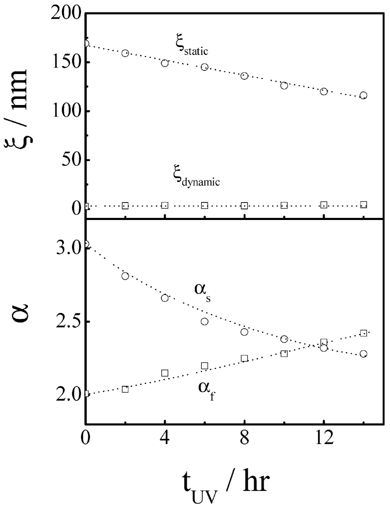

Fig. 3. UV irradiation time dependence of the static and dynamic correlation length, as well as the scaling exponent α_f and α_s during the sol–gel transition, where $\theta = 30°$ and $T = 25$ °C.

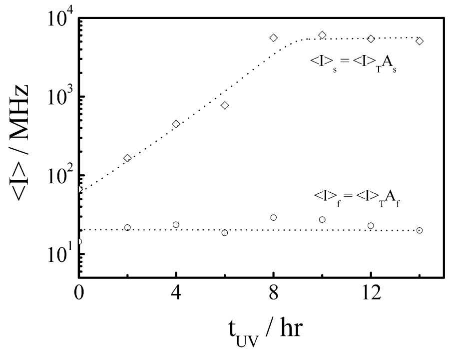

Fig. 4. UV irradiation time dependence of absolute scattered light intensity related to the fast ($\langle I\rangle_{fast}$) and slow ($\langle I\rangle_{slow}$) relaxation, where $\theta = 30°$ and $T = 25$ °C.

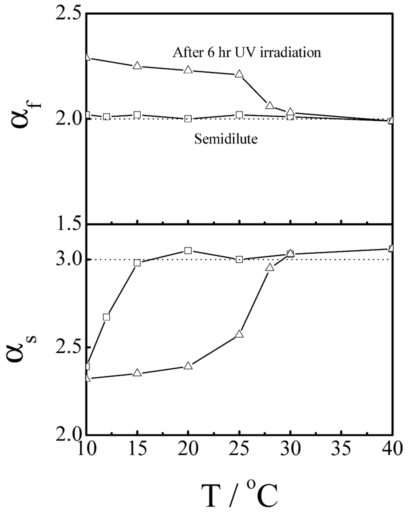

Fig. 5. Temperature dependence of the scaling exponents α_f and α_s at semidilute solution, pre-gel cluster and the gel stages, where $\theta = 30°$.

different blobs become less correlated and the dimension of the density fluctuation increases, leading to the decrease in α_f to 2.0 ± 0.1 and the increase in α_s to 3.0 ± 0.1. As for the semidilute solution, the change of solvent quality does not alter the diffusive nature of the motions of the blobs so that α_f remains. However, α_s drops at ~12 °C because the contraction of the chains in very poor solvent leads to the decrease in the dimension of the density fluctuation.

In summary, we have shown that the slow relaxation modes observed in dynamic LLS during the transition from a semidilute solution to a uniform chemical gel is related to thermally agitated density fluctuation. In addition, we reveal that the previously reported controversial values of the scaling exponent (α_s) between the linewidth of the slow relaxation (Γ_s) and the scattering vector (q) can be attributed to the relative length of $1/q$ (the observation length in LLS) to the dimension of the density fluctuation.

Acknowledgements

The financial support of the Hong Kong Special Administration Region, Research Grants Council, Earmarked Grants (CUHK4257/00P, 2160174) and the CAS Bai Ren Project is gratefully acknowledged.

References

[1] Adam M, Delsanti M. Macromolecules 1977;10:1229.
[2] Amis EJ, Han CC. Polymer 1981;23:1403.
[3] Brown W, Nicolai T. Colloid Polym Sci 1990;267:977. and references cited therein.
[4] de Gennes PG. Scaling concepts in polymer physics. Ithaca, NY: Cornell University Press; 1979.
[5] Heckmeier M, Mix M, Strobl G. Macromolecules 1997;30:4454.
[6] Stepánek P, Brown W. Macromolecules 1998;31:1889. and references therein.
[7] Wheeler LM, Lodge TP. Macromolecules 1989;22:3399. Wheeler LM, Lodge TP. Macromolecules 1992;25:1316.
[8] Chang T, Yu H. Macromolecules 1984;17:115.
[9] Kjoniksen A-L, Nystrom B. Macromolecules 1996;29:7116.
[10] Ngai T, Wu C. Macromolecules 2003;36:848.
[11] Chu B. Laser light scattering, 2nd ed. New York: Academic; 1991.
[12] Pecora R. Dynamic light scattering. New York: Plenum; 1976.
[13] Pusey PN, van Megen W. Physica A 1989;157:705.
[14] Joosten JGH, Mccarthy JL, Pusey PN. Macromolecules 1991;24:6690.
[15] Rouf C, Bastide J, Pujol JM, Schosseler F, Munch JP. Phys Rev Lett 1994;73:830.
[16] Rodd AB, Dunstan DE, Boger DV, Schmidt J, Burchard W. Macromolecules 2001;34:3339.
[17] Adam M, Delsanti M, Munch JP, Durand D. Phys Rev Lett 1998;61:706.
[18] Martin JE, Wilcoxon J, Odinek J. Phys Rev A 1991;43:858.
[19] Shibayama M, Norisuye T. Bull Chem Soc Jpn 2002;75:641. and the references therein.
[20] Bueche F. J Colloid Interface 1970;33:61.
[21] Soni VK, Stein RS. Macromolecules 1990;33:61.
[22] Wu C, Chan KK, Xia K-Q. Macromolecules 1995;28:1032. Wu C, Chan KK, Xia K-Q. Macromolecules 1996;29:1574.