Effect of Cross-Linking on Dynamics of Semidilute Copolymer Solutions: Poly(methyl methacrylate-*co*-7-acryloyloxy-4-methylcoumarin) in Chloroform

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ABSTRACT: 7-Acryloyloxy-4-methylcoumarin (AMC) can undergo a [2 + 2] photodimerization when irradiated with an UV light of 310 nm. Its copolymerization with methyl methacrylate (MMA) resulted in a photo-cross-linkable copolymer P(MMA-*co*-AMC), which enabled us to study the effect of cross-linking on the dynamics of semidilute solutions of such a copolymer in a controllable fashion. For each semidilute copolymer solution studied before the photoreaction, dynamic laser light scattering showed a fast and a slow relaxation mode respectively with line widths Γ_f and Γ_s . They were scalable to the scattering vector q as $\Gamma_f \sim q^{\alpha_f}$ with $\alpha_f \approx 2.0 \pm 0.1$, which is the hallmark of cooperative diffusion relaxation, and $\Gamma_s \sim q^{\alpha_s}$ with $\alpha_s \approx 3.0 \pm 0.2$, which could be related to internal motions of large transient clusters made of the entangled chains. Two relaxation modes were also observed during the photoreaction. The photo-cross-linking of the chains in less concentrated solutions ($<3 \times 10^{-2}$ wt %) only resulted in finite clusters, where α_f and α_s essentially remained, indicating that there was no change in solution dynamics. On the other hand, in more concentrated solutions ($>5 \times 10^{-2}$ wt %), transparent and homogeneous gels were eventually formed after a long time irradiation. As the cross-linking proceeds, the fast relaxation contributes less and less. At the same time, α_f increases, but α_s decreases, revealing that the diffusion relaxation are gradually mixed with the internal motions and finally diminished in the gel state.

Introduction

Following the scaling theories developed by de Gennes and co-workers,[1,2] much attention on the research of polymer solutions has been focused on the so-called semidilute regime,[3,4] which is generally considered to be a low volume fraction of polymer but a strong overlap between chains. The overlap concentration (C^*) has been slightly differently defined in the literature as $3M/(4\pi N_A R_g^3)$, $M/(N_A R_g^3)$, and $[\eta]^{-1}$, where M and R_g are respectively the molar mass and the radius of gyration of polymer chains studied, N_A is the Avogadro constant, and $[\eta]$ is the intrinsic viscosity.[5] In general, $3M/(4\pi N_A R_g^3) < C^* < M/(N_A R_g^3)$. It is known that $R_g \propto M^\nu$ with $0.5 \le \nu \le 0.6$, depending on the solvent quality.[1] Therefore, using polymer chains with a higher molar mass M can lower the overlap concentration C^*, which satisfied both the conditions of a low volume fraction and a high chain overlapping. The concentration range of semidilute solution is not well-defined. Most of investigations were rather arbitrarily limited to a volume fraction no more than 10% (w/v).

Semidilute solution theories are usually presented in terms of static and dynamic screening lengths (ξ_s and ξ_D). Beyond the distance of ξ_s, excluded-volume interactions are screened; namely, the interactions between monomers of one chain are screened by monomers of other chains, while ξ_D is related to the distance of hydrodynamic interactions.[6] Experimentally, ξ_s can be directly obtained from the angular dependence of the scattering intensity in static laser light scattering (LLS),[7,8] small-angle neutron scattering (SANS),[2] or small-angle X-ray scattering (SAXS),[9] while ξ_D is calculated from the cooperative diffusion coefficient (D_c) measured in dynamic LLS using the Stokes−Einstein relation, $\xi_D = kT/6\pi\eta_0 D_c$, where T is the absolute temperature, k is the Boltzmann's constant, and η_0 is the solvent viscosity.[10]

Scaling laws have been applied to the concentration dependence of ξ in semidilute solutions assuming that ξ_s should be independent of the chain length as long as it is much smaller than R_g.[1] In a three-dimensional space, $\xi_s \propto C^{-\nu/(3\nu-1)}$, where ν is the excluded-volume exponent defined before. It has been shown that in the good solvent limit $\nu \approx 0.59$, very close to 0.6 predicted from the scaling theory. Therefore, ξ_s can be scaled to C as $\xi_s \sim C^{-0.75}$ in good solvents.[11−13] Experimentally, most of the previous results collapsed into two master curves, $\xi_s \sim C^{-0.72\pm0.06}$ and $\xi_D \sim C^{-0.70\pm0.04}$, as summarized by Brown and Nicolai.[3,4] The problem is that such a scaling extends well into the concentration range in which the correlation length is even less than the persistence length. In other words, the problem is that the power law even works in the range it should fail according to the scaling theory.[3,4,14,15]

Besides in good solvent, semidilute solutions in the Θ or even a poor solvent condition has also been studied by LLS,[16−18] including block copolymers in selective solvents.[19] However, the interpretation of the results from dynamic LLS is not straightforward because there exist at least two relaxation modes, namely, a fast mode related to the cooperative diffusion and a so-called slow mode attributed to the dynamics of those entangled chains. It has been shown that the fast mode could be well preserved even in the gel state,[20] while the slow mode was system-dependent.[21−24] For example, Konak

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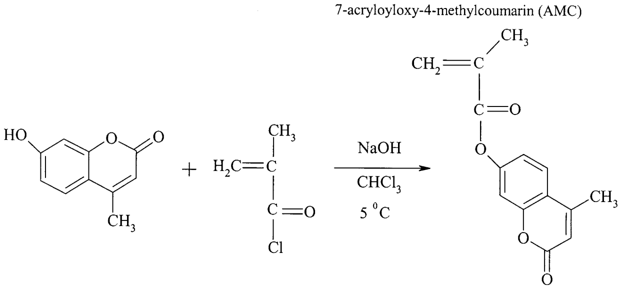
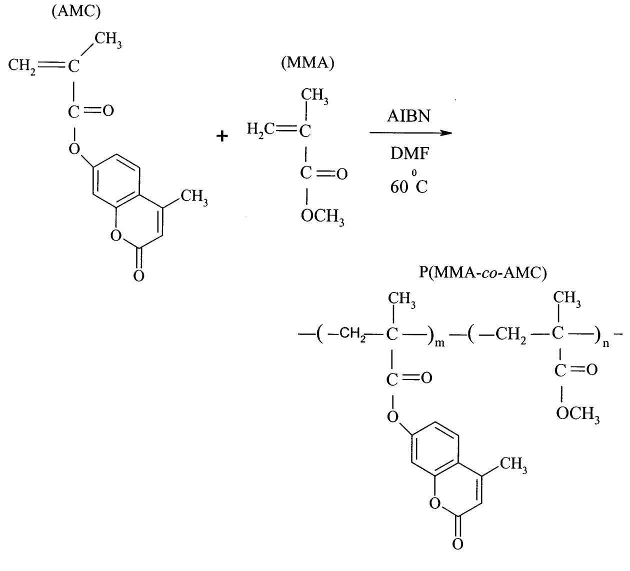
Scheme 1. Synthesis of 7-Acryloyloxy-4-methylcoumarin (AMC)



Scheme 2. Copolymerization of Methyl Methacrylate (MMA) with 7-Acryloyloxy-4-methylcoumarin (AMC)



et al.[21] recently studied semidilute solutions of poly(styrene-*co*-methyl methacrylate) in a selective solvent (acetone) and showed that the slow mode was related to the dynamics of polymer clusters formed by random association, in which Γ_s could be scaled to q as $\Gamma_s \propto q^{\alpha_s}$ with $\alpha_s > 2$ and increasing with the polymer concentration. Nemoto et al.[22] studied aqueous Borax solutions of poly(vinyl alcohol) (PVA) by using LLS and dynamic viscometry and found that α_s was in the range 2−3 when the polymer concentration is around C^*, but approached zero at higher concentrations, which was attributed to its complex environment.

The study of the structure and dynamics of semidilute and concentrated solutions still remains an experimental challenge in LLS partially because it is difficult to clean viscous semidilute solutions and partially because they are strongly system dependent. Most of the past studies were concentrated on polystyrene. Investigation on the dynamics of entangled chains in semidilute solution is important not only in solution theory but also in the gelation study because the entangled chains can be viewed as a transient polymer network. To have a better understanding of the structure and dynamics of semidilute solutions, especially the slow relaxation mode, we recently synthesized a linear poly(methyl methacrylate-*co*-7-acryloyloxy-4-methylcoumarin) [P(MMA-*co*-AMC)] copolymer and studied the dynamics of such a copolymer in semidilute soluitons by dynamic LLS. The advantage of using such a system is relied on the fact that two coumarin groups can undergo a [2 + 2] photodimerization when irradiated with UV light (310 nm).[25] Such a dimerization reaction can be used to bind the copolymer chains together in chloroform in a completely controllable fashion so that we are able to investigate the effect of cross-linking on the fast and slow relaxation modes of semidiluted solutions at each photoreaction stage.

Experimental Section

Materials. 7-Hydroxy-4-methylcoumarin and methacryloyl chloride were purchased from Acros Chemical Co. and used without further purification. Methyl methacrylate (MMA) was purchased from Aldrich Chemical Co. and purified by vacuum distillation. AIBN was also from Aldrich and performed by a recrystallization from methanol. *N*,*N*-Dimethylformamide (DMF) was purified by vacuum distillation after dying with barium oxide. Other solvents and chemicals were used as received.

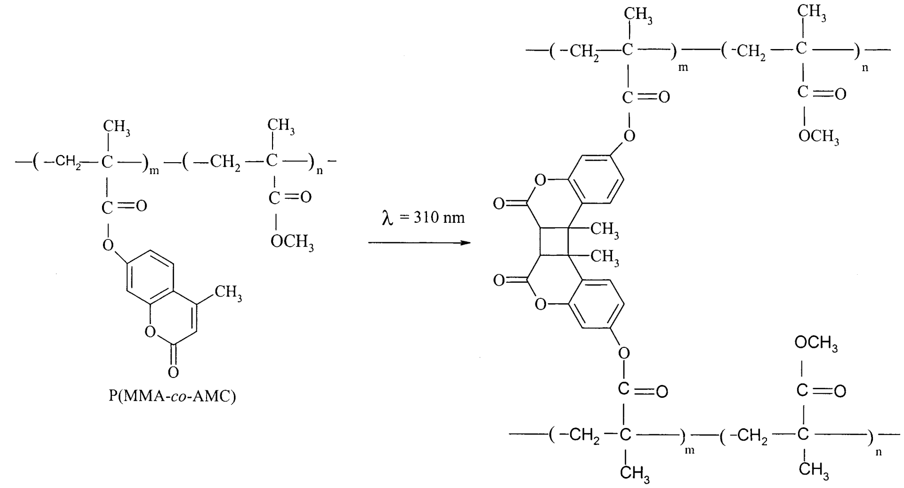
Sample Preparation. The synthesis of photo-cross-linkable copolymer containing 4-methylcoumarin pendant groups involved two steps. The first step is to prepare 7-acryloyloxy-4-methylcoumarin (AMC), as shown in Scheme 1. To a solution of 7-hydroxy-4-methylcoumarin (12.0 g, 68 mmol) in 192 mL of 0.5 N NaOH aqueous solution was added 150 mL of chloroform and then cooled to 5 °C. Under vigorous stirring, methacryloyl chloride (7.1 g, 68 mmol) was injected into the mixture, and the reaction was continued for 1 h. The white solid obtained after evaporating chloroform was recrystallized in acetone.[26,27] In the second step, 7-acryloyloxy-4-methylcoumarin (AMC) was copolymerized with methyl methacrylate (MMA) in DMF by using AIBN as free radial initiator, as shown in Scheme 2.[26] Freshly distilled monomers, MMA, AMC, and AIBN solution ([MMA]:[AMC]:[AIBN] = 9:1:0.0002), were charged into a polymerization tube. After three freeze−thaw cycles of degassing, the tube was sealed off under vacuum. The reaction was carried at 60 °C for ~40 h. The resultant copolymer P(MMA-*co*-AMC) was harvested in methanol and dried overnight in a vacuum. A proper amount of P(MMA-*co*-AMC) was dissolved in chloroform to form a clear solution. The solution was then filtered into a quartz cell (diameter 10 mm) to remove dust. The solution preparation was always under a nitrogen atmosphere. The clarified solution was placed in a photochemical reactor equipped with 10 tubes of 310 nm lamps with a total energy output of ~150 W. The photoreaction, as shown in Scheme 3, was carried out for different desired time periods, and then the solution was studied by laser light scattering.

Laser Light Scattering. A slightly modified commercial LLS spectrometer (ALV/DLS/SLS-5022F) equipped with a multi-τ digital time correlator (ALV5000) and a cylindrical 22 mW UNIPHASE He−Ne laser (λ_0 = 632 nm) was used. The details of the LLS instrumentation and theory can be found elsewhere.[10,28] In static LLS, the excess absolute time-averaged scattered light intensity, known as the excess Rayleigh ratio $R_{vv}(q)$, of a dilute polymer solution at concentration C (g/mL) is related to the weight-average molar mass M_w, the root-mean-square z-average radius of gyration $\langle R_g^2\rangle_z^{1/2}$ (or written as $\langle R_g\rangle$), and the scattering vector q as

$$\frac{KC}{R_{vv}(q)} \approx \frac{1}{M_w}\left(1 + \frac{1}{3}\langle R_g^{\ 2}\rangle q^2\right) + 2A_2C \tag{1}$$

where $K = 4\pi^2n^2(dn/dC)^2/(N_A\lambda_0^4)$ and $q = (4\pi n/\lambda_0)\sin(\theta/2)$ with N_A, dn/dC (=0.132 mL/g), n, and λ_0 being the Avogadro number, the specific refractive index increment, the solvent refractive index, and the wavelength of the light in a vacuum, respectively, and A_2 is the second virial coefficient. The extrapolation of $R_{vv}(q)$ to $q \to 0$ and $C \to 0$ leads to M_w. The plots of $[KC/R_{vv}(q)]_{C\to 0}$ vs q^2 and $[KC/R_{vv}(q)]_{q\to 0}$ vs C respectively lead to $\langle R_g^2\rangle$ and A_2. For finite concentrations, the so-called Zimm plot of $KC/R_{vv}(q)$ is usually used, which incorporates the extrapolation of $C \to 0$ and $q \to 0$ in a single grid. In the present study, linear copolymer chains used for the study of dynamics of semdilute solution were first characterized in

Scheme 3. Photodimerization-Induced Cross-Linking of P(MMA-*co*-AMC) Copolymer Chains in Chloroform



dilute solutions. It is helpful to note that in the semidilute solutions the solution concentration was higher than the overlap concentration C^*, and molecular characteristic properties of individual chains were screened by interchain interaction so that eq 1 is no longer applicable.

In dynamic LLS, the intensity–intensity–time correlation function ($G^{(2)}(\tau)$) [$= \langle I(0)I(\tau)\rangle$] of each copolymer solution at different photoreaction stages was measured in the scattering angle (θ) range 30°–90° at 25 °C. $G^{(2)}(\tau)$ can be related to the normalized field-field autocorrelation function $|g^{(1)}(\tau)|$ ($\equiv [\langle E(0)E^*(\tau)\rangle/\langle E(0)E^*(0)\rangle]$) via the Siegert relation as[10]

$$G^{(2)}(\tau) = A[1 + \beta|g^{(1)}(\tau)|^2] \qquad (2)$$

where A ($\equiv \langle I(0)\rangle^2$) is the measured baseline and β ($\approx$0.95) is a constant related to the coherence of the detection optics. For a polydisperse system, $g^{(1)}(\tau)$ is related to the distribution of the characteristic line width $G(\Gamma)$ by[10,28]

$$|g^{(1)}(t)| = \int_0^\infty G(\Gamma)\mathrm{e}^{-\Gamma t}\,\mathrm{d}\Gamma \qquad (3)$$

For a diffusive relaxation, Γ is related to the translational diffusion coefficient D or the collective diffusion coefficient D_c by $\Gamma = Dq^2$ or D_cq^2, depending on whether the solution is in a dilute ($C < C^*$) or a semidilute ($C > C^*$) regime. In principle, $G(\Gamma)$ can be calculated from the Laplace inversion according to eq 3.[4,10] D or D_c is further related to the hydrodynamic radius R_h by $R_h = k_BT/(6\pi\eta_0D)$ or the dynamic correlation length ξ_D as $\xi_D = k_BT/(6\pi\eta_0D_c)$ as discussed before. It has been shown that, for a semidilute solution or a polymer solution undergoing the cross-linking reaction, $G^{(2)}(\tau)$ can often be described by a combination of a single-exponential function and a stretched exponential function,[29,30] namely,

$$[G^{(2)}(\tau) - A]/A = \beta\{W_f\exp(-\Gamma_f\tau) + W_s\exp[-(\Gamma_s\tau)^b]\}^2 \qquad (4)$$

where W and Γ are the weighting and characteristic line width of the relaxation, respectively, subscripts "s" and "f" denote the fast and slow modes, respectively, $W_f + W_s = 1$, and b ($0 < b < 1$) is related to the width of $G(\Gamma)$ associated with the slow relaxation. A smaller b indicates a broader line width distribution.

Results and Discussion

Figure 1 shows a typical Zimm plot of dilute solutions of copolymer P(MMA-*co*-AMC) in chloroform at 25 °C. On the basis of eq 1, the extrapolation of $[KC/R_{vv}(q)]_{C\to0,q\to0}$ leads to $M_w = 2.12 \times 10^5$ g/mol, and the slopes of $[KC/R_{vv}(q)]_{C\to0}$ vs q^2 and $[KC/R_{vv}(q)]_{q\to0}$ vs C respectively lead to $\langle R_g\rangle = 37.4$ nm and $A_2 = 8.1 \times 10^{-4}$ mol cm^3/g^2. The positive A_2 shows that chloroform is a good solvent for P(MMA-*co*-AMC) at 25 °C. The overlap concentration (C^*) estimated from $M_w/(4\pi\langle R_g\rangle^3N_A/3)$ and $M_w/(\langle R_g\rangle^3N_A)$ is 1.8×10^{-3} and 6.7×10^{-3} g/mL, respectively. Therefore, it is not so difficult in practice to reach the semidilute regime ($C > C^*$) with a relatively low polymer volume fraction.

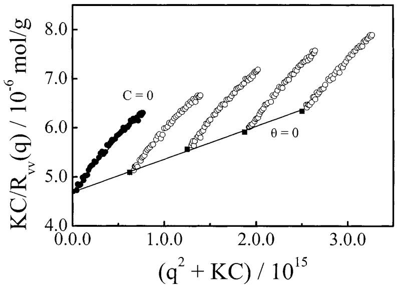


Figure 1. Zimm plot of photo-cross-linkable copolymer poly(methyl methacrylate-*co*-7-acryloyloxy-4-methylcoumarin) [P(MMA-*co*-AMC)] in chloroform, where C ranges from 2.5×10^{-4} to 1.0×10^{-3} g/mL.

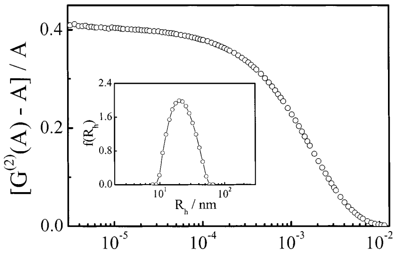


Figure 2. Typical intensity–intensity–time correlation function of photo-cross-linkable copolymer [P(MMA-*co*-AMC)] in chloroform, where $\theta = 15°$ and $C = 2.5 \times 10^{-4}$ g /mL. The inset shows its corresponding hydrodynamic radius distribution.

Figure 2 shows a typical intensity–intensity–time correlation function of a dilute solution of copolymer P(MMA-*co*-AMC) in chloroform (5.0×10^{-4} g/mL) at $\theta = 15°$ and $T = 25$ °C. The inset shows its corresponding hydrodynamic radius distribution ($f(R_h)$) calculated from $G^{(2)}(\tau)$ on the basis of eqs 2 and 3 by using a CONTIN Laplace inversion program in the correlator. The relative width ($\mu_2/\langle\Gamma\rangle^2$) is 0.12, leading to an estimate of $M_w/M_n \approx 1 + 4\mu_2/\langle\Gamma\rangle^2 \approx 1.5$.[32] The average hydrodynamic radius ($\langle R_h\rangle$) is 22.1 nm. The dimensionless ratio $\langle R_g\rangle/\langle R_h\rangle$ is a sensitive index of the chain conformation.[33] It

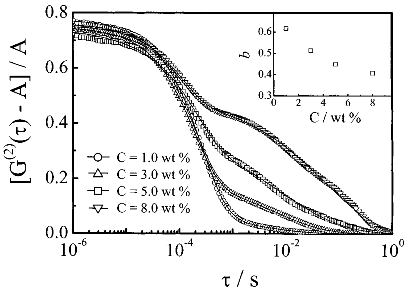


Figure 3. Intensity–intensity–time correlation functions of semidilute solutions of photo-cross-linkable copolymer [P(MMA-*co*-AMC)] in chloroform. The solid lines represent the best fitting of eq 4 where $\theta = 30°$. The inset shows the concentration dependence of the stretching exponent (b) obtained in the fitting of eq 4 (see text for details).

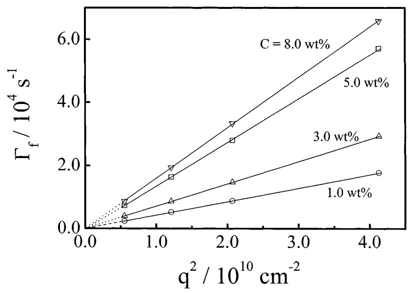


Figure 4. Scattering vector (q) dependence of characteristic line width (Γ_f) of the fast relaxation mode of semidilute solutions of photo-cross-linkable copolymer [P(MMA-*co*-AMC)] in chloroform.

has been known that for flexible random coil chains $\langle R_g\rangle/\langle R_h\rangle \sim 1.5-1.8$, depending on the solvent quality and the chain polydispersity. Here, the ratio of $\langle R_g\rangle/\langle R_h\rangle = 1.68$ clearly shows that P(MMA-*co*-AMC) chains in chloroform at 25 °C have an expected flexible random coil conformation.

Figure 3 shows that as the copolymer concentration increases, the slow relaxation mode gradually appears and moves toward a longer relaxation time, which can be fitted by a stretched exponential function on the basis of eq 4. Previous studies of semidilute solutions suggested that the fast relaxation corresponds to a cooperative diffusion of individual chains, while the slow relaxation might be related to the dynamics of those chains entangled in semidilute solution.[21–24,34] The inset of Figure 3 shows that the stretching exponent b from the fitting of eq 4 decreases with increasing the copolymer concentration, indicating that the copolymer solution becomes more "heterogeneous". In other words, the chains entangled in a more concentrated solution are not able to relax during the delay time window.

Figure 4 shows that the line width of the fast relaxation mode (Γ_f) is a linear function of q^2 and the extrapolation of Γ_f to $q \rightarrow 0$ passes the origin, confirming that the fast relaxation is indeed related to the diffusion. The slope of Γ_f vs q^2 leads to the cooperative diffusion coefficient (D_c) and further to the dynamic correlation length (ξ_D) by $\xi_D = k_BT/6\pi\eta_0D_c$. Figure 5 shows that ξ_D decreases with the copolymer concentration and is scaled to C as $\xi_D \sim C^{-\alpha}$, with $\alpha = 0.70 \pm 0.02$, fairly close to 0.75 predicted by the scaling theory,[1] and agrees well with most of previous experimental results.[3,11–13]

On the other hand, Figure 6 shows that the line width of the slow relaxation mode (Γ_s) is scaled to q as $\Gamma_s \sim q^{\alpha_s}$ with $\alpha_s = 3.0 \pm 0.1$. It is helpful to note that the q-independent as well as the q^2-dependent of Γ_s have

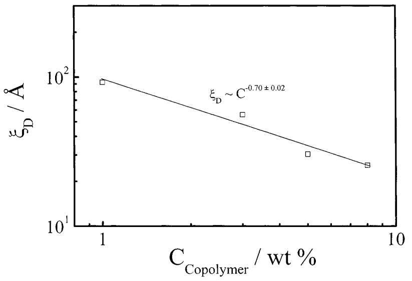


Figure 5. Copolymer concentration dependence of dynamic correlation length (ξ_D) for semidilute solutions of photo-cross-linkable copolymer [P(MMA-*co*-AMC)] in chloroform.

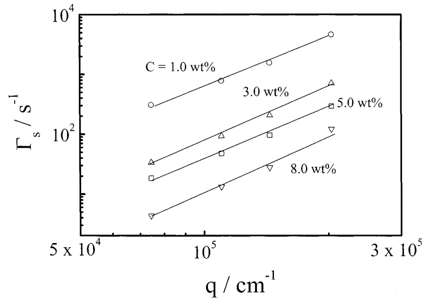


Figure 6. Scattering vector (q) dependence of characteristic line width (Γ_s) of the slow relaxation mode of semidilute solutions of photo-cross-linkable copolymer [P(MMA-*co*-AMC)] in chloroform.

previously been observed.[22,35,36] The higher values of α_s have also been reported for copolymer chains in a selective solvent[21,37] as well as for physical[24,38] and chemical gels,[29–31,39] which was attributed to the formation of large polydispersed clusters. It has been known in LLS that for a given dilute solution, as long as $1/q$ is much smaller than the radius of gyration of a linear chain or a hyperbranched polymer cluster or even a microgel, $\Gamma_s/(q^3k_BT/\eta)$ is independent of both $\langle R_g\rangle$ and q on the basis of the scaling theory,[40,41] where η is the solution viscosity. For a dilute solution, η can be replaced by the solvent viscosity.

It is helpful to note that $1/q$ (~50–135 nm in the scattering angle range 30°–90°) is much larger than the radius of gyration of individual chains ($\langle R_g\rangle \sim 36$ nm). Figure 6 shows that for each copolymer concentration studied Γ_s/q^3 should not be, but is, independent of q. It suggests that the entangled chains might act as transient polymer clusters with a size much larger than $1/q$. On the other hand, Figure 6 shows that the plots of Γ_s vs q for different concentrations do not fall to a single master curve. This is because in semidilute solutions η should depend on the copolymer concentration. It has been known that $\Gamma_s\eta/q^3k_BT$ is a constant when $\langle R_g\rangle q \gg 1$.[41] Therefore, the plot of q^3k_BT/Γ_s vs C should lead to a concentration dependence of η which provides a novel way to determine the local viscosity in a semidilute solution.

Figure 7 shows such a plot in which we know that q^3k_BT/Γ_s has to approach the viscosity (η_0) of chloroform when $C \rightarrow 0$. The inset shows that in the semidilute regime q^3k_BT/Γ_s is scaled to C as $q^3k_BT/\Gamma_s \sim C^{2.0\pm0.2}$, slightly higher than 1.8 predicted for semidilute solutions in the reptation model.[1,42] Therefore, q^3k_BT/Γ_s can be related to the copolymer concentration (C) as $q^3k_BT/\Gamma_s = \eta_0 + 85.3C^{2.0\pm0.2}$. A different concentration dependence of Γ_s was also previously observed. For example, Horkay et al.[43] showed that for poly(vinyl alcohol–vinyl

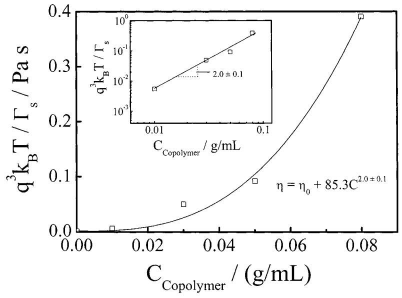


Figure 7. Copolymer concentration dependence of q^3k_BT/Γ_s of semidilute solutions of photo-cross-linkable copolymer [P(MMA-*co*-AMC)] in chloroform. The inset shows the scaling between q^3k_BT/Γ_s and C.

acetate) copolymer in aqueous solutions $1/\Gamma_s \sim C^{3.0}$. We will come back to this point later. Now let us focus on how the fast and slow relaxation modes change when the copolymer chains are gradually photo-cross-linked together.

Figure 8 shows that as the photo-cross-linking reaction proceeds, both the fast and slow relaxation become slower and slower, shifting to a longer delay time. At the same time, the contribution of the slow relaxation increases, indicating the formation of less immobile clusters. The shifting is much faster when the concentration is higher because the interchain photo-cross-linking is enhanced and more effective in a more concentrated solution. Note that the cross-linking extent (CE (%)) is a linear function of the UV irradiation time (t_{UV}); namely, CE (%) = $(3.4 \pm 0.1)t_{UV}$ (h). Since the copolymer concentration was much higher than C^* ($(1.8-6.7) \times 10^{-3}$ g/mL), the copolymer chains must be highly overlapped. Therefore, most of the photodimerization (cross-linking) should be interchain reaction, resulting in randomly, but uniformly branched, clusters.[27] It is interesting to note that the time correlation functions for less concentrated solutions (1.0 or 3.0 wt %) in Figure 8a collapse into a single curve after a long irradiation time, showing that the longest relaxation time or the largest cluster formed is finite. In other words, no gel could be formed in these two copolymer solutions, which has been confirmed by visual flow test. As for the two more concentrated solutions (5.0 and 8.0 wt %), Figure 8b shows that the longest relaxation time increases gradually with the irradiation time, and the solution finally turns into a gel after ~10 h UV irradiation, as shown in the inset by an inverted cell. In the case of C = 8.0 wt %, the fast relaxation nearly disappeared after ~14 h UV irradiation.

One important feature in Figure 8b is that the apparent coherence factor (β) in eq 2; i.e., the intercept of $[G^{(2)}(\tau) - A]/A$ at $\tau \rightarrow 0$ increases during the sol−gel transition, which is opposite to what was commonly observed in previous studies, e.g., by Matin, et al.[30] in the sol−gel transition of TMSO and by Shibayama et al.[44,45] in a bulk cross-linking polymerization of *N*-isopropylacrylamide (NIPA). The previously observed decrease of β was attributed to the contribution from frozen components in the gel network. A chemical gel normally has an inhomogeneous "island" structure and is nonergodic; i.e., the extent of relaxation of $G^{(2)}(\tau)$ and the scattering intensity depend on the sample position. However, the gel formed in the present study is transparent and homogeneous because no specks were detected when we turn the cell to let the laser hits different parts of the gel. More importantly, Figure 8b shows that the gel network formed after a long exposure of UV light can still completely relax at a long decay time of a few seconds. In other words, the gel network can relax a length scale of $1/q$ (~100 nm) within the delay time window used, indicating that it is even dynamically ergodic.

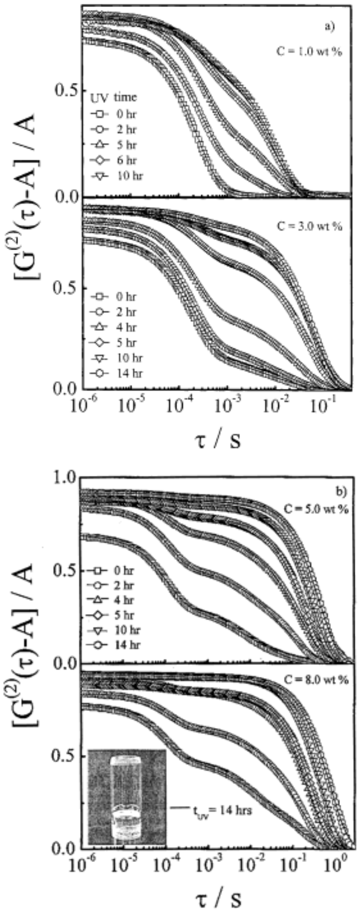


Figure 8. Intensity−intensity−time correlation functions of semidilute solutions of photo-cross-linkable copolymer [P(MMA-*co*-AMC)] in chloroform at different stages of photo-cross-linking (i.e., after different UV irradiation times), where θ = 30°.

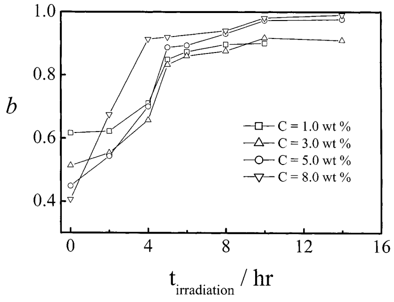


Figure 9. UV irradiation time dependence of the stretching exponent (b) obtained in the fitting of eq 4 for semidilute solutions of photo-cross-linkable copolymer [P(MMA-*co*-AMC)] in chloroform, where θ = 30°.

The solid lines in Figure 8 represent the fitting on the basis of eq 4. As discussed before, the stretching exponent b is related to the polydispersity of the slow relaxation modes. Figure 9 shows that b increases and approaches one as the photo-cross-linking reaction proceeds, especially for the solutions of C = 5.0 and 8.0 wt %. This indicates that the concentration and density fluctuation are suppressed by the photo-cross-linking.

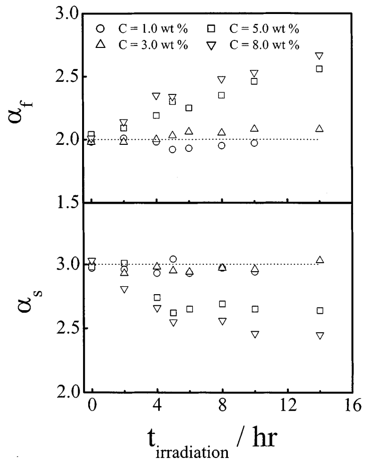


Figure 10. UV irradiation time dependence of the scaling exponents in $\Gamma_f \sim q^{\alpha_f}$ and $\Gamma_s \sim q^{\alpha_s}$ for the fast and slow relaxation modes of semidilute solutions of photo-cross-linkable copolymer [P(MMA-*co*-AMC)] in chloroform.

The resultant solution or gel network is dynamically more homogeneous. Therefore, it relaxes nearly as a single component, and at the same time, the contribution of the fast diffusive relaxation becomes less and less because individual chains are eventually cross-linked as parts of larger clusters or a gel network. For each given UV irradiation time (i.e., at a given reaction stage), each plot of Γ_f or Γ_s vs q, similar to those in Figure 5, can lead to a scaling exponent α_f or α_s.

Figure 10 shows the that for two less concentrated solutions (1.0 and 3.0 wt %), in which no gel was formed, $\alpha_f = 2.0 \pm 0.1$ and $\alpha_s = 3.0 \pm 0.1$. They are very similar to the behaviors of two corresponding solutions in spite of the fact that the photoirradiation-induced cross-linking reaction has resulted in large clusters and gradually reduced the contribution of the fast diffusion mode. Here, the q^3 dependence of Γ_s is definitely associated with internal relaxation of large clusters. A comparison of Figures 6 and 10 confirms that the slow relaxation mode observed in Figure 3 is related to internal motions of the clusters. The only difference is that before the photo-cross-linking reaction, the clusters are transient and formed via the chain entanglements. Our result implies that the chain deentanglement is so slow that the entangled chains can move together as clusters. In other words, we cannot see the deentanglement within the delay time window used in dynamic LLS.

On the other hand, the UV irradiation time dependence of α_f and α_s for two more concentrated solutions (5.0 and 8.0 wt %) has a different pattern; namely, α_f increases, but α_s decreases, as the photoreaction proceeds. This can be attributed to a gradual cross-linking of individual linear chains, which results in larger less mobile clusters and eventually an immobile gel network. At a finite scattering angle, the clusters quickly become comparable to $1/q$ as the cross-linking proceeds. Therefore, the diffusive relaxation starts to mix with internal motions of large clusters. The mixture of internal motions with diffusive relaxation makes the apparent Γ_f more dependent on q so that α_f increases. On the other hand, some of the large clusters become less mobile or immobile, which makes the apparent Γ_s less dependent on q, which explains why α_s decreases as the cross-linking reaction proceeds.

In the fitting of $G^{(2)}(\tau)$ on the basis of eq 4, we also obtain the weighting (W_f) of the diffusion relaxation mode, i.e., the contribution of all components which are mobile and able to relax a length scale of $1/q$ within the delay time window used in dynamic LLS. Figure 11 shows an expected decrease of W_f because more copolymer chains are cross-linked together to form large less mobile clusters and eventually an immobile gel network as the photo-cross-linking reaction proceeds. In an effective cross-linking reaction, most of the chains are interconnected to become part of a gel network, so that the fast and slow relaxation modes should be merged in the gel state.[20,24,46] This is exactly what we observed in the study of two more concentrated solutions. For a given irradiation time, W_f decreases as the copolymer concentration increases, which is understandable because the chance of photo-cross-linking two copolymer chains in a more concentrated solution is higher. Note that for two less concentrated solutions W_f remains finite, but for two more concentrated solutions, $W_f \to 0$ or $W_s \to 1$, after a long UV irradiation. Figure 11 is consistent with Figure 9, even though they represent different parameters; namely, the disappearance of the fast diffusion relaxation of mobile exponents and the formation of a more homogeneous solution or a uniform gel as the photo-cross-linking reaction proceeds.

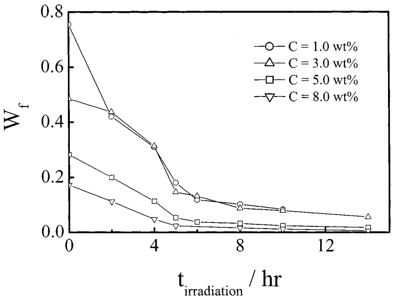


Figure 11. UV irradiation time dependence of relative contribution of the fast relaxation mode (W_f) of semidilute solutions of photo-cross-linkable copolymer [P(MMA-*co*-AMC)] in chloroform, where $\theta = 30°$.

Conclusion

The incorporation of photo-cross-linkable functional group 7-acryloyloxy-4-methylcoumarin (AMC) into a poly(methyl methacrylate) (MMA) chain backbone enables us to study the effect of cross-linking on the dynamics of semidilute solutions at each reaction stage by laser light scattering (LLS). This is because AMC can undergo a controllable [2 + 2] photodimerization when irradiated with UV light of 310 nm. Prior to the photo-cross-linking reaction, dynamic LLS studies of different semidilute solutions of such a copolymer in chloroform showed that there always exist a fast and a slow relaxation mode. The line widths (Γ_f and Γ_s) of these two relaxation modes can be scaled to the scattering vector q as $\Gamma_f \sim q^{\alpha_f}$ with $\alpha_f = 2.0 \pm 0.1$ and $\Gamma_s \sim q^{\alpha_s}$ with $\alpha_s = 3.0 \pm 0.2$, respectively, indicating that they are related to cooperative diffusion of individual mobile chains and internal motions of large "immobile" clusters. The contribution of the slow relaxation increases with the copolymer concentration. As expected, the photoreaction-induced cross-linking of the copolymer chains in a less concentrated copolymer solution ($<3 \times 10^{-2}$ g/mL) can only result in finite polymer clusters. It is interesting to find that the cross-linking has no effect on either α_f or α_s, indicating no change in the solution dynamics. On the other hand, it suggests that the slow relaxation observed before the cross-linking reaction should be related to internal motions of the transient clusters made of entangled chains. Our result shows that the disentanglement of the chains inside these clusters takes a time much longer than the delay time window used in dynamic LLS; i.e., they are not able to move a distant of $1/q$ within the delay time window. In contrast, irradiating a more concentrated solution ($>$5.0 wt %) for a long time can eventually lead to a homogeneous gel. In such a sol−gel transition, there also exist two relaxation modes. The contribution of the fast relaxation decreases as the irradiation time increases. Moreover, as the photo-cross-linking reaction proceeds, α_f increases, but α_s decreases, reflecting a mixture of internal motions of large clusters with diffusion relaxation, and some of the large clusters even become immobile. This is because more copolymer chains were cross-linked together to form large clusters during the photoreaction.

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