Gelation Processes of Polymer Solutions. 1. Photodimerization of Free and Polymer-Bound Anthryl Groups

Nobuhiro Ide, Yoshinobu Tsujii, Takeshi Fukuda,* and Takeaki Miyamoto

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan

Received December 11, 1995; Revised Manuscript Received February 23, 1996[⊗]

ABSTRACT: A copolymer of 2-(9-anthrylmethoxy)ethyl methacrylate with methyl methacrylate ($M_w = 3.1 \times 10^5$, anthryl content = 0.8 mol %) and a low-mass model compound were studied with respect to their photodimerization or photo-cross-linking processes in tetrahydrofuran solution. The number of dimers or cross-links formed by ultraviolet (UV) irradiation was determined by UV absorption spectroscopy. A kinetic study on the model compound indicated the existence of a small amount of side reaction, which should be taken into consideration for a quantitative analysis. The concentration dependence of the initial quantum yield of photo-cross-linking of the polymer suggested that, below the overlap concentration c^*, the intramolecular cross-linking predominates, while at $c > c^*$, the contribution of intermolecular cross-linking increases with increasing c. This was directly confirmed by the light scattering measurements of the molecular weight and radius of gyration of the irradiated polymer. For a 10 wt % solution ($c/c^* \approx 4$), the critical number of cross-links, L_g, of gelation was determined to be about 1.0 per chain, of which the intermolecular contribution is estimated to be ~0.33. This value is fairly close to the Flory−Stockmayer theoretical prediction (about 0.24).

Introduction

A polymer solution often gels upon the introduction of chemical or physical cross-links on the chains. A fundamental question that has been raised for a long time pertains to the critical number of cross-links required to produce a gel, i.e., a branched macromolecule with infinitely large molecular weight. The classical theory of Flory and Stockmayer (FS)[1] predicts the following relations for the cross-linking of prepolymer (vulcanization or four-functional random branching):

$$M_{wo}/M_w = 1 - 2L(M_{wo}/M_{no}) \quad (1)$$

$$L_g = (2M_{wo}/M_{no})^{-1} \quad (2)$$

where M_w and M_n are the weight- and number-average molecular weights, L is the number of cross-links per prepolymer, and the subscripts o and g denote the prepolymer and the critical point of gelation, respectively. Values of L and L_g observed for, e.g., copolymerizations of vinyl and divinyl monomers[2−4] were much larger, typically 1 or 2 orders of magnitude larger than predicted by eqs 1 and 2. This enormous discrepancy between theory and experiment has been attributed mainly to the neglect, in the FS theory, of intramolecular cross-linking or loop formation, which makes no contribution to the increase of molecular weight. Even in a homogeneous polymer solution, there is a difference between the overall and the local concentrations in reactive sites. An extreme case is that of a very dilute solution, in which the local concentration is large within the domain of the polymer chain but is nearly zero outside of it. Hence, reactions in dilute solution would mostly occur intramolecularly, giving virtually no intermolecular cross-links. As the concentration increases, the solution becomes more and more homogeneous, and the number of intermolecular cross-links, L_2, relative to that of intramolecular ones, L_1, would increase, rendering the FS theory a more reliable approximation. In fact, a previous study by us[5] on the gelation of the dihydroxypropylcellulose/borax/aqueous solution, a physically gelling system, has suggested the validity of the FS theory at sufficiently high concentrations of the polymer.

More generally, we would expect that the total number of cross-links, $L_g = L_{g1} + L_{g2}$, at gelation and the L_2/L_1 ratio are functions of the concentration and characteristics of the polymer. Aside from the universality arguments of the critical behavior of gelation,[6,7] the prediction of the critical point and the estimation of the number of effective cross-links are essential to control the reaction of gelling systems and to understand their structure−property relationships. A promising, though laborious, route to this end would be to make experimentally clear the above-mentioned function for particular model systems and draw certain generalities therefrom.

Here we have studied the cross-linking process of anthryl group-carrying poly(methyl methacrylate) (A-PMMA) in solution. It is known that anthryl compounds undergo dimerization on absorbing a 320−400 nm light, while the formed dimers are dissociated by a shorter wavelength light or heat.[8] The dimerization or cross-linking process can be quantitatively followed by ultraviolet (UV) absorption spectroscopy. The high sensitivity of this method allows us to work at a very low anthryl, hence polymer, concentration, enabling us to observe the intramolecular cross-linking process selectively. This information should be useful to analyze the reactions occurring at higher concentrations. Previous studies of relevance which have dealt with the photodimerization of polymer-bound anthryl groups in solution include those by Tazuke and Banba,[9] who treated various oligomeric polyesters, by Kozel and Lashkov,[10] who observed intramolecular reactions, and by Hargreaves and Webber,[11] who noted the photodecomposition of carbonyl chromophores. Regarding the problem of photodecomposition, Fox and Britt[12] have found no low-mass photoproducts cleaved from poly(2-(9-anthryl)ethyl methacrylate), suggesting the absence

---

[⊗] Abstract published in *Advance ACS Abstracts,* April 15, 1996.

Chart 1. Model Polymer A-PMMA

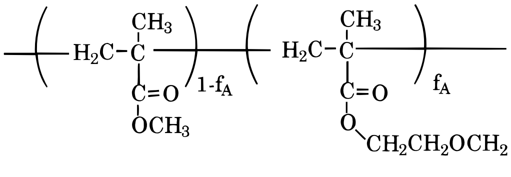
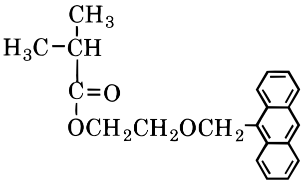


Chart 2. Model Compound A



of undesirable side reactions in this polymer. This observation has led us to prepare 2-(9-anthrylmethoxy)ethyl methacrylate and copolymerize it with methyl methacrylate to give the model polymer A-PMMA (Chart 1). We also studied the photoreaction of the low-mass model compound **A** (Chart 2), which proved useful for the analysis of the polymer systems. To our knowledge, this is the first report that deals with the photo-cross-linking reaction of a high polymer in solution covering a dilute as well as a gelling high-concentration regime.

Experimental Section

Synthesis of Poly(2-(9-anthrylmethoxy)ethyl methacrylate) (A-PMMA). To a dimethyl sulfoxide (DMSO) solution of ethylene glycol (28 mL) were added at 0 °C potassium hydroxide (1.12 g) as an activator and then 9-bromoanthracene (2.31 g), which was synthesized from 9-(hydroxymethyl)anthracene (Aldrich Chemical Co., Milwaukee, WI)[12] and recrystallized from chloroform solution. The reaction was allowed to proceed at room temperature for a few hours until the solution was clear yellow-brown. The reaction mixture was poured into an excess of ice-cold water to recover 9-anthrylmethyl 2-hydroxyethyl ether, which was purified by reprecipitation from tetrahydrofuran (THF) solution into ice-cold water. The monomer, 2-(9-anthrylmethoxy)ethyl methacrylate, was prepared by adding 0.83 mL of methacryloyl chloride (Tokyo Kasei Kogyo Co., Tokyo, Japan) dropwise to a THF solution containing 9-anthrylmethyl 2-hydroxyethyl ether (2.0 g) and triethylamine (3.2 g). After being stirred at 0 °C for 2 h, the reaction mixture was extracted with 30 mL of benzene, washed several times with water, and then concentrated. The obtained crude product was purified by silica gel column chromatography with the eluent a mixture of benzene and hexane (1:3). The copolymer (A-PMMA) of this monomer with methyl methacrylate (MMA) was prepared by radical copolymerization initiated by AIBN initiator in a THF solution (monomer:THF = 8:2 by weight) at 50 °C with N_2 bubbling. The comonomer MMA was distilled under reduced pressure after being washed with aqueous NaOH and dried on silica gel. The copolymer thus obtained was precipitated several times from THF solution into methanol. The weight-average molecular weight, M_w, and the polydispersity index, M_w/M_n, were determined to be 3.1×10^5 by light scattering and 2.1 by gel permeation chromatography (GPC), respectively. The fraction of the anthryl group introduced in the copolymer was estimated to be 0.80 mol % from the absorbance at 365 nm. The compositional distribution in this copolymer should be minimal, since the conversion was kept low (~8%), and since the system itself should not be far from ideal with unit reactivity ratios. The relevant molar extinction coefficient was determined to be 7040 by use of the low-mass model compound **A**. All procedures were carried out in the dark to prevent photobleaching of the anthryl group.

Synthesis of 2-(9-Anthrylmethoxy)ethyl Isobutyrate (A). The low-mass model compound, 2-(9-anthrylmethoxy)ethyl isobutyrate (**A**), was synthesized according to the same procedure as described above, except that isobutyl chloride (Nacalai Tesque, Kyoto, Japan) was used as the acid chloride. It was purified by silica gel column chromatography with ethyl acetate/benzene (1:4) solvent system.

Photoirradiation. As a solvent, spectroscopic grade THF (Dotite Spectrosol) was used without further purification. After a sample solution was degassed by several freeze−pump−thaw cycles below 10^{-5} Torr, photoirradiation was carried out at room temperature in a quartz or Pyrex-glass cell with an optical path length of 1 cm or 1 mm. A 500 W xenon lamp (Ushio Electronics, Osaka, UXL-500D-O) was used as an excitation light source. The light with wavelength ranging from 320 to 400 nm was selected by the following combination of filters: an aqueous filter, a dispersion plate (Sigma Koki, DFSQ1-30C02-1500), and Toshiba UV-33 and UV-D33S filters. The filtered UV light intensity was calibrated by a photometer (International light, IL500) to be 1.02×10^{-7} mol/(s cm^2), from which the number of absorbed photons was calculated according to the spectra of the filtered light and the anthryl chromophore.

Measurements. Absorption spectra were recorded on a Shimadzu UV2200A spectrophotometer. The concentration of anthyrl groups was estimated with the absorption peak at 365 nm (see above). Light scattering measurements were made in THF solvent at 25 °C by a DLS-7000 photometer (Otsuka Electronics, Japan), which was calibrated with benzene. The refractive index increment, d*n*/d*c*, in THF solution of A-PMMA at 25 °C was determined to be 0.0882 mL/g by a DRM1030 differential refractometer (Otsuka Electronics). Proton nuclear magnetic resonance (^{1}H-NMR) spectra were obtained with a Varian VXR-200 spectrometer operating with a frequency of 200 MHz. GPC analysis was made with a Shimadzu high-performance liquid chromatograph, HLC-802UR, installed with TSK-GEL G2000HXL, G3000HXL, G4000HXL, and G5000HXL gel columns (TOHSO, Tokyo, Japan). THF was used as eluent, and a flow rate of 1.0 mL/min was maintained.

Results and Discussion

Before presenting main results, we wish to make some comments on photoinduced side reactions, other than dimerization, in anthryl compounds. We previously studied a copolymer of 9-anthrylmethyl methacrylate with MMA, instead of A-PMMA used here. To prevent photooxidation,[11,14] we deoxygenated a THF solution of this polymer by the freeze−pump−thaw method and sealed it. After irradiation of the UV light, we observed a significant decrease of the polymer molecular weight (by light scattering) and the production of undefined low-mass compounds (by GPC). This suggests the occurrence of main-chain scission, in addition to the decomposition of the carbonyl chromophores.[11] In the case of THF solutions of A-PMMA, degassed and sealed under high vacuum, no such side reaction was observed. We have also studied, by both NMR and UV spectroscopies, DMSO solutions of the model compound **A**, degassed and sealed in an NMR tube and UV irradiated. Figure 1 shows the ^{1}H-NMR spectra taken before and after irradiation. From this result, and from the UV analysis, we confirmed that the amount of dimer produced is equal to the amount of monomer lost. This means that dimerization predominates in this system. However, as will be described later, a low level of side reaction still occurs in degassed solutions of **A** and probably A-PMMA as well, which becomes important at very low concentrations of the anthryl group.

Dimerization Kinetics of Model Compound A. Figure 2 shows the UV spectra of a THF solution of **A**

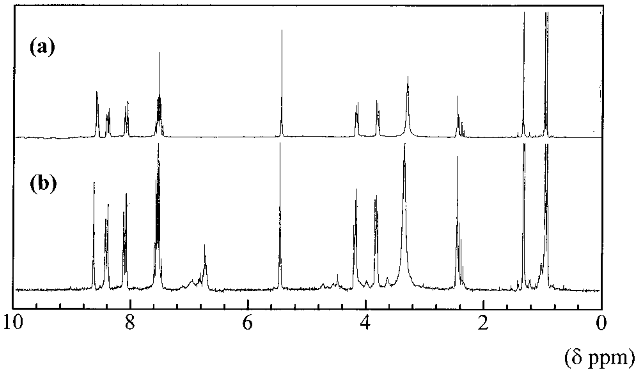


Figure 1. ^{1}H-NMR spectra of the model compound **A** in dimethyl sulfoxide-d_6 solution (a) before and (b) after irradiation.

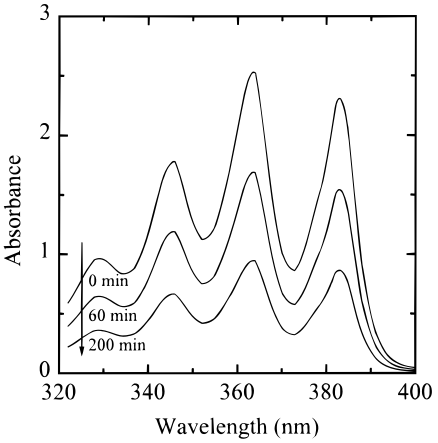


Figure 2. UV spectra of a THF solution of **A** as a function of irradiation time ($[\mathbf{A}]_0 = 3.65 \times 10^{-3}$ mol/L).

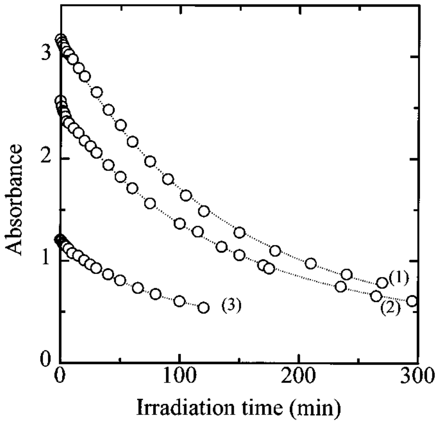


Figure 3. Plot of absorbance versus irradiation time for THF solutions of **A**: $10^3[\mathbf{A}]_0$ = (1) 4.50, (2) 3.65, and (3) 1.71 mol/L.

taken at various irradiation times. We employed the absorption peak around 365 nm to determine the concentration of anthryl group. Examples of the absorbance versus time plot are presented in Figure 3.

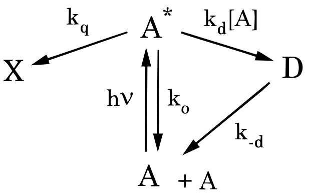


Figure 4. Photoreaction scheme of model compound **A**.

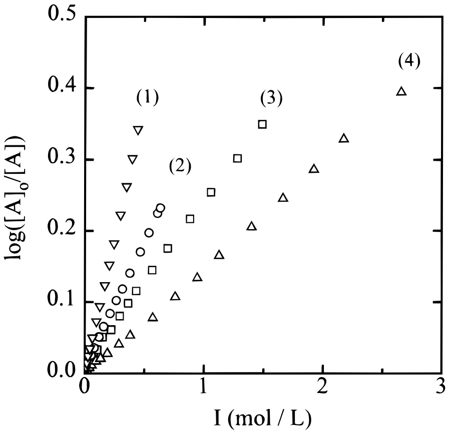


Figure 5. Plot of log($[\mathbf{A}]_o$/[**A**]) vs *I* for THF solutions of *A*: $10^3[\mathbf{A}]_o$ = (1) 0.164, (2) 0.307, (3) 1.71, and (4) 4.50 mol/L.

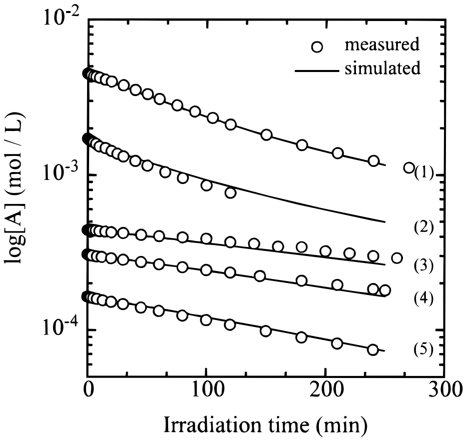


Figure 6. Plot of log [**A**] versus irradiation time for THF solutions of **A**: $10^3[\mathbf{A}]_o$ = (1) 4.50, (2) 1.71, (3) 0.443, (4) 0.307, and (5) 0.164 mol/L. The solid curves were computer-simulated with $k_d/k_o = 0.16$ (mol/L)$^{-1}$, $k_q/k_o = 1.6 \times 10^{-4}$, and $k_{-d} = 1.6 \times 10^{-5}$ s^{-1}.

Now let us assume the photoreaction scheme of **A** in solution shown in Figure 4: upon absorbing the light energy, **A** is excited to **A***, which either dimerizes with **A** with a (second-order) rate constant, k_d, or is deactivated to the ground state with a rate constant k_o. The dimer **D** can be dissociated to two monomers. This rate constant, k_{-d}, was estimated to be 1.6×10^{-5} s^{-1} at 26 °C by observing the UV absorbance of the system preirradiated to produce a sufficient number of dimers and kept in the dark. In an early stage of reaction, we can assume that $[\mathbf{D}] = 0$, and thus the decreasing rate of **A** is quasi-first-order, since $k_d[\mathbf{A}] \ll k_o$ in all the cases studied here:

$$-\mathrm{d}[\mathbf{A}]/\mathrm{d}I \approx 2k_d[\mathbf{A}]/(k_o + k_d[\mathbf{A}]) = 2(k_d/k_o)[\mathbf{A}] \quad (3)$$

Here, *I* is the number of photons absorbed by a unit volume of solution. Figure 5 shows the plot of log($[\mathbf{A}]_o$/[**A**]) vs *I* for the reaction of **A** at 26 °C, where $[\mathbf{A}]_o$ is the initial concentration of **A**. The linearity approximately holds in all cases, but the slope $2(k_d/k_o)$ clearly depends on $[\mathbf{A}]_o$. This indicates a “side route” from **A*** to an unknown product **X** that has no absorbance in the anthracene range. Because of the low concentration of this product **X**, we have not yet been able to directly detect and analyze it, but we are sure of its presence. In fact, computer simulations carried out under the assumption of this “quenching” reaction (rate constant k_q) gave satisfactory results and are presented in Figure 6. In this case, the initial decreasing rate of **A** reads

$$-\mathrm{d}[\mathbf{A}]/\mathrm{d}I = (k_q + 2k_d[\mathbf{A}])/(k_o + k_q + k_d[\mathbf{A}]) \quad (4)$$

$$\approx k[\mathbf{A}] \quad (5)$$

$$k = (k_q/k_o)[\mathbf{A}]^{-1} + 2(k_d/k_o) \quad (6)$$

Equation 5 with eq 6 is based on the approximation that $k_o \gg k_q + k_d[\mathbf{A}]$, and it explains the increase of the quasi-first-order rate constant k with decreasing [**A**] (Figure 5). The simulations in Figure 6 took account of the dimer dissociation with the mentioned rate constant, which was nonnegligible in a latter stage of reaction with large $[\mathbf{A}]_o$. They give the following optimum values of rate constant ratios:

$$k_d/k_o = 0.16 \quad (7)$$

$$k_q/k_o = 1.6 \times 10^{-4} \quad (8)$$

Since the quantum yield of the quenching process ($\Phi_q \approx k_q/k_o$) is very small, this quenching process seems to have remained unnoticed. Nevertheless, it is important at such low concentrations that the quantum yield of dimerization ($\Phi_d \approx (k_d/k_o)[\mathbf{A}]$) is of the same order as Φ_q (see below). Experimental data for polymer systems will be corrected for it by use of the k_q/k_o value in eq 8.

Systems with A-PMMA. Examples of the absorbance versus irradiation time plot for A-PMMA/THF solutions are presented in Figure 7, where some similar data for the model compound **A** (henceforth the "monomer") are also given for comparison. Clearly, the absorbance decreases much faster in the polymer solutions than in the monomer systems, especially at the initial stage of irradiation.

Figure 8 compares the polymer and monomer solutions with respect to the initial values of quantum yield of dimerization, Φ_d, at various concentrations, where, by using eqs 5 and 6, Φ_d is obtained as

$$\Phi_d \approx (k_d/k_o)[\mathbf{A}] = {}^1/_2[(-\mathrm{d}[\mathbf{A}]/\mathrm{d}I) - (k_q/k_o)] \quad (9)$$

Here, a comment may be due on the possible energy migration between anthryl groups. According to the Foerster theory,[15] the energy migration efficiency is proportional to r^{-6}, where r is the distance between chromophores, and the critical distance at which the energy migration has the same probability as internal quenching processes from an excited state is 22 Å. Even for the most concentrated solution (c = 13 wt %, $[\mathbf{A}] = 9.2 \times 10^{-3}$ mol/L) studied in this paper, the average distance between anthryl groups is calculated to be 62 Å, which is 3 times as large as the critical distance. This concentration is much higher than the overlap concentration (c^* = 2 wt %, $[\mathbf{A}] = 1.4 \times 10^{-3}$ mol/L, see below) and hence the local concentration relevant to the intramolecular process. Thus, neither inter- nor intramolecular energy migration should have any contribution to the quantum yield of dimerization in the studied concentration regime. Figure 8 shows a clear difference between the polymer and monomer solutions: in the monomer solution, Φ_d increases in proportion to [**A**], while in the polymer system, Φ_d has a finite, fairly large value even at very low concentrations, stays nearly constant until [**A**] reaches about 2×10^{-3} M, and then starts to increase with increasing [**A**]. This means that the monomeric anthryl groups are randomly distributed in space, while the polymer-bound ones are not. The latter ones are populated in each domain of polymer molecules; thus, even in dilute solution, where intermolecular contacts seldom occur, they can undergo intramolecular dimerization at an appreciable rate. Therefore, in the polymer system, the first relation in eq 9 has to be reinterpreted as

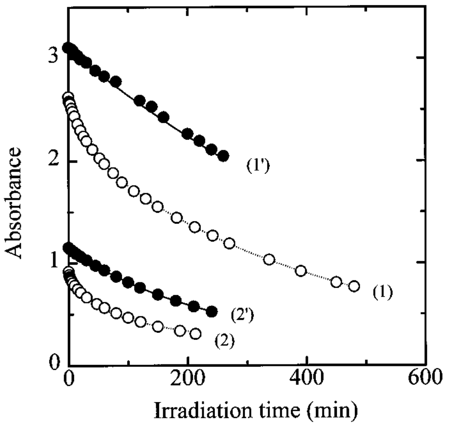


Figure 7. Plot of absorbance versus irradiation time for THF solutions of A-PMMA (○, $10^3[\mathrm{A}]_o$ = (1) 0.373 and (2) 0.130 mol/L) and **A** (●, $10^3[\mathbf{A}]_o$ = (1′) 0.442 and (2′) 0.164 mol/L).

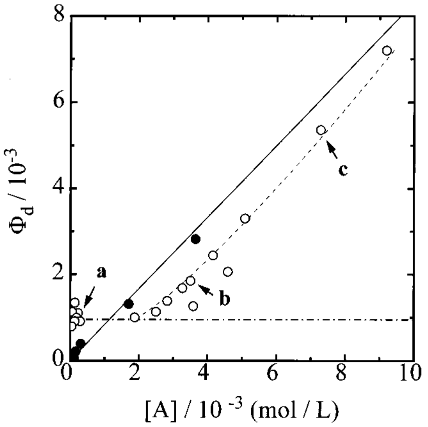


Figure 8. Plot of quantum yield of dimerization Φ_d versus anthryl concentration, [**A**], for A-PMMA (○) and **A** (●). See text for details.

$$\Phi_d \approx (k_d/k_o)[\mathbf{A}]_{\mathrm{eff}} \quad (10)$$

where $[\mathbf{A}]_{\mathrm{eff}}$ is the effective concentration of anthryl groups leading to dimerization reaction. This $[\mathbf{A}]_{\mathrm{eff}}$, and hence the Φ_d vs [**A**] curve, reflects the inhomogeneity of the local concentration of the reactive sites in polymer solution, which should be an important factor to control the critical point of gelation and the gel structure.

The above argument suggests that, in the dilute regime, where Φ_d (or $[\mathbf{A}]_{\mathrm{eff}}$) is constant, intramolecular cross-linking predominantly occurs, and above the concentration at which Φ_d starts to increase (about 2 wt % in concentration of this polymer), intermolecular cross-linking also becomes appreciable. It is interesting to note that the polymer concentration of 2 wt % approximates the overlap concentration c^* computed from $c^* = M_w/[(4\pi N_A/3)\langle S^2\rangle_w^{3/2}]$, with $\langle S^2\rangle_w \approx \langle S^2\rangle_z(M_{no}/M_{wo})$, where $\langle S^2\rangle_w$ and $\langle S^2\rangle_z$ are the weight-average and z-average mean-square radii of gyration of the polymer, and N_A is the Avogadro number (for the $\langle S^2\rangle_z$ value, see below).

To confirm these points, we have carried out light scattering measurements at the points a and b marked in Figure 8. Figure 9 shows the inverse excess scatter-

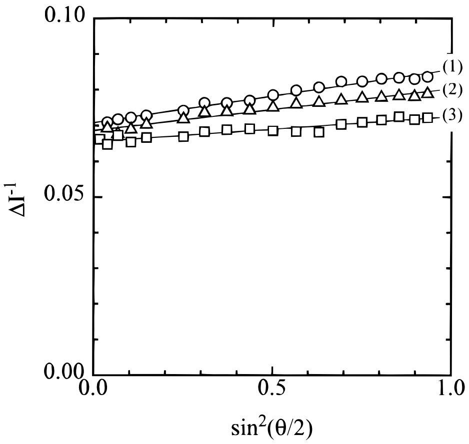


Figure 9. Plot of inverse excess scattering intensity ΔI^{-1} vs $\sin^2(\theta/2)$ for a 0.25 wt % THF solution of A-PMMA: $T = 25.0$ °C; irradiation time t = (1) 0, (2) 45, and (3) 90 min.

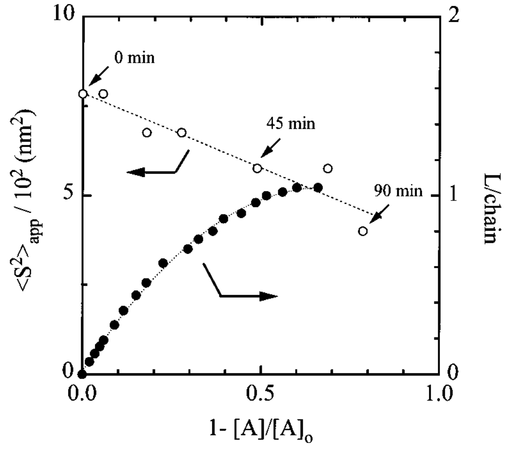


Figure 10. Plot of $\langle S^2\rangle_{app}$ (○) and number of cross-links L per chain (●) versus $1 - [\mathbf{A}]/[\mathbf{A}]_o$ for a 0.25 wt % THF solution of A-PMMA.

ing intensity, ΔI^{-1}, from a 0.25 wt % THF solution of the polymer (point a) as a function of $\sin^2(\theta/2)$. The ordinate intercept of the plot is nearly independent of irradiation time, indicating approximate constancy of molecular weight, whereas the slope of the curve is changed by irradiation. The apparent mean-square radius, $\langle S^2\rangle_{app}$, computed form the ΔI^{-1} vs $\sin^2(\theta/2)$ plot is presented as a function of $1 - [\mathbf{A}]/[\mathbf{A}]_o$ in Figure 10, where the number of cross-links, L, per prepolymer obtained from the absorbance data is also shown. The figure shows that, after 90 min of irradiation, for example, about 1 cross-link per chain is formed intramolecularly (since there is no appreciable increase in M_{app}, Figure 9), which is accompanied by a decrease of $\langle S^2\rangle_{app}$ of about 40%. Figure 11 shows the Zimm plot for the polymer recovered after 300 min of irradiation at the concentration $c = 5.0$ wt % (point b in Figure 8). The M_w and $\langle S^2\rangle_z^{1/2}$ are observed to have increased by factors of 5.3 and 1.9, respectively (see the legend for Figure 11). The L at this irradiation time is estimated to be about 0.75 cross-links per chain. This suggests that, at point b, an appreciable number of intermolecular cross-links are formed. According to the FS theory, however, the number of intermolecular cross-links, L_2, that would bring about this much of an increase in M_w is estimated to be about 0.20 ($M_w/M_{wo} = 5.3$, $M_{wo}/M_{no} = 2.1$ in eq 1), suggesting that the intramolecular reaction still predominates in this concentration regime.

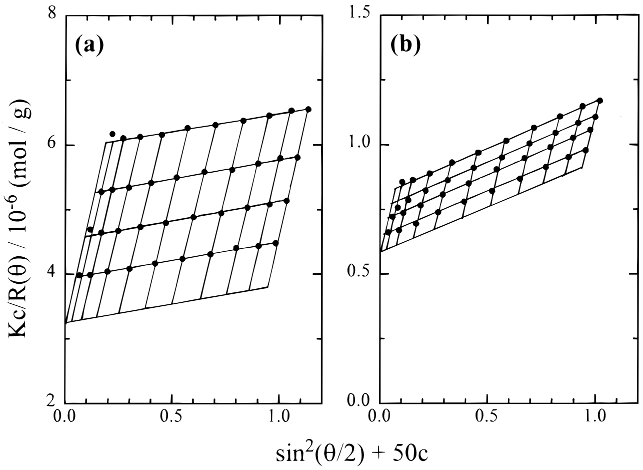


Figure 11. Zimm plot for (a) A-PMMA before irradiation ($M_w = 3.1 \times 10^5$, $\langle S^2\rangle_z^{1/2}$ = 260 Å) and (b) the polymer recovered after 300 min of irradiation in a THF solution with $c = 5.0$ wt % ($M_w = 1.7 \times 10^6$, $\langle S^2\rangle_z^{1/2}$ = 490 Å): solvent, THF; $T = 25.0$ °C.

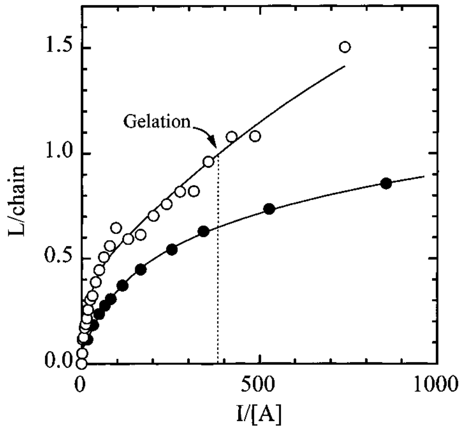


Figure 12. Plot of number of cross-links per chain versus number of photons absorbed per anthryl group for THF solutions of A-PMMA: c = 10 wt % (○) and c = 0.16 wt % (●).

Figure 12 shows the relation between the total number of cross-links, L, per chain and the number of photons absorbed per anthryl groups, observed at the point of c in Figure 8, where $c/c^* \approx 4$. The point shown by the arrowhead in Figure 12 indicates an approximate gel point, above which the system was observed not to flow when tilted. At this "gel point", L is about 1.0. The filled circles in the figure indicate the data obtained for a dilute solution (c = 0.16 wt %), in which almost all cross-linkds are intramolecular ones. If intra- and intermolecular reactions are assumed to be independent of each other, we may subtract from L the contribution of the intramolecular cross-links, L_1, indicated by the dilute solution data and estimate $L_2 = 1.0 - L_1$ to be about 0.33. This value is to be compared with the L_g value of the FS theory, which is 0.24 (eq 2). Presumably, the assumption of independent intra- and intermolecular reactions would not be rigorously correct, because the intermolecular process is considered as a kind of concentration-dependent quenching which will, of course, affect the excited-state lifetime of the chromophore and hence also the intramolecular process. However, that the actual value is close to the FS value may be accepted as a fact for the following reasons: (i) the L value is very small ($L \leq 1.0$), even at the gel point, and (ii) the lifetime of the chromophore should be nearly constant, since Φ_d is less than 0.01 even in the most concentrated solution.

This result would explain the enormous differences observed between the theory and the experiments in other systems.[2−4] It indicates that a main difference comes from the neglect of L_1 in the FS theory and that L_2 is reasonably correlated with the FS theory. In dilute solution, L_1 is overwhelmingly larger than L_2, and hence huge differences between the theory and experiment can be observed. Even in the moderately concentrated solution, L_1 can be much larger than L_2, as Figure 11 indicates. We expect that the relative contribution of intramolecular cross-links would become smaller at higher concentrations, with the L value itself coming closer to the FS theory. Work is in progress to confirm this experimentally and to make clear the effects of concentration, molecular weight, and composition of anthryl groups on the intra- and intermolecular photo-cross-linking and gelation processes of A-PMMA in solution.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan (Grant-in-Aid 05453150).

References and Notes

(1) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(2) Schmidt, M.; Burchard, W. *Macromolecules* **1981**, *14*, 370.
(3) Mrkvickova, L.; Kratochvil, P. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 1675.
(4) Dotson, N. A.; Diekmann, T.; Macosko, C. W.; Tirrell, M. *Macromolecules* **1992**, *25*, 4490.
(5) Sato, T.; Tsujii, Y.; Fukuda, T.; Miyamoto, T. *Macromolecules* **1992**, *25*, 3890, 5970.
(6) See, e.g.: de Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(7) See, e.g.: Stauffer, D.; Coniglio, A.; Adam, M. *Adv. Polym. Sci.* **1982**, *44*, 103.
(8) Bouas-Laurent, H.; Castellan, A.; Desvergne, J. P. *Pure Appl. Chem.* **1980**, *52*, 2633.
(9) Tazuke, S.; Banba, F. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 2463.
(10) Kozel, S. P.; Lashkov, G. I. *Opt. Spectrosc. (USSR)* **1980**, *48*, 607.
(11) Hargreaves, J. S.; Webber, S. E. *Macromolecules* **1984**, *17*, 235.
(12) Fox, M. A.; Britt, P. F. *Macromolecules* **1990**, *23*, 4533.
(13) Bullpitt, M.; Kitching, W.; Doddrell, D.; Adcock, W. *J. Org. Chem.* **1976**, *41*, 760.
(14) Bowen, E. J.; Tanner, D. W. *Trans. Faraday Soc.* **1955**, *51*, 475.
(15) Berlman, I. B. *Energy Transfer Parameters of Aromatic Compounds*; Academic Press: New York, 1973.

MA951817T