Polymer Bulletin 39, 109–116 (1997)

Polymer Bulletin

Local motion of crosslinks for poly(methyl methacrylate) gels by the fluorescence depolarization method

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Received: 31 March 1997/Revised version: 11 April 1997/Accepted: 21 April 1997

Summary

Poly(methyl methacrylate) (PMMA) gels labeled at crosslinks with anthracene were prepared. Anthracene fluorescence depolarization was monitored to probe the local motion of crosslinks for PMMA gels at different equilibrium swelling states. The relaxation times and the activation energies of local motion were measured for PMMA gels at the swollen states in various solvents through fluorescence anisotropy decays. The local motion of PMMA gel at crosslinks became faster with the increase of swelling ratio. When the swelling ratios were almost the same, the mobility of crosslinks was the same irrespective of the molecular weights between crosslinks. These results indicate that the local motion of crosslinks for PMMA gel is mainly governed by the segment density of network chains in the vicinity of crosslinks.

Introduction

Polymer gels have been extensively investigated because of their scientific interest as well as technological significance. In a gel, the polymer chains are connected to each other by the crosslinks, and it is expected that the motion, such as the translational and the rotational diffusion, of a chain is restricted compared with that of a linear chain. Thus, a gel has characteristic properties different from those of a concentrated solution and a bulk [1]. So far, many workers have studied the macroscopic properties of gels such as swelling behavior [2, 3] and mechanical behavior [4, 5]. It is known theoretically and experimentally that the elastic properties of gels are not affected by the quality of the solvent but are determined by the equilibrium swelling ratio, alone [6, 7].

The macroscopic properties of polymer networks are governed by the molecular-scale dynamics at crosslinks [8]. Therefore it is important to understand the local motion of a gel from a microscopic point of view. Recently gels have been studied by means of various methods; e.g., light scattering [9-11], small angle neutron scattering [12], NMR [13, 14], and fluorescence techniques [15, 16]. Such advances in experimental techniques enabled us to get information about microscopic structure and dynamics of polymer gels. Different techniques probe the polymer chain motion occurring on different time scales [17-19]. We have examined the local motion of linear polymer

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chains by the fluorescence depolarization method by introducing fluorescent probes into the polymer chains [20-25]. This method enables us to measure directly the orientational autocorrelation function in a time range of 10^{-12} – 10^{-6} s. Since the conformational transitions of the polymer chain occur in a time range of subnanosecond, the relaxation process measured by this method reflects the local motion of the polymer chains. We have measured the local motion of the chain center for linear polymers such as poly(methyl methacrylate) (PMMA) [20-23], poly(isoprene) [24], and polystyrene [25], etc. in dilute solutions. It was found that the local motion at the center of a chain became faster with the chain expansion, *i.e.*, with the decrease of the segment density [22, 25]. In the present study, we prepared PMMA gels labeled at crosslinks with anthracene and examined the local motion of crosslinks for PMMA gels. The relaxation time of the local motion was measured in various solvents upon establishing swelling equilibrium for the polymers with different molecular weights between crosslinks by means of the time-resolved fluorescence depolarization method. The activation energy for the local motion was estimated. We here discuss the factors that govern the local motion of crosslinks.

Experimental Section

Samples

Anthracene-labeled PMMA gels (Figure 1) were prepared by the free radical copolymerization of methyl methacrylate (MMA; Wako Pure Chemical Industries, Ltd.), ethylene glycol dimethacrylate (EGDMA; Wako Pure Chemical Industries, Ltd.), and 9,10-anthrylenedimethyl dimethacrylate (AnDMA). α,α'-Azobisisobutyronitrile (AIBN; Nacalai Tesque, Inc.) and distilled toluene were used as initiator and solvent, respectively. All the reagents for polymerization were purified before use. AnDMA was synthesized from 9,10-bis(chloromethyl)anthracene (bis(ClMe)An; Tokyo Chemical Industries Co., Ltd.) and methacrylic acid (MAA; Wako Pure Chemical Industries, Ltd.) [26, 27]. Bis(ClMe)An was recrystallized from toluene, and MAA was used as received. The feed ratios of EGDMA to MMA, f_c, were set at 0.3, 0.5, 1.0, 3.0, and 5.0 mol-%. The polymerization was carried out in toluene with [MMA] = 4 M, [AIBN] = 2.8×10^{-2} M, and [AnDMA] = *ca.* 10^{-5} M for 15 h at 60°C in glass tubes under vacuum.

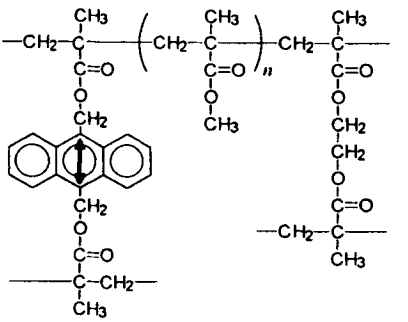

Figure 1. PMMA gels labeled at crosslinks with anthracene. The double-headed arrow indicates the direction of the transition moment for anthracene.

The conversion of the polymerization was *ca.* 95 %. Then all the samples were immersed in toluene (Nacalai Tesque, Inc., spectrophotomeric grade) at room temperature to extract unreacted monomers and sol fraction. The extraction was repeated until the emission of anthracene in the range of 400 – 480 nm was no longer measured from the decanted toluene. The concentration of anthracene probe was less than 10^{-5} M in each gel, so the fluorescence depolarization due to excitation energy migration was negligible. The sample gel of f_c = 0.5 mol-% was swollen to the equilibrium state in four kind of solvents; toluene, chloroform (Dojin, spectrophotomeric grade), acetone (Nacalai Tesque, Inc., spectrophotomeric grade), and acetonitrile (Nacalai Tesque, Inc., spectrophotomeric grade). The sample of f_c = 3.0 mol-% was swollen in toluene and acetonitrile. The other samples were swollen in toluene. All the samples were macroscopically homogeneous and optically clear.

Equilibrium Swelling Measurements

The molecular weight between crosslinks, M_c, was determined from the polymer volume fraction at the swelling equilibrium state for each gel (f_c = 0.3, 0.5 1.0, 3.0, and 5.0 %) swollen in toluene using the Flory-Rehner equation [28]. The Flory-Huginns interaction parameter was estimated to be 0.43 from the value of the second virial coefficient for PMMA/toluene solution reported in the literature [29].

The diameter of the samples, d, was measured at the equilibrium swelling state. The swelling ratio, V/V_0, was determined as

$$\frac{V}{V_0} = \left(\frac{d}{d_0}\right)^3 \tag{1}$$

where V is the volume of the sample at the equilibrium swelling state, and V_0 and d_0 are the volume and the diameter just after preparation, respectively. The molecular weights between crosslinks, M_c, and the swelling ratios, V/V_0, at 20°C for all the samples were given in Table 1. A sample is denoted by PMMA-f_c/swelling solvent in the Table. V/V_0 for the samples of f_c = 0.3, 0.5, and 1.0 % was measured as a function of

Table 1. Crosslinking Agent Fractions, f_c, Molecular Weights between Crosslinks, M_c, and Swelling Ratios, V/V_0, at 20°C

Sample	f_c (%)	$M_c \times 10^{-3}$	V/V_0
PMMA-1.0/toluene	1.0	14	2.85
PMMA-0.5/toluene	0.5	53	4.57
PMMA-0.3/toluene	0.3	120	7.25
PMMA-0.5/chloroform	0.5	53	7.79
PMMA-0.5/acetone	0.5	53	4.13
PMMA-0.5/acetonitrile	0.5	53	2.18
PMMA-3.0/toluene	3.0	1.9	1.18
PMMA-3.0/acetonitrile	3.0	1.9	0.79
PMMA-5.0/toluene	5.0	1.1	0.98

temperature from 10 to 45°C. The temperature dependence of the swelling ratios was less than 15 % in this temperature range.

Time-resolved Fluorescence Measurements and Analysis

The time-resolved fluorescence depolarization measurement was carried out by the single-photon counting system [22, 30]. The second harmonic of Ti:Sapphire laser (Spectra Physics, Tsunami) was used as the light source. The wavelength was 396 nm. The instrumental function has a full width at half maximum of *ca.* 60 ps. The excitation pulse was polarized vertically, and the parallel fluorescence component, $I_{//}(t)$, and the perpendicular one, $I_{\perp}(t)$, were measured alternately to avoid data distortions due to the time drift. The time-resolved fluorescence measurement was made at the equilibrium swelling state for each sample. The measurement of the gels of f_c = 3.0 and 5.0 % was made only at 20°C. For the other samples the temperature range of measurement was from 10 to 40°C. The temperature was kept constant for more than 2 days to ensure the establishment of the swelling equilibrium before the measurements.

The fluorescence anisotropy ratio, $r(t)$, is defined as

$$r(t) = \frac{I_{//}(t) - I_{\perp}(t)}{I_{//}(t) + 2I_{\perp}(t)} \tag{2}$$

We convoluted eq 3 with the instrumental function to analyze the anisotropy ratio, $r(t)$, and fitted it to the experimental anisotropy data by the method of nonlinear-least-squares [20].

$$r(t) = r_0\left[x\exp\left(-\frac{t}{T_1}\right) + (1-x)\exp\left(-\frac{t}{T_2}\right)\right] \tag{3}$$

Equation 3 is an empirical equation, but it fitted the experimental data very well for all the samples. Figure 2 shows an example of $r(t)$ data fitting with eq 3. The mean relaxation time, T_m, is defined as eq 4 and calculated by eq 5 with the best-fit values of x, T_1, and T_2 obtained by fitting of $r(t)$ with eq 3.

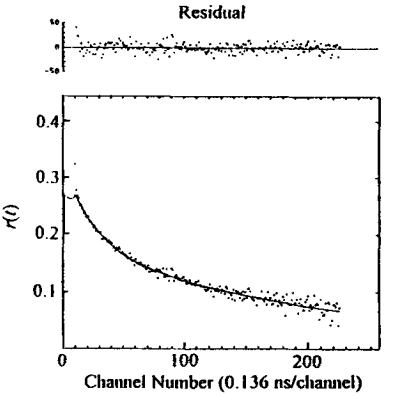

Figure 2. Fluorescence anisotropy decay measured for PMMA-0.5/toluene at 20°C. The dots are the experimental data and the solid line is the fitting curve by the method of nonlinear-least-squares: $r(t) = 0.268\ [\ 0.676\ \exp(-t/27.8) + 0.324\ \exp(-t/3.14)]$.

$$T_m = r_0^{-1}\int_0^\infty r(t)dt \tag{4}$$

$$= xT_1 + (1-x)T_2 \tag{5}$$

Results and Discussion

The local dynamics of gels at crosslinks is discussed in terms of viscosity reduced mean relaxation time, T_m/η, where η is the solvent viscosity. Figure 3 shows a relationship between T_m/η and V/V_0 for PMMA gels at 20°C. Also shown in Figure 3 are the data points for the samples with different M_c's. It is obvious from Figure 3 that T_m/η decreases as V/V_0 and M_c increase, *i.e.*, the mobility at crosslinks becomes greater with the increase of V/V_0 and M_c. First, we compared the mobility of PMMA-0.5s swollen in four kinds of solvents (open symbols in Figure 3) to evaluate the effect of V/V_0 on the local motion. The local motion of PMMA-0.5 at crosslinks becomes faster with the increase of V/V_0, while M_c is the same for these samples. Secondly, the mobilities for PMMA-0.5/chloroform (symbol,□, in Figure 3) and PMMA-0.3/toluene (▼) were compared in terms of V/V_0, M_c, and T_m/η. V/V_0 for PMMA-0.5/chloroform and that for PMMA-0.3/toluene are approximately the same, *i.e.*, 7.79 and 7.25, respectively, while M_c of PMMA-0.5 is 2.3 times lower than that of PMMA-0.3. The mobility of PMMA-0.5/chloroform at crosslinks is roughly the same as that of PMMA-0.3/toluene, that is, the values of T_m/η are 15.8 and 22.0 ns/cP, respectively. This indicates that the mobility of a gel at crosslinks is the same when its swelling ratio is kept constant, even though the molecular weights between crosslinks, M_c, are different. It was experimentally found that T_m/η is proportional to the power of V/V_0 for the gels with the same M_c. The data for the samples except PMMA-5.0/toluene (× in Figure 3) lie on one line independently of M_c. Therefore, it is concluded that the mobility of a gel at

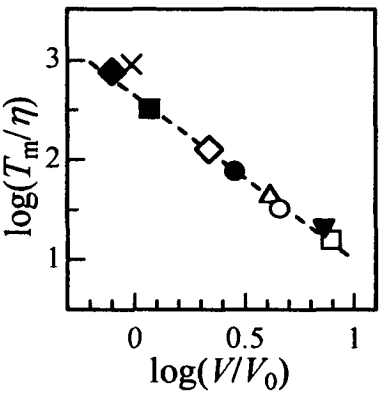

Figure 3. Relationship between reduced relaxation time and swelling ratio for PMMA gels. Symbols: ▼, PMMA-0.3/toluene; ○, PMMA-0.5/toluene; ●, PMMA-1.0/toluene; □, PMMA-0.5/chloroform; △, PMMA-0.5/acetone; ◇ PMMA-0.5/acetonitrile; ■, PMMA-3.0/toluene; ◆, PMMA-3.0/acetonitrile; ×, PMMA-5.0/toluene.

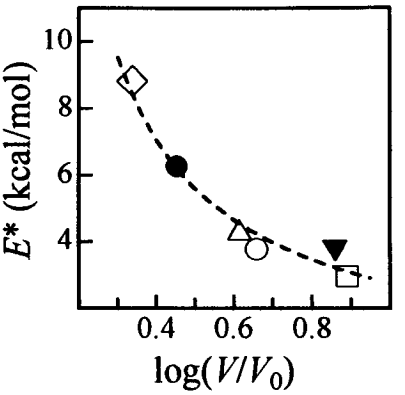

Figure 4. Relationship between activation energy of local motion and swelling ratio. Symbols are the same as in Figure 3.

crosslinks is dependent on its swelling ratio and independent of the molecular weight between crosslinks in the case of large M_c. This implies that the mobility at crosslinks is affected by the segment density in the vicinity of the crosslinks.

The value of $\ln(T_m/\eta)$ was linearly related to $1/T$, where T is the absolute temperature. Then the activation energy, E^*, was estimated by the theory of Kramer's diffusion limit [31]. E^* is related to T_m by the following equation.

$$T_m/\eta = A\exp(E^*/RT) \tag{7}$$

where R is the gas constant. The value of E^* for each sample is plotted against the increase of V/V_0 in Figure 4. E^* becomes smaller with the increase of V/V_0 and is not affected by M_c similarly to the case of the reduced relaxation time, T_m/η, if M_c is large.

The relaxation time and the activation energy for the local motion at crosslinks are

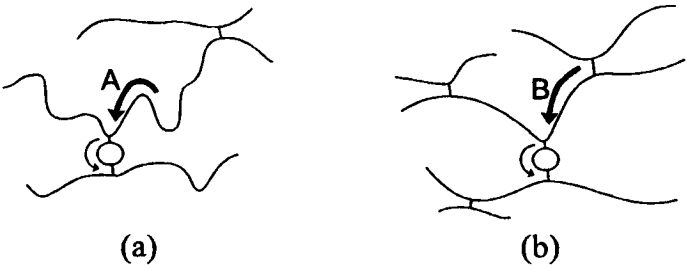

Figure 5. Schematic figure for the local motion of crosslinks for a gel when (a) M_c is large and (b) M_c is small. The labeled crosslinks (circles in this figure) reorient by the micro-Brownian motion of the neighboring network chains (arrows A and B). When the length of network chain between crosslinks is sufficiently long (case (a)), reorientation of the crosslinks is not affected by the neighboring crosslinks. In the case of (b) neighboring crosslinks have an influence on the reorientation of the labeled crosslinks (motion B) because the motion of the crosslinks is constrained by the neighboring one due to the short length between crosslinks.

dependent only on the swelling ratio when M_c is large. When the swelling ratio becomes small, that is, the network chains shrink, the space around the probe is crowded with the network chain segments. The conformational transition of the chain is suppressed by this steric hindrance effect. Thus, the local motion of crosslinks is more constrained and the values of the relaxation time and the activation energy increase. The reorientation of the probe reflects the motion in a short length scale of the network chain, so that the local motion at crosslinks is independent of the length of the network chain between crosslinks, if it is sufficiently longer than the distance scale that influences on the motion of crosslinks (Figure 5a). It is thus summarized that the local motion of a gel at crosslinks is governed by the network chain expansion in the vicinity of crosslinks.

In the last, one case should be noted that M_c becomes smaller. In Figure 3, T_m/η for PMMA-5.0 (×) deviated upwards from the line. For PMMA-5.0 the crosslinks are separated only by about ten segments from each other, and the chain motion that affects the local dynamics of the crosslinks is restricted by the neighboring crosslinks. Therefore the local motion of the labeled crosslinks depends also on the molecular weight between crosslinks (Figure 5b). This point is being studied at present and will be reported elsewhere.

Conclusion

We examined the local chain dynamics of a PMMA gel at crosslinks at the equilibrium swelling state by the fluorescence depolarization method. It was found that the mobility of crosslinks for gels depends only upon the swelling ratio, V/V_0, when the molecular weight between crosslinks, M_c, is large. In the case that M_c is small, the motion of the crosslinks is affected by both V/V_0 and M_c. These results indicate that the local motion of a gel at crosslinks is governed mainly by the segment density of the network chains in the vicinity of crosslinks when the length between crosslinks is long.

Acknowledgement

This work was supported by Grants-in-Aid on Priority-Area-Research 'Photoreaction Dynamics' (06239107) from the Ministry of Education, Science, Sports and Culture.

References

(1) Ferry, J. D. "*Viscoelastic Properties of Polymers*", 2nd Ed.; John Wiley and Sons: New York, **1970**.

(2) Sato, E.; Tanaka, T. *J. Chem. Phys.* **1988**, *89*, 1695.

(3) Kaneko, Y.; Sakai, K.; Kikuchi, A.; Yoshida, R.; Sakurai, Y.; Okano, T. *Macromolecules* **1995**, *28*, 7717.

(4) Geissler, E.; Hecht, A. M. *Macromolecules* **1980**, *13*, 1276.

(5) Urayama, K.; Takigawa, T.; Masuda, T. *Macromolecules* **1993**, *26*, 3092.

(6) Geissler, E.; Horkay, F.; Hecht, A. M.; Zrinyi, M. *J. Chem. Phys.* **1989**, *90*, 1924.

(7) Horkay, F.; Zrinyi, M.; Geissler, E.; Hecht, A. M. *Makromol. Chem., Macromol. Symp.* **1990**, *40*, 195.

(8) Eichinger, B. E. *Ann. Rev. Phys. Chem.* **1983**, *34*, 359.

(9) Tanaka, T.; Hocker, L. O.; Benedek, G. B. *J. Chem. Phys.* **1973** *59*, 5151.

(10) Joosten, J. G. H.; McCarthy, J. L. *Macromolecules* **1991**, *24*, 6690.

(11) Takebe, T.; Nawa, K.; Suehiro, S.; Hashimoto, T. *J. Chem. Phys.* **1989**, *91*, 4160.
(12) Takahashi, H.; Shibayama, M.; Fujisawa, H.; Nomura, S. *Macromolecules* **1995**, *28*, 8824.
(13) Tokuhiro, T.; Amiya, T.; Mamada, A.; Tanaka, T. *Macromolecules* **1991**, *24*, 2936.
(14) Ikehara, T.; Nishi, T.; Hayashi, T. *Polym. J.* **1996**, *28*, 169.
(15) Hu, Y.; Horie, K.; Torii, T.; Ushiki, H.; Tang, X. *Polym. J.* **1993**, *25*, 123.
(16) Hu, Y.; Horie, K.; Ushiki, H.; Tsunomori, F. *Eur. Polym. J.* **1993**, *29*, 1365.
(17) Ediger, M. D. *Ann. Rev. Phys. Chem.* **1991**, *42*, 225.
(18) Fytas, G.; Dorfmüller, Th.; Lin. Y. H.; Chu, B. *Macromolecules* **1981**, *14*, 1088.
(19) Heinrich, G.; Vilgis, T. A. *Macromolecules* **1992**, *25*, 404.
(20) Sasaki, T.; Yamamoto, M.; Nishijima, Y. *Macromolecules* **1988**, *21*, 610.
(21) Sasaki, T.; Nawa, K.; Yamamoto, M.; Nishijima, Y. *Eur. Polym. J.* **1989**, *25*, 79.
(22) Horinaka, J.; Ono, K.; Yamamoto, M. *Polym. J.* **1995**, *27*, 429.
(23) Ono, K.; Sasaki, T.; Yamamoto, M. *Macromolecules* **1995**, *28*, 5012.
(24) Ono, K.; Ueda, K.; Yamamoto, M. *Polym. J.* **1994**, *26*, 1345.
(25) Ono, K.; Okada, Y; Yokotsuka, S.; Sasaki, T.; Yamamoto, M. *Macromolecules* **1994**, *27*, 6482.
(26) Krakovyak, M. G.; Ananieva, T. D.; Skorokhodov, S. S. *Synth. Comm.* **1977**, *7*, 397.
(27) Krakovyak, M. G.; Ananieva, T. D.; Anufrieva, E.; Gotlib, Y.; Nekrasova, T.; Skorokhodov, S. *Macromol. Chem.* **1981**, *182*, 1009.
(28) Flory, P. J. "*Principles of Polymer Chemistry*"; Cornell Univ. Press.: Ithaca, New York, **1953**.
(29) Konak, C.; Tuzar, Z.; Jakes, J. *Polymer* **1990**, *31*, 1866.
(30) O'Conner, D. V.; Phillips, D. "*Time-Correlated Single-Photon Counting*", Academic Press, London, **1984**.
(31) Kramers, H. A. *Physica* **1940**, *7*, 284.