

Physical Aging of Photo-Crosslinked Poly(ethyl acrylate) Observed in the Nanometer Scales by Mach-Zehnder Interferometry

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Deformation in the nanometer scales of photo-crosslinked poly(ethyl acrylate) (PEA) was *in situ* monitored by Mach-Zehnder interferometry (MZI). Upon irradiation with 365 nm, anthracene labeled on the PEA chains undergoes photodimerization, generating the PEA networks. The cross-link kinetics induced by different light intensities was monitored by using a UV-visible spectrometer. On the other hand, the deformation in the nanometer scales of the photo-cross-linked polymer was measured *in situ* by using a Mach-Zehnder interferometer (MZI) under the same experimental conditions. The aging data observed by ceasing irradiation at different stages of the photocuring process reveal a general relationship for the kinetics of aging under different cross-link densities.

KEY WORDS: Poly(ethyl acrylate) / Mach-Zehnder Interferometry / Photocuring / Physical Aging / Microdeformation / Strain Relaxation /

Upon approaching the glassy region, mobility of polymer quickly decreases and eventually almost vanishes as the polymer is vitrified. This phenomenon is often observed in polymers under cooling, thermally curing or photocuring. A number of interesting physical phenomena such as the Kohlrausch-Williams-Watts (KWW) relaxation behavior^{1,2} have been observed in the vicinity of this vitrification process. For this particular case, diffusion becomes size-dependent and the kinetics is no longer expressible by a simple exponential function of time.³ As the cross-link reaction proceeds to a certain point, the polymer enters the glassy state and falls out of equilibrium, exhibiting the so-called physical aging phenomena whose time-evolution is much slower than the time scales of observation.⁴ It is well known that photochemical reactions in the bulk state of polymers often proceed non-uniformly due to the inhomogeneity of the local environments.⁵ This inhomogeneous reaction kinetics, particularly for the case of cross-link, could generate a local transient strain field in these reacting polymers. Depending upon the relative distance from the glass transition temperature (T_g), this local strain field can either completely relax or persist for a long time inside the sample during the course of the reaction. The latter case would be enhanced by the glassy state where the relaxation of the reaction-induced strain becomes extremely slow.

Physical aging of polymer has been extensively investigated by a number of experimental methods. Among them, dilatometry has been widely used to monitor the changes in volume of polymers at different temperatures in the glassy state.⁶⁻⁸ Recently, fluorescence method using probe molecules with the internal rotations sensitive to viscosity was also utilized to examine the aging phenomena of polymers.⁹ Furthermore, an X-ray diffraction method was recently proposed for monitoring the strain distribution in amorphous materials,¹⁰ which would be able to provide a potential tool for studies on physical aging.

Recently, we have developed a Mach-Zehnder interferometer (MZI) equipped with a high-pressure Mercury lamp (350 W, Moritex, Japan) to *in situ* monitor the time-evolution process of the strain in photoreactive polymers.¹¹ In this study, the nanometer deformation was *in situ* observed for a poly(ethyl acrylate) cross-linked with 365 nm UV light of different intensities. The aging phenomena and the corresponding kinetics were observed and analyzed *via* the dependence of the deformation on irradiation time and cross-link density. These experimental data reveal a general relationship for the aging process induced by various cross-link densities.

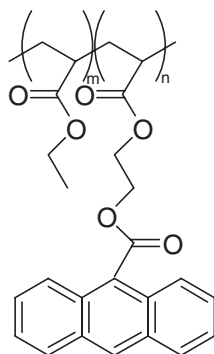
EXPERIMENTAL

Materials

Sample used in this study was an anthracene-labeled poly(ethyl acrylate) derivative (PEA-A). The polymer was synthesized by copolymerization of ethyl acrylate monomer (Wako Pure Chemical Industries, Japan) and 2-chloroethyl acrylate (CEA, Monomer-Polymer & Dajac Labs, Inc, Pennsylvania) in acetone for 30 min at 70 °C with 2, 2'-azobis(isobutyronitrile) as initiator. The former monomer was purified by distillation under vacuum after being dried with calcium hydride, whereas the later was used without further purification. The weight-average molecular weight of the polymer was determined by gel permeation chromatography (GPC) with tetrahydrofuran as diluent and monodisperse polystyrene as a standard for calibration. The weight-average molecular weight and the polydispersity of this PEA-A are respectively $M_w = 1.6 \times 10^5$ and $M_w/M_n = 2.2$. Subsequently, the photoreactive PEA-A was obtained by reacting the chloroethyl moieties of the CEA component with potassium salt of 9-anthracenecarboxylic acid in anhydrous dimethylformamide at 60 °C over 18 h. PEA-A synthesized by this

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Scheme 1. Chemical structure of anthracene-labeled poly(ethyl acrylate) (PEA-A).

procedure was purified by precipitation three times using acetone as good solvent and *n*-hexane as poor solvent. The label content of the resulting polymer PEA-A is 9 anthracenes/chain (0.6 mole % in equivalent) as determined by UV-vis spectrometry (UV-1600, Shimadzu Inc., Japan). The chemical structure of the photo-cross-linkable PEA-A is indicated in Scheme 1. PEA-A films with the thickness 10 μm were prepared by casting toluene solutions of PEA-A followed by drying *in vacuo* at 65 $^{\circ}\text{C}$ for 7 d to remove residual solvent prior to the interferometric experiments. All the experiments were carried out at 25 $^{\circ}\text{C}$.

Photodimerization of Anthracene and Cross-link Kinetics in PEA-A Films

The photodimerization kinetics of anthracenes in PEA-A films was monitored by following the decrease in the optical absorbance $OD(t)$ at 365 nm under irradiation. The normalized optical absorbance $OD_N(t)$ is plotted versus the irradiation time under various light intensities in Figure 1. It was found that the photodimerization kinetics of anthracene can be well fitted to the modified Kohlrausch-Williams-Watts (KWW) stretched exponential function¹² using nonlinear least square with regression on a conventional software for data analysis (Igor Pro, v. 5.0, Wave Metrics Inc.).

$$OD_N(t) = (1 - D) \exp[-(k_0 t)^\beta] + D \quad (1)$$

Here, $OD_N(t)$ is the normalized absorbance defined as $OD(t)/OD_0$ where OD_0 is the initial absorbance of the sample. It should be noted that OD_0 is less than unity for all the samples used in this experiment. D is the baseline of the decay, expressing the limiting absorbance of anthracene monitored at 365 nm. k_0 and β are respectively the average reaction rate and the inhomogeneity index of the cross-link process.

Using the absorbance data of anthracene calculated from eq (1), the irradiation-time dependence of the average cross-link density $\gamma(t)$ was obtained.

$$\gamma(t) = \frac{\alpha [OD(t) - OD_0]}{2 OD_0} \quad (2)$$

Here, $\alpha \approx 9$ is the average number of anthracene labeled per PEA chain and OD_0 is the initial absorbance of the PEA-A

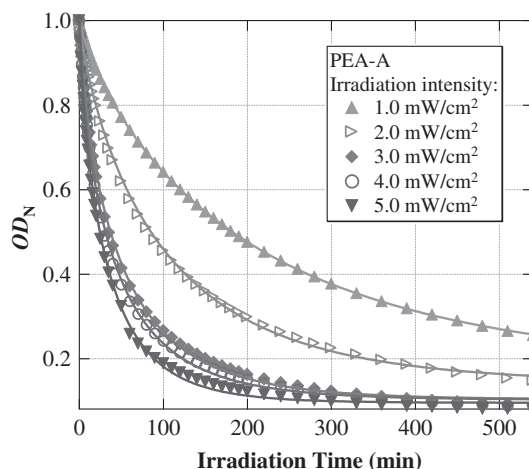


Figure 1. Photodimerization kinetics of anthracene in a PEA-A monitored upon irradiation with various light intensities.

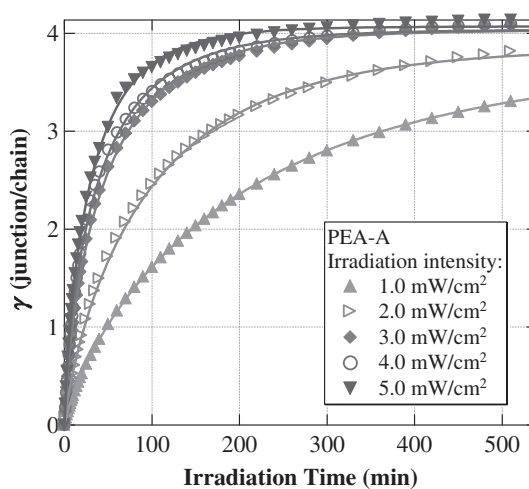


Figure 2. Crosslink kinetics of a PEA-A polymer obtained by irradiation with various light intensities.

sample. The factor 2 in the denominator arises from the fact that two anthracenes moieties on the PEA chains react to form one cross-link junction. γ is, therefore, the average number of junctions between two PEA-chain segments. As shown in Figure 2, the cross-link kinetics observed under several UV light intensities ranging from 1.0 to 5.0 mW/cm^2 can be well fitted to the modified Kohlrausch-Williams-Watts (KWW) stretched exponential function of irradiation time:

$$\gamma(t) = A_\infty [1 - \exp(-k_c t)^\beta] \quad (3)$$

where k_c and β are respectively the mean cross-link rate and the inhomogeneity-index of the process. A_∞ is the limiting cross-link density obtainable under a given UV intensity.

As illustrated in Figure 2, as the irradiation intensity increases, the cross-link density γ also increases and tends to approach a constant value for a given irradiation intensity. For the highest light intensity 5 mW/cm^2 , the cross-link density reaches the limiting value at *ca.* 500 min of irradiation.

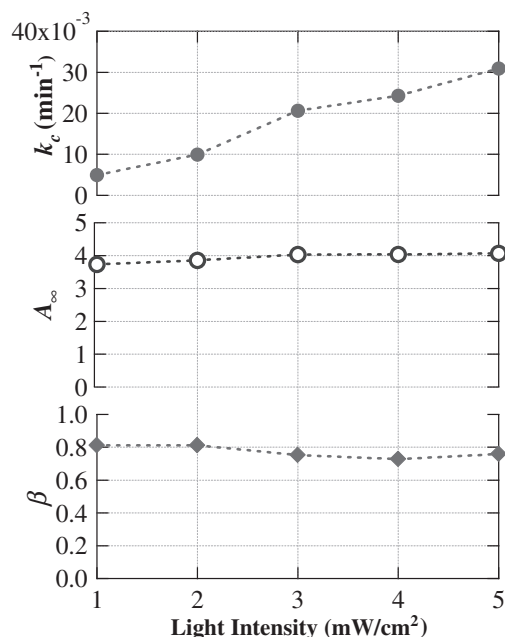


Figure 3. Kinetic parameters obtained by the curve fitting process for a PEA-A film irradiated with various light intensities ranging from 1 to 5 mW/cm².

Furthermore, the cross-link rate k_c gradually increases with increasing the irradiation intensity as shown in Figure 3, whereas both the limiting cross-link density A_∞ and the inhomogeneity parameter β in the modified KWW eq (3) do not significantly change within the range 1~5 mW/cm².

In situ Measurements of the Deformation in the Photo-cross-linked PEA-A

In the experiments using Mach-Zehnder interferometry (MZI), the sample was divided into two parts, the irradiated part for the detection of deformation and the masked part used as reference. The details of instrumentation, measurements and data analysis were reported elsewhere by Inoue *et al.*¹¹ In brief,

irradiation was performed *in situ* via an optical fiber installed at a distance of *ca.* 17 cm from the sample using a UV-reflecting mirror as shown in Scheme 2. The interference fringes recorded by a CCD camera placed after the half-mirror [HM2] reflect the change in optical path length (OPL) of the sample before and after irradiation. There are two factors affecting this optical path length difference (OPLD): the changes in refractive-index Δn and in the sample thickness Δd . From the measurements performed with a prism-coupler (Metricon, Model-2010), it was found that the refractive-index of PEA-A before and after irradiation cross-link is almost unchanged up to the fourth decimal at the wavelength 632.8 nm. Because both Δn and Δd are small, their product could be negligible ($\Delta n \cdot \Delta d \approx 0$). Thus, the OPLD may be approximately expressed as:¹¹

$$OPLD \cong (n_s - n_0)\Delta d + d_0\Delta n \quad (4)$$

where n_s and n_0 are respectively the refractive-index of the sample and air. Since the change in refractive-index Δn of PEA-A before and after irradiation is negligible under this experimental condition, the OPLD can be finally approximated as:

$$OPLD \cong (n_s - n_0)\Delta d \quad (5)$$

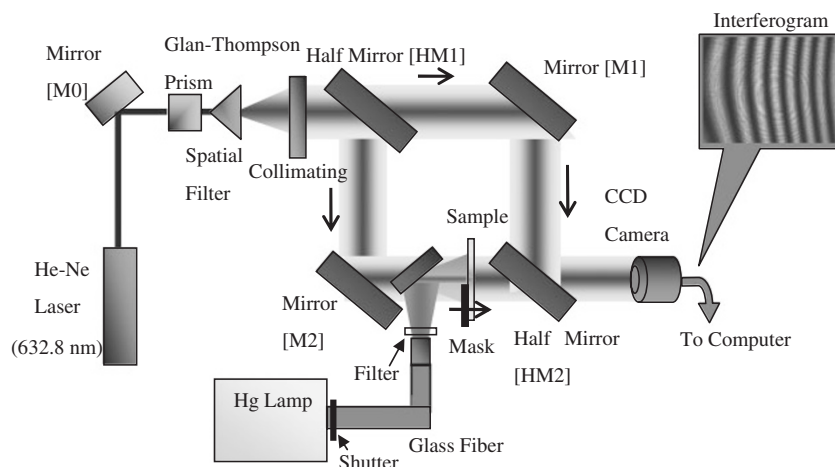
and

$$\Delta d = (d - d_0) \quad (6)$$

Here, d_0 and d are respectively the thickness of the blend before and after the photo-crosslink reaction. The deformation (or the strain) ε defined as ($\Delta d/d_0$) of the cross-linked blends can be calculated from:

$$\varepsilon = \frac{\Delta d}{d_0} = \frac{OPLD}{(n_s - n_0)d_0} = \frac{OPLD}{(n_s - 1)d_0} \quad (7)$$

Finally, from the refractive-index of the sample and OPLD calculated from the interference fringes before and after cross-link, the change in the elastic strain ε with irradiation time was obtained.



Scheme 2. Block diagram of the Mach-Zehnder interferometer used in this work.

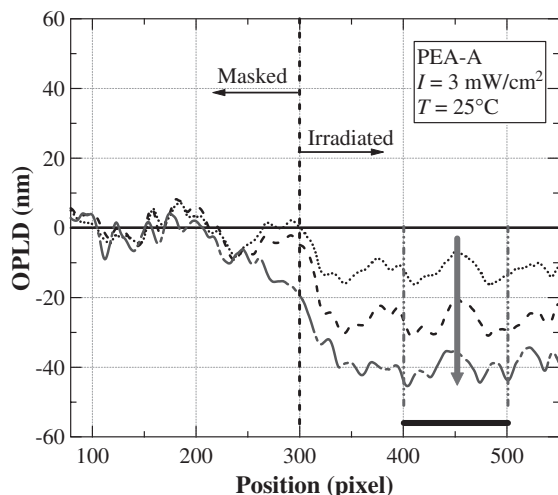


Figure 4. Time-evolution of the optical path length difference (OPLD) obtained for a PEA-A film irradiated over several irradiation-time intervals: (—), 0 min; (···), 20 min; (---), 40 min; (-·-), 60 min. The bar in the range 400~500 pixels indicates the area used for averaging.

RESULTS AND DISCUSSION

Effects of Crosslink on the Deformation of PEA-A

Figure 4 shows the deformation observed *in situ* under the MZI for a PEA-A film during the course of photo-cross-link with the intensity 3.0 mW/cm^2 . Obviously, the OPLD gradually decreases with increasing irradiation time in the irradiated part of the sample. Since the change in refractive-index is negligibly small ($\Delta n \leq 5 \times 10^{-4}$), the OPLD is directly proportional to the strain, according to eq (7). The results shown in Figure 4 indicate that the PEA-A film is gradually shrinking upon photo-cross-link over 20, 40 and 60 min of irradiation with 365 nm. It should be noted that the modulation in the OPLD seen in the irradiated part of the sample arises from the non-uniform thickness of the film in the nanometer scales. To improve the precision of the data, OPLD was averaged over 100 pixels in the area far from the edge of the photomask as indicated by the bar in the figure. By following this procedure, the irradiation-time dependence of the strain ε generated under three different irradiation intensities 1.0, 3.0 and 5.0 mW/cm^2 was calculated using eq (7), and the results are shown in Figure 5. It was found that the strain $\varepsilon(t)$ increases with increasing both the light intensity and irradiation time. Furthermore, the strain can be well described by an exponential function of irradiation time:

$$\varepsilon(t) = \frac{OPLD(t)}{d_0(n_s - n_0)} = Ae^{-k_d t} + B \quad (8)$$

Here, A is a constant, B is the limiting strain obtained at very long irradiation time for a given light intensity and k_d is the rate of deformation induced by the photo-cross-link. From the analysis, it was found that B decreases (*i.e.*, the shrinkage increases) with increasing the irradiation intensity, whereas k_d is almost unchanged at low irradiation intensity and is enhanced under high intensity.

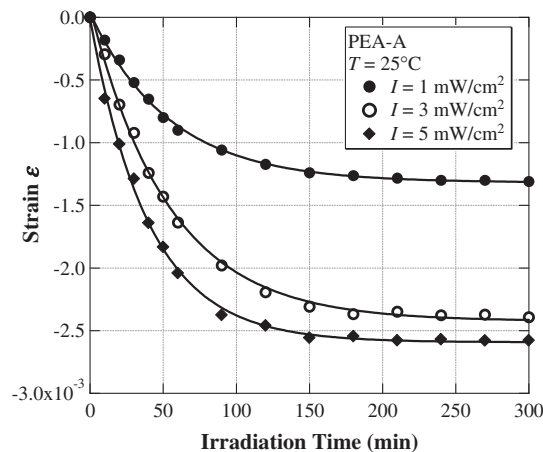
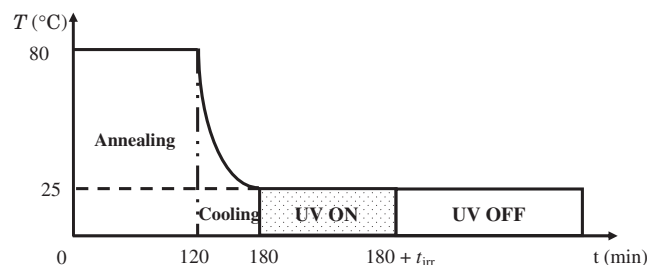


Figure 5. Time-evolution of the deformation observed for a PEA-A film under various light intensities: (●), 1 mW/cm^2 ; (○), 3 mW/cm^2 ; (◆), 5 mW/cm^2 observed at 25°C .



Scheme 3. Irradiation procedure and thermal history of a PEA-A film with the irradiation time t_{irr} as a variable.

Kinetics of Physical Aging Observed by Mach-Zehnder Interferometry

The experimental procedure to study the aging process is schematically illustrated in Scheme 3. Prior to the interferometric experiments, a PEA-A film was annealed at 80°C for 120 min. The sample was then slowly quenched to the experimental temperature 25°C for 60 min. Such a treatment was necessary to eliminate the local strain generated during the course of quenching and also to erase the thermal history of the sample. It is worth noting that before irradiation, the glass transition temperature of PEA-A is -13.0°C as measured by DSC with a heating rate of 10°C/min . Subsequently, the sample was irradiated over a certain period of time (t_{irr}) to set up the cross-link density γ . Then the UV light was turned off and the strain relaxation of the irradiated sample was monitored *in situ* under the M-Z interferometer in the dark. The elapse time t_e is defined as the time after the UV light was turned off, *i.e.*, the time used to observe the strain relaxation of the cross-linked polymer in the dark. Four average cross-link densities $\gamma = 1, 2, 3$ and 4 (per chain) were chosen by stopping irradiation respectively at 10, 30, 80 and 360 min along the photo-cross-link process. As illustrated in Figure 6, the deformation which was obtained by stopping the cross-link process at the irradiation time $t_{\text{irr}} = 10 \text{ min}$ corresponding to $\gamma = 1$, was almost unchanged within 5 h in the dark. However,

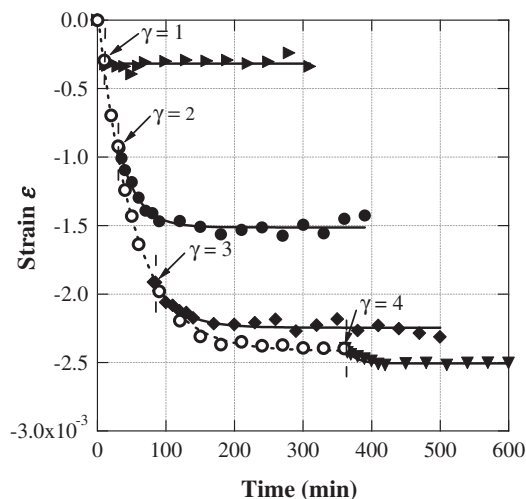


Figure 6. Strain relaxation of a PEA-A film observed under various experimental conditions: (----), continuous irradiation; (—), in the dark.

for higher average cross-link densities $\gamma = 2$ (corresponding to $t_{\text{irr}} = 30$ min), $\gamma = 3$ ($t_{\text{irr}} = 80$ min) and $\gamma = 4$ ($t_{\text{irr}} = 360$ min), the strain ε gradually changes with the elapse time. These experimental results indicate that the sample continues shrinking after the UV light was turned off, a typical behavior of physical aging. For reference, the dependence of the strain on irradiation time under continuous irradiation is displayed as open circles on the same figure obtained with the same experimental conditions. Taking into account that the temperature of the α -relaxation obtained by dielectric relaxation at the frequency 60 kHz surpasses 25°C ,¹³ *i.e.*, the temperature of this MZI experiment, the above results suggest that for the cross-link density $\gamma = 2$, the photocured PEA could enter its glassy state and as a consequence, continues shrinking to approach the equilibrium state after the UV light is turned off. In other word, the glass transition temperature of the photo-cross-linked PEA-A film exceeds the experimental temperature (25°C) at the cross-link density $\gamma > 1$. The time-evolution of the strain after turning off the UV light can be well fit to the following exponential function of elapse time:

$$\varepsilon_a(t) = E \exp(-k_a t) + F \quad (9)$$

where E and F are constant, and k_a is the rate constant characterizing the aging process. It should be noted that in these experiments, the cross-link density increases with irradiation time and consequently determines the history of the sample. These experimental results reveal that the rate of aging k_a decreases when the irradiation process was stopped after a long t_{irr} . Particularly, it is worth noting that the behavior of this aging process can be expressed by a master curve as illustrated in Figure 7 where the strain ε normalized to its maximum ε_{max} was plotted versus the non-dimensionalized elapse time defined as $(t_e \times k_a)$. Here, t_e is the elapse time in the experiment and k_a is the rate constant of the aging process obtained by fitting the data to eq (9). These results clearly

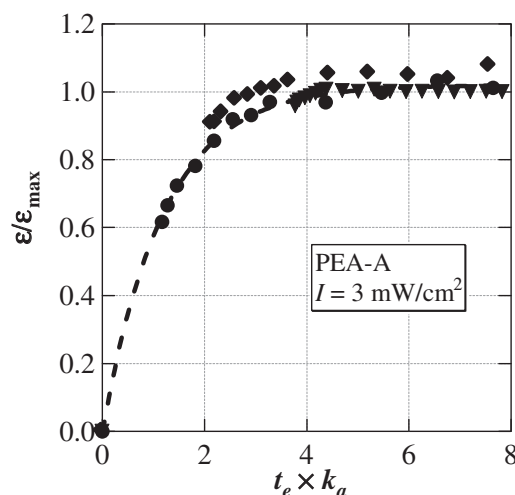


Figure 7. The reduced plot obtained for the physical aging kinetics: (●) $t_e = 30$ min; (◆) $t_e = 80$ min; (▼) $t_e = 360$ min.

indicate that the aging kinetics of PEA can be expressed by a master curve. The general behavior of the dependence of strain on the non-dimensionalized parameter $(t_e \times k_a)$ suggests that there may exist a universal relaxation function behind the data. Because we only have one set of data obtained under a fixed irradiation intensity (3 mW/cm^2), it would be too early to draw any conclusion on the universal behavior of this deformation of photo-crosslinked polymers. Currently, experiments using different light intensities are in progress to elucidate the universal behavior observed for physical aging kinetics of cross-linked polymers.

CONCLUSIONS

In summary, we have shown that the deformation (shrinkage) in the nanometer scales of poly(ethyl acrylate) during the photo-cross-link process can be *in situ* monitored by using Mach-Zehnder interferometry. The kinetics of aging depends on the distance from the equilibrium deformation. In addition, the kinetics can be solely expressed by the rate of the shrinkage process. Further experiments on the deformation kinetics in the nanometer scales are currently in progress and the results will be reported in the near future.

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REFERENCES

1. G. Williams and D. C. Watts, *Trans. Faraday Soc.*, **66**, 80 (1970).
2. "Disorder Effects on Relaxational Processes," R. Richert and A. Blumen Eds., Springer-Verlag, Berlin 1994.
3. M. H. Cohen and G. S. Grest, *Phys. Rev. B: Condens. Matter Mater. Phys.*, **20**, 1077 (1979).
4. a) L. C. E. Struik, "Physical Aging in Amorphous Polymers and Other Materials," Elsevier, Amsterdam, 1978.
b) I. M. Hodge, *Science*, **267**, 1945 (1995).
5. a) C. S. Paik and H. Morawetz, *Macromolecules*, **5**, 171 (1972).
b) L. Lamarre and C. S. P. Sung, *Macromolecules*, **16**, 1729 (1983).
c) H. Yoshizawa, K. Ashikaga, M. Yamamoto, and Q. Tran-Cong, *Polymer*, **30**, 534 (1989).
d) J. S. Royal and J. M. Torkelson, *Macromolecules*, **26**, 5331 (1993).
e) K. Horie and I. Mita, *Adv. Polym. Sci.*, **88**, 77 (1989).
6. A. J. Kovacs, *Fortschr. Hochpolym. Forsch*, **3**, 394 (1963).
7. J. M. Hutchinson, in "The Physics of Glassy Polymers," R. N. Haward and R. J. Young Ed., Chapman & Hall, London, 1997, Chapter 3, pp 85–153.
8. G. B. McKenna, Y. Leterrier, and C. R. Schultheisz, *Polym. Eng. Sci.*, **35**, 403 (1995).
9. E. F. Meyer, A. M. Jamieson, R. Simha, J. H. M. Palmen, H. C. Booji, and F. H. J. Maurer, *Polymer*, **31**, 243 (1990).
10. H. F. Poulsen, J. A. Wert, J. Neufeind, and V. Honkimaki, *Nat. Mater.*, **4**, 33 (2005).
11. K. Inoue, S. Komatsu, X.-A. Trinh, T. Norisuye, and Q. Tran-Cong-Miyata, *J. Polym. Sci., Part B: Polym. Phys.*, **43**, 2898 (2005).
12. K. Kataoka, A. Harada, T. Tamai, and Q. Tran-Cong, *J. Polym. Sci., Part B: Polym. Phys.*, **36**, 455 (1998).
13. N. G. McCrum, B. E. Read, and G. Williams, "Anelastic and Dielectric Effects in Polymeric Solids," John Wiley & Sons, New York, 1967, p 294.