Supporting information for

# Diffusion Processes of Single Fluorescent Molecules in a Polymer-based Thin Material with Three-Dimensional Network

Syoji Ito*[1, 2], Takatsugu Kusumi[1], Satoshi Takei[1, 3], and Hiroshi Miyasaka*[1,4]

[1]Division of Frontiers Materials Science and Center for Quantum Science and Technology under Extreme Conditions, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka, Japan. Fax: +81-6-6850-6244, Tel: +81-6-6850-6243, E-mail: sito@chem.es.osaka-u.ac.jp, miyasaka@ chem.es.osaka-u.ac.jp.

[2]PRESTO, Japan Science and Technology Agency

[3]Electronic Materials Research Laboratories, Nissan Chemical Industries, LTDtd., 635 Sasakura, Fuchu-Machi, Toyama 939-2792, Japan.

[4]CREST, Japan Science and Technology Agency

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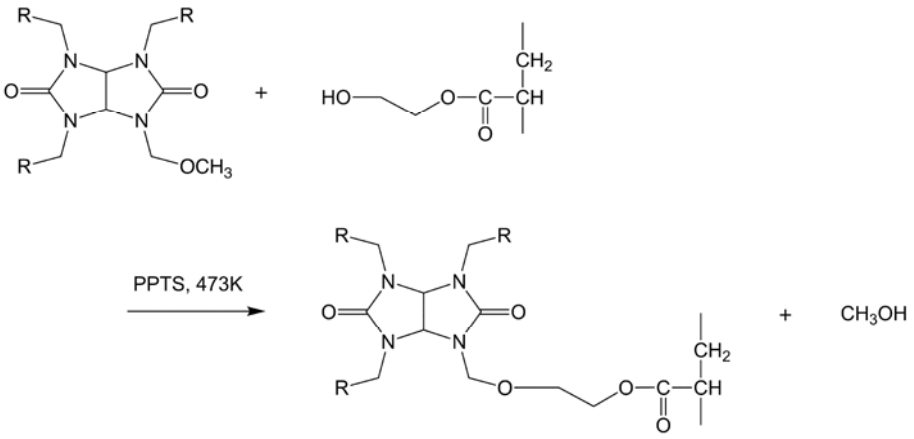
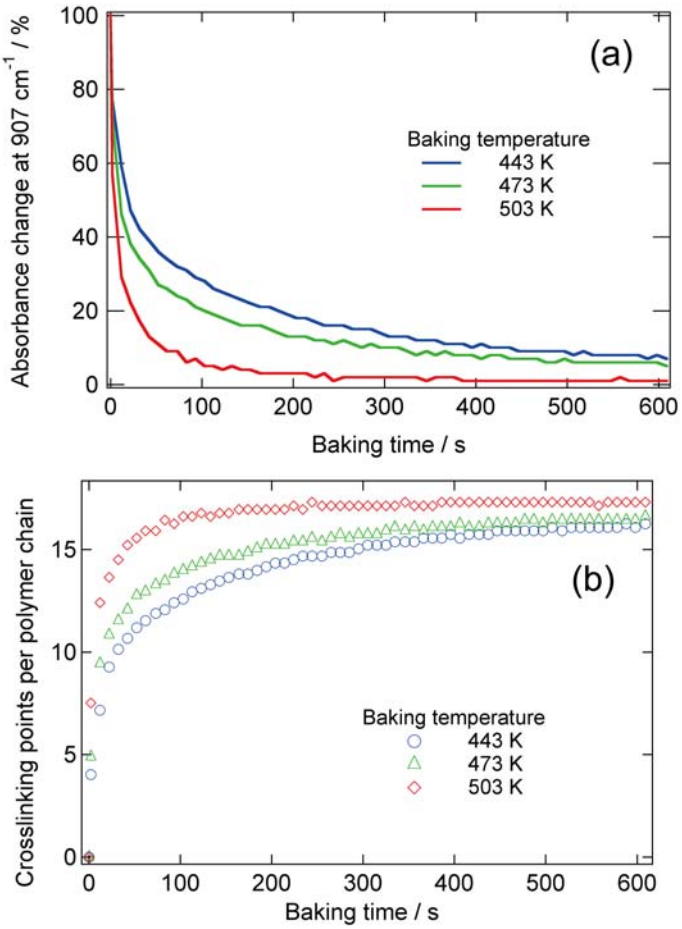
## S1. Samples.




S1. The reaction scheme of network formation between poly-HEA and TMMGU in the presence of PPTS. Poly-HEA, TMMGU, and PPTS were provided from by Nissan Chemical Industry, and PDI was purchased from Aldrich. All the compounds were used without further purification. The measurement of molecular weight distribution by gel permeation chromatography (GPC) provided the following parameters for poly-HEA: MN = 6050, MW = 9800, and dispersity = 1.62. The measurement using a differential scanning calorimeter (DSC320, SII) determined the glass transition temperature to be, Tg = 290 K, for neat poly-HEA. While, n No peak was detected in the signal of DSC signal for the mixture film comprising a mixture of poly-HEA (80 wt%), TMMGU (19 wt%), and PPTS (1 wt%) in the temperature range from 273 to –363 K. This is ascribed to the drop of the glass transition temperature to less than 270 K due to the addition of small molecules, mainly TMMGU.

**S2. Estimation of the number of the crosslinking points.**




S2. (a): Absorbance change at 907 cm$^{-1}$ for a poly-HEA film in the course of thermal network formation (crosslinking) were measured by FTIR. The FTIR spectra for the polymer film were measured in the following manner. First, a sample stage in a FTIR spectrophotometer (Nicolet 5700, Thermo ELECTRON) was heated up to a certain programmed temperature; the preset temperature was maintained by a feedback system. Then, a spin-casted poly-HEA-based film was set on the sample stage. Just after the setting of the sample, the FTIR spectra were obtained every 10 s up to 610 s. The peak at 907 cm$^{-1}$ is assigned to absorption by the methoxy group in the crosslinker (TMMGU). (b): Time course of the increase in average number of crosslinking points in one polymer chain due to thermal network formation. The number of crosslinking points per poly-HEA chain (the number average molecular weight, $M_n$, ~ 6050) was estimated on the basis of the following assumptions: 1) Absorbance at 907 cm$^{-1}$ is proportional to the number of methoxy groups in the sample film and 2) Methoxy groups are annihilated only by the crosslinking reaction.

**S3. The effect of the crosslinking reagent, TMMGU, on the properties of the film.**

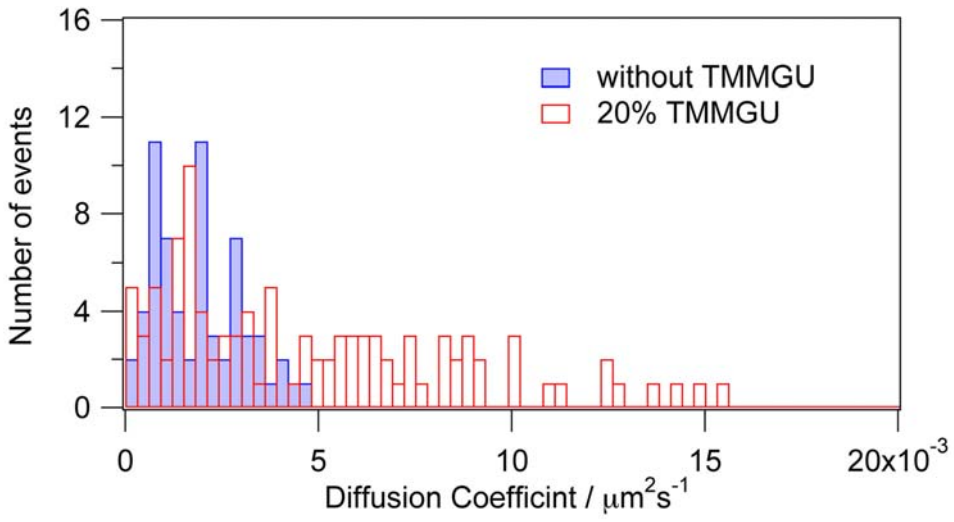



Figure S3. Histograms of translational diffusion coefficients of single PDIs (64 molecules) in neat poly-HEA film (blue bars) and a mixture film of poly-HEA, TMMGU, and PPTS without baking (no network formation). (red bars, the data is the same as in Figure 3). To check the effect of the crosslinking agent on the translational diffusion of the guest molecules, we compared the diffusion coefficients of PDI in films with TMMGU and PTTS without those. The polymer films were prepared by spin-casting at room temperature on well-cleaned cover slips at 2000 rpm for 120 s. Residual solvent in the neat poly-HEA film was removed by vacuum drying, as written in Experimental section in the main text. The average translational diffusion coefficient of PDIs in the neat poly-HEA film was $1.9 \times 10^{-3}$ $\mu m^2 s^{-1}$. This value is less than half of the average translational diffusion coefficient of PDIs in the mixture poly-HEA film ($5.0 \times 10^{-3}$ $\mu m^2 s^{-1}$). The relatively small diffusion coefficient is ascribed to the higher glass transition temperature of the neat poly-HEA (*ca.* 290 K) than that of the mixed material (< 270 K, See S1 in the supporting information).