

Supporting Information

Interfacial Kinetics of a Model Epoxy-Amine Addition Reaction

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1. Materials.

Phenyl glycidyl ether (PGE, Kishida Chemical Co., Ltd.), hexylamine (HA, Wako Pure Chemical Industries, Ltd.), and Coumarin 314 (Sigma-Aldrich) were used as received without further purification.

2. Evaluation of the Kinetics of the Addition Reaction in the Bulk and Interface.

Stoichiometric amounts of phenyl glycidyl ether (PGE) (0.450 g, 3.0 mmol) and hexylamine (HA) (0.152 g, 1.5 mmol) were mixed. Then, the reaction mixture was placed into a homemade NaCl cell. The reaction in the bulk was tracked on the basis of the ratio of the consumption of glycidyl and primary amino groups by Fourier-transform infrared (FT-IR) spectroscopy (Jasco FTIR620). On the other hand, information for the interfacial reaction was evaluated by attenuated-total-reflectance IR (ATR-IR) measurements that used ZnSe as a prism. The FT-IR and ATR-IR measurements were made over the wavenumber range from 7000 to 4000 cm^{-1} with a 4 cm^{-1} resolution at 303 K, 313 K, 323 K, 333 K, and 343 K. The number of scans in FT-IR was 64 times, while the number in ATR-IR was 512 times.

The rate of the reaction for epoxy and amino groups, which is presented in Scheme 1, $(d[(HX)_A]/dt)$ at given time t , is given by equation S1,

$$\frac{d([(HX)_A]_t)}{dt} = k_1 \cdot [HA]_t [E]_t [(HX)_A]_t + k_1' \cdot [HA]_t [E]_t [(HX)_0] + k_2 \cdot [HA2]_t [E]_t [(HX)_A]_t + k_2' \cdot [HA2]_t [E]_t [(HX)_0] \quad \text{S1}$$

where $[E]_t$, $[HA]_t$, and $[HA2]_t$ are the concentrations of epoxy, primary amine, and the secondary amine produced by the addition reaction. The quantity $[(HX)_A]_t$ is the concentration of the hydroxyl groups at a given reaction time t , which is equal to the concentration of the epoxy group consumed after time t because the hydroxyl group is generated via ring opening reaction of the epoxy group while $[(HX)_0]$ is the initial concentration of hydroxyl groups in the system. The k_1 and k_2 in scheme 1 are the reaction rate constants, k_1' and k_2' are the rate constants of the reaction activated by hydroxyl groups present at the initial stage. Here, we assumed that the values of k_1/k_2 and k_1'/k_2' are constant (n), as shown in equation S2.

$$\frac{k_2}{k_1} = \frac{k'_2}{k'_1} = n \quad \text{S2}$$

The n value is 0.5, when the reactivity of hydrogen in primary and secondary amino groups is equal. Thus, n can be written as equation S3.

$$n = 0.5 + \Delta n \quad \text{S3}$$

Then, equation S1 can be rewritten as equation S4,

$$\frac{d[(HX)_A]_t}{dt} = ([PGE]_0 - [(HX)_A]_t)(k_1 \cdot [(HX)_A]_t + k'_1 \cdot [(HX)_0])([HA]_t + n[HA2]_t) \quad \text{S4}$$

where $[PGE]_0$ is the concentration of epoxy at the initial stage. The concentration of primary and secondary amino groups at a given time t will be given stoichiometrically by equation S5.

$$[HA]_t + \frac{[HA2]_t}{2} = [HA]_0 + \frac{[(HX)_A]_t}{2} \quad \text{S5}$$

Substitution of equation S5 into equation S4 gives equation S6.

$$\begin{aligned} \frac{d[(HX)_A]_t}{dt} = & ([PGE]_0 - [(HX)_A]_t) \left([HA]_0 - \frac{[(HX)_A]_t}{2} \right) (k_1 \cdot [(HX)_A]_t \\ & + k'_1 \cdot [(HX)_0]) \left(1 + \frac{2[HA2]_t}{2[HA]_t + [HA2]_t} \right) \end{aligned} \quad \text{S6}$$

Equation 3 in the main text can be obtained by transforming equation S6.

3. The Effect of a Solid Interface on Molecular Diffusion

Coumarin 314, which is a fluorescence probe, was dispersed in a PGE/HA reaction mixture at a concentration of 0.8 mmol/L. Then, the mixture was cast onto a sapphire prism. The concentration of Coumarin 314 was sufficiently low to avoid self-quenching of the dyes. Time-resolved fluorescence anisotropy studies were performed using a light pulse (430 nm, 1.5 ps) generated by a mode-locked Ti/sapphire picosecond laser as an excitation source for the dyes. A streak camera was used to detect the time-resolved fluorescence from excited Coumarin 314 molecules. The pulse light was irradiated on

the reaction mixture from the prism at an incident angle larger than the critical angle, meaning that the fluorescence probe was excited by evanescent waves. Information about the solid substrate interfacial reaction was extracted on the basis of evanescent wave excitation. Thus, the information obtained by the current experiment reflects the molecular motion in the close proximity to the interface. The fluorescence anisotropy ratio (r) is defined as equation S7,

$$r = \frac{I_{VV} - GI_{VH}}{I_{VV} + 2GI_{VH}} \quad \text{S7}$$

where I_{VV} and I_{VH} are the fluorescence intensity of the vertical and horizontal components, and G is a compensating factor. The G value can be obtained from equation S8.

$$G = \frac{I_{HV}}{I_{HH}} \quad \text{S8}$$

Here, I_{HV} and I_{HH} are the fluorescence intensity of the vertical and horizontal components.

The viscosity of the bulk sample was measured by a vibration-type viscometer (Sekonic viscomate VM-10A).