II Pc 05

Dynamic Light Scattering Studies on Network Formation of Bridged Polysilsesquioxanes Catalyzed by Phosphotungstic Acid

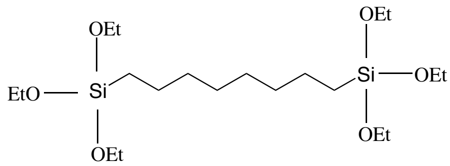
Yusuke Aoki,[1] Tomohisa Norisuye,[1] Qui Tran-Cong-Miyata,[1] Shigeki Nomura[2] and Toshiya Sugimoto[2]

[1] *Department of Polymer Science & Enginnering, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan*

[2] *R&D and Technology Center, Sekisui Chemical Co.,Ltd., 2-1 Hyakuyama, Shimamoto-cho, Mishima-gun, Osaka 618-8589, Japan*

e-mail: nori@ipc.kit.ac.jp

The sol-gel process of 1,8-bis(triethoxysilyl)octane (TES-Oct) catalyzed by phosphotungstic acid (PWA) has been investigated by time-resolved dynamic light scattering(TRDLS). The time-intensity correlation functions (ICFs) exhibited two modes, corresponding respectively to the cooperative diffusion of entangled chains and the translational diffusion of cross-linked clusters. Below the gelation threshold the ICFs were well described by sum of two exponential functions, allowing the successful analysis of the relaxation times and the corresponding relative intensity for both the fast and slow modes. Contrary to the general observation of acid catalyzed systems, the specific gelation process was found for $r_{PWA} = 0.100$ which is defined as the molar ratio of PWA to TES-Oct. Namely, the relative amplitude for the fast relaxation, A_f and the averaged slow relaxation time, $\langle \tau_{slow} \rangle$, exhibit exceptionally larger values in the gelation process, suggesting the existence of the ionized larger clusters found for the base-catalyzed system. Presented in fig 1 were the ICFs obeserved around the gelation threshold with different PWA concentrations. As seen this figure, ICF for r_{PWA}=0.100 contains a larger contribution from the fast mode than others. It was due to unique gelation mechanism catalyzed by PWA as mentioned above. The hydrodynamic radii, R_H, were also evaluated by dilution of the gel forming samples at several sampling points in order to confirm the existence of the larger cluster during the gelation. In addition to the normal increase in R_H in the sol-gel process, it was found that the matrix viscosity and/or hydrodynamic interaction play a significant role in both the slow dynamics, e.g., divergence of $\langle \tau_{slow} \rangle$ in the gelation process, and a power law behavior in the ICF around gelation threshold.



Scheme.1 Chemical structure of TES-Oct.

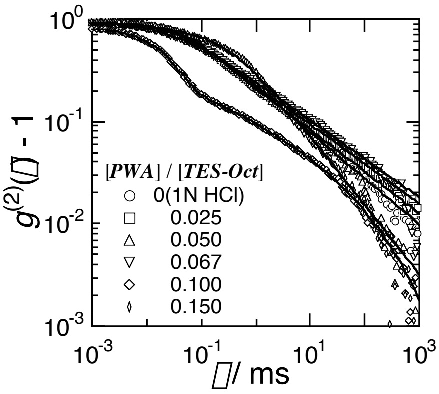


Fig.1 ICF obtained for TES-Oct with different [PWA] / [TES-Oct] around the gelation time.

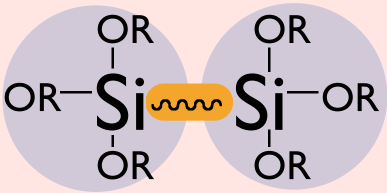
Dynamic Light Scattering Studies on Network Formation of Bridged Polysilsesquioxanes Catalyzed by Phosphotungstic Acid

(Department of Polymer Science & Enginnering, Kyoto Institute of Technology)
Yusuke Aoki, Tomohisa Norisuye and Qui Tran-Cong-Miyata

(R&D and Technology Center, Sekisui Chemical Co.,Ltd.)
Shigeki Nomura and Toshiya Sugimoto

Introduction

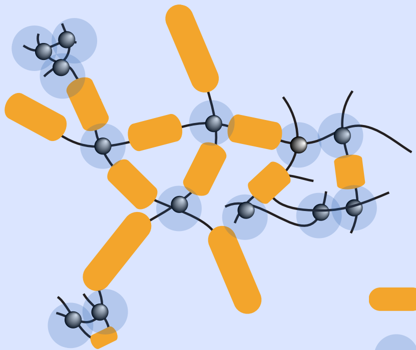
Sol-Gel Precursor



as a catalyst

Sol-Gel Reaction

Bridged Polysilsesquioxane

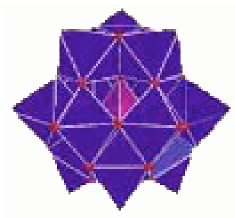


Applications
- optical devices
- catalyst supports
- electrolyte film…

organic group
siloxane unit

phosphotungstic acid

PWA



- ○$H_3(PW_{12}O_{40}) \cdot nH_2O$
- ○proton conductivity
- ○6～29 hydrated water
- ○α-Keggin structure

To control the proton conductivity…

role of PWA ⟷ **reaction kinetics**

to elucidate this …

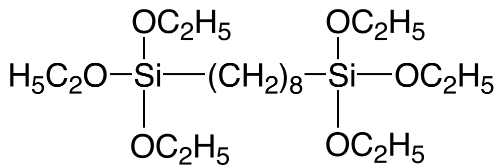
the gelation process has been observed by DLS.

Samples

Sample B

1,8-bis(triethoxysilyl)octane

TES-Oct



\+

2-propanol

stirred in 30min.

experimental conditions

$$\frac{C_{TES}}{C_{Total}} = 18.67\% \text{ (wt/wt)}$$

$$\frac{[H_2O]}{[\text{TES-Oct}]} = 0.5$$

$$\frac{[\text{PWA}]}{[\text{TES-Oct}]} = X$$

(X = 0.025〜0.150)

Sample A

PWA

dried in vacuo
50°C, 3days

\- 23 hydrated
water

Dried PWA

containing 6-bound water

\+

H_2O

2-propanol

stirred in 30min.

Sample A

\+

Sample B

stirred in

0.5min.

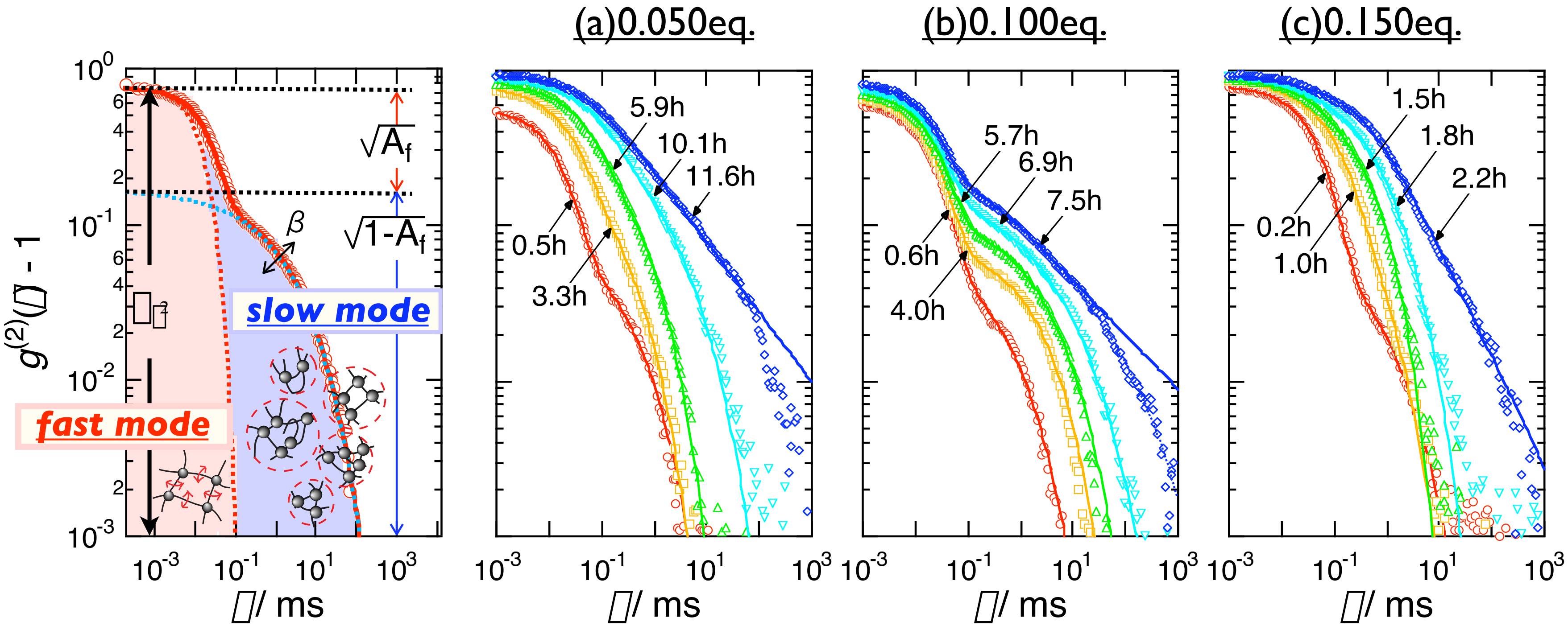
investigated by dynamic light scattering (DLS)

Intensity Correlation Functions (ICF)

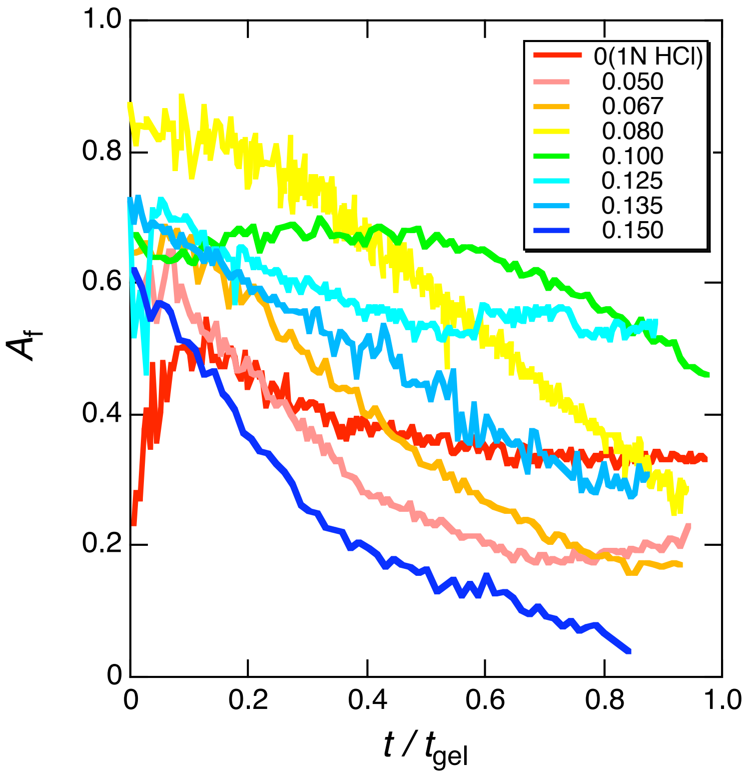
$$g^{(2)}(\tau) - 1 = \sigma_I^2 \left\{ A_f \exp(-\tau/\tau_f) + A_s \exp(-(\tau/\tau_s)^{\beta}) \right\}^2 \qquad (t < t_{gel})$$

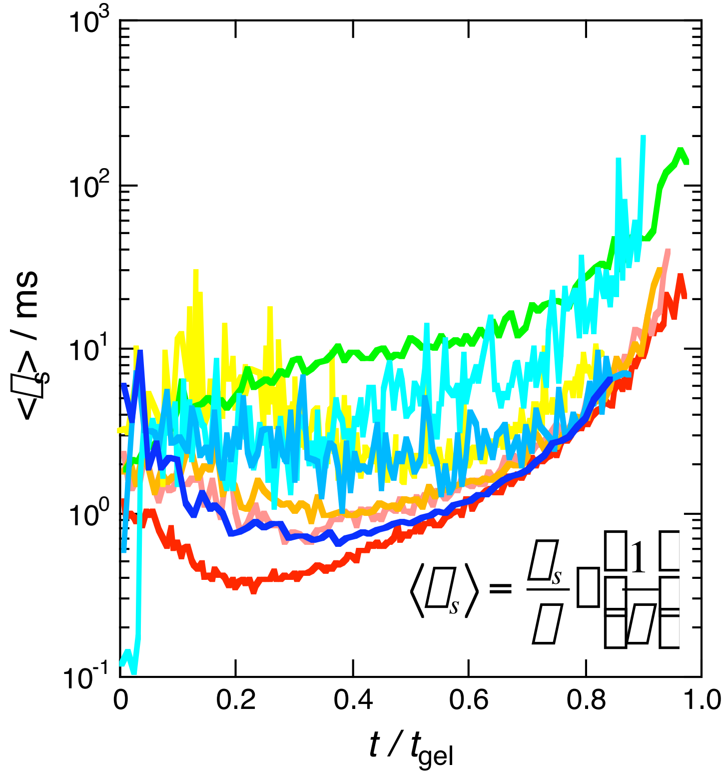
$$A_f + A_s = 1$$

$$g^{(2)}(\tau) - 1 = \sigma_I^2 \left[A_f \exp(-\tau/\tau_f) + A_s (1 + \tau/\tau^*)^{\frac{n_{gel}-1}{2}} \right]^2 \qquad (t \geq t_{gel})$$

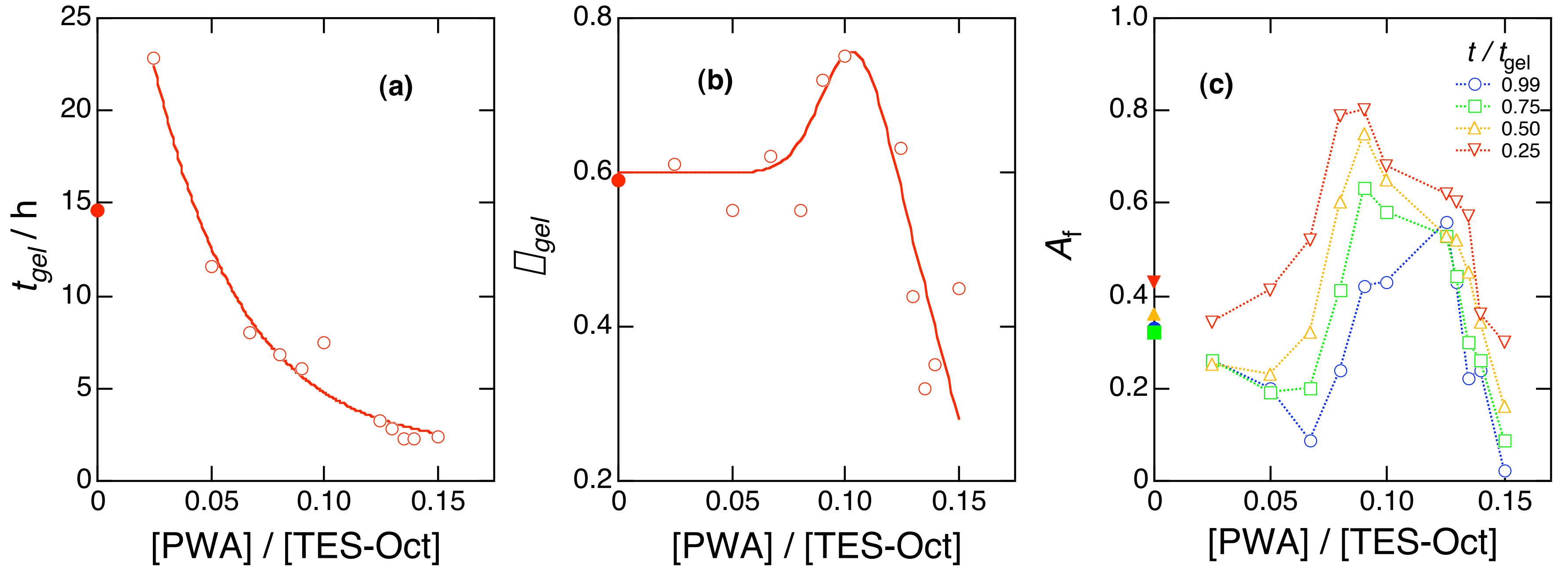


Time evolution of A_f, $<\tau_s>$



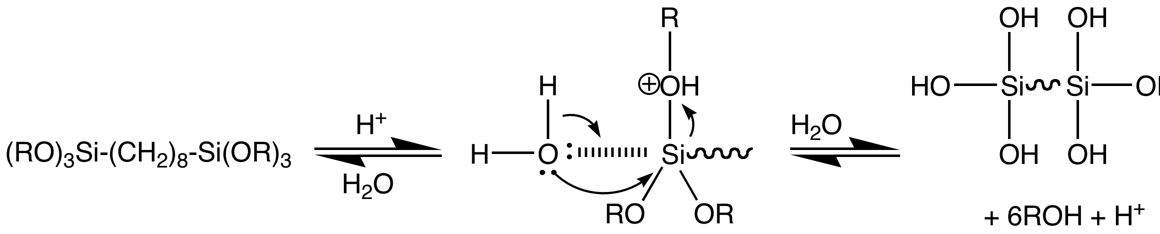


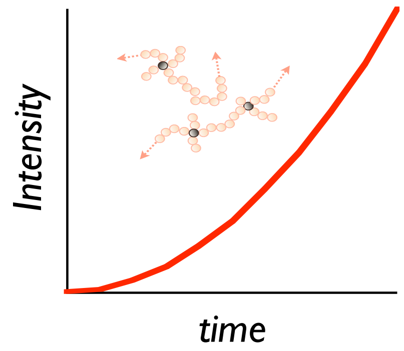
Dependence of (a) t_{gel}, (b) A_f, and (c) α_{gel}, as a function of [PWA] / [TES-Oct]



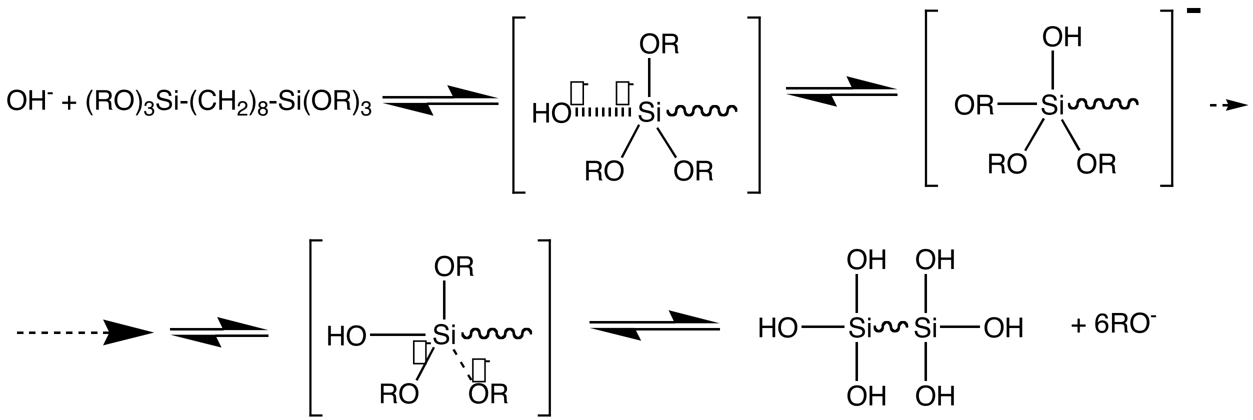
Sol-Gel Reaction Scheme

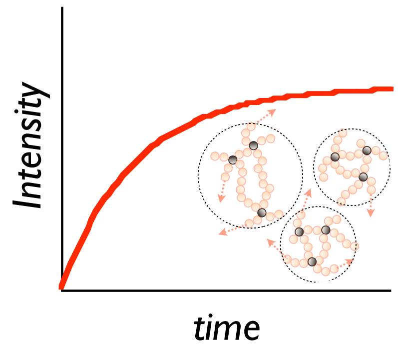
Acid-catalyzed hydrolysis



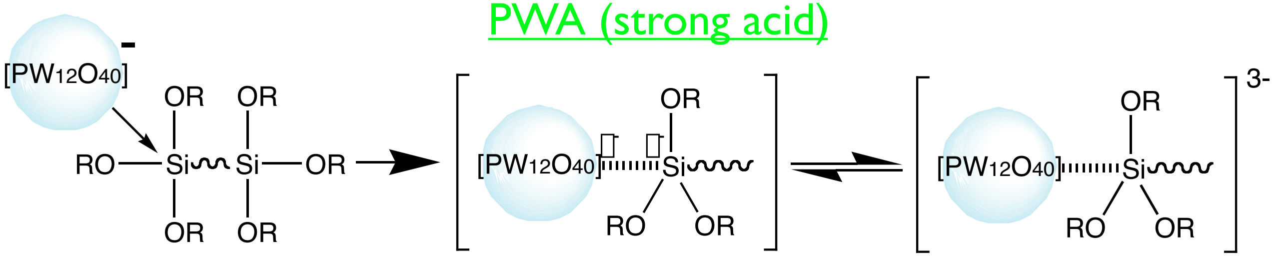


Base-catalyzed hydrolysis

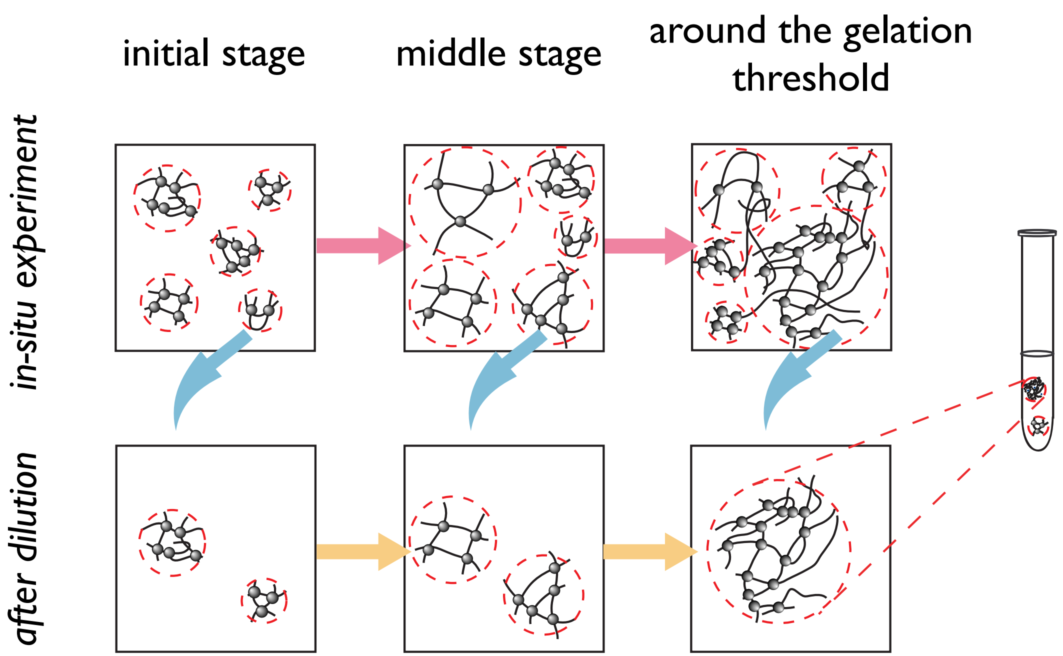




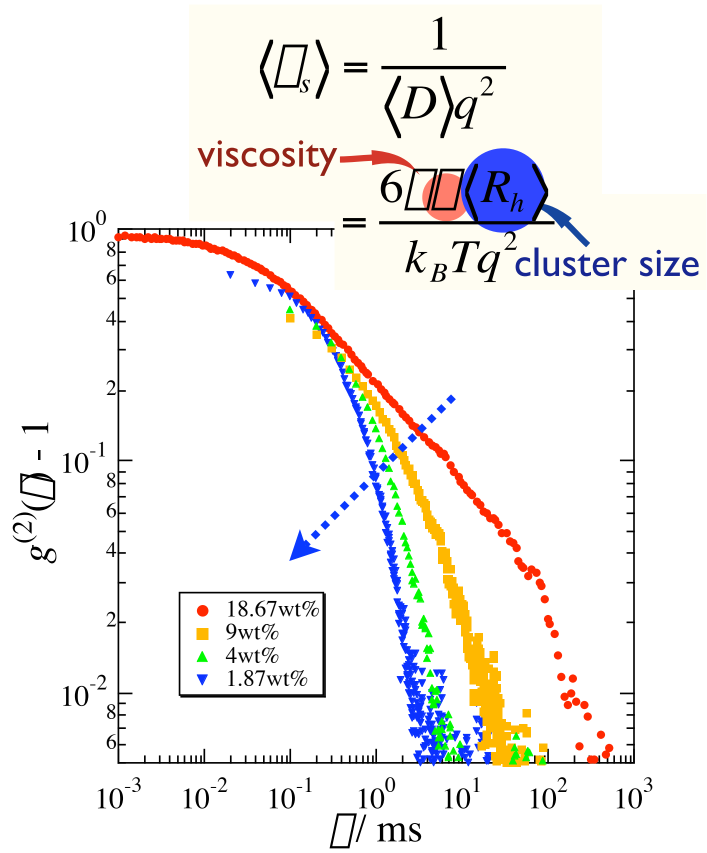
PWA (strong acid)



Experiment for confirming the existence of the larger clusters

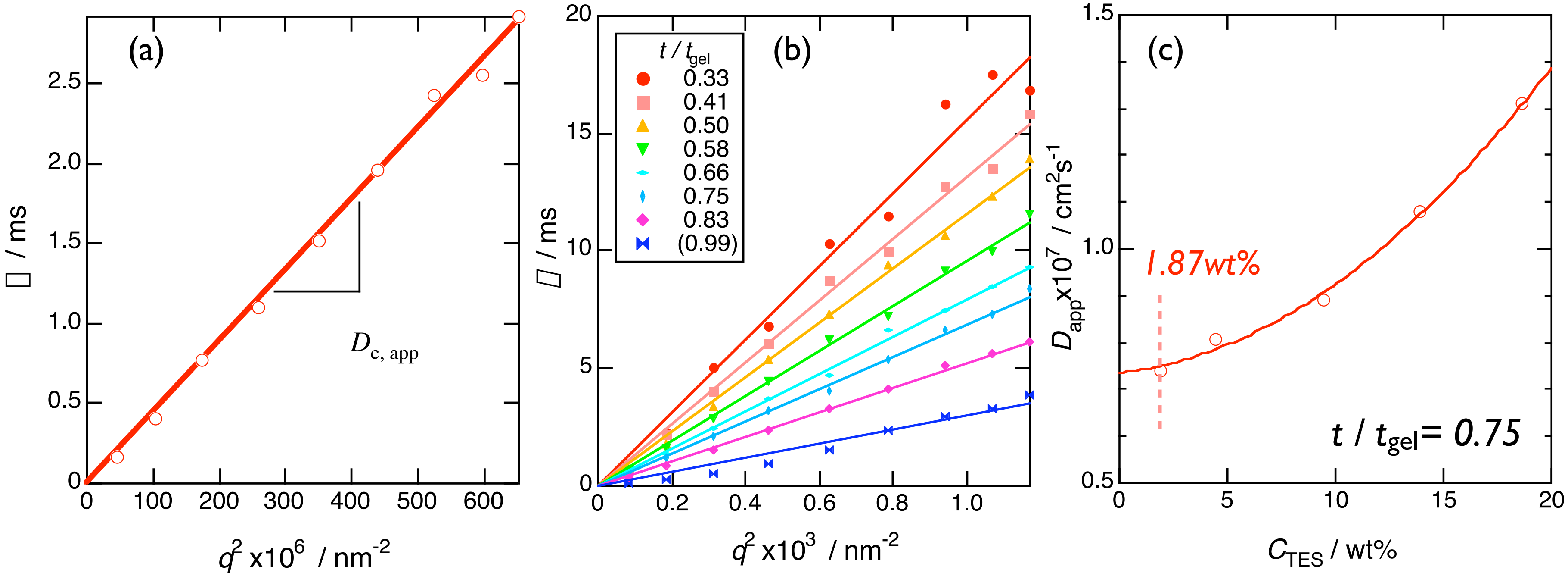


the reaction was quenched by dilution
with a large amount of IPA

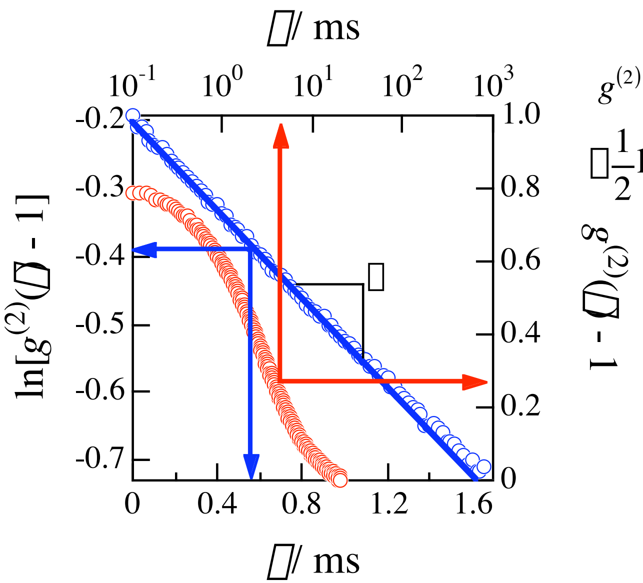


0.050eq around gelation threshold.

Examples of the data analysis for (a) the angular, (b) t / t_{gel} and (c) the concentration dependent experiments

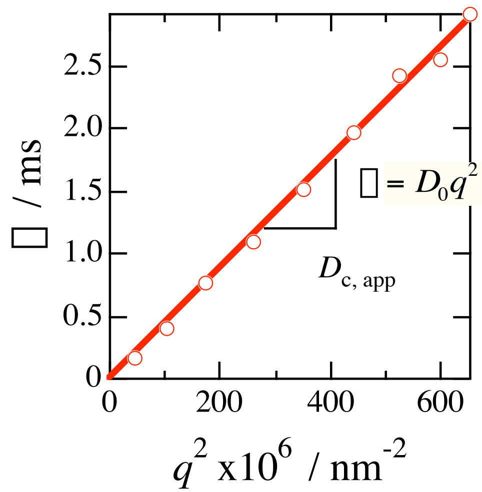


Analysis and time evolution of the hydrodynamic radii of the clusters



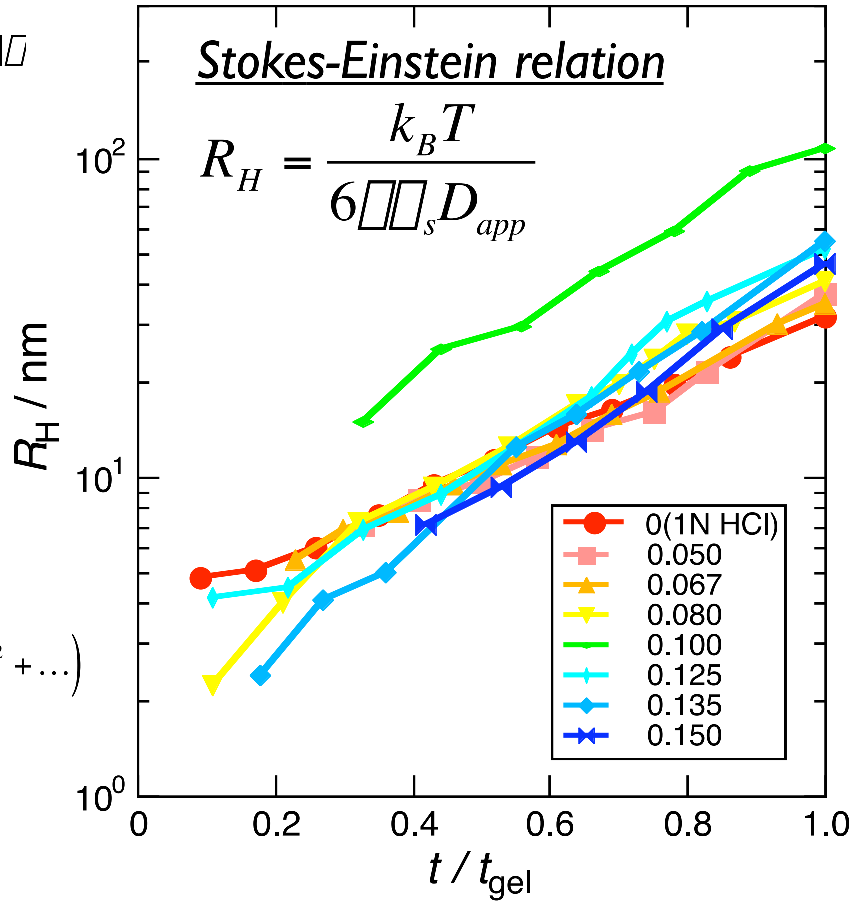
$$g^{(2)}(q,\tau) = 1 + \exp(-2\Gamma\tau)$$

$$-\frac{1}{2}\ln\left\{g^{(2)}(q,\tau) - 1\right\} = \Gamma\tau$$



$$\Gamma = D_0 q^2 (1 + k_D c + \dots)\left(1 - f_D\left(\langle S^2 \rangle_z\right) q^2 + \dots\right)$$

$$qR_g \ll 1 \longrightarrow \Gamma = D_0 q^2$$

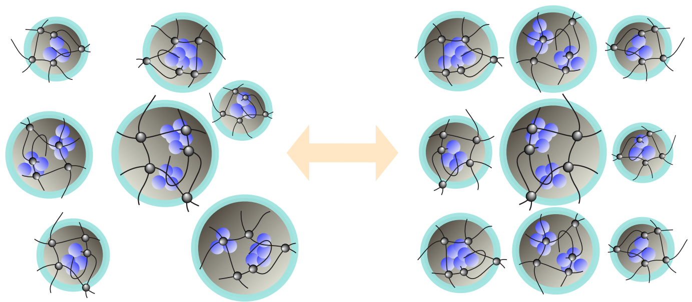


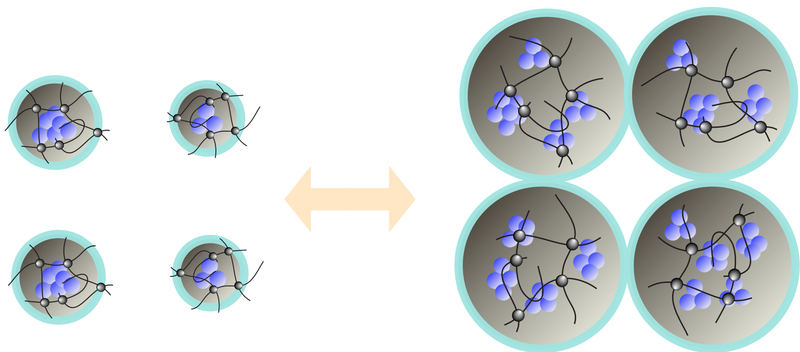
Optimal gelation process for higher conductivity

For 0.100eq...

(1) A_f↑ → *amount of charge*↑→*like base catalyzed system*
τ_s, R_H↑ → *cluster size*↑→*like base catalyzed system*
→ *homogeneous structure!*

may be percolated!





(2) *larger ionic domains*

better proton transport channel ↑

Conclusions

- We have been conducted by DLS for real time observation of the sol-gel process and subsequent cluster dilution analysis for the sol-gel derived polymer composite, 1,8-bis(triethoxysilyl)octane (TES-Oct) containing phosphotungstic acid (PWA).

- Two relaxation modes were observed in the time intensity correlation function, and these modes were successfully analyzed by a combination function of a single exponential function and a stretched exponential function of the reaction time.

- Exceptionally larger values of A_f and $\langle \tau_s \rangle$ were found during the gelation for [PWA] / [TES-Oct] = 0.100. The cluster dilution analysis for quenched samples obtained at several sampling points also supports the above findings.

- In order to design a polymer composite with higher proton conductivity, the most suitable concentration of PWA solutions is demanded.

Macromolecules in press 2003