イオンゲル PMMA/EMITFSI のダイナミクス

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What is ion gel?

Ion gels consist of network polymers and solvents of ionic liquids.

Double characters of ion gels :

stable, soft, transparent, strong film

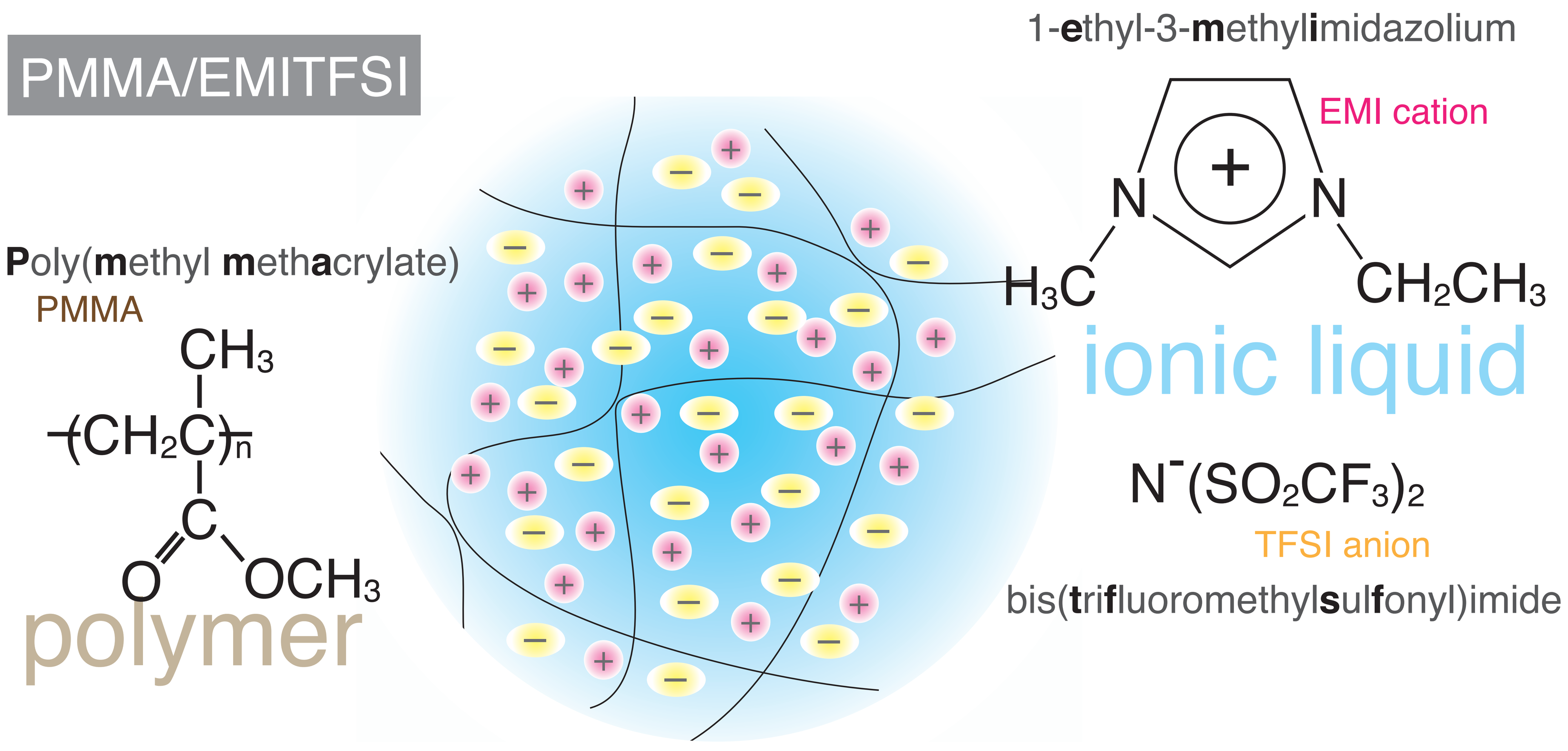
→ properties of gels

nonvolatility, incombustibility, high ionic conductivity

→ properties of ionic liquid

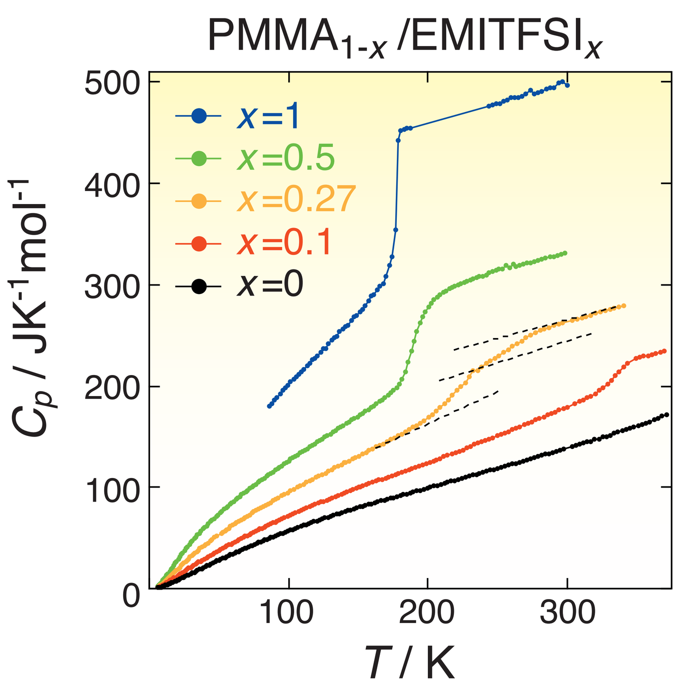
These features attract much attention in applications for various electrochemical devices, actuators, and so on.

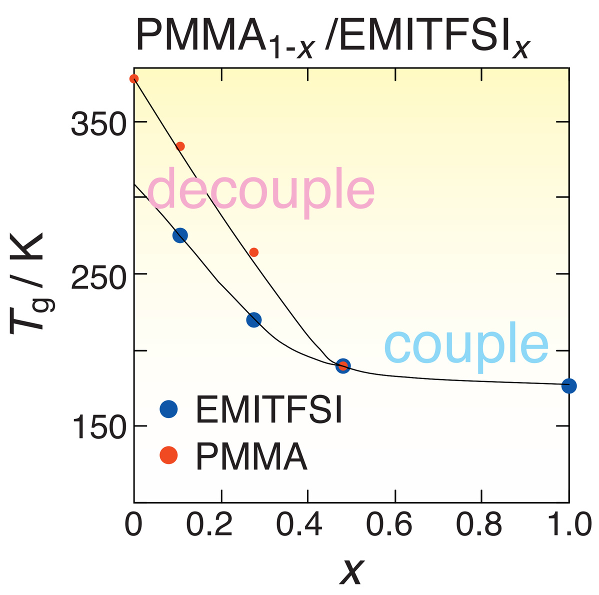
PMMA/EMITFSI



Glass transition

We have measured the heat capacities of PMMA/EMITFSI gels and determined their glass transition temperatures.





The glass transition temperatures, T_g, of PMMA and ionic liquid depend on the mole fraction of ionic liquid, x. The motion of ionic liquid and PMMA are decoupled in the lower x region, but coupled in the higher x region.

Experimental

sample

(from Watanabe group in Yokohama Nat. Univ.)

h-$PMMA_{0.9}$/d-$EMITFSI_{0.1}$
d-$PMMA_{0.9}$/h-$EMITFSI_{0.1}$
h-$PMMA_{0.73}$/d-$EMITFSI_{0.27}$
d-$PMMA_{0.73}$/h-$EMITFSI_{0.27}$

PMMA or EMITFSI were selectively deuterated to observe motion of another component with many H atoms.

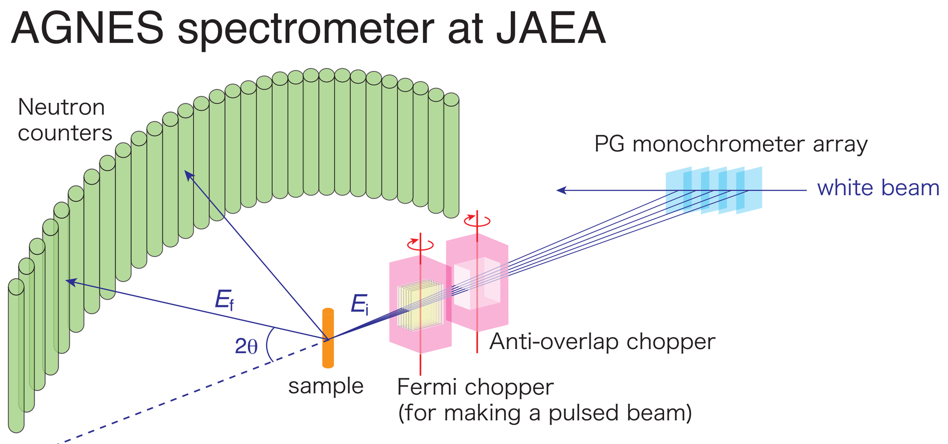
Neutron scattering

Neutrons scattering cross section

	coherent xs	incoherent xs
^{1}H	1.76	80.27
$^{2}H(D)$	5.59	2.05

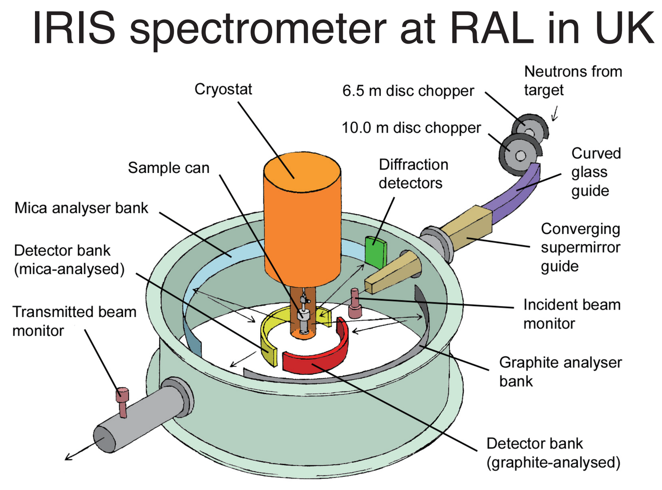
Neutrons are very sensitive to H atom!

AGNES spectrometer at JAEA



Monochrometer : PG(002)
Energy resolution~0.12meV
E_i=4.6meV, $-4<\Delta E<20$meV

IRIS spectrometer at RAL in UK



Analyser : PG(002)
Energy resolution~0.015meV
E_f=1.85meV, $-0.2<\Delta E<1.3$meV

Elastic scattering

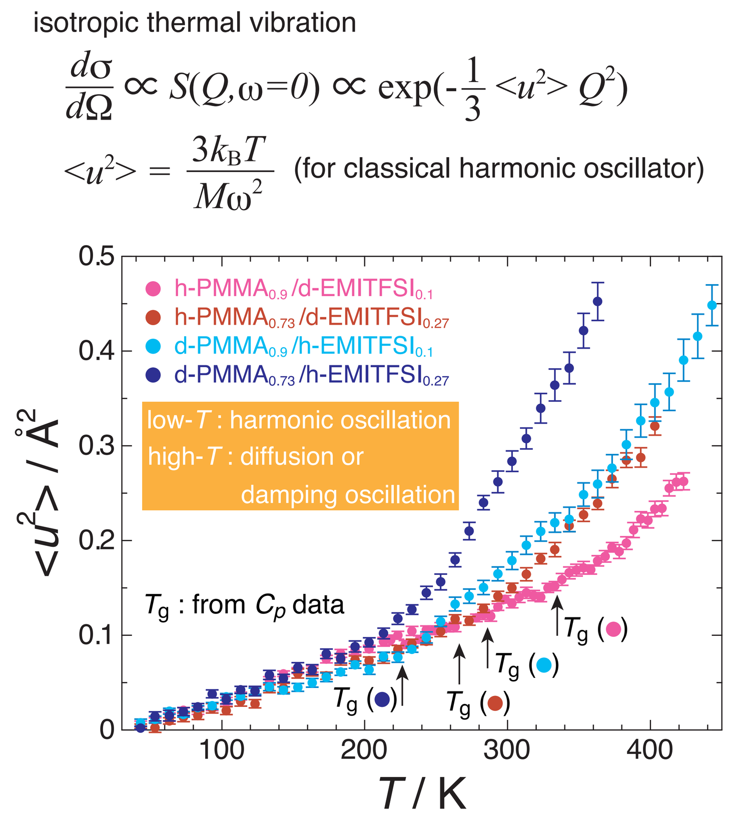
mean square displacements

(incoherent scattering from H atom)

isotropic thermal vibration

$$\frac{d\sigma}{d\Omega} \propto S(Q,\omega=0) \propto \exp(-\frac{1}{3}\langle u^2\rangle Q^2)$$

$$\langle u^2\rangle = \frac{3k_B T}{M\omega^2}$$ (for classical harmonic oscillator)

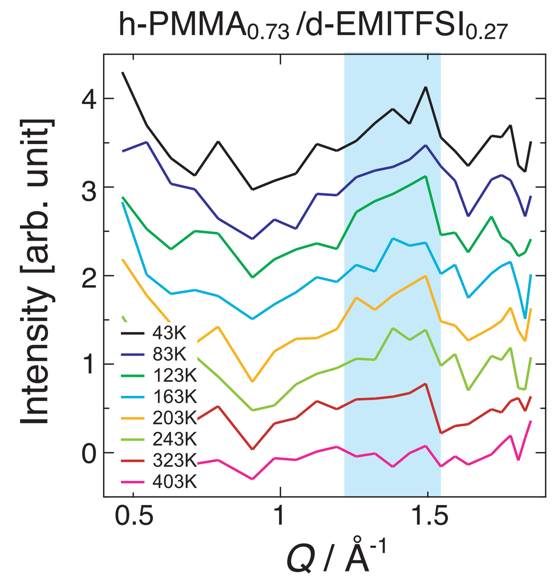


The offset temperatures coincide with T_gs.

strucutures of ion gel

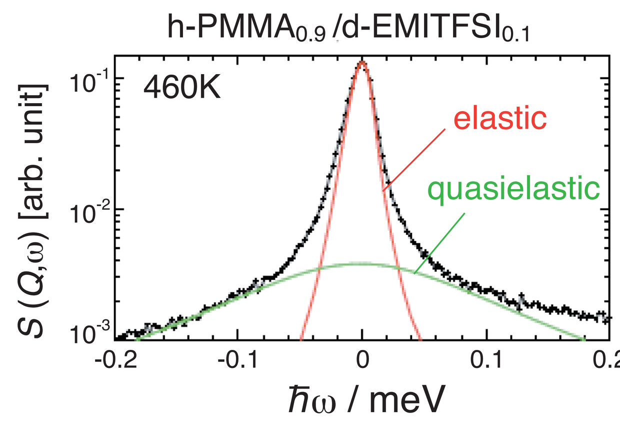
(coherent scattering from nuclei except H atom)

A broad peak is observed around at Q=1.4Å^{-1}.
The peak disappears as T increases.

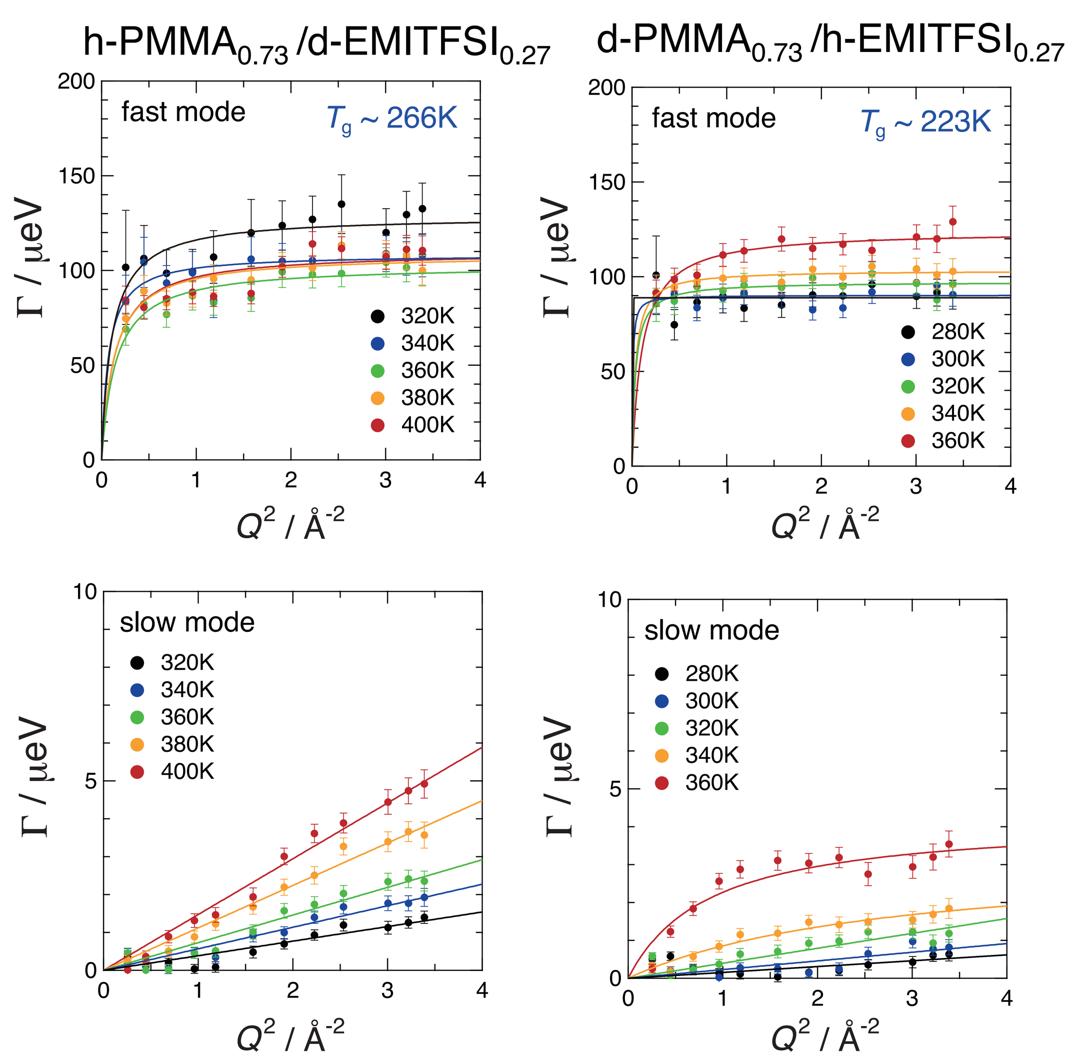


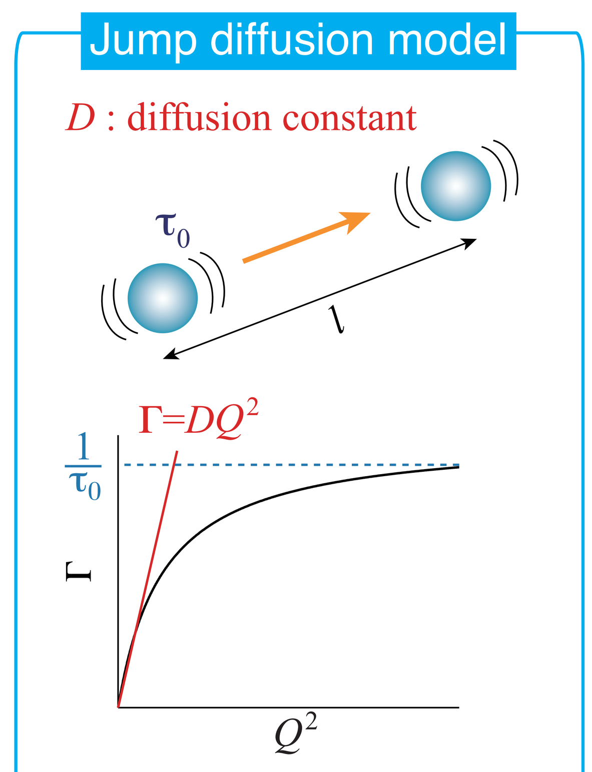
Quasielastic scattering

QENS spectrum of ion gel



We fit the QENS data with assumeing a delta function as an elastic component and two Lorentzians as quasielastic components. From the fitting, we obtained a broad Γ, corresponding to fast relaxation and a sharp Γ, corresponding to slow relaxation.

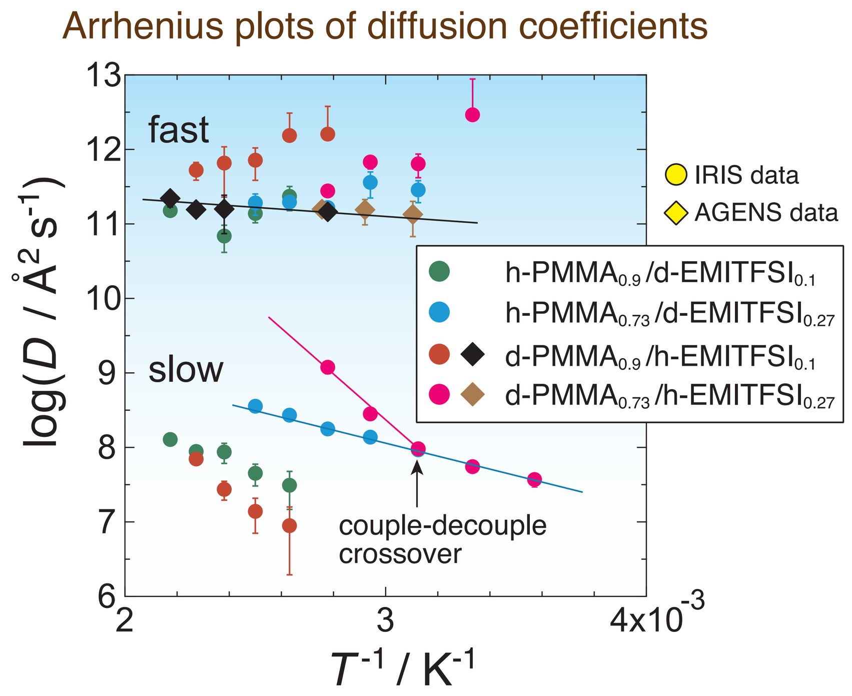




$$S(Q,\omega) = \frac{A\Gamma}{(\hbar\omega)^2+\Gamma^2}$$

$$\Gamma(Q) \approx \frac{DQ^2}{1+D\tau_0 Q^2} \qquad l = \sqrt{6D\tau_0}$$

Arrhenius plots of diffusion coefficients



fast motion : D does not change with T.
→ side-chain motion of PMMA intraionic motion of EMITFSI

slow motion : larger activation energy
→ diffusive motion

The couple-decouple crossover was observed around 320K in $PMMA_{0.73}/EMITFSI_{0.27}$.

↓

The motional coupling cannot be discussed only from the viewpoint of T_gs.

Conclusions

★ Excess increase of mean square displacement, $\langle u^2\rangle$, was observed above the glass transition temperature, T_g, determined by C_p.

★ The fast and slow motions are observed in QENS measurements. It is of interest that the coupling-decoupling crossover was observed at T~320K in the ion gel with x=0.27. We can summerize that the motion of PMMA and EMITFSI are coupled in high concentration and/or low temperature.