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Investigation of Gelling Aqueous Clay Dispersions with Dynamic Light Scattering

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Summary: The gelation process of aqueous clay (Laponite XLS, XLG) dispersions and of a photopolymerization system (*N*-isopropylacrylamide, Irgacure 2959, Laponite XLS) have been investigated by dynamic light scattering. The gelation threshold could be clearly indicated by a change in the shape of the time-intensity correlation function.

Keywords: clay; dynamic light scattering; gelation; nanocomposites; photopolymerization

Introduction

Polymer hydrogels are soft materials containing substantial amounts of water. Poly (*N*-isopropylacrylamide) hydrogels (PNIPAAm) have been extensively studied for the last three decades. Conventional cross-linked hydrogels with organic cross-linkers, e.g. *N, N′*–methylenbisacrylamide, show some serious disadvantages for technical and medical use. The main disadvantage of chemical cross-linked hydrogels is the lack of mechanical toughness. Furthermore, the limited swelling rate at equilibrium and the bad transparency of hydrogels with a high content of cross-linking agent are insufficient for some technical and academic use.

These problems associated with organically cross-linked hydrogels can be solved by nanocomposite hydrogels. Nanocomposite hydrogels made of *N*-isopropylacrylamide and clay were synthesized by free radical polymerization and characterized by several authors.[1–5]

The nanocomposite hydrogels presented here were prepared by *in-situ* free radical polymerization started through photopolymerization ($\lambda > 350$ nm) in the presence of inorganic, exfoliated clay (Laponite XLS) without a need of an organic cross-linking agent. The later aim of this system is the application in photopatterning.

In general, light scattering techniques are very suitable to study the gelation process without disturbing the gelling system. It was pointed out,[6] that four methods in dynamic light scattering (DLS) for the determination of the gelation threshold are applicable: (i) the change in the scattered intensity (occurrence of speckle patterns), (ii) the power-law behavior in the time-intensity correlation function (TCF), (iii) a characteristic broadening of the decay time distribution function, and (iv) the suppression of the initial amplitude of the TCF. Each of these methods is a phenomenon based on the characteristic features of gels, i.e. (i) inhomogeneity, (ii,iii) connectivity divergence, and (iv) nonergodicity.

In DLS, at the gelation threshold, a power law behavior[7] for the TCF is revealed,

$$g_2(t) - 1 = \frac{\langle I(0) \cdot I(t) \rangle}{\langle I \rangle^2} - 1 \propto t^{-\mu}$$

with $0.21 \leq \mu \leq 0.9$[7–9], here $\langle I(t) \rangle$ is the scattering intensity at time t with respect to $t = 0$ and $\langle \ldots \rangle$ denotes a time average.

The power-law behavior, which possesses no characteristic relaxation time, is self-similar. The incipient gel is a self-similar (fractal) distribution of fractal clusters of all sizes, from monomers to the infinite cluster. For many gelling systems a clear power-law behavior in the

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time-intensity correlation function at the gelation threshold was reported.[6,8–11]

Recently, several DLS studies on Laponite suspensions to investigate the phase diagram as well as to monitor aging and gelation have been published.[12–17]

Experimental Details

Raw Materials

N-isopropylacrylamide (NIPAAm) monomer was purchased from Acros Co., Belgium and was purified by recrystallization from *n*-hexane, followed by drying under vacuum.

The inorganic clay, a synthetic hectorite named ''Laponite XLG'' ($[Mg_{5.34}Li_{0.66}Si_8O_{20}(OH)_4]Na_{0.66}$) and ''Laponite XLS'' (consisting of 92.32 wt-% $[Mg_{5.34}Li_{0.66}Si_8O_{20}(OH)_4]Na_{0.66}$ and 7.68 wt-% $Na_4P_2O_7$)[12] respectively, from Rockwood Specialties Inc. was used after washing and freeze-drying. The photoinitiator 2-hydroxy-4′-(2-hydroxyethoxy)-2-methylpropiophenone (Irgacure 2959) from Aldrich was used as received.

Sample Preparation

For investigations by DLS, Millipore water (with a conductivity of 18.2 $\mu\Omega/cm^2$) was used. Oxygen in the pure water was removed by bubbling argon gas for more than 3 h prior to use. Throughout all experiments, oxygen was excluded from the reaction system. For preparation of clay suspensions, different contents of ''Laponite XLG'' or ''Laponite XLS'' were suspended in Millipore water and were stirred for more than 1 h to receive transparent and homogeneous dispersions. We did not observed that a longer dispersion time lead to a better dissolution. For DLS studies the dispersions were filtered using a 1.2 μm nylon membrane filter.

To receive hydrogels by photopolymerization, a transparent aqueous solution consisting of water (30 ml), inorganic clay (Laponite XLS) (0.496 g), NIPAAm (3.0 g) and the photoinitiator Irgacure 2959 (0.08 g) was prepared. The solution was filtered using a 1.2 μm nylon membrane filter and the photopolymerization was carried out under argon atmosphere through UV-irradiation ($\lambda > 360$ nm, mercury UV lamp of 450 W (Osram)) at different exposure times. To avoid inhomogenities in the structure of hydrogels due to the UV irradiation, NMR-tubes (with an outer diameter of 5.0 mm) were used for the photopolymerization and the following DLS investigations. We used ''Laponite XLS'' instead of ''Laponite XLG'' because the photopolymerization is easier to handle when using the non-gelling Laponite derivative.

Dynamic Light Scattering

An ALV DLS/SLS-5000 light scattering system with a He-Ne laser (Uniphase 1145P, output power 22 mW and $\lambda =$ 632.8 nm) as the light source equipped with an ALV-5000/EPP multiple digital time correlator was used. The online DLS experiments were carried out at an angle of $\theta = 90^\circ$ and with an acquisition time of 3 min. The NMR-tubes were immersed in a toluene bath and thermostated at $(20.0 \pm 0.1)\,^\circ C$.

In DLS the measured time-intensity correlation function $g_2(q,t)$ in the self-beating mode is related to the normalized electric field time correlation function $g_1(q,t)$ by Siegert relation

$$g_2(q,t) = B\left(1 + \beta|g_1(q,t)|^2\right)$$

where B is the baseline and β the coherence factor.

For large macromolecules and polydisperse systems one can expect a more complex decay. In that cases, $g_1(q,t)$ is described by a sum of exponential functions reflecting the distribution of relaxation times $G(\Gamma)$ which can be calculated by the Laplace inversion (the CONTIN procedure[18]) of the following expression

$$g_1(q,t) = \int G(\Gamma)\exp(-\Gamma t)d\Gamma$$

For spherical particles the hydrodynamic radius (or the dynamic correlation length ξ for concentrations well above the chain overlapping concentration c^*) can be

calculated by means of the Stokes-Einstein equation

$$R_h(\xi) = \frac{kT}{6\pi\eta_0 D_z}$$

with D_z, k_B, T and η_0 being the translational diffusion coefficient, the Boltzmann constant, the absolute temperature, and the solvent viscosity, respectively.

Results and Discussion

The inorganic clay, a synthetic hectorite, belongs to the 2:1 phyllosilicates (Figure 1). A octahedral layer is encircled by two tetrahedral layers. The lamellar crystal structure is swollen when dispersed in water and gradually cleaved into discrete disk-like particles. Monolayer clay particles are anisotropic platelets 25 nm in a diameter and circa 1 nm thick. The resulting aqueous clay suspensions, composed of exfoliated clay particles, is homogeneous and transparent.[2]

Laponite XLG particles have negatively charged faces and positively polarized edges. As a result, suspensions of Laponite XLG in water (without polymer) form gels when the concentration exceeds 3 wt-%. The reason therefore is the structure of the clay platelets, which tend to form a so-called ''house-of-cards'' structure through ionic interactions, which implies a random structure with short range orientational order (see Figure 1).

On the contrary, Laponite XLS is modified with pyrophosphate ions ($P_2O_7^{4-}$) so that both faces and egdes of the clay particles are negatively charged when the particles are dispersed in an aqueous solution. There is a repulsive electrostatic interaction between the clay particles which forces them to stay separate even at moderate concentrations.

Gelation of Aqueous Clay Suspensions

The TCFs for aqueous clay dispersions with different Laponite XLG contents after 39 hours aging time are shown in Figure 2. The power law behavior was observed between a clay content of 3.0–3.5 wt-%. Taking the most linear behavior in the power law scaling for the gel point in this

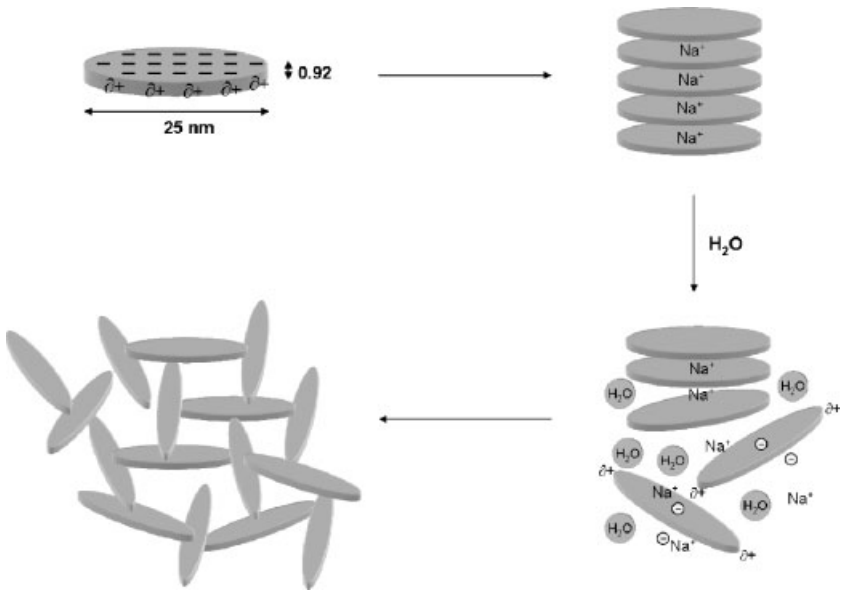

Figure 1.
Schematic representation of the clay (Laponite XLG) aqueous suspension and the formation of the ''house-of-cards'' structure, drawn after ref.[2]

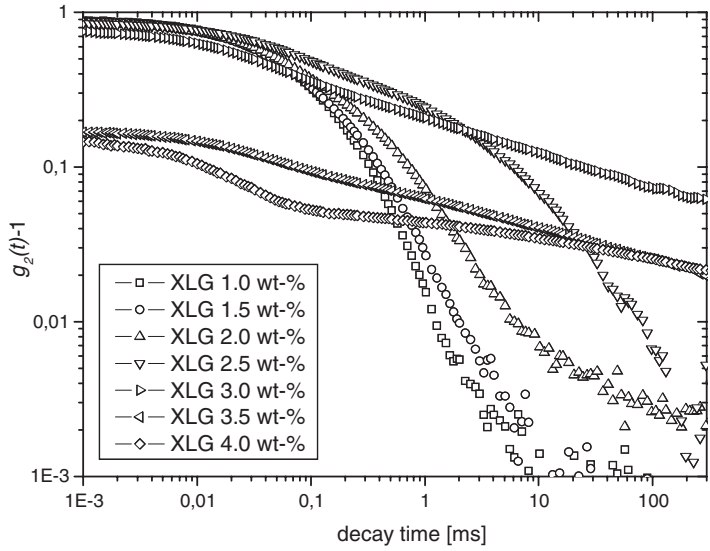

Figure 2.
TCFs for aqueous clay dispersions with different Laponite XLG contents after 39 hours aging time.

special given case one can take the TCF data with a clay content of 3.5 wt-%. Applying a linear fit (between a decay time window of 0.01 and 300 ms with a regression coefficient of 0.9996) to these data an exponent of $\mu = 0.19$ was observed.

A power-law decay, with a concentration dependent scaling exponent, was also observed in the gel phase.[14] We are aware the fact that, at much longer aging times the shape of the TCFs is also changing.[15–17] It means, that the gel point can be also observed at lower concentrations (3.5 wt-%) then in the present study when waiting for exceptional long times. As an example, it was reported that at a solution with 1 wt-% Laponite XLG was gelling after 4 weeks at 25 °C![2] Therefore, we choosed 39 h aging time for all aqueous clay samples.

The Figure 3 shows the radii (correlation length) distribution for the clay dispersions obtained from the data in Figure 2 by CONTIN.

Our correlation lengths were about 25 nm at low clay concentrations (1–1.5 wt-%), which is consistent with the diameter of clay platelets obtained by SAXS results. At all concentrations, peaks lower then 10 nm were observed. We assume, that hydrodynamic radii lower than 10 nm are no real sizes in that clay system and can be probably attributed to internal relaxation modes inside that ''house-of-cards'' network.

With increasing the clay content the distribution is shifting toward larger radii caused by large aggregates. Above the sol-gel transition the distribution is very broad. However, also peaks about 1 μm were reached at high clay concentrations in analogy with results found by Mori et al.[12] These sizes are indicated to be related to the extended clay-gel structure. In summary, the exact assigment of the three peaks to the gel structure is not possible.

No significant change in the TCF (Figure 4) and in the hydrodynamic radii R_h distribution (Figure 5) at all clay concentrations were observed on aqueous solutions of Laponite XLS. Longer aging times than 39 hours arised the same results. The estimated hydrodynamic radii were about 25 nm at all clay concentrations. This is consistent with the diameter of clay platelets (see above) as well as the radii values and a similar radii distribution given in ref.[13]

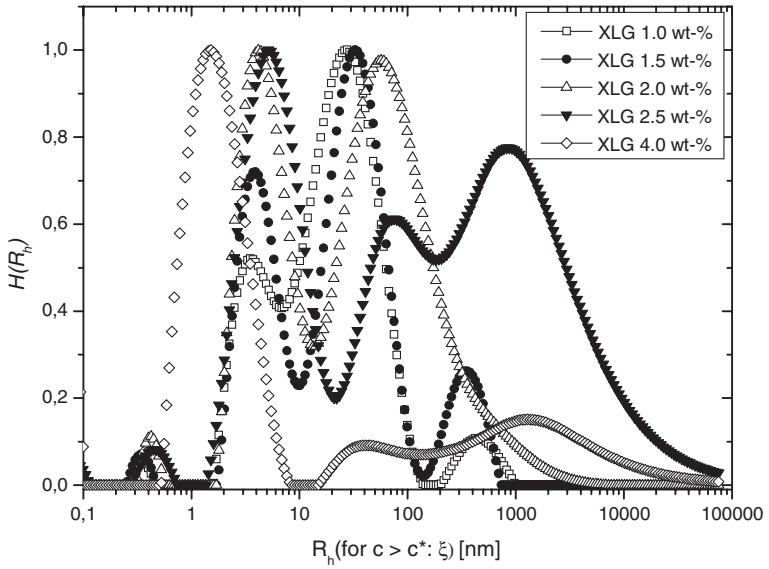

Figure 3.
Hydrodynamic radii R_h (resp. correlation length ξ) distribution for aqueous clay dispersions with different Laponite XLG contents after 39 hours aging time.

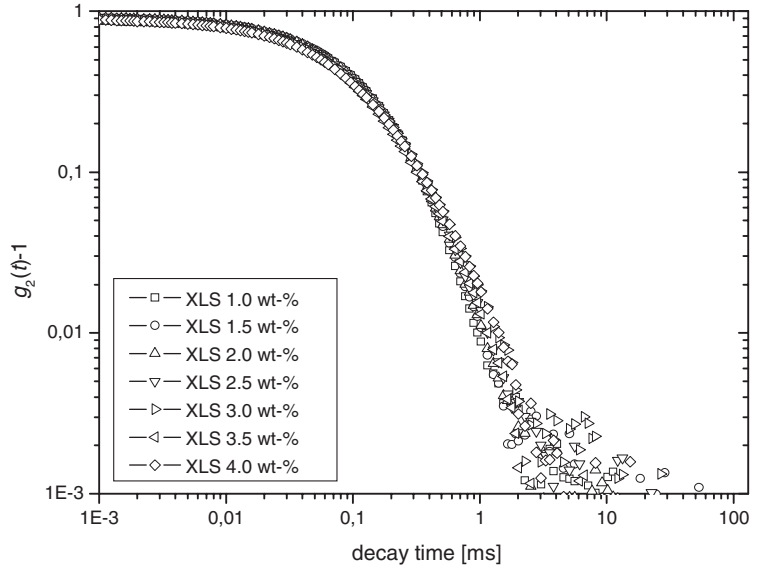

Figure 4.
TCF of aqueous clay (Laponite XLS) dispersions at different clay contents after 39 hours aging time.

Photopolymerization System

We assume similar to Haraguchi et al.[2], that the photoinitiator reacts with the monomer attached on the clay surface and the polymerization starts there. In the Figure 6 the formation of ''clay-brush'' particles in early stages of polymerization is shown. At the end of polymerization process, the polymer chains reaching from one to another clay platelet and forming a stable

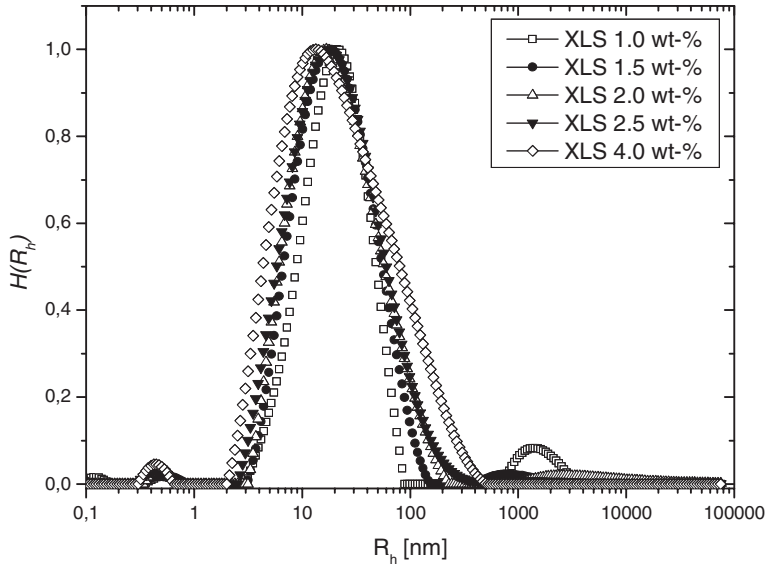

Figure 5.
Hydrodynamic radii R_h distribution of aqueous clay (Laponite XLS) dispersions at different clay contents after 39 hours aging time.

transparent gel. With regard to the inhomogeneities, it can be assumed that the NIPAAm chains are anchored to the clay particles in such way that there is an excess polymer density close to the surface of the platelets. The clay particles act in that process as multifunctional cross-links.

In the Figure 7, the sol-gel transition can be identifed between 49–50 s. A simple tilting test of the tube irradiated after 50 s

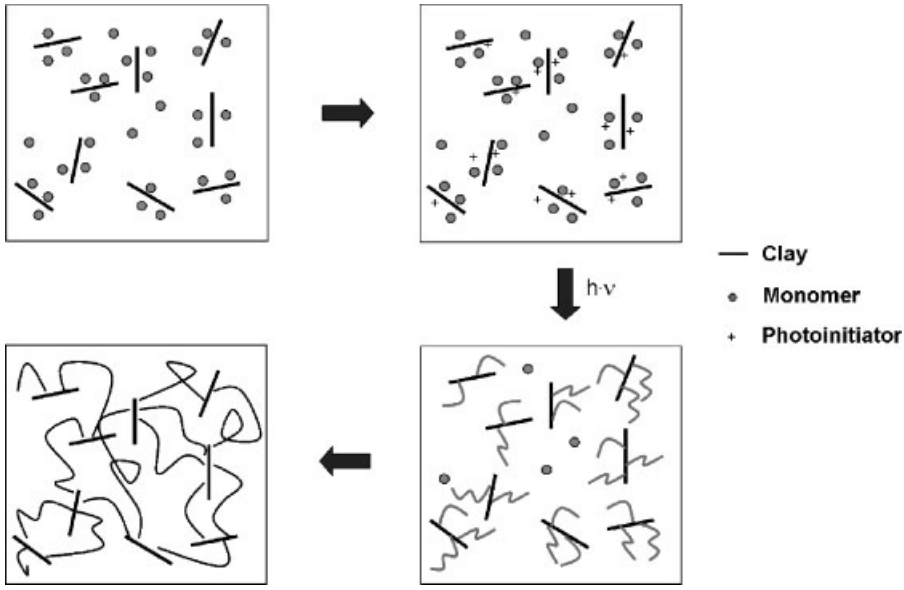

Figure 6.
Mechanism of the photopolymerization process of the aqueous clay (Laponite XLS) dispersion, after Haraguchi et al.[2]

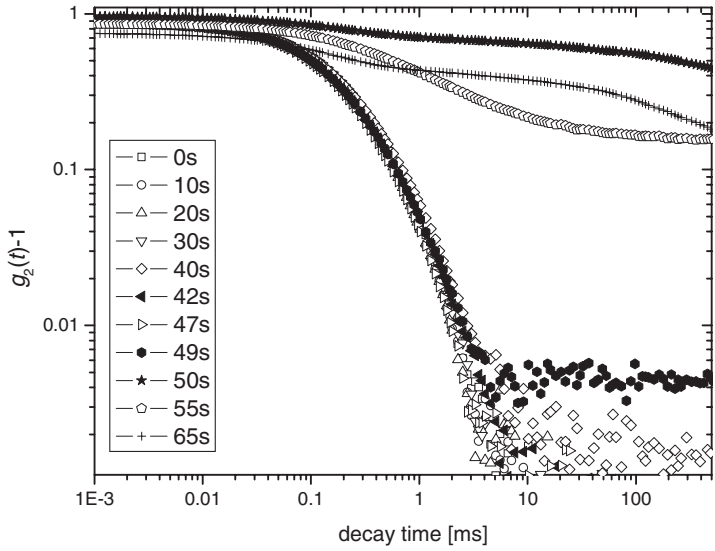

Figure 7.
TCFs of the photopolymerization of the aqueous clay (Laponite XLS) dispersion system after different UV irradiation times.

showed no flow behavior. No continuous change in the shape of the TCFs as usual when monitoring gelling systems and as well as no power law in the TCF was observed on that system, obviously due to the non-fractal structure of the first critical cluster.

Conclusion

Several aqueous clay dispersions, which are gelling have been investigated with dynamic light scattering. Laponite XLS is not able to form gels in aqueous solutions, while Laponite XLG is gelling with a self-similar structure of the critical gel structure, clearly indicated by a power law behavior in the TCF with the lowest exponent up to now ever observed. For more details about the theoretical meaning of μ see the review.[19] It must be mentioned, that contrary no fractal-like organization of colloidal Laponite particles was observed by using static light scattering and rheometry.[20]

The photopolymerization process of the system NIPAAm/Laponite XLS/Irgacure 2959 to receive bulk hydrogels are described for the first time. During gelation monitoring by DLS an abrupt change in the TCFs and no power law was observed. This phenomenon is in further investigation. The obtained gels show thermosensitive behavior and improved mechanical properties.

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