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Growth Process for Fractal Polymer Aggregates Formed by Perfluoro-octyltrimethoxysilane.

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Introduction

The detailed understanding of the reaction process of silane-coupling agent is very important for the practical modification of surface. The growth process of fractal perfluoro-octyltrimethoxysilane (PFOS) polymers has been surveyed and analyzed using the Guinier's approximation by Ogasawara et al. [1]. The principal result is that the growth process of the polymeric precursors occurs in two-steps. In the present study, the time-resolved SAXS spectra for the growth process of fractal PFOS polymers, catalyzed by various HCl -concentrations are reported.

Experimental

1H,1H,2H,2H-perfluorooctyltrimethoxysilane (PFOS) was purchased from Fluka Chemical LTD. and was used without further purification. The five PFOS/ethanol/ $HCl \bullet H_2O$ (1:1:0.4 weight ratio) systems with different HCl -concentrations (0.5, 1.0, and 2.0) were used as an acid-catalyzed reaction mixture at 298 K.

Time-resolved SAXS profiles were measured using a synchrotron radiation X-ray scattering spectrometer (BL-10C) with SAS optics installed at 2.5 GeV storage ring in the PHOTON FACTORY, Tsukuba, Japan.

Results and Discussion

The SAXS spectra of the PFOS sample solutions, catalyzed by the different HCl -concentrations, were time-resolved until phase-separation occurred [1]. The representative SAXS profile1M HCl -catalyzed) is shown in Figure 1[A]. It is found that, in the initial stage of the reaction, the SAXS profiles are characteristic of fractal polymer aggregates. The intensity of each profile in the lower q range increases with time, until finally the profile becomes characteristic of that of a polymeric viscous solutions [2, 3]. Therefore, we may assume that a transition similar to the so-called sol-gel transition occurs in the course of this polymerization process.

In our previous paper [1], we have analyzed these time-resolved SAXS curves, which were obtained by 1M HCl -catalyzed reaction. There a power-law behavior, which is independent of both R_g and $\boldsymbol{a}$ ($\cong 3$ Å), is predicted [16]. We have concluded that the polymeric precursors of PFOS formed by the 1M HCl - catalyzed reaction are mass fractals of dimension $D_f \approx 2$, although the D_f values slightly dependent on the reaction time (D_f = 1.81 – 2.10).

The time-dependence and the HCl -concentration dependence of D_f, which were estimated by Porod's law, are shown in Table 1. It is evident that the D_f value strongly depends upon the reaction time and the HCl - concentration, indicating that the mass-fractal structure of the PFOS polymeric aggregates grow up, depending on the time and HCl – concentration. The time- and HCl - concentration dependence of Rg In Figure 1[B]. The Guinier Rg data evidently show that polymerization of PFOS monomers occurs in a two-steps and that higher HCl -concentration promotes the rate of growth. For example, in the case of the 1.0M HCl -sample system, in the initial stages (below 4300s) of the reaction, formation of small PFOS clusters occurs, while, in the later stages (above 4000s), formation of larger polymeric aggregates rapidly takes place.

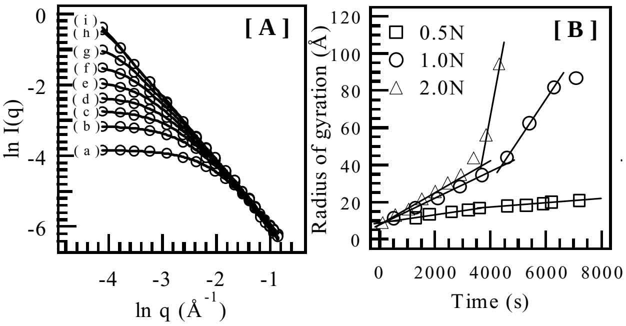

Figure 1 [A]Time-resolved SAXS curves [(*a*) 500s, (*b*) 1300s, (*c*) 2100s, (*d*) 2900s, (*e*) 3700s, (*f*) 4600s, (*g*) 5400s and (*h*) 6300s] for the 1M HCl -catalyzed PFOS-ethanol system. [B] Radius of gyration (Rg) versus time (s)

0.5MHCl	1300s 1.22	2600s 1.47	3600s 1.61	5300s 1.66	6200s 1.74
1.5MHCl	500s 1.82	2100s 1.92	3700s 1.95	5400s 1.82	7100s 2.00
2.0MHCl	300s 1.28	900s 1.58	1500s 1.69	2100s 1.78	2580s 1.78

Table 1 HCl – concentrationand time dependence of fractal dimension D_f.

References

[1] T. Ogasawara et al., J. Colloid Polym. Sci. 278 (2000): 293,
[2] Cohen Addad JP (ed) et al, Physical properties of polymeric gels. Wiley, New York, (1996) pp 87-142
[3] E. Bouchard et al., J. Phys. 47 (1986), 1273

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