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Structure fluctuation of amphiphilic monomer during polymerization

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Introduction

We have proposed the new method to prepare structure controlled membrane named "self-assemble polymerization" in which the ordered structure of self-assemble monomers on substrate is fixed into polymers by irradiating lights such as low energy electron beam, X-ray and ultra-violet light [1,2].

Not only amphiphilic molecules but also molecules including hydrogen bonding, π–π interaction, and metal-legand interaction are possible to form self-assemble structure. However, the alignment of interaction vector among molecules is necessary to be the self-assemble monomer. For the case of amphiphilic molecules consisted of two or three long alkyl chains, the polymers obtained by self-assemble polymerization has anisotropic structure consisted of highly stacked bilayers parallel to film surface.

Experimental

Two types of styrene derivative monomers containing tridodecyl ammonium chloride and phosphonium chloride was synthesis by the reaction of chrolomethylstyrene and N, N' tri n-dodecyl methylamine or tri n-dodecyl methylphosphine used as amphiphilic monomers.

The simultaneous differential scanning calorimetric – small angle X-ray scattering (DSC-XRD) measurement was carried out by the simultaneous DSC [3] setting on SAXS optics at BL-10C, Photon Factory, High Energy Accelerator Research Organization (KEK), Tsukuba, Japan. The wavelength of monochromatic X-ray for DSC-XRD was 0.1488 nm. The scattering X-ray was detected by a one-dimensional position sensitive proportional counter (PSPC, 512 channels, Riga Co. Ltd.). The distance between sample and PSPC was 550 mm, which covered 1.02 nm< $S^{-1} = (2\pi/q)^{-1} = (2\sin\theta/\lambda)^{-1} < 37.8$ nm.

Results

Small angle X-ray scattering (SAXS) profiles of p-tri n-dodecyl ammonium chloride styrene showed multi diffraction peaks with the ratio of 1 : 2 : 3 : 4 until 12th higher diffraction peaks. The SAXS profile indicated that multi layers more than 500 layers stacked parallel to the substrate surface. From the results of SAXS and the structure optimized by semi-empirical molecular orbital calculation, the estimated three-dimensional molecular structure is shown in Fig.1. Amphiphilic molecules formed bilayer with 2.8 nm of layer distance and bilayers stacked parallel to the substrate surface. In the bottom layer, tri n-dodecyl chains faced to the hydrophobic substrate, which was confirmed by the attenuated total reflection Fourier transform infrared spectroscopic measurement (ATR-FTIR).

The scattering theory for multi-lamellar bilayer is proposed by Lemmich [4]. The scattering intensity function $I(q)$ from X-ray scattering of layered systems is interpreted in terms of a form factor $f(q)$ and a structure factor $s(q)$.

$$I(q) = \left\langle \left| f(q) \right|^2 \right\rangle \left\langle s(q) \right\rangle \quad (1)$$

Here, < > denotes averaging over all fluctuations in the system and q is a scattering vector. In order to parameterize the scattering theory for $I(q)$, we apply a simple geometric model in which each of the N repeat units in a stack is taken to consist of four layers with different scattering length densities; b_H (hydrophilic part), b_W (styrene group) and b_L (hydrophobic alkyl chain). The thickness of the layers is assumed to fluctuate independently according to Gaussian distributions with mean values d_H, d_W and d_L, and corresponding standard deviations σ_H, σ_W and σ_L. From the scattering model analysis of SAXS profiles at various temperatures, the optimum molecular structure for self-assemble polymerization was analyzed [5].

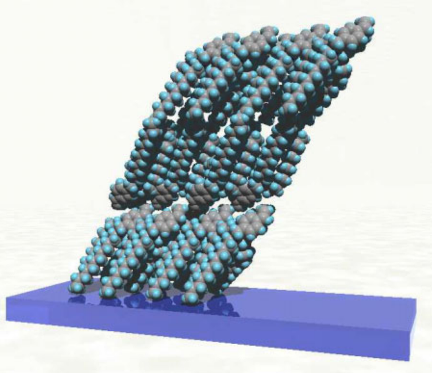

Fig.1 Three-dimensional self-assemble structure of p-tri n-dodecyl ammonium chloride styrene

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