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In-situ polymerization of molecular macroclusters on silica: Poly(N-isopropylacrylamide) nano-films

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Recently, we succeeded to prepare flat and defect-free polymer nano-films by in-situ photo-polymerization of the adsorbed monomers (e.g. acrylic acid) on silica surfaces through hydrogen-bonding in cyclohexane. Our method has advantages such as simplicity, low-cost, applicability to any shape of substrates. In this study, to further develop this method, we prepared poly[N-isopropylacrylamide (NIPAAm)] film by using new procedure which we call solution exchange method (Fig.1). NIPAAm monomers are adsorbed on the silicon prism surface in chloroform and polymerized in cyclohexane by UV irradiation. The increase in the film thickness was monitored following the ν_{NH} peak intensity in ATR-FTIR spectra (Fig.2). The film thickness increased drastically after 3 h UV irradiation, while almost no increase in the thickness in case of adsorption and polymerization was performed in one solution (toluene and cyclohexane). Peak positions of Amide I and II of adsorbed NIPAAm indicated that the solution exchange induced the adsorbed structure similar to the N-methyl acetamide crystal, in which the neighboring double bonds of NIPAAm became close, and should promote the polymerization(Fig.3).

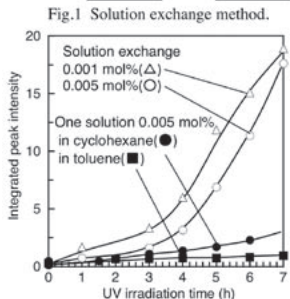
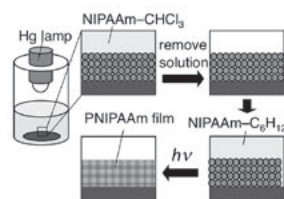


Fig.2 Irradiation time dependence of ν_{NH} peak intensities from ATR-FTR.

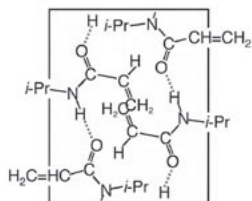


Fig.3 Structure of adsorbed NIPAAm.

Keywords: adsorption, hydrogen bonding, polymer films

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Frank model in faces description of polyethylene and n-alkane crystals

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Crystal face of polyethylene and long-chain n-alkanes often have a lenticular form which doesn't change during its growth (see Fig.- Lenticular forms of $C_{246}H_{494}$ crystals[1]). There are no still explanations to these facts. Two Frank[3] equations which describe dependence of density of the right and left kinks from coordinate of a step have been solved for a step with a constant length with the assumption that the building units delayed by kinks rows cannot be dissolved and that the kinks are not formed in height more

elementary. Mansfield[2] and his followers have been solved Frank equations for a step (and a face) which length increases with some rate. Researchers of polymer crystals used these calculations, they consider such crystals in which the distance between steps is in the order of several sizes of building units - the case when Frank's model is not applicable. Besides coordinate and time independence of normal growth rate of a face assumes a constancy of a summary density of the right and left kinks that also contradicts calculations[2].

[1] Putra E.G.R. *Macromolecules* 2003,36,5214

[2] Mansfield M.L. *Polymer* 1988,29,1755

[3] Frank F.C. *J. Crystal Growth* 1974,22,233



Keywords: crystal growth, crystal shapes, growth kinetics

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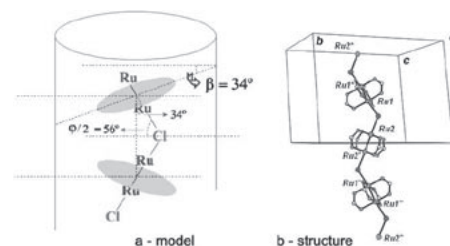
Crystallography validates a model for the supramolecular architecture of polymeric metallomesogens

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Single-crystal analysis is a direct structural probe at a molecular and supramolecular level, most useful in understanding physical properties of advanced crystalline materials but unfortunately precluded in liquid crystals (LC) due to lack of long-range order. Their structural description often consists in models based on physico-chemical arguments, macro-structural information and local-probe evidences. Following this approach, we proposed a model (1) for the remarkable LC columnar phases of diruthenium tri(alkoxy) benzoates ($[Ru_2(3,4,5 (C_nH_{2n+1}O)_3C_6H_4CO_2)_4Cl]_x$) in which the polymeric $\dots Ru_2-Cl-Ru_2-Cl \dots$ strands exhibit zig-zag conformations with a Ru-Cl-Ru angle estimated as 112 (Figure 1). We succeeded now to solve the structure of the n=2 homologue. Its molecular structure corresponds to the typical lantern structure. Each chloride anion is coordinated to the axial positions of two different bimetallic units, giving rise to polymeric strands in a zig-zag conformation (Figure 2); the experimental Ru-Cl-Ru = 118 and Ru-Ru-Cl = 170, 172 angles agree well with the predicted values.

1) M. Rusjan, B. Donnio, B. Heinrich, F. Cukiernik, D. Guillon, *Langmuir* 2002, 18, 10116



Keywords: metallomesogens, diruthenium carboxylates, supramolecular architecture

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