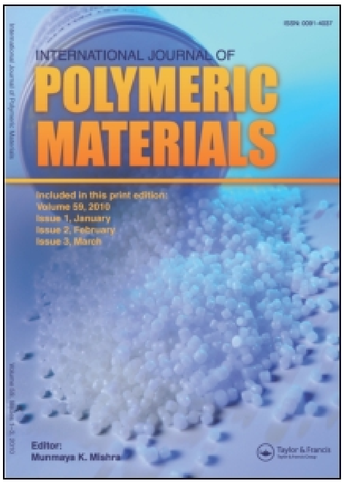
This article was downloaded by:
On: *19 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Structure and Physical Properties of Polymeric Supramolecular Assembly

Tisato Kajiyama[a]; Atsushi Takahara[a]
[a] Department of Materials Physics and Chemistry, Graduate School of Engineering, Kyushu University, Fukuoka, Japan

To cite this Article Kajiyama, Tisato and Takahara, Atsushi(2000) 'Structure and Physical Properties of Polymeric Supramolecular Assembly', International Journal of Polymeric Materials, 46: 1, 233 — 242

To link to this Article: DOI: 10.1080/00914030008054857

URL: http://dx.doi.org/10.1080/00914030008054857

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Intern. J. Polymeric Mater., 2000, Vol. 46, pp. 233-242
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under
the Gordon and Breach Science
Publishers imprint.
Printed in Malaysia.

Structure and Physical Properties of Polymeric Supramolecular Assembly

TISATO KAJIYAMA* and ATSUSHI TAKAHARA

Department of Materials Physics and Chemistry, Graduate School of Engineering, Kyushu University, Higashi-ku, Fukuoka 812-8581, Japan

(Received 25 September 1998)

Progress in structure and properties of polymeric supramolecular assembly in Japan is reviewed.

Keywords: Monolayer; Langmuir-Blodgett film; polymer thin film; rotaxane; dendrimer; supramolecular assembly; scanning force microscopy; surface force

1. STRUCTURE AND PROPERTIES OF POLYMERIC MONOLAYERS

Structure analysis of monolayers on the water surface is important for the structure control of monolayers. H. Yamaoka, H. Matsuoka *et al.* (3084, E794) measured X-ray reflectivity (XR) of amphiphilic diblock copolymer monolayers on the water surface. XR experiments were performed using liquid/vapor interface X-ray reflectometer designed by Yamaoka *et al.* [1]. A LB trough was equipped to the reflectometer, so that *in situ* measurements could be carried out for the spread monolayers on the water surface at different surface pressures. The layer thickness, and surface and interface roughness could be determined on the basis of XR. The amphiphilic diblock copolymers, poly(α-styrene)-poly(decyl 4-vinylpyridine) (P(αMSt)-b-P(4VP-C_{10})) were synthesized by a living anionic polymerization. The Kiessig fringes were observed

---

*Corresponding author.

for specular reflection measurement of P(αMSt)$_{50}$-b-P(4VP-$C_{10}H_{21}I$)$_{50}$ monolayers on the water subphase. The peak position of the Kiessig fringes was shifted to a lower angle with an increase in surface pressure. This indicates that the thickness of monolayer increased with an increase of surface pressure. The thickness and electron density of the P(αMSt)$_{50}$ and P(4VP-$C_{10}H_{21}I$)$_{50}$ layer in the P(αMSt)$_{50}$-b-P(4VP-$C_{10}H_{21}I$)$_{50}$ monolayer at 37 mN m^{-1} were determined by a curve fitting. Though the chain length of P(αMSt)$_{50}$ was 12.6 nm in all-*trans* conformation, the thickness of P(αMSt)$_{50}$ was 1.7 nm being indicative of the coiled conformation at high-surface pressure.

T. Seki, K. Ichimura *et al.* (3086, E794) investigated the photo-induced expansion and contraction responses in a poly(vinyl alcohol) derivative monolayer with azobenzene (Az) side chains at the air-water interface based on surface potential measurements, Brewster angle microscopy (BAM), UV-visible absorption spectroscopy, and the macroscopic area estimations with a Langmuir film balance. Surface potential measurements confirmed the model of photostimulated motions previously proposed. The BAM observation combined with a movable mini-trough allowed precise evaluations of the mechanical response of an isolated domain monolayer at zero pressure, which can be regarded as providing the inherent attributes. In comparison with the corresponding UV-visible spectroscopic data, the expansion process on UV light (365 nm) illumination was found to show a nonlinear response with photoreaction, which was characterized by the existence of an induction period. Initiation of the film expansion required ca. 40% conversion of the *trans*-to-*cis* photoisomerization. This method also confirmed a self-contracting motion on visible light (436 nm) illumination. Based on macroscopic area evaluations monitored at each applied surface pressure, the photoresponding behavior was found to include large artificial distortions. This work clarified, for the first time, the inherent photomechanical response and its cooperativity in the monolayers at the air-water interface.

Scanning force microscopy can be utilized as a novel tool to measure local mechanical properties of monolayers. T. Kajiyama, A. Takahara *et al.* (3269, E824) studied the surface mechanical properties for the immobilized organotrichlorosilane mixed monolayers [2] by using a temperature-controllable lateral force microscope (LFM). Lateral force microscopic measurement was performed for the octadecyltrichlorosilane (OTS)/(2-perfluorooctyl)ethyltrichlorosilane (FOETS) mixed monolayer prepared by the Langmuir method. The monolayers were immobilized onto the Si-wafer. The magnitude of the lateral force increased with an increase in alkyl chain length due to an increase in shear strength among alkyl chains. The temperature dependence of lateral force for the OTS and the FOETS monolayer was evaluated. The magnitude of the lateral force of the OTS monolayer decreased in the temperature from 123–203 K and 313–318 K, that might be attributed to the transformation of crystalline form from rectangular form to hexagonal one and the melting of alkyl chains. On the other hand, in the case of the FOETS monolayer, a decrease in lateral force was observed in the temperature range of 260–280 K, may be due to the melting of fluoroalkyl chains.

2. POLYMER THIN FILMS

N. Okui, T. Kikutani *et al.* (3369, E841) prepared the polyamide thin films onto Cu substrates by alternating vapor deposition polymerization (AVDP) method. Four kinds of bifunctional monomers were deposited alternatively onto the substrate. Polyamides studied were Nylon i, j, k, l where the numbers i, j, k, l indicates the carbon number of diamine, acid dichloride, diamine, and acid dichloride monomers, respectively. The film thickness increased with a number of vapor deposition cycles. Polymerization was confirmed by infrared spectra. Wide-angle X-ray diffraction in symmetrical reflection geometry was carried out in order to characterize crystal form and crystal orientation. The (hkl) diffraction was not observed. Nylon 6, 6, 6, 10 and Nylon 7, 9, 9, 9 showed a scattering peak in a low Bragg angle region which corresponded to the layer spacing. Nylon 6, 6, 10, 10 did not show any apparent diffraction peaks. The film structures was not dependent on the odd/even carbon numbers of each monomer but the repeating unit lengths of nylon systems.

H. Ozaki (3267, E824) prepared a single sheet with one or two-dimensional superstructure formed by a monolayer reaction. Plane or chain molecules vapor-deposited onto a clean surface of cooled graphite formed a monolayer in which they were laid flat and closely packed. They were liable, however, to be desorbed as well as be disordered in aggregation when heated to room temperature in an ultrahigh vacuum. Such a monolayer are considered as a stage for controlled chemical reaction because adequate mobility and aggregation of molecules indispensable for the reaction can be effectuated by regulating the substrate temperature. Two types of monolayer reactions were used to prepare a planar carbon network (an organic monoatomic layer). One dimensional surface topochemical reaction (STR) of lying 17,19-hexatriacontadiyne (HTDY) and two-dimensional STR of 1,15,17,31-dotriacontatetrayne (DTTY) produced a single sheet of a sashlike (atomic sash) and a clothlike macromolecules (atomic cloth), respectively. On the other hand, the surface self assembly of planar macromolecules having polar groups with hydrogen bonds gave a tapelike supermolecule (atomic tape). The atomic tape formation was observed for 1,4-bis((4-carbonylphenyl)-ethynyl)benzene) (BCB). The formation of these superstructures were confirmed by Penning ionization electron spectroscopy (PIES) and scanning tunneling microscopy (STM).

Conjugated polymers are very interesting if one can intentionally modify the size and shape of wave functions of delocalized π electrons. To realize such modification, Munekata *et al.* (3389, E844) prepared crystalline polydiacetylene (PDA) thin films onto semiconductor substrates such as GaAs by a molecular beam deposition. PDA studied was poly(5,7-dodecadiyne-1,12-diyl-bis-butylurethane) polycrystal prepared by photopolymerization. The structure of PDA thin films was investigated with Raman microscopy and atomic force microscopy (AFM). Single crystal wires and sheets with the width and thickness of a few tens of nanometers were prepared in a large area under proper growth conditions.

3. PATTERNING OF ULTRATHIN ORGANIC FILMS

Two dimensional molecular arrangement control of organic thin films is important to design novel molecular devices [3]. Y. Oishi, T. Kunitake *et al.* (3156, E806) proposed a molecular arrangement control method in the organic monolayers by homo and hetero molecular recognitions through hydrogen bonding on the basis of AFM observations. Dialkyl guanidium lipid molecules in the monolayer transferred from pure water were randomly arranged, whereas those in the monolayer transferred from an aqueous solution of sodium oxalate were regularly arranged in a hexagonal packing. This result indicates that the crystallization of the amorphous monolayer on the pure water was induced by the homo recognition of a sodium oxalate template. Furthermore, the two-dimensional molecular patterning with respect to a height difference is presumably formed by rearrangement of the two monolayer components of guanidium and orotate through the hetero recognition of a flavin adenine dinucleotide template.

For the construction of ultrahigh density memory devices, it is indispensable to fabricate memory-recognizable molecular scale pits with unique distributions on number density, volume, and distance in the memory device. T. Kajiyama *et al.* (3307, E831) fabricated nanometer scale pits in the fatty acid monolayers and their Langmuir-Blodgett (LB) films by using a cantilever tip of AFM. The pits were fabricated by a mechanical and an electrical fabrication methods. The mechanical fabrication method was carried out by shaving the lignoceric acid monolayer by the mechanical lateral vibration of cantilever tip, and resulting in the formation of the square shaped pit with $20 \times 20\,\mathrm{nm}^2$. In the case of an electric field-induced fabrication method, the pits were fabricated by applying voltage between metal coated AFM probe tip and thin film substrate. This method can fabricate the small circular pit with $6 \times 8\,\mathrm{nm}^2$ and can control the spatial distribution of pits. From these results, it can be considered that the spatial distribution of nanometer scale pits in the LB film can be controlled by electric field-induced fabrication method.

LB films can be applied to fabricate high-resolution resists for the preparation of integrated circuits with higher densities. T. Miyashita *et al.* (3313, E832) prepared a novel photo-crosslinkable LB film consisting of *N*-dodecylacrylamide and *N*-ω-acryloylundecyl-4-vinylpyridium salt. The photographic property of the cross-linkable polymer LB film was investigated by UV adsorption spectroscopy and profilometry. The photographic sensitivity dose linearly depended on the number of monolayers. The photographic sensitivity per monolayer was determined to be $3.3\,\mathrm{mJ\,cm}^{-2}$. On the other hand, the photographic contrast was 1.7, being irrespective of the number of deposited monolayers. Drawing patterns of the bilayer films using photolithographic technique was observed by AFM. It was demonstrated that the cross-linkable polymeric LB films could be used to create high-resolution molecular patterning with nanometer (layer) thickness.

The ordered patterns of nanosize polystyrene aggregates have been observed by rinsing a mica surface with a dilute polymer solution in benzene. M. Shimomura, S. Nishimura *et al.* (3341, E836) investigated a mesoscopic pattern formation of polyfunctional polymers such as polyhexylthiophane, (azobenzene containing amphiphile/polyanion) ion complex and photocrosslinkable stilbazol copolymers. AFM observation showed a honey comb pattern formation. UV-Vis spectra revealed that the formation of bilayer structure in the polyion complex. The azobenzene showed *cis-trans* isomerization, even in the bilayer membrane. Also, the polyhexylthiophene showed microdot structure.

N. Kimizuka, T. Kunitake *et al.* (3315, E832) reported a newly developed technique for the construction of 2D-molecular assemblies on solid supports. The new technique called Molecular Trans Patterning, consists of pre-organization of molecules or small particles on gel-surfaces, and subsequent transfer of them to solid supports. Silica nano-particles and tobacoo mosaic virus were pre-organized at the surface of agarose gel by solvent casting. The resultant films were successfully transferred onto modified silica surfaces and highly oriented pyrolytic graphite surfaces. 2D-organization of these mesoscopic materials were examined by AFM and scanning electron microscopy (SEM).

4. POLYROTAXANES

Rotaxane are the compounds consisting of noncovalent entities called "rotor" and "axle". Rotaxane containing number of rotors is called polyrotaxane. Cycrodextrin (CD) interacts with various polymers with high specificity, resulting in the formation of a crystalline inclusion complex in which the CD molecules are threaded by a polymer chain [4]. α-CD forms inclusion complexes with poly(ethylene glycol) (PEG), poly(propyrene glycol) (PPG), poly(oxytrimethylene) and poly(tertrahydrofuran), β-CD forms complexes with PPG and polypropyrene. A. Harada, M. Kamachi *et al.* (3237, E819) reported synthesis of novel polyrotaxanes from γ-CD and PPG end capped with 9-anthracences(9An) dimer. The PPG derivatives with 9An-ends and an aqueous solution of γ-CD were stirred in the dark to give a crystalline inclusion complexes. The mixture was exposed with visible light with a Xe lamp. The products precipitated were collected and purified with size exclusion chromatography (SEC) to give pure polyrotaxanes (PPG-γ-DAn). The characterization of PPG-γ-DAn was carried out by ^{1}H-NMR, ^{13}C-NMR, UV-Vis, FT-IR. It was confirmed that γ-CD can thread through the bulky An in the end group of PPG and formed the inclusion complex. Photodimerization of An gave totally different high molecular weight complex.

K. Ito, R. Hayakawa *et al.* (3229, E818) investigated an inclusion-dissociation behavior in a complex formation between molecular nanotubes and linear polymer chains in solutions on the basis of the Flory-Huggins lattice model. It was revealed that the reversible inclusion-dissociation behavior between nanotubes and linear polymers and that the behavior becomes a first order transition in a poor solvent. On the other hand, in the case of a good solvent, the polymer chains were gradually dissociated from or included into the tubes with varying temperatures. The inclusion behavior of linear and star polymers into nanotubes was confirmed by the optical absorption and quasielastic light scattering (QELS) studies. The theoretical curves for the inclusion ratio of nanotubes fitted well to the experimental results obtained from the absorption spectra. QELS, measurement revealed that the size of the inclusion complex for the star polymers was much larger for the linear polymers. This apparently indicates the formation of supramolecular structure consisting of nanotubes and star polymers.

T. Ooya, N. Yui (3245, E820) synthesized polyrotaxanes as novel biodegradable polymers with supramolecular assembly. The synthesis of biodegradable polyrotaxanes consists of three steps: preparation of an inclusion complex consisting of α-CD and amino-terminated PEG, introduction of *L*-phenylalanine (*L*-Phe) at each complex terminal *via* peptide linkages, and hydroxypropylation of α-CDs in the polyrotaxanes. Succinimide ester of benzyloxycarbonyl-*L*-Phe was condensed with the terminal amino groups of the inclusion complex. H^1-NMR and GPC results showed that α-CDs were threaded onto a PEG chain and *L*-Phe moieties were introduced at each terminal of the PEG chain. Further, the amounts of threaded α-CDs were found to be governed by the molecular weight of PEG. The hydroxypropylation of α-CDs improved the solubility of the polyrotaxanes in PBS (pH 7.4). The hydroxypropylated (HP-) polyrotaxanes were characterized by terminal peptide cleavage using papain. *In vitro* degradation of the HP-polyrotaxanes revealed that the HP-α-CDs threaded onto a PEG chain were released only when terminal peptide linkages were cleaved. The kinetics of terminal peptide cleavage were also evaluated by catalytic efficiency. The catalytic efficiency was found to be independent on the molecular weight of the HP-polyrotaxanes but to be affected by terminal hydrophobic moieties. The designed polyrotaxanes might be applicable for the novel drug carriers.

5. DENDRIMERS AND NANOPARTICLE

Dendrimers are hyperbranched macromolecules with a regular tree-like array of branch units [5]. Sugar balls are typical functional dendrimers having molecular recognition ability. K. Aoi, M. Okada *et al.* (3188, E811) prepared sugar ball with various chemical structures. Assembly of AB-type surface block poly(amido amine) dendrimer (generation 2.0) with both *O*-(*N*-acetyl-D-glucosamine)-substituted serine terminal groups for the hydrophilic block and *n*-hexyl groups as the hydrophobic block was investigated. Surface tension of the amphiphilic dendrimer was examined by a drop-weight method. A critical micelle concentration was clearly observed for the dendrimer solution. This indicates that the dendrimer has a potential to form dendrimer monolayer on the water subphase. It was revealed that *n*-hexyl groups behaves effectively as a hydrophobic block on the dendrimer surface. Based on the control on the hydrophobic and hydrophilic balances of sugar ball, the supramolecular assembly of sugar ball can be constructed.

T. Serizawa, M. Akashi *et al.* (3331, E835) studied the monolayer deposition of polystyrene nanosphere onto a polymer surface prepared by a layer-by-layer adsorption method. Quantitative analyses of the adsorption amount by a quartz crystal microbalance (QCM) revealed that the adsorption behavior of the nanospheres was strongly influenced by the concentration and ionic strength in an aqueous solution of the nanosphere. Scanning electron microscopic (SEM) observation revealed that the nanosphere could be adsorbed on the polymer surface with a fairly constant distance due to an electrostatic interaction. The surface properties of polymer surface and the sizes of nanoparticles drastically affected the adsorption behavior.

6. SURFACE FORCES

Nanometer range of interactions and structures of supramolecular assemblies have been studied on the basis of force-distance profiles measured with a surface force apparatus (SFA) [6]. SFA can measure the magnitude of attraction or repulsion forces between two surface directly as a function of the separation, which allows us to analyze the origin of observed forces, for example, van der Waals, electrostatic, and others. Surface force measurements have been also carried out for investigation of specific interaction and nonspecific interaction between proteins, polypeptides and nucleic acid immobilized on the surface. For these purposes, it is necessary to develop a method of attaching the molecules such as proteins on the surface in a desired orientation. SFA has allowed accurate measurement of surface and intermolecular forces. However, only a limited number of system could be investigated because of restriction of the sample geometry. In contrast, force measurement by AFM is relatively easy to use. E. Ishiguro, K. Kurihara *et al.* (3114, E799) prepared LB film which could bind His-tag proteins through specific interaction between metal-chelating lipids and polyhistidine stretches *via* Cu(II) ion and measured forces between protein monolayers by AFM. Measured surface forces between protein monolayers were attributed to the electric double layer force owing to the surface charge and also to steric force due to compression of the protein monolayer. Surface charge density might be in a strong relation to compressibility of the protein monolayer determined from force profiles. This technique would be useful for studies on physical properties of proteins as well as specific biological interactions involving proteins.

M. Hato, S. Ohnishi *et al.* (3110, E7999) have investigated the morphology and surface forces of protein A adsorbed on mica surface in protein solutions of various concentrations. The force-distance curves, measured with a SFA, were interpreted in terms of two different regimes: a "large-distance" regime in which an electrostatic double-layer force dominates, and an "adsorbed layer" regime in which a force of steric origin dominates. To further clarify the forces of steric origin, the surface morphology of the adsorbed protein layer was investigated with AFM because the steric repulsive forces are strongly affected by the adsorption mode of the protein A molecules on mica. At lower protein concentrations of 2 ppm and 10 ppm, protein A molecules were adsorbed "side-on" parallel to the mica surfaces, forming a monolayer with thickness of ca. 2.5 nm. AFM images at higher concentrations of 30 ppm and 100 ppm showed protruding structures from the monolayer. This indicates that the adsorbed protein molecules end-oriented into the solution, with the remainder of each molecule adsorbed side-on to the mica surface. These extending ends of protein A overlapped each other and formed a "quasi-double layer" over the mica surface. These AFM images confirmed the existence of the monolayer of protein A molecules at low concentrations and the "quasi-double layer" with occasional protrusions at high concentrations, which were consistent with the adsorption mode observed in the force-distance curves.

References

[1] Yamaoka, H., Matsuoka, H., Kago, K., Endo, H. and Eckelt, J. (1998). *Physica B*, p. 248.
[2] Kajiyama, T., Ge, S.-R., Kojio, K. and Takahara, A. (1996). *Supramol. Sci.*, **3**, 123.
[3] Wiesendanger, R. (1994). *J. Vac. Sci. Tech.*, **B12**, 515.
[4] Harada, A. (1997). *Adv. Polym. Sci.*, **133**, 142.
[5] Frecht, J. M. J. (1994). *Science*, **263**, 1740.
[6] Israelachvili, J. N. and Tabor, D. (1972). *Nature*, **236**, 106.