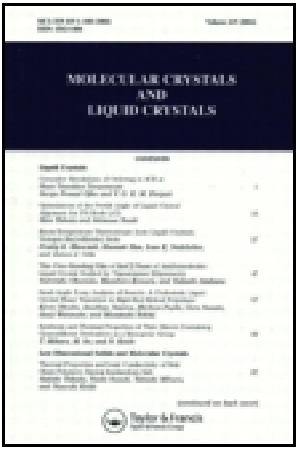

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Molecular Organization of Comb-Like Polymers Containing Long Fluorocarbon Chains in the Thin Films Formed by the LB and Lift-Up Methods

Yoshio Shibasaki [a] , Zhiqin Zhu [a] & Kiyoshige Fukuda [a]

[a] Saitama University, Urawa, 338-8570, Japan

To cite this article: Yoshio Shibasaki, Zhiqin Zhu & Kiyoshige Fukuda (1999): Molecular Organization of Comb-Like Polymers Containing Long Fluorocarbon Chains in the Thin Films Formed by the LB and Lift-Up Methods, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 337:1, 165-168

To link to this article: http://dx.doi.org/10.1080/10587259908023403

Mol. Cryst. and Liq. Cryst., 1999, Vol. 337, pp. 165-168
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

Molecular Organization of Comb-Like Polymers Containing Long Fluorocarbon Chains in the Thin Films Formed by the LB and Lift-Up Methods

YOSHIO SHIBASAKI, ZHIQIN ZHU and KIYOSHIGE FUKUDA

Saitama University, Urawa 338–8570, Japan

Molecular organization in layered structures, which can be caused by side-chain crystallization of a comb-like polymer having long fluorocarbon chains, and the structure of thin films formed by LB and lift-up methods, have been investigated, in comparison with those of poly(octadecylacrylate).

Keywords: molecular organization; comb-like polymers; fluorocarbon chains; thin film; LB method; lift-up method

INTRODUCTION

A comb-like polymer containing a sufficiently long fluorocarbon chain in the side chains is crystallized easily. Because fluorine atom is too large to allow a precise trans zig-zag planar conformation of $-(CF_2-CF_2)_n-$ chain, the side chains are rather rigid and the cohesive force among them is strong[1-3]. In this paper, molecular organization in the thin films formed by the LB and lift-up methods has been examined on the bases of cohesive energy and conformational freedom of the comb-like polymer chains.

EXPERIMENTAL

1H,1H,11H-icosafluoroundecyl acrylate ($H(CF_2)_{10}CH_2OCOCH=CH_2$, $F_{10}A$, mp 44.0-45.4℃); 1H,1H,9H-hexadecafluorononyl acrylate ($H(CF_2)_8CH_2OCOCH=CH_2$, F_8A, mp -21.6℃) were bought from Daikin

Fine Chemicals. F$_{10}$A was used after purification by recrystallization from ethanol solution, while F$_8$A was used as received. Their polymers (PF$_{10}$A and PF$_8$A) and poly(octadecyl acrylate) (PC$_{18}$A) were prepared by γ-ray-irradiation post-polymerization. Thermal properties of these polymers were measured using a Seiko Instruments Model DSC6200 differential scanning calorimeter (DSC). For additional characterization of the film structure, a JEOL FT-IR spectrophotometer Model JIR-100 and a Rigaku diffractometer RAD-B with Cu Kα radiation were used.

Monolayer of PF$_{10}$A was spread from methylethylketone solution (6.3×10^{-4}M) and surface pressure-area (π-A) isotherms were measured using a Lauda film balance. LB films were deposited on a CaF$_2$ plate using a KSV apparatus (LB2200) with a dipping speed of 10 cm min^{-1} at 30 mN m^{-1}. In the case of lift-up method, the CaF$_2$ plate of hydrophobic surface with a ferric stearate monolayer immersed vertically into the dilute solution of PF$_{10}$A, and then it was slowly withdrawn.

RESULTS AND DISCUSSION

Estimation of Cohesive Energy Among Side Chains

Cohesive energies among fluorocarbon chains in the comb-like polymers were estimated by the DSC measurements. Thermal property of PF$_{10}$A,PF$_8$A and PC$_{18}$A are summarized in Table 1, where T$_m$ and T$_c$ are temperatures of melting and crystallization, ΔH_f and ΔH_c are molar heats of fusion and crystallization per repeating unit, respectively, and ΔS_f and ΔS_c are corresponding entropy changes.

Table 1 Thermal Properties of Comb-like Polymers

Sample	T_m	T_c	ΔH_f	ΔH_c	ΔS_f	ΔS_c
	℃		kJmol^{-1}		JK^{-1}mol^{-1}	
PF$_{10}$A	118.2	105.1	12.6	11.4	32.2	30.1
PF$_8$A	54.7	19.9	6.1	3.7	18.5	12.6
PC$_{18}$A	53.7	46.3	22.7	19.3	69.5	60.2

The values of ΔH_c seem to reflect the cohesive energies and those of ΔS_c indicate regularity of lammelar structure formed by side chains. Values of ΔH_c and ΔS_c for PF$_{10}$A are about half of those for PC$_{18}$A. Thus, it can be expected that PF$_{10}$A has a sufficient cohesive energy among the side chains to form the thin solid film with lamellar structure, whereas cohesive energy for PF$_8$A is insufficient.

Film Formation by LB and Lift-up Methods

These comb-like plymers can form stable condensed monolayeres at the air-water interface up to 70 mNm^{-1}. From the π-A isotherms, as shown in Fig.1, it has been found that the monolayer of $PF_{10}A$ has a tendency to condense with the increase of temperature, whereas that of $PC_{18}A$ tends to expand. The limiting areas per side chain of $PF_{10}A$ were 0.23 nm^{-2} at 15℃ and 0.21 nm^{-2} at 25℃, while those of $PC_{18}A$ were 0.27 nm^{-2} at 15℃ and 0.29 nm^{-2} at 25℃. Therefore, formation of LB films at a higher temperature seems to be rather preferable for $PF_{10}A$, while a lower temperature will be better for $PC_{18}A$.

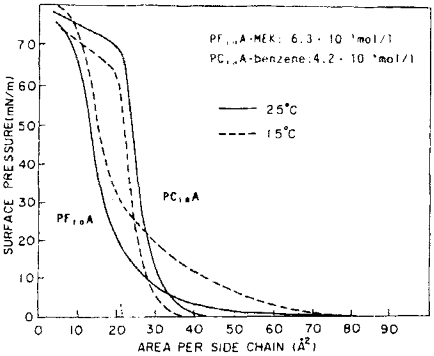

FIGURE 1 π-A isotherms of $PF_{10}A$ and $PC_{18}A$.

In the case of hydrohobic plate, only first cycle was Y-type deposition and followed by X-type deposition. On the contrary, with the hydrophilic plate, first two cycles were Z-type deposition and further deposition was difficult.

The thin film of $PF_{10}A$ formed by the lift-up method has a lamellar structure which is similar to the LB film. This can be ascribed to the adsorption of the comb-like polymers on the solid surface followed by the side-chain crystallization.

Film thickness, as estimated by IR measurements, was decreased with the increasing of lift-up speed, and in the case of speed faster than 0.10 cm min^{-1} the film formation by this method was impossible. The adsorption of comb-like polymer as well as the side-chain crystallization is considered to be a time-consuming process because of the entanglement of comb-like polymer chains. Film thickness increased linearly with the solution concentration.

X-Ray diffraction patterns, as shown in Fig.2, indicate that regularity of the lamellar structure of the $PF_{10}A$ films formed by the lift-up method is less than those in the LB film but better than those in cast film.

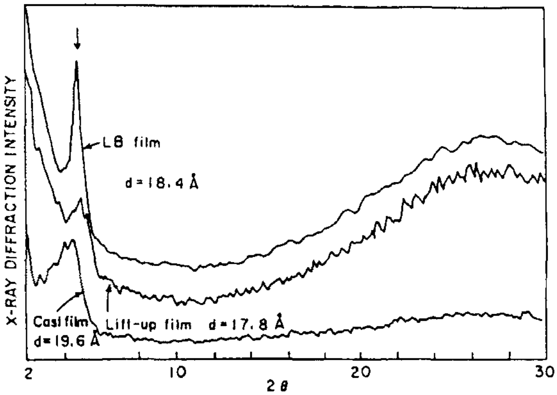

FIGURE 2 X-Ray diffraction patterns for films of $PF_{10}A$.

In these cases, the structure of films is considered as a single layer rather than an interdigitated anti-parallel packing of side chains[4].

Mechanism of film formation on the solid surface by the lift-up method can be considered as follows. When the solid plate is immersed in the solution of $PF_{10}A$, at first the comb-like polymers are adsorbed on the surface, followed by self-organization of long fluorocarbon chains. Additional polymer chains may be deposited successively on the initially adsorbed polymer, and rearranged forming a somewhat ordered lamellar structure. Furthermore, in the lift-up process of solid plate, according to evaporation of solvent the local concentration of $PF_{10}A$ at meniscus on the plate should be increased.

References

[1] J. Schneider, C. Erdelen, H. Ringsdorf and J.F. Rabolt, Macromolecules, **22**, 3475(1989).
[2] Y. Shibasaki, Z.-Q. Zhu and K. Fukuda, J. Nanjing Univ., **31**, 335 (1995).
[3] Y. Shibasaki, H. Saitoh and K. Chiba, J. Thermal Analysis, **49**, 115(1997).
[4] L.D. Budovskaya, V.E. Ivanova, L.N. Oskar, S.V. Lukasov, G.B. Yu, et al., Polymer Sci. U.S.S.R., **32**, 502(1990).