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Investigation into Monolayers and Multilayers of Star-Shaped Graft Copolymer Based on Styrene–Divinylbenzene Microgel Cores

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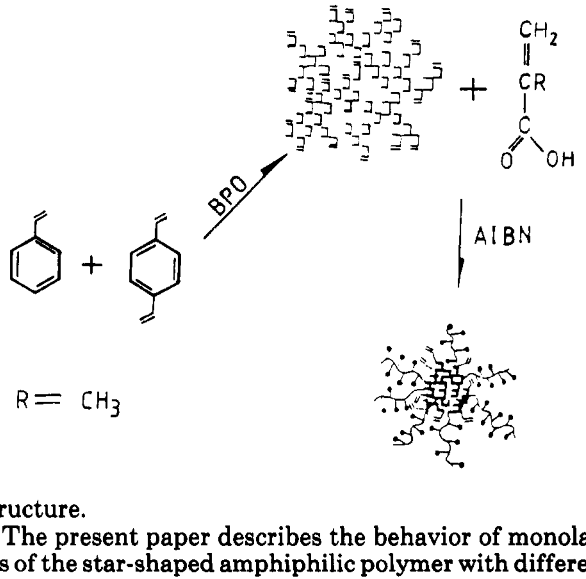
ABSTRACT: A new kind of amphiphilic polymer, composed of a hydrophobic styrene–divinylbenzene (St–DVB) microgel core, several hydrophilic branching chains of poly(methacrylic acid), and some pendent vinyl groups attached to the core, was synthesized by means of free-radical polymerization and grafting. The behavior of the monolayers and multilayers of the amphiphilic polymer was studied by surface pressure–area curves and scanning electron microscopy (SEM). The SEM photographs show that these amphiphilic macromolecules spread on the water surface in aggregations, and these aggregations disperse with the increase in hydrophilic content of the polymer. "Y"-type multilayers of the amphiphilic polymer on substrate were first built by the Langmuir–Blodgett (LB) technique. The layer structure was confirmed by X-ray diffraction. The thickness of one monolayer of the amphiphilic polymer with 30% PMA content is ~29 Å. The LB layers can polymerize further to form a cross-linked layer structure because this kind of amphiphilic polymer is also a kind of macromonomer.

Introduction

Langmuir–Blodgett (LB) films made from amphiphilic molecules with low molecular weights exhibit relatively poor thermal and mechanical stabilities. To overcome this disadvantage, Cemel[1] and many other research groups have pursued the method of forming LB film from suitable monomers and then inducing the film to polymerize by a suitable physical treatment such as UV irradiation. Another method involves the preparation of monolayers of suitable preformed amphiphilic polymers at the air–water interface and then the monolayers are deposited onto suitable substrates by the conventional LB technique.[2-6] Although the behavior of many common polymers such as PS, PMMA, and PVA on air–water interfaces has been investigated,[7,8] it has still proved difficult to spread these polymers onto substrates vertically via compact monolayers and impossible to form ordered LB multilayers.

It is well-known that large amounts of proteins are incorporated in lipid bilayers. If experimental conditions such as pH and temperature are changed, these proteins may aggregate to some extent to form a local stable two-dimensional protein membrane. Taking account of these findings, we designed a new type of amphiphilic polymer. Its hydrophobic part is a soluble styrene–divinylbenzene (St–DVB) microgel, and the hydrophilic part consists of several branched chains of PMA or other hydrophilic polymer. It is an amphiphilic star-shaped graft polymer. Scheme I shows the method of preparation and molecular structure.

Scheme I
Synthetic Process of the Star-Shaped Amphiphilic Polymer



The present paper describes the behavior of monolayers of the star-shaped amphiphilic polymer with different weight percentages of the hydrophilic part and the plasticizing function of stearic acid applied to the polymer monolayers studied by π–A curves and scanning electron microscopy (SEM). A possible model for this polymer monolayer at the air–water interface is proposed in which the hydrophilic chains of the amphiphile dissolve in the water, and its hydrophobic microgel cores float on the

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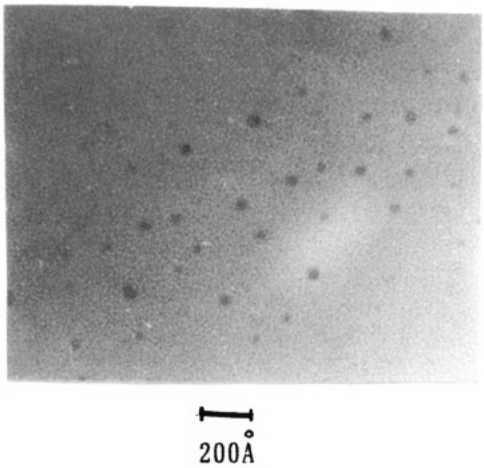


Figure 1. TEM picture of St–DVB microgel.

water surface. With increase in the proportion of the hydrophilic part of the polymer, the hydrophobic gel cores change from aggregation to dispersion, and their shapes vary from spherical to flat, just like "duckweeds" for dispersed monomolecules. The difference from the conventional concept is that the LB film is usually made from simple molecules with well-known structures, but this is the first example of an LB film that is composed of such a complex molecule, namely, a star-shaped graft polymer. Furthermore, because of the large number of vinyl groups left in the microgel, the amphiphilic molecule in the LB film could be polymerized again to form a cross-linked layer structure. Therefore, this star-shaped amphiphilic polymer may be classed as a kind of macromonomer.

Experimental Section

(1) St–DVB Microgel. The experimental conditions for the synthesis of the microgel were stated elsewhere.[9] The microgel prepared had a molecular weight of 15 000 with an average diameter of ~40 Å (Figure 1). Translation diffusion of the St–DVB microgel in a good solvent (tetrahydrofuran) and a Θ solvent (cyclohexane) was studied by photon correlation spectroscopy.[10] It was shown that the microgel took the shape of an ideal sphere in solution, and the equivalent hydrodynamic radius of the microgel in cyclohexane was 67 Å as calculated from the Stokes–Einstein relation. Furthermore, the microgel can be dissolved in solvents such as toluene, benzene, THF, trichloromethane, and so on. Therefore, it is a kind of soluble and spherical gel core with a low cross-linking density.

(2) Grafting on Polymer Microgel. Gel cores (100 mg), AIBN (30 mg), methacrylic acid, (5 mL) and THF (60 mL) were mixed in a reaction flask at 60 °C. After a short time (10–40 min), 10 mg of hydroquinone was added to the solution, and the temperature was lowered to room temperature to quench the reaction. THF was partially evaporated at 35 °C by using a rotary drier coupled to a vacuum pump. The remaining solution was poured into excess methanol to precipitate the amphiphilic polymer. The amphiphilic polymer was dissolved in THF and precipitated in methanol repeatedly to separate it from homopolymer PMA. After drying at 25 °C in a vacuum oven, the amphiphilic polymer was kept at 4 °C.

(3) Preparation of Monolayers. The monolayers were prepared by spreading a drop of the solution of the amphiphilic polymer dissolved in a mixture solution of DMF/chloroform (2:8 (v/v)) with a concentration of 0.5 mg/mL on water. Usually the surface pressure–area (π–A) curves were measured with a commercial LB film balance (Model Jida C-1, Changchun, China) at a compression rate of 4.5×10^{13} nm^2/s and a temperature of the subphase of 20 °C. The transfer ratio of the amphiphilic polymer with different grafting degrees (10–30%) was 1.0. The water was distilled four times from a quartz still.

(4) Preparation of Multilayers. Langmuir–Blodgett multilayers were prepared by means of a commercially available film balance on a pure aqueous subphase or 10^{-3} mol/L of $PbCl_2$ in aqueous solution at 20 °C. Multilayers could be deposited by Y-type deposition on various materials such as silanized quartz, monocrystal silicon, CaF_2 monocrystal, etc. The dipping speed of the substrate was chosen to be ~0.2 cm/min, and the compression pressure at each dipping was 25 mN/m. Between subsequent dips, the samples were allowed to dry in air for 4 h to avoid retransferring the last deposited monolayer to the water surface.

As the grafting degree, the weight percentage of the hydrophilic part, of the amphiphilic polymer varied from 10% to 30%, the transfer ratio was still 1.0, no matter how many times the dipping cycle was repeated. However, when the grafting degree was <10% or >40%, the transfer ratio became <1.0.

(5) Measurements. Infrared spectra were recorded on a FT-5DX spectrophotometer. The IR spectra for LB monolayers deposited on CaF_2 crystals were obtained with 500 scans at a resolution of 2 cm^{-1} under an atmosphere of N_2. The measurements of molecular weights of the microgel were performed on a Knauer membrane osmometer, using toluene as solvent. SEM photos were obtained with a Hitachi X-650 scanning electron microscope at 25 kV, 200 Å gold metalization. Contact angles of water on the surface of LB films were measured on an Erma contact angle meter Type 2 goniometer. Low-angle X-ray diffraction experiments were performed on a D/Max-rA X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å). The number of vinyl groups (N) in the microgel core in the solution was calculated from a standard curve of UV spectra recorded on a Shimadzu UV-260 spectrophotometer according to Malinsk's method.[9] Thus it was easy to obtain the average number of vinyl groups per microgel from $n = N/[(W/M)N_A]$, where N_A is the Avogadro number and M and W are the molecular weight and the weight of the microgel. The branching degree was estimated by determining the number of vinyl groups reduced per microgel core. The degree of grafting (weight percent) was measured and calculated by elemental analysis and from the IR standard curve of a PMA–poly(St–DVB) blend.[9]

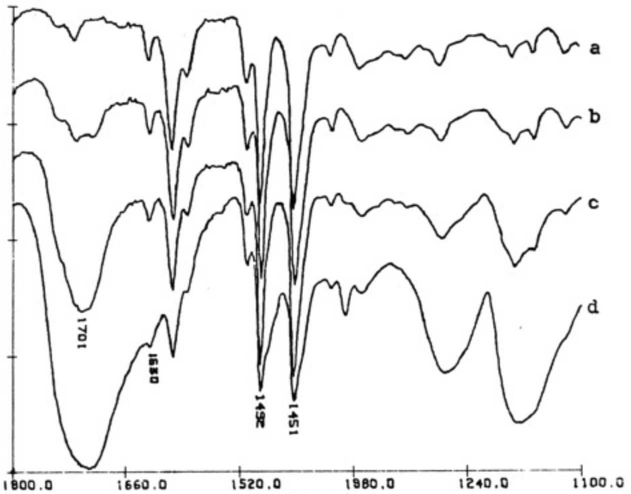


Figure 2. IR spectra of star-shaped amphiphilic polymers with different PMA contents (wt %): (a) 2; (b) 6; (c) 18; (d) 80 (water soluble).

Results and Discussion

Characterization of the Star-Shaped Amphiphilic Polymer. The IR spectrum showed the characteristic C=O absorption of PMA at 1701 cm^{-1} enhanced by the increase in the degree of PMA grafting on the St–DVB microgel core (Figure 2). Even when the graft reaction had finished, there were still many pendent vinyl groups on the microgel core (1630 cm^{-1}, Figure 1 and Table I). By varying the grafting time, we could control the grafting percentage and branching degree (Table I). The solubility of the amphiphilic polymer changed from oil soluble to water soluble with increase of PMA content (Table II).

Table I
Relationship between Grafting Reaction Time and Grafting Degrees of the Amphiphilic Polymers

sample	reacn time, min	PMA content, wt %	$M_n \times 10^{-4}$	branching degree[a]
1	0	0	1.10	0
2	15	6.7	1.18	2
3	20	12	1.25	4
4	25	26	1.49	10
5	35	30	1.57	13

[a] Calculated from variations of vinyl groups. The vinyl groups for an ungrafted microgel core number 62 (average).

Table II
Solubilities of the Star-Shaped Amphiphilic Polymers with Various PMA Contents in Different Solvents

PMA content, wt %	THF	DMF	methanol	water
<5	sol[a]	sol	insol	insol
5–40	insol	sol	insol	insol
55–80	insol	sol	sol	insol
80<	insol	sol	sol	sol

[a] sol = soluble, insol = insoluble.

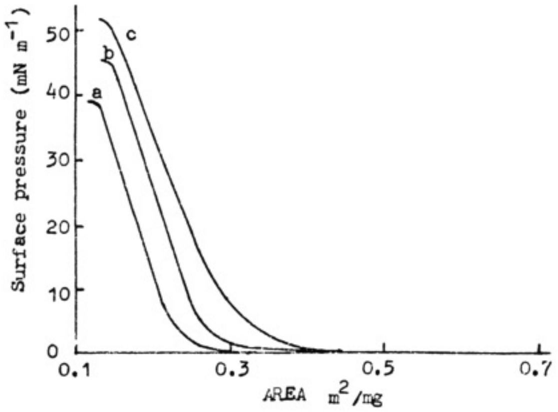


Figure 3. Pressure–area isotherms of star-shaped amphiphilic polymers with different PMA contents (wt %): (a) 15; (b) 24; (c) 30.

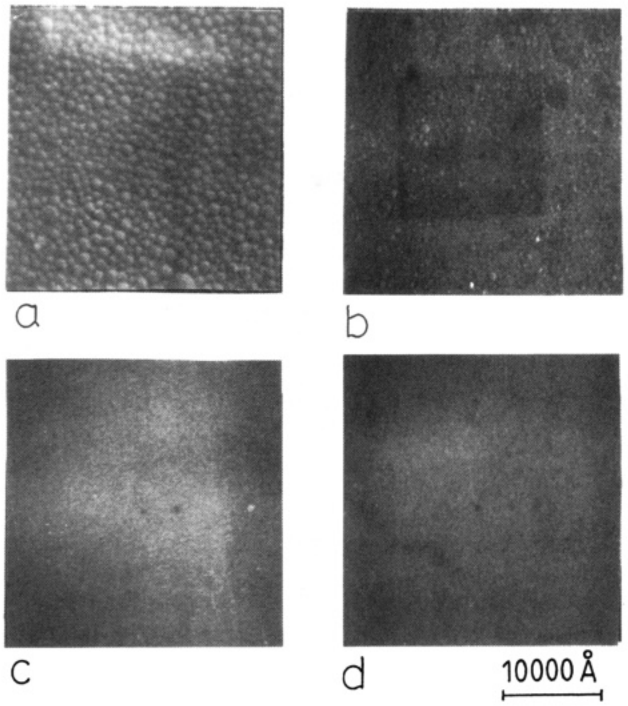


Figure 4. SEM pictures of star-shaped amphiphilic polymer monolayers with different PMA contents (wt %): (a) 9; (b) 15; (c) 24; (d) 30. Deposited on glass, gold covering.

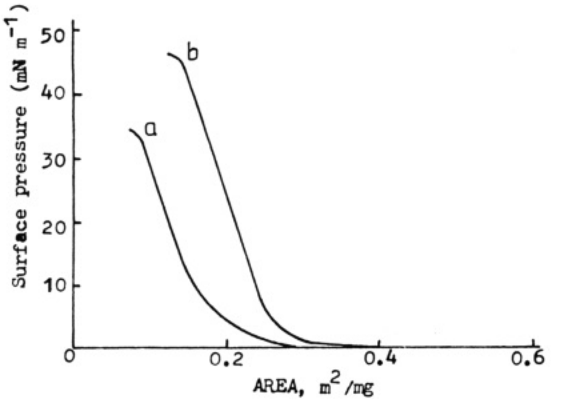


Figure 5. Pressure–area isotherms of star-shaped amphiphilic polymer (24% PMA): (a) from 10^{-3} M $PbCl_2$ subphase; (b) from pure water subphase.

Monolayer Study. (1) Spreading Behavior of Amphiphilic Polymers with Different PMA Contents. The spreading behavior of star-shaped amphiphilic polymers with various PMA contents is shown in Figure 3. The SEM photographs of the monolayers are shown in Figure 4. These figures show that if there are fewer hydrophilic groups, the polymer amphiphiles spread not as monomolecules but as an aggregate at the water surface because of the strong hydrophobic force between the polystyrene gel cores. The diameters of these aggregate domains are ~1000–3000 Å. If the aggregates spread as monolayers of the polymer amphiphile, there are 20–30 amphiphilic molecules in each aggregate domain according to the calculation. The aggregate monolayer domain will decrease sharply with the increase of the hydrophilic component (PMA), and the film becomes very flat. Obviously, this is attributed to the increase of interaction between the hydrophilic chains of the polymer and water molecules, which allows the aggregate domain to become disentangled and dispersed. It should be pointed out that there still remains the possibility of aggregation of the microgel (see Figure 4). We cannot be sure that the amphiphile disperses as a monomolecule because of insufficient resolution of SEM. According to Kumaki's study, if MW < 50 000, the polystyrene particles seem to stand on the water surface or are stacked.[11] Our experimental results confirm his conclusion that, with the increase in the proportion of hydrophilic groups, the shape of the polystyrene microgel on the water surface changes from spherical to flat, and as a result, the molecular area of the amphiphilic polymer increases.

(2) Spreading Behavior of the Amphiphilic Polymer on the Subphase Containing Pb^{2+} Ion. In view of the above results, one can expect that, if there are some metal ions that can combine with carboxyl groups to form insoluble salts in the subphase, it must make it very difficult to disperse the amphiphilic polymer on the water surface, even when there is a high content of PMA. The π–A curves and SEM photographs of the monolayer of the amphiphilic polymer in a pure water subphase and a 10^{-3} mol/L $PbCl_2$ subphase are shown in Figures 5 and 6, respectively. According to expectation, the amphiphilic polymer contracts sharply in the Pb^{2+} subphase, its molecular area decreases sharply, and aggregate domains are formed again due to the formation of lead carboxylate, which is only slightly soluble in water. This result is in accord with the behavior of low molecular weight amphiphilic molecules such as stearic acid on various subphases.[12] The difference between them is that the molecular area of the amphiphilic polymer contracts more

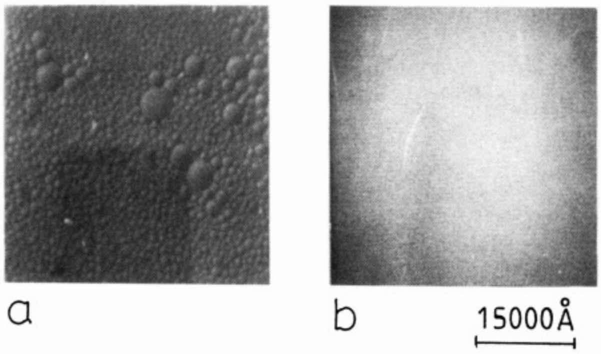


Figure 6. SEM pictures of star-shaped amphiphilic polymer monolayers (24% PMA): (a) transferred from 10^{-3} M $PbCl_2$ subphase; (b) transferred from pure water subphase.

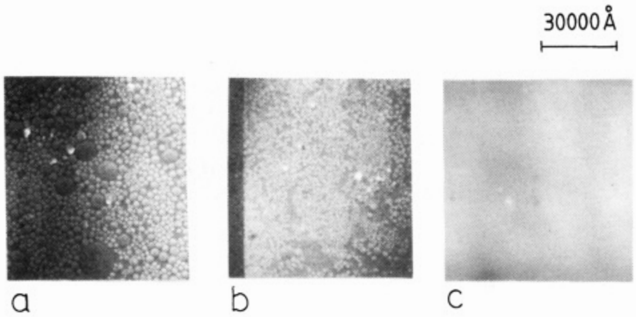


Figure 7. SEM pictures of plasticizing process of stearic acid to amphiphilic polymer monolayer (5% PMA). Stearic acid polymer: (a) 0:100; (b) 4:100; (c) 8:100. Deposited on glass from pure water.

markedly because its number of carboxyl groups is much greater than that of stearic acid.

(3) Plasticizing Function of Stearic Acid Added to Star-Shaped Amphiphilic Polymer. An increased number of hydrophilic groups in amphiphilic polymer can cause their molecular aggregates to disentangle and disperse on the water surface. The introduction of small amounts of low molecular weight amphiphilic molecules probably has the same effect as hydrophilic groups. According to Busse's theory, the plasticizing process is essentially a separation of polymer molecules by the action of low molecular weight molecules.[13] SEM photographs of the plasticizing action of stearic acid on amphiphilic polymers with a 5% PMA content are shown in Figure 7. From this figure, it can be seen that, if there is a high degree of aggregation of the polymer, it does not form a good monolayer. With the addition of 4% stearic acid, the diameters of the aggregate domains decrease sharply from 3000 to 1000 Å, and on adding 8% of stearic acid, the aggregate domains cannot be seen and the film becomes very flat. In general, stearic acid is not a good plasticizer for common polymers. However, because of the orientation of the stearic acid and amphiphilic polymer at the water surface, they can be well mixed in any proportions. The π–A curves (Figure 8) show that the collapse pressure of the mixtures increases with increasing amount of stearic acid in the monolayers, which also confirms that the two compounds have a good compatibility, according to Gabrielli's study.[14]

Multilayer Study. The strong effect of the hydrophobic and hydrophilic parts makes the polymer molecules orientate on a water surface, and its monolayers can easily be transferred onto various materials to form "Y"-type LB multilayers. We measured the contact angles of water for LB films with a hydrophobic outside layer and with a hydrophilic outside layer and found these were 66 and 36°, respectively. Comparing the contact angles with those of polystyrene (84°) and PMMA (50°), we concluded the amphiphilic star-shaped molecules were rearranged to the two-dimensional unsymmetric structure at an air–water interface shown in (Scheme II).

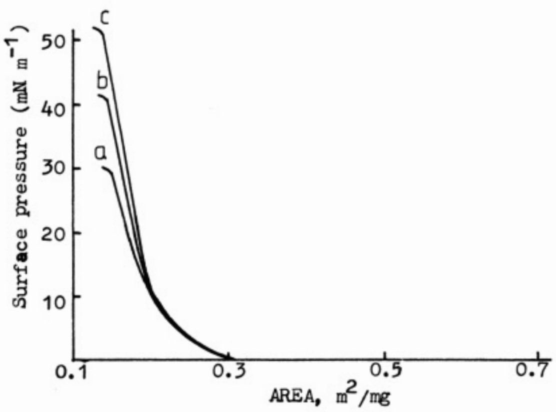


Figure 8. Pressure–area isotherms of mixtures of the amphiphilic polymer (11% PMA) and stearic acid. The weight fractions of stearic acid are (a) $X_E = 0.00$, (b) $X_E = 0.04$, and (c) $X_E = 0.12$.

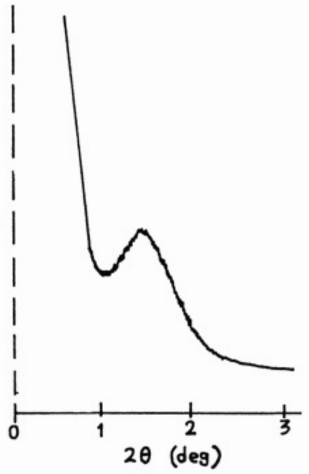
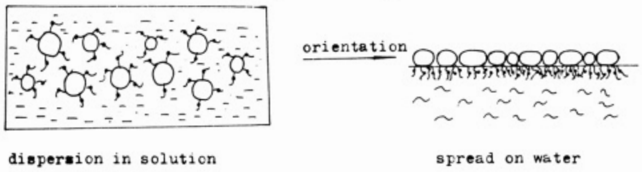


Figure 9. X-ray diffraction pattern of 9 layers of star-shaped amphiphilic polymer LB film (30% PMA) deposited on monocrystalline silicon slide.

Scheme II
Possible Scheme for the Orientation of the Star-Shaped Amphiphilic Polymer



The X-ray diffraction pattern of a 9-layer film is shown in Figure 9. The layer reflection was observed for the amphiphilic polymer with 30% PMA content. The thickness of a monolayer of this polymer is ~29 Å, calculated from the Bragg equation. This showed that the amphiphilic star-shaped polymer could form a two-dimensional ordered structure. Combining the value of the thickness and the molecular area (770 Å) determined by the π–A curve (see Figure 3c), the diameter of the amphiphile spherical particle was found to be 36 Å, which is consistent with the diameter calculated for a gel core with MW = 15 000, assuming the density of PMA approaches that of PSt (1.05 g/cm^3).

The layer reflection could not be observed for the polymer with the same PMA content when it was transferred from the 10^{-3} mol/L $PbCl_2$ subphase. Obvi-

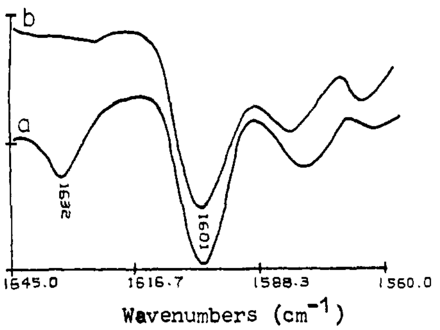


Figure 10. FT-IR spectra of 30 layers of amphiphilic polymer (15% PMA) LB film: (a) room temperature; (b) after a 4-h heat treatment at 100 °C.

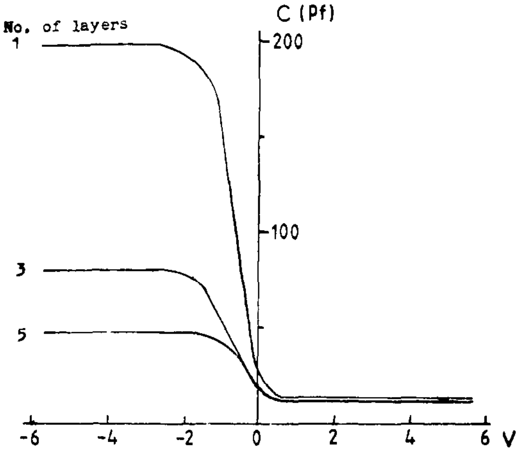


Figure 11. $C-V$ curves for different layer films after a 4-h heat treatment at 200 °C.

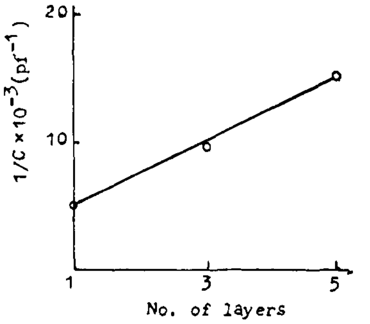


Figure 12. $1/C-n$ curve for amphiphilic polymer LB film after a heat treatment for 4 h at 200 °C.

ously, the forming of the aggregate domain not only increased the thickness of the monolayer but also decreased the degree of order of the film.

Furthermore, this amphiphilic polymer is also a macromonomer. After being deposited on the substrate, the LB layers can polymerize again to form a very stable film. Figure 10 shows that the vinyl groups of the polymer (1632 cm^{-1}) have reacted again after heat treatment, and a cross-linking layer structure has formed. In fact, the multilayers could not be removed from the monocrystalline silicon slide after heat treatment even though a good solvent of the polymer, DMF, was used. The capacitance–voltage ($C-V$) curves of the multilayers of the amphiphilic polymer deposited on silicon covered by an oxidic film of 400 Å still existed after a heat treatment for 4 h at 200 °C (Figure 11). These results show that the cross-linking film has a very strong mechanical stability. Further, from the linear relation of $1/C$ versus the number of layers in Figure 12, it can be seen that good layer reproducibility can be obtained.

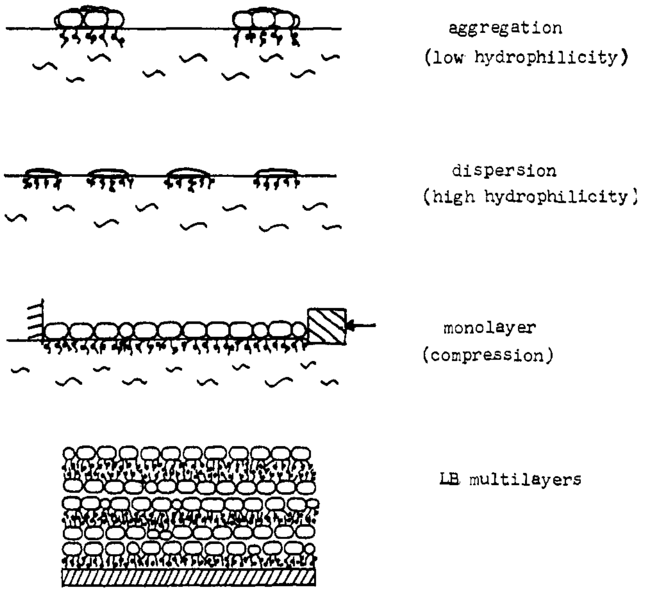


Figure 13. Schematic representation of a possible mechanism for the formation of the star-shaped amphiphilic polymer monolayer and a possible model of its LB multilayers.

The proposed model of this type of monolayer and LB multilayer is different from that currently accepted. This scheme (Figure 13) describes a possible model for the monolayer and multilayer of the polymer; that is, the dispersed polymer monomolecules are like a group of aggregate "duckweeds" floating on the water surface. With an increase in the hydrophilic part of the polymer, the aggregate polymer monolayer domains will be dispersed due to the untangling of the polymer microgel cores, and its molecular area increases as these gel cores become flat. The polymer LB film possesses a layer structure, which becomes thinner as the proportion of the hydrophilic part of the polymer increases.

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Registry No. (St)(DVB)(MA) (graft copolymer), 129834-16-8; stearic acid, 57-11-4.