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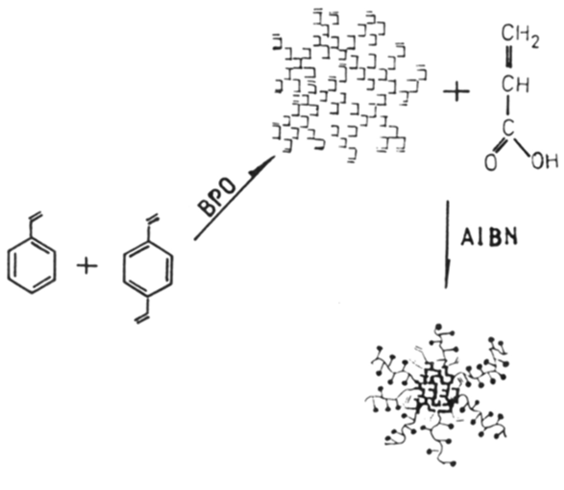
Communications to the Editor

A New Type of Amphiphilic Polymer

Amphiphilic molecules have been applied in many fields for a long time. In the past few years, as for amphiphilic molecules, promising perspectives turned up in the field of Langmuir-Blodgett (LB) monolayers and multilayers. To overcome poor stability of the LB films, ordered polymeric monolayers and multilayers have been prepared through two approaches: polymerizable amphiphilic monomers can be used to build up monomeric model membranes, which can then be converted into polymeric ones by irradiation or other initiating methods;[1-6] on the other hand, oligomeric amphiphiles or preformed amphiphilic polymers with spacer groups can be used to build up polymeric model membranes directly at the air-water interface.[7,8] Herein we describe a new type of amphiphilic polymer first developed in our laboratory. It is a macromolecule; however, it can be polymerized again after forming LB film. Therefore, this amphiphilic polymer combines the characteristics of the two approaches. Its structure is quite different from any previous amphiphilic polymers. Its hydrophilic part can be a poly(acrylic acid) series or other hydrophilic polymers. The hydrophobic part is a spherical gel core, a cross-linking network. The soluble and functional microgel ultrafine particles are being given much attention in recent years. Kakurai[9] et al. had synthesized a soluble, functional microgel core by free-radical polymerization in 1980; however, until now the studies on controlling the structure of a soluble microgel core (molecule weight, degree of cross-linking, numbers of pendent vinyl group, etc.) and studies on grafting of a monomer, especially of a hydrophilic monomer, onto the microgel core through radical initiation have not been reported. Scheme I shows the entire process of preparing this amphiphilic polymer.

Scheme I



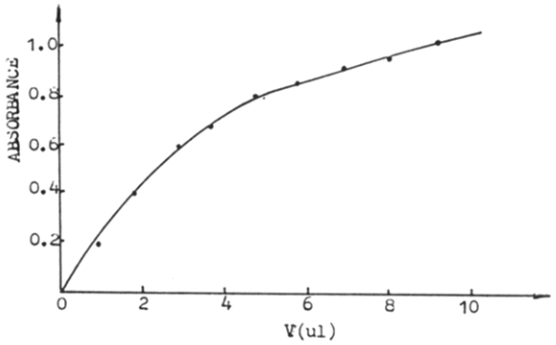


Figure 1. Standard curve of the UV spectra for measuring numbers of vinyl groups = $D_{st}(V \times 10^{-3})/104$ mol. D_{st}: density of styrene.

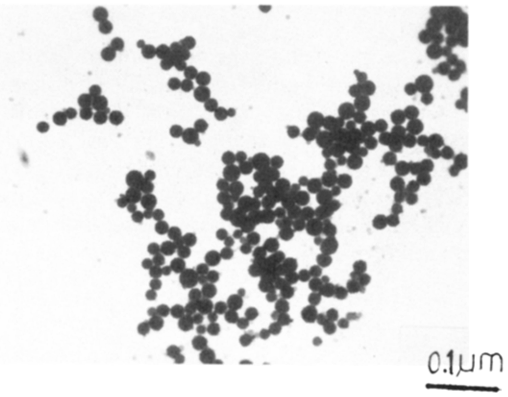


Figure 2. TEM photograph of the gel core.

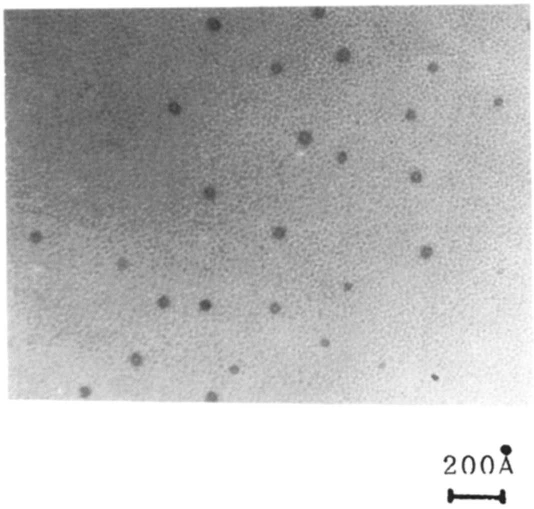


Figure 3. TEM photograph of the gel cores.

The experiment was divided into two steps. First, the gel core was synthesized by copolymerization of styrene and divinylbenzene. The initiator was BPO, which made up an oxidation-reduction system with DMA. Ultrasonic irradiation with a frequency of 25 kHz and N_2 were used in the reaction. A total of 10 mL of styrene, 4 mL of divinylbenzene, 0.3 g of BPO, and 0.15 mL of DMA were added to 25 mL of dioxane at 60 °C. The reaction was continued for 6 h, and methanol was added dropwise to the solution to precipitate the gel core. In IR spectra of the gel core, a signal at 1630 cm^{-1} (C=C) showed the functional vinyl groups for grafting. Analyses calculated for the vinyl groups of the gel core were made by a standard curve of UV spectra according to Malinsk's method[10] (Figure 1). The number of vinyl groups on a molecule was 14-200. Introducing a little $CHCl_3$ reduced the molecular

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Table I
Characteristics of Star-Shaped Polymer of Grafting PAA onto St-DVB Microgel Cores

samples	grafting, wt %	$M_n \times 10^{-4}$	B^a	N^b	water	THF
S-1	92	20.9	45	0	soluble	insoluble
S-2	83	9.9	45	0	soluble	insoluble
S-3	50	3.2	16	29	insoluble	soluble
S-4	19	1.8	10	35	insoluble	soluble
S-5	16	1.7	9	36	insoluble	soluble
S-6	11	1.6	8	37	insoluble	soluble
S-7	10	1.5	7	38	insoluble	soluble
S-8	4	1.4		45	insoluble	soluble

[a] Branching degree of the star-shaped polymer. [b] Number of vinyl groups remaining in the star-shaped polymer.

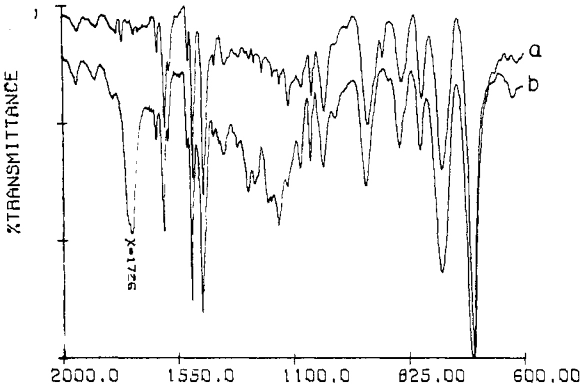


Figure 4. (a) IR spectra of the gel core; (b) IR spectra of the amphiphilic polymer.

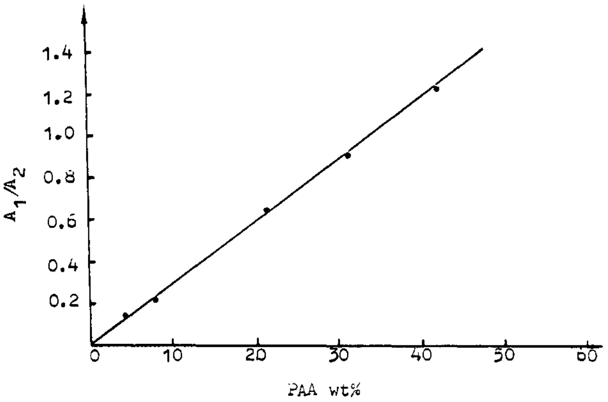


Figure 5. Standard curve of the IR spectrum for measuring wt % of PAA. A_1: the area of the 1726-cm^{-1} band, representing PAA. A_2: the area of the 700-cm^{-1} band, representing the gel core.

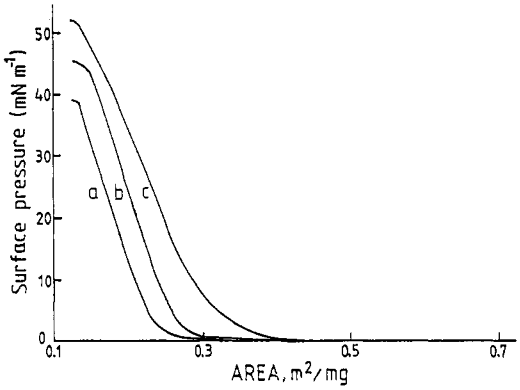


Figure 6. Surface pressure–area isotherms of star-shaped amphiphilic polymer monolayers with different contents of PMA (PMA/St-DVB, w/w): 0.15 (a), 0.24 (b), 0.29 (c), taken from pure water at 20 °C. MW = 15 000.

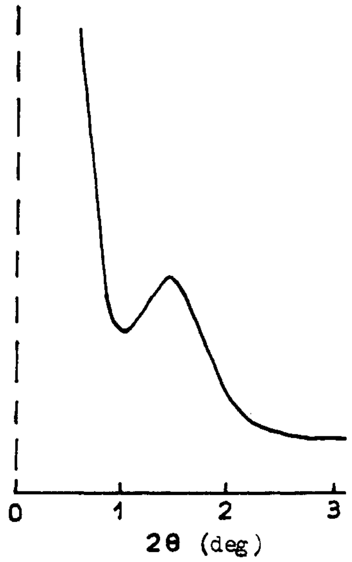


Figure 7. X-ray diffraction pattern of nine layers of a star-shaped amphiphilic polymer LB film deposited onto monocrystalline silicon. PMA content: 29% (w/w) measured by the reflection method.

weight, and adjusting the amount of divinylbenzene controlled the number of vinyl groups per molecule. The gel core with various structures was made. The molecular weight was between 6000 and 100 000, as measured by GPC and MO methods; GPC measurement was conducted in THF solvent, and narrow distribution polystyrene was used as a standard. The gel core was aggregated during the precipitation; the diameter of the aggregated gel core was smaller than 200 Å, as indicated in a TEM photo (Figure 2). After adjusting the ratio of solvent–precipitator carefully and spraying solution onto the carbon film, we got fine particles with diameters at the nanometer level. For instance, for the gel core with a MW 1.5 × 10^4, the average diameter was about 40 Å (Figure 3), only a 5-Å deviation from the value calculated by the compact model.[11] Second, the gel core was grafted with acrylic acid or methacrylic acid by free-radical polymerization. A total of 100 mg of the gel core, 30 mg of AIBN, 5 mL of acrylic acid, and 10 mL of dioxane were mixed in a reaction flask at 70 °C. After 4 min of reaction, excess methanol was poured quickly into the solution to stop the reaction. The amphiphilic polymer was precipitated, washed by methanol, and separated from homopolymer PAA. The characteristic band of the hydrophilic part at 1726 cm^{-1} emerged in the IR spectrum of the amphiphilic polymer (Figures 4 and 5).

There was a hydrophobic–hydrophilic balance in the synthesis of the amphiphilic polymer. In the initial stage, the gel core was hydrophobic and it became amphiphilic with prolongation of reaction time. Finally, it became entirely soluble in water. Only under moderate reaction conditions could amphiphilic polymer be obtained. The synthesis depended on several factors, such as temperature, concentration, time, etc. In fact, even if these factors are taken into consideration, the transformation from am-

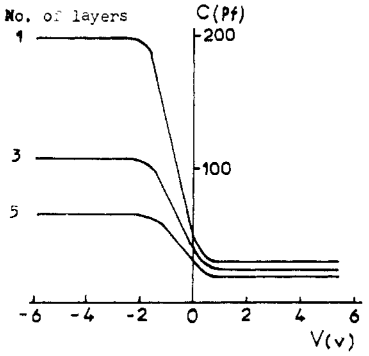


Figure 8. Capacitance-voltage (C/V) curves for different layer films of star-shaped amphiphilic polymer deposited onto a n-$SiSiO_2$ slice, after a heat treatment for 4 h at 200 °C. PMA content: 12%.

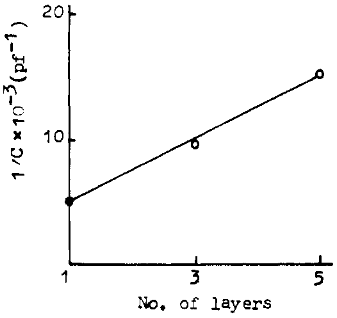


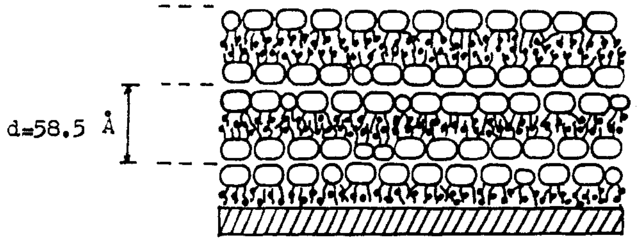
Figure 9. $1/C$–n curve for an amphiphilic polymer LB film after heat treatment for 4 h at 200 °C (according to Figure 8).

phiphilic to hydrophilic was so fast that the critical point of getting amphiphilic polymer was not easily grasped. The puzzle was solved by introduction of a little vinnamic acid (1%), which decreased effectively the reaction speed and hydrophilicity of the grafting chain. At the same time the product could be separated easily.

The degrees of grafting (wt %) were determined by elemental analysis and IR spectroscopy. The degrees of branching were obtained by calculation of the change of vinyl groups on the microgel core. The results are shown in Table I. It was found that the polymer was amphiphilic for degrees of grafting of 10–50%. The polymer was entirely hydrophilic if its degree of grafting reached 83%.

The amphiphilic polymer was spread as a DMF–chloroform (2:8) solution at a concentration of about 0.5 mg/mL at the water–air interface. The surface pressure isotherms of the polymer with different poly(methacrylic acid) (PMA) contents were given in Figure 6. It can be seen that the surface collapse pressure of the polymer monolayers increased from 39 to 51 mN m^{-1} with the increase of the hydrophilic component of the polymer; the molecular area of the polymer also increased with the increase of PMA content. Having strong hydrophobic and hydrophilic groups that could orientate at the water surface, the amphiphilic polymer monolayers were easily transferred onto n-$SiSiO_2$ to form the "Y" type of LB multilayers. We measured the contact angle of water for the LB film, and the hydrophobic outside layer and the hydrophilic outside layer were 66° and 36°, respectively.

Chart I
Model of Star-Shaped Amphiphilic Polymer Multilayers



Comparison with the contact angles of polystyrene (84°) and PMMA (50°) shows that the gel star structure was rearranged to the "duckweed" structure at the air–water interface as shown in (Chart I). X-ray diffraction results (Figure 7) indicated that the thickness for one monolayer of the amphiphilic polymer with a 29% content (wt %) of PMA and a molecular weight of 15 000 (gel part, 11 000; PMA part, 4000) was about 29 Å, and the molecular area determined by a π–A curve was about 770 $Å^2$. The volume of amphiphilic molecule equals that of a spherical particle with a diameter of 36 Å; it was quite consistent with the diameter calculated from the gel core with a MW of 15 000, if one assumes that the density of PMA approaches that of PSt. IR spectra showed that the remaining vinyl groups in the membranes could be cross-linked at 80 °C, so that the membranes increased in thermal stability and mechanical stability. The capacitance–voltage (C–V) curve of the multilayers of the amphiphilic polymer deposited on a silicon oxide semiconductor proved that the membranes were still stable after a heat treatment for 4 h at 200 °C (Figures 8 and 9).

In conclusion, a new amphiphilic polymer has been researched for forming LB model membranes. A more detailed description of broad studies related to monolayers and LB multilayers will be discussed elsewhere.

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