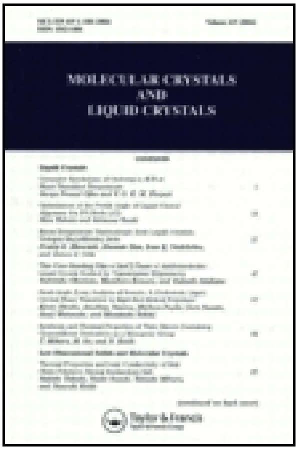

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Preparation of Monolayers of Polysilsisquioxane by the LB Technique

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PREPARATION OF MONOLAYERS OF POLYSILSISQUIOXANE BY THE LB TECHNIQUE

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Abstract Mixing polyphenylsilsisquioxane with arachidic acid is found to improve the spreading characteristics of the polymer. Polysilsisquioxane containing sidegroup of ethylundecylate is shown to form stable monolayer at the air-water interface. SEM and TEM have been used to characterize the properties of polymer aggregates in LB films.

INTRODUCTION

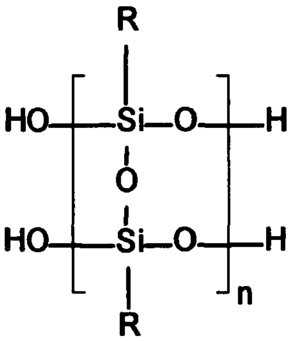
Recently, potential applications of LB films have been expected in many fields.[1] For device applications the LB films need to be very stable and robust. Because polymeric materials are generally tougher than low molecular weight amphiphilic molecules there is considerable interest in the preparation of polymeric LB films.[2] Soluble polysilsisquioxane, a ladder polymer, has many unusual properties, e.g. thermal and oxidative stability, electrical insulating property and selective permeability to gases. In this paper we report the spreading behavior of the polymer in the monolayer and discuss the influence of the substituent and the extra arachidic acid on the polymer aggregates.

EXPERIMENTAL

Polysilsisquioxanes with sidegroups of benzene (abbrev. P_I, $\overline{M}w=2.5\times10^4$) or ethylundecylate (abbrev. P_{II}, $\overline{M}w=5.5\times10^5$) shown in scheme 1 were prepared following the procedures described by Li et al.[3] Arachidic acid (abbrev. AA, 99% purity) was purchased from Sigma Co. and used without further purification. Solvents were of A.R. grade quality. Double-distilled and deionized water was used. Glass slides were treated with chromic acid to ensure that no traces of organic contaminants remained on the substrates.

All of film experiments were carried out on the WM-1 film balance (Southeast Univ., P.R.China). P_I mixed with AA in a given ratio was spread from benzene solution and P_{II} was spread from a 1:2 mixture of toluene and chloroform. After a wait of about 30 min for the solvent to evaporate, the film was compressed at a rate of 50cm²/min and deposited at a speed of 5 mm/min at a constant surface pressure. The transfer ratio of the monolayer was found to be about 0.9.

SEM was done using a Hitachi S-520 microscope. TEM was done using a JEM-100CXII microscope. The film sample for TEM was deposited on a copper mesh coated with Formvar film by horizontal dip at a given constant pressure.



I. $R=C_6H_5$

II. $R=(CH_2)_{10}COOC_2H_5$

SCHEME 1

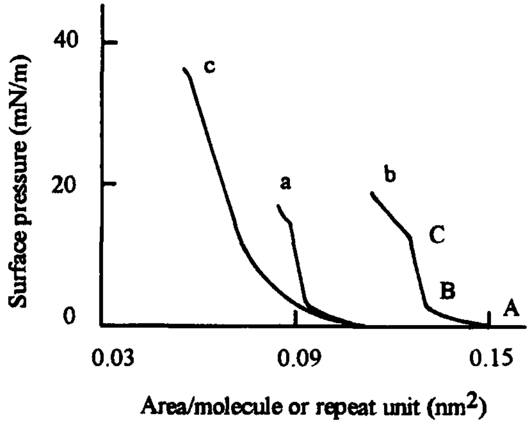


FIGURE 1 Surface pressure versus area isotherms a.P_I; b.P_I:AA=3:1 (mole ratio); c. P_{II}

RESULTS AND DISCUSSION

Figure 1 shows the surface pressure versus area per molecule or repeat unit (brackets part in scheme 1). For the monolayers of pure P_I and P_{II}, limiting areas per repeat unit obtained from extrapolating the condensed region to zero pressure are 0.095nm² and 0.078nm² respectively. These values are small compared with the actual areas of the repeat units, indicating a folded form of polymer chain as the spreading form with or without long sidegroup in the polymer molecule. A plot of the area per repeat unit versus time (not shown here) indicated that the P_I monolayer was not stable and the P_{II} monolayer was stable.

Mixing P_I with arachidic acid gives a stable monolayer below C point (isotherm b in Figure 1). For other molar ratios the shapes of the isotherms and the pressures at C point are similar to isotherm b. In order to estimate a change of the spreading form of the polymer chain, limiting areas per repeat unit for the condensed region below the C point were calculated at various mixing mole ratios by assuming the area of arachidic acid to be constant at 0.205nm²/molecule. The calculation method is as follows,

$$\text{Area per repeat unit} = [A - 20.5 \times (1 - X)]/X \qquad (1)$$

A=area per molecule determined from Figure 1.
X=mole fraction of the polymer repeat unit.

The limiting area per repeat unit obtained increases with decreasing concentration of the polymer in the mixture up to 0.295nm² in 1:10 mole ratio of P_I and AA, that is , the polymer chain becomes an expanded form by dilution with arachidic acid.

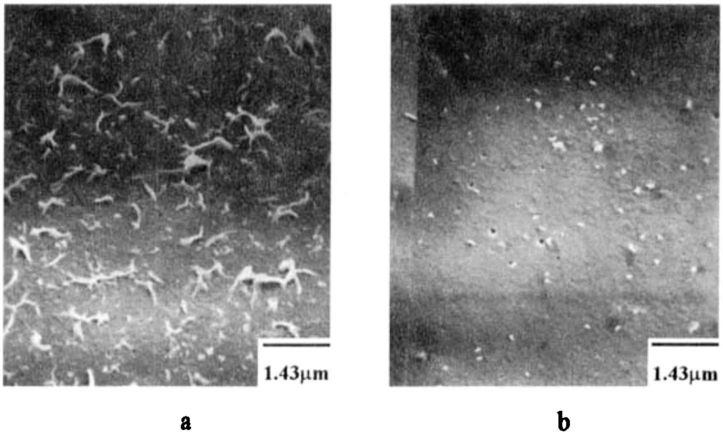


FIGURE 2 SEM pictures of P_I/AA monolayers
P_I:AA (mole ratio): a. 1:1; b. 1:10

In addition, arachidic acid can reduce polymer aggregate patches. SEM micrographs in Figure 2 reveal the existence of polymer aggregate patches in LB films. At high molar fraction of P_I, the film appears inhomogeneous and large aggregate patches. When the mole fraction of P_I decreases, these large patches become small grains. The SEM micrograph of the P_{II} film appears homogeneous.

To confirm the structure of the P_{II} film, we have employed TEM. Figure 3 shows TEM micrographs of P_{II} at different pressures. At low pressure small aggregates of P_{II} are dispersed uniformly. Size of aggregates increases with increasing the pressure. Eventually the aggregates link up mutually to form large aggregate patches.

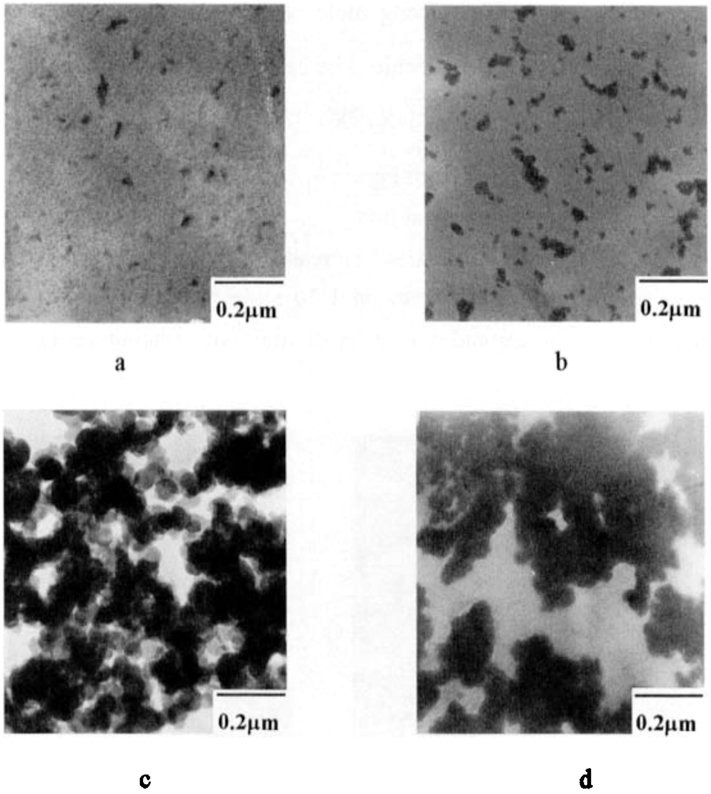


FIGURE 3 TEM pictures of P_{II}
surface pressure (mN/m): a.5; b.10; c.20; d.25

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REFERENCES

1. M.C. Petty, Thin Solid Films, 210/211, 417 (1992).
2. R.H. Tredgold, Thin Solid Films, 152, 223 (1987).
3. G.Li, M.Ye and L.Shi, Chin. J. Polym. Sci., 12, 331(1994).