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Phase Transitions in Poly-*n*-Alkyl Methacrylate Monolayers

Tatsuo NAKAHARA, Kinsi MOTOMURA and Ryohei MATUURA
Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Fukuoka

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The effects of temperature on the surface pressure of monolayers of polymethacrylates with *n*-alkyl groups containing from 9 to 18 carbon atoms have been studied. Two kinds of phase transitions have been observed in the surface pressure-area isotherms. On the basis of the bulk properties of the polymers, these phase changes have been interpreted as the transition of the monolayer to a three-dimensional fluid state and as side-chain crystallization.

Various phases detectable in surface pressure-area isotherms of monolayers have been investigated extensively,[1] and each phase has been well-characterized in a way analogous to the specification of three-dimensional phases. In view of the fact that these investigations of two-dimensional phase transitions have dealt almost exclusively with monomeric substances, however, an accurate description of phases for polymeric systems seemed to be required.

For this purpose the series of poly-*n*-alkyl methacrylates may be useful, since all of the homologous polymers provide uniform and stable monolayers at the air-water interface, and by introducing various side groups their physical states in bulk can be varied systematically; they exhibit vitrified, fluid, and crystalline states at a given temperature with an increase in the side-chain length.[2,3]

In the present paper the phases and phase transitions appearing in monolayers of polymethacrylates with *n*-alkyl groups containing from 9 to 18 carbon atoms have been investigated by measuring the surface pressure. On the basis of bulk properties of the polymers, the interpretation of the observed phases and the phase changes has been attempted.

Experimental

All the *n*-alkyl methacrylate monomers used in this study were prepared from methyl methacrylate by the alcoholysis procedure of Rehberg and Fisher.[4] The polymerization was carried out in bulk by using benzoyl peroxide as a catalyst. The poly-*n*-nonyl methacrylate (PNMA), poly-*n*-dodecyl methacrylate (PDMA), poly-*n*-tetradecyl methacrylate (PTMA), poly-*n*-hexadecyl methacrylate (PHMA), and poly-*n*-octadecyl methacrylate (POMA) prepared in this way were purified by repeating the precipitation, with a dilute benzene solution added to methanol. The degrees of polymerization determined for these polymers by the light-scattering method ranged from 10^4 to 10^5.

The polymers were spread on redistilled water from benzene solutions, and their surface pressure was measured by both modified Wilhelmy-type and Langmuir-type surface balances. The measurements were carried out at various temperatures over the range from 10 to 35°C, each with a constancy of ±0.1°C.

Results and Discussion

The surface pressure-area (π-A) isotherms at different temperatures for all of the polymers are illustrated in Figs. 1 to 5. It has been found that the π-A isotherms shift toward the larger areas with a decrease in the length of side chains when they are compared at the same temperature. This was also found by Crisp, who ascribed this to the secondary cohesion of side chains.[5,6]

While an appreciable temperature dependence of the surface pressure for coherent films was predicted,[7] previous investigations of the temperature effect on surface pressure have mainly been directed to expanded films.[1] In this study the effect

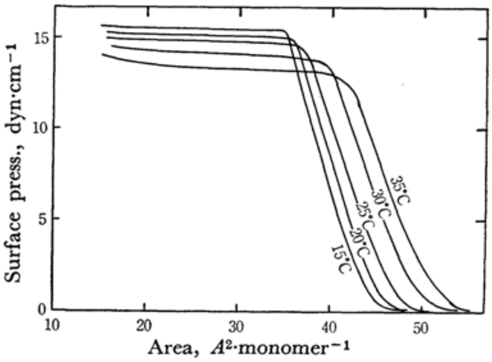

Fig. 1. The π-A isotherms for PNMA at various temperatures.

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[1] W. D. Harkins, "The Physical Chemistry of Surface Films," Reinhold Publishing Co., New York (1952), p. 106.

[2] S. S. Rogers and L. Mandelkern, *J. Phys. Chem.*, **61**, 985 (1957).

[3] S. A. Greenberg and T. Alfrey, *J. Am. Chem. Soc.*, **76**, 6280 (1954).

[4] C. E. Rehberg and C. H. Fisher, *ibid.*, **66**, 1203 (1944).

[5] D. J. Crisp, *J. Colloid Sci.*, **1**, 49 (1946).

[6] D. J. Crisp, *ibid.*, **1**, 161 (1946).

[7] T. Kawai, *J. Polymer Sci.*, **35**, 401 (1959).

of temperature on the π-A isotherms is very remarkable, as may be seen in Figs. 1 to 5. The increase in the occupied area with the temperature may be interpreted in terms of the decrease in cohesive force which was introduced by Motomura and Matuura(8) in deriving the equation of state for a monolayer of a linear polymer with short side chains.

In the cases of PNMA, PDMA, and PTMA, and PHMA at higher temperatures, plateaus appear in the π-A isotherms during isothermal compression, and the films can be compressed to an area less than that of the closely-packed hydrocarbon chain without change in the pressure. It was confirmed also, with a Langmuir-type surface balance, that all the π-A isotherms, including the plateau, could be retraced by slow re-expansion with little hysteresis. Since the temperatures for determining the π-A isotherms were far above both glass temperatures and the melting points of PNMA, PDMA, and PTMA,(2,3) these polymers are considered to form fluid films at air-water interfaces. The π-A isotherms of PHMA at 25—35°C are also in the fluid state, because the melting range covers 16—21°C.(3)

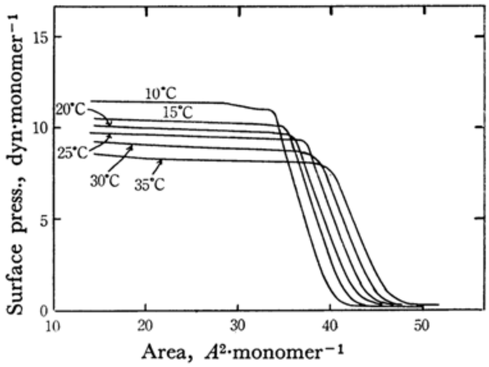

Fig. 2. The π-A isotherms for PDMA at various temperatures.

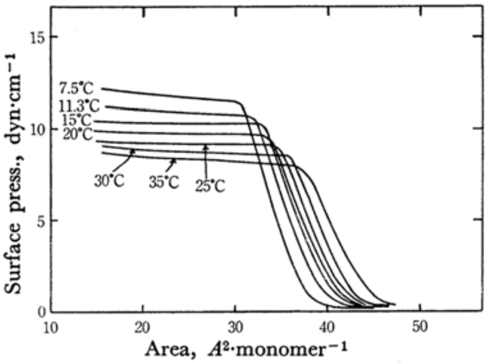

Fig. 3. The π-A isotherms for PTMA at various temperatures.

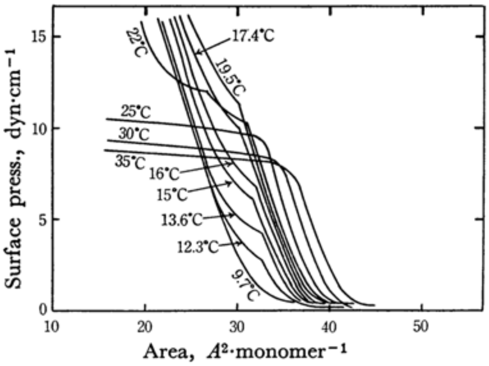

Fig. 4. The π-A isotherms for PHMA at various temperatures.

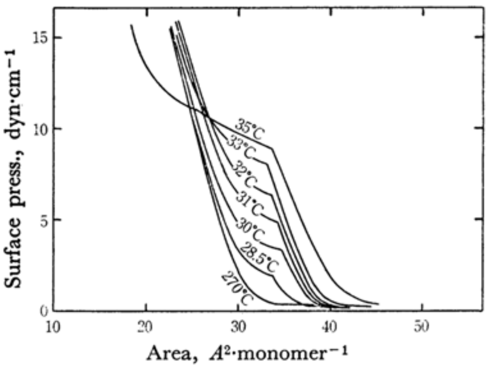

Fig. 5. The π-A isotherms for POMA at various temperatures.

From the above facts, it seems reasonable to consider that the three-dimensional fluid begins to separate from the fluid monolayer at the plateau point of the π-A isotherms of PNMA, PDMA, and PTMA, and of PHMA above 25°C; the fluid monolayer and the bulk fluid are coexistent in equilibrium over the plateau region at a constant pressure. The plots of the equilibrium pressures between the monolayer and the bulk fluid of the polymers against the temperature are shown in

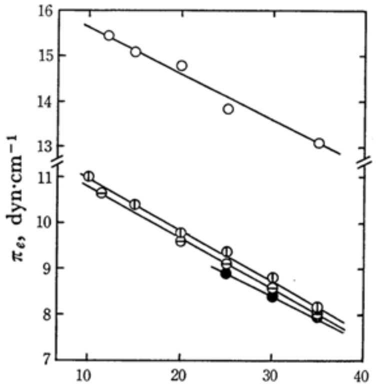

Fig. 6. The plots of the equilibrium pressures against temperature for PNMA (○), PDMA (⦶), PTMA (⊖) and PHMA (●).

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8) K. Motomura and R. Matuura, *J. Colloid Sci.*, **18**, 52 (1963).

TABLE 1. EQUILIBRIUM PRESSURE, AREA, LATENT HEAT AND ENTROPY CHANGE OF TRANSFORMATION FROM TWO- TO THREE-DIMENSIONAL SYSTEMS OF PNMA, PDMA, PTMA AND PHMA AT 25°C

Polymer	π_e dyn·cm^{-1}	A_e A^2·monomer^{-1}	$(\partial\pi_e/\partial T)_p\times 10^2$ dyn·cm^{-1}·deg^{-1}	$\Delta h\times 10^{14}$ erg·monomer^{-1}	$\Delta s\times 10^{12}$ erg·deg^{-1}·monomer^{-1}
PNMA	13.85	39.4	−6.84	8.03	2.69
PDMA	9.35	37.5	−7.50	8.38	2.81
PTMA	9.14	34.9	−7.41	7.70	2.58
PHMA	8.93	33.1	−6.84	6.75	2.26

Fig. 6. The equilibrium pressures are found to decrease linearly with the temperature. The fact that a similar temperature dependence of the pressure was observed in the equilibrium of the monolayers of fatty acids with their lenses[9,10] may well give further support to the coexistence of two- and three-dimensional fluid states.

The latent heat of the phase transition of the film to the bulk fluid may be calculated by using the thermodynamic equation derived by Motomura[11] from an accurate treatment of the phase and phase transition of monolayers; after neglecting minor quantities, the change in enthalpy, accompanying the phase transition is approximately given by:

$$\left(\frac{\partial \pi_e}{\partial T}\right)_p \simeq -\frac{1}{T}\,\frac{h_b-h_f}{A_e} = -\frac{s_b-s_f}{A_e}$$

where h_f and h_b are the enthalpies, s_f and s_b are the entropies of the film and the bulk fluid respectively, and π_e and A_e are the pressure and the area of the monolayer in equilibrium with the bulk fluid. The enthalpy and entropy differences, $\Delta h(=h_b-h_f)$ and $\Delta s(=s_b-s_f)$, both calculated at 25°C, are given in Table 1. The positive entropy change indicates the expected ordered configuration in the monolayers.

The fact that the entropy change of PDMA is the largest suggests that the three-dimensional fluid state of this polymer is most stable among the polymers studied. The change in Δs with the side-chain length seems to have the same tendency as that of the brittle points[12] of these polymers: the brittle points of the homologous polymers were found to decrease with the side-chain length up to PDMA, but, for the polymers with the longer side chains, to increase with the side-chain length.

For PHMA and POMA the π-A isotherms obviously showed a two-dimensional phase change due to the side-chain crystallization. It is reasonable that the phase change in the PHMA and POMA monolayers is detected at temperatures lower than 22°C and 35°C respectively, since the melting range in bulk has been reported to cover 16—21°C for PHMA and 33—34°C for POMA.[3]

In a preceding paper,[13] the crystallization isotherms obtained for the POMA monolayer by measuring the decrease in the area with time at various temperatures and surface pressures were analyzed by the general mathematical treatment of the kinetices of phase changes, and it was concluded that the linear growth was dominant. It was also recognized that the transition point in the π-A isotherm was observed when the induction period of the crystallization was comparable to the experimental time scale.

Thus, the transition pressures in the π-A isotherms of POMA and PHMA are time-dependent, and those found by the usual experimental technique are obviously apparent. It was shown by the crystallization kinetics of the monolayer that the equilibrium transition pressure is the pressure where the induction period of crystallization is infinite, but the temperature dependence of the equilibrium-transition pressure was found to be similar to that of the apparent transition pressure.[13] In order to calculate the heat of fusion, therefore, it might be useful to apply a two-dimensional, Clapeyron-Clausius-type equation[11] to the π-A isotherms measured with a finite rate of compression, since the difference between the areas of crystalline and liquid states is likely to be considered to be approximately equal to that of the equilibrium state.

The heats of fusion thus calculated are -2.0×10^{-13} and -2.7×10^{-13} erg per monomer for PHMA and POMA respectively. A half of the difference between these values, -3.5×10^{-14} erg, may be regarded as approximately the heat of fusion per CH_2 unit. The fact that this value is nearly identical with the heat of fusion per CH_2 unit of paraffin[14] seems to be further confirmation of the side-chain crystallization of PHMA and POMA monolayers.

An anomaly in the π-A isotherm of PHMA at 22°C is considered to indicate that the transition from a two- to a three-dimensional fluid film is quenched by the crystallization, so that the film is stabilized. This transient phenomenon must depend on the experimental time scale, *i. e.,* the rate of compression.

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