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Masayoshi Watanabe,* Yozo Kosaka, Kohei Sanui, and Naoya Ogata
Department of Chemistry, Sophia University
7-1 Kioi-cho, Chiyoda-ku, Tokyo 102, Japan

Kiyoshi Oguchi* and Tomoko Yoden
Research Development Corporation of Japan
c/o Department of Chemistry, Sophia University
7-1 Kioi-cho, Chiyoda-ku, Tokyo 102, Japan

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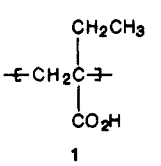
On the Mechanism of Polyelectrolyte-Induced Structural Reorganization in Thin Molecular Films†

We reported in 1985 that polyelectrolyte adsorption can be used to control the structural and functional properties of bilayer membranes prepared from double-chain surfactants in water.[1] In particular, the pH-dependent adsorption of hydrophobic poly(carboxylic acids) on phosphatidylcholine films[2] can be used to design surfactant vesicles that release their contents rapidly and quantitatively in response to changes in environmental parameters such as pH,[1] temperature,[1] or the concentrations of an organic solute, e.g., glucose.[3] Composite thin films prepared in this way offer intriguing technological opportunities in information storage and transfer, in sensing and control (including biosensing), and in medical diagnosis and therapeutics.

Much of our work has concerned the pH-dependent interactions of poly(2-ethylacrylic acid) (PEAA, 1) with bilayer vesicles of natural or synthetic phosphatidylcholines (2). Hydration of dipalmitoylphosphatidylcholine



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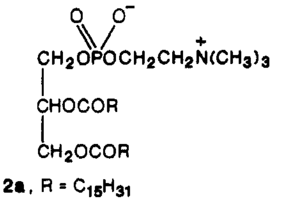

2a, R = $C_{15}H_{31}$
b, R = mixed hydrocarbon chains
c, R = $C_{18}H_{35}$

(DPPC, **2a**) at a concentration of 1 mg/mL in a phosphate-buffered solution of PEAA at pH 7.5 affords a turbid suspension of multilamellar vesicles.[4] Depression of the pH to 6.5 or below causes a marked loss of turbidity (Figure 1); similar treatment of egg yolk phosphatidylcholine (**2b**) vesicles also causes rapid, quantitative loss of vesicle-entrapped carboxyfluorescein, a fluorescent marker.[1,5,6] We have suggested that it is the pH-induced conformational transition of PEAA[7-9] that causes this structural reorganization and the concomitant loss of membrane integrity. We describe in this paper a series of photophysical and calorimetric experiments that support this hypothesis.

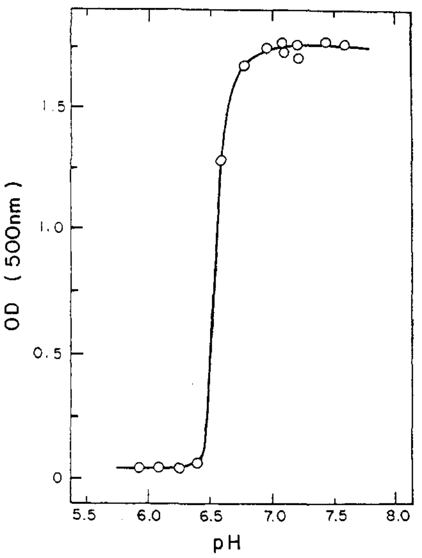

Figure 1. Optical density (500 nm) of a 1 mg/mL suspension of DPPC in phosphate-buffered aqueous PEAA (1 mg/mL).

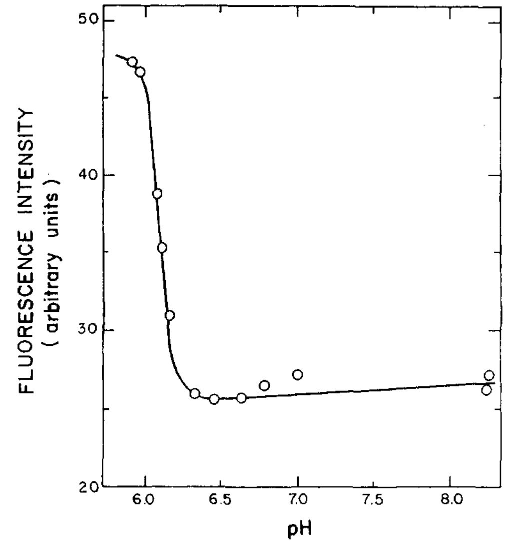

Figure 2. Fluorescence intensity (375 nm) emitted by 5 × 10^{-6} M pyrene in phosphate-buffered solutions of PEAA as a function of pH. Excitation at 337 nm, excitation and emission slit width 3.0 nm.

Thomas and co-workers have shown pyrene to be a useful photophysical probe of polyelectrolyte conformation in aqueous solution.[10-12] Figure 2 shows a plot of the intensity of fluorescence emitted by 5 × 10^{-6} M pyrene in a series of PEAA solutions of varying pH.[13] The large increase in fluorescence intensity at low pH is consistent with Thomas' observations regarding poly(methacrylic acid) (PMAA)[10] and signals the collapse of the PEAA chain from an expanded conformation at high pH to a relatively hydrophobic, globular coil in acidic solutions. The changes in the vibrational fine structure of the fluorescence emission are also consistent with a decrease in the polarity of the pyrene microenvironment at low pH.[14] The midpoint of the conformational transition of PEAA occurs at

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† Part 13 in the series "Interactions of Synthetic Polymers with Cell Membranes and Model Membrane Systems". Part 12: Turek, A. B.; Tirrell, D. A. *J. Bioactive Compatible Polym.* **1986**, *1*, 309.

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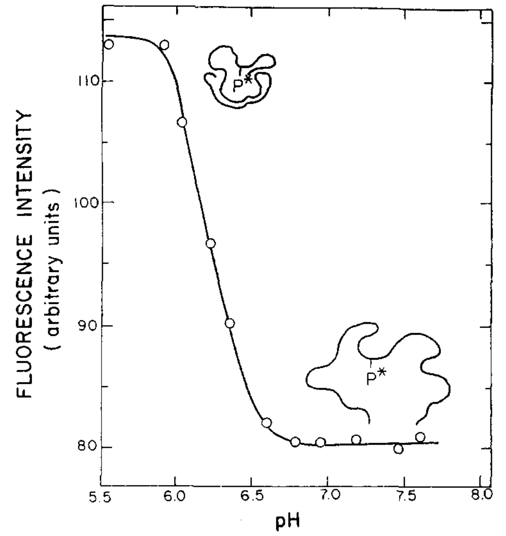

Figure 3. Fluorescence intensity (379 nm) emitted by 2-ethylacrylic acid/1-pyreneacrylic acid copolymer (1 mg/mL) in phosphate-buffered solutions as a function of pH. Excitation at 345 nm, excitation and emission slit width 3.0 nm.

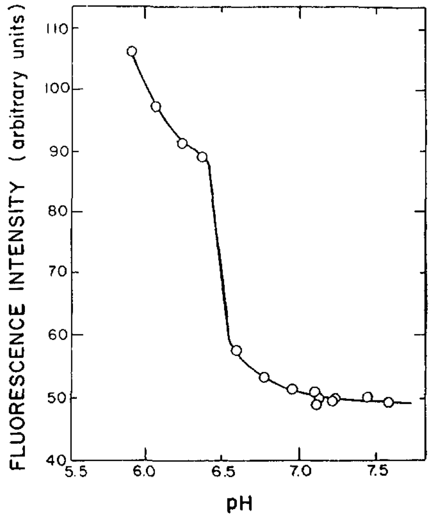

Figure 4. Fluorescence intensity (379 nm) emitted by 2-ethylacrylic acid/1-pyreneacrylic acid copolymer (0.9 mg/mL) in phosphate-buffered suspensions of DPPC (1 mg/mL) as a function of pH. Parameters as in Figure 3.

pH 6.1 under these conditions.

A similar analysis of the fluorescence emitted from a copolymer of 2-ethylacrylic acid and 1-pyreneacrylic acid[15] is shown in Figure 3. The conformational transition is again manifested by a large increment in fluorescence intensity, with the transition midpoint at pH 6.2. The very small difference in the transition midpoints reported by bound and unbound pyrene contrasts somewhat with Thomas' results for poly(methacrylic acid), wherein covalent binding of the fluorophore was found to shift the transition from ca. pH 5.0 to pH 5.7. The origins of this difference in the behavior of PMAA and PEAA are uncertain but may be associated with the increased hydrophobic character of PEAA.[8]

Figure 4 illustrates the effect of added DPPC on the conformational transition of PEAA.[16] The transition midpoint is shifted to pH 6.5 by the addition of an equivalent weight of surfactant. We attribute the shift to hydrogen-bonding interactions between PEAA and the membrane surface; analogous interactions in hydrogen-bonded interpolymer complexes cause similar shifts in the average pK_a of poly(carboxylic acids),[17] and we find that addition of DPPC to aqueous PEAA solutions causes a decrease in the apparent acidity of the chain as determined by potentiometric titration.[18]

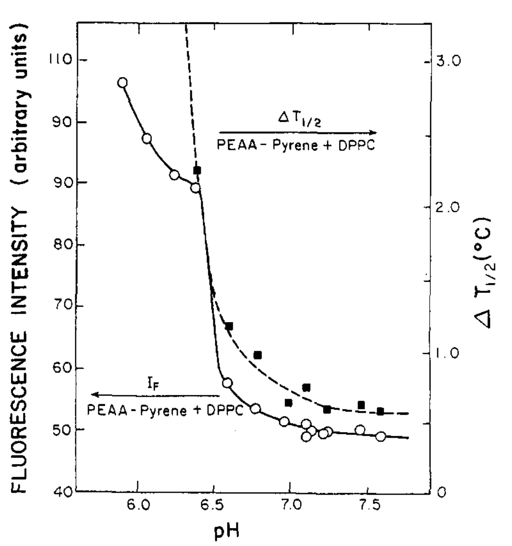

Figure 5. Fluorescence intensity as in Figure 4 (○) and calorimetric transition half-width $\Delta T_{1/2}$ (■) for the same samples. $\Delta T_{1/2}$ at pH 6.25 is 5.5 °C (not shown).

The relation between the conformational state of the polyelectrolyte chain and the degree of structural order in the molecular film is shown in Figure 5. The half-width of the calorimetric phase transition of the film ($\Delta T_{1/2}$) increases sharply at pH 6.5, in excellent agreement with the midpoint of the conformational transition of PEAA. The most reasonable interpretation is that the collapsed polyelectrolyte chain provides a hydrophobic site for "solubilization" of the hydrocarbon tails of the surfactant and in so doing disrupts the structural organization that is characteristic of the pure surfactant film. This suggestion is based on the well-known capacity of poly(methacrylic acid) to solubilize simple hydrocarbons in acidic aqueous solutions[19] and on Thomas' and our own observations, discussed herein, regarding pH-dependent solubilization of aromatic hydrocarbons by hydrophobic polyelectrolytes.

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Registry No. 1, 62607-09-4; 2a, 2644-64-6; pyrene, 129-00-0; (2-ethylacrylic acid)(1-pyreneacrylic acid) (copolymer), 105971-07-1.

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(5) We have shown previously[1] that vesicle disruption occurs at a measurable rate only at temperatures above that of the order-disorder transition of the lipid bilayer. Egg yolk phosphatidylcholine (T_m = −15 °C) is thus more conveniently used in transport experiments than is DPPC (T_m = 41 °C).
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(16) Mixing of the copolymer and DPPC was accomplished in the following manner: 0.9 mL of a 1 mg/mL copolymer solution in the required phosphate buffer (note 4) was mixed at room temperature with 0.1 mL of a 10 mg/mL suspension of DPPC in the same buffer. The mixture was then heated to 50 °C for 10 min with repeated vortex agitation.
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(20) Department of Polymer Science and Engineering.
(21) Department of Physics and Astronomy.

Keith A. Borden,[20] Ki Min Eum,[21] Kenneth H. Langley,[21] and David A. Tirrell*[20]

Department of Polymer Science and Engineering
and Department of Physics and Astronomy
University of Massachusetts
Amherst, Massachusetts 01003

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Identification of a Curie Transition in Vinylidene Fluoride/Tetrafluoroethylene Random Copolymers by Spectroscopic Methods

While copolymers of vinylidene fluoride (VF_2) and trifluoroethylene (TrFE) have been studied extensively,[1–6] only recently[7–9] has a Curie transition been observed in random copolymers of VF_2 and tetrafluoroethylene (TFE). Initial studies on a commercially available 81/19 (mol %) copolymer had mixed results[7,8,10–12] in detecting an observable Curie transition due to its proximity to the crystalline melting point. However, a systematic study[13,14] of VF_2/TFE copolymers over a wide compositional range by X-ray and thermal analysis unequivocally demonstrated the existence of a Curie transition.

Since the random addition of TFE comonomer to a VF_2 backbone does not introduce a new chemical species (as in the case of copolymerization with TrFE) but merely increases the head-to-head defect content, evidence of a Curie transition in VF_2/TFE copolymers further reinforces the notion that poly(vinylidene fluoride) (PVF_2) must also undergo a Curie transition.[7] The fact that it may coincide with the crystalline melting point remains a plausible argument for the lack of any experimental verification of this Curie point in PVF_2. In the commercially available (Kynar 7201) VF_2/TFE (81/19) copolymer, a similar observation can be made, as shown in Figure 1. On the first heating the DSC trace shows an asymmetric melting point curve indicating the presence of a premelting transition at 116 °C. When the sample is cooled (bottom trace), it becomes quite evident that in addition to the crystallization exotherm, there is a second, weaker feature, which might be associated with a paraelectric to ferroelectric phase transition.

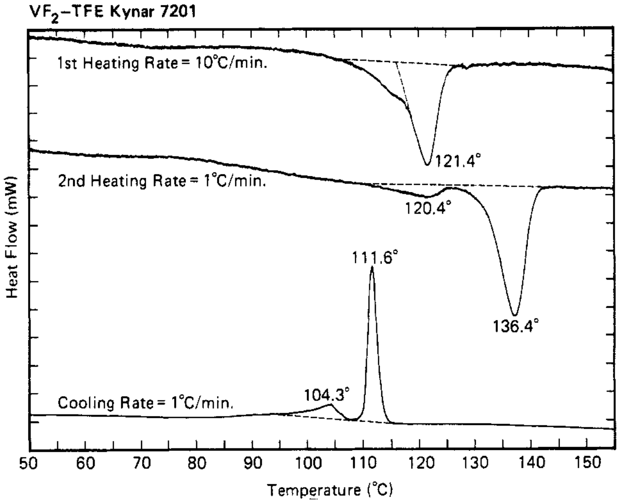

Figure 1. DSC trace of VF_2/TFE copolymer with a 81/19 (mol %) ratio. Top trace, first heating; lower trace, cooling at 1 °C/min; middle trace, sample cooled from the melt at 0.2 °C/min and then heated.

As earlier work[6] indicated, Raman spectroscopy is a nondestructive technique for probing local changes in conformational order which accompany a Curie transition. In fact, bands in the 800–850-cm^{-1} region have been used[6] to investigate the loss of the planar PVF_2 structure in VF_2/TrFE copolymers as the temperature was raised to the Curie point. The intense 841-cm^{-1} asymmetric CF_2 stretching band which is characteristic of the planar form was observed to lose intensity as the 805-cm^{-1} band characteristic of TG and/or TG′ conformations became dominant at the Curie point. It was thus anticipated that similar high-temperature studies could be carried out on the VF_2/TFE copolymers and could be used to establish the absence or existence of a Curie transition.

In order to investigate the transition shown in Figure 1 by Raman spectroscopy, a sample of the Kynar 7201 copolymer was slow cooled from the melt at 0.2 °C/min. This allowed more perfect crystals to form, thereby raising the melting point by 15 °C as shown in the second heating trace of Figure 1. Moreover, of equal importance was the appearance of a well-defined transition at 120.4 °C, easily delineated from the melting point at 136.4 °C. A second portion of this same sample was used for the Raman studies shown in Figure 2. At 83 °C the spectrum is very similar to that observed[6] for the VF_2/TrFE copolymers below the Curie point. As the temperature approaches that of the observed DSC transition (120.4 °C) a dramatic change in the intensity of the bands at 805 and 841 cm^{-1} is observed, with the 805-cm^{-1} band increasing in intensity at the expense of the 841-cm^{-1} band. Lowering the temperature to 108 °C returns the relative intensity of the bands to their original value. The cyclic reversibility and the band intensity variations with temperature suggest that the 120.4 °C transition involves a reversible change in conformation from a planar structure to one of lesser order which includes short TGTG′ sequences. This order–disorder transition is thus identical with that observed[6] in VF_2/TrFE copolymers and can be characterized as a Curie transition.

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