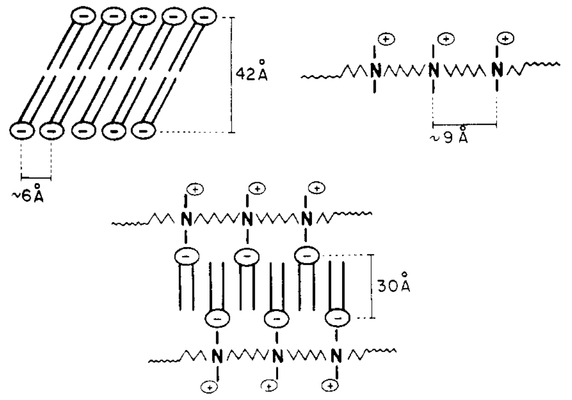
Scheme I



angle reflection at 4.09 Å. Comparison of these features with the diffraction data of previous workers[7-14] identifies this as a lipid phase in which the hydrocarbon chains of apposed monolayers are normal to the bilayer and fully interdigitated.

Acyl chain interdigitation is demonstrated more clearly by a comparison of the electron density profiles calculated from the diffraction patterns in Figure 1. Figure 2A is the profile of the unmodified DPPG bilayer and indicates a phosphate-to-phosphate separation across the bilayer of 42 Å, which is the expected thickness for an L_{β}' bilayer of this chain length.[15] Treatment with ionene-6,6 reduces the bilayer thickness to 30 Å, a result which can be reconciled only with the formation of a gel phase in which the hydrocarbon tails are deeply interpenetrated.

Interdigitation has been observed previously in samples of DPPG neutralized with organic counterions.[8-11] Specifically, preparation of the choline, acetylcholine, or polymyxin salts of DPPG affords interdigitated gel phases. McIntosh and co-workers[13,14] have discussed the requirements which must be met by small molecules which induce the interdigitated phase: such molecules must displace water from the interfacial region without penetrating deeply into the bilayer interior.

Thus the observation of an interdigitated phase in ionene-treated DPPG bilayers—the first indication that *polymeric* additives may induce interdigitation—is consistent with previous results concerning the formation of this unusual gel phase. In fact, the picture of the ionene-6,6-treated bilayer as an interdigitated structure is a pleasing one. One imagines that the approach of ionene-6,6 to the bilayer surface is driven by strong electrostatic forces between the negatively charged phosphate groups of the surface and the ammonium cations bound to the polymer chain. But effective ion pairing at the surface would place the hydrophobic polymethylene spacer of ionene-6,6 in juxtaposition with the polar, hydrated diglycerylphosphate portion of the lipid head group. A position in the hydrocarbon core of the bilayer would be energetically preferred for the spacer, but access to the core is precluded by the high energetic cost of burying an ammonium cation. The solution is a lateral expansion of the bilayer, accompanied by deep interpenetration of the hydrocarbon chains of the lipid (Scheme I). This allows terminal methyl groups of the hydrocarbon chains to take interfacial positions, in contact with the hydrophobic polymethylene spacer, while remaining dehydrated as a result of protective "capping" by the polymer chain.

We are currently exploring the relation of polymer chain structure and the induction of acyl chain interdigitation in DPPG and related bilayers. The consequences of interdigitation in terms of bilayer stability and permeability are also under investigation.

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Registry No. 1, 29322-35-8; 1, SRU, 31622-88-5; DPPG, 4537-77-3.

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Effect of Ultrasonic Irradiation on Ion Binding by Synthetic Polyelectrolytes Using Terbium(3+) as a Fluorescence Probe[1,2]

Interest in the absorption and fluorescence of rare earth metal ions in solution has been greatly stimulated because of their possible use as lasers. In an effort to obtain stronger fluorescence, two general approaches appear possible. The first involves the addition of an agent to the solution, usually an organic ligand, which will absorb energy and transfer it to the rare earth ion. An alternative method is to enhance the absorption and fluorescence of the rare earth ion by suitable changes in its environment.

The extreme sensitivity of certain lanthanide absorption bands to their solution environment is well documented and the phenomenon is referred to as "hypersensitivity".[3] The hypersensitive absorption is greatly increased by three factors: an increasingly basic character of the coordinating

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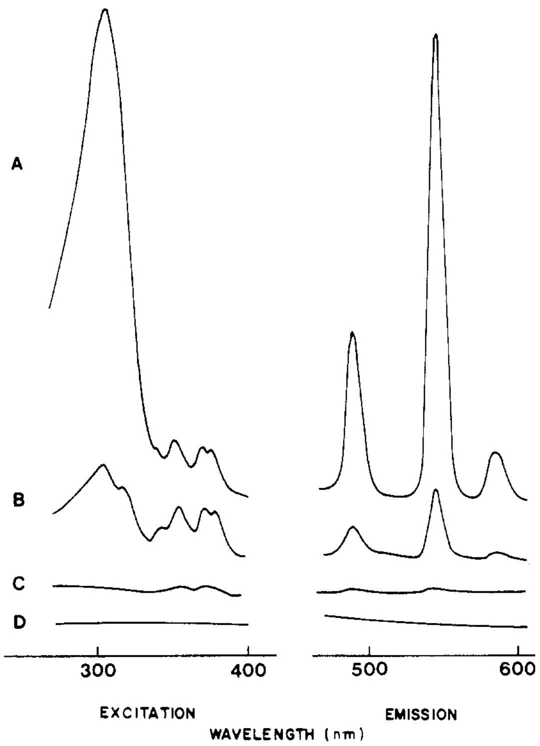


Figure 1. Effect of ultrasonic irradiation on excitation spectra (left) and emission spectra (right) of the Tb^{3+}–polyacrylate system. Poly(acrylic acid) (MW = 450000) was used and it ionized about 95% at pH 9.0. (A) After 20 min of ultrasonic irradiation; (B) before ultrasonic irradiation ([PAA] = 5.0×10^{-2}, [Tb^{3+}] = 1.0×10^{-3} M, and pH ~9.0); (C) [Tb^{3+}] = 1.0×10^{-3}; (D) [PAA] = 5.0×10^{-2}.

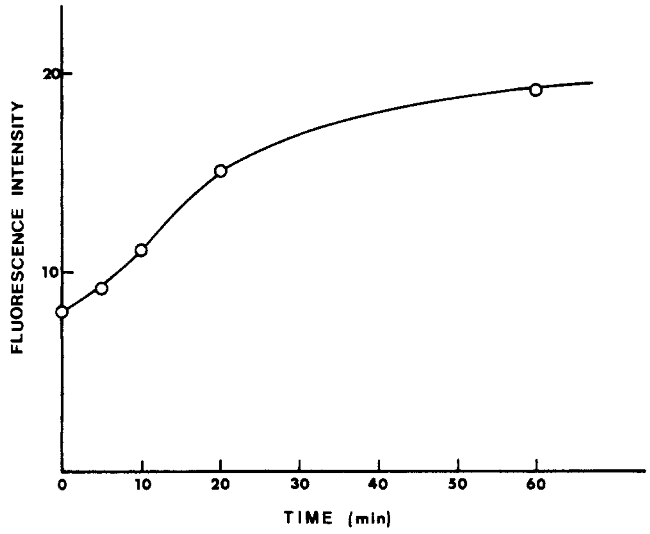


Figure 2. Effect of ultrasonic irradiation on fluorescence intensity of Tb^{3+}.

ligand, a decrease in the metal ion–ligand bond distance, and an increase in the number of coordinated ligands.

Recently we observed that the absorption peak at 310 nm and the fluorescence intensity at 545 nm of Tb^{3+} ions are greatly enhanced when they are bound to synthetic polyelectrolytes[4] and polysaccharides[5] in aqueous solution. These results suggest that the 310-nm absorption band corresponds to the hypersensitive transition of the Tb^{3+} ion and that the ions are site bound on the polyanions.

The absorption peak and the fluorescence intensity of Tb^{3+} in aqueous polyacrylate (PAA) solution do not change upon standing at room temperature. However, it was

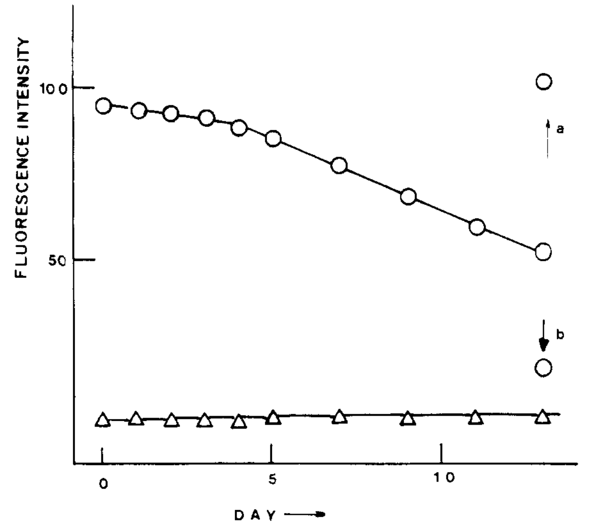


Figure 3. Relationship between fluorescence intensities of Tb^{3+} and time at room temperature: (○) after 20 min, ultrasonic irradiation; (△) without ultrasonic irradiation; (a) after additional 20 min, ultrasonic irradiation; (b) after heating 15 min at 75 °C.

found that when the solution was irradiated with ultrasonic radiation, the intensities were greatly enhanced.

It is well-known that ultrasonic waves have a chemical action on macromolecules.[6] Prolonged exposure of macromolecular solutions to ultrasonic irradiation usually leads to degradation. When the Tb^{3+} polyacrylate solution was exposed to 55 kHz, 100-W ultrasonic irradiation for 10–20 min at 10 °C, the viscosity of the solution was found to be reduced (η_{sp} decreased from 10.35 to 8.98 dL/g after a 60-min irradiation). This indicated that the polymer was degraded by the ultrasonic irradiation. However, in addition to the reduction of the viscosity, the absorption peak at 310 nm and the fluorescence intensity of the 545-nm peak were greatly enhanced (Figure 1). These intensities increased with increasing duration of irradiation (Figure 2). However, it was found that when the irradiated solution was allowed to stand at room temperature, these intensities gradually decreased toward the preirradiation values. Typical data are plotted in Figure 3. These phenomena suggest that the polyacrylate chain was compressed[7] by the ultrasonic irradiation, resulting in increased binding of the Tb^{3+} ions to the nearest carboxylates.

The resulting structure may have a greater coordination number and decreased ion–ligand bond distance, leading to a further increase in the absorption and fluorescence intensity. However, the complex is strained, rendering it thermodynamically unstable. As a result, when the sample was aged at room temperature, the structure rearranged gradually to a more strain-free form, leading to a decrease in the absorption and fluorescence intensities.

When the Tb^{3+} ion was added to the solution of poly(sodium methacrylate) (PMA), only a moderate enhancement of the absorption and fluorescence intensity was obtained.[4] When the PMA–Tb^{3+} solution was irradiated with ultrasonic radiation under the same conditions as for the PAA–Tb^{3+} system, the viscosity of the solution was found to be decreased (η_{sp} decreased from 7.65 to 6.49 dL/g after a 60-min irradiation), but no enhancement in either the absorption or fluorescence intensity was observed.

Complex formation of polyanion with metal ions usually results in an intramolecular coordination (cooperative binding), which leads to a contraction of the polymer chain.[7] Poly(methacrylic acid) is less flexible than poly(acrylic acid) and multidentate complex formation is more difficult.[8] This could explain why irradiation of the

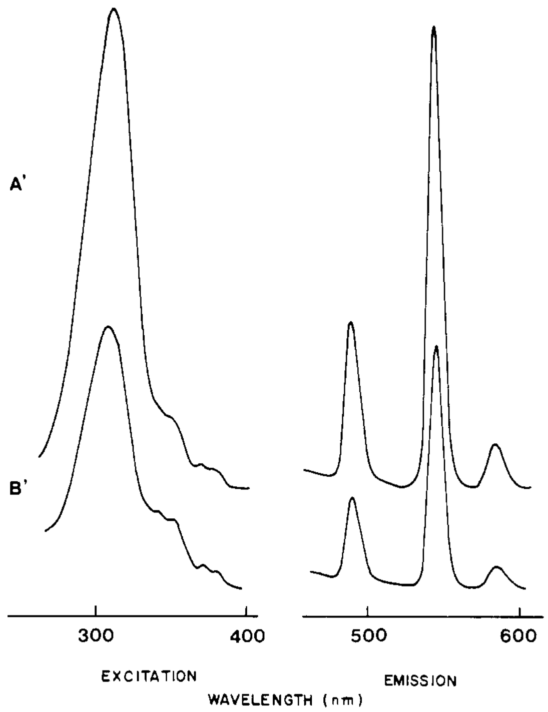
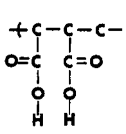


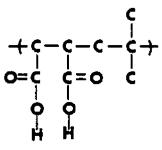
Figure 4. Effect of ultrasonic irradiation on excitation spectra (left) and emission spectra (right) of Tb^{3+} ion in maleic acid–ethylene copolymer. The copolymers MA–E, MA–*i*-Bu, MA-3-MePe were obtained from Monsanto Chemical Co. and their molecular weights were about 100 000. (A′) After 20 min of ultrasonic irradiation, (B′) before ultrasonic irradiation. [COOH] = 5.0 × 10^{-2} M, [Tb^{3+}] = 1.0 × 10^{-3} M, and pH ~9.0.

PMA–Tb^{3+} system with ultrasonic radiation produced no change in fluorescence intensity since the corrdination structure of the Tb^{3+} with the carboxylates did not change.

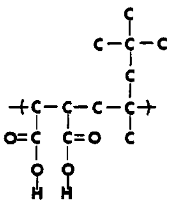
In order to further verify the ultrasonic irradiation effects on the Tb^{3+} ion binding to polyelectrolytes, the fluorescence properties of Tb^{3+} salts of three 1:1 maleic acid–olefin copolymers were investigated. The 1:1 copolymers were maleic acid–ethylene (MA–E) **1**, maleic acid–isobutene (MA–*i*-Bu) **2**, and maleic acid–2,3,3-trimethyl-1-pentene (MA–3-MePe) **3**.


$-\!\!\left[CH(COOH)-CH(COOH)-C-C\right]\!\!-$

1 **MA-E**


$-\!\!\left[CH(COOH)-CH(COOH)-C-C(C)(C)\right]\!\!-$

2 **MA-iBu**


$-\!\!\left[CH(COOH)-CH(COOH)-C-C(C)(C-C(C)(C)-C)\right]\!\!-$

3 **MA-3MePe**

The absorption peak and fluorescence intensity were also found to be greatly increased when Tb^{3+} ions were bound to these copolymers. When solutions of the Tb^{3+}–(MA–E) and Tb^{3+}–(MA–*i*-Bu) systems were irradiated with ultrasonic radiation, the absorption peak and fluorescence intensity were enhanced as found in the Tb^{3+}–PAA system (Figure 4). However, in the case of the Tb^{3+}–(MA-3-MePe) system, neither the absorption nor the fluorescence intensity changed under ultrasonic irradiation. This is believed to be due to the limited flexibility of the chain caused by the bulky methylpentane group. As a result, the coordination structure between Tb^{3+} and carboxylate would not be expected to change under ultrasonic irradiation.

The results reported in this communication show that the coordination structure of flexible synthetic polyelectrolyte salts in aqueous solution rearranges on ultrasonic irradiation. The rare earth ion fluorescence probe technique has been shown to be useful for the elucidation of such structural changes. Multiple experiments along the lines described here are in progress and will be described at a later date.

Acknowledgment. We thank Professor H. Morawetz for helpful discussions.

References and Notes

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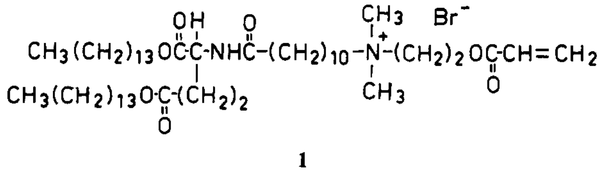
Ordered Cast Films of Polymerized Bilayer Membranes

We describe herein the preparation of highly ordered bilayer films by casting of aqueous dispersions of polymerized bilayer membranes.

It has been shown that a large variety of synthetic amphiphiles undergo spontaneous assemblage to stable bilayer membranes which display physicochemical characteristics similar to those of biolipid bilayers.[1] These aqueous bilayers are often not stable enough to use as functional vesicles, and there are inherent inconveniences in the aqueous bilayer dispersion. These disadvantages have been remedied by two lines of approach: one is polymerized vesicles,[2-6] which are a current target of active investigations for obtaining stable vesicles, and the other technique is immobilization,[7-20] which rendered possible to use bilayers as macroscopic films. The results described in this paper open a new branch in this field by combination of these two approaches.

Amphiphile 1[21] gives by sonication in water colloidal dispersions which are shown by electron microscopy to contain vesicles and lamellae of bilayers. The crystal-to-liquid crystal phase transition temperature, T_c, of the aqueous bilayer was determined to be 42 °C by differential


$$CH_3(CH_2)_{13}OC(=O)-CH\big((CH_2)_2C(=O)O(CH_2)_{13}CH_3\big)-NHC(=O)-(CH_2)_{10}-\overset{+}{N}(CH_3)_2-(CH_2)_2OC(=O)CH=CH_2\ \ Br^-$$

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