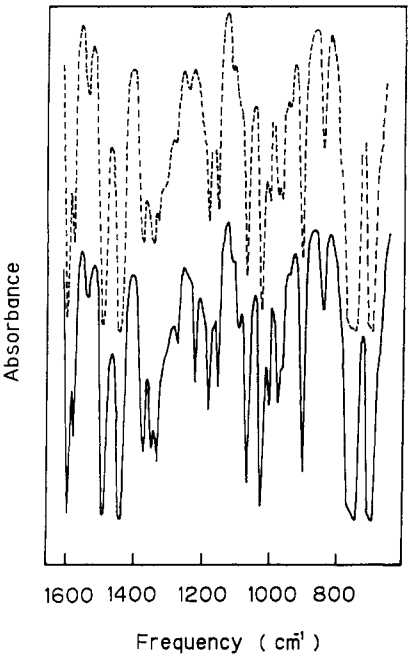

Figure 3. Infared spectra of the new polymer: (—) crystallized sample; (- - -) quenched sample.

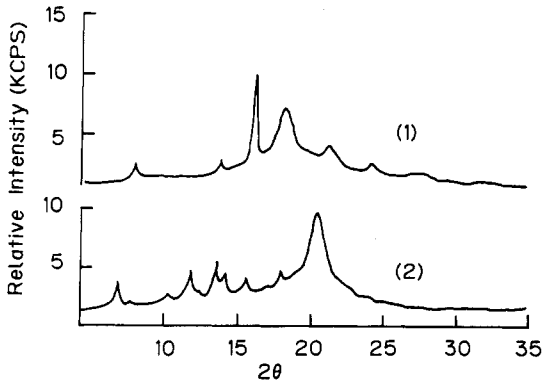

Figure 4. X-ray diffraction spectra of the crystallized sample: (1) isotactic polystyrene; (2) the new polymer.

to a helical conformation were not observed in the crystallized sample, and a new absorption signal was observed at 1200 cm^{-1}. This absorption signal also disappeared in the quenched sample. Therefore, we conclude that the absorption signal at 1220 cm^{-1} is closely associated with the conformation of the new polymer and that this polymer has a conformation different from the helical structure of isotactic polystyrene.

The X-ray diffraction spectra of the new polymer and isotactic polystyrene are shown in Figure 4. The well-defined X-ray diffraction pattern of the new polymer is quite different from that of isotactic polystyrene. The identity period measured from the fiber spectrum of the new polymer is about 5.06 Å, which is much smaller than that of crystallized isotactic polystyrene (6.65 Å), having a threefold helical structure. Furthermore, the identity period is twice as great as that of polyethylene and nearly equal to that of syndiotactic poly(vinyl chloride), having a planar zigzag conformation. We conclude, therefore, that the new polymer has a planar-zigzag conformation in the crystalline state.

The crystallization rate of the new polymer was extremely high in comparison with that of isotactic polystyrene, which is comparable to polyethylene. The melting point of the new polymer is about 270 °C, which is higher than that of isotactic polystyrene by 40 °C.

A more complete characterization and description of the method of preparation of the new polymer are in progress and will be reported shortly.

Registry No. Syndiotactic polystyrene, 28325-75-9.

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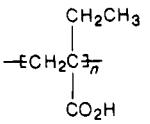
Glucose-Dependent Disruption of Phospholipid Vesicle Membranes†

Poly(α-ethylacrylic acid) (PEAA, 1) undergoes a conformational transition to a globular structure upon acidification of its aqueous solutions.[1,2] The globular polymer



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associates strongly with bilayer vesicles prepared from phosphatidylcholines and phosphatidylglycerols, with profound disruption of bilayer organization.[3,4] The latter phenomenon allows the formulation of phospholipid vesicles that release their contents rapidly and quantitatively in response to small changes in environmental pH.[4] We show herein that this process can be combined with enzymic generation of H^+ to produce vesicles sensitive to low concentrations of neutral organic solutes such as glucose.[5]

Hydration of L-α-dilauroylphosphatidylcholine (DLPC) at a concentration of 2.4 mg/mL in pure water or in aqueous salt solutions affords turbid suspensions of multilamellar vesicles.[6,7] Addition of PEAA[8] and/or the enzyme glucose oxidase (GO)[9] to the hydration medium

† Part 11 in the series "Interactions of Synthetic Polymers with Cell Membranes and Model Membrane Systems". For Part 10, see: Ramaswami, V.; Tirrell, D. A. *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 241.

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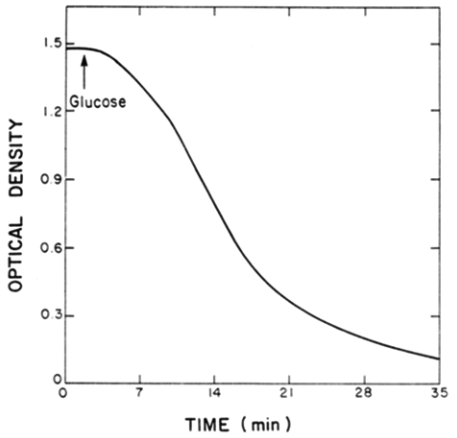

Figure 1. Optical density (400 nm) of an aqueous suspension of DLPC (2.4 mg/mL), PEAA (2.6 mg/mL), and GO (0.7 mg/mL) prior and subsequent to addition of glucose (1.3 mg/mL). Arrow marks time of glucose addition.

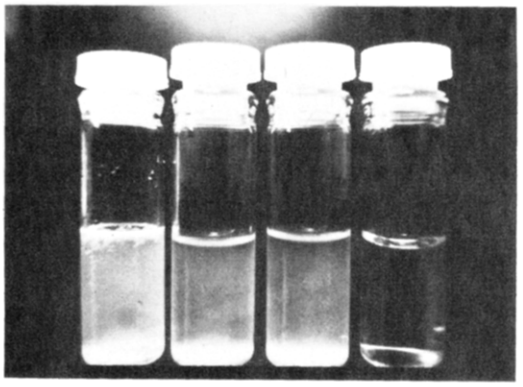

Figure 2. Clarification of DLPC/PEAA/GO suspension upon addition of glucose. From left: DLPC/GO; DLPC/GO + glucose; DLPC/PEAA/GO; DLPC/PEAA/GO + glucose.

causes no significant change in turbidity. Figure 1 is a plot of the optical density (at 400 nm) of an unbuffered DLPC/PEAA/GO (1/1/0.3) suspension vs. time prior and subsequent to addition of glucose[10] at a concentration of 1.3 mg/mL.[11] The optical density of the suspension is reduced rapidly following addition of glucose and reaches a final value less than 10% of the original after approximately 30 min.[12] Figure 2 demonstrates the clarity of the final suspension and presents the results of several control experiments in which no changes in turbidity were anticipated or observed; in particular, the addition of glucose to *polymer-free* DLPC/GO suspensions caused no loss in the turbidity of the suspension.

A full interpretation of these results must await thorough characterization of the aggregates present in the final, acidic suspension; however, disruption of DLPC vesicle membranes in acidic PEAA solutions has been demonstrated previously[4] and is believed to result from lipid solubilization in the compact, hydrophobic polymer coil.[13,14] In the present work, acidificiation occurs via enzymic generation of gluconic acid, with the result that the suspension displays a remarkable sensitivity to low concentrations of glucose.

These results are of interest from several points of view. First, we have shown previously that disruption of vesicle membranes by PEAA is accompanied by rapid, quantitative release of vesicle contents;[4] thus one can imagine therapeutic applications of the present work in self-regulated insulin delivery or diagnostic uses in monitoring of glucose concentrations in physiologic fluids. Second, the behavior of this system bears crude but real analogy to the behavior of hormonal second messenger systems[15] in that the process of interest is mediated not by the added organic solute (glucose) directly but by a second substance (H^+) generated in a specific way via enzymic catalysis. In this crude analogy, glucose plays the role of hormone and H^+ that of second messenger. Finally, this idea is quite general, in that many hydrolytic and oxidative enzymes are known to generate H^+ from a variety of substrates.

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(10) D-Glucose (Gold Label) was used as received from Aldrich Chemical Co. The suspension was saturated with O_2 over a period of 10 min prior to addition of glucose.
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Dendritic Macromolecules:[1] Synthesis of Starburst Dendrimers

A supreme challenge to synthetic chemists has been to design and construct molecular prototypes that mimic key functions in evolutionary chemistry. Host–guest com-

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