

These chemical shift data that support the diad assignments in this copolyester system are collected in Table II.

The presence of diad structure in the ^{13}C NMR spectra of the HBA/HNA copolyesters allows direct determination of primary information on the monomer sequence distribution by spectral deconvolution. These results are summarized in Table III.

In order to quantify the amount of order in these copolyester systems one can define (eq 1a and 1b) Ψ_B and

$$\Psi_B = \frac{(\text{BN})X - (\text{BB})(1 - X)}{(\text{BN})X + (\text{BB})(1 - X)} \quad (1a)$$

$$\Psi_N = \frac{(\text{NB})(1 - X) - (\text{NN})X}{(\text{NB})(1 - X) + (\text{NN})X} \quad (1b)$$

Ψ_N as sequence order parameters based on benzoic or naphthoic units, respectively.¹² (BN), (BB), (NB), and (NN) are the relative numbers of BN, BB, NB, and NN diads in the copolyester and X is the number fraction of B units (i.e., HBA units) in the chain (see Table I).

For a copolyester with infinite polycondensation degree \bar{P}_n , the number of BN diads is equal to the number of NB diads (for a cyclic copolyester this is always true). Furthermore, if $\bar{P}_n = \infty$, eq 2 applies and one can show by

$$(\text{BB})/X^2 = (\text{NN})/(1 - X)^2 \quad (2)$$

simple mathematics that $\Psi_B = \Psi_N$.¹³ However, because the copolyesters A2 and A3 have relatively low \bar{P}_n 's and the deconvolution of the ^{13}C NMR signals has an accuracy of ca. 5%, $\Psi_B \neq \Psi_N$. Therefore, the two values Ψ_B and Ψ_N and the average value $\bar{\Psi} = (\Psi_B + \Psi_N)/2$ are listed separately in Table III and compared with Ψ_B of A1 and Ψ_N of A4. Note that if $\Psi = 1$ the structure is "alternating ordered" (BNBNBN...), if $\Psi = -1$ the structure is "blocky" (BBB...NNN...), and if $\Psi = 0$ the structure is random. As one can see in Table III, the Ψ_B and Ψ_N values of the copolyesters A1-A4 are between +0.04 and -0.02. Since the accuracy of Ψ is ± 0.08 , the measured diad sequence distribution of all four copolyesters, A1-A4, is in agreement with a random arrangement of monomer units. This result is the same inferred by Blackwell et al.⁸ based on X-ray results of melt spun copolyester fibers.

Currently, we are using the NMR methodology in conjunction with specifically labeled monomers to investigate ester interchange in the copoly(HBA/HNA) chain. In particular, we are studying whether equal reactivities of the two monomers HBA and HNA or ester interchange during the reaction lead to the random sequence. Conversely, we are examining conditions that might lead to ordering in the copoly(HBA/HNA) system, as has been observed in the copoly(HBA/PET) system by annealing under specific conditions.¹⁴

Acknowledgment. We thank S. K. Kumar for the helpful discussions concerning the sequence order parameter Ψ , E. Hadziioannou for the DSC measurements, and C. G. Wade for his kind support.

Registry No. 1, 114943-43-0; 2, 116149-25-8; (A1)(A4) (copolymer), 81843-52-9.

References and Notes

- Butzbach, G. D.; Wendorff, J. H.; Zimmermann, H. J. *Polymer* 1986, 27, 1337. Cao, M. Y.; Wunderlich, B. *J. Polym. Sci., Polym. Phys. Ed.* 1985, 23, 521. Blundell, D. J.; Buckingham, K. A. *Polymer* 1985, 26, 1623.
- Davies, G. R.; Ward, I. M. In *Structure and Properties of Oriented Thermotropic Liquid Crystalline Polymers in the Solid State*; Zachariades, A. E., Porter, R. S., Eds.; Marcel Dekker: New York, 1988; Chapter 2.
- Nicely, V. A.; Dougherty, J. T.; Renfro, L. W. *Macromolecules* 1987, 20, 573.

- Quach, L.; Hornbogen, E.; Volkens, W.; Economy, J. *J. Polym. Sci., Polym. Phys. Ed.*, in press.
- McFarlane, F. E.; Nicely, V. A.; Davis, T. G. *Contemporary Topics in Polymer Science*; Plenum: New York, 1977; Vol. 2, p 109.
- Meesiri, W.; Menczel, J.; Gaur, U.; Wunderlich, B. *J. Polym. Sci., Polym. Phys. Ed.* 1982, 20, 719.
- Joseph, E.; Wilkes, G. L.; Baird, D. G. *Polymer* 1985, 26, 689.
- Blackwell, J.; Biswas, A.; Gutierrez, G. A.; Chivers, R. A. *Faraday Discuss. Chem. Soc.* 1985, 79, 73.
- Blackwell, J.; Cheng, M.-M.; Biswas, A. *Macromolecules* 1988, 21, 39.
- Volkens, W.; Lyerla, J. R.; Economy, J.; Dawson, B. *J. Polym. Sci., Polym. Chem. Ed.* 1983, 21, 2249.
- Rosenau-Eichin, R.; Ballauff, M.; Grebowicz, J.; Fischer, E. W. *Polymer* 1988, 29, 518.
- Recently S. Hanna and A. H. Windle (*Polymer* 1988, 29, 207) introduced an order parameter R'_p for copolymers which they called "blockiness." R'_p is based on a logarithmic scale ($R'_p = 1$, random; $R'_p = 0$, alternating; $R'_p = \infty$, blocky) and can be transformed to the "sequence order parameter" Ψ by eq 3

$$\Psi = 1 - \frac{4}{\pi} \arctan(R'_p) \quad (3)$$

However, Ψ has a wider applicability because it can also be determined in the case of A1 and A4 where there is no information about the N- or B-diads, respectively, and, therefore, R'_p cannot be calculated. Furthermore Ψ allows the comparison of different copolymers on a linear scale.

- Note: If $X = 0.5$ ([HBA]/[HNA] = 1), eq 1a and 1b simplify to eq 4:

$$\Psi_B = \Psi_N = \frac{(\text{BN}) - (\text{BB})}{(\text{BN}) + (\text{BB})} = \frac{(\text{NB}) - (\text{NN})}{(\text{NB}) + (\text{NN})} \quad (4)$$

- Lenz, R. W.; Jin, J., II; Feichtinger, K. A. *Polymer* 1983, 24, 327.
- IBM World-Trade Postdoctoral Fellow 1987-1988.

A. Mühlebach,¹⁵ R. D. Johnson, J. Lyerla,* and J. Economy

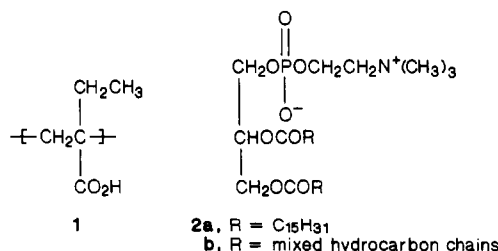
IBM Research Division, Almaden Research Center
650 Harry Road, San Jose, California 95120-6099

Received April 19, 1988;

Revised Manuscript Received July 27, 1988

Photoregulation of the Binding of a Synthetic Polyelectrolyte to Phosphatidylcholine Bilayer Membranes

We have described previously the use of controlled polyelectrolyte adsorption to effect molecular switching in mixtures of hydrophobic polyelectrolytes [e.g., poly(2-ethylacrylic acid) (PEAA, 1)] with bilayer vesicles of natural or synthetic phosphatidylcholines (2). In par-



ticular, we have prepared in this way phosphatidylcholine vesicles that release their contents rapidly and quantitatively in response to changes in pH,^{1,2} temperature,¹ or glucose concentration.³ We describe in the present paper the use of a photosensitive polyelectrolyte to effect photoregulation of the structure and permeability of phosphatidylcholine vesicle membranes.⁴

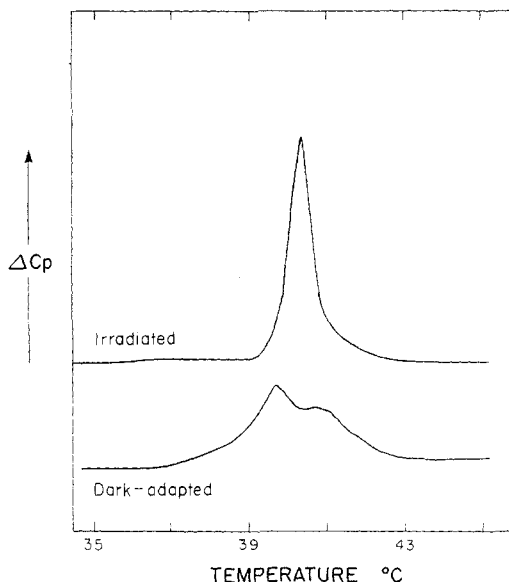
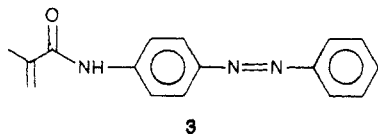


Figure 1. Calorimetric phase transition behavior of DPPC (1 mg/mL) treated with 1 mg/mL of copolymer 4 at pH 7.55. Upper curve: Copolymer 4 irradiated to photoequilibrium with Rayonet 350 nmHg lamps. Lower curve: Dark-adapted 4. Details of sample preparation and calorimetric conditions are given in ref 9.

Radical copolymerization of a 9/1 mixture of 2-ethylacrylic acid (EAA) and *N*-[4-(phenylazo)phenyl]methacrylamide (PAPM, **3**) affords a 24/1 EAA/PAPM co-



polymer (**4**).⁵ The dark-adapted copolymer in water shows the expected absorption spectral maxima at 235 nm ($\epsilon = 11\,200\text{ M}^{-1}\text{ cm}^{-1}$) and 342 nm ($\epsilon = 12\,500\text{ M}^{-1}\text{ cm}^{-1}$). Irradiation at 350 nm⁶ causes a systematic decrease in the intensity of the 342-nm band attributed to the trans isomer of the pendent azobenzene units. Isosbestic points are maintained, and the process is reversible; the absorption spectrum reverts to that of the dark-adapted sample in about 18 h at room temperature in the dark.

Ishihara and co-workers have reported that analogous photoisomerization of copolymers of *N*-[4-(phenylazo)phenyl]acrylamide (PAPA) with acrylic acid causes significant changes in the state of ionization of the chain.⁷ Since we have shown previously that the interactions of PEAA with phosphatidylcholine films are exceedingly sensitive to ionization,^{1,8} it appeared likely that the membrane binding of EAA/PAPM copolymers should be subject to photoregulation.

Figure 1 shows this to be the case. The figure shows calorimetric scans of the order-disorder transitions of dipalmitoylphosphatidylcholine (DPPC, **2a**) membranes treated with dark-adapted and irradiated **4**.⁹ The irradiated sample undergoes a sharp transition similar to that found in pure DPPC membranes,¹⁰ thus minimal membrane reorganization results from addition of the polyelectrolyte carrying largely cis azobenzene residues. On the other hand, dark adaptation (i.e., thermal reversion of the azobenzene units to predominantly trans configurations) yields a disordered film that displays only a broad, poorly defined endotherm.

These results are in accord with our expectations, given the large differences in the solubilities and dipole moments of the cis ($\mu = 3.0\text{ D}$) and trans ($\mu = 0\text{ D}$) forms of azo-

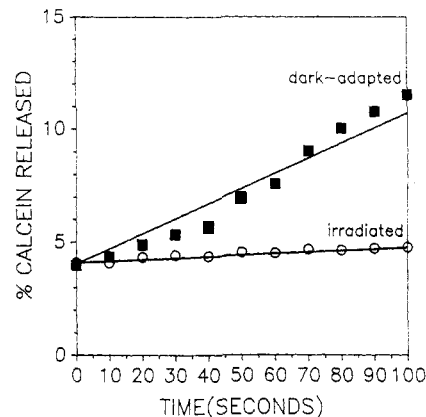


Figure 2. Time-dependent efflux of calcein from unilamellar vesicles of EYPC, pH 7.55: (O) EYPC treated with irradiated **4**; (■) EYPC treated with dark-adapted **4**. Details of sample preparation and methods of determining rates of dye release are given in ref 12.

benzene.¹¹ Increasing the cis fraction of polymer-bound azobenzene units increases local polarity and should stimulate dissociation of carboxylic acid groups bound to the chain. Indeed, Ishihara and co-workers have noted that the pH of unbuffered aqueous solutions of acrylic acid/PAPA copolymers is depressed upon irradiation.⁷ In the present work, the bulk pH is maintained by the large buffer capacity of the system, and changes in carboxylic acid ionization and pendent group hydration are exploited to control the association of the chain with the phosphatidylcholine film.

The binding of hydrophobic polyelectrolytes, e.g., PEAA, to phosphatidylcholine membranes causes large changes in membrane permeability.¹ Figure 2 confirms that the photosensitivity of **4** can be exploited to render membrane permeability sensitive to light. The figure shows the time course of the efflux of the dye, calcein, from unilamellar vesicles of egg yolk phosphatidylcholine (EYPC, **2b**) treated with dark-adapted **4** or with the copolymer irradiated to photoequilibrium.¹² The irradiated sample displays a permeability to calcein which is identical with that of polymer-free EYPC vesicles; this observation is consistent with the calorimetric results in Figure 1 which reveal little structural perturbation of DPPC by the irradiated polyelectrolyte. On the other hand, the permeability of the dark-adapted sample is increased at least 10-fold in comparison with the polymer-free control and the irradiated sample.

The results described herein show that the association of synthetic polyelectrolytes with phosphatidylcholine membranes can be rendered sensitive to light. Photocontrolled polyelectrolyte adsorption can thus be used to effect large changes in the structural organization, and the permeability, of bilayer membranes in water. Work in progress addresses the rate, efficiency, and reversibility of these photoprocesses.

Acknowledgment. This work was supported by a grant from 3M, St. Paul, MN. Support of our research by a Presidential Young Investigator Award of the National Science Foundation (to D.A.T.) is also gratefully acknowledged.

Registry No. **2a**, 2644-64-6; **4**, 116149-26-9.

References and Notes

- (1) Tirrell, D. A.; Takigawa, D. Y.; Seki, K. *Ann. N. Y. Acad. Sci.* **1985**, *446*, 237.
- (2) Devlin, B. P.; Tirrell, D. A. *Macromolecules* **1986**, *19*, 2465.
- (3) Borden, K. A.; Eum, K. M.; Langley, K. H.; Tirrell, D. A. *Macromolecules* **1987**, *20*, 454.

- (4) Higuchi and co-workers have reported very recently on the interaction of a photosensitive poly(glutamate) with vesicles prepared from cationic, double-chain surfactants: Higuchi, M.; Takizawa, A.; Kinoshita, T.; Tsujita, Y. *Macromolecules* 1987, 20, 2888.
- (5) The inherent viscosity of the copolymer used in the present experiments was 0.37 dL/g (0.2% in 50 mM phosphate, pH 7.54, 28 °C).
- (6) Samples were irradiated at room temperature in borosilicate glass vials in a Rayonet RMR 400 mini-reactor equipped with four 350 nmHg vapor lamps and a merry-go-round apparatus. Polymer concentration was 0.5 mg/mL.
- (7) Ishihara, K.; Matsuo, T.; Tsunamitsu, K.; Shinohara, I.; Negishi, N. *J. Polym. Sci., Polym. Chem. Ed.* 1984, 22, 3687.
- (8) Seki, K.; Tirrell, D. A. *Macromolecules* 1984, 17, 1692.
- (9) Calorimetric samples were prepared by adding 1.5 mg of DPPC to 1.5 mL of a 1.0 mg/mL solution of the copolymer in 50 mM potassium phosphate buffer, pH 7.55. This suspension was heated to ca. 45 °C for 1 min and agitated on a vortex mixer for 1 min. The heating and agitation were repeated 3 times, and the sample was degassed under vacuum. Calorimetric scans were recorded on a Microcal MC-1 scanning microcalorimeter at a heating rate of 15 °C/h.
- (10) Mabrey, S.; Sturtevant, J. M. *Methods Membr. Biol.* 1978, 9, 237.
- (11) Hartley, G. S. *Nature (London)* 1937, 140, 281; *J. Chem. Soc.* 1938, 633.
- (12) Samples for determination of dye release rates were prepared by adding 15–20 mg of EYPC to 2.0 mL of a 200 mM calcein solution in 50 mM potassium phosphate buffer, pH 7.14. The sample was agitated on a vortex mixer at room temperature for 3 min and sonicated (Branson Sonifier) at 0 °C for 30 min at 30 W. The sample was then centrifuged in a Beckman JA-20 rotor at 15 000 rpm and 10 °C for 30 min. The top 1.5 mL of the sample was placed on a Sepharose CL-4B column (1.6 × 20 cm) and eluted at 5 °C with 50 mM phosphate buffer; 1.5-mL fractions were collected. Unilamellar vesicles with entrapped calcein eluted in fractions 15–27 as determined by following the optical density of the fractions at 250 nm. Vesicle fractions were adjusted to pH 7.55 with 0.1 N NaOH. Unilamellar vesicles (0.75 mL) were added to 0.75 mL of a 1.0 mg/mL polymer solution in 50 mM phosphate buffer, pH 7.55. The fluorescence of the samples at 530 nm was monitored as a function of time on a Perkin-Elmer MPF-66 spectrometer, with excitation at 495 nm.
- (13) Department of Chemistry.
- (14) Department of Polymer Science and Engineering.

Michael S. Ferritto¹³ and David A. Tirrell*¹⁴

Department of Chemistry and
Department of Polymer Science and Engineering
University of Massachusetts
Amherst, Massachusetts 01003

Received March 25, 1988

Poly[(3,5-di-*tert*-butyl-4-hydroxyphenyl)-acetylene]: Formation of a Conjugated Stable Polyradical

There is currently a great interest in preparing organic polymers containing a stable radical.^{1–3} Poly[(4-hydroxyphenyl)acetylene] is theoretically expected^{4,5} through its oxidation to yield a π -conjugated organic polyradical or a macromolecule having its full spin proportional to its molecular weight. However, poly[(4-hydroxyphenyl)acetylene] and its derivatives have not been synthesized. This paper describes the synthesis of poly[(3,5-di-*tert*-butyl-4-hydroxyphenyl)acetylene] (1) and the formation of its polyradical as shown in the idealized Scheme I.

4-Acetyl-2,6-di-*tert*-butylphenyl acetate (2a) prepared as in the literature⁶ was converted by a Vilsmeier reaction⁷ to β -chloro-3,5-di-*tert*-butyl-4-acetoxycinnamaldehyde (2b).⁸ The aldehyde was hydrolyzed to yield (3,5-di-*tert*-butyl-4-acetoxycinnamyl)acetylene (2c).⁹ 2c was deacetylated with LiAlH₄ in THF to give (3,5-di-*tert*-butyl-4-hydroxyphenyl)acetylene (2d).¹⁰

Scheme I

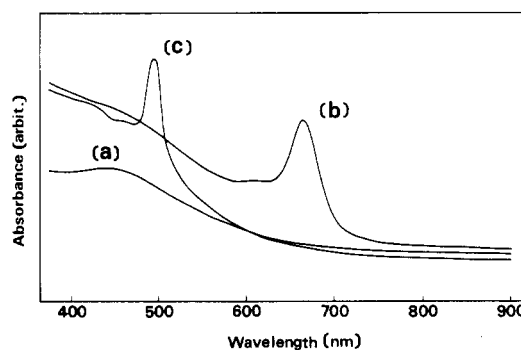
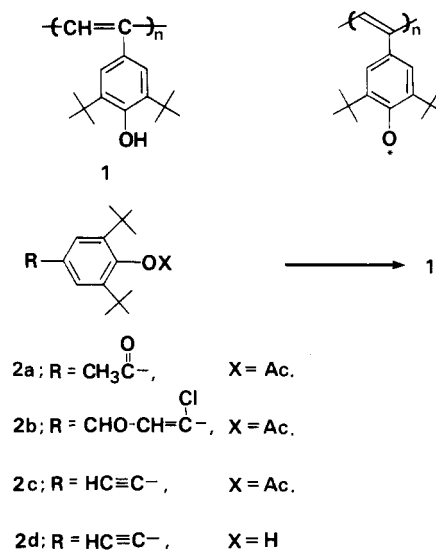


Figure 1. UV-vis spectra of 1: (a) 1 in benzene; (b) 1 in the methanol containing excess KOH; (c) 1 after the oxidation with fresh PbO₂ in benzene.

2d was polymerized with WCl₆ in CCl₄, according to the polymerization procedure for substituted acetylenes.¹¹ 1 was obtained as a dark red powder and was soluble in CHCl₃, benzene, tetrahydrofuran, alcohol, and acetone. The structure represented in 1 was confirmed by elemental analysis and IR.¹² The molecular weight of 1 was 1–3 × 10⁴ (GPC, polystyrene standard) with $M_n/M_w = 1.6–2.0$.

UV-vis spectra of 1 (Figure 1) showed a broad absorption with a maximum at 450 nm that extended to 600 nm, which indicates a fairly long π -conjugated system in the main chain. Treatment of the polymer solution with excess alkali yields the dark green phenolate anion of 1 ($\lambda_{\max} = 655$ nm). Careful oxidation of 1 with fresh PbO₂ under an oxygen-free atmosphere gives a deep brownish solution. A strong absorption band appeared at 495 nm, corresponds to the 2,6-di-*tert*-butyl-4-phenylphenoxy radical ($\lambda_{\max} = 496$ nm¹³), and occurs at wavelengths longer than that of 2,6-di-*tert*-butyl-4-alkylphenoxy radicals ($\lambda_{\max} =$ ca. 400 nm¹⁴). This indicates that the phenoxy substituent is conjugated with the polyacetylene main chain to some extent. The absorption intensity of the oxidized 1 solution suggested formation of the phenoxy radical of 1 in high concentration and stayed constant upon standing at room temperature over a day. This radical formation of 1 is in contrast to the radical formation of the corresponding low molecular phenols, e.g. 3,5-di-*tert*-butyl-4-hydroxycinnamate; the latter had been reported to give bisquinone methides irreversibly.¹⁵ The sterically crowded structure of 1 probably suppresses bond formation between unpaired electrons.

ESR spectra of the oxidized 1 solutions show strong broad absorptions with hyperfine splitting, which give a