itiator ratio. A proportional relation was observed between the composition of the polymer (^{1}H NMR) and the mole ratio of methyl methacrylate and 1,2-epoxypropane reacted. A similar result was obtained in the block copolymerization of methyl methacrylate and epoxyethane.

When δ-valerolactone was employed in the second stage of polymerization, the reaction proceeded rather sluggishly. For example, a living polymer of methyl methacrylate was prepared by polymerization initiated with (TPP)AlMe (0.025 mol/L solution in CH_2Cl_2) at 100% conversion, where the molar amount of the monomer was 40 times that of the initiator ($\bar{M}_n = 3700$, $\bar{M}_w/\bar{M}_n = 1.13$). To this living prepolymer was added δ-valerolactone with a mole ratio to the prepolymer of 100. After 10 days at 30 °C under irradiation with visible light, the GPC of the reaction mixture showed a sharp elution curve at an increased molecular weight ($\bar{M}_n = 5000$, $\bar{M}_w/\bar{M}_n = 1.11$), with disappearance of the peak due to the starting prepolymer of methyl methacrylate. The ^{1}H NMR analysis of the polymer obtained by the reprecipitation of the product from CH_2Cl_2/methanol also confirmed the formation of poly(methacrylate)–polyester block copolymer, the contents of methyl methacrylate and δ-valerolactone[8] units being 74% and 26%, respectively, exactly the same as calculated from the GPC results.

These results demonstrate unprecedented versatility in the application of aluminum porphyrin to the synthesis of various block copolymers.

Registry No. (TPP)AlMe, 108971-21-7; (methyl methacrylate)(propylene oxide) (block copolymer), 115678-83-6; (methyl methacrylate)(δ-valerolactone) (block copolymer), 115678-84-7.

References and Notes

(1) See, for example: (a) Suzuki, T.; Murakami, Y.; Tsuji, Y.; Takegami, Y. *J. Polym. Sci., Polym. Lett. Ed.* **1976**, *14*, 675. (b) Gomes, A. S.; Coutinho, F. M. B.; Marinho, J. R. D. *J. Polym. Sci., Polym. Lett. Ed.* **1987**, *25*, 237.

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(5) For poly(methyl methacrylate), ^{1}H NMR in $CDCl_3$ δ 3.6 (OCH_3), 2–1.8 (CH_2), 1.1–0.8 (CH_3).

(6) For poly[oxy(methylethylene)], ^{1}H NMR in $CDCl_3$ δ 3.5–3.4 (CH and CH_2) and 1.1 (CH_3).

(7) The attempted synthesis of the block copolymer by the polymerizations of propylene oxide initiated with (TPP)AlCl (1, X = Cl) followed by methyl methacrylate (upon irradiation or in the dark) under similar conditions was unsuccessful.

(8) For poly(δ-valerolactone), ^{1}H NMR in $CDCl_3$ δ 4.1 (OCH_2), 2.3 ($CH_2C(O)$), 1.7 ($CH_2(-CH_2)_2-CH_2$).

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Diad Sequence Distribution in Copolyesters of 4-Hydroxybenzoic Acid and 6-Hydroxy-2-naphthoic Acid

Liquid-crystalline aromatic copolyesters based on 4-hydroxybenzoic acid (HBA) and 6-hydroxy-2-naphthoic acid (HNA) have been the subject of numerous physical and mechanical property investigations.[1,2] Important to the interpretation and understanding of these measurements is knowledge of the composition and the monomer sequence distribution in this copolyester system. This is made apparent by the recent ^{13}C NMR results[3,4] on the (60/40) copolyester of 4-hydroxybenzoic acid and poly(ethylene terephthalate) (PET) which demonstrate this copolyester to be compositionally heterogeneous with certain fractions displaying a nonrandom sequence distribution. These results correct initial reports of a homogeneous structure with a random sequence distribution[5] and aid in explaining many of the indirect observations of a nonrandom sequence distribution in the commercial copoly(HBA/PET).[6,7] The sequence distribution in copoly(HBA/HNA) is inferred to be random on the basis of X-ray fiber patterns.[8] However, the X-ray data provide only indirect information on the sequence distribution and only for crystalline regions of the sample. Furthermore, such X-ray data on the 2/1 copolyester of HBA and biphenol terephthalate (BPT)[9] suggest a random sequence of monomers while ^{13}C solid-state NMR has suggested some blockiness in this copolyester.[10] In light of the confusion manifest in the literature on the HBA/PET copolyester system and the different observations of the (HBA/BPT) microstructure, it is critical to have a direct measurement of the sequence distribution in the copolyesters of HBA and HNA.

Table I
Characterization of Copolyesters A1–A4

copolyester	polycondensn conditns[a]	DSC,[b] T, °C (ΔH, J/g)	solubil,[c] %	X[d]	$\bar{M}_n$[e]
A1	c = 4.5%, 18 h, 340 °C	–	0.4	0.48	>30K
A2	melt, 10 min–1 h, 280–340 °C, vacuum	285 (2.6)	2.0	0.73	10.3K
A3	c = 18%, 24 h, 245 °C	260 (1.2)	3.7	0.48	21K
A4	c = 4.5%, 18 h, 340 °C	–	0.2	0.47	>30K

[a] c, concentration (wt %) in therminol-66 (high-boiling inert aromatic hydrocarbon from Monsanto Co., St. Louis, MO). [b] Crystal–nematic transition temperature and enthalpy; –, no endotherm observed (however, see text for annealing results). [c] Weight percent in PFP at 100 °C. [d] Composition: number fraction of HBA units in the copolyester, determined by ^{1}H NMR analysis, see footnote *e* below. Note: The fraction of HBA units can also be determined from the ^{13}C NMR spectrum by using the relative intensities of other carbon signals, e.g., a and b in Figure 1b,c. [e] Determined by ^{1}H NMR end-group analysis of copolyester samples, hydrolyzed in $CD_3OD/D_2O/NaOD$ (12:3:1): Kricheldorf, H. R.; Schwarz, G. *Makromol. Chem.* **1983**, *184*, 475. Accurate determination of end-group signal intensity limits the technique to $M_n \lesssim 30$K.

In this paper, we report the first direct measurement (via ^{13}C NMR spectroscopy) of the diad sequence distribution of commercially available as well as synthesized copolyesters of HBA and HNA.

Four copolyesters have been examined in this study: the commercially available Vectra from Hoechst-Celanese Co., Summit, NJ (designated **A2**), and three copolyesters synthesized in-house (designated **A1**, **A3**, **A4**). Table I lists the polycondensation conditions, crystal–nematic transition temperatures and enthalpies, solubilities in pentafluorophenol, compositions, and number-average molecular weights of these copolyesters. The copolyester **A1** was synthesized from 4-acetoxy-[α-^{13}C]benzoic acid (50% ^{13}C) and 6-acetoxy-2-naphthoic acid; copolyester **A4** from 4-acetoxybenzoic acid and 6-acetoxy-[α-^{13}C)-2-naphthoic acid (50% ^{13}C). The copolyester **A3** was synthesized from

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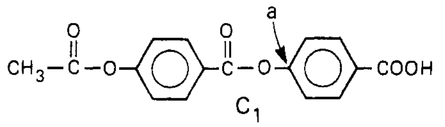
Table II
Chemical Shifts and Assignments of Model Compounds 1 and 2 and Copolyesters A1-A4

1



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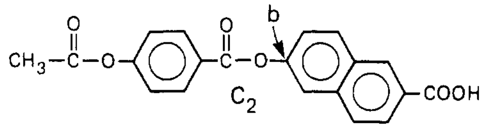
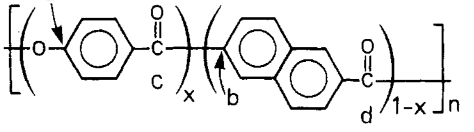


A1-A4



carbon[a]	1	2	A1	A2	A3	A4
a	154.0			154.4	154.6	
b		149.4		149.7	149.8	
c_1	164.5		164.7	164.7	164.7	
c_2		165.3	165.4	165.4	165.4	
d_1				166.3	166.3	166.3
d_2				165.5	165.6	165.6

[a] c_1, benzoic–benzoic diads (BB); c_2, benzoic–naphthoic diads (BN); d_1, naphthoic–benzoic diads (NB); d_2, naphthoic–naphthoic diads (NN).

monomers unenriched in the ^{13}C isotope. The "as synthesized" copolymers **A1** and **A4** had very high molecular weight owing to the high polycondensation temperature and did not show any endothermic transitions in DSC between 50 and 500 °C. The reason for this lack of crystallinity is the fast cooling after the polycondensation reaction. However, by annealing the samples at 210 °C for 24 h, the crystallinity could be improved and a crystal–nematic transition observed at ca. 260 °C (ΔH = 4.2 J/g). **A3** crystallized readily due to the lower molecular weight. The model dimers (compounds **1** and **2**, see Table II) were synthesized by condensation of 4-acetoxybenzoyl chloride with 4-hydroxybenzoic acid or 6-hydroxy-2-naphthoic acid, respectively.

To obtain data on the sequence distribution, ^{13}C NMR spectra of the copolyesters **A1**–**A4** dissolved in pentafluorophenol (PFP) at 100 °C were measured at 80 °C on a Bruker AM 500 FT-NMR spectrometer operating at 125.8 MHz for ^{13}C. The (inverse-gated) proton-decoupled spectra were obtained under quantitative conditions using an rf pulse of 45° combined with a relaxation delay between pulses of 20 s. (The measured relaxation times from inversion–recovery experiments ranged from 2.5 to 3.1 s for the carboxyl carbons.) In each case 1K–20K FID's were accumulated. A DMSO-d_6 insert was used for the lock signal. Chemical shifts are reported with respect to TMS, corrected for temperature effects.

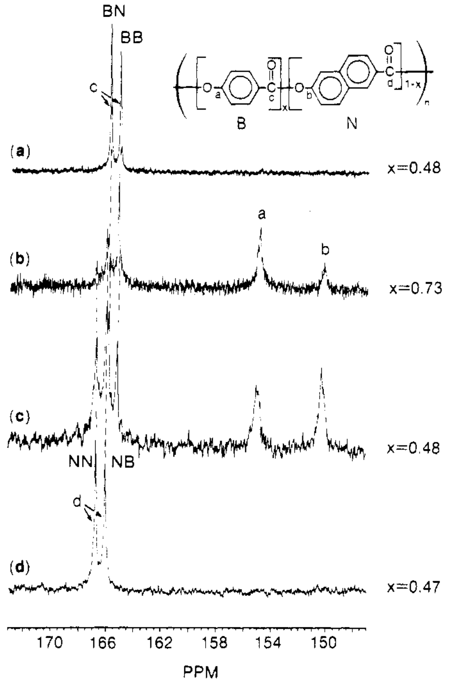


Figure 1. ^{13}C NMR spectra in the carboxyl carbon region of the copolyesters **A1**–**A4** (a–d) in PFP at 80 °C. x is the fraction of HBA units in the copolyester.

In Figure 1b is shown the ^{13}C NMR spectrum over the chemical shift range ca. 173–147 ppm of the commercial copolyester **A2**. The carboxyl carbons of the polymer give rise to four distinct resonances covering a total chemical shift range of 1.6 ppm. The resonances are assigned to the four diads: BB, BN, NB, NN (B = benzoic acid unit, N = naphthoic acid unit). Sensitivity of the carboxyl carbon chemical shift to sequence effects in aromatic copolyesters has been reported previously.[5,11] Support for the resonance line assignments in Figure 1b derives from comparison of the chemical shifts to those in the synthesized copolyesters **A1**, **A3**, and **A4**, and the model dimers **1** and **2** (see Table II). Relative to the spectrum of **A2**, the spectrum of **A3** (Figure 1c) shows the enhanced intensities of the resonances assigned to NN, NB, and BN diads with respect to BB diad intensity, as would be expected based on the higher naphthoic acid content in **A3**. The spectra of the copolyesters with the ^{13}C-enriched carboxyl's (Figure 1a,d) display the respective BB, BN (**A1**) and NN, NB (**A4**) diad resonances. (Note that the natural abundance carbon resonances are below the noise level in Figure 1a,d.) The observed chemical shifts of the internal carboxyl group in the dimer of acetoxybenzoic acid (**1**) and the mixed dimer of acetoxybenzoic–naphthoic acid (**2**) (see Table II) provide further proof of the assignment of the BB and BN diads.

Table III
Diad Sequence Distribution and Order Parameters for the Copolyesters A1-A4

	diads[a]				seq order param[b]		
copolyester	(BB)	(BN)	(NB)	(NN)	Ψ_B	Ψ_N	$\overline{\Psi}$
A1	22 ± 2 (23.0)	26 ± 3 (25.0)	(25.0)	(27.0)	0.04		
A2	52 ± 5 (53.3)	19 ± 2 (19.7)	21 ± 2 (19.7)	8 ± 12 (7.3)	<0.01	−0.02	−0.01
A3	22 ± 2 (23.0)	24 ± 2 (25.0)	24 ± 2 (25.0)	28 ± 3 (27.0)	<0.01	<0.01	<0.01
A4	(22.1)	(24.9)	25 ± 2 (24.9)	28 ± 3 (28.1)		<0.01	

[a] Diad content in percent (sum of all diads = 100%); calculated values for random copolyester in parenthesis. The relative intensities were determined by a spectral deconvolution program, LINESIM, written by Dr. Peter Barron, Griffith University, Brisbane, AUS. The reproducibility was usually within ±5% and always <±10%, the value indicated in the table. [b] For definition see eq 1a and 1b in the text; a propagation of error analysis based on the data on relative intensities in the table and 2% error in compositional analysis yielded an error of ±0.08 in Ψ.

Macromolecules 1988, *21*, 3117-3119 **3117**

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

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

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

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

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

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]

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

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(12) 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

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

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.

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

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

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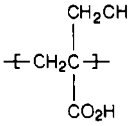
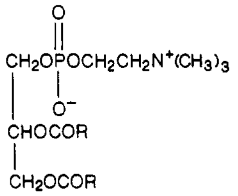
Photoregulation of the Binding of a Synthetic Polyelectrolyte to Phosphatidylcholine Bilayer Membranes

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 particular, 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]



$$-\!\!\left[\mathrm{CH_2}\overset{\overset{\textstyle \mathrm{CH_2CH_3}}{|}}{\underset{\underset{\textstyle \mathrm{CO_2H}}{|}}{\mathrm{C}}}\right]\!\!-$$

1



$$\begin{array}{l}\mathrm{CH_2OP(=O)(O^-)OCH_2CH_2N^+(CH_3)_3} \\ | \\ \mathrm{CHOCOR} \\ | \\ \mathrm{CH_2OCOR}\end{array}$$

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

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