(m, 4 H); mass spectrum for $C_7H_{12}ClNO$ m/e 161.

General Procedure for Polymerization. Since all the polymerizations were carried out under the same conditions, only the polymerization of **8b** is described here as an example. A polymerization tube containing **8b** (2.0 g, 5.68 mmol) and ethylene glycol ditosylate (0.2 mg, 5.4×10^{-7} mol) was degassed under high vacuum (ca. 10^{-5} mm) overnight and then sealed. The sealed tube was heated in a thermal bath at 130 °C for 6 h, at 140 °C for 3 h, and finally at 160 °C for 3 h. The mixture slowly thickened and solidified to a pure white mass in the first period of heating. The product was dissolved in dichloromethane, precipitated by adding to excess methanol, and vacuum dried at 100 °C overnight to give **11b** in quantitative yield.

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Modification of Low-Density Polyethylene Film Using Polymerizable Surfactants[1]

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ABSTRACT: Ultraviolet-induced polymerization (254 nm) of aqueous dispersions comprised of 1,2-bis[11-(methacryloyloxy)undecyl]-*sn*-glycero-3-phosphocholine (**1**), 1,2-bis(heptadeca-10,12-diynoyl)-*sn*-glycero-3-phosphocholine (**2a**), 1,2-bis(heneicosa-10,12-diynoyl)-*sn*-glycero-3-phosphocholine (**2b**), 1,2-bis(hexacosa-10,12-diynoyl)-*sn*-glycero-3-phosphocholine (**2c**), bis[10-(methacryloyloxy)decyl] hydrogen phosphate (**4**), or bis[11-(methacryloyloxy)undecyl]dimethylammonium dimethyl phosphate (**5**) in the presence of low-density polyethylene film (PE) provides a simple and effective means for producing hydrophilic polyethylene surfaces. These modified films show excellent stability toward 1:1 $CHCl_3$–CH_3OH at room temperature, maintaining their hydrophilicity and surfactant content. On the basis of (1) the similarity between the expected loading for monolayer coverage (estimated from collisional areas that have been calculated from pressure–area isotherms for monomeric monolayers constructed at the air–water interface) and the measured surfactant content for each film, (2) the requirement that **2a–c** be properly aligned for effective topotactic polymerization, and (3) the apparent film thickness of polymerized **2b** deposited onto a siliconized silicon oxide surface and its resulting hydrophilicity, it is proposed that each surface bears an ordered polymerized surfactant coating, approaching monolayer coverage. Attempted modification of PE with 1-palmitoyl-2-[11-(methacryloyloxy)undecyl]-*sn*-glycero-3-phosphocholine (**3**) and dimethylhexadecyl[11-(methacryloyloxy)undecyl]ammonium dimethyl phosphate (**6**) failed to alter the film's surface.

Introduction

Surface structure and composition play a major role in defining many of the physical properties and ultimate uses of solid organic polymers. In particular, features such as wetting,[3] weathering,[4] adhesion,[5] dye adsorption,[5] friction,[5] electrostatic charging,[6] permeation,[7] and biocompatibility,[8,9] which are important for engineering and biotechnological applications, are largely influenced by surface characteristics. Despite this fact, current methods available for modifying polymer surfaces in a well-defined manner remain limited.[10]

In this paper we described a new method for modifying the surface of low-density polyethylene film.[10,11] Our *rationale* behind this new approach is summarized in Scheme

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Scheme I

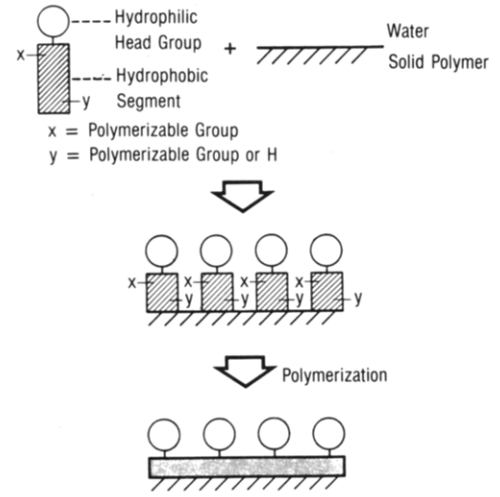
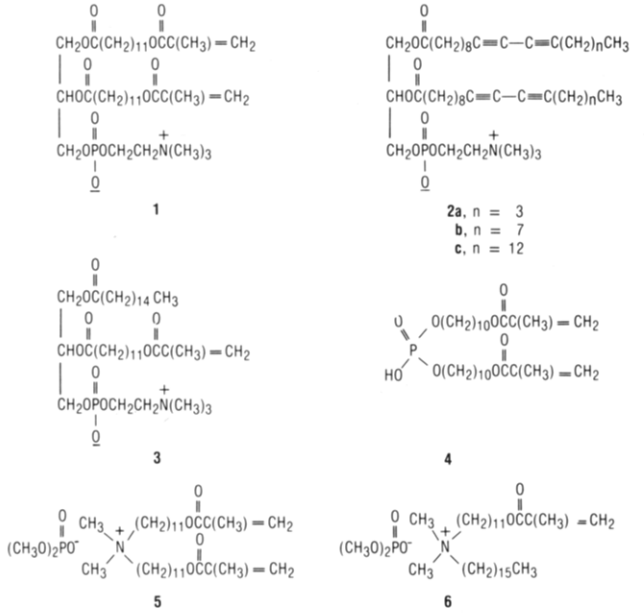


Chart I



I. Dispersal of surfactant molecules in water leads to the formation of aggregates (generally micelles when a single aliphatic chain is employed or vesicles when two chains are present), where hydrophobic interactions are maximized.[12] On the basis of analogy to the behavior of lipids in oil/water mixtures,[13] we reasoned that if a solid hydrophobic polymer were placed in contact with such aqueous solutions, an adsorbed monolayer of surfactant might form spontaneously at the solid–liquid phase boundary. We further reasoned that if the surfactant contained a polymerizable moiety, subsequent polymerization could, in principle, secure the monolayer to the polymer surface via (1) extended nonpolar interactions, (2) covalent linking to alkyl radicals generated on the original surface, and/or (3) insolubility (if a cross-linked network were produced).[14]

In order to explore this idea, we have focused our efforts on the surface modification of low-density polyethylene through the use of polymerizable surfactants **1**–**6** (Chart I). Low-density polyethylene film (PE) was specifically chosen for this investigation for several reasons. First, PE is hydrophobic and flexible, yet sufficiently strong mechanically that it can be handled without special precautions. Second, PE has very low solubility in all common solvents at room temperature and in several solvents at elevated temperatures. A thorough cleaning of the film before and after treatment should, therefore, be possible. Third, PE is readily available, inexpensive, and relatively well-characterized;[15–18] it is a mosaic of crystalline and amorphous regions. A typical sample having a density of 0.919 g/cm^3 is approximately 50% crystalline. Fourth, polyethylene is widely used industrially. New and milder methods for modifying PE could find immediate and direct applications. Phospholipids **1** and **2**, having a choline moiety at the head group, were chosen for initial studies.[11] Each of these molecules would be expected to confer a "cell-membrane-like" environment at the surface of PE. If surface modification were successful, the resulting polymers could prove valuable, especially for biological, biochemical, and biotechnological applications that require a high degree of biocompatibility. Surfactants **4**–**6** extend the range of lipids to include ammonium and phosphate at the head groups. In addition, while compounds **1**, **2**, **4**, and **5** are capable of producing cross-linked networks, analogous surfactants **3** and **6** are expected to yield only linear polymers. Thus, a comparison of the efficacy of these surfactants may indicate whether cross-linking is a prerequisite for successful modification of low-density polyethylene film. Finally, all of the methacrylate-based sufactants should be effectively polymerized either in an organized assembly or in a relative disorder state. In contrast, the conjugated diacetylene-based lipids require proper alignment for efficient topotactic polymerization.[19–23] Comparison of the loading of both classes of surfactants onto PE could yield useful insight into the probable surface structure that exists in each case.

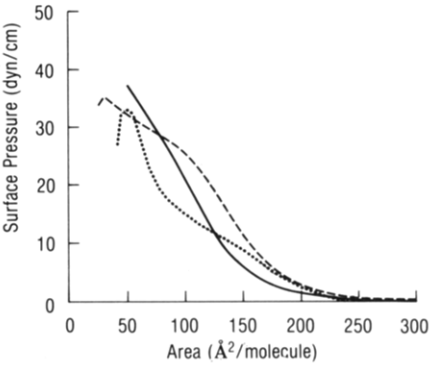


Figure 1. Surface pressure–area isotherms for **1** (···), **4** (– – –), and **5** (—).

Results

Polymerizable Surfactants. Synthetic procedures used for the preparation of **1** and **3** were similar to those previously described.[24] Surfactants **2**, **4**, **5**, and **6** were prepared by straightforward and unexceptional synthetic methods which are described in the Experimental Section.

Monolayer Properties. Surface pressure–area isotherms for **1**, **2**, **4**, and **5** were recorded on a computerized MGW Lauda film balance and are reported in Figures 1 and 2. Analysis of these curves was made by using the semiempirical two-dimensional gas equation (1) and the Langmuir "duplex layer" equation which describe the gaseous and the liquid-expanded monolayer states, respectively. Here, Π is the experimentally measured surface pressure, Π_0 is the position of the horizontal asymptote of the hyperbola which characterizes the liquid-expanded region, A is the measured surface area for a given surface pressure, n is the number of moles of surfactant at the air–water interace, A_0 is the molar collisional area of the surfactant, $R = 8.3143 \times 10^7$ ergs mol^{-1} K^{-1}, and i is an empirical constant which is thought to reflect segmental

Table I
Surfactant Properties at the Air-Water Interface

surfactant	state	surf press. range, dyn/cm	A_0, Å^2	i	Π_0, dyn/cm
1	liquid expanded	1.2–8.0	75 ± 5	3.3	−7.5 ± 0.5
2a	liquid expanded	2.0–29.6	33.0 ± 0.3	2.9	−12.8 ± 0.2
2b	liquid expanded	3.6–28.8	38.0 ± 0.4	3.0	−12.7 ± 0.2
2c	liquid expanded	3.0–30.3	45.3 ± 0.8	2.0	−21.1 ± 1.3
4	gaseous	1.0–11.9	128 ± 1	0.8	−0.13 ± 0.05
5	gaseous	1.1–15.7	94 ± 1	1.1	−0.37 ± 0.05

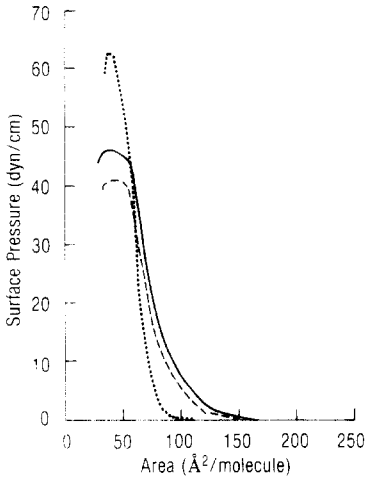


Figure 2. Surface pressure–area isotherms for **2a** (– – –), **2b** (—), and **2c** (···).

motion. A nonlinear least-squares fit of the data for the surface pressure regions specified in Table I was excellent in all cases.[25] Computed values of i and Π_0 listed in Table I for **1**, **2a**, **2b**, and **2c** are typical of saturated phosphatidylcholines and clearly reflect a liquid-expanded state; corresponding values for **4** and **5** establish the presence of a gaseous monolayer state. Also listed in Table I are the collisional areas which have been calculated for each surfactant.

$$\Pi(A - nA_0) = nRT \quad (1)$$

$$(\Pi - \Pi_0)(A - nA_0) = inRT \quad (2)$$

Polyethylene Film Modification. In all of the experiments described in this work, 2 × 10 cm or 2 × 5 cm pieces of commerical low-density polyethylene film 3-mil (Petrothene NA 344-55, 0.920 g/cm^3, 2.0 melt index) were employed. Immersion of PE into an aqueous dispersion of **1** followed by UV irradiation (2537 Å, 1 h), removal, and washing with water and 1:1 $CHCl_3$–CH_3OH afforded a film whose lipid content was constant, when dispersion concentrations in the range 0.23–0.39 mM were used (Table II). Careful phosphorus analysis of the film (see Experimental Section) indicated a loading corresponding to ca. 2.7 × 10^{14} lipids/cm^2 of *geometrical* surface area. Control experiments performed with polyethylene plus aqueous dispersions of polymerized **1**, or nonpolymerized **1** (in the absence of UV light), and polyethylene plus 1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine (with UV irradiation) showed negligible phospholipid incorporation and retention of the hydrophobic surface. Exposure of PE modified with **1** (PE/**1**) to 5.4 M HCl for 24 h led to the quantitative removal of phosphorus from the film.

Using similar procedures, we successfully modified PE with surfactants **2a**, **2b**, **2c**, **4**, and **5** (Table II). Within experimental error, a constant loading of **2a** was observed with dispersions in the range 0.33–0.87 mM and was equivalent to ca. 1.8 × 10^{14} lipids/cm^2. Lipids **2b** and **2c** exhibited constant loadings of ca. 1.9 × 10^{14} and 1.4 × 10^{14}/cm^2, respectively, with surfactant concentrations

Table II
Lipid Content and Surface Hydrophilicity of Modified PE[a]

lipid	lipid, mM	bound lipid × 10^{14}	contact angle, deg A	S	R	adsorbed lipid × 10^{14}
1	0.13	0.1				
	0.16	0.5				
	0.19	2.1				
	0.23	2.4				
	0.26	2.7				
	0.29	2.8				
	0.39	2.7	63	58	13	7.2
2a	0.07	1.0				
	0.13	0.5				
	0.20	1.1				
	0.27	1.0				
	0.33	1.7				
	0.40	1.3				
	0.47	2.2	62	58	28	2.6
	0.53	2.1				
	0.87	1.7				
2b	0.06	2.3				
	0.12	1.7				
	0.18	1.6	70	60	37	
	0.23	2.0				
	0.35	1.8				5.1
	0.47	2.0				
	0.58	2.0				
2c	0.05	1.2				
	0.10	1.1				
	0.15	1.6	73	65	37	
	0.20	1.4				
	0.30	1.6				5.1
	0.40	1.6				
	0.50	1.5				
4	0.09	3.4				
	0.18	4.7				
	0.28	6.0				
	0.37	3.8				
	0.55	4.0	66	47	24	11.8, 5.5, 4.8, 4.9
	0.73	3.0				
5	0.15	0.5				
	0.23	0.7	59	52	18	
	0.31	1.1				
	0.46	1.4				
PE[b]			93	91	87	

[a] Bound (UV treated) and adsorbed lipid refers to the number of lipids/cm^2 of geometrical surface area. Contact angles refer to advancing (A), stationary (S), and receding (R). [b] Untreated polyethylene.

within the range 0.06–0.58 and 0.05–0.50 mM, respectively. Phosphate ester **4** gave a constant loading of ca. 4.2 × 10^{14} lipids/cm^2 with 0.09–0.73 mM. The quaternary ammonium salt **5** produced a loading of 1.4 × 10^{14}/cm^2 with a surfactant concentration of 0.46 mM; higher concentrations of this dispersion could not be used for surface modification experiments due to their inherent instability. Attempted modification of PE with **3** and **6**, using surfactant concentrations of up to 0.26 and 0.34 mM, respectively, failed to produce positive results; i.e., the film remained hydrophobic and no significant incorporation of lipid could be detected by phosphorus analysis.

Stationary (sessile drop), advancing, and receding contact angles measured for water on the surface of surfac-

tant-modified PE as well as untreated PE are reported in Table II. A substantial increase in surface hydrophilicity, after lipid treatment, is clearly evident in all cases. Contact angles which are reported represent the average of at least three separate drops, where both sides of each drop were measured and where the contact angles varied by less than 3°. While most water droplets indicated a uniform coating, some droplets showed a variation in contact angle of as much as 9°. Thus macroscopically, these modified films are not perfectly homogeneous over the entire surface. The basis for this heterogeneity is not presently clear; possible sources include (a) morphological heterogeneity of the commercial unmodified PE surface used, (b) the presence of tiny air bubbles which form occasionally at the film–water interface during UV irradiation, and (c) nonuniform coating at the molecular level.

In an effort to obtain direct evidence for lipid adsorption onto PE *prior* to polymerization, the following additional experiments have been carried out. Clean strips (2 × 10 cm) of PE were immersed in sonicated aqueous dispersions of **1**, **2a**, **2b**, **2c**, and **4** for 1 h at room temperature. The film was then removed and washed by gentle agitation in 40 mL of distilled water (two times) and then analyzed for phosphorus content. Data reported for **1** and **2** represent single experiments; adsorption results for **4** are from four separate experiments. Qualitatively, lipid adsorption in each case is within a factor of about 3 of that found for the analogous modified (UV treated) surfaces.

Thin-layer chromatography of each of the UV-treated dispersions (silica gel, 65:25:4 $CHCl_3/CH_3OH/H_2O$) showed a single spot at the origin, indicating complete polymerization. In the case of the conjugated diacetylene-based phospholipids, yellow photoproducts were obtained;[21] the polymeric nature of the photoproduct of **2b** was further indicated by its lack of solubility in chloroform, dimethyl sulfoxide, *N*,*N*-dimethylformamide, and methanol.[26] Polyethylene film modified with **2a**, **2b**, and **2c** showed no detectable color by visual inspection.

Modification of Silicon Plates with 2b. Optically polished silicon plates (SIL) (1.25 × 2.50 × 0.30 cm) were siliconized via treatment with 10% dichlorooctamethyltetrasiloxane in hexane to give SIL-sil.[27] Immersion of this hydrophobic surface into an aqueous dispersion of **2b** (0.14 mM) followed by UV irradiation and workup, using procedures similar to those used for PE modification, afforded SIL-sil/**2b**. For purposes of comparison, a monolayer of **2b** was constructed at the air–water interface and transferred directly to a SIL-sil plate (single passage from air into water at a rate of 5 cm/min, where the surface pressure was maintained at 30 dyn/cm during the transfer) using conventional Langmuir–Blodgett methods.[21,28] The transfer ratio, defined as the decrease in area of the monolayer at the air–water interface divided by the total geometrical surface area of the plate that passes through this interface, was 1.1. This silicon plate, bearing a supported monolayer (while in the aqueous phase of the film balance), was then placed inside a quartz tube. After removal of residual lipid at the air–water interface, the tube and its contents were removed from the film balance and irradiated (254 nm) to give LB-SIL-sil/**2b**. The average film thickness of polymerized **2b** in four SIL-sil/**2b** plates was 28 Å (Table III). All four plates were hydrophilic, exhibiting an average stationary contact angle for water of 46°. Examination of two LB-SIL-sil/**2b** plates, by ellipsometry and contact angle analysis, strongly suggests that only a small fraction of the lipid remains on the siliconized surface after irradiation; i.e., almost negligible lipid thicknesses were observed, and the surfaces were only modestly and nonuniformly hydrophilic (Table III). Similarly, while a monolayer of **2b** could be transferred to PE via Langmuir–Blodgett methods, subsequent UV treatment in water resulted in the complete loss of the lipid, as evidenced by phosphorus analysis and by retention of the hydrophobic surface.

Table III
Modification of Silicon Plates with 2b

	film thickness,[a] Å [stationary contact angle, deg][b]			
plate no.	SIL	SIL-sil	SIL-sil/**2b**	LB-SIL-sil/**2b**
1	18 ± 0 [26]	22 ± 2 [74]	15 ± 2 [41]	
2	18 ± 0 [15]	26 ± 1 [78]	35 ± 2 [49]	
3	19 ± 1 [20]	26 ± 1 [78]	29 ± 1 [47]	
4	17 ± 0 [17]	24 ± 1 [73]	33 ± 3 [46]	
5	19 ± 1 [21]	21 ± 1 [77]		4 ± 1 [61]
6	17 ± 1 [26]	25 ± 1 [83]		0 [59]

[a] Film thickness represent average values of 10 separate measurements at different locations along the surface of the plate; SIL, SIL-sil, SIL-sil/**2b** and LB-SIL-sil/**2b** refer to the outermost silicon oxide, siliconized, vesicle-deposited polymeric lipid, and Langmuir–Blodgett–deposited polymeric lipid layers, respectively. [b] Stationary contact angles measured for water.

Discussion

Ultraviolet-induced polymerization of aqueous dispersions of **1**, **2**, **4**, and **5** in the presence of PE provides a simple and effective means for producing hydrophilic polyethylene surfaces. These modified films show excellent stability toward 1:1 $CHCl_3$–CH_3OH at room temperature, maintaining their hydrophilicity and surfactant content. Comparison of the results obtained with **1** and **3** and with **5** and **6** suggests that two polymerizable moieties per surfactant are needed for successful surface attachment. While examination of a larger variety of lipids is required before meaningful generalizations can be made, these results suggest that cross-linking plays a key role in this surface modification process.

Surfactants **2a**, **2b**, and **2c** require proper orientation for efficient topotactic polymerization. Intense blue and red colors, commonly observed during UV treatment, are frequently taken as direct evidence for such polymerization.[19-23] Yellow photoproducts of conjugated diacetylenes have also been attributed to topotactic polymerization.[21,22] The absence of blue and red photoproducts in the *aqueous dispersions* of **2** may be the result of the high radius of curvature associated with small vesicles (extensive sonication) and/or the fact that no prior cooling of the dispersion was performed. Both of these factors have been correlated with the effectiveness of topotactic polymerization for conjugated diacetylene-based phospholipids in the vesicle state.[23,26,29,30] Interestingly, very brief exposure of a solid sample of **2b** to UV light (254 nm) resulted in the successive formation of blue and red colors. The lack of solubility of the UV photoproduct of **2b** derived from the aqueous dispersions provides strong indirect evidence that polymerization has occurred. All attempts at clarifying the nature of this product via resonance Raman spectroscopy have failed thus far, due to the strong fluorescence of the sample. The absence of color in PE/**2** cannot be used as evidence for or against topotactic polymerization at the film surface (the UV–vis spectrum of PE/**2b** did not show any significant absorption). Langmuir–Blodgett multilayer construction experiments have

Table IV
Comparison of A_0 vs. A_{PE}

surfactant	A_0,[a] Å^2	A_{PE},[b] Å^2
1	75 ± 5	37 ± 6
2a	33.0 ± 0.5	56 ± 9
2b	38.0 ± 0.4	53 ± 9
2c	45.3 ± 0.8	71 ± 5
4	128 ± 1	24 ± 4
5	94 ± 1	71 ± 12

[a] Collisional area (see Table I). [b] Area occupied per lipid assuming monolayer coverage on a *flat* PE surface.

shown that for molecules similar to **2**, approximately six layers of polymeric lipid are required before a pink color (becoming yellow when heated) is "apparent to the eye".[21] While we are unable to establish that polymers of **2**, deposited on PE, bear the ene–yne backbone which is characteristic of poly(diacetylenes), the predisposition of conjugated diacetylenes toward topotactic polymerization in an ordered state makes such a polymerization pathway likely.

All of the data presented in the Results, when taken together, strongly suggest that each surface bears an ordered polymerized surfactant coating, approaching monolayer coverage. That the true surface of the PE film (i.e., the polyethylene–water interface) is the site of lipid attachment is indicated by the lability of PE/**1** toward HCl. If we define a "surface" group on PE as one that can interact with a reagent that would be expected to be insoluble in the bulk polymer (e.g., HCl) and that is dissolved in a nonswelling solvent (e.g., water), the fact that HCl is capable of promoting the complete release of phosphorus from PE/**1** requires that **1** be located at the water–hydrocarbon interface.[10b]

The native surface of cleaned polyethylene film is clearly not flat at the molecular level.[10] To a first approximation, however, its geometrical area can be taken as a reasonable estimate of its true surface area.[10] If we then define A_{PE} as the area of polyethylene surface that is occupied by each surfactant molecule, a direct comparison can be made with the collisional areas calculated from the pressure–area isotherms. Inspection of the data presented in Table IV reveals reasonable agreement between A_0 and A_{PE} values for **1**, **2a**, **2b**, **2c**, and **5**. Polymerized phosphate ester **4** appears to occupy considerably less space on the PE surface than its monomeric counterpart at the air–water interface. The very high collisional area observed for this surfactant is a likely result of intramolecular hydrogen bonding between the hydroxyl moiety in the head group with its ester functionalities. At the PE/water phase boundary, competing interaction of the ester groups with the hydrophobic PE surface could provide a means for "straightening out" the surfactant, promoting interlipid interaction, and thus lead to a more condensed state; each phosphate ester would, therefore, be expected to take up less area on the PE surface. The similarity between the A_0 and A_{PE} values further suggests that the polymeric lipid coatings are in *intimate* contact with the PE film. If the polymer chains of **1**, **2**, **4**, and **5** were extended out and away from the surface, there would have to be either (1) the same number of chains/cm^2 having approximately the same degree of polymerization or (2) a different density of chains with fortuitous molecular weight distributions, resulting in similar loading. Both situations seem highly improbable.

Ellipsometry data obtained for SIL-sil/**2b** strongly suggest the presence of an ordered monolayer coating of lipid (Table III). While the absolute values of these thicknesses must be regarded as approximate due to anisotropic and adsorption effects,[31,32] these numbers, nonetheless, compare reasonably well with monolayer thicknesses reported for closely related poly(diacetylenes) prepared via Langmuir–Blodgett deposition.[32]

In preliminary experiments, the use of purified vesicle dispersions of **1** and **2b** (gel filtration through Sephadex G-50, where void volume fractions were employed) gave identical loadings on PE as compared with nonfiltered samples. These results suggest that the vesicles themselves, and not unassociated or micellar monomers, serve as the source of lipid for surface modification. Elegant studies described by Schindler have demonstrated that vesicles comprised of 1,2-dioleoyl-*sn*-glycero-3-phosphocholine are capable of depositing a densely packed lipid monolayer at an air–water interface.[33] We hypothesize that an analogous process takes place at the polyethylene film–water phase boundary, resulting in a tightly packed adsorbed monolayer that is subsequently polymerized. Adsorption data reported in Table II provide strong evidence for lipid adsorption prior to polymerization, which is consistent with such a hypothesis. Finally, it is interesting to note the failure of UV treatment to stabilize a monolayer of **2b** supported on PE and on SIL-sil (Langmuir–Blodgett transfer). One possible explanation for this result is that under UV polymerization conditions, the lipid desorbs and equilibrates into the bulk aqueous phase.[33] In contrast, irradiation of both PE and SIL-sil in the presence of aqueous dispersions of **2b** yields strongly hydrophilic surfaces, with a loading on PE approaching monolayer coverage. In these latter cases, an excess amount of lipid present in water may make it possible to maintain a compact adsorbed monolayer at the solid hydrophobic surface.[33]

The surface modification procedure described herein was conceived from the idea of polymerizing a surfactant monolayer adsorbed onto a hydrophobic solid support (Scheme I). All of the data described in the Results are consistent with such a model and make a strong case for surface structures consisting of organized polymerized surfactant monolayers. Alternative pathways for lipid deposition which must also be considered, however, include (i) a "peeling" process in which oligomer (prepolymer) is transferred from adsorbed vesicles to the solid support followed by cross-linking and/or grafting and (ii) adsorption of oligomer from the bulk aqueous phase followed by cross-linking and/or grafting. At the present time we are unable to distinguish between these mechanistic possibilities.

Studies now in progress are aimed at defining (a) the degree of order and uniformity within these surfaces at the molecular level,[34] (b) the precise mechanism and nature of the lipid attachment to the support, and (c) the applicability of this technique for the modification of other organic as well as inorganic solid surfaces.

Experimental Section

General Methods. Unless stated otherwise, all reagents and chemicals were obtained commercially and used without further purification. Distilled water was purified by filtration through a "Milli-Q" reagent water purification system (Millipore Co.). *sn*-Glycero-3-phosphorylcholine (GPC) was prepared from egg lecithin and converted into its $CdCl_2$ complex as previously described.[25] The following chemicals were obtained from Aldrich Chemical Co. and used directly: methacryloyl chloride, 1,10-dodecanediol, pyridinium dichromate, ethyl chloroformate, 4-(dimethylamino)pyridine, dicyclohexylcarbodiimide, methyl dichlorophosphate, 11-bromoundecanol, 40% dimethylamine, copper(I) chloride, 70% ethylamine–hydroxylamine hydrochloride. Dichlorooctamethyltetrasiloxane (Surfasil) was obtained commercially (Pierce Chemical Co.) and used without further puri-

fication. A cation-exchange resin AG MP-50 (50–100 mesh, hydrogen form) and an anion-exchange resin AG1-X2 (100–200 mesh, chloride form) were obtained from Bio-Rad Laboratories. Tetrahydrofuran (Aldrich Chemical Co.) was purified by distillation over sodium hydride. Chloroform (Aldrich Chemical Co.) was distilled over P_2O_5 prior to each reaction. *N,N*-Dimethylformamide (Baker Scientific) was dried over $MgSO_4$ and distilled under reduced pressure. All ^1H NMR, IR, and UV spectra were recorded with Varian EM 360, Beckman Acculab 7, and Bausch & Lomb Spectronic 2000 spectrometers, respectively. UV–vis spectra were recorded with a Perkin-Elmer Model 320 spectrophotometer, equipped with an integrating sphere. Chemical shifts are reported in ppm relative to tetramethylsilane. Melting points were determined with an Electrothermal melting point apparatus and are uncorrected. Chloroform used in depositing the surfactants onto the walls of the glass flasks was HPLC grade (Fisher Scientific Co.). All surfactants were dispersed in pure water via vortex mixing, followed by sonication to constant turbidity, using a bath-type Heat Systems Model W-375 R sonicator (50 °C) and procedures similar to those previously described.[11,25] Elemental analyses were performed by Midwest Microlab, Indianapolis, IN. Chromatographic separations were carried out with Merck silica gel TLC plates (F-254) and Merck Type 60, 230–400 mesh. All column chromatographic purifications were carried out by "flash" chromatographic methods.[35] All ultraviolet treatments were carried out with a Rayonet photochemical reactor (Southern N.E. Ultraviolet Co., Hamden, CT) equipped with 16 2537-Å Rayonet photochemical reactor lamps. The temperature inside the photoreactor during UV irradiation increased to ca. 40 °C. Commercial low-density polyethylene film, 3-mil (Petrothene NA 344-55, 0.920 g/cm^3, 2.0 melt index) was obtained from Luetzow Industries (Milwaukee, WI) and cut into 2 × 10 cm pieces. This film was cleaned by (1) heating for 2 h in refluxing 1:1 $CHCl_3$–CH_3OH, (2) extraction (Soxhlet) with $CHCl_3$ for 12 h, and (3) drying (6 h, 78 °C (0.1 mm)). Contact angles were measured with a specially assembled apparatus involving an optical projection technique to magnify a droplet of water placed on the film. Values were determined after washing each film in 1:1 chloroform–methanol, air-drying (ca. 3 min) and oven-drying (0.5 min, 40 °C). Angles were measured after a 1-min contact time with the water droplet. The base of each droplet on the film surface was 4.0 mm. When projected on the screen, the measured base was 24 cm. Reported contact angles represent the angle between the base line of the drop (deposited via a micropipet) and the tangent to the drop. Advancing angles were measured just prior to the advance of the drop when its volume is increased; the receding angles were measured after the removal of a small volume of the drop, just prior to a decrease in the length of the base of the drop. Manipulations of the drop were affected via a micropipet.

1,2-Bis(heneicosa-10,12-diynoyl)-*sn*-glycero-3-phosphocholine (2b). To a solution of 10-undecynoic acid[36] (4.55 g, 25 mmol) in 10% aqueous KOH (25 mL) was added 150 mg of hydroxylamine hydrochloride and 750 mg of copper(I) chloride in 70% ethylamine (7.9 mL) under a nitrogen atmosphere. A solution of 1-iodo-1-decyne[37] (6.6 g, 25 mmol) in methanol (15 mL) was added dropwise to the reaction mixture with cooling (0 °C). The mixture was then acidified with 2 M H_2SO_4 and extracted with ether. The organic layer was dried over $MgSO_4$ and evaporated. The residue was recrystallized from hexane to yield 4.38 g (55%) of heneicosa-10,12-diynoic acid: NMR ($CDCl_3$) δ 0.87 (t, 3 H, CH_3), 1.33 (br s, 24 H, CH_2), 2.0–2.5 (m, 6 H, $CH_2C{=}O$ and $CH_2C{\equiv}C$); IR (Nujol) $\nu_{C=O}$ 1680 cm^{-1}; mp 49.5–50.5 °C.

Heneicosa-10,12-diynoic acid (0.305 g, 0.96 mmol) and *sn*-glycero-3-phosphorylcholine–$CdCl_2$ (GPC–$CdCl_2$) (112 mg, 0.24 mmol) were stirred with dicyclohexylcarbodiimide (247 mg, 1.2 mmol) and 4-(dimethylamino)pyridine (59 mg, 0.48 mmol) in dry $CHCl_3$ (4 mL) at room temperature for 2 days. The mixture was diluted with 10 mL of 4:5:1 $CHCl_3$–CH_3OH–H_2O, applied to a column of AG-MP-50 (1 × 18 cm), and eluted with the same solvent system. The eluate was concentrated under reduced pressure and the residue purified by column chromatography (silica gel, 9:1 $CHCl_3$–CH_3OH followed by 65:25:4 $CHCl_3$–CH_3OH–H_2O) to give 0.116 g (56%) of **2b**: NMR ($CDCl_3$) δ 0.88 (t, 6 H, CH_3), 1.3 (br s, 48 H, CH_2), 2.33 (m, 12 H, CH_2CO and $CH_2C{\equiv}C$), 3.37 (br s, 9 H, $N(CH_3)_3$), 3.6–4.5 (m, 8 H, CH_2O and CH_2N), 5.53 (m, 1 H, CHO); IR (Nujol) $\nu_{C=O}$ 1710, $\nu_{choline}$[38] 1100, 1045, 970 cm^{-1}. Anal. Calcd for $C_{50}H_{84}NO_8P$: N, 1.63; P, 3.61. Found: N, 1.83; P, 3.46.

1,2-Bis(heptadeca-10,12-diynoyl)-*sn*-glycero-3-phosphocholine (2a). Procedures used for the synthesis of **2a** were similar to those described above for the preparation of **2b**. The yield of heptadeca-10,12-diynoic acid was 60%. NMR ($CDCl_3$) δ 0.9 (br s, 3 H, CH_3), 1.33 (br s, 16 H, CH_2), 2.23 (br s, 6 H, CH_2CO and $CH_2C{\equiv}C$), 11.2 (br s, 1 H, CO_2H); IR (neat) $\nu_{C=O}$ 1700 cm^{-1}. The isolated yield of the product based on GPC–$CdCl_2$ was 86%: NMR ($CDCl_3$) δ 0.90 (t, 6 H, CH_3), 1.33 (br s, 32 H, CH_2), 2.23 (m, 12 H, CH_2CO and $CH_2C{\equiv}C$), 3.4 (br s, 9 H, $(CH_3)_3N^+$), 3.7–4.6 (m, 8 H, CH_2O and CH_2N^+), 5.0–5.3 (m, 1 H, CHO); IR (neat) $\nu_{C=O}$ 1730, $\nu_{choline}$ 1090, 1060, 970 cm^{-1}. Anal. Calcd for $C_{42}H_{68}NO_8P$: N, 1.88; P, 4.15. Found: N, 2.01; P, 3.50.

1,2-Bis(hexacosa-10,12-diynoyl)-*sn*-glycero-3-phosphocholine (2c). Procedures used for the synthesis of **2c** were similar to those described above for the preparation of **2b**. The isolated yield of the product based on GPC–$CdCl_2$ was 58%: NMR ($CDCl_3$) δ 0.90 (t, 6 H, CH_3), 1.27 (br s, 68 H, CH_2), 2.0–2.5 (m, 12 H, CH_2CO and $CH_2C{\equiv}C$), 3.4 (br s, 9 H, $(CH_3)_3N^+$), 3.7–4.5 (m, 8 H, CH_2O and CH_2N^+), 5.1–5.3 (m, 1 H, CHO); IR (Nujol) $\nu_{C=O}$ 1710, $\nu_{choline}$ 1090, 1055, 965 cm^{-1}. Anal. Calcd for $C_{60}H_{104}NO_8P$: N, 1.40; P, 3.10. Found: N, 1.52; P, 3.07.

Bis[10-(methacryloyloxy)decyl] Hydrogen Phosphate (4). Methyl dichlorophosphate (0.18 mL, 1.8 mmol) was added to dry pyridine (1.8 mL) at −20 °C and the mixture was stirred for 15 min.[39] To this mixture was then added 0.885 g (3.66 mmol) of 10-(methacryloyloxy)decanol[40] in dry pyridine (1.8 mL) which had been precooled to −20 °C. The temperature was then gradually raised to room temperature (15 min), and the mixture was stirred overnight. After pyridine was removed under reduced pressure, 20 mL of dilute HCl was added to the residue. Subsequent extraction with $CHCl_3$, followed by drying of the organic layer over $MgSO_4$ and concentration under reduced pressure, afforded crude **4**. Purification by chromatography (silica gel, 9:1 $CHCl_3$–CH_3OH) furnished 0.33 g (17%) of **4**: NMR ($CDCl_3$) δ 1.3 (br s, 32 H, CH_2), 1.93 (m, 6 H, $CH_3C{=}$), 3.6–4.4 (m, 4 H, CH_2O), 4.1 (t, 4 H, CH_2OCO), 5.5 (m, 2 H, vinyl), 6.03 (m, 2 H, vinyl); IR (neat) $\nu_{C=O}$ 1715, $\nu_{C=C}$ 1630 cm^{-1}. Anal. Calcd for $C_{28}H_{51}PO_8$: C, 61.52; H, 9.40; P, 5.67. Found: C, 59.34; H, 9.29; P, 5.80.

Bis[11-(methacryloyloxy)undecyl]dimethylammonium Dimethyl Phosphate (5). A mixture of 11-bromoundecanol (5.0 g, 20 mmol) in THF (50 mL) and 40% dimethylamine (250 mL) was allowed to stand at room temperature overnight. The product mixture was extracted with methylene chloride, and the organic layer was dried ($MgSO_4$) and concentrated under reduced pressure. Distillation afforded 2.3 g (55%) of 11-(dimethylamino)undecanol (114–120 °C (0.15 mm)): NMR ($CDCl_3$) δ 1.27 (br s, 18 H, CH_2), 2.17 (br s, 8 H, NCH_3 and NCH_2), 3.22 (s, 1 H, OH), 3.55 (t, 2 H, CH_2O).

A mixture of 11-(dimethylamino)undecanol (0.267 g, 1.24 mmol) and 11-bromoundecanol (0.622 g, 2.48 mmol) in toluene (5 mL) was heated at 100 °C for 21 h. The resulting bis(11-hydroxyundecyl)dimethylammonium bromide (0.484 g, 84%) precipitated from solution and was filtered, washed with chloroform, dried, and esterified directly with methacryloyl chloride without further purification.

Bis(11-hydroxyundecyl)dimethylammonium bromide (129 mg, 0.277 mmol) was heated with methacryloyl chloride (0.268 g, 2.3 mmol) for 2 h at 90 °C. After removal of unreacted methacryloyl chloride and liberated HCl, under reduced pressure, the residue was chromatographed (silica gel, 6:1 $CHCl_3$–CH_3OH), affording 0.171 g of bis[11-(methacryloyloxy)undecyl]dimethylammonium halide. Subsequent passage through 16 mL of an anion-exchange resin bearing dimethyl phosphate (see below), using 4:5:1 $CHCl_3$–CH_3OH–H_2O as the eluent, afforded, after solvent evaporation, 180 mg (0.277 mmol, 100%) of **5**: NMR ($CDCl_3$) δ 1.3 (br s, 36 H, CH_2), 1.93 (m, 6 H, $CH_3C{=}$), 3.3 (br s, 6 H, NCH_3), 3.53 (d, 6 H, CH_3OPO), 3.4–3.8 (m, 4 H, NCH_2), 4.1 (t, 4 H, OCH_2), 5.53 (m, 2 H, vinyl), 6.07 (m, 2 H, vinyl); IR (neat) $\nu_{C=O}$ 1710, $\nu_{C=C}$ 1630 cm^{-1}. Anal. Calcd for $C_{34}H_{66}NO_8P$: N, 2.16; P, 4.78. Found: N, 1.78; P, 3.61.

A column of AG1-X2 (16-mL wet volume, 0.8 mequiv/mL) was eluted with 2 M NaOH (100 mL) and washed thoroughly with distilled water. The resin was then treated with dimethyl hy-

drogen phosphate (2.65 g, 21 mmol) in 5 mL of water and washed sequentially with water and 4:5:1 $CHCl_3$–CH_3OH–H_2O. Dimethyl hydrogen phosphate was prepared as follows: Dimethyl chlorophosphate (21.9 g, 0.15 mmol)[41] in 50 mL of acetone was added dropwise to 100 mL of water with stirring. The reaction was exothermic and was stirred for 2 h (without external cooling). Water was removed under reduced pressure, affording dimethyl hydrogen phosphate (19 g, 0.15 mol, 100%) as a highly viscous liquid.

Dimethylhexadecyl[11-(methacryloyloxy)undecyl]ammonium Dimethyl Phosphate (6). Dimethylhexadecyl [11-(methacryloyloxy)undecyl]ammonium bromide[42] was converted into its dimethyl phosphate form via ion exchange using procedures similar to those described above for the preparation of **5**: NMR ($CDCl_3$) δ 0.88 (m, 3 H, CH_3), 1.23 (s, 46 H, CH_2), 1.93 (m, 3 H, CH_3C=), 3.28 (br s, 6 H, CH_3N), 3.52 (d, 6 H, CH_3OPO), 3.3–3.7 (m, 4 H, CH_2N), 4.1 (t, 2 H, CH_2O), 5.5 (m, 1 H, vinyl), 6.07 (m, 1 H, vinyl).

Preparation of Monolayers and Pressure–Area Isotherms. Surface pressure isotherms were recorded with a computerized MGW Lauda film balance (23 °C). The surfactants were spread on a pure water surface (previously saturated with air) from a 9:1 (v/v) hexane–ethanol solution containing approximately 1 mg of lipid/mL.[43] The rate of monolayer compression was 1.2 cm^2/s.

Modification of Low-Density Polyethylene Film. The following representative procedure, described for the loading of **2b** onto PE, was used in all cases. Surfactant **2b** (15 mg) was dissolved in 10 drops of $CHCl_3$ and placed in a 25-mL thin-walled round-bottomed flask. The lipid was then coated onto the walls of the flask by evaporating off the solvent (a stream of nitrogen was used initially, followed by drying under reduced pressure (12 h, 22 °C, 0.1 mm)). Degassed and distilled water (15 mL) was then added, and the mixture was vortex mixed, degassed with a stream of nitrogen, sonicated for 1 h (bath-type sonicator) at 50 °C, and cooled to room temperature. An appropriate volume of the dispersion was then added directly to 25-mL quartz test tubes, each containing a strip of clean polyethylene film. In order to avoid bubble formation on the surface of the film, it is important to add the dispersion slowly down the walls of the tube [the PE film (20 mm in width) was conveniently held in place by using 19-mm-diameter tubes]. The dispersion was then carefully diluted with distilled water to appropriate concentrations for surface modification studies. Each tube was sealed with a No-Air stopper, and the vapor phase was then carefully purged with nitrogen for 10 min. The tubes were allowed to stand at room temperature for 1 h and were then placed in a Rayonet photochemical reactor and irradiated for 1 h (2537 Å). Within experimental error, extending the contact time of PE in the presence of 0.15 mg/mL of **1** to 6 h, prior to irradiation, did not significantly affect the loading. The films were then removed from the tubes, gently hand shaken in air for ca. 15 s, and washed by immersing them into distilled water (ca. 100 mL) and gently agitating them (each film was moved in and out of the wash six or seven times). To prevent contamination of the surface, all films were handled with stainless steel forceps. The washing procedure was repeated four times, using, in each case, freshly distilled water. Finally, each strip was immersed in 1:1 $CHCl_3$–CH_3OH for 24 h at room temperature, transferred directly to a Pyrex tube, slowly pyrolyzed, and analyzed for phosphorus.[11] An appropriate calibration for phosphorus analysis was made, using sodium hydrogen phosphate as the standard; within experimental error, dipalmitoyl-*sn*-glycero-3-phosphocholine produced the same calibration curve. The calibration curve data were obtained by adding known quantities of the phosphorus compound to a Pyrex tube containing a 2 × 10 cm strip of clean PE, pyrolyzing the mixture, and analyzing for phosphorus content;[11] the error in the "bound" and "adsorbed" lipid values reported in Table II is estimated to be ca. 20%. Blank experiments carried out in the absence of the phosphorus standard and in the absence of PE film, showed an apparent phosphorus content in the reagent solutions of 0.0046 μmol for a given analysis, equivalent to 0.69×10^{14} lipids/cm^2. Control experiments carried out in the absence of the phosphorus standard but in the presence of a cleaned and unmodified 2 × 10 cm strip of PE film indicated an apparent phosphorus content in the film (after subtraction of the blank value from the reagent solution) of 0.0029 μmol, equivalent to 0.44×10^{14} lipids/cm^2 of PE surface.

Modification of Silicon Plates with 2b. Optically polished silicon plates, SIL (Infrared Optics, Farmingdale, NY) were washed with 1:1 $CHCl_3$–CH_3OH and air-dried. The oxide surface was siliconized via treatment with 10% dichlorooctamethyltetrasiloxane in hexane (20 min, room temperature) to give SIL-sil.[26] Immersion of SIL-sil in an aqueous dispersion of **2b** (0.14 mg/mL) followed by UV irradiation (254 nm) and washing, using procedures similar to those used for PE modification, afforded SIL-sil/**2b**. In a related experiment, a monolayer of **2b** was constructed at the air–water interface of a computerized MGW Lauda film balance and transferred directly to a SIL-sil plate by single passage of the plate from air into water at a rate of 5 cm/min.[28] The surface pressure was maintained at 30 dyn/cm during the transfer; the transfer ratio was 1.1. While in the aqueous phase of the film balance this silicon plate was then placed inside a quartz tube. After removal of residual lipid at the air–water interface, the tube and its contents were removed from the film balance and irradiated (254 nm), and the plate was washed in the usual manner to give LB-SIL-sil/**2b**.

Ellipsometry Measurements. Ellipsometry measurements were performed with an L116A-85F dual-mode automatic ellipsometer (Gaertner Scientific) equipped with a 6328-Å laser light source and SC6A, GC5A, and GC8A programs for data analysis; the incidence angle used in all cases was 70°. The average thickness of the oxide layer present on the silicon plates was measured with the SC6A program. The thickness of the siliconized layers was determined by using a one-layer program (GC5A), where the refractive index of the siliconized layer was fixed at 1.38; apparent optical constants used for the Si–SiO_2 (SIL) layer were determined by using a SUBCA program and were $n_s = 3.88$ and $k_s = 0.15$ at 6328 Å. The thicknesses of polymerized **2b** were determined by using a two-layer program (GC8A), where the refractive index and measured thickness of the siliconized layer plus the refractive index of the lipid layer ($n = 1.52$)[32] were all fixed.

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Registry No. 1, 80294-17-3; **2a**, 96557-16-3; **2a** (homopolymer), 96557-22-1; **2b**, 96557-17-4; **2b** (homopolymer), 96557-23-2; **2c**, 96614-19-6; **2c** (homopolymer), 96614-20-9; **4**, 90046-26-7; **4** (homopolymer), 90046-27-8; **5**, 96557-18-5; **5** (homopolymer), 90046-29-0; **6**, 96557-20-9; $CdCl_2$, 10108-64-2; PE (homopolymer), 9002-88-4; 10-undecynoic acid, 2777-65-3; 1-iodo-1-decyne, 67826-81-7; heneicosa-10,12-diynoic acid, 28393-00-2; heptadeca-10,12-diynoic acid, 28393-06-8; methyl dichlorophosphate, 677-24-7; 10-(methylacryloyloxy)decanol; 56927-66-3; 11-bromoundecanol, 1611-56-9; dimethylamine, 124-40-3; 11-(dimethylamino)undecanol, 29823-94-7; bis(11-hydroxyundecyl)dimethylammonium bromide, 96557-21-0; dimethyl phosphate, 813-78-5; dimethylhexadecyl[11-(methylacryloyloxy)undecyl]ammonium bromide, 74875-67-5.

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Stereoselectivity of the Model Catalytic Site Proposed for the Isospecific Ziegler–Natta Polymerization of the α-Olefins

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ABSTRACT: The coordination of C-3 branched α-olefins to the model catalytic site, proposed by some of us for the isospecific Ziegler–Natta polymerization, is considered. We point out that the model is able to account for the stereoselectivity of the catalyst in the presence of a chiral monomer (3-methyl-1-pentene). The model would be also able to account for the relative reactivities of the C-3 branched monomers in the polymerization initiation steps.

Introduction

In previous papers,[1-5] a model for the catalytic site for the Ziegler–Natta polymerization of the α-olefins, which accounts for the observed isospecific behavior, has been proposed. Such a model is able to explain a large number of factual observations (e.g., type of tacticity errors along a mainly isotactic chain,[1] maintenance of isotacticity after an ethylene insertion,[1] similarity of the general behavior of $TiCl_3$ and $MgCl_2$–Lewis base supported catalysts[4]) and above all was able to give correct predictions[1,3] relative to the stereospecificity of polymerization initiation steps (when the alkylating groups are CH_3, C_2H_5, or i-C_6H_9), confirmed by the experimental data obtained by Zambelli and co-workers.[6]

It is well-known that the isospecific catalysts are also partially stereoselective: in the presence of racemic monomers, polymers are obtained, which can be partially resolved into optically active fractions.[7-10] Recently a detailed study relative to the isotactic polymerization of (*RS*)- and (*S*)-3-methyl-1-pentene has been published.[11] In particular, quantitative data have been reported relative to the initiation step on Ti–methyl bonds, which was characterized as nonenantioselective but partially diastereoselective. In other words both *si* and *re* attack of the

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