$$\sum_{j=1}^{N} H_{ij}B_{ij} = \sum_{j=1}^{N} H_{kj}B_{kj} \qquad i \neq k \tag{10a}$$

$$\sum_{j=1}^{N} (\mathbf{H}^{-1})_{ij}B_{ij} = \sum_{j=1}^{N} (\mathbf{H}^{-1})_{kj}B_{kj} \qquad i \neq k \tag{10b}$$

From eq 1, 3, and 9 we get

$$D_{\mathrm{t,K}}/D_{\mathrm{t}} = (\sum_{j=1}^{N} H_{ij})[\sum_{j=1}^{N} (\mathbf{H}^{-1})_{ij}] \tag{11}$$

for any i. Since matrix **H** is symmetric

$$\sum_{i=1}^{N} (\sum_{j=1}^{N} H_{ij})[\sum_{j=1}^{N} (\mathbf{H}^{-1})_{ij}] = \sum_{j=1}^{N} \sum_{l=1}^{N} \sum_{i=1}^{N} H_{ji}(\mathbf{H}^{-1})_{il} \tag{12}$$

and, consequently, for structures satisfying eq 8

$$D_{\mathrm{t,K}}/D_{\mathrm{t}} = (1/N)\sum_{j=1}^{N} \sum_{l=1}^{N} \delta_{jl} = 1 \tag{13}$$

In order to show easily the equivalence between eq 4 and 7, we should add some other conditions. Thus we will be restricted to structures for which

$$|\mathbf{R}_i| = |\mathbf{R}_k| \qquad i \neq k \tag{14}$$

Then all the elements B_{ii} are identical. Taking also into account eq 4, 7, and 10 and noticing that $B_{ij} = B_{ii} \cos \alpha_{ij}$, where α_{ij} is the angle defined by vectors $\mathbf{R}_i$ and $\mathbf{R}_j$, we find

$$[\eta]/[\eta]_{\mathrm{app}} = \sum_{j=1}^{N} \sum_{l=1}^{N} H_{ij}(\mathbf{H}^{-1})_{il} \cos \alpha_{ij} \cos \alpha_{il} \tag{15}$$

or

$$[\eta]/[\eta]_{\mathrm{app}} = (1/2)\sum_{j=1}^{N} \sum_{l=1}^{N} \{[\cos (\alpha_{ij} + \alpha_{il}) + \cos (\alpha_{ij} - \alpha_{il})]H_{ij}(\mathbf{H}^{-1})_{il}\} \tag{16}$$

Many symmetrical structures have C_2 symmetry axes defined by the center of masses and each one of the hydrodynamic units. In all these cases

$$\sum_{j=1}^{N} H_{ij} \sin \alpha_{ij} = 0$$

$$\sum_{j=1}^{N} (\mathbf{H}^{-1})_{ij} \sin \alpha_{ij} = 0$$

and

$$\sum_{j=1}^{N} \sum_{l=1}^{N} H_{ij}(\mathbf{H}^{-1})_{il} \sin \alpha_{ij} \sin \alpha_{il} = 0 \tag{17}$$

Equations 16 and 17 lead to

$$[\eta]/[\eta]_{\mathrm{app}} = \sum_{j=1}^{N} \sum_{l=1}^{N} \cos (\alpha_{ij} - \alpha_{il}) H_{ij}(\mathbf{H}^{-1})_{il} \tag{18}$$

For planar structures satisfying eq 8, 14, and 17 the simplification $\alpha_{ij} - \alpha_{il} = \alpha_{jl}$ gives

$$[\eta]/[\eta]_{\mathrm{app}} = (1/N)\sum_{j=1}^{N} \sum_{l=1}^{N} \cos \alpha_{jl} \sum_{i=1}^{N} H_{ij}(\mathbf{H}^{-1})_{il} = 1 \tag{19}$$

Equation 19 is applicable to structures formed by units placed at the vertices of regular polygons.

Some structures satisfying eq 8, i.e., with $D_{\mathrm{t,K}} = D_{\mathrm{t}}$, do not yield $[\eta]/[\eta]_{\mathrm{app}} = 1$. This is the case of a rectangular structure (for which eq 17 is not valid) or a nonplanar flexible ring composed by N units joined through statistical segments. Another interesting instance is the straight rod with large N. In this structure eq 8 holds asymptotically while the two formulas for the intrinsic viscosity are not equivalent.

Nevertheless, the equivalence between eq 4 and 7 applies for some nonplanar structures of higher symmetry. Thus in the very simple case of four units disposed at the vertices of a tetrahedron the elements of matrices **H** and $\mathbf{H}^{-1}$ have only two different values since off-diagonal terms are all identical. Then

$$\sum_{j=1}^{N} H_{ij}(\mathbf{H}^{-1})_{ij} = H_{ii}(\mathbf{H}^{-1})_{ii} + 3H_{ik}(\mathbf{H}^{-1})_{ik} = 1 \tag{20}$$

and

$$\sum_{j=1}^{N} H_{ij}(\mathbf{H}^{-1})_{kj} = H_{ii}(\mathbf{H}^{-1})_{ik} + H_{ik}(\mathbf{H}^{-1})_{ii} + 2H_{ik}(\mathbf{H}^{-1})_{ik} = 0 \tag{21}$$

for any $k \neq i$. On the other hand, since $\cos \alpha_{ik} = -{}^{1}/{}_{3}$ for $i \neq k$

$$\sum_{j=1}^{N} \sum_{l=1}^{N} H_{ij} \cos \alpha_{ij}(\mathbf{H}^{-1})_{il} \cos \alpha_{il} = H_{ii}(\mathbf{H}^{-1})_{ii} - H_{ii}(\mathbf{H}^{-1})_{ik} - H_{ik}(\mathbf{H}^{-1})_{ii} + H_{ik}(\mathbf{H}^{-1})_{ik} \tag{22}$$

Subtracting eq 21 from eq 20, comparing the result with eq 22, and taking into account eq 15 lead to $[\eta]/[\eta]_{\mathrm{app}} = 1$. Similar, though considerably more elaborate demonstrations could be worked out for other regular polyhedral structures.

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Alternating Copolymerization of 7,7,8,8-Tetracyanoquinodimethane with Methyl Methacrylate in Acetonitrile

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In previous papers, we reported spontaneous alternating copolymerizations of 7,7,8,8-tetracyanoquinodimethane (TCNQ) in acetonitrile with donor monomers such as styrene (St), 2-chloroethyl vinyl ether (CEVE), phenyl vinyl ether (PhVE), and vinyl acetate (VAc),[1,2] indicating that TCNQ acts as a powerful electron-acceptor monomer. Moreover, 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane ($TCNQF_4$),[3] a much stronger electron acceptor than TCNQ, was found to copolymerize in an alternating

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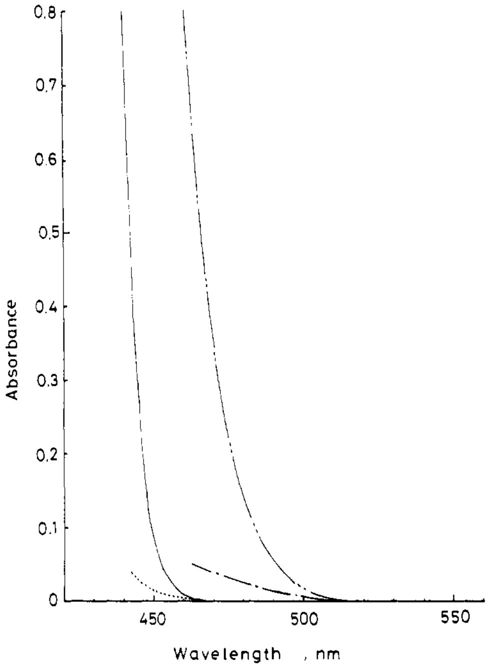

Figure 1. UV–vis spectra of mixtures of TCNQ with MMA and of TCNQF$_4$ with MMA in dichloromethane: (···) difference spectrum between TCNQ and a mixture of TCNQ with MMA and (—) spectrum of TCNQ; (– – –) difference spectrum between TCNQF$_4$ and a mixture of TCNQF$_4$ with MMA and (–·–) spectrum of TCNQF$_4$. Concentrations of solutions employed are [TCNQ] = 1.27×10^{-3} mol/L, [TCNQF$_4$] = 1.26×10^{-3} mol/L, and [MMA] = 0.5 mol/L.

fashion not only with donor monomers such as St, PhVE, and VAc but also with so-called acceptor monomers with small positive *e* values such as methyl methacrylate (MMA) (*e* = 0.4[4]) and methyl acrylate (MA) (*e* = 0.6[4]). On the other hand, radical homopolymerization of MMA with TCNQ as an initiator and its kinetics were studied by Koyama and Nishimura,[5] suggesting that TCNQ and MMA react with each other to give a free radical species. Therefore, it is requisite to study in detail the polymerization behavior between TCNQ and MMA even though TCNQ is a weaker electron acceptor than TCNQF$_4$.

In this note, alternating copolymerizations of TCNQ with MMA and MA are described.

Experimental Section

TCNQ was prepared according to the method of Acker and Hertler[6] and purified by recrystallization from ethyl acetate (three times) and sublimation (twice) (mp 294–296 °C). MMA and MA were purified from commercial products by conventional methods.[7] *α,α'*-Azobis(isobutyronitrile) (AIBN) was recrystallized from ethanol. Acetonitrile was refluxed over phosphorus pentoxide and then distilled at 81.5 °C.

The polymerization procedure was as follows: Given amounts of TCNQ, comonomer (MMA or MA), and AIBN and 10 mL (or 20 mL) of acetonitrile were placed in an ampule, which was degassed completely by the freeze–thaw method (three times) and sealed. The ampule was set in a bath thermostated at 60 °C for the time of polymerization and then opened. The reaction mixture was poured into excess methanol to precipitate the copolymer. The copolymer was purified by reprecipitation with *N,N*-dimethylformamide (DMF) as a solvent and methanol as a precipitant and dried under reduced pressure.

The copolymer composition was established by elemental analysis. Solution viscosity for the copolymer was determined in DMF using an Ostwald viscometer at 30 °C. ^{1}H NMR measurement for the copolymer of TCNQ with MMA and the homopolymer of MMA was carried out in dimethyl-*d*$_6$ sulfoxide and chloroform-*d*, respectively, using tetramethylsilane as an internal standard.

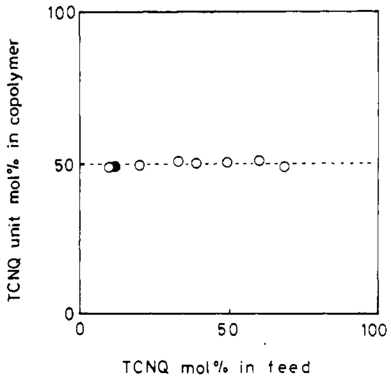

Figure 2. Copolymer composition curve of the TCNQ–MMA system: (○) with initiator; (●) without initiator.

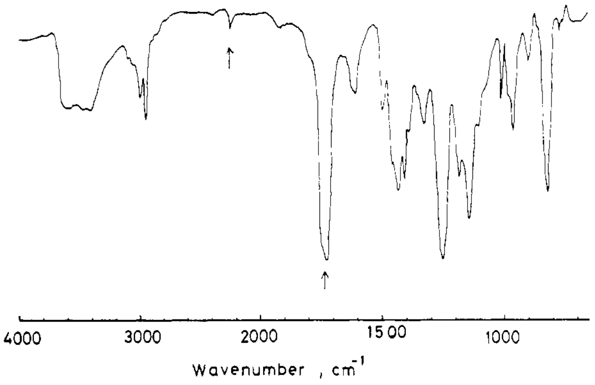

Figure 3. IR spectrum of the copolymer of TCNQ with MMA (KBr disk).

Results and Discussion

When the yellow TCNQ solution in dichloromethane was mixed with the MMA solution in dichloromethane, no apparent development in color was observed, as noted by Koyama and Nishimura.[5] However, the difference UV–vis spectrum between the TCNQ solution and the mixture solution of TCNQ with MMA, as shown in Figure 1, shows additional absorption (an increase in intensity) below 460 nm; similar behavior for the TCNQF$_4$–MMA case occurs for wavelengths below 510 nm. For the latter case the additional absorption could be treated successfully with the Benesi–Hildebrand equation to give values of the association constant (K_{CT} = 0.40 at 20 °C and 0.33 at 30 °C) for the charge-transfer complex formation. It is conceivable that the additional absorption (an increase in intensity) is indicative of a charge-transfer interaction between TCNQ and MMA as well as between TCNQF$_4$ and MMA.

Table I summarizes the results of copolymerization of TCNQ with MMA and Figure 2 shows the composition diagram of this copolymerization, indicating a typical picture of an alternating copolymerization. The products were obtained as white powders, are soluble in acetonitrile, acetone, and DMF, and are insoluble in chloroform, benzene, and methanol. The IR spectrum of the product obtained (run no. 1) is shown in Figure 3, where absorptions at 2250 and 1730 cm^{-1} were assigned to the nitrile group and to the ester-carbonyl group, respectively, indicating incorporation of both TCNQ and MMA units into the copolymer. The ^{1}H NMR spectra of the product obtained (run no. 1) and the homopolymer of MMA, prepared by its polymerization with AIBN in benzene at 60 °C, are shown in traces 1 and 2 of Figure 4, respectively; in the former, absorptions at 1.7, 3.35, 3.7, and 8.0 ppm were assigned to the *α*-methyl, the methylene, and the methoxy protons of the MMA unit and the phenylene

Table I
Copolymerization of TCNQ with MMA in Acetonitrile[a] at 60 °C

run no.	monomer feed, mg TCNQ	monomer feed, mg MMA	amt of TCNQ, mol %	time, h	polym yield, mg	conversn, %	% H	% C	% N	TCNQ in copolymer, mol %	η_{sp}/C,[b] dL·g^{-1}
1[c]	103.0	453.5	9.9	15.8	49.4	8.9	3.41	67.51	18.20	48.8	0.14
2[c]	102.2	203.2	19.7	16.1	22.8	7.5	3.73	67.12	18.29	49.5	0.06
3[c]	102.5	102.6	33.3	21.8	12.1	5.9	3.66	66.68	18.69	51.2	
4[c]	206.9	155.9	39.3	23.2	37.1	10.2	3.85	66.76	18.54	50.6	0.07
5[c]	206.4	104.0	49.3	23.4	18.5	6.0	3.76	67.13	18.55	50.6	0.05
6[c]	205.8	67.0	60.1	72.1	34.3	12.6	3.80	67.34	18.80	52.0	
7[c]	206.5	46.3	68.6	92.5	12.2	4.8	3.95	66.47	18.20	48.8	
8[d]	137.9	501.2	11.9	91.7	83.4	13.0	3.87	67.63	18.20	48.8	0.20
9[d]	103.1	553.0	8.4	16.3	trace						

[a] 10 mL for run nos. 1–5, 8, and 9 and 20 mL for run nos. 6 and 7. [b] DMF solvent. t = 30 °C. C = 0.12–0.26 g/dL. [c] AIBN: 2 mg for run nos. 1–5 and 4 mg for run nos. 6 and 7. [d] Without initiator.

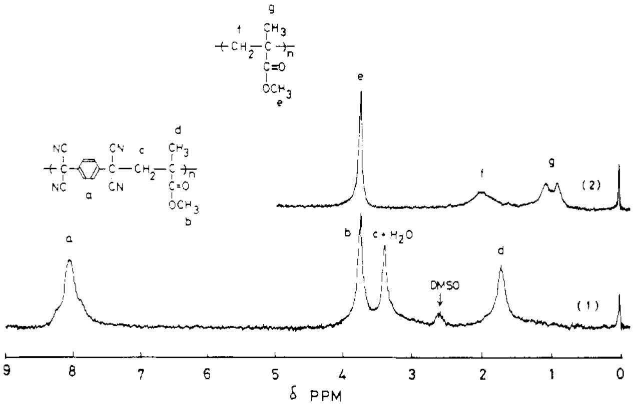

Figure 4. ^{1}H NMR spectra of (1) copolymer of TCNQ with MMA in dimethyl-d_6 sulfoxide and (2) homopolymer of MMA in chloroform-d.

protons of the TCNQ unit, respectively. The methylene and α-methyl protons of the MMA unit in the copolymer were found to be much more subject to deshielding than the corresponding protons of the homopolymer of MMA. The deshielding conceivably arises from a powerful electron withdrawal by the neighboring dicyanomethylene groups when the MMA unit is sandwiched between TCNQ units in the copolymer. Similar behavior was observed in alternating copolymers between TCNQ and St,[1] TCNQF$_4$ and St,[3] TCNQF$_4$ and MMA,[3] and 7,7,8,8-tetrakis(methoxycarbonyl)quinodimethane and St.[8] It can be concluded, therefore, that the copolymer between TCNQ and MMA is indeed alternating. In addition, an alternating copolymer of TCNQ with MMA could be obtained without a free radical initiator when the time of the polymerization was very long.

Copolymerization between TCNQ and MA, with a higher positive e value (e = 0.6[4]) than that of MMA (e = 0.4[4]), was attempted, because TCNQF$_4$ and MA successfully gave alternating copolymer in the presence of a free radical initiator such as AIBN.[3] Neither copolymer nor the homopolymer of MA was obtained, and only the starting materials were recovered. Since TCNQ is less electron accepting than TCNQF$_4$ and MA is more electron accepting than MMA, probably TCNQ could not interact so effectively with MA that their copolymerization does not take place.

The rate of spontaneous alternating copolymerization of TCNQ with MMA was compared with that of TCNQF$_4$ with MMA. The time to decrease by 18% the concentration of the TCNQ solution for the alternating copolymerization of TCNQ with MMA ([TCNQ] = 2.72 × 10^{-5} mol/L, [MMA] = 0.0255 mol/L, 39.5 °C) was found to be 6 days (8640 min). The times to decrease by half and 18% the concentration of the TCNQF$_4$ solution for the alternating copolymerization of TCNQF$_4$ with MMA ([TCNQF$_4$] = 2.52 × 10^{-5} mol/L, [MMA] = 0.0260 mol/L, 39.5 °C) were measured as 34.5 and 7.5 min,[3] respectively. Thus, the copolymerization of TCNQ with MMA takes place about $^1/_{1000}$th as fast as that of TCNQF$_4$ with MMA. Moreover, in the previous study[3] of spontaneous alternating copolymerizations between TCNQF$_4$ and St and between TCNQF$_4$ and MMA, the former (4 min for the time to decrease by half the monomer concentration) was found to react about 9 times as rapidly as the latter (34.5 min). It can be pointed out, therefore, that these alternating copolymerizations are influenced significantly by the difference in polar character between acceptor and donor monomers.

In our kinetics studies of the spontaneous alternating copolymerizations involving the TCNQF$_4$–St,[3] p-dioxene–maleic anhydride (MAnh),[9] and 1,2-dimethoxyethylene–MAnh[9] systems, we found the rate of copolymerization to be as follows: $R_p = k_p[\text{acceptor}]^{3/2}[\text{donor}]^{3/2}$. The monomer orders in this equation allowed us to propose the following polymerization reaction scheme:[9] The initiation is a bimolecular reaction between donor and acceptor monomers, the propagation is the radical addition reaction of the polymer radical with the charge-transfer complex between donor and acceptor monomers, and the termination is the bimolecular reaction between polymer radicals. However, it was calculated from the data of runs 1–5 in Table I that the copolymerization rate approximately is expressed in the following equation: $R_p = k_p \cdot [\text{TCNQ}]^{0.6}[\text{MMA}]^{1.25}$. The monomer orders in the rate equation are different from the expected values in the above-mentioned scheme. It was reported previously[3] that the alternating copolymerization of TCNQF$_4$ with St takes place about 190 times as rapidly as that of TCNQ with St and obeys three-halves-order kinetics instead of first-order kinetics for the latter case.[1] This change in monomer order in the copolymerization rate was considered to be responsible for the very slow rate of the latter case, because the latter case could successfully be fit to three-halves-order kinetics, too, in its reexamination. However, participation of other unknown causes should be taken into account. Additional studies of alternating copolymerization of many other donor–acceptor monomer pairs are anticipated to give a clue to find real causes.

Registry No. TCNQ, 1518-16-7; MMA, 80-62-6.

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Communications to the Editor

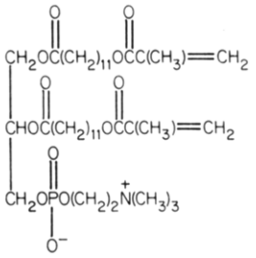
Polymer-Supported Membranes. A New Approach for Modifying Polymer Surfaces[1]

In this communication we describe a new and an extraordinarily simple technique for modifying surfaces of solid organic polymers.[2] Our method involves the polymerization of suitable lipid molecules adsorbed at aqueous–insoluble polymer phase boundaries. Resulting surfaces are termed *polymer-supported membranes.*

Surface structure and composition play a significant role in defining many of the physical properties and ultimate uses of 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.[2]

We have conceived of a new synthetic technique for altering polymer surfaces. Our general approach is outlined in Scheme I.[10] A lipid molecule composed of a hydrophilic head group, a hydrophobic segment, and one or more polymerizable groups is dispersed in an aqueous–hydrophobic, insoluble polymer two-phase mixture. In analogy to the behavior of lipids in oil/water mixtures,[11] a monolayer is expected to form at the phase boundary. Subsequent polymerization secures the membrane to the polymer surface (1) through extended hydrophobic interactions, (2) through covalent linking to alkyl radicals generated on the original surface, and/or (3) by virtue of the insolubility of the newly formed cross-linked network (when lipids with two or more polymerizable groups are employed).[12]

In order to test the feasibility of polymer-supported membranes, we attempted the synthesis of phosphatidylcholine-modified polyethylene film. Commercial low-density polyethylene film, 3-mil (Petrothene NA 344-55; 0.920 g/cm^3; 2.0 melt index),[13] was (1) cut into 2 × 10 cm pieces, (2) heated for 2 h in refluxing 1:1 $CHCl_3$–CH_3OH (3) extracted (Soxhlet) with $CHCl_3$ for 12 h, and (4) dried [6 h, 78 °C (0.1 mm)]. Resulting strips were each placed into 25-mL quartz test tubes, followed by addition of 20 mL of a vesicle dispersion of bis[12-(methacryloyloxy)dodecanoyl]-L-α-phosphatidylcholine (1).[14–16] Each tube was purged with nitrogen for 10 min, sealed with a No-Air stopper, placed in a Rayonet photochemical reactor, and irradiated for 1 h (2537 Å).[16] 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). 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.[17]



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Scheme I

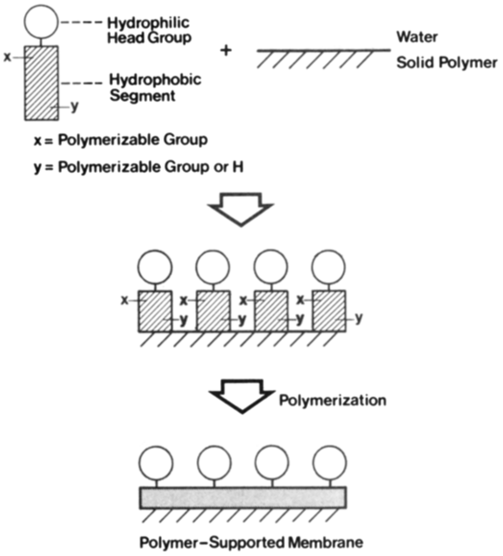

Figure 1 shows the number of lipid molecules immobilized per cm^2 of geometrical area as a function of lipid concentration used in the aqueous dispersion. A maximum loading is reached at ca. 1.5 × 10^{14}/cm^2. Exposure of the modified film to 5.4 M HCl for 24 h led to the quantitative removal of phosphorus derived from 1.[19,20] If a "surface" group is defined as one that can interact with a reagent which would be expected to be insoluble in bulk polyethylene (i.e., HCl) and which is dissolved in a solvent that does not swell polyethylene (i.e., water), this result provides strong evidence that 1 is secured to the polymer surface (i.e., at the polyethylene–water interface) and not within the film.[2b] In contrast, 1 polymerized onto polyethylene was completely stable to water, 1% aqueous sodium dodecyl sulfate, THF, and 1:1 $CHCl_3$–CH_3OH at room temperature for 24 h. As expected, phosphatidylcholine-modified polyethylene is hydrophilic. The contact angle for water measured on this surface was 35°; unmodified polyethylene had a contact angle of 100°.[21] Control experiments performed with polyethylene plus dispersions of polymerized 1, or nonpolymerized 1 (in the absence of

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