Amphiphilic Polymers from Long-Chain (*Z*)-2-Alkoxyvinyl Acetates

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Received September 6, 1995; Revised Manuscript Received January 17, 1996[⊗]

ABSTRACT: Five new (*Z*)-2-alkoxyvinyl acetates (isopropyl, butyl, hexyl, decyl, and 10-undecenyl derivatives) have been prepared by a retro-Diels−Alder technique. The synthesis of typical detergent derivatives with long alkyl residues is markedly improved by using cyclopentadiene instead of anthracene for the Diels−Alder reaction. Amphiphilic polymers were obtained by cationic homopolymerization of the long-chain derivatives. As a result of their molecular arrangement, these polymers show a decidedly hydrophobic character. However, a highly water-soluble polymer with detergent properties resulted if the amphiphilic geometry of the homopolymer of the 10-undecenyl derivative was changed by oxidative cleavage of the terminal side-chain double bond.

Introduction

The tendency of amphiphilic compounds to associate spontaneously when in contact with an aqueous medium leads to a number of promising applications.[1−3] Organized structures can thereby be formed, such as Langmuir−Blodgett films and vesicles resembling the arrangement of phospholipids in biomembranes. Polymerizable amphiphilic compounds present an opportunity to stabilize these associated structures by polymerization, so that stable membrane models can be tailor-made in order to imitate the efficacy of biological membranes. If such polymers (prepared by linking a great number of amphiphilic units with a C−C backbone) are water-soluble, they form micelles in aqueous solution and exhibit surfactant properties.[4] A current procedure for the synthesis of these polysoaps is the alternating copolymerization of hydrophilic and hydrophobic monomers, e.g., the copolymerization of long-chain alkyl vinyl ethers with maleic acid derivatives.[5] We have now shown that the homopolymerization of appropriate, asymmetrically substituted (*Z*)-1,2-ethenediol derivatives yields polymers with a novel amphiphilic structure, featuring a strictly alternating sequence of hydrophilic and hydrophobic groups at every carbon atom of the main chain. In this respect, the synthesis and polymerization of (*Z*)-2-alkoxyvinyl acetates with long alkyl substituents are of interest.

Results and Discussion

Often amphiphilic polymers are prepared that carry the hydrophilic groups at the polymer backbone. This arrangement has been called "head" arrangement.[4] Such structures should be easily obtainable from (*Z*)-2-alkoxyvinyl esters.

A. Polymers with an Amphiphilic "Head" Arrangement. (*Z*)-2-Alkoxyvinyl acetates **5** are prepared by a retro-Diels−Alder technique, which allows a general approach to symmetrically and unsymmetrically (*Z*)-1,2-dioxy-substituted olefins.[6,7] Starting material is diol **1**, which is easily accessible by Diels−Alder reaction of vinylenecarbonate with anthracene, followed by saponification of the carbonate ester.[8] Diol **1** is converted into cyclic acetals **2** by reaction with aldehydes or acetone. Reductive ring-opening of the 1,3-dioxolane ring by $AlCl_3/LiAlH_4$ leads to glycol monoethers **3** with the desired unsymmetrical substitution pattern. Their acetate esters **4** undergo a retro-Diels−Alder reaction at 350 °C to yield the free (*Z*)-1,2-ethenediol dienophiles **5**. This synthetic strategy was successfully used for the preparation of the new (*Z*)-2-alkoxyvinyl acetates **5b**−**e** (see Scheme 1).

Unlike ethyl derivative **5a**, the homologous compounds **5b**−**e**, with longer alkyl substituents, are partially fragmented by a subsequent retro-ene reaction before being distilled off from the thermolysis residue. Two different retro-ene reactions can occur, depending on whether the vinyl ether or the vinyl ester function of the monomer is involved. Whereas the cleavage of the alkyl−oxygen bond yields the olefins **6** and acetoxyacetaldehyde **7**, ketene and the respective alkoxyacetaldehydes **8** are formed by cleavage of the acyl−oxygen bond (see Scheme 2). The thermolysis products were identified by NMR spectroscopy after chromatographic separation of the mixture. The two aldehydes **7** and **8** were found in all the condensates, whereas the corresponding olefins **6**, due to their high volatilities, could be detected only in the case of decyl derivative **5e**. The amounts of aldehydes **7** and **8** in the product mixtures increase with the alkyl chain lengths of monomers **5** (see Table 1). The fragmentation into ketene and alkoxyacetaldehyde **8** is favored over the other retro-ene pathway.

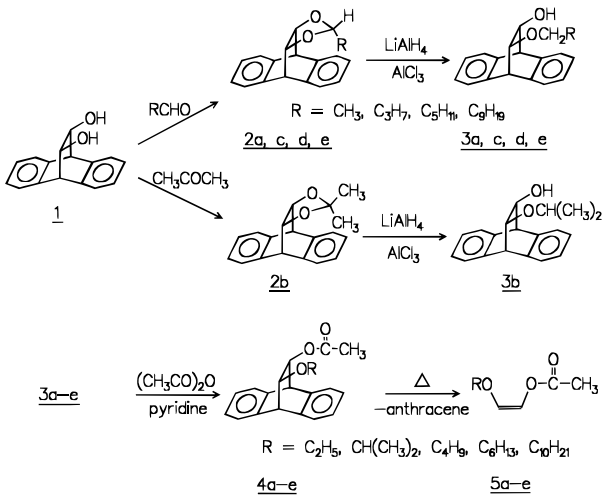
Acceleration of the distillation process by reducing the pressure lowers considerably the percentage of side products, but under these conditions, unreacted starting material **4e** is also found in the distillate. As a result of these contrary effects, there is an optimum pressure of 100−150 hPa for the thermolysis of decyl derivative **4e**.

Like (*Z*)-2-ethoxyvinyl acetate (**5a**),[9] the three homologous linear derivatives **5c**−**e** can be polymerized by cationic initiation (see Scheme 3 and Table 2). Polymerization can be initiated by $SnCl_4$ in toluene at −10 to −20 °C as in the case of **5a**,[9] but higher molecular weights are achieved if the cationic polymerization is carried out in methylene chloride at −30 to −40 °C with the BF_3−diethyl ether complex as initiator. This effect can be explained on the basis of a decreased number of chain transfer reactions as a result of the lower polymerization temperatures. A more detailed systematic explanation of the molecular weights achieved for the different monomers and polymerization condi-

[⊗] Abstract published in *Advance ACS Abstracts,* March 1, 1996.

0024-9297/96/2229-2776$12.00/0

Scheme 1. Synthesis of (*Z*)-2-Alkoxyvinyl Acetates 5 by a Retro-Diels–Alder Technique



Scheme 2. Fragmentation of (*Z*)-2-Alkoxyvinyl Acetates 5 by Retro-Ene Reactions

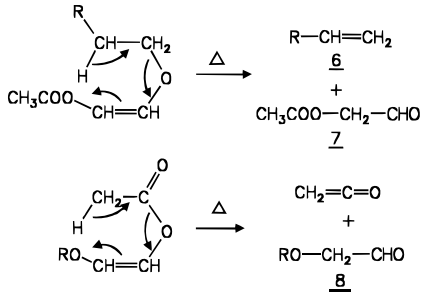
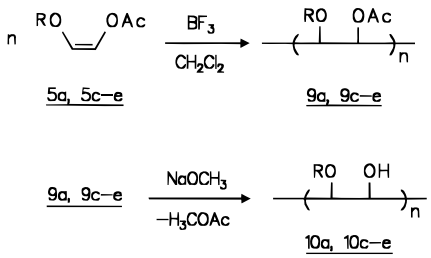


Table 1. Product Distributions and Yields of the Thermolytic Distillations of Anthracene Cycloadducts 4

		product distribution (%) in the thermolysate			yield of pure
starting material	pressure at thermolysis	monomer	aldehydes	starting material	monomer (%)
4a	atm	100			87
4b	atm	95	5		78
4c	atm	90	10		68
4d	atm	80	20		44
4e	atm	65	35		26
4e	150 hPa	80	<5	20	37

Scheme 3. Preparation of Polymers 10a,c–e with a Strictly Alternating Sequence of Hydrophilic and Hydrophobic Groups at the Polymer Backbone



tions (temperature, initiator amount) is not possible at present since there are not enough data available yet.

In accordance with the cationic polymerization of **5a**,[9] unusually long polymerization times of 100 h are necessary, and the products show surprisingly narrow molecular weight distributions (M_w/M_n = 1.1–1.3), indicating the existence of long-lived acetoxonium ions in the polymerization mixture[9] (see Scheme 4). Acetoxonium ions of similar structure are known to be formed from β-acetoxy cations and are well investigated in nucleophilic substitution reactions, especially in carbohydrate chemistry.[10] In agreement with other β-substituted vinyl ethers with branched substituents,[11] **5b** gives only oligomeric products under the same polymerization conditions due to sterical restraints.

The homopolymerization of **5c–e** gives at least 95% of head-to-tail linked products. This conclusion can be drawn from ^{1}H- and ^{13}C-NMR spectroscopy because side signals arising from head-to-head linked units are not detected. This fact applies to the broad main-chain signals as well as to the sharp side-chain signals. Deacetylation of polymers **9c–e** yields the new poly(1-hydroxy-2-alkoxyethylenes) **10c–e** (see Scheme 3), which can be regarded as strictly alternating copolymers consisting of hydroxymethylene and alkoxymethylene units, such that hydrophilic and hydrophobic groups are alternating at every carbon atom of the polymer backbone.

In spite of their amphiphilic chemical structure, these materials show a decidedly hydrophobic character (see Table 3). Decyl derivative **10e**, for example, is soluble only in apolar organic solvents such as hexane, chloroform, and diethyl ether, but is insoluble in water, ethanol, and even acetone. The similarities to the properties of long-chain polyvinyl ethers arise from the fact that the long hydrophobic alkyloxy substituents tend to arrange in a "bottle-brush" conformation around the polymer backbone.[4] Thus, the hydrophilic head groups are shielded inside the polymer coil, and their influence on the solubility is negligible (Figure 1a). An amphiphilic arrangement of the substituents (Figure 1c) is unfavorable because of the high side-chain density of the polymer.[12] The shielding of the head groups is shown particularly by the fact that the solubility of the materials scarcely changes on converting the hydroxy functions into the more polar sulfate esters **11** by reaction with the SO_3–pyridine complex. These sulfate esters have not been characterized in detail because the expected solubility changes did not occur.

B. Polymers with an Amphiphilic "Tail-End" Arrangement. It is expected that water-soluble amphiphilic polymers are accessible on the basis of (*Z*)-1,2-ethenediol derivatives if the hydrophilic groups are located at the ends of the lipophilic alkoxy substituents. This means a change of the amphiphilic molecular architecture from a "head" geometry[4] (with the polar functional groups bound to the polymer backbone, Figure 1a) to a "tail-end" geometry[4] (Figure 1b).

The starting material for this novel amphiphilic polymer is monomer **16**. As the yields for the retro-Diels–Alder reactions producing the monomers **5d,e** are not as good as those for **5a–c**, **16** is prepared by a somewhat modified retro-Diels–Alder approach, which is especially advantageous for the synthesis of long-chain alkyl derivatives with low volatility. The initial Diels–Alder reaction with vinylenecarbonate is carried out with cyclopentadiene instead of anthracene. After hydrolysis of the carbonate ester, diol **12** results,[13] which is converted to ester–ether derivative **15** by a reaction pathway analogous to that for the corresponding anthracene cycloadducts (see Scheme 5). It is to be expected that masking with cyclopentadiene is advantageous for the synthesis of monomers **5d,e** as well.

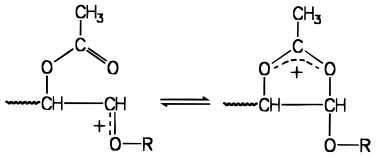
In the first step of this synthesis, **12** is reacted with 10-undecenal to give diastereomeric acetals **13a,b** with

Table 2. Cationic Homopolymerizations of Monomers 5a,c−e and 16

monomer	initiator[a]	initiator amount[b] (%)	temp (°C)	M_n (GPC)[c] (g/mol)	M_n (VPO)[d] (g/mol)	P_n (GPC)	M_W/M_n (GPC)	yield (%)
5a	$SnCl_4$	0.9	−18	4200	nd[e]	32	1.12	nd[e]
5a	$SnCl_4$	0.9	−3	5700	5900	44	1.15	65
5a	BF_3	0.5	−30	9500	10300	73	1.15	68
5c	$SnCl_4$	0.5	−5	4500	nd[e]	28	1.30	75
5c	BF_3	0.5	−25	17500	nd[e]	111	1.61	69
5d	BF_3	0.5	−30	23000	nd[e]	124	1.15	62
5e	$SnCl_4$	0.9	−6	11300	11200	47	1.09	75
5e	BF_3	0.9	−30	17600	nd[e]	73	1.29	73
5e	BF_3	0.5	−30	28600	27800	118	1.26	83
16	BF_3	0.6	−30	6600	nd[e]	26	1.85	66

[a] Polymerization system: $SnCl_4$ in toluene or BF_3 in methylene chloride. [b] Molar ratio initiator/monomer. [c] Determined in tetrahydrofuran using polystyrene as standard. [d] Determined by vapor pressure osmometry in toluene at 45 °C, benzil as standard. [e] Not determined.

Scheme 4. Possible Stabilized Structures of the Cation of the Growing Polymer Chain



a diastereomeric excess of 82%. The measurement of nuclear Overhauser enhancements (^{1}H-NMR) proves to be helpful for the identification of the stereoisomers. The main isomer, **13a**, shows a *syn* arrangement of all hydrogen atoms at the 1,3-dioxolane ring (see Scheme 6). An enrichment of *anti* isomer **13b** is found when the mixture is heated in the presence of water and catalytic amounts of *p*-toluenesulfonic acid. Under thermodynamic control there is a *syn*−*anti* ratio of 57:43. It is noteworthy that the acetalation of diols **17**[14] and **1**[7] yields the *syn* stereoisomers exclusively. The corresponding *anti*-acetals can be synthesized by subsequent equilibration processes as well.[7,14] It was found that this procedure leads to a *syn*−*anti* ratio of 60:40 for acetals **2** derived from diol **1**.

Reductive ring-opening of acetals **13a,b** and the subsequent acetylation of glycol monoether **14** are carried out as described for the anthracene analogues **2** and **3**. The final retro-Diels−Alder reaction of the herein synthesized norbornene derivative **15** can be carried out as gas-phase thermolysis at 560 °C/10^{-2} hPa. This reaction technique has an essential advantage over thermolytic distillation used for anthracene cycloadducts **4** since it gives high chemical yields for typical surfactant derivatives with long alkyl substituents; for example, **16** is obtained with a chemical yield of 77%.

The cationic homopolymerization of **16** with the BF_3−diethyl ether complex as initiator leads to short polymer chains consisting of polymerized vinyl ether units. Interestingly, the other olefinic double bond of monomer **16**, which is accessible to an electrophilic attack as well, is unchanged in the polymer side chains. An interference of this double bond in the polymerization process by chain transfer and termination reactions, however, is suggested by the fact that molar masses of only 7000 g/mol are obtained under the polymerization conditions used for the other monomers, **5c−e.**

Homopolymer **18** is converted to an amphiphilic product with "tail-end" geometry by an oxidative cleavage of the side-chain double bonds with $KMnO_4$ in a nonaqueous medium. The resulting polycarboxylic acid **19** undergoes irreversible cross-linking reactions on drying, so an immediate conversion to the stable carboxylate is advisable. The use of sodium methanolate in methanol for the deprotonation of the polymer simultaneously results in cleavage of the acetate esters and furnishes **20** (see Scheme 7). This amphiphilic polymer is highly soluble in water. Water−methanol mixtures are also suitable solvents as long as the water content exceeds 20%.

The existence of micelles in aqueous solutions of amphiphilic polymers can be detected from changes of the UV−vis spectrum of the trimethynecyanine dye pinacyanol chloride.[15] The UV−vis spectrum of an aqueous, 2×10^{-5} M pinacyanol chloride solution shows characteristic absorption bands at 520, 545, and 600 nm. On addition of polymer **20** to this solution, these three bands disappear. They are replaced by two bands at 560 and 610 nm which are typical for the absorption spectrum of the dye in an apolar solvent or in the apolar environment within a micelle. When a more than 50-fold molar excess of amphiphilic monomeric units with regard to the dye is used, these bands are predominant in the UV−vis spectrum. At lower polymer concentrations, however, they lose intensity in favor of a band at 495 nm, since the number of micelles is insufficient to contain all dye molecules. Thus, the latter band is indicative of dye molecules which interact with polymer subunits but are not located inside a micelle.

From a practical point of view, the solubilization of substances which are normally insoluble or poorly soluble in water is one of the key properties of surfactants. As a typical anionic polysoap, **20** is capable of solubilizing the azo dyes (dimethylamino)azobenzene (DMAB) and 1-(*o*-toluylazo)-2-naphthol (Orange OT) in an aqueous solution (see Table 4). After equilibration at 40 °C, the homogeneous polymer solution (10 g/L) contains 4.52 mmol of DMAB or 4.71 mmol of Orange OT, calculated per mole of amphiphilic monomeric subunits. Hence, for DMAB, polymer **20** attains a solubilization capacity comparable to that of an aqueous solution of sodium laurate (10 g/L), as an example of a common low-molecular-weight surfactant with an analogous chemical structure (3.14 mmol at 30 °C; 5.24 mmol at 50 °C). For Orange OT, **20** exceeds the sodium laurate value (2.22 mmol at 30 °C).[16] At lower concentrations, polymer **20** exhibits even higher solubilization capacities per mole of amphiphilic monomer subunits because solubilization sites are made available more efficiently in a dilute polysoap solution.[17] The solubilization capacity of currently used polysoaps[17] is slightly higher than that found for polymer **20**, because the free hydroxy functions of polymer **20** give the main chain a high polarity, which impairs the hydrophobic environment available inside the micelles.[4] It is thus expected that more efficient polysoaps can be synthesized by converting the hydroxy groups of polymer **20** into apolar ether functions.

Table 3. Solubilities of Poly(1-hydroxy-2-alkoxyethylenes) 10a,c−e[a]

polymer	H_2O	H_2O/MeOH	MeOH	EtOH	PrOH	Et_2O	THF	acetone	$CHCl_3$	petroleum ether
10a	+	+	+	+	nd[b]	−	−	−	−	−
10c	−	−	+	+	+	nd[b]	+	+	+	−
10d	−	−	−	+	+	+	+	+	+	+
10e	−	−	−	−	+	+	+	−	+	+

[a] MeOH, methanol; EtOH, ethanol; PrOH, 2-propanol; Et_2O, diethyl ether; THF, tetrahydrofuran. [b] Not determined.

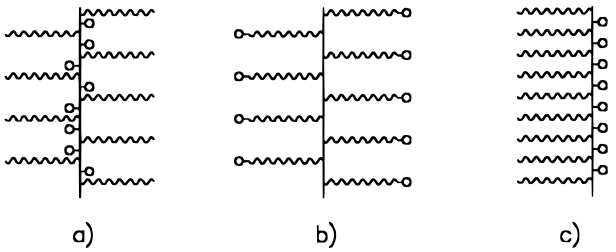
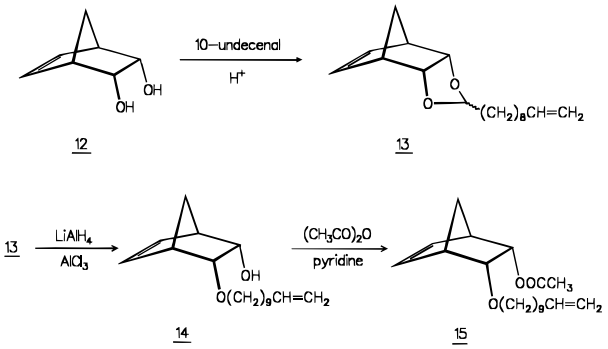
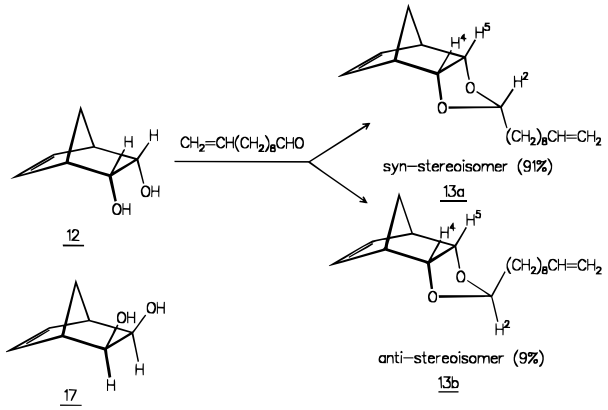


Figure 1. Arrangements of amphiphilic polymers: "bottle-brush" conformation of polymers with "head" geometry (a) or "tail-end" geometry (b) and amphiphilic conformation of a polymer with "head" geometry (c).

Scheme 5. Conversion of Diol 12 into the Unsymmetrically Substituted Ester−Ether Derivative 16



Scheme 6. Stereochemistry of Cyclic Acetals 13a,b Resulting from Acetalation of Diol 12



Conclusions

The hitherto unknown (*Z*)-2-alkoxyvinyl acetates **5b−e** and **16** have been synthesized by thermolysis of appropriate Diels−Alder cycloadducts. It was pointed out as an example for **16** that the synthetic pathway to long-chain alkyl derivatives is considerably improved by the use of cyclopentadiene as diene component instead of anthracene. Except for **5b**, these β-substituted vinyl ethers proved to be susceptible to cationic homopolymerization in spite of their sterically demanding substituents. After deacetylation, the resulting polymers **10c−e** have a novel amphiphilic structure, characterized by a strictly alternating sequence of hydrophilic and hydrophobic substituents at every carbon atom of the main chain. The solubility of these products is strongly determined by the position of the polar head groups. Polymer **20**, for example, with an amphiphilic "tail-end" geometry, is water-soluble and exhibits good surfactant properties.

Scheme 7. Preparation of Polysoap 20 with an Amphiphilic "Tail-End" Geometry

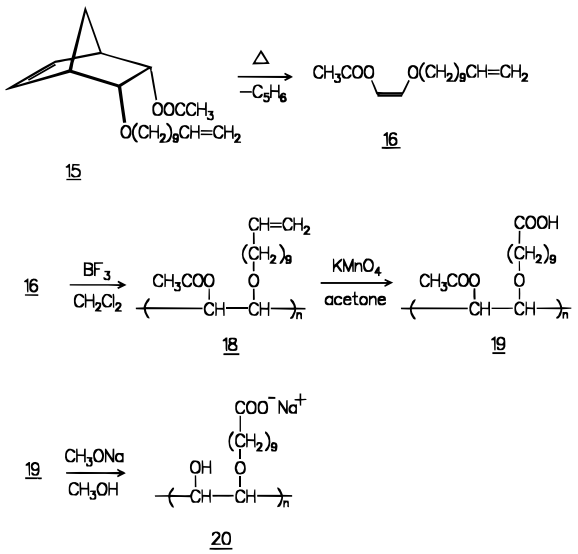


Table 4. Solubilization Capacities of Polymer 20 for (Dimethylamino)azobenzene (DMAB) and for 1-(*o*-Toluylazo)-2-naphthol (Orange OT) in Aqueous Solution at 40 °C

polymer concn (g/L)	solubilized amount (mg/L)		molar ratio (%)[a]	
	DMAB	Orange OT	DMAB	Orange OT
2.5	13.3	13.6	0.595	0.523
5.0	24.9	27.3	0.558	0.525
10.0	40.4	49.0	0.452	0.471

[a] With amphiphilic subunits.

Experimental Section

Elemental analyses were performed at the microanalytical laboratories of the Faculty of Natural Sciences of the Heinrich-Heine-University, Düsseldorf. ^{1}H- and ^{13}C-NMR spectra were recorded on a Varian VXR 300 spectrometer. Melting points were determined using a Büchi 510 apparatus. Mass spectra were obtained on a Varian MAT CH-50 and a MAT 311-A, and IR spectra were recorded on a Perkin-Elmer 1420. For vapor pressure osmometry (VPO), the Knauer osmometer was used.

(*Z*)-9,10-Dihydro-9,10-ethanoanthracene-11,12-diol (**1**) was prepared as described by Patton.[8]

(*Z*)-2-Ethoxyvinyl acetate (**5a**) was prepared according to a published procedure.[9]

The 2-substituted 4,5-(9,10-Dihydro-9,10-anthrylene)-1,3-dioxolanes **2b−e** were prepared as described by Field[18] for compound **2b**.

***syn*-4,5-(9,10-Dihydro-9,10-anthrylene)-2-propyl-1,3-dioxolane (2c)**. Yield 88%; mp 117−8 °C; MS (70 eV) m/z =

292 [M^+]. Anal. Calcd for $C_{20}H_{20}O_2$ (292.4): C, 82.16; H, 6.90. Found: C, 82.26; H, 7.10.

***syn*-4,5-(9,10-Dihydro-9,10-anthrylene)-2-pentyl-1,3-dioxolane (2d)**. Yield 89%; mp 124−5 °C; MS (70 eV) m/z = 320 [M^+]. Anal. Calcd for $C_{22}H_{24}O_2$ (320.4): C, 82.47; H, 7.55. Found: C, 82.12; H, 7.75

***syn*-4,5-(9,10-Dihydro-9,10-anthrylene)-2-nonyl-1,3-dioxolane (2e)**. Yield 87%; mp 78−9 °C; MS (70 eV) m/z = 376 [M^+]. Anal. Calcd for $C_{26}H_{32}O_2$ (376.5): C, 82.94; H, 8.57. Found: C, 82.92; H, 8.83

The new *(Z)*-12-alkoxy-9,10-dihydro-9,10-ethanoanthracen-11-ols **3b**−**e** were prepared according to a procedure published for derivative **3a**.[7] The compounds were purified by recrystallization from hexane **(3b**−**d)** or methanol **(3e)**.

***(Z)*-12-Isopropyloxy-9,10-dihydro-9,10-ethanoanthracen-11-ol (3b)**. Yield 93%; mp 155−6 °C; MS (70 eV) m/z = 280 [M^+]. Anal. Calcd for $C_{19}H_{20}O_2$ (280.4): C, 81.40; H, 7.19. Found: C, 81.29; H, 7.11

***(Z)*-12-Butyloxy-9,10-dihydro-9,10-ethanoanthracen-11-ol (3c)**. Yield 88%; mp 120−1 °C; MS (70 eV) m/z = 116 [M^+ − anthracene]. Anal. Calcd for $C_{20}H_{22}O_2$ (294.4): C, 81.60; H, 7.53. Found: C, 81.74; H, 7.58.

***(Z)*-12-Hexyloxy-9,10-dihydro-9,10-ethanoanthracen-11-ol (3d)**. Yield 84%; mp 96−7 °C; MS (70 eV) m/z = 322 [M^+]. Anal. Calcd for $C_{22}H_{26}O_2$ (322.4): C, 81.95; H, 8.13. Found: C, 81.65; H, 8.04.

***(Z)*-12-Decyloxy-9,10-dihydro-9,10-ethanoanthracen-11-ol (3e)**. Yield 92%; mp 78−9 °C; MS (70 eV) m/z = 200 [M^+ − anthracene]. Anal. Calcd for $C_{26}H_{34}O_2$ (378.6): C, 82.49; H, 9.05. Found: C, 82.47; H, 9.30.

Preparation of the (*Z*)-12-Alkoxy-9,10-dihydro-9,10-ethanoanthracen-11-yl Acetates 4b−**e**. A mixture of 41 g (0.4 mol) of acetic anhydride, 36 g (0.45 mol) of pyridine, and 0.1 g of 4-(dimethylamino)pyridine was added to an ice-cooled solution of 0.20 mol of the alcohols **3b**−**e** in 100 mL of dry methylene chloride. Afterward, the mixture was heated under reflux for 7 h. After the usual workup, the acetates were obtained as oils, which gradually crystallized in the cases of **4b**−**d**. These substances were further purified by recrystallization from 2-propanol, whereas the syrupy decyl derivative **4e** was purified by distillation.

***(Z)*-12-Isopropyloxy-9,10-dihydro-9,10-ethanoanthracen-11-yl Acetate (4b)**. Yield 90%; mp 86−7 °C; MS (70 eV) m/z = 262 [M^+ − CH_3COOH]. Anal. Calcd for $C_{21}H_{22}O_3$ (322.4): C, 78.23; H, 6.88. Found: C, 78.39; H, 6.85.

***(Z)*-12-Butyloxy-9,10-dihydro-9,10-ethanoanthracen-11-yl Acetate (4c)**. Yield 88%; mp 105−6 °C; MS (70 eV) m/z = 336 [M^+]. Anal. Calcd for $C_{22}H_{24}O_3$ (336.4): C, 78.54; H, 7.19. Found: C, 78.76; H, 7.32.

***(Z)*-12-Hexyloxy-9,10-dihydro-9,10-ethanoanthracen-11-yl Acetate (4d)**. Yield 93%; mp 70−1 °C; MS (70 eV) m/z = 144 [M^+ − anthracene − CH_2CO]. Anal. Calcd for $C_{24}H_{28}O_3$ (364.5): C, 79.09; H, 7.74. Found: C, 79.05; H, 7.73.

***(Z)*-12-Decyloxy-9,10-dihydro-9,10-ethanoanthracen-11-yl Acetate (4e)**. Yield 93%; bp 183−5 °C/0,05 hPa; MS (70 eV) m/z = 360 [M^+ − CH_3COOH], 242 [M^+ − anthracene], 200 [M^+ − anthracene − CH_2CO]; ^{1}H-NMR ($CDCl_3$) δ 0.88 (t, 3H, CH_3), 1.15−1.35, 1.4−1.5 (m, 14H + 2H, (CH_2)$_8$CH$_3$), 1.92 (s, 3H, CH_3CO), 3.34, 3.60 (AB, 2H, OCH_2), 3.81 (dd, J = 7.7 Hz, J' = 3.0 Hz, 1H, CHOCH$_2$), 4.35 (d, 1H, benz CHCHOCO), 4.47 (d, 1H, benz CHCHOCH$_2$), 5.02 (dd, J = 7.7 Hz, J' = 3.0 Hz, 1H, CHOCO), 7.09−7.18, 7.25−7.33 (m, 4H + 4H, arom H); ^{13}C-NMR ($CDCl_3$) δ 14.13 (1C, *C*H$_3$), 20.88 (1C, *C*H$_3$CO), 22.68, 26.07, 29.33, 29.41, 29.57, 29.62, 29.83, 31.91 (8C, (*C*H$_2$)$_8$CH$_3$), 48.45 (1C, benz *C*HCHOCO), 48.59 (1C, benz *C*HCHOCH$_2$), 70.56 (1C, OCH$_2$), 70.74 (1C, *C*HOCO), 75.48 (1C, *C*HOCH$_2$), 124.60, 124.64, 125.45, 125.69, 126.07, 126.25, 126.58, 126.69, 138.91, 139.70, 140.02, 140.35 (12C, arom C). Anal. Calcd for $C_{28}H_{36}O_3$ (420.6): C, 79.96; H, 8.63. Found: C, 79.96; H, 8.61.

Preparation of the (*Z*)-2-alkoxyvinyl Acetates 5b−**e**. The acetates **4b**−**d** were heated to 350 °C on a metal bath under atmospheric pressure and inert conditions. For **4e**, a pressure of 100−150 hPa was used. At 350 °C, the products **5b**−**e** distilled off together with anthracene and the products of a subsequent retro-ene reaction (acetoxy- and the respective alkoxyacetaldehyde). After the anthracene residue was filtered off, the products **5b**−**e** were obtained analytically pure by distillation.

For the identification of the retro-ene side products, the thermolysate mixtures were separated by gradient chromatography (silica gel; eluent, hexane−methylene chloride, 100:0 to 50:50). The alkoxyacetaldehydes as main side products could be isolated analytically pure by distillation of the thermolysate mixtures (butyloxyacetaldehyde, bp 68−70 °C/75 hPa; hexyloxyacetaldehyde, bp 42−4 °C/1.2 hPa; decyloxyacetaldehyde, bp 51−2 °C/0.05 hPa). All side products were characterized by their NMR spectra.

***(Z)*-2-Isopropyloxyvinyl Acetate (5b)**. Yield 78%; bp 77−9 °C/24 hPa; MS (70 eV) m/z = 144 [M^+], 102 [M^+ − CH_2-CO]. Anal. Calcd for $C_7H_{12}O_3$ (144.2): C, 58.32; H, 8.39. Found: C, 57.79; H, 8.19.

***(Z)*-2-Butyloxyvinyl Acetate (5c)**. Yield 68%; bp 90−1 °C/24 hPa; MS (70 eV) m/z = 158 [M^+], 116 [M^+ − CH_2CO]. Anal. Calcd for $C_8H_{14}O_3$ (158.2): C, 60.74; H, 8.92. Found: C, 60.67; H, 8.93.

***(Z)*-2-Hexyloxyvinyl Acetate (5d)**. Yield 44%; bp 78−9 °C/1.2 hPa; MS (70 eV) m/z = 186 [M^+], 144 [M^+ − CH_2CO]. Anal. Calcd for $C_{10}H_{18}O_3$ (186.2): C, 64.49; H, 9.74. Found: C, 64.32; H, 9.71.

***(Z)*-2-Decyloxyvinyl Acetate (5e)**. Yield 34%; bp 84−6 °C/0.05 hPa; MS (70 eV) m/z = 242 [M^+], 200 [M^+ − CH_2CO]; ^{1}H-NMR ($CDCl_3$) δ 0.88 (t, 3H, CH_3), 1.20−1.42, 1.62−1.72 (m, 14H + 2H, (CH_2)$_8$CH$_3$), 2.17 (s, 3H, CH_3CO), 3.82 (t, J = 6.8 Hz, 2H, OCH_2), 5.63 (d, J = 3.8 Hz, 1H, =CHOCH$_2$), 6.49 (d, J = 3.8 Hz, 1H, =CHOCO); ^{13}C-NMR ($CDCl_3$) δ 14.13 (1C, *C*H$_3$), 20.71 (1C, *C*H$_3$CO), 22.70, 25.64, 29.34, 29.36, 29.56, 29.65, 31.92 (8C, (*C*H$_2$)$_8$CH$_3$), 73.70 (1C, OCH$_2$), 117.18 (1C, =*C*HOCO), 133.15 (1C, =*C*HOCH$_2$), 167.72 (1C, CH$_3$*C*O); IR (cm^{-1}) $1/\lambda$ = 1755 (C=O), 1685 (C=C). Anal. Calcd for $C_{14}H_{26}O_3$ (242.4): C, 69.38; H, 10.81. Found: C, 69.28; H, 10.94.

Preparation of the Poly(1-acetoxy-2-alkoxyethylenes) 9a,c−**e**. In 15 mL of dry methylene chloride (or toluene) was dissolved 15−20 mmol of monomers **5**. The solution was maintained under inert conditions and cooled to the polymerization temperature indicated. Subsequently, the specified amount of freshly distilled BF_3−diethyl ether complex (or $SnCl_4$) was added through a septum. After a polymerization time of 100 h, the initiator was hydrolyzed by adding 5 mL of a methanol−water mixture (1:1). The solution was then filtered through a membrane filter (cellulose, 0.8 μm). For purification, the polymer was reprecipitated by adding its solution in tetrahydrofuran to a 10-fold excess of petroleum ether **(9a)**, methanol−water (1:1) **(9c)**, methanol **(9d)**, or methanol−acetone (2:1) **(9e)**. Polymers **9a**,**c** were obtained as solids, whereas **9d,e** had a waxlike consistency.

Poly(1-acetoxy-2-decyloxyethylene) (9e): ^{1}H-NMR ($CDCl_3$) δ 0.88 (t, 3H, CH_3), 1.15−1.4 (14H, (CH_2)$_7$CH$_3$), 1.4−1.7 (broad, 2H, OCH$_2$CH_2), 1.9−2.2 (broad, 3H, CH_3CO), 3.1−4.2 (broad, 3H, CHOCH_2), 4.8−5.4 (broad, 1H, CHOCO); ^{13}C-NMR ($CDCl_3$) δ 14.12 (1C, *C*H$_3$), 20.5−21.5 (1C, *C*H$_3$CO), 22.7, 26.2, 29.4, 29.8, 29−31, 32.0 (8C, (*C*H$_2$)$_8$CH$_3$), 68−73 (1C, O*C*H$_2$), 72−75 (1C, *C*HOCO), 74−78 (1C, *C*HOCH$_2$), 169−171.5 (1C, CH$_3$*C*O).

Preparation of the Poly(1-hydroxy-2-alkoxyethylenes) 10c−**e**. In 50 mL of dry tetrahydrofuran was dissolved 3−4 g of polymers **9c**−**e**. A solution of 430 mg (8 mmol) of sodium methanolate in 50 mL of dry methanol was added, and the mixture was heated under reflux for 20 h. Afterward the polymers **10c**−**e** were precipitated by adding the mixture to an excess of water **(10c)** or methanol **(10d,e)**.

Poly(1-hydroxy-2-hexyloxyethylene) (10d). Anal. Calcd for $(C_8H_{16}O_2)_n$ (144.2)$_n$: C, 66.63; H, 11.18. Found: C, 66.42; H, 11.46.

Poly(1-hydroxy-2-decyloxyethylene) (10e): ^{1}H-NMR ($CDCl_3$) δ 0.88 (t, 3H, CH_3), 1.2−1.4 (broad, 14H, (CH_2)$_7$CH$_3$), 1.45−1.7 (broad, 2H, OCH$_2$CH_2), 3.3−4.0 (broad, 3H, CHOCH_2), 4.0−4.4 (broad, 1H, CHOH); ^{13}C-NMR ($CDCl_3$) δ 14.13 (1C,

CH_3), 22.7, 26.3, 29.5, 29.8, 30−32, 32.0 (8C, $(CH_2)_8CH_3$), 69−74 (2C, OCH_2, CHOH), 76−80 (1C, $CHOCH_2$). Anal. Calcd for $(C_{12}H_{24}O_2)_n$ $(200.3)_n$: C, 71.95; H, 12.08. Found: C, 71.65; H, 12.27.

Sulfation of Poly(1-hydroxy-2-butoxyethylene) 10c. In 25 mL of dry tetrahydrofuran was dissolved 1.8 g of polymer **10c**. After the addition of 2.7 g (1.1 equiv with regard to free hydroxy functions) of the SO_3−pyridine complex, the mixture was heated under reflux for 2 h. Afterward, the precipitated sulfated polymer **11** was filtered off and dissolved in 40 mL of dry methanol. The unreacted SO_3−pyridine complex was separated by adding this solution to a suspension of $BaCO_3$ in 30 mL of water. After the $BaCO_3/BaSO_4$ solid was filtered off, the solvents and free pyridine were evaporated in vacuo. The sulfated polymer **11** was identified by the characteristic S=O bands of its IR spectrum ($1/\lambda$ = 1240, 1190, 1060 cm^{-1}). Polymer **11** was soluble in water−methanol (1:1) but insoluble in water.

endo-cis-5-Norbornene-2,3-diol **(12)** was prepared as described by Lambert and Mark[13] and Patton.[8]

Compounds **13**−**15** were prepared by analogy with their corresponding anthracene cycloadducts, **2**−**4**. The liquids were purified by distillation.

***endo*-4,5-(4-Cyclopenten-1,3-ylene)-2-(9-decenyl)-1,3-dioxolane (13)**. Yield 84%; bp 107−8 °C/0.05 hPa; MS (70 eV) m/z = 276 [M^+], 210 [$M^+ - C_5H_6$]; ^{1}H-NMR ($CDCl_3$) (*syn* isomer **13a)** δ 1.2−1.45 (m, 12H, $CH_2(CH_2)_6CH_2$), 1.5−1.6 (m, 2H, O_2CHCH_2), 1.49, 1.68 (AB, J = 9.6 Hz, norbornene CH_2), 2.03 (m, 2H, $CH_2CH{=}CH_2$), 2.99 (m, 2H, bridgehead CH), 4.61 (m, 2H, CHO), 5.02 (t, J = 4.7 Hz, 1H, O_2CH), 4.92, 4.98 (2ddt, 2H, $CH{=}CH_2$), 5.80 (ddt, 1H, $CH{=}CH_2$), 6.13 (m, 2H, $CH{=}CH$); ^{1}H-NMR ($CDCl_3$) (*anti* isomer **13b**) δ 3.06 (m, 2H, bridgehead CH), 4.76 (m, 2H, CHO), 5.23 (t, J = 4.8 Hz, 1H, O_2CH); ^{13}C-NMR ($CDCl_3$) (*syn* isomer **(13a)** δ 24.17, 28.90, 29.10, 29.35, 29.45, 29.58 (6C, $CH_2(CH_2)_6CH_2$), 33.12 (1C, O_2CHCH_2), 33.80 (1C, $CH_2CH{=}CH_2$), 45.73 (2C, bridgehead CH), 47.27 (1C, norbornene CH_2), 81.86 (2C, CHO), 109.57 (1C, O_2C), 114.10, 139.17 (2C, $CH{=}CH_2$), 134.58 (2C, $CH{=}CH$); ^{13}C-NMR ($CDCl_3$) *anti* isomer **(13b)** δ 36.03 (1C, O_2CHCH_2), 45.53 (1C, norbornene CH_2), 46.68 (2C, bridgehead CH), 82.50 (2C, CHO), 111.29 (1C, O_2CH), 135.44 (2C, $CH{=}CH$). Anal. Calcd for $C_{18}H_{28}O_2$ (276.4): C, 78.21; H, 10.21. Found: C, 78.19; H, 10.22.

***endo-cis*-3-(10-Undecenyloxy)-5-norbornen-2-ol (14)**. Yield 97%; bp 112−4 °C/0.05 hPa; MS (70 eV) m/z = 212 [$M^+ - C_5H_6$]. Anal. Calcd for $C_{18}H_{30}O_2$ (278.4): C, 77.65; H, 10.86. Found: C, 77.62; H, 11.03.

***endo-cis*-3-(10-Undecenyloxy)-5-norbornen-2-yl Acetate (15)**. Yield 71%; bp 125−6 °C/0.05 hPa; MS (70 eV) m/z = 320 [M^+], 254 [$M^+ - C_5H_6$]; ^{1}H-NMR ($CDCl_3$) δ 1.2−1.4 (m, 13H, $O(CH_2)_2(CH_2)_6CH_2$, norbornene CH), 1.45−1.55 (m, 2H, OCH_2CH_2), 1.51 (m, 1H, norbornene CH), 2.0−2.1 (m, 2H, $CH_2CH{=}CH_2$), 2.03 (s, 3H, CH_3CO), 3.01, 3.06 (2m, 2H, bridgehead CH), 3.35, 3.45 (AB, J = 9.4 Hz, OCH_2), 3.98 (dd, J = 7.4 Hz, J' = 3.6 Hz, 1H, $CHOCH_2$), 5.15 (dd, J = 7.4 Hz, J' = 3.9 Hz, 1H, CHOCO), 4.92, 4.99 (2ddt, 2H, $CH{=}CH_2$), 5.81 (ddt, 1H, $CH{=}CH_2$), 6.25 (m, 2H, $CH{=}CH$); ^{13}C-NMR ($CDCl_3$) δ 20.97 (1C, CH_3CO), 25.99, 28.92, 29.12, 29.41, 29.43, 29.54, 29.79 (7C, $CH_2(CH_2)_7CH_2$), 33.81 (1C, $CH_2CH{=}CH_2$), 42.33 (1C, norbornene CH_2), 45.47, 45.72 (2C, bridgehead CH), 70.91 (1C, OCH_2), 74.03 (1C, CHOCO), 78.92 (1C, $CHOCH_2$), 114.11, 139.17 (2C, $CH{=}CH_2$), 134.02, 135.01 (2C, $CH{=}CH$), 171.17 (1C, CH_3CO). Anal. Calcd for $C_{20}H_{32}O_3$ (320.5): C, 74.96; H, 10.07. Found: C, 74.84; H, 10.17.

***(Z)*-2-(10-Undecenyloxy)vinyl Acetate (16)**. Acetate **15** was slowly evaporated at 0.01 hPa (1.5 g/h). The vapor was passed through a quartz tube (250 mm long, 24 mm diameter) filled with quartz chips and heated to 560 °C. The thermolysis product **16** condensed at room temperature, whereas the cyclopentadiene was collected separately in a trap at −196 °C. **16** was purified by distillation. Yield 77%; bp 94 °C/0.05 hPa; MS (70 eV) m/z = 254 [M^+], 212 [$M^+ - CH_2CO$]. Anal. Calcd for $C_{15}H_{26}O_3$ (254.4): C, 70.83; H, 10.30. Found: C, 70.84; H, 10.36.

Poly[1-acetoxy-2-(10-undecenyloxy)ethylene] **(18)** was prepared as described for the poly(1-acetoxy-2-alkoxyethylenes) **9a,c**−**e**. Anal. Calcd for $(C_{15}H_{26}O_3)_n$ $(254.4)_n$: C, 70.83; H, 10.30. Found: C, 70.92; H, 10.54.

Poly[1-acetoxy-2-(9-carboxynonyloxy)ethylene] (19). A solution of 5.90 g (37.3 mmol) of $KMnO_4$ in 200 mL of dry acetone was added to an ice-cooled solution of 2.75 g (10.8 mmol) of **18** in 100 mL of dry acetone. The mixture was stirred at room temperature overnight and then poured into 350 mL of water. After acidification with sulfuric acid, the MnO_2 precipitate was reduced with sodium disulfite. Afterward acetone was removed in vacuo. The precipitated gel-like polymer was washed with 1 N HCl, dissolved in a mixture of tetrahydrofuran and methanol (8:1), reprecipitated by addition to an excess of 1 N HCl, and finally washed with water. Yield 78%; ^{1}H-NMR (acetone-d_6) δ 1.25−1.5, 1.5−1.7 (broad, 10H + 4H, $CH_2(CH_2)_7CH_2$), 1.9−2.2 (broad, 3H, CH_3CO), 2.28 (t, broad, 2H, CH_2COOH), 3.3−4.1 (broad, 3H, $CHOCH_2$), 4.8−5.4 (broad, 1H, CHOCO); ^{13}C-NMR (acetone-d_6) δ 20.6−22.0 (1C, CH_3CO), 25.7, 26.9, 30.7, 29.5−31.5 (7C, $CH_2(CH_2)_7CH_2$), 34.45 (1C, CH_2COOH), 69,0−73.5 (1C, $CHOCH_2$), 72.5−75.0 (1C, CHOCO), 75.0−77.5 (1C, $CHOCH_2$), 169.5−171.5 (1C, CH_3CO), 175.60 (COOH); IR (cm^{-1}) $1/\lambda$ = 1745, 1710 (C=O). Anal. Calcd for $(C_{14}H_{24}O_5)_n$ $(272.3)_n$: C, 61.74; H, 8.88. Found: C, 62.69; H, 9.15.

Poly[sodium-1-hydroxy-2-(9-carboxylatononyloxy)ethylene] (20). A solution of 860 mg (15.9 mmol) of sodium methanolate in 80 mL of dry methanol was added to a solution of 1.7 g (6.3 mmol) of **19** in 20 mL of tetrahydrofuran. The mixture was heated under reflux for 24 h and afterward diluted with 20 mL of water. The polymer was precipitated by pouring into an excess of acetone−hexane (1:1) and was washed with methanol. **20** was obtained as a colorless powder. Yield 1.3 g (82%); ^{1}H-NMR (D_2O) δ 1.2−1.5, 1.45−1.75 (broad, 10H + 4H, $CH_2(CH_2)_7CH_2$), 2.18 (t, broad, 2H, CH_2COO), 3.3−4.0 (broad, 3H, $CHOCH_2$), 3.9−4.4 (broad, 1H, CHOH); ^{13}C-NMR (D_2O) δ 26−28, 29−32 (7C, $CH_2(CH_2)_7CH_2$), 38.85 (1C, CH_2COO), 69−75.5 (2C, $CHOCH_2$, CHOH), 77−81 (1C, $CHOCH_2$), 184−185 (COO); IR (cm^{-1}) $1/\lambda$ = 1565, 1420 (C=O).

Examination of the Spectral Changes of Pinacyanol Chloride. The absorption spectrum of an aqueous 2×10^{-5} M solution of pinacyanol chloride was registered in the range of 400−750 nm on a Perkin Elmer spectrophotometer 554. Subsequently, specified amounts of polymer **20** were added to samples of this solution, so that the resulting molar ratios of amphiphilic monomer subunits and dye molecules were from 5:1 to 500:1. After an equilibration time of 20 min, the spectra of these solutions were measured. The polymer-free solution of pinacyanol chloride shows absorption bands at 520, 545, and 600 nm. In the presence of 10^{-4} mol/L amphiphilic monomeric units, a band at 495 nm is predominant in the spectrum. At higher polymer concentrations, this band loses intensity in favor of the typical micelle bands at 560 and 610 nm.

Solubilization Experiments of the Azo Dyes (Dimethylamino)azobenzene (DMAB) and 1-(*o*-Toluylazo)-2-naphthol (Orange OT). An excess of azo dye was added to aqueous solutions of polymer **20** (c = 2.5, 5.0, and 10.0 g/L). After an equilibration time of 14 days at 40 °C, the undissolved dye was separated by centrifugation, and the clear colored polymer solutions were diluted with an equal amount of ethanol. The dye concentrations of these solutions were determined by UV−vis spectrometry according to the Lambert−Beer law. The absorbance was measured at λ = 419 nm for DMAB (ϵ = 24 340) and at λ = 497 nm for Orange OT (ϵ = 20 000).

Acknowledgment. Support of this investigation by the "Fonds der Chemischen Industrie" is gratefully acknowledged.

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MA951324O