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(27) K_{EDA} for *N*-vinylcarbazole/dimethyl 1,1-dicyanoethylene-2,2-dicarboxylate = 0.19 L·mol^{-1}.[3]
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Photochemical Synthesis of Block Polymers of Poly(bisphenol A carbonate) with Vinyl Monomers

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ABSTRACT: The photochemical synthesis of block polymers of poly(bisphenol A carbonate) (PC) and polyvinyl monomers is based on the incorporation of benzoin methyl ether (BME) in the PC main chain. On photolysis these light-sensitive PCs degrade, and the number of chain scissions per macromolecule corresponds to their NMR analytical BEM content. Upon photolysis in the presence of vinyl monomers (methyl methacrylate, ethyl acrylate, acrylonitrile), block polymers were obtained of which the composition, molecular weights, and some physical properties have been determined. The method is selective and highly efficient.

The selective incorporation of light-sensitive groups within a condensation polymer offers on photolysis the possibility of formation of macroradicals which may initiate the polymerization of vinyl monomers[1] with the production of block polymers. Depending on the mode of termination of these monomers and on the number of incorporated photolabile groups, the overall structure of the resulting block polymers will be different. If the polymer contains only one photolabile group per macromolecule, the final structure will be of the AB or/and A–B–A type, corresponding to respectively disproportionation and addition termination. If the number of light-sensitive groups exceeds unity, the block polymer mixture will also contain B–A–B triblocks and $(A–B)_n$ multiblocks, resulting from the middle labile group. These different possibilities are represented in Figure 1.

In these systems homopolymer formation will be very limited; it may result in the initiation step from a transfer reaction between the macroradical and the vinyl monomer, e.g., hydrogen transfer, or in the propagation reaction from transfer between a growing chain and the monomer. The method requires therefore an adequate choice of photolabile group and of vinyl monomer. A high quantum yield of photolysis of the photolabile groups enhances considerably the selectivity of the method. Prolonged irradiation may indeed induce undesirable side reactions, e.g., hydrogen abstraction, formation of homopolymers, or graft polymers.

A first example of this method was based on the incorporation of ketooxime ester groups in a poly(tetrachlorobisphenol A adipate). On photolysis in the presence of styrene high yields of block polymers were obtained; only 5–10% homopolystyrene was formed.[2,3] Mezger and Cantow described the incorporation of diaryl disulfide groups in a cellulosic prepolymer; on irradiation in the presence of styrene or of chloroprene these groups produce multiphase block polymers.[4] Similarly, Vlasov et al. prepared symmetric polypeptide chains containing photolabile disulfide or azo groups which on photolysis in the presence of several vinyl monomers produce polypeptide–polyvinyl block polymers.[5]

In the present paper photochemical block polymerization was based on the incorporation of *p,p'*-dihydroxybenzoin methyl ether groups (BME) in poly(bisphenol A carbonate). Its photolysis in the absence and presence of vinyl monomers as well as the formation of polycarbonate–polyvinyl block polymers will be considered successively.

Experimental Section

Chemicals. Vinyl monomers were freshly distilled under reduced nitrogen atmosphere before use. Bisphenol A was recrystallized from toluene. Tetrahydrofuran was distilled after refluxing over sodium metal for 2 h. Pyridine and acetone were dried over molecular 4A sieves. The other substances (chemical pure grade) were used without further purification.

Syntheses. *p,p'*-Dihydroxybenzoin methyl ether (BME) was prepared in a four-step synthesis: (a) methoxymethylation of *p*-hydroxybenzaldehyde, (b) benzoin condensation of the protected hydroxybenzaldehyde, (c) methylation of the secondary alcohol, and (d) deprotection of the phenol group.

(a) 4-(Methoxymethoxy)benzaldehyde was prepared by condensation of 4-hydroxybenzaldehyde in chloroform solution with dimethoxymethane in the presence of *p*-toluenesulfonic acid following the method of Yardly:[6] yield 72%; bp 97–100 °C/1 mmHg. (b) 4,4'-Dimethoxymethoxybenzoin was prepared by condensation of the preceding compound in the presence of potassium cyanide:[7] yield 42%; mp 85–87.5 °C.

Anal. Calcd for $C_{18}H_{20}O_6$: C, 65.05; H, 6.07; O, 28.88. Found: C, 64.97; H, 6.14; O, 28.92. (c,d) 4,4'-Dimethoxymethoxybenzoin was methylated quantitatively by methyl iodide in anhydrous tetrahydrofuran in the presence of silver oxide.[8] The resulting yellow oil was hydrolyzed at 75 °C in 50% acetic acid for 10–15 min in the presence of sulfuric acid as catalyst.[7] After recrystallization from benzene, the yield was 66%, mp 189–192 °C.

4,4'-Bis((chlorocarbonyl)oxy)benzoin Methyl Ether. BME (1 g, 3.9 mmol) was dissolved in 30 mL of anhydrous tetrahydrofuran, and 6.2 g of phosgene (6.3×10^{-2} mol) was introduced. A solution of *N,N*-dimethylaniline in 30 mL of anhydrous tet-

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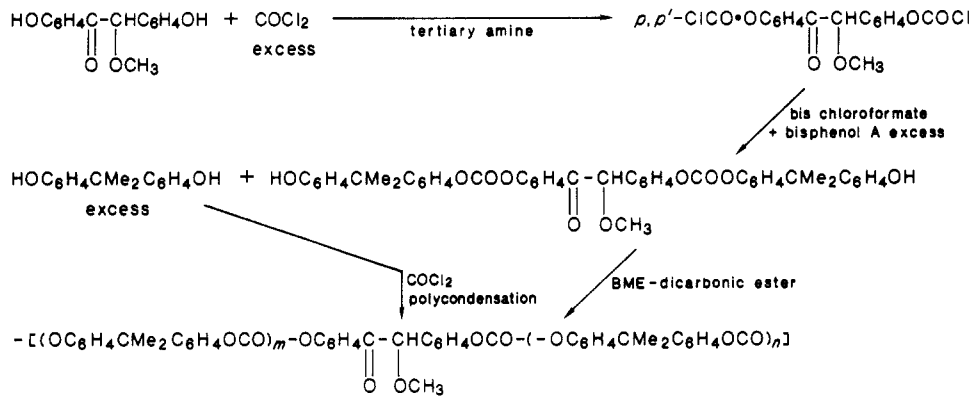
Scheme I



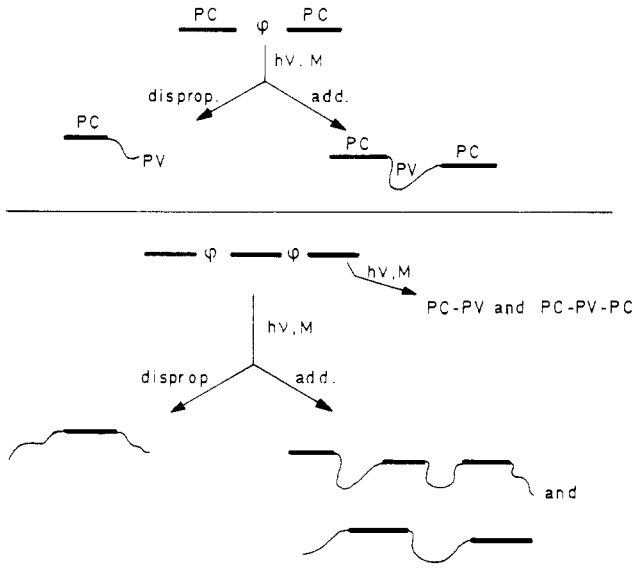


Figure 1. Structure possibilities of block polymers and influence of the number of light-sensitive groups: PC, light-sensitive condensation polymer; PV, polyvinyl sequence; φ, photolabile group.

rahydrofuran was then added dropwise within 1 h at 0 °C; stirring was continued for 6 h at room temperature. Dry nitrogen was bubbled through the reaction mixture for 30 min at 30 °C. After the solvent was removed, the residue was extracted with 100 mL of benzene. After being washed 3 times with 5% hydrochloric acid and then with distilled water, the solution was dried with anhydrous sodium sulfate. After the solvent was removed, a heavy yellow oil (1.3 g) was obtained, for which the purity exceeds 95% as checked by NMR: yield 57%.

Incorporation of BME into Poly(bisphenol A carbonate) (BME–PC). 4,4′-Bis((chlorocarbonyl)oxy)benzoin methyl ether must be first transformed into the bis(bisphenol A)–BME dicarbonic ester by reaction with a large excess of bisphenol A. It is assumed that the reactivity of the BME–dicarbonic ester is equal to that of bisphenol A itself. In a second condensation step with phosgene, a polycarbonate with incorporated BME is obtained. The content of incorporated BME groups depends on the BME–dicarbonic ester/bisphenol A ratio of the mixture.

4,4′-Bis((chlorocarbonyl)oxy)benzoin (1 g, 2.6 mmol) and 17.9 g of bisphenol A (7.0×10^{-2} mol) were dissolved in 100 mL of anhydrous tetrahydrofuran. A solution of 1.2 g pyridine (1.6×10^{-2} mol) in 30 mL of anhydrous tetrahydrofuran was added dropwise within 45 min at room temperature. Stirring was continued for 15 h. After removal of the solvent, the residual brown oil was dissolved in 150 mL of pyridine. Under stirring, 11.6 g of phosgene (0.12 mol) was bubbled through that solution at 30 °C within 2 h; stirring was continued for two more hours. The slurry mixture was poured in 2 L of water and the polymer filtered off. After being washed successively with 1% hydrochloric acid and water, the polymer was dried under vacuum. Further purification proceeded by dissolving the polymer in dichloromethane and reprecipitating it in methanol; after a period of drying, 15 g of polycarbonate (BME–PC) was obtained.

Photochemical Block Polymerization. One gram of BME–PC was dissolved in dichloromethane containing the required amount of vinyl monomer. Dry nitrogen was bubbled through for 20 min at 0 °C. The mixture was irradiated for 1 h at room temperature with a high-pressure mercury lamp equipped with a cut-off filter (>300 nm). The polymer was precipitated into 300 mL of methanol, filtered, washed with methanol, and dried under vacuum at 70 °C. In the case of acrylonitrile, *N,N*-dimethylformamide was used instead of dichloromethane.

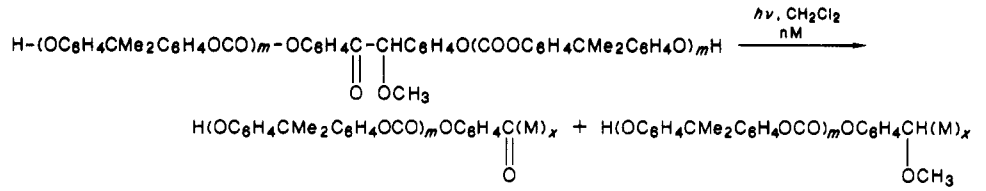
NMR spectra were taken with a Varian 390 EM spectrometer. Infrared (IR) spectra were measured with a Perkin-Elmer 521 spectrophotometer and ultraviolet spectra with a Perkin-Elmer Hitachi 200 double-beam spectrophotometer. Transmission electron microscopy was carried out with a JEOL JEM 100U. Melting points were measured with a Leitz–Wetzler melting point microscope (Model 1146). Glass transition temperatures were measured under nitrogen atmosphere at a heating rate of 10 °C/min with a Perkin-Elmer DSC-2X differential scanning calorimeter. Molecular weights of polymers were determined either with gel permeation chromatography (GPC) (Waters Associates chromatograph, Model 200), vapor pressure osmometry (Corona/Wescan Model 232A), or by viscometry. The photoirradiation was carried out with a high-pressure mercury lamp (Osram 200W). The cut-off filter (Hoya Glass works) or interference filter (Schott and Gen., Mainz Glass Werke) was used. The light intensity was measured with a IL P 700 fluxmeter with a PT 171 C sensor. Mechanical properties were measured with an Instron Model 1121. Impact strength was measured with a Pendulum impact-tester 7565 k for films of 0.2-mm thickness. Films were cast from dichloromethane solution and dried under vacuum for 10 days at 40 °C.

Results and Discussion

In order to assure the incorporation of the 4,4′-dihydroxybenzoin methyl ether (BME) within a poly(bisphenol A carbonate), one has to transform it into its bis(bisphenol A) dicarbonic ester, which has a similar reactivity to that of bisphenol A itself for further condensation. Preliminary experiments of direct condensation of a mixture of BME and bisphenol A with phosgene were indeed unsuccessful on account of the lower reactivity of BME compared to that of bisphenol A. No incorporation of BME could be detected either by ultraviolet spectroscopy or by GPC differences before and after irradiation. Consequently, BME was first treated with a large excess of phosgene (20-fold) to produce the dichloroformate. Subsequently, this dichloroformate was reacted with a large excess of bisphenol A. The reaction mixture, consisting of the bis(bisphenol A) dicarbonic ester and the excess of bisphenol A, was again treated with phosgene for the formation of BME–PC, i.e., polycarbonate with incorporated BME (see Scheme I).

The photolysis of BME has a quantum yield of 0.74;[9] it is almost complete after 0.5 h in our experimental con-

Scheme II



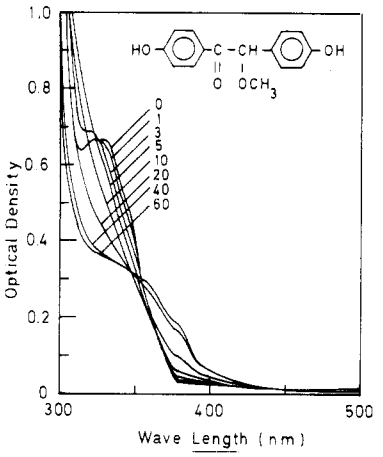


Figure 2. Ultraviolet absorption spectra of *p,p'*-dihydroxybenzoin methyl ether and influence of time of irradiation. High-pressure Hg lamp; interference filter 337 nm, 1.21×10^{-3} mol/L in dioxane.

Table I
Data from Photolysis of BME-Poly(bisphenol A carbonate)

$\bar{M}_{n0}$	$\bar{M}_{ni}$	N_s[a]	BME group/ macromolecule[b]
33 600	14 800	1.27	1.26
50 600	28 600	0.77	0.84

[a] Calculated $N_s = (M_{n0}/M_{ni}) - 1$. [b] ^{1}H NMR results.

ditions (Figure 2). In agreement with that, the intrinsic viscosities of BEM-containing polycarbonates decrease with time of irradiation of their chloroform solution; under the same irradiation conditions polycarbonate homopolymers remain unchanged (Figure 3). Two different BEM–PC polymers with 0.84 and 1.26 BEM groups per macromolecule (determined by NMR) have been photolyzed, and their number-average molecular weights before (M_{n0}) and after irradiation (M_{ni}) were determined by gel permeation chromatography. The numbers of chain scission per macromolecule, N_s, calculated on the basis of the equation

$$N_s = (M_{n0}/M_{ni}) - 1$$

were respectively 0.77 and 1.27; these values correspond very satisfactorily with the NMR data (Table I). When these BME–PC polymers are decomposed in the presence of a vinyl monomer, polycarbonate–polyvinyl block polymers are formed. In the case of a termination reaction by disproportionation, the reaction proceeds as in Scheme II. Some experimental results with methyl methacrylate have been reported previously.[10] It was shown that the polymethacrylate weight fraction increases with the monomer concentration and that it remains constant after 1 h of

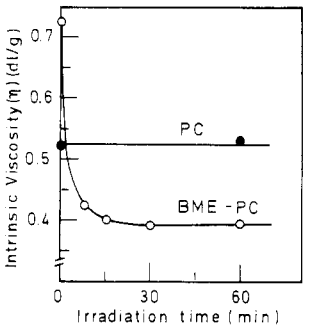


Figure 3. Photodegradation of BME–PC in chloroform at 20 °C ($\lambda_{irr} > 300$ nm). Decrease of intrinsic viscosity with time of irradiation. PC line corresponds to polycarbonate without BME groups.

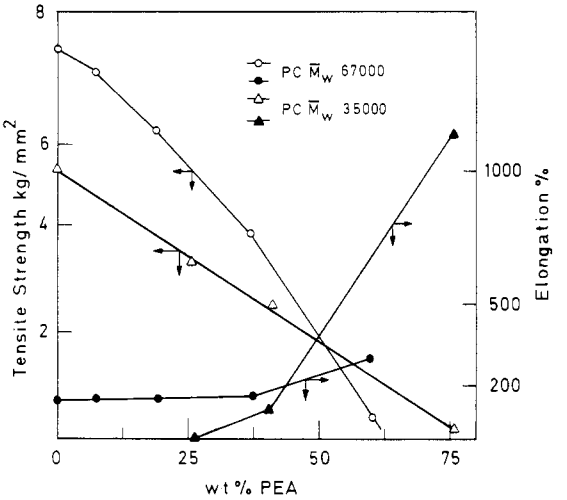


Figure 4. Influence of the composition of PC–PEA block polymers on mechanical properties.

irradiation. The acetophenone link $PCOC_6H_4COCH_2C(CH_3)(COOCH_3)$ resulting from the monomer addition to the benzoyl radical does not compete with the benzoine cleavage in forming block polymers. The reaction products were almost pure block polymers; on prolonged extraction with boiling acetone only 10–11 g as a weight fraction was soluble; it contained 5 mol % PC. These PC–PMMA block polymers show on differential scanning calorimetry two independent glass transition domains corresponding to PMMA (around 90 °C) and partially crystalline PC (175 °C). The mechanical properties of a PC–PMMA (58/42) block polymer was compared to those of the corresponding homopolymers (Table II). As expected, the block polymers present intermediate properties. The role of the poly(methyl methacrylate) sequence is predominant for

Table II
Mechanical Properties of PC57–PMMA43 Block Polymers

polymer	$\bar{M}_n$	$\bar{M}_w$	dispersity, $= \bar{M}_w/\bar{M}_n$	tensile strength, kg/mm²	elongation, %	impact strength, J/mm²
polycarbonate	28 600	66 900	2.32	7.3	147	3.6
PC57-PMMA43	48 300	138 000	2.86	5.2	117	0.24
poly(methyl methacrylate)	35 000	77 300	2.22	4.6	23	0.14

Table III
Synthesis and Mechanical Properties of Poly(bisphenol A carbonate)-Poly(ethyl acrylate) Block Polymers

[BME], 10^3 mol·L^{-1}	[EA] mol·L^{-1}	yield, g	PC mol %	PC NMR wt %	MW × 10^3 $\bar{M}_{n\,calcd}$	MW × 10^3 $\bar{M}_n$ (GPC)	MW × 10^3 $\bar{M}_w$	tensile strength, kg/mm^2	elongation, %	impact strength, J/mm^2
1.25			100			14.8	34.9	5.1	5	
	0.31	1.32	52	74	20.2	19.8	53.5	3.3	3	
	0.62	1.78	36	59	25.1	20.7	61.3	2.5	110	
	1.54	3.8	11	24	61.9	33	137	0.2	1136	
0.535			100			28.6	66.9	7.3	147	3.6
	0.15	0.92	83	92.5	30.9	30.7	83	6.9	154	2.4
	0.31	1.06	62.5	81	35.3	34.5	86.2	5.8	154	2.6
	0.62	1.54	40	63	45.5	49.8	136	3.9	161	3.1
	1.54	2.79	21	40	71	54.4	171.4	0.4	299	

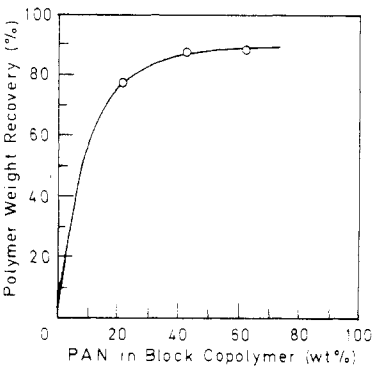


Figure 5. Solvent resistance of PC–PAN block polymer and dependence on block composition. Extraction was with boiling chloroform for 10 h.

the tensile and impact strengths.

The same block polymerization method was used with ethyl acrylate in order to obtain PC–PEA block polymers with hard and soft sequences. Therefore, two BME–PCs of 33 600 and 50 600 number-average molecular weight with respectively 1.26 and 0.84 BEM groups per macromolecule were photolyzed in dichloromethane (1 g/30 mL) containing increasing amounts of monomer. The experimental data are given in Table III and Figure 4.

In this table the M_n and M_w values refer to the BME–PC polymers after photochemical decomposition in the absence of monomer (first line of each series) and after photochemical block polymerization. By assuming that the basic PC sequences in the block polymers correspond to the molecular weight of the polycarbonate after photodecomposition in absence of monomer, molecular weights can be calculated on the basis of their chemical composition. Although M_n values as determined by gel permeation chromatography may be controversial, the comparison between the experimental and calculated M_n values shows a fair correspondence, except at relatively high monomer concentration. In most cases, the calculated M_n values are higher than the experimental ones, contrary to the case of the PC–PMMA block polymers. Concerning the mechanical properties of these block polymers, preliminary measurements on polycarbonate homopolymers of increasing molecular weight have confirmed that low molecular weight polymers have very low tensile strength; it increases considerably when the molar mass M_n exceeds 17 500 and reaches then a level of strength which increases only slightly with further increase of molecular weight.

A similar observation applies also to elongation properties. Such dependence upon the molar mass is well-known for many polymers and was already described by Golden et al. in the case of the polycarbonates.[11] Therefore, the second series of PC–PEA blocks of Table III, in which the PC sequence amounts to a molecular weight of 28 600, likely presents more reliable data than the first series (PC 14 800) concerning their observed mechanical properties. The tensile strength decreases with increasing PEA content, while the elongation shows little change up to 50 wt % PEA and then rises considerably at higher PEA content.

The morphology of these PC–PEA block polymers has been observed by electron microscopy and shows two distinct phases; the contrast was improved by developing the PC crystals in an acetone atmosphere. On increasing the PEA content, the lamellar size decreases, and the borderline between crystalline amorphous regions becomes more and more vague.

Acrylonitrile has been the third monomer to be used by the same synthetic procedure, in order to improve the solvent resistance of polycarbonates. In this case, however, *N,N*-dimethylformamide was used as the solvent instead of dichloromethane for the block polymerization. The solvent resistance was examined by Soxhlet extraction with boiling chloroform, which is known as an excellent solvent of polycarbonate. The results are shown in Figure 5. After 10 h of extraction, the polymer weight recovery amounted to about 80 wt % by incorporating only 20 wt % polyacrylonitrile. Under the same conditions, polycarbonate homopolymer dissolves completely within a few minutes. The solvent resistance is thus considerably improved without affecting the overall properties of the polycarbonate.

In conclusion, this photochemical method permits the synthesis of many block polymers for which the PC block lengths can be regulated by the BME content of the prepolymers and the polyvinyl sequences by the polymerization conditions. The basic selectivity and high efficiency of this method are both of particular interest.

Acknowledgment. We gratefully acknowledge the financial support of the Ministry of Scientific Programmation and the grant of a postdoctorate fellowship of the Asahi Glass Ltd. (T.D.).

Registry No. BME, 95972-61-5; 4-(methoxymethoxy)benzaldehyde, 6515-21-5; 2-hydroxybenzaldehyde, 123-08-0; dimethoxymethane, 109-87-5; 4,4′-dimethoxymethoxybenzoin, 98437-94-6; 4,4′-bis((chlorocarbonyl)oxy)benzoin methyl ether, 95972-63-7; (4,4′-bis((chlorocarbonyl)oxy)benzoin methyl ether)(phosgene)(bisphenol A) (copolymer), 115982-98-4; (4,4′-bis((chlorocarbonyl)oxy)benzoin methyl ether)(phosgene)(bisphenol A)(methyl methacrylate) (block copolymer), 115982-99-5; (4,4′-bis((chlorocarbonyl)oxy)benzoin methyl ether)(phosgene)(bisphenol A)(ethyl acrylate) (block copolymer), 116004-67-2; (4,4′-bis((chlorocarbonyl)oxy)benzoin methyl ether)(phosgene)(bisphenol A)(acrylonitrile) (block copolymer), 115983-00-1.

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Photopolymerization of Vesicles Prepared from *n*-Hexadecyl 11-(4-Vinylbenzamide)undecyl Hydrogen Phosphate and from Mixtures of Dioctadecyldimethylammonium Bromide and *n*-Hexadecyl 11-(4-Vinylbenzamide)undecyl Hydrogen Phosphate

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ABSTRACT: Surfactant vesicles, prepared from *n*-hexadecyl 11-(4-vinylbenzamide)undecyl hydrogen phosphate (**4**) and from mixtures of **4** and dioctadecyldimethylammonium bromide (**2**), have been photopolymerized by exposure to a 450-W xenon lamp or to repetitive, 265-nm, 20-ns laser pulses. Changes in the temperature, the pH, and the composition of the vesicles, as well as polymerization, profoundly affected the ^{31}P NMR spectra. Thus, a high-resolution signal at −10.95 ppm (relative to 1.0×10^{-2} M methylenediphosphonic acid) was observed at 70 °C for vesicles prepared from **4** at pH 5.8. Decreasing the temperatures decreased the motion of the phosphorus head group due to "liquid-to-solid" phase transition and broadened the ^{31}P NMR line width. Increasing the pH or incorporating **2** into **4** vesicles caused a downfield shift and line narrowing. Polymerization manifested in broadening of the ^{31}P NMR line width. Irradiation of vesicles, prepared from **4** and from mixtures of **4** and **2**, resulted in time, composition, and temperature-dependent changes of the absorption spectra. Absorbances due to the styrene moiety decreased exponentially with increasing photolysis. The pseudo-first-order rate constants, k_ψ values, calculated for steady-state irradiations, remained independent of the amount of **4** in vesicles prepared from mixtures of **4** and **2** at 23 °C, but it increased with increasing amounts of **4** at 70 °C. Breaks in the Arrhenius plots for the photopolymerization of vesicles prepared from 40:60 **4**/**2** showed the presence of two-phase transitions, indicating unequal distribution of surfactants. The first transition, having a phase transition temperature of 48 ± 2 °C, corresponded to the value determined for vesicles prepared from 40:60 **4**/**2** surfactant mixtures. The second transition, having a phase transition temperature of 65 ± 3 °C, was suggested to be due to patches of **4** assembled at higher temperatures. Data obtained in the repetitive 10-Hz laser photolysis allowed the assessment of the degrees of polymerization of **4** to be approximately 2. Number-averaged molecular weights of 3010 and 1500 and corresponding degrees of polymerizations of 5.1 and 2.5 were also determined from vapor phase osmometry measurements in photopolymerized vesicles prepared from **4** and from a 40% **4** and 60% **2** mixture. Irradiation with repetitive laser pulses at different frequencies afforded values for the propagation and termination rate constants for **4** in MeOH and for vesicles prepared from **4** and from a 40% **4** and 60% **2** mixture.

Introduction

Potential industrial applications have prompted the interest in polymerized vesicles.[1-6] The ability of polymerized vesicles to provide stable compartments of different microenvironments has been exploited in controlled release and delivery of drugs and other materials, immunorecognition, catalysis, transport, and artificial photosynthesis.[7-9]

Vesicles are closed-bilayer, single (SUVs), or multilamellar (MLVs) structures prepared from naturally occurring phospholipids or synthetic surfactants.[10] A vesicle-forming surfactant contains, typically, two C12–C20 hydrocarbon chains and a phosphate, sulfate, or quaternary ammonium head group. Introduction of vinyl, methacrylate, diacetylene, isocyano, and styrene moieties in the hydrocarbon chains or in the head groups led to polymerizable surfactants.[1-6,11] Vesicles prepared from polymerizable surfactants could subsequently be polymerized in their bilayers or across their outer or outer and inner head groups. Alternatively, exchanging the vesicle counterions by appropriate monomers and subsequent polymerization introduced the concept of polymer-coated vesicles.[12-15] Polymerized and polymer-coated vesicles showed enhanced stabilities and permitted some degree of permeability and morphology control.[1-5]

Optimization of permeability control requires an understanding of the kinetics and the structural changes which accompany vesicle polymerizations. These mechanistic details are being scrutinized in several laboratories.[15-24] Attention is focused in our laboratories to styrene-containing surfactants. We have found the photopolymerization of vesicles prepared from **1** (dioctadecyldimethylammonium bromide (**2**) functionalized by a styrene moiety in the head group) to result in pulling some 10–20 aryl groups together and thereby creating surface clefts.[20] Subsequently, we showed the degree of polymerization for vesicles prepared from an analogous surfactant (**3**) to vary between 10 and 20.[15] Larger degrees of polymerization were observed for vesicles prepared from mixtures of **2** and vinylbenzoic acid as well as from mixtures of **3** and vinylbenzoic acid.[15]

Polymerizations of vesicles prepared from a negatively charged surfactant (**4**) and from mixtures of **4** and **2** are the subject of the present report. ^{31}P NMR spectroscopy has provided structural information on vesicles prepared

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