Macromolecules **2000,** *33,* 4285−4287

Highly Hydrophobic Surface Material: Poly(phytanyl methacrylate)†

Kiyoshi Yamauchi,* Fusashi Akiyama, and Takahiro Kitano

Department of Bioapplied Chemistry, Faculty of Engineering, Osaka City University, Sumiyoshi-ku, Osaka 558-8585, Japan

Received November 16, 1999
Revised Manuscript Received March 8, 2000

Introduction

Long isopranyl chains, $-[CH_2CH_2CH(CH_3)CH_2]_nH$, feature the hydrophobic moiety of archaebacterial membrane lipids. The microorganisms proliferate in such extreme habitats as hot springs and salt lakes.[1,2]

In the course of the studies on the liposomes made of the abnormal lipids and their model compounds, we found that the assemblies were very stable at high temperature and high NaCl concentration (0−5.5 M).[3−5] We have experienced also that the membranes were weakly stained by uranyl acetate and phosphotungstic acid to result in low-contrast images in comparison with the membranes prepared from straight alkyl chain analogues.[6] These phenomena might indicate that the polyisopranyl comounds are more hydrophobic than straight chain analogues. Indeed, aqueous solutions of the surfactants bearing a phytanyl group (Phy) were lower significantly in surface tension than that of straight-chain surfactants, viz., 25−30 vs 38−45 dyn/cm at ambient temperature.[6,7] In this paper we wish to describe a new type of highly hydrophobic surface material, poly(phytanyl methacrylate) (Figure 1).

Experimental Section

1-Decanol, 1-eicosanol, and phytol were purchased from Sigma-Aldrich, Japan. Phytanyl alcohol was prepared by the Raney Ni-catalyzed hydrogenolysis of the phytol with the procedure mentioned previously.[4] Thin-layer chromatography (TLC) and column chromatography were conducted using a silica gel-precoated sheet [Merck GF254 Art 5735 (type 6)] and silica gel [Merck Art 7734 (70−230 mesh)], respectively. TLC spots were visualized by spraying a 0.0012% aqueous solution of Rhodamin 6G. ^1H NMR (400 MHz) spectra were recorded on a JEOL α-400 spectrometer from a dilute solution in $CDCl_3$ with tetramethylsilane as a internal standard. Fast atom bombardment mass spectra (FABMS) were obtained by using a JEOL HX-100 in a positive ion-detection mode, where a sample in glycerol on a standard FAB target was subjeced to a beam of xenon atoms produced at 8 kV and 2 mA. The molecular weights of polymers were determined by a gel permeation chromatograph, Toyo-Soda 8000, using THF as a solvent. Contact angles were measured by the use of Kyowa Kaimen Kagaku model CA-A contact-angle meter at 20 ± 1 °C. Other instruments used were a Jasco A202 infrared spectrometer and a Rigaku DSC-8240 differential scanning calorimeter.

Preparation of Monomers. a. Phytanyl methacrylate. To a cooled mixture of phytanyl alcohol (3.0 g, 10.0 mmol) and triethylamine (2.0 mL, 14 mmol) in an ice water bath was added methacryloyl chloride (1.3 mL, 13.3 mmol). The reaction mixture was stirred below 10 °C for 45 min and then at room temperature overnight. The resulting solution was fractionated between water and dichloromethane. The organic layer was washed successively with 2.2 M hydrochloric acid, saturated sodium hydrogen carbonate, and water and then dried on anhydrous sodium sulfate. The solution was concentrated to afford the residue which was subjected to a silica gel column chromatography using a mixture of hexane and ethyl acetate (20:1 v/v) as a developing solvent. The title monomer was obtained as a colorless oil to show a single homogeneous spot in TLC with a relative mobility of 0.56 (hexane and ethyl acetate, 20:1 v/v), yield, 2.6 g (70%). ^1H NMR: δ 0.909−0.836 (complex m, 15H, $5CH_3$), 1.94 (s, 3H, α-CH_3), 4.176 (m, 2H, OCH_2, 2H), 6.090 and 5.539 (two s, 2H, $C{=}CH_2$). IR (neat): 2940 (s), 1725 (s), 1637 (w), 1465 (m), 1380 (m), 1325 (w), 1300 (m) and 1175 (s) cm^{-1}. FABMS: m/z 366 ($C_{24}H_{46}O_2^+$ ion; relative intensity, 10%). Calcd for $C_{24}H_{46}O_2$: C, 78.62; H, 12.64. Found: C, 78.33; H, 12.69.

b. Decyl Methacrylate. 1-Decanol (3.0 g, 19 mmol), methacryloyl chloride (2.2 mL, 23 mmol), and triethylamine (3.3 mL, 24 mmol) were treated in a manner similar to that mentioned above to afford the title compound as the colorless oil, which was homogeneous to show a single spot in TLC; mobility, 0.62 (hexanes−ethyl acetate, 15:1 v/v); yield 3.2 g (75%). ^1H NMR: δ 0.881 (t, J = 6.8 Hz, 3H, CH_3), 1.255 [s, 14H, $CH_3(CH_2)_7$], 1.669 (m, 2H, OCH_2CH_2), 1.947 (s, 3H, α-CH_3), 4.136 (t, 2H, OCH_2), 5.547 and 6.097 (two s, 2H, $={}CH_2$). IR (neat): 2940 (s), 1725 (s), 1637 (w), 1460 (m), 1380 (w), 1300 (m), 1275 (m), and 1140 (s) cm^{-1}. FABMS: m/z 226 ($C_{14}H_{26}O_2$ ion; relative intensity, 2%). Calcd for $C_{14}H_{26}O_2$: C, 74.28; H, 11.57. Found: C, 74.35; H, 11.58.

c. Eicosanyl Methacrylate. 1-Eicosanol (1.5 g, 5.0 mmol) and methacryloyl chloride (0.7 mL, 7.1 mmol) were allowed to react in the presence of triethylamine (1.0 mL, 7.2 mmol) in a manner similar to that mentioned above to provide the title monomer as an analytically pure substance. Relative mobility in TLC 0.49 (hexanes−ethyl acetate, 15:1 v/v); yield 1.4 g (77%); mp 33.8−35.1 °C. ^1H NMR ($CDCl_3$): δ 0.880 (t, J = 6.8 Hz, 3H, CH_3), 1.255 [s, 34H, $CH_3(CH_2)_{17}$], 1.668 (t, J = 6.8 Hz, 2H, OCH_2CH_2), 1.945 (s, 3H, α-CH_3), 4.136 (t, 2H, OCH_2), 5.548 and 6.098 (two s, 2H, $={}CH_2$). IR (neat): 2940 (s), 1725 (s), 1637 (w), 1460 (m), 1380 (w), 1300 (m), 1275 (m) and 1140 (s) cm^{-1}. FABMS: m/z 366 ($C_{24}H_{46}O_2^+$ ion; relative intensity, 20%). Calcd for $C_{24}H_{46}O_2$: C, 78.62; H, 12.64. Found: C, 78.50; H, 12.74.

Preparation of Polymers. The methacrylate monomers were polymerized as described typically below. Phytanyl methacrylate (0.21 g, 0.57 mmol), a benzene solution of azobis(isobutyronitrile) (AIBN, 1 mg/mL, 0.09 mL, ca. 0.57 μmol), and benzene (0.12 mL) were placed in a glass tube; cf. initiator: monomer = 1:1000 mol/mol; solvent: monomer = 1:1 g/v. The glass tube was cooled, flashed with nitrogen gas, and thawed. After repeating the freeze−nitrogen gas flashing−thaw cycle three times, the tube was sealed and shaken at 50 °C for 20 h. Subsequently, the contents of the tube were diluted with a small amount of hexane and poured into methanol to result in separating the polymer as the precipitates. The polymer was purified by dissolving in hexane and precipitating from methanol and finally dried under reduced pressure (about 1 mmHg) overnight. The yields and molecular weights of the polymers are listed in the Table 1.

Contact Angle and Zisman's Critical Surface Tension. A chloroform solution of the aforementioned polymers (0.1 M) was spread on a glass plate (3−4 mg of polymer /cm^2) and dried in a desiccator (silica gel) overnight under reduced pressure and ambient temperature. A liquid drop (5 μL) was placed by means of a microsyringe on the coated glass which was in an closed environmental chamber [height−width−depth: 7 cm × 4 cm × 5 cm; 100% humidity with respect to the liquid]

---

† Abbreviations. FABMS: fast atom bombardment mass spectra; M_N, M_W, and M_Z: number-, weight-, and Z-average molecular weights, respectively; PMMA, poly(C10MA, poly(C20MA), and poly(PhyMA): poly(methyl methacrylate), poly(decyl methacrylate), poly(eicosyl methacrylate), and poly(phytanyl methacrylate), respectively.

* To whom the correspondence should be addressed.

10.1021/ma991939b CCC: $19.00

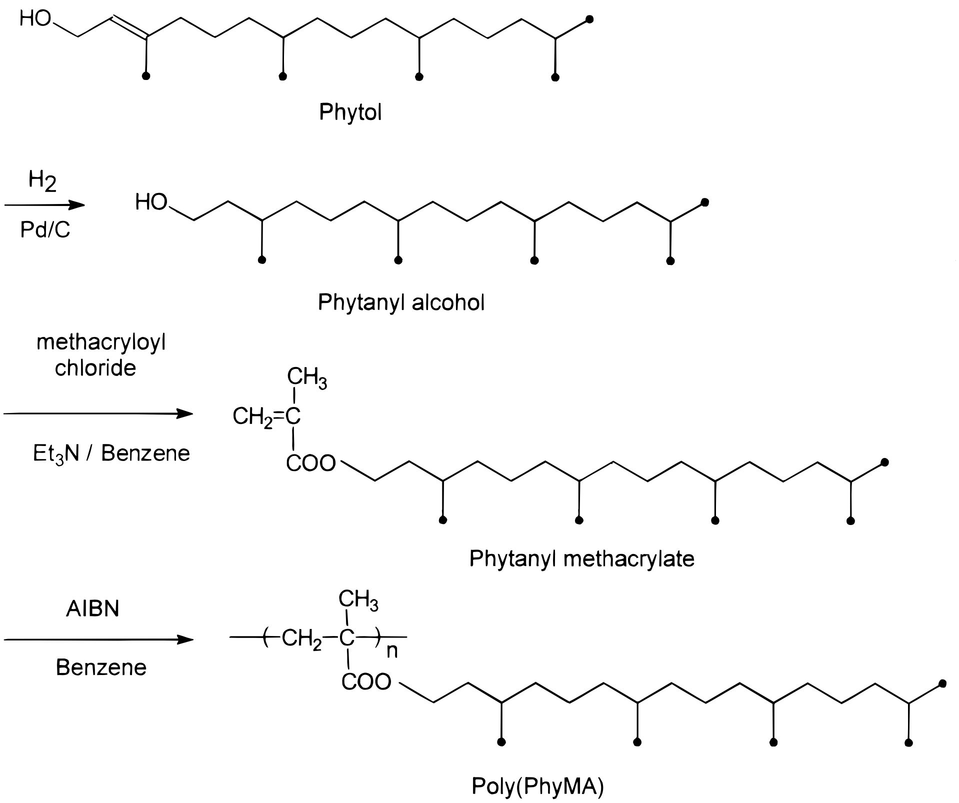

Figure 1. Reactions for preparation of poly(PhyMA).

Table 1. Contact Angle (to Water) and Molecular Weights of Various Poly(alkyl methacrylate)s

polymer[a]	$\theta \pm 3°$ at 20 ± 1 °C	$10^4 M_N$	$10^4 M_W$	$10^4 M_Z$	yield (%)
poly(PhyMA)	124°	89	220	400	67
poly(C20MA)	104	150	340	560	53
poly(C10MA)	112	58	120	160	81
PMMA[c]	67	99			
glass	22				

[a] C10 and C20 are n-$C_{10}H_{21}$ and n-$C_{20}H_{41}$ groups, respectively. M_N, M_W, and M_Z are the number-, weight-, and Z-average molecular weights, respectively. [b] The PMMA was available from Aldrich Co., product number 18226-5.

equipped with optically clear windows. After taking 60–100 s as an equilibration time,[8] a contact angle of water was measured three times at different sites at 19–21 °C and averaged, with an experimental error of less than ±3°. During the measurements taking about 10 min, the drift of the contact angle was negligible. The Zisman plot[9,10] was performed upon measuring the contact angles of heptane, octane, nonane, decane, undecane, dodecane, tetradecane, and hexadecane. The plots are shown typically in Figure 2. All these solvents were distilled prior to use. Surface energy (to air; γ_s) and interface energy (to water, γ_{sl}) of various poly(alkyl methacrylate)s were calculated according to Andrade's equation.[11,12]

Results and Discussion

The long-chain alcohols such as phytanyl alcohol were condensed with methacryloyl chloride in the presence of triethylamine to produce the corresponding methacryl esters in a semiquantitative yield (70–77%). The monomers were isolated by silica gel column chromatography; cf. the distillation, even under a reduced pressure, did not give the monomers as analytically pure substances.

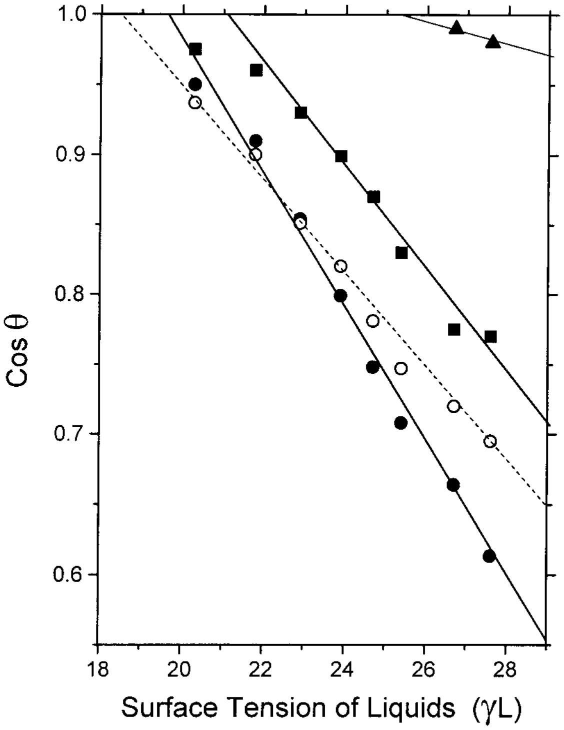

Figure 2. Zisman plots of various n-alkanes (C_nH_{2n+2}, $n = 7$, 8, 9, 10, 11, 12, 14, and 16) on poly(PhyMA) (●), poly(C10MA) (■), poly(C20MA) (▲), and Teflon (poly(tetrafluoroethylene)) (○). The data of PTFE were cited from the literature.[9]

Polymerization of the alkyl methacrylates took place readily in the presence of AIBN. Perhaps because of subtle differences in polymerization conditions, the molecular weights of the PMMA, poly(C20MA), and poly(PhyMA) were varied considerably as seen in Table 1 [the PMMA was a commercial product.]. Nonetheless, the polymers may be large enough for examination of the hydrophobicity of polymer coatings on a glass plate. As expected, the contact angle (θ) of water on the poly-

Table 2. Zisman's Critical Surface Tension of Various Poly(alkyl methacrylate)s

polymers[a]	γ_c (dyn/cm)
poly(hexafluoropropylene)	16.2
poly(tetrafluoroethylene)	18.5
poly(PhyMA)	19.6 ± 0.6
poly(C10MA)	21 ± 0.7
poly(trifluoroethylene)	22
poly(C20MA)	25 ± 0.7
poly(ethylene)	33
poly(vinyl alcohol)	37
PMMA	39
poly(vinyl chloride)	40
nylon 6-6	46

[a] The γ_c values of poly(C10MA), poly(C20MA), and poly(PhyMA) were determined by the Zisman's plot in the present study. Other values were cited from the literature.[9]

Table 3. Surface Energy (to Air; γ_s) and Interface Energy (to Water, γ_{sl}) of Various Poly(alkyl methacrylate)s[a]

polymers[b]	γ_s (dyn/cm)	γ_{sl} (dyn/cm)
glass	170	20
water	73	0
nylon 6-6	40	5.1
poly(trifluorochloroethylene)	38	5.6
PMMA	36	6.2
poly(vinyl chloride)	35	6.9
poly(ethylene)	33	7.6
poly(tetrafluoroethylene)	24	13
poly(C20MA)	10	28
poly(C10MA)	7	35
poly(PhyMA)	4	44
air	0	73

[a] The γ_s and γ_{sl} were obtained according to Andrade's method.[11,12]

(long alkyl methacrylate)s was larger than that of PMMA. The poly(PhyMA), however, was abnormal; viz., despite that the phytanyl chain had the same C and H composition as the eicosyl chain, the polymer provided the surface which was more hydrophobic than poly(C20MA). The Zisman critical surface tensions (γ_c) of various substances are shown in Table 2. It would be worth noting that poly(PhyMA) was comparable in γ_c with poly(tetrafluoroethylene). Surface energies (γ_s of air/substance interface and γ_{sw} of water/substance interface) are calculated according to Andrade and coworkers' method as seen in Table 3.

We have not been able to explain well the unique surface property of poly(PhyMA) though it should have originated from the phytanyl chain. It might be caused by the fluid and bulky structure. As aforementioned, the isopyranyl chain is the main feature of the lipids of the archaebacteria which thrive in extreme environments. It has often been shown in the physicochemical studies that the phytanyl chains of the lipids are in a liquid crystalline state over a wide temperature range (from as low as −40 to 70 °C), suggesting a high-entropy (S) state of the membranes[4−6,13,14] [The poly(PhyMA) did not exhibit any phase transitions in the temperature range, either.] In addition, the Langmuir adsorption isotherm study of the archaebacterial lipids showed that a phytanyl chain occupied as large as 100 Å^2, which was significantly larger than straight-chain analogues (40−60 Å^2). In other words, the phyanyl chains are packed loosely in comparison with the straight chains; hence, an enthalpy (H) of the phytanyl chain may be considered smaller than that of the straight chain and accords with the phase transition study of the archaebacterial lipid membranes.[4−6] Since the surface energy (γ) is defined as the Gibbs free energy per unit length ($G = H - TS$), it may be considered that the surface tension of poly(PhyMA) is smaller than that of poly(n-alkyl methacrylate) such as poly(C20MA). We have currently been studying the surface properties of phytanyl chain-bearing compounds.

References and Notes

(1) Langworthy, T. A. In *The Bacteria;* Woese, C. R., Wolfe, R. S., Eds.; Academic Press: San Diego, 1985; Vol. VIII, pp 459−497.

(2) De Rosa, M.; Gambacorta, A.; Gliozzi, A. *Microbiol. Rev.* **1996**, *50*, 70−80.

(3) Yamauchi, K.; Sakamoto, Y.; Moriya, A.; Yamada, K.; Hosokawa, T.; Higuchi, T.; Kinoshita, *M. J. Am. Chem. Soc.* **1990**, *112*, 3188−3191.

(4) Yamauchi, K.; Doi, K.; Kinoshita, M.; Kii, F.; Fukuda, H. *Biochim. Biophys. Acta* **1992**, *1110*, 171−177.

(5) Yamauchi, K.; Doi, K.; Kinoshita, M. *Biochim. Biophys. Acta* **1996**, *1283*, 163−169.

(6) Yamauchi, K. *J. Jpn. Oil Chemist' Soc.* **1997**, *46*, 539−550.

(7) Yamauchi, K.; Onoue, Y.; Tsujimoto, T.; Kinoshita, M. *Colloids Surf., B: Biointerfaces* **1997**, *10*, 35−38.

(8) Kabza, K.; Gestwicki, J. E.; McGrath, J. L. *J. Chem. Educ.* **2000**, *77*, 63−65.

(9) Zisman, W. A. *Ind. Eng. Chem.* **1963**, *55*, 18−38.

(10) Zisman, W. A. In *Encyclopedia of Polymer Science and Technology*; Mark, H. F., Gaylord, N. G., Bikales, N., Eds.; Interscience Publishers: New York, 1964; Vol. I, pp 450−477.

(11) Smith, L.; Doyle, C.; Gregonis, D. E.; Andrade, J. D. *J. Appl. Polym. Sci.* **1982**, *26*, 1269−1276.

(12) Andrade, J. D.; Lee, H. B.; Jhon, M. S.; Kim, S. W.; Hibbs, J. B. *Trans. Am. Soc. Artif. Intern. Organs* **1973**, *19*, 1−7.

(13) Yang, L. L.; Haug, A. *Biochim. Biophys. Acta* **1979,** *573*, 308−320.

(14) Chen, J. S.; Barton, P. G.; Brown, D.; Kates, M. *Biochim. Biophys. Acta* **1974**, *352*, 202−217.

MA991939B