1156 *Macromolecules* **2006,** *39,* 1156−1159

Contact Angle of Poly(alkyl methacrylate)s and Effects of the Alkyl Group

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Received October 6, 2005; Revised Manuscript Received December 7, 2005

ABSTRACT: The contact angle (θ) of water on the surface of various poly(alkyl methacrylate)s was measured in order to obtain a relationship between the chain length of the alkyl group and the surface energy of the polymers, where the alkyl is an n-C_nH_{2n+1} ($n = 1$, 2, 4, 6, 8, 10, 12, 14, 16, 18, and 20) group and a phytanyl or (3*RS*,7*RS*,11*RS*)-3,7,11,15-tetramethylhexadecyl group. Generally, the plotting of θ vs alkyl chain length gave a bell-shaped curve to show the maximum θ at a certain poly(alkyl methacrylate). The θ of each polymer, however, varied characteristically with temperature; hence, the polymer providing the maximum θ was altered to another polymer by changing temperature. The complex phenomenon was analyzed by the means of DSC, ESCA, XRD, and RAS IR spectra, etc. of the polymers to reveal that the contact angle was dramatically enhanced when the polymer state was changed to a noncrystalline (melt) state from a crystalline state. In other words, the polymer, which possesses long alkyl groups with random packing, was found to provide a highly hydrophobic surface. Especially, poly(phytanyl methacrylate) was fit to these conditions to express a very large θ (120−125°) over a wide temperature range (10−60 °C), being the most hydrophobic hydrocarbon material ever prepared.

Introduction

Achaea (formally called archaebacteria), proliferate in such extreme habitats as hot springs and salt lakes.[1,2] At a molecular level, the archaeal lipids are unique in hydrocarbon chain structure. Namely, unlike eubacterial and eukaryotic lipids, which bear chiefly straight chain fatty acids in the hydrophobic moiety, archaeal lipids possess universally a polyisopranyl chain such as a phytanyl group [(3*R*,7*R*,11*R*)-3,7,11,15-tetramethylhexadecyl].[2,3] Conceivably, the microorganisms may require the unique lipids in order to cope with the extreme habitats. During the course of the physicochemical study of archael lipid membranes, we found that the substances having the phytanyl group expressed an abnormally low surface energy[4,5] as well as highly thermostable and salt-tolerant properties.[6−9] For instance, a water droplet on poly(phytanyl methacrylate) (PPhyMA) showed a contact angle (θ) of about 122° at ambient temperature; such a high hydrophobic surface has never been achieved by other hydrocarbon materials. Being impressed by the unique surface phenomenon, we studied the contact angle of water on various poly(n-alkyl methacrylate)s (PC*n*MA) and PPhyMA to obtain a basic knowledge of the relationship between the hydrophobicity and the structure of the hydrocarbon group (Figure 1).

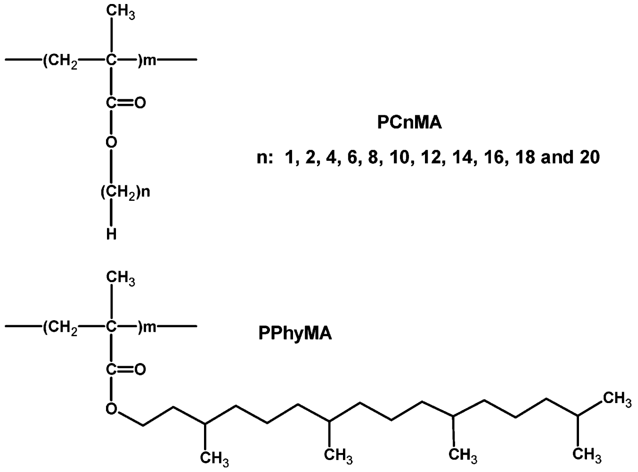

Figure 1. The polymers used in the contact angle study.

Experimental Section

Monomers. Commercially available n-alkyl methacrylates (C*n*MA, $n = 1$−8, 12, 18; Tokyo Kasei Co.) were purified by distillation or by silica gel column chromatography using a mixture of hexanes−ethyl acetate (20:1 v/v). The C*n*MA ($n = 10$, 14, 16, and 20) were prepared in a following typical procedure. To a cooled mixture of 1-eicosanol (9.0 g, 30 mmol), triethylamine (6.0 mL, 43 mmol),and benzene (about 100 mL) in an ice water bath was added methacryloyl chloride (4.5 mL, 46 mmol). The reaction mixture was stirred below 0 °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 aqueous hydrochloric acid, saturated sodium hydrogen carbonate, and water and then dried on anhydrous sodium sulfate. The solution was concentrated to afford a 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 to afford eicosyl methacrylate as an analytically pure substance (5.5 g, 50%): mp 34.5−35.0 °C; R_f (a mixture of hexane and ethyl acetate, 20:1 v/v) 0.5. The ^{1}H and ^{13}C NMR spectra as well as FABMS spectrum of the product were consistent with the assigned structure. Similarly, C*n*MA ($n = 10$, 14, and 16) were obtained as colorless oil in a yield of 51−82%. PhyMA was produced as a oil in a yield of 82% from a reaction of methacryloyl chloride and (3*RS*,7*RS*,11*RS*)-3,7,11,15-tetramethylhexadecyl alcohol or phytanyl alcohol (vide infra); the monomer was purified by means of column chromatography with the physical constants mentioned elsewhere.[4] The phytanyl alcohol was obtained in a following manner. A suspension of phytol (25.1 g, 84.8 mmol) in ethanol (100 mL) containing Raney-Ni (ready for use, Fluka A.G., 3.5 g) was stirred under atmospheric pressure of hydrogen at room temperature for 10 h. After removal of the catalyst by filtration

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10.1021/ma052168g CCC: $33.50

Table 1. Molecular Weight and Distribution of PC*n*MA and PPhyMA[a]

polymer	$M_n \times 10^{-5}$	$M_w \times 10^{-5}$	M_w/M_n
PPhyMA	2.7	5.2	1.9
PC1MA	2.6	5.3	2.2
PC2MA	1.8	5.3	2.8
PC4MA	2.6	4.8	1.9
PC6MA	2.7	5.4	2.0
PC8MA	3.1	5.5	1.8
PC10MA	1.4	3.9	2.8
PC12MA	2.9	5.6	1.9
PC14MA	1.7	5.0	2.9
PC16MA	1.6	4.8	2.9
PC18MA	3.2	5.6	1.7
PC20MA	1.9	4.7	2.4

[a] M_n and M_w were measured by means of a gel permeation chromatograph (Tosoh 8000 GPC system) using tetrahydrofuran as a solvent and polystyrene for calibration.

with Celite, the filtrate was concentrated to give a residue which as applied to a silica gel column. Elution with a mixture of hexane and ethyl acetate (5:1 v/v) gave phytanyl alcohol (22.0 g, 87%): IR (neat) ν 3342, 2952, 2924, 2866, 1462, 1378, 1367, 1057, 760 cm^{-1}; 90 MHz ^{1}H NMR (90 MHz, CDCl$_3$) δ 0.79−0.80 (m, 15H), 1.08−1.63 (m, 24H), 3.55 (t, J = 6.7 Hz, 2H); FABMS (negative ion detection mode, triethanolamine as a matrix) m/z 297 [M − H]$^-$, rel int 30.

Preparation of PC*n*MA and PPhyMA - General Procedure. A mixture of a monomer (9.5 mmol), benzene (9.5 mL), and AIBN (40 mg) was shaken at 50 °C for 20 h. The resulting solution was poured into methanol to precipitate the corresponding polymer, which was purified by a precipitation procedure (toluene and methanol for dissolution and precipitation, respectively) and kept under reduced pressure until use; the molecular weight was determined by means of a gel permeation chromatography (Table 1).

Coating of the Polymers on Glass. A toluene solution of the polymer (0.1 M, 100 μL) was spread and dried on a glass plate (2.2 cm × 2.2 cm) by means of a spin-coater (Mikasa, 1H-2) at ambient temperature. The resulting plate was stored in a desiccator under reduced pressure at ambient temperature. The polymer coatings were nominally smooth under observation using a scanning electron microscope (Shimadzu, EPM-810) and a color laser 3D profile microscope (Keyence, VK-8510); observation magnitude, 1 and 0.5 (×10^4), respectively (data are omitted).

Contact Angle Measurement. The contact-angle-meter (Kyowa Interface Science Ltd., model CA-A) consisted of an optical microscope and a box (width 5 cm, depth 2.5 cm, height 1.5 cm) with a hatch, where the two side walls facing each other were glass windows for observation and the other walls, including the bottom one, were made of stainless steel and thermocontrolled with circulating water (experimental error, ±0.5 °C). A few water droplets were placed inside the box to fill with water vapor. The polymer coating on glass was placed on the bottom of the box, and the box was closed with a lid. About 1 min after placing a water droplet of about 1.5 mm diameter, the contact angle was measured. The magnitude of the contact angle remained almost unchanged during the measurement, which took about 2 min. The contact angles of three to five different positions were measured and averaged. Experimental error was usually ±1°, which is small enough to be hidden by the symbol in the related figures shown below.

Polymer Characterization. *Electron Spectroscopy for Chemical Analysis (ESCA).* A 4 wt % toluene solution of the polymer was spread on an aluminum sheet (5 mm × 5 mm) using a spin-coater. The sheet was dried under reduced pressure and mounted to a Shimadzu ESCA 750 instrument to record the adsorption bands for the C1s and O1s at an analytical voltage of 8 kV, current of 30 mA, and about 25 °C.

Differential Scanning Calorimetry (DSC). The polymer (2−5 mg) was placed in an aluminum pan, and the endothermic phase transition temperature was recorded by means of a Rigaku DSC-8240 calorimeter. The temperature was scanned from −130 to 70 °C at a rate of 10 °C/min under a constant flow of N$_2$ gas.

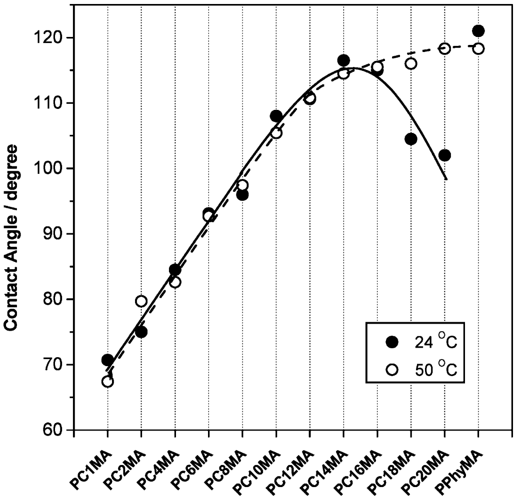

Figure 2. The contact angle of various poly(alkyl methacrylate)s at 24 and 50 °C.

X-ray Diffractometry (XRD). X-ray diffraction patterns of the polymers were recorded with a Shimazu XD-610 diffractometer, which was operated at 30 kV and 20 mA at a 2θ scanning rate of 4.00°/min at about 25 °C.

Reflection and RAS IR Spectroscopies. A 0.5 wt % toluene solution of the polymer was spin-coated on a glass plate that had been vapor-coated with Pt. After drying the specimen in a desiccator, the reflection and the RAS spectra were recorded by means of a Fourier transform IR spectrometer, JASCO Janssen Micro FTIR, under the conditions of 128 scans, a polarizer angle of 90°, apodization of CS, and 25 °C.

Results

Polymer Coatings on Glass. PC*n*MA (n = 1−14) and PPhyMA gave a transparent coating in the temperature range from 0 to 80 °C. By contrast, PC16MA (ca. 21 °C), PC18MA (36 °C), and PC20MA (50 °C) gave opaque and transparent coatings below and above the temperature in parentheses, respectively. The temperature approximately corresponded to the phase transition temperature (T_m) of these polymers (vide infra).

Effect of Alkyl Chain Length on Contact Angle (θ). Figure 2 (● line) displays the θ of water droplet on various PC*n*MA at 24 °C. The angle increased to about 115° as the alkyl chain increased its length from methyl to *n*-hexadecyl groups. However, θ leveled off gradually and even decreased in the polymers bearing long *n*-hexadecy, *n*-octadecyl, and *n*-eicosyl chains. By contrast, the θ at 50 °C increased with the increasing alkyl chain without showing a bell-shaped line (see ○ line). PPhyMA was the most hydrophobic polymer of all, giving about 120°, and its θ was insensitive to temperature.

Effect of Temperature on θ. PPhyMA gave a very large θ over a wide range of temperatures (Figure 3, ▲ line). By contrast, the θ value of C*n*MA was affected strongly by temperature. For instance, the θ value of PC18MA jumped from 100° to 118° at around 37 °C, as shown (● line). The θ value of PC20MA was abruptly changed at about 48 °C (■ line).

Phase Transition Temperature of Polymers. Table 2 lists the phase transition temperature and the endothermic phase transition energy of various PC*n*MAs and PPhyMA that were obtained from the DSC thermographs (Figure 4). These indicate that the endothermic adsorption energy of the polymer (n = 12−20) increased steadily as its alkyl chain length became

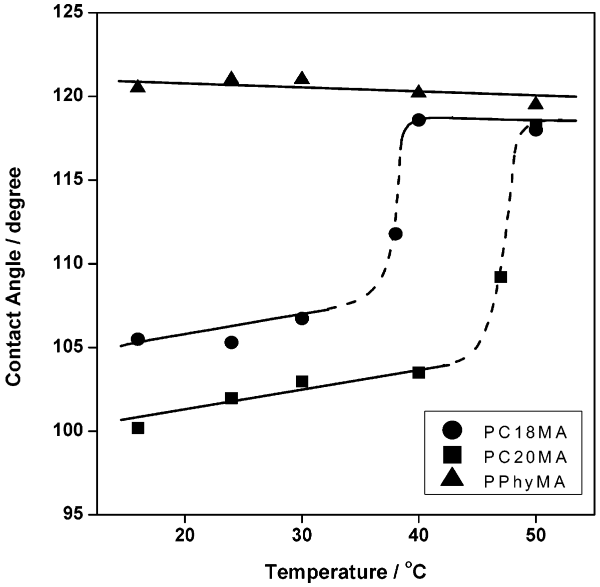

Figure 3. The effect of temperature on the contact angle of PC18MA, PC20MA, and PPhyMA.

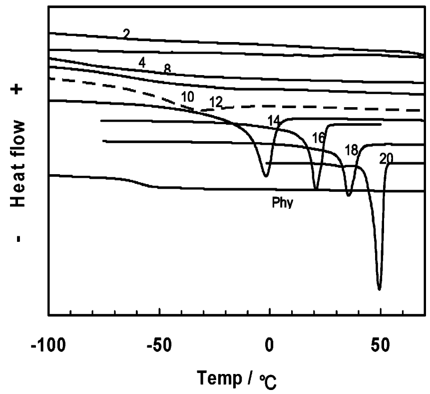

Figure 4. DSC of various poly(*n*-alkyl methacrylate)s; the letters along the lines mean a kind of the alkyl groups, for example, 10 for PC10MA.

Table 2. Differential Scanning Calorimetric Data of Various Polymers

polymer	T_m (°C)	transition energy overall (kJ/mol)	transition energy per CH_2 group (J/mol)
PC*n*MA ($n = 1, 2, 4, 6, 8, 10$)	not detected	–	–
PC12MA	−33.4	3.6	300
PC14MA	−1.8	8.2	586
PC16MA	20.8	15.4	963
PC18MA	35.7	23.7	1320
PC20MA	49.4	40.2	2010
PPhyMA	not observed	–	–

longer, although the polymers ($n = 1-10$) did not show a clearly definable transition peak. PPhyPC displayed a baseline shift at around −65 °C, perhaps due to a glass phase transition.

Packing State of Alkyl Groups of Polymers. The wide-angle X-ray diffraction spectra (XRD) of the polymers at about 25 °C is shown in Figure 5. Table 3 lists a *d* spacing that was calculated from the diffraction degree (2θ). PC*n*MA ($n = 2-16$) gave a diffraction peak at 18°−19° that became increasingly sharp with increasing the alkyl chain length. On the other hand, PC18MA and PC20MA exhibited an intense peak at 22° in the fashion very similar to the octadecyl alcohol crystals (a sharp adsorption at 22°). From the 2θ values, a distance between the neighboring alkyl chain was calculated as 4.2 Å for PC18MA and C20MA and 4.6−5.0 Å for PC*n*MA ($n = 2-16$). PC*n*MA ($n = 1-4$) showed the additional 2θ value (or 6.6−7.1 Å), which was presumably attributed to a packing distance between the polymer backbones.

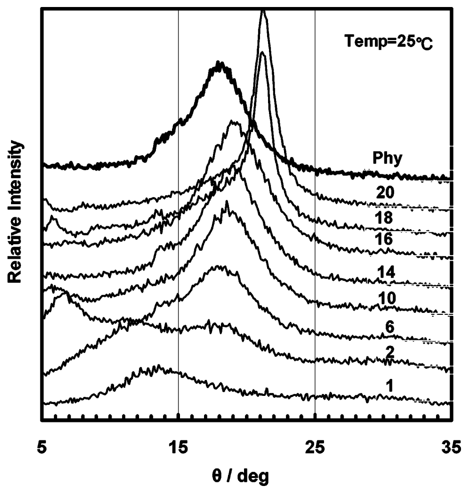

Figure 5. XRD of various poly(*n*-alkyl methacrylate)s at 25 °C; the letters along the lines mean a kind of the alkyl groups, for example, 20 for PC20MA.

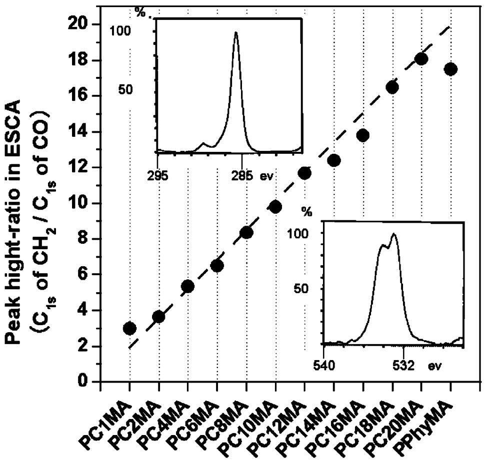

Figure 6. The peak-height ratio of the C1s of the $(CH_2)_nCH_3$ group to the C1s of the −COO− moiety of PC*n*MAs and PPhyMA in ESCA. As examples, the C1s and O1s peaks of PC16MA are displayed in the upper and lower insets, respectively.

Table 3. Diffraction Angle and *d* Spacing of Various Polymers from Estimated from XRD Spectra

polymer	2θ/deg	*d* spacing	polymer	2θ/deg	*d* spacing
PC1MA	13.5	6.6	PC12MA	19.2	4.6
PC2MA	12.4/17.7	7.1/5.0	PC14MA	19.1	4.6
PC4MA	13.5/18.1	6.6/4.9	PC16MA	19.3	4.6
PC6MA	17.9	5.0	PC18MA	21.1	4.2
PC8MA	17.7	5.0	PC20MA	21.3	4.2
PC10MA	18.5	4.8	PPhyMA	18.2	4.9

Atomic Elements on the Polymer Surface. Figure 6 (inset) shows the ESCA of a PC16MA coating as an example, where the C1s of the $(CH_2)_nCH_3$ carbon moiety and the C1s of the CO carbon moiety appeared at 285.4 and 289.4 eV, respectively. The O1s of the C(O)O moiety appeared at 533.0 and 534.1 eV in a similar magnitude. The intensity ratio [C1s of the $(CH_2)_n$-CH_3 moiety/the C1s of the CO carbon moiety] of various PC*n*MAs and PPhyMA is shown in the main panel of Figure 6. It was seen clearly that the surface of the polymer coatings

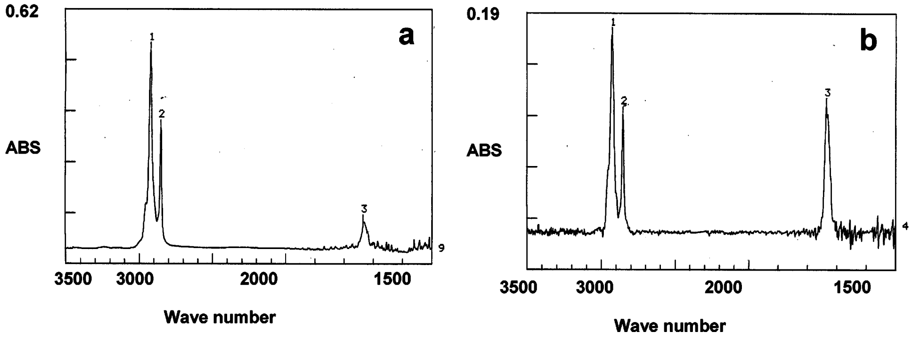

Figure 7. FTIR spectra of PC16MA at 25 °C: (a) reflection mode and (b) RAS mode.

was progressively occupied by the $CH_3(CH_2)_n$ moiety upon increasing the *n* number of the alkyl chain, or the hydrophilic ester oxygen atom was not likely present in the surface region.

Orientation of Alkyl Group in Polymer Coatings. The transmission FTIR spectra of the polymers having an alkyl groups longer than a decyl group showed a strong adsorption at 2900 cm^{-1} and weak adsorption at 1730 cm^{-1}, which are assignable to the CH_2 stretching of the alkyl group and the C═O stretching of the polymers, respectively. By contrast, the magnitude of these band intensities was reversed in the RAS−FTIR spectra; viz., the 2900 cm^{-1} peak was weakened while the1730 cm^{-1} peak was enhanced. A typical example is shown in Figure 7a,b for PC16MA. The polymers that had the short alkyl chain ($n < 10$) did not show such an intensity enhancement in RAS IR spectra (data are omitted).

Discussion

Since all of the polymers (PC*n*MA, $n = 1{-}20$) and PPhyMA were similar in M_n, M_w, and M_w/M_n, their surface properties may be discussed without considering an effect of molecular weight, if any (Table 1). Viewing overall, the surface tension of poly(alkyl methacrylate)s was dependent on the alkyl chains and affected significantly by temperature (see Figures 2 and 3). In detail, (i) PPhyMA gave always a very large contact angle (θ) over a wide temperature range and (ii) the θ value of the PC*n*MA was dependent on temperature and jumped to a higher level at a certain temperature, as seen typically in PC18MA and PC20MA (Figures 2 and 3). The θ values of PC*n*MA ($n = 1{-}14$) at 24 °C were similar to those at 50 °C (the ● and ○ lines of Figure 2); the result may be taken to suggest that the decrease of the surface tension of water with increasing temperature (about −0.5%/°C) did not affect significantly the θ of the polymers, perhaps also of PC*n*MA ($n = 16{-}20$ and Phy). The appearance of the bell-shaped curve (Figure 2, ● line) is thus explained by the dependence of the contact angle on temperature. As seen in the DSC thermogram (Table 2 and Figure 4), the jumping of θ seemed to occur around the T_m; in other words, the hydrophobicity of the polymers was abruptly increased when temperature became higher than the T_m. The transition entropy per a CH_2 group ($\Delta S = \Delta H/T_m$ per methylene group) was increased with increasing alkyl chain length (Table 2), suggesting that the longer chain was packed with a higher order (at the temperature $< T_m$). Indeed, the X-ray refraction spectrum was sharpened and *d* spacing (between the neighboring chains) was shortened with increasing alkyl chain length (Figure 5, Table 3), suggesting strongly that the long alkyl chains assumed a highly ordered crystalline state. It would be worth noting that PPhyMA gave a diffraction scattering at $2\theta = 18.2°$, although the polymer did not display a well-defined T_m except a baseline shift at around −65 °C. There was no NMR evidence for the regular structure of the phytanyl chain. PPhyMA may thus be ascribed to take a fluid liquid crystalline state in the wide temperature range examined. A similar DSC thermogram was observed in the liposomal membranes made of the phytanyl-group-containing archaeal phospholipids.[6−9] In other words, the θ is considered to jump to a high level when the crystalline packing was melted at T_m. The ESCA (Figure 6) and the RAS−IR (Figure 7) indicated the unique packing mode of the alkyl chains; viz., the hydrocarbon moiety of the polymers are located on the surface region of the coating and the ester moieties was embedded away from the surface, presumably orienting the long axis of the alkyl chains toward the surface (*z*-direction). Similar orientation has been suggested in the X-ray study of lipid membranes.[10]

It is anticipated on the basis of this study that a highly hydrophobic hydrocarbon material may be designed by choosing the hydrocarbon chain that is long and has a low T_m. The T_m may be decreased by branching the chain by a short alkyl group(s), as typified by the phytanyl group.

Acknowledgment. The authors thank to Ms. Yuki Fukunaga of the Analytical Laboratory of OCU for the RAS-IR measurement.

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MA052168G