METHYLATION OF SEPIOLITE AND PALYGORSKITE WITH DIAZOMETHANE

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Abstract—The methylation of the fibrous clays, sepiolite and palygorskite, should be facilitated by their large content of surface silanol groups and the low acidity and inaccessibility of coordinated water molecules. Infrared spectroscopy showed that the reaction of diazomethane with these clays resulted in the methylation of their silanol surface groups. The grafting of CH_3 groups on the surfaces of these clays produced a decrease in the surface area due primarily to the lowering of the microporosity.

Key Words—Diazomethane, Methylation, Palygorskite, Porosity, Sepiolite, Silanol.

INTRODUCTION

The formation of organo-mineral derivatives by the reactions of clays with organic reagents was originally used to elucidate details of clay mineral structure. The first work of this type was carried out by Berger (1941) who attempted to methylate H-montmorillonite with diazomethane. On the basis of the hydrophobic properties shown by the clay after reaction with diazomethane, Berger (1941) interpreted the reaction as a methylation of hydroxyl groups of the clay. Edelman (1947) and Deuel (1952) suggested that Berger's results supported the existence of the Edelman-Favejee structure; however, surface hydroxyls as well as the Edelman-Favejee model appeared to be excluded by X-ray powder diffraction data for smectites and vermiculites. The methylation claimed by Berger was later disputed by Brown *et al.* (1952) and by Greenland and Russell (1955), but it was supported by Aragón de la Cruz (1965).

The reaction of diazomethane with clays has been the subject of much controversy. Greenland and Russell (1955), like Martín-Vivaldi and Hendricks (1952), suggested that the reaction of diazomethane with clay resulted in the polymerization of the diazomethane in the interlayer space of the clay. This reaction was more recently confirmed by Bart *et al.* (1979) who showed by infrared (IR) spectroscopy that polymethylene chains were formed in the interlayer space of montmorillonite treated with diazomethane. These authors attributed the polymerization reaction to the acidity of the residual water in the interlayer of montmorillonite (Mortland, 1968).

The unsuccessful attempts to verify methylation of clay minerals with diazomethane might be due to the low content of surface silanol groups ($\equiv Si-OH$) of the minerals used (smectites, vermiculites, and kaolinites). Silanol surface groups are susceptible to methylation, as was found by Fripiat *et al.* (1960) for silica. Based on the above considerations, the reaction of diazo-

methane with sepiolite and palygorskite was examined. These minerals are fibrous clays that have a high density of surface silanol groups (Ahlrichs *et al.*, 1975; Serna *et al.*, 1977) and that contain adsorbed water that is less acidic and less accessible than that of montmorillonite. Ruiz-Hitzky and Fripiat (1976) and Fernandez-Hernandez and Ruiz-Hitzky (1979) showed that silanol groups of sepiolite react with organic reagents, such as organo-chlorosilanes, epoxides, and isocyanates, to give true organo-mineral derivatives.

MATERIALS AND METHODS

The clays used were sepiolite from Vallecas, Spain, and palygorskite from Torrejón, Spain, supplied by Tolsa, S.A., Spain. Solutions of diazomethane in ether (~6 M) were freshly prepared from Diazald (Aldrich Co., Inc., Milwaukee, Wisconsin) and stored at −5°C. The reaction of diazomethane with the clays was carried out as follows: a 1-g sample of clay predried at 110°C for 24 hr was suspended in 10 ml of ether cooled to −5°C. Ten milliliters of the diazomethane-ether solution was added, and the mixture was stored in a refrigerator for 12–24 hr and shaken regularly. Successive treatments were carried out until the yellow color of diazomethane remained for 24 hr. The samples were washed with ether and dried at 60°C after each treatment. The IR spectra of the original and treated clays were recorded using a Perkin-Elmer 377 spectrometer from 4000 to 400 cm^{-1} on self-supporting films prepared by drying an aqueous suspension of the clays (1% w/v) on a flat Mylar sheet.

The carbon contents of the original and treated clays were determined in a Hewlett-Packard 185 microanalyzer using 0.6 mg of sample weighed in a Cahn G-model electrobalance. Surface areas of the original and treated samples were obtained from the analysis of the N_2 adsorption-desorption isotherms. The samples were outgassed at room temperature and equilibrated under a vacuum ($<10^{-4}$ torr) for at least 2 hr before the
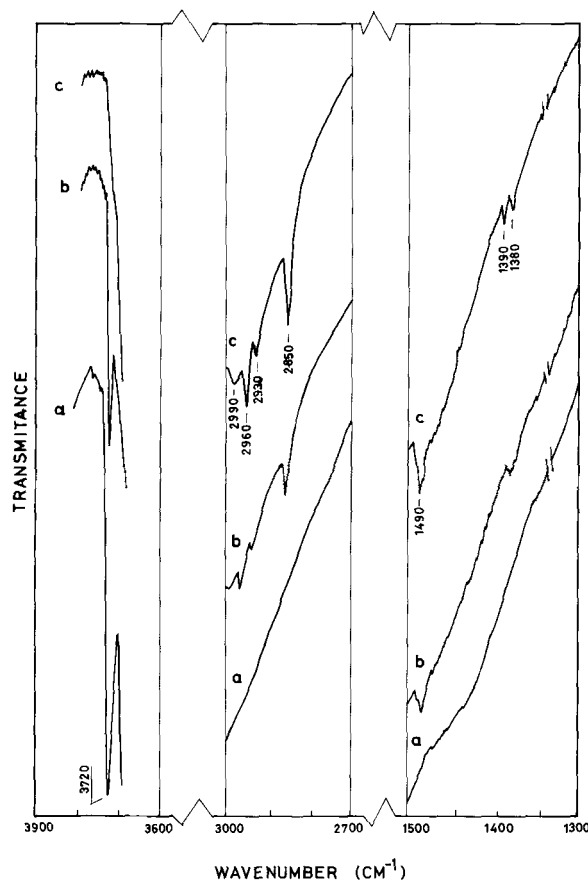
591

Figure 1. Infrared spectra of Vallecas sepiolite (self-supporting films). (a) untreated; (b) after 3 diazomethane treatments; (c) after 5 diazomethane treatments.

Figure 2. Infrared spectra of Torrejón palygorskite (self-supporting films). (a) untreated; (b) after 5 diazomethane treatments.

adsorption-desorption isotherms were measured. The isotherms were obtained at 77 K using a conventional volumetric apparatus. Surface areas were calculated using BET (Brunauer *et al.*, 1938) and t-plot (Lippens and de Boer, 1965) procedures. A cross-sectional area of 16.2 Å² for the N_2 molecule was assumed. The t-plot was also used for qualitative assessment of microporosity of the samples. Mesopore analysis was carried out using the methods of Dollimore and Heal (1970) and Lippens *et al.* (1964), assuming cylindrical and slit-shape geometry for the pores, respectively.

RESULTS AND DISCUSSION

The course of the reactions of sepiolite and palygorskite with diazomethane was followed by IR spectroscopy and by the change in surface area.

Infrared spectroscopy

The spectra of the two clays before and after several treatments with diazomethane are shown in Figures 1 and 2. The spectra show two significant feat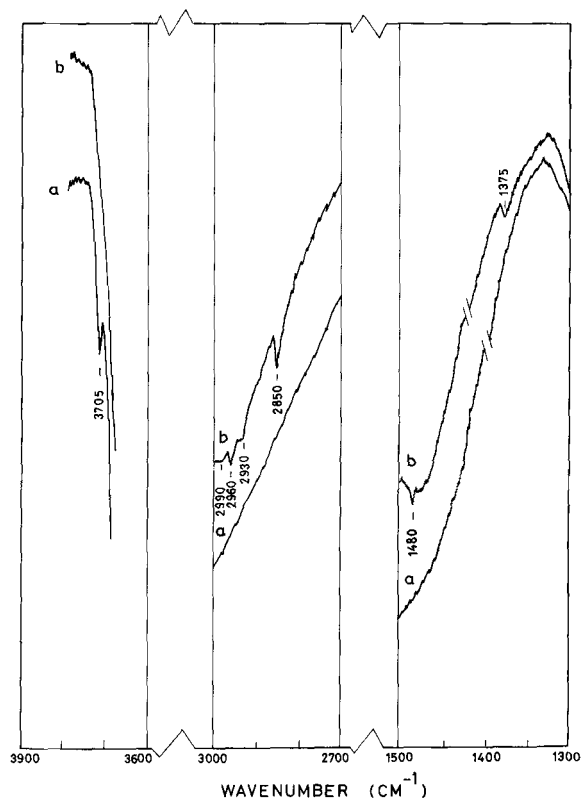ures: (1) the development and increase with successive treatments of new IR bands at 2960, 2930, 2850, 1490, and 1380 cm⁻¹, and (2) the decrease and disappearance of the 3720-cm⁻¹ sepiolite and 3705-cm⁻¹ palygorskite bands corresponding to the OH-stretching vibrations of surface silanol groups. The number of successive treatments needed for the total disappearance of the silanol groups (as observed by IR spectroscopy) was not exactly determined due to the variability of the diazomethane solution concentration (this reagent is highly unstable even at −5°C; Gaynor and MacTavish, 1981). The IR features of the silanol groups, however, always disappeared after 5–7 treatments for sepiolite and 3–5 treatments for palygorskite.

The absorption bands at 2960 and 2850 cm⁻¹, which appeared in the clays after reacting with diazomethane, correspond to the asymmetric and symmetric C–H stretching vibration of CH_3 groups. The more intense 2850-cm⁻¹ band is a highly characteristic feature of the methoxyl O–CH_3 group. The weak bands at 2990 and 2930 cm⁻¹ (Figures 1 and 2) are possibly due to the lone pair effect (Bellamy, 1980) of the oxygen surface atoms of the clay framework. This observation indicates considerable variation of orientation of the C–H bonds of the surface methoxyl groups. Furthermore, none of the C–H stretching bands observed (2990, 2960,
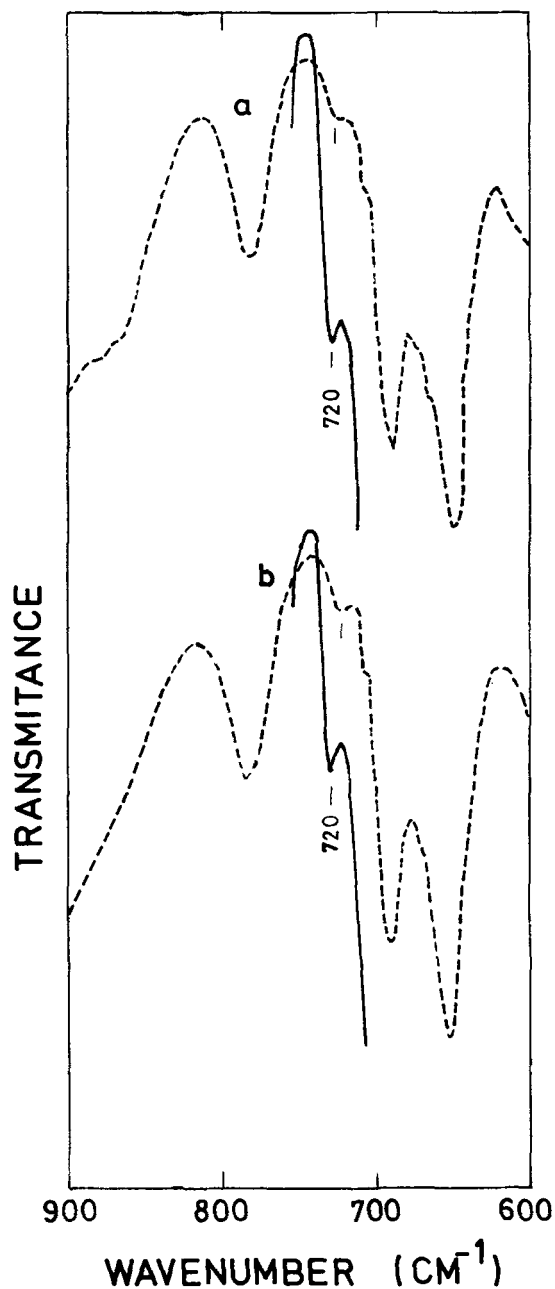
Figure 3. Infrared spectra of Vallecas sepiolite (self-supporting films). Dotted lines = (a) untreated, (b) after 5 diazomethane treatments; full lines = with ordinate expansion ×5.
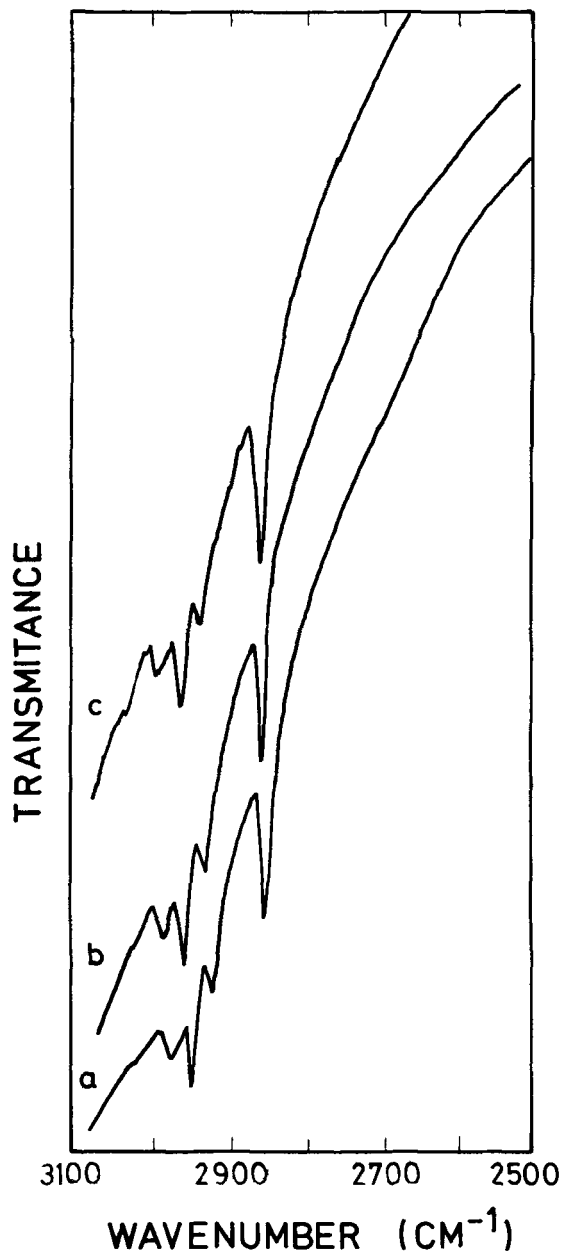

Figure 4. Infrared spectra of Vallecas sepiolite. (a) methylated sepiolite; (b) sample (a) after 48-hr extraction with xylene; (c) sample (a) after 48-hr extraction with hexane.

2930, and 2850 cm^{-1}) for the methylated clays exhibited dichroism, indicating that the axes of the C–H bonds were at angles significantly less than 90° to the (100) plane of the crystals. The bands at 1490 and 1380 cm^{-1} are due to the asymmetrical and symmetrical deformation modes of the C–H bond in the CH$_3$ groups.

Although the 2930-cm^{-1} band is somewhat indicative of the CH$_2$-groups of polymethylene chains, the formation of such chains should have produced a band at 720 cm^{-1} (rocking mode). The spectral features of the sepiolite and palygorskite in the region of 720 cm^{-1}, however, were practically unchanged after methylation, as shown in Figure 3 for sepiolite. To clarify whether some polymethylene chains were formed by the polymerization of diazomethane on the surface of the methylated clays, a sample of methylated sepiolite was extracted with xylene and hexane for 48 hr. This
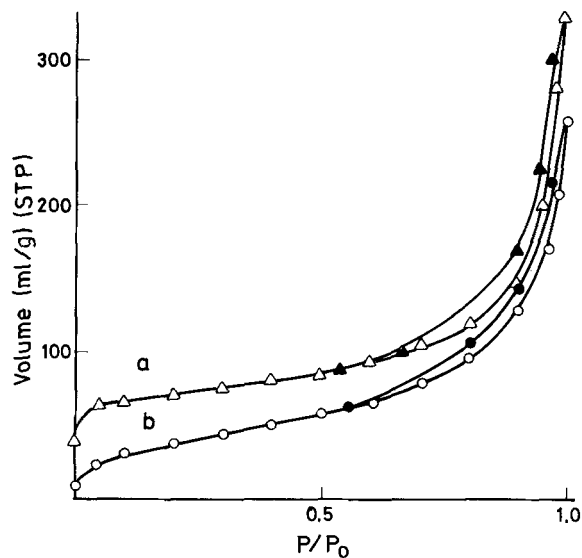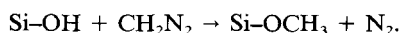
Figure 5. Nitrogen adsorption-desorption isotherms at 77 K. (a) original sepiolite; (b) after 5 diazomethane treatments. Open symbols = adsorption; closed symbols = desorption.

Figure 6. t-plots corresponding to the nitrogen adsorption isotherms at 77 K of Figure 5.

extraction procedure, which was used previously for extracting polymethylene chains from the interlayer space of montmorillonite (Bart *et al.,* 1979), did not change the IR spectrum of the methylated sepiolite (Figure 4). Similar results were obtained for a sample of methylated palygorskite, apparently confirms that the C–H bands of the methylated sepiolite and palygorskite correspond to CH_3 groups grafted onto the surface.

Based on the IR data, the reaction of diazomethane with sepiolite and palygorskite appears to be a true methylation reaction of the surface silanol groups by the following reaction:

$$Si–OH + CH_2N_2 \rightarrow Si–OCH_3 + N_2.$$

Nitrogen adsorption-desorption isotherms

The substitution of the OH groups on the surface by the larger OCH_3 groups should have produced changes in the texture of these fibrous clays. This effect was indicated by the results of the N_2 adsorption-desorption isotherms of the untreated and treated clays. Typical N_2 adsorption-desorption isotherms of sepiolite are shown in Figure 5. Similar curves were obtained for palygorskite. All isotherms show hysteresis loops and have characteristic shapes of the Type IV isotherm, according to the BDDT classification (Brunauer *et al.,* 1940). The corresponding t-plots are shown in Figure 6. Values of t (statistical thickness of the adsorbed N_2 layer on the nonporous reference sample) were obtained from the standard isotherms reported by Lecloux and Pirard (1979) for different C_{BET} values (C_{BET} is a parameter of the BET equation related to the adsorbent-adsorbate) interaction. For all samples, a
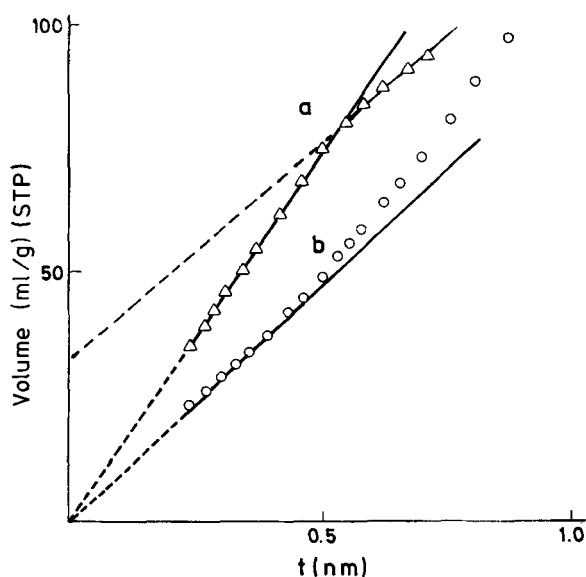
straight line passing through the origin was obtained at low relative pressure. For the original sample, the corresponding t-plot (Figure 6a) shows a downward deviation indicating its microporous character. On the other hand, the t-plots corresponding to methylated samples show an upward trend indicating the absence of microporosity (Figure 6b).

The total surface area, S_t, calculated by the t-method, for all samples, was found to be in good agreement with that obtained by the BET equation, S_{BET}. The total surface area, S_t, and external surface, S_{ex}, were calculated from the slopes of the initial steep line and the less steep line after intersection in the t-plot, respectively (Figure 6a). The surface area due to micropores, S_{mp}, was obtained from the difference ($S_t - S_{ex}$). Cumulative surface area (mesoporous contribution), S_{cum}, in the mesopore range were calculated by the method of Lippens *et al.* (1964) which gave more consistent data for the samples examined than the Dollimore and Heal (1970) method. All these parameters and the carbon content are summarized in Tables 1 and 2 for untreated and treated clays.

With an increasing number of treatments, the total surface area (S_{BET} or S_t) first decreased indicating a blocking of the surface area available to N_2 molecules (Tables 1 and 2). The major portion of this decrease was apparently due to the disappearance of the micropores, which occurred in both clays during the first treatment with diazomethane (Hermosín and Cornejo, 1984). The large decrease of the C_{BET}-constant values after the first treatment indicates that the surface of the clay became much more inert as the methylation proceeded, thereby indicating that the OH surface groups were being substituted by OCH_3 groups.

Table 1. Textural parameters and carbon content of sepiolite before and after diazomethane treatment.

Treat-ment	C (%)	S_{BET} (m²/g)	C_{BET}[1]	S_t (m²/g)	S_{mp} (m²/g)	S_{cum} (m²/g)
0	1.05	229.3	531	232.7	99.9	142.0
1	1.63	169.5	214	176.6	—	142.1
3	1.93	126.0	54	125.3	—	131.8
4	2.03	139.5	43	140.7	—	129.7
5	2.05	147.8	46	146.9	—	151.8
7	2.05	147.5	45	147.1	—	151.2

[1] C_{BET} is a parameter of the BET equation; see text.

Table 2. Textural parameters and carbon content of palygorskite before and after diazomethane treatment.

Treat-ment	C (%)	S_{BET} (m²/g)	C_{BET}[1]	S_t (m²/g)	S_{mp} (m²/g)	S_{cum} (m²/g)
0	1.02	111.0	976	124.8	93.9	70.0
1	1.44	64.3	160	66.3	—	60.3
3	2.01	44.4	35	45.9	—	47.0
4	2.04	52.1	45	50.7	—	51.2
5	2.04	51.8	43	50.3	—	50.0

[1] C_{BET} as in Table 1.

The methylation reaction also affected the S_{cum} values (Tables 1 and 2), which showed a minimum after 3 treatments, increasing slightly thereafter. The S_{BET} values had a similar trend. This surface area change can be explained by considering that in the first treatment the methylation occurred in the most accessible positions such as edges or open channels, thereby preventing the N_2 from entering the micropores and smaller mesopores. As the methylation proceeded in subsequent treatments, the substitution of OCH_3 for OH groups on the surface became more complete. Taking into account the hydrophobic character of methoxylated surface of clays examined, a diminishing of particles aggregation could be expected, and, thus, the total or mesoporous surface area should have increased slightly, which was observed for both clays.

Density of Si–OH groups

On the basis of the increase of C content of the methylated samples, the number of surface silanol groups that had been methylated could be calculated. Complete methylation was assumed for the samples which showed no Si–OH IR bands. These samples were the sepiolite after 5 treatments and the palygorskite after 4 treatments. In this way, a value of 2.2 Si–OH/ 100 Å² for sepiolite and 4.5 Si–OH/100 Å² for palygorskite were obtained. These data support the models suggested by Serna and VanScoyoc (1979) which predicted more surface Si–OH in palygorskite than in sepiolite, in contrast to the previous estimate of Ahlrichs *et al.* (1975) and Serna *et al.* (1977) and as is suggested by IR evidence. The reason for this disagreement, as suggested by Serna and VanScoyoc (1979), is that more crystal imperfections exist in sepiolite than in palygorskite. Thus, as shown in Tables 1 and 2, whereas the total surface area (S_{BET} or S_t) of sepiolite is almost twice that of palygorskite, the surface due to micropores is practically the same for both minerals. The difference lies in the contribution from the mesoporous surface. The conclusions drawn here, however, about the surface changes observed in these particular minerals could be different if sepiolite and palygorskite from other sources are studied.

On the other hand, some surface silanol groups were probably not methylated because of steric hindrance. It is not possible to methoxylate every silanol group because of the larger volume of OCH_3 groups. Nonsubstituted silanols, however, were perturbed by the methoxyl groups and were not observed by IR spectroscopy. On the basis of the above considerations, the reaction of diazomethane with sepiolite and palygorskite appears to produce a true methylation of their surface silanol groups, leaving the surface of these fibrous clays covered with OCH_3 groups grafted on to the surface OH sites. The organo-mineral derivatives obtained from this reaction are true methylated clays. In addition, methylation of sepiolite and palygorskite with diazomethane causes a decrease in their porosity and hence a large decrease in their surface area. Results obtained here suggested that in the reaction of smectites with diazomethane previously reported by Berger (1941), some surface silanol groups could have been methylated; however, the degree of methylation of those smectites should have been very small compared with the amount of polymethylene chains formed. Hence, the methoxyl groups were not detected by IR spectroscopy.

ACKNOWLEDGMENTS

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