Short communication

# Phenyl tris-2-methoxydiethoxy silane as an additive to PC-based electrolytes for lithium-ion batteries

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## Abstract

Phenyl tris-2-methoxydiethoxy silane (PTMS) has been studied as an additive to the PC-based electrolyte of lithium ion batteries with graphite anode. An electrolyte of 1.0 M $LiPF_6$ in propylene carbonate (PC):dimethyl carbonate (DMC) (1:1 v/v) containing phenyl tris-2-methoxydiethoxy silane can suppress the co-intercalation of PC. The main reason for this suppression is that silane can form a cross-polymerized network of Si−O−Si bonds on the graphite surface, thus restraining PC molecules from co-intercalating with lithium ions into graphite electrodes. The electrochemical properties of the modified electrolyte were characterized by cyclic voltammetry, charge/discharge tests, SEM, XPS and FT-IR.
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*Keywords:* Silane; Lithium-ion batteries; Electrolyte additive; Propylene carbonate

## 1. Introduction

With the rapid growth of the portable electronics market in recent years, lithium-ion batteries have become the most attractive rechargeable battery system with the ability to provide high voltage, high energy density and low self-discharge [1]. The electrolyte used in lithium-ion batteries is a key factor influencing the performance of the cell. In spite of possessing many favorable characteristics such as superior ionic conductivity at low temperature, low price and high boiling point, propylene carbonate (PC) is not a suitable electrolyte component for lithium-ion batteries with a graphite anode. This is due to the fact that upon first charging of the lithium-ion batteries PC tends to co-intercalate into graphite, accompanied by severe exfoliation of graphite layers and then leading to the destruction of the graphite structure [2–4]. Several ways have been explored to overcome the inherent incompatibility of PC with graphite in the lithium ion battery system. One way is to modify the surface

of the graphite by means such as coating to prevent the direct contact of PC with the graphitic structure [5,6]. Another way to suppress PC decomposition is to add some additives to the electrolytes. The main action of these additives is to form an effective solid electrolyte interphase (SEI) film during the first cycling process prior to the decomposition of PC. These additives include halogenated alkene compounds [7], ethylene sulfite (ES) [8], propylene sulfite (PS) [9], vinylene compounds (VCs) [10–12], chloroethylene carbonate [13,14], tetrachloroethylene (TCE) [15], acrylonitrile [16] and fluoroethylene carbonate [17].

Recently, research on film forming electrolyte additives for lithium ion batteries has focused on silane compounds [18,19]. They are known to have similar properties to crown ethers and cryptands as far as formation of complexes with metal cations is concerned [20–22]. It was claimed that a unique mechanism of this beneficial effect, aside from electropolymerization, was condensation (polymerization) of podand molecules *via* silicon atoms, leading to the formation of a network on the graphite surface. In addition, they can act as fire-retardant to improve the safety performance of lithium-ion batteries.

In this paper, a new film-forming additive, phenyl tris-methoxydiethoxy silane (PTMS), is examined for non-aqueous electrolytes-based lithium-ion batteries with graphite anodes.

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The performance of graphitic anodes was markedly improved in PC-based electrolytes after adding an amount of PTMS.

## 2. Experimental

Phenyl tris-methoxydiethoxy silane was obtained by reaction of phenyltrichlorosilane with anhydrous diethylene glycol monomethyl ether, according to the following chemical equation:

$$PhSiCl_3 + 3H(OCH_2CH_2)_2OCH_3$$

$$\rightarrow PhSi(OCH_2CH_2OCH_2CH_2OCH_3)_3 + 3HCl \qquad (1)$$
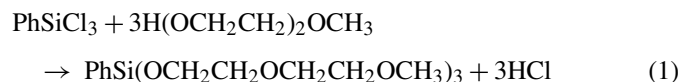
To anhydrous diethylene glycol monomethyl ether cooled to $0\,°C$, phenyltrichlorosilane (0.33 equivalent) was added dropwise over 4 h with continuous stirring. Afterwards, the mixture was heated to boiling for about 6 h to remove gaseous HCl. The obtained product was purified by vacuum distillation and the purity of the obtained compound was verified by elemental analysis and FTIR methods (not discussed here) [23–26].

Electrolyte was prepared by dissolving $LiPF_6$ in a mixture of PC–DMC (1:1 v/v) with the PTMS (10% v/v). The concentration of $LiPF_6$ was 1.0 M. The electrolyte preparation was carried out in a glove box filled with dry argon (water content less than 10 ppm).

The electrodes were prepared by coating a slurry consisting of original CMS (an artificial graphite from heat-treatment at $2800\,°C$, Shanshan Co. Ltd., Shanghai, China), acetylene black (5 wt.%) and PVDF binder (5 wt.%) in a solvent of N-methyl-2-pyrrolidone onto a copper foil current collector. After drying under ambient conditions, round discs of 1 cm diameter and 170 μm thickness were cut off and further dried under vacuum at $120\,°C$ for 12 h.

Electrochemical performance evaluation was carried out with coin-type half-cells, which were assembled in an argon-filled glove box, using the round discs as working electrodes. Lithium foil (450 μm thickness) was used as the counter and reference electrode, and Celgard 2400 as the separator. The discharge and charge was galvanostatically measured in the electrolyte by a Land CT2001A tester at about $0.1\,mA\,cm^{-2}$ at the voltage range of 0.001–2.0 V *vs.* $Li/Li^+$. Cyclic voltammograms were measured with the same cells with CHI400 electrochemical analyzer between 1.5 and 0 V at a scan rate of $0.03\,mV\,s^{-1}$.

A scanning electron microscope (SEM) (Philips XL 300) was used to inspect the surface morphology of the electrodes. In addition, XPS (PHI-5000C ESCA system) was used to analyze the components of the SEI formed at the surface of the graphitic anode during cycling. FTIR was performed on a Nicolet Nexus 470FTIR spectrometer with powder pressed KBr pellets. Before experiments, cells were disassembled in a glove box, washed with dimethyl carbonate, and dried in vacuum at $40\,°C$ for 8 h.

## 3. Results and discussion

Fig. 1 displays the first discharge–charge curves of the graphite electrode in the 1.0 M $LiPF_6$/PC:DMC (1:1 v/v) without electrolyte (a) and (b) with 10% (v/v) PTMS. In the first case



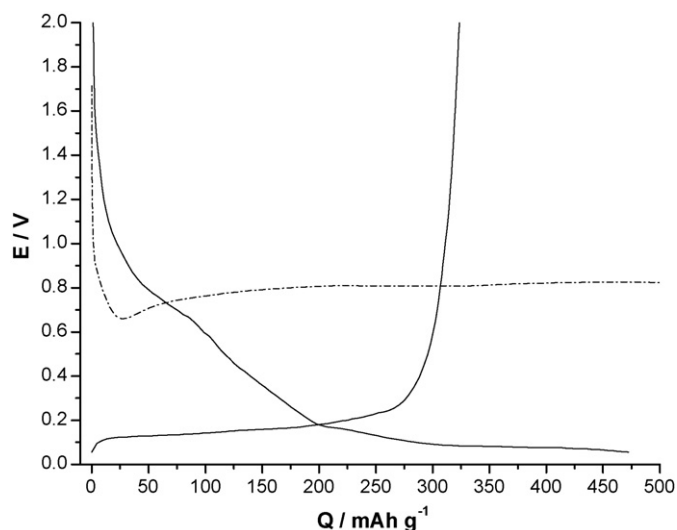Fig. 1. Charge–discharge curves of the graphite electrode in 1.0 M $LiPF_6$/PC:DMC (1:1 v/v) electrolyte without additive (dash dot line) and with 10% (v/v) of PTMS (solid line) in the first cycle at $0.1\,mA\,cm^{-2}$ (0.25 C) in 1.0 M $LiPF_6$ solution of PC–DMC (1:1 v/v).

there is a long plateau at about 0.80 V. It is well known that this long plateau is due to the co-intercalation of the $Li^+$ ions solvated by PC and PC decomposition, then leading to exfoliation of the graphite electrode [2]. There is no intercalation of lithium in the graphitic carbon. As a result, no charge capacity can be obtained. However, a dramatic change is observed when 10% by volume of PTMS is added to the electrolyte. The plateau at about 0.80 V corresponding to PC decomposition disappears almost completely. A large capacity below 0.20 V, corresponding to the intercalation of lithium ion into graphite, is obtained, with a reversible capacity of $323\,mAh\,g^{-1}$, and Coulombic efficiency of 68%. In the following six cycles, the Coulombic efficiencies are 85, 82, 83, 89, 85 and 81%, respectively. This is much different from the cycling behavior of the graphite electrode in EC-based electrolyte. The main reason seems to be that the SEI film was not well formed in the first cycle, since in Fig. 1 there is a slope between 0.8 and 0.2 V, which is the main reason of the irreversible capacity.

The cycle performance of graphite electrode in 1.0 M $LiPF_6$/PC:DMC (1:1 v/v) electrolyte is shown in Fig. 2. It is clear that the reversible capacity does not present clear evidence of declining at $0.1\,mA\,cm^{-2}$ (about 0.25 C) between 0.001 and 2.0 V. As mentioned above, the Coulombic efficiency in each cycle is not close to 100%. The main reason may be that the content of PTMS (10%) is much larger than that of normal additive such as VC, usually 1 or 2%, which is consistent with the above results of Coulombic efficiencies during cycling. If PC still decomposes or co-intercalates, the reversible capacity fades evidently.

Fig. 3 shows the cyclic voltammogram for the graphite anode in 1.0 M $LiPF_6$/PC:DMC (1:1 v/v) electrolyte added with 10% (v/v) of PTMS in the first cycle. For comparison, the cyclic voltammogram of the graphite anode in the above electrolyte without the additive in the first cycle, is also given. In the case of the electrolyte without the additive, there is a large irre-
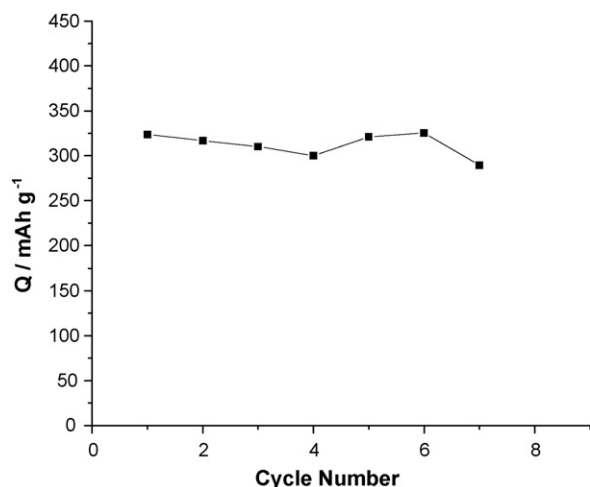
Fig. 2. Cycling performance of Li/graphite cells using 1.0 M LiPF$_6$/PC:DMC(1:1 v/v) with 10% (v/v) of PTMS as electrolytes *vs.* cycle number, which was recorded at a constant charge/discharge current density of 0.1 mA cm$^{-2}$ (0.25 C) and cutoff voltage 0.001–2.0 V *vs.* Li/Li$^+$.
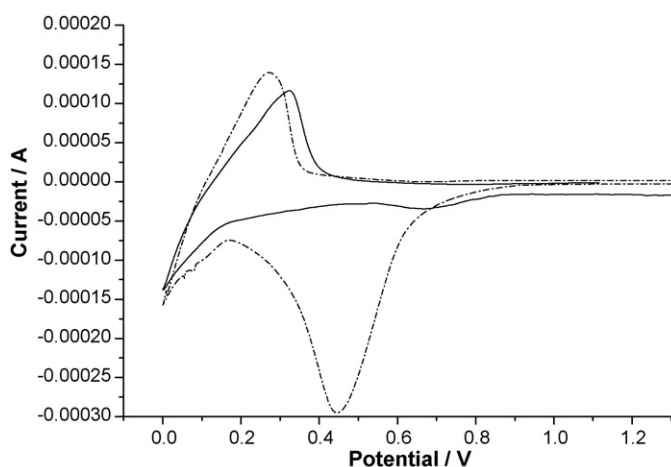


Fig. 3. Cyclic voltammograms of graphite electrode in 1.0 M LiPF$_6$/PC:DMC (1:1 v/v) electrolyte without additive (dash dot line) and with 10% (v/v) PTMS added (solid line) for the first cycle at a scan rate 0.03 mV s$^{-1}$.

versible peak near 0.45 V *vs.* Li/Li$^+$, which definitely can be ascribed to PC decomposition and graphite exfoliation [5,6,27]. In contrast, the cyclic voltammogram of electrolyte with PTMS demonstrates a different performance. One distinct current peak is present near 0.70 V *vs.* Li/Li$^+$, and the irreversible peak near 0.45 V *vs.* Li/Li$^+$ disappears. This peak at 0.70 V is due to the reduction process, leading to the cross-polymerization of PTMS and the formation of a SEI film. These results are consistent with previous results [8–17]. During the following cycles, the peak at 0.7 V does not disappear completely, it just becomes weaker and weaker, which is partially consistent with the above results that the Coulombic efficiency is not near 100% after the first cycles due to too large content of PTMS, which is still reduced to form a thicker SEI film, leading to irreversible capacity. Further research is needed to get a clear understanding of this phenomenon.

SEM micrographs of graphitic anodes before and after cycles are shown in Fig. 4. In Fig. 4a it can be seen clearly that the surface of the graphite electrode before charge/discharge is very smooth. However, after cycling, it is observed that the graphite surface is completely covered with a layer of SEI film as shown in Fig. 4b.

The components of the SEI were further investigated by XPS. The concentration of Si element is as high as 1.45%, which obviously indicates the additive was reduced and became a part of the SEI film. Fig. 5a shows the X-ray photoelectron spectra for Si$_{2p}$. This shows that silicon on the surface of CMS after cycling in the electrolyte containing PTMS exists in the forms of Si−O−Si, Si−O$_x$ and C−Si−O, corresponding to binding energy peaks of 102.0, 102.5 and 103.5 eV, respectively [28]. From the O$_{1s}$ spectra (Fig. 5b), the binding energy peak at 533.5 eV can be attributed unambiguously to the Si−O−Si bonding. Furthermore, the binding energy peaks at 532.8 and 531.4 eV correspond to C−O−C and Si−O−C, respectively.

The FTIR spectrum of the graphite electrode after several cycles is presented in Fig. 6. The broad band at 1000–1100 cm$^{-1}$ can be ascribed to the Si−O stretches in a SiO$_x$ network on the electrode surface [29,30], the C−H stretches associated with the terminal phenyl groups appear above 3000 cm$^{-1}$, and bands at 1456 and 1593 cm$^{-1}$ can be attributed to ring deformation modes



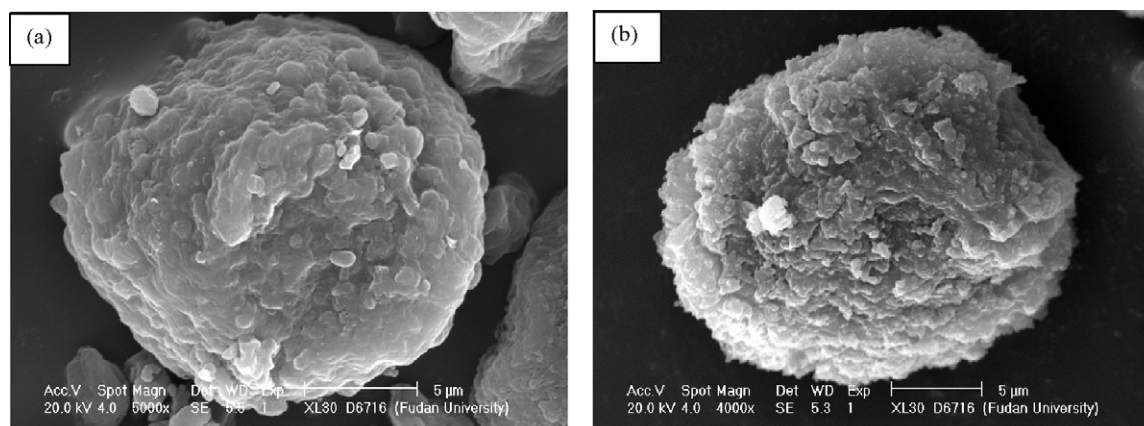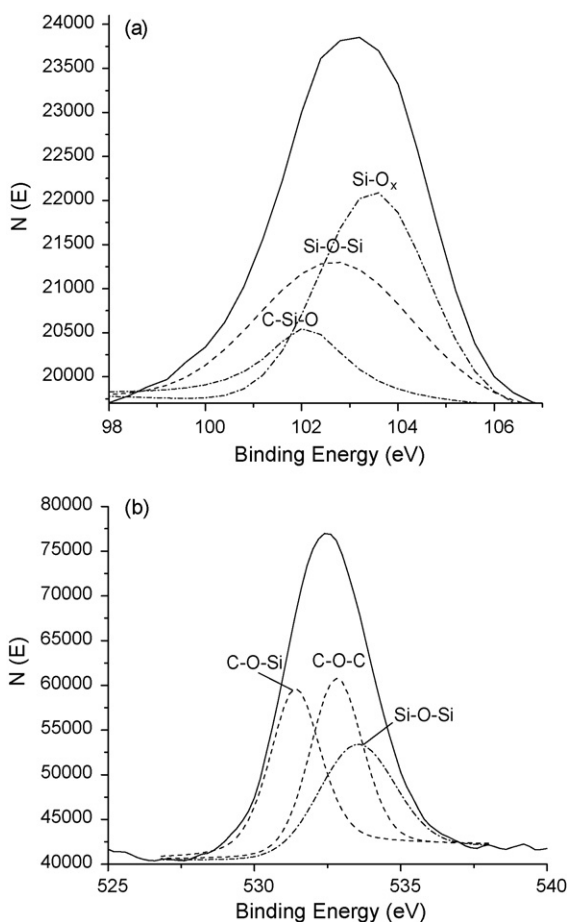Fig. 4. SEM micrographs of graphite electrodes (a) before cycle and (b) after 10 cycles.

Fig. 5. XPS spectra of (a) $Si_{2p}$ and (b) $O_{1s}$ for the SEI of the graphitic electrode after cycling.

of the phenyl substituent. The strong bands at 2800–3000 cm$^{-1}$ are known to be characteristic for the $-CH_2-$ chains that are present in PTMS [31,32]. Other functionalities were identified by absorptions at 967 cm$^{-1}$ (Si–O–C) and 1083 cm$^{-1}$ (Si–C, overlapping with features due to Si–O bonds that are inevitably present). In the case of the graphite electrode prior to cycling, after soaking in the electrolyte with PTMS for 12 h, it was
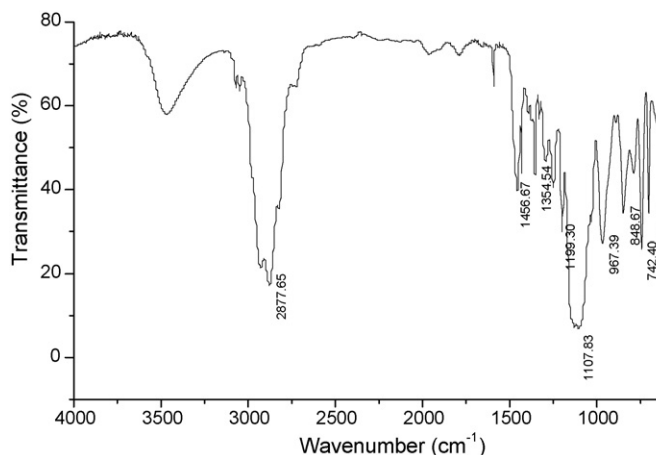
washed by DMC and water. From the FTIR, no evidence of PTMS or silane could be found. As a result, we assume that the presence of bonds such as Si–O–C, Si–C and Si–O is evidence of the reduction of PTMS on the surface of the graphite electrode, thereby constituting partial components of SEI films.

On the basis of the above results, it is clear that the silane forms a cross-polymerized network of Si–O–Si bonds on the graphite surface during the reduction process in the first cycle. Because of steric effects [33–37], not all molecules are individually linked to the surface, but rather form a cross-polymerized network of molecules combining with the graphite surface in the form of C–O–Si, Si–C and Si–O covalent bonds. The cross-polymerized network can effectively prevent PC molecules from co-intercalation into the graphite electrodes.

## 4. Conclusion

A new additive, phenyl tris-2-methoxydiethoxy silane (PTMS), to PC-based electrolyte was developed for lithium-ion batteries containing graphitic anodes. It has been demonstrated that PTMS may effectively restrain PC molecules from co-intercalating with lithium ions into graphite electrodes. The graphite electrodes present good electrochemical performance when 1.0 M LiPF$_6$/PC:DMC (1:1 v/v) with 10% (v/v) of PTMS was used as the electrolyte. This behavior results from the strong interaction existing between PTMS and the electrode surface. PTMS probably acts as a part of the SEI film. After addition of PTMS to the electrolyte, the silane head groups are incorporated into a cross-linked network of Si–O–Si bonds, which probably has some kind of Li$^+$ selective channels. PTMS therefore seems very attractive and provides a good way to improve the electrochemical performance of graphitic carbon at low temperature.

## References

[1] Y. Nishi, J. Power Sources 100 (2001) 101.
[2] A.N. Dey, B.P. Sullivan, J. Electrochem. Soc. 117 (1970) 222.
[3] H.L. Zhang, C.H. Sun, F. Li, C. Liu, J. Tan, H.M. Cheng, J. Phys. Chem. C 111 (2007) 4740.
[4] J.O. Besenhard, H.P. Fritz, J. Electroanal. Chem. 53 (1974) 329.
[5] J. Gao, L.J. Fu, H.P. Zhang, T. Zhang, Y.P. Wu, H.Q. Wu, Electrochem. Commun. 8 (2006) 1726.
[6] J. Gao, H.P. Zhang, L.J. Fu, T. Zhang, Y.P. Wu, T. Takamura, H.Q. Wu, R. Holze, Electrochim. Acta 52 (2007) 5417.
[7] A. Naji, J. Ghanbaja, P. Willmann, D. Billaud, Electrochim. Acta 45 (2000) 1893.
[8] G.H. Wrodnigg, J.O. Besenhard, M. Winter, J. Electrochem. Soc. 146 (1999) 470.
[9] G.H. Wrodnigg, T.M. Wrodnigg, J.O. Besenhard, M. Winter, Electrochem. Commun. 1 (1999) 148.
[10] R. Oesten, U. Heider, M. Schmidt, Solid State Ionics 148 (2002) 391.



Fig. 6. FTIR spectrum for the graphite electrode after seven cycles.

[11] Y. Naruse, S. Fujita, A. Omaru, US Patent 5,714,281, 1998.

[12] D. Aurbach, K. Gamolsky, B. Markovsky, Y. Gofer, M. Schmidt, U. Heider, Electrochim. Acta 47 (2002) 1423.

[13] Z.X. Shu, R.S. McMillan, J.J. Murrary, J. Electrochem. Soc. 142 (1995) L161.

[14] Z.X. Shu, R.S. McMillan, J.J. Murrary, I.J. Davidson, J. Electrochem. Soc. 143 (1996) 2230.

[15] Y.S. Hu, W.H. Kong, Z.X. Wang, X.J. Huang, L.Q. Chen, Solid State Ionics 176 (2005) 53.

[16] H.J. Santner, K.C. Moller, J. Ivanco, M.G. Ramsey, F.P. Netzer, S. Yamaguchi, J.O. Besenhard, M. Winter, J. Power Sources 119 (2003) 368.

[17] R. McMillan, H. Slegr, Z.X. Shu, W.D. Wang, J. Power Sources 81–82 (1999) 20.

[18] G. Schroeder, B. Gierczyk, D. Waszak, M. Walkowiak, Electrochem. Commun. 8 (2006) 1583.

[19] G. Schroeder, B. Gierczyk, D. Waszak, M. Kopczyk, M. Walkowiak, Electrochem. Commun. 8 (2006) 523.

[20] G.W. Gokel, O. Murillo, Podands Compr. Supramol. Chem. (1996) 1.

[21] J.W. Steed, J.L. Atwood, Supramolecular Chemistry, Wiley, New York, 2000.

[22] J.L. Atwood, J.W. Steed, Encyclopedia of Supramolecular Chemistry, Marcel Dekker Inc., New York, 2004.

[23] B. Leska, B. Gierczyk, K. Eitner, V.I. Rybachenko, G. Schroeder, Supramol. Chem. 16 (2004) 303.

[24] G. Schroeder, B. Gierczyk, B. Leska, J. Incl. Phenom. 35 (1999) 327.

[25] B. Gierczyk, G. Schroeder, G. Wojciechowski, B. Łeska, V. Rybachenko, B. Brzezinski, J. Mol. Struct. 516 (2000) 153.

[26] G. Schroeder, B. Leska, B. Gierczyk, K. Eitner, G. Wojciechowski, B. Rrozalski, F. Bartl, B. Brzezinski, J. Mol. Struct. 508 (1999) 129.

[27] M. Yoshio, H.Y. Wang, K. Fukuda, Y. Hara, Y. Adachi, J. Electrochem. Soc. 147 (2000) 1245.

[28] C.D. Wagner, D.E. Passoja, H.F. Hillery, T.G. Kinisky, H.A. Six, W.T. Jansen, J.A. Taylor, J. Vasc. Sci. Technol. 21 (1982) 933.

[29] J.F. Brown Jr., L.H. Vogt Jr., P.I. Prescott, J. Am. Chem. Soc. 86 (1964) 1120.

[30] B. Fabre, G.P. Lopinski, D.D.M. Wayner, Chem. Commun. (2002) 2904.

[31] P.G. Pai, S.S. Chao, Y. Takigi, G. Lucovsky, J. Vasc. Sci. Technol. A4 (1985) 689.

[32] S.Y. Lee, M.T.J. Harris, J. Colloid Interface Sci. 293 (2006) 401.

[33] B.J. Ravoo, D.N. Reinhoudt, S. Onclin, Angew. Chem. Int. Ed. 44 (2005) 6282.

[34] M.J. Stevens, Langmuir 15 (1999) 2773.

[35] P. Silberzan, L. Leger, D. Ausserre, J.J. Benattar, Langmuir 7 (1991) 1647.

[36] C.P. Tripp, M.L. Hair, Langmuir 8 (1992) 1120.

[37] C.P. Tripp, M.L. Hair, Langmuir 11 (1995) 1215.