Ethylene and propylene polymerization catalyzed by a model Ziegler–Natta catalyst prepared by gas phase deposition of magnesium chloride and titanium chloride thin films

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Received 16 July 1995; accepted 23 August 1995

Model Ziegler–Natta catalysts are prepared by gas phase deposition of ultra-thin $TiCl_4$/$MgCl_2$ films in UHV conditions. A monolayer of $TiCl_4$ chemisorbed on a solid solution of titanium and magnesium chloride is formed in this way. The reduction and alkylation of $TiCl_4$ by its reaction with a liquid layer of $AlEt_3$ condensed on the halide film is monitored by XPS. Most of the $TiCl_4$ is reduced by $AlEt_3$ and is incorporated in the mixed titanium/magnesium chloride. The model catalyst is active in the polymerization of ethylene and propylene at 300 K, both in the absence and in the presence of $AlEt_3$ in the reaction cell. The polymers that form over the catalyst film have been characterized by Raman spectroscopy. The weak signals from methyl end groups and unsaturations suggest high molecular weight for both polymers. The polypropylene film has a high degree of isotacticity even without the use of any electron donor. For the propylene polymerization reaction the overall turnover frequency is in the range between 0.1 and 1 molecule/(site s).

Keywords: ethylene and propylene polymerization; model Ziegler–Natta catalyst; XPS studies of $TiCl_4$; interaction with aluminum alkyl; Raman spectroscopy of polymers

1. Introduction

The Ziegler–Natta heterogeneous catalytic system is composed of titanium chloride in the 3+ oxidation state that is partially alkylated during the reaction with an aluminum alkyl. It is extensively used to polymerize ethylene and propylene to homo- or co-polymers [1–3]. In the so-called third and fourth generation catalysts, $TiCl_4$ is chemisorbed on "activated" magnesium chloride, a defective form of $MgCl_2$ with high Miller index planes exposed at the surface. The $TiCl_4$ is reduced and alkylated by reaction with AlR_3 (generally triethyl aluminum) to produce the active catalyst. One or more Lewis bases (electron donors) are added to the system

to control the stereoselectivity of the monomer insertion in the case of propylene polymerization.

The molecular level study of the physical and chemical properties of this catalyst is complicated by its complexity and its sensitivity to oxygen and moisture in the ambient. We have started surface science studies of the Ziegler–Natta catalyst by which we build up, step by step, a model system in a controlled environment. Ultra-thin films of magnesium chloride and titanium chloride are prepared by gas phase deposition onto a polycrystalline gold foil under ultra-high vacuum (UHV) conditions. Extremely clean, oxygen free, magnesium and titanium chloride films, a few monolayers thick, are prepared in this way.

Modern surface science techniques can be used to characterize the model catalyst surface. We have studied the growth of these halide films and discussed the results in previous papers [4–6]. Ordered monolayer and multilayer $MgCl_2$ films are chlorine terminated and do not chemically interact with $TiCl_4$. The irradiation of these films with low energy electrons (1 keV) stimulates the preferential desorption of chlorine, producing a magnesium rich surface that readily chemisorbs $TiCl_4$ molecules at 330 K. A fraction of this chemisorbed $TiCl_4$ reacts with the reduced and defective electron irradiated magnesium chloride film, with the formation of a mixed titanium/magnesium chloride. The $TiCl_4$ molecules are chemisorbed with a heat of adsorption of about 38 kcal/mol, exhibiting optimal thermal stability in the temperature range typically used for the polymerization reaction (300–350 K).

In this paper we describe the interaction of our model Ziegler–Natta catalyst with triethyl aluminum. X-ray photoelectron spectroscopy (XPS) measurements show that $TiCl_4$ is reduced and incorporated in the mixed titanium/magnesium chloride film, when a liquid layer of $AlEt_3$ is deposited on the surface of the model catalyst at 300 K. In this way we obtain a surface that is active in the catalytic polymerization of ethylene and propylene at 300 K. The polymers so produced have been characterized by Raman spectroscopy. From the amount of polymer obtained, we estimated a turnover frequency of about 0.1–1 molecule/(surface site s).

2. Experimental apparatus and procedure

The experimental apparatus consists of a preparation chamber where the thin $MgCl_2$ and $TiCl_4$ films are deposited, a PHI 5300 XPS system for the film elemental composition and oxidation state analysis, and a reaction cell where the catalytic polymerization activity tests are performed. The three sections of the apparatus are interconnected through gate valves and two transfer arms allow for the movement of the sample from one section to the others, without breaking vacuum. The preparation chamber has a background pressure of 1×10^{-9} Torr, provided by a turbomolecular pump and an ion pump. The sample can be heated by an electron beam

heater. The chamber is equipped with a Knudsen cell for the sublimation of $MgCl_2$ (source), and electron gun for the irradiation of the deposited films and a leak valve for the introduction of $TiCl_4$ into the chamber at controlled pressure. A short tube brings the actual gas inlet from the leak valve right in front of the sample. Since the pressure is measured by an ionization gauge positioned about 20 cm away from the sample, the actual pressure at the sample surface during the $TiCl_4$ deposition is considerably higher than the measured pressure. The analysis chamber is equipped with a differentially pumped ion gun, an X-ray source and a spherical capacitance electron energy analyzer. During the XPS analysis the chamber has a base pressure of 1×10^{-9} Torr. The reaction cell consists of a $2\frac{3}{4}$ inches six-way cross kept at a standard background pressure of 5×10^{-8} Torr by two sorption pumps and a turbomolecular pump. A pressure transducer allows to monitor the pressure in the range 1×10^{-3}–1×10^{3} Torr. The polymerization reaction is carried out in batch mode, with stagnant gas phase.

The surface of the substrate (gold polycrystalline foil) is cleaned by Ar-ion bombardment and subsequent heating in UHV to anneal the surface defects. $MgCl_2$ is sublimed from the Knudsen cell and deposited on the substrate held at 300 K. In this way, we can prepare extremely clean $MgCl_2$ films, a few monolayers thick [4,5]. The magnesium chloride film, still held at 300 K, is then irradiated with a beam of 1 keV electrons and a current density of 50 $\mu A/cm^2$, which corresponds to a flux of 3×10^{14} electron/(cm^2 s). The beam is rastered over the entire surface of the sample (about 0.5 cm^2) to obtain uniform exposure. At the same time $TiCl_4$ is leaked into the chamber at a pressure of 5×10^{-8} Torr. In these conditions we reach the maximum uptake of titanium chloride in about 15 min [6].

The sample is then transferred to the reaction cell to be exposed to triethyl aluminum. The reservoir of $AlEt_3$ is heated to about 370 K to increase its vapor pressure. When the $AlEt_3$ is introduced in the reaction cell, it condenses on the sample surface held at 300 K: in a short time a liquid film becomes visible on top of the titanium chloride/magnesium chloride film. The pressure of the aluminum alkyl vapor ranges between 2 and 6 Torr. This condition is maintained for a period between 5 and 30 min. During this step of the model catalyst preparation, the active catalytic sites are formed on the film surface. The cell is then quickly evacuated and the sample is transferred to the analysis chamber.

The polymerization is carried out in the reaction cell, with the model catalyst held at 300 K. Both ethylene and propylene have been polymerized. The reaction is successful both in the presence and in the absence of $AlEt_3$ in the gas phase. When $AlEt_3$ is present in the reaction mixture, it is introduced in the reaction cell as described earlier. In both cases, the monomer is introduced at the pressure of 760 Torr and is allowed to react for 10–60 h.

At every step of the model catalyst preparation, the elemental composition and the oxidation states of the atoms in the deposited film are monitored by XPS. The Al K_α excitation radiation (1486.6 eV) is used for the XPS analysis. The photons of this radiation have sufficient energy to excite the Mg $KL_{23}L_{23}$ Auger transition.

The Au $4f_{7/2}$ peak at 84.0 eV is taken as reference for the energy scale. The polyethylene and polypropylene films grown on the model catalyst are characterized by Raman spectroscopy, using the 514.5 nm line of an argon laser as excitation radiation.

3. Results

3.1. PREPARATION OF $TiCl_4/MgCl_2$ ULTRA-THIN FILMS

The deposition and growth of monolayer and multilayer $MgCl_2$ films on a gold polycrystalline substrate have been already described [4,5]. The electron irradiation induced $TiCl_4$ deposition onto monolayer and multilayer $MgCl_2$ films has also been reported [6].

Table 1 summarizes the atomic compositions of the deposited films at the different stages of preparation of the model Ziegler–Natta catalyst, as measured by XPS. These compositions are calculated from the peak areas corrected by the cross section of the different elements [7]. Ten monolayers of $MgCl_2$ are deposited on the gold substrate. This film is then irradiated with 1 keV electrons and $TiCl_4$ is introduced in the preparation chamber at the pressure of 5×10^{-8} Torr for 30 min. Titanium chloride is deposited in this way on the halide film, with Ti accounting for 26% of the atomic composition.

Fig. 1 shows the Ti 2p region of the XPS spectrum recorded at two different stages of the model catalyst preparation. The lower curve refers to the $TiCl_4/MgCl_2$ film after the titanium chloride deposition. Two double peaks are present, indicating two different chemical environments for the deposited titanium atoms. The doublet at 458.3 and 464.4 eV is due to the $2p_{3/2}$ and $2p_{1/2}$ photoelectrons from titanium atoms in $TiCl_4$ in its molecular solid state [6,8,9]. We identify this state as chemisorbed $TiCl_4$. The doublet at 455.9 and 461.9 eV is due to the $2p_{3/2}$ and $2p_{1/2}$ photoelectrons from titanium atoms in a solid solution that we have previously characterized and called mixed titanium/magnesium chloride ($TiMg_xCl_y$) [6]. Here, the titanium atoms are more electron rich (reduced) than in $TiCl_3$, which

Table 1
Atomic composition of the deposited film at the different stages of preparation of the model Ziegler–Natta catalyst

Stage of preparation of the model Ziegler–Natta catalyst	Atomic composition (%)							
	$Ti_{458.3\,eV}$	$Ti_{455.9\,eV}$	Ti_{tot}	Mg	Cl	Al	C	O
1: $MgCl_2$ 10 ML	–	–	–	36	64	–	–	–
2: 1 + $TiCl_4$	12	14	26	1	73	–	–	–
3: 2 + $AlEt_3$	5	16	21	1	58	2	16	2

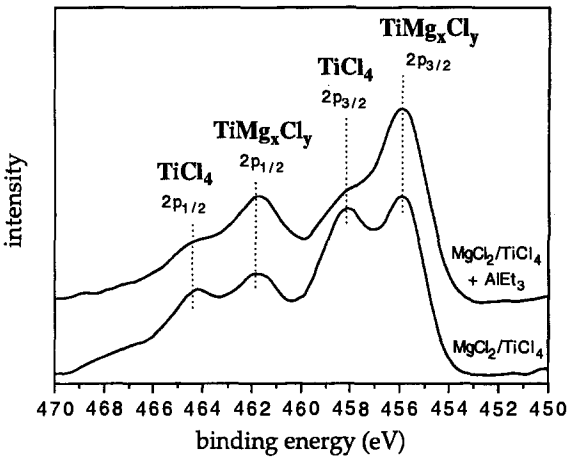

Fig. 1. Ti 2p region of the XPS spectra obtained from the model Ziegler–Natta catalyst before and after the reaction with $AlEt_3$.

shows the Ti $2p_{3/2}$ peak at 457.6 eV [8]. After deconvolution of the Ti 2p XPS peak in asymmetric Gaussian–Lorentzians, we estimated that 45% of the Ti in the deposited film is present as $TiCl_4$.

3.2. $AlEt_3$ REACTION WITH $TiCl_4/MgCl_2$ ULTRA-THIN FILMS

After the electron irradiation induced $TiCl_4$ deposition on $MgCl_2$ film, the sample is transferred to the reaction cell to be exposed to relatively high pressure of triethyl aluminum. The temperature difference between the reservoir of $AlEt_3$ and the sample allows for the deposition of a liquid layer of aluminum alkyl on the halide film surface. High exposure to $AlEt_3$ seems to be needed in order to obtain the active catalytic site. The titanium chloride/magnesium chloride film prepared as described in the previous section has been exposed to a liquid layer of $AlEt_3$ for 5 min. The cell is then quickly evacuated and the sample is transferred to the analysis chamber. The elemental composition of the model catalyst after this treatment is reported in table 1. We measure a substantial build-up of carbon (16%), while only traces of Al and O are present. From the position of the Al 2p peak (74.1 eV) and the O 1s peak (531.5 eV) we deduce that aluminum oxide, hydroxide or oxichloride could be present at the catalyst surface [10–15]. The intensity of the Ti 2p signal is now 87% of the value measured after the electron induced $TiCl_4$ deposition. Considering the mean free path of the Ti 2p photoelectrons, this drop can be explained by the formation of approximately one complete monolayer of ethyl chains on top of the sample, after reaction of Ti atoms at the film surface with $AlEt_3$. The intensity of the C 1s signal is in agreement with this interpretation. The drop of the Cl 2p is more marked than the loss of the Ti 2p signal, possibly due to the reduction of most of the $TiCl_4$.

The upper curve of fig. 1 shows the Ti 2p region of the XPS spectrum after reaction of the $TiCl_4/MgCl_2$ film with $AlEt_3$. The same features discussed in the previous section are present, with a doublet at 458.3 and 464.4 eV due to chemisorbed $TiCl_4$ and a doublet at 455.9 and 461.8 eV due to Ti atoms in the mixed titanium/magnesium chloride. Part of the Ti^{4+} has been reduced by the aluminum alkyl and incorporated in the mixed chloride. Only 24% of the Ti in the deposited film is now present as $TiCl_4$.

3.3. ETHYLENE AND PROPYLENE POLYMERIZATION REACTION ACTIVATED BY MODEL ZIEGLER–NATTA CATALYSTS

The model Ziegler–Natta catalyst proved to be active for the polymerization of ethylene and propylene. The model system, prepared as described above, is transferred to the reaction cell and pure C_3H_6 is introduced in the reactor at 760 Torr. No $AlEt_3$ is added to the reaction mixture. After 10 h of reaction, the cell is evacuated. A very thin polymeric film grows onto the same area of the sample where the electron beam was rastered during the electron irradiation induced $TiCl_4$ deposition on the $MgCl_2$ film. Fig. 2 shows the XPS spectrum of the sample after polymerization: only C is detected. The detailed analysis of the C 1s region indicates that two peaks are present at 286.0 and 285.8 eV, with 1.5 eV full width at half maximum. They are respectively due to carbon atoms in methyl and methylene groups (higher energy peak) and to carbon atoms in methyne groups (lower energy peak) [16]. These peaks are shifted of 1.0 eV from the literature values due to the local charging of the sample surface under X-ray irradiation. A satellite peak is present at about 275 eV.

Polypropylene can be synthesized in larger amount by adding $AlEt_3$ to the reaction mixture. Two monolayers of $MgCl_2$ are deposited from the gas phase on the

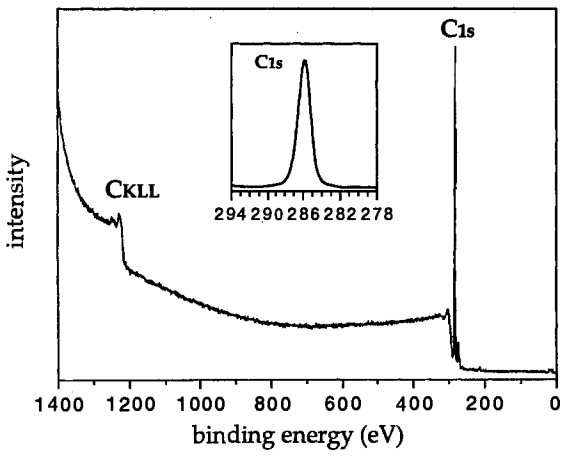

Fig. 2. XPS spectrum from the catalyst after propylene polymerization reaction.

gold substrate as described earlier. Titanium chloride is deposited by electron irradiation of the $MgCl_2$ film in the presence of 5×10^{-8} Torr of $TiCl_4$ for 10 min. Titanium chloride is then reduced and alkylated by exposure to a liquid layer of $AlEt_3$ for 20 min at 300 K. Without evacuation of the reaction cell, propylene is introduced in the reactor at 760 Torr and the mixture is allowed to react for 60 h. A polymer film, roughly 100 μm thick, grows in this way. The polymer is concentrated mostly on the electron irradiated area of the sample, but patches of polymer are also visible on the sample holder, in areas a few millimeters away from the model catalyst surface. The polymer grown in this way has been analyzed by Raman spectroscopy and the relative spectrum is shown in fig. 3. The good quality of the polypropylene produced is confirmed by the small concentration of unsaturations present in the macromolecular chain. Also, this spectrum suggests a high degree of isotacticity in this polypropylene film [17]. Further characterization of the polymer is presently in progress.

A very similar procedure has been followed to produce a model catalyst for the polymerization of ethylene. Titanium chloride is deposited on electron irradiated $MgCl_2$ three monolayers film in presence of 1×10^{-8} Torr of $TiCl_4$ for 15 min. The $TiCl_4/MgCl_2$ film is then exposed to a liquid layer of $AlEt_3$ for 5 min at 300 K. Ethylene is introduced in the reaction cell at 760 Torr without evacuation of the alkyl aluminum. The mixture is allowed to react for 15 h. In these conditions a polymer film grows on the model catalyst surface. The Raman spectrum of the polyethylene obtained in this way is shown in fig. 4. Again, the small concentration of unsaturations and methyl end groups is indicative of high molecular weight polymeric chains.

In the case of polymerization in the presence of $AlEt_3$ in the reaction mixture, there should be the possibility that the reaction is catalyzed by the aluminum alkyl, with no participation of the titanium chloride in the catalytic loop. To demonstrate that this is not the case, a blank reaction has been run, in which a gold foil is exposed to $AlEt_3$, with the formation of a liquid film on the foil surface. After

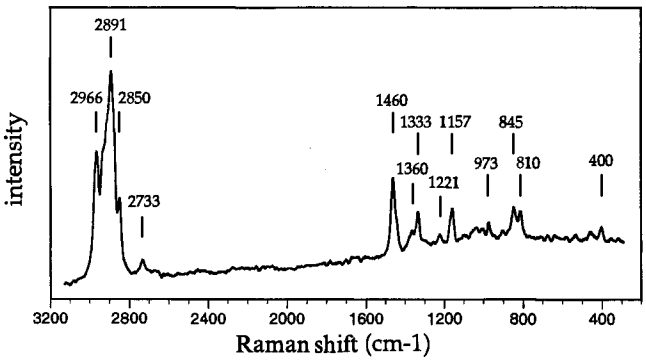

Fig. 3. Raman spectrum of isotactic polypropylene grown on the model Ziegler–Natta catalyst surface.

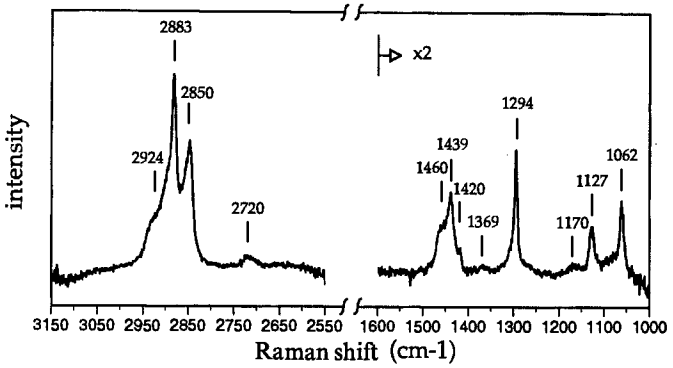

Fig. 4. Raman spectrum of polyethylene grown on the model Ziegler–Natta catalyst surface.

5 min, C_2H_4 is introduced in the reaction cell at 760 Torr, without evacuation of the alkyl aluminum. In this case no polymer is formed on the Au substrate after 16 h at 300 K.

As a first effort to measure the overall polymerization reaction turnover frequency (average rate of monomer insertion per active site per second), we quantified the amount of polymer produced by gravimetric analysis. The polypropylene film grown on the model catalyst in the absence of $AlEt_3$ is dissolved in mesitylene at 400 K. From the catalyst weight difference before and after the polymer dissolution, we estimate that 300 μg of polymer are produced in 10 h. This corresponds to a film of 6 μm in thickness grown on the 0.5 cm^2 area of the model catalyst. Assuming constant rate of polymerization during the reaction period and a catalytic active site density of 10^{15} sites/cm^2 on the model surface, we estimate a turnover frequency of 0.2 molecule/(site s).

4. Conclusion

We report here the first successful polymerization of ethylene and propylene on a model Ziegler–Natta catalyst, prepared by gas phase deposition in UHV conditions. The extremely well controlled environment in which the model catalyst is prepared allows us to obtain a clean, relatively easy to characterize model surface. XPS has proved to be particularly advantageous for monitoring the interaction of $TiCl_4$ with alkyl aluminum, for the synthesis of the active site. A liquid layer of $AlEt_3$ has to be deposited on the $TiCl_4/MgCl_2$ film in order to obtain the desired active sites for the polymerization reaction. The reason for this great excess of aluminum alkyl exposure is under study.

Although it is not possible to exclude the loss of part of the titanium deposited during electron irradiation, by reaction with $AlEt_3$ and formation of some volatile products, our results are consistent with the accepted description of alkyl aluminum as the agent needed for the reduction and alkylation of $TiCl_4$. The active sites

for Ziegler–Natta polymerization are obtained in this way. Only traces of Al are left on the catalyst surface in the form of aluminum oxide, hydroxide or oxichloride, with the oxygen coming from impurities present in the reaction cell during the reaction of the $TiCl_4/MgCl_2$ film with triethyl aluminum.

The polyethylene and polypropylene films grown on the model catalyst have been characterized by Raman spectroscopy. The weak signals from methyl end groups and unsaturations suggest a high molecular weight for both polymers. The polypropylene has a high degree of isotacticity, even without the use of any electron donor during the catalyst preparation or in the reaction mixture, usually added to improve the stereoselectivity of the catalytic surface.

The rate of the overall propylene polymerization reaction has been estimated from the amount of polymer produced. Due to the assumptions that we made, there is a large uncertainty in this value. However, the turnover frequency should be in the range between 0.1 and 1 molecule/(site s). When $AlEt_3$ is added to the monomer in the reactor, the amount of polymer produced is increased by roughly 100 fold. Further studies are under way to understand whether this is due to a faster polymerization reaction or to the longer life of the model catalyst.

Acknowledgement

The authors would like to thank Dr. J.W. Ager of the Materials Sciences Division at the Lawrence Berkeley Laboratory for the Raman spectroscopy analysis of our samples. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division, of the US Department of Energy under Contract No. DE-AC03-76SF00098. The authors would also like to acknowledge support from MONTELL, Inc.

References

[1] P.C. Barbé, G. Cecchin and L. Noristi, Adv. Polym. Sci. 81 (1986) 1.
[2] J.J.A. Dusseault and C.C. Hsu, JMS-Rev. Macromol. Chem. Phys. C 33 (1993) 103.
[3] *Encyclopedia of Polymer Science and Engineering*, Vol. 13, 2nd Ed. (Wiley, New York, 1988) p. 464.
[4] E. Magni and G.A. Somorjai, Appl. Surf. Sci. 89 (1995) 187.
[5] E. Magni and G.A. Somorjai, Surf. Sci. Lett., in press.
[6] E. Magni and G.A. Somorjai, Surf. Sci., in press.
[7] ESCA Operator's Reference Manual. ESCA Version 4.0 and Multi-Technique Version 2.0, Perkin-Elmer Corporation, Physical Electronics Division, Eden Prairie, MN 55344 (1988).
[8] C. Mousty-Desbuquoit, J. Riga and J.J. Verbist, Inorg. Chem. 26 (1987) 1212.
[9] C. Mousty-Desbuquoit, J. Riga and J.J. Verbist, J. Chem. Phys. 79 (1983) 26.
[10] V.I. Nefedov, J. Electron Spectry. Relat. Phenom. 25 (1982) 29.
[11] G.E. McGuire, G.K. Schweitzer and T.A. Carlson, Inorg. Chem. 12 (1973) 2450.

[12] V.I. Nefedov, Y.V. Salyn, G. Leonhardt and R Scheibe, J. Electron Spectry. Relat. Phenom. 10 (1977) 121.
[13] J.A. Taylor, J. Vac. Sci. Technol. 20 (1982) 751.
[14] C.D. Wagner, D.E. Passoja, H.F. Hillery, T.G. Kinisky, H.A. Six, W.T. Jansen and J.A. Taylor, J. Vac. Sci. Technol. 21 (1982) 933.
[15] T.L. Barr, Appl. Surf. Sci. 15 (1983) 1.
[16] G. Beamson and D. Briggs, in: *High Resolution XPS of Organic Polymers* (Wiley, New York, 1992) p. 56.
[17] P.J. Hendra and J.K. Agbenyega, in: *The Raman Spectra of Polymers* (Wiley, New York, 1993).