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Surface modification of propene/1,7-octadiene copolymer by metathesis reactions

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Dedicated to Prof. Dr. Klaus Hummel on occasion of his 70th birthday

Abstract

In this work, we investigated the possibility to modify polyolefin surfaces by ring-opening metathesis polymerization (ROMP). We copolymerized propylene with a small amount of 1,7-octadiene in order to get a polyolefin with vinyl groups in the side-chains. By reaction of the ruthenium–carbene complex $RuCl_2(PCy_3)_2(=CHPh)$ **1** with the vinyl side groups, new carbene complexes were generated, thus creating the active sites for ROMP on the polyolefin surface. This procedure made it possible to graft polymers with different functionalities under mild conditions onto the hydrophobic polypropylene surface. The thickness of the modification depended mainly on the concentration of the active sites at the surface, on the time of treatment with monomer solution and finally on the solvent used for this treatment. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Polyolefins are of great technical interest due to their variable properties and rather low prices. Because these polymers are highly hydrophobic, their surfaces have to be modified for special applications. They are often treated by different methods like corona, flame or plasma treatment [1] before a final coating can be applied.

Highly active well-defined carbene complexes have been synthesized since the 1980's. Mainly, the molybdenum carbene complexes $Mo(CH-t-Bu)(NAr)(OCCH_3(CF_3)_2)_2$ and $Mo(CH-t-Bu)(NAr)(OC(CH_3)_3)_2$ (Ar = 2,6-$C_6H_3-i-Pr_2$) [2] and the ruthenium–carbene complex $RuCl_2(PCy_3)_2(=CHPh)$ (**1**) [10] have proved to be highly active for ring-opening polymerization of a great number of different cyclic monomers [3].

Many investigations have been carried out to fix these well-defined complexes on different carriers. Recently, molybdenum carbene complexes have been supported on the inorganic carrier Al_2O_3 [4]. Because of relatively low stability of molybdenum carbene complexes in long-time experiments [5], we were more interested in the less sensitive ruthenium–carbene complexes. These complexes have been successfully supported by exchange of phosphine ligands on an inorganic carrier (SiO_2) [6] or polymeric material (cross-linked polystyrene)

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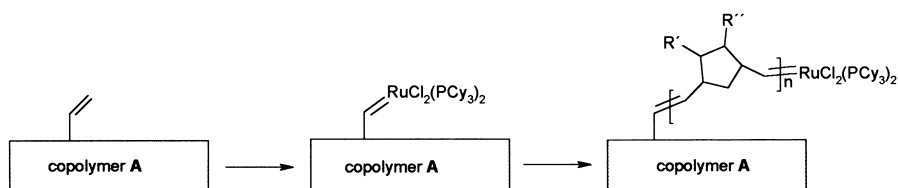*E-mail address:* stelzer@ictos.tu-graz.ac.at (F. Stelzer).

Fig. 1. Scheme of surface modification via metathesis.

[7]. For ring-closing metathesis, they were also fixed temporarily via the carbene moiety [8]. The ruthenium complex **1** was chosen for the investigations described in this paper because of its high resistance to all varieties of chemical functionalities. It has already been shown previously that ROMP can be used to convert hydrophilic inorganic surfaces into a hydrophobic surface via a surface bound metathesis initiator [9]. The ruthenium–carbene complex **1** [10] was chosen for the investigation to modify the surface of polyolefins towards a more hydrophilic one. To achieve this, the idea was to fix a ROMP initiator at the surface of a polyolefin via an exchange of the alkylidene group (Fig. 1). This was facilitated by incorporating vinylic side groups via copolymerization of propene and 1,7-octadiene [11]. Using the heterogeneous $TiCl_4/MgCl_2$ catalyst with Et_3Al as cocatalyst should avoid cross-linking of the polymer chains and decrease the number of ring-closing.

The procedure presented in this paper makes it possible to graft various monomers including some sensitive ones, which are usually instable at high temperatures or under high energetic irradiation. The monomers used in this work are presented in Fig. 2. When employing cyclooctene, rubber-like polymer covering the surface of the copolymer was obtained. Further-
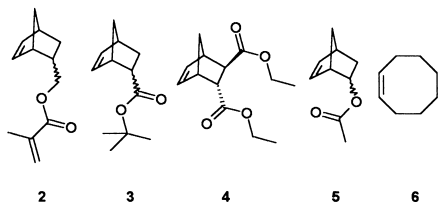
more, a norbornene derivative with methacrylic side chains was polymerized to get a layer of fixed polynorbornene with nonreacted methacrylic moieties. The groups could be cross-linked in a second step with any other methacrylic resin. These two examples demonstrate the great possibilities of this method.

We were also interested in covering the hydrophobic polyolefin surface by a hydrophilic layer up to 50 μm in order to avoid a reorientation of polar groups in the bulk when exposed to hydrophobic environment [1].

2. Experimental

2.1. Chemicals

Dicyclopentadiene, cyclooctene, ethyl acrylate, *tert*-butyl acrylate and fumaric acid diethyl ester were obtained from Fluka, 2-norbornenylacetate (*endo*, *exo* mixture) from Sigma Aldrich. $RuCl_2(PCy_3)_2(=CHPh)$ was obtained from Strem Chemicals. These chemicals were used directly without undergoing further purification if not mentioned differently.

$TiCl_4/MgCl_2$ catalyst (3% Ti) was a gift of PCD Linz. Propene (grade 2.8 from Linde) was purified just before feeding the reactor through columns filled with molecular sieves and Cu contact from BASF. Heptane was dried by distillation from Na/K alloy. Et_3Al solution in heptane was obtained from Fluka.

Solvents and liquid monomers were degassed before use. All operations involving ruthenium–carbene complexes were carried out under argon using Schlenk techniques or in a dry-box under nitrogen.

Fig. 2. Monomers employed for surface modification via metathesis.

2.2. Instrumentation

Infrared spectra were performed on a Perkin-Elmer Spectrum One FTIR. The copolymer films, made in a heated press at 170°C, showed a thickness of ca. 50 μm. The IR spectra of samples with a thickness of 4 mm were measured with an Harrick Slit Pea Single Reflection ATR unit (silicon hemisphere).

High-temperature NMR measurements were performed on a Bruker AM-270. The samples were dissolved in deuterated tetrachloroethane and measurements were carried out at 103°C. Other NMR measurements were performed on a Bruker MSL-300, a Varian Gemini 200 or a Bruker WH-52.

The melting temperature of polymers was determined on a Polymer Laboratories Simultaneous Thermal Analysis STA 625 with heating rates of 5°/min.

Cross-linking of methacrylic moieties was achieved with a 1300 W Heraeus high-pressure mercury lamp and determined by IR.

2.3. Synthesis of ROMP monomers

Synthesis of 2-methyl-acrylic acid bicyclo-[2.2.1]hept-5-en-2-yl methyl ester (**2**) (*endo*, *exo* mixture).

A detailed description of the preparation of **2** is reported elsewhere [12]. For the final purification a distillation was performed (Spaltrohr distillation system) (bp = 75°C/0.2 mm Hg). To avoid radical polymerization during distillation the mixture was degassed and 10 mg of 2,6-di-*tert*-butyl-cresol was added as a stabilizer.

^{1}H NMR (300 MHz): δ: 6.0 ppm (1H, s), 5.8 ppm (1H, dd), 5.7 ppm (1H, dd), 5.1 ppm (1H, s), 3.5–4.1 ppm (2H, m), 2.6 ppm (1H, s), 2.5 ppm (1H, s), 2.1 ppm (1H, m), 1.8 ppm (3H, s), 1.5 ppm (1H, m), 1.3 ppm (1H, d), 0.92 (1H, d), 0.25 ppm (1H, m).

Synthesis of bicyclo[2.2.1]hept-5-ene-2-carboxylic acid *tert*-butyl ester (**3**) (*endo*, *exo* mixture) 26.5 g cyclopentadiene (401 mmol) and 60 g *tert*-butyl acrylate (476 mmol) were

mixed with 5 ml CH_2Cl_2 and stirred for 16 h at room temperature. Finally, the product was distilled in vacuum (bp = 85°C/0.2 mm Hg).

^{1}H NMR (90 MHz): δ: 6.10 ppm (1H, m), 5.89 ppm (1H, m), 3.10 ppm (1H, br s), 2.82 ppm (2H, m), 1.7–1.9 ppm (2H, m), 1.34 ppm (9H, s), 1.2–1.3 (1H, m), 0.90 ppm (1H, m).

Synthesis of *endo*, *exo* bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid diethyl ester (**4**).

The procedure is similar to that of **3**, except fumaric acid diethyl ester was used for Diels–Alder reaction with cyclopentadiene. The mixture was then distilled in vacuum (bp = 72°C/0.15 mm Hg) and used without further purification.

^{1}H NMR (90 MHz): δ: 6.28 ppm (1H, dd), 6.07 ppm (1H, dd), 4.17 ppm (4H, q), 3.34 ppm (1H, dd), 3.25 ppm (1H, m), 3.12 ppm (1H, m), 2.68 ppm (1H, m), 1.62 ppm (1H, m), 1.42 ppm (1H, m), 1.28 ppm (6H, m).

2.4. Copolymerization of propene / 1,7-octadiene (copolymer **A**)

Copolymerizations of propene and 1,7-octadiene were performed in a 0.5 dm^3 stainless Büchi steel reactor. After evacuation and purging with nitrogen the reactor was filled with 190 ml heptane and heated to 60°C. 10 ml 1,7-octadiene and 1 ml of Et$_3$Al-solution (3 mmol/ml in heptane) were then added. When the propene pressure remained constant, the polymerization was started by breaking a small glass phiole. The phiole had been filled with 50 mg heterogeneous catalyst and fixed inside the reactor. A propeller-like stirrer was used at 900 rpm for stirring the reaction mixture. Propene pressure was kept constant at 4 bar by a Büchi press flow gas controller bpc 6002 and temperature was controlled by a julabo MS thermostat. The polymerization was terminated after 60 min by degassing the reactor and adding a small amount of methanol. The resulting copolymer **A** grains were washed with methanol and aqueous NaOH and finally dried in vacuum for 16 h at room temperature.

2.5. Supporting of carbene complexes

Copolymer **A** was pressed at 170°C to ca. 50 μm films or 4-mm-thick plates under normal atmosphere. These samples were added to a solution of **1** in heptane (2 mg/ml) under nitrogen atmosphere. The films were kept in solution for 30 min during which the colour turned light purple. Finally the samples were washed three times with heptane over a period of 60 min without loss of the purple colour.

2.6. Ring-opening metathesis polymerization

The pretreated samples (1 cm^2 squares) were transferred into 2 ml of solution made from monomers **2**–**6** in heptane (usually about 200 mg monomer/ml heptane). Gradually, new swollen films of polymers **p2**–**p6** became visible at the surface. The polymerizations were terminated after 8 h by removing the films from the monomer solution and exposing to air. When polymerizing **2**, 1 mg 2,6-di-*tert*-butyl-cresol was added as a stabilizer.

2.7. Extraction of ROMP samples

The samples obtained above were extracted with tetrahydrofuran (20 ml) at 50°C for 1 h. In addition, to investigate the removable part of ROMP samples, some films were kept in boiling THF for 16 h.

2.8. Cross-linking of methacrylic groups

Copolymer **A** films modified with methacrylic polymers were swollen in a THF solution of 2-hydoxy-2-methyl-1-phenyl-propan-1-one for 10 min. After removing the solvent in vacuum, the films were irradiated with a 1300 W UV lamp for 10 min.

The cross-linking of the methacrylic groups was followed by FT-IR spectroscopy each minute.

2.9. Treatment of copolymer **A**/**p3** samples with HCl/dioxane

Copolymer **A** films modified with polymer **p3** were treated with a mixture of 10 ml concentrated hydrochloric acid and 30 ml dioxane under reflux for 1 h. To finish, the samples were washed with THF.

3. Results and discussion

3.1. Copolymerization of propene / 1,7-octadiene (copolymer **A**)

The consumption of propene in copolymerization with 1,7-octadiene was followed by a gas-flow meter and is shown in Fig. 3. After a maximum at the beginning, the activity gradually decreased. Compared to a homopolymerization of propene [13], a loss of activity was found when adding 1,7-octadiene. The microstructure of the copolymer was investigated by ^{13}C NMR analysis (Fig. 4). The total amount of octadiene incorporated was about 1.4 mol% (compared to 4 mol% octadiene in reactor feed). Half of the octadiene showed intramolecular cyclization, the remaining 50% were incorporated by single addition polymerization of one vinyl group. Hence, the copolymer had 0.7 mol% of 5-hexenyl groups, which could be used
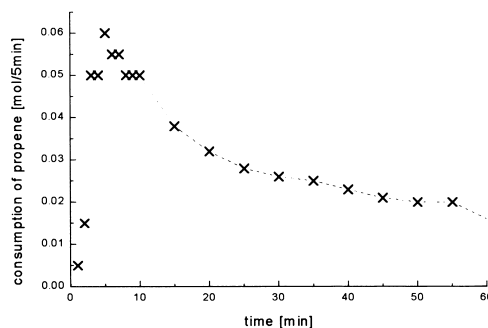

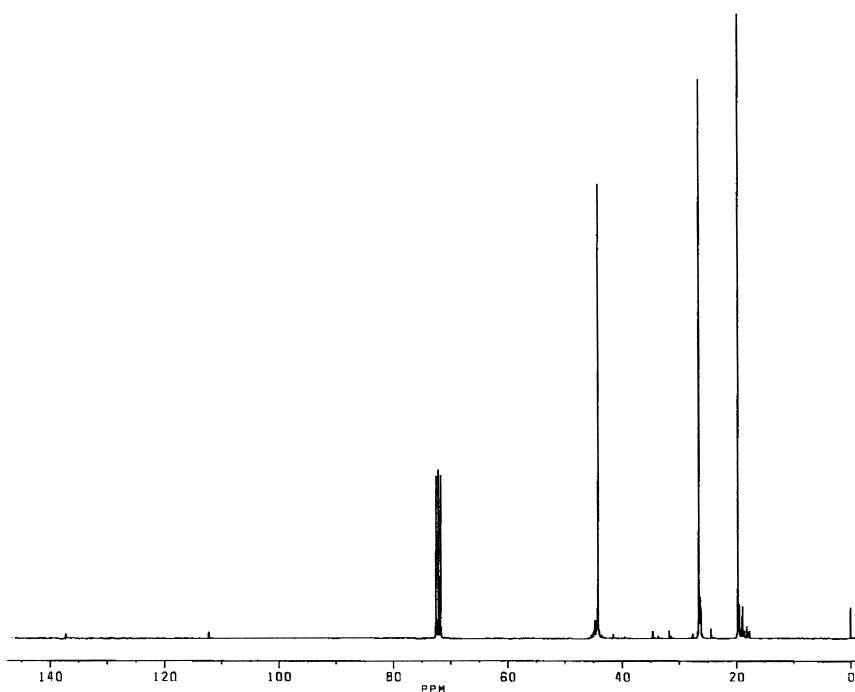Fig. 3. Consumption of propene vs. time in copolymerization with 1,7-octadiene.

Fig. 4. 75 MHz ^{13}C NMR of highly isotactic copolymer **A** in $C_2D_2Cl_4$ as solvent.

for further modification. Furthermore, the polypropene main-chain was highly isotactic and 81% mm pentads were found. When investigating the copolymer by FT-IR spectroscopy, the
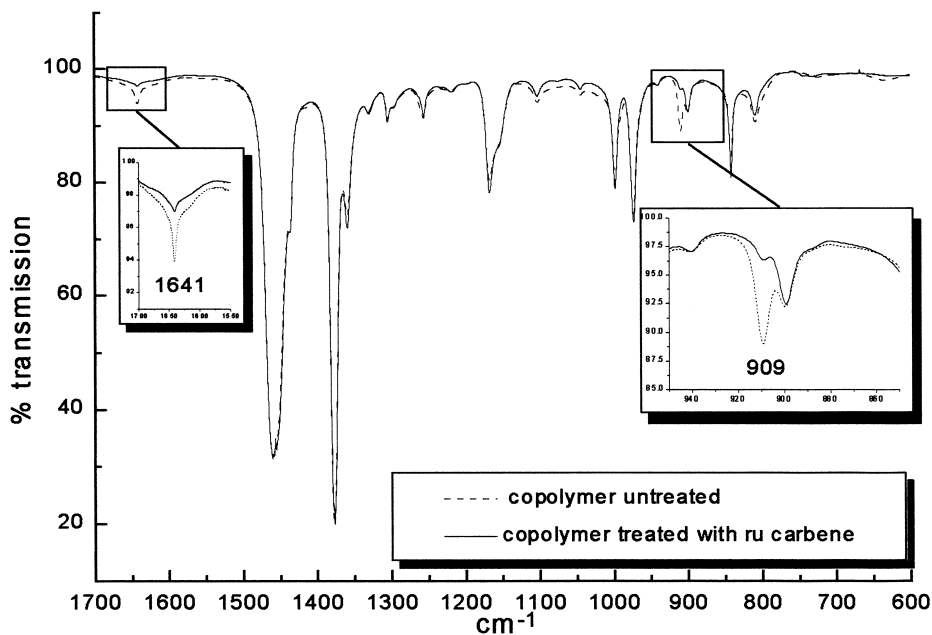

Fig. 5. FT-IR spectra of a 50 μm film of copolymer **A** before and after treatment with ruthenium carbene solution.
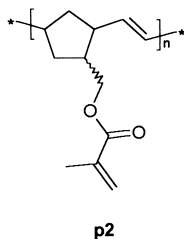
p2

Fig. 6. Grafted polymer carrying a methacrylic moiety.

vinyl groups were clearly identified by the C–H vibration at 909 cm^{-1} (CH_2=CHR) and C=C stretching at 1641 cm^{-1} (CH_2=CHR) (Fig. 5). This clear identification of the reactive groups was useful to observe the reaction with the carbene complex. Thermal characterization of copolymer **A** showed a melting temperature of 138°C (onset of melting peak), ΔH = 49 J/g (2nd heating run). Comparing ΔH to a completely crystalline polypropylene (209 J/g, [14]), the copolymer showed a rather low crystallinity due to cyclic and hexenyl units.

3.2. Supporting of carbene complexes

The reaction of the ruthenium–carbene complex with the vinyl groups of the copolymer **A** (according to Fig. 1) was monitored by FT-IR spectroscopy. In order to monitor this, a 50 μm film was treated with a solution of **1** for 1 h. Following the intensity of C–H vibration of the vinyl group at 909 cm^{-1}, the exchange of the alkylidene moiety was identified by a nearly complete disappearance of the peak (Fig. 5).

Furthermore, the loss of the C=C vibration at 1641 cm^{-1} was observed. Unfortunately, carbene signals could not be detected by IR due to their low intensity. Following the reaction using high temperature NMR spectroscopy was not possible because **1** is not stable at the high temperatures required. Nevertheless, based on the evidence, we assume a more or less complete conversion of the vinylic side groups.

3.3. Ring-opening metathesis of 2-methyl-acrylic acid bicyclo[2.2.1]hept-5-en-2-yl methyl ester **2**

We were interested in a method to graft a polymer carrying a cross-linkable group in a side-chain onto a polyolefin surface under mild conditions, i.e. room temperature. Since methacrylic groups do not react with the ruthenium–carbene complex in an acyclic cross-metathesis-substituted polynorbornene bearing, the photochemical cross-linkable moiety (Fig. 6) was grafted on the copolymer surface. To avoid radical polymerization during the modification procedure, 2,6-di-*tert*-butyl-cresol was added as a stabilizer.

By varying the concentration of **2** and the reaction time, we were able to produce polymer layers of different thickness. Using high concentrations of **2** (400 mg/ml), the film of **p2** on the surface of a 4-mm-thick sample grew up to 50 μm. Fig. 7 shows a cut through such a sample, where the polymer was coloured by swelling the cut in THF containing the red dye sudan.

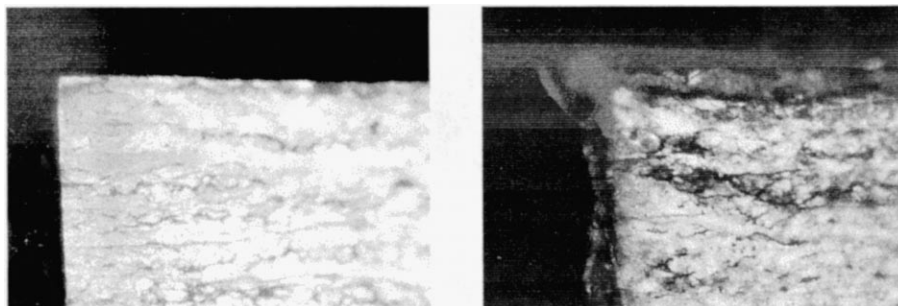Fig. 7. Left: copolymer **A** before modification; right: cut through copolymer **A** sample modified by a about 50 μm film of ROMP polymer (gray) [pictures obtained by polarized optical microscopy].
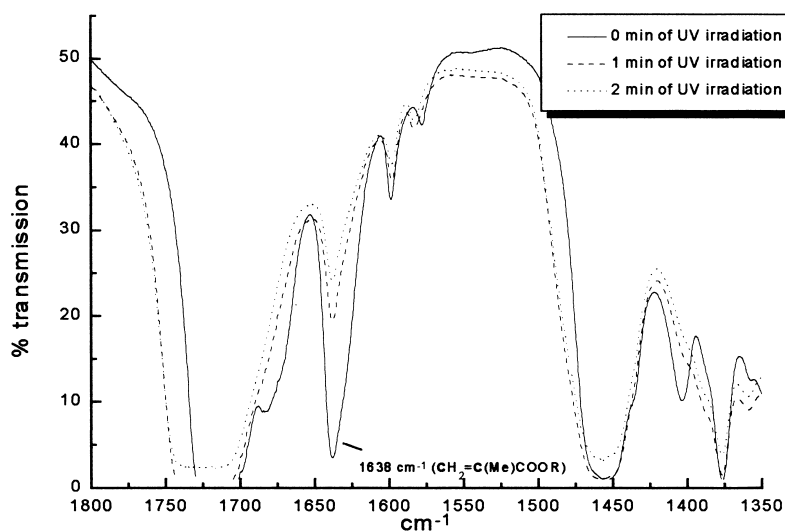
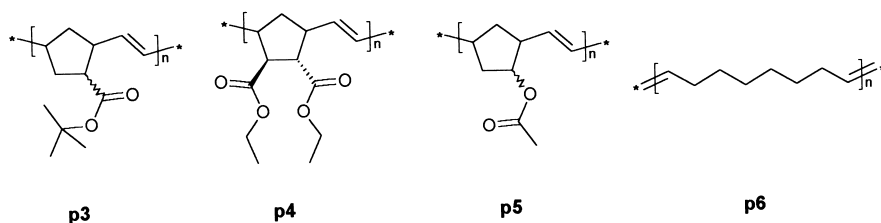Fig. 8. FT-IR spectra of cross-linking of methacrylic groups of **A**/**p2**.

Fig. 9. Further ROMP polymers grafted on the surface.

The methacrylic moiety provided us the possibility to cross-link the polymer obtained via ROMP to get a very hard but transparent layer on the polyolefin sample. Cross-linkage of the metharyclic groups when exposed to UV-irradiation was investigated by FT-IR spectroscopy by following the loss of intensity of the peak at 1637 cm^{-1} ($CH_2 = C(Me)COOR$) (Fig. 8). We also tested the mechanical properties of the samples with cross-linked layers. When bending occurred the samples broke, but the cross-linked layer did not split off.

3.4. Ring-opening metathesis polymerization of other monomers

Furthermore, we were polymerized monomer **3**, **4**, **5** and **6** (Fig. 9) on the surface of the copolymer to obtain **A**/**p3**, **A**/**p4**, **A**/**p5** and **A**/**p6**.

When grafting **p3** on the surface, a ROMP polymer with a *tert*-butyl ester moiety was obtained. The carboxylic acid can then be generated by treating such esters with strong acids in water. Here, a sample of copolymer **A**/**p3** was treated with HCl/dioxane to obtain a polymer with carboxylic groups (Fig. 10). This should enhance the hydrophilicity of the samples, be-
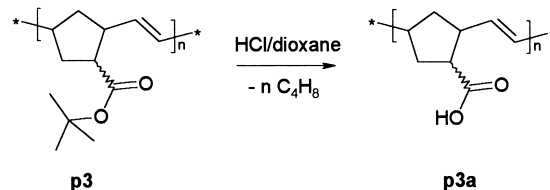
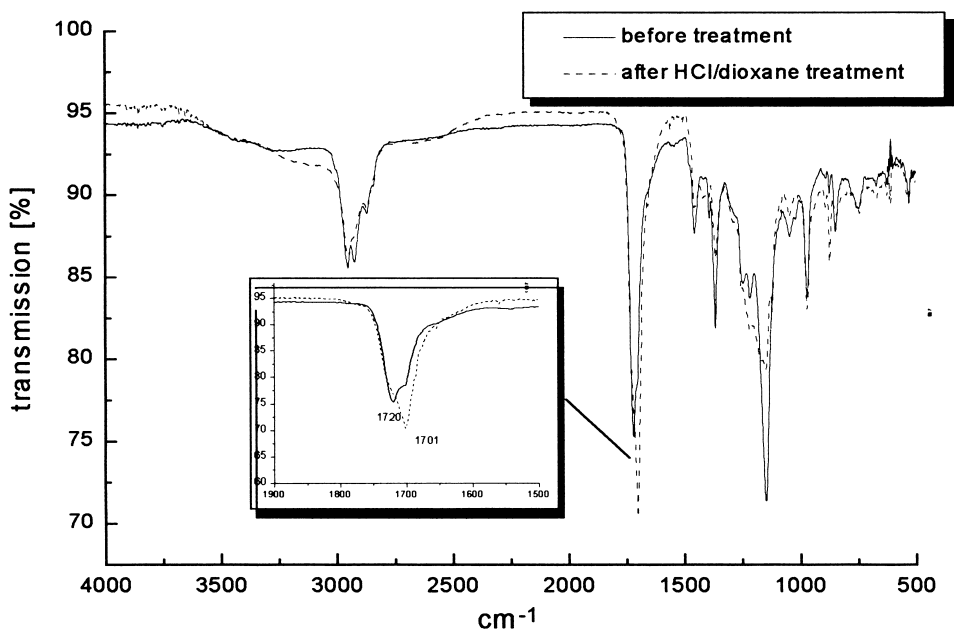Fig. 10. Modification of **A**/**p3** by hydrochloric acid.

Fig. 11. FT-IR spectra before and after treatment of copolymer **A/p3** sample by HCl/dioxane.

cause many applications require a hydrophilic surface. Fig. 11 shows the IR spectra before and after HCl treatment. The carbonyl peak of the carboxylic acid at 1701 cm^{-1} was found.
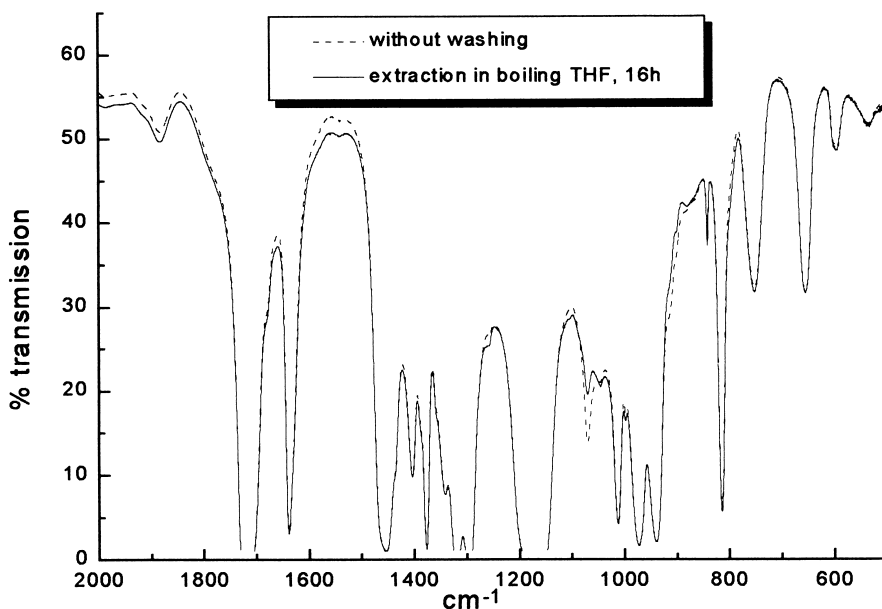

Fig. 12. FT-IR spectra of 50 μm film of **A/p2** before and after extraction in boiling THF.

By covering the polyolefin surface with poly-(octenamere) (**p6**), we got a rubber like surface. This should provide better compatibility with natural and synthetic rubbers, thus yielding interesting properties of such blends.

3.5. Extraction of romp polymers

As it cannot be excluded that a homopolymer was formed by non reacted carbene complexes during the described method, the removable part of polymer was determined. For doing this, the modified polymer films were extracted with THF for 16 h. Films before and after extraction showed no differences in the polymer peaks in the FT-IR spectra (Fig. 12). In addition, no polymer was found in the THF solution. We can now assume, that if some homopolymer was formed by nonreacted ruthenium–carbenes inside the copolymer **A**, entangled polymer chains must have been formed that could not be removed.

4. Conclusions

In this work, we were investigating a new method for grafting ROMP polymers on a polyolefin carrying vinyl groups. We showed that the fixing of the carbene complex **1** was possible via exchange of the alkylidene moiety. Hence, ROMP of different monomers can be initiated at the surface of the polyolefin samples. In order to test the possibilities of this new method, a number of monomers with various functionalities were investigated. Layers of grafted ROMP polymers bearing ester or methacrylic moieties were grown up to a thickness of 50 μm.

Surface modification via ROMP should make it possible to graft, e.g. norbornene derivatives carrying bioactive carbohydrates, aminoacids, or other defined functionalities onto the surface of polyolefins.

Acknowledgements

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