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Reactions of Titanocene Derivatives with Molecular Carboxylic Acids and Copolymers Bearing Carboxylic Acid Groups

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Linear, soluble copolymers containing titanium are of interest for use in targets for inertial-confinement fusion (ICF) experiments because the titanium is a useful spectroscopic probe for studying the nuclear fusion process. We have studied the reactions of dichlorotitanocene and diphenyltitanocene with carboxylic acids to determine if these can be used to prepare such polymers. Model reactions of dichlorotitanocene with *p*-toluic acid show that both mono- and di-carboxylates are formed. We have prepared a soluble titanium-containing copolymer via the reaction of poly(styrene-*co*-methacrylic acid) with an excess of dichlorotitanocene but attempts to remove the excess molecular titanocene from the copolymer result in crosslinking of the copolymer. Model reactions of benzoic and pivalic acids with diphenyltitanocene demonstrate that monosubstituted carboxylato(phenyl)titanocenes are formed but that these products are stable only at low temperatures and decompose readily at ambient temperature. Proton NMR studies of the reaction of diphenyltitanocene and benzoic acid at -20 °C indicate that this reaction is second order, suggesting that the reaction does not proceed through a benzyne intermediate. © 1997 by John Wiley & Sons, Ltd.

Keywords: laser fusion; titanium; metal-containing polymer; titanocene; carboxylic acid

INTRODUCTION

Soluble, linear, carbon-based copolymers containing elements such as chlorine, iodine or transition metals are of interest for use in the production of targets for laser inertial-confinement fusion (ICF) experiments.[1–3] In a typical ICF implosion experiment, a small plastic microballoon target containing gaseous deuterium (D_2) or deuterium–tritium (DT) is symmetrically exposed to extremely high-power radiation from a laser source. This radiation ablates the capsule wall and compresses the gaseous fuel to very high densities and temperatures, resulting in the initiation of nuclear fusion. Dopant atoms incorporated in the inner wall of the capsule can provide spectroscopic probes of the dynamics of the capsule implosion process.[3] Copolymers containing titanium are particularly interesting diagnostic materials because incorporation of titanium into the inner capsule wall or ‘mandrel’ gives rise to a relatively simple K-shell spectroscopic signal from the titanium atoms that are mixed into the hot, dense plasma during the implosion.[3]

To allow mandrel preparation using the available methods, the copolymers must have properties like those of polystyrene.[1,2] These include solubility in organic solvents such as methylene chloride and tetrahydrofuran, and sufficient mechanical strength to form stable microshells that serve as target mandrels. In addition, the titanium contents of the copolymers must be between 0.1 and 1.0 atom % (i.e. 0.1–1.0 titanium atoms per 100 total atoms) to allow observation of the K-shell spectra of titanium atoms in the plasma. Few, if any, titanium-containing polymeric materials described in the literature have this combination of characteristics. Some soluble polymeric materials

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containing titanium have been reported but their structures suggest that their mechanical properties are likely to be much different from those of polystyrene.[4–8] Many titanium-containing polymers have been reported for use in catalysis, but these are crosslinked insoluble resins.[7–13] Others, prepared by the interfacial condensation of diols with dichlorotitanocene[14] have one titanium atom per repeat unit, and thus have a titanium concentration that is generally too high to use as a diagnostic material for ICF. In addition, these polymers exhibit solubility and mechanical properties significantly different from polystyrene. Vinyl monomers have been prepared[15,16] and some are commercially available (Gelest, Inc., Tullytown, PA, USA), but no information concerning their copolymerization with styrene has been reported. Our attempts to prepare titanium-containing copolymers from styrene and vinyl titanate monomers will be described in a subsequent report (K. E. Branham, J. W. Mays, G. M. Gray and R. Cook, unpublished results).

In this paper, we describe our attempts to prepare linear, titanium-containing polymers via the reaction of dichlorotitanocene and diphenyltitanocene with copolymers with carboxylic acid substituents. Because many of the reactions of these titanocene derivatives with carboxylic acids have not been studied in detail, we also report the results of our studies of the titanocene derivatives with molecular carboxylic acids.

EXPERIMENTAL

Materials and methods

Triethylamine (Aldrich) was dried by refluxing for at least 12 h over calcium hydride. Tetrahydrofuran (THF, Fisher) and *p*-dioxane were dried by distillation from sodium and benzophenone. Toluene, benzene, hexanes and petroleum ether (all from Fisher) were dried over molecular sieves and sparged with dry nitrogen gas prior to use. Benzoic acid ($PhCO_2H$), toluic acid (CH_3-*p*-$C_6H_4CO_2H$), sodium *p*-toluate [Na(CH_3-*p*-$C_6H_4CO_2$)] (all from Aldrich) and azobisisobutyronitrile (AIBN, Kodak) were purified by recrystallization and dried under vacuum prior to use. Diphenyltitanocene (Cp_2TiPh_2), was prepared by literature methods[17,18] and was recrystallized from methylene chloride/hexanes prior to use. Methacryloyl chloride was prepared by the reaction of methacrylic acid (Fisher) and benzoyl chloride (Fisher) and was purified by distillation immediately after synthesis.[19] Pivalic acid [$(CH_3)_3CCO_2H$], dichlorotitanocene (Cp_2TiCl_2) and phenyl-lithium (all from Aldrich) were used as received. All air- or water-sensitive materials were handled either in a Vacuum Atmospheres dry box or in Schlenk glassware under a nitrogen or argon atmosphere or on a vacuum line.

Characterization methods

The ^1H NMR spectra were recorded on a GE NT-300, wide-bore, multinuclear NMR spectrometer and are referenced to internal tetramethylsilane (TMS). Chemical shifts downfield from that of TMS are reported as positive. A spectral width of 2000 Hz was used, and 16 000 data points were taken for each spectrum. Typically, 16 scans were run for each sample. The infrared spectra of solid samples in KBr disks were run on a Nicolet IR44 FT-IR spectrometer. A spectral window from 48000 cm^{-1} to 400 cm^{-1} was used for each spectrum and 16 scans were run for each analysis. KBr pellets were approximately 0.5–1.0 mm in thickness and contained 0.1–1.0% (w/w) of the compound being characterized. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA, USA.

Size-exclusion chromatography (SEC) was carried out on a system incorporating a Waters 510 pump, a Waters 410 differential refractive index detector and two Waters linear Ultrastyragel columns in series at 30 °C at a flow rate of 1 ml min^{-1}. Injections of 20 μl of THF solutions containing between 0.1% and 0.2% (w/v) of the polymer were used. The weight-average (M_w), number-average (M_n) and *z*-average (M_z) molecular weights and polydispersities (M_w/M_n) are based on a polystyrene calibration curve.

Reaction of dichlorotitanocene with sodium *p*-toluate

A mixture of Cp_2TiCl_2 (750 mg, 3.00 mmol) and Na(CH_3-*p*-$C_6H_4CO_2$) (475 mg, 3.00 mmol) was placed in a 100 ml round-bottom flask attached to a swivel-frit assembly. On a vacuum line, 60 ml of toluene was vacuum-transferred into the flask. This mixture was stirred overnight in a water bath at 50 °C. The solution was then cooled to room temperature and filtered on the swivel-frit to remove NaCl. The orange filtrate was concentrated until solids began to appear in the solution, slowly cooled to $-80\,^{\circ}C$ and filtered on the swivel-frit to yield an orange–red solid on the frit and an orange solution in the flask. The toluene was removed from the orange solution under vacuum and the solid on the frit was washed with petroleum ether. The swivel-frit and the flask were taken into the dry box, the orange–red solid (380 mg) containing a mixture of Cp_2TiCl_2 and the substituted products was removed and the flask containing the residue from the filtrate was placed in a clean swivel-frit. Toluene was vacuum-transferred into this flask to yield an orange solution. This was filtered and then the toluene was removed under vacuum to give a mixture of the substituted products as an orange solid (620 mg). The ^1H NMR spectrum of a $CDCl_3$ solution of this solid indicated that it was a mixture of Cp_2TiCl_2 [^1H NMR ($CDCl_3$): δ 6.59 (Cp, s, 10H)], $Cp_2TiCl[OC(O)C_6H_4$-*p*-CH_3][δ 7.79 (CH, d, $|^3J(HH)| = 12$ Hz, 2H); 7.20 (CH, d, $|^3J(HH)| = 12$ Hz, 2H); 6.57 (Cp, s, 10 H); 2.39 (Me, s, 3H)] and $Cp_2Ti[OC(O)C_6H_4$-*p*-$CH_3]_2$ [δ 7.94 (CH, d, $|^3J(HH)| = 12$ Hz, 4H); 7.25 (CH, d, $|^3J(HH)| = 12$ Hz, 4H); 6.61 (Cp, s, 10 H); 2.44 (Me, s, 6H)]. Only a trace of Cp_2TiCl_2 was present. Integration of the Cp resonances indicated that the ratio of $Cp_2TiCl[OC(O)C_6H_4$-*p*-$CH_3]$ to $Cp_2Ti[OC(O)$-C_6H_4-*p*-$CH_3]_2$ was 55:45.

Reaction of dichlorotitanocene with *p*-toluic acid in the presence of triethylamine

All operations were performed in a dry box. First, Cp_2TiCl_2 (750 mg, 3.00 mmol) was dissolved in 40 ml of THF in a 100 ml round-bottom flask and 0.50 ml (3.6 mmol) of NEt_3 was added to this solution. Next, CH_3-*p*-$C_6H_4CO_2H$ (410 mg, 3.00 mmol) was dissolved in 20 ml of THF and transferred to an addition funnel. This solution was added slowly to the Cp_2TiCl_2/NEt_3 solution over a 30-min period. After the addition was completed, the reaction mixture was stirred overnight in the dry box and then filtered. The THF was removed from this solution under vacuum to yield a sticky solid. This solid was washed with petroleum ether to give 1.160 g of the final product. The ^1H NMR spectrum of a $CDCl_3$ solution of this product indicated that this reaction yields the same three complexes as did the reaction of Cp_2TiCl_2 and $Na(CH_3$-*p*-$C_6H_4CO_2)$ but that the ratio of $Cp_2TiCl[OC(O)C_6H_4$-*p*-$CH_3]$ to $Cp_2Ti[OC(O)C_6H_4$-*p*-$CH_3)_2$ was higher (65:35).

Preparation of poly(styrene-*co*-methacryloyl chloride)

The following materials were placed in a 1-l three-necked round-bottom flask equipped with a magnetic stir bar, a thermometer adaptor and thermometer, a reflux condenser, and a gas inlet: 500 ml of dry benzene, 45.0 g (432 mmol) of inhibitor-free styrene, 5.00 g (47.8 mmol) of inhibitor-free methacryloyl chloride and 0.125 g (0.800 mmol) of AIBN. The system was purged with nitrogen for approximately 2 h, then heated to 50 °C in an oil bath. After 48 h, a second aliquot of AIBN (0.129 g, 0.800 mmol, in 5 ml of benzene) was added to the reaction mixture. Two more charges of AIBN were added at 48-h intervals. After 14 days, the copolymer was precipitated by pouring the reaction mixture into 1.6 l of hexanes in the dry box. The excess liquid was decanted, and the solid copolymer was collected and dried in a vacuum oven to yield 14.7 g of poly(styrene-*co*-methacryloyl chloride). SEC (THF): M_n, 21 000; M_w, 36 000; M_w/M_n, 1.7. Elemental analyses: C, 80.66, H, 7.33 Cl, 7.88%. From the C and Cl analyses, the styrene/methacryloyl chloride ratio was calculated to be 0.75:0.25 and 0.77:0.23. The average of these was used in the stoichiometry calculations in the next section.

Preparation of poly(styrene-*co*-methacrylic acid) and reaction with dichlorotitanocene

The following materials were placed in a 500 ml round-bottom flask and heated to reflux: 4.00 g of poly(styrene-*co*-methacryloyl chloride) (approximately 9.20 mmol of methacryloyl chloride), 200 ml of THF, 20 ml of triethylamine and 20 ml of deionized water. This mixture was refluxed until IR analysis of solid samples showed bands characteristic of carboxylic acid residues [IR (KBr disk): ν, 1810, 1740 cm^{-1}] and no band characteristic of acid chloride residues [IR (KBr disk): ν, 1800 cm^{-1}]. Next, the reaction mixture was transferred to a separatory funnel, and concentrated HCl was added until two phases formed and the THF phase became acidic to litmus paper. The THF phase was then evaporated to dryness, and the resulting solid was carefully dried on the vacuum line to remove traces of water. This solid polymer was dissolved in 250 ml of dry, distilled THF and 2.00 ml (14 mmol) of triethylamine and 3.54 g (14 mmol) of Cp_2TiCl_2 [^{1}H NMR ($CDCl_3$): δ 6.59 (Cp, s)] were added to this solution in the dry box. This mixture was stirred under nitrogen for five days until the color of the solution had changed from bright red to orange and considerable white solid (Et_3NHCl) had formed. The white solid was removed by filtration under nitrogen, and the clear filtrate was poured into 700 ml of hexanes in the dry box of precipitate the copolymer. The excess liquid was decanted, and the orange solid isolated and dried under vacuum. This solid was dissolved in 100 ml of THF, and this solution was poured into 700 ml of hexanes in the dry box to precipitate the polymer again. The excess liquid was decanted, and the solid isolated and dried under vacuum to yield 1.8 g of the final product. ^{1}H NMR ($CDCl_3$): δ 7.18 (phenyl, bs); 6.59, 6.46, 6.44, 6.43 (Cp groups, all s); 2.20, 1.95, 1.75 (methyne, methylene and methyl, all bs). SEC (THF): M_n, 21 000; M_w, 41 000; M_z 86 000; M_w/M_n, 1.9.

Reaction of diphenyltitanocene with benzoic acid in refluxing dioxane

This reaction was conducted by a modification of literature procedures.[20,21] A solution of 1.27 g (3.83 mmol) of Cp_2TiPh_2 and 0.49 g (4.0 mmol) of benzoic acid in 100 ml of dioxane was prepared under argon gas in a 250 ml Schlenk flask and purged with argon for 1 h. By this time the reaction mixture had become lighter, indicating that a reaction was taking place at room temperature. Next, the flask was equipped with a reflux condenser and the solution was subjected to reflux for 2 h under argon. The reaction mixture was allowed to cool and the dioxane removed *in vacuo*. A black powdery solid was obtained in a quantitative yield.

^{1}H NMR study of the reaction of diphenyltitanocene with benzoic acid at 21 °C

A solution of 13.0 mg (0.0392 mmol) of Cp_2-$TiPh_2$ in 0.8 ml of $CDCl_3$ was prepared in the dry box in a 5 mm NMR tube, and a ^{1}H NMR spectrum of this solution was run [^{1}H NMR ($CDCl_3$): δ 6.92 (phenyl, m, 10H); 6.20 (Cp, s, 10 H)]. Next 5.0 mg (0.040 mmol) of $PhCO_2H$ was added, and the reaction was followed by ^{1}H NMR spectroscopy. After 15 min, the resonances due to Cp_2TiPh_2 and $PhCO_2H$ [^{1}H NMR ($CDCl_3$): δ 8.13 (phenyl, m, 2H); 7.62 (phenyl, m, 1H), 7.48 (phenyl, m, 2H)] had disappeared, and new resonances due to benzene [^{1}H NMR ($CDCl_3$): δ 7.36 (CH, s, 6H)] and $Cp_2TiPh[OC(O)Ph]$ {^{1}H NMR ($CDCl_3$): δ 7.90 [C(O)–phenyl, m, 2H]; 7.52 [C(O)–phenyl, m, 1H]; 7.48 [C(O)–phenyl, m, 2H]; 7.10 (Ti-phenyl, m, 5H); 6.37 (Cp, s, 10 H)} had appeared. After 3 h, the orange solution had become much darker, and a ^{1}H NMR spectrum indicated that a variety of new, unidentified products were being formed. A final ^{1}H NMR spectrum, recorded 24 h after the solution was prepared, was extremely complex and indicated that none of the $Cp_2TiPh(OC(O)Ph)$ remained in the solution.

^{1}H NMR study of the reaction of diphenyltitanocene with benzoic acid at −20 °C

A solution of 20.4 mg (0.0615 mmol) of Cp_2TiPh_2 in 0.40 ml of $CDCl_3$ was prepared in the dry box in a 5 mm NMR tube fitted with a septum cap. At the same time, a solution of 7.50 mg (0.0615 mmol) of $PhCO_2H$ in 0.4 ml of $CDCl_3$ was prepared in a vial fitted with a septum cap. The $PhCO_2H$ solution was added to the Cp_2TiPh_2 solution in the NMR tube using a syringe, and then the tube was placed in the NMR probe at −20 °C. The reaction was monitored over 2.5 h using ^{1}H NMR spectroscopy, and the course of the reaction was followed by integrating the Cp resonances of the Cp_2TiPh_2 and $Cp_2TiPh[OC(O)Ph]$ complexes. These data are given in Table 1, and a plot of the $1/[Cp_2TiPh_2]$ vs time is shown in Fig. 1. No decomposition of the product was observed during this time.

To determine how stable the product was at −20 °C, the sample was removed from the probe, transported to a freezer in a dry ice/acetone bath and stored for six days. Then, a final ^{1}H NMR spectrum was recorded at −21 °C. This spectrum was identical to that of the solution taken six days earlier.

^{1}H NMR study of the reaction of diphenyltitanocene with pivalic acid at 21 °C

A solution of 18.5 mg (0.0557 mmol) of Cp_2TiPh_2 in 0.5 ml of $CDCl_3$ was prepared in the dry box. At the same time a solution of 5.70 mg (0.0559 mmol) of $(CH_3)_3CCO_2H$ in 0.5 ml of

Table 1. Data from the reaction of diphenyltitanocene with benzoic acid at −20 °C

Time (min)	Integration of the Cp resonance of $Cp_2Ti\ Ph(OC(O)Ph)$[a]	Integration of the Cp resonance of Cp_2TiPh_2[a]	Mole fraction[b] of $Cp_2\ Ti\ Ph(OC(O)Ph)$	Mole fraction of Cp_2TiPh_2
0	0.00	1.00	0.00	1.00
18	1.00	1.15	0.47	0.53
34	1.00	0.65	0.61	0.39
57	1.00	0.36	0.74	0.26
88	1.00	0.23	0.81	0.19
148	1.00	0.13	0.88	0.12

[a] These data were normalized to the initial value of the integral.

[b] The mole fractions can be converted to molarities by multiplying by the initial concentration of the Cp_2TiPh_2, 0.0767 M

$CDCl_3$ was also prepared in the dry box [^1H NMR ($CDCl_3$): δ 1.23 (methyl, s)]. The solutions were mixed in a 5-mm NMR tube in the dry box, and then the tube was placed in the NMR probe. The reaction was monitored using ^1H NMR spectroscopy. After 13 min, resonances for $Cp_2TiPh(OC(O)C(CH_3)_3)$ [^1H NMR ($CDCl_3$): δ 7.00 (phenyl, m, 6H); 6.24 (Cp, s, 10H); 1.17 (methyl, s, 9H)] and benzene [^1H NMR ($CDCl_3$): δ 7.36 (s)] as well as those from the starting materials were observed. After 2 h 40 min, the resonance for $(CH_3)_3CCO_2H$ completely disappeared and $Cp_2TiPh[OC(O)C(CH_3)_3]$ was the major product. This solution still contained a small amount of Cp_2TiPh_2 and two unidentified singlets at 6.40 ppm and 0.69 ppm. After 22 h 40 min, significant decomposition had occured and a variety of new resonances in the 6–8 ppm region had appeared although some $Cp_2TiPh[OC(O)C(CH_3)_3]$ was still present in the solution.

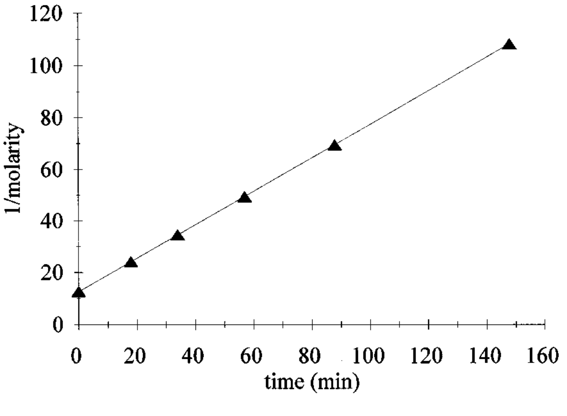


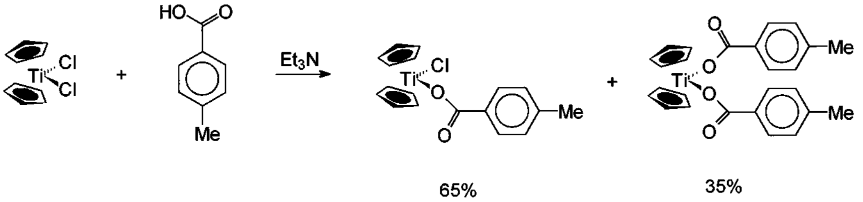
Figure 1 Plot of $1/[Cp_2TiPh_2]$ versus time (min) for the reaction of Cp_2TiPh_2 and $PhCO_2H$ at −20 °C.

RESULTS AND DISCUSSION

There are two general routes to the preparation of linear polymers containing transition-metal complexes as substituents: macromolecular modification and the polymerization of metal-containing monomers. Macromolecular modification, the method investigated in this report, involves the coordination of groups on polymer chains to metal precursor complexes. The appeal of macromolecular modification for the preparation of titanium-containing copolymers is that the reactive titanium-complex substituents are introduced after the polymerization has taken place and, thus, do not have to survive under the polymerization conditions.

The ideal titanium precursor complex for preparing linear titanium-containing copolymers by macromolecular modification should contain only one coordination site, to avoid crosslinking of the polymer through the metal center. Unfortunately, no titanium(IV) complexes with a single reactive group are readily available.

Several literature reports suggest that titanocene derivatives of the type Cp_2TiX_2 can react with carboxylic acids to form both mono- and dicarboxylates.[20–25] These results suggest that it may be possible to prepare soluble titanium-containing copolymers by reacting these titanocenes with copolymers bearing carboxylic acid residues if the first X group is replaced at a significantly higher rate than is the second. Two copolymers that contain carboxylic acid residues and have mechanical properties much like those of polystyrene are poly(styrene-*co*-methacrylic acid) and poly[styrene-*co*-(4-carboxystyrene)]. These copolymers can be prepared with reasonable molecular weights, polydispersities and



[1]

comonomer compositions using well-known free-radical polymerization methods.

In order to determine whether the reactions of titanocene derivatives and copolymers bearing carboxylic acid residues can be used to prepare soluble linear polymers, we have studied the reactions of Cp_2TiCl_2 with CH_3-*p*-$C_6H_4CO_2H$ and $Na(CH_3$-*p*-$C_6H_4CO_2)$, and the reactions of Cp_2TiPh_2 with $PhCO_2H$ and $(CH_3)_3CCO_2H$, as models for reactions with polymers containing either carboxystyrene or methacrylic acid groups. We have also carried out the reaction of Cp_2TiCl_2 with the poly(styrene-*co*-methacrylic acid) copolymers. The results of these studies are discussed in detail below.

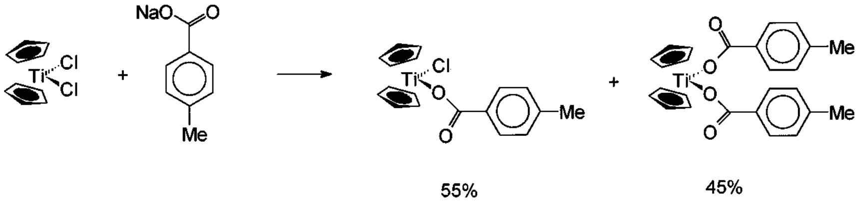
Reaction of dichlorotitanocene with *p*-toluic acid and sodium *p*-toluate

The 1:1 reactions of Cp_2TiCl_2 with either Ch_3-*p*-$C_6H_4CO_2H$ or $Na(CH_3$-*p*-$C_6H_4CO_2)$ in THF gave (in addition to unreacted Cp_2TiCl_2) mixtures of mono- and di-substituted products, as determined from integration of the cyclopentadienyl ^1H NMR resonances (Eqns [1] and [2]). Analysis of the product mixture obtained from the reaction of CH_3-*p*-$C_6H_4CO_2H$ and Cp_2TiCl_2 indicated that 65% of the product was the monosubstituted titanocene, $Cp_2TiCl[OC(O)C_6H_4$-*p*-$CH_3]$, and 35% of the product was the disubstituted titanocene, $Cp_2Ti[OC(O)C_6H_4$-*p*-$CH_3]_2$. The ratio of mono- to di-substituted products obtained from the reaction of $Na(CH_3$-*p*-$C_6H_4CO_2)$ with Cp_2TiCl_2 was 55:45. The difference in the relative amounts of the mono- and di-substituted products in these two reactions is probably due to the greater nucleophilicity of the $Na(CH_3$-*p*-$C_6H_4CO_2)$ relative to the $[(CH_3CH_2)_3NH]^+[O_2CC_6H_4$-*p*-$CH_3]^-$ which results in a lower selectivity for displacing the chloride from Cp_2TiCl_2.

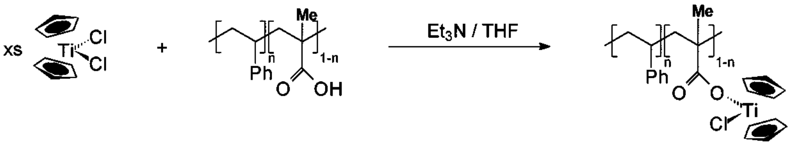
Reaction of dichlorotitanocene with poly(styrene-*co*-methacrylic acid) copolymers

Although the reaction of Cp_2TiCl_2 with CH_3-*p*-$C_6H_4CO_2H$ did not give only the monosubstituted complex, more of this complex was formed. This suggested that it might be possible to prepare linear chlorotitanocene-substituted copolymers if an excess of Cp_2TiCl_2 was used. Indeed, the reactions of a poly(styrene-*co*–methacrylic acid) copolymer (M_w, 36 000; M_w/M_n, 1.7) with a 50% excess of dichlorotitanocene and under reasonably high dilution conditions yielded a soluble, linear polymer (M_w=41 000, M_w/M_n=1.9) (Eqn [3]). The small changes in M_w and M_w/M_n are strong evidence that the functionalization proceeds without crosslinking under these conditions. The small increase in M_w is probably due to incorporation of the heavier Cp_2TiCl groups into the methacrylic acid repeat units. A slight increase in M_w/M_n is expected for a polymeric material contaminated with a molecular substance such as Cp_2TiCl_2.

The ^1H NMR spectra of this material show resonances due to Cp_2TiCl_2 at 6.59 ppm and resonances at 6.46 ppm, 6.44 ppm, 6.43 ppm and 6.25 ppm assigned to Cp_2TiCl groups bound to carboxylate groups in the copolymer. The presence of several resonances for bound titanocene groups is most likely due to some 'blocky' character in the copolymer which would give rise to different microstructures along the polymer chain. We were unable to estimate confidently



[2]



[3]

the ratio of free titanocene complexes to bound complexes because all of the Cp resonances fall on top of one of the broad resonances due to phenyl protons in styrene repeat units, making accurate integration impossible.

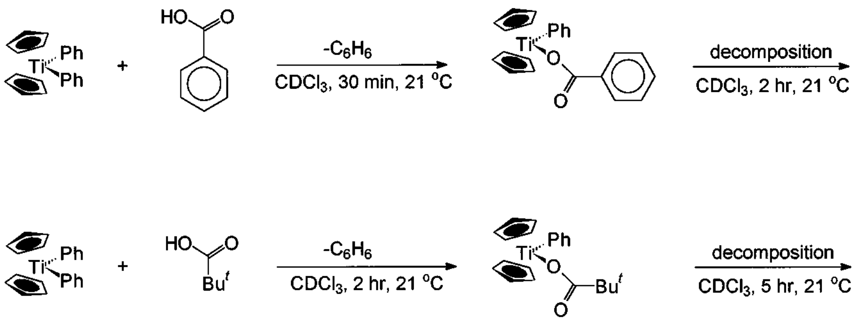
All attempts to separate the Cp_2TiCl_2 from the copolymer by reprecipitation were unsuccessful. All reprecipitation attempts resulted in the isolation of insoluble materials, presumably due to crosslinking in the absence of excess Cp_2TiCl_2. Elemental analysis of the soluble mixture would not allow estimation of the ratio of free to bound titanocene complexes. Only a total percentage of titanium could be determined. These data were not obtained because this approach showed little promise for successfully preparing soluble and homogeneous materials. It does not appear that this method will allow preparation of materials suitable for mandrel production because the presence of a molecular contaminant in the titanium-containing copolymer may have adverse effects on the quality of mandrels prepared from such a material.

Reaction of benzoic and pivalic acids with diphenyltitanocene

When heated to temperatures greater than 80 °C, Cp_2TiPh_2 loses benzene to form benzynetitanocene.[22] This complex reacts with protic acids, HXR (X = O, N; R = alkyl, aryl), to form the corresponding $Cp_2TiPh(XR)$ complexes.[20,21,23] These results suggested that the reaction of benzynetitanocene with carboxylic acids should yield carboxylato(phenyl)titanocenes, $Cp_2TiPh[OC(O)R]$. However, Shakshooki[24] has reported that carboxylic acids react with Cp_2TiPh_2 to form bis(carboxylato)titanocenes, $Cp_2Ti[OC(O)R]_2$, but no experimental details or spectroscopic data were provided. Thus, before attempting to react Cp_2TiPh_2 with carboxylic acid-functionalized polymers, we attempted to resolve these conflicting reports by studying the reactions of Cp_2TiPh_2 with $PhCO_2H$ and $(CH_3)_3CCO_2H$ as models for the polymers. Our initial attempt to prepare benzoato(phenyl)titanocene from Cp_2TiPh_2 and $PhCO_2H$ was carried out in refluxing dioxane under an argon atmosphere. Under these conditions, a benzyne complex would be formed.[21] This reaction did not yield the desired $Cp_2TiPh[OC(O)Ph]$ complex. Both the ^1H NMR spectrum of the reaction mixture residue, which contained a number of Cp resonances, and the dark color of the isolated product suggested that decomposition had occurred.

The color of the diphenyltitanocene solution in the previous reaction changed after benzoic acid was added at room temperature but before heating was begun. This suggested that these compounds would react at ambient temperature and that the reaction probably would not involve a benzyne intermediate because these do not form below 80 °C. In order to determine if a reaction was occurring at ambient temperature, we followed the reactions of Cp_2TiPh_2 with $PhCO_2H$ and $(CH_3)_3CCO_2H$ at 21 °C using ^1H NMR spectroscopy. These studies indicated that the carboxylato(phenyl)(titanocenes were the initial products formed in these reactions (Eqn [4]). The reaction of Cp_2TiPh_2 with $PhCO_2H$ was quite clean and was complete after 15 min at 21 °C. The reaction of Cp_2TiPh_2 with $(CH_3)_3CCO_2H$ was complete after 2 h 40 min at 21 °C as measured by the disappearance of the ^1H NMR resonance of the $(CH_3)_3CCO_2H$. However, this reaction was not as clean as that of Cp_2TiPh_2 and $PhCO_2H$, and ^1H NMR resonances for Cp_2TiPh_2 and by-products (6.34 and 0.69 ppm) were observed after those of the $(CH_3)_3CCO_2H$ had disappeared. The rate of reaction of Cp_2TiPh_2 with carboxylic acids appears to be influenced by steric effects, with the bulkier $(CH_3)_3CCO_2H$ reacting much more slowly.

The carboxylato(phenyl)titanocenes are not stable at room temperature and decompose to form numerous unidentified products (Eqn [4]). The rate of decomposition, like the rate of the formation, also depends on the steric bulk of the carboxylic acid, with $Cp_2TiPh[O(O)CPh]$ decomposing more rapidly than $Cp_2TiPh[O(O)CC(CH_3)_3]$. This decomposition does not appear to involve the formation of bis(carboxylato)titanocenes. We have prepared an authentic sample of the bis(benzoato)titanocene



[4]

from dichlorotitanocene and benzoic acid[25] but see no ^1H NMR resonances in the NMR spectra of any of the solutions corresponding to the Cp groups in this complex [^1H NMR ($CDCl_3$): δ 6.63]. These results are in contrast to those of Shakshooki.[24] The instabilities of the carboxylato(phenyl)titanocenes do not appear to be due to the solvent, as similar results were obtained when the reactions were carried out in tetrahydrofuran-d_g. Because the processing of mandrels requires that the polymers be stable at elevated temperatures, no studies of the reactions of diphenyltitanocene and poly(styrene-*co*-methacrylic acid) copolymers were carried out.

Although these reactions are not useful for the preparation of linear titanium-containing polymers for laser fusion experiments, their mechanisms are of interest. As mentioned above, the rate of the reaction depends on the nature of the carboxylic acid and the reaction occurs rapidly at ambient temperature. To gain more insight into the mechanism, we followed the reaction of Cp_2TiPh_2 with $PhCO_2H$ at -20 °C using ^1H NMR spectroscopy. The integrations for the cyclopentadienyl resonances of Cp_2TiPh_2 and $Cp_2TiPh[OC(O)Ph]$ and the mole fractions of these complexes are given in Table 1. A plot of $1/[Cp_2TiPh_2]$ versus the time is given in Fig. 1. Because the initial concentrations of the two reactants were the same, the reaction is second order overall, and presumably first order in each component. The rate constant for this reaction, determined by a linear regression analysis of the data, is $0.646 \pm 0.007\ \text{M}^{-1}\ \text{min}^{-1}$ ($r^2 = 0.999$). These data support the suggestion, made above, that the reaction does not proceed via a benzyne-titanocene because this reaction would be expected to exhibit unimolecular kinetics.[22] The data are consistent with a mechanism in which a rate-determining nucleophilic attack of the $PhCO_2H$ on the Cp_2TiPh_2 is followed by the rapid elimination of benzene from the molecule.

CONCLUSIONS

The reactions of dichloro- and diphenyltitanocene with carboxylic acids are not a useful route for the formation of stable, linear titanium-containing polymers. Both chlorides in the dichlorotitanocene are displaced by carboxylic acids unless excess dichlorotitanocene is present. This results in insoluble, crosslinked polymers. Diphenyltitanocene does react with carboxylic acids to form carboxylato(phenyl)titanocenes. However, these complexes are unstable and decompose at ambient temperatures. This means that polymers containing such groups would not be stable under the conditions used in mandrel production.

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