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The cyclopentadienyltitanium trichloride/MAO-catalysed polymerisation of methyl acrylate and copolymerisation with styrene and isoprene

Ian D. Cunningham (✉), Khatereh Fassihi

Chemistry, University of Surrey, Guildford, GU2 7XH, UK
e-mail: i.cunningham@surrey.ac.uk, Fax: +44 (0)1483 686851

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Summary

The polar electron-deficient alkene methyl acrylate was readily polymerised in good yield by the $CpTiCl_3$-MAO system to give a polymer with a relatively low molecular weight, but reasonable polydispersity. The polymer appears to be atactic. The same system also gave a random sequence 1:1 copolymer of methyl acrylate and styrene, which according to NMR and SEM studies was a true copolymer rather than a blend.

Introduction

The cyclopentadienyltitanium trichloride-methylaluminoxane ($CpTiCl_3$-MAO) system is an efficient and versatile one for the polymerisation of alkenes such as styrene [1, 2], 1-vinylcyclohexene [3], 1,3-butadiene [2] and 4-methylpenta-1,3-diene [2, 4]. In particular, polymerisation of styrene yields the syndiotactic polymer [5]. Until recently, the alkenes polymerised or co-polymerised [6, 7, 8] by $CpTiCl_3$-MAO and related (*e.g.* metallocene) homogeneous catalysts have been non-polar relatively electron-rich ones; there has been little evidence of analogous polymerisation of polar electron-deficient alkenes. In addition, whilst free-radical, anionic and, more recently [9] ‘living’ polymerisation procedures for the homopolymerisation of acrylates are well-established, efficient *co-polymerisation* is still problematic [10]. A patent reports the co-polymerisation of styrene and a variety of acrylates and methacrylates using MAO and $(Me_5Cp)Ti(OMe)_3$, but little detail is given [11]. Interestingly, a more recent paper described the homopolymerisation of methyl methacrylate and its copolymerisation with styrene in the presence of the somewhat more esoteric catalyst system, Zn-reduced $(Me_5Cp)TiMe_3$+$Ph_3C^+B(C_6F_5)_4^-$, but levels of acrylate incorporation were low [12].

Given the established versatility and ready availability of the $CpTiCl_3$-MAO system, we wished to explore its potential for polymerisation of acrylates, and to attempt electron-deficient and electron-rich alkene co-polymerisation. In this report we describe the efficient polymerisation of methyl acrylate by the $CpTiCl_3$-MAO system, and the co-polymerisation of methyl acrylate with styrene and isoprene.

Experimental part

Materials

Methyl acrylate (Acros, 99% stabilised with 200 ppm monomethyl ether hydroquinone), isoprene (Aldrich, 99%) and cyclopentadienyltitanium trichloride (Aldrich, 97%) were used as received. Toluene (BDH) was distilled under N_2 from P_2O_5 (Fisher Scientific) and the fraction at 108 °C collected. Styrene (Aldrich, 99%) was dried by distillation at *ca.* 30 mmHg from CaH_2 (Aldrich). The HCl/methanol solution used in the workup was prepared by bubbling HCl gas (generated by dropping hydrochloric acid into *conc.* sulphuric acid) into methanol (BDH). The MAO (Aldrich, 10% w/w solution in toluene) was used as received.

Measurements

Gel Permeation Chromatography was carried out using THF as mobile phase on a Millipore with RI Detector ERC – 7516, Erma Optical Works Ltd. The pump delivery speed was 1.0 cm^3 min^{-1}, the injection volume = 20 mm^3 and the sample was 0.02 g in 1 cm^3 of THF. NMR spectra were obtained at 300 MHz using a Bruker AC 300 Spectrometer. The solvent was $CDCl_3$ and the reference TMS; samples were prepared by dissolving *ca.*10 mg sample in *ca.* 0.5 solvent in a 5 mm NMR tube. IR spectra were obtained using a Perkin Elmer 2000 FTIR spectrophotometer.

Polymerisation of methyl acrylate

The polymerisation of styrene was carried out using a slight modification of the method of Zambelli *et al.* for polystyrene [1].

A 3-necked 250 cm^3 round-bottomed flask was set up with a stopper, a septum and a connection to a vacuum pump, manometer and dry N_2 supply. Methyl acrylate (10.0 cm^3, 9.6 g, 112 mmoles) and sodium-dried toluene (15 cm^3) were placed in the flask along with a stirring bar. To this was added cyclopentadienyl titanium trichloride ($CpTiCl_3$) (9.0 mg, 0.041 mmoles). The apparatus was evacuated and filled with N_2 three times before a slow flow of N_2 was allowed across the system. The 10% MAO/toluene (0.9 cm^3, *ca.* 1.2 mmoles) was added carefully through the septum, with the tip of the needle *below* the surface of the solvent. The reaction was quickly heated to 50 °C on an oil bath and maintained at this temperature, with stirring, for 4 h. Upon cooling, the reaction was opened to the air and HCl/methanol solution (*ca.* 25 cm^3) was carefully added. The solution was allowed to stir at room temperature for 20 min after which the precipitated solid was collected by vacuum filtration. It was allowed to dry in the air or in an oven at 60 °C. The product was a a rubbery solid (4.9 g, 51%); ^1H NMR showed traces of residual toluene, so a small sample was dissolved in chloroform and precipitated by addition of hexane to give poly(methyl acrylate) as a white solid. IR (KBr) υ cm^{-1}: 2960-2850 (aliphatic H), 1730 (ester C=O); ^1H NMR ($CDCl_3$) ppm: 1.4 –1.6 (*ca.* 0.5 H, br m), 1.6-1.8 (*ca.* 1 H, br s), 1.8-2.0 (*ca.* 0.5 H, br m), 2.2-2.4 (1 H, br s), 3.66 (3 H, br s).

Co-polymerisation

The co-polymerisation of methyl acrylate and styrene was carried out similarly, except that methyl acrylate (15 cm^3, 14.34 g, 166 mmoles) and styrene (15 cm^3, 13.635 g, 131 mmoles) were used in place of just methyl acrylate. Samples were analysed after 72 h. Similarly, the co-polymerisation of methyl acrylate and isoprene involved methyl acrylate (15 cm^3, 14.34 g, 166 mmoles) and isoprene (15 cm^3, 10.215 g, 150 mmoles).

Results and discussion

Polymerisation

Heating of methyl acrylate, with $CpTiCl_3$ and MAO, in toluene under N_2 at 50 °C for 4 h followed by workup in acidified methanol gave poly(methyl acrylate) as a rubbery solid in 51% yield [13]. An infrared spectrum was comparable to a reference spectrum [14]. The yield here is higher than in other published reports. For example, the Zn-reduced $(Me_5Cp)TiMe_3/Ph_3C^+B(C_6F_5)_4^-$ system polymerised methyl methacrylate to *ca.* 22%, and yield was limited by deactivation of the catalyst after 30 minutes [12].

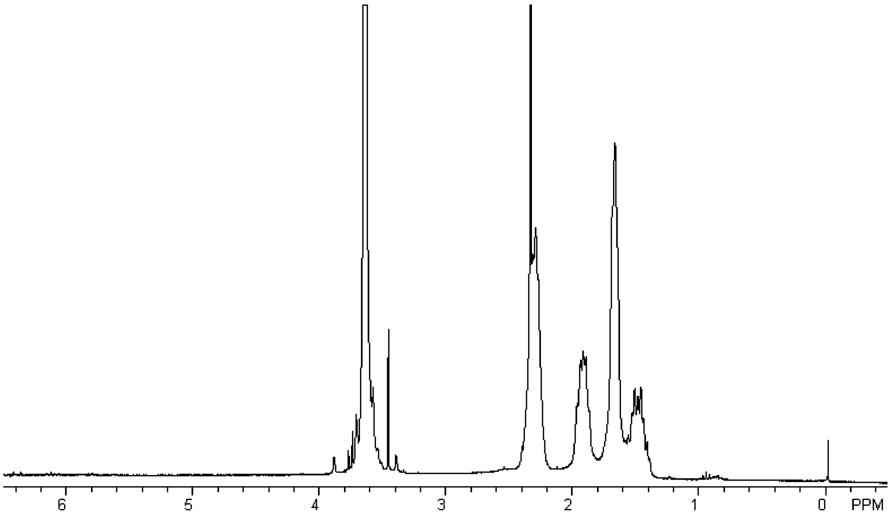

Figure 1. H NMR spectrum of poly(methyl acrylate)

In our case the deactivation occurs after 4 h, and extending the reaction time to 24 h resulted in only a slight yield increase to 55%. Furthermore, our system polymerises methyl acrylate under dilute (toluene) conditions, in contrast to the above system where neat monomer is required. The product proved to be fairly intractable when pure, but a H NMR spectrum prior to complete removal of solvent toluene shows the main spectral features of the polymer (Figure 1). The peak at 3.55 ppm is assigned to the ester methyl hydrogens, and that at 2.25 ppm to the methine (α-H) hydrogens (the sharp peak is due to residual toluene). The remaining signals, due to the methylene hydrogens are distributed over three distinct signal groups centred at 1.85, 1.60 and 1.45 ppm. Multiplet signals centred at 1.85 and 1.45 ppm are characteristic of two non-equivalent β-H in a *m* environment ($H_{a'}$, $H_{a''}$) (Figure 2), while the signal at 1.60 ppm is characteristic of two equivalent β-H in a *r* environment (H_a). The *m* and *r* signals integrate approximately equally.

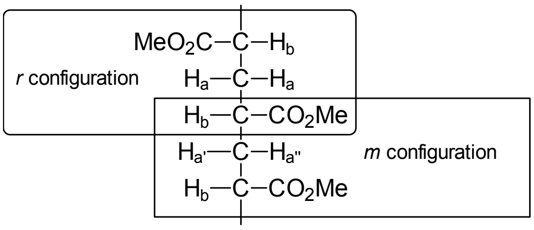

Figure 2. H NMR environments in poly(methyl acrylate)

Clearly the polymer is neither syndiotactic or isotactic, and while an atactic polymer is most likely, the relative narrowness of the peaks (peak at 1.60 ppm is ca. 0.075 ppm at ½ height) allows the possibility of true heterotacticity (e.g. mrmrmr).

GPC analysis gave $M_n = 7800$, $M_w = 15000$, PDI = 1.9. This is a rather small polymer and corresponds to a DP of 91-174, although the polydispersity is reasonable compared to some literature values for this type of catalyst system [1, 7, 12, 15].

Copolymerisation

Copolymerisation of methyl acrylate and styrene under similar conditions, but for 72 h, gave a rubbery solid product in 32% yield. The infrared spectrum of the product showed a strong carbonyl peak at 1729 cm^{-1} characteristic of poly(methyl acrylate), but also peaks 3000-3100 cm^{-1} and at 1602 cm^{-1} characteristic of polystyrene. The H NMR spectrum clearly shows broad peaks characteristic of both polymerised styrene (Ar-H at 6.5 – 7.6 ppm) and polymerised methyl acrylate ($CO_2C\underline{H}_3$ at 3.1 – 3.8 ppm) in addition to a region of peaks (1.0 – 2.5 ppm) from both types of polymer. Repeated washing with acetone did not change the ratio of the polystyrene to poly(methyl acrylate) peaks, which remained at *ca.* 1:1. The $CO_2C\underline{H}_3$ signal at 3.1 – 3.8 ppm is much broader and less well-defined than in the poly(methyl acrylate).

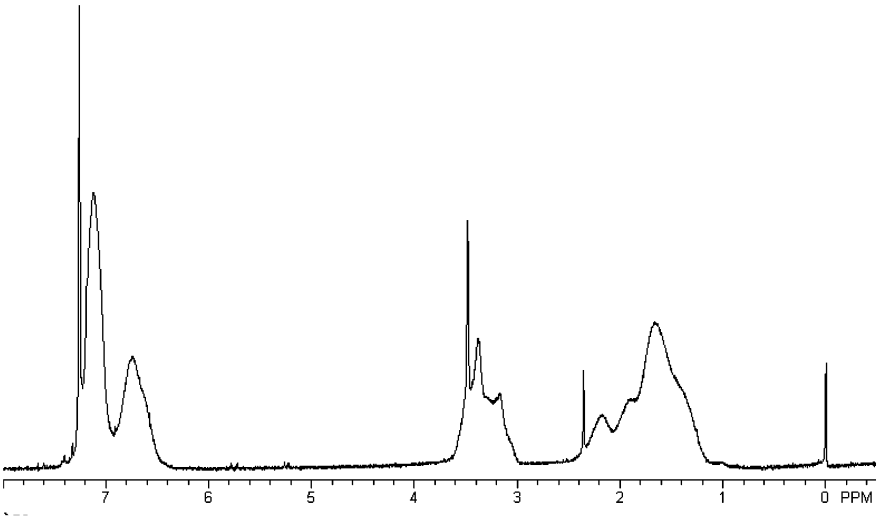

Figure 3. H NMR spectrum of methyl acrylate-styrene co-polymer

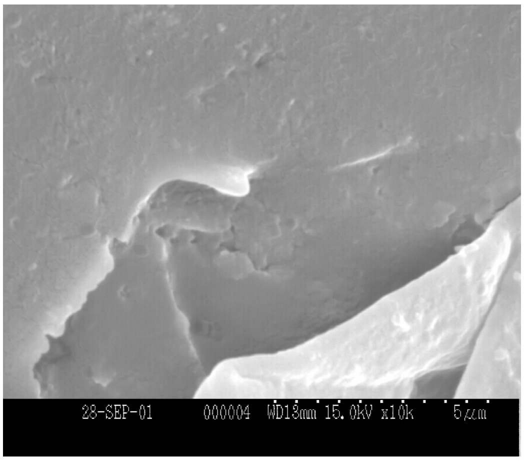

Figure 4. SEM image of methyl acrylate-styrene copolymer (the image spans 12 µm)

The broadness of the peaks, particularly that for the ester methyl group, suggests copolymer with a random sequence distribution, probably without stereoregularity. The H NMR spectrum also argues against a simple blend of polystyrene and poly(methyl acrylate), and indeed against a block copolymer, since both of these would give an NMR spectrum that is a superimposition of those for polystyrene and poly(methyl acrylate).

The methyl acrylate-styrene copolymer was examined using a Scanning Electron Microscope and showed homogeneity down to sub-µm resolution (Figure 4) [16].

The copolymerisation here contrasts with that for the Zn-reduced $(Me_5Cp)TiMe_3/Ph_3C^+B(C_6F_5)_4^-$ system, where a similar mixture of methyl methacrylate and styrene gave only low yields of low M_n atactic polystyrene homopolymer [12].

Copolymerisation of methyl acrylate and isoprene (2-methylbuta-1,3-diene) gave a rubbery solid in 7% yield after 72 h at 50 ^{o}C. The infrared spectrum showed peaks due to =C-H and C=O at 3021 and 1729 cm^{-1}, respectively. The H NMR spectrum is shown in Figure 5.

The NMR shows clearly the presence of =C-H signals (5.10 ppm) and $–CO_2C\underline{H}_3$ signals (3.65 ppm) as well as a fairly clearly defined spectrum at 1.4 – 2.6 ppm. The single, if broad, =C-H peak suggests 1,4 polymerisation of the isoprene, and integration indicates an approximate 2:1 ratio of isoprene to methyl acrylate units. However, the contrast between the broadness of the =C-H signal and relative sharpness of the $–CO_2C\underline{H}_3$ signal might be indicative of a blend of homopolymers, although examination by SEM again showed homogeneity down to sub µm levels.

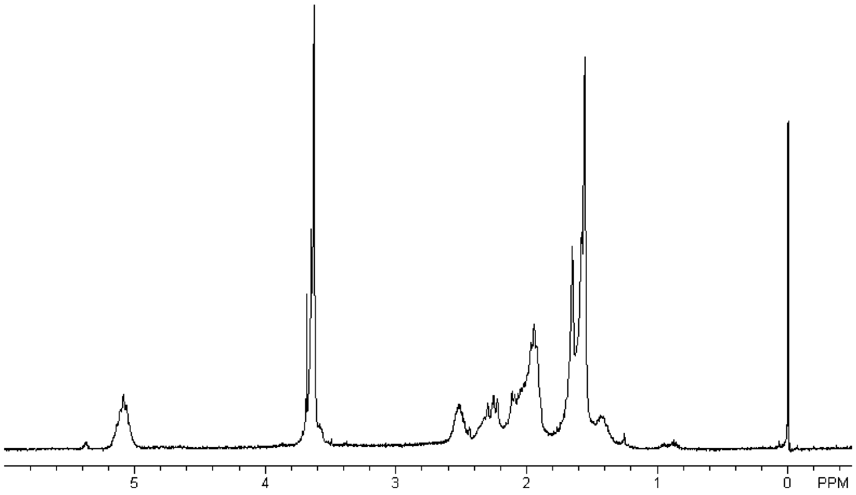

Figure 5. H NMR spectrum of methyl acrylate-isoprene co-polymer

A styrene-isoprene copolymer was also prepared in low yield (4% after 72 h). It gave a H NMR spectrum showing broad Ar-H, =C-H and aliphatic C-H signals similar to published spectra [6].

Conclusions

The readily-available $CpTiCl_3$/MAO catalyst system, extensively used hitherto for the polymerisation of electron-rich alkenes, has been shown to effect polymerisation of the polar electron-deficient alkene methyl acrylate. The polymer was obtained in good yield, and despite a relatively low molecular weight (M_n = 7800), showed PDI = 1.9, although there was no evidence of stereoregularity. A 1:1 methyl acrylate-styrene random sequence copolymer was also prepared in fair yield, and showed homogeneity to below μm resolution. Work is currently under way to elucidate the mechanism of these polymerisations.

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