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Approaches to highly polar polymers with low glass transition temperatures. 1. Fluorinated polymers via a combination of ring-opening metathesis polymerisation and hydrogenation

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Dedicated to Prof. Ian M. Ward on the occasion of his 75th birthday

Abstract

The synthesis and hydrogenation of two fluorinated polymers is described. The products were characterised through a detailed study of their ^{1}H-, ^{13}C- and ^{19}F-NMR spectra, together with thermal and GPC analysis. Hydrogenation resulted in a significant lowering of the glass transition temperatures of the polymers.

Keywords: Hydrogenation; ROMP; Fluoropolymers

1. Introduction

Many polar polymers fall into the category of costly, but technologically valuable, speciality materials [1]. The homo- and co-polymers of vinylidene fluoride exemplify the situation; thus, the fluorinated elastomers based on copolymers of vinylidene fluoride, are important speciality polymers in many applications including, inter alia, seals and gaskets in hydraulic systems; whereas the piezo and pyro electric properties of the poled homopolymer of vinylidene fluoride are useful for application in devices such as hydrophones, piezoelectric loudspeakers and microphones and in pyroelectric sensors. One of the objectives of our work in this area is to establish routes to polar polymers displaying low glass transition temperatures, such materials might be additions to the range of elastomers and/or suitable for exploitation as electrostrictive materials [2,3]. The work described here concerns the ring-opening metathesis polymerisation (ROMP) of partially fluorinated bicyclo[2.2.1]hept-2-ene monomers, to give partially fluorinated poly(1,3-cyclopentylene vinylene)s, followed by hydrogenation of the double bonds to give saturated polar polymers. The ROMP of bicyclo[2.2.1]hept-2-enes with polar substituents, such as nitrile, amide, imide, ester, pyridyl, acid anhydride, chlorine, bromine and fluorine units is well established [4–8]. The first syntheses of the kind of materials of interest here were carried out by Wilson; monomers were obtained via Diels-Alder reaction of cyclopentadiene and fluorinated alkenes, and underwent ring opening metathesis polymerisation with classical initiator systems based on the reactions of tungsten and molybdenum chlorides with tin or aluminium based alkylating agents [4,5]. This approach to the synthesis of fluorinated polymers has been expanded [7] and reviewed [8]. Generally the polymers produced in this early work were obtained in good yields, however, due to the fluorine atom substitution, the relatively bulky substituted cyclopentane and rigid vinylene units in the backbone, the T_gs obtained were well above room temperature, thus a modification of monomers or polymers was required in order to lower the T_g. The hydrogenation of the double bonds in these polymers was investigated because it was expected that the transformation of the rigid double bonds into single bonds would increase the conformational mobility thereby increasing the flexibility of the polymer backbone. An additional anticipated benefit of hydrogenation was improved photo-oxidative stability consequent on the removal of two tertiary allylic C–H bonds per repeat unit. The outcome of this approach is described in this report.

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2. Experimental

2.1. General considerations

Cyclopentadiene was freshly prepared by thermal cracking from dicyclopentadiene purchased from Aldrich. Hexafluoropropene and 1,1,1-trifluoropropene were purchased from Bristol Organics Ltd, and used without further purification. Tetraphenyltin was purified by successive soxhlet extractions with toluene, dried under vacuum and stored in a glove box operating with an atmosphere of nitrogen having <1 ppm water and <1 ppm oxygen. Tungsten hexachloride and molybdenum pentachloride (99.9 +) were purchased from Aldrich, used without further purification and stored in the glove box. The different stock solutions were freshly prepared prior to use. Toluene was distilled from sodium and stored over molecular sieves. *p*-Trifluorotoluene was distilled prior to use and stored over molecular sieves. *p*-Toluenesulphonylhydrazide was dried under vacuum at room temperature overnight prior to use.

2.2. Monomoer syntheses

5,5,6-Trifluoro-6-trifluoromethyl bicyclo[2.2.1]hept-2-ene. Freshly distilled cyclopentadiene (4.43 g, 5.5 ml, 67 mmol) was injected into an oxygen-free Carius tube containing hydroquinone (0.45 g). Hexafluoropropene (21 g, 100 mmol) was vacuum transferred into the Carius tube, which was sealed under vacuum. The Carius tube was placed in a furnace at 180 °C for 72 h. After cooling and 'hot-spotting' to open the tube, the contents were flash distilled to give 5,5,6-trifluoro-6-trifluoromethylbicyclo[2.2.1]hept-2-ene as a colourless liquid mixture of *exo* and *endo* isomers (12.50 g, 87%); bp = 140 °C; lit. [9] 140–140.5 °C; capillary GC showed two peaks, $t_R = 4.68$ min, 67.5% *exo* adduct; $t_R = 4.76$ min 32.2% *endo* adduct. Found: C, 44.6; H, 2.8; F, 52.8%; $C_8H_6F_6$ requires C, 44.5; H, 2.8; F, 52.7%. ^{1}H NMR: (*exo*; δ/ppm) 6.24 (2H, s, –CH=); 3.27 (2H, s, C–H); 2.30 (2H, s, $-CH_2-$); (*endo*; δ/ppm) 6.34 (2H, s, –CH=); 3.13 (2H, s, C–H); 2.05 (2H, s, $-CH_2-$). ^{19}F NMR: (*exo*; δ/ppm): −169.5 (1F, q, $J^3_{FF} = 6.8$ Hz, C–F); (2F, ABq, $J^2_{FF} = 237.85$ Hz, $\delta = -109.07$ ppm, $J^3_{FF} = 12.79$ Hz, $\delta = -108.23$ ppm, $J^3_{FF} = 5.26$ Hz, $-CF_2-$); −76.01 (3F, dd, $J^3_{FF} = 13.17$ Hz, $J^4_{FF} = 8.27$ Hz, CF_3); (*endo*; δ/ppm): −170.3 ppm (1F, s, C–F); −107.9 (2F, d, $J^3_{FF} = 6.8$ Hz); −74.7 (3F, td, 14.30 and 6.7 Hz). ^{13}C NMR: 135.9 (C3 *exo*/*endo*, dd, $J^3_{C-F} = 5.8$ and 1.4 Hz); 134.4 (C2 *exo*, d, $J^3_{C-F} = 22.5$ Hz); 134.08 (C2 *endo*, d, $J^3_{C-F} = 7.9$ Hz); 124.85 (C6 *endo*, ddd, $J^1_{C-F} = 272.3$ and 265.9 Hz, $J^2_{C-F} = 16.8$ Hz); 124.7 (C6 *exo*, td, $J^1_{C-F} = 271.15$ and 265.9 Hz, $J^3_{C-F} = 16.8$ Hz); 121.8 (C8 *exo*, qd, $J^1_{C-F} = 283.2$ Hz, $J^3_{C-F} = 32.1$ Hz); 121.88 (C8 *endo*, qd, $J^1_{C-F} = 283.2$ Hz, $J^3_{C-F} = 25.26$ Hz); 95.4 (C6 *exo*/*endo*, dm, $J^1_{C-F} = 209.3$ Hz); 49.01 and 48.82 (C4 *endo* or *exo*, two doublets with $J^2_{C-F} = 84$ Hz and $J^2_{C-F} = 82$ Hz, respectively); 48.82 (C4 *endo* or *exo*, t, $J^2_{C-F} = 88$ Hz); 47.6 (C1 *endo*, d, $J^2_{C-F} = 86$ Hz); 46.9 (C1 *exo*, d, $J^2_{C-F} = 78$ Hz); 44.8 (C7 *endo* or *exo*, s); 42.3 (C7 *endo* or *exo*, s); IR: C–H stretch 3080 cm^{-1}, CH=CH stretch 1610–1631 cm^{-1}, C–F stretches 1390–1000 cm^{-1}. MS: $M^+ = 216$ ($M_{100\%}$, 66, retro Diels-Alder), 196, 176, 164, 144, 126, 94.

5-Trifluoromethylbicyclo[2.2.1]hept-2-ene. Freshly distilled cyclopentadiene (15 g,67 mmol) and hydroquinone (0.45 g) were mixed in a Carius tube. 3,3,3-Trifluoropropene (6.43 g,100 mmol) was introduced by vacuum transferred and the tube was sealed from the vacuum line and heated at 180 °C for 72 h. After cooling and opening by 'hot-spotting' the contents of the tube were flash distilled to give a 62:38 mixture of the *exo* and *endo* isomers of 5-trifluoromethylbicyclo[2.2.1]hept-2-ene (II) (8.5 g, 52% yield) as a colourless liquid (bp = 118 °C, lit. [10] 119 °C). ^{1}H NMR was complex with much overlapping of peaks (*exo*; vinyl hydrogens, δ/ppm): 6.21 (1H, m, –CH=); 6.19 (1H, s, –CH=); 2.00 (1H, m, CH_2, C7); (*endo*; vinyl hydrogens, δ/ppm): 5.95 (2H, m, =CH–). ^{19}F NMR: Two peaks at −68.28 ppm (*endo* $J^3_{F-H} = 9.78$ Hz) and −66.15 ppm (*exo*, $J^3_{F-H} = 10.16$ Hz). ^{13}C NMR (δ/ppm): 138.2 (C3 *endo*); 137.62 (C2 *endo*); 136.45 (C3 *exo*); 131.93 (C2 *exo*); 128.56 (C8 *endo*, q, $J^1_{C-F} = 278$ Hz); 128.1 (C8 *exo*, q, 277.6 Hz); 50.06, 46.2, 43.5, 43.3, 43.0, 42.7, 42.5, 42.2, 41.4 (C5, C6, C3, C4 *endo*/*exo*); 27.8 (C7 *exo*); 27.3 (C7 *endo*). GC–MS EI + : Two signals, identical MS (M^+ 162); 66 (100% retro Diels-Alder), 93, 77, 51, 39, 27.

2.3. General procedure for ring-opening metathesis polymerisation

Ph_4Sn (2 equiv.) was placed in a dry ampoule equipped with a magnetic stirrer and flushed with dry oxygen-free nitrogen. WCl_6 or $MoCl_5$ (0.01 M solution in toluene, 1 equiv.) was injected via a rubber seal. After the required activation time (10–15 min for the tungsten based catalyst, when the colour changed from blue-black to dark-brown and 5 min for the molybdenum based catalyst, when the colour changed from black-green to dark-brown), the monomer or mixture of monomers (500 equiv.) was injected and the solutions were stirred vigorously. The solutions became more viscous until the stirrer stopped. After quenching the reaction by addition of a few drops of MeOH, the contents of the ampule were poured in acetone and dissolved. The acetone solutions were partially rotary evaporated to give viscous solutions and the polymers were precipitated by dropwise addition of the viscous solution to a 5-fold excess of cold *n*-hexane, recovered by filtration and dried under vacuum.

2.4. General procedure for the hydrogenation of the polymers

The polymers were dissolved in trifluorotoluene (50 ml

for 1 g of polymer) and placed in an oxygen-free three-necked flask equipped with a reflux condenser and a magnetic stirrer. *p*-Toluenesulphonylhydrazide (15–20 times the weight of the polymer) was added in small aliquots at intervals of 30 min while the solution was stirred at reflux (102 °C). The mixture was cooled to room temperature and the contents of the flask were poured directly into a 10-fold excess of cold methanol and stirred for 30 min. The precipitated solid was recovered by filtration and dried in a vacuum oven at 50 °C overnight. The products were re-dissolved in the minimum amount of acetone or benzene and re-precipitated in a 5-fold excess of cold methanol. The white solids obtained were recovered by filtration and dried in a vacuum oven at 50 °C overnight to give the saturated or partially saturated polymers.

3. Results and discussion

3.1. Ring opening metathesis polymerisations

We have studied two systems in this work, both polymerisations have been described previously [4,5,7,8], however the improved NMR spectroscopic capabilities that have become available allow us to present a more detailed analysis of the polymer chain microstructures than was previously possible.

3.2. Monomer syntheses and characterisation

5,5,6-Trifluoro-6-trifluoromethyl bicyclo[2.2.1]hept-2-ene was synthesised via the Diels-Alder reaction of perfluoropropene with cyclopentadiene to give, a 32:68 mixture of the racemic *endo* and *exo* isomers, respectively, see Fig. 1, and Section 2. Analysis by GC–MS confirmed the molecular formulae of the products, M^+ 216, both isomers exhibited a base peak at *m/e* 66 ($C_5H_6^+$), arising from a retro Diels-Alder reaction of the parent ion, a fragmentation mode characteristic of bicyclo[2.2.1]hept-2-enes. IR spectroscopy showed the characteristic, vinylic C–H stretch (3080 cm^{-1}, weak), saturated CH stretch (2970–2850 cm^{-1}) and C–F stretches (1390–1000 cm^{-1}, strong).

Analysis of the ^{19}F NMR spectrum gave two sets of signals in a ratio of ca. 60:40, corresponding to the *exo* and *endo* isomers, respectively. The stereochemical assignment of these adducts was based on earlier work by Stone and Smart [11]. The ^{13}C NMR spectrum was analysed on the basis of the carbon–fluorine coupling constants, the carbons bearing a fluorine atom and a trifluoromethyl group appear as a complex doublet of multiplets at 95.4 ppm with a coupling constant of 209.2 Hz for J^1_{C-F}, the CF_2 carbon appears as two groups of doublets of doublet of doublets centred at 124.8 ppm, the observed coupling constants for the major isomer *exo* are $J^1_{C-F} = 272.3$ and 265.9 Hz and $J^2_{C-F} = 16.8$ Hz, the couplings for the minor *endo* isomer could not be resolved. The trifluoromethyl carbons appear as two groups of quartets of doublets centred at 122.28 and 121.88 ppm with C–F couplings $J^1_{C-F} = 283.5$ Hz and $J^2_{C-F} = 32.1$ Hz for the major *exo* signals and $J^1_{C-F} = 282.6$ Hz and $J^2_{C-F} = 31.3$ Hz for the minor *endo* signals. The *exo* and *endo*-isomers co-distil and have similar GC retention volumes. The isomers were not separated but, since the objective is to make a low T_g material, the copolymerisation of the *exo*/*endo* mixture might help this objective.

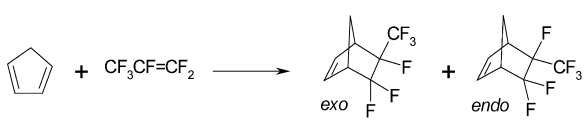

Fig. 1. Synthesis of a racemic *exo* and *endo* mixture of 5,5,6-trifluoro-6-trifluoromethylbicyclo[2.2.1]hept-2ene.

5-Trifluoromethylbicyclo[2.2.1]hept-2-ene was synthesised via a Diels-Alder reaction between 1,1,1-trifluoropropane and cyclopentadiene, see Fig. 2. The GC–MS analysis confirmed the existence of two products with the same molecular formulae M^+ 162, both exhibited the expected base peak at *m/e* 66 ($C_5H_6^+$).

The IR spectrum showed the expected vinylic C–H stretch (3080 cm^{-1}, weak), saturated CH stretch (2970–2850 cm^{-1}) and C–F stretches (1390–1000 cm^{-1}, strong). The ^{19}F NMR spectrum showed two signals in the trifluoromethyl region revealing the presence of the *endo* and *exo* isomers [5]. The signal at −66.3 ppm, $J^2_{H-F} = 9.78$ Hz (62%) and was assigned to the *exo* isomer; the minor *endo* component was seen at −68.2 ppm, $J^2_{H-F} = 10.16$ Hz (38%). The ^1H NMR spectrum was very complex, displaying extensive overlapping of peaks and, while it was consistent with the assignment given above, was not analysed in detail. The ^{13}C NMR spectrum was analysed on the basis of the carbon–fluorine coupling constants of the trifluoromethyl carbon, which appears as two low intensity quartets centred at 128.56 and 128.06 ppm with $J^1_{C-F} = 278$ and 277.6 Hz, respectively, for the major and minor isomers.

3.3. Ring-opening metathesis polymerisations

The scheme for the ROMP of 5,5,6-trifluoro-6-trifluoromethyl bicyclo[2.2.1]hept-2-ene is shown in Fig. 3. This monomer was polymerised following the procedure described above to give, from WCl_6/Ph_4Sn initiation, poly(4,4,5-trifluoro-5-trifluoromethyl-1,3-cyclopentylene vinylene) (**Ia**) as a white powder in a 55% mass recovery. The characterisation of this polymer is discussed below.

With $MoCl_5/Ph_4Sn$ initiation a sample of poly(4,4,5-

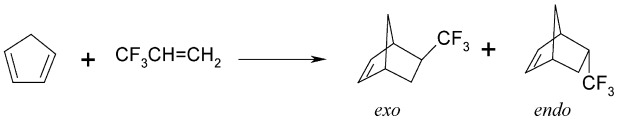

Fig. 2. Synthesis of 5-trifluoromethylbicyclo[2.2.1]hept-2-ene.

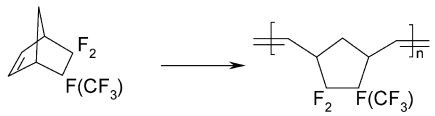

Fig. 3. Scheme for ROMP of 5,5,6-trifluoromethylbicyclo[2.2.1]hept-2-ene.

trifluoro-5-trifluoromethyl-1,3-cyclopentylenevinylene) (**Ib**) with a different microstructure was obtained as a white powder, in 30% mass recovery. The characterisation of this polymer is discussed below.

The ROMP of 5-trifluoromethylbicyclo[2.2.1]hept-2-ene is shown schematically in Fig. 4. The polymerisation was carried out at room temperature using the initiator derived from tungsten hexachloride (1 equiv.) in toluene using tetraphenyltin (2 equiv.) as a co-initiator. After the required activation time when the solution of the catalyst mixture became dark brown the monomer (500 equiv.) was injected into the reaction vessel. The dark brown solution became gradually more viscous and the polymerisation was taken as completed when the stirrer stopped. The contents of the ampoule were quenched with few drops of methanol, and the product was dissolved in acetone and precipitated in cold hexane to give a white solid (85% yield).

The characterisation of polymer (**III**) is discussed below.

3.4. Polymer hydrogenations

Hydrogenation of polymers allows the generation of new products with novel properties [12]. Polymer crystallinity tends to increase on hydrogenation but glass transition temperatures can either increase or decrease, depending upon the starting material. Industrial hydrogenations are carried out using cobalt or nickel catalysts at elevated temperature and pressure but these methodologies were not suitable for the small-scale work reported here. A convenient non-catalytic hydrogenation is based on the in situ generation of diimide from *p*-toluensulfonylhydrazide in a solvent above 90 °C. Double bonds are reduced and *cis* to *trans* isomerisation of any remaining vinylenes is promoted. Attachment of hydrazide fragments to the polymer chains, which can be minimised by the addition of an antioxidant, depolymerisation and cyclisation are possible side reactions. The hydrogenation scheme for the polymers (**Ia**) and (**Ib**) to give polymers (**IIa**) and (**IIb**) is shown schematically in Fig. 5. The materials were dissolved in 1,1,1-trifluorotoluene and hydrogenated using diimide as described in Section 2. Once the hydrogenation process was completed the contents of the flasks were poured into a 10-fold excess of methanol and stirred for 30 min, to dissolve

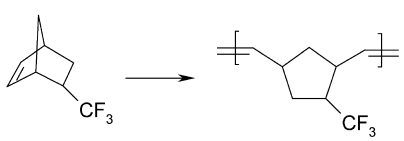

Fig. 4. Synthesis of poly(5-trifluoromethylbicyclo[2.2.1]hept-2-en) (**III**).

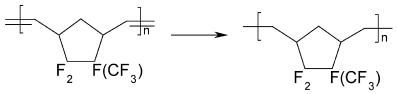

Fig. 5. Scheme for the hydrogenation of polymer (**Ia**) and (**Ib**).

the residual $CH_3C_6H_4SO_2H$, leaving a white precipitate, which was recovered by filtration, dissolved in toluene or acetone and reprecipitated in cold methanol to give the polymers (**IIa**) and (**IIb**).

Low intensity vinyl signals were visible between 5 and 6 ppm in the ^{1}H NMR spectra of the products and integration indicated extents of hydrogenation of 83% for polymer (**Ia**) and 95% hydrogenation for polymer (**Ib**). The characterisation of these polymers is discussed below.

The hydrogenation of poly(5-trifluoromethyl-1,3-cyclopentylenevinylene) (**III**) is shown schematically in Fig. 6. ^{1}H NMR spectroscopic analysis revealed that the hydrogenation of polymer (**III**) was complete within the sensitivity of the analytical technique. The resulting polymer (**IV**) was a white solid, which was recovered by precipitation into cold methanol.

3.5. Structural characterisation of the polymers

3.5.1. NMR spectroscopy

We have previously investigated the microstructure of a wide range of partially fluorinated poly(1,3-cyclopentylenevinylene)s [7,8]. Such polymers can be characterised by elemental analysis, infrared (IR), ^{1}H NMR and ^{19}F NMR spectroscopy, however the most valuable analytical probe for the determination of chain microstructure is ^{13}C NMR spectroscopy [6]. The repeat unit for polymers (**Ia** and **Ib**), shown in Fig. 7, has eight different carbon environments. The classical ROMP initiators used in this work are not well defined and probably contain different initiating species, this can give rise to a great variety of structures as a result of incorporating monomer residues in different configurations. Moreover, the monomers exists as a mixture of *endo* and *exo* isomers both of which are racemic. On incorporation into the polymer the vinylene unit can be *cis* or *trans*, the fluorinated cyclopentane unit can be incorporated in a head–tail, head–head or tail–tail fashion, the trifluoromethyl group can be *syn* or *anti* with respect to the adjacent vinylene carbons and the incorporated unit can be derived from an *R* or *S* monomer. This gives rise to an enormous range of possible structures and it is not surprising that at the time of the original work the NMR spectra of polymer (**I**) could not be sufficiently well resolved to allow anything other than a general confirmation of chain structure.

However, since these polymers were first reported

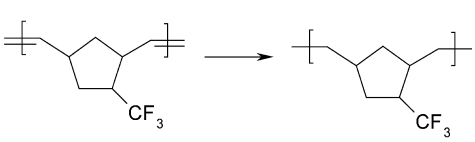

Fig. 6. Hydrogenation of polymer (**III**).

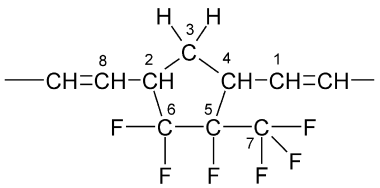

Fig. 7. The carbon environments for the polymers (**I**).

improved NMR facilities have become available and more detailed assignment of the signals is possible and is presented here. Previous experience in the polymerisation of 5,5,6-trifluoro-6-trifluoromethyl[2.2.1]hept-2-ene indicated that the polymer (**Ib**) synthesised using the $MoCl_5$ derived initiating system displays mainly *trans* double bonds, and polymer (**Ia**) initiated using the WCl_6 derived catalyst gives a mixture of *cis* and *trans* double bonds [4,5].

The NMR spectra obtained from both polymers were rather complicated; we start the analysis with the ^{19}F NMR spectra, shown in Fig. 8, which are the easiest to interpret. Three sets of signals can be seen and assigned, those for $-CF_3$ occur between -70 and -80 ppm, those for the difluoromethylene group between -100 and -130 ppm and those for C–F units between -160 and -200 ppm. The signals for the trifluoromethyl groups in the spectrum of polymer (**Ib**) appear as two broad doublets displaying coupling with the adjacent fluorine atom. The smaller signal occurs at -77.2 ppm and the larger at -73.0 ppm both with ($J^2_{FF} = 50.4$ Hz) and with relative integrated intensities of 20:80, respectively. In case of the polymer (**Ia**) the signals of the trifluoromethyl groups appear as two broad multiplets at -73.8 and -77.2 ppm, with relative integrated intensities of 46:54, respectively. From the integrated intensities of the signals, the relative proportions of structures (i) and (ii), shown in Fig. 9, incorporated into the polymer can be determined and hence the relative incorporation of *exo* and *endo* monomers from the monomer feed.

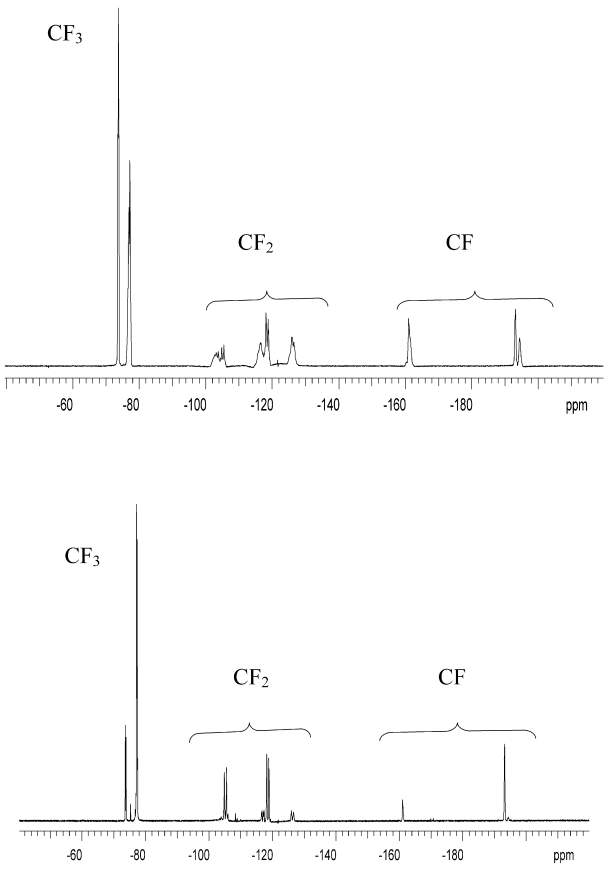

Fig. 8. The ^{19}F NMR spectra of polymer (**Ia**) (above) and (**Ib**) (below).

The mechanism and stereochemical regulation of ROMP of bicyclo[2.2.1]hept-2-enes is now well established [6,13], the accepted mechanism is depicted in Fig. 10. The transition metal carbene initiator approaches the double bond from the *exo*-direction forming a metallocyclobutane, which opens to give a new propagating metallocarbene chain end after incorporating one monomer unit. Ozonolysis experiments revealed that in poly(1,3-cyclopentylene vinylene)s the cyclopentane ring has a *cis*-1,3-structure. From scheme shown in Fig. 10 the *endo*-substituents R2 and R3 will be on the same side of the ring as the carbon–carbon double bond in the polymer chain. That is to say, the racemic monomer (±)-*exo* gives the repeat unit structure (i), Fig. 9, and the monomer (±)-*endo* gives the structure (ii).

The integration of the signals from the trifluoromethyl group in the polymer (**Ia**) gives a 46:54 ratio for structures (i) and (ii), respectively, and the integration for polymer (**Ib**) gives a 20:80 ratio for the same pair of signals. The monomer feed had a 43:57 mixture of *exo* and *endo* isomers, respectively, so under the experimental conditions employed, the $WCl_6/2Ph_4Sn$ initiator system does not discriminate significantly between *endo* and *exo* monomers; whereas with the less reactive $MoCl_5/2Ph_4Sn$ initiator the *endo* monomer was incorporated to a significantly greater extent. An explanation for this observation is not immediately obvious but, on the basis of the mechanism outlined in Fig. 10, it seems unlikely to be a simple steric effect.

The ^{19}F NMR spectrum of polymer (**Ib**) with mainly *trans* double bonds is much simpler to interpret than that of (**Ia**), the signals assigned to the difluoromethylene groups appear as two major group of signals at -104.5 ppm ($J^2_{FF} = 250.3$ Hz) and -118.5 ppm ($J^2_{FF} = 250.3$ Hz, $J^3_{FF} = 58.7$ Hz). Minor signals were observed at &116.3 ppm ($J^2_{FF} = 244.6$ Hz, $J^3_{FF} = 76.1$ Hz) and -125.7 ppm ($J^2_{FF} = 260.4$ Hz), the integration of both groups of signals gives a ratio of 21:79 which is consistent with that determined from the trifluoromethyl group

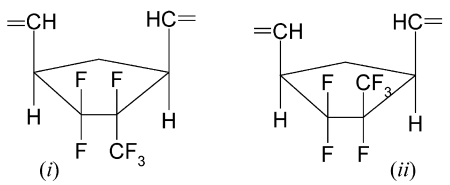

Fig. 9. Polymer repeat unit structures in polymers **Ia** and **Ib**.

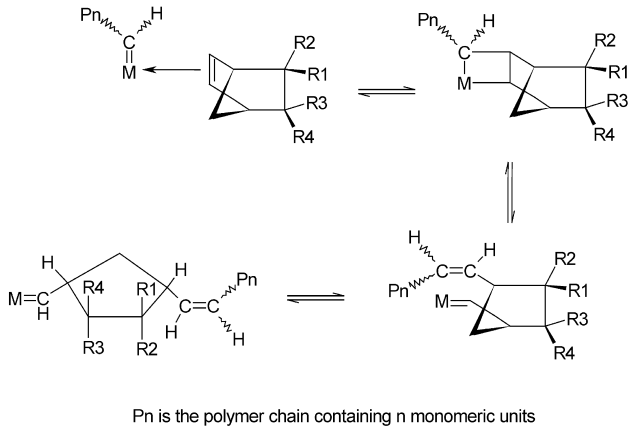

Fig. 10. A summary of the assembly mechanism in ROMP of norbornenes.

integrations. The signals arising from the difluoromethylene group in the spectrum of polymer (**Ia**) have the same shift as those in polymer (**Ib**), although there is considerable overlapping and an accurate integration cannot be made. The signals from the CF group are well-resolved in both spectra and appear as three broad singlets with different intensities, the singlet at −193 ppm in both spectra is assigned to the repeat unit (i) in Fig. 9, and when the relative intensities of these signals are compared with the sum of the other signals the incorporation ratio of *endo* and *exo* isomers obtained is entirely consistent with the previous determinations.

In the ^{13}C NMR spectrum of polymer (**Ib**), shown in Figs. 11 and 12, using the numbering system given in the figure the signals due to the trifluoromethyl carbons C7 are partially distinguished as a quartet of doublets at 122 ppm, with coupling constants $J^1_{C-F} = 280.3$ Hz and $J^2_{C-F} = 32.98$ Hz. An overlapped shoulder is observed in each signal, and this observation is attributed to the presence of the minor component, structure (i), see Fig. 9. In the signals assigned to the carbon C6, a doublet of doublets of doublets, is observed at 124.5 ppm with $J^1_{C-F} = 269$ and 260 Hz and $J^2_{C-F} = 33$ Hz, one part of this signal overlapping with the multiplet arising from the vinyl carbons. The

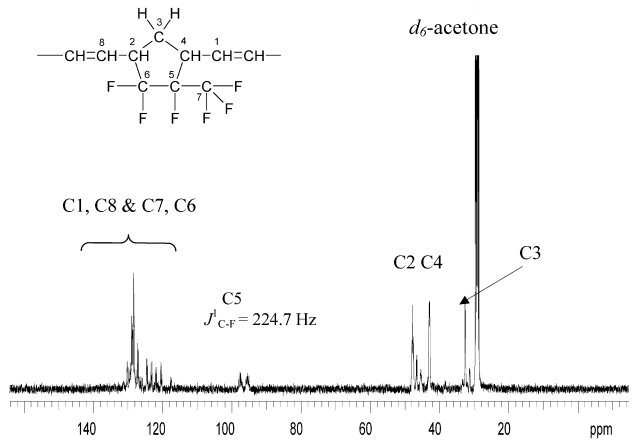

Fig. 11. The ^{13}C NMR spectrum of polymer **Ib**.

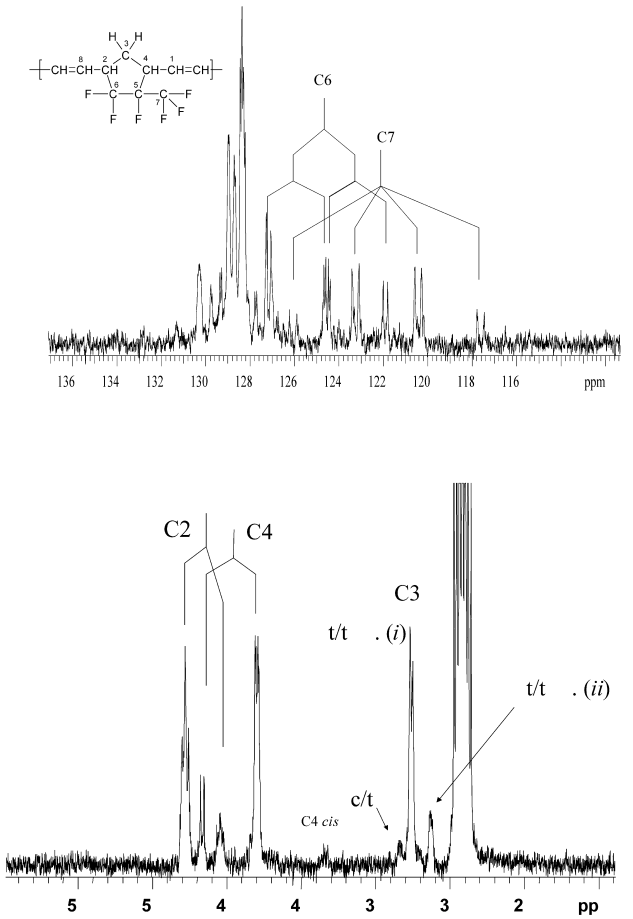

Fig. 12. The expanded ^{13}C NMR spectrum of the vinyl region of polymer (**Ib**) (above) and the saturated region (below).

carbon C5 appears at 96.5 ppm as a doublet of multiplets with $J^1_{C-F} = 225$ Hz.

The vinyl carbons C1 and C8 appear as a complex multiplet of signals between 127 and 132 ppm.

In the methylene region, shown in Fig. 12, seven broad signals with different intensities are observed. The signals due to the methylene carbon C3 are readily assigned between 30 and 35 ppm, the major and minor signals at 32.6 and 31.3 ppm, respectively, are assigned to carbon C3 in a *trans–trans* sequence of double bonds, the integrated intensity ratio of these signals is 86:14 which, within experimental error, is consistent with the ratio of structures (i) and (ii), obtained from other signal integrations. A very small signal is also observed at 33.5 ppm as a multiplet, which is assigned to carbon C3 in a *cis/trans* sequence [6]. The four broad signals between 40 and 50 ppm appear as two major and two minor signals and are assigned to the allylic carbons C2 and C4 in *trans* vinylene sequences, the assignments are based on the multiplicities and intensities observed and the fact that allylic carbons adjacent to *trans* double bonds appear at lower frequency than their *cis* equivalents. This leads to the conclusion that the signal at 47.8 ppm (triplet, $J^2_{C-F} = 24.2$ Hz) is assigned to carbon C2 and the doublet at 43.0 ppm ($J_{C-F} = 23.7$ Hz) is assigned to

the carbon C4. The two minor signals at 46.6 ppm (doublet, $J^2_{C-F} = 23.7$ Hz) and 45.46 ppm (multiplet) were assigned to the C2 and C4 carbons in the minor component, structure (i), see Fig. 9, and the integrated intensity ratios ca. 20:80 correspond with the established incorporation ratio of the two repeat units. Finally, the low intensity signal observed at 38.48 ppm is assigned to carbon C4 in a *cis* vinylene sequence as was confirmed from the analysis of the ^{13}C NMR spectrum of polymer **IIa**.

In the ^{13}C NMR spectrum of the polymer (**IIa**), shown in Figs. 13 and 14, the signal of the CF_3 group, carbon C7 is partially resolved as a quartet of multiplets centred at 121.5 ppm with a coupling constant $J^1_{C-F} = 285.8$ Hz, and the partially resolved signal of the carbon C6 appears as a triplet of multiplets centred at 124.2 ppm with $J^1_{C-F} = 271$ Hz. The signal of the carbon C5 appears at 98 ppm as a doublet of multiplets with $J^1_{C-F} = 201.9$ Hz. The vinylic carbons C1 and C8 appear as a set of broad signals between 125 and 132 ppm. The methylene carbon C3 signal is much more complex than the analogous signal in the 'high *trans*' polymer (**IIb**). Two groups of three signals are seen due to the existence of the different configurations of the trifluoromethyl and different *cis*:*trans* vinylene sequences. The sets of three signals are attributed to the three possible *cis*–*cis*, *cis*–*trans* ≡ *trans*–*cis*, and *trans*–*trans* sequences for C3 in structures (i) and (ii); see assignments in Fig. 9. The signals for the saturated carbons C2 and C4 appear between 36 and 50 ppm displaying eight broad signals (two overlapped). The integration of the signals from carbon C2 at 45.5 and 48 ppm gives a 36:64 ratio for the incorporation of structures (i) arising from *exo*-monomer and (ii) from *endo*-monomer, respectively, see Fig. 9, and indicates an increased incorporation of structure (i) in *trans* vinylene sequences of polymer (**IIa**) compared to the 20:80 ratio in polymer (**IIb**).

The other signals are assigned to the carbons C2 and C4 in a *cis* double bond environment, but the overlapping of the signals does not allow integration. Clearly from a simple comparison of the spectra of polymers (**IIa**) and (**IIb**), the former displays a much more complex microstructure than the latter, which is

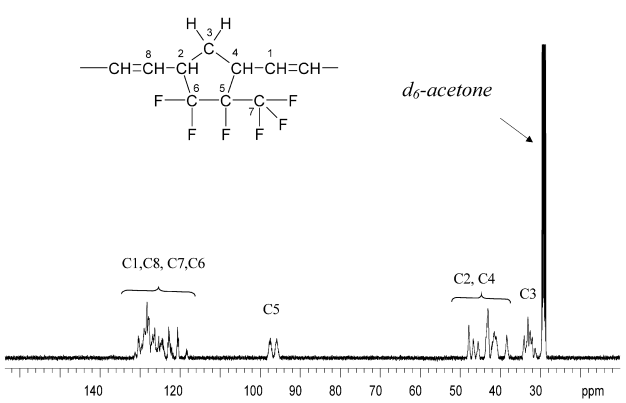

Fig. 13. The ^{13}C NMR spectrum of polymer (**Ia**) with assignments.

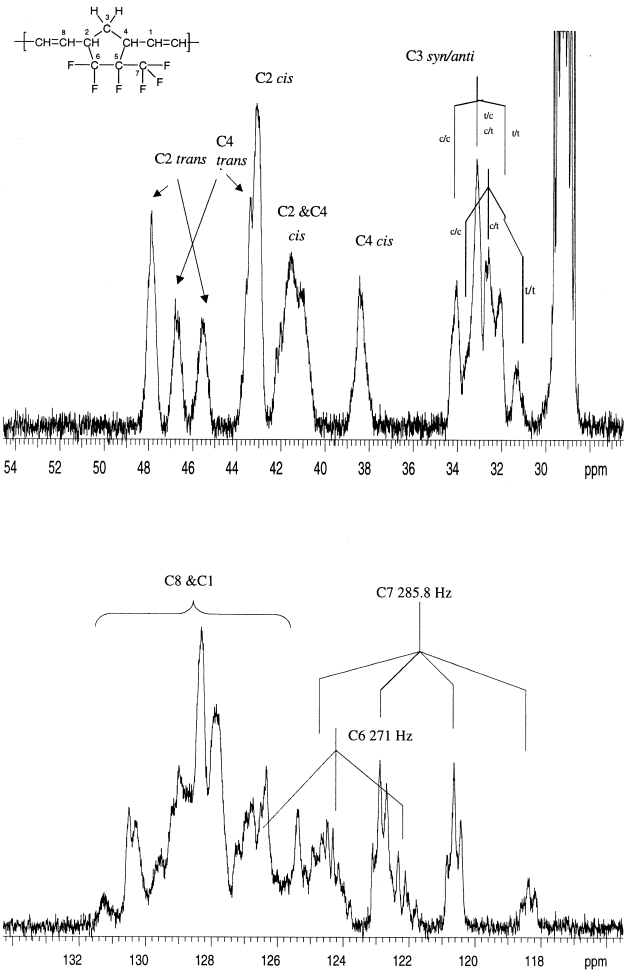

Fig. 14. Assigned signals for the expanded ^{13}C NMR spectrum of polymer (**Ia**) in the saturated region (above) and the vinylic region (below).

consistent with the higher reactivity and lower selectivity typically displayed by tungsten based initiators systems as compared to their molybdenum analogues.

The analysis of the ^1H NMR spectrum of polymers (**IIa**) and (**IIb**) was consistent with the microstructural assignment based on ^{19}F and ^{13}C NMR spectroscopy but added no new insights and is not discussed here. However, the hydrogenation of these polymers was conveniently monitored by the disappearance of the signals assigned to the vinyl hydrogens at 5.9 ppm. The signals in the saturated region of the spectrum (1–4 ppm) also undergo change in the expected manner; the vinylene signals decrease in intensity and new methylene signals appear. The spectra of polymers (**IIa**) and (**IIb**) are shown in Figs. 15 and 16, respectively.

The relative intensities of the vinyl hydrogens at 5.9 ppm compared to the well-resolved signal centred at 2.5 ppm were used to calculate the extent of hydrogenation, giving values of 95 and 83% for polymers (**IIb**) and (**IIa**), respectively. The hydrogenation of the polymers was also monitored by ^{13}C NMR spectroscopy. The partially hydrogenated polymers displayed new signals between 20

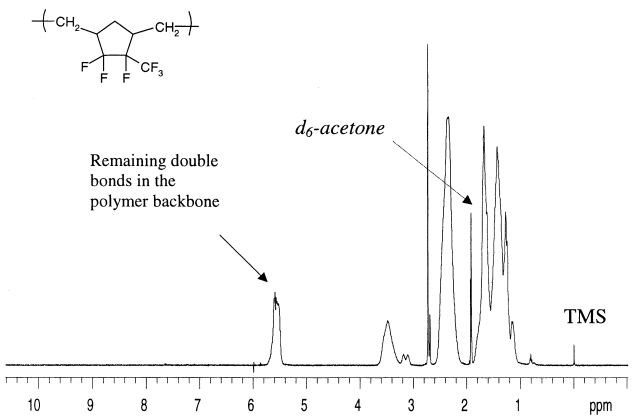

Fig. 15. The ^{1}H NMR spectrum of polymer (**IIa**).

and 30 ppm assigned to the newly created CH_2 carbons, as well as decreased intensity of the signals from carbons C1 and C8 in the vinyl region; however, the spectra did not provide any new insights nor were they useful for quantitative analysis of the hydrogenation and they are not reproduced here.

The numbering system used to identify the carbon environments of polymer (**III**) in ^{13}C NMR spectroscopy are shown schematically in Fig. 17.

In the ^{13}C NMR spectrum of polymer (**III**), Fig. 18, two groups of signals are observed. The signals between 136 and 122 ppm were assigned to the vinylene carbons C1 and C8, and the trifluoromethyl carbon C7; the signals between 50 and 30 ppm were assigned to the ring carbons (C2, C3, C4, C6 and C5). The resonance due to the carbon of the trifluoromethyl group is partially resolved as two quartets centered at approximately 129 ppm with $J^{1}_{C-F} = 284.9$ Hz attributed to the two different repeat units arising from *endo* and *exo* monomer incorporation, see the discussion of the ^{19}F NMR spectrum.

The remaining signals arise from vinyl carbons C1 and C8, since *endo* and *exo* monomer incorporation, *cis* and *trans* vinylenes, head–tail, head–head and tail–tail placements are to be expected a complex multiplet is to be expected and is indeed seen, in the high resolution spectrum

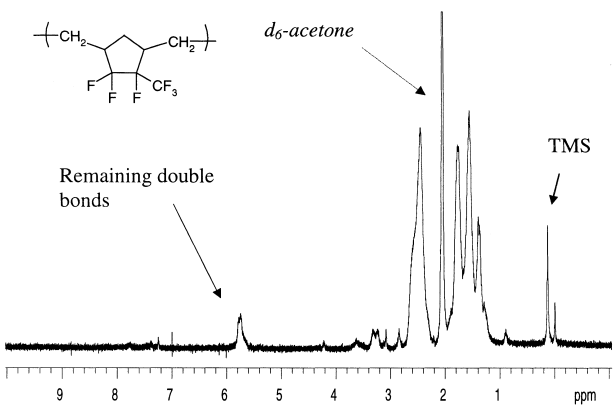

Fig. 16. The ^{1}H NMR spectrum of polymer (**IIb**).

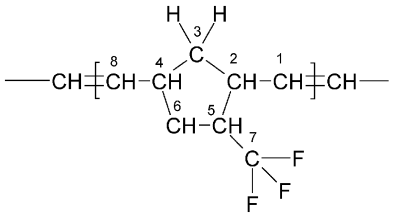

Fig. 17. Carbon environments for polymer (**III**).

of this region the expected number of signals is resolved but individual signals cannot be assigned. The assignment of the saturated region in the ^{13}C NMR spectrum followed from the earlier work of Blackmore and, while it is consistent with the rest of the analysis, it adds nothing to our understanding and so is not reproduced here.

The ^{19}F NMR spectra of polymers (**III**) and (**IV**) shown in Figs. 19 and 20, respectively, display two signals in the relative intensity ratio 63:37 assigned to the structures (i) and (ii), respectively, in Fig. 21. The situation is analogous to that discussed above for polymers (**I**). Similar relative intensities and shifts are observed in both spectra; however, the signals in the spectrum of the saturated polymer display small shoulders, which are tentatively assigned to H–H or

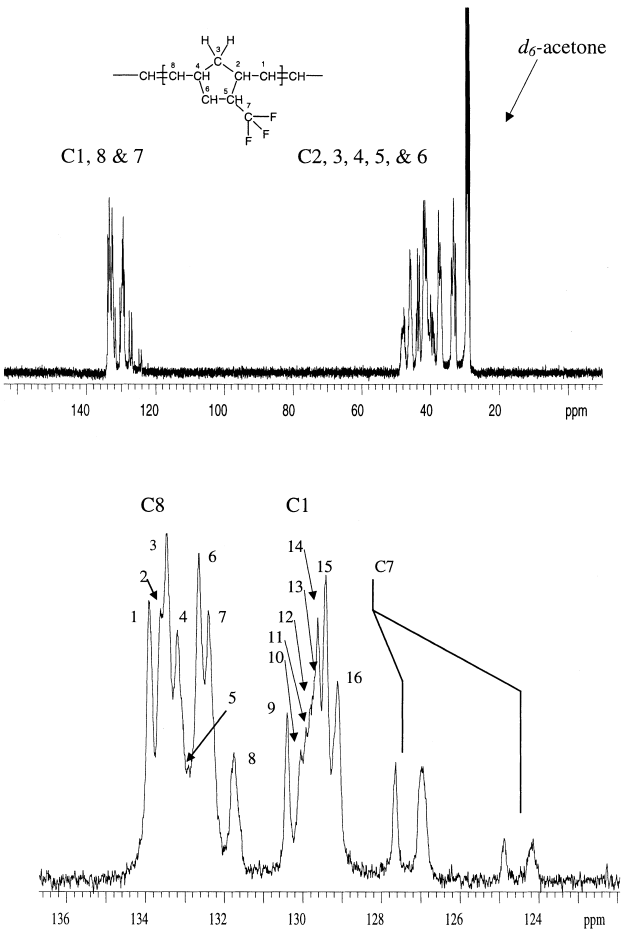

Fig. 18. The ^{13}C NMR spectrum of polymer (**III**), whole spectrum (above), vinyl and CF_3 region (below).

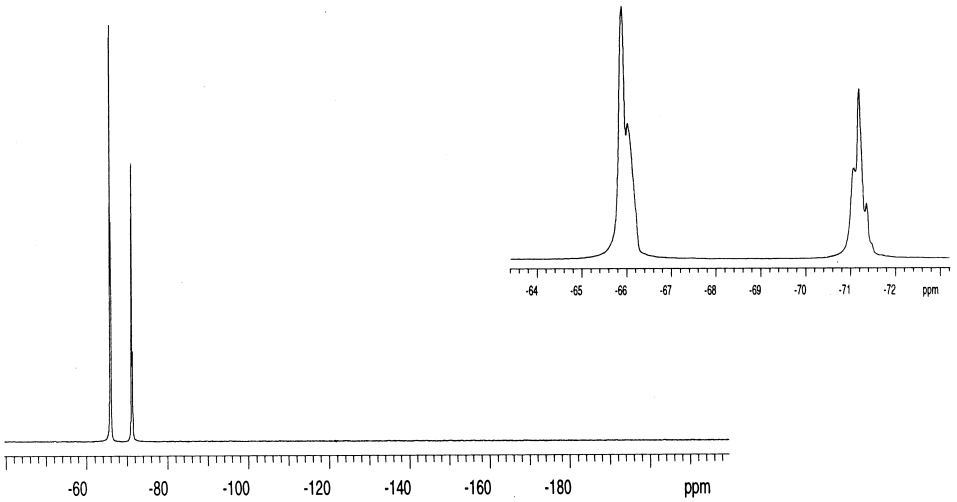

Fig. 19. The ^{19}F NMR spectrum of polymer (**III**).

T–T sequences of ca. 17 and 4%, respectively, for the repeat units derived from the structures (i) and (ii) in Fig. 21.

As discussed for the ROMP of 5,5,6-trifluoro-6-trifluoromethylbicyclo[2.2.1]hept-2-ene monomer, the structure (i), which is the major structure in the polymer, is derived from the *exo* monomer and the structure (ii) from the *endo* monomer; since the initial monomer mixture had a 61:38 *exo*:*endo* ratio, it can be seen that, under the experimental conditions of the polymerisation, the $WCl_6/2Ph_4Sn$ initiator system does not discriminate between the *exo* and *endo* isomers of 5-trifluormethylbicyclo[2.2.1]hept-2-ene.

The ^{1}H NMR spectrum of polymer (**III**), Fig. 22, displays a complex multiplet at 5.5 ppm, attributed to the distribution of *cis* and *trans* double bond configurations along the backbone. The C_{sp3}–H hydrogens, H_{bced}, were assigned by analogy with earlier work [7].

The ^{1}H NMR spectrum of the material obtained after hydrogenation shows that in this case the extent of reaction approached 100%, see Fig. 23. Very low intensity signals are still observed between 5 and 6 ppm, suggesting the existence of traces of residual double bonds in the polymer, but the amount is too small to measured reliably, probably less than 1%. It can be seen that the diimide hydrogenation of polymer (**III**) was much more efficient than the analogous process with polymers (**Ia**) and (**Ib**). This observation may be a consequence of shielding of the double bonds in polymers (**Ia**) and (**Ib**) by the fluorinated substituents.

3.5.2. Elemental analysis

The results of the elemental analysis for the polymers are shown in Table 1. The percentages obtained are generally only moderately consistent with the expected values and suggest that there may be some contamination or degradation in some samples; for example, the low %C values for **Ia** and **Ib** may indicate oxidation before analysis which is commonly observed for norbornene ROMP products, it is sometimes difficult to remove the last traces of solvent from these materials and analysis for fluorine by the potassium

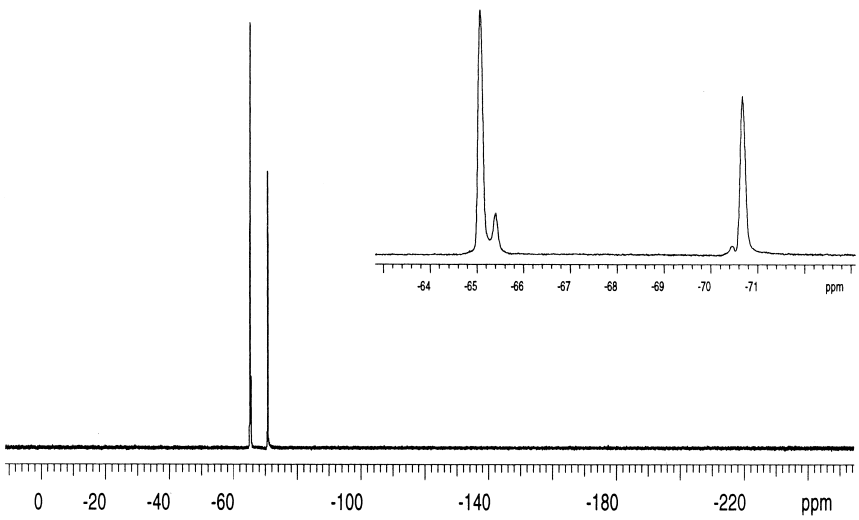

Fig. 20. The ^{19}F NMR of the saturated polymer (**IV**).

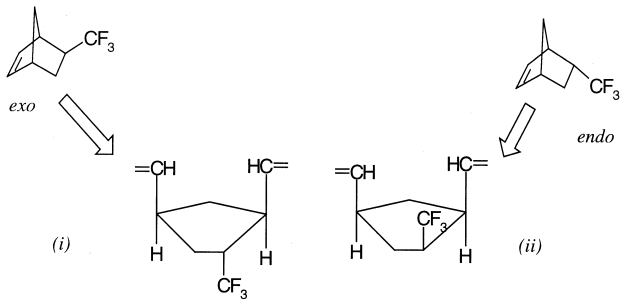

Fig. 21. Polymer structures.

fusion method has previously proved difficult for this class of polymer. However, the %C and %H values for the target polymers, **IIa**, **IIb** and **IV**, i.e. the hydrogenated polymers are all good, which was pleasing.

3.5.3. IR spectroscopy

IR spectroscopic examination of the polymers reported here was consistent with the assigned structures but added little to understanding and so spectra are not reproduced. Thus, comparison of the IR spectra of polymers (**Ia**) and (**IIa**) showed an increased intensity and broadening of the peak at 2930 cm^{-1} associated with C–H stretching in (**IIa**) due to the increased proportion of CH_2 groups. Also the expected a decrease in the intensity of the peaks associated with the –CH=CH-out-of-plane bending modes between 600 and 900 cm^{-1} was observed in the transformation of (**Ia**) into (**IIa**). Similar effects were observed on comparison of the spectra of polymers (**III**) and (**IV**). In both systems the –CH=CH-stretching mode in the polymers was too weak to be detected.

3.5.4. GPC and thermal characterisation

The polymers were characterised by gel permeation chromatography (GPC) using a Viscotek Trisec TDA 301 chromatograph with DMF eluent and poly(styrene) calibration. Thermal analysis was carried out using Perkin-Elmer Pyris 1 DSC and TGA instruments. The results are collated and compared in Table 2.

Polymers **Ib**, **IIb** and **IV** were not soluble in any of the

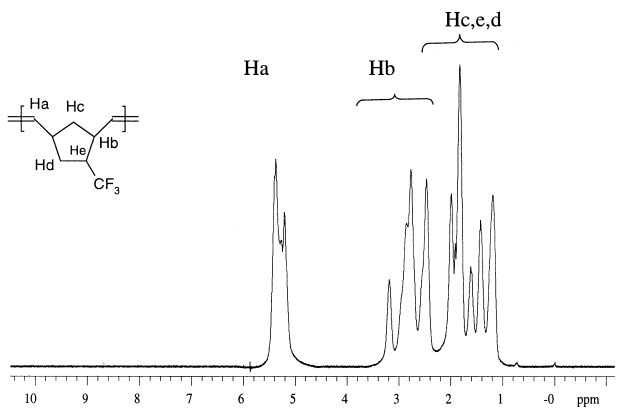

Fig. 22. The ^{1}H NMR spectrum of polymer (**III**).

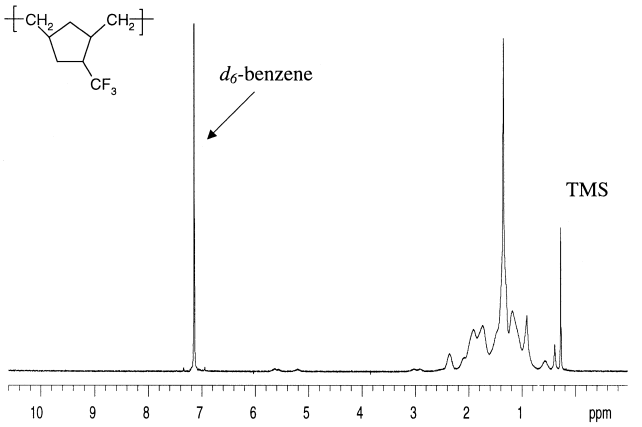

Fig. 23. The ^{1}H NMR spectrum of saturated polymer (**IV**).

available chromatography solvents, but **Ia**, **IIa** and **III** were soluble in dry DMF and the molecular weights obtained for the reprecipitated polymers indicate that the products were genuine high polymers, as expected. The value of the molecular weights for the hydrogenated polymer **IIa** is greater than that for the precursor which indicates that the molecular weights can only be taken as approximate estimates but does suggest that there was little or no chain degradation during the hydrogenation stage. Curiously, and in contrast to expectation, the hydrogenated polymers were revealed to be less thermally stable by thermogravimetry than the precursors. No glass transition process was observed in the DSC analysis of polymers (**Ib**) and (**IIb**).

The experimental evidence demonstrated that the partial hydrogenation (83%) of the double bonds in **Ia** leads to a lowering of T_g by 36 °C, unfortunately the effect for the high trans vinylene content polymer **Ib** is not available since the T_g could not be detected by DSC. However, complete hydrogenation of III to a leads to a lowering of T_g by 37 °C adding further support to the proposal that hydrogenation of this type of polymer is a reasonable way to increase the chain mobility and lower the T_g.

4. Conclusions

The objectives of the work were achieved in that two bicyclo[2.2.1]heptene monomers bearing fluorinated substituents were successfully polymerised by ROMP and their chain microstructures characterised in detail. The very

Table 1
Elemental analysis results

Polymers	C (%) (expected)	H (%) (expected)	F (%) (expected)
Ia	46.79 (44.4%)	2.60 (2.78%)	50.61(52.78%)
Ib	45.78 (44.4%)	2.43 (2.78%)	52.11 (52.78%)
IIa	44.01 (44.04%)	3.37 (3.67%)	48.68 (52.29%)
IIb	44.10 (44.04%)	3.56 (3.67%)	51.76 (52.29%)
III	60.55 (59.26%)	5.54 (5.56%)	34.72 (35.18%)
IV	58.82 (58.84%)	7.34 (6.71%)	28.21 (34.77%)

Table 2
DSC, GPC and TGA analysis results

Polymer	T_g (DSC) (°C)	GPC			TGA % wt loss at 300 °C
		M_n	M_w	PDI	
Ia	161	154,000	240,000	1.6	<0.3
Ib	–	–	–	–	<0.4
IIa	125	172,000	479,000	2.8	9
IIb	–	–	–	–	6
III	90	26,000	61,000	2.3	<1.2
IV	53	–	–	–	2

active WCl_6/Ph_4Sn initiator system giving an approximately 50:50 distribution of *cis* and *trans* vinylenes, a random incorporation of possible repeat units and no discrimination between *endo* and *exo* monomer incorporation, whereas the $MoCl_5/Ph_4Sn$ system gave a high *trans* vinylene content and a marked discrimination in favour of *endo* isomer incorporation. These polymers were successfully hydrogenated using diimide and, in agreement with expectation, hydrogenation resulted in a significant (36/37 °C) lowering of T_g in both the cases, where T_g could be determined by DSC; the hydrogenation of the high *trans* vinylene polymer gave a material in which the T_g could not be detected. Somewhat disappointingly the hydrogenated polymers appear to be, on the basis of thermogravimetry, somewhat less thermally stable than their precursors.

Acknowledgements

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