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NMR spectroscopic characterisation of the microstructure of poly(dimethyl 7-oxabicyclo[2.2.1]hept-2-ene-*exo, exo*-5,6-dicarboxylate)

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SUMMARY

Samples of title polymer have been prepared by ring-opening metathesis polymerisation of dimethyl 7-oxabicyclo[2.2.1]hept-2-ene-*exo,exo*-5,6-dicarboxylate I using a ruthenium catalyst. Comparison of the NMR spectra obtained from samples prepared in two different solvents enables the differences in polymer microstructure to be established. When tetrahydrofuran is used as solvent, a highly tactic polymer with high *trans* vinylene content is produced. In contrast, when ethanol/water is used as solvent, the polymer exhibits an atactic microstructure and contains approximately equal amounts of *cis* and *trans* vinylene bonds.

INTRODUCTION

Ring-opening metathesis polymerisation (ROMP) is an area of polymer science where suitable transition metal catalysts have been demonstrated to be able to produce stereoregular polymers from certain monomers (1). For polymers based on the ring-opening of 7-oxabicyclo[2.2.1]heptene derivatives, a number of structural features need to be considered including double bond configuration, *exo/endo* substituents, head/tail effects (for asymmetrically substituted monomers) and tacticity (2). We now report part of an investigation into how the microstructure of poly(dimethyl 7-oxabicyclo[2.2.1]hept-2-ene-*exo,exo*-5,6-dicarboxylate) II (see Figure 1) can be controlled by changing reaction conditions such as catalyst, solvent and temperature. Details are given of carbon-13 NMR studies on samples which have been polymerised in different solvents systems.

EXPERIMENTAL

Preparation of Polymer (II)

The structures of monomer I and polymer II are shown in Figure 1 below.

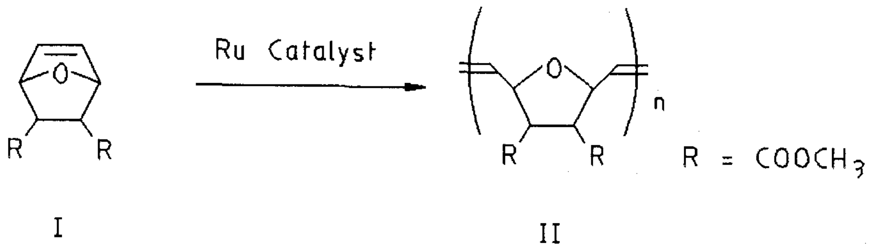

Figure 1: ROMP of monomer I to give polymer II

Sample IIA - in tetrahydrofuran

0.4g monomer I and 2ml tetrahydrofuran (THF) were added to a small Schlenk tube containing a magnetic stirrer. The solution was deoxygenated by three freeze-pump-thaw

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cycles and kept under nitrogen. The solution was then heated to 60°C on a water bath. 0.025g ruthenium trichloride catalyst was added, the tube was sealed and the contents stirred. After 5 hours, an excess of distilled water was added to the flask in order to precipitate the polymer **IIA** which was washed repeatedly with distilled water and dried under vacuum. The polymer was purified by dissolution in tetrahydrofuran and precipitation into an excess of distilled water. The yield of polymer was 69%. The molecular weight was determined to be 300,000 by gel permeation chromatography.

Sample **IIB** - in ethanol/water

0.020g ruthenium trichloride catalyst and 2.5ml ethanol/distilled water (1:1) were added to a small Schlenk tube containing a magnetic stirrer. 0.153ml 1-hexene was added (as a chain transfer agent to limit the polymer molecular weight), and the mixture was deoxygenated by three freeze-pump-thaw cycles and kept under nitrogen. The tube was then stirred at 60°C for 30 minutes. 0.5g monomer **I** was added and the tube was sealed and stirred at 60°C. After 70 minutes, an excess of degassed, distilled water was added in order to precipitate the polymer **IIB** which was washed repeatedly with distilled water and dried under vacuum. The product was purified by dissolution in tetrahydrofuran and precipitation into an excess of distilled water. The yield of polymer was 90%. The molecular weight was determined to be 160,000 by gel permeation chromatography.

NMR Measurements

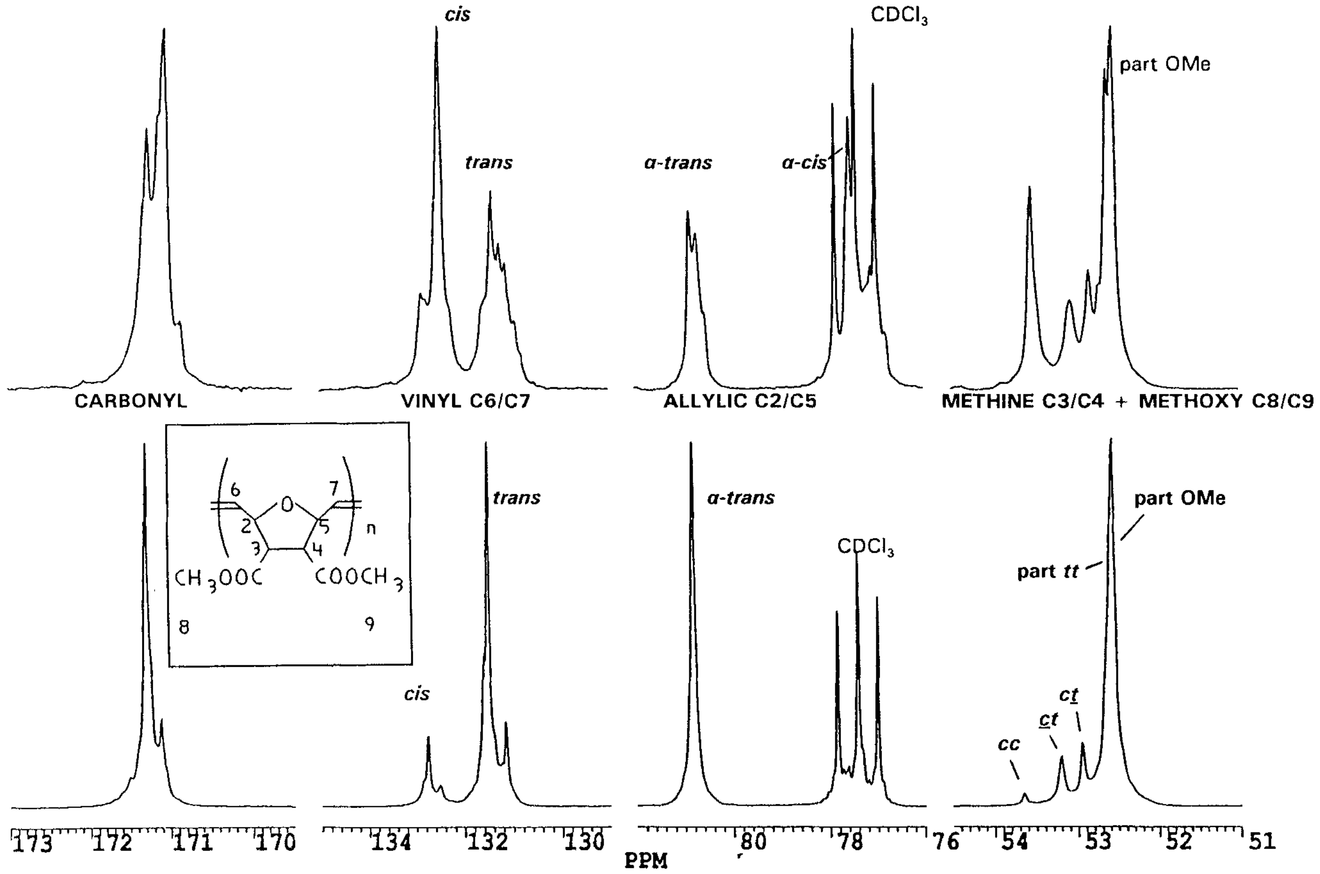
Carbon-13 NMR measurements were performed using a Bruker AC300 spectrometer operating at c. 75 MHz. Spectra were recorded on 15-20% w/v solutions of polymer in deuterochloroform using a 10 mm multinuclear probehead. No special precautions were taken to ensure quantitative signal intensities. However, integration of the carbon-13 spectra of representative oxanorbornene polymers indicates that, apart from the carbonyl resonances, the observation conditions chosen (30 degree pulses, 3 s recycle delay, broadband proton decoupling) result in reliable signal intensities.

RESULTS AND DISCUSSION

Carbon-13 NMR spectra of the polymer samples are discussed in preference to their proton NMR spectra since the latter yield little in the way of microstructural information. Before proceeding with the analysis of the carbon-13 spectra, a brief discussion of the microstructural features of these polymers is necessary. Each carbon type can be expected to give rise to a set of resonances (which are not necessarily fully resolved) due to a combination of i) double bond configuration, ii) sequence effects, and iii) tacticity effects (2,3). Explicitly, sequence effects relate to the configurations of a sequence of neighbouring double bonds. For example, a pair of adjacent double bonds can have tt, ct (tc), or cc configurations (where c = *cis*, t = *trans*); the chemical shift of a given carbon may then be sensitive to such differences in sequence. Tacticity effects arise from the fact that the allylic carbons are chiral and that allylic carbons on adjacent rings may have the same (isotactic or m diad) or opposite (syndiotactic or r diad) chirality. Again, carbon-13 chemical shifts are known to be sensitive to these tacticity effects. Chemical shift sensitivity to longer range sequence and tacticity effects is also possible. One problem encountered in carbon-13 NMR studies of microstructure is that the magnitudes of the sequence and tacticity effects upon chemical shift are often similar. It then proves difficult to divorce the two effects (3). It is worth noting that stereochemical constraints during the ROMP polymerisation result in *syn* relationships between the two vinylic-allylic bonds associated with a given monomer unit. Similarly, the two methyl ester moieties within each repeat unit are also *syn*. An *anti* relationship exists between the methyl ester substituents and the vinylic-allylic bonds in each repeat unit.

The carbon-13 spectra of **IIA** and **IIB** are shown in Figure 2, along with the carbon numbering system employed. Each spectrum comprises sets of resonances in the following regions: vinylic carbon C6/C7, 130 - 134 ppm; allylic carbon C2/C5, 77 - 82 ppm; methine carbon C3/C4, 52 - 54 ppm; ester carbonyl C8/C9, 171 - 172 ppm; methoxy carbon C10/C11, 52 - 53 ppm. Feast and Harrison have reported similar carbon-13 NMR spectra for an analogous polymer system containing 60%, 75% and 90% *trans* vinylenes in the backbone (3), but were unable to make detailed microstructural

Figure 2: Carbon-13 NMR Spectra of Sample **IIA** (bottom) and **IIB** (top)



assignments. Comparison of the vinylic carbon resonances observed for the two samples studied in this work yields useful information concerning microstructural differences.

Sample **IIB** gives rise to two sets of vinylic carbon resonances which are assigned to *cis* (signals to high frequency) and *trans* (signals to low frequency) double bonds on the basis of chemical shift (2,3). However, each set then comprises a number of signals which presumably reflect differing tacticities and/or a distribution in the configuration of adjacent double bonds. In contrast, the vinylic carbons in **IIA** give rise to two much simpler set of signals (here, the *cis* set is much weaker than the *trans* set in keeping with results from proton NMR measurements).

The observation of a significantly simpler set of carbon resonances for sample **IIA** is consistent with it being highly tactic (1). Thus, as an initial premise, tacticity effects can be ignored in the analysis of its spectrum. In the first instance, the vinylic carbons are expected to exhibit triad chemical shift sensitivity to double bond sequence (i.e. the shift of a vinylic carbon is sensitive to the configuration of the double bond to either side of it). The following sequences therefore need to be considered: ccc, cct, tct, ctc, ctt, and ttt. These six sequences should, in theory, give rise to eight resonances after noting that the central vinylic carbons in both the cct and ctt sequences are inequivalent. Examination of the vinylic carbon resonances in **IIA**, after application of resolution enhancement (Figure 3), indicates that an assignment based solely on configurational sequence effects is not inconceivable. If such an assignment is correct, then it supports the premise that the sample is highly tactic (i.e. highly iso- or syndiotactic). In order to develop this argument further it is necessary to make some assignments to the observed signals, as shown in Figure 3. Considering the t-centred sequences first, and given that the polymer has a high

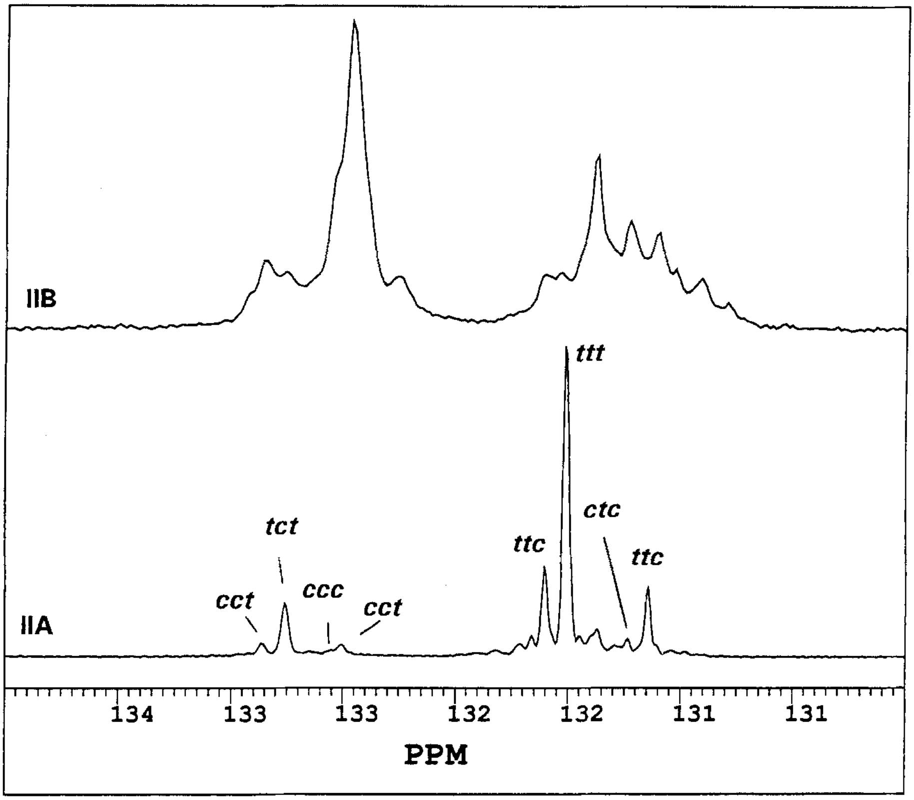


Figure 3: Resolution-Enhanced Carbon-13 NMR Spectra of Samples **IIA** (bottom) and **IIB** (top): Vinyl Carbon Resonances.

trans double bond content (proton NMR measurements reveal that *trans* vinlyenes account for 82% of all double bonds), the most abundant sequence is expected to be ttt, followed by ttc. (This is certainly true for a random distribution of double bonds; calculation reveals that, even in the case of an 'alternating' microstructure, the ttt sequence will still dominate because of the high *trans* vinylene content). Thus, the most intense signal is assigned to the former signal, whilst the two next most intense signals are assigned to the latter sequence. (The high frequency ttc signal is assumed to coincide with a minor signal due to the presence of small amounts of other tacticities since it shows slightly higher intensity than the low frequency ttc signal). Similar arguments apply for the assignment of the tct and cct sequences. The two remaining sequences, ctc and ccc, are more difficult to assign since they are expected to have the lowest abundance. They have therefore been assigned on the basis of regularity in chemical shift behaviour, as follows.

Changing from the ttt sequence to the ttc sequence results in chemical shift changes (expressed in Hz for convenience) in the two central vinylene carbons of +6.8 and -27.9 Hz. The smaller shift change can be assigned to the central vinylene carbon on the t-side of the ttc sequence since this is more remote from the site of change of double bond configuration. Following these changes through, the ctc sequence is expected to resonate at (6.8 - 27.9) = -21.1 Hz with respect to the ttt sequence, as shown schematically in Figure 4. A corresponding peak is clearly observed at -21.0 Hz. A similar process has also been applied in order to assign the signal due to the ccc sequence. (Here, the assignment is less convincing since the ccc sequence is expected to have very low abundance). The observed sequence abundances resulting from the above assignments are given in Table I, along with abundances calculated assuming random incorporation of *cis* and *trans* double bonds.

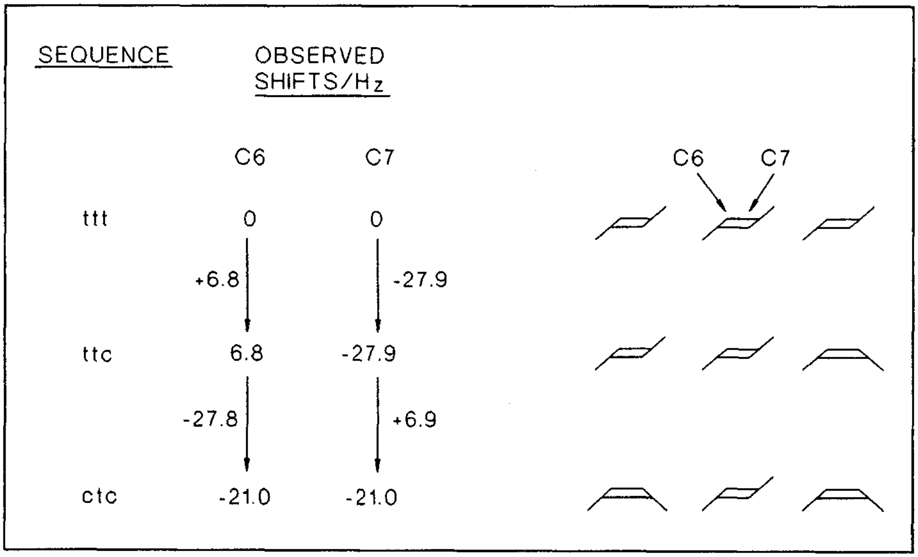


Figure 4: Schematic showing regularity of chemical shift behaviour in *trans*-centred vinylene triads.

The good agreement between calculated and observed abundances provides firm support for chemical shift assignments made solely on the basis of configurational sequence distribution. Furthermore, this agreement also indicates that the *cis* and *trans* vinylenes occur in random fashion along the polymer backbone. Hence, the double bond configuration resulting from ring-opening of incoming monomer is not influenced by the nature of vinylene configuration of the preceding monomer unit in the propagating polymer.

TABLE I: Observed and Calculated Double Bond Sequence Abundances for Sample **IIA** (based on [t] = 0.82, [c] = 0.18 and assuming random incorporation of c and t double bonds).

sequence	observed abundance	calculated abundance
ccc	0.01	0.01
cct	0.05	0.05
tct	0.10	0.12
ctc	0.03	0.03
ttc	0.25	0.24
ttt	0.56	0.55

If the same considerations are applied to sample **IIB**, then the same set of vinylene resonances would be expected, except that they would have different relative intensities compared to **IIA**. That a host of additional resonances are observed implies that **IIB** is not highly tactic (i.e. the presence of more than one tacticity gives rise to the additional signals). Detailed assignments of the vinylene resonances for **IIB** are now in progress.

In summary, the earlier premise that the high *trans* content polymer **IIA** is highly tactic is fully justified on the basis of the above evidence. The distinction as to whether **IIA** is predominantly isotactic or syndiotactic has yet to be made and does not follow directly from its carbon-13 NMR spectrum. Work is in hand to make this distinction.

Further information on the microstructure of these polymers is available from the methine carbon resonances due to C3/C4 (see Figure 2). These occur in the region 52 - 54 ppm which unfortunately overlaps with the OMe group signal. However, from integration, it is clear that the methine carbons give rise to four distinct resonances in both samples (one of which is masked by the OMe signal at c. 52.6 ppm. The signals observed for sample **IIA** are much sharper than those for **IIB**, giving further support to the observation that **IIA** is more highly tactic than **IIB**. The observation of four resonances is in keeping with chemical shift sensitivity to the configuration of the double bond on each side of the five-membered ring. In this case, three sequences, tt, ct and cc need to be considered. In the cc and tt sequences, C3 and C4 are equivalent, so that they each give rise to one resonance. In the ct case, C3 and C4 are inequivalent, and therefore should give rise to two signals of equal intensity. Given that **IIA** has high *trans* content, peak assignments shown in Figure 2 are straightforward. The broadening observed in the peaks for sample **IIB** presumably reflects an increase in the number of carbon environments as a result of the presence of more than one tacticity.

A similar set of four resonances has been observed by Feast and Harrison for an analogous polymer system (3). The relative intensities of the four peaks, as a function of *trans* vinylene content, appear to be in keeping with the assignments discussed above.

Examination of the resonances due to allylic and carbonyl carbon in samples **IIA** and **IIB** indicates that these are not sensitive to double bond sequence distribution (note that the resonances due to allylic carbon *α* to *cis* vinylene are masked by the deuterochloroform signal). However, the differences in the forms of these signals in **IIA** and **IIB** again indicate that former is more highly tactic than the latter. For example, the *trans* allylic carbon in **IIA** resonates as a single peak; in **IIB** a range of shifts are observed, reflecting an atactic microstructure.

CONCLUSIONS

Ruthenium-catalysed ring-opening metathesis polymerisation of dimethyl 7-oxabicyclo[2.2.1]hept-2-ene-*exo,exo*-5,6-dicarboxylate leads to polymers whose microstructure is highly dependent on the nature of the solvent employed. Detailed NMR analysis reveals that when THF is used as solvent a highly tactic polymer with high *trans* vinylene content results. The vinylene bond configuration resulting from ring-opening of incoming monomer is not influenced by the nature of the double bond configuration of the preceding monomer unit. In contrast, when ethanol/water is used as solvent, approximately equal amounts of *cis* and *trans* vinylene bonds are formed in the polymer. In addition, the polymer now exhibits an atactic microstructure.

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