Preparation of Poly[(1,1-dipropyl)butane-1,4-diyl], ($Pr_2CCH_2CH_2CH_2$)$_n$, *via* Regiospecific Ring Opening Polymerisation of 3,3-Dipropylcyclobutene

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A general route to 3,3-disubstituted cyclobutenes is described and 3,3-dipropylcyclobutene is subjected to ring opening metathesis polymerisation (ROMP) using the Schrock initiator, Mo(=CHR)(=NAr)(OR′)$_2$, where R is $C_6H_5C(Me)_2$-, Ar is 2,6-diisopropylphenyl and R′ is (Me)$_3$C- to give a polymer which is completely regiospecific (HT) and stereospecific (*trans*); the polymer is reduced to poly[(1,1-dipropyl)butane-1,4-diyl], which shows evidence of unusual properties associated with the conformational control exerted by the quaternary centres.

There is increasing interest in controlling the shapes of flexible molecules with conformational locks.[1,2,3] We have shown that quaternary centres exert extensive control over the conformations of nearby bonds to the extent that tetrapropylmethane or the related $\mathrm{Pr}^n_4\mathrm{N}^+$ ion has only two significantly populated conformations (with D_{2d} and S_4 symmetry).[4] These conformers differ by only 1.06 kJ mol^{-1}, but the next conformation lies 8.62 kJ mol^{-1} higher in energy. We have suggested that polymers of the type [$(RCH_2CH_2)_2CCH_2CH_2$]$_n$ and [$(RCH_2CH_2)_2CCH_2CH_2CH_2$]$_n$ might have unusual properties associated with conformational control of both the main chain and the side chains by the quaternary centres. For the [$(RCH_2CH_2)_2CCH_2CH_2CH_2$]$_n$ case in particular one can readily predict that: (*a*) The CH_2-CH_2-CH_2 unit in the main chain should exist exclusively in an *anti, anti* (tt) conformation. It has been shown that this is the case for the CH_2OCH_2 unit in poly(3,3-disubstituted)oxetanes.[5] (*b*) Four structures **A**–**D** are possible at each quaternary centre (Fig. 1). The main chain conformation imposes certain conformations on the side chains. In general, these structures will all have energies which differ by far less than the *gauche/anti* (*g/t*) difference, although this may be modified for particular side chains; thus the poly-**B** structure is improbable for ($Pr_2CCH_2CH_2CH_2$)$_n$, due to interations between the propyl groups from next-but-one quaternary centres (Fig. 2). (*c*) On the other hand, the energy barriers for interconversion of **A**–**D** are much higher than those for conversion of *gauche* to *anti* conformers, since passage through at least one strained conformer with a g^+g^- (*syn*-pentane) interaction is necessary. These polymers should therefore have unusual chain dynamics as well as unusual structures. We report the first synthesis of a hydrocarbon polymer which can test these predictions.

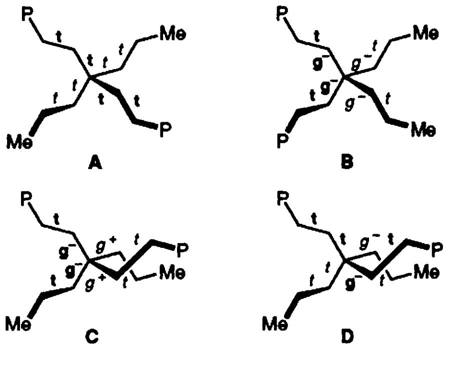


Fig. 1 The four possible conformations, **A**–**D**, around a quaternary centre in the polymer ($Pr_2CCH_2CH_2CH_2$)$_n$; **P** is the remaining polymer chain. Torsion angles along the main chain are shown **bold**, those in the Pr–C–Pr unit are in *italics*.

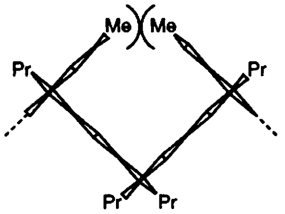
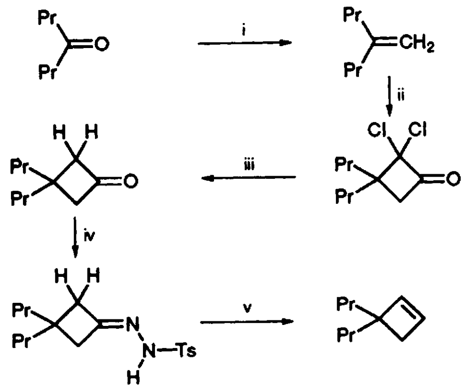


Fig. 2 The poly-**B** structure for ($Pr_2CCH_2CH_2CH_2$)$_n$, showing interactions between the propyl groups from next-but-one quaternary centres

3,3-Dipropylcyclobutene was prepared as shown in Scheme 1, using modifications of established routes.[6] Cycloaddition of dichloroketene to 1,1-dipropylethene was found not to compete well with dimerisation of the ketene, and good yields of the cycloadduct were only obtained when trichloroacetyl chloride was added slowly by syringe pump to a sonicated solution of the alkene containing zinc powder.[7] Dechlorination proceeded smoothly, but the Shapiro reaction[8] only gave good yields when lithium tetramethylpiperidide was used as the base.[9] The *p*-toluenesulfonylhydrazone was at least as good as the 2,4,6-triisopropylbenzenesulfonylhydrazone in this reaction. This synthesis should be quite general and has been completed for 3,3-dialkylcyclobutenes with alkyl = Et, Bu^n and $PhCH_2CH_2$. ROMP of 3,3-dipropylcyclobutene was initially carried out with several first generation catalysts such as WCl_6/Et_3Al.[10] Soluble polymers were formed but it was apparent from the complex ^{13}C NMR spectra in the alkene region that polymerisation was neither stereospecific nor regiospecific. ROMP using well-defined Schrock initiator Mo[=CHCPh(Me$_2$)](=N-2,6-di-Pr^{i}C$_6$H$_3$)(Bu^{t}O)$_2$[11] however, gives much more promising results. The polymerisation reaction produces a living polymer, which was capped with benzaldehyde. The ^{13}C NMR spectrum, Fig. 3(*a*), of the polymer shows only two strong signals in the alkene region which indicates that the polymer obtained is clearly regiospecific (HT, see later) and stereospecific (*trans*, IR out-of-plane vinyl absorption at 977 cm^{-1}) and can be represented by **1**; the small peaks in Fig. 3(*a*) are due to the end groups. ROMP using Mo(=CHCPh(Me$_2$))(=N-2,6-di-i-PrC$_6$H$_3$)(O-C(CF$_3$)$_2$Me)$_2$[12] as initiator gives polymer which is largely *cis* but does contain some *trans* [Fig. 3(*b*)].



Scheme 1 *Reagents*: i, Ph$_3$P=CH$_2$, 60%; ii, Cl$_2$C=C=O from Zn powder and Cl$_3$CCOCl with sonication, Et$_2$O, 60%; iii, Zn/HOAc, 90%; iv, *p*-toluenesulphonylhydrazide, THF, 70%; v, lithium 2,2,6,6-tetramethylpiperidide, THF, 60%

Diimide reduction of **1** was carried out with *p*-toluenesulfonylhydrazide in xylene[13] at 110 °C; it was necessary to use a large excess of *p*-toluenesulfonylhydrazide (40 equiv.), added in portions over 3 d to get complete hydrogenation to **2**. The ^{13}C NMR spectrum of **2** shows signals at 39.4, 37.9, 37.5 (quaternary carbon), 16.4, and 15.1 (Me); four methylene signals are expected if **2** is HT (five if it was entirely HHTT), there must be a coincidence of the signals for the $CH_3\mathit{CH}_2CH_2$ and $CH_2\mathit{CH}_2CH_2$ groups.

As recovered by precipitation from chloroform into methanol, polymers **1** and **2** are insoluble in common solvents at room temperature, but dissolve on heating or after being melted. GPC analysis of **1** in chloroform shows M_n = 51700 (relative to polystyrene standards), M_W/M_n = 1.27. The GPC analysis of **2** in the same solvent is comparable to that of **1**, showing that neither crosslinking nor chain scission has occurred during the hydrogenation step. Both **1** and **2** show good thermal stability at elevated temperatures; thus, when subjected to thermogravimetric analysis, **1** exhibits 2% mass loss at 290 °C and 96% mass loss at 380 °C, whereas **2** shows 2% mass loss at 349 °C and 96% mass loss at 456 °C.

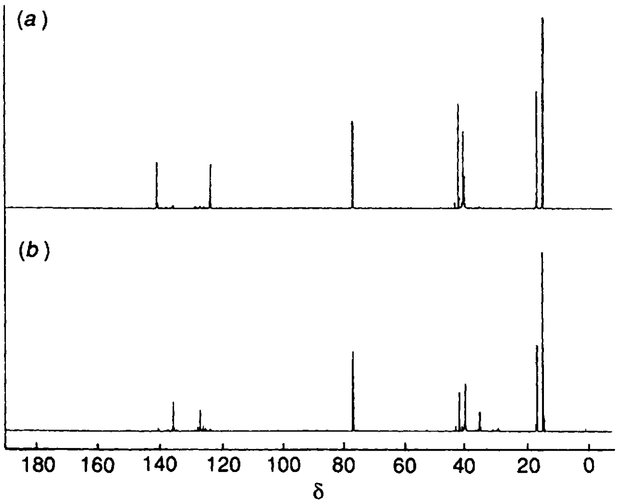
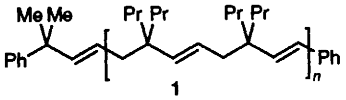


Fig. 3 (*a*) ^{13}C NMR spectrum (125 MHz, CDCl$_3$) of the polymer **1** from ROMP of 3,3-dipropylcyclobutene using the initiator Mo[=CHCPh(Me$_2$)](=N-2,6-di-Pr^i-C$_6$H$_3$)(Bu^{t}O)$_2$, capped with benzaldehyde. (*b*) Polymer prepared in the same way but using Mo[=CHCPh(Me$_2$)](=N-2,6-di-Pr^{i}C$_6$H$_3$)(O-C(CF$_3$)$_2$Me)$_2$ as initiator.



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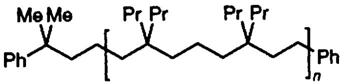

2

The differential scanning calorimetry trace (DSC, Perkin-Elmer DSC7) for **1** recovered by reprecipitation shows a large melting endotherm at 102 °C (55 J g^{-1}) which is absent from the trace of a sample quenched from the melt. When a quenched sample of **1** was annealed for 2 h at 80 °C and the DSC rerun, only a small endotherm appears at 99 °C along with another smaller endotherm at 102 °C. The DSC trace for **2** shows a melting endotherm at 136 °C (36 J g^{-1}), but when annealed for 17 h at 100 °C it shows two melting endotherms at 127 °C and 136 °C. These preliminary results indicate (i) that both polymers are crystalline, (ii) that crystallisation from the melt appears to be relatively slow, and (iii) suggest that several crystalline forms of these hydrocarbon polymers may be accessible.

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