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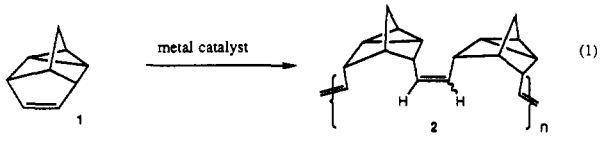
Communications to the Editor

Synthesis and Epoxidation of Cis-Enriched Polydeltacyclene

The epoxidation of polyolefinic compounds is an area of current interest due to the ability to modify the physical properties of the polymer.[2] The chemical reactivity imparted by the highly strained epoxide is also of great importance. For example, the synthesis of epoxy resins provides commercially important materials with a diverse range of applications including their use as thermosetting resins, as protective coatings, and as matrices in composites. Polyepoxides are essential components in many adhesives and are used as stabilizers and plasticizers for vinyl resins.[3]

As part of our interest in the synthesis and utility of a new polymer, polydeltacyclene **2**, prepared via a ring opening metathesis polymerization (ROMP),[4] we have investigated the behavior of **2** toward epoxidizing agents in order to prepare highly strained and rigid polyepoxy polymers. In this article, we report the synthesis and characterization of cis-enriched polydeltacyclene and the reactivity of **2** and polynorbornene with dimethyldioxirane.

We have recently shown that deltacyclene, **1**, can be efficiently polymerized in the presence of ruthenium trichloride to yield polydeltacyclene **2** as a mixture of cis and trans isomers, eq 1.[5] This result is in contrast to



(1)

the behavior of norbornene, which gives predominantly the trans polyolefin in the presence of ruthenium trichloride.[6] Since our monomer had behaved quite differently compared to norbornene, it was of interest to examine the olefin stereoselectivity in the presence of other catalysts that have been successfully used to effect highly cis stereoselective polymerizations of norbornene.[4a]

Changing the catalyst from $RuCl_3$ to WCl_6/Ph_4Sn[7,8] effected a smooth polymerization of deltacyclene and provided a white solid in good yield (73%) and of moderate molecular weight M_w = 20 000. Analysis of the ^1H NMR spectrum indicated a more selective reaction had taken place, yielding **2**, with the cis geometry predominating. Three peaks at 5.46, 5.55, and 5.64 ppm corresponding to the isomeric olefinic protons were observed, and integration of these peaks indicated a 70:30 cis/trans mixture. Integration of signals at 2.47 and 2.18 ppm, which we assign to the allylic protons, provided a second means of measuring the stereoselectivity of the reaction. In the ^{13}C NMR spectrum, the signals at 11.1, 14.8, and 16.2 ppm are assigned to cyclopropane carbons while those at 35.8, 41.1, 43.7, and 48.2 ppm are assigned to aliphatic carbons. Expansion of the region between 129.4 and 132.8 ppm revealed five peaks, which are assigned to the olefinic carbons.

$ReCl_5$ was substantially more cis stereoselective than the tungsten or ruthenium catalysts. The reaction was most effectively carried out by addition of deltacyclene to a flask containing the catalyst in the glovebox at room temperature *in the absence of any solvent*. Under these conditions a solid was isolated in moderate yield (48%), which, by ^1H and ^{13}C NMR, was >95% *cis*-**2**. A low molecular weight material (M_w = 6000) was also obtained in ca. 20% yield.[9] The GPC of pure *cis*-**2** indicated that the polymer was of very high molecular weight (M_w = 986 000). The ^1H NMR spectrum showed a single resonance at 5.48 ppm, which was assigned to the cis olefinic hydrogens and a signal at 2.48 ppm for the allylic protons (Figure 1A). The ^{13}C NMR spectrum (Figure 1C) contains six peaks at 11.3, 16.3, 35.7, 40.7, 43.8, and 131.2 ppm, which indicates a highly stereoregular polymer was formed. It is interesting to note that *cis*-**2** is substantially less soluble in chloroform, THF, or benzene than is the cis/trans polymer. We have not yet found a catalyst that is highly trans selective to compare the properties of *cis*-**2** and *trans*-**2**.

We have also examined the reactivity of the *cis*-polydeltacyclene/*trans*-polydeltacyclene toward oxidizing agents with the goal of preparing a polyepoxide, Table I. The partially epoxidized material starting from *cis*-**2**/*trans*-**2** proved to be quite sensitive to one of the most commonly used epoxidizing agents, i.e., *m*-chloroperbenzoic acid (MCPBA).[3] The use of a two-phase buffered system[10] was also ineffective at inhibiting decomposition of the epoxidized polymer if greater than 10–15% of the olefins were epoxidized. Acid-catalyzed opening of the epoxide is a likely source of the instability.

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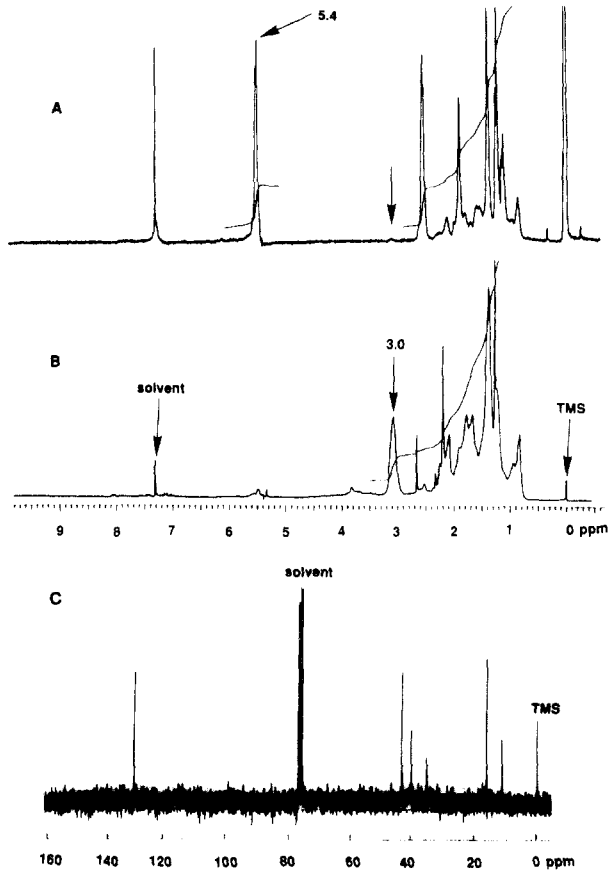


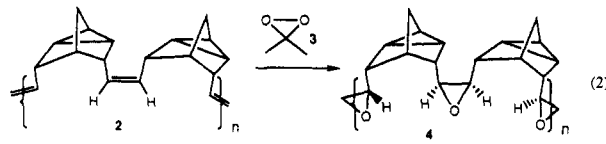
Figure 1. NMR spectra in $CDCl_3$ of (A) *cis*-polydeltacyclene **2** (^1H at 200 MHz), (B) *cis*-polydeltacyclene epoxide **4** (^1H at 200 MHz), and (C) *cis*-polydeltacyclene **2** (^{13}C at 50.1 MHz).

Table I
Epoxidation of Polydeltacyclene (PDC) and Polynorbornene (PNB) with Dimethyldioxirane (DMD)

entry	polymer	olefin ratio cis:trans	equiv of DMD[a]	olefin reacted[b] (cis:trans), %
1	PDC	50:50	0.2	30:0
2	PDC	50:50	0.3	60:0
3	PDC	50:50	1.0	decomposn
4	PDC	70:30	1.0	decomposn
5	PDC	100:0	1.0	100:0
6	PDC	100:0	0.5	30:0
7	PDC	100:0	0.1	10:0
8	PNB	90:10	1.0	100:100
9	PNB	90:10	0.7	70:0
10	PNB	30:70	1.0	100:70

[a] Dimethyldioxirane used as a solution in acetone. [b] The amount of olefin reacted is as a percentage of the amount of that olefin, i.e., 30% of 50:50 cis/trans means 15% of the total starting material.

In considering milder epoxidizing agents, we were intrigued by recent reports on the use of dimethyldioxirane for the epoxidation of highly sensitive organic molecules.[11] We are aware of no studies on the utility of this reagent in polymer chemistry. When we subjected a chloroform solution of *cis*-**2**/*trans*-**2** to a solution of distilled dimethyldioxirane in acetone at room temperature, we observed varying amounts (15–30%) of polyepoxide depending on the molar ratio of polymer/dioxirane. Integration of the signal at 3.00 ppm (which is assigned to the hydrogens on the epoxide-bearing carbon) vs the total area between 5.4–5.8 ppm for the olefinic protons provides a measure of the degree of epoxidation. Examination of the ^1H NMR spectra revealed that only the cis olefins were reactive under these conditions. Steric factors have been proposed to be more important for the epoxidation with dimethyldioxirane than with MCPBA and have been used to explain the increased rate of reaction of cis vs trans olefins.[12] The integral for the trans olefinic signal was unchanged while a decrease was noted for the signal assigned to the cis protons. A new olefinic signal also appeared at 5.73 ppm, which was assigned to a trans olefinic hydrogen which is adjacent to a monomer repeat unit where the olefin has been epoxidized. Attempts to fully epoxidize *cis*-**2**/*trans*-**2** led to decomposition of the polymer. However, if 100% *cis*-**2** was treated under identical conditions, we were able to effect complete epoxidation, yielding polyepoxide **4**, eq 2; the ^1H NMR spectrum is shown in Figure 1B. The

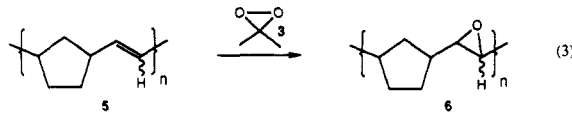


(2)

resonance for the allylic protons has shifted upfield, and a new signal has appeared at 3.00 ppm compared to the polyolefin, **2**.

Since dimethyldioxirane is known to be stereospecific (i.e., cis olefins yield cis epoxides), the isomerism observed must result from epoxidation of the two faces of the olefin designated as *re* and *si*. This leads to multiple resonances due to different local environments for the diads represented by *rere*, *resi*, *sisi*, and *sire*.[2a] Nevertheless, it is clear from the ^{13}C NMR that a cyclopropane is retained in the polyepoxide, an epoxide has been formed as shown by signals at ca. 57 ppm, and the olefin has completely reacted.

The high selectivity exhibited by this reagent toward polydeltacyclene led us to compare its behavior toward *cis*- and *trans*-polynorbornene, entries 8–10. We prepared the polymers using literature procedures[4a,6,7] and subjected 90:10 and 30:70 cis/trans mixtures of **5** to dimethyldioxirane. It was possible to selectively react the cis olefin without any reaction of the trans olefin by controlling the amount of dioxirane, entry 9. However, unlike polydeltacyclene, it was possible to effect complete epoxidation of *cis*-polynorbornene/*trans*-polynorbornene with dimethyldioxirane to yield **6**, eq 3.



(3)

Finally, in order to make this methodology more attractive by avoiding the distillation of dimethyldioxirane, we examined the utility of an in situ method described by Murray.[11a,b] When *cis*-polydeltacyclene was treated with Oxone in a benzene/acetone/water/$NaHCO_3$ mixture,[13] epoxide **4** was isolated in 66% yield with >95% of the olefins epoxidized. Similar results were obtained for polynorbornene epoxidation.[14]

Thus the use of dimethyldioxirane would appear to be a general and very simple method for the epoxidation of polyolefinic compounds. In those instances where a controlled amount of epoxidation is desired, purified dioxirane is the preferred reagent. The extra convenience of the in situ method suggests it will have wider applicability. Studies are in progress on the physical and chemical properties of these polyepoxides, the results of which will be reported in due course.

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(9) The ^1H and ^{13}C NMR spectra of this polymer indicated the presence of the cyclopropyl ring but no olefinic double bonds. Thus far, the determination of the structure for the minor product has eluded us in spite of extensive spectroscopic analysis. The low molecular weight material was most efficiently separated from the high molecular weight material by vigorously swirling the flask containing the two materials and quickly decanting the light fluffy solid, which proved to be the low molecular weight polymer. The amount of this undesired material was a function of the dryness of the reaction conditions. If a drop of water was added to the reaction mixture, the saturated polymer was the only product isolated. We also found that $ReCl_5$ from Aldrich gave substantially less of the saturated polymer than the catalyst purchased from Alfa.
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(13) A typical experimental is as follows: *cis*-**2** (1.3 mmol) was dissolved in benzene (100 mL). Water (30 mL), acetone (20 mL), and sodium bicarbonate (214 mmol) were added followed by Oxone (73 mmol). The reaction mixture was stirred vigorously for 3 h. The solids were removed by filtration, and the solution was extracted with benzene. The benzene was dried over magnesium sulfate before removing the volatiles to yield the polyepoxide **4** in 66% yield.
(14) When polynorbornene (70:30 trans/cis) was epoxidized using ca. 25% as much Oxone as that described in ref 13, the reaction was 50% completed (once again we noted the cis olefin was more reactive than the trans olefin).

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Complex Formation between Poly(ethylene glycol) and α-Cyclodextrin

Since the discovery of cyclodextrins (α-CD, β-CD, and γ-CD), a great number of inclusion complexes with low molecular weight compounds, both organic[1] and inorganic,[2] have been prepared and characterized. However, there are no reports, to our knowledge, on the formation of complexes of CDs with polymers except for the examples in which a monomer was polymerized in situ within a cyclodextrin complex.[3,4] We have found that α-cyclodextrin forms complexes with poly(ethylene glycol) (PEG) of various molecular weights to give stoichiometric complexes in high yields.

When aqueous solutions of PEG were added to a saturated aqueous solution of α-CD at room temperature, the solution became turbid and the complexes were obtained as precipitates when the average molecular weight of PEG was between 400 and 10 000. This is the first observation that cyclodextrin forms complexes with polymers in a solid state. α-CD does not form complexes with the low molecular weight analogues, ethylene glycol,[5] diethylene glycol, and triethylene glycol. β-CD did not form complexes with PEG of any molecular weight.

The rate of the complex precipitation depends on the molecular weight of PEG. The rates were followed by absorbance at 700 nm. Figure 1 shows the effects of molecular weights on the rates of the turbidity development after mixing the α-CD solution and PEG solution. The

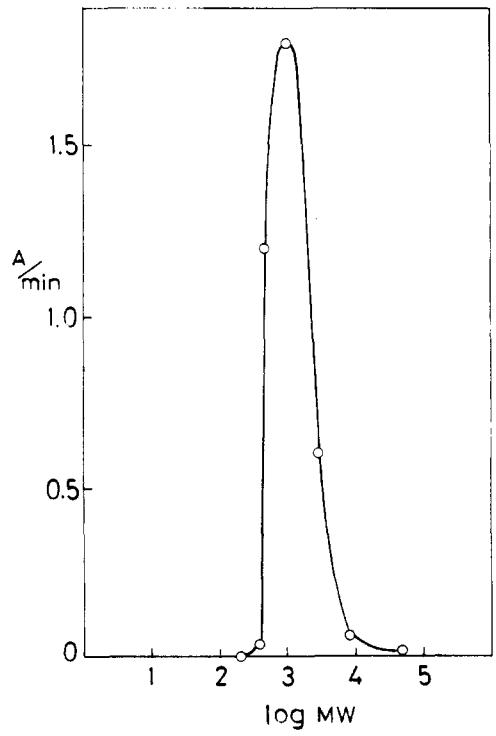

Figure 1. Rate of turbidity development after mixing the saturated α-CD solution and PEG solution. α-CD solution 2 mL, 10 mg of PEG/0.1 mL of H_2O, monitored at 700 nm.

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