Metathesis Polymerization of 7-Oxa-2,3-bismethoxycarbonylbicyclo[2.2.1]hepta-2,5-diene: Synthesis of Novel Conjugated Polyenes

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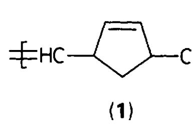
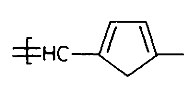
Novel high-molecular-weight polymers are readily made by the alkene metathesis reaction using 7-oxa-2,3-bismethoxycarbonylbicyclo[2.2.1]hepta-2,5-diene as the monomer and Ru and Os chlorides as catalysts; these polymers are readily dehydrogenated using dichlorodicyanobenzoquinone to afford novel purple–red conjugated polyenes.

Although cyclo-octatetraene has been metathesis polymerized by well-defined tungsten alkylidene initiators to give polyacetylene directly,[1] the most favoured method using metathesis catalysts and ring-opening polymerization is that where a processable precursor polymer is first formed which by one single effective reaction, retro-Diels–Alder, is converted into polyacetylene.[2] We have recently attempted to use general indirect methodology of this kind with the aim of synthesizing novel polyacetylenes.

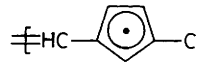
Bicyclo[2.2.1]hepta-2,5-diene rapidly forms the high-molecular-weight polymer (**1**) using a variety of metathesis catalysts.[3] The tertiary hydrogen atoms are easily removed using dehydrogenating agents such as iodine, t-butylperbenzoate with UV irradiation, and dichlorodicyanobenzoquinone (DDQ),[4] to make black paramagnetic materials which were assigned structures (**2**) and/or (**3**).[5] Unfortunately (**1**) is not very soluble and (**2**)/(**3**) is an intractable black solid whose structure is difficult to elucidate. However, because of the



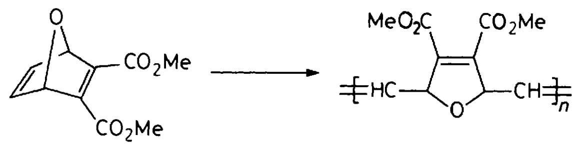
(1)



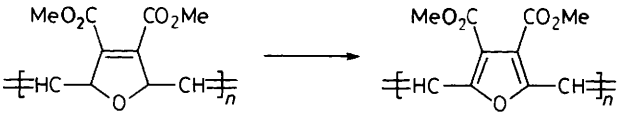
(2)



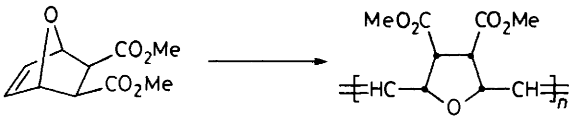
(3)



(4) **(5)**



(5) **(6)**



exo **(7)** **(8)**

apparent ease of dehydrogenation of (**1**) using DDQ we decided to apply this methodology to functionalized bicycloheptadiene monomers in the belief that they would afford highly soluble ring-opened polymers. This requires the presence of heteroatoms and polar groups, a feature which usually militates against efficient metathesis.

We now report that 7-oxa-2,3-bismethoxycarbonylbicyclo-[2.2.1]hepta-2,5-diene (**4**), easily synthesized from readily available starting materials,[6] is rapidly converted in virtually quantitative yield to high-molecular-weight ring-opened polymer (**5**) using $OsCl_3$, and in good yield using $RuCl_3{\cdot}3H_2O$ catalysts,† though surprisingly $IrCl_3{\cdot}3H_2O$ as catalyst is inactive. The colourless fibrous materials thus obtained are soluble in a wide range of organic solvents and give well defined ^{13}C and ^{1}H NMR spectra.

The ^{13}C NMR spectra of these polymers are reproduced in Figures 1 and 2. As with other ring-opened polymers containing symmetrically substituted repeat units[7] the signals for the bridgehead carbon atoms C(1,4) adjacent to *cis* and *trans* double bonds are well separated, with *trans* always downfield of *cis*. Assuming the same line order as in these other cases,[7] one may assign the signals at δ 82.00 and 85.98 to C(1,4) *cis* and *trans* respectively.‡

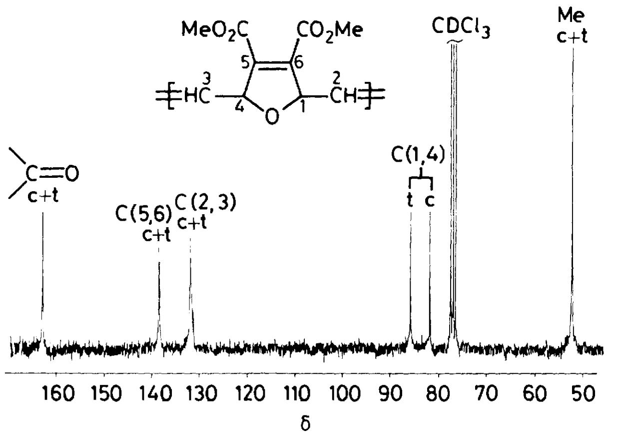


Figure 1. ^{13}C NMR spectrum of 50% *trans* (**5**) prepared from (**4**) using $OsCl_3$ as catalyst.

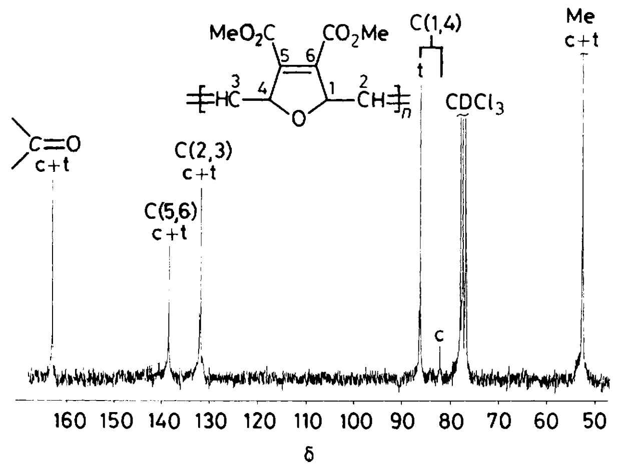


Figure 2. ^{13}C NMR spectrum of 90% *trans* (**5**) prepared from (**4**) using $RuCl_3{\cdot}3H_2O$ as catalyst.

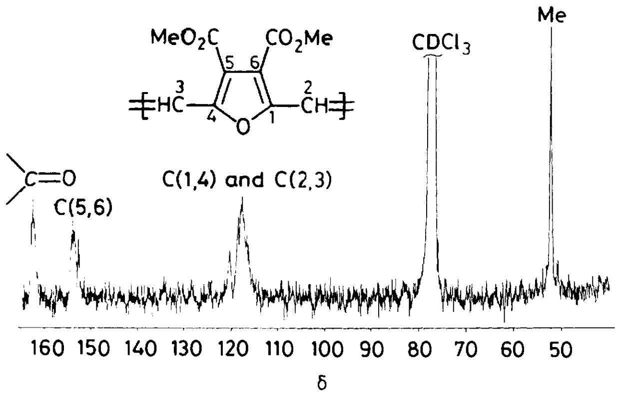


Figure 3. ^{13}C NMR spectrum of dehydrogenated polymer (**6**) prepared from 50% *trans* (**5**).

This assignment means that the polymer prepared using the Os catalyst, Figure 1, has a main chain *trans* double bond content of 50%, and that prepared using the Ru catalyst, Figure 2, a *trans* content of greater than 90%, in accord with previous work using these catalysts.[8] Signals at δ 52.52 and 162.80 are assigned to the methyl and carbonyl respectively and an off-resonance experiment allows one to distinguish

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† In the case of Ru catalysed polymerization equal volumes of 1 M monomer solution in chlorobenzene and 0.13 M catalyst solution in ethanol were heated overnight in a sealed tube at 100 °C. In Os catalysed polymerization 1.6 M monomer solutions in chlorobenzene were mixed with 0.05 M catalyst solution in ethanol and heated for two hours in a sealed tube at 70 °C. In both cases polymers were isolated by precipitation in methanol.

‡ All spectra were taken using $CDCl_3$ solutions with tetramethylsilane (TMS) as internal standard.

between C(2,3) at δ 131.80 and C(5,6) at δ 138.32, as well as supporting the other assignments.

^{1}H NMR spectra of these polymers have the methyl signal at δ 3.78 and a broad singlet at δ 5.91 attributable to the bridgehead protons. The 90% *trans* polymer has one alkenic proton signal at δ 5.47 while the 50% *trans* polymer has two alkenic proton signals at δ 5.47 and 5.57, confirming that both *cis* and *trans* double bonds are present. The ^{1}H NMR spectra therefore confirm that the polymers are genuinely metathesis ring-opened and not 1,4-epoxide ring-opened.

Benzene solutions of (**5**) gently refluxed with a stoicheiometric amount of DDQ over five minutes became wine-red and eventually purple–red in colour. Precipitation in methanol afforded a quantitative yield of a deep-red polymer ($\lambda_{max.}$ = 460 nm) which after further reprecipitation and washing was shown by microanalysis to be essentially free from DDQ. The ^{13}C NMR spectrum, Figure 3, shows complete conversion of the starting material (**5**) resulting in a new set of signals that, although broad, are consistent with the structure of the conjugated polyene (**6**) and may be assigned realistically as shown in Figure 3.

The material is moderately paramagnetic giving a symmetrical signal with a g value of 2.0027, as expected for a polyacetylene. The polymer is readily hydrogenated to a colourless derivative using toluene-*p*-sulphonhydrazide.[9] We have also prepared and ring-open polymerized (**7**), the dihydro derivative of (**4**), using Ru and Os catalysts; however, the polymer (**8**) thus obtained is not formed so readily and so cleanly (some 1,4-epoxide ring-opening is indicated in the ^{13}C NMR spectrum) and significantly does not dehydrogenate under the conditions used to dehydrogenate (**5**). This result parallels our experience in the attempted dehydrogenation of poly(norbornene) and poly(norbornadiene)[5] where the latter dehydrogenates but not the former, emphasising the importance of ring unsaturation for these hydrogen abstraction reactions.

Novel conjugated, soluble polymers are very much in demand for research into their intriguing optical and electronic properties. We have here a very easy general synthesis of a novel type of polyacetylene where there is opportunity of varying both the nature of the polar substituents and skeletal hetero atom.[10]

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