The Structure of Polymers Derived from exo- *and* endo-*Dicyclopentadiene*

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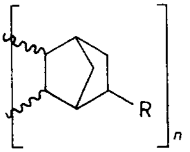
The polymerization of exo- *and* endo-*dicyclopentadiene with* $BF_3.Et_2O$ *and* $PdCl_2\ (\phi CN)_2$ *has been studied. All of the polymers except one are formed by 1,2-polymerization of the bicycloheptene double bonds. Polymerization of* endo-*dicyclopentadiene with* $BF_3.Et_2O$ *leads to a polymer containing* exo *fused cyclopentene rings and it is suggested that this is a 1,3-polymer. This is the first time unequivocal evidence has been provided to support the formation of a 1,3-polymer from a bicycloheptene by cationic polymerization.*

THE structure of polymers produced by the cationic polymerization of bicyclo-[2,2,1]-heptene and related compounds has previously been reported[1] to be (I).

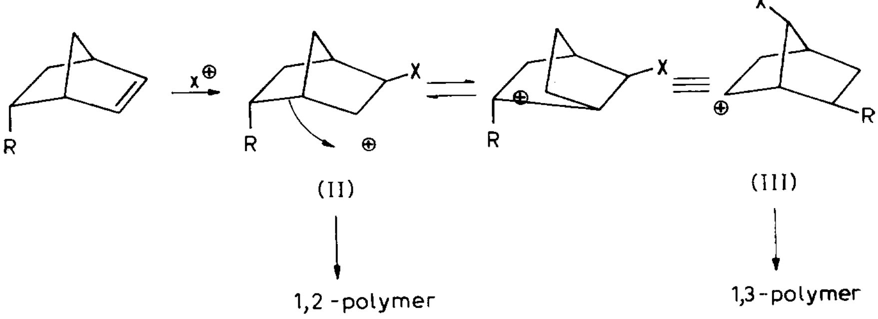


(I)

The evidence for the presence of the 1,2-disubstituted bicycloheptane repeat unit in these polymers is limited.

Addition of the initiator X^+ to the double bond of a substituted bicycloheptene leads to (II), which can then rearrange as shown to give (III). If (II) acts as the propagating species then clearly the polymer incorporates the bicycloheptane unit into its backbone by 1,2-substitution. If, however, rearrangement of (II) occurs before it propagates then (III) will be the active propagating species and the bicycloheptane units will be attached by 1,3-substitution to the polymer backbone. The possibility of a species similar to (III) acting as the propagating carbonium ion in a bicycloheptene polymerization has been considered by Kennedy and Makowski[1] but was thought to be unlikely on the basis of infra-red evidence.

SCHEME I

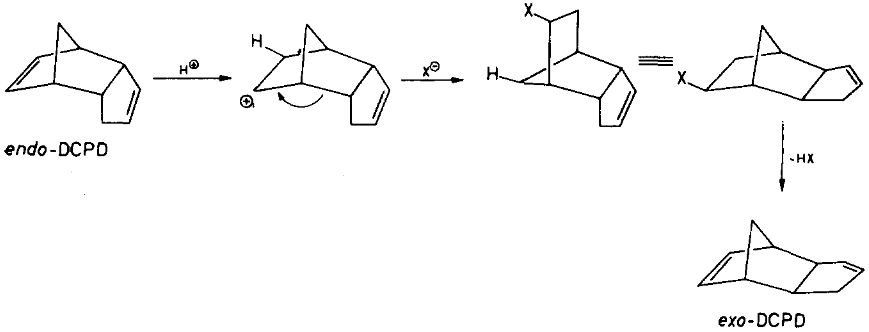


We now present evidence for the participation of a propagating carbonium ion of type (III) in the cationic polymerization of *endo*-dicyclopentadiene.

From Scheme I it will be noted that the *endo* substituent R is converted to an *exo* substituent when (II) rearranges to (III). Thus, in order to aid in following whether the rearrangement (II) → (III) has occurred, it is convenient to choose the substituent R in such a way that the change *endo* → *exo* can be identified clearly and unequivocally. For this reason we have chosen to study the polymerization of the two isomeric dicyclopentadienes (DCPD).

On the addition of HX to *endo*-dicyclopentadiene, rearrangement occurs and the product obtained is X substituted dihydro-*exo*-dicyclopentadiene. This reaction is used for the isomerization *endo* → *exo* dicyclopentadiene[2], as indicated in Scheme II.

SCHEME II



We have prepared polymers from *exo*- and *endo*-dicyclopentadiene using $BF_3.Et_2O$ and $PdCl_2$ $(\phi CN)_2$ as initiators. The palladium compound has recently been described by McKeon and Starcher[3] as an active initiator for the polymerization of bicycloheptenes.

EXPERIMENTAL

The n.m.r. spectra were recorded using chloroform solutions of the polymers at 30°C on a Varian Associates 220 Mc/s spectrometer. The i.r. spectra were measured using a Perkin–Elmer 257 grating infra-red spectrophotometer and the molecular weights determined by vapour pressure osmometry in *o*-dichlorobenzene on a Mechrolab vapour pressure osmometer, Model 302.

Commercially available (British Drug Houses Ltd) *endo*-dicyclopentadiene and boron trifluoride etherate were purified by distillation in vacuum before use. Palladium dichloride dibenzonitrile was prepared as in the literature[4] and *exo*-dicyclopentadiene was prepared by conversion of the *endo* dimer to chlorodihydro-*exo*-dicyclopentadiene[2] followed by elimination of hydrogen chloride by potassium *tert.* butoxide in dry dimethylsulphoxide[5].

Polymerizations

Using $BF_3.Et_2O$—$BF_3.Et_2O$ ($\frac{1}{2}$ cm^3) was added at room temperature to the stirred diene (2 g) in a flask flushed with dry, oxygen-free nitrogen. Stirring was continued for half an hour. The solid mass that was formed was dissolved in chloroform, the colour discharged by adding a few drops of triethylamine and the polymer precipitated by pouring the solution into vigorously stirred methanol. The polymer was purified by reprecipitation and then dried in a stream of warm, dry, oxygen-free nitrogen. Yields of polymer: 1·2 g from *endo* dimer and 1·4 g from *exo* dimer.

Using $PdCl_2$ (ϕCN)$_2$ (*Cf. ref.* 3)—A mixture of the diene (5 g) and $PdCl_2$ (ϕCN)$_2$ (0·1 g) was stirred at 170°C (*endo* dimer) or 130° (*exo* dimer) in an atmosphere of dry, oxygen-free nitrogen for 3½ hours. The viscous reaction mixture was diluted with chloroform, the solution decolourized by boiling with activated charcoal and filtering, and the polymer precipitated by pouring the warm solution into vigorously stirred methanol. The polymer was purified and dried as described above. Yields of polymer: 1·4 g from *endo* dimer and 3·2 g from *exo* dimer.

RESULTS

Physical data on the polymers are collected in *Table 1*.

Table 1. Physical properties of poly-DCPDs

Monomer	*Initiator*	*Polymer label*	*Analysis** %C	%H	*Unsaturation†* %	*Mol. wt (VPO) Solvent* o-*dichlorobenzene*
exo-DCPD	$PdCl_2$ (ϕCN)$_2$	A	90·37	9·13	54·0	1 950±100
	$BF_3.Et_2O$	B	91·58	9·21	46·6	1 450±40
endo-DCPD	$PdCl_2$ (ϕCN)$_2$	C	91·14	9·21	48·4	860±30
	$BF_3.Et_2O$	D	90·17	9·37	40·0	820±50

*Requires C, 90·9 per cent; H, 9·1 per cent.

†Expressed as a percentage of initial double bonds which remain unreacted; determined by n.m.r.

The infra-red spectra of these polymers in the region 850 to 650 cm^{-1} are recorded in *Figure 1*.

The presence of bands at 1 620 and 3 020 cm^{-1} and the absence of one at 1 580 cm^{-1} in the spectra of all the polymers showed that all the bicycloheptene double bonds had been consumed in the polymerization. The remaining unsaturation is due entirely to cyclopentene double bonds.

DISCUSSION

de Kock and Veermans[6] studied the infra-red spectra of a series of substituted dihydro-*exo*- and dihydro-*endo*-dicyclopentadienes and showed that whilst compounds in the *exo* series have a weak band at 740 cm^{-1} and a stronger band at 700 to 690 cm^{-1} the corresponding bands in the spectra of the *endo* series have their relative intensities reversed. They used this evidence to suggest that *endo*-dicyclopentadiene is incorporated in the *exo* form into ethylene–propylene–DCPD terpolymers.

From the similarity of their spectra in *Figure 1*, it is clear that polymers B and D contain essentially the same structural units. Polymer A is similar to B and D but polymer C is unique in this series. From de Kock and Veermans' results we conclude that A, B and D possess an *exo* fused cyclopentene ring and that C contains an *endo* fused ring. This assignment is supported by the n.m.r. spectra of these polymers in chloroform solution. As part of our study of the n.m.r. of compounds containing the bicycloheptane nucleus we have shown that the shift of the allylic proton indicated

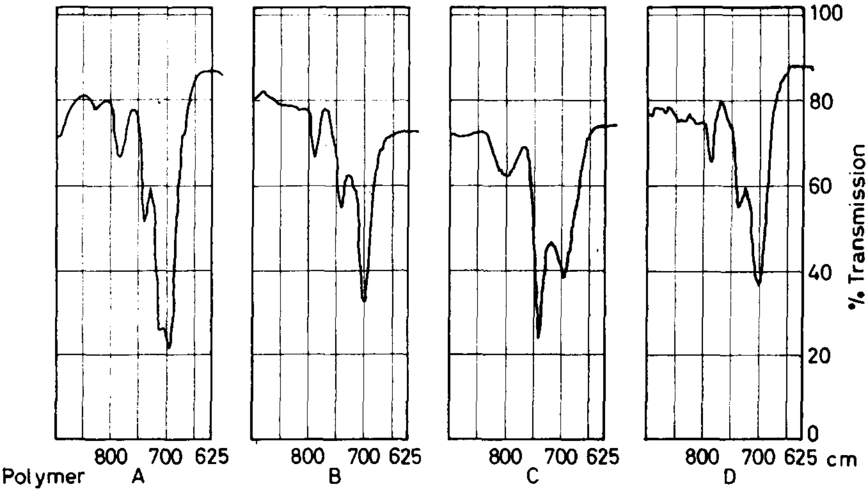
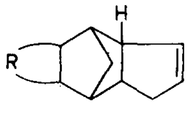


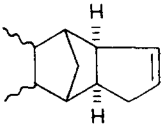
Figure 1—The i.r. spectra of polymers in *Table 1* (K Br disc)



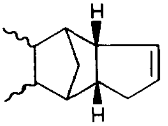
(IV)

in (IV) in compounds where the cyclopentene ring is *endo* fused to the bicycloheptane nucleus is 6·9 to 7·1τ whereas when the fusion of the cyclopentene ring is *exo* the corresponding proton lies[7] at 7·4 to 7·6τ. In the n.m.r. spectra of polymers A, B and D the lowest field peak protruding from the methylene envelope is at 7·45τ (it is impossible to obtain a precise integral because of the methylene envelope tail) whereas, in the spectrum of C a broad resonance centred at 7·02τ and equivalent to one proton is seen almost separated from the methylene envelope. These resonances we assign to the allylic proton mentioned above and this chemical shift evidence supports our proposal that only polymer C possesses cyclopentene rings *endo* fused to the bicycloheptane.

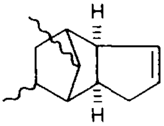
We have thus shown that no rearrangement has occurred on polymerization of *exo*-dicyclo-pentadiene with either initiator. With *endo*-dicyclopentadiene rearrangement to the *exo* configuration has occurred during polymerization with $BF_3.Et_2O$ but not with $PdCl_2(\phi CN)_2$. Referring back to Scheme I it will be remembered that we pointed out that where no rearrangement occurs the bicycloheptane nucleus will be joined to the polymer backbone by 1,2-substitution, whereas if rearrangement does take place the attachment will be by 1,3-substitution. Thus, as a result of our infra-red and n.m.r. measurements we suggest that polymers A and B have repeat units of the type (IX) and that C has repeat units as (X), i.e. these are all 1,2-polymers. Polymer D, however, has been formed by rearrangement and we thus propose that its repeat unit has the 1,3-structure (XI).



(IX)



(X)



(XI)

From *Figure 1* it is clear that polymer A is not absolutely identical with B since an additional structural vibration band is evident at 710 cm^{-1}. It seems possible that $BF_3.Et_2O$ initiated polymer possesses *trans* 1,2 links in the backbone whereas polymer A has *cis* 1,2 links although as yet we have no additional evidence to support this proposal.

Since it is well established that bicycloheptenes can rearrange after the addition of a positive species to the double bond[8] it seems possible that the 1,3-polymerization mechanism proposed above is more common in the cationic polymerization of bicycloheptenes than has previously been realized. The difficulty has been in identifying that rearrangement has occurred.

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