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STEREOREGULAR FLUOROPOLYMERS: 6. THE RING-OPENING POLYMERIZATION OF N-PENTAFLUOROPHENYLBICYCLO[2.2.1]HEPT-5-ENE-2,3-DICARBOXIMIDE*

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SUMMARY

Exo-N-pentafluorophenylbicyclo[2.2.1]hept-5-ene-2,3-dicarboximide(I) readily undergoes metathesis ring-opening polymerization when exposed to conventional metathesis catalysts such as WCl_6/Me_4Sn and $MoCl_5/Me_4Sn$; by contrast, its endo isomer (II) is not homopolymerized but can be copolymerized with (I). The microstructures of the resulting polymers are established and discussed.

INTRODUCTION

The background and motivation for this study was set out in the first paper of this series [1-5]. An initial objective is to establish the polymerizability of a range of fluorinated monomers with a variety of initiator systems and to investigate the microstructures of the products. This paper continues this survey theme with an examination of the ring-opening metathesis polymerization of N-pentafluorophenylbicyclo-[2.2.1]hept-5-ene-2,3-dicarboximides (I) and (II). A fairly wide range of substituted monomers are subject to metathesis ring-opening polymerization [6,7], but to date imides have attracted little attention [8].

RESULTS AND DISCUSSION

Monomer Synthesis

Exo-N-pentafluorophenylbicyclo[2.2.1]hept-5-ene-2,3-dicarboximide(I) was prepared via the reaction of pentafluoroaniline with exo-bicyclo-

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* Dedicated to Emeritus Professor W.K.R. Musgrave on the occasion of his 70th birthday.

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[2.2.1]hept-5-ene-2,3-dicarboxyanhydride. The anhydride was obtained via the literature route and purified by successive recrystallizations from chlorobenzene [9]. Monomer I was recovered as a white crystalline solid with correct elemental analysis. The infra-red spectrum of the product showed characteristic bands due to olefinic C-H (3070 cm^{-1}), carbonyl (1790 cm^{-1}), CH=CH (1650 cm^{-1}) and C-F (1300 cm^{-1}). Its mass spectrum gave a breakdown pattern typical of a norbornene derivative, with a base

TABLE 1

^{19}F NMR shifts for Monomer I recorded at 56.45 MHz, $CFCl_3$ external reference

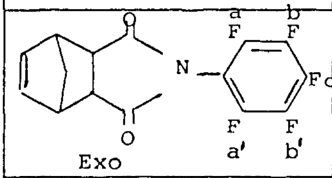
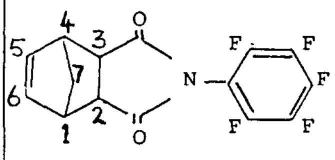
Compound	Shift/ ppm	Multiplicity	Inte- gral	Assign- ment
 Exo	161.7	m	2	b,b'
	151.4	t, J_{cb}=20.7Hz	1	c
	143.3	d, J_{ab}=22.6Hz	2	a,a'

TABLE 2

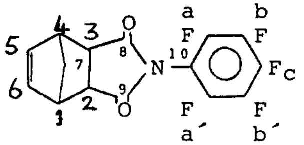
^{1}H NMR spectrum and assignments for Monomer I, recorded at 300.13 MHz, TMS internal reference

Compound	Shift/ ppm	Multiplicity	Inte- gral	Assign- ment
 Exo	6.36	Resolved into 3 lines separated by 1.76Hz	1	5,6
	3.45	s	1	2,3
	2.90	s	1	1,4
	1.61	Abq, δ_A=1.65, δ_B=1.58, J_{AB}=10.1Hz, A limb split into doublets,J,1.4Hz	1	7

peak at m/e = 66 arising from a retro Diels Alder reaction. The ^{19}F, ^{1}H and ^{13}C NMR spectra were assigned in a routine manner and confirm the structure as I. Shifts and assignments are tabulated in Tables 1, 2 and 3 respectively. Low intensity signals observed in the spectra (not tabulated) are assigned to a small proportion of the endo isomer present.

TABLE 3

^{13}C NMR shifts and assignments for Monomer I, recorded at 75.46 MHz, TMS internal reference

Compound	Shift/ ppm	Multiplicity	Assignment
 Exo	174.8	s	8,9
	144.7	d, $^{1}J_{C-F}$=251Hz	a, a'
	140.9	d, $^{1}J_{C-F}$=257Hz	c
	138.5	d, $^{1}J_{C-F}$=254Hz	b, b'
	137.9	s	5,6
	107.4	s	10
	43.1	s	7
	48.6	s	2,3
	45.9	s	1,4

Endo-N-pentafluorophenylbicyclo[2.2.1]hept-5-ene-2,3-dicarboximide was prepared via an analogous route. The Diels Alder reaction of maleic anhydride with cyclopentadiene was carried out at low temperature (0-5°C) to yield endo-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxyanhydride [10], reaction of the anhydride with pentafluoroaniline in glacial acetic acid gave the endo imide (II). The infra-red spectrum and mass spectrum were similar to those obtained for the exo isomer. The ^{19}F, ^{1}H and ^{13}C NMR data for the adduct are tabulated in Tables 4, 5 and 6 respectively. The ortho fluorines (a and a') give resonances at different positions indicating that they are not equivalent. Therefore, it seems that there are probably conformational preferences in this system, and that repulsion between the carbonyl groups and ortho fluorines results in a preferred conformation in which the plane of the ring is perpendicular to the plane of the carbonyl groups. The ^{19}F NMR of the exo adduct gave one doublet for the ortho fluorines, indicating that they were magnetically equivalent. It is possible that there is hindered rotation in both adducts, but the difference in environment of the ortho fluorines in the exo isomer is not sufficient to allow them to be resolved as separate signals, whereas in the endo case the environments are significantly different. This may be seen more clearly by consulting molecular models. The repulsion between the carbonyl group and the pentafluorophenyl ring would not be expected to be large and the barrier to rotation should be relatively easily overcome. However, variable temperature NMR studies on both forms caused no apparent effect on the spectra. Examination of the ^{13}C NMR data (Table 6) to determine if the ortho carbons gave separate resonances, was performed but the relevant signals could not be easily identified due to their low intensity. Hence, the explanation of the multiplicity observed in the ^{19}F NMR spectrum remains somewhat uncertain in detail although the structural assignment is unambiguous.

TABLE 4

^{19}F NMR shifts and assignments for Monomer II, recorded at 56.45 MHz, $CFCl_3$ external reference

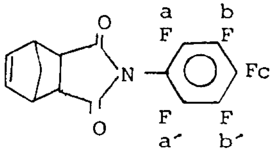
Compound	Shift/ ppm	Multiplicity	Integral	Assignment
 Endo	161.5	d of d of d, J_{ab}=20.7Hz J_{bc}=20.7Hz, $J_{a'b}$=5.6Hz	2	b,b´
	151.9	t, J_{cb}=20.7Hz	1	c
	143.3	d of d of d, $J_{a'b'}$=20.7Hz $J_{a'b}$=5.6Hz, $J_{a'a}$=5.6Hz	1	a´
	141.2	d of d of d, J_{ab}=20.7Hz $J_{ab'}$=5.6Hz, $J_{aa'}$=5.6Hz	1	a

TABLE 5

^1H NMR shifts and assignments for Monomer II recorded at 300.13 MHz, TMS external reference

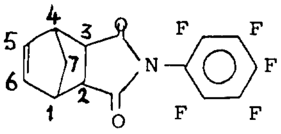
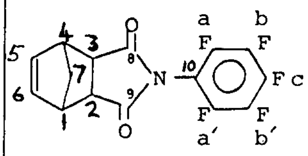
Compound	Shift/ ppm	Multiplicity	Inte-gral	Assign-ment
 Endo	6.25	s	1	5,6
	3.54	d, $J_{1,6}$ = 1.5 Hz	1	2,3
	3.51	d, $J_{1,6}$ = 1.5 Hz	1	1,4
	1.63	ABq, δ_A = 1.72, δ_B = 1.55 J_{AB} = 8.8Hz	1	7

TABLE 6

^{13}C NMR shifts and assignments for Monomer II recorded at 75.46 MHz, TMS internal reference

Compound	Shift/ ppm	Multiplicity	Assignment
	174.5	s	8,9
	143.7	d, $^1J_{C-F}$ = 256Hz	a, a′
	142.2	d, $^1J_{C-F}$ = 256Hz	c
	138.0	d, $^1J_{C-F}$ = 255Hz	b, b′
	134.9	s	5,6
	107.3	s	10
	52.2	s	7
	46.9	s	2,3
	45.6	s	1,4

Polymerizations

Castner and Calderon [9] observed that pure endo-5-norbornene-2,3-dicarboxyanhydride was relatively inert to metathesis polymerization, whereas the exo isomer readily polymerized. The same authors also found that when a mixture of exo and endo isomers was polymerized, the conversion was dependent upon the amount of exo isomer present. In these experiments the recovered monomer clearly indicated that the exo isomer had been preferentially polymerized, but some endo monomer had also been incorporated. They concluded that the barrier to endo/endo linking during chain propagation was either in the carbene to metallocycle transition state, or due to steric restrictions in the polymer chain itself. Exo and endo-N-pentafluorophenylbicyclo[2.2.1]hept-5-ene-2,3-dicarboximides (I) and (II) were exposed to metathesis catalysts, as detailed in Table 7.

TABLE 7
Polymerization of exo and endo-N-pentafluorophenylbicyclo[2.2.1]hept-5-ene-2,3-dicarboximide

Monomer (mmole)	Catalyst (mmoles)	Cocatalyst (mmole)	Solvent[a] (cm^3)	Temp[b] (°C)	Time (hrs)	Yield[c] (%)
exo (10.58)	WCl_6(0.071)	Me_4Sn(0.142)	C,(20.8)	RT	24	45
exo (5.56)	$MoCl_5$(0.034)	Me_4Sn(0.068)	C,(11.4)	60	0.75	89
exo (1.9 + endo 1.9)	$MoCl_5$(0.038)	Me_4Sn(0.076)	C (12)	60	1.75	39
endo (4.04)	$MoCl_5$(0.080)	Me_4Sn(0.160)	C,(11.1)	60	24	-
endo (6.14)	WCl_6(0.041)	Me_4Sn(0.084)	C, (15)	60	36	-

[a] C - chlorobenzene, CE - 1:1 (vol for vol) mixture of chlorobenzene and ethanol.

[b] Approximate temperature. Some polymerizations were notably exothermic, no monitor of temperature was placed in the vessel.

[c] After reprecipitation and drying under vacuum for at least 24 hours.

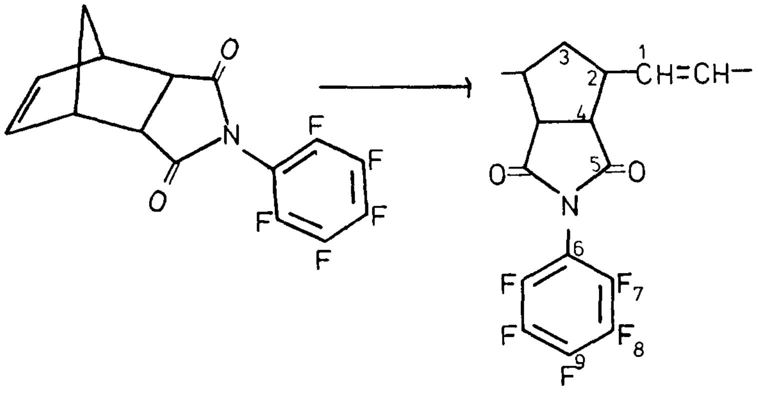
The exo isomer was readily polymerized using W and Mo based catalysts. However, attempts to polymerize the monomer with $RuCl_3$ and

$OsCl_3$ catalysts proved unsuccessful. The endo isomer could not be polymerized via $MoCl_5/Me_4Sn$ or WCl_6/Me_4Sn catalysis, in any of several attempts. A mixture of exo and endo isomers was polymerized using $MoCl_5/Me_4Sn$ as catalyst, giving a relatively low yield of polymer. These results are analogous to those obtained by Calderon and Castner with the anhydrides [9].

Polymer Characterization

The infrared spectra of the polymers recorded in Table 7 are shown in Figure 1. No structurally useful assignments could be made on the basis of these spectra, other than to confirm the presence of expected functional groups. In particular, the C-H out of plane bending region for the *cis* and *trans* vinylenes, which is often useful in this class of polymers, did not yield any information due to the overlap of other absorbances. It is clear that all three materials are very similar in basic structure.

^{13}C NMR spectroscopy was more useful in providing structural information on these polymers. The spectrum of the polymer obtained via $MoCl_5$ catalysis is shown in Figure 2, and the chemical shifts and assignments recorded in Table 8. The repeat unit of the polymer and the numbering system used when assigning spectra is shown below. The basis



on which the ^{13}C NMR spectra of substituted polynorbornenes may be assigned has been discussed in detail by Ivin [6], this is a particularly clear and unambiguous example. The C5 resonance in Figure 2 is easily

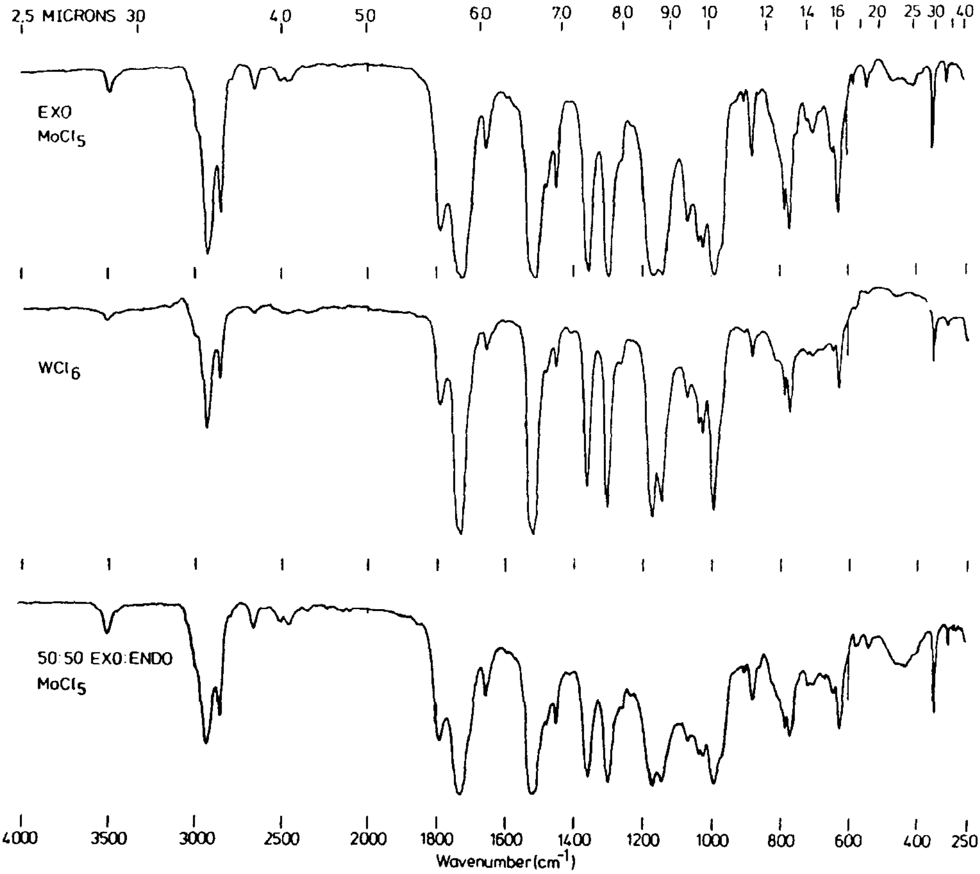


Fig. 1. Infrared spectra of polymers listed in Table 7.

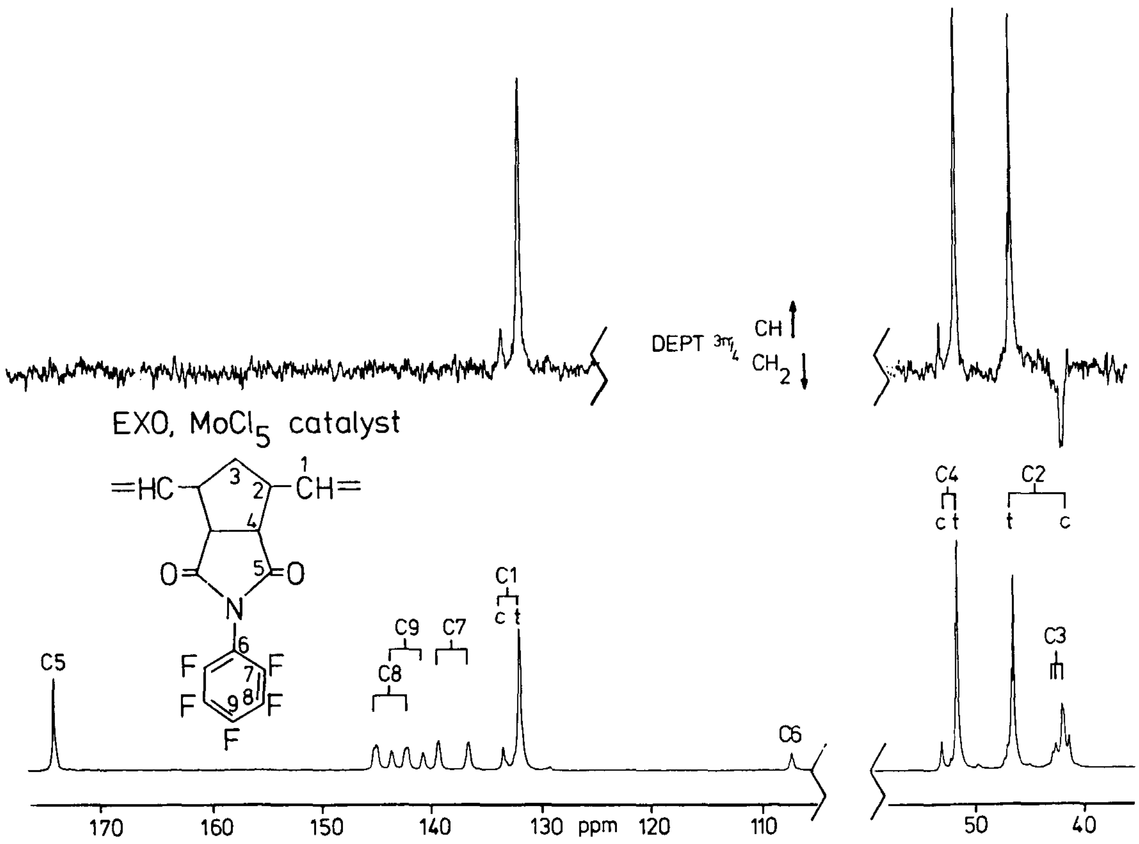


Fig. 2. ^{13}C NMR spectrum of poly(exo-N-pentafluorophenylbicyclo[2.2.1]hept-5-ene-2,3-dicarboximide) prepared via $MoCl_5/Me_4Sn$ initiation, recorded at 90.56 MHz in $(CD_3)_2CO$ solution with TMS as internal reference

TABLE 8

^{13}C NMR chemical shifts and assignments of samples of poly(N-pentafluorophenylbicyclo[2.2.1]hept-5-ene-2,3-dicarboximide

Monomer/Catalyst			Assignment
Exo(I)/$MoCl_5$	Exo(I)/WCl_6	Exo(I)/Endo(II)/ $MoCl_5$	
174.62	174.61	174.61	C5 exo
		173.2	C5 *endo*
143.57, $^{1}J_{C-F}$=263Hz	143.5, $^{1}J_{C-F}$=251Hz	143.4, $^{1}J_{C-F}$=250Hz	C8
142.13, $^{1}J_{C-F}$=258Hz	142.06, $^{1}J_{C-F}$=255Hz	142.1, $^{1}J_{C-F}$=259Hz	C9
137.32, $^{1}J_{C-F}$=254Hz	137.8, $^{1}J_{C-F}$=253Hz	138.0, $^{1}J_{C-F}$=252Hz	C7
133.36	133.30	133.30	C1, *cis*
	132.35)		
131.88	131.81)	131.86	C1, *trans*
		131.27	endo
		129.10	endo
107.14	107.10	107.00	C6
	53.02		C4 ct
52.90	52.87	52.89	C4 cc
	52.05		C4 tc
51.41	51.41	51.40	C4 tt
	49.55	49.55	endo
		47.17	endo
46.95	46.95	46.95	)
46.56		46.56	) C2, *trans*
46.38	46.40	46.38	)
		45.19	endo
		44.87	endo
	42.78		C3, cc
42.47	42.47	42.46	C3, ct≡tc
41.91)	41.90	41.89	C3, tt
41.78)			
41.27	41.33	41.26	C2, *cis*
	40.63		endo

distinguished as the lowest field signal. The carbons of the pentafluorophenyl group are observed as low intensity doublets and are assigned by analogy with related compounds. The C6 resonance appears at ≃107 ppm, and is absent in the DEPT spectrum. The vinylene carbon signal is resolved into *cis* and *trans* environments as indicated, giving a value of σ_C, the proportion of *cis* vinylene units, of 0.09. At high field the C4 *cis* and *trans* environments are assigned to the signals at 52.90 and 51.41 ppm respectively. A low intensity peak, observed adjacent to the *trans* signal may be a tc or ct resonance. These signals give a σ_C value of 0.09. The *trans* allylic carbon signal is observed at 46.56 ppm, and consideration of the expected 5 ppm upfield shift of the *cis* environment, allows the C2 *cis* signal to be assigned to the peak at 41.27 ppm; this signal overlaps with the methylene carbon signals, but the DEPT spectrum confirms the assignment. The C2 *trans* signal appears to be resolved into two peaks, with a low intensity shoulder. This fine structure may be a consequence of the resolution of the tt and tc adjacent vinylene effects and/or meso/racemic dyads. The σ_C value for this carbon is 0.12. The C3 resonance is resolved into 3 peaks assigned to the cc, tc≡ct and tt environments. The cc peak was not detected by the computer and the integral for this peak was estimated; the value of σ_C from this carbon is 0.15. The tt peak is resolved into two signals of approximately equal intensity, which is probably a result of m/r splitting, and indicates that the polymer is atactic.

The overall conclusion from this analysis is that the polymer has a high *trans* vinylene content. The values of σ_C calculated from the C3 and C2 signals are not very reliable since the peaks overlap, and consequently the integrals are inaccurate. However, all σ_C values indicate a high *trans* double bond content, and the resolution of the C3 resonance suggests the polymer is probably atactic.

Figure 3 shows the spectrum of the polymer derived via WCl_6 initiation. The C5, C6, C7, C8 and C9 resonances are assigned by analogy with the $MoCl_5$ derived polymer. The C1 resonance is again resolved into *cis* and *trans* environments, and the *trans* signal is observed as two peaks, a consequence of long range *cis*/*trans* vinylene effects or meso/racemic dyad splitting. The vinylene signals give a value of σ_C of

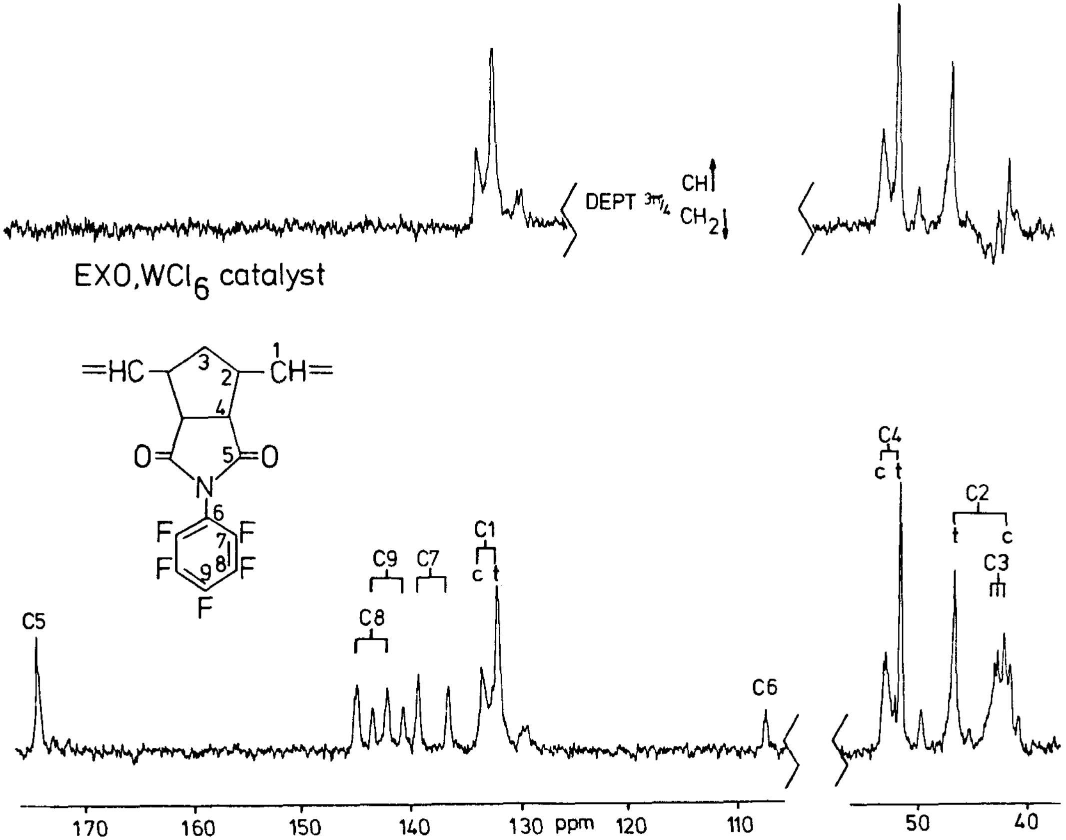


Fig. 3. ^{13}C NMR spectrum of poly(exo-N-pentafluorophenylbicyclo[2.2.1]hept-5-ene-2,3-dicarboximide) prepared via WCl$_6$/Me$_4$Sn initiation, recorded at 90.56 MHz in (CD$_3$)$_2$CO solution with TMS as internal reference

0.36. The C4 resonance appears as four signals assigned to the cc, ct, tc, and tt environments of this carbon; a value of $\sigma_c = 0.39$ is obtained. Carbons C2 and C3 are assigned by comparison with the spectrum of the polymer derived from $MoCl_5$ initiation, and give σ_c values of 0.23 and 0.49 respectively. There are significant discrepancies in the σ_c values; overlap of the C2 and C3 carbon signals makes the integrals and hence σ_c values derived from these carbons unreliable. The C1 and C4 signals are well resolved, and the values of σ_c calculated from these carbon signals are in reasonable agreement. Hence, it can be concluded that the polymer has ca 35 to 40% of *cis* vinylenes. Signal broadening and the occurrence of fine structure for most of these signals probably implies that the polymer is atactic.

The ^{13}C NMR of the polymer produced by polymerizing a mixture of exo and endo isomers via $MoCl_5/Me_4Sn$ initiation is shown in Figure 4. The shifts and assignments are recorded in Table 8. The spectrum is very similar to that obtained from polymerization of the exo isomer using $MoCl_5$ as catalyst, except some of the weak peaks have increased in intensity. These peaks can be confidently assigned to carbons associated with endo units, and by comparison of the integral of the exo and endo signals, it is apparent that the exo isomer has been preferentially incorporated into the polymer chain. The signals of the carbons derived from endo isomer are marked (e) on the spectrum and those associated with the exo isomer are assigned by analogy with the previous spectra. The σ_c values were 0.17 for the vinylene carbons, 0.23 for C4, 0.17 for C2, and 0.23 for C3. The overlap of signals with endo carbon resonances makes the reliability of the values uncertain, but it is apparent that the vinylenes adjacent to exo units have predominantly *trans* stereochemistry.

Thus, the conclusion to be drawn from analysis of the spectra is that the $MoCl_5$ based catalysts give a high *trans* vinylene content, and WCl_6 derived polymers give a mixture of *cis* and *trans* double bonds. The polymerization of a mixture of exo and endo isomers shows that exo monomer is preferentially incorporated into the chain.

The GPC results for the polymers listed in Table 7 are recorded in Table 9.

The results show that the materials produced are genuine high polymers, having a fairly large molecular weight distribution.

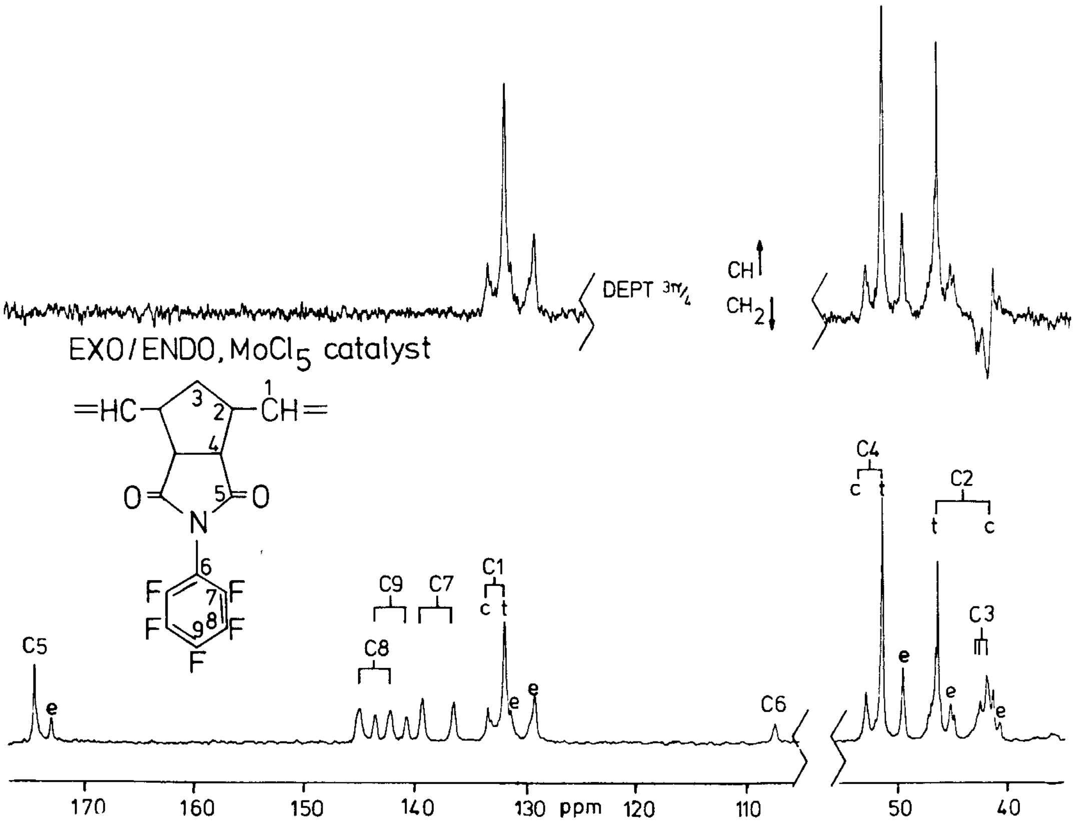
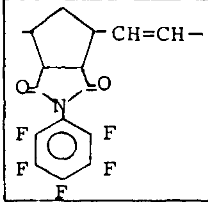


Fig. 4. ^{13}C NMR spectrum of the polymer produced from MoCl$_5$ initiation of an exo/endo mixture of N-pentafluorophenylbicyclo[2.2.1]hept-5-ene-2,3-dicarboximide, recorded at 90.56 MHz in $(CD_3)_2CO$ solution with TMS as internal reference.

TABLE 9

GPC data[a] for polymers prepared in this work

Polymer	Catalyst	$\bar{M}_n \times 10^5$	$\bar{M}_w \times 10^5$	$\bar{M}_w/\bar{M}_n$
	exo, WCl_6/Me_4Sn	1.99	8.80	4.42
	exo, $MoCl_5/Me_4Sn$	3.05	12.60	4.13
	endo + exo, $MoCl_5$	1.05	3.50	3.33

[a] THF solutions (ca. 1%), Polymer Laboratories PL-gel columns 10^5, 10^3, 500 A pore size in series, RI detector, $\bar{M}_n$ values are 'polystyrene equivalent'.

EXPERIMENTAL

Synthesis of exo-N-pentafluorophenylbicyclo[2.2.1]hept-5-ene-2,3-dicarboximide(I) (nc)

Exo-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxyanhydride (15.2g, 0.09 moles) in glacial acetic acid (70 cm^3) and pentafluoro-aniline (17g, 0.09 moles) in glacial acetic acid (20 cm^3) were mixed together in a 250 cm^3 round-bottomed flask, and heated to reflux for 2 hours. The solution changed colour during this period from a pale yellow to a deep orange. The solution was allowed to cool and the product precipitated by the dropwise addition of water. The product was recovered by filtration and recrystallised several times from a 50:50 mixture of acetic acid and water to give: exo-N-pentafluorophenylbicyclo[2.2.1]hept-5-ene-2,3-dicarboximide (I) as a white crystalline solid (18.9g, 0.058 moles, 64%); m.p. 116°C; [Found, C, 54.6; H, 2.2; N, 3.9; F, 28.4; $C_{15}H_8F_5NO_2$ requires C, 54.7; H, 2.4; N, 4.2; F, 28.5]; m/e 329 (M^+); ν_{max}, 3060 cm^{-1} (vinyl C-H stretch), 3000 cm^{-1} (C-H stretch), 1790 cm^{-1} (CO-N-CO) and 1300 cm^{-1} (C-F).

Synthesis of endo-N-pentafluorophenylbicyclo[2.2.1]hept-5-ene-2,3-dicarboximide(II) (nc)

Endo-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxyanhydride (8.6g, 0.05 moles) in glacial acetic acid (40 cm^3) and pentafluoroaniline (9.5g, 0.05 moles) in glacial acetic acid (10 cm^3) were mixed together in a 100 cm^3 round-bottomed flask and heated to reflux for 2 hours. The solution was allowed to cool and the product recovered in the same way as the exo adduct (see above) to give: endo-N-pentafluorophenylbicyclo-[2.2.1]hept-5-ene-2,3-dicarboximide(II); as a white crystalline solid (10.5g, 0.032 moles, 64%); m.p. 133^oC; [Found: C, 54.8; H, 2.3; N, 3.9; F, 29.0; $C_{15}H_8F_5NO_2$ requires, C, 54.7; H, 2.4; N, 4.2; F, 28.5]; m/e 329 (M^+); ν_{max} 3050 cm^{-1} (vinyl C-H stretch), 1780 and 1720 cm^{-1} (CO-N-CO-), 1300 cm^{-1} (C-F).

Polymerization Procedure

The experimental procedure, necessary precautions, solvent purification and catalyst generation have been described in detail previously [1]. Details of particular experiments are recorded in the script. The polymers produced were purified by repeated precipitation from butanone solution into methanol.

CONCLUSION

N-Pentafluorophenylbicyclo[2.2.1]hept-5-ene-2,3-dicarboximides are polymerized by conventional metathesis catalysts based on WCl_6 and $MoCl_5$ activated with $(CH_3)_4Sn$. The exo isomer is readily polymerized, and whereas the endo isomer does not homopolymerise under these conditions it can be incorporated into polymers when an exo/endo mixture is initiated with the $MoCl_5/(CH_3)_4Sn$ system. The $MoCl_5$ derived initiator leads to a polymer with ca. 90% trans vinylene units which is probably atactic. The WCl_6 derived initiator gives rise to an atactic polymer with $\geq$60% trans vinylenes.

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