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The synthesis and characterisation of poly(1,4-cyclopentenylene-5,6-ethylidene-2,3-disodium dicarboxylate)s and pendant functional group isomerisation

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Summary

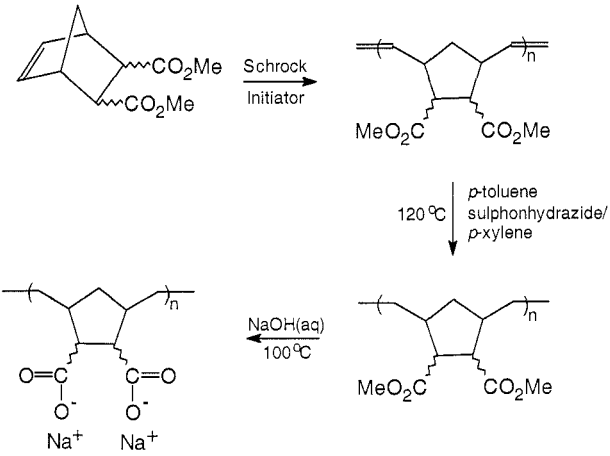
Poly(1,4-cyclopentenylene-5,6-ethylidene-2,3-disodium dicarboxylate)s have been synthesised from the *exo,exo-*, *endo,endo-* and *exo,endo-* isomers of dimethyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylates in a three step process involving ring opening metathesis polymerisation, hydrogenation and hydrolysis. *Exo,exo-* and *endo,exo-* pendant functional group stereochemistries were unchanged throughout these processes, whereas, the polymers derived from the *endo,endo*-monomer underwent fragmentation during hydrogenation and isomerisation during hydrolysis to give to the more stable *endo,exo-* form of the polymer.

Introduction

The objective of this work was the controlled synthesis and characterisation of water-soluble polymers with well-defined molecular weights in which the steric relationship of pendant carboxylate groups with respect to each other and the polymer backbone were specified. These materials were required for a study of the influence of polymer structure and molecular weight on the crystallization of inorganic salts from aqueous solutions; the results of that study are reported elsewhere [1, 2]. The synthetic route selected is shown in Scheme 1. The first step was the living ring opening metathesis polymerisation (ROMP) of *exo,exo-*, *endo,endo-* and *endo,exo-* isomers of dimethyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylates using the Schrock initiator, Mo(CH-^{t}Bu)(NAr)(O-^{t}Bu)$_2$, following the methodology established by Schrock and co-workers [3]. The products of this step were obtained in a range of molecular weights and with narrow molecular weight distributions. *p*-Toluene sulphonylhydrazide, as a precursor to diimide [4], allowed complete hydrogenation of the double bonds in the second step. This step reduced the risk of oxidative cross linking and degradation reactions in the subsequent manipulations. The final stage was the hydrolysis of the esters using aqueous NaOH.

Significant degradation of molecular weight was observed during the hydrogenation step for the polymer derived from the *endo,endo*-monomer but not in the case of the

other two polymers. This difference in behaviour can be attributed to the greater steric compression in the *endo,endo*-monomer derived polymer compared to the polymers derived from the *endo,exo*- and *exo,exo*-monomers. Further evidence supporting this hypothesis of steric compression was provided by the isomerisation of the *endo,endo*- carboxylate functionalities to the more stable *endo,exo*- configuration during the hydrolysis stage.



Scheme 1. A schematic representation of the polymer syntheses undertaken in this study.

Results and discussion

Monomers were synthesized via Diels-Alder reaction between cyclopentadiene and the appropriate dienophiles and the product stereochemistries confirmed by single crystal X-ray structure determinations on the free acids [2, 5]. Poly(dimethyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate)s were obtained via living ROMP following Schrock's method [3], see Table 1. The Mn values of the hydrogenated polymers derived from *exo,endo*-and *exo,exo*-monomers were, within experimental error, the same as those of their precursors. Whereas for the hydrogenated *endo,endo*-polymer the Mn (89,100) was about half that of its precursor (174,100) and the PDI was broader, (1.5) compared to (1.01); for lower molecular weight polymers the effect was less significant. This evidence indicates that the polymer fragmented during hydrogenation. The reason for this is not clearly understood but merits comment. We know from detailed analysis of the ^{1}H and ^{13}C NMR signals associated with polymer repeat units that the *cis:trans* vinylene distributions in these unsaturated poly(ester)s varies with monomer structure. For polyesters derived from the *exo,exo*-monomers high *trans* vinylene content was found (Schrock *et al* estimate ca.95% based on the ^{1}H NMR spectrum, we estimate 88% based on the ^{1}H and ^{13}C NMR data) whereas for both the *endo,endo*- and *exo,endo*-monomer derived polymers we estimate a 50:50 distribution of *cis* and *trans* vinylenes compared to the Schrock group's estimate of 80% trans for the *endo, endo*- case (they were unable to analyse the data for the *exo,endo*- case). The discrepancies in the values between our two groups may be a consequence of the quality of the spectra and/or the use of different solvents for synthesis; however, the general trend is clear, *exo,exo*-monomer derived polymers

have a very high trans vinylene content (ca. 90 – 95%) whereas both other systems have a significant proportion of *cis* vinylenes (20 to 50%). A *trans* dyad gives minimal steric strain and greater flexibility in the backbone of the polymer; whereas, a *cis* dyad, which has four contiguous syn substituents on each five membered ring, inevitably experiences more steric strain and a stiffer backbone. The conditions for diimide hydrogenation, *para*-xylene at 120°C, are quite severe and a large stiff and sterically compressed polymer molecule may experience sufficient stress to fragment under these condition. This explanation is speculative but is consistent with the facts.

Table 1. Number average molecular weights and polydispersity indices, PDI = M_w/M_n for polymers synthesised in this study

	Step 1 – Dimethyl Ester[a]		Step 2 – Hydrogenated[b]		Step 3 – Hydrolysed[c]	
	Mn	PDI	Mn	PDI	Mn	PDI
exo/exo	182,000	1.24	184,900	1.28	160,000	1.47
	71,400	1.12	68,200	1.11		
	7,700	1.10	7,700			
endo/endo	174,000	1.01	89,100	1.51	73,000	1.70
	57,700	1.02	52,000	1.05	48,400	1.22
	6,000	1.12				
exo/endo	275,400	1.12	220,500	1.34	147,200	1.54
	68,600	1.03	65,500	1.04		
	4,900	1.07	5,900	1.08		

[a] Viscotek Differential Refractometer/Viscometer dual detector (Model 200), THF solution, [b] RI detector, $CHCl_3$ solution; for both a & b measurements 10μm mixed styrene/divinyl benzene gel columns and PS calibration standards supplied by Polymer Laboratories Ltd., Church Stretton, plc were used. [c] recorded by Polymer Laboratories Ltd using Differential Refractometer, aqueous 0.2M $NaNO_3$, 0.1M NaH_2PO_4 adjusted to pH 7 with NaOH as eluent, 2 x PL aquagel-OH mixed columns 8μm 300 x 7.5 mm, PEO calibrants.

The hydrogenated polymers were hydrolysed in refluxing aqueous NaOH. Where the Mn of final products were measured (Table 1, ref 6) the values for the hydrolysed polymers were, within experimental error, the same as the values for their precursors although there was some broadening of the dispersity; thus these polymers were not substantially degraded during hydrolysis.

^1H and ^{13}C NMR spectroscopies were used to characterise the intermediate and final polymeric products. Successful hydrogenation is indicated in the ^1H NMR spectrum (see experimental) by the loss of signals corresponding to the vinylic hydrogen atoms ($H_{5,6,}$~ 5.5ppm) and in the ^{13}C NMR spectrum (Figure 1) by the loss of the vinylic carbon atom resonances ($C_{5,6}$ ~ 130ppm). These signals are replaced by peaks corresponding to hydrogen and carbon atoms in a saturated environments 1ppm≤ $\delta H_{5,5',6,6'} \leq$ 3ppm for ^1H NMR and 33.48ppm and 29.96ppm for ^{13}C NMR. Therefore, the evidence for hydrogenation is clear and unambiguous from both ^1H and ^{13}C NMR spectroscopic analyses. Conclusive evidence of full hydrolysis comes from the ^{13}C NMR spectra in which no methoxy methyl carbon atom peaks (29ppm ≤ $\delta C_{5,6}$ < 39ppm) can be seen.

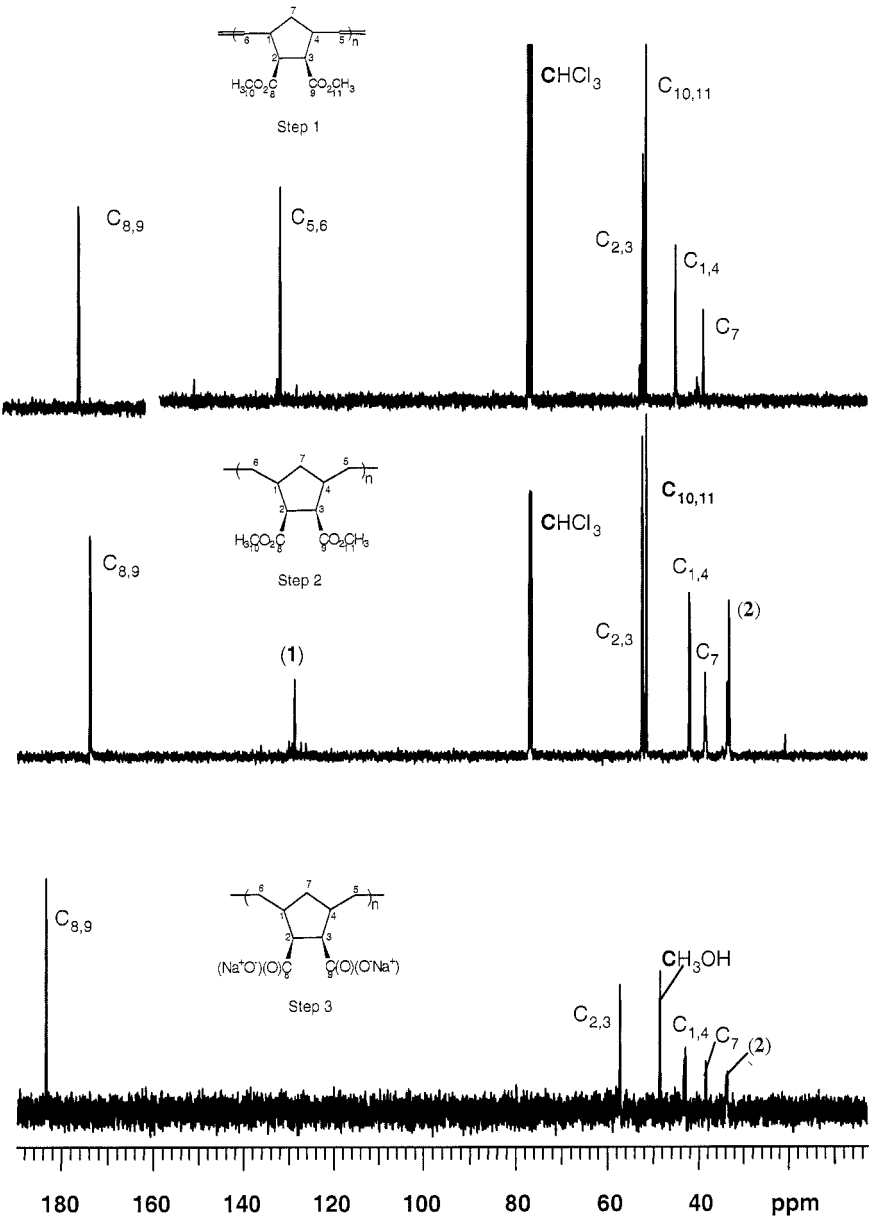


Figure 1. ^{13}C NMR spectra for the products of Step 1 (top), Step 2 (middle) and Step 3 (bottom) in the synthesis of poly(*exo,exo*-1,4-cyclopentenylene-5,6-ethylidene-2,3-disodium dicarboxylate)s. Residual solvent, *p*-xylene, (**1**) $C_{2,3,5,6}$ and (**2**) methyls.

Since the spectrum of the product of hydrolysis of poly(*endo,endo*-1,4-cyclopentenylene-5,6-ethylidene-2,3-dicarboxylate) is identical to that of poly (*endo,exo*-1,4-cyclopentenylene-5,6-ethylidene-2,3-disodium dicarboxylate), see Figure 2, it is evident that the hydrolysis of the *endo,endo*- polymer results in the isomerisation of the functional groups to give a polymeric product with 50:50 *endo,exo*- pendant functional group content. This epimerization at the CH alpha to the ester is consistent with our earlier hypothesis *vide supra* that the *endo,endo*- polymer, is subject to steric stress leading to fragmentation during hydrogenation and isomerisation during hydrolysis.

Experimental

Organic reagents were purchased from Aldrich Chemical Co. and used as received. Polymerisations and manipulations were carried out under a dry nitrogen atmosphere. ^{1}H and ^{13}C NMR spectra were recorded using a Varian VXR 400 MHz spectrometer run at 400MHz and 100 MHz respectively. Chemical shifts are given in parts per million (δ) and referenced to TMS at 0 ppm or to the HOD peak at 4.75ppm in spectra where D_2O was used. Coupling constants are in Hertz. SEC chromatography measurements were carried out at 308K as specified in the footnote to Table 1. Samples were dissolved in degassed THF (0.1%w/w) and filtered through a 0.2μm polypropylene-backed PTFE filter. Full assignment of the ^{1}H and ^{13}C NMR spectra was carried out with the aid of DEPT, ^{1}H COSY and HETCOR spectra and the analyses of polymers synthesised in step 1 were consistent with literature data [3,7]. The starting monomers were synthesised following established routes [2,3]. Details of polymer syntheses, yields and analytical parameters are recorded below for typical experiments. Analogous samples, see Table 1, had similar yields and analytical characteristics.

Step 1. Preparation of poly (bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid dimethyl ester)

This reaction involved the living ring opening metathesis polymerisation of the three isomers of dimethyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate using the initiator, $Mo(CH\text{-}^{t}Bu)(NAr)(O\text{-}^{t}Bu)_2$, as reported by R.R. Schrock [3]. The only difference was that dry benzene was used as the solvent in this work as opposed to toluene or THF in the earlier study.

Exo,exo-Poly(dimethyl 1,4-cyclopentenylene-5,6-ethylidene-2,3-dicarboxylate) was obtained as white fibrous material after reprecipitation twice from THF into methanol and drying; yield 88%; M_n 182,000, PDI 1.24 (SEC); found C,62.33; H,6.75% calc. for $(C_{10}H_6O_4)_n$ C, 62.85; H,6.71%. ^{1}H NMR, ($CDCl_3$, 400MHz) δ(ppm): 5.39 (s, 1.7H, $H_{5,6\ trans}$), 5.22 (m, 0.3H, $H_{5,6\ cis}$), 3.61 (s, 6H, $H_{8,9}$), 3.30 (bm, 0.3H, $H_{1,4\ cis}$), 2.93 (bm, 1.7H, $H_{2,3\ trans}$), 2.81 (bm, 1.7H, $H_{1,4\ trans}$), 2.81 (bm, 0.3H, $H_{2,3\ cis}$, assigned from COSY spectrum) 2.04 (bm, 1H, $H_{7\ or\ 7'}$), 1.26 (bm, 1H, $H_{7\ or\ 7'}$). ^{13}C NMR, ($CDCl_3$, 100MHz) δ(ppm): 173.09 (s, $C_{8,9\ trans}$), 172.92 (s, $C_{8,9\ cis}$), 132.80 (s, $C_{5,6\ trans/cis}$), 131.96 (s, $C_{5,6\ trans/trans}$), 128.28 (s, $C_{5,6\ cis/trans}$), 53.07 (s, $C_{2,3\ cis/trans}$), 52.42 (s, $C_{2,3\ trans/trans}$), 51.74 (s, $C_{10,11}$), 45.22 (s, $C_{1,4\ trans/cis}$), 45.16 (s, $C_{1,4\ trans/trans}$), 40.58 (s, $C_{1,4\ cis/trans}$), 39.15 (s, C_7).

Endo,endo Poly(dimethyl 1,4-cyclopentenylene-5,6-ethylidene-2,3-dicarboxylate) was obtained as white material with the texture of crepe paper after reprecipitation twice

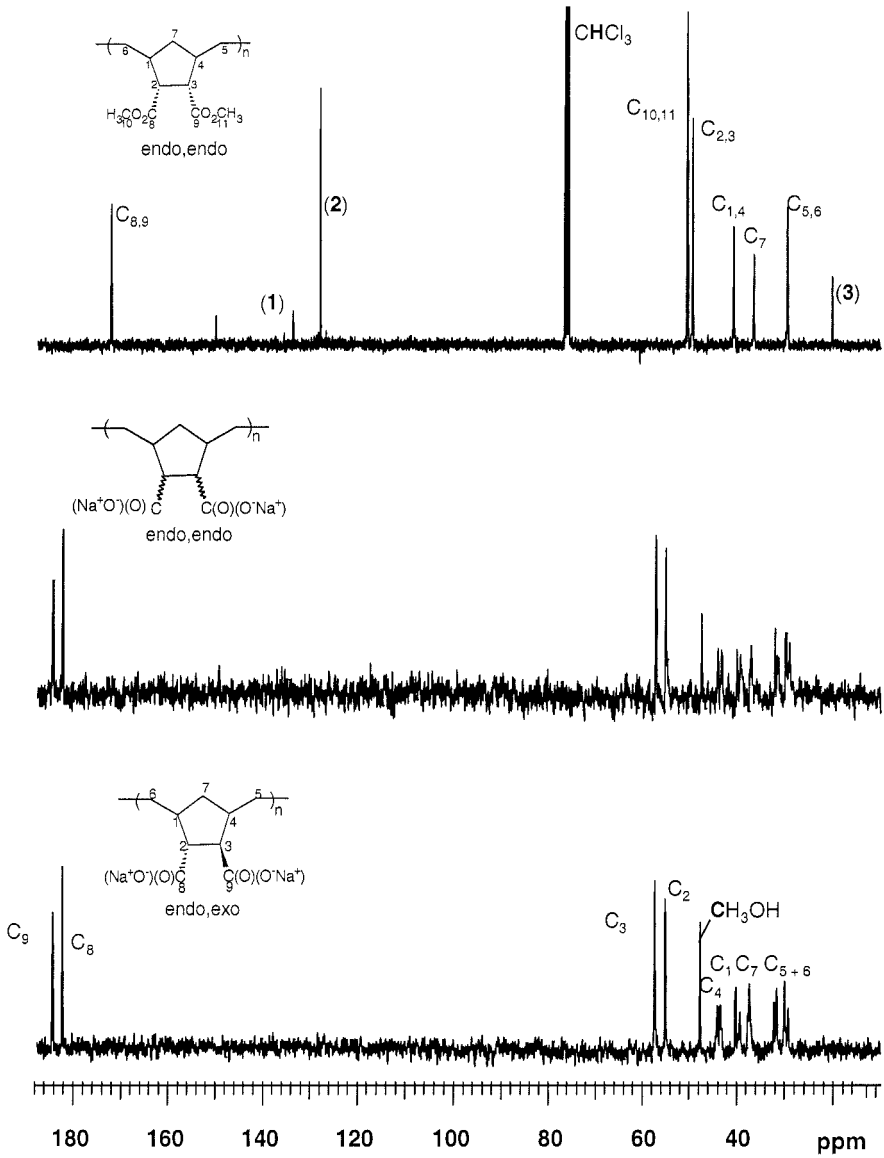


Figure 2. ^{13}C NMR spectra for poly(dimethyl *endo,endo*-1,4-cyclopentenylene-5,6-ethylidene-2,3-dicarboxylate) (top); its hydrolysis product (middle) and poly(*endo,exo*-1,4-cyclopentenylene-5,6-ethylidene-2,3-disodium dicarboxylate) Residual solvent, *p*-xylene, (**1**) $C_{1,4}$; (**2**) $C_{2,3,5,6}$ and (**3**) methyls

from THF into methanol and drying; yield 92%; M_n 174,000, PDI 1.01 (SEC); found C,61.98; H,6.73% calc. for $(C_{10}H_6O_4)_n$ C, 62.85; H,6.71%. ^1H NMR ($CDCl_3$, 400MHz) δ(ppm): 5.51 (bm, 2H, $H_{5,6}$), 3.64 (bm, 6H, $H_{8,9}$), 3.09 (bm, 2H, $H_{2,3}$), 2.84 (bm, 2H, $H_{1,4}$ assigned from COSY spectrum), 1.92 (bm, 2H, $H_{7,7'}$). ^{13}C NMR ($CDCl_3$, 100MHz) δ(ppm): 172.64 (m, $C_{8,9}$), 131.77 (m, $C_{5,6}$), 51.31 (s, $C_{10,11}$, assigned from COSY spectrum), 51.28 (m, $C_{2,3}$), 44.61 (m, $C_{1,4}$), 37.96 (m, C_7).

Endo,exo Poly(dimethyl 1,4-cyclopentenylene-5,6-ethylidene-2,3-dicarboxylate) was obtained as white material with the texture of crepe paper after reprecipitation twice from THF into methanol and drying; yield 62%; M_n 275,400, PDI 1.12 (SEC); found C,62.49; H,6.80% calc. for $(C_{10}H_6O_4)_n$ C, 62.85; H,6.71%. - ^{1}H NMR, ($CDCl_3$, 400MHz) δ(ppm): 5.32 (3 x bm, 2H, $H_{5,6}$), 3.67 (dm, 6H, $H_{8,9}$), 3.24 (bm, 1H, $H_{2,3}$), 2.96 (bm, 2H, $H_{1,4 \text{ and } 2,3}$), 2.70 (bm, 1H, $H_{1,4}$), 1.97 (bm, 1H, H_7), 1.49 (bm, 1H, $H_{7'}$). ^{13} C NMR , ($CDCl_3$, 100MHz) δ(ppm): 174.28 (m, $C_{8,9\ exo}$), 173.21 (m, $C_{8,9\ endo}$), 132.54 (dm, $C_{5,6 \text{ cis or trans}}$), 130.08 (m, $C_{5,6 \text{ cis or trans}}$), 52.50 (m, $C_{1,4\ cis}$), 52.31 (bd, $C_{2,3 \text{ cis or trans}}$), 51.75 (m, $C_{10,11}$), 46.74 (m, $C_{1,atrans}$), 44.43 (m, $C_{2,3 \text{ cis or trans}}$), 39.13 (m, C_7).

Step 2. Hydrogenation of poly(bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid dimethyl ester)

The polymers synthesised in step 1 were hydrogenated by heating with *p*-toluene sulphonylhydrazide at 120°C in *p*-xylene solution under a dry nitrogen atmosphere and with continuous stirring. The duration of heating was varied according to the amount of polymer used and was carried out until all vinylenes were hydrogenated as judged by ^{1}H NMR analysis

Exo,exo-poly(dimethyl 1,4-cyclopentenylene-5,6-ethylidene-2,3-dicarboxylate was obtained as a colourless, transparent, adhesive solid after precipitation from hot p-xylene into methanol, decantation and drying under vacuum. 57% yield, M_n 184,900, PDI 1.28 ^{1}H NMR ($CDCl_3$, 400MHz) δ(ppm): 3.68 (bm, 6H, $H_{8,9}$), 2.67 (bd, 2H, $H_{2,3}$), 2.21 (2bm, 2H, $H_{1,4}$), 1.55 (bm, 2H, $H_{5,6}$), 1.17 (bt, 1H, H_7), 0.80 (bm, 1H, $H_{7'}$). ^{13}C NMR, ($CDCl_3$, 100MHz) δ(ppm): 173.95 (m, $C_{8,9}$), 134.51 (s, *p*-xylene, C_1), 128.74 (s, *p*-xylene, C_2), 52.52 (s, $C_{10,11}$), 51.68 (s, $C_{2,3}$), 42.27 (d, $C_{1,4}$), 38.69 (s, $C_{7 \text{ or 6 and 5}}$), 33.73 (s, $C_{7 \text{ or 6 and 5}}$), 20.82 (s, *p*-xylene, CMe).

Endo,endo-poly(dimethyl 1,4-cyclopentenylene-5,6-ethylidene-2,3-dicarboxylate was obtained as a colourless, transparent, adhesive solid after precipitation from hot p-xylene into methanol, decantation and drying under vacuum. 88% yield, M_n 89,100, PDI 1.51 ^{1}H NMR ($CDCl_3$, 400MHz) δ(ppm): 3.68 (bm, 6H, $H_{8,9}$), 3.05 (bm, 2H, $H_{2,3}$), 2.08 (2bm, 4H, $H_{1,4 \text{ cis and trans, } 5,6}$), 1.40 (2bm, 4H, $H_{7,7',5,6}$) ^{13}C NMR [see appendix B19] ($CDCl_3$, 100MHz) δ(ppm): 173.10 (m, $C_{8,9}$), 134.51 (s, *p*-xylene, C_1), 128.74 (s, *p*-xylene, C_2), 51.12 (s, $C_{10,11}$), 50.07 (s, $C_{2,3}$), 41.20 (m, $C_{1,4}$), 37.05 (s, $C_{7 \text{ or 6 and 5}}$), 30.18 (s, $C_{7 \text{ or 6 and 5}}$), 20.82 (s, *p*-xylene, CMe).

Endo,exo- poly(dimethyl 1,4-cyclopentenylene-5,6-ethylidene-2,3-dicarboxylate was obtained as a colourless, transparent, adhesive solid after precipitation from hot p-xylene into methanol, decantation and drying under vacuum. 98% yield, M_n 220,500, PDI 1.34 ^{1}H NMR ($CDCl_3$, 400MHz) δ(ppm):3.67 (dm, 6H, $H_{8,9}$), 3.15 (bm, 1H, $H_{2,3}$), 2.78 (bm, 1H, $H_{2,3}$), ~2.0 (bm, 1H, $H_{1,4}$), 1.20 (bm, 2H, $H_{1,4 \text{ and } 5,6}$), 1.63 (bm, 1H, $H_{6',5'}$), 1.35 (bm, 2H, $H_{5,6 \text{ and } 7}$), 1.09 (bm, 2H, $H_{5,6 \text{ and } 7'}$). ^{13}C NMR ($CDCl_3$, 100MHz) 45.22 (s, $C_{1,4 \text{ trans/cis}}$), 45.16 (s, $C_{1,4 \text{ trans/trans}}$), 40.58 (s, $C_{1,4 \text{ cis/trans}}$), 39.15 (s, C_7).

Step 3. Base hydrolysis of poly(1,4-cyclopentenylene-5,6-ethylidene-2,3-dicarboxylic acid dimethyl ester)

Poly(1,4-cyclopentenylene-5,6-ethylidene-2,3-dicarboxylic acid dimethyl esters), were hydrolysed in refluxing aqueous NaOH (10% w/w), reactions were terminated when full dissolution of the polymer had occurred, ca. 4 hrs.

Exo,exo-poly(disodium 1,4-cyclopentenylene-5,6-ethylidene-2,3-dicarboxylate) was

obtained as a white powdery hygroscopic solid after precipitation from aqueous solution into a three fold excess of methanol, centrifugation, decantation and drying under vacuum. Yield 80%. M_n 160,000 PDI 1.47. Elemental analysis proved unsatisfactory but the hydrolysis was shown to be complete by the absence of -OCH_3 signals in the ^1H NMR spectrum. ^1H NMR, (D_2O, 400MHz) δ(ppm): 2.36 (bm, 2H, $H_{2,3}$), 1.91 (bm, 3H), 1.31, 1.25, 1.04, 0.96, 0.60 (bm, 5H). ^{13}C NMR, (D_2O, 100MHz) δ(ppm): 183.46 (s, $C_{8,9}$), 57.21 (s, $C_{2,3}$), 43.00 (d, $C_{1,4}$), 38.34 (s, C_7), 33.55 (bd, $C_{5,6}$).

Endo,exo- poly(disodium 1,4-cyclopentenylene-5,6-ethylidene-2,3-dicarboxylate) was obtained from the hydrolysis of the *endo,endo*-polyester, see Results and Discussion section and Figure 2, as a white powdery hygroscopic solid after precipitation from aqueous solution into a three fold excess of methanol, centrifugation, decantation and drying under vacuum. Yield 92%. M_n 73,000, PDI 1.70. Elemental analysis proved unsatisfactory but the hydrolysis was shown to be complete by the absence of -OCH_3 signals in the ^1H NMR spectrum. ^1H NMR, (D_2O, 400MHz) δ(ppm): 2.70 (t, 1H, H_2), 2.30 (t, 1H, H_3), 2.01, 1.90, 1.70 (bm, 4H), 1.37, 1.30, 1.19, 1.03, 0.90, 0.78 (bm, 4H). ^{13}C NMR, (D_2O, 100MHz) δ(ppm): 185.26 (s, C_9), 183.17 (m, C_8), 58.22 (s, C_3),55.97 (s, C_2), 44.75 (m, C_4), 40.69 (m, C_1), 38.23 (m, C_7), 32.94 (m, $C_{5\text{ or }6}$), 30.68 (m, $C_{5\text{ or }6}$).

Endo,exo--poly(disodium 1,4-cyclopentenylene-5,6-ethylidene-2,3-dicarboxylate) was obtained as a white powdery hygroscopic solid after precipitation from aqueous solution into a three fold excess of methanol, centrifugation, decantation and drying under vacuum. Yield 82%. M_n 147,200, PDI 1.54. Elemental analysis proved unsatisfactory but the hydrolysis was shown to be complete by the absence of -OCH_3 signals in the ^1H NMR spectrum. ^1H NMR, (D_2O, 400MHz) δ(ppm): 2.70 (t, 1H, H_2), 2.30 (t, 1H, H_3), 2.01, 1.90, 1.70 (bm, 4H), 1.37, 1.30, 1.19, 1.03, 0.90, 0.78 (bm, 4H). ^{13}C NMR, (D_2O, 100MHz) δ(ppm): 185.24 (s, C_9), 183.16 (m, C_8), 58.18 (s, C_3), 55.97 (s, C_2), 44.65 (m, C_4), 40.73 (m, C_1), 38.27 (m, C_7), 32.92 (m, $C_{5\text{ or }6}$), 31.01 (m, $C_{5\text{ or }6}$).

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References and notes

1. Feast WJ, Heywood BR, Hesselink JL and Rannard SP *in preparation*
2. Megson JL, (1997) Ph.D. Thesis Durham University
3. Bazan GC, Schrock RR, Cho HN, Gibson VC (1991) *Macromolecules,* 24: 4495.
4. Gastel FJC, Klunder AJH and Zwanenburg, B (1991) *Rec. Trav. Chim. Pays-Bas,* **110**, 175-184.
5. Dr A.S. Batsanov personal communication.
6. Aqueous SEC measurements were carried out by Polymer Laboratories Ltd., Church Stretton, SY6 6AX, UK; the analysts were only told the solubility of the polymers and the fact that they were polyelectrolytes.
7. Ivin KJ and Mol JC (1997) in Olefin Metathesis and Metathesis Polymerisation, Academic Press.