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Cyclic polyesters: Part 8. Preparation and characterization of cyclic oligomers in six aromatic ester and ether–ester systems

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Cyclic oligomers of tetraethylene glycol terephthalate (TEGT), tetraethylene glycol isophthalate (TEGI), tetraethylene glycol orthophthalate (TEGO), decamethylene terephthalate (DMT), decamethylene isophthalate (DMI) and decamethylene orthophthalate (DMO) were prepared successfully and cleanly from a ring-chain equilibrium reaction in dilute solution of chlorobenzene. The reactions were monitored by gel permeation chromatography (GPC) and proton nmr and ^{13}C NMR spectroscopy, and the molar cyclic concentrations $[M_x]$ deduced ($x = 1-10$). The cyclic oligomers were also analysed by fast atom bombardment mass spectrometry (FAB-MS), matrix assisted laser desorption ionization–time of flight mass spectometry (MALDI–TOF MS) and differential scanning calorimetry (DSC). The existence of the cyclic oligomers was proven by all of the above methods. In addition, it was found that small amounts of linear species were formed, especially in the TEGT system.

(Keywords: cyclic esters; cyclic ether–esters; gel permeation chromatography)

INTRODUCTION

In this paper, the synthesis and characterization of cyclic and linear oligomers of tetraethylene glycol terephthalate (TEGT), tetraethylene glycol isophthalate (TEGI), tetraethylene glycol orthophthalate (TEGO), decamethylene terephthalate (DMT), decamethylene isophthalate (DMI) and decamethylene orthophthalate (DMO) are described. The structure of the six repeat units are shown in *Figure 1*. This is part of a study of large ring molecules[1–3], particularly macrocyclic ether–esters[4–12]. The main aim of this present work was to establish the experimental conditions required to prepare a range of new macrocycles so that in the future preparative GPC will be used to isolate individual compounds for further investigation. One of the other systems (DMT) was the subject of a previous paper[9], where its equilibrium cyclic concentrations were measured and discussed in terms of the Jacobson–Stockmayer theory[13,14].

The early work on cyclic polyethers was pioneered by Pederson[15]. Since then the field has expanded rapidly and a large number of macrocyclic compounds have been prepared and their cation complexation properties extensively studied[16]. Some of the cyclic oligomers described here have been made previously, but not by the same method. Bradshaw and Thompson[17] made the TEGT cyclic monomer and dimer along with many other cyclic monomers and dimers by reacting isophthaloyl chloride and 5-nitroisophthaloyl chloride (acid chlorides) with tri-, tetra-, penta-, and hexaethylene glycols. Frensch and V ögtle[18] did a similar synthesis at around the same time. Bradshaw also synthesized the TEGO cyclic monomer by reacting a diacid chloride with a glycol. Piepers and Kellogg also synthesized the TEGO cyclic monomer[19], but used acid bromides and dicaesium salts of dicarboxylic acid to perform a "Hantzsch" type synthesis. The TEGO cyclic dimer was made by Ogowa[20] by a template synthesis using tris(2-methoxyphenyl)bismuthane which also acts as a dehydrating agent. The dicarboxylic acid anhydride and tetraethylene glycol in toluene solution gave both the monomer and the dimer. The TEGI cyclic monomer was synthesized by the same mechanism as in refs[11,12] by Ninagawa *et al.*[21] The PDO cyclic monomer[22] and dimer[23] were both synthesized by Drewes and Coleman by condensing the dipotassium salt of orthophthalic acid with the appropriate alkyldibromide. No evidence of higher oligomers can be found in the literature, and nothing for the DMT and DMI systems.

The mechanism used here to make the cyclic oligomers is depolymerization of linear polyesters. Carothers and coworkers discovered that linear polyesters could be depolymerized using certain metal catalysts to yield the cyclic monomeric and dimeric cyclics[24,25]. The best depolymerization catalysts were the divalent salts of tin, manganese, iron, magnesium and cobalt[25]. Our reactions, however, are done in dilute solution so that intramolecular reactions are preferred over intermolecular reactions, so higher cyclic oligomers are formed. The cyclics described in this paper could be used for ring opening polymerization reactions, for complexing with metal ions and for topological studies such as entrapping them into networks[26,27]. They could also be divided into sharp fractions by preparative GPC to give materials suitable for further chemical and physical investigations.

EXPERIMENTAL

Materials

Dimethyl terephthalate, dimethyl isophthalate, dimethyl phthalate, 1,10-decandiol and tetraethylene glycol were

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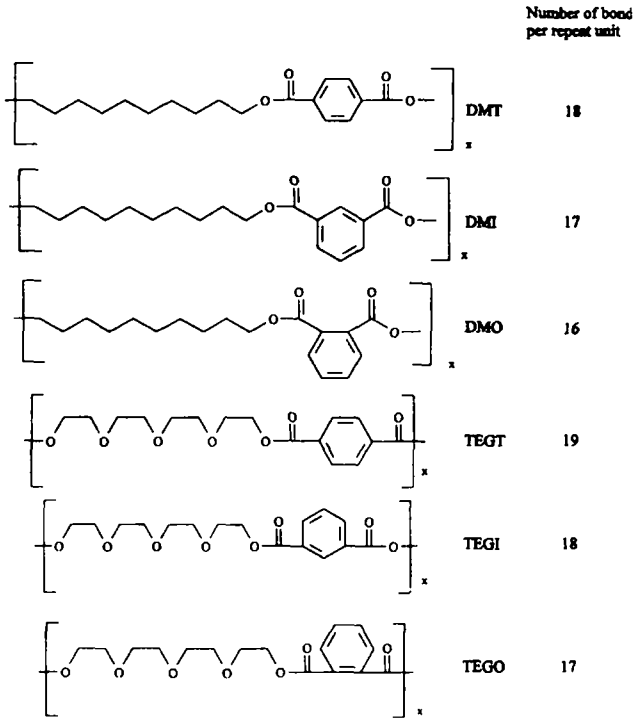


Figure 1 Schematic representation of the isomers of tetraethylene glycol phthalate (TEGP) and polydecamethylene phthalate (DMP) showing the number of bonds per repeat unit in each case

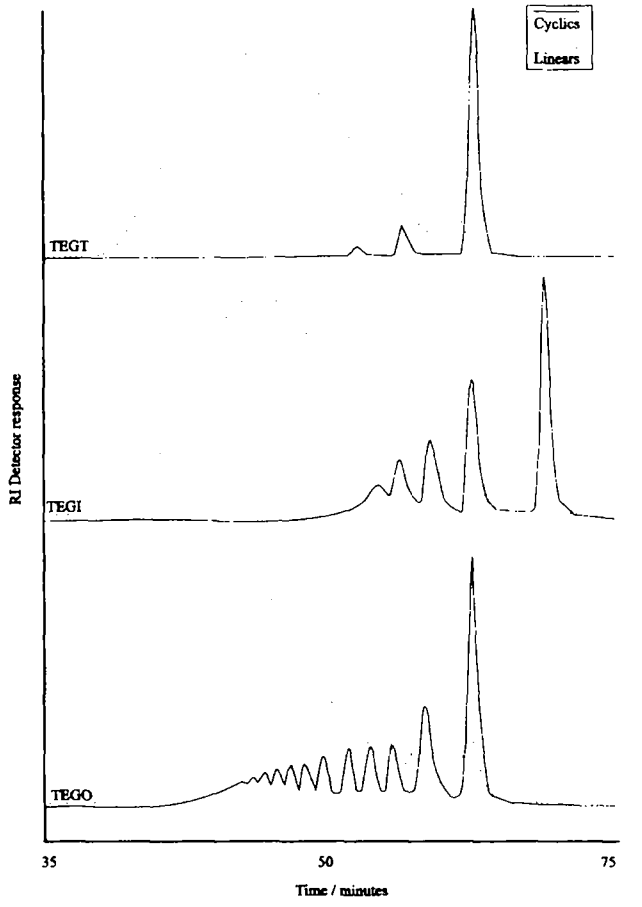


Figure 2 GPC taces of the TEGP ring-chain reaction products at 100:1 dilution in chlorobenzene

obtained from Fluka Chemicals Ltd. The catalyst used was dibutyltin oxide, and this was obtained from Aldrich. All of the above reagents were used as received.

Preparation of high mass linears

The high mass linears were prepared by a condensation polymerization reaction between the relevant dimethyl ester and tetraethylene glycol. The relevant dimethyl ester and tetraethylene glycol or 1,10-decandiol were added in equimolar proportions to a four necked reaction vessel, which was equipped with an overhead stirrer, a thermometer and a distillation head. The reaction vessel was purged with dry nitrogen and the temperature raised to 140°C with stirring to establish thorough mixing and melting of the monomers. The catalyst, dibutyltin oxide (0.5 wt%) was then added and the temperature raised to 160°C for 48 h under vacuum to remove methanol from the system. The products were then allowed to cool to room temperature under a nitrogen atmosphere. The molar masses of the linear polymers of TEGT, TEGI and TEGO were found to be ca. 30 000, and that of DMT, DMI, DMO to be ca. 40 000 by gel permeation chromatography (GPC).

Preparation of cyclic oligomers by solution transesterification

The high mass linear polymers obtained as described above were refluxed in dilute solution of chlorobenzene (100:1 w/w and 30:1 w/w) with further catalyst (0.5% w/w).

Gel permeation chromatography

The instrument was set up with four mixed-E 3μ analytical columns, an ERC 7515A refractive index (RI) detector, a Polymer Laboratories LC1150 HPLC pump and a Spark Holland Basic Marathon Auto Injector. This system was run with Caliber V7.0 software. The flow rate was 0.5 ml min^{-1}. All of the above equipment was supplied by Polymer Laboratories.

Nuclear magnetic resonance spectroscopy

^{1}H – NMR spectra were obtained on a Joel 270 MHz spectrometer, using deuterated chloroform as the solvent. The spectra were processed and analysed using Winnmr V3.0 software from Bruker.

Differential scanning calorimetry

The linear and cyclic products were analysed thermally on a Polymer Laboratories Thermal Sciences STA 625, using Trace2 (V4.0) software. The samples were cooled with liquid nitrogen and the heating rate used in each case was 10° min^{-1}.

Mass spectroscopy

FAB MS spectra were obtained using a NOBA matrix and $CHCl_3$ as the solvent. Matrix-assisted laser desorption ionization time of flight mass spectrometry (MALDI–TOF-MS) was carried out on a Kratos Kompact 111 spectrometer in refletron mode. This instrument incorporates a 337 nm nitrogen laser with a 3 ns pulse duration and an electron multiplier detector. The sample was deposited in a 0.1 M 2,5-dihydroxybenzoic acid matrix from an acetone/water mixture, apart from DMT which was deposited from a chloroform/acetone mixture. 0.4 μl of the matrix was deposited on a plate. This was dried in the oven for 30 s. The polymer solutions were made up at a concentration of 1 mg ml^{-1}, and 0.4 μl put on top of the dried matrix. This was then dried in an oven for 2 min. The spectrometer was calibrated internally using bovine insulin (5734) and sodium (22.9898). The width of the peaks in the region of 4000 Da at half peak height is approximately 4 Da.

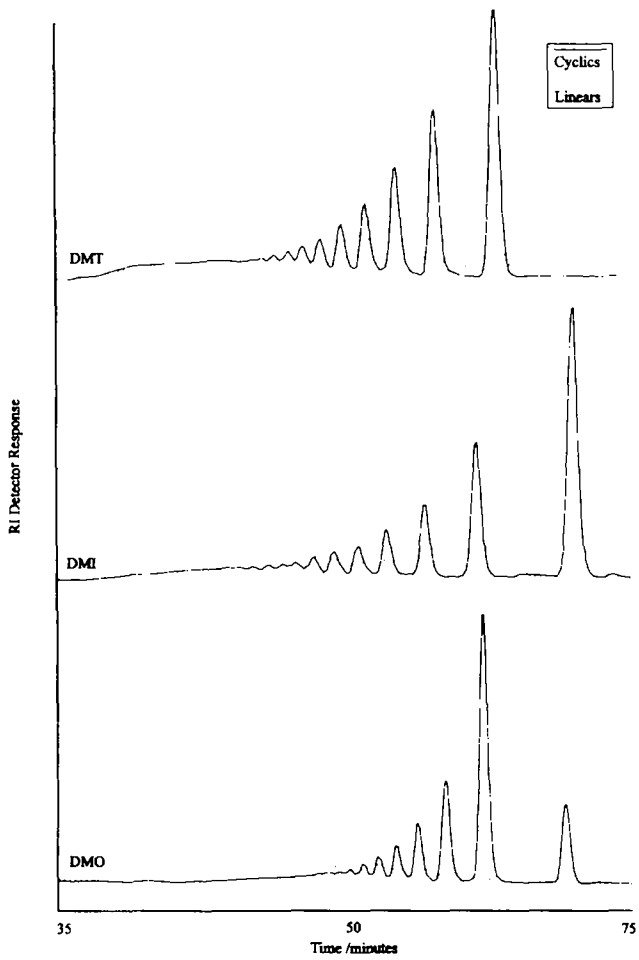


Figure 3 GPC traces of the DMP ring-chain reaction products at 100:1 dilution in chlorobenzene

RESULTS AND DISCUSSION

Ring-chain reactions

The products from the melt polymerization and ring-chain transesterification reactions were analysed by GPC as described in the previous section. The results are shown in *Figures 2 and 3*. The concentrations of the resolved cyclic species were determined by peak area estimates using the GPC Caliber software supplied by Polymer Laboratories Ltd, which assumes that all the cyclic species give similar responses using the refractive index detector. The distribution of the oligomers is detailed in *Table 1*.

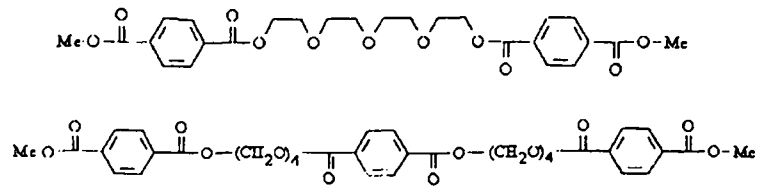
Table 1 TEGP and DMP cyclic oligomer M, distribution

	Percentage of each oligomer by weight					
x	TEGT	TEGI	TEGO	DMT	DMI	DMO
1	—	19	—	—	36	16
2	82	10	28	32	17	51
3	11	6	16	21	9	19
4	3	5	8	14	3	11
5	1	4.5	8	10	3	6
6	< 1	3	7	7	2	4.3
7	—	3	6.5	5	2	3.1
8	—	2.5	6	4	2	2.4
9	—	2	4.5	3.5	1.5	1.7
10	—	2	3.5	3	0.9	1.2
11	—	1.5	3	2.1	0.5	1
12	—	1	2	1.1	0.5	0.9

Table 2 Mass of the tetraethylene glycol phthalate cyclic oligomers

Number of repeat units	Mass (g) M	Mass (g) (MNa)$^+$	Mass (g) (M-H_2O)$^+$
1	324	347	306
2	648	671	630
3	972	995	954
4	1296	1319	1278
5	1620	1643	1602
6	1944	1967	1926
7	2268	2291	2250
8	2592	2615	2574
9	2916	2939	2898
10	3240	3263	3222

whilst the first species to occur in both TEGT and TEGO is the dimer. This is supported by the distributions of the oligmers shown by GPC in *Figure 2*. Molecular modelling by "Chem-X" shows that the virtual monomers of TEGT and TEGO are highly strained and therefore unlikely to form, while the monomer of TEGI is much less strained. This is shown in *Figure 5*. MALDI–TOF mass spectra (shown in *Figure 6*) again indicate that cyclic species with a repeat unit of 324 are present. The MALDI–TOF spectra however also show that there is a small amount of linear species present. These occur at 194 *m/z* greater than the cyclic oligomers, and can be attributed to the linear species shown below in *Table 3*. The linears have methylester terminated phthalate groups at either end of the chain. An exception to this is the TEGI linear species at 834 *m/z*, which is proton terminated. An example of this is given below.



Linear species associated with TEGT x=1 and 2

Characterization of cyclic oligomers

Mass spectrometry. The mass spectra of the cyclic oligomers of TEGT, TEGI, and TEGO are shown in *Figure 4*. It can be seen that there are peaks corresponding to (M)$^+$, (MNa)$^+$ and (M-H_2O)$^+$ for some species. The peaks are summarized in *Table 2*.

From the FAB-MS spectra shown in *Figure 4*, it can be seen that the first cyclic oligomer of TEGI is the monomer,

The same analaysis can be carried out for the DMT, DMI and DMO cyclic oligomers. The FAB-MS spectra of these are shown in *Figure 7*. *Table 4* summarizes the peaks found in these spectra. It can be seen that with DMT the first cyclic oligomer to form is the dimer, whereas DMI readily forms the monomer. DMO, however, forms a small amount of monomer with the higher oligomers forming the usual Gaussian distribution.

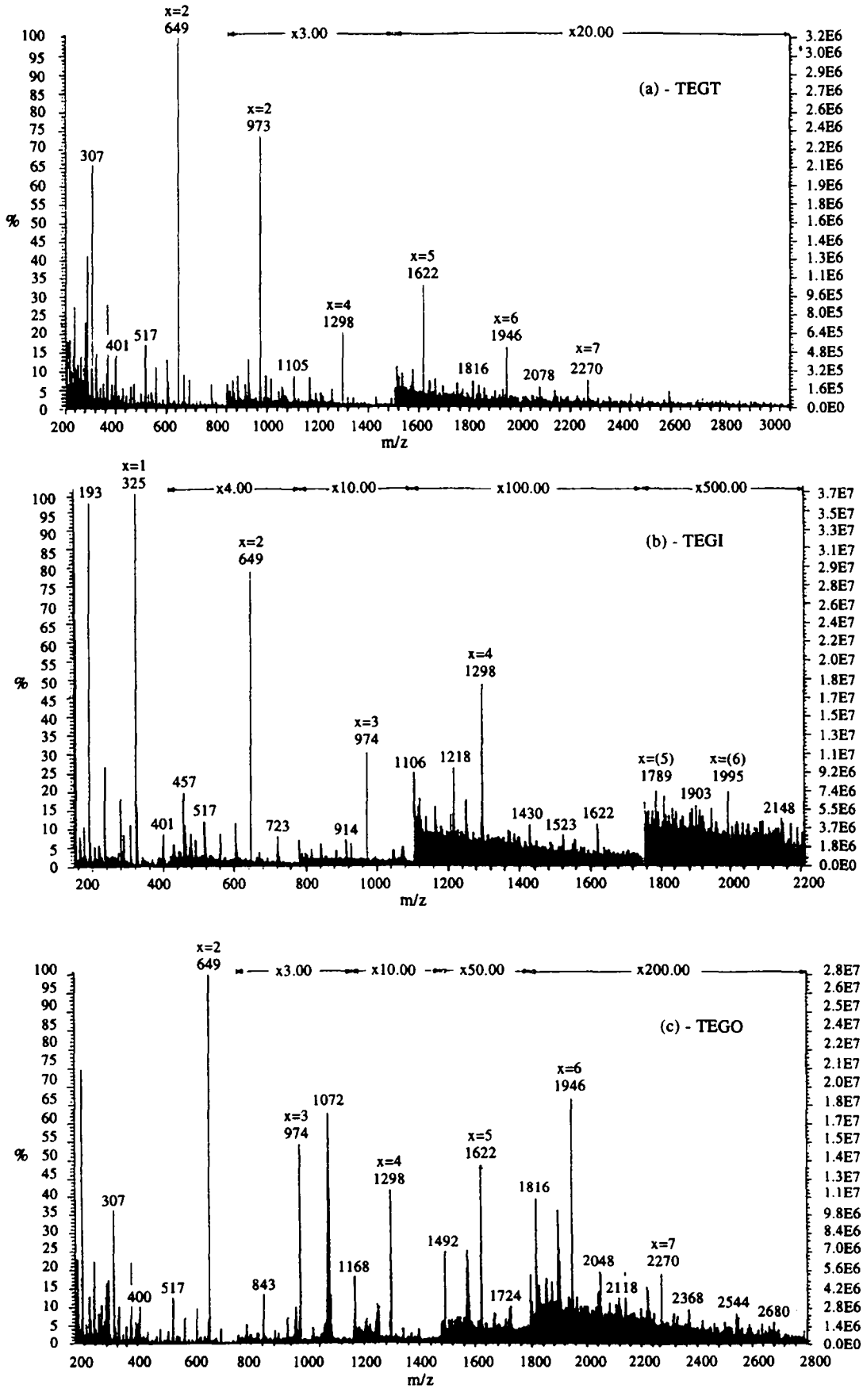


Figure 4 FAB-MS of the TEGP ring-chain reaction products

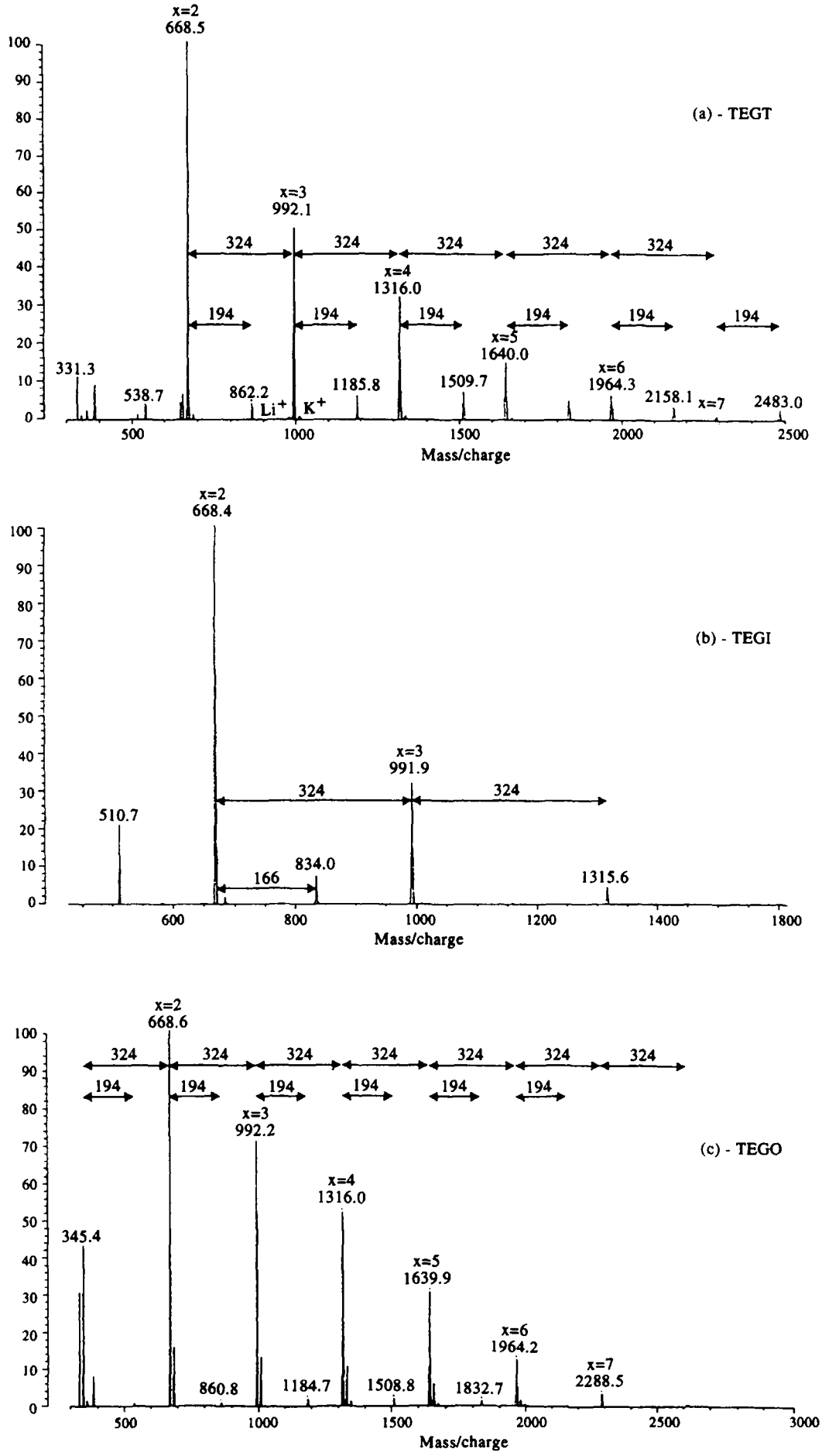


Figure 5 MALDI–TOF mass spectra of the TEGP cyclic oligomers

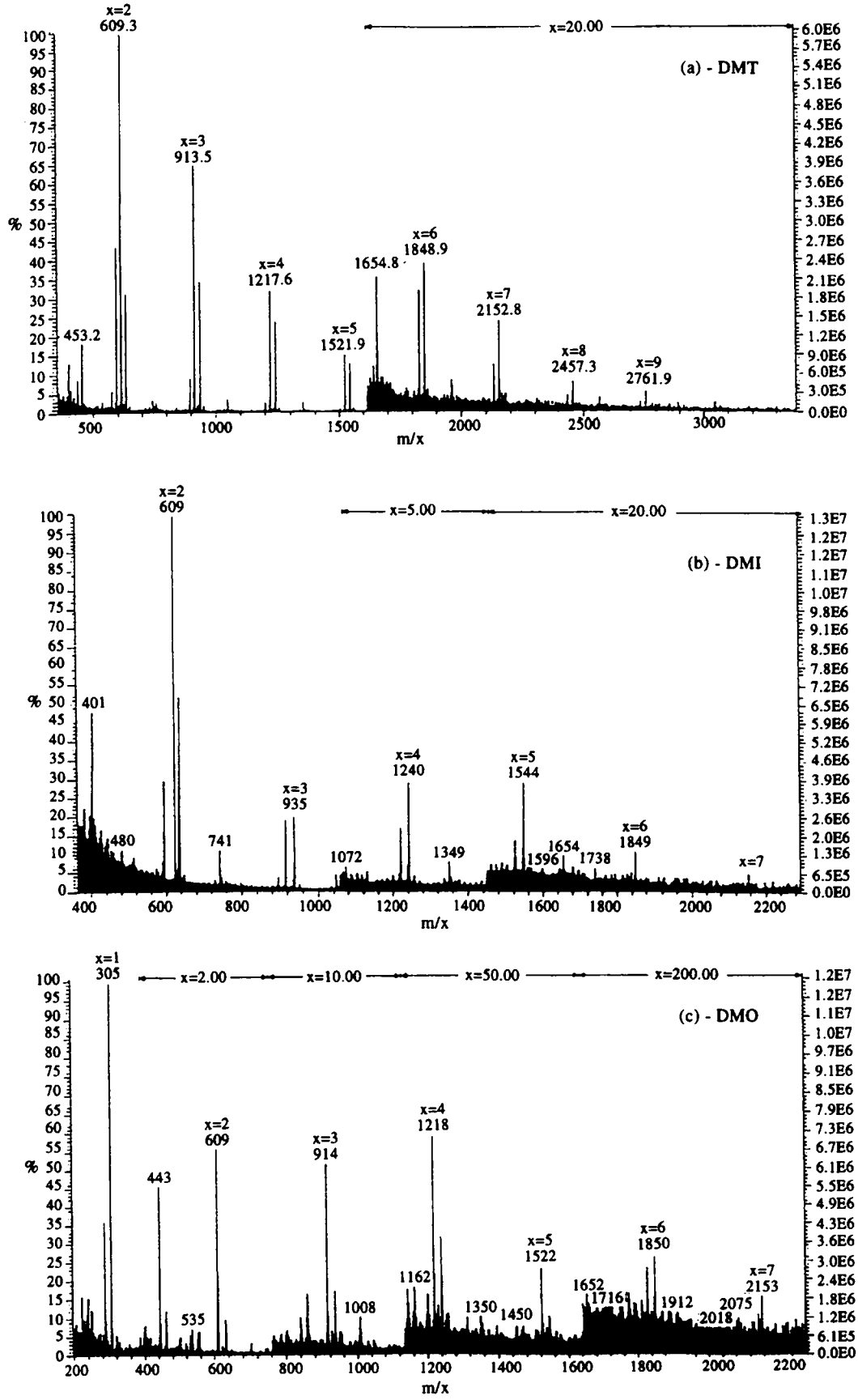


Figure 6 FAB mass spectra of the DMP cyclic oligomers

The MALDI–TOF mass spectra of the DMP cyclics are shown in *Figure 8* and the peaks are summarized below in *Table 5*.

Nuclear magnetic resonance spectroscopy. Figure 9 shows the proton NMR spectra of (a) the high mass linears before cyclization and (b) the cyclics of TEGT. The proton NMR spectra of the three high mass linears show that the methyl ester proton peaks attributed to the dimethyl ester

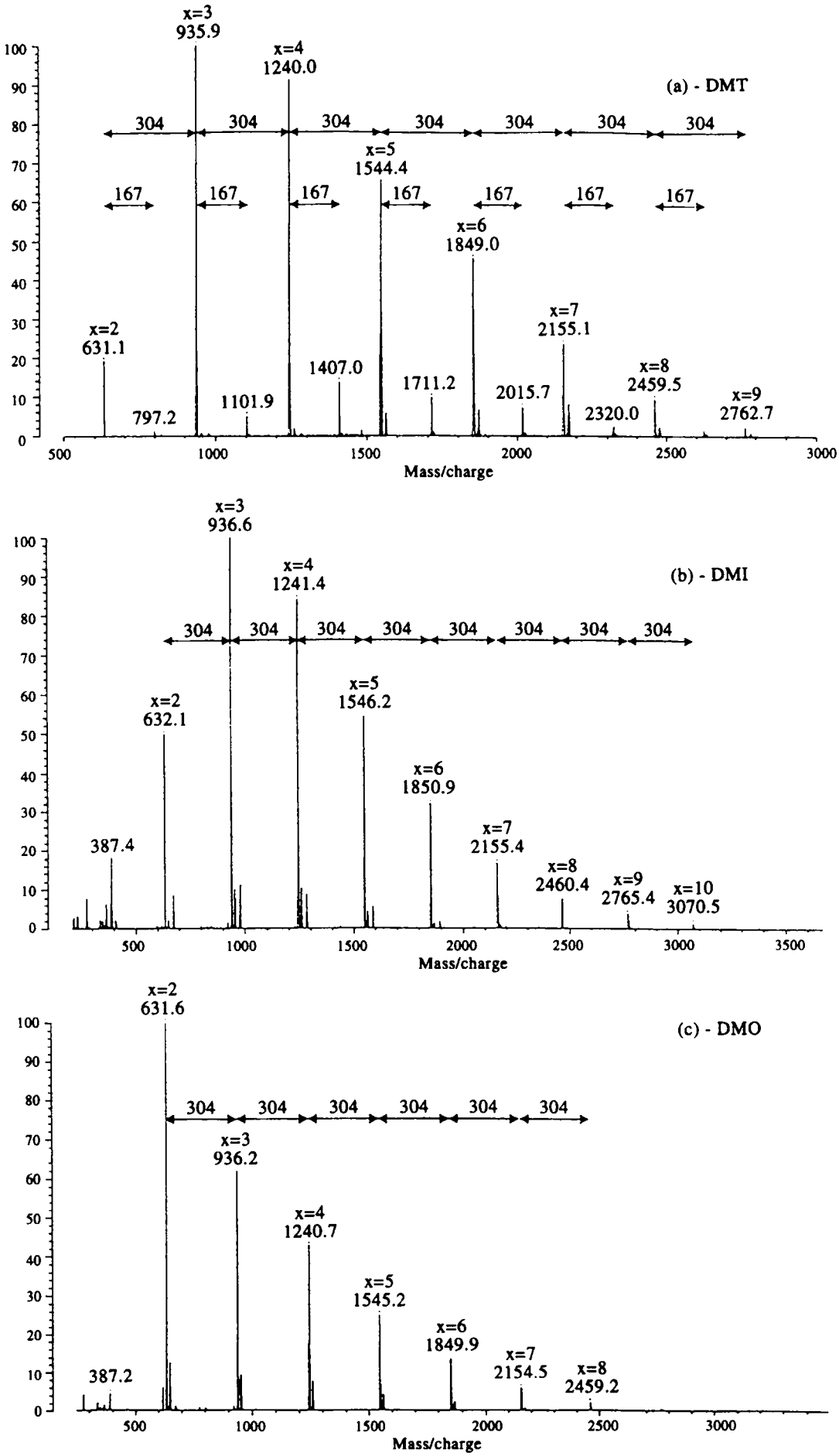


Figure 7 MALDI–TOF mass spectra of the DMP ring-chain reaction products

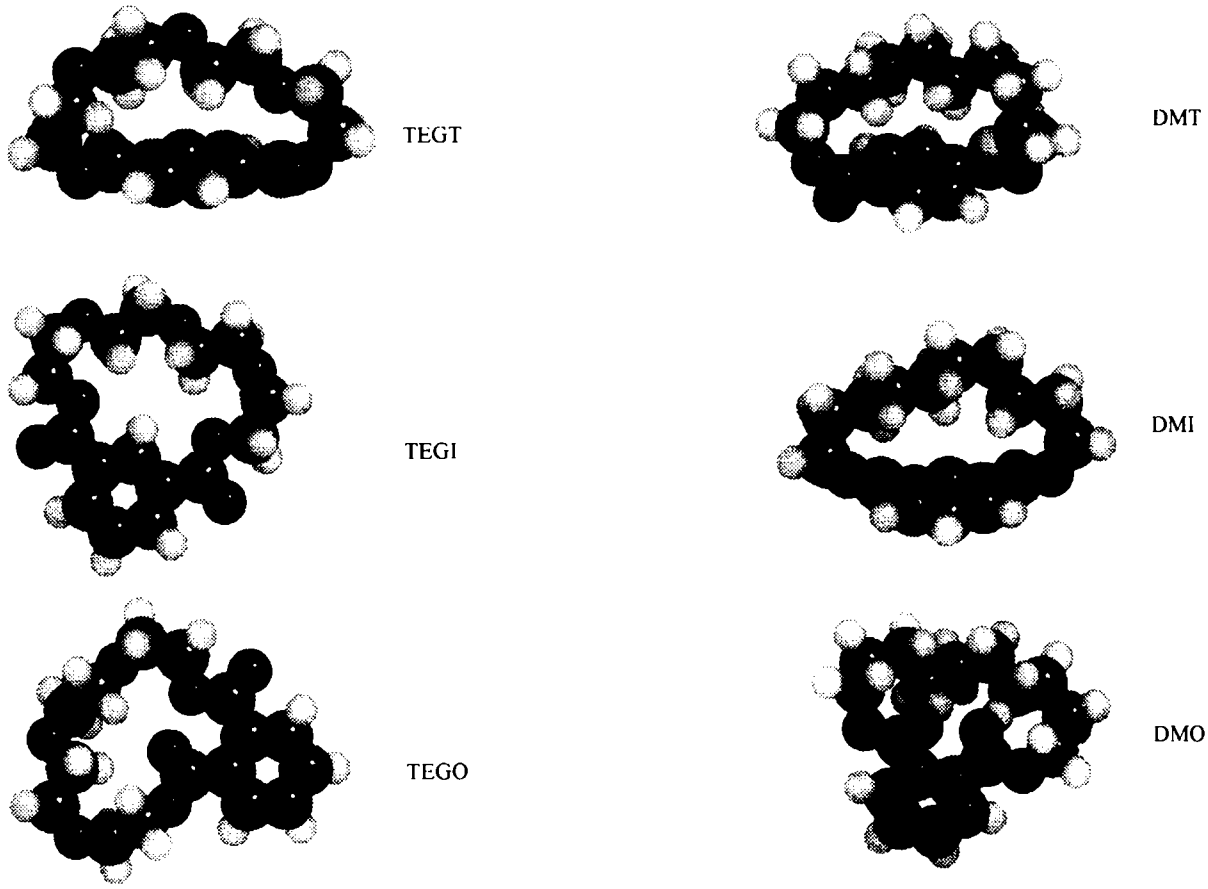


Figure 8 CPK solid diagram for molecular modelling by Chem-X of the cyclic monomers

Table 3 Summary of peaks from MALDI–TOF mass spectra of cyclics M_x and the corresponding linear species

x	Cyclic species peak *m/z*	Linear species peak *m/z*	Percentage linears
		TEGT	
2	668	862	3
3	992	1186	8
4	1316	1510	19
5	1640	1834	25
6	1964	2158	34
7	2289	2483	61
8	2613	2807	77
		TEGI	
2	668	834	4
3	992	—	No linear
4	1316	—	No linear
5	1640	—	No linear
		TEGO	
1	345	—	No linear
2	668	861	1
3	992	1185	3
4	1316	1509	4
5	1640	1833	4
6	1964	—	No linear
7	2288	—	No linear

Note that all the peaks are for the sodiated molecular ion $(MNa)^+$, except the peak for the TEGI $x = 2$ linears which shows an unsodiated peak at 834 *m/z*. Also note that additional peaks for TEGI are listed than those that can be seen in *Figure 5*(b). These are found by expansion of the MALDI–TOF spectra.

Table 4 Mass of the decamethylene phthalate cyclic oligomers

Number of repeat units	Mass (g) M^+	Mass (g) $(MNa)^+$	Mass (g) $(M\text{-}H_2O)^+$
1	304	327	286
2	608	631	590
3	912	935	894
4	1216	1239	1198
5	1520	1543	1502
6	1824	1847	1806
7	2128	2151	2110
8	2432	2455	2414
9	2736	2759	2718
10	3040	3063	3022

starting material have disappeared at 3.9028 ppm, 3.8588 ppm and 3.8004 ppm from TEGT, TEGI and TEGO, respectively. Similarly, the peak due to the diol protons in tetraethylene glycol at 3.5553 ppm has disappeared in all three linear spectra. Predictable downfield shifts have occurred due to the condensation polymerization reaction such as the TEG ethylene oxide protons shifting from 3.5553 to 3.6590 ppm in TEGT. The high mass linear polymers show a singlet due to methyl ester end groups which disappear in the cyclic spectra. These occur at 3.9378 ppm, 3.9387 ppm, and 3.9082 ppm in TEGT, TEGI and TEGO linears, respectively. The absence of the characteristic methyl ester end group peaks confirm the cyclic topology of the molecules. Similarly, the proton NMR spectra of linear DMT, DMI, DMO show peaks at 3.9513 ppm, 3.9549 ppm and 3.9091 ppm which disappear in the corresponding cyclic spectra. The ^{13}C DEPT spectra, which are shown in *Figure 10*, back up these observations. The three dimethyl ester starting material peaks have disappeared in the linear product. These linear products show peaks attributable to methyl

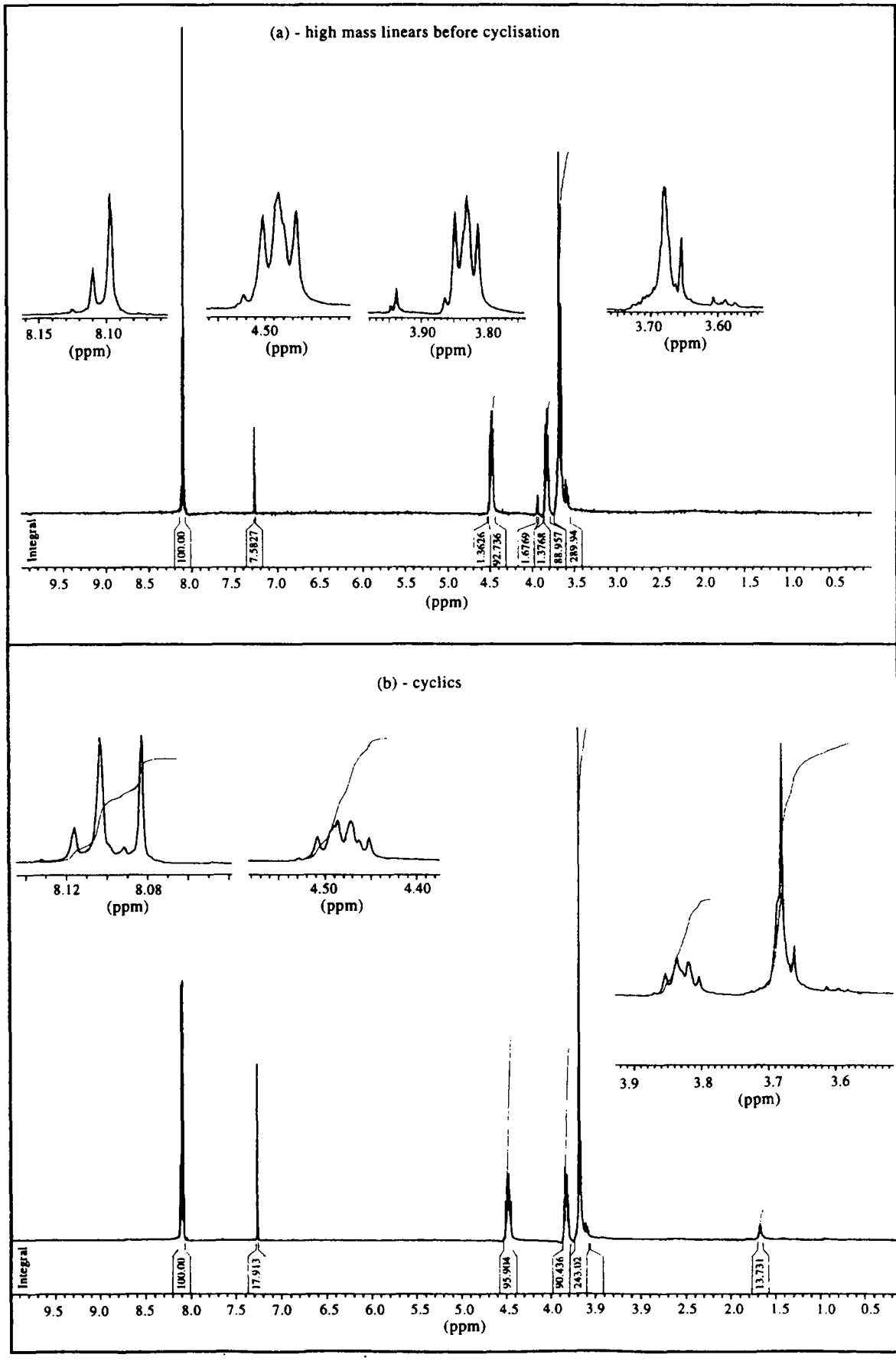


Figure 9 Proton nmr spectrum of TEGT (a) high mass linears before cyclisation and (b) cyclics

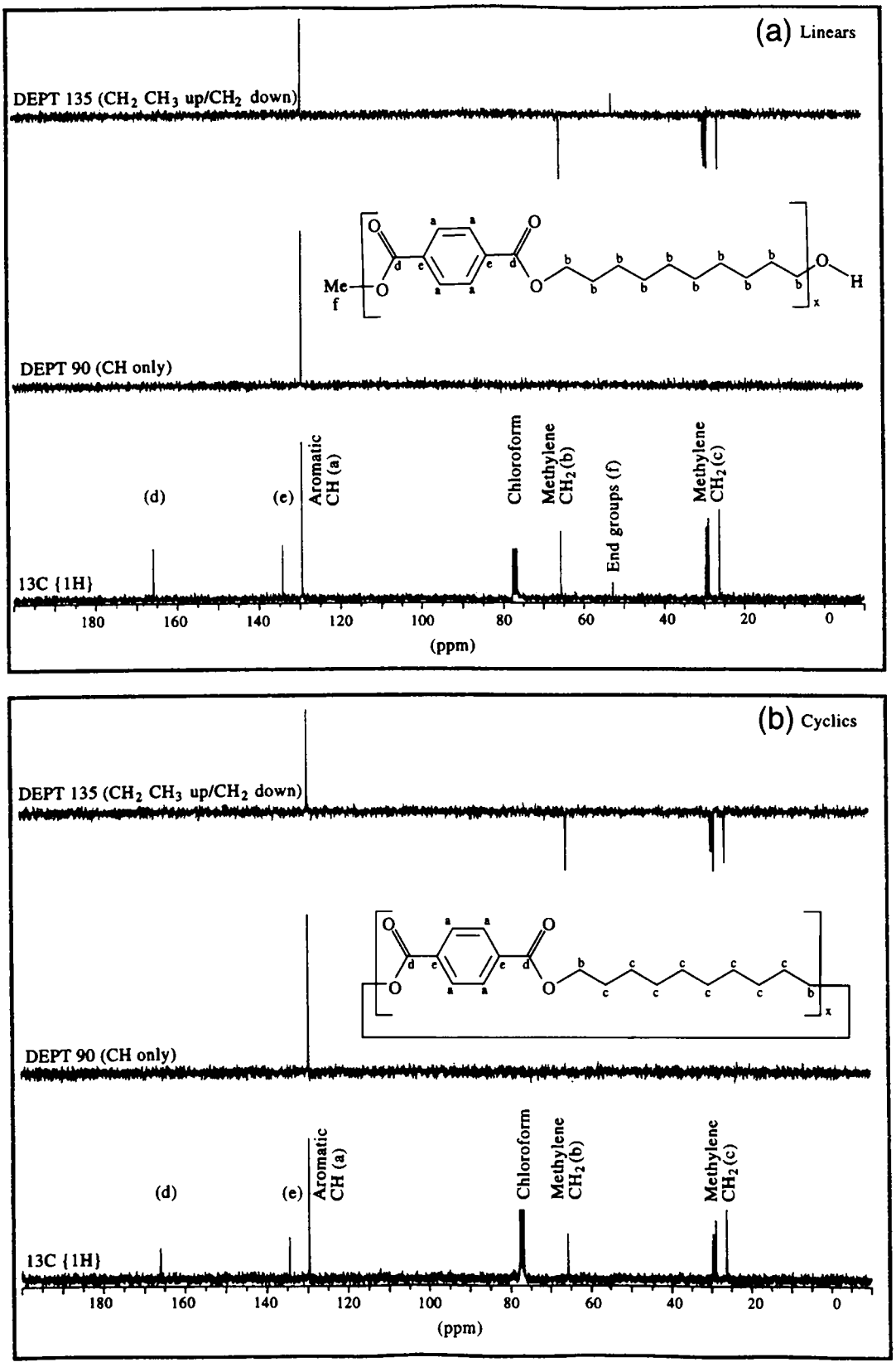


Figure 10 ^{13}C DEPT nmr spectra of PDT (a) high mass linears before cyclisation and (b) cyclics

ester end groups at 52.6409 ppm which are not found in the cyclic species.

Differential scanning calorimetry. An example of the results of the DSC analysis is shown in *Figure 11*. The results are summarized in *Table 6* below.

The DSC results show that the cyclics are much more crystalline than the high mass linears. This is due to the lack of chain entanglements in the cyclic oligomers. The phenyl groups can stack and arrange themselves in a more orderly fashion and hence are more crystalline. These characterization methods show that the tetraethylene glycol phthalate

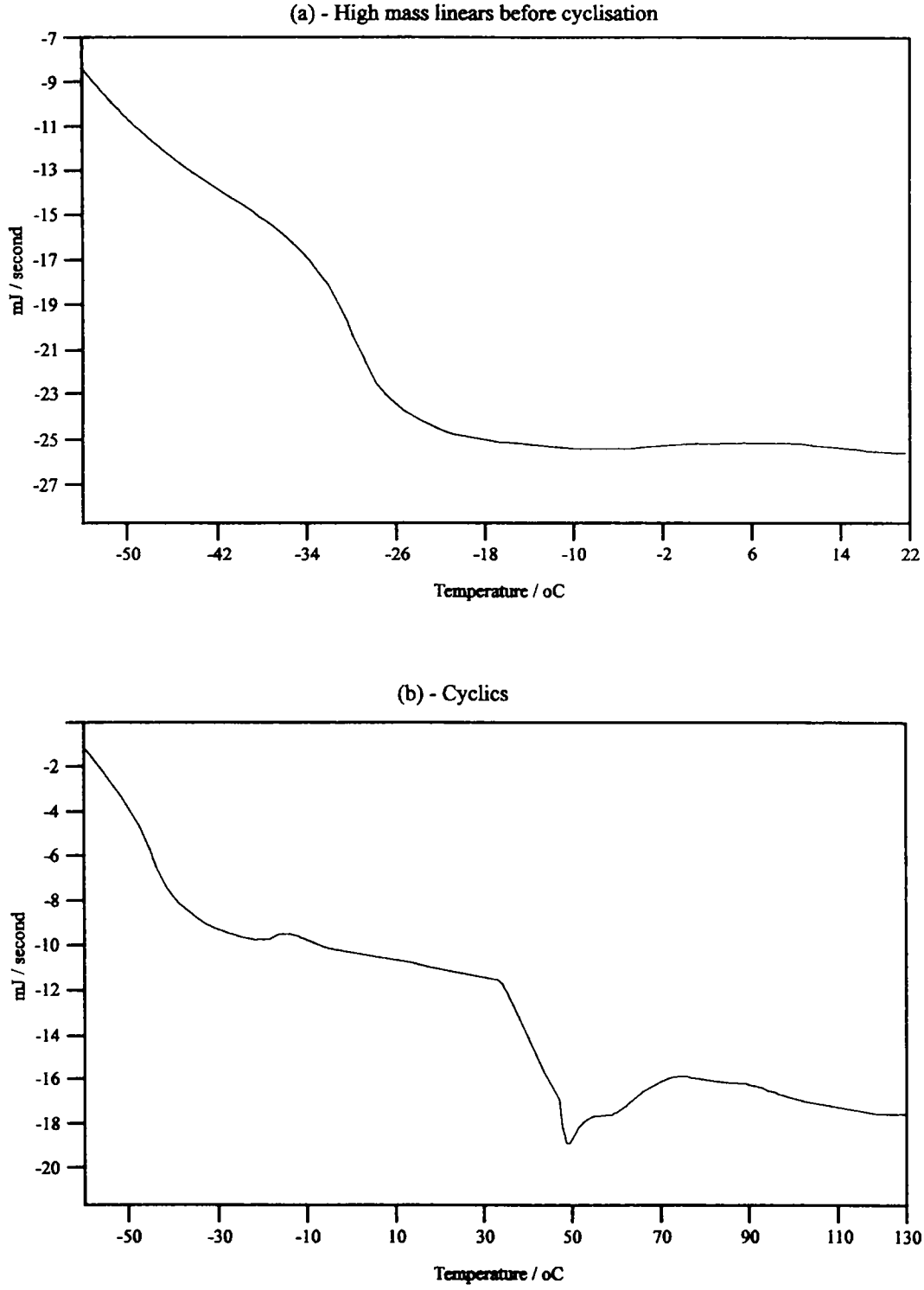


Figure 11 DSC traces of TEGT (a) high mass linears before cyclisation and (b) cyclics

and decamethylene phthalate systems produce large cyclic species, but MALDI–TOF mass spectrometry shows that they contain small amounts of linear oligomers, particularly in the case of TEGT.

Analysis of results

The investigations described here have led to the determination of the molar cyclic concentrations of the cyclics $[O(CH_2O)_4OC_6H_4C]_x$ and $[OC_{10}H_{20}OCOC_6H_4]_x$ with $x = 1-10$. This was done from GPC tracings by analysing peak areas of individual cyclic species, as well as the area of the whole reaction produced by the caliber GPC software supplied by Polymer Laboratories. Plots of the logarithms of the molar cyclic concentrations $[M_x]$ against the logarithms of the number of skeletal bonds for TEGT, TEGI and TEGO are shown in *Figure 12*, and *Figure 13* shows the same plot for DMT, DMI, DMO. Both sets of cyclic oligomers have 18 skeletal bonds per repeat unit and so can easily be compared. The log $[M_x]$ *versus* log n plot for each system gives a mean slope close to -3.0 in the region $x = 32-180$ compared to the Jacobson–Stockmayer limiting value of -2.5. The higher oligomers are present in much lower concentrations and hence there is a great uncertainty in their experimental $[M_x]$ values.

Table 5 Summary of peaks from MALDI-TOF mass spectra of cyclics M_x and the corresponding linear species.

x	Cyclic species peak *m/z*	Linear species peak *m/z*	Percentage linears
		DMT	
2	631.3	794.1	3.4
3	936.1	1101.9	5.5
4	1240.7	1406.8	9.8
5	1545.1	1711.3	12
6	1849.9	2106.1	14
7	2154.5	2321.2	8.5
8	2459.2	2594.8	14
		DMI	
2	632.1	671.7	18
3	963.6	976.9	12
4	1241	1281.4	10
5	1546.2	1586.2	6
6	1850.9	1910.9	5
7	2155.4	2195.4	1
8	2460.4	—	No linears
9	2765.4	—	No linears
10	3070.5	—	No linears
		DMO	
2	631.6	671.5	1
3	963.2	—	No linears
4	1240.1	—	No linears
5	1545.2	—	No linears
6	1849.9	—	No linears
7	2154.5	—	No linears
8	2459.2	—	No linears

Table 6 Summary of results from DSC analysis where T_{cm} is crystalline melting point and T_g is glass transition temperature. The linears are the high mass linears before cyclization

Oligomer	Transition	Temperature (°C)
TEGT linears	T_g	− 30
TEGT cyclics	T_{cm}	48.5
TEGI linears	T_g	− 23
TEGI cyclics	T_{cm}	81
TEGO linears	T_g	− 26
TEGO cyclics	T_{cm}	52
DMT linear	T_{cm}	121
DMT cyclics	T_{cm}	92
DMI linears	T_{cm}	53
DMI cyclics	T_{cm}	98
DMO linears	T_g	− 33
DMO cyclics	T_{cm}	60

Further investigations of these cyclic materials are in progress.

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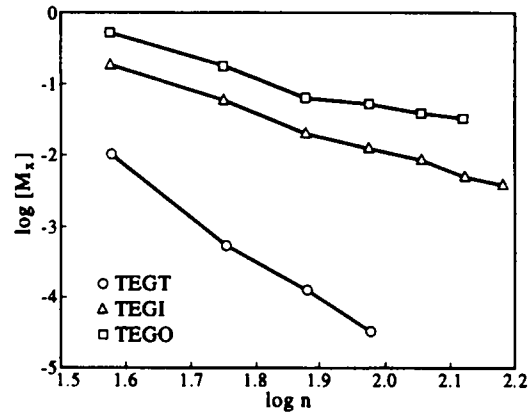

Figure 12 Plot of log [M_x] against log n for TEGT, TEGI and TEGO ring chain reaction products at 100:1 dilution in chlorobenzene

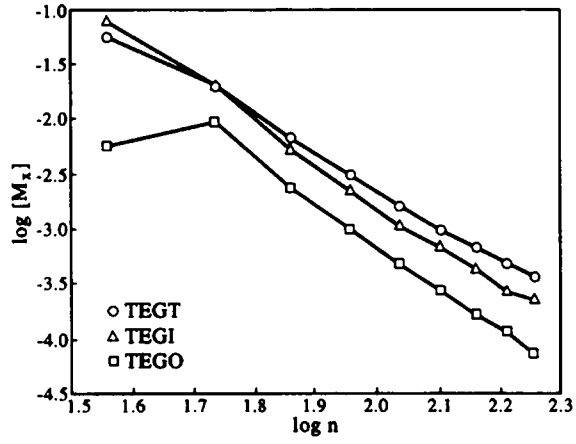

Figure 13 Plot of log [M_x] agaist log n for DMT, DMI and DMO ring chain reaction products at 100:1 dilution in chlorobenzene

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