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Preparation and characterization of aliphatic diphenyl esters intended as precursors for polyesters

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An extensive number of aliphatic diphenyl esters, $C_6H_5OOC(CH_2)_nCOOC_6H_5$ ($n = 0, \ldots, 8, 10, 11, 12, 14$), have been prepared in pure form. The crystalline melting points of these esters exhibit an odd–even temperature behaviour, with the higher-melting even series (n even) displaying a minimum for $n = 8$ while the odd series shows an almost monotonic slow increase. High-resolution ^{13}C nuclear magnetic resonance (n.m.r.) spectroscopy of the esters in $CDCl_3$ and C_6D_6 allows all non-symmetrical carbons to be resolved, even the seven different methylenes for $n = 14$. This unusual spectral sensitivity is primarily based on similar data from phenyl esters, interpreted as the results of an apparent macrocyclic conformation of the larger diphenyl esters. High-performance size exclusion chromatography (s.e.c.) of diphenyl esters, phenyl esters, aromatic and linear hydrocarbons in tetrahydrofuran, toluene and chloroform points to specific phenyl ester–solvent interactions, which obscure a potential s.e.c. conformational analysis of the diphenyl esters.

(Keywords: diphenyl esters; phenyl esters; preparation; crystalline melting points; ^{13}C nuclear magnetic resonance; size exclusion chromatography)

INTRODUCTION

The use of diesters in polycondensation reactions often offers an advantageous approach for a more convenient synthesis of polyesters owing to their more tractable physical properties with respect to those of other precursors. Our previous experiments, concerned with the preparation of comb-shaped polyesters starting from a glycol with a long side-chain and acid chlorides, dimethyl esters and diphenyl esters of aromatic dicarboxylic acids, unambiguously revealed that the best results were obtained using the latter method[1]. This can be seen as a result either of the superior leaving-group character of the phenoxide group compared with the alkoxide one, or of the low volatility of the diphenyl ester (comparable with that of the glycol), which avoids fortuitous loss of functionality with subsequent unwanted variation of the stoichiometric ratio of the reactants.

Following the previous work on aromatic comb-shaped polyesters[2] we considered it valuable to extend the work to the synthesis and characterization of diphenyl esters of homologous aliphatic, linear dicarboxylic acids, devoting particular attention to their purity, since this is a prerequisite for obtaining high polymers via polycondensation results. Monofunctional impurities limit chain growth and final product quality is affected by even small concentrations of impurities, either organic or inorganic.

In this paper we report the synthesis, characterization and solution behaviour of a series of diphenyl esters of linear, aliphatic carboxylic acids intended as precursors for an extended range of comb-shaped aliphatic polyesters. Subsequent reports will describe the synthesis and characterization of these polyesters.

EXPERIMENTAL

Preparation and purification of dichlorides

Commercially available dichlorides were distilled under vacuum to obtain colourless products, which were kept under N_2 at −20°C until use. Oxalyl chloride (Aldrich, >99% (gold label)) was used directly from the glass ampoule (*caution*: highly toxic!) without further treatment. Some dichlorides (pimeloyl, dodecanedioyl, tridecanedioyl, tetradecanedioyl and hexadecanedioyl) were synthesized from the corresponding dicarboxylic acids by boiling with a 100% molar excess of thionyl chloride until a liquid mixture was obtained. After 1/2 h reflux the excess thionyl chloride was distilled off and the resulting crude dichloride purified as above.

Preparation of diphenyl esters

The esters were, except for diphenyl malonate, prepared from the dichlorides under N_2 in the following general way as exemplified with diphenyl pimelate.

Pimeloyl chloride (32.9 g, 0.167 mol) was dissolved under N_2 in 60 ml of anhydrous benzene (Carlo Erba,

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p.a., distilled from K/Na, stored under N_2) and transferred to a 500 ml three-necked round flask equipped with a reflux condenser, a pressure equilibrating addition funnel, a magnetic stirring bar and previously flushed with N_2. Phenol (33.4 g, 0.355 mol; Carlo Erba, p.a.) was dissolved in 40 ml of anhydrous benzene and transferred to the funnel. Anhydrous pyridine (30 ml, 0.371 mol; Carlo Erba, p.a., distilled from KOH and stored under N_2) was additionally added to the funnel. The phenol and pyridine solution was added to the pimeloyl chloride solution in 1 h with rapid stirring, causing a mildly exothermic reaction. Stirring was continued for 3 h. The reaction mixture was then heated to 60°C and filtered through a sintered glass filter. After careful washing with hot benzene the combined filtrates were concentrated to ~50 ml by evaporation under N_2. Addition of 300 ml of n-heptane and heating to boiling dissolves almost all the diphenyl pimelate. After decanting the hot solution the remaining ester is dissolved by repeating the procedure twice with additional 100 ml of n-heptane and finally 50 ml of n-heptane. The ester precipitates upon cooling. The recovered ester is recrystallized from 400 ml of n-heptane. After filtration and drying under vacuum, 36.9 g (71%) diphenyl pimelate is recovered.

Diphenyl oxalate has a low solubility in boiling n-heptane (1–2 g/100 ml). In some cases when the hydrocarbon solvent did not result in the desired degree of diester purity, as revealed by the d.s.c. traces, other solvents, methanol or ethanol, were successfully employed.

Diphenyl malonate was prepared from malonic acid, phenol and phosphorus oxychloride in accordance with a procedure developed for the corresponding succinate[3]. Since diphenyl malonate failed to precipitate from the recovered benzene solution in any concentration, this part was modified. Toluene was used as solvent and the toluene solution, decanted from the phosphoric acid residue, was washed three times with 5% KOH solution (one-tenth of its volume). The toluene solution is then washed three times with water and dried with anhydrous Na_2SO_4 overnight. After filtration the toluene is removed on a Rotavapor and the diphenyl malonate recovered and recrystallized with n-hexane as above.

All diphenyl esters were finally purified by distillation under vacuum (200–250°C/0.5–1 mbar). The purified esters were characterized by d.s.c., ^{13}C n.m.r. and s.e.c.

Preparation of phenyl esters

A series of reference phenyl esters of saturated fatty acids (butyric, capric, caprylic, decanoic, lauric, myristic and stearic) was prepared as described for the diphenyl esters and purified by vacuum distillation. The phenyl esters were also characterized by ^{13}C n.m.r. and s.e.c.

INSTRUMENTATION

Differential scanning calorimetry (d.s.c.)

D.s.c. measurements were carried out on a Perkin–Elmer DSC-4 instrument equipped with an Intracooler-I apparatus. The traces of the different diphenyl esters in the form of fine crystalline powder were recorded at a heating rate of 5°C min^{-1}.

^{13}C nuclear magnetic resonance (n.m.r.) spectroscopy

Spectra were recorded at 62.896 MHz on a Bruker AC 250 spectrometer at 300 K on 20% (w/v) solutions in $CDCl_3$ or C_6D_6 in 5 mm i.d. tubes. A pulse width of 3.5 μs ($\approx$90°), a 0.92 s data acquisition and a 2 s pulse repetition were used to obtain $\approx$1000 scans. Chemical shifts are referenced to the central resonances of $CDCl_3$ or C_6D_6 (76.90 or 128.40 ppm, respectively, from $(CH_3)_4Si$).

Size exclusion chromatography (s.e.c.)

S.e.c. characterization of esters was performed with a Knauer HPLC-PUMP FR-30 fitted with a Rheodyne 7010 Sample Injection Valve and a series of PLgel 5μ columns (7.5 mm i.d.) from Polymer Laboratories in a thermostatically controlled oven: 30 cm 1000 Å, 30 cm 500 Å, and 60 cm 100 Å. Detection was accomplished with a Knauer High Temperature Differential-Refractometer. Concentrations of solutes were nominally 0.5% (w/v) in analytical-grade solvents. All experiments were run at 30°C.

RESULTS AND DISCUSSION

The preparation of the diphenyl esters used (see Experimental section) ensures pure products. Diphenyl malonate could not be prepared by the standard route, probably due to the acidity of the malonic methylene protons, so a procedure originally developed for the diphenyl succinate[3] was adopted; see Experimental.

An indication of the diphenyl ester purity was obtained from the d.s.c. traces, which all showed sharp single endotherms. The relevant melting temperatures taken at the peak maximum are listed in *Table 1*.

The dependence of the crystalline melting points, t_m, on the spacing of the ester groups is depicted in *Figure 1*.

The initial part of this homologous series with $n = 0, \ldots, 8$ clearly demonstrates the odd–even effect of the melting behaviour of diphenyl esters (see *Figure 1*). The part with n = 10, 11, 12 also shows this effect. In the even series a distinctive minimum for DPSE ($n = 8$) at 68.0°C is observed after the initial rather high value of 140.8°C for DPOX followed by a slow increase in melting point for the subsequent larger homologues. The odd members admittedly fewer in numbers, on the other hand, show an almost monotonic slow increase in melting point. It seems reasonable to expect that, with increasing number of methylene groups, the melting points of the diphenyl esters will approach that of linear polyethylene.

Table 1 Crystalline melting points of diphenyl esters

Diphenyl ester	Abbreviated form	n^a	t_m (°C)
Oxalate	DPOX	0	140.4
Malonate	DPMA	1	49.1
Succinate	DPSC	2	125.0
Glutarate	DPGL	3	54.0
Adipate	DPAD	4	108.8
Pimelate	DPPI	5	53.0
Suberate	DPSU	6	73.0
Azelate	DPAZ	7	60.8
Sebacate	DPSE	8	68.0
Dodecanedioate	DPDD	10	76.6
Tridecanedioate	DPTD	11	72.4
Tetradecanedioate	DPTTD	12	84.2
Hexadecanedioate	DPHXD	14	86.4

[a] Number of methylene groups

All diphenyl esters were characterized by ^{13}C n.m.r. With the exception of DPOX the spectra in general contain one carbonyl, four aromatic and a varying number of aliphatic carbon resonances, as exemplified with the spectra of DPHXD in *Figure 2*.

The ^{13}C chemical shifts of all the diphenyl esters are collected in *Table 2*.

Owing to the symmetry in this homologous series of esters, several pairs of esters have the same number of resonances. However, both the chemical shifts and the relative intensities of the methylene resonances in these pairs differ conclusively.

Because of the close proximity of the second carbonyl group, the carbonyl resonances of the smallest diphenyl esters, especially DPOX but also DPMA, are strongly shielded compared to the resonances in the larger esters with $n \geq 10$. However, carbonyl resonance shielding is observed in all the intermediate esters, DPGL through DPSE, as well, although the shielding decreases with increasing length of the methylene chain. Whereas the shielding in the first five or six esters, DPOX through DPPI, is anticipated to be influenced by substitutional effects, such effects generally vanish with increasing distance and normally cease to exert any influence when

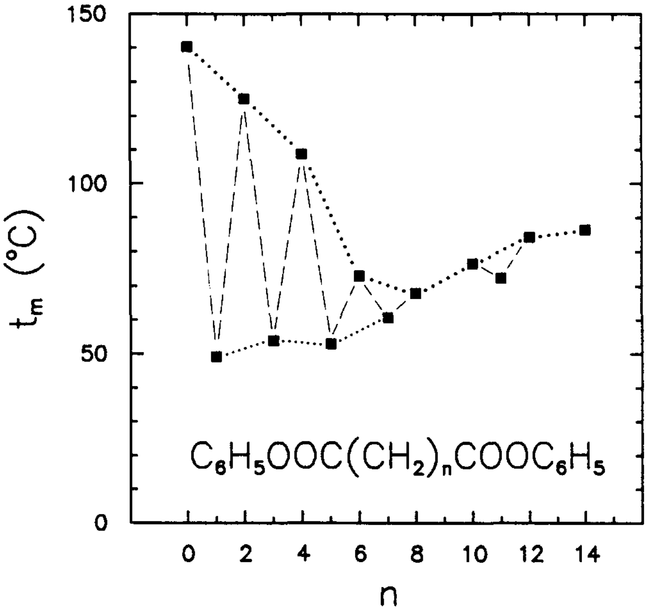

Figure 1 Dependence of crystalline melting points on spacing of ester groups in diphenyl esters of aliphatic dicarboxylic acids

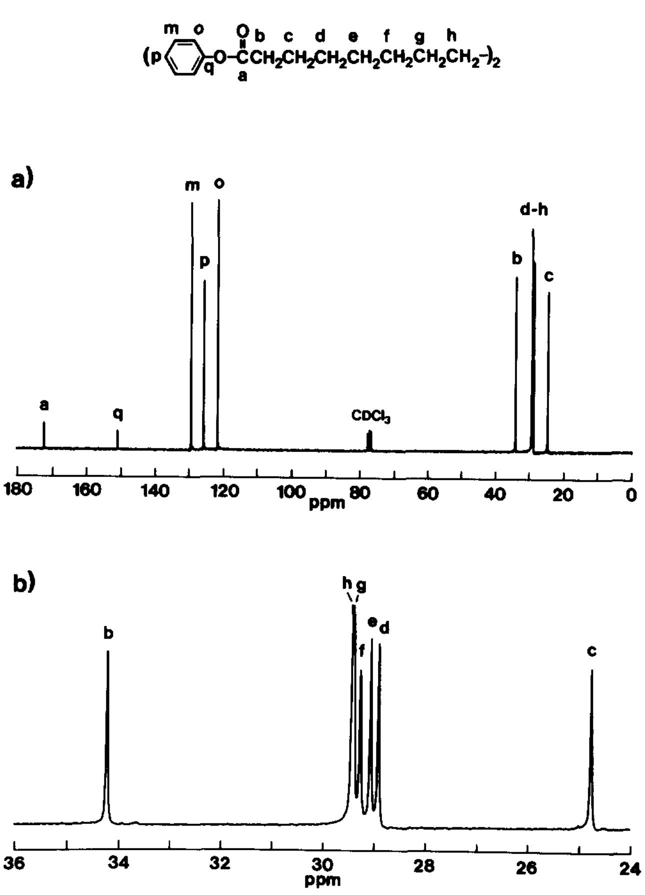

Figure 2 62.90 MHz ^{13}C n.m.r. spectrum of diphenyl hexadecanedioate in $CDCl_3$: (a) full spectrum; (b) expansion of methylene carbon region

Table 2 62.90 MHz ^{13}C n.m.r. chemical shifts of diphenyl esters (ppm in $CDCl_3$)

										Phenyl			
Sample	n^a	$-O-\overset{O}{\overset{\parallel}{C}}-$	$-CH_2-$	$-CH_2-$	$-CH_2-$	$-CH_2-$	$-CH_2-$	$-CH_2-$	$-CH_2-$	$-O-CH=$	*ortho*	*meta*	*para*
DPOX	0	155.54								149.83	120.76	129.61	126.77
DPMA	1	164.60	41.50							150.27	121.19	129.42	126.18
DPSC	2	170.59	29.19							150.50	121.35	129.31	125.79
DPGL	3	171.13	33.03	19.84^b						150.45	121.33	129.23	125.65
DPAD	4	171.40	33.70	24.05						150.49	121.30	129.16	125.53
DPPI	5	171.72	33.89	24.30	28.25^b					150.54	121.33	129.17	125.51
DPSU	6	171.84	34.05	24.50	28.49					150.58	121.35	129.16	125.47
DPAZ	7	171.96	34.15	24.66	28.70^c					150.62	121.38	129.20	125.47
DPSE	8	172.02	34.20	24.73	28.85	28.89				150.63	121.40	129.21	125.51
DPDD	10	172.06	34.23	24.77	28.92	29.05	29.20			150.65	121.40	129.20	125.51
DPTD	11	172.07	34.22	24.76	28.90	29.05	29.23	29.31^b		150.63	121.39	129.18	125.49
DPTTD	12	172.07	34.22	24.77	28.92	29.07	29.26	29.36		150.64	121.40	129.18	125.49
DPHXD	14	172.07	34.22	24.78	28.92	29.07	29.28	29.41	29.43	150.63	121.40	129.18	125.48

[a] Number of methylene groups
[b] Peak intensity $\sim\frac{1}{2}$ of that of the other methylenes in sample
[c] Peak intensity $\sim 1\frac{1}{2}$ of that of the other methylenes in sample

Table 3 62.90 MHz ^{13}C n.m.r. chemical shifts of diphenyl esters (ppm in C_6D_6)

										Phenyl			
Sample	n[a]	$-\mathrm{O}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-$	$-CH_2-$	$-CH_2-$	$-CH_2-$	$-CH_2-$	$-CH_2-$	$-CH_2-$	$-CH_2-$	$-O-CH=$	*ortho*	*meta*	*para*
DPAZ	7	171.78	34.72	25.41	29.42	29.45[b]				151.97	122.23	129.92	126.05
DPSE	8	171.79	34.79	25.50	29.61	29.70				151.99	122.35	129.93	126.05
DPHXD	14	171.79	34.83	25.59	29.77	30.03	30.25	30.41	30.46	152.00	122.35	129.89	126.02

[a] Number of methylene groups
[b] Peak intensity ~$\frac{1}{2}$ of that of the other methylenes in sample

Table 4 62.90 MHz ^{13}C n.m.r. chemical shifts of phenyl esters (ppm in $CDCl_3$)

	Ester						
	Butyrate	Caproate	Caprylate	Decanoate	Laurate	Myristate	Stearate
n[a]	3	5	7	9	11	13	17
$-\mathrm{O}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-$	171.92	172.02	172.05	172.05	172.04	172.04	172.04
$-CH_2-$	36.09	34.16	34.24	34.24	34.25	34.26	34.27
$-CH_2-$	18.31	24.44	24.79	24.80	24.81	24.82	24.83
$-CH_2-$	13.46[b]	31.08	28.76	28.95	28.97	28.98	28.99
$-CH_2-$		22.12	28.90	29.10	29.12	29.13	29.14
$-CH_2-$		13.70[b]	31.50	29.27	29.32	29.33	29.35
$-CH_2-$			22.43	29.10	29.46 (2)[c]	29.52 (3)[c]	29.57 (7)[c]
$-CH_2-$			13.88[b]	31.71	29.20	29.47	29.48
$-CH_2-$				22.50	31.77	29.22	29.24
$-CH_2-$				13.91[b]	22.54	31.79	31.81
$-CH_2-$					13.94[b]	22.55	22.56
$-CH_3$						13.95	13.96
Phenyl							
$-O-CH=$	150.65	150.65	150.67	150.67	150.69	150.70	150.70
ortho	121.42	121.38	121.40	121.40	121.42	121.42	121.43
meta	129.21	129.16	129.18	129.18	129.18	129.19	129.19
para	125.52	125.46	125.48	125.48	125.48	125.48	125.49

[a] Number of methylene groups plus terminal methyl
[b] Terminal methyl
[c] Number of methylene groups in this peak

a methylene chain contains >5 units[4]. The same arguments hold for the aromatic carbon resonances, where the final values are initially observed in DPAZ with an eleven-atom spacing between the phenoxy carbons. Also evident from *Table 2* is the multiplicity of the methylene group resonances in the longest diphenyl esters with $n = 10$, 11, 12 and 14. All these observations cannot be explained merely by assuming a random coil of the diphenyl esters in $CDCl_3$ solution.

Accordingly, the solution behaviour of some of the esters in an aromatic solvent, C_6D_6, was additionally examined. *Table 3* lists the ^{13}C chemical shifts of DPAZ, DPSE and DPHXD in C_6D_6. Here we are able to observe the expected four non-equivalent methylene groups in DPAZ, which could not be observed in $CDCl_3$ (compare *Table 2*). Surprisingly, all the carbonyls have nearly the same chemical shift, whereas we still observe the methylene group multiplicity in DPHXD.

In an attempt to understand these observations, reference was made to results obtained under exactly the same experimental conditions (in $CDCl_3$) of a series of phenyl esters of linear, saturated fatty acids. The phenyl ester end of long fatty acids is equal in chemical structure to each end of the long diphenyl diesters and accordingly expected to exhibit the same ^{13}C shielding behaviour as these long diphenyl ester ends. *Table 4* lists the ^{13}C chemical shifts of this series of phenyl esters.

The assignments are based on the aliphatic additivity constants[4], starting from butyrate, and substantiated by similar observations in a homologous series of methyl esters of linear, saturated fatty acids[5]. A detailed inspection of *Table 4* reveals that in the phenyl ester series already the carbonyl in caprylate reaches the chemical shift value observed in the rest of the series; however, also the carbonyl in caproate is close to this value. The data of the aromatic resonances are even more striking inasmuch as the phenyl resonances are virtually insensitive to the size of the fatty acid chains ranging from 5 to 17 carbons. Also the development of the resonances of the methylene groups in α- and β-positions to the carbonyl, which already in caprylate ($n = 7$) reach the values observed in all the larger phenyl esters, is the expected one for an increasing, homologous hydrocarbon-based series of compounds where ^{13}C chemical shift development is governed by additivity effects only[4]. We also conclude that five methylene groups counting from each end are the ultimate resolution for the fatty acid chain of phenyl esters.

When we now compare the resonances of the two chemically exactly equal phenyl ester ends in large diesters ($n \geq 10$) with those in large monoesters ($n \geq 11$), we observe a small, but consistent, deshielding of carbonyl and phenoxy carbon resonances of diesters compared with monoesters. However, for the α- and β-methylene carbons we observe the reverse effect, a small, but consistent, shielding. This shielding of α- and β-methylene groups in diesters is interpreted as the result of a rotational isomeric equilibrium state leading to some sort of apparent macrocyclic order. Further support for this conclusion is the observation that the methylene groups spaced from the carbonyls by six methylene units in DPHXD resonate at 29.43 ppm (*Table 2*), a shielding of 0.14 ppm compared with the central methylene groups of the linear stearate chain (29.57 ppm, *Table 4*). In a comparative experiment we observe only five methylene resonances in hexadecane with the six unresolved central methylene resonances resonating at 29.68 ppm. Carbon resonances of large alicyclic hydrocarbons have previously been reported[6] to be shielded compared with their linear analogues. For example, in cycloheptadecane the methylene carbons were found to resonate at 27.9 ppm (recorded in CS_2) as compared to ≈ 30 ppm for the central methylene carbons of the long-chain alkanes.

The most convincing support for the macrocyclic conformation of the diphenyl esters in $CDCl_3$, however, comes from ^{13}C n.m.r. investigations of polyesters prepared from 2-octadecyl-1,3-propanediol and DPTTD or DPHXD[7]. In these ^{13}C spectra only five methylene groups originating from the carboxylic precursors are resolved; the central four or six groups in each carboxylic unit, respectively, fall in one peak. This is in line with the normal ^{13}C spectral sensitivity to substitution at distances of up to four bonds in polymer main chains observed in polymers in general[8] as well as in polyesters in particular[9]. In the high-molar-mass comb-shaped polyesters, no cyclic conformation of the individual carboxylic units is possible.

The apparent macrocyclic conformation of the diphenyl esters in $CDCl_3$ solution is envisaged with almost parallel phenyl rings. We argue that the presence of the second parallel phenyl ring can well explain the observed resonance deshielding of carbonyl and phenoxy carbons as compared with the monoesters. Similar conformations have recently been identified as conducive to intramolecular excimer formation in the structurally very similar dibenzoates with two to six methylene units between the ester groups[10].

Another potential way of investigating solution behaviour of the diphenyl esters is high-performance size exclusion chromatography (s.e.c.) on a column combination with high efficiency for characterization of small molecules.

Figure 3 depicts the s.e.c. separation of four different mixtures of diphenyl esters in tetrahydrofuran (THF). The resolving power of this column combination is clearly illustrated by the nearly baseline separation of all the constituents of the two even series in which the members only differ by four methylene units. These results are combined in *Figure 4* in the conventional calibration curve relating log(relative molecular mass), log(M_r), to peak elution volume, V_r.

Except for the two smallest members, DPOX ($n = 0$) and DPMA ($n = 1$), the diphenyl esters fall on a perfectly linear calibration curve.

The observed deviations of DPOX and DPMA from the linear calibration curve make these molecules appear larger in THF solution than indicated by their molecular masses. In the case of DPOX a 'rod-like' structure is anticipated with the two vicinal carbonyls in an antiparallel conformation minimizing dipole–dipole interaction and making room for the phenyl rings as well.

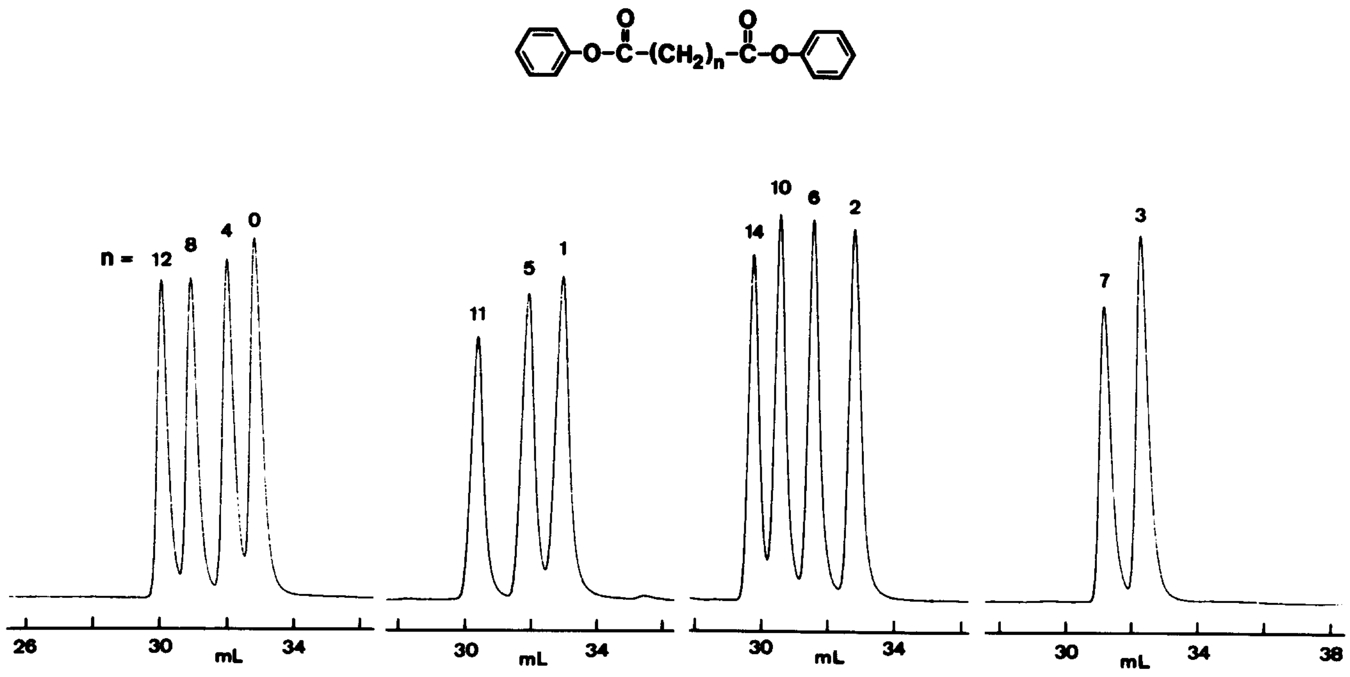

Figure 3 S.e.c. separation of four diphenyl ester mixtures on 30 cm 1000 Å, 30 cm 500 Å and 60 cm 100 Å PLgel 5μ columns. Solute concentrations, ≈ 5 mg ml^{-1}; mobile phase, tetrahydrofuran; flow rate, 1 ml min^{-1}; detection, refractive index

Table 5 List of compounds in s.e.c. calibration curves in *Figures 4*, *5* and *6*

Sample family	Composition	Members present (n)
Diphenyl esters	$C_6H_5OOC(CH_2)_nCOOC_6H_5$	0,1,2,3,4,5,6,7,8,10,11,12,14
Phenyl esters	$C_6H_5OOC(CH_2)_nCH_3$	2,4,6,8,10,12,16
Aromatic hydrocarbons	$C_6H_5(CH_2)_nCH_3$	1,2,3,5,7,11
n-Alkanes	$CH_3(CH_2)_nCH_3$	6,8,10,12,14,18,22

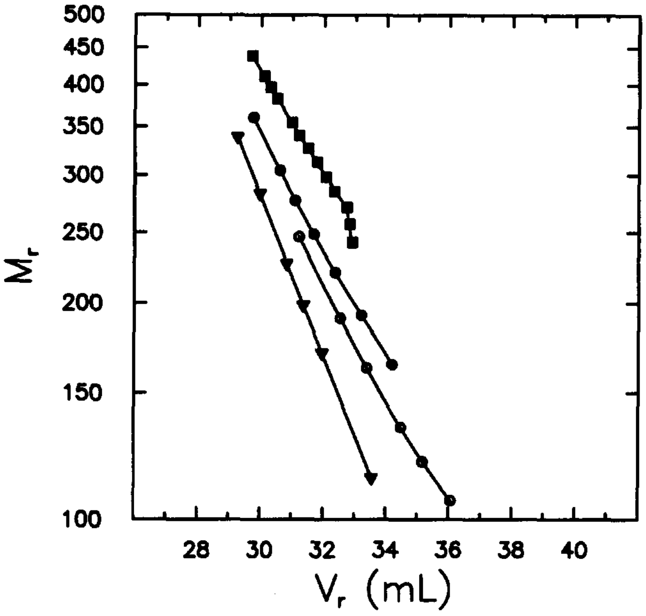

Figure 4 S.e.c. calibration curves for diphenyl esters (■), phenyl esters (●), aromatic hydrocarbons (○) and n-alkanes (▼). The individual compounds are listed in *Table 5*. Mobile phase, THF; flow rate, 1 ml min^{-1}

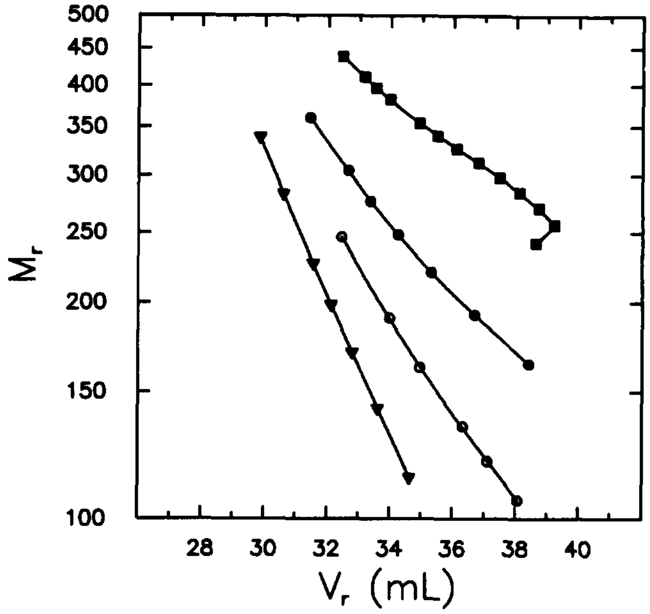

Figure 5 S.e.c. calibration curves for diphenyl esters (■), phenyl esters (●), aromatic hydrocarbons (○) and n-alkanes (▼). The individual compounds are listed in *Table 5*. Mobile phase, toluene; flow rate, 1 ml min^{-1}

Also DPMA could be envisaged in some sort of 'rod-like' conformation due to restricted internal rotations around single bonds.

In order to investigate further the resolving power of the column system in the effective molecular size range in question, three other families of compounds (composition and members utilized are listed in *Table 5*) structurally related to the diphenyl esters were analysed. The calibration curves for phenyl esters, aromatic hydrocarbons and n-alkanes are only slightly curved or perfectly linear in the investigated ranges, as also shown in *Figure 4*. Although these last three calibration curves substantiate the vital importance of size and shape as compared with absolute molecular mass, we are not able to deduce any preferential conformations in THF solutions of the diphenyl esters forming the linear part of the calibration curve in *Figure 4*.

A similar s.e.c. investigation was performed using toluene as mobile phase. The resulting calibration curves depicted in *Figure 5* are all differently shifted towards larger elution volumes as compared with the behaviour in THF (*Figure 4*).

Under ideal s.e.c. conditions only the change of conformational entropy of the solute contributes to the distribution coefficient[11]. Non-size exclusion effects can be caused by enthalpic interactions between solute and packing and solute–mobile phase interactions ('differential solvation')[12]. Enthalpic interactions are minimized if the mobile phase is a good solvent for the solute and at the same time solvates the column packing (gel). In practice the mobile phase and the gel should have approximately the same solubility parameter[11], δ. The values of δ for THF, toluene and chloroform in (cal cm^{-3})$^{1/2}$ are 9.1, 8.9 and 9.3 respectively, compared with 9.1 for poly(styrene-*co*-divinylbenzene)[13], the gel.

The calibration curves for the diphenyl esters and the n-alkanes in THF, toluene and chloroform (obtained at similar conditions) are compared in *Figure 6*.

A closer inspection reveals that the n-alkane calibration curves are perfectly linear, with nearly the same slopes. The displacements of these curves on the elution volume axis are interpreted as the different swelling of the gel exerted by the solvents. Moreover the displacements correlate with the δ values of the solvents: the lowest value results in the largest displacement (toluene).

It is obvious from *Figure 6* that the swelling of the gel only accounts for a part of the relative displacements of the diphenyl ester calibration curves, and in the case of toluene only a rather small part.

The degree of shifting is apparently somewhat dependent on the relative content of phenyl ester in a compound, inasmuch as the largest differences are observed in the smallest diphenyl esters and phenyl esters. Although DPOX deviates from the behaviour of the rest of the diphenyl esters, it is clearly seen that the solvent plays a very important role, even when normally accepted s.e.c. solvents (THF, toluene and chloroform) are selected. These observations point to specific mobile phase–phenyl ester interactions; however, a more de-

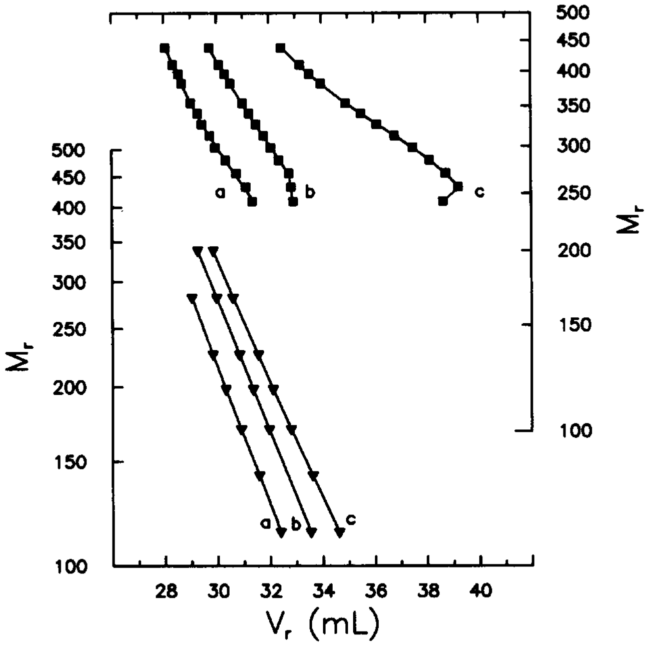

Figure 6 S.e.c. calibration curves for diphenyl esters (■) and n-alkanes (▼). Mobile phases, (a) chloroform, (b) THF and (c) toluene; flow rate, 1 ml min^{-1}

tailed analysis of these phenomena was outside the scope of this work.

In conclusion, the chromatographic experiments described in this report are not able to shed light on the larger diphenyl ester conformations in the examined solvents; on the other hand, they show that high-performance s.e.c. can be employed for the analysis of diphenyl esters. This result can make a fruitful analytical contribution to the characterization of reaction mixtures involving diphenyl esters, in particular when these latter are used in polycondensation reactions.

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