

Synthesis of Difuran Diesters from Furfural, and Their Evaluation as Plasticizers for Polyvinyl Chloride

R. D. SANDERSON, D. F. SCHNEIDER,* and I. SCHREUDER

Department of Chemistry and Institute for Polymer Science, University of Stellenbosch, Stellenbosch 7600, South Africa

SYNOPSIS

The compounds 1,1-bis[5-(2-ethylhexyl, 2-octyl, hexyl, and butyl)carboxylate-2-furyl]ethane, and 5,5'-dihexylcarboxylate-2,2' bifuran were synthesized from furfural and characterized for their plasticizing abilities toward polyvinyl chloride (PVC) by dynamic mechanical thermal analyses (DMTA) with di-(2-ethylhexyl) phthalate (DOP) as the standard of reference. DMTA gave values for the depression of the glass-transition temperature (T_g) per mass fraction of plasticizer, and it also yielded a set of parameters, relative to those of DOP, which describe the compatibility of the furan diesters with PVC. These values are compared to those of DOP and furan diesters incorporating only one furan ring in the molecular structure, which have previously been tested by this method. The difuran plasticizers are less efficient in lowering T_g than the monofuran plasticizers or DOP, with 1,1-bis[5-(2-octyl)carboxylate-2-furyl]ethane the least efficient and 1,1-bis(5-hexylcarboxylate-2-furyl)ethane the most efficient. On average the compatibility toward PVC is better than that of DOP, and similar to that of analogous monofuran structures. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

We have recently reported¹ our initial results on the synthesis of a range of long-chain furan diesters and the evaluation of these diesters as plasticizers for polyvinyl chloride (PVC). These studies are aimed at finding new applications for furfural, a compound available in potentially very large quantities from plant residues. Our initial results revealed that when a furan ring is substituted for the benzene ring of conventional plasticizers, an improvement in compatibility toward PVC is realized, although little difference in plasticizing efficiency was found. We now communicate additional results in connection with our synthesizing endeavors toward new furan-based plasticizers incorporating two furan moieties, and an evaluation of the abilities of these diesters as plasticizers for PVC.

EXPERIMENTAL

Instrumentation and Materials

Melting points were determined on a Gallenkamp melting point apparatus; melting and boiling points are uncorrected. Nuclear magnetic resonance (NMR) spectra were measured in deuteriochloroform relative to tetramethyl silane as internal standard. ¹H- and ¹³C-NMR spectra were recorded on a Varian VXR 51 Fourier transform (FT)-spectrometer at 300 MHz and a Varian FT 80 spectrometer at 80 MHz, respectively. All mass spectra and accurate mass measurements were recorded on a Varian MAT 311 A mass spectrometer. Refractive indices and densities of the difuran diesters were measured on an Abe refractometer and with a dilatometer, respectively. Silica gel (0.063–0.200 mm, Merck), was used for column chromatography and analytical thin layer chromatographic separations were performed on silica gel plates (0.2 mm, Merck 60 F254). All solvents were purified and fractionally distilled prior to use, and petroleum ether refers to the fraction boiling at 40–60°C. The paste PVC

* To whom correspondence should be addressed.

resin, Lucovyl PB 1702, was plasticized on an Apex hydraulic press, and dynamic mechanical thermal analysis (DMTA) scans were run on a PL Dynamic Mechanical and Thermal Analyzer in shear mode at a heating rate of 5°C/min.

1,1-Bis[5-(2-ethylhexyl)carboxylate-2-furyl]ethane 2a

A mixture of 1,1-bis(5-carbomethoxy-2-furyl)ethane² (5.00 g, 18.0 mmol), 2-ethylhexanol (9.36 g, 71.9 mmol), potassium carbonate (0.99 g, 7.2 mmol), and benzylhexadecyldimethylammonium chloride (0.30 g, 0.72 mmol)³ was stirred for 10 h at 80°C (oil-bath temp.) under vacuum (60 mmHg) in a reaction flask fitted with a Vigreux column. Progression of the esterification was monitored by thin-layer chromatography (TLC) on silica gel with ether-petroleum ether (1 : 1) as mobile phase and by spraying the chromatoplate with acidic potassium dichromate. The reaction mixture was poured into water (40 mL), extracted with ether (3 × 20 mL), the combined ether extracts dried (MgSO₄), and the ether and excess 2-ethylhexanol removed by distillation under vacuum. Chromatography of the brown residue on silica gel yielded upon elution with ether-petroleum ether (1 : 9) **1,1-bis[5-(2-ethylhexyl)carboxylate-2-furyl]ethane 2a**: (7.70 g, 90.3%), b.p. 200–210°C (air-bath temp.) at 7 × 10⁻⁶ mmHg, *d* 1.027, *n*_D²³ 1.4968, *δ*_H 0.895 (6 H, t, J 4.5 Hz, 2× CH₃); 0.923 (6 H, t, J 7.5 Hz, 2× CH₃), 1.26–1.46 (16 H, m, 8× CH₂); 1.680 (2 H, h, J 6.1 Hz, 2× CH); 1.681 (3 H, d, J 7.3 Hz, CH₃); 4.169 (2 H, dd, J 10.9, 5.9 Hz, 2× OCH); 4.208 (2 H, dd, J 11.0, 5.8 Hz, 2× OCH); 4.364 (1 H, br q, J 7.2 Hz, CH); 6.213 (2 H, dd, J 3.5, 0.7 Hz, 2× = CH); and 7.066 (2 H, d, J 3.4 Hz, = CH); *δ*_C 144.01 (C-2), 108.10 (C-3), 118.57 (C-4), 158.85 and 159.65 (C-5 and C-6), 67.25 (C-7), 38.99 (C-8), 30.57 (C-9), 29.00 (C-10), 23.00 (C-11), 14.03 (C-12), 24.03 (C-13), 11.09 (C-14), 33.82 (C-15), 17.93 (C-16), (Found: M⁺, 474.2966. C₂₈H₄₂O₆ requires M, 474.2981).

1,1-Bis[5-(2-octyl)carboxylate-2-furyl]ethane 2b

A mixture of 1,1-bis(5-carbomethoxy-2-furyl)ethane² (5.00 g, 18.0 mmol), 2-octanol (9.36 g, 71.9 mmol), potassium carbonate (0.99 g, 7.2 mmol), and tetrabutylammonium hydrogen sulfate (0.24 g, 0.72 g)³ was stirred for 24 h at 110°C (oil-bath temp.) under vacuum (60 mmHg) in a reaction flask fitted with a Vigreux column. The reaction mixture was worked up as for **2a**, chromatographed on silica gel, and eluted with ether-petroleum ether (1 : 9) to give

1,1-bis[5-(2-octyl)carboxylate-2-furyl]ethane 2b (6.87 g, 80.5%), b.p. 200–210°C (air-bath temp.) at 8 × 10⁻⁶ mmHg, *d* 1.020, *n*_D²³ 1.4930, *δ*_H 0.873 (6 H, t, J 6.7 Hz, 2× CH₃), 1.304 (6 H, d, J 6.2 Hz, 2× CH₃), 1.22–1.37 (16 H, m, 8× CH₂), 1.678 (3 H, d, J 7.3 Hz, CH₃), 1.64–1.88 (4 H, m, 2× CH₂), 4.363 (1 H, br q, J 7.2 Hz, CH), 5.097 (2 H, sx, J 6.4 Hz, 2× OCH), 6.202 (2 H, dd, J 3.4, 0.9 Hz, 2× = CH), and 7.057 (2 H, d, J 3.4 Hz, 2× = CH); *δ*_C 144.33 (C-2), 118.39 (C-3), 108.04 (C-4), 158.43 and 159.59 (C-5 and C-6), 71.75 (C-7), 36.06 (C-8), 25.41 (C-9), 29.16 (C-10), 31.79 (C-11), 20.08 (C-12), 14.04 (C-13), 22.63 (C-14), 33.84 (C-15), 17.99 (C-16), (Found: C, 71.0; H, 8.5%; M⁺, 474.2980. C₂₈H₄₂O₆ requires C, 70.85; H, 8.9%; M, 474.2981).

1,1-Bis(5-butylcarboxylate-2-furyl)ethane 2d

A mixture of 1,1-bis(5-carbomethoxy-2-furyl)ethane² (3.5 g, 12.6 mmol), butanol (5.59 g, 75.5 mmol), potassium carbonate (0.69 g, 5 mmol), and tetrabutylammonium hydrogen sulfate (0.17 g, 0.5 mmol)³ was stirred for 5 h at 80°C (oil-bath temp.) under vacuum (140 mmHg) in a reaction flask fitted with a Vigreux column. The reaction mixture was worked up as for **2a**, chromatographed on silica gel, and eluted with ether-petroleum ether (1 : 9) to give **1,1-bis(5-butylcarboxylate-2-furyl)ethane 2d** (4.00 g, 87.7%), b.p. 200°C (air-bath temp.) at 8 × 10⁻⁶ mmHg, *d* 1.102, *n*_D²³ 1.5080, *δ*_H 0.961 (6 H, t, J 7.3 Hz, 2× CH₃), 1.435 (4 H, sx, J 7.4 Hz, 2× CH₂), 1.680 (3 H, d, J 7.3 Hz, CH₃), 1.715 (4 H, qn, J 7.0 Hz, 2× CH₂), 4.281 (4 H, t, J 6.7 Hz, 2× OCH₂), 4.363 (1 H, br q, J 7.3 Hz, CH), 6.207 (2 H, dd, J 3.5, 0.7 Hz, 2× = CH), and 7.083 (2 H, d, J 3.4 Hz, 2× = CH); *δ*_C 143.98 (C-2), 108.15 (C-3), 118.71 (C-4), 158.78 and 159.67 (C-5 and C-6), 64.64 (C-7), 30.82 (C-8), 19.21 (C-9), 13.73 (C-10), 33.81 (C-11), and 17.94 (C-12), (Found: C, 66.85; H, 7.05%; M⁺, 362.1732. C₂₀H₂₆O₆ requires C, 66.3; H, 7.2%; M, 362.1729).

Hexyl Furoate 3

A mixture of furfural (1.00 g, 10.4 mmol), sodium cyanide (2.71 g, 55.2 mmol), acetic acid (0.99 g, 16.5 mmol), manganese dioxide (18.98 g, 218.3 mmol), and hexanol (30 mL) was stirred at room temperature⁴ while progression of the reaction was monitored by TLC on silica gel with ether-petroleum ether (1 : 1) as mobile phase. After 14 h celite (5 g) was added, the suspension filtered, and the filter pad washed with ether (100 mL). The filtrate was subsequently washed with water (50 mL), the

water layer extracted with ether (2×40 mL), the combined organic phases dried (MgSO_4), and the solvent and excess of hexanol removed by distillation under vacuum. Chromatography of the residue on silica gel with ether–petroleum ether (1 : 4) as eluent yielded a colorless liquid (1.56 g) that was distilled to yield **hexyl furoate 3** (1.50 g, 73.5%), b.p. 135°C (air-bath temp.) at 7 mmHg (lit.⁵ $105\text{--}107^\circ\text{C}$ at 1 mmHg).

1,1-Bis(5-hexylcarboxylate-2-furyl)ethane 2c

To hexyl furoate (3.38 g, 17.2 mmol) in conc. sulfuric acid (30 mL) at 0°C , acetaldehyde (0.66 g, 15.1 mmol) was added dropwise with stirring during 50 min. After removal of the ice-bath, stirring was maintained for a further 8 h while progression of the reaction was monitored by TLC on silica gel with ether–petroleum ether (1 : 1) as mobile phase. The mixture was poured on ice, extracted with ether (4×100 mL), the combined ether extracts washed with 10% aqueous sodium hydrogen carbonate (50 mL), dried (MgSO_4), filtered, and the solvent evaporated to yield a dark brown oil (3.45 g). Chromatography on silica gel with ether–petroleum ether (1 : 19) as eluent gave **1,1-bis(5-hexylcarboxylate-2-furyl)ethane 2c** (2.44 g, 67.5%), b.p. 220°C (air-bath temp.) at 8×10^{-6} mmHg, d 1.054, n_D^{23} 1.5006, δ_H 0.894 (6 H, t, J 7.0 Hz, $2 \times \text{CH}_3$), 1.29–1.44 (12 H, m, $6 \times \text{CH}_2$), 1.679 (3 H, d, J 7.3 Hz, CH_3), 1.723 (4 H, qn, J 7.1 Hz, $2 \times \text{CH}_2$), 4.269 (4 H, t, J 6.8 Hz, $2 \times \text{OCH}_2$), 4.363 (1 H, br q, J 7.2 Hz, CH), 6.207 (2 H, dd, J 3.5, 0.8 Hz, $2 \times = \text{CH}$), and 7.082 (2 H, d, J 3.4 Hz, $2 \times = \text{CH}$); δ_C 144.01 (C-2), 108.16 (C-3), 118.69 (C-4), 158.78 and 159.69 (C-5 and C-6), 64.97 (C-7), 28.73 (C-8), 25.63 (C-9), 31.47 (C-10), 22.56 (C-11), 14.01 (C-12), 33.84 (C-13), and 17.97 (C-14), (Found: M^+ , 418.2330. $\text{C}_{24}\text{H}_{34}\text{O}_6$ requires M , 418.2355).

5,5'-Dihexylcarboxylate-2,2'-bifuran 5

A mixture of 5,5'-diformyl-2,2'-bifuran^{6,7} (0.8 g, 4.4 mmol), sodium cyanide (2.224 g, 45 mmol), acetic acid (0.79 g, 13.2 mmol), manganese dioxide (15.608 g, 179 mmol), and hexanol (100 mL) were stirred at room temperature⁴ while progression of the reaction was monitored by TLC on silica gel with ether–petroleum ether (1 : 1) as mobile phase. After 26 h celite (10 g) was added, the suspension filtered, and the filter cake washed with ether (100 mL). The filtrate was subsequently washed with water (100 mL), the aqueous layer extracted with ether (100 mL), the combined organic phases dried (MgSO_4), and

the solvent and excess of hexanol removed by distillation under vacuum. Chromatography of the residue on silica gel with ether–petroleum ether (1 : 9) as eluent yielded a white solid (0.576 g), which was recrystallized from hexane to give **5,5'-dihexylcarboxylate-2,2'-bifuran 5** (0.472 g, 28.7%), m.p. 63.2°C , δ_H 0.907 (6 H, t, J 7.0 Hz, $2 \times \text{CH}_3$), 1.30–1.44 (12 H, m, $6 \times \text{CH}_2$), 1.756 (4 H, qn, J 7.0 Hz, $2 \times \text{CH}_2$), 4.317 (4 H, t, J 6.7 Hz, $2 \times \text{CH}_2$), 6.890 (2 H, d, J 3.7 Hz, $2 \times = \text{CH}$), and 7.228 (2 H, d, J 3.6 Hz, $2 \times = \text{CH}$); δ_C 144.78 (C-2), 109.29 (C-3), 119.35 (C-4), 148.29 (C-5), 158.49 (C-6), 65.32 (C-7), 28.73 (C-8), 25.65 (C-9), 31.49 (C-10), 22.43 (C-11), 14.02 (C-12), (Found: C, 67.75; H, 7.2%; M^+ , 390.2066. $\text{C}_{22}\text{H}_{30}\text{O}_6$ requires C, 67.65; H, 7.75%; M , 390.2042).

Sample Preparation for DMTA

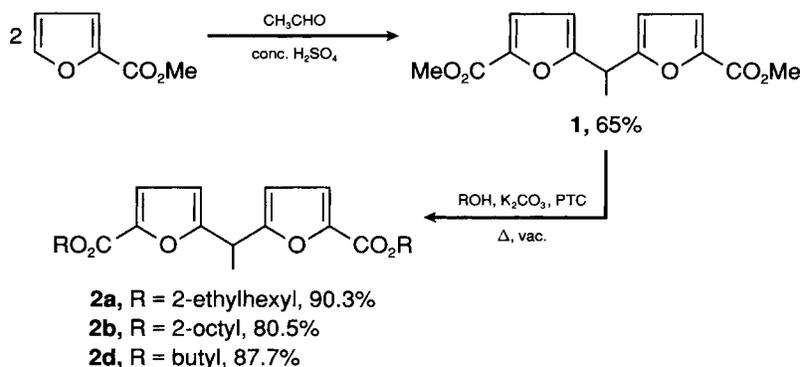
Four ca. 0.5-g plasticized PVC samples, containing diester in 25, 40, 55, and 70 phr, were prepared from each of the difuran diesters. Where the plasticizer was a fluid, resin and plasticizer were stirred thoroughly with a spatula to a smooth paste, which was then transferred to a mold, 1.2-mm thick with four 1×2 cm rectangular cavities. Plasticization was effected in a hot press at 145°C and 5 MPa in 10 min.

In the case of the solid plasticizer, 2 mL of chloroform was added to the resin–plasticizer mixture, the resulting viscous solution thoroughly stirred, and the solvent evaporated over 48 h. The residue was finely ground with a mortar and pestle and plasticization effected in the hot press as above. The PVC with no added plasticizer required 20 min at 160°C and 5 MPa in the press to anneal.

RESULTS AND DISCUSSION

Synthetic Routes

A literature report² concerning the acid catalyzed condensation of a series of aldehydes with methyl furoate described a useful procedure by which bis(carboalkoxyfuryl)alkanes of type **1** could be synthesized from methyl furoate. These reaction products evidently resulted from a double acid catalyzed electrophilic substitution of the aromatic rings via intermediate hydroxyesters. In our hands the condensation of acetaldehyde and methyl furoate¹ gave, after refluxing the brown reaction product in methanol with activated charcoal and repeated recrystallization from a mixture of water and methanol, a 65% yield of off-white crystals of pure 1,1-bis(5-carbomethoxy-2-furyl)ethane **1**, m.p. 82°C



Scheme 1

(lit.² 81°C) (Scheme 1). This compound was transesterified with 2-ethylhexanol, 2-octanol, and butanol according to a general base catalyzed method under phase transfer conditions.^{1,3} The plasticizers **2a**, **2b**, and **2d** were obtained in yields of 90, 80, and 88%, respectively, and were purified by chromatography and distillation under high vacuum. All proposed structures were rigorously confirmed by ¹H and ¹³C NMR spectroscopy, high resolution mass spectroscopy, and elemental analyses whenever possible.

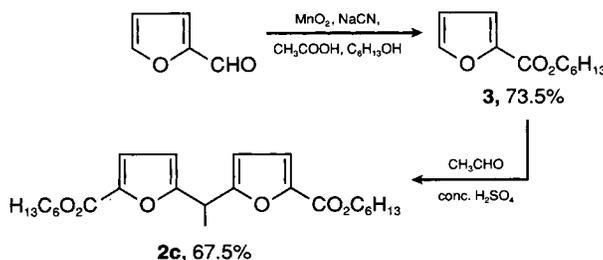
In an effort to realize shorter reaction routes from furfural to the plasticizer molecules, the one pot conversion⁴ of aldehydes to the corresponding methyl esters by treatment of carbonyl compounds with sodium cyanide, acetic acid, and manganese dioxide in methanol, was implemented for the synthesis of methyl furfuroate. These conditions improved our synthesis of methyl furfuroate from furfural and yields of 95% could routinely be realized. By applying the same reaction conditions, but utilizing hexanol as solvent instead of methanol, hexyl furfuroate **3** (Scheme 2) was synthesized from furfural in 74% yield. Acid catalyzed condensation of **3** with acetaldehyde gave the plasticizer, 1,1-bis(5-hexylcarboxylate-2-furyl)ethane **2c**, in 68% yield.

In our efforts to devise reaction routes to additional long-chain difuroate diesters as potential plasticizers, the oxidative coupling of furan derivatives to bifurans utilizing palladium(II) acetate both as oxidizing agent and as catalyst,^{6,7} was next investigated. The bifuran **4**, m.p. 262°C (lit.⁷ 265°C) was obtained in a catalytic yield of 561% by applying these reagents to furfural in the presence of copper(II) salts and O₂ as reoxidants. The transformation of **4** into the long-chain difuran diester **5** (Scheme 3) was effected in 29% yield by treatment of the dialdehyde **4** with sodium cyanide, acetic acid, and manganese dioxide in hexanol.⁴

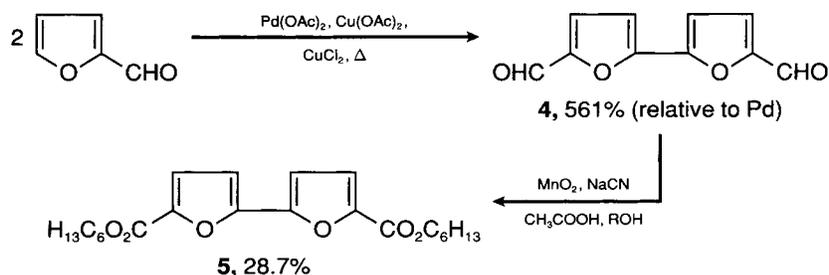
CHARACTERIZATION AS PLASTICIZERS

Data Analysis

The results of DMTA are shown in Figures 1–5. The main event in each of the storage and loss modulus curves is the glass transition, and T_g was measured as the onset temperature of the glass transition in the storage modulus. The linearity of the graph of T_g vs. concentration^{8,9} gave a value for the depression of T_g per mass percent plasticizer for each of the



Scheme 2



Scheme 3

materials tested. The T_g of unplasticized PVC was measured as 87°C . This value was used as the zero point of the depression of T_g at 0% plasticizer, and further T_g 's were measured at plasticizer levels of 25, 40, 55, and 70 phr, giving further values of depression. By plotting these values versus mass percent plasticizer, a straight line through the origin and the four data points was obtained for each diester tested (Fig. 6), with the slope equal to the depression of T_g per mass percent plasticizer, in $^\circ\text{C}$. The results are summarized in Table I. Similar results on furan diesters that have previously been synthesized and tested by this method¹ are given in

Table I, together with an efficiency value for di(2-ethylhexyl) phthalate (DOP), our standard of reference.

It is known furthermore that if a plasticizer is miscible with a polymer, a blend of the two should show a single T_g ,⁸ and that sharp transitions suggest good compatibility, while broad transitions are typical of less compatible blends. In order to quantify this trend, the width at half height of the maximum of the damping curve ($\tan \delta$) was measured for each sample in $^\circ\text{C}$ (see Figs. 1-5). The damping curves were used because these have good definition in the temperature range over which the glass transition

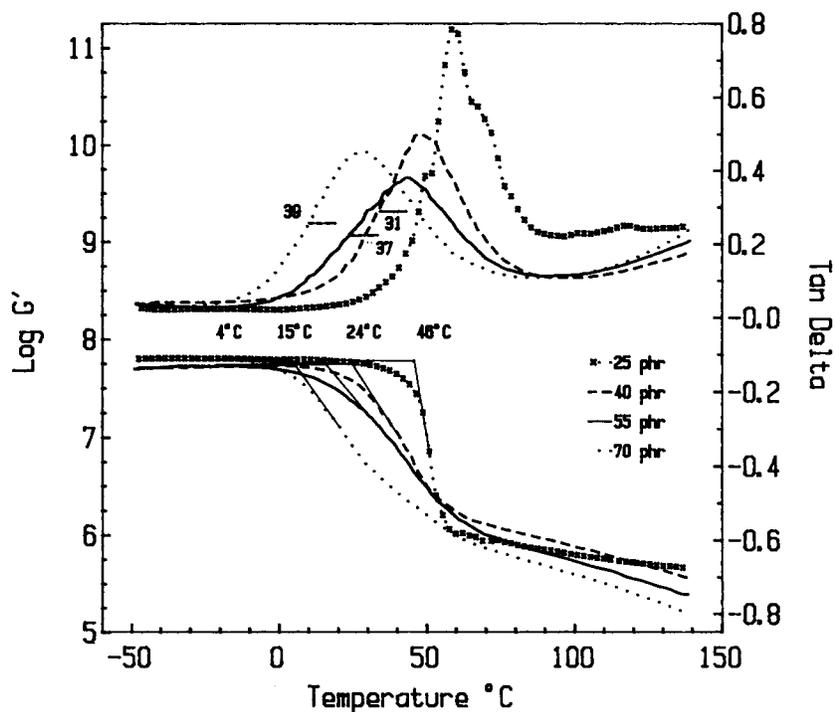


Figure 1 DMTA data for **2a**. The storage moduli (lower set of curves) are drawn on the left y-axes ($\log G'$), and the determined T_g values are indicated. Loss moduli ($\tan \delta$) are drawn on the right y-axes, and the width (in $^\circ\text{C}$) at half height of the damping peak is indicated for each sample.

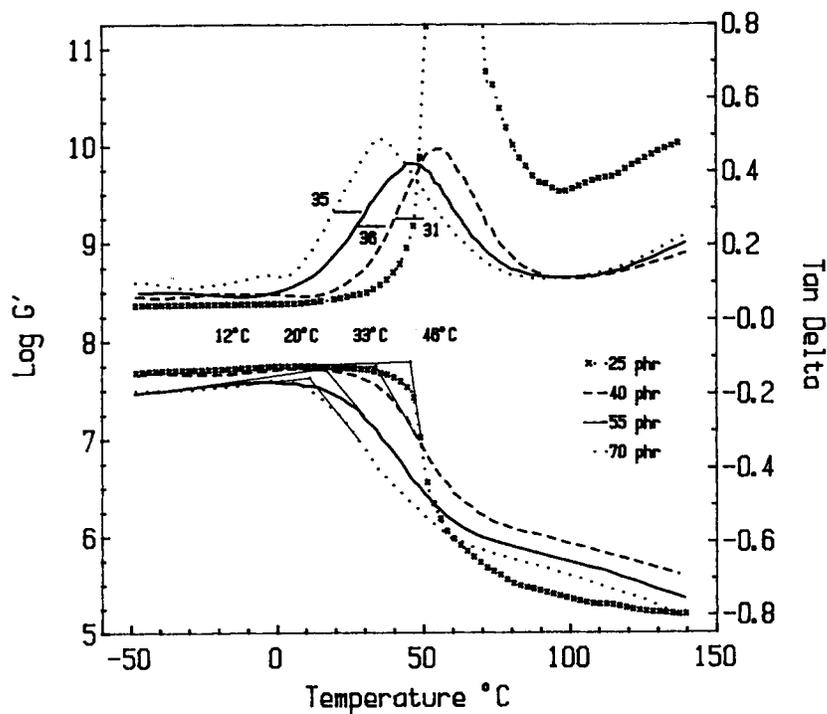


Figure 2 DMTA data for **2b**. The storage moduli (lower set of curves) are drawn on the left y-axis ($\log G'$), and the determined T_g values are indicated. Loss moduli ($\tan \delta$) are drawn on the right y-axis, and the width (in $^{\circ}\text{C}$) at half height of the damping peak is indicated for each sample.

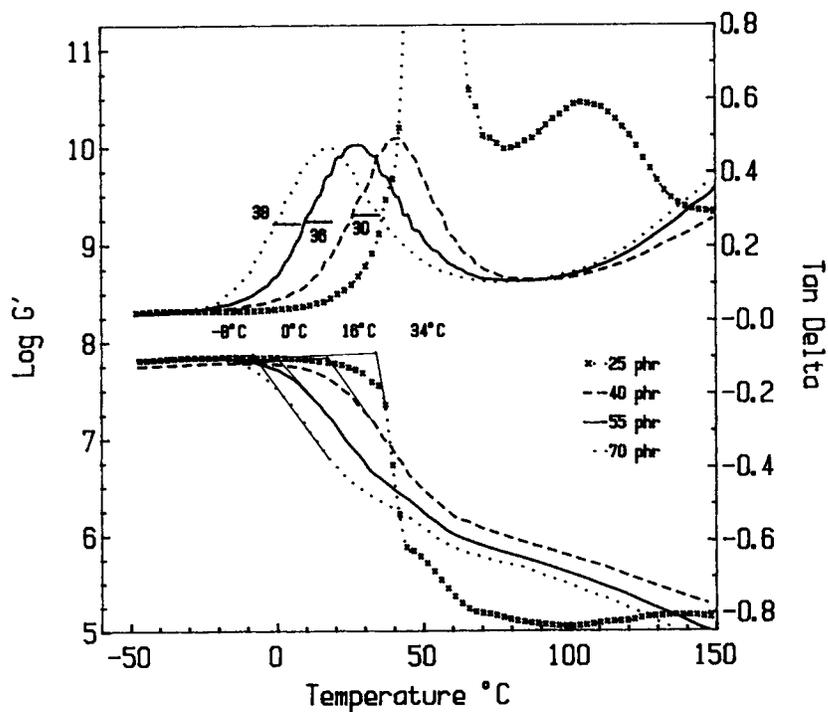


Figure 3 DMTA data for **2c**. The storage moduli (lower set of curves) are drawn on the left y-axis ($\log G'$), and the determined T_g values are indicated. Loss moduli ($\tan \delta$) are drawn on the right y-axis, and the width (in $^{\circ}\text{C}$) at half height of the damping peak is indicated for each sample.

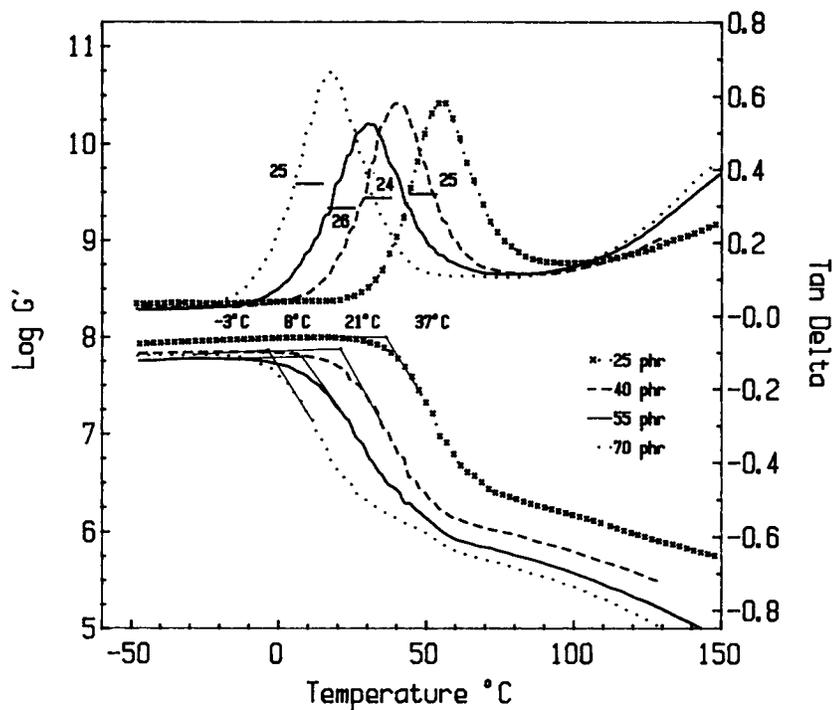


Figure 4 DMTA data for **2d**. The storage moduli (lower set of curves) are drawn on the left y-axes ($\log G'$), and the determined T_g values are indicated. Loss moduli ($\tan \delta$) are drawn on the right y-axes, and the width (in $^{\circ}\text{C}$) at half height of the damping peak is indicated for each sample.

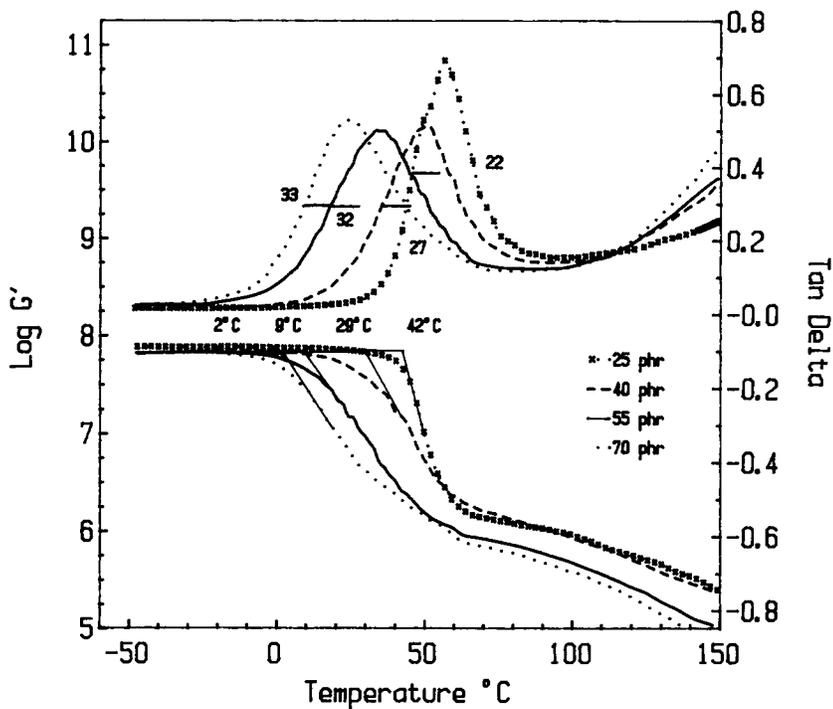


Figure 5 DMTA data for **5**. The storage moduli (lower set of curves) are drawn on the left y-axes ($\log G'$), and the determined T_g values are indicated. Loss moduli ($\tan \delta$) are drawn on the right y-axes, and the width (in $^{\circ}\text{C}$) at half height of the damping peak is indicated for each sample.

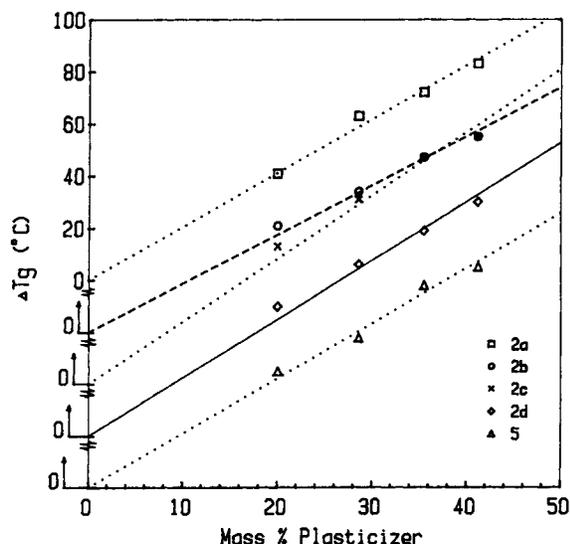


Figure 6 Processing of DMTA data: depression of T_g vs. mass % plasticizer. For clarity each plasticizer is represented with its own y -axes. Y/x values as well as the standard error for each regression are summarized in Table I.

takes place. Samples that exhibited anomaly in their damping curves were disregarded, i.e., 25 phr **2c** in Figure 3. For each diester, the δ °C value at each concentration was divided by the δ °C value at the corresponding plasticizer level of DOP in order to obtain dimensionless compatibility numbers versus DOP, for example:

1. width at half height for DOP at 55 phr, 38°C;
2. width at half height for **2c** at 55 phr, 36°C;
3. compatibility number vs. DOP at 55 phr, 38°C/36°C = 1.06.

The δ °C values for DOP¹ at 25, 40, 55, and 70 phr, in ascending order of concentration, are 25, 29, 38, and 35°C. By this method three or four compatibility numbers (different concentrations) vs. DOP were obtained for each difuran diester. Their average gives one numerical quantity, and an increasing value indicates higher compatibility towards PVC. The results are shown in Table I.

Solubility parameters of the four liquid plasticizers were calculated according to published methods^{10,11} and are given in Table I. It was necessary to obtain a molar attraction constant for the furan ring, and a value of 673 (cal/cm³)^{1/2} mol⁻¹ was computed from the known solubility parameter and density of furan.¹¹ An averaged value¹⁰⁻¹² of 9.55 was used as the solubility parameter for PVC.

DISCUSSION

The diesters **2a–2d** are odorless, clear oils, thermally stable as illustrated by their distillation at high temperature, and they are fluorescent under UV light. The bifuran **5** is a low-melting white solid. On the plasticization of PVC with the difuran diesters some color formation was observed, and pure **2a**, **2b**, **2c**, and **2d** discolored to light red or yellowish oils on long exposure to air and light. No stabilizers were added to the plasticizer-resin preparations.

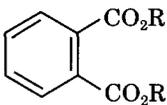
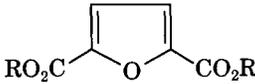
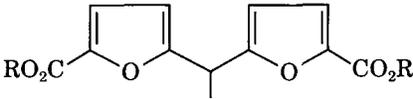
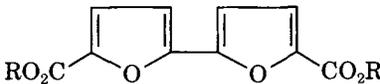
From the DMTA curves displayed in Figures 1–5 it is obvious that PVC that has been plasticized by the long-chain difuran diesters displays viscoelastic behavior typical of compatible compositions. In each of the storage and loss modulus curves there is one main event, namely the glass transition, that is followed by an ill-defined rubbery plateau and an area of elastic or rubbery flow. In some plots part of the damping curve of the 25-phr sample is off scale as these glass transitions are sharp, and give very high damping maxima.

Table I reveals that the 2-ethylhexyl substituted difuran diester **2a** is considerably less efficient in lowering T_g than either DOP, our standard of reference, or the 2-ethylhexyl substituted furan diester (**i**). Confirmation of the decrease in efficiency when moving from a mono- to a difuran structure is obtained by comparing values for **2b–2d** to those of (**ii**)–(**iv**). A factor contributing to such a decrease is high molecular weight, which generally leads to lower plasticizing efficiency.^{9,13}

It is further found that the 2-octyl substituted compound **2b** exhibits less efficiency in lowering T_g than the 2-ethylhexyl substituted **2a**, echoing the drop over the similarly substituted (**i**) and (**ii**) as well as DOP and di(2-octyl) phthalate (DCP).¹³ The two compounds are of equal molecular weight, but where the carboxylate group in **2a** is connected to a primary carbon that of **2b** is connected to a secondary one. It is possible that its lower plasticizing efficiency results from inhibition in free rotation around this ester bond, giving a less flexible compound not as able to create free volume. The remainder of the difuran diesters follow a similar trend to that of their monofuran analogs; the hexyl substituted compound is the most efficient in the series, and the butyl substituted compound only a little less efficient than it.

DMTA data mostly indicates a higher compatibility toward PVC from the furan diesters than from the reference standard, DOP. This is expected as the furan ring is more polar than the benzene ring, leading to greater solvency in the polar PVC resin.

Table I

Compound	R=	Efficiency ΔT_g /Mass %	Compatibility (DMTA)	Density	Solubility Parameter δ	$\delta - \delta_{PVC}$
						
DOP	2-Ethylhexyl	2.45 ± 0.06	1.00	0.985	8.9	0.7
						
(i)	2-Ethylhexyl	2.41 ± 0.08	1.09	0.994	9.3	0.2
(ii)	2-Octyl	2.23 ± 0.08	1.07	0.986	9.2	0.4
(iii)	Hexyl	2.52 ± 0.14	1.07			
(iv)	Butyl	2.45 ± 0.12	1.34			
						
2a	2-Ethylhexyl	2.04 ± 0.08	0.95	1.027	9.6	-0.1
2b	2-Octyl	1.83 ± 0.07	1.00	1.020	9.6	0.0
2c	Hexyl	2.33 ± 0.11	0.98	1.054	10.0	-0.4
2d	Butyl	2.18 ± 0.10	1.27	1.102	10.4	-0.9
						
5	Hexyl	2.11 ± 0.19	1.11			

An unexpected finding is that instead of an improvement the move from a mono- to a difuran structure has a detrimental effect on compatibility toward PVC. To illustrate, **2a** has a smaller compatibility number than (i), **2b** is less than (ii), and so forth, even though the difuran diesters embody a higher proportion of compatibilizing groups, namely the furan rings. Moving down in the ranges (i)–(iv) and **2a**–**2d**, we do however find that the increase in the aromatic relative to aliphatic character of the molecular structures is accompanied by an increase in compatibility, with the butyl substituted (iv) and **2d** the most highly compatible in the two respective ranges. The general DMTA prediction of good compatibility between the furan diesters and PVC is confirmed by inspection of the differences in solubility parameter between PVC and those of the respective furan diesters (Table I). A general estimation is that plasticizer and polymer

must be within 1–2 δ -units of each other for mutual solubilization, and inspection of Table I reveals all values to be within 1 δ -unit of that of PVC, again leading to the expectation of high compatibility.

This work was supported in part by a grant from the Foundation for Research and Development, South Africa, and we thank C. G. Smith Chemicals for their financial support, helpful suggestions, and continued interest in the project.

REFERENCES

1. R. D. Sanderson, D. F. Schneider and I. Schreuder, *J. Appl. Pol. Sci.*, **53**, 1785 (1994).
2. S. Pennanen and G. Nyman, *Acta Chem. Scand.*, **26**, 1018 (1972).
3. J. Barry, G. Bram, and A. Petit, *Tetrahedron Lett.*, **29**, 4567 (1988).

4. E. J. Corey, N. W. Gilman, and B. E. Ganem, *J. Am. Chem. Soc.*, **90**, 5616 (1968).
5. R. C. Weast, *CRC Handbook of Chemistry and Physics*, 67th ed., CRC Press, Boca Raton, FL, 1986.
6. I. V. Kozhevnikov, *React. Kinet. Catal. Lett.*, **4**, 451 (1976).
7. I. V. Kozhevnikov, *React. Kinet. Catal. Lett.*, **4**, 415 (1976).
8. H. E. Bair, in *Thermal Characterization of Polymeric Materials*, E. A. Turi, Ed., Academic Press, New York, 1981, pp. 878-884.
9. J. R. Darby and J. K. Sears, in *Encyclopedia of PVC*, Vol. 1, L. I. Nass, Ed., Marcel Dekker Inc., New York, 1976, pp. 451-452.
10. P. A. Small, *J. Appl. Chem.*, **3**, 71 (1953).
11. J. Brandrup and E. H. Immergut, *Polymer Handbook*, 2nd ed., Wiley, New York, 1975, pp. IV-337.
12. J. R. Darby and J. K. Sears, in *Encyclopedia of PVC*, Vol. 1, L. I. Nass, Ed., Marcel Dekker Inc., New York, 1976, pp. 397-405.
13. L. J. Krauskopf, in *Encyclopedia of PVC*, Vol. 1, L. I. Nass, Ed., Marcel Dekker Inc., New York, 1976, pp. 518-523.

Received June 27, 1994

Accepted September 6, 1994