

Synthesis and Evaluation of Some Functionalized Difuran Diesters as Plasticizers for PVC

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SYNOPSIS

Butyl, hexyl, and 2-ethylhexyl diesters of 1,1-bis(5-carboxyl-2-furyl)-2,2-dichloroethene, hexyl and 2-ethylhexyl diesters of 1,1-bis(5-carboxyl-2-furyl)ketone, and the hexyl diester of 1,1-bis(5-carboxyl-2-furyl)methane were synthesized from furfural and evaluated for their plasticizing abilities toward PVC, by the application of dynamic mechanical thermal analysis and [di(2-ethylhexyl) phthalate] as a standard of reference. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

During our previous investigations^{1,2} we observed that upon plasticizing PVC with difuran diesters that possess tertiary benzylic-type hydrogen substituents α to the furan ring, an undesired red or yellowish tint was acquired by the resin. It is known that conditions that prevail during the processing of PVC resins, i.e. high temperature and the presence of atmospheric oxygen, are favorable for initiating autooxidation, and that plasticizers possessing tertiary or other reactive hydrogen substituents are particularly susceptible to homolytic interactions that may contribute to color development. To diminish the possibility of yellowing, it was accordingly decided to synthesize a few series of plasticizers devoid of hydrogen substituents α to the furan ring. Another incentive toward the synthesis of these plasticizers was to investigate the influence of functional groups in the molecular backbone on final plasticizer performance.

EXPERIMENTAL

Instrumentation and Materials

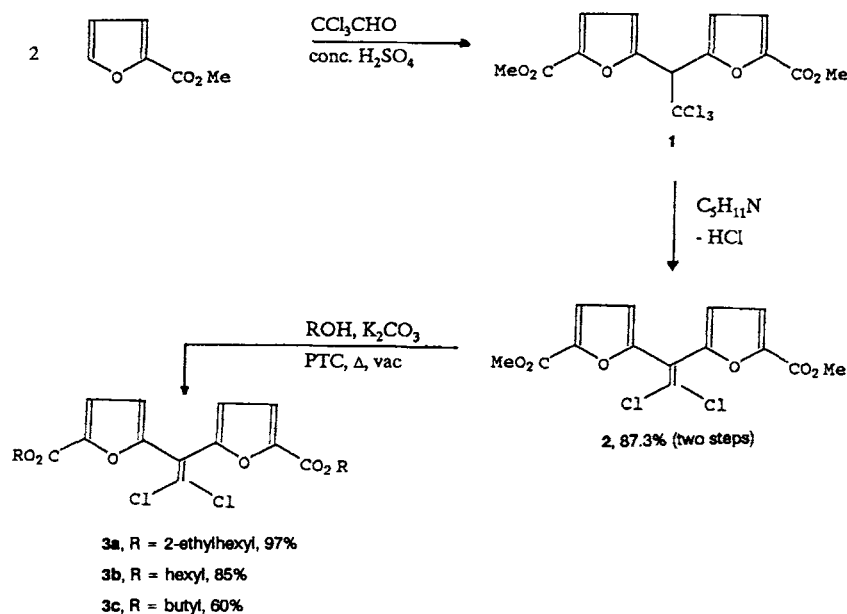
Melting points were determined on a Gallenkamp melting point apparatus; melting and boiling points

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 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 were measured on an Abe refractometer and densities of the furan diesters were determined with a dilatometer. 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 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]-2,2-dichloroethene 3a

A mixture of 1,1-bis(5-carbomethoxy-2-furyl)-2,2-dichloroethene^{3,4} (2.51 g, 7.21 mmol), 2-ethylhexanol (7.56 g, 58.1 mmol), potassium carbonate (0.40 g, 2.9 mmol), and tetrabutylammonium hydrogen sulfate (0.12 g, 0.29 mmol)⁵ was heated at 130°C to

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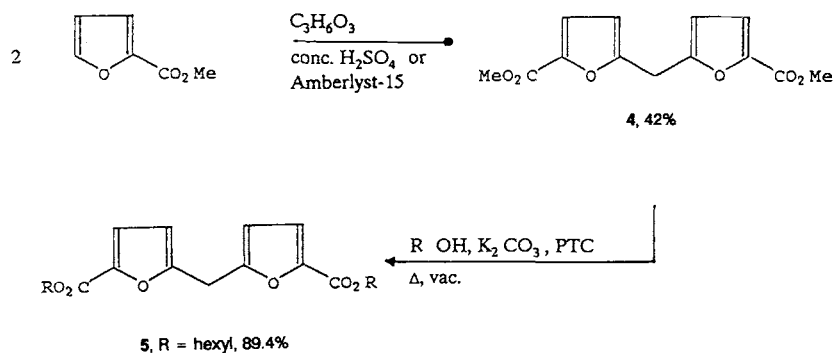
Scheme 1

homogenize the reaction mixture and then stirred in a reaction flask fitted with a Vigreux column for 5 h at 110°C (oil-bath temp.) under vacuum (120 mm Hg). Progression of the reaction was monitored by thin layer chromatography (TLC) on silica gel with ether-petroleum ether (1 : 1) as mobile phase and spraying the chromatoplate with acidic potassium dichromate. The reaction mixture was poured into water (30 mL), extracted with ether (3 × 20 mL), the combined ether extracts dried (MgSO₄), and the ether and excess of hexanol removed by distillation under vacuum. Chromatography of the brown residue on silica gel yielded, upon elution with ether-petroleum ether (3 : 17), 1,1-bis[5-(2-ethylhexyl)carboxylate-2-furyl]-2,2-dichloroethene **3a** (3.81 g, 97%), bp 255°C (air-bath temp.) at 6 × 10⁻⁶ mm Hg with a slight degree of deterioration, *d* 1.120, *n*_D²³ 1.5302, δ_{H} 0.895 (6 H, t, J 7.2 Hz, 2 × CH₃), 0.917

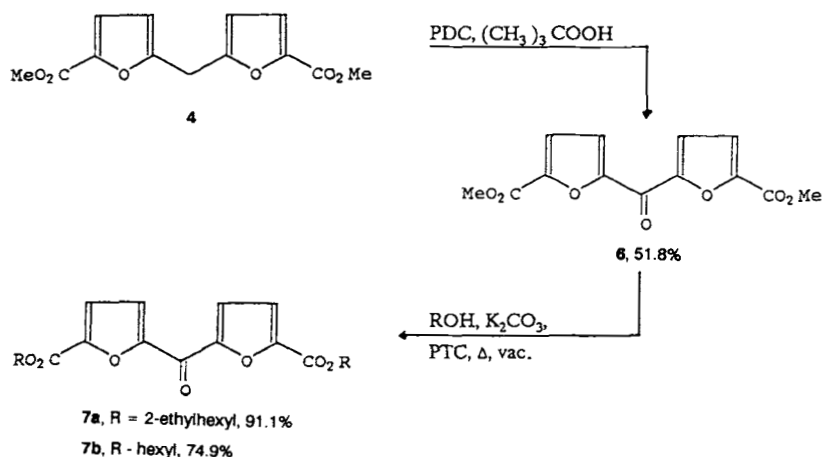
(6 H, t, J 7.4 Hz, 2 × CH₃), 1.25–1.45 (16 H, m, 8 × CH₂), 1.673 (2 H, h, J 6.0 Hz, 2 × CH), 4.180 (2 H, dd, J 5.9, 10.9 Hz, 2 × OCH), 4.225 (2 H, dd, J 5.7, 10.9 Hz, 2 × OCH), 6.666 (2 H, d, J 3.6 Hz, 2 × =CH), and 7.187 (2 H, d, J 3.6 Hz, 2 × =CH); δ_{C} 144.85 (C-2), 114.69 (C-3), 118.41 (C-4), 150.73 (C-5), 158.47 (C-6), 67.48 (C-7), 38.94 (C-8), 30.54 (C-9), 28.99 (C-10), 22.98 (C-11), 14.03 (C-12), 23.97 (C-13), 11.07 (C-14), 120.66 (C-15), 127.12 (C-16). Found: *M*⁺, 540.2046. C₂₈H₃₈O₆Cl₂ requires *M*, 540.2045.

1,1-Bis(5-hexylcarboxylate-2-furyl)-2,2-dichloroethene **3b**

A mixture of 1,1-bis(5-carbomethoxy-2-furyl)-2,2-dichloroethene^{3,4} (3.0 g, 8.69 mmol), hexanol (7.11 g, 69.5 mmol), potassium carbonate (0.48 g, 3.5



Scheme 2



Scheme 3

mmol), and tetrabutylammonium hydrogen sulfate (0.12 g, 0.35 mmol)⁵ was heated at 130°C to homogenize the reaction mixture and then stirred in a reaction flask equipped with a Vigreux column for 5 h at 100°C (oil-bath temp.) under vacuum (170 mm Hg). The reaction was worked-up as above, chromatographed on silica gel and eluted with ether-

petroleum ether (3 : 17) to give 1,1-bis[5-hexylcarboxylate-2-furyl]-2,2-dichloroethene **3b** (3.59 g, 85%), bp 255°C (air-bath temp.) at 6×10^{-6} mm Hg, d 1.167, n_D^{23} 1.5410, δ_H 0.896 (6 H, t, J 7.0 Hz, $2 \times \text{CH}_3$), 1.29–1.42 (12 H, m, $6 \times \text{CH}_2$), 1.724 (4 H, qn, J 7.0 Hz, $2 \times \text{CH}_2$), 4.283 (4 H, t, J 6.7 Hz, $2 \times \text{OCH}_2$), 6.656 (2 H, d, J 3.6 Hz, $2 \times =\text{CH}$), and

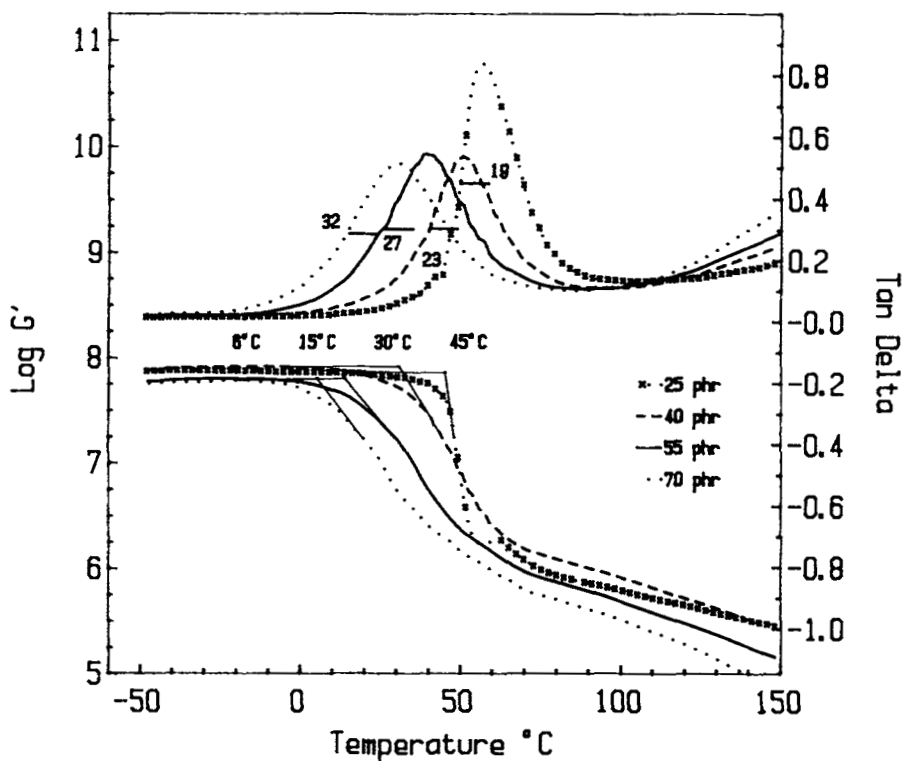


Figure 1 DMTA data for **2a**. The storage moduli (lower set of curves) are drawn on the left y axes ($\log G'$), and the determined T_g values are indicated. Loss moduli ($\tan \delta$) are drawn on the right y axes, and the width (in °C) at half height of the damping peak is indicated for each sample.

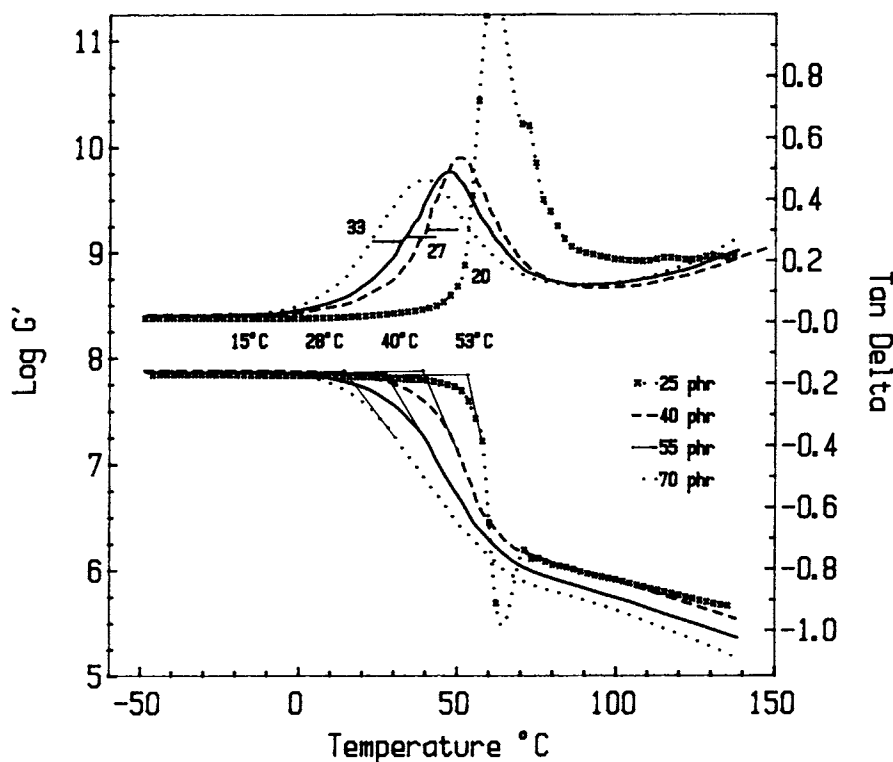


Figure 2 DMTA data for **2b**. The storage moduli (lower set of curves) are drawn on the left y axes ($\log G'$), and the determined T_g values are indicated. Loss moduli ($\tan \delta$) are drawn on the right y axes, and the width (in $^{\circ}\text{C}$) at half height of the damping peak is indicated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

7.196 (2 H, d, J 3.6 Hz, $2\times =\text{CH}$); δ_{C} 144.89 (C-2), 114.75 (C-3), 118.50 (C-4), 150.70 (C-5), 158.29 (C-6), 65.19 (C-7), 28.67 (C-8), 25.61 (C-9), 31.44 (C-10), 22.56 (C-11), 13.99 (C-12), 120.67 (C-13), and 127.12 (C-14). Found: C, 59.9%; H, 6.5%; M^+ , 484.1478. $\text{C}_{24}\text{H}_{30}\text{O}_6\text{Cl}_2$ requires C, 59.4%; H, 6.25%; M, 484.1419.

1,1-Bis(5-butylcarboxylate-2-furyl)-2,2-dichloroethene **3c**

A mixture of 1,1-bis(5-carbomethoxy-2-furyl)-2,2-dichloroethene^{3,4} (2.43 g, 7.0 mmol), butanol (10.42 g, 140.6 mmol), potassium carbonate (0.39 g, 2.8 mmol), and tetrabutylammonium hydrogen sulfate (0.10 g, 0.29 mmol)⁵ was heated at 130°C in a reaction flask to homogenize the reaction mixture and then stirred as above for 5 h at 100°C (oil-bath temp.) under vacuum (240 mm Hg). The reaction mixture was worked-up as before, chromatographed on silica gel, and eluted with ether-petroleum ether (3 : 17) to give 1,1-bis(5-butylcarboxylate-2-furyl)-2,2-dichloroethene **3c** (1.80 g, 60.0%), bp 245°C (air-bath temp.) at 5×10^{-6} mm Hg, d 1.221, n_{D}^{23}

1.5535, δ_{H} 0.957 (6 H, t, J 7.4 Hz, $2\times \text{CH}_3$), 1.432 (4 H, sx, J 7.4 Hz, $2\times \text{CH}_2$), 1.714 (4 H, qn, J 7.0 Hz, $2\times \text{CH}_2$), 4.293 (4 H, t, J 6.6 Hz, $2\times \text{OCH}_2$), 6.663 (2 H, d, J 3.6 Hz, $2\times =\text{CH}$), and 7.199 (2 H, d, J 3.6 Hz, $2\times =\text{CH}$); δ_{C} 144.85 (C-2), 114.73 (C-3), 118.51 (C-4), 150.72 (C-5), 158.35 (C-6), 64.93 (C-7), 30.72 (C-8), 19.17 (C-9), 13.69 (C-10), 120.66 (C-11), and 127.17 (C-12). Found: C, 56.55%; H, 5.3%; M^+ , 428.0800. $\text{C}_{20}\text{H}_{22}\text{O}_6\text{Cl}_2$ requires C, 55.95%; H, 5.15%; M, 428.0794.

Bis(5-carbomethoxy-2-furyl)methane **4**

Methyl furoate¹ (5.0 g, 39.6 mmol) and amberlyst-15 (10 g) in benzene (40 mL) were treated dropwise with trioxane (1.04 g, 11.6 mmol) in benzene (10 mL) during 30 min and the reaction mixture stirred at reflux temperature for a further 48 h while progression of the reaction was monitored by TLC on silica gel with ether-petroleum ether (1 : 1) as mobile phase. The amberlyst-15 was removed by filtration, washed with ether (50 mL), the combined filtrates dried (MgSO_4), and the solvents removed by distillation. Chromatography of the residue on silica

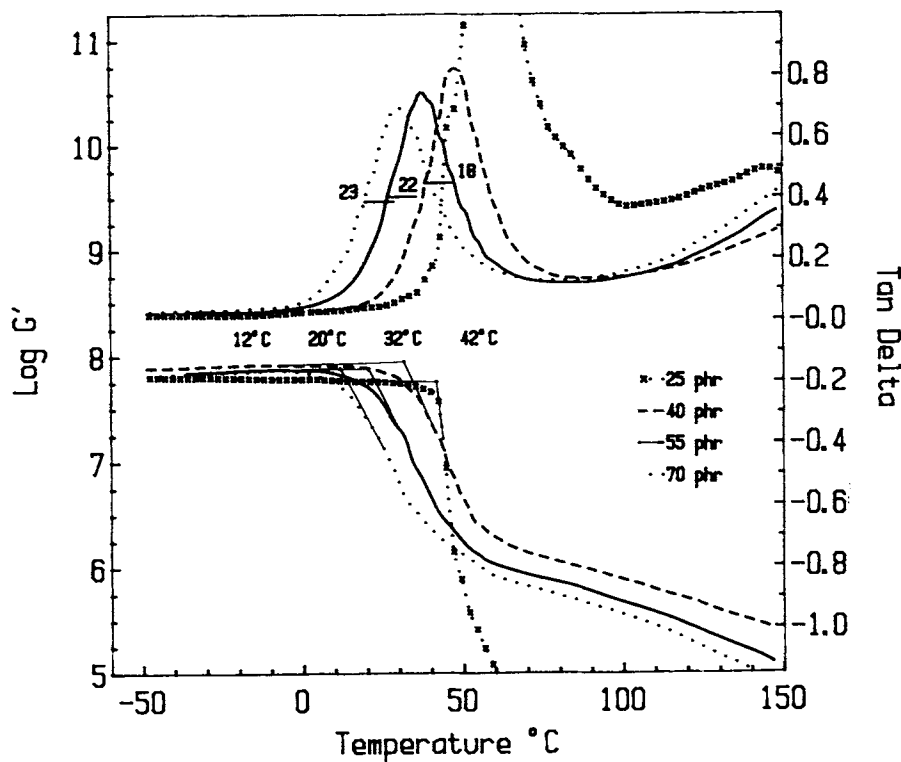


Figure 3 DMTA data for **2c**. The storage moduli (lower set of curves) are drawn on the left y axes ($\log G'$), and the determined T_g values are indicated. Loss moduli ($\tan \delta$) are drawn on the right y axes, and the width (in $^{\circ}\text{C}$) at half height of the damping peak is indicated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

gel with ether-petroleum ether (1 : 1) as eluent yielded bis(5-carbomethoxy-2-furyl)methane **4** (1.10 g, 21%), mp 120°C (lit.³ 121°C).

Bis(5-hexylcarboxylate-2-furyl)methane **5**

A mixture of bis(5-carbomethoxy-2-furyl)methane³ **4** (3.00 g, 11.4 mmol), hexanol (4.64 g, 45.4 mmol), potassium carbonate (0.63 g, 45.4 mmol), and tetrabutylammonium hydrogen sulfate (0.154 g, 0.45 mmol)⁵ was stirred in a reaction flask equipped with a Vigreux column for 2.5 h at 100°C (oil-bath temp.) under vacuum (90 mm Hg). The reaction mixture was worked-up as before, chromatographed on silica gel, and eluted with ether-petroleum ether (1 : 9) giving bis(5-hexylcarboxylate-2-furyl)methane **5** (4.11 g, 89.4%), bp 230°C (air-bath temp.) at 7×10^{-6} mm Hg, d 1.069, n_D^{25} 1.5040, δ_{H} 0.897 (6 H, t, J 7.0 Hz, $2 \times \text{CH}_3$), 1.22–1.59 (12 H, m, $6 \times \text{CH}_2$), 1.731 (4 H, qn, J 7.1 Hz, $2 \times \text{CH}_2$), 4.157 (2 H, br s, CH_2), 4.280 (4 H, t, J 6.8 Hz, $2 \times \text{OCH}_2$), 6.257 (2 H, dt, J 3.4, 0.8 Hz, $2 \times =\text{CH}$), and 7.097 (2 H, d, J 3.4 Hz, $2 \times =\text{CH}$); δ_{C} 144.25 (C-2), 109.62 (C-3), 118.85 (C-4), 154.68 (C-5),

158.73 (C-6), 65.03 (C-7), 28.73 and 28.02 (C-8 and C-13), 25.62 (C-9), 31.48 (C-10), 22.57 (C-11), and 14.00 (C-12). Found: C, 68.5%; H, 8.0%; M^+ , 406.2273. $\text{C}_{23}\text{H}_{32}\text{O}_6$ requires C, 68.3%; H, 7.9%; M , 406.2266.

Bis(5-carbomethoxy-2-furyl)ketone **6**

To a stirred suspension of bis(5-carbomethoxy-2-furyl)methane³ **4** (4.0 g, 15.1 mmol) and celite (18 g) in benzene (150 mL) was added pyridinium dichromate (22.7 g, 60.3 mmol)^{6,7} followed by the dropwise addition during 15 min of *tert*-butyl hydroperoxide (5.43 g, 60.3 mmol) at 10°C . The reaction mixture was stirred for a further 17 h at room temperature, filtered, and the filter pad extracted by refluxing with chloroform (5 min). Evaporation of the solvent from the combined filtrates yielded a dark brown viscous mass, which was repeatedly crystallized from ethanol and a mixture of chloroform and ethanol to yield bis(5-carbomethoxy-2-furyl)ketone **6** (2.18 g, 51.8%), mp 210.8°C , δ_{H} 3.977 (6 H, s, $2 \times \text{CH}_3$), 7.320 (2 H, d, J 3.7 Hz, $2 \times =\text{CH}$).

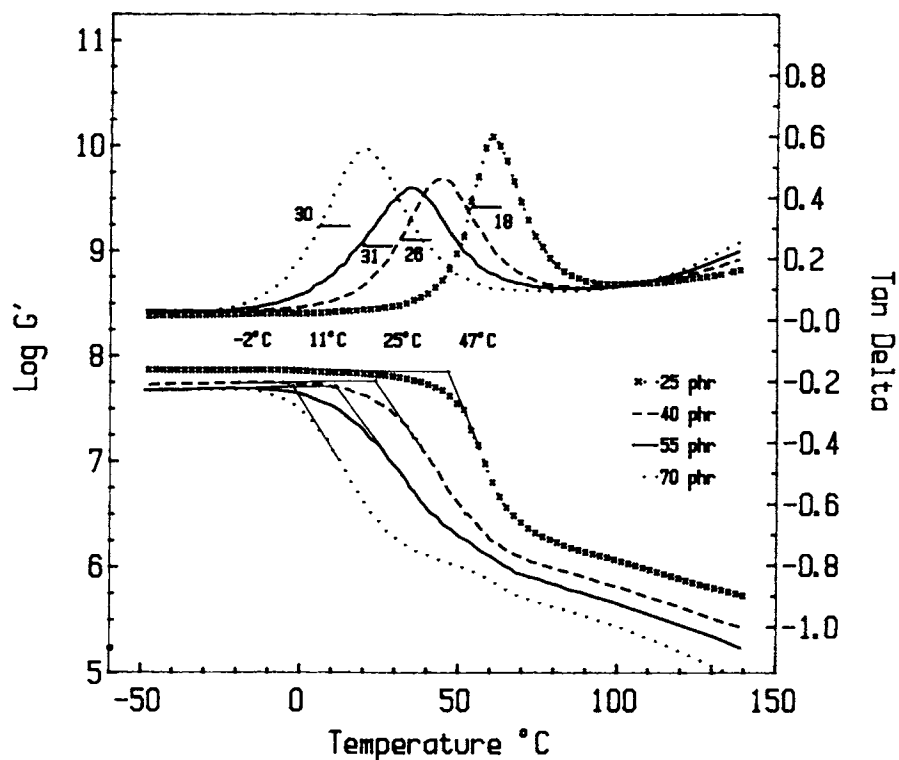


Figure 4 DMTA data for **2d**. The storage moduli (lower set of curves) are drawn on the left y axes ($\log G'$), and the determined T_g values are indicated. Loss moduli ($\tan \delta$) are drawn on the right y axes, and the width (in $^{\circ}\text{C}$) at half height of the damping peak is indicated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

Bis[5-(2-ethylhexyl)carboxylate-2-furyl]ketone **7a**

A mixture of bis(5-carbomethoxy-2-furyl)ketone **6** (1.54 g, 5.5 mmol), 2-ethylhexanol (14.44 g, 111 mmol), potassium carbonate (0.31 g, 2.2 mmol), and benzylhexadecyldimethylammonium chloride (0.09 g, 0.22 mmol)⁵ was stirred in a reaction flask equipped with a Vigreux column for 2 h at 120°C (oil-bath temp.) under vacuum (80 mm Hg). The reaction mixture was worked-up as before, chromatographed on silica gel, and eluted with ether-petroleum ether (1 : 9) to give a pale yellow solid (2.40 g) which was recrystallized from hexane to yield pure bis[5-(2-ethylhexyl)carboxylate-2-furyl]ketone **7a** (2.13 g, 80.9%), mp 62.5°C , δ_{H} 0.911 (6 H, t, J 7.1 Hz, $2 \times \text{CH}_3$), 0.954 (6 H, t, J 7.4 Hz, $2 \times \text{CH}_3$), 1.28–1.57 (16 H, m, $8 \times \text{CH}_2$), 1.744 (2 H, h, J 6.0 Hz, $2 \times \text{CH}$), 4.270 (2 H, dd, J 5.9, 11.0 Hz, $2 \times \text{OCH}$), 4.311 (2 H, dd, J 5.7, 10.8 Hz, $2 \times \text{OCH}$), 7.276 (2 H, d, J 3.7 Hz, $2 \times =\text{CH}$), and 7.679 (2 H, d, J 3.7 Hz, $2 \times =\text{CH}$); δ_{C} 147.56 (C-2), 120.51 and 118.47 (C-3 and C-4), 152.27 (C-5), 158.13 (C-6), 68.15 (C-7), 38.96 (C-8), 30.54 (C-9), 29.01 (C-10), 23.01 (C-11), 14.05 (C-12), 23.94 (C-13), 11.06

(C-14), and 168.12 (C-15). Found: C, 68.2%; H, 7.6%; M^+ , 474.2586. $\text{C}_{27}\text{H}_{38}\text{O}_7$ requires C, 68.35%; H, 8.05%; M , 474.2618.

Bis(5-hexylcarboxylate-2-furyl)ketone **7b**

A mixture of bis(5-carbomethoxy-2-furyl)ketone **6** (3.20 g, 11.5 mmol), hexanol (23.50 g, 230 mmol), potassium carbonate (0.64 g, 4.6 mmol), and tetrabutylammonium hydrogen sulfate (0.16 g, 0.46 mmol)⁵ was stirred in a reaction flask equipped with a Vigreux column for 3.5 h at 120°C (oil-bath temp.) under vacuum (200 mm Hg). The reaction mixture was worked-up as before and chromatography on silica gel with ether-petroleum ether (1 : 4) as eluent yielded a white solid (3.60 g) which was recrystallized from a mixture of hexane and chloroform to give bis(5-hexylcarboxylate-2-furyl)ketone **7b** (3.01 g, 62.6%), mp 90.3°C , δ_{H} 0.910 (6 H, t, J 7.1 Hz, $2 \times \text{CH}_3$), 1.31–1.47 (12 H, m, $6 \times \text{CH}_2$), 1.786 (4 H, qn, J 7.0 Hz, $2 \times \text{CH}_2$), 4.367 (4 H, t, J 6.8 Hz, $2 \times \text{OCH}_2$), 7.291 (2 H, d, J 3.7 Hz, $2 \times =\text{CH}$), and 7.677 (2 H, d, J 3.7 Hz, $2 \times =\text{CH}$); δ_{C} 147.60 (C-2), 120.53 (C-3), 118.53 (C-4), 152.26

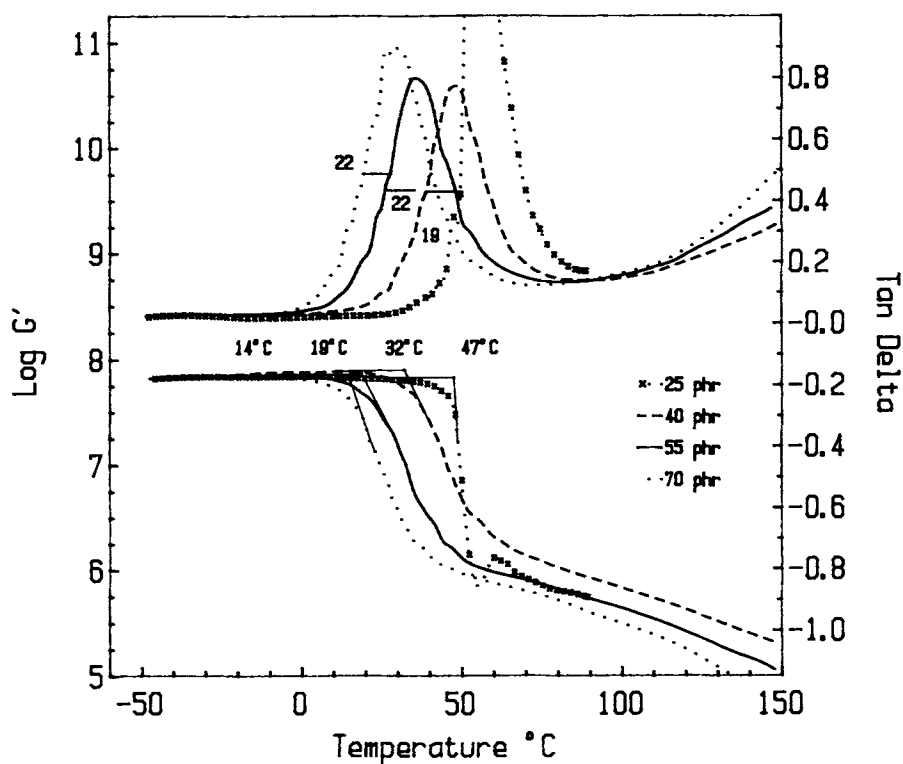


Figure 5 DMTA data for **5**. The storage moduli (lower set of curves) are drawn on the left y axes ($\log G'$), and the determined T_g values are indicated. Loss moduli ($\tan \delta$) are drawn on the right y axes, and the width (in $^{\circ}\text{C}$) at half height of the damping peak is indicated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

(C-5), 158.07 (C-6), 65.91 (C-7), 28.67 (C-8), 25.63 (C-9), 31.48 (C-10), 22.58 (C-11), 14.02 (C-12), and 168.13 (C-13). Found: C, 66.65%; H, 7.1%; M⁺, 418.1998. C₂₃H₃₀O₇ requires C, 66.0%; H, 7.2%; M, 418.1991.

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 1.2-mm thick mold with four 1 × 2 cm rectangular cavities. Plasticization was effected in a hot press at 145 $^{\circ}\text{C}$ and 5 MPa in 10 min.

In the case of a 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 $^{\circ}\text{C}$ and 5 MPa in the press to anneal.

RESULTS AND DISCUSSION

Synthetic routes

We previously reported the synthesis of a range of ethylidene-bridged difuran diesters, together with an evaluation of their abilities to plasticize PVC.² These compounds were obtained by the condensation of acetaldehyde with 2M methyl furoate in concentrated sulfuric acid, followed by transesterification to yield long-chain difuran diesters. In the present study chloral was condensed with methyl furoate according to the method of Pennanen and Nyman³ to give 1,1-bis(5-carbomethoxy-2-furyl)-2,2,2-trichloroethane **1**. Hydrochloric acid was eliminated from the crude product mixture by treatment with piperidine⁴ to furnish a white solid (87% yield) which was repeatedly crystallized from dioxane to give the pure unsaturated diester **2** in 59% yield⁴ (Scheme 1). The plasticizers **3a**, **3b**, and **3c** were now obtained by transesterification of **2** with 2-ethylhexanol, hexanol, and butanol, respectively.⁵ These reactions were catalyzed by solid potassium carbonate and performed under phase transfer con-

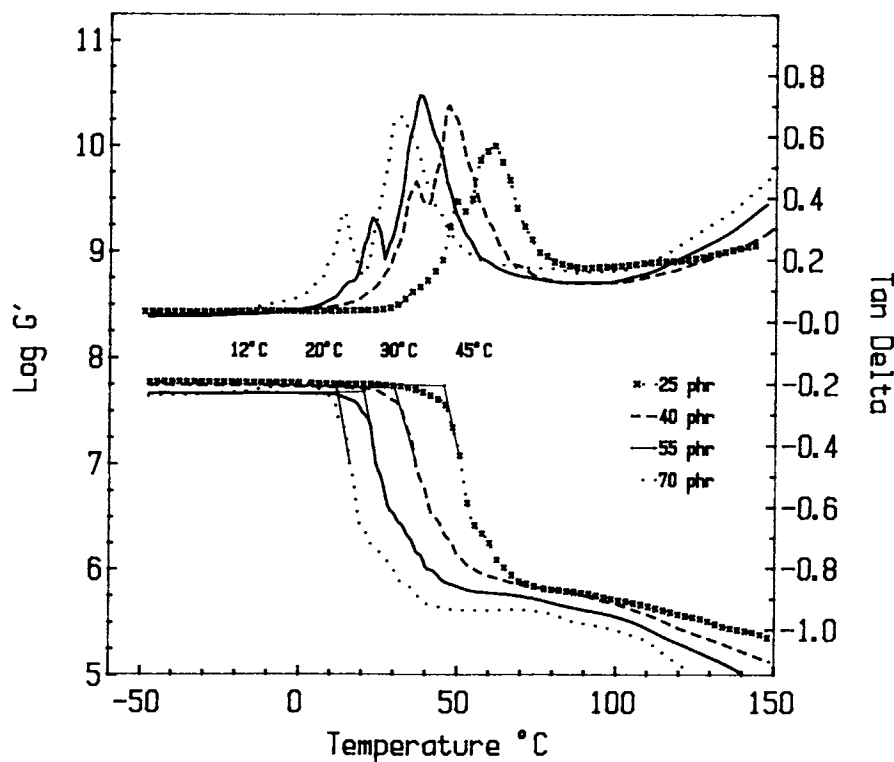


Figure 6 Processing of DMTA data: depression of T_g vs. mass % plasticizer. For clarity each plasticizer is represented with its own y axes. Y/x values as well as the standard error for each regression are summarized in Table I.

ditions. The absence of solvent allowed a vacuum to be applied, which facilitated the continuous removal of the generated methanol, thereby shifting the reaction equilibrium toward the formation of the long-chain diesters **3a**, **3b**, and **3c**.

The need to synthesize bis(5-carbomethoxy-2-furyl)methane **4** was inspired by the possibility of oxidizing^{6,7} its reactive methylene group, and thereby yielding a difuran plasticizer with a carbonyl bridge connecting the two furan rings. A condensation reaction of trioxane with 2*M* methyl furoate in conc. sulfuric acid (Scheme 2) was therefore performed according to the literature procedure³ to give, after chromatography and crystallization from ethanol, pure **4** in 37% yield. In an effort to eliminate the use of large quantities of sulfuric acid, the condensation of methyl furoate with trioxane and acetaldehyde in the presence of a strongly acidic cation exchange resin, e.g. amberlyst-15, was explored. Under these conditions only the more reactive trioxane gave the desired coupling product **4**, in a low yield of 21%. Transesterification of **4** with hexanol under the usual reaction conditions gave the long-chain difuran diester **5** in 89% yield (Scheme 2).

The reactive methylene group of **4** was successfully oxidized to a keto-group (Scheme 3) by implementation of a procedure previously reported by Chidambaram and Chandrasekaran.⁶ Treatment of **4** with a 1 : 1 ratio of *tert*-butyl hydroperoxide and pyridinium dichromate⁷ gave the keto-diester **6**, in 52% yield. A relatively large excess of long-chain alcohol had to be used in the transesterification of **6** with 2-ethylhexanol and hexanol in order to solubilize this high melting compound, and the desired diesters **7a** and **7b** were produced in yields of 81 and 63%, respectively, as pure compounds. The structures of the difuran plasticizers were rigorously confirmed by ¹H- and ¹³C-NMR, high resolution mass spectrometry, and in some cases by elemental analyses.

Characterization as Plasticizers

Data Analysis

The results of DMTA are shown in Figures 1–6. 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

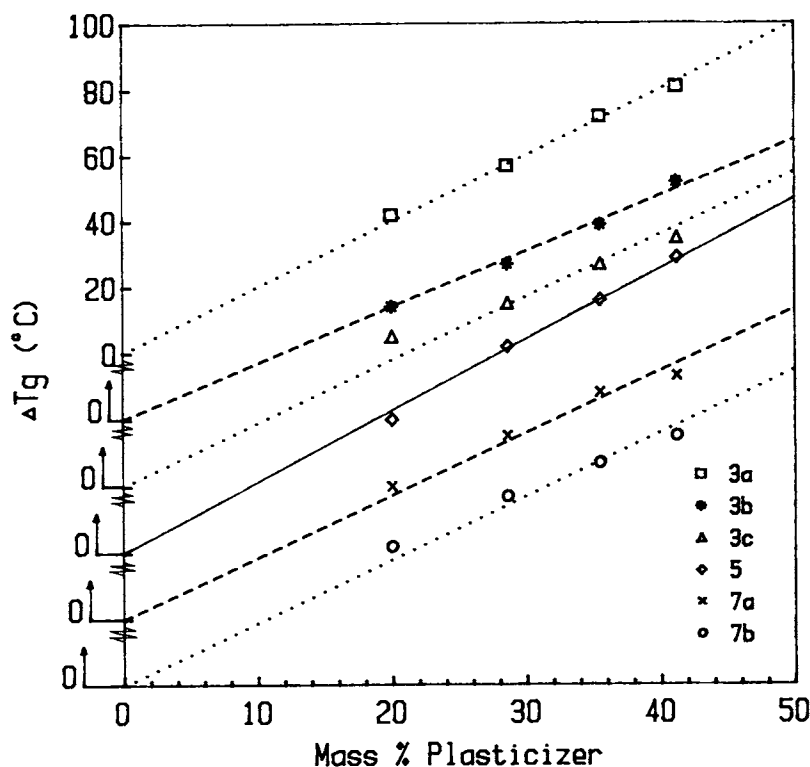


Figure 7

the storage modulus. The linearity of the graph of T_g vs. concentration,⁸ gave a value for the depression of T_g per mass percent plasticizer for each of the materials tested. The glass transition temperature of unplasticized PVC was measured as 87°C, and this value was used as the zero point of the depression of T_g at 0% plasticizer. Further T_g s were measured at plasticizer levels of 25, 40, 55, and 70 phr, giving further values of depression. By plotting depression of T_g vs. mass percent plasticizer, a straight line through the origin and the four data points was obtained for each diester tested (Fig. 7), with the slope equal to the depression of T_g per mass percent plasticizer in °C. Y/x values as well as the standard error for each regression are summarized in Table I. Similar results on furan and difuran diesters that have previously^{1,2} been synthesized and tested by this method are given in Table I, together with an efficiency value for di(2-ethylhexyl) phthalate (DOP), our standard of reference.

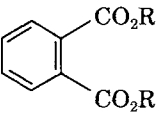
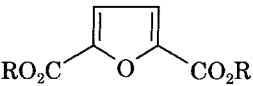
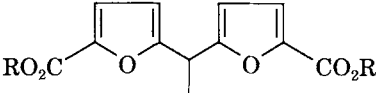
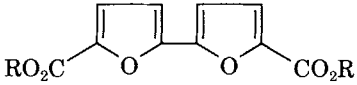
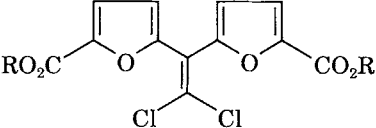
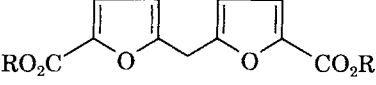
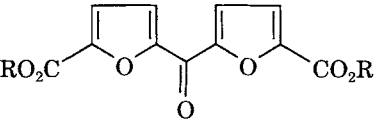
Furthermore it is known that if a plasticizer is miscible with a polymer, a blend of the two should show a single T_g ,⁸ and that sharp transitions suggest good compatibility, while broad transitions are typical of less compatible blends. To quantify this trend, the width at half the height of the maximum of the damping curve ($\tan \delta$) was measured for each sample

in °C (see Figs. 1–6). The damping curves were used because these have good definition in the temperature range over which the glass transition takes place. Samples that exhibited anomaly in their damping curves were disregarded, i.e. 25 phr **3c** 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 to obtain dimensionless compatibility numbers vs. DOP, for example: width at half height for DOP at 55 phr, 38°C; width at half height for **3b** at 55 phr, 27°C; and compatibility number vs. DOP at 55 phr, 38°C/27°C = 1.41.

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. Three or four compatibility numbers (different concentrations) vs. DOP were obtained for each difuran diester. The average gives one numerical quantity, and an increasing value indicates higher compatibility toward polyvinyl chloride (PVC). The results are shown in Table 1.

Solubility parameters of the four liquid plasticizers were calculated according to the method of Small,^{9,10} 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

Table I

Compound	R =	Efficiency $\Delta T_g/\text{Mass } \%$	Compatibility (DMTA)	Density	Solubility Parameter δ	$\delta - \delta_{\text{pvc}}$
						
DOP	2-Ethylhexyl	2.45 ± 0.6	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			
						
(v)	2-Ethylhexyl	2.04 ± 0.08	0.95	1.027	9.6	-0.1
(vi)	2-Octyl	1.83 ± 0.07	1.00	1.020	9.6	0.0
(vii)	Hexyl	2.33 ± 0.11	0.98	1.054	10.0	-0.4
(viii)	Butyl	2.18 ± 0.10	1.27	1.102	10.4	-0.9
						
(ix)	Hexyl	2.11 ± 0.19	1.11			
						
3a	2-Ethylhexyl	2.00 ± 0.10	1.27	1.120	9.9	-0.3
3b	Hexyl	1.70 ± 0.10	1.31	1.167	10.3	-0.8
3c	Butyl	1.90 ± 0.28	1.62	1.221	10.7	-1.1
						
5	Hexyl	2.14 ± 0.11	1.22	1.069	10.1	-0.6
						
7a	2-Ethylhexyl	1.87 ± 0.19	1.61			
7b	Hexyl	1.90 ± 0.21				

density of furan.¹⁰ An averaged value of 9.55 was used as solubility parameter for PVC.⁹⁻¹¹

Discussion

The chlorinated compounds **3a**, **3b**, and **3c**, and the methane-bridged **5** are clear, viscous oils that are fluorescent under UV light; the ketones **7a** and **7b** are white solids, with melting points 62.5 and 90°C, respectively. At temperatures above 230°C some thermal degradation occurred during the high vacuum distillation of **3a**, **3b**, and **3c**, giving a reddish tone to these compounds. This tone persisted in the final plasticized articles. Some color formation was also observed on plasticization of PVC with the ketones **7a** and **7b** and the methane-bridged **5**. The series **3a-3c** and **7a** and **7b** are devoid of reactive hydrogen substituents α to the furan ring. It can therefore be inferred that although homolytic interaction of such reactive hydrogens probably does contribute to color development during processing, this cannot be the only mechanism by which this occurs. No stabilizers had been added to the plasticizer-resin preparations. PVC samples plasticized with the hexyl substituted ketone **7b** (mp 90°C) had clouded up and stiffened a month after plasticization, and were heated at 100°C for 2 min before scanning as usual.

The DMTA data in Figures 1-4 and 6 illustrates that PVC that has been plasticized by the three chlorinated diesters, the keto diester **7a**, and the methane-bridged **5**, display viscoelastic behavior typical of a compatible composition. The high-melting ketone **7b** provides an exception (Fig. 6), as each concentration exhibits two maxima in its damping curve ($\tan \delta$). These are difficult to assign. For the remainder of the compounds, in each of the storage and loss modulus curves there is one main event, namely the glass transition, that is followed by a badly 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 five functionalized difuran diesters are to various extents less efficient in lowering T_g than DOP, the standard of reference. This is partly attributed to higher molecular weight, which tends to favor a lower plasticizing efficiency.^{12,13} A factor that further lowers the efficiency is the stiffness of the two furan rings when connected by keto and dichloroethene bridging groups with ensuing conjugation. Ethane or methane bridging groups rotate freely (sp³ hybridized), and the free

volume created in these more mobile systems has a positive effect on plasticizing efficiency.

The glass transitions of the keto- and chlorinated diesters, as represented by their compatibility numbers, are sharp when compared to those of the non-functionalized furan diesters or DOP (Table I). The keto- and chlorinated diesters evidently form intimate systems of plasticizer and resin, as the extra polarity imparted by the functional groups leads to greater solvency in, and hence compatibility with, the polar PVC resin. In the case of the keto-diester **7b** (mp 90°C), however, plasticization is visibly not permanent. Here the plasticizer's intermolecular forces are stronger than the plasticizer-resin forces, and at room temperature there is slow crystallization of the plasticizer in pockets in the PVC resin, resulting in clouding up and stiffening of the plastic.

The general DMTA prediction of good compatibility between the difuran diesters and PVC is confirmed by inspection of the differences in solubility parameter between PVC and those in **3a**, **3b**, **3c**, and **5** (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 or close to 1 δ -unit of that of PVC, predicting high compatibility.

CONCLUSION

We synthesized and tested as plasticizers for PVC three chlorinated, two keto, and one alkyl difuran diester. It was ascertained that the functionalized diesters are considerably more soluble in the polar PVC resin than their nonfunctionalized analogs, but the efficiency of these compounds in lowering T_g is less. The methane-bridged compound exhibited efficiency and compatibility data comparable to that of other alkyl difuran diesters.

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