

Synthesis and Evaluation of Dialkyl Furan-2,5-Dicarboxylates as Plasticizers for PVC

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SYNOPSIS

Di(2-ethylhexyl), di(2-octyl), dihexyl, and dibutyl furan-2,5-dicarboxylate were synthesized from furfural and characterized for their plasticizing abilities toward PVC by dynamic mechanical thermal analysis (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 for DOP, which describe the compatibility of the furan diesters with PVC. The efficiency in lowering T_g as exhibited by di(2-ethylhexyl) furan-2,5-dicarboxylate is similar to that of its benzenoid analog, DOP, and was determined at 2.41 and 2.45°C per mass % plasticizer, respectively. All four furan diesters were found to be more compatible toward PVC than toward DOP, with dibutyl furan-2,5-dicarboxylate the most highly compatible.

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INTRODUCTION

Furfural is a valuable chemical that can be obtained in good yields¹⁻³ from plant residues such as sugar cane bagasse, oat hulls, corn husks, or wood. Considering that these raw materials are renewable and largely underutilized, the use of furan derivatives for the polymer industry becomes an attractive alternative to petroleum-based technologies. World production of furfural is constrained by the limited demand for this compound, but production can be significantly expanded if new markets for furfural or its derivatives can be established.

The present investigation deals with the synthesis of several long-chain furan diesters from furfural and the evaluation of these diesters as plasticizers for PVC. An incentive was whether an improvement would be realized in the plasticizing ability as a result of the polarity of the furan ring as compared to the benzene ring in conventional plasticizers. Application of the furan moiety as a functional element in a plasticizer for PVC is novel, and in order to compare its behavior to that of the benzene moiety, we

initially synthesized and evaluated di(2-ethylhexyl) furan-2,5-dicarboxylate, a molecule possessing a structure related to that of di(2-ethylhexyl)phthalate, the well-established plasticizer known as DOP. Thermal analysis, in particular, DMTA, was the chosen technique for evaluating the plasticizing abilities of the furan diesters toward PVC.

EXPERIMENTAL

Instrumentation and Materials

Melting points were determined on a Gallenkamp melting-point apparatus; melting and boiling points are uncorrected. Nuclear magnetic resonance spectra were measured in deuteriochloroform relative to tetramethylsilane as the 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

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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. Paste PVC resin, Lucovyl PB 1702, was plasticized on an Apex hydraulic press, and DMTA scans were run on a PL dynamic mechanical and thermal analyzer in the shear mode at a heating rate of 5°C/min.

Syntheses

Methyl Furoate 2

A mixture of furoic acid⁴ (8.94 g, 79.7 mmol), amberlyst-15 (12.8 g), and methanol (80 mL) was refluxed for 10 h. The amberlyst-15 was removed by filtration and washed with ether (150 mL) and the solvents from the combined filtrates removed by distillation. Treatment of the residue with saturated, aqueous sodium hydrogen carbonate (30 mL) was followed by extraction with ether (2 × 30 mL), the combined extracts washed with water (30 mL) and dried (MgSO₄), and the solvent evaporated to yield methyl furoate **2** (7.75 g, 77%), bp 83°C at 19 mmHg (lit., Ref. 5, 83°C at 19 mmHg).

Di(2-ethylhexyl)furan-2,5-dicarboxylate 6a

A mixture of dimethyl furan-2,5-dicarboxylate^{6,7} (4.56 g, 24.8 mmol), 2-ethylhexanol (12.90 g, 99.1 mmol), potassium carbonate (1.37 g, 9.9 mmol), and benzyltrimethylhexadecylammonium chloride (0.41 g, 0.99 mmol)⁸ was stirred in a reaction flask fitted with a Vigreux column for 4 h at 90°C (oil-bath temp) under vacuum (60 mmHg). Progression of the transesterification was monitored by TLC on silica gel with ether-petroleum ether (1 : 1) as the 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 of 2-ethylhexanol removed by distillation under vacuum. Chromatography of the brown residue on the silica gel yielded upon elution with ether-petroleum ether (1 : 9) di(2-ethylhexyl)furan-2,5-dicarboxylate **6a** (7.73 g, 82.1%), bp 190–200°C (air-bath temp) at 8 × 10⁻⁶ mmHg, *d* 0.994, *n*_D²³ 1.4779, δ H 0.901 (6 H, t, J 7.0 Hz, 2 × CH₃), 0.934 (6 H, t, J 7.5 Hz, 2 × CH₃), 1.26–1.48 (16 H, m, 8 × CH₂), 1.713 (2 H, h, J 6.1 Hz, 2 × CH), 4.225 (2 H, dd, J 10.9, 6.0 Hz, 2 × OCH), 4.269 (2 H, dd, J 10.9, 5.7 Hz, 2 × OCH), and 7.179 (2 H, s, 2 × =CH); δ C 118.13 (C-4), 147.20 (C-5), 158.13 (C-6), 67.83 (C-7), 39.06 (C-

8), 30.60 (C-9), 29.09 (C-10), 23.07 (C-11), 14.05 (C-12), 24.02 (C-13), and 11.07 (C-14).

Found: M⁺, 380.2562. C₂₄H₃₆O₅ requires M, 380.2563.

Di(2-octyl)furan-2,5-dicarboxylate 6b

A mixture of dimethyl furan-2,5-dicarboxylate^{6,7} (4.00 g, 21.7 mmol), 2-octanol (11.31 g, 86.8 mmol), potassium carbonate (1.20 g, 8.6 mmol), and tetrabutylammonium hydrogen sulfate (0.30 g, 0.86 mmol)⁸ was stirred for 10 h at 100°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 **6a**, chromatographed on silica gel, and eluted with ether-petroleum ether (1 : 9) to give di(2-octyl)furan-2,5-dicarboxylate **6b** (6.91 g, 83.7%), bp 190–200°C (air-bath temp) at 5 × 10⁻⁶ mmHg, *d* 0.986, *n*_D²³ 1.4744, δ H 0.876 (6 H, t, J 6.8 Hz, 2 × CH₃), 1.333 (6 H, d, J 6.2 Hz, 2 × CH₃), 1.20–1.42 (16 H, m, 8 × CH₂), 1.67–1.77 (4 H, m, 2 × CH₂), 5.147 (2 H, sx, J 6.3 Hz, 2 × OCH), and 7.161 (2 H, s, =CH); δ C 117.93 (C-4), 147.34 (C-5), 157.85 (C-6), 72.77 (C-7), 35.96 (C-8), 25.40 (C-9), 29.13 (C-10), 31.75 (C-11), 19.99 (C-12), 14.05 (C-13), and 22.60 (C-14).

Found: M⁺, 380.2562. C₂₄H₃₆O₅ requires M, 380.2563.

Dihexyl Furan-2,5-dicarboxylate 6c

A mixture of dimethyl furan-2,5-dicarboxylate^{6,7} (2.58 g, 14.0 mmol), hexanol (5.77 g, 56.5 mmol), potassium carbonate (0.78 g, 5.6 mmol), and tetrabutylammonium hydrogen sulfate (0.19 g, 0.56 mmol)⁸ was stirred for 5 h at 100°C (oil-bath temp) under vacuum (180 mmHg) in a reaction flask fitted with a Vigreux column. The reaction mixture was worked up as for **6a**, chromatographed on silica gel, and eluted with ether-petroleum ether (1 : 9), yielding the diester **6c** (3.63 g, 80.0%), which could be recrystallized from hexane to give pure dihexyl furan-2,5-dicarboxylate **6c**, mp 31.4–32.2°C, δ H 0.900 (6 H, t, J 7.1 Hz, 2 × CH₃), 1.27–1.45 (12 H, m, 6 × CH₂), 1.756 (4 H, qn, J 7.1 Hz, 2 × CH₂), 4.327 (4 H, t, J 6.8 Hz, 2 × OCH₂), and 7.189 (2 H, s, 2 × =CH); δ C 118.21 (C-4), 147.07 (C-5), 158.17 (C-6), 65.69 (C-7), 28.65 (C-8), 25.59 (C-9), 31.47 (C-10), 22.57 (C-11), and 14.00 (C-12).

Found: C, 66.55%; H, 8.15%; M⁺, 324.1908. C₁₈H₂₈O₅ requires C, 66.65%; H, 8.7%; M, 324.1937.

Dibutyl Furan-2,5-dicarboxylate 6d

A mixture of dimethyl furan-2,5-dicarboxylate^{6,7} (3.00 g, 16.3 mmol), butanol (4.83 g, 65.2 mmol),

potassium carbonate (0.900 g, 6.5 mmol), and tetrabutylammonium hydrogen sulfate (0.221 g, 0.6 mmol)⁸ was stirred for 8 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 **6a**, chromatographed on silica gel, and eluted with ether-petroleum ether (1 : 9), yielding the diester **6d** (3.03 g, 69.4%), which could be recrystallized from hexane to give pure *dibutyl furan-2,5-dicarboxylate* **6d**, mp 41.5–42.5°C, δ H 0.970 (6 H, t, J 7.4 Hz, 2× CH₃), 1.451 (4 H, sx, J 7.5 Hz, 2× CH₂), 1.747 (4 H, qn, J 7.2 Hz, 2× CH₂), 4.339 (4 H, t, J 6.7 Hz, 2× OCH₂), and 7.189 (2 H, s, 2× =CH); δ C 118.21 (C-4), 147.06 (C-5), 158.18 (C-6), 65.39 (C-7), 30.72 (C-8), 19.17 (C-9), and 13.71 (C-10).

Found: C, 62.95%; H, 7.05%; M⁺, 268.1307. C₁₄H₂₀O₅ requires C, 62.65%; H, 7.5%; M, 268.1311.

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 furan diesters as well as from DOP. 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 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°C and 5 MPa in the press to anneal.

RESULTS AND DISCUSSION

Syntheses

The key step in the viable synthesis of long-chain furan diesters from furfural is obviously substitution at C-5 of the furan nucleus. The direct hydroxy-methylation of either furfural or furfuryl alcohol with formaldehyde under acid catalysis was not regarded as a viable option due to the ease with which these materials polymerize in acidic media,⁹ and the more stable methyl furoate was therefore chosen as the starting material.

The first step toward the synthesis of methyl furoate was the oxidation of furfural to furoic

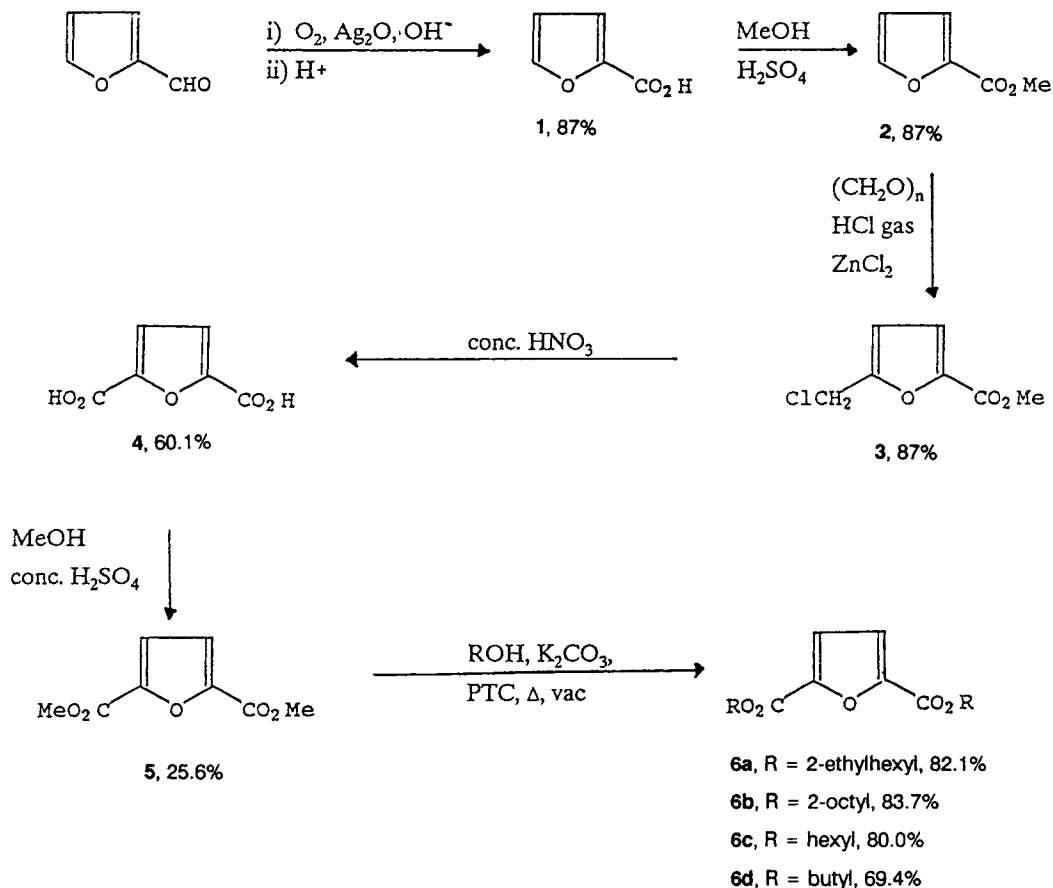
acid (Scheme 1), which can be carried out according to a large number of reported literature procedures.^{4,10–21} We found the oxidation of furfural with oxygen and silver oxide as the catalyst in aqueous alkaline solution⁴ to be a very convenient and high-yielding method, producing furoic acid **1** in 87% yield after recrystallization from carbon tetrachloride. The silver oxide was recirculated with no loss in yield of furoic acid. A high-purity product was also obtained by oxidizing furfural directly with silver oxide under phase-transfer catalysis¹⁴ to give furoic acid in 85% yield after recrystallization. Base-catalyzed Cannizzaro condensation of furfural^{22,23} gave in our hands an unsatisfactory yield of 25% furoic acid with a concomitant formation of furfuryl alcohol (36%). Although methyl furoate **2** could be synthesized in high yield (87%) according to the standard acid-catalyzed esterification procedure,^{6,7} the strongly acidic ion-exchange resin, Amberlyst-15, was conveniently utilized instead of sulfuric acid.

The next step in our synthetic scheme, the regioselective chloromethylation of methyl furoate at the five position, was effected by passing a stream of gaseous hydrochloric acid through a reaction mixture comprising methyl furoate, paraformaldehyde, and zinc chloride in chloroform, producing methyl 5-chloromethylfuroate **3** in 87% yield, which is in good agreement with literature reports.^{6,24–28} Oxidation of **3** with concentrated nitric acid^{6,24–28} gave furan-2,5-dicarboxylic acid **4** in 60% yield. Acid-catalyzed diesterification of crude **4** gave pure dimethyl-2,5-furandicarboxylate^{6,7} **5** in 26% yield only after repeated crystallization from a mixture of benzene and hexane.

The potentially difficult transesterifications^{29,30} of dimethyl-2,5-furandicarboxylate were efficiently effected in the presence of solid potassium carbonate under phase-transfer conditions with no added solvent.³⁰ The absence of solvent allows the reaction to be performed under vacuum and the continuous removal of the generated methanol resulted in a complete shift of the reaction equilibrium toward the long-chain esters that were produced in satisfactory-to-excellent yields. Confirmation of the proposed structures of the potential plasticizers was derived from ¹H- and ¹³C-NMR, high-resolution mass spectroscopy data and elemental analyses.

Characterization as Plasticizers: Data Analysis

The results of dynamic mechanical and thermal analysis, or 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



Scheme 1

as the onset temperature of the glass transition in the storage modulus. The linearity of the graph T_g vs. plasticizer concentration^{31,32} gave a value for the depression of T_g per mass percent plasticizer for each of the materials tested. The glass transition 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 vs. 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 °C. Y/x values as well as the standard error for each regression are summarized in Table I.

Furthermore, it is known that if a plasticizer is miscible with a polymer, a blend of the two should show a single T_g ,³¹ and that sharp transitions suggest good compatibility, whereas broad transitions are typical of less compatible blends. To quantify this trend, we measured the width at half-height of the maximum of the damping peak (tan delta) for each

sample in °C (see Figs. 1–5). The damping curves were used as these have a good definition in the temperature range over which the glass transition takes place. The sample 25 phr **6a** (Fig. 2) exhibited anomaly in its damping curve and was disregarded. 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 vs. DOP, e.g.:

Width in at half-height for DOP at 55 phr	38°C
Width in at half-height for 6a at 55 phr	34°C
Compatibility number vs. DOP at 55 phr	$38^\circ\text{C}/34^\circ\text{C} = 1.12$

By this method, three or four compatibility numbers (different concentrations) vs. DOP were obtained for each furan diester. Their average gives one numerical quantity, where an increasing value indicates higher compatibility toward PVC. The results are shown in Table I.

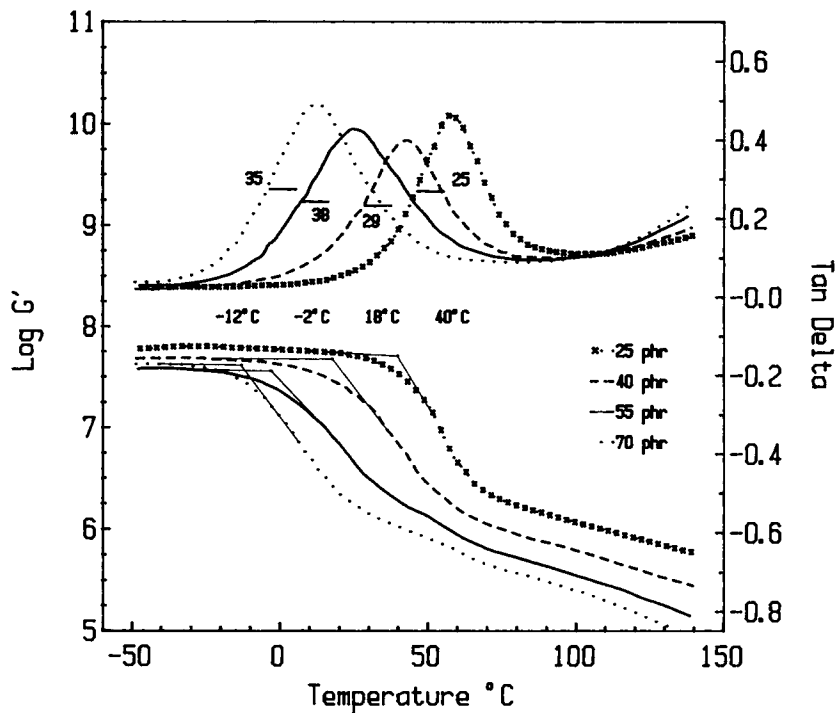


Figure 1 DMTA data for DOP. The storage moduli (lower set of curves) are drawn on the left y-axes ($\log G'$), and the determined T_g values are indicated. Loss moduli (tan delta) are drawn on the right y-axes, and the width (in °C) at half-height of the damping peak is indicated for each sample.

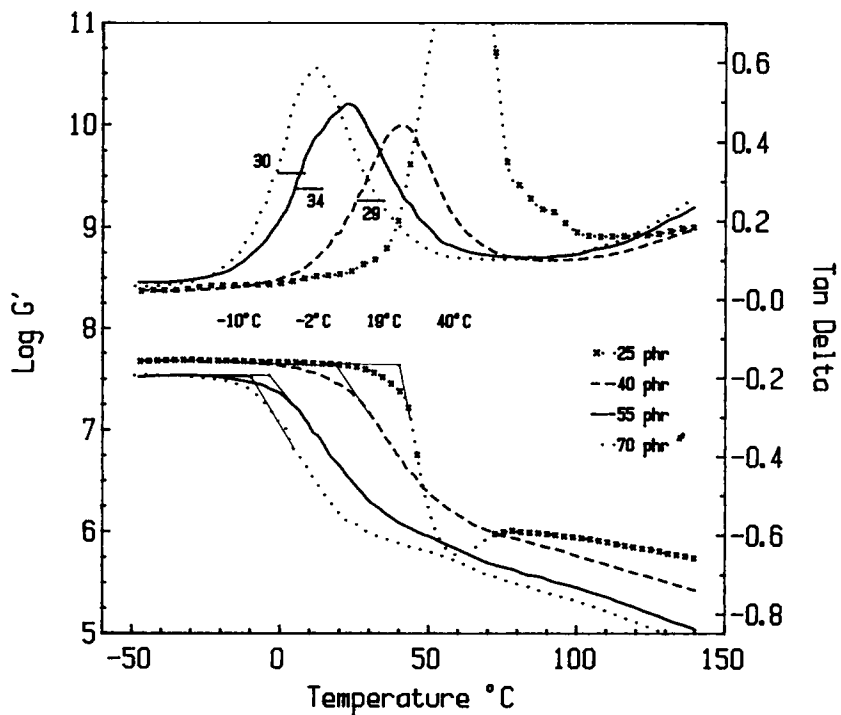


Figure 2 DMTA data for 6a. The storage moduli (lower set of curves) are drawn on the left y-axes ($\log G'$), and the determined T_g values are indicated. Loss moduli (tan delta) are drawn on the right y-axes, and the width (in °C) at half-height of the damping peak is indicated for each sample.

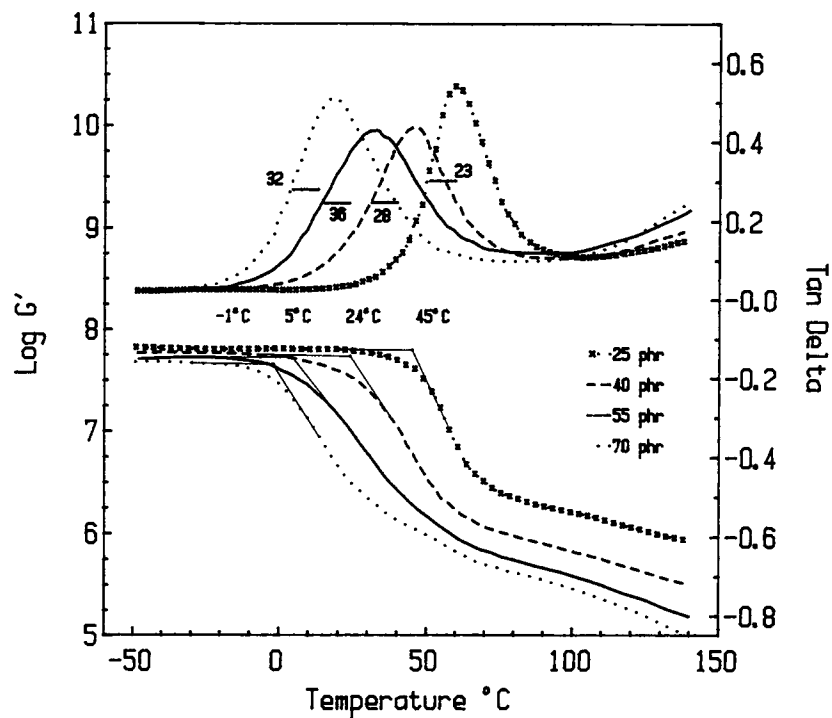


Figure 3 DMTA data for **6b**. The storage moduli (lower set of curves) are drawn on the left y-axis ($\log G'$), and the determined T_g values are indicated. Loss moduli (tan delta) are drawn on the right y-axis, and the width (in $^{\circ}\text{C}$) at half-height of the damping peak is indicated for each sample.

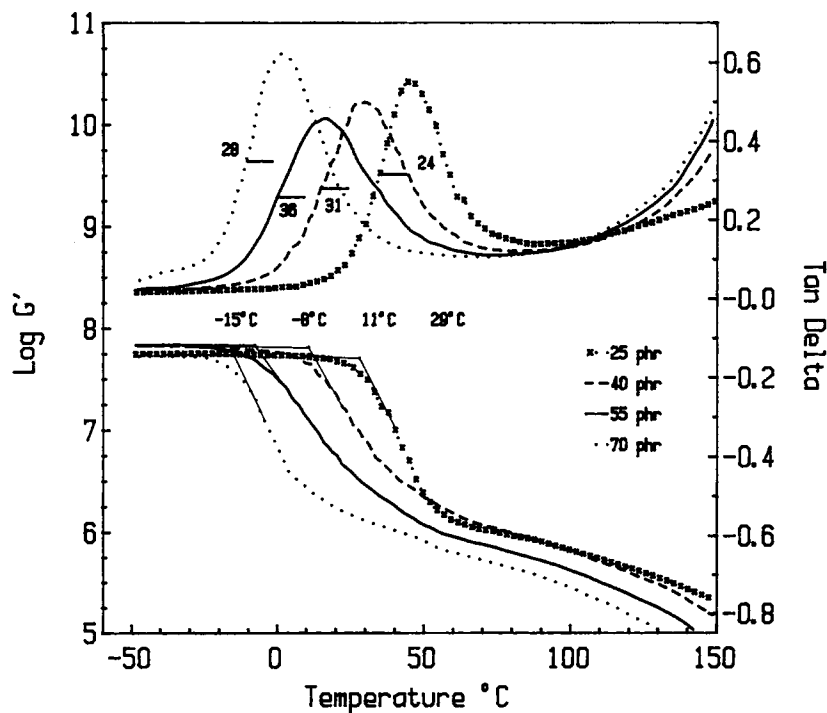


Figure 4 DMTA data for **6c**. The storage moduli (lower set of curves) are drawn on the left y-axis ($\log G'$), and the determined T_g values are indicated. Loss moduli (tan delta) are drawn on the right y-axis, and the width (in $^{\circ}\text{C}$) at half-height of the damping peak is indicated for each sample.

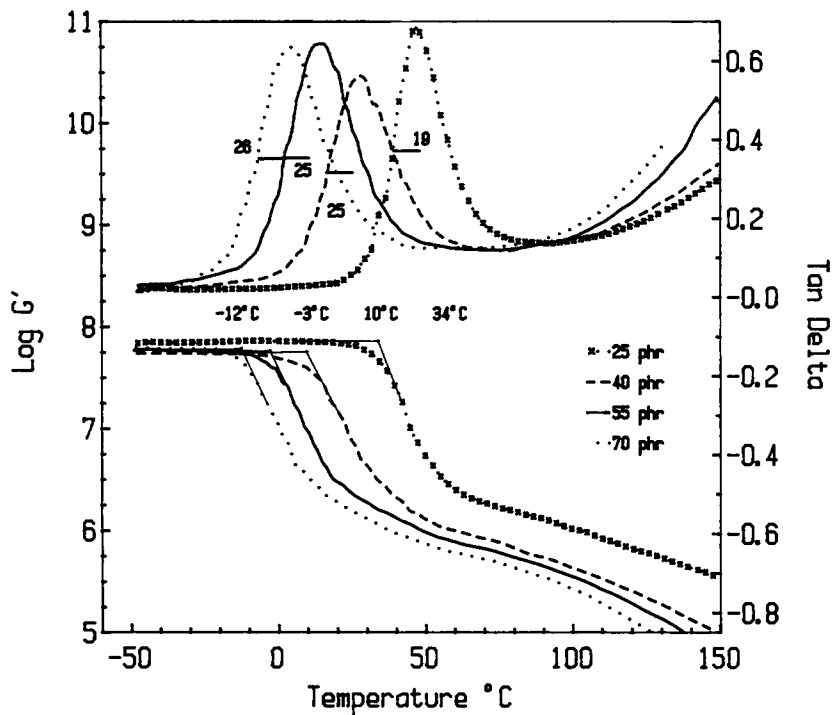


Figure 5 DMTA data for 6d. The storage moduli (lower set of curves) are drawn on the left y-axis ($\log G'$), and the determined T_g values are indicated. Loss moduli (tan delta) are drawn on the right y-axis, and the width (in $^{\circ}\text{C}$) at half-height of the damping peak is indicated for each sample.

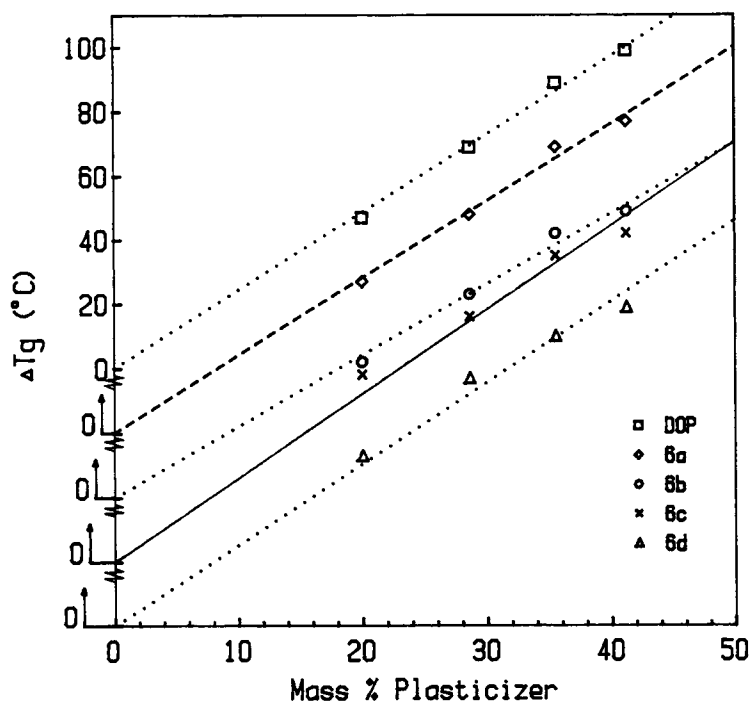
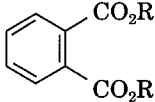
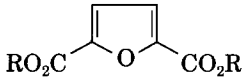


Figure 6 Processing of DMTA data: Depression of T_g vs. mass % plasticizer. For clarity, each plasticizer is represented with its own y-axis. Y/x values as well as the standard error for each regression are summarized in Table I.

Table I Summary of the Relative T_g Lowering Efficiency, Compatibility, and the Difference in Solubility Parameter Displayed by DOP and the Furan Diesters **6a-d** Toward PVC

Compound	R =	Efficiency (ΔT_g /mass %)	Compatibility (DMTA)	Solubility Parameter δ	$\delta - \delta_{PVC}$	
	DOP	2-Ethylhexyl	2.45 ± .06	1.00	8.9	0.7
	6a	2-Ethylhexyl	2.41 ± .08	1.09	9.3	0.2
	6b	2-Octyl	2.23 ± .08	1.07	9.2	0.4
	6c	Hexyl	2.52 ± .14	1.07		
	6d	Butyl	2.45 ± .12	1.34		

Solubility parameters for the liquid plasticizers were calculated according to the method of Small^{33,34} and are also given in Table I. It was necessary to obtain a molar attraction constant for the furan ring, and a value of $673 \text{ (cal/cm}^3)^{1/2} \text{ mol}^{-1}$ was computed from the known solubility parameter and density of furan.³⁴ An averaged value of 9.55 (Refs. 33–35) was used as the solubility parameter for PVC.

DISCUSSION

The furan diesters **6a** and **6b** are odorless, clear oils, whereas **6c** and **6d** are low-melting white solids. **6a** and **6b** are thermally stable, as illustrated by their distillation at high temperature, and they display the unusual characteristic of being fluorescent under UV light. On the plasticization of PVC with the furan diesters, some color formation was observed and pure **6a** and **6b** discolored to light red or yellowish oils on long exposure to air and light. No stabilizers had been added.

From the DMTA curves displayed in Figures 1–5, it is obvious that PVC which has been plasticized by the long-chain furan diesters displays viscoelastic behavior closely comparable to that of DOP. In each of the storage and loss modulus curves, the main event is the glass transition, which is followed by an ill-defined rubbery plateau and an area of elastic or rubbery flow. Table I shows that DOP and the 2-ethylhexyl-substituted plasticizer **6a** are very similar in their efficiency in lowering T_g , revealing that there is no great difference in the behavior of benzene and furan rings as regards this application. We do, how-

ever, find that the 2-ethylhexyl-substituted plasticizer **6a** is more efficient in lowering T_g than is the 2-octyl substituted **6b**. The two compounds are of equal molecular mass, but where the ester group in **6a** is connected to a primary carbon, that of **6b** is connected to a secondary one. The lower plasticizing efficiency of **6b** may be attributed to some inhibition in the free rotation around this ester bond, giving a less flexible compound less able to create free volume. In the homologous DOP and di(2-octyl)phthalate (DCP), it is also DCP that exhibits less efficiency.³⁶ We furthermore find that the hexyl-substituted **6c** is the most efficient in lowering T_g of all five plasticizers tested, and the butyl-substituted **6d** is less efficient than is **6c**. The value for **6d** is surprising as it is contrary to the general trend that a decrease in the molecular mass of a plasticizer leads to an increase in plasticizing efficiency.^{32,36}

From Table I it is seen that of the structurally related diesters **6a** and DOP, **6a** has the higher compatibility toward PVC. This is expected as the furan ring is more polar than is the benzene ring, leading to greater solvency in the polar PVC resin. As we move down in the range from the octyl-substituted **6a** and **6b** to the hexyl-substituted **6c** and the butyl-substituted **6d**, there is an increase in the aromatic relative to aliphatic character of the molecular structure and, therefore, also an increase in polar character. Accordingly, there is an increase in compatibility from compounds **6a** and **6b** to **6c**, and the butyl-substituted **6d** is very highly compatible.

The general DMTA prediction of good compatibility between the furan diesters and PVC is sec-

onded by inspection of the difference in the solubility parameter between PVC and that of DOP, **6a** and **6b** (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 the three values to be within 1 δ -unit of that of PVC, predicting high compatibility. Once again, it appears that the two furan diesters are the most compatible toward PVC.

To conclude, then, four long-chain furan diesters have been synthesized using furfural as starting material and their plasticizing abilities toward PVC evaluated using di-(2-ethylhexyl)phthalate (DOP) as the standard of reference. In terms of efficiency, no major improvement is seen by substituting a furan for a benzene ring, but an improvement over DOP in compatibility is shown by all the furan diesters, especially by the butyl substituted **6d**. An investigation concerning the syntheses and evaluation as plasticizers of compounds incorporating two furan rings in the plasticizer backbone will be addressed in a subsequent publication.

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REFERENCES

- H. F. Mark, N. M. Bikales, C. G. Overberger, G. Menges, and J. I. Kroschwitz, Eds., *Encyclopedia of Polymer Science and Engineering*, 2nd ed., Wiley, New York, 1987, Vol. 7, pp. 454–473.
- M. Baoqi and J. Shuying, *J. Cell. Chem. Technol.*, **23**, 277 (1989).
- A. Gandini, *Adv. Polym. Sci.*, **25**, 47 (1977).
- R. Andrisano, *Boll. Sci. Fac. Chim. Ind. Bologna*, **7**, 66 (1949); *Chem. Abstr.*, **44**, 9404h (1950).
- R. C. Weast, *CRC Handbook of Chemistry and Physics*, 67th ed., CRC Press, Boca Raton, FL, 1986.
- V. I. Lutkova and N. N. Shmagina, *Plast. Massy*, **4**, 56 (1960); *Chem. Abstr.*, **55**, 502d (1961).
- G. Gonis and E. D. Amstutz, *J. Org. Chem.*, **27**, 2946 (1962).
- J. Barry, G. Bram, and A. Petit, *Tetrahedron Lett.*, **29**, 4567 (1988).
- A. Madzhidov, A. Abduvaliev, and A. S. Sultanov, *Uzbeksk. Khim. Zh.*, **9**, 72 (1965); *Chem. Abstr.*, **63**, 4232b (1965).
- H. Arita and T. Odawara, *Jpn. Pat.* 1130/1950; *Chem. Abstr.*, **47**, 2214d (1953).
- V. A. Zverev and V. I. Mil'man, *Elektrokhimiya*, **16**, 1867 (1980); *Chem. Abstr.*, **94**, 54844n (1981).
- H. Baba, *Kagaku Kenkyusho Hôkoku*, **33**, 168 (1957); *Chem. Abstr.*, **52**, 7267g (1958).
- K. Nakagawa, S. Mineo, and S. Kawamura, *Chem. Pharm. Bull.*, **26**, 299 (1978).
- S. Julia, A. Ginebra, and J. Pallas, *Afinidad*, **36**, 326 (1979); *Chem. Abstr.*, **92**, 93483x (1980).
- H. V. Udupa, K. S. Udupa, and D. C. Trivedi, *Indian IN 156 218/1985*; *Chem. Abstr.*, **105**, 14284u (1986).
- V. Prabha, S. K. Gupta, M. Kohli, and K. G. Gupta, *Res. Bull. Panjab Univ. Sci.*, **37**, 87 (1986); *Chem. Abstr.*, **107**, 3981j (1987).
- Z. Csürös, R. Soós, E. Fogassy, and G. T. Szabó, *Period. Polytech. Chem. Eng.*, **18**, 249 (1974).
- D. K. Mansurova and K. M. Makhkamov, *Mater. Resp. Nauchno-Tekh. Konf. Molodykh. Uch. Pererab. Nefti Neftekhim.*, **1**, 105 (1976); *Chem. Abstr.*, **89**, 179769v (1978).
- T. Wei, C. Zhao, Y. Li, J. Zhang, and W. Yan, *Shanxi Daxue Xuebao, Ziran Kexueban*, **29**, 102 (1985); *Chem. Abstr.*, **104**, 209132e (1986).
- D. Dinelli, *Ann. Chim. Appl.*, **29**, 448 (1939); *Chem. Abstr.*, **34**, 19037 (1940).
- A. P. Dunlop, U.S. Pat. 2,407,066 (1942).
- B. S. Funiss et al., *Vogel's Textbook of Practical Organic Chemistry*, 4th ed., Longman, London, 1984, p. 792.
- C. E. Carraher, *J. Chem. Ed.*, **55**, 269 (1978).
- O. Moldenhauer, G. Trautmann, W. Irion, R. Pfluger, H. Döser, D. Mastaglio, and H. Marwitz, *Liebigs Ann. Chem.*, **580**, 169 (1953).
- Y. Hachihama, T. Shono, and K. Hyono, *Technol. Rep. Osaka Univ.*, **8**, 475 (1958); *Chem. Abstr.*, **53**, 18933h (1959).
- A. Tundo, *Boll. Sci. Fac. Chim. Ind. Bologna*, **14**, 63 (1956); *Chem. Abstr.*, **51**, 5748g (1957).
- R. Andrisano, *Boll. Sci. Fac. Chim. Ind. Bologna*, **7**, 58 (1949); *Chem. Abstr.*, **44**, 9404d (1950).
- R. Andrisano, *Ann. Chim.*, **40**, 30 (1950); *Chem. Abstr.*, **45**, 7563a (1951).
- J. A. Abedi and N. M. Roscher, *Synth. Commun.*, **19**, 1539 (1989).
- J. Barry, G. Bram, and A. Petit, *Tetrahedron Lett.*, **29**, 4567 (1988).
- H. E. Bair, in *Thermal Characterization of Polymeric Materials*, E. A. Turi, Ed., Academic Press, New York, 1981, pp. 878–884.
- J. R. Darby and J. K. Sears, in *Encyclopedia of PVC*, L. I. Nass, Ed., Marcel Dekker, New York, 1976, Vol. 1, pp. 451–452.
- P. A. Small, *J. Appl. Chem.*, **3**, 71 (1953).
- J. Brandrup and E. H. Immergut, *Polymer Handbook*, 2nd ed., Wiley, New York, 1975, pp. IV–337.
- J. R. Darby and J. K. Sears, in *Encyclopedia of PVC*, L. I. Nass, Ed., Marcel Dekker, New York, 1976, Vol. 1, pp. 397–405.
- L. J. Krauskopf, in *Encyclopedia of PVC*, L. I. Nass, Ed., Marcel Dekker, New York, 1976, Vol. 1, pp. 518–523.

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