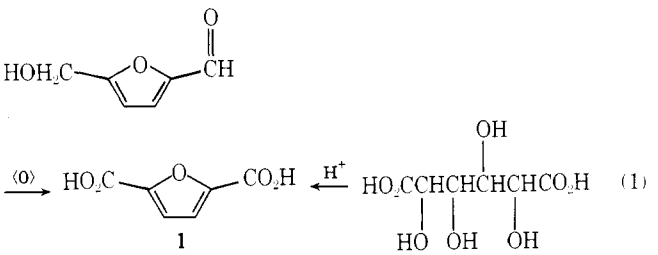
Polyesters Derived from Furan and Tetrahydrofuran Nuclei

J. A. Moore* and J. E. Kelly

Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12181. *Received December 2, 1977*

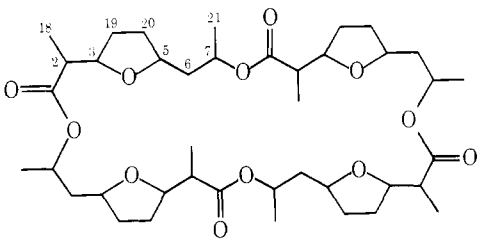
ABSTRACT: Polyesters derived from 2,5-furandicarboxylic acid and 2,5-bis(hydroxymethyl)furan or 1,6-hexanediol, as well as polyesters derived from *cis*- and *trans*-tetrahydrofuran-2,5-dicarboxylic acid and ethylene glycol or *cis*- and *trans*-hydroxymethyltetrahydrofuran have been prepared and characterized. The sensitivity of these heterocyclic monomers to traces of oxygen at high temperatures demonstrated in this work makes solution polymerization the most effective route for the preparation of such polymers. Thermal analysis shows that the polymer with the lowest glass transition temperature (T_g) in the completely reduced furan system is that in which diacid and diol are both of the *cis* configuration.

In view of the constraints placed upon the limited petrochemical resources of the world, it seemed advisable to us to investigate the conversion of plentiful regenerable plant cellulose or cellulose derivatives to intermediates useful for the preparation of polymers. As initial components of interest we chose furan-2,5-dicarboxylic acid (1) and its derivatives. This



material can be prepared by conversion of sucrose[1] or glucose[2] to 5-hydroxymethylfurfural which is then oxidized. Oxidation of glucose to saccharic acid followed by cyclization also yields 1[1] (eq 1).

2,5-Tetrahydrofuran esters are also of biological interest because of the presence of similar structures in nonactin, **2**, a naturally occurring, ion-binding macrocyclic antibiotic.[3-6]



nonactin
2

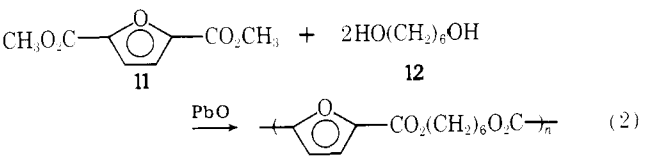
In addition, the stereochemistry of the tetrahydrofuran monomers should have an effect on the physical properties of the saturated polyesters. The all-*trans* polyester should be higher melting and more ordered than the *cis* polyester, because the *trans* polyester would be expected to be more elongated and better able to pack. Polyesters composed of *cis* and *trans* monomers should have physical properties intermediate between the all-*cis* and all-*trans* polymers.

It was the purpose of this work to synthesize, purify, and characterize various 2,5-disubstituted furan and tetrahydrofuran monomers, such as diacids, diols, diesters, and diacid chlorides. These monomers were polymerized using melt-transesterification or solution polymerization techniques. Further study of these polymers is continuing and the results will be reported at a later date.

Results and Discussion

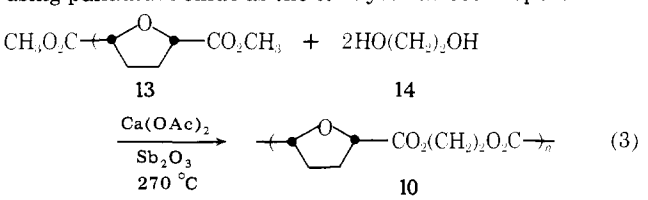
Because the nomenclature[7] of these materials is cumbersome, the structures and names of the polymers will be listed in Table I and for the remainder of this discussion the polymers will be referred to by number.

The first polymerization method attempted for the synthesis of the polymers which are shown in Table I was melt-transesterification. To assess the stability of the diacids to various conditions and types of catalyst systems polymerization with aliphatic diols was done.[8] Lead dioxide was used initially but a polymer was obtained which had $[\eta]^{25}_{CHCl_3}$ 0.17 (eq 2). A mixture of calcium acetate and antimony oxide has been shown to be an effective catalyst for the preparation of poly(ethylene terephthalate)[9] and in this work it was found that **4** could be synthesized as a white fibrous, film-forming



polymer having $[\eta]^{25}_{CHCl_3}$ 0.4 using this catalyst and a maximum temperature of 279 °C. When the temperature was allowed to exceed 300 °C, the resulting polymer had $[\eta]^{25}_{CHCl_3}$ = 0.1.

Because the calcium acetate and antimony oxide catalyst at 279 °C was an effective system for eq 2, this procedure was employed for eq 3. However, under these conditions, a black, insoluble solid was obtained which would only swell in chloroform or hexafluoroisopropyl alcohol. When an oxygen scavenger, triphenylphosphine, was added and the maximum temperature reached only 250 °C the resulting polymer was found to be partially soluble in chloroform or hexafluoroisopropyl alcohol. The soluble polyester had $[\eta]^{25}_{CHCl_3}$ 0.21 and was found to be a tacky semisolid which adheres to glass and metal. The insoluble portion of the polyester was a black gel which would swell in chloroform or hexafluoroisopropyl alcohol. It should be mentioned that the synthesis of **10** from **13** and **14** employing melt-transestification techniques and using palladium oxide as the catalyst has been reported.[8]

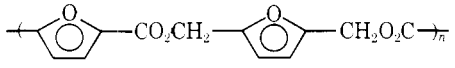


Because ethylene glycol is known to be stable under the conditions of polymerization (eq 2)[9] the observed blackening

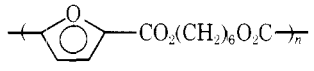
0024-9297/78/2211-0568$01.00/0

Table I
Polymeric Nomenclature and Structure

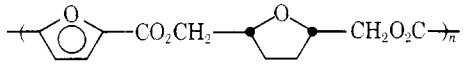
Poly(2,5-furandiylcarbonyloxymethylene-2,5-furandiylmethyleneoxycarbonyl (3)



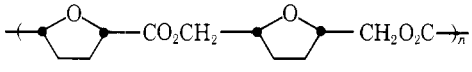
Poly(2,5-furandiylcarbonyloxyhexamethyleneoxycarbonyl (4)



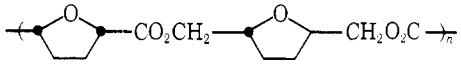
Poly[2,5-furandiylcarbonyloxymethylene(*cis*-tetrahydro-2,5-furandiyl)methyleneoxycarbonyl] (5)



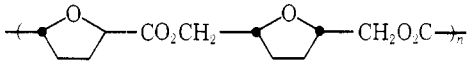
Poly[(*cis*-tetrahydro-2,5-furandiyl)carbonyloxymethylene-(*cis*-tetrahydro-2,5-furandiyl)methyleneoxycarbonyl] (6)



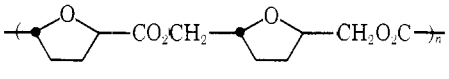
Poly[(*cis*-tetrahydro-2,5-furandiyl)carbonyloxymethylene-(*trans*-tetrahydro-2,5-furandiyl)methyleneoxycarbonyl] (7)



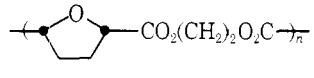
Poly[(*trans*-tetrahydro-2,5-furandiyl)carbonyloxymethylene(*cis*-tetrahydro-2,5-furandiyl)methyleneoxycarbonyl] (8)



Poly[(*trans*-tetrahydro-2,5-furandiyl)carbonyloxymethylene(*trans*-tetrahydro-2,5-furandiyl)methyleneoxycarbonyl] (9)

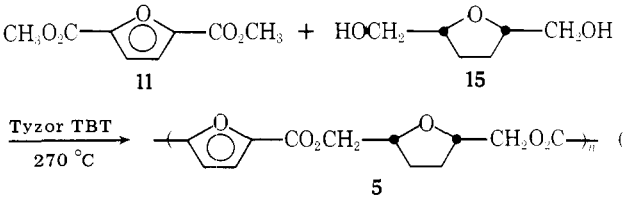


Poly[(*cis*-tetrahydro-2,5-furandiyl)carbonyloxyethyleneoxycarbonyl] (10)

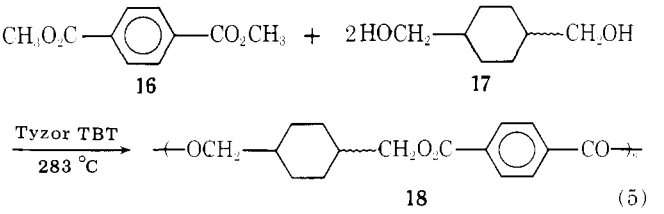


and gellation is most probably caused by instability inherent in the tetrahydrofuran monomer. An oxygen scavenger seemed to impede the gellation and therefore the observed discoloration and cross-linking may be due to oxidative cleavage, most likely involving the hydrogen atoms at the 2 and 5 positions of the heterocyclic ring.

To investigate the assumption that the tetrahydrofuran ring is unstable to the conditions of melt-transesterification further, reaction 4 was performed. Tyzor TBT (*tert*-butyl titanate) was chosen as the catalyst because titanate catalysts have been shown to be effective[10] for reaction 5 which is similar to (4). The product of the heterocyclic system, **6**, was found to be a shiny, black, brittle, insoluble solid. Because the



(4)



(5)

$[\eta]^{30}$ 0.5 in phenol/tetrachloroethane (40:60)[13]

furan diester, **11**, was previously shown to yield a high molecular weight polymer at 270 °C and a soluble polyester even at 300 °C (reaction 2), the observed blackening and cross-linking most probably stems from inherent instability of the tetrahydrofuran ring.

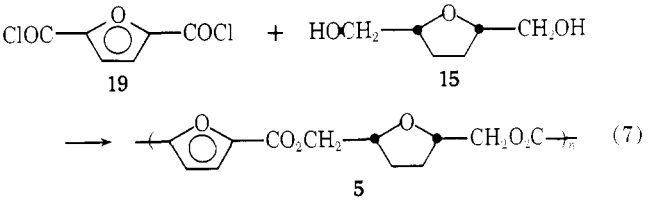
Reaction 6 was also carried out

$$11 + 15 \xrightarrow[230\ °C]{PbO} 5 \qquad (6)$$

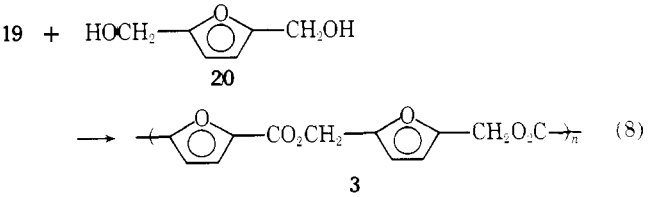
These conditions were milder then those previously described (reaction 4), and a brown, tacky, semisolid material, soluble in chloroform and acetone, was obtained, the intrinsic viscosity of which must be ≤0.07 because of its acetone solubility. [It was found, experimentally, that when polymer **5** had an intrinsic viscosity of 0.07 or greater, it was no longer soluble in acetone (see Table II).] Blackening was observed in this system within the first 3 h of heating at temperatures above 160 °C.

Based on the above polymerization results, it appears that 2,5-disubstituted tetrahydrofuran monomers are not good candidates for melt-transesterification polymerizations unless oxygen is completely excluded and the maximum polymerization temperature is maintained at, or below, 200 °C.

Solution polymerization of diacid chlorides and diols was investigated next. These processes are usually carried out at, or below, room temperature. Therefore, decomposition should not be a problem. The variables which affect this process were examined with several polymers to optimize the polymerization conditions. Reaction 7 was carried out using different solvents and the results of these experiments are summarized in Table II. The highest values for the intrinsic viscosity of polymer **5** were obtained when either chloroform or hexamethylphosphoric acid triamide was used as the polymerization solvent. These two solvents and some others were used in the preparation of polymer **3** [eq 8]. The results of these experiments are shown in Table III.



(7)



(8)

Based on the results shown in Tables II and III, chloroform was chosen as the solvent most useful for all the solution polymerizations. It was found that polymers **4** through **10** were soluble in chloroform. Only two solvents have, as yet, been found for polymer **3** (the intrinsic viscosity of which is equal to or greater than 0.12), hexafluoroisopropyl alcohol or a mixture of phenol and tetrachloroethane (40:60), neither of

Table II
Polymerization of 2,5-Furandicarbonyl Chloride with 2,5-*cis*-Bis(hydroxymethyl)tetrahydrofuran in Various Solvents

Solvent	Base	Temp, °C	$[\eta]^{25}_{CHCl_3}$	Polymer solvents
C_2H_5O-C_2H_5	$(C_2H_5)_3N$	23	0.04[a]	$CHCl_3$
$CHCl_3$	$(C_2H_5)_3N$	23	0.07	CH_3COCH_3 $CHCl_3$, insoluble in CH_3COCH_3
HMPA[b]	$(C_2H_5)_3N$	23		No polymer could be isolated
HMPA		23	0.07	$CHCl_3$

[a] The polymer precipitated during the polymerization. [b] Hexamethylphosphoric acid triamide. This material can be both solvent and base.

Table III
Polymerization of 2,5-Furandicarbonyl Chloride with 2,5-Bis(hydroxymethyl)furan in Different Solvents

Solvent	Base	Temp, °C	$[\eta]^{25}_{P/TCE}$[a]	Polymer solvents and Color
$CHCl_3$	$(C_2H_5)_3N$	23	0.12	(CF_3) CHOH, P/TCE; white[d]
DMF[b]	$(C_2H_5)_3N$	0	No polymer could be isolated	
DMF	$(C_2H_5)_3N$	150	No polymer could be isolated	
TCE/TMSO[c]	$(C_2H_5)_3N$	23	0.12	$CHCl_3$;[e] brown
HMPA		70	0.12	$CHCl_3$;[e] brown

[a] P/TCE is an abbreviation for a mixture of phenol and tetrachloroethane (40; 60). [b] Dimethylformamide. [c] Tetrachloroethane and tetramethylene sulfone (50:50). [d] The polymer precipitated from the polymerization solution. [e] No viscosity measurements were made, but it was clear that the inherent viscosity was less than 0.12 because the polymer was soluble in chloroform.

Table IV
Polymerization of 2,5-Furandicarbonyl Chloride with 2,5-*cis*-Bis(hydroxymethyl)tetrahydrofuran using Different Acid Acceptors[a]

Acid acceptor	$[\eta]^{25}_{CHCl_3}$	Polymer solvents and Color
Pyridine	<0.07	$CHCL_3$, CH_3COCH_3; white
DABCO[b]	No polymer could be isolated	
N-Methylmorpholine	0.07	$CHCl_3$; yellow
$(C_2H_5)_3N$	0.07	$CHCl_3$; white

[a] All the reactions were performed using chloroform as the polymerization solvent at 0 °C. [b] 1,4-Diazabicyclo[2.2.2]octane.

which is a useful polymerization solvent. Therefore, chloroform was chosen for the solution polymerization of **19** and **20** even though polymer **3** precipitated during the polymerization.

Polymerization (reaction 7) was carried out with a number of acid acceptors. The results of these experiments are shown in Table IV.

As can be seen from Table IV, the highest intrinsic viscosities were obtained when either *N*-methylmorpholine or triethylamine were used as the acid acceptors. However, because a colorless polymer was obtained using triethylamine, it was used as the acid acceptor for all subsequent solution polymerizations.

Table V
Solution Polymerization Methods

Method	Polymerization eq	$[\eta]^{25}$	Viscosity solvent
A	6	0.07	$CHCl_3$
B	6	0.10	$CHCl_3$
A	7	0.12	P/TCE
B	7	0.17	P/TCE

Table VI
Solution Polymerization Results

Polymer	$[\eta]^{25}_{CHCl_3}$	% conversion
3	0.17[a]	91
4	0.16	90
5	0.10	90
6	0.05	70
7	0.06	70
8	0.10	70
9	0.10	70
10	0.20	90

[a] Determined in P/TCE.

Two solution polymerization methods were used. Method A involved a slow, dropwise addition of a solution of diol, triethylamine, and chloroform to a stirred solution of diacid chloride in chloroform at 0 °C, under nitrogen. Two moles of triethylamine were used for each mole of diacid chloride. The addition was normally done at a rate of 0.5 mL/min. If this procedure was carried out at room temperature, the polymerization solution became slightly yellow, but the molecular weights of the polymers, as reflected by their intrinsic viscosities, remained the same. Upon completion of the addition of the diol solution, the polymerization solution was stirred overnight before the polymer was precipitated. Method B involved preparing two solutions of equal volume. One solution contained the diacid chloride and chloroform. The other solution contained the diol and 2 mol of triethylamine for every mol of diol and chloroform. The diol solution was added, all at once, to the diacid chloride solution with stirring, but without cooling. This system was stirred for 4 h then more triethylamine was added and the system was allowed to stand undisturbed for 6 days. Then more triethylamine was added and the system was briefly stirred and allowed to stand undisturbed for another 6 days before the polymer was precipitated. A comparison of methods A and B is shown in Table V for polymerizations 7 and 8.

As can be seen from Table V, the solution polymerization method which yielded the highest molecular weights (as indicated by intrinsic viscosity) used chloroform as solvent, excess triethylamine as the acid acceptor, and a 2-week polymerization time. Table VI lists all the polymers which were synthesized by this method, their intrinsic viscosities, and the yields in which they were obtained.

It should be pointed out that the polymers in Table VI are of relatively low viscosity and have little ability to form cohesive films.

The isolation and purification of polymers **6** through **9** was different than that used for polymers **3, 4, 5,** and **10.** All the polymers listed in Table VI precipitated from light petroleum ether as flocculent white solids, but polymers **6** through **9** were found by NMR to contain large amounts of triethylamine hydrochloride. The triethylamine hydrochloride could not be removed by washing with water because these polymers are water soluble. Drying the polymers *in vacuo* (0.02 Torr) at 60

°C over concentrated sulfuric acid failed to remove the triethylamine hydrochloride. Therefore, the polymers were dissolved in methylene chloride and were esterified with excess diazomethane. The solvent was removed and the polymers were isolated as brown, sticky, semisolids after drying. The presence of triethylamine hydrochloride completely changes the physical appearance of polymers **6** through **9.** In their pure state, the polymers are sticky, semisolids but in the presence of triethylamine hydrochloride they were isolated as fluffy white solids in which no apparent phase separation was observed. This behavior may be taken as indicating a strong affinity of these polymers for triethylamine hydrochloride.

Differential scanning calorimetry was performed on these polymers. None of the polymers with the exception of **10** exhibit a well-defined melting transition. The melting transition exhibited by **10** (at 150 °C) was found to be reproducible on cooling and reheating. The all-aromatic polyester **3** decomposed to a black insoluble material at about 200 °C, while the remaining polyesters **4** and **5** which contained the furan ring generally decomposed at about 250 °C, yielding black, insoluble solids. The all-aliphatic polyesters, **6** through **9,** have glass transition temperatures at, or below, 0 °C ranging from a low of −15 °C for the all-*cis* polyester **6** to a maximum of 0 °C for polymer **10.** *trans*-Tetrahydrofuran units seem to raise the glass transition slightly over that of the *cis*-tetrahydrofuran units. None of the aliphatic polyesters show definite melting points and all decompose to black insoluble materials at temperatures between 200 and 250 °C. It should be noted that both *cis*- and *trans*-poly(1,4-cyclohexylenedimethylene terephthalate) (**18**) have been synthesized and it was reported[11] that the glass transition temperature of the *trans* polyester was about 10 °C higher than that of the *cis* polyester. This is in agreement with the results found for polymers **6** (*cis*) and **9** (*trans*).

Conclusions

From the results of this initial study it can be concluded that polyesters based on the fully aromatic furan-2,5-dicarboxylic acid (and its dichloride) may be useful as a polymerization component particularly if lower temperature processes are used. Temperatures generally necessary for effective melt polycondensations are too high for use with the materials studied here. The partially reduced furan nuclei are too sensitive to aerobic oxidation at these temperatures and are amenable to polymerization only by solution polymerizations at relatively low temperatures. The furan alcoholic components are generally too unreactive to be converted to high polymer by these procedures.

The examples studied here which combined the furan diacid with alphatic diols seem to indicate that a careful study of this homologous series of polyesters may yield interesting materials. The thermal analysis data, in general, bear out the general ideas broached in the introductory section. Thus the polymer in the reduced furan series with the lowest glass transition is the all-*cis* polymer. Surprisingly, the T_g values of the other polymers vary only slightly with the sequence of isomeric acid and diol in the chain. The difference in T_g values for the all-*cis* and all-*trans* polymers is approximately the same as the difference reported for the *cis* and *trans* isomers of cyclohexylenedimethylene terephthalate.

Experimental Section

All melting points were determined with a Scientific Glass Co. capillary melting point apparatus using open capillary tubes. Boiling points and melting points are uncorrected. Infrared spectra were obtained on a Perkin-Elmer Model 137 spectrophotometer; the wave numbers reported are the ν_{max} of strong and medium bands and important shoulders. Nucler magnetic resonance spectra were recorded on a Varian Model T-60 spectrophotometer using tetramethylsilane or dimethyl sulfoxide as internal standard. Refractive indices were measured with an Abbe refractometer. Ultraviolet spectra were measured with a Micro Tek Unicam Model Sp. 800A ultraviolet spectrophotometer. Differential scanning calorimetry (DSC) was performed using a Dupont Model 900 Thermal Analyzer. The side-arm polymerization tubes used for melt polymerizations were of the following dimensions: overall length, 32 cm; bulb, 6 cm in length, 2 cm in diameter for a total volume of 13.5 mL; neck, 20.5 cm in length, 1 cm in diameter; side arm, 5 cm in length, 1 cm in diameter. The side arm was located 20.5 cm above the top of the bulb. The polymerization tubes were made of Pyrex glass with a thickness of 0.8 mm. The gas chromatograph used was an F and M Research Chromatograph Model 810, having a constant gas flow rate of 3 mL/min. The drybox used was made by the Kewaunee Scientific Equipment Co. Unless otherwise specified, any reference to solvent removal, evaporation of solvent, or concentration of solutions implies that the solvent was removed by vacuum rotary evaporation using a Büchi Rotovapor R type KRV 65/45. The blender used was a Waring commercial blender.

Diethyl ether, benzene, and dioxane were purified by distillation from sodium hydride. Chloroform was purified by washing it with water, drying it over anhydrous sodium sulfate, and then distilling it from calcium hydride. Triethylamine was purified by distillation from phosphorus pentoxide under nitrogen. Tetrachloroethane was purified by washing it sequentially with dilute acid, water, dilute base, and water and then by drying it over anhydrous sodium sulfate. Dry benzene (5% by weight) was added and the azeotrope was fractionally distilled. Only the benzene-free (as determined by NMR) fractions were used. Hexane was purified by repeated warming and stirring over fresh portions of concentrated sulfuric acid, until the acid layer no longer became discolored. The supernatant hexane was then washed with water, dried over anhydrous sodium sulfate, and distilled from phosphorus pentoxide. Dimethylformamide was distilled under nitrogen from phosphorus pentoxide. Tetramethylene sulfone was purified by warming, with stirring, over potassium permanganate and the remaining insoluble material was removed by filtration. The filtrate was distilled from phosphorus pentoxide (110 °C, 0.05 Torr). Hexamethylphosphoric acid triamide (HMPA) was purified by distillation from active (heated at 159 °C for 6 hr) molecular sieves (70 °C, 0.05 Torr). Nitrogen gas was dried by passage through fresh, concentrated sulfuric acid. Dry, deoxygenated nitrogen gas was prepared by bubbling nitrogen through Fieser's solution and then over sodium hydroxide pellets and finally by bubbling through 100 mL of fresh, concentrated sulfuric acid. Pyridine was purified by distillation from barium oxide. 1,4-Diazabicyclo[2.2.2]octane (DABCO) was purified by sublimation, *N*-methylmorpholine was purified by distillation from phosphorus pentoxide under nitrogen, and tetrahydrofuran was purified by distillation from lithium aluminum hydride. Thionyl chloride was purified by distillation from triphenylphosphite (1 mL of $P(OPh)_3$/70 mL of thionyl chloride).

Furan and tetrahydrofuran diacids were prepared and purified generally as described in the literature.[12] Following the procedure outlined by Sorenson and Campbell[13] ethylene glycol was purified by refluxing over sodium metal (100 g of ethylene glycol/1 g of sodium) and subsequent distillation (760 Torr, 192 °C). 1,6-Hexanediol was purified by distillation through a Nester/Faust adiabatic-annular spinning band distillation column (0.02 Torr, 110 °C). The resulting white solid had mp 43–45 °C (lit.[14] 43 °C) and was analyzed by gas chromatography (column: 5% Carbowax 20M column temp = 200 °C; injection port = 290 °C; detector = 280 °C; attenuator = 1.6×10^2; and 0.1 μL of sample was injected) exhibiting one symmetrical peak. Polymer grade 2,2-bis(4-hydroxyphenyl)propane (bis(phenol A)) was dried *in vacuo* at 40 °C over phosphorus pentoxide for 16 h, mp 152–3 °C (lit.[15] 152–3 °C).

2,5-Bis(hydroxymethyl)furan. Generally according to the method of Gagnaire and Monzeglio[12] dimethyl-2,5-furan dicarboxylate, 15 g (0.081 mol), was converted to a greenish solid, 8.1 g, 78% yield. (Collection and continuous ether extraction of the precipitated alumina from hydrolysis of the reaction mixture was necessary to obtain this amount of product.) The solid crystallized from ethyl acetate as white flakes: mp 79 °C (lit.[12] mp 79 °C); IR (KBr) 1400 (broad –OH), 3000, 1560 (aromatic), 1400 (broad), 1240, 1390, 1000, 970, 920, 810, 755 cm^{-1}; NMR (Me_2SO-d_6) δ 6.2 (s, 2 H, ring), 5.13 (t, 2 H, OH), 4.7 (d, 4 H, $-CH_2O-$); M^+ 128 (3), $\lambda_{max}^{C_2H_5OH}$ 225 nm (ϵ_{max} 825). The diol was sublimed at 70 °C (0.05 Torr), mp 79–80 °C.

2,5-*cis*-Bis(hydroxymethyl)tetrahydrofuran. Generally according to the procedure of Gagnaire and Monzeglio,[12] dimethyl-2,5-*cis*-tetrahydrofuran dicarboxylate, 16.3 g (0.089 mol), was converted to 10.9 g of a clear, colorless oil: 94% yield; n^{25}_D 1.4660; bp 80 °C (0.05 Torr); IR (neat) 3400, 2900 (broad –OH), 1560, 1100, 1050

(broad), 1000, 880, 810 cm^{-1}; NMR (Me_2SO-d_6) δ 1.71 (m, 4 H, $-CH_2$ ring), 3.39 (t, 4 H, $-CH_2O-$), 3.83 (m, 2 H, -CH- ring *cis*),[18] 4.55 (t, 2 H, -OH); UV, only end absorption was observed in ethanol. The product was purified by distilling it twice (50 °C oil bath temperature, 0.0 5 Torr) and was analyzed by gas chromatography (column: 15% isodecylphthalate, column temperature = 100 °C, injector port = 260 °C, detector = 250 °C, attenuator 4 × 10, and 0.1 μL of sample was injected) exhibiting one symmetrical peak.

2,5-*trans*-Bis(hydroxymethyl)tetrahydrofuran. Dimethyl-2,5-*trans*-tetrahydrofuran dicarboxylate, 9.12 g (0.049 mol), was dissolved in 150 mL of dry ether and was reacted with lithium aluminum hydride, 4.5 g, in 300 mL of dry ether as described for the *cis* isomer. After extraction and distillation (80 °C oil bath temperature, 0.025 Torr) 5.3 g of a clear, colorless oil was obtained: 84%; IR (neat) 3000 (broad OH), 1450, 1230, 1060, 990, 800 cm^{-1}; NMR (Me_2SO-d_6) δ 1.73 (m, 4 H, $-CH_2-$), 3.41 (d, 4 H, $-CH_2O-$), 3.91 (m, 2 H, -CH *trans*),[18] 4.53 (broad s, 2 H, OH); n^{25}_D 1.4774; UV, only end absorption was observed in ethanol. The diol was purified by distilling it twice under the above conditions.

2,5-Furandicarbonyl Chloride. 2,5-Furandicarboxylic acid, 7.8 g (0.05 mol), was suspended in 250 mL of dry ether with stirring. Phosphorus pentachloride (95%), 30 g, was added at a rate so that the system could be kept at, or below, room temperature with an ice–water bath. The mixture was stirred for 10 h. The ethereal solution was filtered, 250 mL of light petroleum ether was added, and the solution was concentrated to about 35 mL. Purified hexane, 35 mL, was added and the solid which precipitated was collected by suction filtration. A second crop of material was precipitated when the above filtrate was concentrated to a volume of about 20 mL and stored at −20 °C. The total yield of white, solid diacid chloride was 7.2 g, 75% yield. The diacid chloride crystallized from purified hexane as white needles: mp 76–80 °C (lit.[16] 80 °C); IR (KBr) 3000, 1750 (-COCl), 1560 (aromatic), 1200, 1000, 970, 840 cm^{-1}; NMR ($CDCl_3$) δ 7.53 (s); $\lambda_{max}^{C_6H_{14}}$ 380 nm (ϵ_{max} 2300).

2,5-*cis*-Tetrahydrofurandicarbonyl Chloride. Into a 25-mL round-bottom flask was placed 2.5–3.0 mL of oxalyl chloride and 15 mL of dry ether. The solution was briefly stirred and 2,5-*cis*-tetrahydrofurandicarboxylic acid, 0.8 g (0.005 mol), was added slowly, with cooling (ice–water bath). The mixture was stirred for 3 h, concentrated, and distilled (75 °C oil bath temperature, 0.03 Torr) yielding 0.83 g of a clear, colorless liquid: 85% yield; IR (neat) 3000, 1800 (COCl), 1450, 1280, 1250, 1100, 1010, 980, 940, 910, 840, 750 cm^{-1}; NMR ($CDCl_3$) δ 2.43 (m, 4 H, $-CH_2-$ ring), 4.7 (m, 2 H, CH); n^{25}_D 1.4923; UV, only end absorption was observed in purified hexane.

2,5-*trans*-Tetrahydrofurandicarbonyl Chloride. Purified thionyl chloride, 30 mL, was placed in an oven-dried, 50-mL, round-bottom flask equipped with a reflux condenser (protected by a calcium chloride drying tube) and a magnetic stirring bar. 2,5-*trans*-Tetrahydrofurandicarboxylic acid, 1.0 g (0.006 mol), was added all at once with stirring and the system was refluxed for 3 h. The resulting clear solution was then evaporated to an oil which was placed in a distillation apparatus. The system was evacuated (0.02 Torr) at room temperature resulting in the formation of a solid in the distillation pot. The system was heated to 50–60 °C at which temperature the solid sublimed and was collected on a cold finger. Upon completion of the sublimation, the pressure in the system was brought to 1 atm with dry nitrogen. The sublimed material was collected in a drybox and purified by sublimation under the previously described conditions. A white solid was obtained: 1.0 g; 81% yield; mp (sealed tube) 55–62 °C; IR (CCl_4) 3000, 2400, 1800 (-C(O)Cl), 1500, 1250, 1100, 970 cm^{-1}; NMR ($CDCl_3$) δ 2.41 (m, 4 H, $-CH_2$ ring), 5.0 (m, >CH ring); UV, only end absorption was observed in purified hexane.

Poly(2,5-furandiylcarbonyloxymethylene-2,5-furandiylmethyleneoxylcarbonyl) (3). Method A. 2,5-Bis(hydroxymethyl)-furan, 1.43 g (0.0117 mol), was placed in an oven-dried, 25-mL, round-bottom flask equipped with a magnetic stirring bar and a 50-mL pressure-equalizing dropping funnel which was fitted with a drying tube filled with calcium chloride. Purified chloroform, 10 mL, and purified triethylamine, 2.145 g (0.0220 mol), were added with a pipet into the flask and the mixture was cooled with an ice–water–methanol bath with stirring. 2,5-Furandicarbonyl chloride, 2.156 g (0.0117 mol), dissolved in 10 mL of purified chloroform, was added dropwise through the addition funnel to the cooled diol solution over the course of 1 h. The solution became more viscous and a white solid began to precipitate. The system was allowed to stir overnight. The polymer was isolated by adding the chloroform solution to 500 mL of light petroleum ether with vigorous stirring. A white flocculent solid precipitated which was isolated by suction filtration and washed twice in a Waring blender (1-L capacity) with 150 mL of distilled water for 2 min. The polymer was dried over phophorus pentoxide at 40 °C and 0.05 Torr for 3 days. A white solid, 2.8 g, 96% yield, was obtained which was soluble in a mixture of tetrachloroethane, phenol (50:50), ($[\eta]^{25}$ 0.12), and hexafluoroisopropyl alcohol but insoluble in chloroform to any appreciable extent.

Method B. 2,5-Bis(hydroxymethyl)furan, 1.54 g (0.012 mol), was placed in an oven-dried, 125-mL Erlenmeyer flask equipped with a magnetic stirring bar. Purified chloroform, 60 mL, and purified triethylamine, 2.43 g (0.024 mol), were added all at once with stirring. 2,5-Furandicarbonyl chloride, 2.32 g (0.012 mol), dissolved in 20 mL of purified chloroform, was placed in an oven-dried, 50-mL, Erlenmeyer flask equipped with a drying tube filled with calcium chloride. The diacyl chloride solution was added all at once to the diol suspension with stirring but without cooling. The 50-mL Erlenmeyer flask was washed with 10 mL of purified chloroform and this was also added to the 125-mL Erlenmeyer flask. Upon addition of the diacyl chloride, the polymerization flask was sealed with a ground glass stopper and a clear, yellow solution resulted which warmed spontaneously to about 60 °C.

After stirring for 4 h, an additional 2.0 g of purified triethylamine was added and the stoppered mixture was allowed to stand undisturbed for 6 days. At the end of this time, 7.3 g of purified triethylamine was added with a pipet and the solution was mixed briefly and was allowed to stand for an additional 6 days. The polymer was isolated by precipitation into light petroleum ether, washing with distilled water, and drying *in vacuo* (60 °C, 0.05 Torr) over phosphorus pentoxide. The resulting white solid, 2.7 g, 91% yield, had $[\eta]^{25}$ 0.17 in a mixture of phenol/tetrachloroethane (50:50): IR (KBr) 3100, 1720 ($-CO_2$), 1580 (aromatic), 1430, 1360, 1280, 1260, 1220, 1150, 1120, 1030, 970, 800, 760 cm^{-1}; NMR ($CDCl_3$) δ 7.3 (s, 2 H), 6.4 (s, 2 H), 5.21 (s, 4 H, $-CH_2O-$); $\lambda_{max}^{(CF)_2CHOH}$ 267 nm (ϵ_{max} 1774); DSC, mp 180–200 °C dec.

Poly(2,5-furandiylcarbonyloxyhexamethyleneoxycarbonyl) (4). In analogy to a procedure outlined by Sorenson and Campbell[9] purified 1,6-hexanediol, 3.2 g (0.032 mol), was placed in a side-arm polymerization tube. Dimethyl-2,5-furan dicarboxylate, 2.5 g (0.016 mol), 0.0062 g (0.000039 mol) of calcium acetate, and 0.01 g (0.000034 mol) of antimony oxide were added and the system was heated with a fluidized sand bath (190–200 °C), under nitrogen, for 6 h. The nitrogen flow was discontinued and the system was evacuated to less than 1 Torr at 200 °C. The temperature was maintained at 200 °C for 1 h and was then raised to 275 °C over the course of 2 h. The system was heated at 275 °C for an additional 2 h. Upon cooling, a hard, greenish solid was obtained which was found to be soluble in halogenated hydrocarbons. The polymer was dissolved in chloroform, filtered by gravity, and isolated by suction filtration as a white, fibrous mass after precipitation into light petroleum ether. This procedure was repeated and the polymer was dried *in vacuo* (0.02 Torr) at 40 °C for 16 h over paraffin wax shavings. The resulting white, fibrous solid, 1.6 g, 50% yield, had $[\eta]^{25}_{CHCl_3}$ 0.40. Brittle fibers could be drawn from the polymer melt and transparent, flexible films could be cast from a 20% (by weight) solution of the polymer in chloroform: IR (KBr) 3000, 1730 (CO_2-), 1580 (aromatic), 1470, 1370, 1270, 1230, 1140, 1020, 980, 820, 770 cm^{-1}; NMR ($CDCl_3$) δ 1.6 (m, 8 H, $-CH_2-$), 4.3 (m, 4 H, $-CH_2O$), 7.2 (s, 2 H, aromatic); $\lambda_{max}^{CHCl_3}$ 264 nm (ϵ_{max} 1525); DSC, sharp endothermic transition at 150 °C.

Material with $[\eta]^{25}_{CHCl_3}$ 0.17 was found by gel permeation chromatography (methylene chloride solvent, polystyrene calibration) to have an apparent $\overline{M}_n$ = 7 438, $\overline{M}_w$ = 18 860, $\overline{M}_z$ = 45 054, $\overline{M}_w/\overline{M}_n$ = 2.54.

Poly[2,5-furandiylcarbonyloxymethylene(*cis*-tetrahydro-2,5-furandiyl)methyleneoxycarbonyl] (5). (a) Into a side-arm polymerization tube was placed 5.32 g (0.00410 mol) of 2,5-*cis*-bis(hydroxymethyl)tetrahydrofuran, 3.73 g (0.0203 mol) of dimethyl-2,5-furan dicarboxylate, 0.005 g of Tyzor-TBT (*tert*-butyl titanate, Dupont), and 0.005 g of sodium isopropoxide. In analogy to a procedure outlined by Sorenson and Campbell[10] the system was heated under nitrogen to 175 °C for 3 h. A brown liquid resulted which was heated at 215 °C for 15 min. Vacuum was applied to 0.05 Torr and the temperature was increased to 280 °C for 3 h. A black liquid was obtained which solidified on cooling to form a shiny, brittle, insoluble solid: IR (KBr) 3400, 1720 ($-CO_2-$), 1580 (aromatic), 1440, 1370, 1260, 1210, 1140, 1080, 1010, 980, 760 cm^{-1}

(b) 2,5-*cis*-Bis(hydroxymethyl)tetrahydrofuran, 1.7230 g (0.0131 mol), 2.64 g (0 026 mol) of purified triethylamine, and 2.510 g (0.0131 mol) of 2,5-furandicarbonyl chloride were reacted according to method B. The resulting white solid, 3.0 g, 90% yield, was found to be soluble in halogenated hydrocarbons and had $[\eta]^{25}_{CHCl_3}$ 0.10: IR (KBr) 3400, 1720 ($-CO_2-$), 1580 (aromatic), 1440, 1370, 1260, 1210, 1140, 1080, 1010, 980, 760 cm^{-1}; NMR ($CDCl_3$) δ 2.0 (m, 4 H, $-CH_2$ ring),

4.4 (m, 6 H, $-CH_2O$, >CH ring), 7.2 (2 H aromatic); $\lambda_{max}^{CHCl_3}$ 264 (ϵ_{max} 1340); mp 250 °C dec.

Poly[(*cis*-tetrahydro-2,5-furandiyl)carbonyloxymethylene-(*cis*-tetrahydro-2,5-furandiyl)methyleneoxycarbonyl] (6). In a drybox 2,5-bis(hydroxymethyl)tetrahydrofuran, 1.306 g (0.0098 mol), 1.948 g (0.0098 mol) of 2,5-*cis*-tetrahydrofurandicarbonyl chloride, and 2.00 g (0.019 mol) of purified triethylamine were reacted according to method B. The polymer precipitated as a flocculent white solid by addition to excess light petroleum ether and was collected by suction filtration. This white solid, however, was contaminated with triethylamine hydrochloride. The solid, therefore, was dissolved in methylene chloride and treated with excess diazomethane. The resulting solution was evaporated to an oil which was dried *in vacuo* (0.02 Torr), at room temperature, over sulfuric acid, sodium hydroxide, and paraffin wax for 24 h. The polymer was then dried *in vacuo* (0.02 Torr) at 60 °C over sulfuric acid and sodium hydroxide at 60 °C for 48 h. A sticky, semisolid, brown material was obtained, 1.8 g, 70% yield, which had $[\eta]^{25}_{CHCl_3}$ 0.045: IR (neat) 3400, 3000, 1780, 1730, 1600, 1430, 1340, 1250, 1190, 1140, 1080, 1050, 1000, 790 cm^{-1}; NMR ($CDCl_3$) δ 5.0 (m), 4.6 (m), 4.2 (s), 3.8 (s), 3.7 (s), 3.6 (m), 2.5 (d), 2.2 (m), 1.9 (m), 1.4 (m); UV, only end absorption was observed in chloroform; DSC, the polymer had a glass transition at −15 °C and decomposed with weight loss at 200 °C.

[Poly[(*cis*-tetrahydro-2,5-furandiyl)carbonyloxymethylene(*trans*-tetrahydro-2,5-furandiyl)methyleneoxycarbonyl] (7). As described for all-cis polymer, 2,5-*trans*-bis(hydroxymethyl)-tetrahydrofuran, 1.346 g (0.0102 mol), 2.01 g (0.0102 mol) of 2,5-*cis*-tetrahydrofurandicarbonyl chloride, and 2.06 g (0.0204 mol) of purified triethylamine were reacted. The polymer was isolated, treated with diazomethane, and dried. A sticky, semisolid, brown material was obtained, 1.8 g, 70% yield, which had $[\eta]^{25}_{CHCl_3}$ 0.06: IR (neat) 3600, 3000, 1730 ($-CO_2-$), 1600, 1450, 1270, 1170, 1060, 940, 880 cm^{-1}; NMR ($CDCl_3$) δ 4.6 (m, 2 H, $>CHCO_2-$ ring), 4.0 (s, 4 H, $-C(O)-OCH_2-$), 3.7 (s), 3.6 (m, 2 H, > $CHCH_2$ ring), 2.2 (m, 4 H, $-CH_2CHCO_2-$ ring), 1.8 (m, 4 H, $-CH_2CHCH_2O$ ring); UV, only end absorption was observed in chloroform; DSC, the polymer had a glass transition at −8 °C and decomposed with weight loss at 185 °C.

Poly[(*trans*-tetrahydro-2,5-furandiyl)carbonyloxymethylene(*cis*-tetrahydro-2,5-furandiyl)methyleneoxycarbonyl] (8). As described for the all-cis polymers, 2,5-*cis*-bis(hydroxymethyl)-tetrahydrofuran, 1.810 g (0.0137 mol), 2.701 g (0.0137 mol) of a mixture of 2,5-*cis*-tetrahydrofurandicarbonyl plus 2,5-*trans*-tetrahydrofurandicarbonyl chloride (less than 4% cis as determined by NMR), and 2.77 g (0.0274 mol) of purified triethylamine were reacted. The polymer was isolated, treated with diazomethane, and dried. A sticky, semisolid brown material was obtained, 2.4 g, 70% yield, which had $[\eta]^{25}_{CHCl_3}$ 0.01: IR (neat) 3500, 2000, 1730 ($-CO_2-$), 1600, 1450, 1350, 1280, 1200, 1070, 1000, 920, 860 cm^{-1}; NMR ($CDCl_3$) δ 4.7 (n, 2 H, $-CHCO_2$ ring), 4.1 (s, 4 H, $-CH_2CH_2-$), 2.2 (m, 4 H, CH_2CHCO_2- ring), 1.8 (m, 4 H, $-CH_2CHCH_2O-$ ring); UV, only end absorption was observed in chloroform; DSC, the polymer had a glass transition at −3 °C and decomposed with weight loss at 225 °C.

Poly[(*trans*-tetrahydro-2,5-furandiyl)carbonyloxymethylene(*trans*-tetrahydro-2,5-furandiyl)methyleneoxycarbonyl] (9). As described for the all-cis polymer, 2,5-*trans*-bis(hydroxymethyl)tetrahydrofuran, 1.403 g (0.0106 mol), 2.095 g (0.0106 mole) of a mixture of 2,5-*cis*-tetrahydrofurandicarbonyl chloride plus 2,5-*trans*-tetrahydrofurandicarbonyl chloride (less than 4% cis as determined by NMR), and 2.14 g (0.0212 mol) of purified triethylamine were reacted. The polymer was isolated, treated with diazomethane, and dried. A sticky, semisolid, brown material was obtained, 1.9 g, 70% yield which had $[\eta]^{25}_{CHCl}$ 0.1: IR (neat) 3500, 3000, 1730 ($-CO_2-$), 1600, 1450, 1350, 1270, 1200, 1080, 1000, 940, 880 cm^{-1}; NMR ($CDCl_3$) δ 4.7 (m, 2 H, $>CHCO_2$ ring), 4.1 (s, 4 H, $-CO_2CH_2$), 3.7 (s), 3.5 (m, 2 H, $>CHCH_2O-$ ring), 2.2 (m, 4 H, $-CH_2CHCO_2-$ ring), 1.8 (m, 4 H, $-CH_2CHCH_2-$ ring); UV, only end absorption was observed in chloroform; DSC, the polymer had a glass transition at −5 °C and decomposed with weight loss at 230 °C.

Poly[(*cis*-tetrahydro-2,5-furandiyl)carbonyloxethyleneoxycarbonyl] (10). A side-arm polymerization tube was charged with dimethyl-2,5-*cis*-tetrahydrofuran dicarboxylate, 2.0 g (0.011), 0.006 g (0.00039 mol) of calcium acetate, 0.006 g (0.002 mol) of antimony oxide, 0.006 g (0.00023 mole) of triphenylphosphine, and 1.2 g (0.022 mol) of purified ethylene glycol. The system was heated under nitrogen at 180 °C for 4 h. The pressure was lowered to 0.3 Torr and the system was heated at 210 °C for 1 h and at 250 °C for 2 h. A black, tacky material was obtained on cooling which was found to be partially (~30%) soluble in chloroform. The chloroform–polymer mixture was filtered by gravity and the filtrate was poured into an excess of light petroleum ether, resulting in the formation of a tacky material which was dried *in vacuo* (0.02 Torr) at 40 °C for 16 h over paraffin wax shavings. The resulting tacky material, 0.4 g (20% yield), was found to have $[\eta]^{25}_{CHCl_3}$ 0.21: IR (KBr) 3400, 3000, 1730 (–CO–), 1440, 1370, 1270, 1190, 1090, 850, 760 cm^{-1}; NMR ($CDCl_3$) δ 2.23 (m, 4 H, $-CH_2-$ ring), 4.40 (s, 4 H, $-CH_2O-$), 4.50 (m, 2 H, >CH ring); UV, only end absorption was observed in chloroform; DSC, the polymer had a glass transition at 0 °C and decomposed with weight loss at 250 °C.[17]

Acknowledgment. Partial support of this work in the form of a Goodyear Fellowship to J.E.K. is thankfully acknowledged.

References and Notes

(1) W. N. Haworth and W. G. M. Jones, *J. Chem. Soc.*, 667 (1944).
(2) J. Harris, J. F. Seaman, and L. L. Zoch, *For. Prod. J.*, **10**, 125 (1960); *Chem. Abstr.*, **54**, 10322a (1960)
(3) P. Muller and D. O. Rudin, *Biochem. Biophys. Res. Commun.*, **26**, 398 (1967).
(4) B. T. Kilbourn, J. D. Dunitz, L. A. R. Pioda, and W. Simon, *J. Mol. Biol.*, **30**, 559 (1967).
(5) J. H. Prestegard and I. Chan, *Biochemistry*, **8**, 3921 (1969).
(6) J. H. Prestegard and I. Chan, *J. Am. Chem. Soc.*, **92**, 4440 (1970).
(7) IUPAC Macromolecular Nomenclature Commission, *Macromolecules*, **6**, 149 (1973).
(8) T. Shono, K. Hono, and Y. Hachihama, *Kogyo Kagaku Zasshi*, **63**, 176 (1960); *Chem. Abstr.*, **56**, 4707 (1962).
(9) W. R. Sorenson and T. W. Campbell "Preparative Methods of Polymer Chemistry", 2nd ed, Interscience, New York, N.Y., 1968, p 132.
(10) Reference 9, p 133.
(11) F. E. Critchfield and R. D. Lundberg, French Patent 2 026 275 (1970); *Chem. Abstr.*, **74**, 14265b (1971).
(12) D. Gagnaire and P. Monzeglio, *Bull. Soc. Chim. Fr.*, **2**, 474 (1965).
(13) Reference 9, p 131.
(14) R. C. Weast, Ed., "Handbook of Chemistry and Physics", 4th ed, The Chemical Rubber Publishing Co., Cleveland, Ohio, 1965, p C-358.
(15) Reference 14, p C-486.
(16) Reference 14, p C-333.
(17) For a preparation of this polymer by a novel route see: J. A. Moore and J. E. Kelly, *J. Polym. Sci., Polym. Lett. Ed.*, **16** (3), 115 (1978).