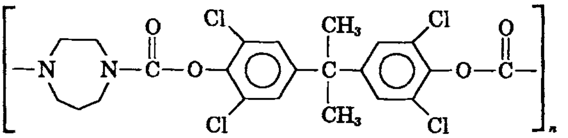
Polyurethanes from Aromatic Bischloroformates*

PAUL W. MORGAN,[†] *Textile Fibers Department, E. I. duPont de Nemours and Co., Wilmington, Delaware 19898*

Synopsis

Linear polyurethanes, having high molecular weight, were prepared by interfacial polycondensation from halogen substituted aromatic bischloroformates and aliphatic diamines, piperazines, and aromatic diamines. Examples of specific intermediates are hexamethylenediamine, piperazine, homopiperazine (see formula), *m*-phenylenediamine, and the bischloroformates of 2,2-bis(4-hydroxy-3,5-dichlorophenyl)propane, 2,2-bis(4-hydroxy-3,5-dibromophenyl)propane, and 2,2-bis(4-hydroxyphenyl)hexafluoropropane:



In comparison with corresponding unhalogenated polyurethanes, the polymers from this study, particularly those based on piperazines, had high glass transition and softening temperatures. Polyurethanes in this class, like most ring-containing polyurethanes, do not have sufficient thermal stability at their high melting points for easy melt forming. They were more soluble in a variety of common solvents and had excellent resistance to ultraviolet light. Surprisingly, the irregularity introduced into the polymer chain by the use of such intermediates as homopiperazine (formula above) or 2-methylpiperazine did not inhibit crystallization. On the other hand the symmetry provided by *trans*-2,5-dimethylpiperazine greatly reduced solubility in many solvents. Several polyamides and a polyurea from homopiperazine are included.

INTRODUCTION

The term, polyurethane, is generally associated with such materials as elastomers (spandex), hard and soft foams, coatings, paints, and adhesives. In this work polyurethane is used to mean the more limited field of linear, nonelastomeric polymers. Beginning in the 1930s German chemists studied and developed wholly aliphatic polyurethanes, using primarily the reaction of diisocyanates and glycols.[1] These polymers were nylonlike but melted below 200°C. Wittbecker and Katz[2,3] found that higher melting polyurethanes could be prepared from ring-containing diamines and aliphatic or aromatic bischloroformates by interfacial polycondensation. The application of low temperature polymerization procedures to polyurethane preparation has been reviewed by Morgan to 1965[4] and the review extended for the interfacial process to 1974

---

[*] Presented in part as the Carothers Award lecture before the Delaware Section of the ACS, Wilmington, DE, May 18, 1988.

[†] Present address: 822 Roslyn Ave., West Chester, PA 19382.

Journal of Applied Polymer Science, Vol. 40, 1771–1782 (1990)

CCC 0021-8995/90/9-101771-12$04.00

by Tanada and Yokoyama.[5] Lyman[6] succeeded in preparing polyurethanes melting above 200°C from aromatic diisocyanates and ethylene glycol by a high temperature solution process. Matzner and co-workers[7–9] described the synthesis of many high melting polyurethanes by the reaction of bischloroformates and diamines in solvents at elevated temperatures with magnesium powder as a catalyst.

Although, as indicated, several processes are available to produce the high-melting polyurethanes, melt-spinning could be used only on a small scale with a few polymers because of limited thermal stability. Solvent spinning was accomplished easily,[10] but many of the polymers lacked solubility in generally acceptable spinning solvents. Furthermore, fabrics from some polymers showed discoloration upon ironing after a bleaching treatment and others based on aromatic intermediates were prone to discoloration by sunlight. Research on aromatic polyesters[11] had demonstrated that chlorine substituents in the bisphenols ortho to the hydroxyl groups would yield light-stable polyesters which were high melting and crystallizable and had greatly increased solubility. Examination of the use of substituents in aromatic polyurethanes to effect improvement in properties was begun.[12,13]

RESULTS AND DISCUSSION

A wide variety of polyurethanes from aromatic bischloroformates (Table I) was prepared and examined for dilute solution viscosity, melting behavior (Tables II–IV), solubility characteristics (Tables VI and VII), and light stability (Table VIII). Because homopiperazine (1,4-diazacycloheptane) was available in good quality, a number of polyamides and a polyurea were prepared (Table V). Fiber preparation and evaluation are discussed in the following paper.

Polymer Preparation. Interfacial polymerization was used to prepare the polymers. Preferred solvents for the organic phase were chloroform, 1,2-dichloroethane, and 1,1,2-trichloroethane. Most of the polymers were prepared only once or twice from available diamines. Selected polymers were made repeatedly in attempts to get maximum molecular weight or to adjust the inherent viscosity to a desired range for fiber spinning (0.75–1.1 dL/g in *m*-cresol). With one exception (polymer 5, Table II) only those polymers with inherent viscosities of 0.3 dL/g or above are reported.

The purity of the intermediates and solvents was found to be the dominant factor in determining molecular weight. The phase volume ratios had only a

TABLE I
Bisphenol Bischloroformates

Bisphenol	Bischloroformate melting point (°C)
Hydroquinone	100
2,2-Bis(4-hydroxyphenyl)propane	96–98
2,2-Bis(4-hydroxy-3-chlorophenyl)propane	52
2,2-Bis(4-hydroxy-3,5-dichlorophenyl)propane	165–166
2,2-Bis(4-hydroxy-3,5-dibromophenyl)propane	161–162
2,2-Bis(4-hydroxyphenyl)hexafluoropropane	71–72

TABLE II
Polyurethanes from 2,2-Bis(4-Hydroxy-3,5-Dichlorophenyl)propane Bischloroformate by Interfacial Polycondensation

Polymer no.	Diamine	Yield (%)	η_{inh} (dL/g)[a]	PMT (°C)
1	Ethylene	93	0.45[b]	240
2	Hexamethylene	90	0.84[b]	212
3	9,9-Bis(aminopropyl)fluorene	99	0.41	186
4	*m*-Xylylene	99	0.45	254
5	*p*-Xylylene	87	0.14	270
6	$\alpha,\alpha,\alpha',\alpha'$-Tetramethyl-*p*-xylylene		0.37	220
	Bis(4-aminocyclohexyl)methane[c]			
7	30% *trans-trans* isomer	97	0.76	240
8	50% *trans-trans* isomer	99	1.74	
9	70% *trans-trans* isomer	98	1.52[b]	254
10	100% *trans-trans* isomer	97	1.0	278
11	*m*-Phenylenediamine	96	0.31	240
12	Bis(4-aminophenyl)methane	97	0.40	245
13	2,2-Bis(4-aminophenyl)propane	99	0.57	205
14	1,2-Bis(4-aminophenyl)ethane	98	0.31	224
15	Piperazine	71	2.02[b]	> 400
16	2-Methylpiperazine	99	1.47[b]	> 400
17	2-Ethylpiperazine	97	0.43	316
18	*trans*-2,5-Dimethylpiperazine	98	3.0[b]	> 400
19	Homopiperazine	100	1.88[b]	> 400

[a] Determined in *m*-cresol.
[b] Highest value from several preparations.
[c] Separation and characterization of isomer mixtures in Ref. 14.

moderate effect in the range 300/100–100/300 mL. This is probably because the polymers were soluble in the solvents employed and the aromatic bischloroformates have good hydrolytic stability. However, 1 mol sodium carbonate/mol byproduct hydrogen chloride gave higher molecular weights than sodium hydroxide. For polymerizations in which the diamine had limited water solubility, a portion of the organic solvent was added to the aqueous phase. Successful polymerizations could be scaled up proportionately 10 times or more to produce polymers with equivalent inherent viscosities and yields. The true yields of polymers are believed to be essentially 100% and the somewhat lower yields recorded result from mechanical losses. Detergents were not needed to assist mixing and should be avoided because residues left in the polymers can have an effect on thermal stability and discoloration by light.

Since the polymers were usually formed in solution, such solutions could be separated from the aqueous phase without polymer isolation and used directly for spinning or film casting. Tetrahydrofuran was found to be a preferred spinning solvent and highly concentrated polyurethane solutions were prepared in tetrahydrofuran–water systems and spun after removal of the water phase. Tetrahydrofuran alone is completely water-miscible but in the presence of dissolved polymer intermediates, acid acceptors and byproduct salts, two phases are formed.[4,15]

Solubility. The polyurethanes from halogen-substituted bisphenols were soluble in a variety of common solvents such as chlorinated aliphatic hydro-

TABLE III
Polyurethanes from Other Halogenated Bischloroformates

Polymer no.	Diamine	Yield (%)	η_{inh} (dL/g)[a]	PMT (°C)
	From 2,2-Bis(4-hydroxy-3-chlorophenyl)propane chloroformate			
20	2-Methylpiperazine	99	1.11	348 dec
	From 2,2-Bis(4-hydroxy-3,5-dibromophenyl)propane bischloroformate			
21	2-Methylpiperazine	98	0.51	326
22	*trans*-2,5-Dimethylpiperazine	95	0.54	> 400
	From 2,2-Bis(4-hydroxyphenyl)hexafluoropropane bischloroformate			
23	Ethylene	97	0.31	220
24	Hexamethylene	90	0.80[b]	160
25	9,9-Bis(aminopropyl)fluorene	98	0.54	190
26	Bis(4-aminocyclohexyl)methane, 70% *trans–trans* isomer	99	1.16	210
27	Piperazine	99	0.57	260
28	2-Methylpiperazine	99	1.45[b]	318
29	2-Ethylpiperazine	89	0.82	285
30	*trans*-2,5-Dimethylpiperazine	99	1.60	300
31	Homopiperazine	93	0.51	250
32	*m*-Phenylenediamine	100	0.30	238
33	*N,N'*-Diphenyl-*p*-phenylenediamine[c]	93	0.40	245

[a] Determined in *m*-cresol.
[b] Highest value from several preparations.
[c] Preparation by reaction in *o*-dichlorobenzene at 170°C for 4.5 h without acid acceptor.

carbons, phenols, cyclic aliphatic ethers, and some organic acids (see Table VI for solubility tests on a group of piperazine polyurethanes). They were insoluble in aliphatic ketones and alcohols and acyclic ethers. The range of solubility

TABLE IV
Polyurethanes from Nonhalogenated Bischloroformates

Polymer no.	Diamine	Yield (%)	η_{inh} (dL/g)[a]	PMT (°C)
	From 1,4-Phenylene bischloroformate			
34	Piperazine[b]	86	0.99	> 375
35	Homopiperazine	91	0.63	348
36	*trans*-2,5-Dimethylpiperazine[b]	100	3.47	> 350
	From 2,2-Bis(4-hydroxyphenyl)propane bischloroformate			
37	Piperazine[b]	—	0.46	250
38	Homopiperazine	80	0.67	222
39	2,2-Bis(4-aminophenyl)propane	92	1.18	230

[a] *m*-Cresol except no. 34 which was in *sym*-tetrachloroethane-phenol (66/100 w/w).
[b] Reference 2.

TABLE V
Comparison of Homopiperazine Polyamides and a Polyurea with Like Polymers from Other Piperazines[a]

		Homopiperazine			Methylpiperazine		Piperazine		*trans*-2,5-Dimethylpiperazine	
Polymer class	Reactant	Yield (%)	η_{inh} (dL/g)	PMT (°C)	η_{inh} (dL/g)	PMT (°C)	η_{inh} (dL/g)	PMT (°C)	η_{inh} (dL/g)	PMT (°C)
Polyamide	Sebacyl chloride	~ 50	0.94	100	1.01	120	1.10	200	1.60	165
	Isophthaloyl chloride	72	1.34	242	0.60	275	0.65[b]	260	1.44	315
	5-*tert*-Butylisophthaloyl chloride	96	0.37	265						
	5-Chloroisophthaloyl chloride	70	0.90	260						
	Terephthaloyl chloride	97	1.29	320	1.92	> 375	1.35	> 400	3.14	> 400
	Bis(4-chlorocarbonylphenyl) sulfone	100	0.37	272	1.43	> 350	1.28	> 380	2.62	> 350
Polyurea	Bis(4-isocyanatophenyl)methane	97	0.37	262					1.3	350 dec

[a] Data for other piperazine polymers is from Ref. 4.

[b] η_{sp}/c.

TABLE VI
Solubility Tests on Polyurethanes from Piperazines[a]

Solvent[b]	Pip-2U	Pip-DPPU	Pip-TeClDPPU	MePip-TeClDPPU	HomoPip-TeClDPPU	DMePip-TeClDPPU[c]
Methylene chloride	++	−	++	−	+	−
Chloroform	++	−	++	−	−	−
1,2-Dichloroethane	−	−	ps	−	++	−
1,1,2-Trichloroethane	+	−	++	−	++	+
Tetrahydrofuran	−	−	+ poor	++	++	+
1,3-Dioxolane	−	−	+	+	+	−
1,4-Dioxane	−	−	−	−	+	−
Acetonitrile	−	−	ins	−	ins	−
Acetone	−	−	ins	−	ins	−
Methyl ethyl ketone	−	−	−	−	sw hot	−
Cyclohexanone	+ hot	+ hot	ps hot	−	++	−
Acetophenone	−	+ hot	−	−	−	−
γ-Butyrolactone	−	+ hot	−	−	−	−
Benzene	ins	−	−	−	+[d]	−
Toluene	−	−		−	ps	−
Pyridine	−	−	+ hot	−	−	−
Thiophene	−	−	−	−	+	−
Phenol	−	−	−	−	+	−
m-Cresol	+	+	+	+	+	+
Dimethyl sulfoxide	−	+ hot	−	−	ins	−
Tetramethylene sulfone	−	+ hot	ins	−	sw	−
Dimethylformamide	+ hot	+ hot	ps	−	++	−
Dimethylacetamide	−	−	sw	−	+	−
Dimethylacetamide-5% LiCl	−	+ hot	ps	−	+	−
Tetrafluoropropanol	+	−	−	−	sw	−
Formic acid	++ hot	−	ins	−	−	−
Trifluoroacetic acid	++	−	−	−	−	−
$CHCl_3$-methanol (88/12, v/v)	++	−	−	−	−	−
TrCE-methanol (1/1, v/v)[e]	−	−	++	−	−	−
TrCE-formic acid (7/3, v/v)[e]	++	+	++	−	++	++

[a] Polymer codes: Pip = piperazine; MePip = 2-methylpiperazine; HomoPip =homopiperazine; DMePip = *trans*-2,5-dimethylpiperazine; 2U = urethane from ethylene glycol; DPPU = urethane from 2,2-bis(4-hydroxyphenyl)propane; TeClDPPU = urethane from 2,2-bis(4-hydroxy-3,5-dichlorophenyl)propane.

[b] Solubility codes: ++, ≥ 20% by wt; +, ≥ 10% by wt; ps, partly soluble; sw, swollen; ins, insoluble; −, no information. Tests at room temperature unless otherwise indicated.

[c] Care must be taken in isolation to avoid crystallization and change solubility.

[d] Amorphous polymer. Crystalline, oriented fiber is insoluble in benzene and toluene.

[e] TrCE is 1,1,2-trichloroethane.

TABLE VII
Variation of Inherent Viscosity with Solvent for the Polyurethanes from Homopiperazine and Methylpiperazine with 2,2-Bis(4-Hydroxy-3,5-Dichlorophenyl)propane

Solvent	Homopiperazine η_{inh} (dL/g)[a]	Methylpiperazine η_{inh} (dL/g)[a]
sym-Tetrachloroethane-phenol (40/60, w/w)	1.16	
1,1,2-Trichloroethane	1.03	
m-Cresol	1.00	1.25
1,2-Dichloroethane	0.85	
Cyclohexanone	0.77	
Tetrahydrofuran	0.76	1.15
Dimethylacetamide	0.64	1.04
Dimethylformamide	—	0.92

[a] Inherent viscosities determined at 30°C and a concentration of 0.5 g/100 mL solvent.

was greater than for corresponding polyurethanes without halogen substitution. The polymers were amorphous as prepared. However, many would crystallize upon heating at 230–250°C for short periods. They were then less soluble or insoluble in many of the same solvents. Even though solutions with equally high solids content may be attained in several solvents, the quality of the solutions may vary. This is indicated by the variation of inherent viscosity de-

TABLE VIII
Discoloration of Polymers on Exposure to Light in the Fade-Ometer

No.	Polymer film or fiber[a]	Exposure hours	Color
1	DPP-I (ester)	2	Yellow
2	TeClDPP-I (ester)	> 800[b]	None
3	DDM-2U (urethane)	20	Yellow
4	DDM-TeClDPPU	26	Trace color
		84	Pale yellow
5	DDE-TeClDPPU	20	Trace color
		80	Yellow
6	DDP-2U	20	None
		80	Yellow tint
7	DDP-DPPU	16	Pale yellow
		60	Yellow
8	DDP-TeClDPPU	200	Trace color
9	Pip-2U	> 1000	None
10	Pip-DPPU	60	Trace color
11	Pip-TeClDPPU	> 1000	None
12	MePip-TeClDPPU	> 1000	None
13	HomoPip-TeClDPPU	> 1000	None

[a] Codes for compositions: DPP = 2,2-bis(4-hydroxyphenl)propane; TeClDPP = 2,2-bis(4-hydroxy-3,5-dichlorophenyl)propane; I = isophthalate; DDM = bis(4-aminophenyl)methane; 2U = urethane of ethylene glycol; DDE = 1,2-bis(4-aminophenyl)ethane; DPPU = urethane of DPP; DDP = 2,2-bis(4-aminophenyl)propane; TeClDPPU = urethane of TeClDPP; Pip = piperazine; MePip = 2-methylpiperazine; HomoPip = homopiperazine.

[b] Reference 11.

termined in several solvents, as illustrated in Table VII, and experience with concentrated spinning solutions for which there were important differences in viscosities and in solvent evaporation rates.

Melting Temperatures. The polyurethanes described here were amorphous as prepared and they vary appreciably in molecular weight. Comparisons of melting temperatures of the polymers must be made with those conditions in mind.

The melting points of the polyurethanes with ring substitution in the bisphenols were high, ranging from around 190 to above 400°C. Often the melting temperatures of the halogenated polymers were higher than for the unhalogenated analogs (e.g., polymers 15 and 19 vs. 37 and 38, Tables II and IV). On the other hand, the differences in melting points were insignificant or even reversed in some instances (polymers 13 and 39, Tables II and IV). The piperazine polyurethanes were particularly high melting ($\sim$ 300 to $>$ 400°C). These polymers were much more readily crystallized than the non-chlorine-substituted polymers and may have crystallized as the temperature was raised in the melting test. Methyl substitution of the piperazine or any disorder introduced by the homopiperazine unit did not lower the melting point below 400°C, but ethyl substitution lowered the melting point to 316°C (polymer 17). One example indicates that symmetrical substitution gives a greater increase in melting point than unsymmetrical substitution (polymers 16 and 20, Tables II and III). Among the nonpiperazine polymers of Table II, the ethylene polymer melts higher than that based on hexamethylenediamine, as would be expected (polymers 1 and 2; see also Table III, polymers 23 and 24). The polymer from *p*-xylylenediamine melts higher than that from *m*-xylylenediamine (polymers 4 and 5). For the polymers from bis(4-aminocyclohexyl)methane, melting points increase some with increasing *trans–trans* isomer content (polymers 7, 9, and 10).

Fluorine substitution on the isopropylidine group did not greatly change the range of melting temperatures for those polyurethanes for which data on comparable nonhalogenated polymers is available (Table III; compare polymer 27 with 37). Except for the piperazine polymers the melting points are comparable to many of the polyurethanes based on 2,2-bis(4-hydroxy-3,5-dichlorophenyl)propane (Table II).

Table V provides a comparison of the melting temperatures of several polyamides and a polyurea of homopiperazine with those from other piperazines in the literature. The homopiperazine amides are the lowest melting of the group. The melting temperatures of the amides from the other piperazines do not occur in a consistent order.

Thermal Stability. Few, if any, ring-containing polyurethanes which melt above 200°C can be melt-processed for sustained periods of time without severe degradation. Polymers melting from 200 to 250°C, and perhaps a little higher in some cases, can be melt-pressed into films and even extruded on a very small scale into fibers with particular care to minimize the heating time. Although no detailed study of thermal stability was made, none of the halogenated polyurethanes were sufficiently stable at the melting temperature for melt spinning. Some of those with low melting points could be melt-pressed into films.

Light Stability. Many polymers are discolored and/or degraded in terms of molecular weight upon exposure to sunlight or an artificial source of ultraviolet light. One solution to this deficiency is to find a light-stabilizing additive. A better alternative is to find a similar, more stable polymer. Wholly aromatic polyesters, such as the isophthalate of 2,2-bis(4-hydroxyphenyl)propane (Table VIII, polymer 1), become yellow very rapidly in light. When the ring positions adjacent to the hydroxyl group in the phenol are substituted with chlorine groups (polymer 2), light stability is markedly improved.[11] The ester links in unsubstituted aromatic polyesters undergo a rearrangement to ortho-hydroxybenzophenone units, which produce the color.[16-18] The reaction is prevented by chlorine or other substituents. The rearrangement is similar to a Fries rearrangement but proceeds by a different mechanism.

Polyurethanes derived from aromatic diamines with aliphatic or aromatic bischloroformates are colored in varying degrees by exposure to ultraviolet light (polymers 3–8). Replacement of a methylene link by an isopropylidene link between aromatic rings in the diamine improves light stability (polymer 6 vs. 3 and polymer 8 vs. 4). Ortho chlorine substitution in the bischloroformate also improves stability (polymer 8 vs. 7). Chlorine-substituted diamines have not been examined because of the difficulty in synthesizing high polymers.

The nonaromatic polyurethane from piperazine and ethylene bischloroformate has outstanding light stability, both as to coloration and degradation in molecular weight (polymer 9; Ref. 10). Comparison of the polyurethane from piperazine with an unsubstituted bisphenol with the related wholly aromatic polyurethane (polymer 10 vs. 7) shows only a modest improvement in light stability. Polyurethanes from piperazines and chlorine-substituted aromatic bischloroformates have exceptional resistance to coloration by ultraviolet light (polymers 11, 12, and 13). Fibers from the latter group of polymers also have good retention of physical properties upon light exposure.

EXPERIMENTAL

Diamines and Bisphenols

Most of the intermediates were available from reagent supply companies or other commercial sources and were purified by known means. Physical constants are given in such sources as Ref. 4, 7, and 19. Some of the diamines are quite hygroscopic, e.g., ethylenediamine, hexamethylenediamine, piperazine, and homopiperazine, and are best handled by preparing an assayed aqueous solution after purification.

Preparation of Bischloroformates[7,20,21]

Low Temperature Procedure. Phosgene (64 mL; 0.9 mol) was collected in an 800-mL, round-bottom flask equipped with stirrer, dropping funnel, and a dry-ice condenser. The flask was cooled externally by an ice-salt bath and an additional metal pan was placed beneath the whole apparatus. The exit from the condenser was connected by tubing to a scrubbing trap through which water was flowing. Cold tetrahydrofuran (50 mL) was added to the phosgene. A solution of 156 g (0.42 mol) of 2,2-bis(4-hydroxy-3,5-dichlorophenyl)propane in a mixture of tetrahydrofuran (100 mL) and dimethylaniline (100 mL) was prepared. This solution was dripped into the stirred phosgene solution for 2 h and the mixture was stirred for another 30 min. The dry ice was removed from the condenser. Residual phosgene was purged from the system with dry nitrogen and hydrolyzed in the water scrubber. The slurry then was poured into 1 L of ice and water. The precipitated bischloroformate was collected, washed well with cold water, and freed from water by air drying and vacuum drying. The product was recrystallized from hexane and had a maximum melting point of 165–165.5°C.

High Temperature Procedure. This procedure[20] was carried out in a Special Services Laboratory by technicians experienced in the safe use of high pressure equipment. 2,2-Bis(4-hydroxy-3,5-dichlorophenyl)propane (200 g) was placed in a cylindrical Hasteloy alloy pressure vessel. To this was added 5 mL of dimethylformamide and 250 mL of phosgene. The reaction was allowed to proceed in the sealed bomb at 130–140°C for 8–12 h. Hydrogen chloride and phosgene were discharged with water scrubbing and the solid residue was recrystallized from hexane to which was added 10% by volume of 1,2-dichloroethane. The yield of pure bischloroformate was 80–90%.

This type of preparation can be carried out with basic ion exchange resins, such as Amberlite IRA-400, as the catalyst.[21] The time required may be somewhat longer but the crude product has less color.

Polymer Preparation

Homopiperazine (2.50 g; 0.025 mol as a 17% aqueous solution), 5.30 g of sodium carbonate, and 250 mL of water were placed in a blender. As the blender was started a solution of 12.28 g of 2,2-bis(4-hydroxy-3,5-dichlorophenyl)propane bischloroformate in 100 mL of 1,2-dichloroethane was added as rapidly as possible. The mixture was stirred at high speed for 4 min and an equal volume of hexane was added to precipitate the polymer. The polymer was washed thoroughly with water by repeated shredding in the blender and filtration. The granular product was dried under vacuum at 80°C. The yield was 12.95 g (97%) and the inherent viscosity was 1.75 (*m*-cresol).

Many preparations were carried out with this formulation. However, high molecular weight polymers may be obtained with other phase ratios and at other concentration levels, provided that the intermediates are pure. For optimum results these variables must be explored.

Direct Preparation of a Spinning Solution

In a 200-mL centrifuge tube, equipped with a disc stirrer and cooled by an ice bath, was placed 45 mL of tetrahydrofuran, 7 mL of water, 5.0 g of 2-methylpiperazine, and 7.50 g of finely divided calcium hydroxide. To this was added over a period of 2 min with rapid stirring 24.55 g of 2,2-bis(4-hydroxy-3,5-dichlorophenyl)propane bischloroformate dissolved in 40 mL of tetrahydrofuran. A portion of solvent (10 mL) was used to rinse in residual bischloroformate. Stirring was continued 2 h. The small aqueous phase was a pasty mass and settled as a cake when the solution was centrifuged.

A second polymerization was carried out with 3.75 g of calcium hydroxide. After this mixture was centrifuged, there was obtained a bright polymer solution and a separated aqueous phase with a small amount of unused calcium hydroxide. Most of the aqueous phase was removed with a pipette. The two polymer solutions were combined and used for dry-spinning of fibers. The inherent viscosity of the polymer was 1.04 dL/g.

Characterization Tests

Dilute Solution Viscosity. Inherent viscosity, $\eta_{\text{inh}} = \ln(\eta_{\text{rel}})/c$, values were determined in *m*-cresol at 30°C and a concentration *c* of 0.5 g of polymer per 100 mL of solution, unless otherwise specified.

Polymer Melt Temperature. Polymer melting was determined on dry powdered polymer on a chrome-plated gradient temperature bar and is noted as the temperature at which the polymer under moderate sliding pressure leaves a molten or waxy trail adhering to the bar.[22]

Light Stability. The light stability of fibers and films was tested by exposing them in a Model FDA-R Fade-Ometer (Atlas Electric Devices Co., Chicago, IL) equipped with a xenon arc. The equipment was operated in accordance with the standard procedure for dyed textiles except that the samples were mounted on 91-pound white Bristol Index board and clipped, top and bottom, in the usual position. Fibers were wound on the cardboard in the longer, vertical direction for physical testing. For observing development of color, fibers were wound in a mat in the shorter direction and strips of film were stapled to the cardboard face. For the color test a portion of the film or fiber was shielded by a strip of cardboard which could be lifted for observations. The machine gave a light exposure equivalent to 53 standard sunlight h in 20 h of operating time, as determined by the use of U. S. Bureau of Standards colored papers.

HEALTH AND SAFETY CONSIDERATIONS

No unusual safety precautions were needed for most of this work. Some of the solvents present breathing and contact hazards and should be handled so as to minimize exposure. Tetrahydrofuran, in particular, can cause serious liver damage. Furthermore, tetrahydrofuran forms peroxides with the consequent danger of violent explosions. It should be stabilized with metallic sodium and stored in brown bottles. Tests for peroxide should be made frequently and contaminated solvent discarded. See appropriate manuals on solvent toxicities and purification procedures.

Phosgene is an especially volatile and toxic material. It is available in special cylinders for laboratory use and should be handled in small quantities as outlined in the Experimental section. Warnings should be in place on laboratory doors and on any access to the building roof where hood vents are located. No activities should be in progress on the roof. A plan should be agreed upon for laboratory and building evacuation should an accidental spill occur.

The author is indebted to W. H. Bonner and W. H. Behnke for data on the polyurethane from 2,2-bis(4-aminophenyl)propane and 2,2-bis(4-hydroxyphenyl)propane chloroformate, to M. Katz for solubility data on the polyurethane from piperazine and ethylene glycol chloroformate, and to W. F. Dryden for excellent technical assistance.

References

1. R. J. W. Reynolds, in *Fibres from Synthetic Polymers,* R. Hill, Ed., Elsevier, New York, 1953, pp. 158–169.
2. E. L. Wittbecker and M. Katz, *J. Polym. Sci.,* **40,** 367 (1959).
3. E. L. Wittbecker, U.S. Pat. 2,731,445 (1956); assigned to the Dupont Co.

4. P. W. Morgan, *Condensation Polymers by Interfacial and Solution Methods,* Wiley-Interscience, New York, 1965.

5. T. Tanada and T. Yokoyama, in *Interfacial Synthesis,* F. Millich and C. H. Carraher, Jr., Eds., Dekker, New York, 1977, Vol. II, pp. 231–268.

6. D. J. Lyman, *J. Polym. Sci.,* **45,** 49 (1960).

7. M. Matzner, R. P. Kurkjy, and R. J. Cotter, *Chem. Rev.,* **64,** 645 (1964).

8. M. Matzner and R. Barclay, Jr., *J. Appl. Polym. Sci.,* **9,** 3321 (1965).

9. M. Matzner, R. Barclay, and C. N. Merriam, *J. Appl. Polym. Sci.,* **9,** 3337 (1965).

10. E. L. Wittbecker, W. S. Spliethoff, and C. R. Stine, *J. Appl. Polym. Sci.,* **9,** 213 (1965).

11. W. Sweeny, U.S. Pat. 3,234,167 (1966); assigned to the Dupont Co.; *Chem. Abstr.,* **64,** 14343e (1966).

12. P. W. Morgan, U.S. Pat. 3,391,111 (1968); assigned to the Dupont Co.

13. P. W. Morgan, U.S. Pat. 3,395,122 (1968); assigned to the Dupont Co.

14. A. E. Barkdoll, D. C. England, H. W. Gray, W. Kirk, Jr., and G. M. Whitman, *J. Am. Chem. Soc.,* **75,** 1156 (1956).

15. P. W. Morgan, in *Encyclopedia of Polymer Science and Engineering* Wiley, New York, 1987, Vol. 8, pp. 221–237.

16. H. Kobsa, *J. Org. Chem.,* **27,** 2293 (1962).

17. S. B. Maerov, *J. Polym. Sci.,* **A3,** 487 (1965).

18. J. Lo, S. N. Lee, and E. M. Pearce, *J. Appl. Polym. Sci.,* **29,** 35 (1984).

19. J. K. Stille and T. W. Campbell, *Condensation Monomers,* Wiley-Interscience, New York, 1968, pp. 208–210.

20. C. W. Stephens, U.S. Pat. 3,211,774 (1967); assigned to the Dupont Co.; *Chem. Abstr.,* **64,** 655f (1966).

21. C. W. Stephens and W. Sweeny, U.S. Pat. 3,211,775 (1965); assigned to the Dupont Co.

22. W. Sorenson and T. W. Campbell, *Preparative Methods of Polymer Chemistry,* 2nd Ed., Wiley-Interscience, New York, 1968, pp. 57–59, Method A.

Received March 24, 1989
Accepted August 23, 1989