U). We thank Ulla Jacobsson, Department of Organic Chemistry, for running the NMR shift correlation spectrum and Lars Göran Danielsson, Department of Analytical Chemistry, who performed the atomic absorption analysis.

Registry No. DXO, 35438-57-4; DXO (homopolymer), 121425-66-9; DXO (SRU), 121425-79-4; DDXO (homopolymer), 121425-68-1; Bu_2SnO, 818-08-6; Sn-OKt, 301-10-0; $(i\text{-PrO})_4Ti$, 546-68-9; zinc acetate, 557-34-6; aluminum isopropoxide, 555-31-7; tetrahydro-4*H*-pyran-4-one, 29943-42-8.

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Synthesis and Characterization of a Thermotropic, Liquid-Crystalline Polyester Comprising Phenyl Benzoate Groups Connected via a Tris(ethylene oxide) Spacer

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ABSTRACT: A new, thermotropic, liquid-crystalline dimer and high molecular weight polymer in which the rigid, mesogenic unit is connected via a tris(ethylene oxide) spacer have been synthesized. The polymer was fully characterized by IR, NMR, GPC, and dilute solution light scattering and viscometry. Experimental data indicate $\bar{M}_w \approx 100\,000$ and $\bar{M}_w/\bar{M}_n = 1.9$. The dimer revealed monotropic behavior with a nematic → isotropic transition temperature of 125.6 °C and an associated enthalpy of 0.45 kcal/mru, whereas the polymer exhibited a nematic range of approximately 3 °C, with a corresponding nematic → isotropic transition temperature of 141 °C and an associated enthalpy of 0.51 kcal/mru. Comparison of these values with the ones for the corresponding polymer with an even-numbered decamethylene spacer group indicates not only a lower nematic-to-isotropic transition temperature but, more importantly, a much lower (ca. one-third) enthalpy and entropy of the nematic-to-isotropic transition. These findings are consistent with the model of highly extended chain conformations for main-chain, thermotropic polymers with alkylene spacers and indicate little tendency for conformational order and lower orientational order in the polymer with the more flexible ethylene oxide based spacer.

Introduction

Main-chain, liquid-crystalline polymers comprising rigid units connected via flexible spacers have been studied in great detail in recent years. For this class of polymers it is now well established that the spacer groups play critical roles in determining the stability of the liquid-crystalline state over the isotropic state.[1-4] Furthermore, the spacer groups are not merely playing the role of solvent but rather participate actively in the ordering process in the nematic state. Previous studies have shown that the stability and molecular order of nematic states in semiflexible, thermotropic polymers are dominated primarily by the characteristics of highly extended conformers, which are favored due to steric packing considerations.[5-7] In addition, conformational ordering in the nematic state is found to be the most significant feature differentiating polymer liquid crystals from their monomeric analogues. Hence, the nature of molecular order in nematic polymers and its dependence on chemical structure are of utmost importance. In this context, we felt it would be of great interest to alter the nature of the spacer group by substituting the alkylene-type spacer with a more flexible ethylene oxide based spacer.

Although main-chain, liquid-crystalline (LC) polymers incorporating flexible spacers based on ethylene oxide have been previously reported in the literature,[8-12] many of these incorporate relatively long, rigid mesogens, which exhibit both smectic and nematic mesophases and yield relatively high isotropic transition temperatures (>250 °C). A model dimer and high molecular weight polymer in which the rigid mesogenic unit is short enough to yield a nematic phase in a temperature regime well below the onset of thermal decomposition would be desirable (see structures below). Furthermore, these structures would permit direct comparison with the previously studied alkylene-based spacer systems with an identical mesogenic group.

Results and Discussion

The chemical composition of the homopolymer was confirmed both by IR and ^1H NMR. The IR spectrum of the homopolymer exhibits the characteristic absorption bands one would expect for a polymer composed of aro-

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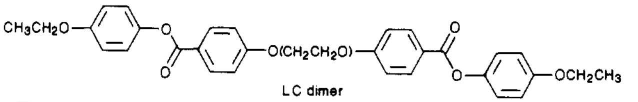
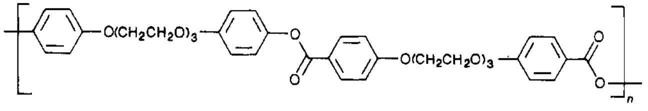


LC dimer



LC polyester

matic ester, aromatic ether, and alkyl ether linkages. Much more detailed information is obtained from the ^{1}H NMR data for the homopolymer; see Figure 1. Resonances that might be attributed to a significant number of end groups are clearly absent. Furthermore, one can clearly distinguish the various protons associated with the two respective monomer molecules. Thus, for the diacid portion of the polymer molecule, the resonances associated with the aromatic protons ortho to the carbonyl group and the aromatic protons ortho to the ether moiety are clearly displayed at a chemical shift of 8 and 7 ppm, respectively. The resonances of the alkyl protons α, β, and γ to the aromatic group occur at 4.1, 3.8, and 3.7 ppm, respectively. In the case of the diphenol portion of the polymer molecule, the proton resonances associated with the aromatic protons ortho to the oxygen can be observed as a multiplet centered at a chemical shift of 6.8 ppm with the corresponding alkyl resonances at 4.0, 3.8, and 3.7 ppm, respectively. Integration of the peaks at 8, 7, 6.8, 4.1, 4.0, 3.8 and 3.7 ppm yields the expected ratio of 2:2:4:2:2:4:4.

In order to ascertain the formation of a high molecular weight polymer via the interfacial polymerization reaction, the unfractionated polyester was thoroughly characterized by size exclusion chromatography, low-angle laser light scattering, and viscometry. Characterization of the solution behavior was facilitated by the fact that the polymer was readily soluble in a number of organic solvents, i.e., chloroform, *N*-methylpyrrolidinone, tetrahydrofuran (hot), and dioxane.

The absolute weight-average molecular weight, $\bar{M}_w$, was determined on the unfractionated polymer in *N*-methylpyrrolidone and chloroform by low-angle light scattering. The excess Rayleigh factor was measured for five concentrations and extrapolated to infinite dilution, yielding $\bar{M}_w = 105000 \pm 10000$ and $\bar{M}_w = 116000 \pm 10000$ in NMP and chloroform, respectively. The light-scattering measurements were straightforward and showed classical behavior; see Figure 2.

The intrinsic viscosity ($[\eta] = 103$ mL/g) was determined in NMP by extrapolation of reduced and inherent viscosities for four concentrations to infinite dilution. The polymer exhibited classical viscosity behavior and the observed $[\eta]$ is consistent with molecular weight data reported for poly(ethylene terephthalate) (PET); i.e., the Mark–Houwink constants reported in the literature for PET in various good solvents predict $[\eta] = 110 \pm 10$ mL/g for a $\bar{M}_w = 100000$.[13,14]

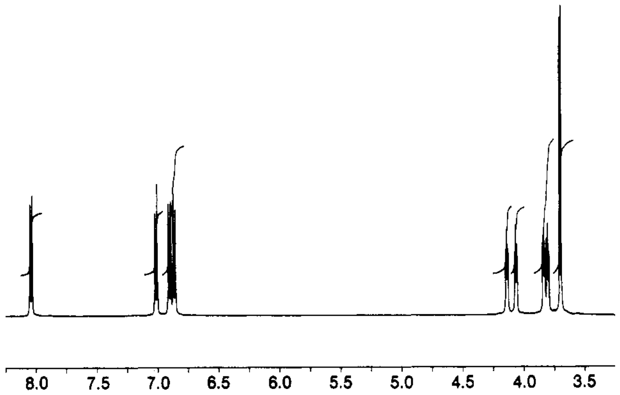


Figure 1. 500-MHz ^{1}H NMR spectrum of the LC polyester in CDCl$_3$.

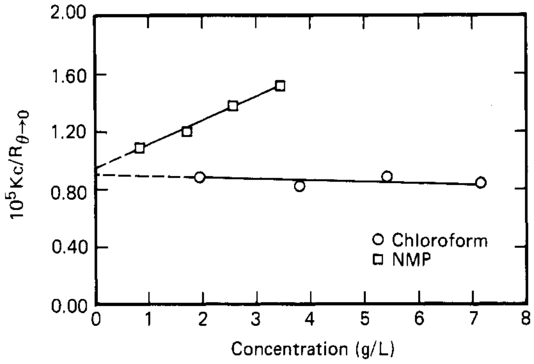


Figure 2. Low-angle light-scattering determination of the LC polyester in NMP and CHCl$_3$.

Table I
SEC Data Relative to Polystyrene for the LC Polyester in Tetrahydrofuran and Chloroform

	THF	CHCl$_3$
$\bar{M}_{peak}$	89000	113000
$\bar{M}_w$	88000	131000
$\bar{M}_w\backslash\bar{M}_n$	1.91	2.21
$\bar{M}_z/\bar{M}_w$	1.55	1.76

The polydispersity of the unfractionated polymer was determined by size exclusion chromatography (SEC) with tetrahydrofuran (THF) and chloroform as mobile phases and styrene/divinylbenzene (PLGel) columns calibrated with a series of 15 narrow-distribution polystyrene standards. In THF, the columns, refractive index detector, and sample injection compartment were all held at 50 °C, since the polymer would precipitate at lower temperatures. The distribution obtained was very similar in shape and width to a most-probable distribution with $\bar{M}_w/\bar{M}_n = 1.9$. These results were confirmed by measurements using chloroform, in which the polyester remains soluble at room temperature. The SEC data in chloroform are compared with those obtained in THF in Table I. The larger values obtained for the molecular weights relative to polystyrene and for the polydispersity index in chloroform are probably due to the greater solubility of the LC polyester in this solvent. Although the molecular weights are relative to polystyrene, comparison with the light-scattering results suggests that the correction factor is not large, i.e., less than a factor of 2. Size exclusion chromatography separates by hydrodynamic volume, which may be expressed as the product $[\eta]M$ or, by use of the Mark–Houwink parameters K and a, by KM^{1+a}, where K and a are dependent on polymer, solvent, and temperature. SEC results relative to polystyrene make no correction for changes in K and a from polystyrene to the polymer being measured. The polydispersity results are only affected by changes in the exponent a in the Mark–Houwink relation. Flexible polymers in good solvents may be expected to have $a \approx 0.7$. The light-scattering results suggest that both THF and chloroform are relatively poor solvents for the LC polymer in the thermodynamic sense, so that the exponent a may be less than the value of 0.7 expected for polystyrene in THF or chloroform; both are good solvents for polystyrene. If the value for a were as small as 0.5 (Gaussian coil with no excluded volume), the real dispersivity $\bar{M}_w/\bar{M}_n$ would still only increase by about 30%. Alternatively, the exponent a may be somewhat larger than 0.7 due to the

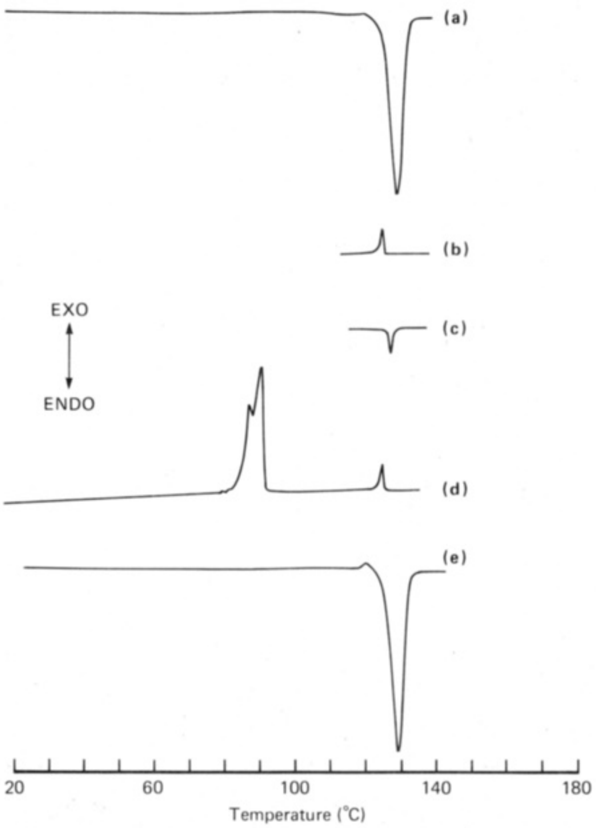


Figure 3. DSC thermograms of the model dimer: (a) initial heating from room temperature to 140 °C; (b) cooling from 140 to 110 °C; (c) heating from 110 to 140 °C; (d) cooling from 140 to room temperature; (e) heating from room temperature to 140 °C. Heating and cooling rates were 5 °C/min.

"stiffness" (long rigid segment) of the polymer in comparison to polystyrene. In this case, the reported apparent dispersivity might be too large. However, it is unlikely that *a* would be any larger than 0.9, so that deviations in this direction are also expected to be small. Thus, the dispersivity value is relatively insensitive to small changes in the Mark–Houwink exponent *a*.

Differential scanning calorimetry (DSC) in conjunction with high-temperature microscopy of both the model dimer and the polymer yielded additional information as to the magnitude and nature of phase transitions observed. The model dimer exhibited monotropic behavior on initial melting with a crystalline-to-isotropic melting transition at 124–129 °C and a transition enthalpy of approximately 27.5 cal/g. Upon cooling, a new transition occurs at 125.6 °C and an associated enthalpy of 1.3 cal/g, indicating a phase change to a mesomorphic state, which then supercools for approximately 40 °C before crystallization occurs at about 80–90 °C, employing a cooling rate of 5 °C/min. However, if the material is only allowed to cool to just below the isotropic-to-mesomorphic transition, the material can be cycled back and forth yielding reproducible transition temperatures of 125.6 °C with an average associated enthalpy of 1.3 cal/g; see Figure 3. Reheating of the melt-crystallized material yields a similar crystal-to-isotropic transition temperature and enthalpy, indicating identical behavior for the solution and melt-crystallized dimer. The observed mesophase-to-isotropic transition enthalpy of 1.3 cal/g is consistent with a nematic mesophase, which was confirmed by high-temperature microscopy. Figure 4 illustrates the mesophase observed between crossed polars at 124 °C upon cooling from the isotropic phase. The nematic nature of this mesophase can be inferred from disclinations of strength $\pm{}^{1}/_{2}$ and ± 1.

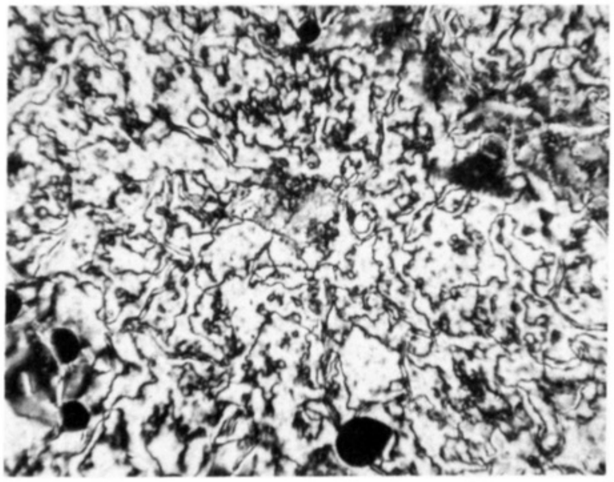


Figure 4. Nematic texture of the dimer mesophase at 125 °C, observed between crossed polars. Magnification = 91×.

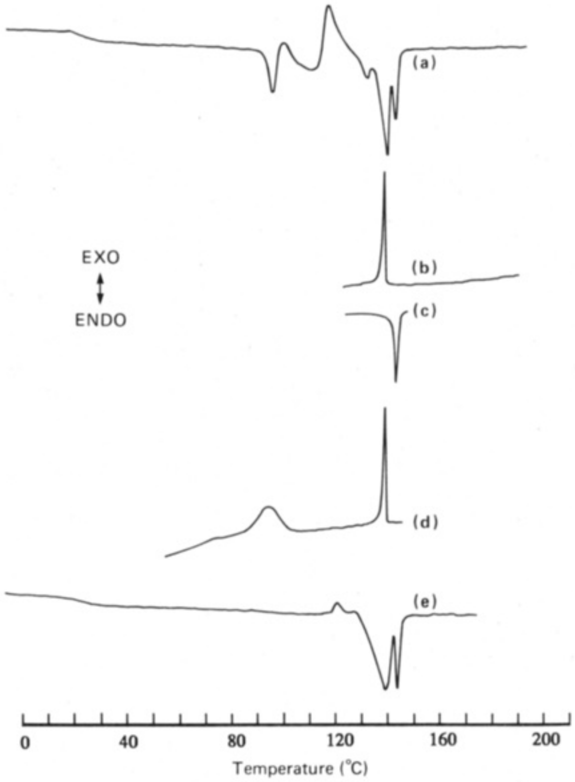


Figure 5. DSC thermograms of the LC polyester: (a) initial heating from 0 to 200 °C; (b) cooling from 200 to 125 °C; (c) heating from 125 to 150 °C; (d) cooling from 150 °C to room temperature; (e) heating from 0 to 175 °C. Heating and cooling rates were 5 °C/min.

Similar experiments with the high molecular weight polymer yielded rather surprising results. Initial heating of the polymer revealed a glass transition temperature at approximately 25 °C followed by a series of exo- and endotherms until the polymer finally exhibited a nematic to isotropic transition at approximately 141 °C (see Figure 5). Upon cooling from the isotropic state, a distinct phase transition to a mesophase can be observed at 140.6 °C with an associated enthalpy of 1.5 cal/g. This mesophase again supercools for approximately 40 °C and crystallization occurs at 90 °C, using a cooling rate of 5 °C/min. However, similar to the model dimer thermal behavior, cooling to just below the initial mesophase transition allows repeated cycling through the transition, yielding a reproducible transition temperature and enthalpy of 140.6 °C and 1.5 cal/g, respectively. Most interesting is the behavior of the

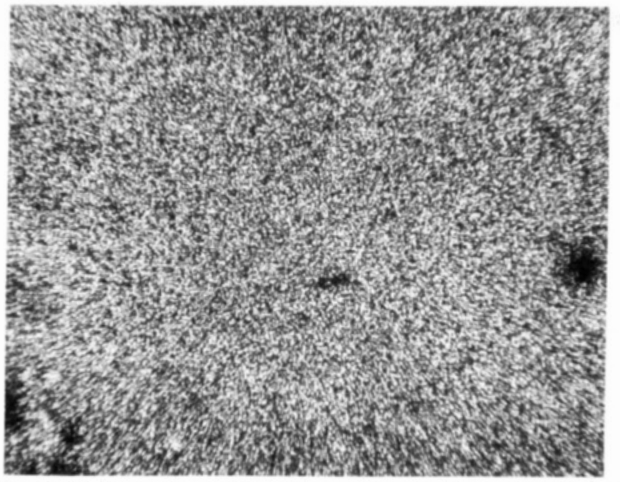


Figure 6. Nematic texture of the LC polyester at 140 °C, observed between crossed polars. Magnification = 91×.

homopolymer if it is allowed to slowly crystallize by cooling the material from the isotropic state at 5 °C/min. Upon reheating this material from room temperature, one now observes the T_g at 25 °C, a small exotherm most likely due to further crystallization, followed by melting of the polymer to the nematic phase and finally the isotropic phase. The multiplicity of phase transitions prior to the latter two endotherms as observed upon initial heating of the polymer have completely disappeared. Such behavior is not uncommon, since the virgin polymer has partially crystallized from solution. Subsequent heating to the isotropic phase and slow cooling results in removal of this history and yields a melt-crystallized sample. It is likely that the crystalline melting point will depend on the thermal history of the sample, but the isotropic–nematic transition upon cooling should be independent of the sample history. Observation of the polymer at 140 °C between crossed polars reveals a birefringent texture with somewhat similar microstructure as observed for the model dimer (Figure 6). This texture is nematic in nature; however, features are much finer as compared to the model dimer. This observation is consistent with general observations made comparing polymeric mesogens with low molecular weight analogues.

Comparison of the thermodynamic data of the tris(ethylene oxide) based spacer system with the decamethylene spacer system reveals striking differences between the two systems, as listed in Table II. It should be noted that the repeat unit, as referred to in Table II, stoichiometrically corresponds to half the true chemical polymer repeat unit illustrated in the Introduction. The repeat unit as defined for the thermodynamic calculations refers to the sequence comprising one rigid unit and one flexible unit. In the case of the alkylene based systems, one observes a large increase in both the nematic-to-isotropic transition temperature, $T_{N\to I}$, and the enthalpy change, $\Delta H_{N\to I}$, in going from monomer to dimer. A similar increase is noted in comparing the dimer with the polymer. This trend is in general accordance with observations published for a number of semiflexible liquid-crystalline polymer systems. A similar comparative analysis of the ethylene oxide spacer based system yields striking differences, especially in comparing the model dimer with the high molecular weight polymer. Thus, there is only a relatively small difference in the nematic-to-isotropic transition temperature and enthalpy between the dimer and polymer. Furthermore, the magnitude of observed nematic-to-isotropic transition enthalpy and entropy changes for both the dimer and the polymer is less than one-third of those for the analogous decamethylene spacer polymer.

Table II
Comparison of the Thermodynamic Data for Decamethylene and Tris(ethylene oxide) Based LC Polyesters

	spacer = $-O(CH_2CH_2)_5O-$[a]			spacer = $-O(CH_2CH_2O)_3-$		
	$T_{N\to I}$	$\Delta H_{N\to I}$[b]	$\Delta S_{N\to I}$[c]	$T_{N\to I}$	$\Delta H_{N\to I}$[b]	$\Delta S_{N\to I}$[c]
monomer	79 °C	0.18	0.51	79 °C	0.18	0.51
dimer	148 °C	0.82	1.95	126 °C	0.41	1.03
polymer	215 °C	1.60	3.28	141 °C	0.51	1.23

[a] Results from ref 2. [b] kcal/mol of repeat unit (mru). [c] cal/(mru K).

Conclusion

These findings are consistent with the model of flexible spacer group participation in the ordering process in the nematic state. Since the nematic-to-isotropic transition enthalpy is derived from both orientational and conformational energy contributions, these results indicate that the more flexible ethylene oxide based spacer group exhibits much less tendency for conformational ordering in the nematic state and a lower order parameter than the corresponding alkylene based spacer groups, which were found to assume highly extended conformations.[5-7] Detailed investigations of conformational and orientational order in the tris(ethylene oxide) based dimer and polymer employing the ^1H NMR and ^2H NMR measurements of deuterium-labeled spacer groups will be reported in a separate paper,[15] together with the calculations of the thermodynamic properties based on the rotational isomeric state model.

Experimental Section

1,2-Bis(2-chloroethoxy)ethane was obtained from Aldrich Chemical and used as received. Methyl *p*-hydroxybenzoate and *p*-(benzyloxy)phenol were obtained from Eastman Kodak and were employed without further purification.

The ^1H NMR spectrum of the polymer was obtained on a Bruker AM-500 using deuteriochloroform as a solvent, a pulse width of 5.0 μs (60° pulse), and a pulse repetition rate of 4.3 s.

Melting points of all monomer intermediates were determined on a Hoover Melting Point Apparatus and are uncorrected.

Thermal analyses were obtained on a Du Pont System employing a Model 1090 controller coupled with a DSC module.

Size exclusion chromatography of the unfractionated polymer was obtained on a Waters 150 C using THF as the mobile phase. The columns, refractive index detector, and sample injection compartment were held at 40 °C.

Weight-average molecular weights were obtained on 0.5-μm filtered samples with a Chromatix KMX-6 and experimentally determined differential refractive index increments of 0.107 and 0.158 for *N*-methylpyrrolidinone and dioxane, respectively.

Mesophase textures were observed on a Zeiss microscope coupled with a Mettler FP 52 hotstage and a Mettler FP 5 temperature controller.

1,2-Bis[2-(4-carboxyphenoxy)ethoxy]ethane (I). Bis(chloroethoxy)ethane (1.87 g, 0.010 mol), 4.56 g (0.030 mol) of methyl *p*-hydroxybenzoate, and 5.53 g (0.040 mol) of potassium carbonate were suspended in 50 mL of dry dimethyl sulfoxide (DMSO) and heated under argon and constant stirring at 140 °C for 10 h. The reaction mixture was then poured into ice–water and the precipitate filtered and sucked dry on the filter. The crude material was now twice recrystallized from absolute ethanol, filtered, and then suspended in 100 mL of a 10 wt % KOH solution in 90% methanol and refluxed for 5 h. The mixture was then poured into cold water and the clear solution acidified with dilute aqueous HCl, yielding a finely divided white precipitate. This was filtered and dried in vacuo at 70 °C for 24 h, yielding 3.28 g (84.2%) of the free diacid. For analytical purposes, a sample was recrystallized from dioxane, mp 227–229.5 °C.

1,2-Bis[2-[4-(chloroformyl)phenoxy]ethoxy]ethane (II). Diacid I (2.5 g, 0.006 mol) was suspended in 25 mL of ethyl acetate containing 5 g of thionyl chloride. The mixture was refluxed for approximately 6 h until the solution had turned clear and no more gas evolution was evident. The excess ethyl acetate and thionyl chloride were evaporated under vacuum, and the residue was crystallized from isopropyl ether and then toluene/hexane to yield 1.5 g (55%) of the diacyl chloride, mp 66–67 °C.

1,2-Bis[2-(4-benzyloxyphenoxy)ethoxy]ethane (III). (Benzyloxy)phenol (6.00 g, 0.030 mol), 1.87 g (0.010 mol) of bis(chloroethoxy)ethane, and 5.53 g (0.040 mol) of potassium carbonate were suspended in 50 mL of dry DMSO and heated under argon and with constant stirring for 10 h at 140 °C. The reaction mixture was then poured into cold water and allowed to stand overnight in the refrigerator. The precipitate was then filtered and vacuum dried at 50 °C for 24 h, yielding 3.83 g (75%) of product. The material was then recrystallized once from absolute ethanol before proceeding to the next step, mp 108–109 °C.

1,2-Bis[2-(4-hydroxyphenoxy)ethoxy]ethane (IV). III (5.14 g, 0.010 mol) was dissolved in 75 mL of dry THF with slight warming in a 250-mL round-bottom flask equipped with a three-way stopcock and gas balloon. Next, 2.1 g of 10 wt % Pd on charcoal was added. The flask was now evacuated and filled with hydrogen via the balloon. This flushing procedure was repeated twice, before opening the flask to the hydrogen supply. The hydrogenolysis was followed by TLC employing a hexane/ethyl acetate solvent system. Once the reaction was complete, the reaction mixture was filtered and the solvent evaporated on a rotary evaporator. The crude material was then recrystallized from 300 mL of xylenes and dried under vacuum, yielding 3.0 g (89.8%) of product, mp 112.5–113.5 °C.

Dimer Synthesis. Diacyl chloride II (4.27 g, 0.010 mol) was dissolved in 50 mL of dry THF and added dropwise to a solution of 2.80 g (0.020 mol) of *p*-ethoxyphenol and 2.02 g (0.020 mol) of triethylamine in 50 mL of dry THF. The temperature was maintained at 0 °C throughout the addition via external cooling with ice. The reaction mixture was then allowed to reach ambient temperature and stirring was continued for an additional 16 h. The solvent was then removed on a rotary evaporator and the residue slurried in water, filtered, and finally dried under vacuum at 75 °C. The crude product was then dissolved in 75 mL of dry THF and passed through a basic alumina column of activity I. The resulting solution was stripped and the white material recrystallized from toluene yielding 5.95 g of final product, mp 125.5–126.5 °C.

Polymer Synthesis. Diphenol IV (1.672 g, 0.0050 mol) and 0.400 g (0.010 mol) of NaOH were dissolved in 250 mL of deionized water. This solution was added to a 1-quart Waring blender. Next, 1.5 g of Adogen was added to the mixture with slow stirring, followed by crushed ice to provide internal cooling. Diacyl chloride II (2.136 g, 0.0050 mol) dissolved in 25 mL of dichloromethane was now added in one portion while the blender speed was increased to a maximum. The suspension was stirred for 5 min and then poured into 500 mL of acetone. The precipitate was filtered and then redissolved in 125 mL of hot THF. The polymer precipitated from the THF solution upon cooling and was filtered after standing overnight. The material was then dried under vacuum 50 °C for 24 h yielding 2.9 g of off-white polyester.

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Registry No. I, 101678-92-6; II, 105744-17-0; III, 121030-38-4; IV, 29239-84-7; (II)(IV) (copolymer), 121030-40-8; (II)(IV) (SRU), 101797-81-3; LC dimer, 121030-39-5; $ClCH_2CH_2(OCH_2CH_2)_2Cl$, 112-26-5; methyl *p*-hydroxybenzoate, 99-76-3; *p*-ethoxyphenol, 622-62-8; 4-(benzoyloxy)phenol, 2444-19-1.

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