Synthesis and Characterization of Soluble Aromatic Polyesters Containing Oligophenyl Moieties in the Main Chain

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ABSTRACT: A series of rigid aromatic polyesters containing substituted oligophenyls was prepared. Aliphatic and aromatic side groups were used to increase the solubility. New oligophenyldiols were synthesized by coupling aromatic Grignard reagents with aromatic halides, using palladium complexes as catalysts. The polyesters were prepared by melt polycondensation and characterized by viscosimetry, thermal analysis, and dynamic mechanical analysis. The temperature dependence of the intrinsic viscosity, in the range 30-85 °C, was sensitive to the type and position of the side groups. Polyesters with aromatic substituents were stable up to 400 °C. The glass transition temperatures of the polyesters with aromatic side groups were in the range 150-250 °C. Dynamic mechanical analysis showed that in the cases where aromatic substituents were used to increase solubility, the obtained polymers appear to have useful mechanical properties at high temperatures. The glass transitions appeared in the range 150-220 °C, while a plateau modulus in the range of 10^8 Pa was obtained at high temperatures (up to 350 °C).

Introduction

Rigid polymers have attracted much attention because of their outstanding mechanical properties.[1,2] The unusual properties are due to the highly anisotropic structure which results in a parallel packing of the macromolecular chains. Increase of the chain rigidity results in reduction of the chain folds and in better orientability.[3]

In a certain class of stiff macromolecules, e.g. aromatic polyesters, such a rigidity increase could be performed by the introduction of oligophenyl units in the main chain. Such a modification of the polymer structure is expected to decrease further the solubility and increase the melting point. Even in the cases of aromatic-aliphatic polyesters, introduction of the unsubstituted terphenyl unit in the main chain led to insoluble products.[4,5] In all cases of rigid polymers, the limited solubility in common organic solvents and the very high melting points hinder their applications.

Many efforts have been made to increase the processability of stiff polymers either by the interruption of the rigid character (introducing kinks of flexible units in the main chain)[2,6-10] or by attachment of lateral substituents.[11-27] The second method has found wider application. It mainly concerns of the introduction of flexible side groups onto the polymer backbone which lead to a dramatic increase in solubility and decrease of the glass transition temperature. The length and the nature of the side chains have been examined.[20] The main problem of such a modification is the relatively low thermal stability because of the presence of the aliphatic side chains attached on a thermally stable polymer backbone. Alternatively, aromatic substituents have also been used with some success for the solubilization of aromatic polyesters[13] and recently have attracted increased attention.[23,26,27] Depending on the position and the density of substitution, the resulting polyesters in some cases are amorphous with very good solubility in common solvents and low transition temperatures.[27]

The question about the rigidity or semirigidity of the aromatic polyesters attracted considerable attention in recent years. Estimation of the persistence length in some substituted aromatic polyesters gave much lower values than the expected, obtained from theoretical calculations.[13,28-32] Variation of the persistence length with the kind of substituent was observed in some cases.[13,31] In order to have an idea about the limits for the rigidity increase of the aromatic polyesters, polymers containing oligophenyl units in the main chain are required.

In the present work, we describe the preparation and characterization of aromatic polyesters containing oligophenyl moieties in the main chain in combination with the attachment of different side groups in order to increase solubility. Among the different types of the substituents, aromatic groups are preferred because they provide thermal stability. For that reason new oligophenyldiols (shown in Scheme 1) have been synthesized. 2′,3′,5′-Triphenyl-*p*-terphenyl-4,4″-diol (**2**) was synthesized by metalation of the respective 4,4″-dibromo-*p*-terphenyl derivative with *n*-butyllithium, reaction with trimethyl borate, and subsequent oxidation of the diboronic compound with hydrogen peroxide. 2″,3″,5″-Triphenyl-*p*-quinquephenyl-4,4⁗-diol (**4**) was synthesized using the palladium-catalyzed coupling of 4,4″-dibromo-2′,3′,5′-triphenyl-*p*-terphenyl with either (*p*-(benzyloxy)phenyl)magnesium bromide or (*p*-methoxyphenyl)magnesium bromide. The diol was obtained by catalytic hydrogenolysis in the former case and by the ether cleavage of the methoxy groups with pyridine hydrochloride mediated methyl ether cleavage in the later. Finally, 2,5-diphenylterephthalic acid was synthesized by Pd(dppf)Cl_2-catalyzed coupling of 2,5-dibromo-*p*-xylene with phenylmagnesium bromide and subsequent oxidation of the methyl groups. Polymer synthesis was performed in melt, using either the acetyl derivatives of the synthesized diols and the diacids or the oligophenylene diols with the appropriate diacid dichlorides. The obtained polymers were studied by thermal analysis, viscosimetry, X-ray diffraction, and dynamic mechanical analysis.

Experimental Section

Materials. Chemicals were purchased from Aldrich and used as received. 2,5-Dihexylterephthalic acid,[33] 2′,3′,5′-triphenyl-4,4″-dibromo-*p*-terphenylene,[34] and the catalyst dichloro[1,1′-bis(diphenylphosphino)ferrocene]palladium [$PdCl_2$(dppf)][35] were synthesized according to known procedures. Tetrahydrofuran

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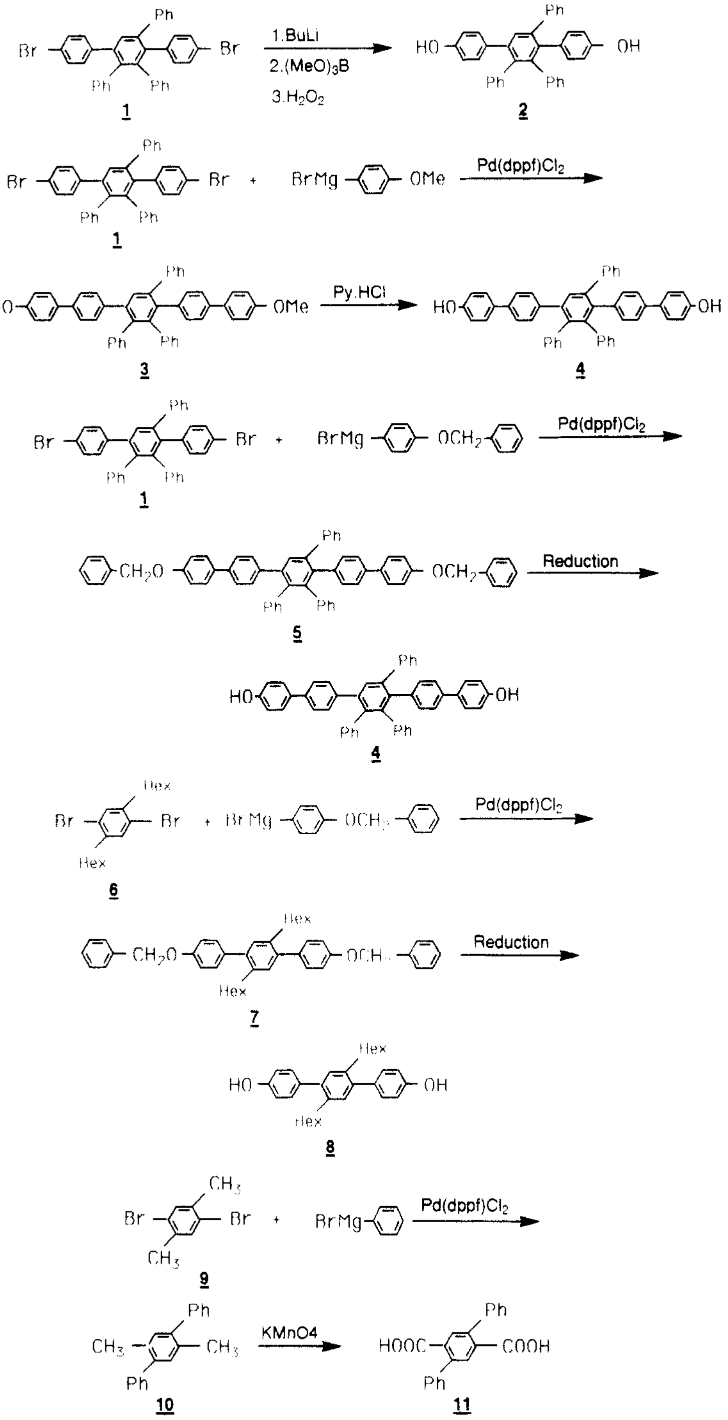
Scheme 1



was distilled from sodium in the presence of benzophenone directly into the reaction flask.

Monomer Synthesis. 2′,3′,5′-Triphenyl-*p*-terphenyl-4,4″-diol (2). 2′,3′,5′-Triphenyl-4,4″-dibromo-*p*-terphenyl (1) (5.15 g, 8.4 mmol) was dissolved in freshly distilled THF (110 mL) under nitrogen. The solution was cooled to −70 °C. *n*-BuLi 1.6 M in hexanes (21 mL) was added dropwise in 10 min. The cooling bath was removed, and the mixture was stirred at room temperature for 1 h. The suspension was cooled again to −70 °C, and trimethyl borate (12 mL) was added within 20 min. The resulting solution was stirred at room temperature for 20 h. After hydrolysis with diluted HCl and neutralization with NaOH, 80 mL of 10% hydrogen peroxide was added, and the mixture was stirred for 1 h. Removal of the solvents under reduced pressure, filtration, washing with water, and drying gave a white solid. Recrystallization from toluene–hexane gave 3.2 g of the desired product 2 (yield 78%), mp 247–248 °C.

FTIR (KBr, cm^{-1}): 3418, 3022, 1610, 1516, 1440, 1424, 1382, 1256, 1172, 1104, 1074, 1018, 838, 764, 702, 552, 534.

The diacetyl derivative of the diol 2 was synthesized using acetyl chloride and triethylamine. The product was recrystallized from toluene–hexane, mp 223–225 °C.

FTIR (KBr, cm^{-1}): 3022, 1752, 1512, 1432, 1368, 1194, 1166, 1018, 1008, 912, 852, 762, 700, 600, 548. ^{1}H NMR (CDCl$_3$): δ = 2.18 (s; 3 H), 2.25 (s; 3 H), 6.7 (d; 2H), 6.9 (m; 14 H), 7.2 (m; 7 H), 7.55 (s; 1H). ^{13}C NMR (CDCl$_3$): δ = 21.00, 119.94, 120.62, 125.53, 125.79, 126.45, 126.79, 127.05, 127.75, 129.98, 130.88, 131.37, 131.51, 131.56, 132.41, 137.58, 138.65, 139.30, 139.49, 139.86, 140.13, 140.17, 141.02, 141.51, 142.02, 148.88, 149.42, 168.70, 169.04.

4,4⁗-Dimethoxy-2″,3″,5″-triphenyl-*p*-quinquephenyl (3). 2′,3′,5′-Triphenyl-*p*-terphenyl (1) (2.0 g, 3.2 mmol) and PdCl$_2$(dppf) (32 mg) were degassed, the reaction flask filled with argon (3 times), and freshly distilled THF (20 mL) was added and heated to obtain a solution. The solution was cooled at room temperature and (*p*-methoxyphenyl)magnesium bromide (13 mmol) in THF was added in 10 min. The mixture was refluxed for 2 days. Hydrolysis and addition of methanol gave a solid which was isolated by filtration, washed with hexane, and dried in vacuo. Recrystallization from toluene–hexane gave 1.6 g (73%) of pure compound 3 which had mp 278–279 °C.

FTIR (KBr, cm^{-1}): 3026, 2958, 2834, 1766, 1606, 1580, 1500, 1440, 1288, 1248, 1196, 1178, 1038, 822, 804, 770, 702, 612, 534. ^{1}H NMR (DMSO-d_6): δ = 3.78 (s; 3 H), 3.82 (s; 3 H), 7.0 (m; 16H), 7.25 (m; 9H), 7.50 (m; 5H), 7.60 (s; 2H). ^{13}C NMR (DMSO-d_6): δ = 55.08, 114.19, 114.28, 124.17, 125.20, 125.42, 125.76, 126.35, 126.51, 126.91, 127.17, 127.45, 127.65, 129.54, 130.07, 130.73, 130.95, 131.03, 131.46, 131.59, 131.68, 136.38, 137.53, 138.00, 138.57, 138.96, 139.45, 139.53, 139.72, 139.87, 140.31, 141.15, 141.80, 158.71, 158.83.

2″,3″,5″-Triphenyl-*p*-quinquephenyl-4,4⁗-diol (4). 4,4⁗-Dimethoxy-2″,3″,5″-triphenyl-*p*-quinquephenyl (3) (1.17 g) was heated together with 4.1 g of pyridine hydrochloride at reflux for 1 day. The solid was washed with water, filtered out, and dried in vacuo. Recrystallization from 95% ethanol gave 0.67 g (60%) of 4, mp 268–270 °C.

4,4⁗-Bis(benzyloxy)-2″,3″,5″-triphenyl-*p*-quinquephenyl (5). 2′,3′,5′-Triphenyl-*p*-terphenyl (1) (6.0 g, 9.7 mmol) and PdCl$_2$(dppf) (76 mg) were degassed flushed with argon (3 times) and then dissolved with heating in freshly distilled THF (60 mL). The mixture was cooled at room temperature and (*p*-(benzyloxy)phenyl)magnesium bromide (40 mmol) in THF was added within 30 min. The mixture was heated at reflux for 1 day. The yellow suspension was quenched with methanol, and the solid was filtered out and dried in vacuo. Recrystallization from THF gave 7.2 g (90%) of 5, mp 273–274 °C.

FTIR (KBr, cm^{-1}): 1604, 1498, 1452, 1378, 1286, 1244, 1176, 1028, 824, 738, 698, 536.

2″,3″,5″-Triphenyl-*p*-quinquephenyl-4,4⁗-diol (4). 4,4⁗-Bis(benzyloxy)-2″,3″,5″-triphenyl-*p*-quinquephenyl (5) (4.02 g) and 0.4 g of 10% Pd on activated C were suspended in DMA (50 mL), and the mixture was reduced with H$_2$ at 40 °C for 24 h. The catalyst was removed by filtration, and the diol was precipitated with 1% HCl solution, filtered out and dried in vacuo. Recrystallization from THF–hexane gave 2.9 g (93%) of 4, mp 268–270 °C.

Anal. Found (calc): C, 89.09 (89.32); H, 5.17 (calc 5.69). FTIR (KBr, cm^{-1}): 1610, 1500, 1440, 1256, 1172, 826, 750, 702, 532.

The diacetyl derivative of the diol 4 was synthesized using acetyl chloride and triethylamine. The product was recrystallized from chloroform–hexane, mp 298–300 °C. FTIR (KBr, cm^{-1}): 3028, 1760, 1496, 1432, 1368, 1198, 1108, 1066, 1004, 910, 838, 802, 754, 700, 534. ^{1}H NMR (CDCl$_3$): δ = 2.22 (s; 3 H), 2.25 (s; 3 H), 6.82 (m; 12H), 7.0 (m; 13H), 7.3 (d; 2 H), 7.38 (d; 2H), 7.45 (d; 2H), 7.55 (s; 1H). ^{13}C NMR (CDCl$_3$): δ = 20.93, 121.49, 121.59, 125.27, 125.56, 126.06, 126.19, 126.58, 126.89, 127.55, 127.76, 129.81, 130.23, 131.33, 131.39, 131.84, 136.90, 137.88, 138.29, 138.80, 139.07, 139.22, 139.76, 140.09, 140.17, 140.67, 140.76, 141.49, 141.75, 149.75, 149.91, 169.23.

2′,5′-Dihexyl-*p*-terphenyl-4,4″-diol (8). 2,5-Dihexyl-1,4-dibromobenzene (6) (6.6 g, 16.5 mmol) and PdCl$_2$(dppf) (125 mg) were degassed and filled with argon (3 times) and dissolved in freshly distilled THF (20 mL). In the above solution (*p*-(benzyloxy)phenyl)magnesium bromide (55 mmol) in THF was added within 30 min. The mixture was heated at reflux for 1 day and was quenched with 10% HCl. The product was extracted with CH$_2$Cl$_2$, washed with water, and dried over MgSO$_4$. The organic solvents were removed under reduced pressure, and the solid was triturated with methanol, filtered out, and dried in vacuo. Recrystallization from chloroform–ethanol gave 4.5 g (45%) of 7.

Hydrogenolysis of 7 with Pd on activated carbon as catalyst and recrystallization from toluene–hexane gave 2.5 g (80%) of 8, mp 137–138 °C (lit.^{36} mp 139.5 °C).

2,5-Diphenylterephthalic Acid (11). 2,5-Dibromo-*p*-xylene (9) (5.0 g, 18.9 mmol) and PdCl$_2$(dppf) (170 mg) were degassed, flushed with argon (3 times), and then dissolved in freshly distilled THF (90 mmol). (*p*-(Benzyloxy)phenyl)magnesium bromide (90 mmol) in THF was added within 30 min. The mixture was heated at reflux for 1 d and quenched with diluted HCl. The obtained suspension was triturated with methanol, filtered out, and dried in vacuo to give 4.5 g (92%) of 10.

Table 1. Intrinsic Viscosities in *o*-Dichlorobenzene, at Various Temperatures of the Synthesized Polymers

polymer	[*n*] (mL/g) 30 °C	60 °C	85 °C
Ia	105	102	82
Ib	120	115	100
Ic	130	130	108
Id	148	146	120
IIa	55	41	35
IIb	102 (100)^a	85	74
IIc	130	115	96
IId	135		
IIIa	130	73	54
IIIb	164	109	70
IIIc	200 (164)^a	146	136
IIIc	(160)^b	(135)^b	(115)^b
IVa	40^c	40	
IVb	222^c		

^{a} In chloroform. ^{b} In 1,1,2,2-tetrachloroethane. ^{c} In chloroform–trifluoroacetic acid, 90–10.

Oxidation of 10 with KMnO$_4$ in pyridine–water (9:1) and recrystallization from 95% ethanol gave 3.2 g (55%) of the desired product 11, mp 303–305 °C.

Anal. Found (calc): C, 75.09 (75.46); H, 4.42 (4.43). FTIR (KBr, cm^{-1}): 3026, 1686, 1482, 1418, 1246, 910, 798, 754, 698, 562. ^{1}H NMR (DMSO-d_6): δ = 7.23 (m; 10H), 7.38 (s; 2H). ^{13}C NMR (DMSO-d_6): δ = 127.22, 127.29, 127.88, 127.95, 128.02, 130.60, 130.66, 133.87, 133.94, 139.35, 139.40, 168.24, 168.32.

Polymer Synthesis. Melt Polymerization. A 1.01 mmol amount of the diacetyl derivative, 1.00 mmol of the respective diacid, and 5 mg of Mg as catalyst were placed into a vessel equipped with magnetic stirring, gas inlet/outlet, and vacuum inlet. The flask was evacuated, filled with argon, and immersed in a metal bath at 260 °C (for polymer **IV** at 295 °C). The resulting clear melt were stirred at this temperature for 0.5 h under a very slow stream of argon. When stirring became impossible due to increased viscosity, heating was continued at 280–300 °C for an additional 3 h. Finally, vacuum was applied for 3 h while the reaction mixture was kept at 300 °C. After cooling at room temperature the polymer was dissolved in chloroform, the solution was filtered through glass wool, and the polymer was precipitated in excess of methanol. In the case of polymer **IV** the insoluble part was significant. The polymer was thoroughly washed by methanol and dried to constant weight in vacuo at 60 °C. The results for the various polymers are shown in Table 1.

Polymer and Monomer Characterization. Intrinsic viscosities of the polymers (Chart 1) were measured in chloroform, *o*-dichlorobenzene, and 1,1,2,2-tetrachloroethane at various temperatures as specified in Table 1, with an Ubbelohde-type viscometer in a Schott Gerate AVS 310.

Molecular weights were determined using a Waters 600E gel-permeation chromatograph coupled with a Model 901 photodiode array detector at 254 nm and calibrated with monodisperse polystyrene standards through "Ultrastyragel" columns with 500, 10^4, and 10^5 Å at 25 °C with THF as solvent.

The ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AM 300 spectrometer, using TMS as the internal standard. FTIR spectra were recorded using a Perkin Elmer PC 16 instrument (KBr pellets).

Thermal properties of the polymers were determined by differential scanning calorimetry and thermogravimetric analysis on a Du Pont 990 thermal analyzer equipped with 910 DSC and 951 TGA accessories. Polymer samples of about 10 mg each were examined under a nitrogen flow. The glass transition temperature was taken as the median value of the straight portion of the ΔC_p step observed. The decomposition temperature was obtained as onset of deviation from the baseline.

X-ray measurements were made using Ni-filtered Cu Kα radiation and a θ–θ goniometer.

Dynamic mechanical analyses were performed using a Rheometrics RSA II solid analyzer under nitrogen or air atmosphere at 1 Hz in the temperature range of −100 to +400 °C.

Chart 1

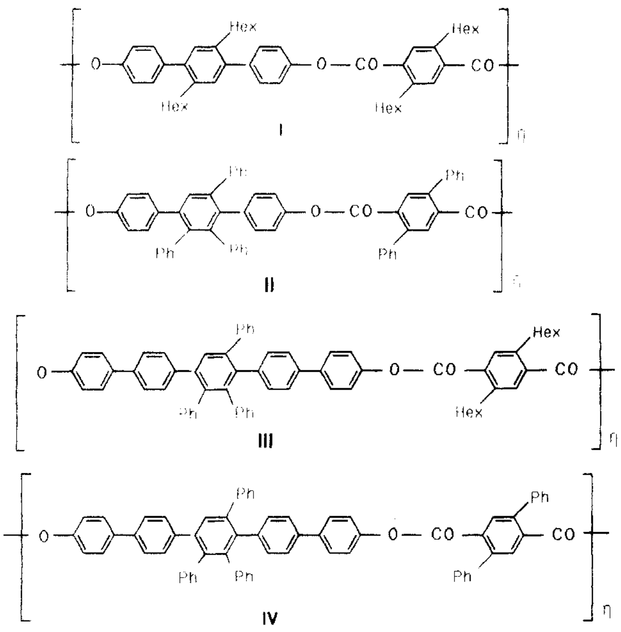


Table 2. Molecular Weights of Polymers Ib,c by GPC Measurements

polymer	M_n[a]	M_w	M_z	M_w/M_n
Ib	27 000	73 500	196 000	2.7
Ic	33 000	72 000	200 000	2.2

[a] In tetrahydrofuran; values obtained from calibration with polystyrene standards.

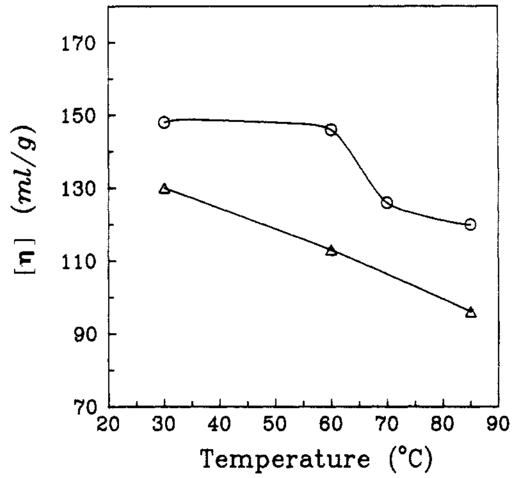


Figure 1. Intrinsic viscosity variation with the temperature for polymers **I** (○) and **II** (△).

Results and Discussion

In order to ensure solubilization of the desired polymeric structures, new substituted oligophenyldiols were required. Two synthetic pathways have been chosen. One of them was based on the conversion of the dibromo derivatives to diboronic esters and final oxidation of the carbon–boron bond to the desired diol.[37] The other one is based on the palladium-mediated coupling of aromatic dibromides with aromatic Grignard reagents. Such reactions are known to be catalyzed by nickel complexes.[38] In our case catalysis with palladium complexes and more specifically[39] with $PdCl_2(dppf)$ proved to be much more effective with respect to yields and purity of the obtained products. The last method was used for the preparation of the 2″,3″,5″-triphenyl-*p*-quinquephenyl-4,4⁗-diol (**4**) and also for a more facile synthesis of the previously described 2′,5′-dihexyl-*p*-terphenyl-4,4″-diol (**8**).[36] Two Grignard reagents have been used, namely the (*p*-methoxyphenyl)magnesium bromide and the (*p*-(benzyloxy)phenyl)magnesium bromide. The second one has the advantage of a more easy removal of the O-protecting group for the generation of the desired diols. Attempts to use the cheaper 4,4″-dichloro-*p*-terphenyl instead of the dibromo derivative were without success.

Finally, using the same palladium-mediated coupling of the 2,5-dibromo-*p*-xylene with excess of phenylmagnesium bromide and subsequent oxidation of the methyl groups, the 2,5-diphenylterephthalic acid was also synthesized. On the other hand, coupling of 2,5-dibromo-*p*-xylene with phenylboronic acid in the presence of $Pd(PPh_3)_4$[40] gave almost the same yield. In the last case the amount of the expensive catalyst used was higher, and also the more expensive phenylboronic acid was needed. All the above described preparations are shown in Scheme 1. Characterization of monomers has been made by elemental analysis, FTIR spectroscopy, and ^1H and ^{13}C NMR spectrometry.

All of the homopolyesters were prepared by the melt polycondensation reactions of either the diols with the respective diacid chlorides or the diacetyl derivatives of the diols with the diacids. All polymers except **IV** were soluble in common chlorinated organic solvents like chloroform, 1,1,2,2-tetrachloroethane, and *o*-dichlorobenzene. Polymer **I** is also soluble in solvents like tetrahydrofuran and toluene, while polymer **IV** needs mixtures of chloroform with trifluoroacetic acid. The very good solubility of the synthesized products arises because of the presence of the bulky substiuents, *n*-hexyl or phenyl groups, in both the diol and terephthalic moieties which reduce the interaction between the polyester chain. The phenyl substituents suppress the crystallization tendency which is evident from the X-ray diffractograms of the polymers **II** and **IV**.

The obtained solubility is desirable for ease of characterization in solution as well as in the solid state. Polymers with intrinsic viscosities higher than 130 mL/g give clear free-standing films after casting from solutions in chloroform.

The results are shown in Table 1. As shown there, in all examined cases polymers with high intrinsic viscosity values, up to 220 mL/g, are obtained. These values suggest that the synthesized polymers had sufficiently high molecular weights so that their mechanical and thermal properties can be compared without concern for the secondary effects caused by molecular weight.

Because of the solubility of the prepared polymers, it was possible to evaluate their molecular weights by GPC and in case of polymer **I** even by using tetrahydrofuran as solvent. The results for polymer **I** are shown in Table 2 and are based on calibration with polystyrene standards. The obtained values are in good agreement with those obtained by Bhowmik and Han[27] for related polymers having biphenyl units in the main chain but are overestimated as we have seen in our previous work.[32] For that reason no further work on the other polymers has been made.

A viscosimetric study has been made for the synthesized polymers. Polymer **I** shows the same temperature dependence of the intrinsic viscosity values as was found previously for related polymers having substituents only in the terphenyldiol moieties.[32] More specifically, the [η] values for the polymer **I** is almost the same as 30 °C and at 60 °C and changes rather sharply at higher temperatures, as shown in Figure 1. This change shows that probably a transition occurs at that temperature. In contrast to

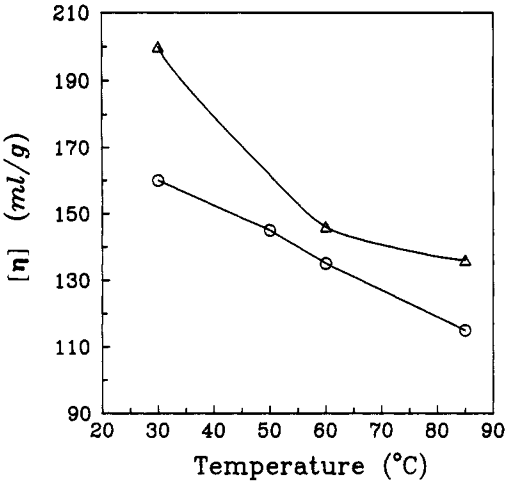


Figure 2. Intrinsic viscosity variation with the temperature for polymer **III**: (△) in *o*-dichlorobenzene; (○) in 1,1,2,2-tetrachloroethane.

polymer **I**, in polymer **II** which differs only in the kind of the substituents but has the same structure of the main chain, the temperature dependence of the [η] differs completely. In this case, a decrease of the [η] values with the temperature was observed as also shown in Figure 1. For both polymers the solvent used was *o*-dichlorobenzene. Measurements in chloroform have also been made at 30 °C giving the same results. These results are in agreement with the rigid nature of the studied polymers, because it is known that for rigid polymers the viscosity values are independent of the solvent.[29] Polymer **III** shows a drastic decrease of the [η] values with the temperature when the measurements were performed in *o*-dichlorobenzene. Measurements in chloroform at 30 °C gave lower values than those obtained in *o*-dichlorobenzene while in 1,1,2,2-tetrachloroethane the same value at 30 °C was obtained. As shown in Figure 2 the temperature dependence of [η] in 1,1,2,2-tetrachloroethane solutions resembles more that observed for polymer **II** despite the presence of the aliphatic substiuents in polymer **III**. The reason for the discrepancy between *o*-dichlorobenzene and tetrachloroethane solutions can be attributed to the limited solubility of the studied polymer in *o*-dichlorobenzene at 30 °C, which is also evident from the segregation observed in the higher molecular weight sample when it was left at that temperature. In any case further work is in progress to also study with other techniques the observed phenomenon.

Finally, in polymer **IV** it was impossible to measure the temperature dependence of [η] because at 30 °C the solution gelled and the obtained measurements were not reproducible even in very diluted solutions. Only addition of 10% trifluoroacetic acid had improved the solubility at 30 °C, but in a such solvent it was impossible to carry out measurements at higher temperatures.

A first approach for structural characterization has been made by X-ray methods with the "as prepared" powders. Polymer **I** shows weak diffraction peaks which indicate the presense of a small fraction of crystalline or mesomorphic material, as shown in Figure 3. Polymers **II–IV** are essentially amorphous in the powdered form as shown also in Figure 3. It is recognized that additional work is needed to characterize more specifically the structures formed.

Thermal analysis has been made by means of DSC and TGA. For polymer **I** there was no evidence for a glass transition in the conventional sense. The DSC thermogram shown in Figure 4 does not show any detectable T_g or melting endotherm up to 300 °C, which is in agreement with previous work on the polymer with the same backbone and aliphatic substiuents only on the terphenyldiol moiety.[25]

On the other hand, polymers with only aromatic substiuents like polymer **II** show classical glass transitions at 218 °C while in polymer **IV** a transition at 265 °C has appeared. Polymer **III** having both aromatic and aliphatic substituents on the diol and diacid moieties, respectively, shows a glass transition at 150 °C. This fact shows that the presence of the aliphatic side groups do not hinder the apperance of the glass transition in all cases.

The thermal stability of the synthesized polymers has been examined in an inert atmosphere. The obtained results are shown in Figure 5 and Table 3. As expected, polymer **I** with four hexyl groups per repeat unit has a considerable weight loss at temperatures higher than 400 °C. As shown in Table 3 more than 65% of the weight has been lost at 500 °C, which is significantly higher than the calculated amount for the removal of the side chains. Polymer **III** with two hexyl groups per repeat unit shows

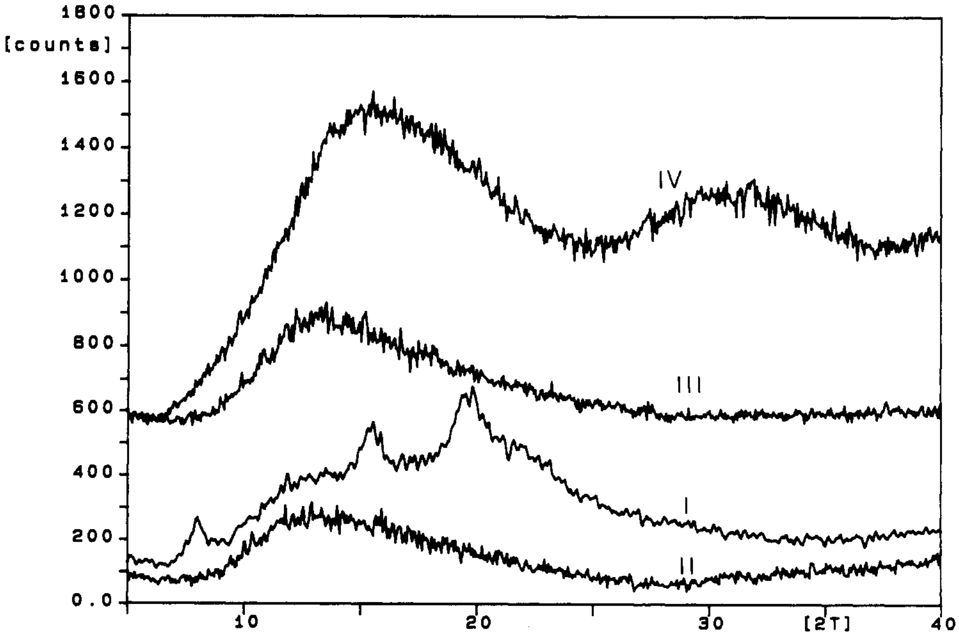


Figure 3. Wide-angle X-ray scattering curves for the synthesized polymers.

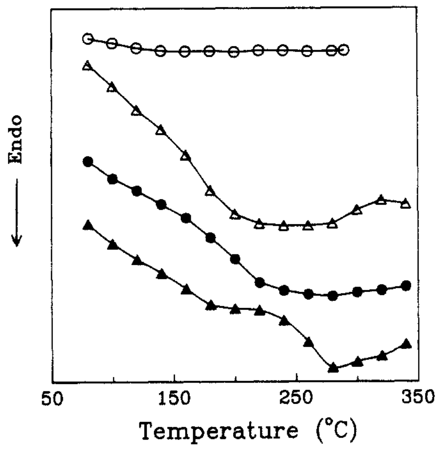


Figure 4. DSC thermograms of the studied polymers: (○) I; (●) II; (△) III; (▲) IV.

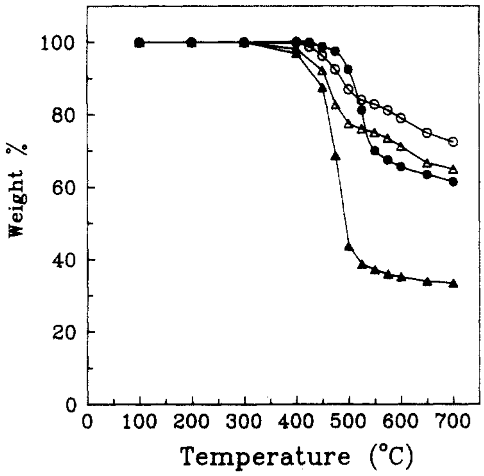


Figure 5. TGA thermograms of the studied polymers: (▲) I; (●) II; (△) III; (○) IV.

Table 3. Thermal Properties of the Synthesized Polymers

polymer	T_g (°C)	T_d (°C)	T_{max} (°C)	weight loss at 500 °C
I		330	475	66
II	218	400	575	8
III	150	350	480	23
IV	265	400	500	13

a considerable reduction of the weight loss to 25% at 500 °C. An obviously better situation is obtained for polymers with aromatic substiuents as shown in Figure 5 and Table 3. The weight loss at 500 °C is about 10%, while at higher temperatures polymer **IV** shows better thermal stability.

More detailed information may be obtained from measurements of the dynamic mechanical behavior of the film forming samples as a function of temperature. Films of about 100 μm thickness were prepared by casting from chloroform solutions. These films were studied for their mechanical relaxation properties by means of a Rheometrics mechanical spectrometer. The mechanical relaxation spectra of polymer **I** are shown in Figure 6. Three relaxations are observed at −60, 60, and ca. 350 °C based on tan δ and E'' peaks. Two lower and broader relaxations are observed in tan δ but not in E''. The relaxation processes can be approached by treating results obtained for other related polymers.[3,20,25] The low-temperature tan δ peak is typical for aromatic polyesters especially bearing aliphatic side chains. This peak is associated with a small decrease in E', which was also observed in the case of poly(2-alkyl-1,4-phenyleneterephthalates)[20] (PAPhT) and are attributed to the reorientation of the carbonyl groups and/or to rotational motions of the end groups of the side chains. The second tan δ peak at 60 °C is associated with a step decrease in E'. This transition has been assigned to the mobility of the side chains accompanied by some conformational rearrangements of the main chain.[3,25,32] The main transition at about 350 °C could be indicative of either a glass or a melting transition. At those temperatures, the polymer particles softened and coalesced, a fact which supports the melting transition. Such a transition was also observed in the case of PAPhT[20] at 290 °C. As expected, the melting transition is shifted to higher temperature, showing the influence of the introduction of the terphenyl unit in the polymer backbone.

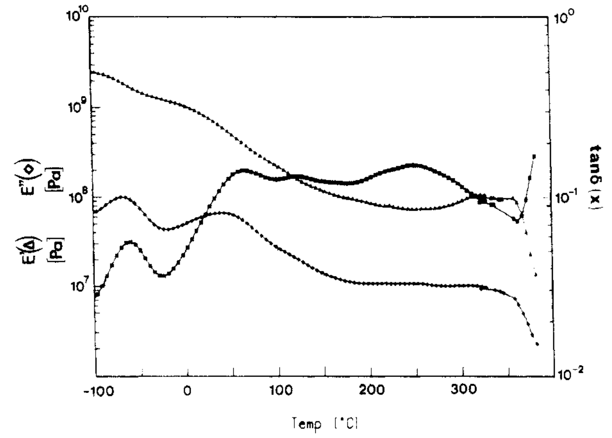


Figure 6. Mechanical–dynamical spectra of polymer **I**.

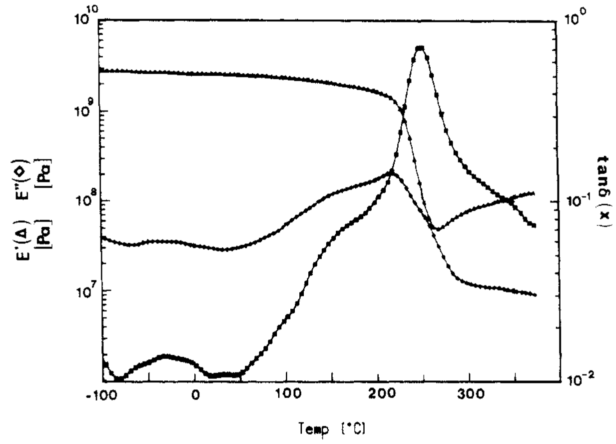


Figure 7. Mechanical–dynamical spectra of polymer **II**.

Keeping the same polymer backbone and using aromatic substituents, as in polymer **II**, results in the relaxation spectra changing completely as shown in Figure 7. A broad transition is observed at low temperatures and is shifted to −30 °C which fits much more the β relaxation process observed in aromatic polyesters, without any effect on the E' value. A shoulder is observed at 150 °C. The E' remaining constant up to 200 °C and the glass transition appearing at 220 °C are in very good agreement with the values obtained by DSC. At higher temperature E' shows a plateau with a positive deviation which could be regarded as an experimental effect rather than as a crosslinking procedure.

In any case, this sample shows quite high E' values (about 10^8 Pa) even at temperatures higher than 350 °C. Comparison of the E' values for polymers **I** and **II**, over the entire temperature range, shows the influence of the substituents on the mechanical properties. The presence of the aromatic substituents brings about solubility of the aromatic polyester and at the same time preserves the mechanical properties of these materials.

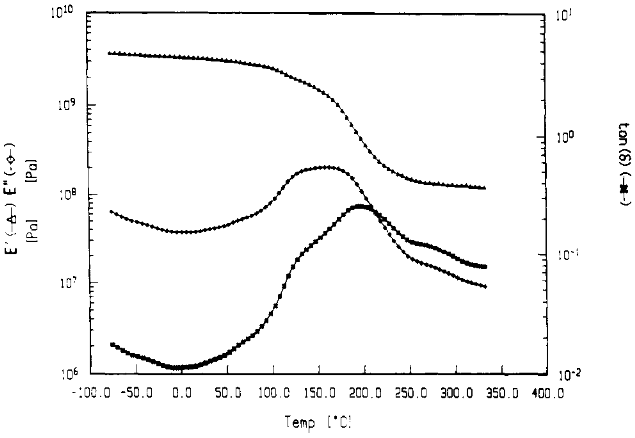


Figure 8. Mechanical–dynamical spectra of polymer **III**.

Modification of the polymer structure by the introduction of the quinquephenyl unit, as in polymers **III** and **IV**, allows the effect of the rigidity increase in combination with the presence of the various substiuents on the mechanical properties to be examined. The relaxation spectra of polymer **III** are shown in Figure 8. This polymer bears two aliphatic side groups on the diacid unit, and despite that no transition at –60 °C and at 60 °C believed to be due to the presence of the aliphatic side chains is observed. A broad glass transition at about 150 °C is observed in very good agreement with the DSC measurements. It should be noted that the presence of the quinquephenyl unit was expected to increase further the polymer rigidity.

The results show that the mechanical behavior of this material is inferior to that of polymer **II**, despite the presence of the bulky quinquephenyl unit in the former case. The lowering of the transition temperature in polymer **III** compared to polymer **II** can be attributed to the presence of the aliphatic substituents on the diacid part. At low temperatures, the effect of the aliphatic side chains could be suppressed because of the increased rigidity of polymer **III**, but at higher temperatures where the side groups become more mobile, the space requirements of them and the increased free volume result in the lowering of the transition temperatures. This clearly supports the view that the kinds and the positions of the substituents strongly affect the behavior of the main chain and subsequently the obtained mechanical properties of the polymers.

In the case of polymer **IV**, limited solubility in common organic solvents led to low quality of the films and therefore no DMA measurements could be obtained.

Conclusions

Soluble aromatic polyesters bearing aromatic or aliphatic substituents were obtained by melt polycondensation of terphenyl- or quinquephenyldiols with disubstituted aromatic diacids. The temperature dependence of the intrinsic viscosity for the synthesized polymers seems to be sensitive to the type of the side groups. The polyesters obtained from the aromatic substituted diols yield observable glass transitions, while those obtained from aliphatic substituted diols do not show a glass transition determined by conventional means. Dynamic mechanical analysis has shown that the kind of substituent used greatly affects the mechanical behavior of the polymers prepared. Polyesters with aliphatic substituents on the diol part show secondary transitions at low temperatures but no glass transition, while those with aromatic substituents on the diol part show the main transitions (T_g) well above 150 °C, depending on the substitution on the diacid part. In all cases, a plateau modulus in the range of 10^8 Pa is present up to 350 °C, showing the high rigidity maintained at high temperature of these soluble polymers.

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