Synthesis and Characterization of Processable Aromatic−Aliphatic Polyethers with Quinquephenyl Segments in the Main Chain for Light-Emitting Applications

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ABSTRACT: New aromatic−aliphatic polyethers containing alkyl- or alkoxy-substituted oligophenyl units were synthesized. The polyethers were characterized by viscosimetry, gel permeation chromatography, thermal and mechanical analysis, NMR, and UV−vis luminescence spectroscopy. The type of the side chain as well as the length of the flexible spacer influence the thermal and mechanical behavior of the synthesized polyethers. In all examined cases, the isotropization transition as well as the glass transition temperature show an odd−even effect depending on the spacer segment length. The polymers are soluble in common solvents and form free-standing films that combine high modulus (E') at room temperature with blue photoluminescence. High fluorescence quantum yield ($\varphi = 0.82$) was obtained for the polyethers studied, which is comparable to values reported in the literature for substituted poly(*p*-phenylenes). The type of the substitutent affects the maximum of the fluorescence peak, which is in the range 370−430 nm.

Introduction

In recent years there has been considerable interest in photonic properties of conjugated polymers.[1−6] These materials combine the processability and mechanical properties of polymers with the electronic properties of organic semiconductors, so they are attractive materials as active layers in electroluminescent devices.[7,8] In addition to poly(*p*-phenylenevinylene) and its derivatives, which are the most extensively studied polymers for their photonic properties, other conjugated polymers such as poly(alkylthiophene)s[9,10] and poly(*p*-phenylene)s[11−14] have also been investigated for their electroluminescent properties. Current research interests in photonic polymers are focused on the tailoring of spectral characteristics, improvement of processability and stability, increasing the quantum yield in photoluminescence, and finally improving the efficiency in electroluminescent devices.[15]

An efficient method to control the conjugation length combined with improved processability is the synthesis of copolymers bearing phenylenevinylene,[16,17] oligothiophene,[10] or oligophenylene[18,19] segments linked by a flexible spacer. Such rigid-flexible copolymers can form various morphologies.

It is known that polymers bearing oligophenylene units in the main chain are insoluble, and liquid crystalline properties appeared at high temperatures even in the case with aromatic−aliphatic structure.[20] To avoid these problems, aliphatic side chains have been attached in the rigid part of the polymers. Extensive work on the effect of the side chains on the properties of wholly aromatic polyesters has shown that the type of the substituents greatly affects their thermal[21,22] and mechanical properties.[23,24] In this respect, we have chosen alkyl and alkoxy substituents as side groups for the terphenyl and quinquephenyl monomers[25,26] to study their influence on the thermal properties of the synthesized polymers.

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In the present paper we report on the synthesis and properties of soluble aromatic−aliphatic polyethers bearing oligophenyl segments in the main chain. New substituted quinquephenyl diol diacetates were synthesized and polymerized with α,ω-dibromides using phase transfer catalyst. These polyethers combine solubility and film-forming properties with liquid crystalline behavior at temperatures where the polymers are thermally stable. Moreover, they are blue-light-emitting polymers, and the combination of light emission and orientation on a molecular level is a promising concept for new optical applications.

Experimental Section

Materials. Chemicals were purchased from Aldrich or Merck and were used as received unless otherwise specified. 2,5-Dialkyl-1,4-phenyldiboronic acid,[27] 2,5-dialkoxy-1,4-phenyldiboronic acids,[28] and 4-acetoxy-4′-bromobiphenyl[29] were synthesized according to known procedures. 1,10-Dibromodecane and 1,12-dibromododecane were recrystallized from methanol. Tetrahydrofuran (THF) was distilled from sodium in the presence of benzophenone directly into the reaction flack.

Monomer Synthesis. *2″,5″-Dihexyloxy-p-quinquephenyl-4,4″″-diol diacetate (**1**).* 2,5-Dihexyloxy-1,4-phenyldiboronic acid 3.66 g (10 mmol), 4-acetoxy-4′-bromobiphenyl 6.98 g (24 mmol), and tetrakis(triphenylphosphine)palladium 0.46 g were put together in a flask that was deaerated and filled with argon. Toluene (40 mL) and 2 M sodium carbonate (20 mL) were added, and the mixture was refluxed under argon for 24 h. After cooling, the precipitate was filtered off and washed with hexane and methanol. Recrystallization from toluene − hexane gave 4.26 g (61%) of the desired product **1**, mp 147−149 °C. ^{1}H NMR ($CDCl_3$): δ 0.84−0.87 (m, 6H), 1.2−1.4 (m, 16H), 2.3 (s, 6H), 3.9−4.0 (m, 4H), 7.0 (s, 2H), 7.1−7.2 (d, 4H), 7.6−7.7 (m, 12H). FTIR (cm^{-1}): 2928, 2856, 1756, 1604, 1506, 1488, 1368, 1202, 1166, 1056, 1004, 912, 834, 804, 742, 674, 582, 520.

*2″,5″-Didodecyloxy-p-quinquephenyl-4,4″″-diol diacetate (**2**).* Compound **2** was synthesized from 2,5-didodecyloxy-1,4-phenyldiboronic acid (10 mmol) by the methodology just described. Recrystallization from toluene − hexane gave 6.23 g (72%) of

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the desired product **2**, mp 140−141 °C. ^{1}H NMR ($CDCl_3$): δ 0.87−0.91 (m, 6H), 1.21−1.45 (m, 36H), 1.7−1.8 (m, 4 H), 2.3 (s, 6H), 3.9−4.0 (m, 4H), 7.05 (d, 2H), 7.18−7.22 (m, 4H), 7.61−7.76 (m, 12H). FTIR (cm^{-1}): 2922, 2850, 1742, 1488, 1370, 1228, 1208, 1166, 1056, 1006, 914, 834, 804, 722, 582, 516.

*2″,5″-Dihexyl-p-quinquephenyl-4,4″″-diol diacetate (**3**).* 2,5-Dihexyl-1,4-phenyldiboronic acid 3.34 g (10 mmol), 4-acetoxy-4′-bromobiphenyl 6.98 g (24 mmol), and tetrakis(triphenylphosphine)palladium 0.46 g were put together in a flask that was deaerated and filled with argon. Toluene (40 mL) and 2 M sodium carbonate (20 mL) were added and the mixture was refluxed under argon for 24 h. The organic layer was washed with water and dried over $MgSO_4$. The organic solvent was removed under reduced pressure. Recrystallization from toluene − hexane gave 3.66 g (55%) of the desired product **3**, mp 95−97 °C. ^{1}H NMR ($CDCl_3$): δ 0.78−0.84 (m, 6H), 1.2−1.6 (m, 16H), 2.4 (s, 6H), 2.5−2.6 (m, 4 H), 7.2−7.3 (m, 2H), 7.4−7.5 (d, 4H), 7.6−7.7 (m, 12H). FTIR (cm^{-1}): 2924, 2854, 1758, 1606, 1504, 1484, 1368, 1218, 1168, 1006, 912, 838, 804, 580, 518.

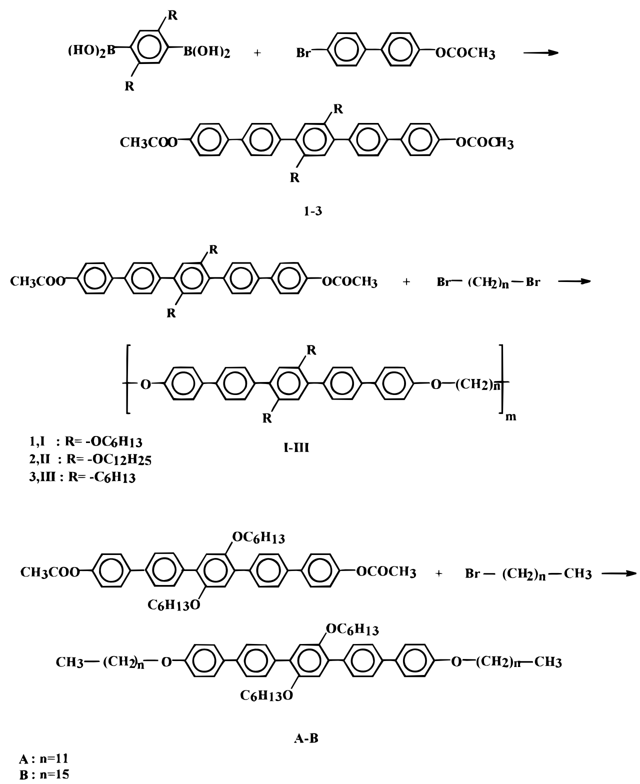
Synthesis of Model Compounds. *4,4″″-Didodecyloxy-2″,5″-dihexyloxy-p-quinquephenyl (**A**).* Monomer **1** (0.4 g, 0.57 mmol), 1-bromododecane (0.42 g, 1.7 mmol), and tetrabutylammonium hydrogen sulfate (0.077 g, 0.2 mmol) were placed into a vessel equipped with a magnetic stirring, an inlet/outlet, and a vacuum inlet. The flask was evacuated and filled with argon several times and then *o*-dichlorobenzene (2 mL) and 10 N NaOH (1 mL) were added. The reaction mixture was vigorously stirred at 90 °C for 12 h under argon. After cooling, the precipitate was filtered off and dried under reduced pressure to yield 80% (0.43 g). ^{1}H NMR ($CDCl_3$): δ 0.88−0.93 (m, 12H), 1.25−1.6 (m, 52H), 1.8−1.87 (m, 4H), 3.97−4.05 (m, 8H), 6.97−7.03 (m, 4H), 7.08 (s, 2H), 7.59−7.74 (m 12H). FTIR (cm^{-1}): 2918, 2848, 1608, 1508, 1488, 1466, 1384, 1246, 1206, 1178, 1052, 942, 822, 720, 518.

*4,4″″-Dihexadecyloxy-2″,5″-dihexyloxy-p-quinquephenyl (**B**).* Compound **B** was synthesized from monomer **1** (0.57 mmol) and 1-bromohexadecane (1.7 mmol) by the aforementioned methodology in a yield of 84% (0.51 g). ^{1}H NMR ($CDCl_3$): δ 0.83−0.92 (m, 12H), 1.2−1.6 (m, 64H), 1.7−1.72 (m, 8H), 3.95−4.06 (m, 8H), 7.02 (d, 4H), 7.07 (s, 2H), 7.6−7.7 (m, 12H). FTIR (cm^{-1}): 2922, 2852, 1606, 1508, 1490, 1466, 1384, 1274, 1248, 1208, 1176, 1116, 1070, 1000, 822, 720, 636.

Polymer Synthesis. A 1 mmol amount of the diacetyl derivatives (**1**−**3**), 1 mmol of the respective dibromide, and 0.4 mmol of tetrabutylammonium hydrogen sulfate[30,31] were placed into a vessel equipped with a magnetic stirring, an inlet/outlet, and a vacuum inlet. The flask was evacuated and filled with argon several times and then *o*-dichlorobenzene (2 mL) and 10 N NaOH (1 mL) were added. The reaction mixture was vigorously stirred at 90 °C for 12 h under argon. The mixture was diluted with chloroform, and the organic layer was washed with water, diluted hydrochloric acid, and water (3 times). The polymer was separated by precipitation into a 10-fold excess of methanol, washed with methanol, and dried under reduced pressure for 24 h.

Polymer and Monomer Characterization. Intrinsic viscosities of the polymers were measured in chloroform at 30 °C with an Ubbelohde-type viscometer in a Scott Gerate AVS 310. Molecular weight estimations were determined by size exclusion chromatography (SEC) with a Waters 600E pump using a 901 photodiode array UV detector at 254 nm and calibrated with monodisperse polystyrene standards through "ultragel" columns with 500, 10^4, and 10^5 Å at 25 °C, with tetrahydrofuran as solvent. The ^{1}H and ^{13}C NMR spectra were recorded with a Varian VXR 300 spectrometer, with deuterated chloroform as solvent and as an internal standard. The FTIR spectra were obtained using a Perkin-Elmer 1600 spectrometer. The tensile tests were performed using a J. J. Tensile Tester type 5001 according to ASTM D882−67. Dynamic mechanical properties were determined by RSA II Mechanical spectrometer of Rheometric Scientific Ltd. Thermal properties of the polymers were determined by DSC SP equipped with AutoCool accessory from Rheometric Scientific Ltd. The UV spectra were recorded on a SLM Aminco 3000 Array spectrophotometer. Fluorescence was measured on a SLM Aminco SPF-500 spectrofluorometer.

Scheme 1



Results and Discussion

Synthesis of Monomers and Model Compounds. The acetoxy-fuctionalized substituted quinquephenyl diols (**1**−**3**) were synthesized by the Suzuki coupling[32] of 2,5-disubstituted-1,4-phenylbisboronic acids with 4-acetoxy-4′-bromobiphenyl mediated by tetrakis(triphenylphosphine) palladium, as shown in Scheme 1. The monomers were characterized using FTIR, and ^{1}H and ^{13}C NMR spectroscopy. Model compounds, such as the ones shown in Scheme 1 (A, B) were synthesized to study their thermal behavior.

Polymer Synthesis and Characterization. Polyethers based on the quinquephenyl diols **1**−**3** were selected to be studied instead of the more common polyesters because of the presence of the carbonyl function in the latter and because it is known that carbonyl moieties are fluorescence quenchers. Polymerizations of equivalent amounts of monomers **1**−**3** with aliphatic α,ω-dibromides (also shown in Scheme 1) were carried out using the phase transfer catalyst tetrabutylammonium hydrogen sulfate.[30,31] Diacetoxy monomers were used instead of the respective diols because these monomers were proved to be more effective.[18] Attempts to polymerize the diols have led to polymers with lower molecular weights and lower yields (**IIIf$_1$**). The reaction time was prolonged to facilitate the elimination of the acetyl groups. The molecular weights obtained are sufficiently high so that the influence of the molecular weight to the phase transition temperatures is avoided. Film-forming materials are obtained in all cases where intrinsic viscosity values are >40 mL/g. Polyethers with spacer length above six methylene units are soluble in common solvents such as chloroform and tetrahydrofuran at room tempera-

Table 1. Viscosimetric and GPC Characterization of the Synthesized Polymers

polymer	n	$[\eta]^a$ (mL/g)	$\bar{M}n^b$	$\bar{M}w$	$\bar{M}w/\bar{M}n$
Ia	7	65	37 000	64 000	1.7
Ib	8	71	27 000	52 000	1.9
Ic	9	46	13 000	36 000	2.8
Id	10	41	12 000	30 000	2.5
Ie	11	82	34 000	75 000	2.2
If	12	48	20 000	56 000	2.8
IIa	7	48	16 000	41 000	2.6
IIb	8	63	32 000	59 000	2.7
IIc	9	71	34 000	64 000	1.9
IId	10	85	43 000	84 000	2.0
IIe	11	75	35 000	65 000	1.9
IIf	12	74	25 000	44 000	1.8
IIId	10	60	21 000	43 000	2.0
IIIe	11	78	32 000	52 000	2.4
IIIf	12	54	23 000	36 000	2.3
IIIf$_1$	12	19	8 000	10 000	1.2

[a] In $CHCl_3$ at 30 °C. [b] In THF based on PS standards.

ture. This solubility is obviously due to the attachment of the side chains, because polyethers based on α,ω-dibromoalkanes and 4,4′-dihydroxybiphenyl exhibit very low solubility even at high temperatures. Polyethers with two methylene units as spacer have very low solubility and the reaction yield was low.

The characterization of the synthesized polymers using viscosimetry and size exclusion chromatography is shown in Table 1. In most cases, relatively high intrinsic viscosity values (40−85 mL/g) were obtained. Monomodal distributions were obtained by SEC in all examined cases. Molecular weight estimates based on calibration with polystyrene standards were in the range 12.000−43.000 ($\bar{M}n$). Using universal calibration, reduced $\bar{M}n$ values were calculated, showing the semiflexible behavior of these polymers. Polydispersity indexes $\bar{M}w/\bar{M}n$ of ∼2 have been calculated in consistence with a polycondensation reaction.

Structural characterization of the synthesized polymers was performed using ^1H and ^{13}C NMR spectroscopy. Polyethers with hexyloxy and dodecyloxy side groups show two overlapped triplets at 4.0 ppm due to $-CH_2-O-$ of the side chains and the main chain, whereas the hexyl substituted polyethers exhibit one triplet at 2.6 ppm due to $-CH_2-$ of the side chains attached to the phenylene ring and one more triplet at 4.0 ppm due to the main chain $-CH_2-O-$ protons. Similarly, in the aromatic region, polyethers **I** and **II** show two multiple peaks at 7.0 and 7.6 ppm, whereas polyether **III** shows two doublets at 7.0 and 7.4 ppm, one singlet at 7.2 ppm, and one multiplet at 7.6 ppm, as expected from the absence of the oxygen atom in the side chains. The ^{13}C NMR for polyether **Ia** with the most probable assignment of the peaks is shown in Figure 1.

Thermal Properties. The thermal transitions of the polymers were monitored by DSC between −50 and 250 °C with a heating and cooling rate of 20 °C/min. Glass transitions were detected between 30 and 70 °C for the different substituents and spacer length. Because these transitions are quite broad, dynamic mechanical analysis has been used to elucidate the influence of the various structural characteristics of the synthesized polyethers on the glass transition temperature.

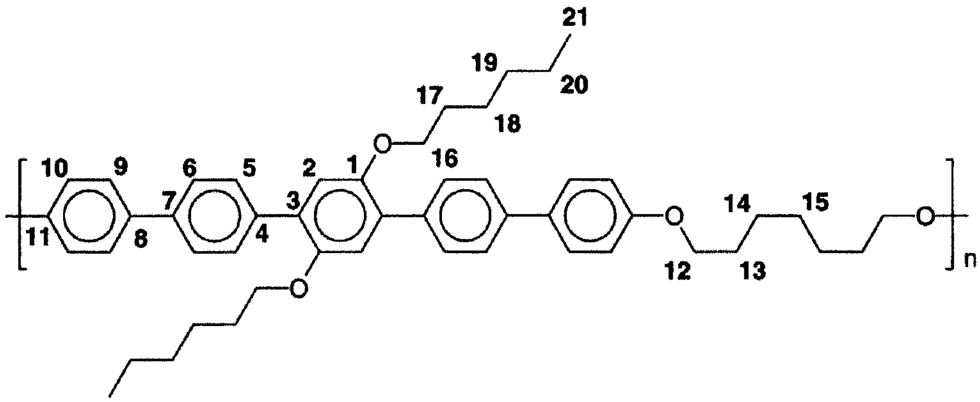
The model compounds of polyether **I**, namely model **A** and **B**, were also studied by DSC, and the results are shown in Table 2 and Figure 2. During the first and second heating scans, compound **A** shows a weak peak at 54 °C and a sharp endotherm at 116 °C. Compound **B** shows a weak endotherm at 32 °C and two endotherms at 88 and 103.5 °C during the first heating run but only one endotherm at 105 °C during the second heating scan, as shown in Figure 2. Because the hexyloxy side groups do not give side chain melting, the endotherms at 54 and 32 °C are due to the presence of the dodecyloxy and hexadecyloxy groups, respectively. However, it should be noted that contrary to the present results, transitions at higher temperatures are expected as the aliphatic group is increased from 12 to 16 carbon atoms.

With regards to the polymers, depending on the spacer segment length as well as the kind of the side chains, the polyethers studied show one or more endothermic transitions during the second heating scans. The first and second heating scans of the polyethers are almost identical. During the cooling, sharp multiple exotherms were obtained in most cases. The results are shown in Figures 3 and 4 (second heating) and 5 (cooling). It is seen that during the second heating scans as the length of the spacer segment increases, the transitions are moved to lower temperatures. Polyethers **Ia**−**Ic** show weak transitions with low ΔH values (see Table 2), whereas **Id**−**If** show multiple endotherms (see Figure 3), with significantly higher enthalpies. In all cases examined the isotropization transitions show an odd−even effect, as shown in Figure 6.

The influence of the kind of the substituents is well demonstrated in Figure 3 where polyethers with hexyl and hexyloxy side chains and the same spacer length are presented. In the case of hexyl-substituted polyethers **IIId**−**IIIf**, only one endotherm at temperatures lower than the alkoxy-substituted analogue was obtained.

As expected, the introduction of the bulkier dodecyloxy side group in polyethers leads to lower transition temperatures, as seen in Table 2. It is known, that side chains with more than eight carbon atoms are able to crystallize, and their melting appeared as an endotherm[33−35] in the range 50−100 °C. In our case, there are no such endotherms, even in the case of the dodecyloxy-substituted polyethers. This result is probably due to the fact that at this temperature range, the polyethers are above their glass transition temperature and thus the mobility caused by the main chain motions destroys the ordering of the side chains. However, it should be noted that in studies on the side-chain crystallization in flexible[34] as well as in semiflexible polymers,[35] side-chain melting was observed for polymers with dodecyl or octadecyl substituents despite the low glass transition temperatures of those polymers. Another explanation for the absence of any side-chain melting in polymer **II** can be the density of substitution and the length of the oligophenylene part because here the rigid part is interrupted by the flexible spacer. In a theoretical work[36] concerning poly(*p*-2,5-dialkylphenylene)s it was shown that if the main chain length is shorter than sexiphenylene there is no side-chain ordering. Of course, in this case there is a much more dense substitution because every phenylene ring is substituted, which is not the case in our study.

Comparing the thermograms of the polyethers examined, it is clear that the presence of the oxygen atom in the side chains influences their thermal behavior. So the alkoxy substituted polymers show multiple endotherms whereas the alkyl-substituted analogues show



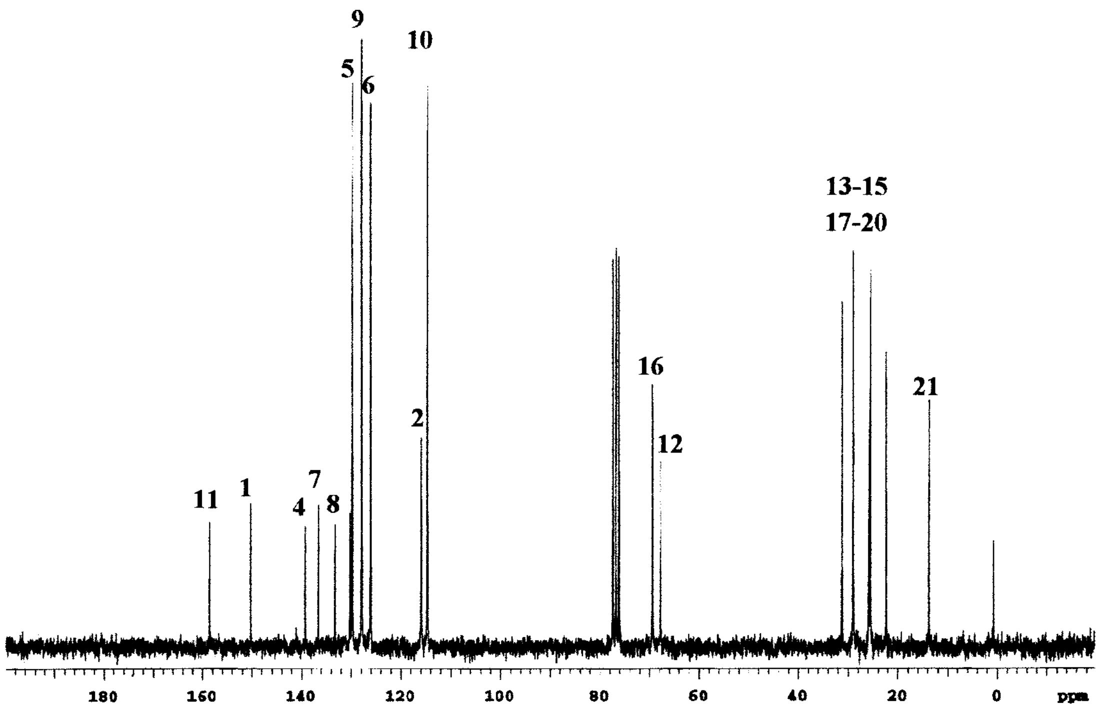


Figure 1. ^{13}C NMR spectrum of polyether **Ia** with the assignment of the peaks.

only one endotherm. It is known from related studies on alkyl- and alkoxy-substituted aromatic polyesters with oligophenyl units in the main chain[24−26] that the alkoxy-substituted polyesters show multiple endotherms in analogy with polyethers **I** and **II**, whereas the hexyl-substituted polyesters are amorphous.[24] This result indicates that in the case of alkoxy-substituted polymers, an ordering involving the side chains possibly takes place, whereas in the hexyl-substituted polyethers, their thermal behavior is mainly due to the rigid−flexible nature of their main chain.

Based on the cooling runs presented in Figure 5 it is clear that in all cases multiple exotherms are obtained regardless of the kind of the side chains. Especially in the case of polyether **IIIe** and **IIIf**, two sharp exotherms, much more intense compared with the ones obtained for polyethers **I** and **II** with the same spacer length, are observed. From these results we conclude that various phases are formed during the cooling runs of these rigid−flexible polyethers. Because thermal analysis and optical microscopy do not give conclusive evidence for the possible liquid crystalline phases formed in these polymers, further study using X-ray diffractometry is in progress.

Mechanical Properties. Detailed information about the mechanical behavior of the synthesized polyethers may be obtained from the dynamic mechanical analysis and the stress−strain measurements of the film-forming samples. Films of ~100 μm thickness were prepared either by casting from solutions or by melt pressing at ~250 °C. These films were studied for their mechanical relaxation properties and the results were identical for melt-pressed and solution-cast films.

As a first example, the viscoelastic spectra of the polyether **I** with various spacer lengths (e.g. $n = 8$, $n = 11$, and $n = 12$) are presented in Figure 7 by means of the temperature dependence of the storage (E') and loss (E'') modulus. In addition to a broad relaxation at low temperatures, a relaxation that is dependent on the spacer length is obtained at temperatures in the range 30−70 °C. Based on the structural characteristics of these polyethers, the later relaxation could be either a

Table 2. DSC Data Obtained from the Second Heating Scan

polymer	n	$T_g{}^a$ (°C)	T_1 (°C)	T_2 (°C)	T_3 (°C)	ΔH_1 (J/g)	ΔH_2 (J/g)	ΔH_3 (J/g)
A		–	54	116	–	1.2	67.5	–
B		–	32	105	–	15.7	47.7	–
Ia	7	59	188	–	–	3.6	–	–
Ib	8	68	182	205	219	1.6	7.5	5.0
Ic	9	53	166	–	–	2.3	–	–
Id	10	56	164	185	199	3.3	25.3	5.7
Ie	11	48	172	180	–	8.4	2.2	–
If	12	54	166	185	–	1.3	22.1	–
IIa	7	–	138	150	–	6.8	9.2	–
IIb	8	45	154	168	–	1.0	22.0	–
IIc	9	–	119	133	–	2.6	19.4	–
IId	10	–	131	146	161	8.4	10.8	3.2
IIe	11	–	107	126	–	3.3	21.1	–
IIf	12	–	134	149	–	21.7	2.4	–
IIId	10	–	156	–	–	16.9	–	–
IIIe	11	33	124	–	–	3.0	–	–
IIIf	12	–	148	–	–	17.8	–	–
IIIf$_1$	12	–	122	–	–		–	–

^{a} From DMA measurements.

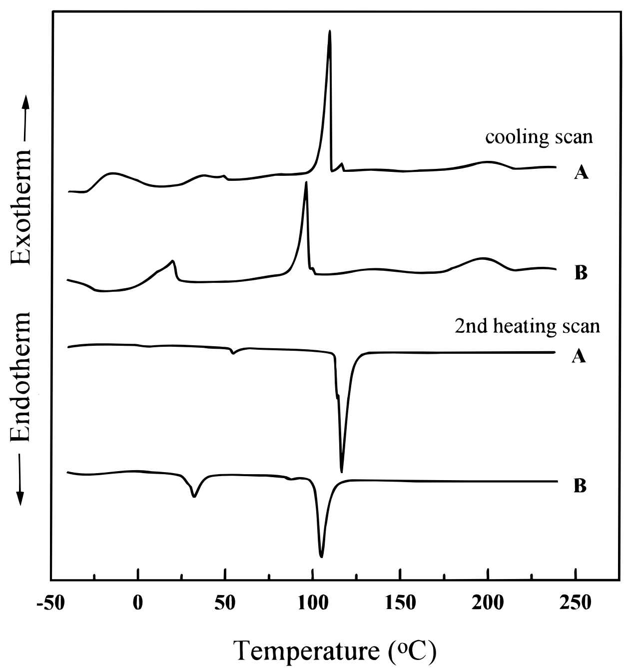


Figure 2. DSC curves of model compounds **A** and **B** during the cooling and the second heating scan.

primary or a secondary relaxation because of the presence of aliphatic side groups. In analogy to aromatic polyesters bearing aliphatic side chains, transitions in this temperature range are assigned to the mobility of the side chains accompanied by some conformational rearrangements of the main chain.[23−25,36,37] To ascertain whether this is a primary relaxation process associated with the glass transition temperature (T_g) the E''_{max} dependence on frequency was determined to obtain an apparent activation energy for this relaxation. The results, see Figure 8, show an Arrhenius type temperature-frequency dependence with an activation energy of 88 kcal/mol (368 kJ/mol), characteristic of an α-relaxation. Based on these results, the influence of the spacer length on the T_g is shown in Figure 6 where there is a weak odd−even effect instead of the expected decrease[38] of T_g as the spacer length is increased.

The effect of the substituents on T_g can be checked using polyethers with the same spacer length bearing

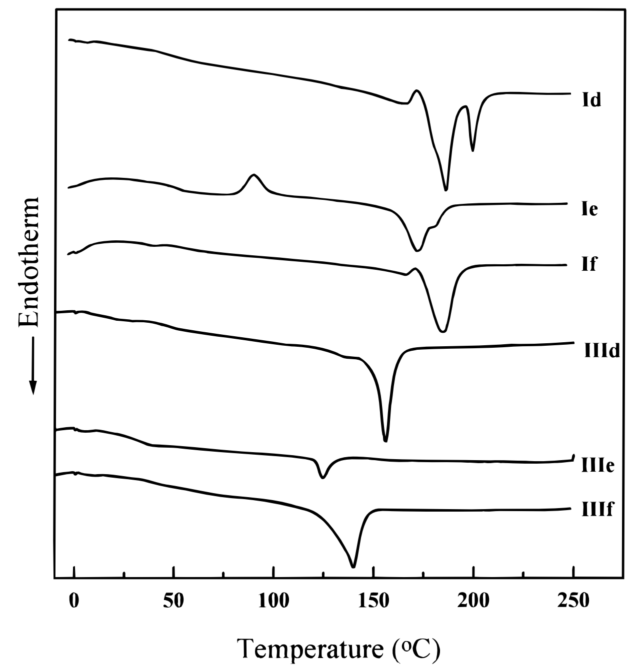


Figure 3. DSC curves of polyether **I** and **III** during the second heating scan.

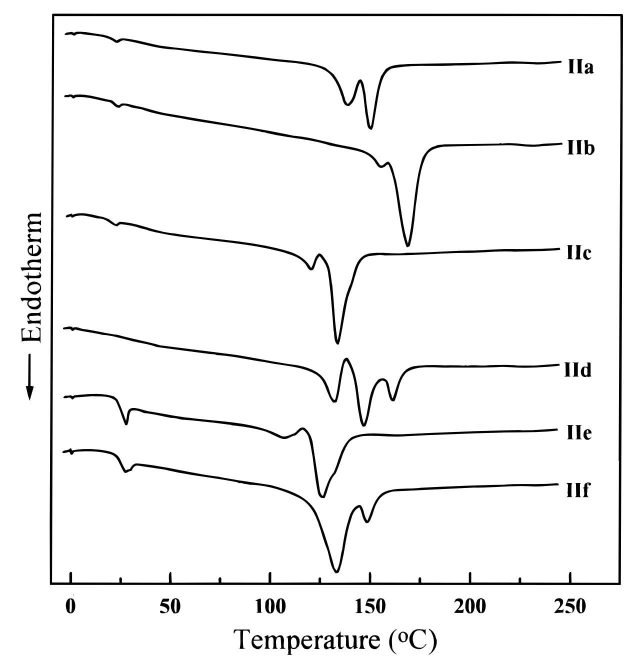


Figure 4. DSC curves of polyether **II** during the second heating scan.

hexyloxy, dodecyloxy, and hexyl side chains. An example is shown in Figure 9 which displays the E' and E'' values for polyethers **Ib** and **IIb** at various temperatures. Polyether **Ib** shows a T_g at 68 °C, whereas the presence of the bulkier dodecyloxy group results in a decrease of the T_g at 45 °C for **IIb**. Similarly, the T_g of the hexyl-substituted polyethers is lower than that of hexyloxy-substituted polyethers (48 °C for **Ie** and 33 °C for **IIIe**). Figure 9 also reveals the influence of the side chains on the storage modulus. Thus, the presence of the bulkier dodecyloxy side groups results in a looser packing of the polymeric main chains and this leads to a decrease of the modulus compared with the polyether with hexyloxy side groups.

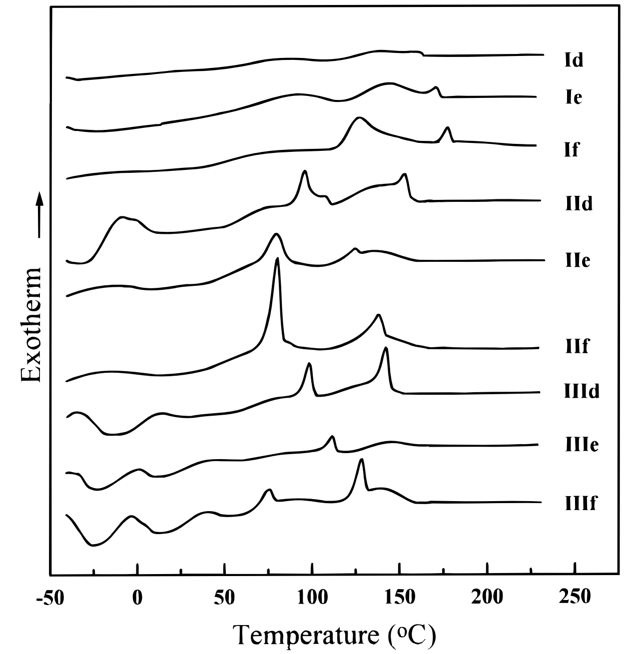


Figure 5. DSC curves of polyethers **I**, **II**, and **III** during the cooling scan.

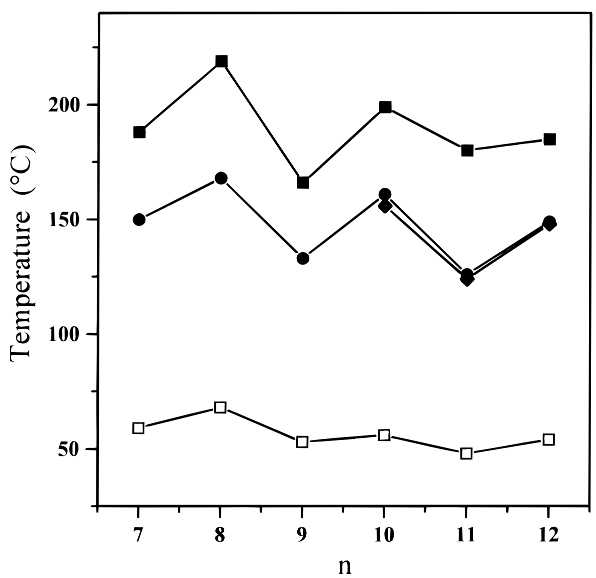


Figure 6. Variation of the glass transition temperature (open symbols) and the isotropization temperature (filled symbols) with the number of the methylene units in polymers **I** (-■-, -□-), **II** (-●-), and **III** (-◆-).

The stress–strain properties of polyether **IIIe** were measured to get an estimate of the mechanical properties at large deformation, and the results are shown in Figure 10. The tensile strength value (σ_b) of 14 MPa and especially the elongation at break (ϵ_b) of 150% show the thermoplastic nature of this material.

Optical Properties in Solution. The UV–vis absorption spectra of the polymers studied were recorded using chloroform solutions. The absorption maximum appeared at 332, 331, and 289 nm for polyethers **Ia**, **IIa**, and **IIIe**, respectively. The solutions show photoluminescence with maxima at 417 (**Ia**), 417, 428 (**IIa**), and 372 (**IIIe**) nm as shown in Figure 11. The type of the substituent affects the maximum of the fluorescence peak showing that the presence of the electron-donating oxygen atoms increase the electronic density in the

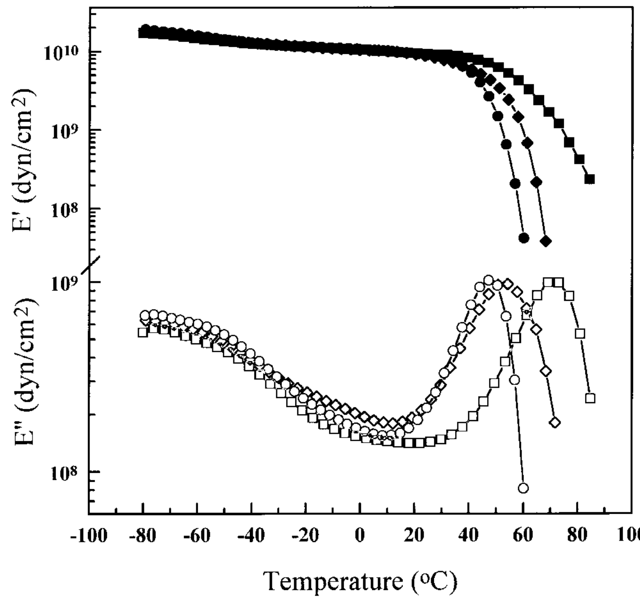


Figure 7. Temperature dependence of storage E' and loss E'' moduli at 10 Hz of polyethers **Ib** (-■-, -□-), **Ie** (-●-, -○-), and **If** (-◆-, -◇-).

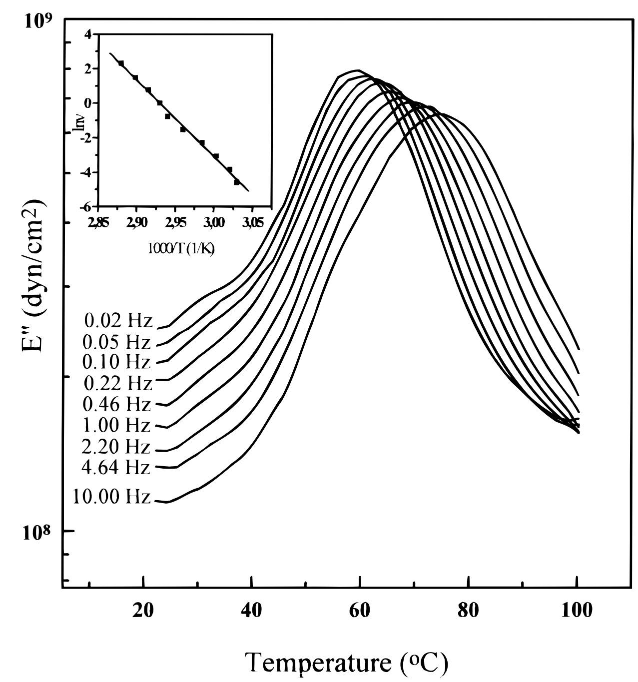


Figure 8. Frequency dependence of loss modulus E'' of polyether **Ib**. Insert: Arrhenious diagram.

chromophore. Such a behavior has also been observed in the case of alkyl- and alkoxy-substituted poly(phenylenevinylene)s[39] polymers and oligomers where the alkoxy-substituted derivatives show a red shift of the emitted light compared with the alkyl-substituted ones.

Comparison of the emission maxima of the studied polymers can be performed with the substituted poly(*p*-phenylene)s reported in the literature. In this respect, the observed maxima for the polyethers studied are in good agreement with those for substituted poly(*p*-phenylene)s.[13,14] Another comparison involves polymers bearing the oligophenyl segments longitudinally attached to the main chain.[18] In this case, polyethers with quinquephenyl moieties show an emission maxi-

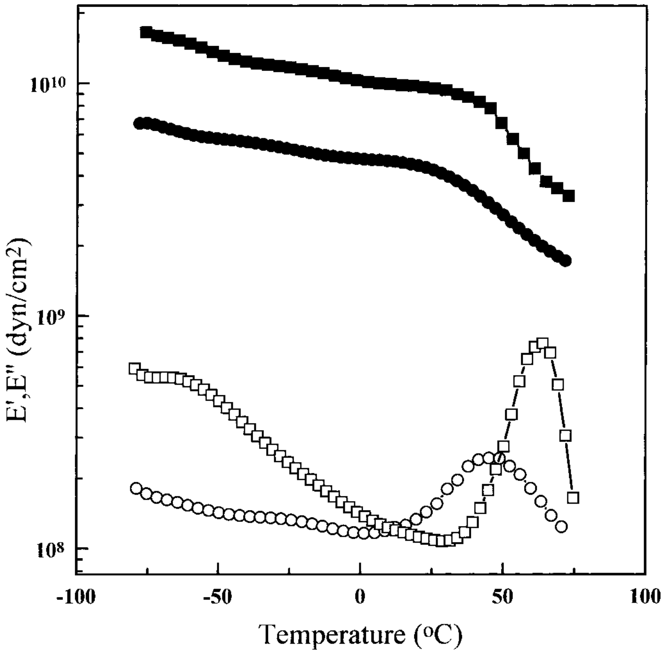


Figure 9. Temperature dependence of storage E' and loss E'' moduli at 10 Hz of polyethers **Ib** (-■-, -□-) and **IIb** (-●-, -○-).

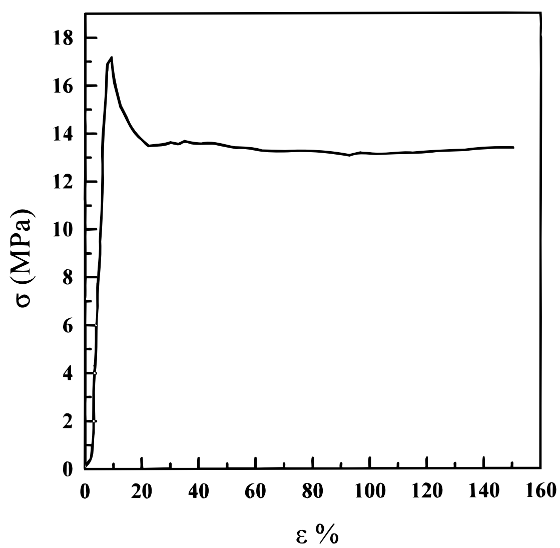


Figure 10. Stress–strain curves of polyether **IIIe**.

mum at 407 nm that compares well with the values of the alkoxy-substituted polyethers of this study.

A very interesting point of the photonic behavior of the synthesized polyethers is related to the fluorescence quantum yield. The obtained value of $\varphi = 0.82$ in solution for polyether **Ia** shows the improved photonic behavior of the polyethers studied, where despite the presence of a nonconjugate part in the polymeric chain, the quantum yield is similar to the one obtained for substituted poly(*p*-phenylene)s.[13,14]

Conclusions

In conclusion, new aromatic–aliphatic polyethers containing substituted oligophenyl units in the main chain were synthesized by reacting the diacetyl derivative of substituted quinquephenyl diols with α,ω-dibromides. The polymers show solubility and film-forming properties. The kind of the side chains and the length of the spacer affect the thermal behavior of the studied polymers. These blue-light-emitting polyethers have high quantum yield that compares well with the values reported for substituted poly(*p*-phenylene)s. The kind of the substituent affects the maximum of the fluorescence peak showing that alkoxy-substituted polymers show a red shift of the emitted light compared with the alkyl-substituted ones. Due to the solubility and the ability to melt at medium temperatures, these polymers were easily processable with good film-forming properties. Their mechanical properties were also measured, and the polymers have a T_g at 30–70 °C. The enhanced processability and the good mechanical properties facilitate the fabrication of light-emitting devices by spin casting or melt processing.

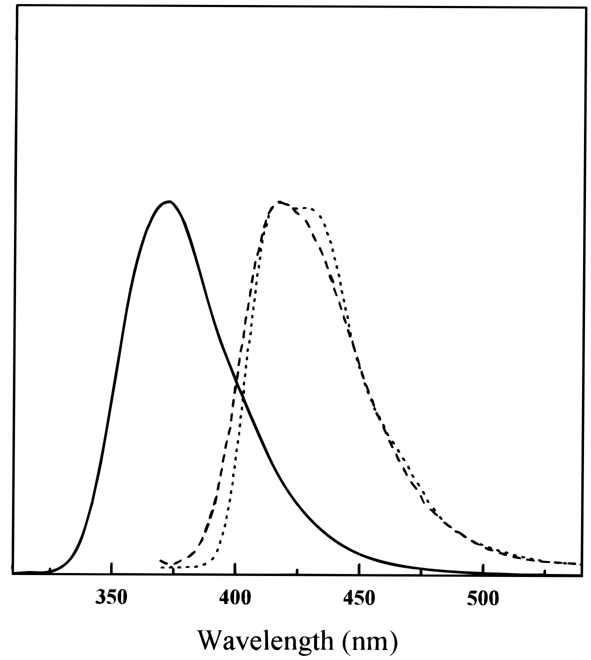


Figure 11. Fluorescence emission spectra in THF solutions of polyethers **Ia**. (- - -), **IIa** (- - - -), and **IIIe** (—).

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