Novel Poly(phenylene vinylenes) with Well-Defined Poly(ε-caprolactone) or Polystyrene as Lateral Substituents: Synthesis and Characterization

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ABSTRACT: New macromonomers containing dialdehyde functionalities placed at the middle or at the end of the chains were synthesized in two reaction steps. First, using ring-opening polymerization (ROP) of ε-caprolactone (CL) or atom transfer radical polymerization (ATRP) of styrene (St) in the presence of proper initiators provided well-defined low molecular weight polymers with dibromobenzene moieties. In the second step, using Suzuki couplings of these dibromobenzene functions with 4-formylphenyl boronic acid, macromonomers having 4,4′-dicarbaldehyde terphenyl moieties were obtained. Poly(phenylenevinylene)s (PPVs), with lateral subtituents PSt or PCL chains respectively, were synthesized by following a Wittig polycondensation in combination with bis-(triphenylphosphonium) salts in the presence of potassium *tert*-butoxide. The resulting PPVs were soluble in common organic solvents at room temperature as were the starting macromonomers. All of the starting and intermediate polymers and the final PPVs were characterized by using ¹H and ¹³C NMR, IR, GPC, DSC, and TGA measurements. Optical properties of the polymers were followed by UV and fluorescence spectroscopy. The studied PPVs show a blue or green fluorescence in solution.

Introduction

Current interest in conjugated polymers is related to the substantial π-electron delocalization along their backbones which gives rise to interesting optical[1] and nonlinear optical properties[2,3] and allows them to become good electronic conductors typically when oxidized or reduced.[4] These properties lead to a variety of practical applications such as information storage and optical signal processing, substitutes for batteries[5,6] and materials for solar energy conversion.[7] Furthermore, electroluminiscence[8−10] from conjugated polymers is a rapidly expanding field of interest since the first report of polymeric light-emitting diodes (PLEDs) based on poly(*p*-phenylene-vinylene) (PPV) by Burroughes et al.[11] Among the many kinds of conjugated polymers,[12,13] PPVs and its derivatives are still one of the most frequently used class in light-emitting diodes (LEDs)[13] due to their good film-forming properties, relatively high photoluminescence (PL) and electroluminescence (EL) quantum efficiencies, as well as good color tunability through molecular structure designs. They also show good mechanical properties and high chemical and thermal stability which allows the fabrication of electronic devices such as flexible LEDs.[14,15] Despite this progress, PPV LEDs still have some disadvantages. PPV itself has a rigid structure and is inherently insoluble, thus making it impossible to process these materials into the thin films required for the most applications. As a result, considerable effort has been directed toward the preparation of well-defined conjugated polymers with improved solubility, processability and stability. The incorporating of relatively long and flexible side chains onto the polymer backbone is a common technique for preparing fusible and soluble rigid-rod conjugated polymers.

For example simple linear alkyl or alkoxy groups as side chains for PPV derivatives have been often reported.[14,16,17]

Taking into account the interest not only in the synthesis of new types of polymers, but also in the modification of commodity polymers to improve their properties to meet the requirements for high-tech applications, polystyrene (PSt) or poly(methyl methacrylate) (PMMA) has been used in which nanostructured photoactive conjugated oligo(phenylenevinylene) segments are attached as side chains to the backbone.[18,19] On combining a stiff, insoluble, rodlike polymer with a soft coil (such as polystyrene or poly(ε-caprolactone)), it is possible to form a new polymer with novel and interesting properties.

The macromonomer technique has proved to be useful for preparing graft copolymers[20,21] Macromonomers can be prepared by a wide range of methods namely, anionic,[22] cationic,[23] ring opening,[24] group transfer,[25,26] free radical,[27] metathesis,[28,29] and step-growth[30] polymerization, and chain scission[30] processes. Recent developments in controlled/living radical polymerization[31,32] have provided the possibility synthesizing well-defined macromonomers with controlled functionalities, via radical routes as well. Among the various controlled radical polymerization routes, atom transfer radical polymerization (ATRP) is the most versatile because of its simplicity and applicability to many vinyl monomers.[33−35]

We have previously reported the synthesis of polyphenylenes (PPs) with polystyrene (PSt) side chains starting from ATRP initiators as 1,4-dibromo-2,5-bis(bromomethyl)benzene[36] or benzene-2,5-dibromomethyl-1,4-bis(boronic acid propanediol diester).[37] Ring-opening polymerizations as "living" methods were also applied to monomers such as THF or ε-caprolactone employing appropriate initiators.[38,39] The aim was to obtain macromonomers with PTHF or PCL side chains that were then used in the synthesis of PPs with complex composition and topology.[40−43] By oxidative or electrochemical polymerization of pyrrolyl and naphtyl functionalized macromonomers, fully

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Scheme 1. Synthesis of PCL Brominated Macromonomer 1 by ROP of ε-Caprolactone and a PSt One (2) by ATRP of Styrene
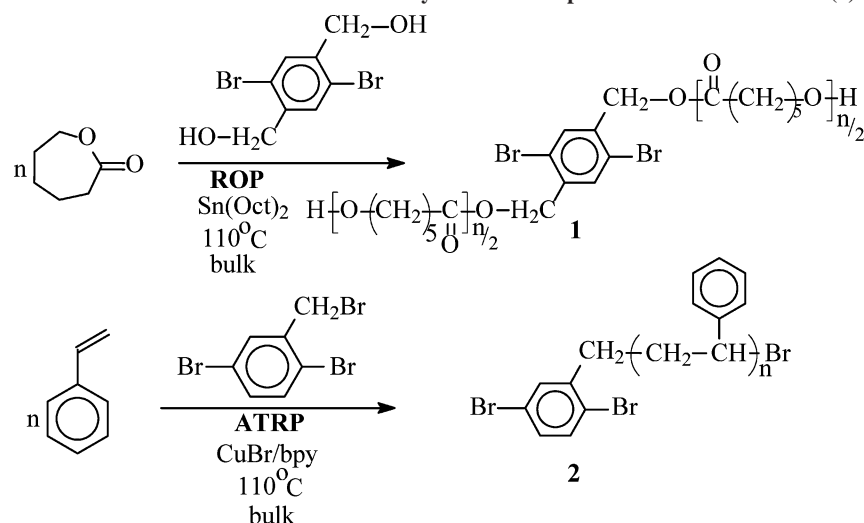
conjugated poly(Schiff base)s with polymeric segments as substituents were obtained.[44,45] Poly(thienylphenylene)s having as lateral substituents the respective PSt, PCL or POx chains were obtained also by oxidative polymerization of modified macromonomers using 2-thiophene boronic acid.[46] It is appropriate to react the above-mentioned arylbromine functional well-defined polymers, obtained by ATRP or ROP, with (4-formylphenyl)boronic acid in a Suzuki type coupling. By applying this strategy aldehyde-functional macromonomers required for the synthesis of PPVs by Wittig reaction with bis-(triphenylphosphonium) salts in the presence of potassium *tert*-butoxide, have been obtained and are described below. These novel soluble and processable PPVs with PCL- or PSt-based macromolecular side chains showed good luminescent properties.

Experimental Section

Materials. All the solvents were purified and dried by the usual methods.

Sn(Oct)$_2$ (Sigma), CuBr (Aldrich), 2,2′-bipyridine (bpy) (Fluka), 1,4-bis(bromomethylbenzene) (Aldrich), 2,5-dibromo-*p*-xylene (Aldrich), triphenylphosphine (PPh$_3$) (Acros), 4-formylphenylboronic acid (Aldrich), Pd(PPh$_3$)$_4$ (Fluka), and potassium *tert*-butoxide (Aldrich) were used as received.

The synthesis of 2,5-dibromo-1,4-(dihydroxymethyl)benzene, the initiator for ROP of ε-caprolactone (Scheme 1) was described elsewhere.[40] Mp (DSC): 217−218 °C. ^{1}H NMR (acetone-d_6) (δ, ppm): 7.74 (s, 2H, Ar), 4.65 (s, 4*H*, CH$_2$), 3.29 (s, 2*H*, OH).

The preparation of 1,4-dibromo-2-(bromomethyl)benzene, the initiator for ATRP of styrene (Scheme 1), was reported elsewhere.[42] Mp (DSC): 94−95 °C. ^{1}H NMR (CDCl$_3$): δ = 7.58 (s, 1H, Ar*H*-3-position), 7.43−7.40 (d, 1H, Ar*H*-5 position), 7.28−7.26 (d, 1H, Ar*H*-6 position), 4.51 (s, 2H, C*H*$_2$Br).

1,4-Dibromo-2,5-bis(bromomethyl)benzene, was prepared by bromination of methyl groups of 2,5-dibromo-*p*-xylene using *N*-bromosuccinimide (NBS).[47] Mp: 160−161 °C. ^{1}H NMR (CDCl$_3$): δ (ppm): 7.65 (s, 2H, aromatic) 4.5 (s, 4H, CH$_2$).

Ring-Opening Polymerization (ROP) of ε-caprolactone (CL) (1). A 6 mL (5.8252 g, 51 mmol) sample of monomer (CL), 0.638 g (2.04 mmol) of bifunctional initiator (2,5-dibromo-1,4-(dihydroxymethyl)benzene), and a catalytic amount of Sn(Oct)$_2$ ([OH]/ [Sn(Oct)$_2$] = 200/1 molar ratio) were added under nitrogen in previously flamed and nitrogen- purged Schlenk tubes equipped with a magnetic stirrer. The CL polymerizations were carried out in bulk at 110 °C. After 24 h the mixtures were diluted with CH$_2$Cl$_2$ and poured into a 10-fold excess of cold methanol. The polymer (**1**) was collected after filtration and dried at room temperature in

vacuum for 3 days. DP$_n$(H NMR) = 26, $M_{n,H NMR}$ = 3264; $M_{n,GPC}$ = 3640, M_w/M_n = 1.32.

ATRP of Styrene (2). A round-bottom-flask equipped with magnetic stirrer and a lateral neck with tap was used. The system was vacuumed and backfilled with dry nitrogen several times. Catalyst (CuBr, 0.215 g, 1.5 mmol), ligand (bipyridine (bpy), 0.704 g, 4.5 mmol) initiator (1,4-dibromo-2-(bromomethyl)benzene, and styrene (10 mL, 87.5 mmol) were introduced under an inert atmosphere. The flask was placed in an oil bath warmed at 110 °C and stirred at that temperature for 55 min. The mixture was then diluted with THF and poured into 10-fold methanol. The solid was collected after filtration and was dried at 40 °C in a vacuum oven overnight. Polymer **2** was purified by passing through a silica gel column using THF as eluent and reprecipitation into methanol (yield, 35%, $M_{n,th}$ = 2360). DP$_n$(H NMR) = 19.5, $M_{n,H NMR}$ = 2270; $M_{n,GPC}$ = 2400, M_w/M_n = 1.3

Synthesis of Aldehyde-Functional Polymers (3, 4) by Suzuki Coupling Reaction. A 100 mL three-necked round-bottom flask equipped with a condenser, a rubber septum, a nitrogen inlet−outlet and a magnetic stirrer was charged with 1 M NaHCO$_3$ (10 mL,) aqueous solution and THF (15 mL). The solvents (THF and NaHCO$_3$ solution (aq)) were previously bubbled with nitrogen over a period of 30 min, and the mixture was refluxed under nitrogen for 4 h.

A 20 mL three-necked round-bottom flask equipped in the same way as the previous one was charged under inert atmosphere with 0.208 mmol of polymer (0.6789 g of **1** or 0.755 g of **2**), 0.156 g (1.04 mmol) of 4-formylphenylboronic acid, and 0.01 g (0.008 mmol) of Pd(PPh$_3$)$_4$. The solvent mixture (4 mL) was introduced with a syringe through the septum. The mixture was refluxed under nitrogen for 4 days, maintaining vigorous stirring and with the exclusion of oxygen and light. The aldehyde functionalized polymers (**3** or **4**) were separated by precipitation in cold methanol, filtrated, and dried. Further purification was performed by passing the polymer through a silica gel column using THF as eluent and reprecipitation in methanol.

Synthesis of *p*-xylylenebis(triphenylphosphonium bromide) (5) and 2,5-dibromo-*p*-xylylenebis(triphenylphosphonium bromide) (6). In a 100 mL round-bottom flask equipped with a condenser and a magnetic stirrer was introduced 0.02 mol of 1,4 bis(bromomethylbenzene) or 1,4-dibromo-2,5-bis(bromomethyl)-benzene, 9.82 g (0.042 mol) of PPh$_3$ and 40 mL of DMF as solvent. First, by slightly heating, the mixture was solved and a white precipitate was observed. Then the heating was continued until reflux with stirring for 4 h. The white precipitate was filtered and washed several times with diethyl ether.

5: ^{1}H NMR (CDCl$_3$): δ 7.76−7.4 (m, 30H, PPh$_3$), 6.83 (s, 4H, Ar), 5.37−5.2 (d, 4H, C*H*$_2$).

Table 1. Molecular Weights of the Polymers Calculated from ^{1}H NMR and GPC Data

starting macromonomer	$M_{n,^1H\ NMR}$	$M_{n,GPC}$, PD	−CHO funct macromonomer	color	$M_{n,^1H\ NMR}$	$M_{n,GPC}$, PD	PPV	color	$M_{n,GPC}$, PD
1	3264	3640, 1.32	**3**	white	3314	3720, 1.36	**7**	bright yellow	28320, 2.59
							8	dark yellow	32000, 2.31
2	2270	2400, 1.3	**4**	white	2420	2480, 1.34	**9**	bright green	18600, 3.05

Scheme 2. Synthesis of the Aldehyde Functionalized Macromonomers from the Bromine Functionalized Ones (PCL (1, 3) or PSt (2, 4)
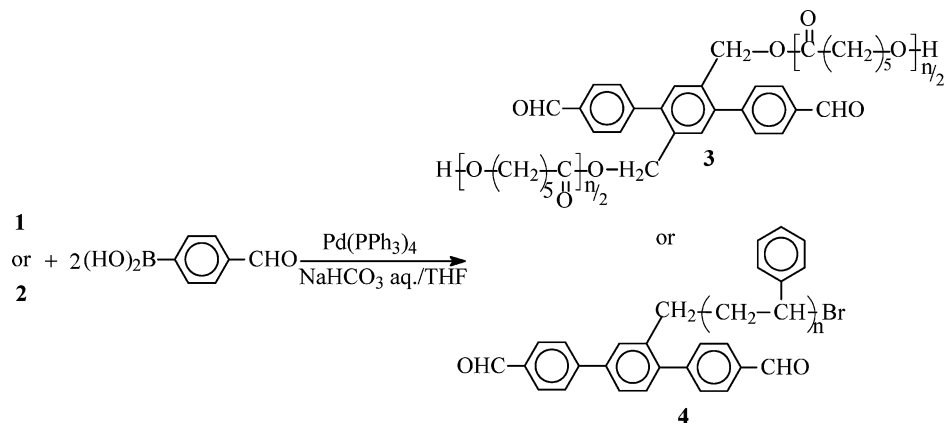
6: ^{1}H NMR (CDCl$_3$): δ (ppm): 7.92−7.38, (m, 30H, PPh$_3$), 7.36−7.32 (s, 2H, Ar), 5.66−5.58, (d, 4H, C*H*$_2$).

General Procedure for the Synthesis of PPV with PCL or PSt Side Chains by Wittig Reaction (7−9). To a solution of 0.2 mmol of **3** or **4** and 0.2 mmol of **5** or **6** in 3 mL of dry THF was added 0.135 g (1.2 mmol) of *t*-BuOK in 1 mL of THF dropwise under nitrogen, and the reaction mixture was stirred for 24 h at room temperature. Because during that time the viscosity of the reaction mixture increased, 1 mL of dry THF was introduced, under nitrogen; an appropriate stirring speed was then maintained. This operation was repeated two more times at 6 h intervals. Finally, after 48 h from the beginning of the reaction the mixture was poured into cold methanol to precipitate the polymer (**7**, **8**, or **9**). Further purification was achieved by passing the polymer through a silica gel column using THF as eluent and reprecipitating in methanol.

Analysis. ^{1}H NMR spectra were recorded in CDCl$_3$ with tetramethylsilane, using a Bruker AC250 (250.133 MHz). FT-IR spectra were recorded on Perkin-Elmer FT-IR Spectrum One spectrometer. Molecular weights were determined by gel permeation chromatography (GPC) equipped with Waters Styragel columns (HR series 2, 3, 5E) with THF as the eluent at a flow rate of 0,3 mL/min and a Waters 410 Differential refractometer detector. The UV spectra were measured using an IBM 9420 spectrometer or a Shimadzu UV 2600PC spectrometer. Emission and excitation spectra were obtained using a Perkin-Elmer LS 50B spectrometer with xenon lamp light source. The maximum absorbance of polymer solution was maintained at *A* < 0.1 in order to minimize errors due to internal filter effects.

Results and Discussion

The first step in the synthesis of PPVs with macromolecular side chains was to obtain dibromo functionalized polymers (**1** or **2**) (Scheme 1). To obtain the desired functionalities, combined with proper molecular weights and polydispersities, controlled polymerization methods were used. Polymer **1** was synthesized by ROP of ε-caprolactone by using [2,5-dibromo-(4-hydroxy-methyl)phenyl)]methanol as bifunctional initiator, in the presence of stannous octoate. PSt-based macromonomer **2** was synthesized by ATRP of styrene by using 1,4-dibromo-2-(bromomethyl)benzene as initiator in the presence of CuBr/bpy as catalytic system.

In both cases the GPC traces are unimodal and narrow, indicating that no important side reactions occurred (see Supporting Information).

As these polymers were intended to be used in further reactions, efforts were directed toward obtaining low molecular weights, combined with convenient yields. Some characteristics are presented in Table 1. In the case of the PCL macromonomer (**1**), the molecular weight calculated from ^{1}H NMR spectrum was considered more reliable and used for further calculations.

The reaction between aryl halides and aryl boronic acids (Suzuki coupling)[48] is a most convenient method for C−C coupling. The reaction is simple and insensitive to moisture. Furthermore, this coupling reaction can be applied to monomers carrying functional groups.[49] We have employed this method in the synthesis of polyphenylenes, in which a macromonomer having a 2,5-dibromo-1,4-phenylene moiety or a 2,5-diboronic acid phenylene one was reacted with an aromatic diboronic acid or an aromatic dibrominated one, respectively.[36−43,50]

Similar macromonomers possessing end-chain or midchain dibromo aromatic moieties were reacted with mono boronic acids having different functionalities (−NH$_2$ or −CHO) and yielded respective amino or aldehyde telechelics.[44] Moreover, by applying the same strategy, and using 1-naphthyl boronic acid as a reaction partner for a 2,5-dibromophenylene center functionalized PSt-based macromonomer, a polymer containing a conjugated sequence (naphthalene−1,4-phenylene−naphthalene) was synthesized.[51] This macromonomer could be further used in oxidative polymerization and a polymer containing a rigid backbone with PSt side chains as substituents was obtained.

In the present work, PCL or PSt macromonomers containing either a center or an end chain conjugated sequence (triphenylene) (**3** or **4** in Scheme 2) could be prepared by Suzuki coupling of **1** and **2**, respectively with 4-formylphenylboronic acid. The reaction conditions (high excess of boronic acid and long reaction times) were chosen to ensure a complete functionalization. A slight increase of molecular weights was noticed for **3** and **4** as compared to **1** and **2**, due to the introduction of new end groups (Table 1).

As the conjugated sequences contain aldehyde groups at both ends, the functionalized polymers are candidates for synthesis of conjugated polymers with macromolecular side chains (PPVs or Schiff base type polymers). We applied the Wittig method in combination with *p*-xylylenebis(triphenylphosphonium bromide) (**5**) or 2,5-dibromo-*p*-xylylenebis (triphenylphosphonium

Scheme 3. Synthesis of PCL Substituted PPVs
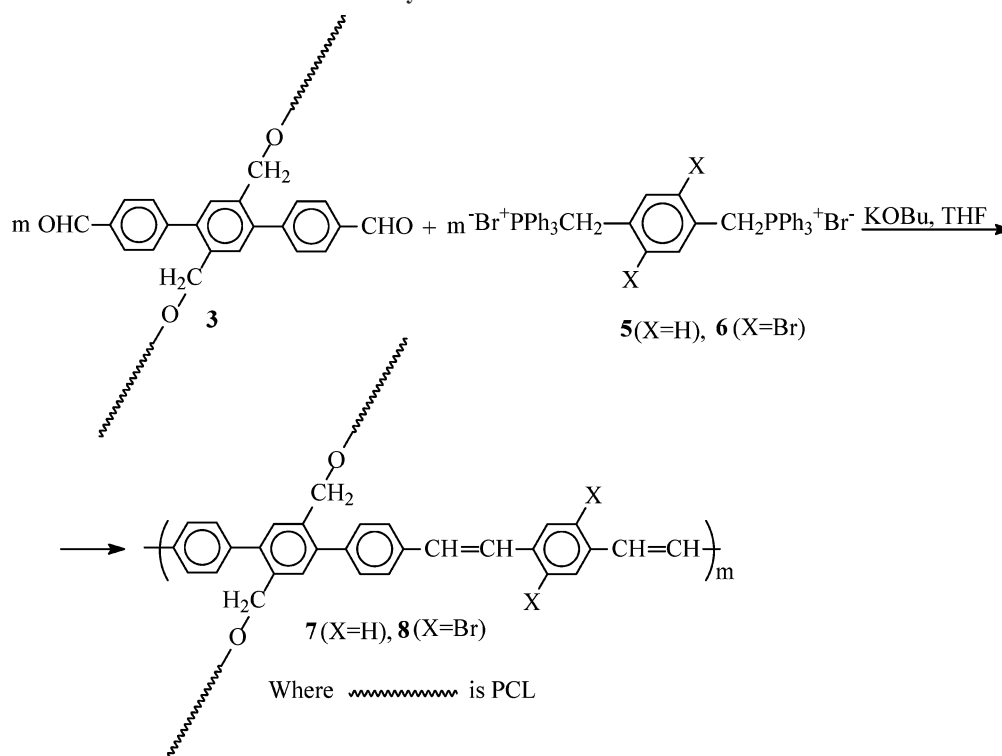
Scheme 4. Synthesis of PPV with PSt as Side Chains
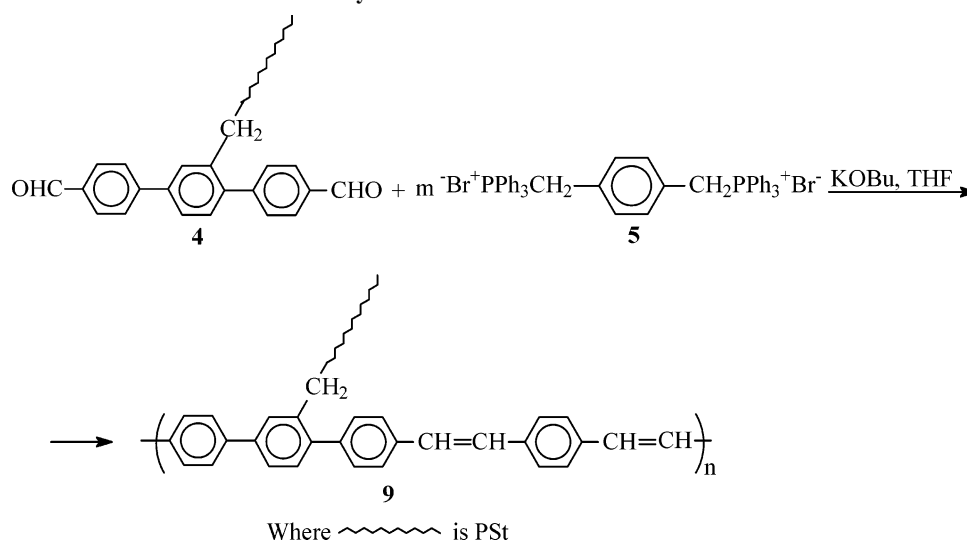
bromide) (**6**) and PPVs having as lateral substituents the respective PCL (**7**, **8** in Scheme 3) or PSt (**9** in Scheme 4) chains were synthesized.
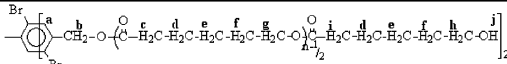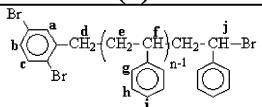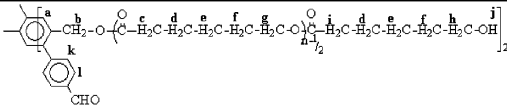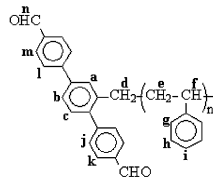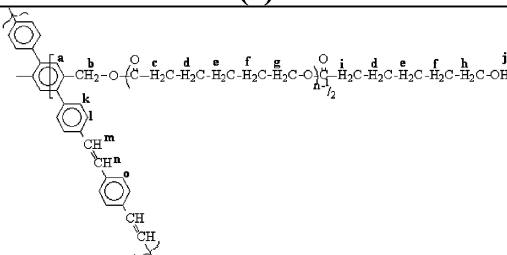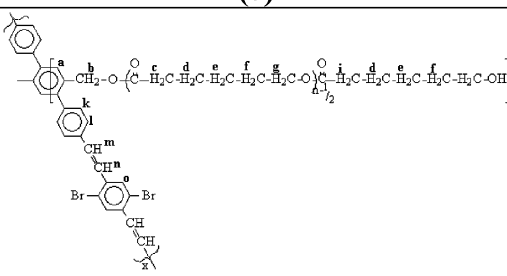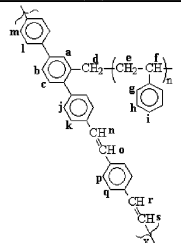
The polymerization reaction was performed in THF in the presence of *t*-KOBu. Colored polymers, listed in Table 1, with good solubility in common organic solvents and good film forming properties (similar to those of the starting macromonomers) were obtained. The solutions of the polymers also show fluorescence under daylight and UV light (366 nm): blue for polymer **7** and **8** (less for the latter) and green for polymer **9**. This behavior is interesting as the composition of these polymers contains 85−90% PCL or PSt. It can be noted that when polyphenylenes with macromolecular side chains were obtained starting from such macromonomers,[36−43,50] they usually resulted as white polymers, similar to the starting materials (see Supporting Information).

Characteristics of the PPVs are shown in Table 1. The molecular weights measured by GPC based on PSt standards, should be taken as minimum estimate because of the highly branched or comblike structure of the obtained structures.

NMR Analysis. ^{1}H NMR spectra data of the polymers are listed in Table 2 (for details, see Supporting Information). In the case of the dibrominated PCL-based macromonomer **1**, the protons belonging to the rest of the initiator (**a** and **b**) are clearly in evidence and their integrals were compared with those of O−CH_2 protons in the PCL chain. Polymerization degree was calculated to be 26, corresponding to a molecular weight of $M_{n,H\ NMR} = 3264$.

The ^{1}H NMR spectrum of the aldehyde functionalized polymer (**3**) also confirms the proposed structure. The aldehyde proton **m** at 10.1 ppm, the new aromatic signals **l** and **k** at 7.99 and 7.56 ppm, together with **a** and **b** protons originating from

Table 2. Spectral Characterization of Macromonomers and the Final PPVs

Polymer	^{1}H-NMR δ (ppm)	FT-IR %T (cm^{-1})
(1)	a(7.58), b(5.15), c(2.20~2.35), d+f(1.60~1.70), e(1.39~1.50), g(4.06), h(3.64), i(2.45)	3440, 2943,2865, 1723, 1470, 1418, 1397, 1365, 1293, 1239, 1176, 1107, 1046, 960, 930, 838, 730, 675
(2)	a+b+c+g+h+i(6.21~7.24), d+e+f(1.10~2.50), j(4.50)	3058, 3025, 2970, 2851, 2848, 1937, 1867, 1798, 1665, 1598, 1489, 1446, 1372, 1177, 1051, 1066, 1026, 910, 808, 760, 758, 697
(3)	a(7.46), b(5.07), c+i(2.27~2.33), d+f(1.60~1.68), e(1.36~1.42), g(4.06), h(3.64), k(7.56), l(7.99), m(10.10)	3440, 2982, 2944, 2865, 1723, 1607, 1572, 1470, 1418, 1397, 1365, 1293, 1239, 1175, 1106, 1045, 960, 933, 838, 731, 710
(4)	a+b+c+g+h+i(6.21~7.24) d+e+f(1.10~2.50), j+k+l+m(7.69~7.98), n+o(10.02~10.07)	3058, 3025, 2970, 2851, 2848, 1937, 1867, 1802, 1798, 1702, 1665, 1598, 1489, 1446, 1208, 1070, 1028, 910, 836, 816, 760, 758, 697,621
(7)	a+m$_{cis}$(7.09~7.22), b(5.10), c+i(2.22~2.37), d+f(1.57~1.68), e(1.36~1.39), g(4.06), h(3.64), o+k+n$_{trans}$(7.35~7.48), l(7.60), m$_{trans}$(7.68), n$_{cis}$(6.61~6.65)	3435, 2980, 2943, 2865, 1723, 1460, 1418, 1366, 1293, 1240, 1185, 1092, 1045, 960, 840, 730
(8)	a+k+m$_{trans}$+n$_{trans}$(7.40~7.46), b(5.12), c+i(2.22~2.37), d+f(1.57~1.68), e(1.36~1.39), g(4.06), h(3.64), o+l(7.61~7.94), l(7.60), m$_{cis}$(6.64~6.75), n$_{cis}$(7.12~7.15)	3435, 2982, 2962, 2867, 1723,1460, 1418, 1396, 1366, 1293, 1240, 1186, 1088, 1015, 960, 932, 860, 799, 730
(9)	a+b+c+g+h+i+j+m+o+r+s(6.28~ 7.19) d+e+f(1.10~2.50), k+l(7.55~7.63), p+q(7.40~7.46)	3058, 3025, 2970, 2923, 2851, 2848, 1937, 1867, 1798, 1665, 1598, 1489, 1446, 1084, 910, 818, 760, 758, 697, 620

the rest of the ROP initiator, permitted a recalculation of the polymerization degree of PCL is similar to the starting one. This result proves not only that during the Suzuki reaction no degradation process of the PCL chain occurred, but also that the functionalization of the polymer was complete.

The ^{1}H NMR spectrum of PPV **7** shows different signals in the aromatic region as comparing with **3**. The aldehyde peak from 10.1 ppm in the spectrum of **3** has disappeared, in this case due to the consumption of this group during the Wittig reaction. The peaks in around 7.0−7.8 ppm are broader and partial overlapping due to the increasing of polydispersity of the new polymer together with increase in conjugation length. Some authors observed the possibility of *cis−trans* conformations in the case of PPV; it has been reported that the *cis* proton appears usually around 6.5 ppm.[52−55] In our case, the small doublet at 6.65−6.61 ppm suggests that some *cis* conformations
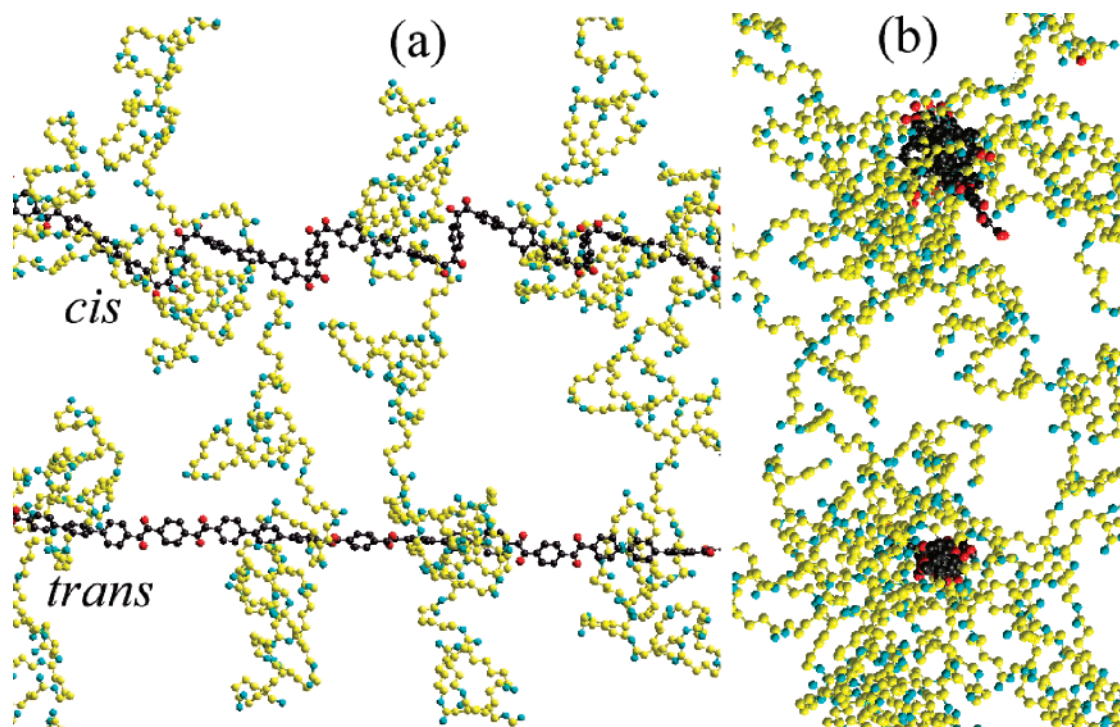
Figure 1. Three-dimensional ball-and-stick models of **7** in *cis* and *trans* conformations, top (a) and frontal (b) images.

at the newly formed vinylic bonds also appeared ($\mathbf{n}_{cis}$). Although protons in the *trans* conformation are not sharply defined ($\mathbf{n}_{trans}$ appears together with other aromatic protons, while $\mathbf{m}_{trans}$ is too close to the **l** ones to permit a precise integration) an evaluation of the *cis* percentage could be done by comparing the integral of $\mathbf{n}_{cis}$ with the integral of **b** protons.

$$I_{\mathbf{b}}/4 = (I_{\mathbf{n}_{cis}} + I_{\mathbf{n}_{trans}})/2 \qquad (1)$$

Thus,

$$\% \ cis = 2I_{\mathbf{n}_{cis}} \times 100/(I_{\mathbf{b}} - 2I_{\mathbf{n}_{cis}}) \qquad (2)$$

where $I_{\mathbf{b}}$ and $I_{\mathbf{n}_{cis}}$ are the integrals of the protons from 5.0 to 5.1 ppm and at 6.65−6.61 ppm, respectively.

The same calculations can be made by comparing the integral of $\mathbf{n}_{cis}$ with that of all the other protons between 7 and 7.8 ppm, as every repeating unit has 18 aromatic protons. In the case of **7** it was found that about 50% of the double bonds are in a *cis* conformation. Taking in account the macromolecular nature of the PPV substituents, the result is probably due to sterical hindrance. As the protons **b** and **h** of the initial macromonomer are still clearly resolvable, their integrals were used also for verifying the polymerization degree of PCL and was found again to be 26. This fact shows that no degradation of the polymer chain took place during the formation of the PPV.

For a better understanding of the spatial arrangement of the PPV main chain in *cis* or *trans* conformations of the vinylene bonds, as well as the distribution of PCL side chains around the rigid core, model molecules for polymer fragments were obtained by molecular mechanics (MM+). The three-dimensional ball-and-stick models are shown in Figure 1 obtained after energy minimization. The shown copolymers, obtained by the copolymerization of a macromonomer with a low molecular weight partner, are graft copolymers, an interesting class of self-assembling materials with domain sizes in the nanometer regime.[40] In general, graft copolymers are considered as special branched polymers that are expensive to produce commercially.

However, the introduction of branches onto a polymer chain facilitates control over the processability and rheological properties and moreover such copolymers show different morphologies due to the microscopic phase separation in the solid state and selective solvation in solution. This intrinsic morphology can be used to design materials for nanoscale devices. In the models presented in Figure 1 in both cases (*cis* and *trans* conformation) the molecule structure is of "hairy-rod" type with a pronounced cylindrical symmetry in the case of the *trans* conformation. The literature has reported the backbone of cylindrical symmetry of the hairy-rod molecules can be modified by attaching long or short side chains.[55] The slight deviation from the cylindrical symmetry of the backbone observed in Figure 1 (*cis*) could be due to the type of conformation of the vinylene double bond. By comparing with conventional polymers, the importance of such cylindrical objects consists in that their diameter is on the order of a few nanometers rather than few angstroms. As a consequence, the rigidity is so high that the persistence length of an individual chain is not on the order of 10 nm, but may instead exceed 50 nm. Such cylindrical rods, due to their high bending moduli, could potentially be used for constructions on the nanometer scale.[43]

In the case of the other PCL substituted PPV, **8**, in which bromine atoms alternates with polymeric substituents, the ^{1}H NMR spectrum also shows that some double bonds are in the *cis* conformation. The intensity of signals from 7.12 to 7.15 ppm ($\mathbf{n}_{cis}$) and 6.64−6.75 ppm ($\mathbf{m}_{cis}$) regions could be compared again with the intensity of the **b** proton peak. In this case, also the **o** protons belonging to the bromine substituted ring appear separately from the other aromatic protons, so the percentage of double bonds in the *cis* conformation (75%) could be calculated. The increase in the amount of *cis* vinylene linkages comparing with polymer **7** can be due to the presence of bulky bromine atoms as side groups near the PCL ones.

In the ^{1}H NMR spectrum of the polystyrene starting macromonomer **2** (Table 2), obtained by ATRP, the peak from about 4.5 ppm corresponding to the final Ar−C*H* proton, directly linked to the final bromine atom, was used for calculating the
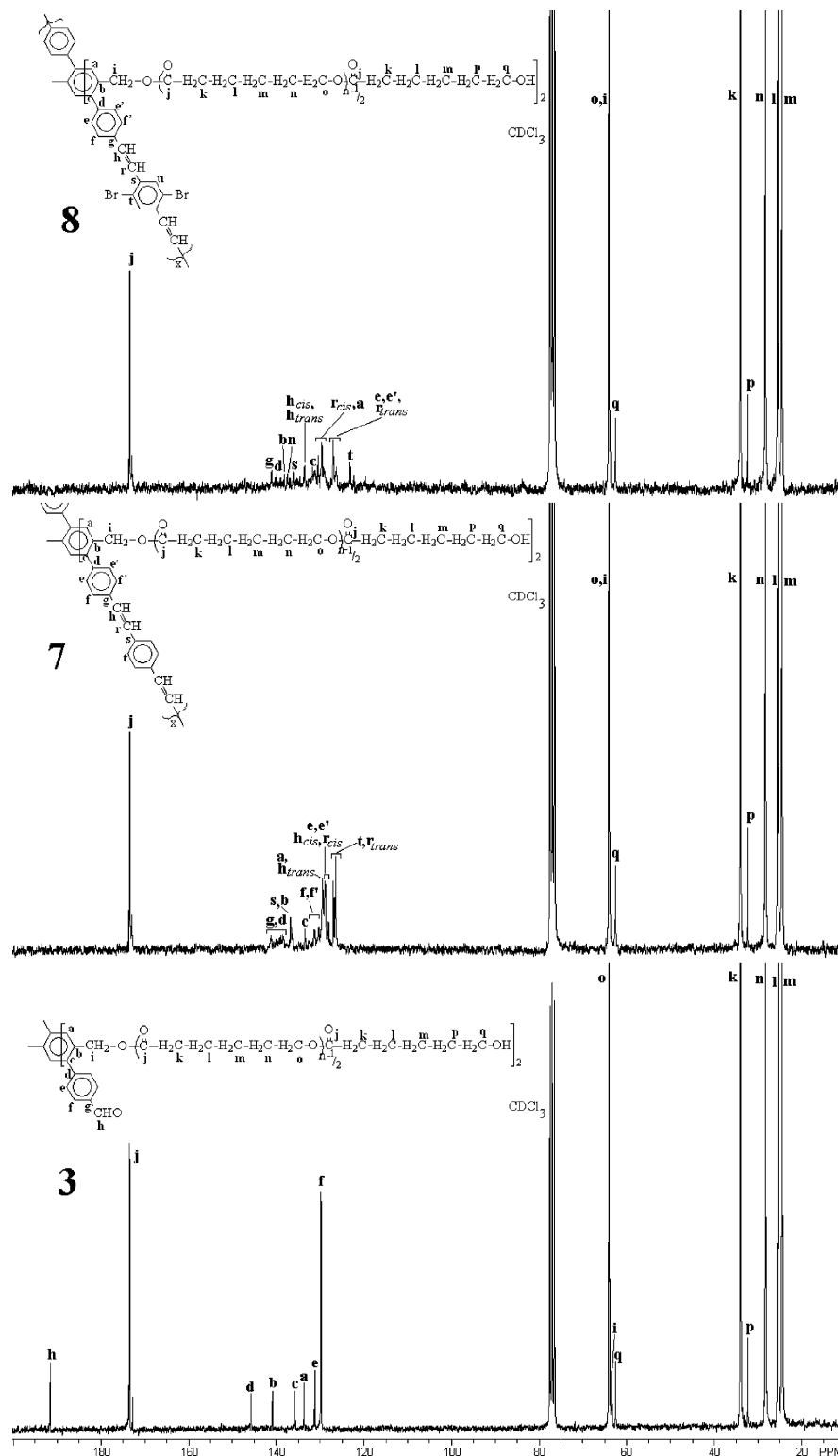
Figure 2. ^{13}C NMR spectra of PCL polymers **3**, **7** and **8**.

molecular weight of the polymer. The result is close to that found from GPC. The spectrum of the aldehyde functionalized polymer **4** shows clear peaks of the newly introduced end groups. As the substitution at the benzene ring originating from the ATRP initiator is not symmetrical as in the case of PCL polymer **3**, the peaks from the aromatic region that are outside the PSt main signals (beyond 7.3 ppm) can be the result of contributions of several aromatic protons (**m**, **k**, **l**, **j**). Despite this the peaks of the aldehyde protons appear very clearly at 10.02−10.07 ppm and could be used for calculating the

molecular weight of **4**. As in the case of **3**, the slight increase of molecular weight as comparing to the starting **2**, can be due to the introducing new end groups in the polymer chain.

Because of the partially overlapping of the protons of the conjugated chain with the aromatic ones in the PSt repeating units, together with the increase of polydispersity, the spectrum of **9** offers less information regarding the final polymer structure. In this case it is not possible to determine whether *cis* conformation are also present. Despite this, the different arrangement of the aromatic protons from the region beyond

7.3 ppm (the region uncovered by PSt), together with GPC data and the results of other analyses, indicates that the desired PPV was formed.

^{13}C NMR analysis can also give information on the polymers structures. Figure 2 present the spectra of PCL-based PPVs (**7** and **8**) in comparison with the aldehyde functionalized macromonomer (**3**). The spectrum of macromonomer **3** presents not only the usual signals of PCL (173.47 ppm, **j**; 129.8 ppm, **f**; 62.47 ppm, **o**; 34.05 ppm, **k**; 26.23 ppm, **n**; 25.59 ppm, **l**; 24.47 ppm, **m**), but also peaks of the carbons originating from the end groups (191.55, **h**; 145.63 ppm, **d**; 140.94 ppm, **b**; 135.66 ppm, **c**; 133.6 ppm, **a**; 131.14 ppm, **e**; 62.28 ppm, **q**; 32.17 ppm, **p**) proving the proposed structure. In the case of the ^{13}C NMR spectra of PCL-based PPVs **7** and **8**, the number of peaks in the aromatic region significantly increases in this region (150−125 ppm), while the signal from 173.47 ppm of the aldehyde carbons from **3**, disappears. Although the distribution of the peaks suggests in both cases the existence of *cis−trans* conformations, no certain conclusions regarding this aspect can be depicted from the spectra. ^{13}C NMR spectra of the PSt-based polymers are even more complicated. Because of the asymmetrical substitution of the PSt chain on the benzene ring, all the aromatic carbons of the end groups differ. Moreover, some of the aromatic carbons of the end groups in the case of **4** or of the conjugated main chain in the case of **9** are covered by the aromatic carbons of PSt itself. Despite this in the case of **4,** the aldehyde carbons appear separately at 181.6 ppm and this peak disappears in the case of PPV **9**. Also, some of the carbons of the end groups or conjugated PPV main chain could be identified in the domains not covered by the aromatic signals of PSt (144 ppm; 132 and 123 ppm; 117 ppm) proving the proposed structures, but no information on the cis−trans conformations is obtained.

IR Analysis. IR spectra of PCL-based polymers (**1**, **3**, **7**, **8**) (Table 2 (for details, see Supporting Information)) display strong specific peaks for CL repeating units (e.g., 1723 cm^{-1}, $\nu_{C=O}$; 1293 cm^{-1}, $\nu_{C-O(as)}$; and 1046 cm^{-1}, $\nu_{C-O,sym}$, etc.). In the case of the aldehyde functionalized polymer a new signal at 1607 cm^{-1} is attributed to $\nu_{C=O}$ from the CHO group. The shifting of this absorbance to lower frequency than usual is explained in this case by the association of this carbonyl group by intramolecular hydrogen bonding with the final OH groups in the PCL moieties. Also, we notice new peaks compared to the starting macromonomer. The absorption at 1572 cm^{-1} can be attributed for $\nu_{C=C}$ of the new aromatic rings from the rest of the boronic acid that are in conjugation with the initial benzene ring from the center of the polymer chain. On the other hand, the peak at 838 cm^{-1} from the spectrum of **1**, that could be attributed to the γ_{CH} of 1,2,4,5-tetrasubstituted benzene ring, is more intense in the case of **3**, due to the γ_{CH} of the new para-disubstituted benzene rings.

In the spectra of PPV type polymers **7** and **8** the absorbance attributed to the aldehyde group in **3**, has almost disappeared. Because of the presence of intense PCL peaks in the regions around 965−980 cm^{-1} (*trans*-γ_{CH} for vinylene bonds) and 675−730 cm^{-1} (*cis*-γ_{CH} for vinylene bonds), less information on their conformation can be obtained from the IR spectra of these polymers. Despite this, a new peak at 860 cm^{-1} in the case of **8**, or 1460 cm^{-1} for both **7** and **8**, can be attributted to a *cis* conformation of the vinylene bonds. Also, the new peak from 1015 cm^{-1} can be due to the *trans* conformation in the PPV main chain.

The IR spectra of **2**, **4**, and **9** (Table 2) display the usual absorptions of PSt at 3058, 3025 (aromatic CH stretching), 2970,

Table 3. Thermal Properties of the Synthesized Polymers

polymer	mp^a (°C)	T_g^a (°C)	IDT^b (°C)	T_{w10}^c (°C)	$Y_{c\,800}^d$ (%)
1	51		270	340	2
3	50		318	378	0
7	41		302	390	9
8	38.5		231	262	11
2		91	180	375	3
4		99	250	377	13.6
9		120	300	405	8

^{a} From DSC analysis ^{b} Initial degradation temperature (IDT) ^{c} The temperature at which the weight loss is 10% (T_{w10}) ^{d} The percent of char yield at 800 °C (Y_C)

2851, 2848 (aliphatic CH stretching), 1937, 1867, 1798, 1665, and 760 (out-of-plane hydrogen deformation), 1598, 1489, 1446 (in-plane-bend -stretching vibrations of phenyl ring), 758, and 697 cm^{-1} (out-of-plane hydrogen deformation).

The absorptions from 808 and 910 cm^{-1} in the spectrum of **2** are characteristic of out-of-plane deformations (γ_{CH}) of the CH bonds of a 1,2,4-trisubstituted aromatic ring. The latter signal is also present in the spectra of **4** and **9.** New peaks appear in the case of IR spectra of **4** and **9** (with small intensities in the latter) in the region 800−850 cm^{-1} due to the presence of p-disubstituted benzene rings (γ_{CH}).

The appearance of an intense absorption at 1702 cm^{-1} ($\nu_{C=O}$) in the spectrum of **4** indicates the presence of aldehyde groups. This peak disappears in the spectrum of PPV **9**. Because of the overlapping of PSt absorptions with those of the double bonds from the main PPV chain, as well as the broadening of the peaks, no information about *cis−trans* conformations can be obtained from the IR spectrum of **9**.

Thermal Analysis. The thermal behavior of the polymers was followed by differential scanning calorimetry (DSC) (30−300 °C) and thermogravimetric analysis (TGA) (30−600 °C), under nitrogen, with a heating rate of 10 °C/min. Some characteristics are presented in Table 3.

The endothermic peaks characteristic of the melting phenomenon of the PCL chains are evidenced at 51, 47, 41, and 38.5 °C in the DSC traces of **1**, **3**, **7**, and **8**, respectively. A decrease of the melting temperature of PCL with the increasing of the complexity of polymers can be seen. The introduction of the conjugated end group in the case of **3** can disturb the length of ordering of PCL chains, so the melting point decreases as compared with **1**. The phenomenon is more evident in the case of PPVs. The PCL molecules are linked to a rigid conjugated chain, at certain distances so the lengths of ordering and consequently the melting points are decreased. The Br substituents (that alternate with PCL ones) linked at the PPV chain of **8**, also has an influence on this characteristic. In the case of the PSt-based compounds the T_g of this polymer is slightly shifted to higher values as the complexity of the molecules increases. This behavior can be a consequence of the decreasing of mobility of PSt segments in the new polymers.

The thermal stability of the synthesized polymers containing oligomeric side chains of PSt or PCL are presented in Table 3. In the case of the series containing PSt (**2**, **4**, and **9**) an increase of the initial degradation temperature (IDT) and the temperature for 10% weight loss (T_{w10}) for compounds **4** and **9** can be observed. For the starting macromonomer **2** the IDT and T_{w10} have been reported as 180 and 375 °C, respectively,[36] whereas in the new synthesized macromonomer **4**, the IDT substantially increased at 250 °C. This fact could be attributed to the triphenylene sequence contained in its structure. The highest values for IDT and T_{w10} were registered for the PPV **9** (300 and 400 °C, respectively). A similar trend can be observed for
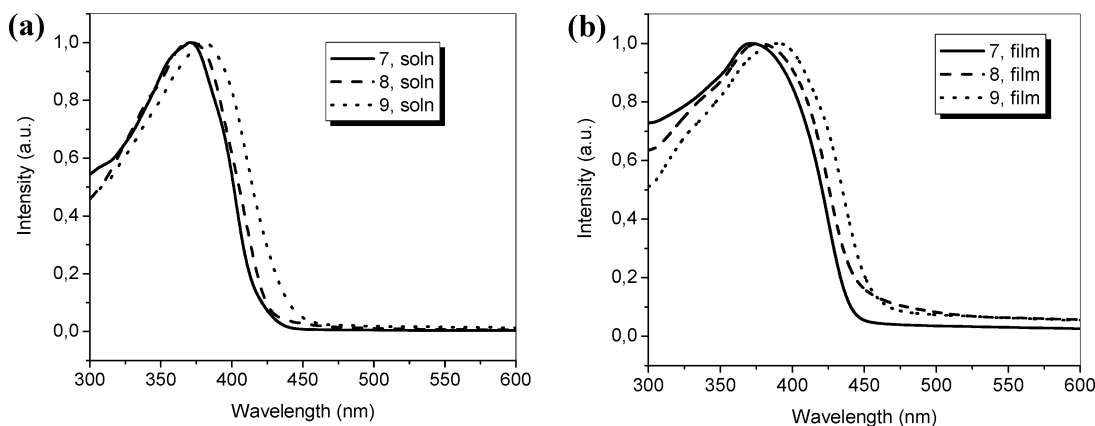
Figure 3. UV−vis spectra for **7**−**9** in chloroform at room temperature (a) and as solid films cast on quartz plates (b). Spectra are normalized for comparison.
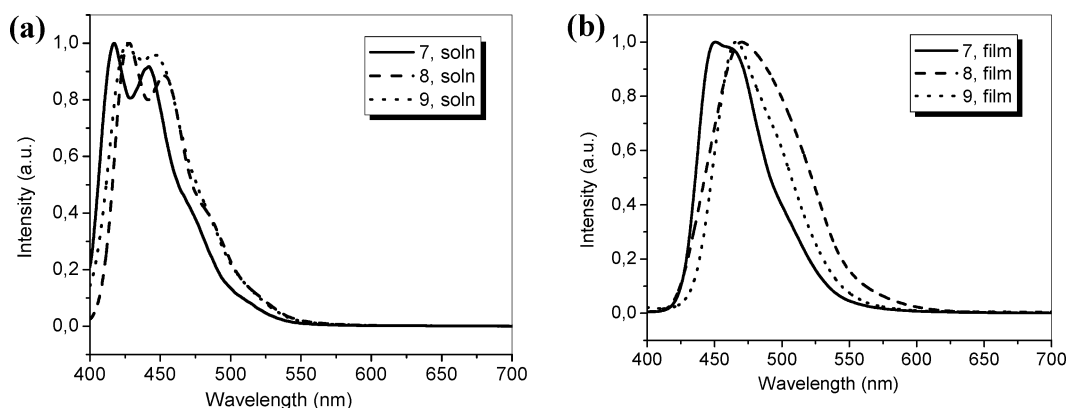

Figure 4. Photoluminescence spectra for **7**−**9** in chloroform (a) and as solid films cast on quartz plates (b).

Table 4. Photophysical Properties of Polymers in THF Solutions (0.04 g/L)

starting macromonomer		aldehyde functionalized macromonomer			PPV		
code	λ_{max}^{abs} (nm)	code	λ_{max}^{abs} (nm)[a]	λ_{max}^{PL} (nm)	code	λ_{max}^{abs} (nm)[a]	λ_{max}^{PL} (nm)
1	212, 225	**3**	212; 284[a]	356	**7**	212; 378	450
					8	212; 378	460
2	257	**4**	257; 293[b]	360	**9P**	257; 388[b]	456

[a] Excitation wavelength for PL spectra of PCL polymers [b] Excitation wavelength for PL spectra of PSt polymers

the series containing PCL. The lowest values (IDT = 231 °C; T_{w10} = 262 °C) were obtained for the polymer **8** that contains near to the PCL side chains also Br atoms directly connected to the phenylene ring, the loss of which is expected at a lower temperature. For the polymer **7**, the IDT value is comparable with that one of the macromonomer **3**. At was reported in the case of polyphenylenes with PCL side chains,[39] the thermal degradation of the polymeric structure starts with the substituents. It can be concluded from the data presented in Table 3 that the thermal stability of PPVs **7** and **9** is similar to that of poly(biphenylenevinylene) derivatives reported by Yamamoto et al. (ca. 300 °C).[57]

Optical Properties. The absorption and emission spectra of the polymers were investigated in THFand CHCl₃ solutions and in films. Starting brominated polymers **1** and **2** show UV absorptions situated between 250 and 300 nm with tails until 280−320 nm (see Supporting Information). Generally, a substituted group affects the electronic and optical properties of a polymer by its electronic nature and its size (steric hindrances). In our case, macromonomers are of the ε-caprolactone or styrene type and short chains contain as a terminal or central group a mono- or disubstituted 1,4-dibrombenzene ring. Therefore, the observed UV absorptions are mainly assigned to the phenyl rings

from short polystyrene chains (in macromonomer **2**) and from the terminal groups (in both dibrominated macromonomers).

Aldehyde functionalized macromonomers **3** and **4** differ from the corresponding **1** and **2** by replacement of bromine atoms with 4-substituted phenylene rings and a conjugation in the triphenylene sequence is possible. As a result, new maxima appear in the UV spectra. Table 4 summarizes UV absorption and emission data for the macromonomers, monomers and polymers measured in THF solutions.

The Wittig polycondensation of **3** and **4** led to PPVs having absorption spectra with the same maxima as the corresponding monomers, however new maxima can be observed assigned to the conjugated chain and also the absorption range is larger and red-shifted comparatively with their monomers. A clear bathochromic shift of the λ_{max} emission is observed for all polymers with respect to macromonomers due to extending of the conjugation length.

The UV spectra of PPVs **7**−**9** in CHCl₃ solutions and for films are presented in Figure 3 while the photoluminescence spectra under excitation wavelength of 370 nm are shown in Figure 4. The peak wavelengths are listed in Table 5.

The PL spectra of all polymer films showed a red shift and some broadening of the emission bands in comparison to their

Table 5. Photophysical Properties of 7−9 in CHCl₃ Solutions and in Film

polymer	λ_{max}^{abs} (nm)[a]	λ_{max}^{abs} (nm)[b]	λ_{max}^{PL} (nm)[a]	λ_{max}^{PL} (nm)[b]
7	373	380	418	451
8	373	376	428	470
9	382	390	428	467

[a] Chloroform solution. [b] Neat film on quartz

solution spectra. The red shifts in PL are due to intermolecular interactions in the films.

Conclusions

PPVs, with well-defined PSt or PCL chains as lateral subtituents, were synthesized by combination of controlled polymerization methods, namely ATRP and ROP, respectively and Wittig polycondensation. The structures of such complexed macromolecules have been fully characterized as they showed excellent solubility in common organic solvents at room temperature. Because of the extended conjugation, they exhibit a bathochromic shift in the emission spectra both in solution and thin films and behave as blue or green luminescent materials. The high solubility and the optical properties of the PPVs graft copolymers imply that they are promising materials for PLEDs and may find many applications in various areas.

Supporting Information Available: Figures showing GPC traces, ¹H NMR, FT-IR, and UV spectra of macromonomers and final PPVs are included, and photos of the PCL and PSt substituted PPVs in solid and solution form. This material is available free of charge via the Internet at http://pubs.acs.org.

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