

# Synthesis and Characterization of Luminescent Rod–Coil Block Copolymers by Atom Transfer Radical Polymerization: Utilization of Novel End-Functionalized Terfluorenes as Macroinitiators

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**Abstract:** Two novel, rigid, photoluminescent, substituted terfluorene derivatives were synthesized by utilizing direct bromination and Suzuki coupling reactions. These oligomers were used as initiators for the atom transfer radical polymerization (ATRP) of styrene and *tert*-butyl acrylate. Thus, diblock and triblock rod–coil block copolymers were prepared with well-defined struc-

ture, as far as their size and shape is concerned. Molecular weights up to approximately 21 000 and polydispersity indices not exceeding 1.5 in most cases

**Keywords:** atom transfer radical polymerization • block copolymers • fluorescence • phase separation • polymerization • radical reactions

were obtained. The copolymers emit blue light in solution, and their luminescence properties remain practically invariable when passing from solution to the solid state. No ground-state aggregation or excimer formation were observed in the solid state, even after annealing at high temperatures.

## Introduction

Light-emitting organic materials have been extensively studied in the past few years, with the focus mainly on their potential use in photoluminescent and electroluminescent devices.<sup>[1–3]</sup> The most recent developments in polymeric light-emitting diode (PLED) materials require the synthesis of conjugated polymers that allow thin film deposition with controlled and reproducible techniques, and which produce highly efficient blue light with low driving voltage. Oligo- and polyfluorene (PF) derivatives, in general, have been found to be excellent candidates for fulfilling the above requirements, since they emit blue light both in solution and in the solid state, exhibit thermal stability, and produce light with high quantum yields.<sup>[4]</sup> Although polyfluorene (PF) derivatives were investigated for electrooptical devices<sup>[5a]</sup> shortly after the discovery of electroluminescence in polymers by Friend, Holmes, and co-workers,<sup>[1a]</sup> no intensive work was devoted to this field for a long time, owing to some structure irregularities.<sup>[5b]</sup> However, new research efforts have recently been

initiated towards the study of various PF homopolymers and copolymers.<sup>[6–10]</sup>

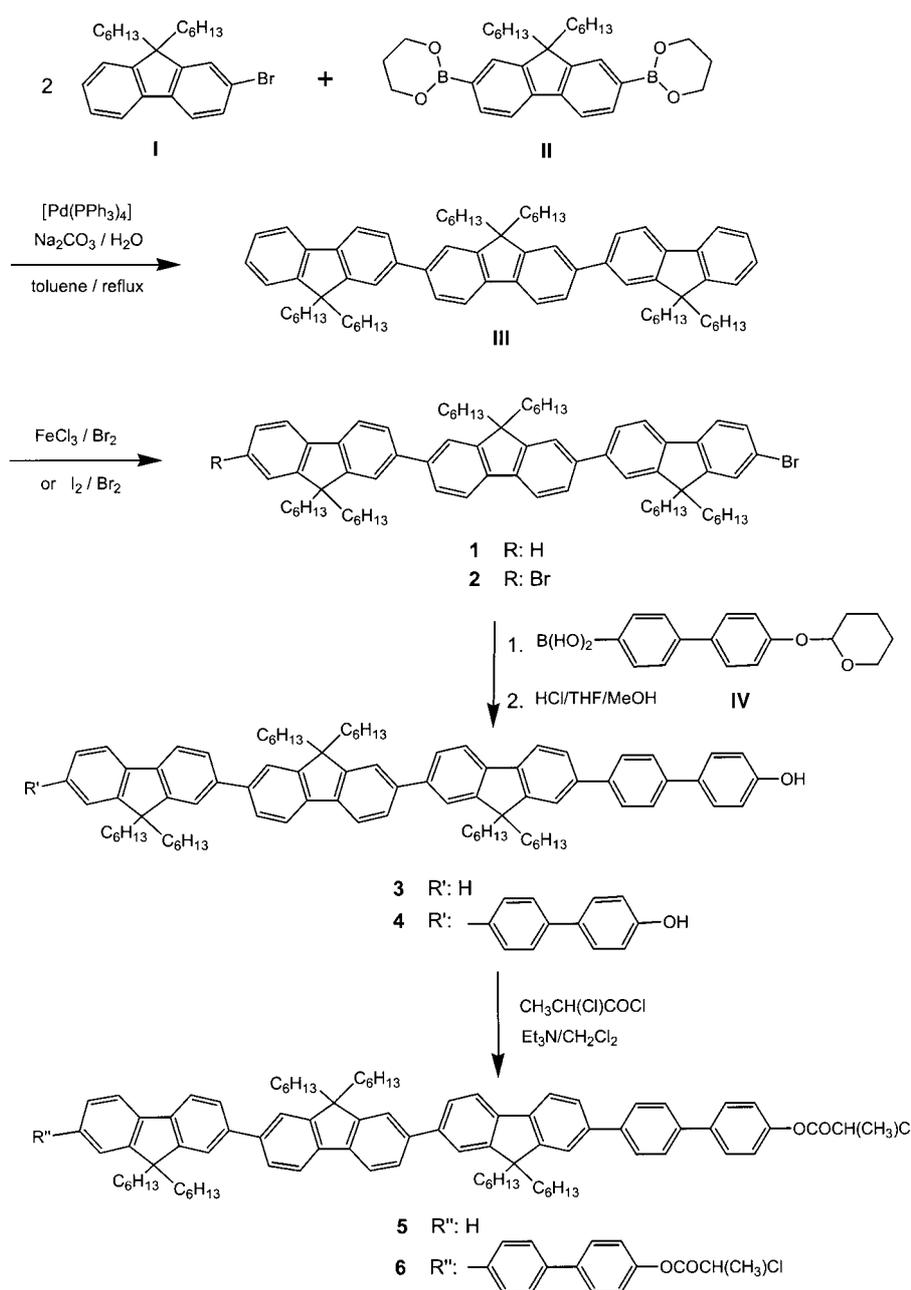
The application of these materials is hindered by their tendency to form aggregates, either during annealing or upon passage of current, which lead to a red-shifted and less efficient emission.<sup>[4a, 11]</sup> To minimize this tendency for aggregation, several attempts have been made to use bulky substituents,<sup>[12]</sup> copolymerization techniques,<sup>[8g, 13]</sup> dendrimer attachment,<sup>[8c, 14]</sup> or an oligomer approach.<sup>[3, 11, 15]</sup>

Among the above methods, the copolymer approach, and especially the synthesis of rod–coil copolymers<sup>[7a, 16, 17]</sup> with well-defined conjugated segments as their rod portion, combines the advantages of polymers, such as easy processing and the absence of crystallization in the devices, with the advantages of the oligomer approach, such as solubility and well-defined conjugation length. Moreover, with a proper combination of the structures of the rigid, conjugated segment and the coil part, unique morphologies can be obtained (such as liquid crystals and honeycomb structures).<sup>[16a]</sup> The incorporation of a light-emitting oligomer into a block copolymer structure can also reduce the size of the luminescent clusters to nanoscale dimensions, minimizing interchain interactions and subsequently the tendency to aggregate.

In our work we chose atom transfer radical polymerization (ATRP)<sup>[18]</sup> to prepare rod–coil copolymers that bear a substituted terfluorene derivative as the light-emitting rigid block. More specifically, compounds **3** and **4** (see Scheme 1) were synthesized and used as initiator precursors for the polymerization of styrene and *tert*-butyl acrylate (*t*BA) by ATRP, which resulted in diblock and triblock rod–coil

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Scheme 1.

copolymers that emit light. The triblock copolymers were found to emit blue light in both solution and the solid state; they did not form any excimers or aggregates after thermal treatment of their films.

## Results and Discussion

In recent years a variety of controlled radical polymerization techniques have been developed.<sup>[18, 19]</sup> These advances in polymer chemistry allowed the synthesis of new, well-defined macromolecules of varying topology and chemical structure, which were difficult or even impossible to obtain with traditional polymerization techniques. ATRP belongs to this category as one of the most popular controlled rad-

ical polymerization methods.<sup>[18, 19a, 19b]</sup> The synthetic process that ATRP utilizes does not demand strict reaction conditions. On the other hand, adjustment of the reaction conditions (proper catalytic system, initiator, solvent, molecular ratio between the reactants), can lead to a linear increase in the molecular weight with conversion and quite low polydispersities because of the activation–deactivation step during polymerization. This allows the preparation of macromolecules with varying composition (block, gradient, statistical, alternating copolymers) and topology (star, comb, graft, dendritic, hyperbranched copolymers).<sup>[18, 19a]</sup>

In this work novel, rigid, mono- and bifunctional luminescent oligofluorene-based initiators for ATRP of various vinyl monomers were synthesized in satisfactory yields by well-known organic reactions (Scheme 1). The substituted terfluorene **III** and its precursors were synthesized and purified based on known procedures.<sup>[7c, 16d, 15c]</sup> The substituted terfluorene **III** was directly brominated by two different synthetic methods.<sup>[7c, 8e]</sup> Despite the previously known difficulties in the synthesis and purification of brominated oligofluorene products, we managed to isolate compound **2** by column chromatography and to characterize it by <sup>1</sup>H and

<sup>13</sup>C NMR spectroscopy. Furthermore, having carefully selected the stoichiometry of the reactants, the monobromo compound **1** was selectively obtained along with a certain amount of unreacted hexahexylterfluorene. The assumption of dibromoterfluorene formation cannot be excluded in this stage. This mixture, after it was separated from any other by-products by column chromatography, was used in the next step.

The <sup>1</sup>H NMR spectra of **III** and **2** clarify the structure of the brominated product. The multiple peak appearing in the range  $\delta = 7.3–7.4$  ppm of the spectrum of **III** is assigned to the protons at the 6-, 7-, 8-, 6'-, 7'-, and 8''-positions (Figure 1a).<sup>[15a]</sup> This peak is completely absent in the spectrum of **2**, and a new multiple peak appears at  $\delta = 7.48$  ppm because of the change in the chemical shift of the protons that are

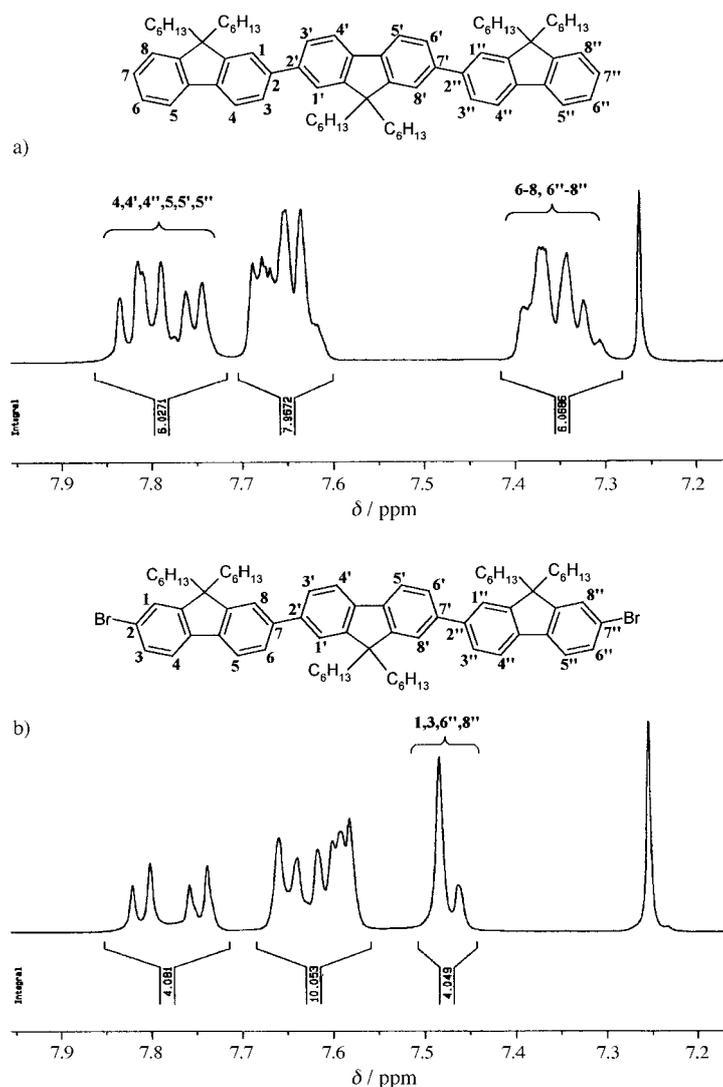


Figure 1.  $^1\text{H}$  NMR spectra (aromatic region) in  $\text{CDCl}_3$  at room temperature a) of **1** and b) of **2**.

adjacent to the inserted bromine atoms (Figure 1b). Integration showed that the multiple peak at  $\delta = 7.35$  ppm in the spectrum of **1** results from six protons and the corresponding one at  $\delta = 7.48$  ppm in the spectrum of **2** results from four protons. This shows that two bromine atoms have been inserted. In addition, the peak assigned to the protons in the 1-, 3-, 6'', and 8''-positions of **2** seems to consist of two separate peaks, one singlet and one doublet, which overlap one another. This proves that the bromination occurred in the 7- and 7''-positions to give the 2,7''-dibromotrifluorene derivative. If the bromine atoms were introduced in the 6-, and 6''-positions there would be two doublet peaks at  $\delta = 7.48$  ppm. Therefore, it is clear that the desired product **2** was obtained. The results obtained from  $^{13}\text{C}$  NMR spectroscopy are in accordance with the corresponding ones from the  $^1\text{H}$  NMR spectra and further support the conclusion that the isolated compound **2** is selectively and totally brominated in the 7- and 7''-positions of **1**.

To increase the persistence and conjugation length, as well as to introduce the proper end-functionalization for this

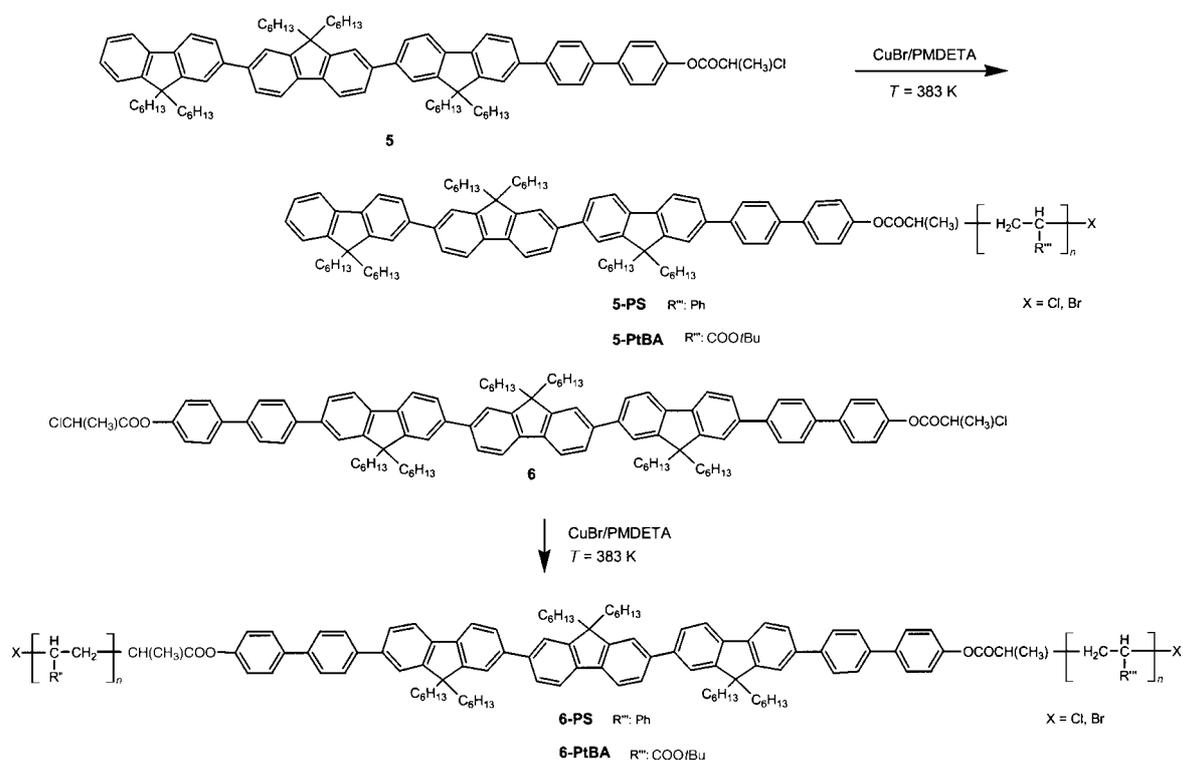
trimer, both **1** and **2** were subjected to Suzuki coupling<sup>[20a]</sup> with boronic acid **IV**<sup>[20b]</sup> to give the mono- and bifunctionalized initiator precursors (**3** and **4**) for ATRP, with eight and ten phenyl rings in the main chain, respectively. After applying proper modifications to the end-groups of these precursors, the resulting mono- and bifunctional initiators (**5** and **6**) were used to synthesize diblock and triblock polystyrene and poly(*tert*-butyl acrylate) (PtBA) copolymers with controlled structure and shape (Scheme 2).

The structures of the initiators were confirmed by  $^1\text{H}$  NMR spectroscopy. A characteristic change upon transformation of **3** to **5** (and **4** to **6**) is the shift of the signal due to the aromatic protons next to the oxygen substituent from  $\delta = 6.95$  to 7.15 ppm. In the spectrum of **5** the integration ratio (4:1) of the signals at  $\delta = 2.05$  ppm, due to the six methylenic groups that are adjacent to the 9-, 9', and 9''-positions, and at  $\delta = 1.80$  ppm, due to the terminal methyl group of the main chain, shows that the OH end group was substituted, resulting in a monofunctional initiator. The corresponding integration ratio for the initiator **6** was 2:1 (Figure 2a), confirming that the preparation of a bifunctional initiator was also achieved.

An important issue in oligo- and polyfluorene synthesis is that the alkyl substitution in the 9(H)-position of the fluorene units should be complete to prepare materials with thermostability and optimized optical properties. In cases where the aforementioned substitution is deficient, there can be partial oxidation of the C(9) center to a carbonyl group, either during the workup procedure in air or by thermal treatment of the material.<sup>[4a]</sup> The resulting fluorenone moieties, known as keto defects, act as quenching sites for optical excitations or charges, since they have the ability to "trap" singlet excitons and reduce the population in the excited state.<sup>[12a]</sup> This would lead to the appearance of a low-energy band in the yellow/orange region of the photoluminescence spectrum. In our case, the absence of signals at about  $\delta = 3.5$  ppm or at about  $\delta = 180$  ppm, assigned to H(9) and C(9)=O, respectively, from the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the precursor compounds and the final initiators, indicate that the synthesized rods are oxidatively stable, defect-poor oligofluorene derivatives.

The synthesized diblock and triblock copolymers and their molecular characteristics are given in Table 1. Molecular weights up to about 21 000 were obtained, and for the PS copolymers the polydispersity index (PDI) did not exceed 1.5. Polymerization of *t*BA gave relatively lower molecular weights. The different architecture of the block copolymers as well as the different monomers used for polymerization provide the opportunity to control the overall morphology and properties of the final material. With the previously discussed synthetic method one can easily explore the relationship between structure and properties by tailoring various chemical and physicochemical parameters, such as the aspect ratio of the rigid-rod block, the glass transition temperature, and the molecular weight of the flexible chains, to obtain the desired final properties.

The incorporation of the initiator into the polymeric chain and the initiation efficiency were confirmed by  $^1\text{H}$  NMR spectroscopy and size exclusion chromatography. In Figure 2 the  $^1\text{H}$  NMR spectra of the initiator **6** and the copolymer **6-PS 2** are presented. Most of the characteristic signals of the rigid



Scheme 2.

block (Figure 2a), that is signals in the aromatic region in the range of  $\delta = 7.57\text{--}7.78$  ppm and in the aliphatic region at  $\delta = 1.05$  and  $0.70$  ppm, are clearly shown in the spectrum of the copolymer (Figure 2b). The integration ratio of the protons in the aromatic region ( $\delta = 7.55\text{--}7.90$  ppm) to those of the terminal  $\text{CH}_3\text{--CH}_2\text{--}$  groups of the hexyl substituents is as expected (1:1). It is also clear that the signal at  $\delta = 4.6$  ppm, which is assigned to the terminal protons next to the halogen atoms of the initiator, has totally disappeared after the polymerization, while a new signal, due to the substituted initiator, has appeared at  $\delta = 3.7$  ppm. This is consistent with the fact that no trace of the initiator is apparent in the SEC chromatograms of the copolymers. As an example, the SEC chromatogram of **6-PS 1** is presented in Figure 3.

The thermal behavior of the synthesized initiators and copolymers has been studied by differential scanning calorimetry (DSC; Figure 4). Initiator **5** displays an endotherm at  $154.5^\circ\text{C}$  during the first heating scan, while only a glass transition temperature ( $T_g$ ) at  $38.5^\circ\text{C}$  is obtained during the second heating scan. For the initiator **6**, only a  $T_g$  at  $43.0^\circ\text{C}$  was obtained for both the first and the second heating scans. The higher  $T_g$  of **6** is consistent with its more rigid structure.

The DSC thermograms of the diblock and triblock copolymers are also depicted in Figure 4. Information for the phase separation of these copolymers can be extracted from these thermograms. Two  $T_g$  values were detected in most cases, one in the temperature range of the oligofluorene  $T_g$  value and the other one arising from the PS phase. This indicates that a phase separation, on the scale where  $T_g$  is sensitive, is obtained in these copolymers.

Initiator **6** and its respective polystyrene copolymers were investigated with absorption and emission spectroscopy in

dilute solution and in the solid state. In Figure 5 the luminescence spectra of **6** and **6-PS 1** are compared with those of hexahexyl-terfluorene in both solution and the solid state. All three spectra in solution (Figure 5a) have a characteristic progressive vibronic structure, which is related to the vibrational stretching of the  $\text{C}=\text{C}$  bond (about  $1600\text{ cm}^{-1}$ ).<sup>[4a]</sup> The bathochromic shift of  $14\text{ nm}$  in the spectrum of the initiator relative to that of the terfluorene indicates an increase in the effective conjugation length<sup>[15a]</sup> after the incorporation of the two biphenyl units at the 2- and 7'-positions, as has already been well proven by NMR spectroscopy. The fact that the emission spectra of the initiator and the respective copolymer are almost identical shows that the flexible chains do not affect the luminescent properties of the chromophore, as was expected. In the solid state (Figure 5b), the spectrum of the terfluorene oligomer is red-shifted by  $20\text{ nm}$ , that of the initiator exhibits a red shift of  $10\text{ nm}$ . This difference could mainly be attributed to the larger torsion angle between the phenylene rings of the biphenyl units, which suppresses the formation of totally planar species.<sup>[21]</sup>

As far as the copolymer's spectrum is concerned there seems to be almost no difference between the solution and solid states (Figure 5c). We believe that the reason for the minimal differences between these two spectra is that the intermolecular interactions between chromophore units, resulting from the formation of aggregates, are significantly diminished. This means that the rigid block gets diluted into the polystyrene matrix, almost as if it were diluted in  $\text{CHCl}_3$ . Similar cases in which the emission spectra of polyfluorene derivatives in solution and in the solid state had little difference have been reported recently.<sup>[22]</sup> In these cases,

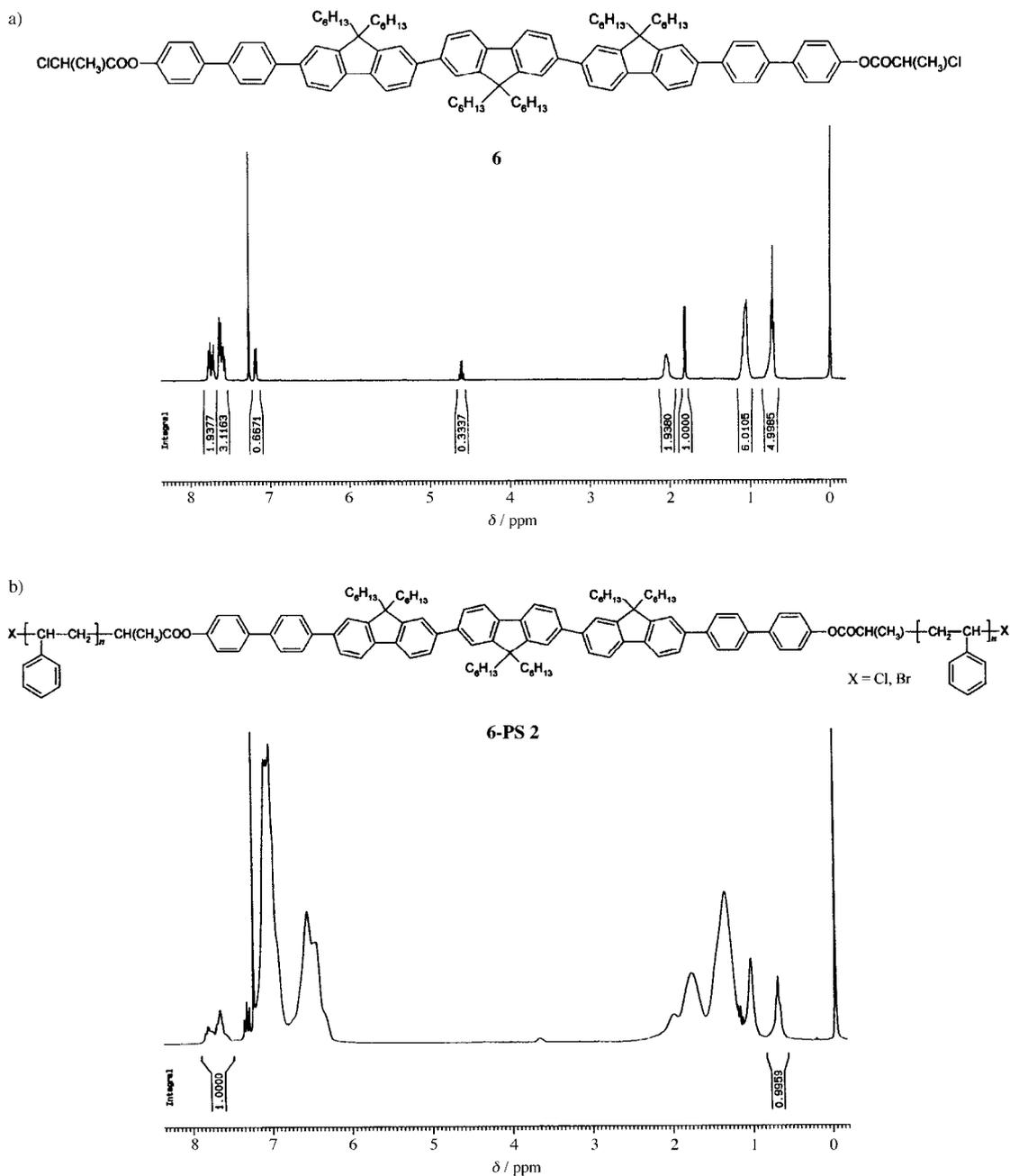


Figure 2. <sup>1</sup>H NMR spectra in CDCl<sub>3</sub> at room temperature of **6** (top) and **6-PS 2** (bottom).

Table 1. Reaction conditions and molecular weight characteristics of the synthesized block copolymers.

Polymer <sup>[a]</sup>	monomer/solvent (v/v)	GPC results <sup>[d]</sup>		
		<i>M</i> <sub>n</sub>	<i>M</i> <sub>w</sub>	PDI
<b>5-PS 1</b>	1.5	4150	5000	1.20
<b>5-PS 2</b>	2	9950	14900	1.50
<b>6-PS 1</b>	2	15500	21450	1.38
<b>6-PS 2</b>	1.5	21000	29600	1.41
<b>5-PtBA 1</b>	2 <sup>[b]</sup>	2500	3050	1.22
<b>6-PtBA 1</b>	10 <sup>[c]</sup>	5200	8600	1.65

[a] Reaction conditions: Diphenyl ether, CuBr, PMDETA, 110 °C. [b] DMF was used as a solvent. [c] Instead of DPE, 10% w/v ethylene carbonate (EC) was used. Reaction temperature: 90 °C. [d] Molecular weights and polydispersity indices were determined with size exclusion chromatography experiments (CHCl<sub>3</sub>, room temperature) using polystyrene standards for instrument calibration.

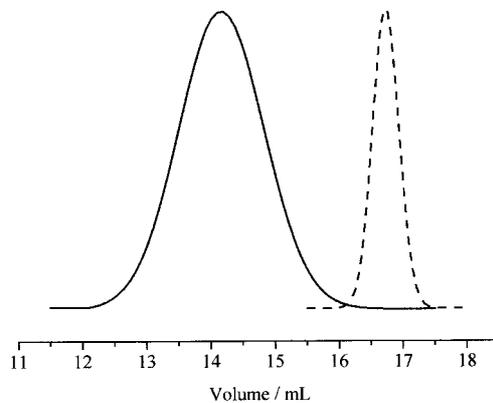


Figure 3. Size-exclusion chromatograms of the copolymer **6-PS 1** (solid line) and the initiator **6** (dashed line).

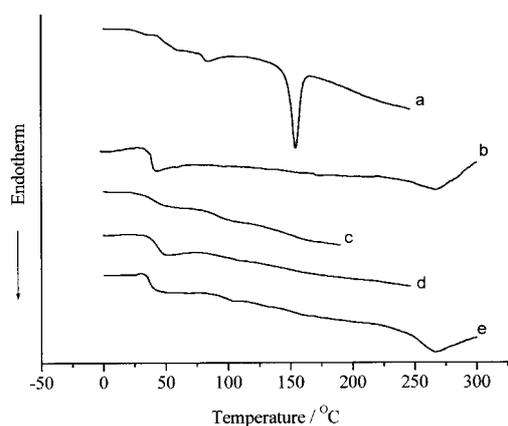


Figure 4. DSC thermograms of a) **5** (first run), b) **5** (second run), c) **5-PS 2** (second run), d) **6** (first run), e) **6-PS 1** (second run). The first and second heating rates were  $20^{\circ}\text{Cmin}^{-1}$ .

instead of *n*-hexyl groups, bulky aliphatic or aromatic chains, or even dendrimers were used as substituents in the 9-position of the fluorene species in order to prevent packing of the polymer backbone because of  $\beta$ -phase formation.<sup>[4a, 8c, 14a]</sup>

To further support the deduction that our copolymers are capable of producing pure blue light as a result of the inhibition of aggregate formation by their flexible polymer chains, we investigated the thermal resistance of the copolymers towards aggregate formation in the solid state.<sup>[22]</sup> For that reason a **6-PS 1** copolymer film was cast from  $\text{CHCl}_3$  onto a quartz substrate and annealed for half an hour at  $140^{\circ}\text{C}$ , which is a temperature much higher than  $T_g$  ( $T_{g,6-PS1} = 96.1^{\circ}\text{C}$ ). From its photoluminescence spectrum before and after annealing (see Supporting Information) it is obvious that no peak that could be attributed to excimer or aggregate formation is present.

## Conclusion

Rod–coil diblock and triblock copolymers containing substituted terfluorene derivatives as the rod block have been synthesized by utilizing atom transfer radical polymerization. These copolymers have the ability to emit blue light when excited in the near-UV region both in solution and in the solid state. Despite the use of nonbulky substituents in the 9-position of the fluorene units, the photoluminescent characteristics in the solid state exhibit minimal differences when compared with those in solution, mainly because of the incorporation of the emissive unit into polystyrene or *Pt*BA flexible chains. Furthermore, DSC measurements revealed the presence of a phase separation in the synthesized block copolymers, making these materials very promising for luminescence applications.

## Experimental Section

**General:** Compounds **I**, **II**, **III**, and **IV** were synthesized based on known procedures.<sup>[7c, 15c, 16d, 20b]</sup> Styrene, *t*BA, and DMF (Merck) were vacuum-distilled from finely powdered calcium hydride. Dichloromethane was washed with concentrated sulfuric acid, then with dilute sodium hydroxide,

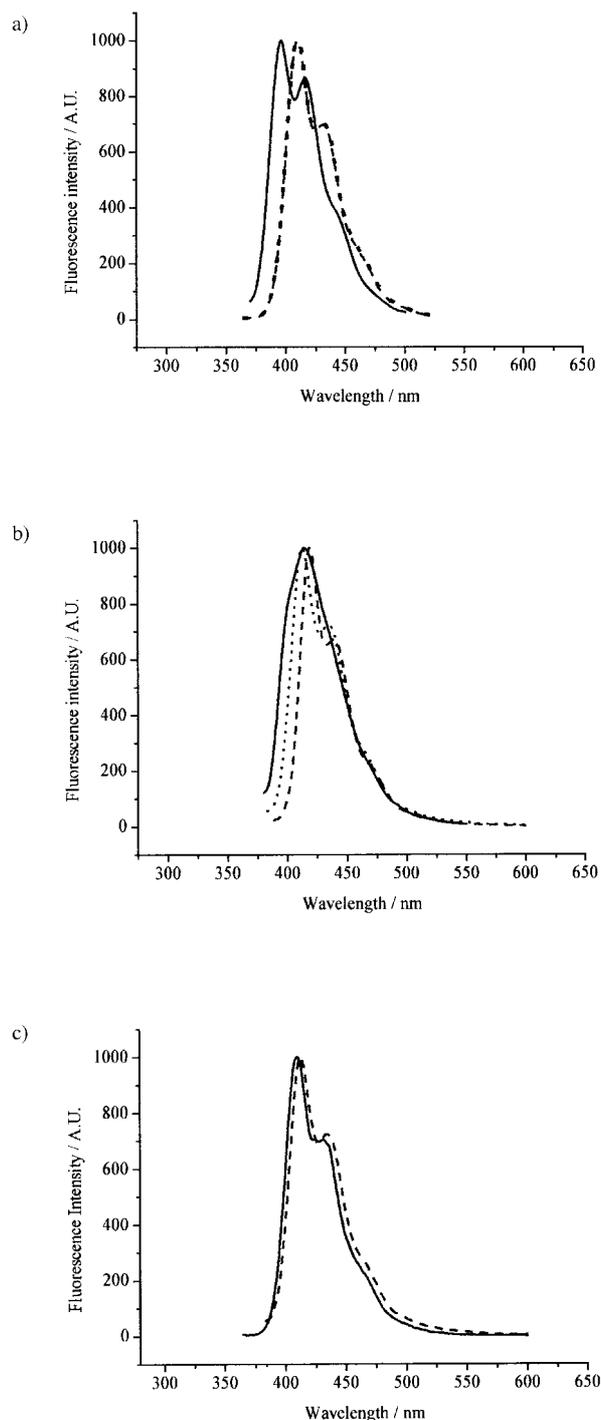


Figure 5. Fluorescence spectra at room temperature of **III** (solid line), initiator **6** (dashed line), and triblock copolymer **6-PS 1** (■) dissolved in  $\text{CHCl}_3$  (a) and as thin films cast from  $\text{CHCl}_3$  onto a quartz substrate (b). c) Fluorescence spectrum at room temperature of **6-PS 1** in  $\text{CHCl}_3$  (solid line) and as thin film cast from  $\text{CHCl}_3$  onto a quartz substrate (dashed line). Excitation wavelength was 360 nm.

and finally with water; it was then dried over sodium hydroxide and calcium chloride pellets and fractionally distilled. Diphenyl ether (Merck) was stored over molecular sieves ( $4 \text{ \AA}$ ) and purged with argon for 30 min before the polymerization was started.  $\text{CuBr}$  (Aldrich), *N,N,N',N'*-pentamethyldiethylene triamine (PMDETA, Aldrich), and all the other reagents and solvents were used as received. All reactions were run under inert atmosphere ( $\text{N}_2$ , Ar). Silica gel 60 (Merck, 0.082–0.2 mm) was used as the stationary phase for column chromatography.

**Physical characterization:** The structures of the synthesized compounds were clarified by high-resolution  $^1\text{H}$  NMR spectroscopy with a Bruker Avance DPX 400 MHz spectrometer and by  $^{13}\text{C}$  NMR spectroscopy with a Bruker Avance DPX 75 MHz. Fluorescence was measured on an SLM Aminco SPF-500 spectrofluorometer. The concentrations of the solutions used for these measurements were  $10^{-7}\text{ M}$  in chromophore units. Molecular weights ( $M_n$  and  $M_w$ ) were determined by gel permeation chromatography (Ultrastayragel columns with 500 and  $10^4 \text{ \AA}$  pore size;  $\text{CHCl}_3$  (analytical grade) was filtered through a  $0.5 \mu\text{m}$  millipore filter and samples were passed through a  $0.2 \mu\text{m}$  millipore filter; flow  $1 \text{ mL min}^{-1}$ ; room temperature) using polystyrene standards for calibration.

**Synthesis of 2-bromo-9,9',9'',9'''-hexahexyl-7,2':7'',2'''-terfluorene (1):** Compound **III** (2.40 g, 2.40 mmol) was dissolved in  $\text{CCl}_4$  (10 mL), and then  $\text{I}_2$  (70 mg, 0.28 mmol) and  $\text{Br}_2$  (0.12 mL, 384 mg, 2.4 mmol) were added. The reaction proceeded in the dark for 48 h. Aqueous sodium sulfite solution was added to the mixture to remove the unreacted  $\text{Br}_2$ . The organic solution was separated and washed with sodium sulfite solution and water. The crude product was obtained after evaporation of the solvent and was dried under vacuum at  $70^\circ\text{C}$ . The glassy, yellow-orange compound was partially purified by column chromatography (hexane/toluene, 10:1) and was used for the next stage.

**Synthesis of 2,7''-dibromo-9,9',9'',9'''-hexahexyl-7,2':7'',2'''-terfluorene (2):** Compound **III** (2.32 g, 2.32 mmol) was dissolved in  $\text{CHCl}_3$  (10 mL) and  $\text{FeCl}_3$  (12.6 mg, 0.078 mmol) and  $\text{Br}_2$  (0.29 mL, 0.90 g, 5.66 mmol) were added to the mixture. The reaction proceeded in the dark for 48 h. From this point the same workup procedure was followed as in the synthesis of Compound **1**. The glassy, yellow-orange compound was purified by column chromatography (hexane/toluene, 10:1). The yield was 1.50 g (1.30 mmol, 56%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS):  $\delta = 7.81$  (d,  $J(\text{H,H}) = 8.0 \text{ Hz}$ , 2H), 7.75 (d,  $J(\text{H,H}) = 8.0 \text{ Hz}$ , 2H), 7.62 (m, 10H), 7.48 (m, 4H), 2.05 (m, 12H), 1.10 (m, 36H), 0.75 ppm (m, 30H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS):  $\delta = 153.28$ , 151.83, 151.14, 141.04, 140.39, 140.09, 139.86, 139.24, 130.02, 126.29, 126.24, 126.19, 121.53, 121.47, 121.06, 120.99, 120.01, 55.54, 40.28, 31.44, 29.62, 23.83, 22.54, 13.97 ppm.

**Synthesis of 4-(tetrahydropyran-2-yloxy)-1,1'-biphenyl-4'-yl-boronic acid IV:** 4'-bromo-[1,1'-biphenyl]-4-ol (15 g, 0.06 mol) was dispersed in  $\text{CH}_2\text{Cl}_2$  (300 mL), and 3,4-dihydro-2H-pyran (16.3 mL, 0.18 mol) and ( $\pm$ )-camphor-10-sulfonic acid (0.41 g, 1.76 mmol) were added. The reaction proceeded in the dark under argon atmosphere at room temperature for 18 h. Approximately half of the solvent was removed by evaporation, and diethyl ether (150 mL) was added. A tenfold excess of 1N aqueous NaOH solution was added to the mixture, which was vigorously stirred for 18 h. The organic layer was collected and washed with plenty of water. The solution was dried over magnesium sulfate and after the complete evaporation of the solvent a dark-brown viscous liquid was obtained, to which hexane was added. The mixture was stirred overnight to produce a colorless solid material (THP-protected 4'-bromo-[1,1'-biphenyl]-4-ol, yield: 14.78 g, 44.4 mmol, 74%). This compound was converted to **IV** according to the following procedure: in a previously dried three-neck round-bottom flask equipped with a thermometer, a dropping funnel with a rubber septum, a gas inlet/outlet, and a magnetic stirring bar, 4-(tetrahydropyran-2-yloxy)-4'-bromo-1,1'-biphenyl (11.50 g, 34.5 mmol) was dissolved in THF (200 mL). The system was degassed three times and filled with argon. The funnel was then charged with *n*BuLi (1.6N solution in hexane, 33 mL, 52.6 mmol). The system was cooled to  $-80^\circ\text{C}$  and the *n*BuLi was added dropwise over about 20 min. The temperature was allowed to rise to  $-40^\circ\text{C}$  and was maintained at that temperature for approximately 3 h. The mixture was cooled again to  $-80^\circ\text{C}$  and trimethyl borate (10 mL, 88.6 mmol) was added dropwise. The suspension was allowed to reach room temperature while stirring overnight under argon atmosphere. Deionized water was added to the yellowish solution so as to hydrolyze the excess trimethyl borate along with the boronic ester groups. The crude product was extracted with ethyl acetate. The acetate solution was washed with water, dried over magnesium sulfate, and the solvent was removed by evaporation. Hexane was added to the white-yellow solid and the latter was filtered, washed with hexane, and dried under vacuum. The yield was 8.20 g (27.5 mmol, 80%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS):  $\delta = 7.52$  (half of AA'XX', 2H), 7.47 (half of AA'XX', 2H), 7.41 (half of AA'XX', 2H), 7.12 (half of AA'XX', 2H), 5.47 (t,  $J(\text{H,H}) = 2.8 \text{ Hz}$ , 1H), 3.92 (m, 1H), 3.62 (m, 1H), 1.45–2.10 ppm (3m, 6H).

**Synthesis of 2-(4'-hydroxy-1,1'-biphenyl-4-yl)-9,9',9'',9'''-hexahexyl-7,2':7'',2'''-terfluorene (3):** A vessel containing compound **1** (1.10 g, 1.02 mmol) along with **IV** (0.91 g, 3.06 mmol), and tetrakis(triphenylphosphine)palladium (0.06 g, 0.05 mmol) was degassed and filled with argon three times. Previously deoxygenated toluene (50 mL) and aqueous sodium carbonate solution (2N, 0.55 g  $\text{Na}_2\text{CO}_3$ , 5.19 mmol) were added, and the mixture was heated at reflux under argon for 48 h. After the mixture had been cooled, the organic layer was separated and washed with water. The toluene solution was dried over magnesium sulfate and the solvent was removed by evaporation. The reddish liquid was dried under reduced pressure at  $70^\circ\text{C}$ . The intermediate product, which bears the tetrahydropyran-yloxy group, was quantitatively deprotected by using a tenfold excess of concentrated hydrochloric acid and THF/MeOH (4:1) as a solvent mixture at reflux for 12 h. The organic solvents were evaporated, and the crude solid was filtered, washed with plenty of water and methanol, and dried under vacuum. The material obtained was purified using column chromatography (toluene/ethyl acetate, 6:1) to give **3**. The yield was 0.57 g (0.49 mmol, 48%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS):  $\delta = 7.81$  (m, 8H), 7.65 (m, 12H), 7.56 (half of AA'XX', 2H), 7.32 (m, 3H), 6.94 (half of AA'XX', 2H), 2.05 (m, 12H), 1.11 (m, 36H), 0.77 ppm (m, 30H).

**Synthesis of 2,7''-bis(4'-hydroxy-1,1'-biphenyl-4-yl)-9,9',9'',9'''-hexahexyl-7,2':7'',2'''-terfluorene (4):** A vessel containing compound **2** (0.84 g, 0.73 mmol) along with **IV** (0.65 g, 2.18 mmol) and tetrakis(triphenylphosphine)palladium (0.04 g, 0.035 mmol) was degassed and filled with argon three times. Previously deoxygenated toluene (30 mL) and aqueous sodium carbonate solution (2N, 0.40 g  $\text{Na}_2\text{CO}_3$ , 3.77 mmol) were added to the mixture. The workup procedure is similar to that of the synthesis of **3**. The white-yellow solid obtained was purified using column chromatography (toluene/ethyl acetate, 4:1) to give **4**. The yield was 0.46 g (0.34 mmol, 47%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS):  $\delta = 7.74$  (m, 12H), 7.60 (m, 18H), 6.94 (half of AA'XX', 2H), 2.05 (m, 12H), 1.11 (m, 36H), 0.77 ppm (m, 30H).

**Preparation of the initiators 5 and 6:**  $\text{Et}_3\text{N}$  (65  $\mu\text{L}$ , 0.47 mmol) and 2-chloropropionyl chloride (CPC, 280  $\mu\text{L}$ , 2.9 mmol) were added in three equal portions every 6 h to a cooled (ice bath) solution of **3** (170 mg, 0.15 mmol) or **4** (200 mg, 0.15 mmol) in  $\text{ClCH}_2\text{CH}_2\text{Cl}$  (20 mL). The system was refluxed for 48 h after the last addition. The red solution was concentrated by evaporation of most of the solvent. Methanol (20 mL) was added to the residue and the colorless precipitate was isolated, washed with methanol, and dried under vacuum. Column chromatography (toluene/hexane, 1:1) gave **5** (155 mg, 0.12 mmol, 80%) and **6** (167 mg, 0.11 mmol, 73%) as colorless solids.

**5:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS):  $\delta = 7.81$  (m, 8H), 7.65 (m, 12H), 7.57 (half of AA'XX', 2H), 7.32 (m, 3H), 7.15 (half of AA'XX', 2H), 4.60 (q,  $J(\text{H,H}) = 6.8 \text{ Hz}$ , 1H), 2.05 (m, 12H), 1.81 (d,  $J(\text{H,H}) = 6.8 \text{ Hz}$ , 3H), 1.11 (m, 36H), 0.77 ppm (m, 30H); elemental analysis calcd (%) for  $\text{C}_{90}\text{H}_{108}\text{O}_2\text{Cl}$  (1257.43): C 85.96, H 8.67; found: C 85.85, H 8.73.

**6:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS):  $\delta = 7.74$  (m, 12H), 7.60 (m, 18H), 7.15 (half of AA'XX', 2H), 4.60 (q,  $J(\text{H,H}) = 6.8 \text{ Hz}$ , 2H), 2.05 (m, 12H), 1.81 (d,  $J(\text{H,H}) = 6.8 \text{ Hz}$ , 6H), 1.11 (m, 36H), 0.77 ppm (m, 30H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS):  $\delta = 151.81$ , 149.93, 140.92, 140.65, 140.52, 140.33, 139.93, 139.36, 139.07, 138.92, 128.15, 127.61, 127.50, 126.18, 125.97, 121.45, 120.01, 55.34, 52.33, 40.41, 31.46, 29.68, 23.85, 22.54, 21.39, 13.97 ppm; elemental analysis calcd (%) for  $\text{C}_{108}\text{H}_{120}\text{O}_4\text{Cl}_2$  (1517.15): C 83.12, H 7.99; found: C 82.96, H 7.82.

**ATRP of styrene and tBA using the rigid macroinitiators:** A mixture of the initiator **5** (0.2 mmol) or **6** (0.1 mmol), CuBr (0.2 mmol), and PMDETA (0.2 mmol) was degassed. The solvent (3.5 mL) and the monomer (7.0 mL) were added with a syringe. The reaction mixture was heated (temperatures are specified in Table 1) for 18 h. After cooling to room temperature, THF (10–15 mL) was added to dissolve the polymer. The suspension was filtered to remove most of the catalyst. Styrene copolymers were precipitated by the addition of methanol (20-fold excess by volume). The tBA copolymers were obtained by pouring the filtered solution into a mixture of methanol and water (50:50 v/v; 20-fold excess by volume). Then the precipitated tBA copolymers were dissolved in diethyl ether. The solution was washed with plenty of water, and diethyl ether was evaporated to give the final tBA block copolymers.

## Acknowledgements

This work was partially supported by the Operational Program for Education and Initial Vocational Training on “Polymer Science and Technology” -3.2a, 33H6, administered through the Ministry of Education and Religious Affairs in Greece.

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Received: August 2, 2002 [F4309]