5758 *Macromolecules* **2002,** *35,* 5758−5762

Synthesis of Luminescent Rod−Coil Block Copolymers Using Atom Transfer Radical Polymerization

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Received February 19, 2002; Revised Manuscript Received April 12, 2002

ABSTRACT: The synthesis of luminescent rod−coil diblock and coil−rod−coil triblock copolymers containing oligo(*p*-phenyleneethynylene) as the rodlike block and polystyrene as the coil was achieved via atom transfer radical polymerization using oligo(*p*-phenyleneethynylene)s as the initiators substituted with 2-halogenopropionyloxy or 4-(bromomethyl)benzyloxy groups.

Introduction

Rod−coil block copolymers attract interest because of the expected[1] and experimentally found[2−4] richness of self-assembling morphologies. The formation of the peculiar supramolecular structures is driven by the incompatibility of the rod and the coil blocks and the tendency of the rod blocks to order into anisotropic structures.[5] Thus, rod−coil block copolymers offer the opportunity for engineering materials with novel properties and functions. Of particular interest to us are rod−coil block copolymers with luminescent rod blocks. These may offer a way to a rational design of materials with optoelectronic properties with the additional feature of easy processing of the materials. Several examples of such copolymers with for example oligo(*p*-phenylenevinylene)s,[4] oligo(*p*-phenyleneethynylene)s,[6] oligo(phenylquinoline),[3] and oligo(*p*-phenylene)[7a] as the rod block have been reported. As expected, the optoelectronic properties vary with the supramolecular morphology.[3] Because the optical properties are also depending on the length of the π-conjugated rod block, monodisperse rod blocks appear as the most promising modules. Additional low polydispersity of the coil will enhance the control over the morphology. For achieving this goal different techniques can be used. For example, premade, anionically polymerized and therefore narrowly distributed coil blocks were attached to monodisperse rods,[4,6a] and controlled radical polymerization techniques were used for formation of the coil block with the rod block acting as the initiator.[4c,7a] We have described the attachment of narrowly dispersed polyisoprene to derivatized monodisperse oligo(*p*-phenyleneethynylene)s (oligoPPEs)[6a] and the use of atom transfer radical polymerization (ATRP)[9] of styrene with rodlike α,ω-difunctionalized quinquephenylene or heptaphenylene[7a] as the initiator to obtain rod−coil diblock and coil−rod−coil triblock copolymers. Herein we present that ATRP can be applied to *p*-phenyleneethynylene-based compounds as the initiators. The initiators were prepared from suitably difunctionalized oligomers **1a** and **2a** that are readily available on the gram scale.[10a] Longer rods and blocks with other architectures[10b] can be envisaged as a possible extension of the presented synthetic route.

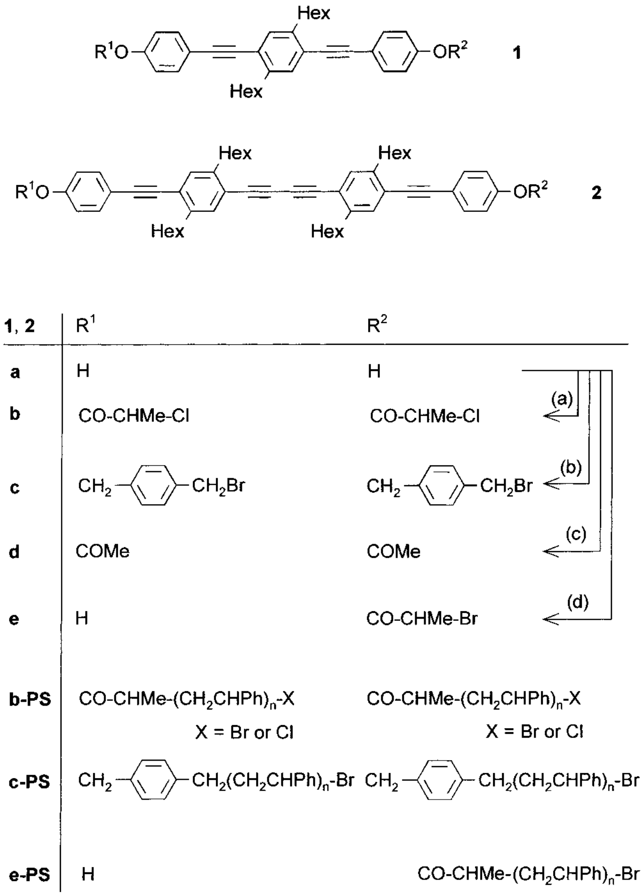
Results and Discussion

Our target was the synthesis of luminescent rod−coil diblock and coil−rod−coil triblock copolymers based on oligoPPE as the rodlike building block. For this purpose we modified the hexyl-substituted oligoPPEs **1a** and **2a** that carry terminal hydroxyl groups in order to obtain mono- and difunctional initiators for ATRP of vinyl monomers. The ATRP active groups 2-halogenopropionyl and 4-(bromomethyl)benzyl were attached either through the reaction of diol **1a** with 2-chloropropionyl chloride to give **1b** or through the reaction of the diol **1a** or **2a** with α,α'-dibromo-*p*-xylene to give the diether products **1c** and **2c** (Scheme 1). In both cases the reagents were used in large excess. The monofunctionalized inititator **1e** was prepared through the reaction of **1a** with only 1.1 equiv of 2-bromopropionyl chloride.

The structures of the initiators were proven by ^{1}H NMR spectroscopy. A characteristic change upon transformation of **1a** into **1b** is the shift of the signal due to the aromatic protons next to the oxygen substituent from 6.81 (**1a**) to 7.15 ppm. The integration ratio 2:3 of the signal at 2.79 ppm that is due to the benzylic protons of the hexyl substituents and at 1.83 ppm that is due to the methyl groups of the propanoyl group shows that both OH groups were substituted, giving a difunctional initiator. The ^{1}H NMR spectrum of the monofunctionalized initiator **1e** is essentially the sum of the ^{1}H NMR spectrum of **1a** and of **1b**, e.g., showing two AA′XX′ systems in the aromatic region and a signal for the OH group. The integration ratio of the signals at 2.80 and 1.82 ppm was found to be 4:3. Thin-layer chromatography showed only one spot. Therefore, it is excluded that the isolated material is a 1:1 mixture of **1a** and **1b**. The transformation of **1a** or **2a** into **1c** or **2c** was accompanied by a downfield shift of the aromatic protons next to the oxygen substituent from 6.81 (**1a**) or 6.85 (**2a**) to 6.95 ppm (**1c**, **2c**). The signal at 5.08 ppm is assigned to the OC**H**$_2$ groups. The integration ratio of this signal and the signals at 2.80 ppm (benzylic protons of the hexyl substituents) and at 4.50 ppm (C**H**$_2$-Br) was found to be 1:1:1. Furthermore, the ratio for the signals at 4.50 ppm (C**H**$_2$Br) and at 0.90 ppm (C**H**$_3$) is 2:3. These data are in agreement with the difunctionalized inititators **1c** and **2c**.

10.1021/ma020256k CCC: $22.00

Scheme 1[a]



[a] Key: (a) ClMeCH−COCl, Et_3N, CH_2Cl_2; (b) α,α′-dibromo-*p*-xylene, K_2CO_3, acetone; (c) MeCOCl, Et_3N, CH_2Cl_2; (d) BrMeCH−COCl, Et_3N, CH_2Cl_2.

The functionalized rods were used as ATRP initiators in the presence of CuBr and an amine to polymerize styrene and ethyl acrylate (Scheme 1). Multiple alterations of the reaction conditions [bipyridine (bipy) or *N,N,N′,N′,N″*-pentamethyldiethylenetriamine (PMDETA); polymerization in diphenyl ether or in the bulk] were made as to achieve the best possible control of the polymerization (Table 1). CuBr was chosen also for **1b** that carries chlorine substituents because halogen exchange is expected to increase the rate of initiation relative to the rate of propagation leading to better control over the polymerization.[11] A wide range of molecular weights were obtained using the different catalytic systems. When CuBr/PMDETA was used, the polymerization of styrene with the initiators **1b** and **1c** gave coil−rod−coil triblock copolymers with high molecular weights, while with CuBr/bipy the obtained molecular weights did not exceed 10 000. Triblock copolymers with low molecular weights were also obtained when the initiator **2c** was used along with CuBr/PMDETA. Regardless of the catalytic system used, the polydispersity index ranged between 1.30 and 1.65. The polymerization of styrene using **1e** as the initiator resulted in rod−coil diblock copolymers. As found in the case of the difunctional initiators, CuBr/PMDETA gave higher molecular weight polymer than CuBr/bipy with a polydispersity index of 1.23 and 1.19, respectively.

To prove the incorporation of the rigid initiator into the polymeric chain, a sample of **1b-PS 3** was examined with size exclusion chromatography (SEC) using different wavelengths for detection, i.e., 254 and 350 nm. While at 254 nm both blocks, polystyrene and oligoPPE, absorb light, at 350 nm only the oligoPPE absorbs light. The obtained SEC traces (Figure 1) show no difference, proving that the oligoPPEs are incorporated into the polymers. This conclusion is supported by the ^{1}H NMR spectrum of **1b-PS 4** (Figure 2), which shows characteristic signals of the oligoPPE block, i.e., signals at 0.88, 2.80, and 7.45 ppm with the expected ratio of 3:2:2.

As shown in Figure 3, SEC does not reveal residual initiator. This indicates a high initiation efficiency. The workup procedure (precipitation with methanol) is not expected to remove residual initiator because of the low solubility of the inititator in methanol. Accordingly, the ^{1}H NMR spectra of **1b-PS**, as for example the spectrum of **1b-PS 4** (Figure 2), show no signal for residual C**H**Cl groups at 4.6 ppm, indicating that the polymers are indeed triblock copolymers. New broad signals at about 4.4 and 4.3 ppm are probably due to the methinic protons that are adjacent to the halogen atom. The same signals are also found in the ^{1}H NMR spectrum of polystyrene prepared by ATRP using α,α′-dibromo-*p*-xylene as an initiator (Figure 2).

Since the T_g of the coil block has a significant influence on the ability of these copolymers to self-assemble,[1] ethyl acrylate was chosen as another vinyl monomer to be polymerized with the rod initiators. The polymerization of ethyl acrylate with **1b** or **1c** as initiators gave unsatisfying results. SEC and NMR spectra revealed residual **1b** or **1c** in the product. Column chromatography allowed for removal of the initiator. However, the product is most probably a mixture of rod−coil and coil−rod−coil block copolymers with very much varying lengths of the coil blocks. In agreement with a mixture of di- and triblock copolymers is the ^{1}H NMR spectrum which shows multiple signals for the aromatic protons.

A matter of concern when using compounds **1b**,**c**,**e**, and **2c** as initiators in these controlled radical polymerizations was that the C≡C bonds may not be completely inert under the reaction conditions, although it has been reported that they usually require the use of metathesis catalyst in order to react efficiently.[12] The Raman spectrum of **1b-PS** showed an intense signal at 2205 cm^{-1} that is assigned to the C≡C bonds (Figure 4). To detect potential participation of the C≡C bonds in the radical polymerization, styrene was polymerized through ATRP (CuBr, bipy, diphenyl ether at 130 °C) with α,α′-dichloro-*p*-xylene as the initiator in the presence of diester **1d**. The product was examined with SEC using 254 and 350 nm as detection wavelengths (Figure 5). While upon detection at 254 nm two well-separated signals due to polymer and compound **1d** are detected, only a signal due to **1d** is detected at 350 nm. Incorporation of **1d** by chain transfer reactions or through the radical addition to the C≡C bond would result in two signals at both wavelengths.[13] This proves that the C≡C bonds do not participate in the polymerization process. Additionally, the rather narrow molecular weight distributions obtained when using **1b**,**c**, and **2c** as initiators in the polymerization of styrene exclude addition to C≡C bonds which should result in branching and/or cross-linking and therefore in broad and possibly multimodal distributions.

The initiators as well as the polystyrene block copolymers were investigated with absorption and emission spectroscopy in dilute solution. The UV absorption spectrum of copolymer **1c-PS** and the emission spectra

Table 1. Reaction Conditions and Molecular Weight Characteristics of the Synthesized Block Copolymers

polymer	$[\text{styrene}]_0/[\text{I}]_0$	amine	styrene/DPE[c] (v/v)	$M_{n,\text{theo}}$[d]	GPC results M_n	M_w	PDI
1b-PS 1[a]	525	PMDETA	3	54 600	53 600	69 850	1.30
1b-PS 2[b]	146	PMDETA	3	15 200	11 400	18 500	1.62
1b-PS 3[b]	58	bipy	3	6 050	5 500	7 900	1.44
1b-PS 4[b]	58	bipy	3	6 050	6 200	9 200	1.48
1e-PS 1[a]	350	bipy	1	36 400	1 300	1 550	1.19
1e-PS 2[a]	525	PMDETA	3	54 600	44 600	54 800	1.23
1c-PS 1[a]	960	PMDETA	3	99 850	93 700	137 800	1.47
1c-PS 2[a]	1311	PMDETA	3	136 350	33 500	53 700	1.60
2c-PS 1[a]	1311	PMDETA	6	136 350	2 700	4 200	1.56
2c-PS 2[b]		PMDETA	bulk	136 350	3 100	5 100	1.65
2c-PS 3[b]		PMDETA	bulk	227 250	13 600	18 600	1.37

[a] Reaction temperature: 110 °C. [b] Reaction temperature: 130 °C. [c] DPE: diphenyl ether. [d] $M_{n,\text{theo}} = 104([\text{styrene}]_0/[\text{I}]_0)$ or $M_{n,\text{theo}} = 104(\text{mmol}_{\text{styrene}}/\text{mmol}_{\text{initiator}})$ (for bulk polymerization) assuming complete monomer conversion.

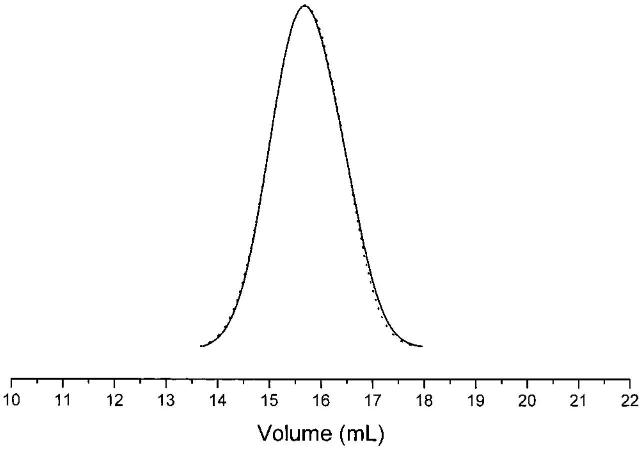


Figure 1. SEC chromatograms of **1b-PS 3** in THF recorded at 254 nm (—) and 350 nm (- - -).

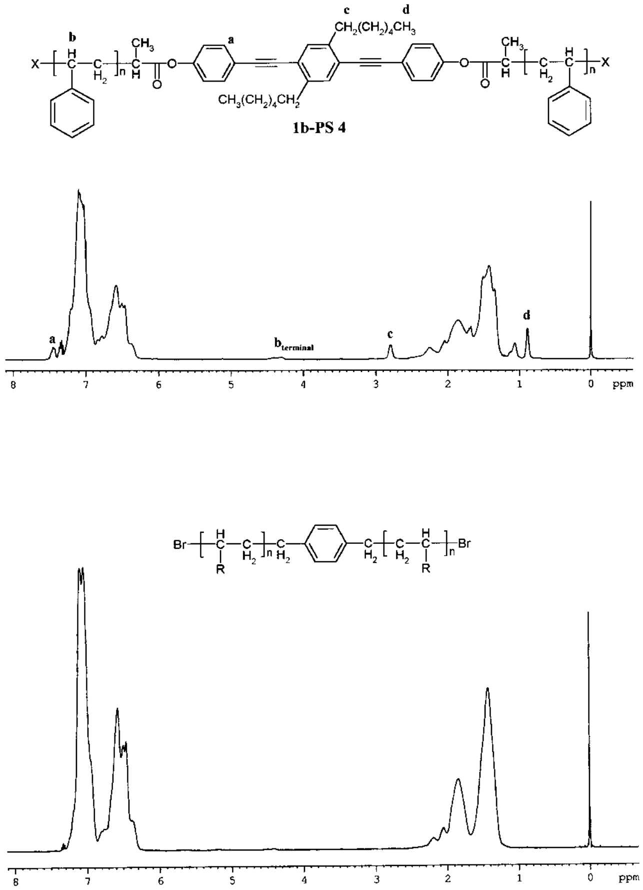


Figure 2. ^{1}H NMR spectra in $CDCl_3$ at room temperature (top) of copolymer **1b-PS 4** and (bottom) of polystyrene (M_n = 6500, PDI = 1.51) obtained through ATRP using α,α′-dibromo-*p*-xylene as an initiator.

of the copolymers **1b-PS**, **1c-PS**, and **2c-PS** are presented in Figure 6. In contrast to the absorption spectra, the emission spectra exhibit two well-distinguished bands which is probably due to vibronic coupling.[6a,d,14] There is a 40−50 nm red shift of the emission of the copolymer **2c-PS** compared to that of **1b-PS** and **1c-PS** due to the longer conjugation length of the rod block. The 7 nm blue shift of the emission spectrum of the copolymer **1b-PS** compared to that of the copolymer **1c-PS** is attributed to the different contribution of an ether and an ester group to the electronic density of the rigid conjugated part. The emission spectra of the initiators and their corresponding copolymers are essentially identical. This is taken as an additional proof for the integrity of the CC triple bonds in the block copolymers.

Preliminary examination of the photoluminescence of the copolymers in solid state (thin films) was also performed. To investigate the impact of the molecular architecture of the copolymers on luminescence properties, we compared the emission spectra of the diols **1a** and **2a** with those of the respective copolymers **1b-PS**, **1c-PS**, and **2c-PS**. We observed that the overall spectra of the copolymers are blue-shifted (5−25 nm) and much narrower than one of the diols (Figure 7). This would probably indicate that the intermolecular interactions between chromophores due to the formation of aggregates[15] are diminished. A more detailed study of the luminescence of these copolymers is in progress.

Conclusions

OligoPPEs carrying 2-halogenopropionyloxy or 4-(bromomethyl)benzyloxy as ATRP active functionalities were prepared and used as initiators in the polymerization of styrene and ethyl acrylate. While in the case of styrene all of the initiator was consumed, the efficiency of initiation of the polymerization of ethyl acrylate was very low. The CC triple bonds of the rod block do not interfere with the polymerization. The combination of PMDETA/CuBr turned out to give polymers with higher molecular weight than the combination bipy/CuBr. Since the obtained polydispersities are somewhat broad, this polymerization method allows mainly to control the shape and the type of the blocks of the copolymers.

Experimental Section

Physical Characterization. The NMR spectra were obtained at 300 or 400 MHz in $CDCl_3$ at room temperature. For signal assignment the carbon multiplicity [quaternary (q-C),

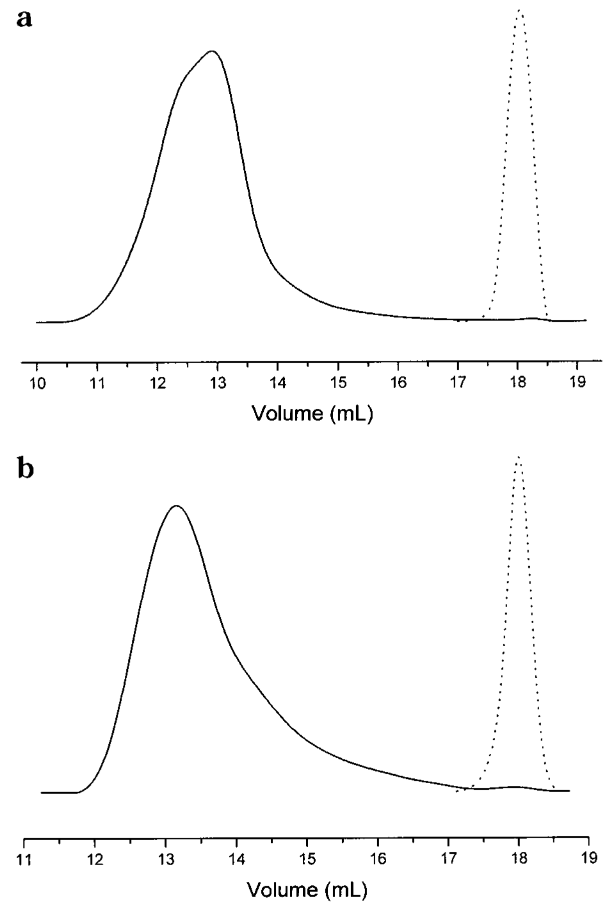


Figure 3. SEC chromatograms of (a) copolymer **1b-PS 1** (—) and the initiator **1b** (- - -) and (b) copolymer **1c-PS 2** (—) and initiator **1c** (- - -).

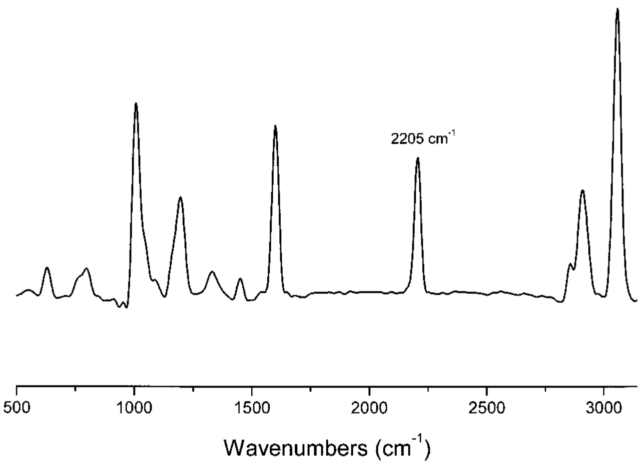


Figure 4. Micro-Raman spectrum of **1b-PS** copolymer film cast on a KBr disk and irradiated with a linearly polarized monochromatic radiation at 514.5 nm.

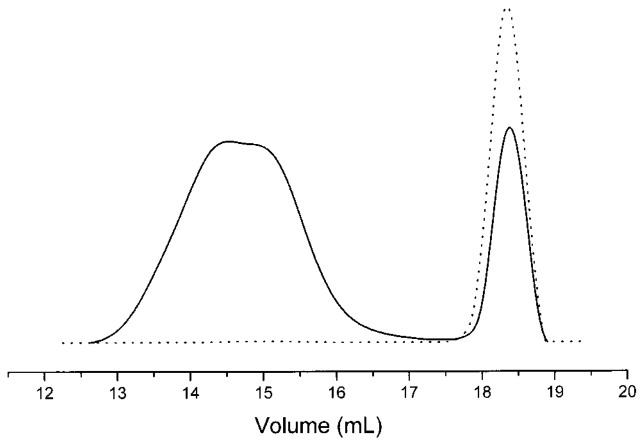


Figure 5. SEC chromatograms detected at 254 nm (—) and 350 nm (- - -) of the product obtained through ATRP polymerization of styrene in the presence of **1d**. Reaction conditions: α,α′-dichloro-*p*-xylene as the initiator, CuBr, bipyridine, diphenyl ether, 130 °C. M_n = 13 600, M_w = 20 200, PDI = 1.48.

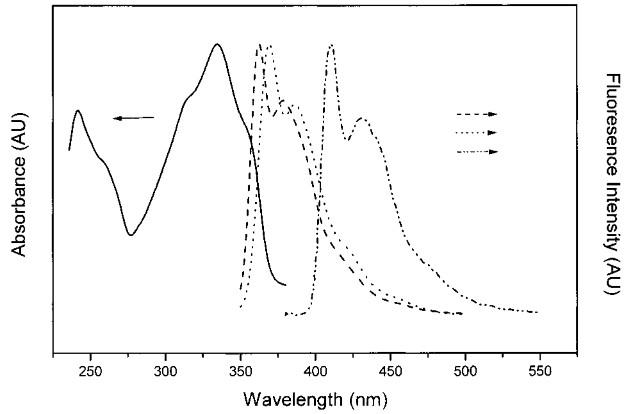


Figure 6. Absorption spectrum of **1c-PS** (—) and fluorescence spectra of **1b-PS** (- - -), **1c-PS** (···), and **2c-PS** (-··-) copolymers dissolved in $CHCl_3$. Excitation wavelengths were 340 nm (**1b-PS** and **1c-PS**) and 370 nm (**2c-PS**).

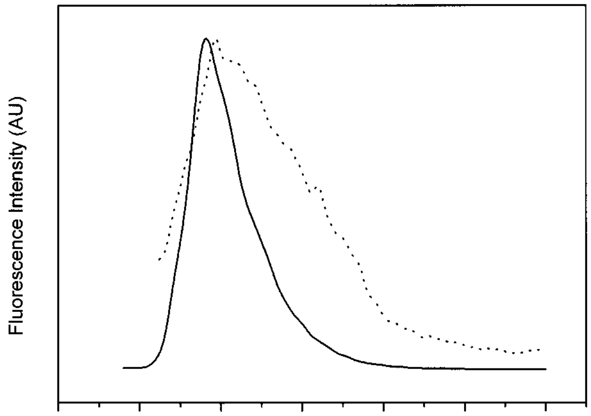


Figure 7. Fluorescence spectra of **1c-PS 1** (—) and **1a** (···) as thin films cast from $CHCl_3$. Excitation wavelength was 330 nm.

tertiary (CH), secondary (CH_2), primary (CH_3)] was determined with DEPT-135 experiments. Molecular weights (M_n and M_w) were determined through gel permeation chromatography (Ultrastyragel columns with 500 and 10^4 Å pore size; THF was distilled from sodium/benzophenone and samples were passed through a 0.5 μm Millipore filter; 1 mL/min flow; room temperature) using polystyrene standards for calibration.

Materials. Compounds **1a** and **2a** were synthesized according to known procedures.[7b] Styrene and ethyl acrylate (Merck) were vacuum-distilled from finely powdered calcium hydride. Methylene chloride was washed with concentrated sulfuric acid and then with dilute sodium hydroxide and finally with water, dried over sodium hydroxide and calcium chloride pellets, and fractionally distilled. Diphenyl ether (Merck) was stored over molecular sieves (4 Å) and purged with argon for 30 min before the polymerization was started. CuBr (Aldrich), 2,2′-bipyridine (bipy, Merck), *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA, Aldrich), and all the other reagents and solvents were used as received. All reactions were run under an inert atmosphere (N_2, Ar). Silica gel 60 (Merck, 0.082−0.2 mm) was used as the stationary phase for column chromatography.

Preparation of the Initiators. Initiator 1b. To a cooled (ice bath) solution of **1a** (125 mg, 0.26 mmol) and Et_3N (75 μL, 0.54 mmol) in CH_2Cl_2 (20 mL) was added 2-chloropropionyl chloride (280 μL, 2.9 mmol). The reaction mixture was stirred for 1 h at 0 °C and for a further 12 h at room temperature. The red solution was condensed by evaporation of most of the solvent. Ethanol (20 mL) was added to the residue, and the colorless precipitate was isolated, washed with ethanol, and dried under vacuum. Column chromatography (toluene) gave **1b** (145 mg, 85%) as a colorless solid; mp 117−118 °C. ^{1}H NMR: $\delta = 0.88$ (m, 6H), 1.2−1.5 (m, 12H), 1.69 (m, 4H), 1.83 (d, $J = 7.0$ Hz, 6H), 2.80 (m, 4H), 4.62 (q, $J = 7.0$ Hz, 2H), 7.14 (half of AA′XX′, 4H), 7.36 (s, 2H), 7.55 (half of AA′XX′, 4H). ^{13}C NMR: $\delta = 14.3$ (CH_3), 21.3 (CH_3), 22.6 (CH_2), 29.2 (CH_2), 30.6 (CH_2), 31.7 (CH_2), 34.1 (CH_2), 52.2 (CH), 88.8 (q-C), 92.9 (q-C), 121.3 (CH), 121.7 (q-C), 122.4 (q-C), 132.3 (CH), 132.7 (CH), 142.3 (q-C), 150.1 (q-C), 168.3 (q-C). $C_{40}H_{44}O_4Cl_2$ (659.694): calcd C, 72.83; H, 6.72; found C, 72.96; H, 6.82.

Initiator 1e. Following the procedure given for the preparation of **1b**, monofuntional initiator **1e** (108 mg, 68%) was obtained through the reaction of **1a** (125 mg, 0.26 mmol) with 2-bromopropionyl chloride (30 μL, 0.29 mmol) and Et_3N (75 μL, 0.54 mmol) in CH_2Cl_2 (20 mL) as a colorless solid; mp 75−77 °C. ^{1}H NMR: $\delta = 0.89$ (m, 6H), 1.2−1.5 (m, 12H), 1.71 (m, 4H), 1.82 (d, 3H), 2.80 (m, 4H), 4.67 (q, 1H), 5.22 (s, 1H, OH), 6.81 (half of AA′XX′, 2H), 7.15 (half of AA′XX′, 2H), 7.35 (s, 2H), 7.42 (half of AA′XX′, 2H), 7.55 (half of AA′XX′, 2H).

Compound 1d. Following the procedure given for the preparation of **1b**, however omitting chromatography, **1d** (245 mg, 84%) was obtained through the reaction of **1a** (250 mg, 0.52 mmol), Et_3N (150 μL, 1.08 mmol), CH_2Cl_2 (50 mL), and acetyl chloride (370 μL, 5.2 mmol) as a colorless solid; mp 134−135 °C. ^{1}H NMR: $\delta = 0.88$ (m, 6H), 1.2−1.5 (m, 12H), 1.69 (m, 4H), 2.32 (s, 6H), 2.80 (m, 4H), 7.10 (half of AA′XX′, 4H), 7.35 (s, 2H), 7.55 (half of AA′XX′, 4H).

Initiator 1c. A solution of **1a** (150 mg, 0.31 mmol) in acetone (10 mL) was added dropwise to a mixture of α,α′-dibromo-*p*-xylene (820 mg, 3.1 mmol) of K_2CO_3 (47 mg, 0.34 mmol) in acetone (15 mL). The reaction mixture was refluxed for 24 h. Most of the solvent was removed by evaporation. Through the addition of methanol (20 mL) the crude product was precipitated. The solid was isolated, washed well with of water and methanol, and then dispersed in a 10-fold excess by volume of hot methanol (60 °C), and the mixture was stirred for 12 h at 60 °C. The solid was isolated and finally purified with column chromatography (toluene/hexane 1:1 v/v) to give **1c** (196 mg, 75%) as a colorless solid; mp 148−150 °C. ^{1}H NMR: $\delta = 0.88$ (m, 6H), 1.2−1.5 (m, 12H), 1.69 (m, 4H), 2.78 (m, 4H), 4.50 (s, 4H) 5.08 (s, 4H), 6.94 (half of AA′XX′, 4H), 7.33 (s, 2H), 7.41 (s, 8H), 7.46 (half of AA′XX′, 4H). ^{13}C NMR: $\delta = 14.1$ (CH_3), 22.6 (CH_2), 29.2 (CH_2), 30.6 (CH_2), 31.7 (CH_2), 33.0 (CH_2), 34.1 (CH_2), 69.5 (CH_2), 87.4 (q-C), 93.7 (q-C), 114.9 (CH), 116.1 (q-C), 122.5 (q-C), 127.8 (CH), 129.3 (CH), 132.1 (CH), 132.9 (CH), 136.9 (q-C), 137.6 (q-C), 142.0 (q-C), 158.6 (q-C).

Initiator 2c. Compound **2c** was prepared according to the procedure given for **1c**, using a solution of **2a** (240 mg, 0.31 mmol) in acetone (10 mL) and a mixture of α,α′-dibromo-*p*-xylene (820 mg, 3.1 mmol) and K_2CO_3 (47 mg, 0.34 mmol) in acetone (15 mL). Column chromatography (toluene/ethyl acetate 4:1 v/v) gave **2c** (254 mg, 72%) as a colorless solid; mp 124−126 °C. ^{1}H NMR: $\delta = 0.88$ (m, 12H), 1.2−1.5 (m, 24H), 1.66 (m, 8H), 2.76 (m, 8H), 4.50 (s, 4H) 5.08 (s, 4H), 6.94 (half of AA′XX′, 4H), 7.32 (s, 2H), 7.36 (s, 2H), 7.41 (s, 8H), 7.45 (half of AA′XX′, 4H). ^{13}C NMR: $\delta = 14.09$ (CH_3), 14.11 (CH_3), 22.6 (CH_2), 29.0−34.1 (9 signals, CH_2), 69.6 (CH_2), 78.2 (q-C), 81.7 (q-C), 87.2 (q-C), 94.6 (q-C), 115.0 (CH), 115.9 (q-C), 120.8 (q-C), 123.8 (q-C), 127.8 (CH), 129.3 (CH), 132.1 (CH), 133.0 (CH), 133.3 (CH), 136.9 (q-C), 137.7 (q-C), 142.0 (q-C), 143.6 (q-C), 158.7 (q-C).

ATRP of Styrene and Ethyl Acrylate Using the Rigid Macroinitiators. A mixture of the initiator (0.1 mmol), CuBr (0.2 mmol), and bipyridine (0.6 mmol) or *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (0.2 mmol) was degassed. Diphenyl ether (if used) and the monomer were added via a syringe. The reaction mixture was heated (temperatures are specified in Table 1) for 12 h. After cooling to room temperature, THF (2−4 mL) was added to dissolve the polymer. The suspension was filtered for removing most of the catalyst. Styrene copolymers were precipitated through the addition of methanol (20-fold excess by volume). Ethyl acrylate copolymers were precipitated by pouring the filtered solution into a mixture of methanol and water (50:50 v/v; 20-fold excess by volume). The precipitated ethyl acrylate copolymers were dissolved in diethyl ether. The solution was extracted with plenty of water, and diethyl ether was evaporated to give the ethyl acrylate copolymers.

Acknowledgment. This work was 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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MA020256K