Macromolecules **1999,** *32,* 9054−9058

Communications to the Editor

Synthesis of Rigid−Flexible Triblock Copolymers Using Atom Transfer Radical Polymerization

P. K. Tsolakis, E. G. Koulouri, and J. K. Kallitsis*

Department of Chemistry, University of Patras,
265 00 Patras, Greece

Received April 1, 1999
Revised Manuscript Received October 26, 1999

Introduction. Diblock copolymers have been extensively studied both theoretically[1] and experimentally[2] mainly because of the observed microphase separation phenomena. Although most AB diblocks can be better described as flexible−semiflexible block copolymers due to conformational asymmetry caused by the different statistical segment length of each block, block copolymers consisting of a flexible coil block and a rigid rod block, named as rod−coil copolymers, have been classified as a separate class and have indeed attracted scientific interest.[3] Lately, diblock, as well as triblock, rod−coil copolymers have found to self-assemble into ordered macromolecular or even supramolecular structures that possess regularity in size and shape.[4] This regularity in structure can be achieved by controlling the block lengths. The synthesis of such block copolymers with predefined and well-controlled molecular weights for each block requires appropriate polymerization techniques.

Atom transfer radical polymerization (ATRP) is accepted as an efficient technique for the controlled radical polymerization of various monomers resulting in polymers with predetermined molecular weights and narrow polydispersities.[5] Since various molecules can be modified in order to fulfill the requirements of an ATRP initiator,[6] rigid oligophenylenes, which are also known for their luminescent properties, can be modified and used as initiators for the synthesis of rigid−flexible block copolymers.

In this communication the synthesis of ABA rigid−flexible triblock copolymers using ATRP polymerization is presented. More specifically, modified oligophenylenes were used as rigid macroinitiators for the ATRP polymerization of styrene. The polymers obtained were characterized using ^{1}H and ^{13}C NMR, GPC, and luminescence measurements.

Experimental Section. Materials. 4,4″-Dibromo-2′,3′,5′-triphenyl-*p*-terphenyl (**1**),[7] 2″,5″-dihexyloxy-*p*-quinquephenyl-4,4⁗-diol diacetate (**5**)[8] and 4-acetoxy-4′-bromobiphenyl[9] were synthesized according to known procedures. Styrene (Merck) was vacuum distilled from finely powdered calcium hydride. Tetrahydrofuran (THF) was distilled under sodium in the presence of benzophenone directly into the reaction flask.

Preparation of Macroinitiators. Synthesis of Rigid Initiators 4 and 6. A 0.48 g sample of DMAP in dry methylene chloride was mixed with 2.0 mL (14.4 mmol) of TEA in a dry three-neck round-bottom flask equipped with a condenser, a dropping funnel, a gas inlet/outlet, and a magnetic stirring bar. The dropping funnel was filled with a dilute dispersion of 1.03 g (1.3 mmol) of 2‴,3‴,5‴-triphenyl-*p*-heptaphenyl-4,4′′′′′′-diol in 150 mL of dry CH_2Cl_2 or 0.8 g (1.3 mmol) of 2″,5″-dihexyloxy-*p*-quinquephenyl-4,4⁗-diol in 100 mL of dry CH_2Cl_2. After the mixture was to 0 °C, 1.5 mL (14.4 mmol) of 2-bromopropionyl chloride was added and the dilute dispersion was added to the yellow mixture dropwise under argon for approximately 2 h. Subsequently, the temperature was allowed to reach room temperature, and the reaction was continued for at least 24 h. The dark-red solution was condensed by evaporation. The rigid initiators were precipitated in methanol, filtered off, washed with water and methanol, and dried under vacuum. The yield was 0.90 g (0.85 mmol) and 0.81 g (0.9 mmol), respectively. **4**: FTIR (cm^{-1}) 3026, 1760, 1600, 1490, 1442, 1378, 1338, 1240, 1198, 1168, 1138, 1072, 1002, 898, 814, 734, 698. **6**: mp 171−173 °C; FTIR (cm^{-1}) 2958, 2864, 1764, 1488, 1388, 1262, 1214, 1082, 802.

Polymerizations. ATRP of Styrene Using the Synthesized Rigid Macroinitiators. A round-bottom flask equipped with a U-tube, a rubber septum, a magnetic stirring bar, and a gas inlet/outlet was burned under vacuum. In the flask, 0.1064 g (0.1 mmol) of **4** or 0.0884 g (0.1 mmol) of **6** was placed along with 0.0287 g (0.2 mmol) of CuBr and 0.0937 g (0.6 mmol) of bipyridine. The system was degassed three times and flushed with argon. Equal volumes of the solvent and the monomer were transferred to the flask via syringe. The reaction mixture was then immersed in a oil bath and heated at 110 °C for 24 h. After cooling to room temperature, THF (2−4 mL) was added to the reaction mixture to dissolve the polymer. The suspension was filtered in order to remove the catalyst and precipitated in a large excess of methanol. The polymers were dried under vacuum at room temperature. The results for the different polymers synthesized are depicted in Table 1. NMR characterization of the copolymers was also performed. For example, the ^{1}H NMR spectrum of QPPS 1 in C_2Cl_4 is shown in Figure 1b.

Measurements. The structures of reactants, macroinitiators, and block copolymers were characterized by high-resolution ^{1}H NMR spectroscopy, using a Bruker Avance DPX 400 MHz spectrometer and DMSO-d_6, C_2Cl_4, or $CDCl_3$ as solvents. The ^{13}C NMR spectra were obtained by a Bruker Avance DPX 100 MHz spectrometer using $CDCl_3$ as a solvent. The number-average ($\bar{M}_n$) and weight-average ($\bar{M}_w$) molecular weights of block copolymers were determined by GPC using a Shimadzu-10A gel permeation chromatograph equipped with three Ultrastyragel columns (10^5, 10^4, and 500 Å pore size).

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* Corresponding author. Telephone: +003061 997121. Fax: +003061 997122. E-mail: J.Kallitsis@chemistry.upatras.gr.

10.1021/ma990481a CCC: $18.00

Table 1. Molecular Weight Characteristics of the Synthesized Triblock Copolymers

	NMR results		GPC results		
polymer	$\bar{M}_n$	$\bar{M}_w$ (LS detector)	$\bar{M}_n$	$\bar{M}_w$	PDI
QPPS 1[a]	8800	13600	9200	10800	1.17
QPPS 2[b]	7300	27700	12700	27500	2.15
QPPS 3[c]	9400	49600	20600	43400	2.10
QPPS 4[c]	10200	16800	7900	13200	1.67
QPPS 5[a]	23200		17100	21600	1.26
HPPS 1[a]	8000	11000	8000	9500	1.19
HPPS 2[a]	3300		7500	9900	1.33
HPPS 3[a]	5700	20000	7100	8800	1.24
HPPS 4[d]	2400	9500	2100	2950	1.41

[a−d] Catalytic systems used: [a] CuBr, bipy; [b] Cu^0/CuBr$_2$, bipy; [c] Cu^0, bipy; [d] CuCl, dT−bipy.

Measurements were performed in THF solvent at room temperature with 1 mL/min flow. Calibrations of both chromatographs were based on polystyrene standards. $\bar{M}_w$ values were also obtained by a LS detector. FTIR spectra were obtained using a Perkin-Elmer 1600 spectrometer. The UV spectra were recorded on a SLM Aminco 3000 Array spectrophotometer. Fluorescence was measured on a SLM Aminco SPF-500 spectrofluorometer.

Results and Discussion. In our approach to prepare rigid−flexible triblock copolymers, the rigid part was selected to be the central block. This rigid part, which acts as an initiator for the ATRP polymerization, also possesses photoluminescence. In that respect the photonic properties of the final copolymer can be controlled by changing the molecular structure of the initiator. Moreover, using different monomers and a different length of the flexible block, the overall morphology of the final copolymer can also be controlled. Existing[10] or new synthesized oligophenylenes were modified in order to introduce end functionalities capable of acting as atom transfer radical polymerization initiators.

On the basis of previous experience on oligophenylene synthesis,[10−12] α,ω-acetoxy functionalized oligophenylenes with five or seven rings were prepared (Scheme 1), using Suzuki coupling.[13] Hydrolysis of these acetoxy end groups and esterification of the resulting hydroxy end groups with acyl chlorides,[6] containing proper CHBr groups, led to molecules capable of acting as ATRP initiators. These synthesized initiators were characterized by ^{1}H and ^{13}C NMR, FTIR, and GPC measurements.

To study the different phase phenomena in block copolymers, low polydispersity is a prerequisite. In rod−coil block copolymers low polydispersities are also needed in order to study their possible supramolecular assembling. Among different controlled radical polymerizations, we have chosen the atom transfer radical polymerization, since it has been accepted as an efficient method for the “living” polymerization of a large number of monomers, giving polymers with polydispersities ranging from 1.05 to 1.5.[5b] Different catalytic systems that are known to be effective for the ATRP of styrene monomer[5] were tested. The obtained polymers were characterized by ^{1}H and ^{13}C NMR and GPC measurements. The results reported in Table 1 show that in our case the best catalytic system was proven to be that of CuBr/bipy.

The structure elucidation of the synthesized polymers was based on the NMR experiments. The ^{1}H NMR spectra of a typical quinquephenyl initiator **6**, and the respective polymer after the ATRP polymerization, QPPS 1, are presented in Figure 1, where the assignment of the peaks of the initiator is included. The signal of the methylene protons in α-position to the oxygen of the aliphatic side chains and the signal of the methinic protons of the active side of the initiator are located at 4.0 and 4.7 ppm respectively with an integration ratio of 2/1. After the polymerization the signal at 4.7 ppm disappeared and a new signal at 3.6 appeared due to the substituted initiator. The ratio of the signal at 4.0 to that at 3.6 remains 2/1. The absence of the signal at 4.7 ppm confirms the effectiveness of the reaction and consequently the formation of triblock copolymers. The new signal around 4.3 ppm that appears is probably due to the terminal methinic and/or methylene protons of the polystyrene that are adjacent to Br.

Size exclusion chromatography was used in order to examine the effectiveness of the synthetic process in obtaining triblock copolymers with narrow polydispersities. The data given in Table 1 show that narrow polydispersities were accomplished in cases where CuBr/bipy was used as catalytic system, excluding the possibility of different species to be present. Molecular weights were obtained using either a light scattering (LS) detector or a refractive index (RI) detector and calibration based on polystyrene standards. Molecular weights in the range of 2000−20000 correspond in triblock copolymers with flexible blocks of ca. 500−9500 $\bar{M}_w$. Additional molecular weight determination was performed by ^{1}H NMR based on the signals of the different protons of the initiator and the polystyrene. More specifically, in the case of the QPPS copolymers, the calculations were based on the comparison of the signal at 4.0 ppm due to the methylene protons in α-position to the oxygen of the aliphatic side chains of the initiator with the signal at 6.7 ppm of the two aromatic protons in o-position of the polystyrene blocks in the copolymer. In the case of HPPS copolymers, the signals of the aromatic protons of the initiator, which appear above 7.5 ppm, were compared to the aliphatic protons of the polystyrene blocks. The calculated values presented in Table 1 show that in some cases these results are in excellent agreement with the results obtained by SEC.

The rigid part of the synthesized copolymers can be considered as a chromophore, which gives photophysical properties to these copolymers, such as photoluminescence. Photoactive rod−coil copolymers have been previously studied.[4e,14] This can also be used for monitoring the movements of the whole molecule in solution as well as in solid state. In this communication we present the UV absorption and the photoluminescence spectra of both QPPS 1 and HPPS 1 (Figure 2). Judging from the UV absorption maxima at 358 nm and at 345 nm as well as from the luminescence maxima at 405 nm and at 395 nm of the QPPS and the HPPS, respectively, these results are not consistent with what was expected. Both absorption and emission maxima of the HPPS were expected to be red shifted rather than those of the QPPS, considering the length of the oligophenylene part. However, the presence of the three phenyl substituents distorts not only the planarity but also the linearity of the oligophenylene, as has been previously observed in a similar case by crystal structure analysis.[15] Moreover, the electron rich oxygen atoms increase the electronic density of the oligophenylene in QPPS and so the UV absorption as well as the photoluminescence maxima of the QPPS are shifted to higher wavelengths. As is

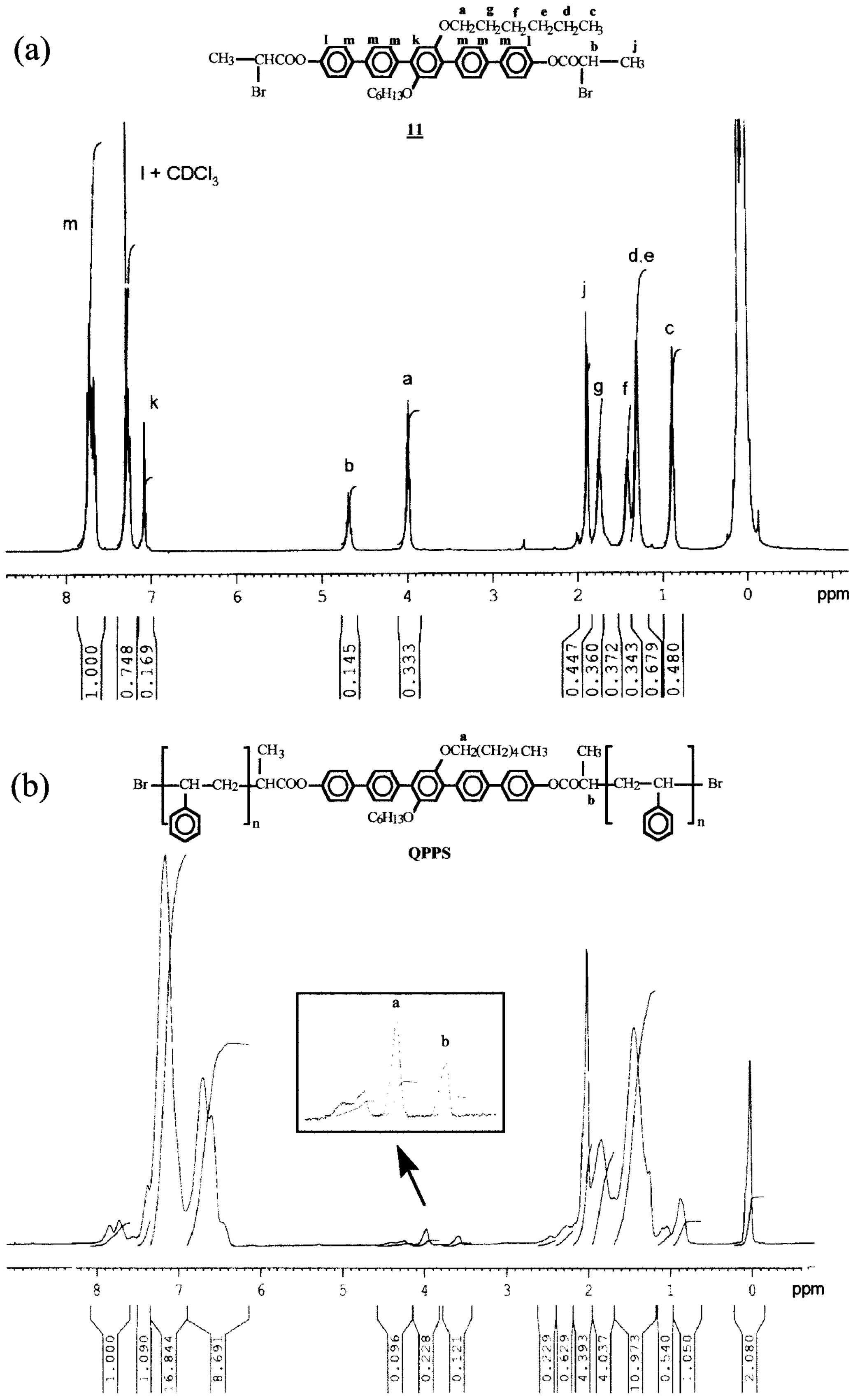


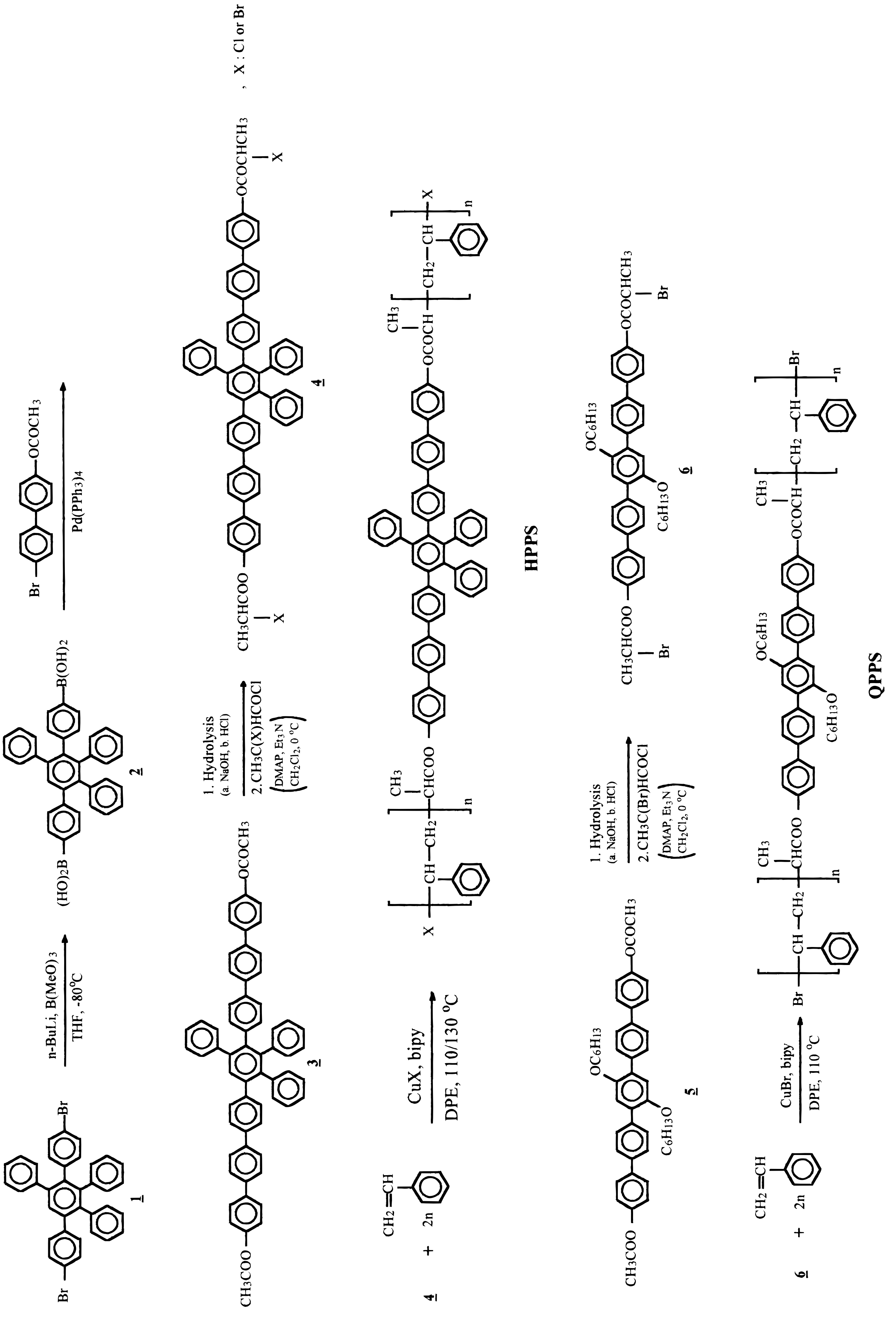
Figure 1. (a) ^{1}H NMR spectrum of the quinquephenyl macroinitiator in $CDCl_3$. (b) ^{1}H NMR spectrum of triblock copolymer QPPS 1 in C_2Cl_4.

shown by the photoluminescence spectra, polymers with blue light emission are obtained in the case of QPPS.

Finally, further work is now in progress in order to characterize fully the synthesized copolymers in solution as well as in the solid state.

Conclusions. A simple method for the synthesis of rigid–flexible block copolymers has been presented. This method is based on atom transfer radical poly-

Scheme 1


Br
Br
1
n-BuLi, B(MeO)3
THF, -80°C
(HO)2B
B(OH)2
2
Br
OCOCH3
Pd(PPh3)4
CH3COO
OCOCH3
3
1. Hydrolysis
(a. NaOH, b. HCl)
2. CH3C(X)HCOCl
(DMAP, Et3N
CH2Cl2, 0 °C)
CH3CHCOO
X
OCOCHCH3
X
4
, X : Cl or Br
4
+ 2n
CH2=CH
CuX, bipy
DPE, 110/130 °C
X
CH
CH2
CH3
CHCOO
n
OCOCH
CH3
CH2
CH
X
n
HPPS
CH3COO
OC6H13
C6H13O
OCOCH3
5
1. Hydrolysis
(a. NaOH, b. HCl)
2. CH3C(Br)HCOCl
(DMAP, Et3N
CH2Cl2, 0 °C)
CH3CHCOO
Br
OC6H13
C6H13O
OCOCHCH3
Br
6
6
+ 2n
CH2=CH
CuBr, bipy
DPE, 110 °C
Br
CH
CH2
CH3
CHCOO
n
OC6H13
C6H13O
OCOCH
CH3
CH2
CH
Br
n
QPPS

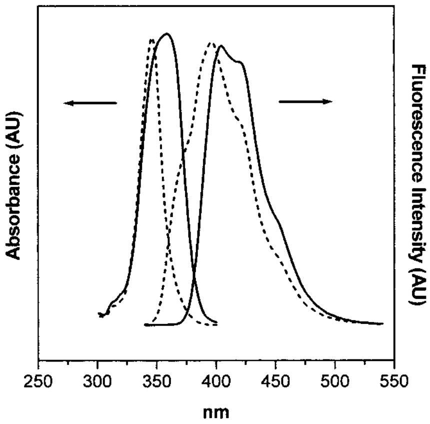


Figure 2. Absorption and emission spectra of triblock copolymer QPPS 1 (—) (λ_{exc} = 378 nm) and HPPS 1 (···) (λ_{exc} = 357 nm) in $CHCl_3$.

merization of styrene using monodispersed α,*ω*-bromo-functionalized oligophenylenes as initiators. Rigid−flexible copolymers with low polydispersities, which also show blue light emission, are obtained using the above-described methodology.

Acknowledgment. The authors would like to thank Prof. C. Tsitsilianis for the use of GPC. This work was supported in part 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.

Supporting Information Available: Text giving Synthesis and characterization of diboronic acid **2**, diester **3**, 2′′′,3′′′,5′′′-triphenyl-*p*-heptaphenyl-4,4′′′′′′-diol, and 2′′,5′′-dihexyloxy-p-quinquephenyl-4,4′′′′-diol, NMR characterization of the initiators **4** and **6,** and ^{13}C NMR spectral data of the QPPS 1 copolymer. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA990481A