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SYNTHESIS OF AMPHIPHILIC COIL-ROD-COIL BLOCK COPOLYMERS USING ATOM TRANSFER RADICAL POLYMERIZATION

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ABSTRACT

Coil-rod-coil block copolymers composed from luminescent rigid units and acrylate flexible blocks have been synthesized using atom transfer radical polymerization. α,ω-Difunctionalized oligophenylenes properly modified to act as ATRP initiators have been used for the polymerization of the various acrylates. Copolymers with controlled shape and in some cases, relatively low polydispersities have been obtained as proved by size exclusion chromatography and NMR. In cases, where t-butyl acrylate blocks have been used as the flexible part, selective hydrolysis resulted in coil-rod-coil copolymers containing poly(acrylic acid) blocks. The solution behavior of the synthesized copolymers was explored in various solvents. The poly(acrylic acid) copolymers in aqueous solutions form large aggregates, while in organic selective solvents for the flexible block, monomolecular micelles seem to be formed.

Key Words: Polymer syntheses; Rod-coil copolymers; Atom Transfer Radical; Polymerization; Luminescence

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INTRODUCTION

Rod-coil block copolymers have attracted great scientific interest because of their ability to self-assemble in solution or bulk state. Their inherent immiscibility results in microphase separation phenomena, which are the main cause of the appearance of ordered macromolecular or even supramolecular structures [1]. These structures can vary in size and shape but possess regularity and a certain periodicity, which is controlled by the particular chemical nature and the physicochemical interactions between the blocks of the polymer chains. Furthermore, the aggregation behavior that is expected in a selective solvent depends on the volume fraction of the different kinds of blocks [2]. Because of their chemical structure the rigid blocks can combine a variety of properties such as electrical and optical ones [3].

In order to achieve regularity in structure, a number of different methods have been utilized. Condensation reactions between well-defined end-functionalized polymers have been used for synthesizing rod-coil copolymers [4]. Living anionic polymerization techniques have been applied in rod-coil block copolymer synthesis, using end-functionalized oligomers as macroinitiators [5]. Controlled radical polymerization techniques have also been utilized for synthesizing rod-coil copolymers [6]. Atom Transfer Radical Polymerization (ATRP) is an example of these controlled polymerization methods that can be easily used for the synthesis of block copolymers of various architectures [7]. This needs either the use of an end-functionalized homopolymer or modification of an oligomer precursor in order to fulfill the ATRP initiator requirements. One of the advantages of ATRP is that a large variety of monomers can be used, some of which cannot be polymerized with other techniques (e.g. anionic polymerization). Acrylates is one characteristic example of such monomers.

We have already synthesized modified oligophenylene derivatives with five and seven rings and used them as fluorescent, rigid, bifunctional macroinitiators to polymerize styrene with ATRP [8]. We now extend this work towards the direction of synthesizing novel coil-rod-coil (CRC) triblock copolymers using different monomers such as ethyl acrylate and tert-butyl acrylate. Selective hydrolysis of tert-butyl groups led to water-soluble CRC copolymers that emit blue light. The ability of these copolymers to self-assemble in micellar structures was examined by static light scattering (SLS) in a variety of polar, selective solvents for the flexible block.

EXPERIMENTAL

Materials

The two rigid oligophenylenes used as macroinitiators were synthesized according to known procedures [8]. Tert-butyl acrylate and ethyl acrylate

(Merck) was vacuum-distilled from finely powdered calcium hydride. Tetrahydrofuran (THF) for GPC measurements was distilled under sodium in the presence of benzophenone and passed through a 0.5 μm millipore filter. Methylene chloride (CH_2Cl_2, Merck) was washed with concentrated sulfuric acid, with dilute sodium hydroxide and water, dried over sodium hydroxide and calcium chloride pellets overnight and fractionally distilled. Diphenyl ether (Merck) was stored over molecular sieves and purged with argon for 30 minutes before polymerization. CuBr (Aldrich), 2,2′-bipyridine (bipy, Merck), N,N,N′,N′,N″-pentamethyldiethylene triamine (PMDETA, Aldrich) and all the other reagents and solvents were used as received.

Polymerizations

ATRP of Tert-butyl Acrylate and Ethyl Acrylate Using Monodisperse Oligophenylenes as Rigid Macroinitiators

A round-bottom flask equipped with a U-tube, rubber septum, magnetic stirring bar and a gas inlet/outlet was flamed under vacuum. In the flask 0.1 mmol of the initiator was added along with 0.2 mmol of CuBr and 0.6 mmol bipyridine (or 0.2 mmol PMDETA). The system was degassed three times and flushed with argon. The solvent (if used) and the monomer were transferred to the flask via a syringe. The reaction mixture was then immersed in an oil bath and heated at a standard predetermined temperature (110°C, in most cases) for 12 hours. 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 most of the catalyst. Tert-butyl acrylate and ethyl acrylate copolymers precipitated in methanol/water 50:50 v/v. Then they were dissolved in diethyl ether and the solution was washed with plenty of water. Diethyl ether was evaporated and the copolymers were obtained and then dried under vacuum at room temperature. The results for the different polymers synthesized are depicted in Table 1.

Measurements

The structure of block copolymers was characterized by high-resolution ^1H NMR spectroscopy, using a Bruker Avance DPX 400 MHz spectrometer. The solvents used were $CDCl_3$ and DMSO-*d6*. The number-average ($\bar{M}_n$) and weight-average ($\bar{M}_w$) molecular weights of block copolymers were determined by gel permeation chromatography using a Polymer Lab apparatus equipped with three Ultrastyragel columns (500, 10^4 and 10^5 Å pore size). Measurements were performed in THF as an eluent at room temperature with 1 mL/min flow rate. Calibration procedure was based on polystyrene standards. Viscosity measurements were performed in water at 25°C with an

Table 1. Molecular Characteristics of the Synthesized Triblock Copolymers

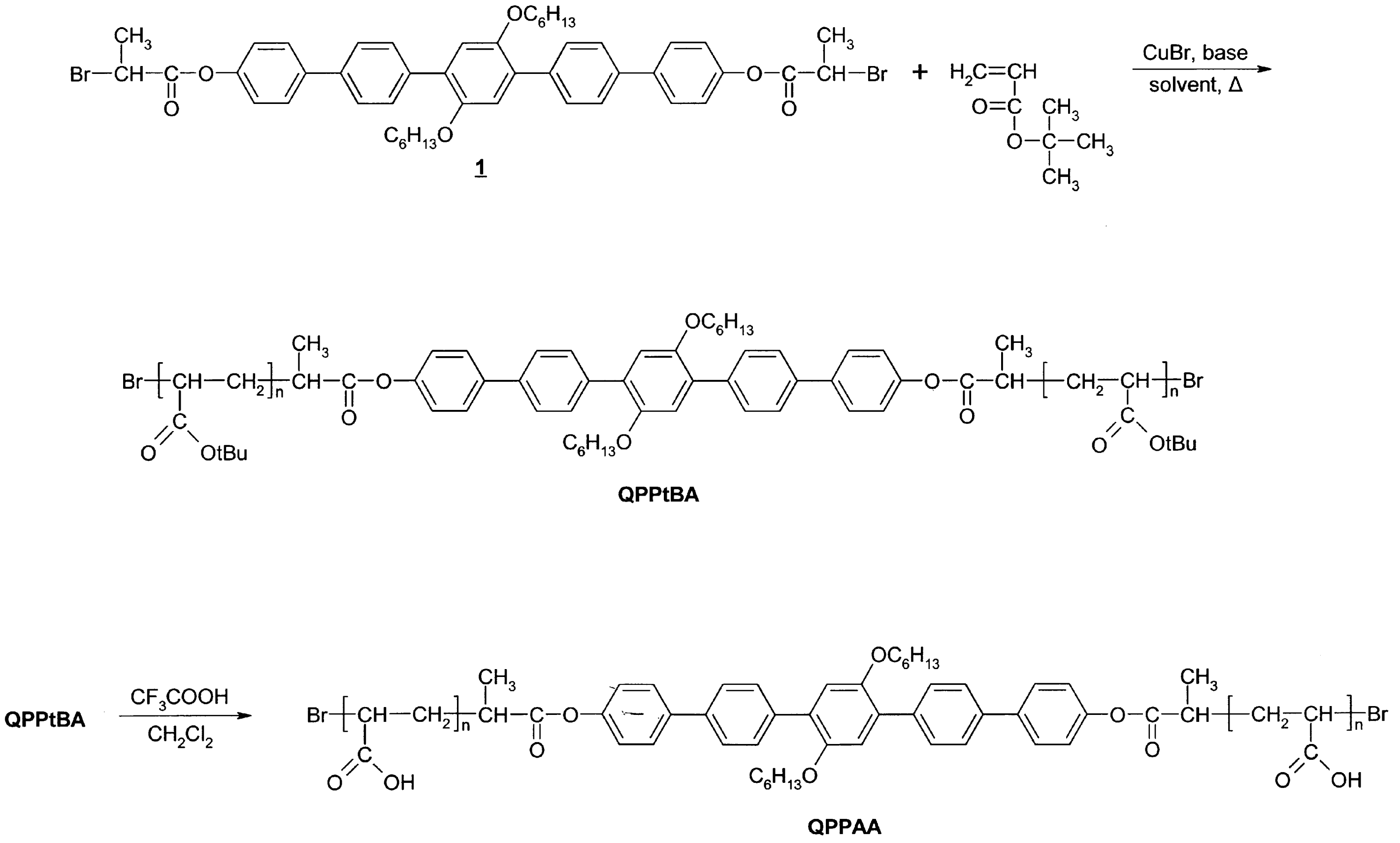
	GPC Results		
Polymer	$\bar{M}_n$	$\bar{M}_w$	PDI
QPPtBA 1[a]	21,000	3,9000	1.86
QPPtBA 2[b]	9100	16,000	1.76
QPPtBA 3[c]	12,500	16,350	1.31
QPPtBA 4[d]	15,650	21,400	1.37
QPPtBA 5[c]	2100	2600	1.24
QPPtBA 6[e]	4200	7000	1.67
HPPtBA 1[f]	15,300	22,100	1.44
HPPtBA 2[c]	5000	6600	1.32
HPPtBA 3[g]	8250	14,550	1.76
HPPtBA 4[h]	128,000	230,000	1.80
HPPtBA 5[d]	12,000	19,350	1.61
HPPEA 1[i]	29,500	37,350	1.27

[a–i]Reaction conditions used: [a] bipy, bulk; [b] bjpy DPE/tBA 1:2; [c] bipy, EC (10% w/v); [d] PMDETA, EC (20% w/v); [e] bipy, toluene; [f] bipy, DPE/tBA 1:2, 105°C; [g] bipy, EC (60% w/v), reaction time: 30 min; [h] PMDETA, EC/DPE/tBA 4:1:2, reaction time: 30 min; [i] PMDETA, DPE, 90°C.

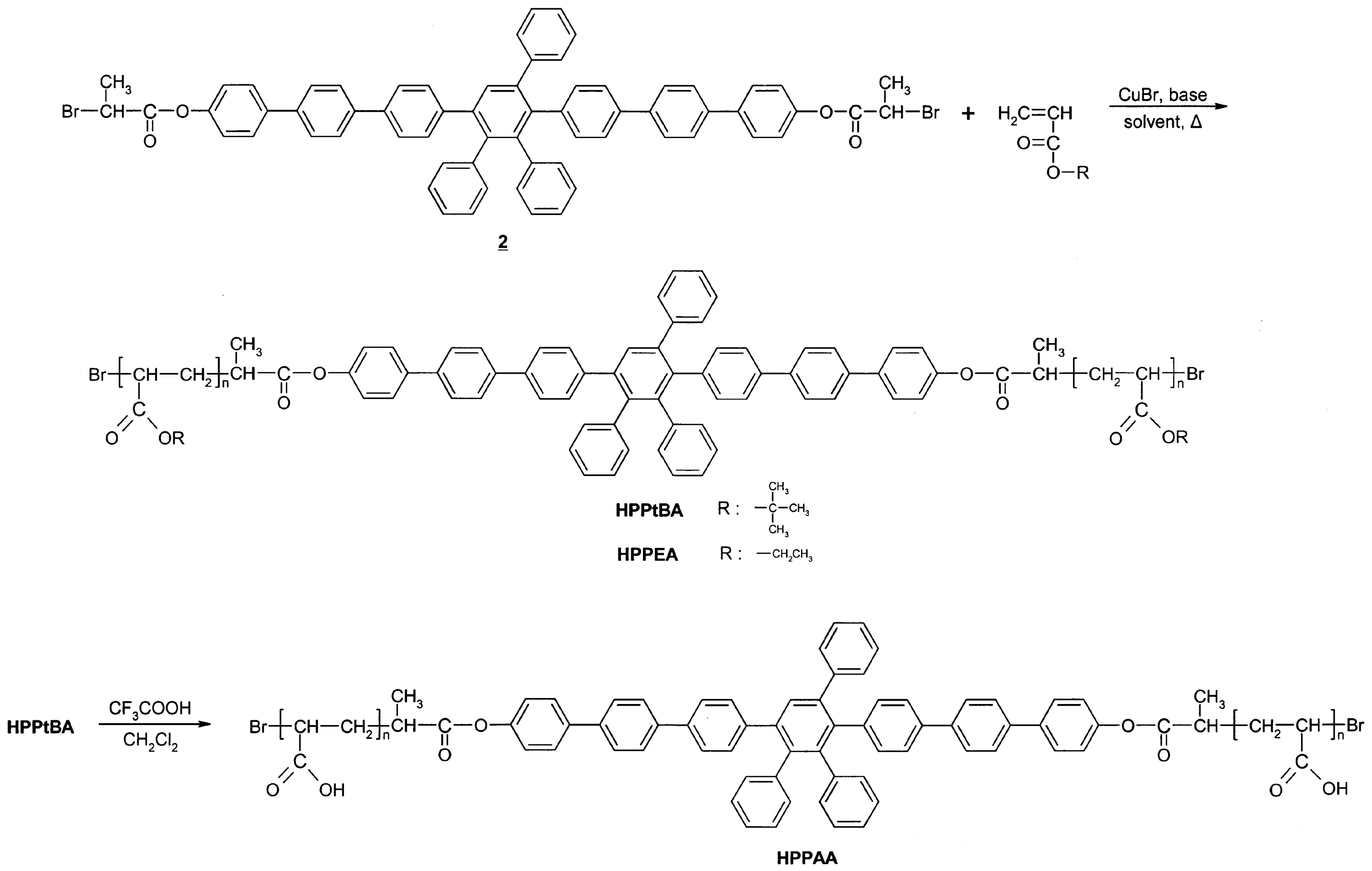
Ubbelohde-type viscosimeter in a Scott Gerate AVS 310. SLS experiments were carried out using a thermal regulated (±0.1°C) spectrogoniometer model SEM RD (Sematech, France) equipped with a He-Ne laser (633 nm). Refractive index increments *dn/dc* required for the SLS measurements were obtained by means of a Chromatic KMX-16 differential refractometer operating at 633 nm.

RESULTS AND DISCUSSION

Two different kinds of modified, monodisperse, rigid oligophenylene derivatives were used as ATRP macroinitiators in order to polymerize acrylic monomers, such as tert-butyl acrylate and ethyl acrylate. ATRP was selected as to develop flexible acrylate blocks on both sides of the rigid block resulting rather in the control of the overall shape of the final triblock copolymer than in narrow polydispersities. The modification of the rods used has been presented in a previous work (8). α,ω-Dibromo-functionalized quinquephenylene and heptaphenylene initiators 1 or 2 reacted with a monomer in the presence of a complex of cuprous bromide (CuBr) and an organic base as a ligand (bipyridine or pentamethyldiethylene triamine) so as to give triblock CRC copolymers [Sch. 1 and 2]. A variety of different polymerization



Scheme 1. Polymerization of tert-butyl acrylate and selective hydrolysis of the resulting triblock copolymers using substituted quinquephenyl initiator.



Scheme 2. Polymerization of tert-butyl and ethyl acrylate and selective hydrolysis of the resulting tert-butyl acrylate triblock copolymers using substituted heptaphenyl initiator.

conditions were used. Factors such as ligand, solvent, solvent/monomer ratio and temperature were altered, thus obtaining copolymers of a wide range of molecular weight and different polydispersities [Table 1]. In some cases, low polydispersity indices were obtained, meaning that regularity in length of the flexible block has been also achieved.

The difficulty in performing ATRP with tert-butyl acrylate is that the catalytic systems used are heterogeneous in bulk or in non-polar solvents [7e]. Moreover, the solubility of the heptaphenylene derivative is limited in non-polar solvents, and thus mainly polar solvents were preferred. It is observed that when a large amount of polar solvent (such as ethylene carbonate, EC) was added, larger polydispersities were introduced and high conversion of the monomer occurred very fast, probably caused by slow deactivation of the propagating radical species [9].

The ligand also plays a very important role in these systems. When using pentamethyldiethylene triamine (PMDETA) instead of bipyridine (bipy) the propagation rate is accelerated from its early stages, thus contributing to the poor control of the polymerization if the initiator did not have the time to get diluted.

So, we concluded that in order to control all these parameters properly, limited amount of polar solvent along with bipy as a ligand should be used. Relatively elevated temperature was preferred to assist in the initiator's solubilization.

The effectiveness of the method used has been checked using ^{1}H-NMR spectroscopy and size exclusion chromatography. From the ^{1}H-NMR spectrum of a representative sample of the HPPtBA copolymer series (see Fig. 1a) in $CDCl_3$ it is obvious that the signal at 4.7 ppm due to the hydrogen of CHBr groups of $\underline{2}$ has been totally disappeared, meaning that the formation of triblock copolymers has been achieved. Furthermore, the incorporation of the initiator onto the flexible chains is proven by the signals of its aromatic protons in the region of 6.8–7.3 ppm. The residual signal at approximately 4.1 ppm is possibly due to the methinic and/or methylene protons that are adjacent to the halogen atom.

Size exclusion chromatography was utilized to calculate molecular weights and polydispersities. The results are shown in Table 1. Molecular weights based on calibration with PS standards are presented, although in polyacrylates it has been observed that molecular weights are underestimated by this calibration. As it was expected, no trace of initiator is apparent in the chromatogram shown in Fig. 2. This demonstrates that the initiation stage was efficient and all the initiator quantity has been reacted.

Poly(tert-butyl acrylate) triblock copolymers were selectively hydrolyzed in order to obtain water soluble copolymers. For the hydrolysis of the tert-butyl ester groups we have used trifluoroacetic acid (CF_3COOH) in methylene chloride (CH_2Cl_2). Trifluoroacetic acid is considered to be a selective reagent for the hydrolysis of tert-butyl

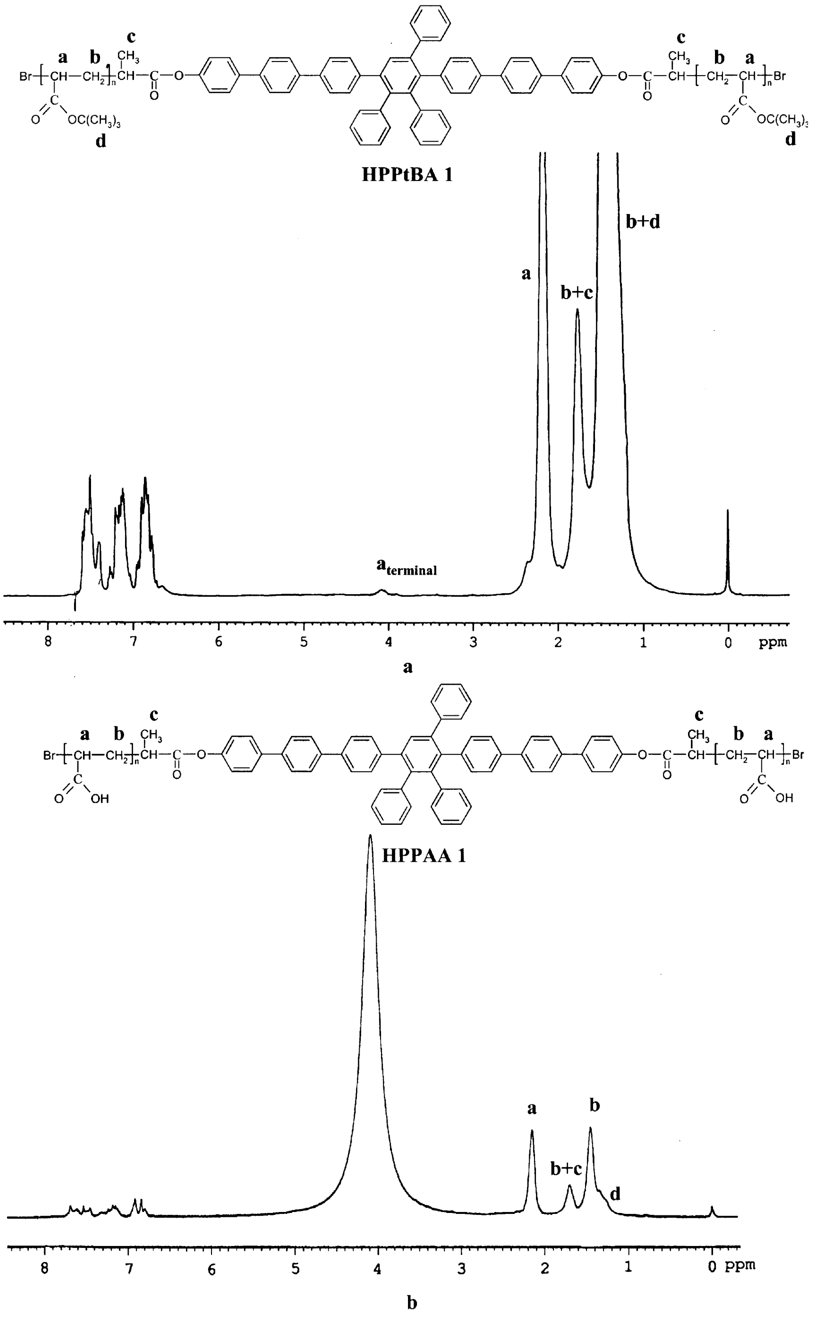


Figure 1. (a) ^{1}H-NMR of HPPtBA 7 in $CDCl_3$; (b) ^{1}H-NMR of HPPAA 7 in DMSO-*d6*/$CDCl_3$ 80:20 v/v.

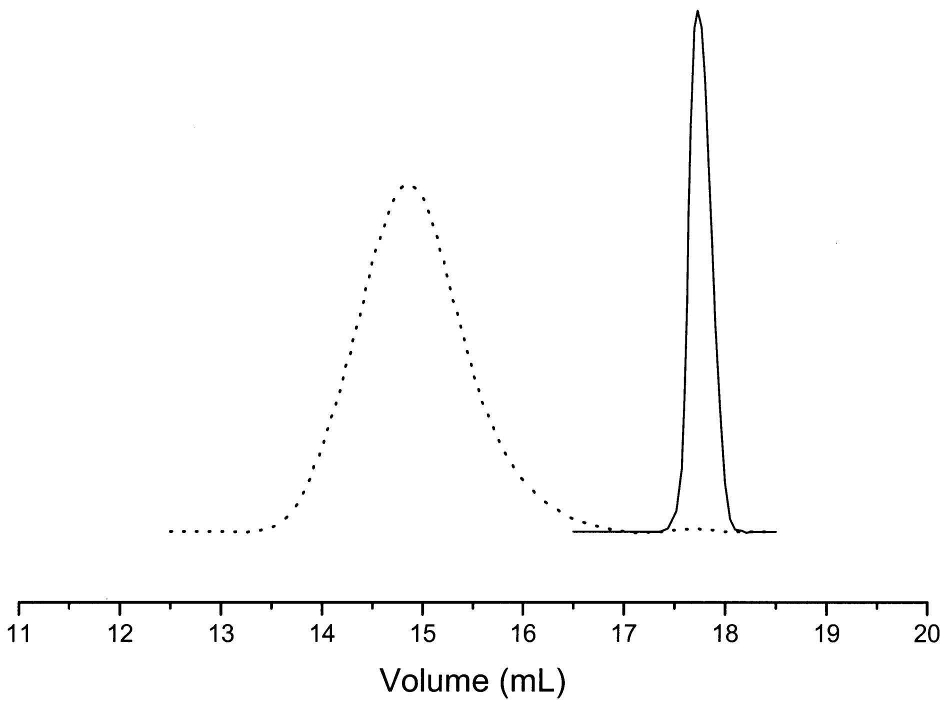


Figure 2. SEC chromatograms of the quinquephenylene initiator **1** (—) and the respective tert-butyl acrylate triblock copolymer QPPtBA 3 (····).

ester groups. Nevertheless, we tried to verify if there was any cleavage at the junction between the rigid block and the flexible ones during the hydrolysis of the poly(tert-butyl acrylate) to poly(acrylic acid). From the ^{1}H-NMR spectrum of the respective polyacrylic acid copolymer HPPAA 7 (DMSO-*d6*/$CDCl_3$ 80:20 v/v) shown in Fig. 1b we compared the integration ratio of the signal at 2.2 δ (protons of the CH groups of the acrylate flexible backbone) to those of all aromatic protons of the copolymer (6.8–7.4 δ) in both the HPPtBA 7 and HPPAA 7 spectra. It was clear that this ratio remained practically invariable after the hydrolysis, namely the copolymer was still a triblock one.

It was also observed that there was a remaining signal of the methyl protons of the tert-butyl groups at approximately 1.4 δ in the HPPAA 7 spectrum (Fig. 3). From this peak, we calculated that the hydrolysis of tert-butyl ester groups occurred at about 97%.

The solution behavior of the hydrolyzed sample QPPAA 1 was examined by viscosity measurements in dilute aqueous solution. In Fig. 4, the inherent viscosity, η_{inh}, has been plotted as a function of concentration. A typical polyelectrolyte behavior was observed [10].

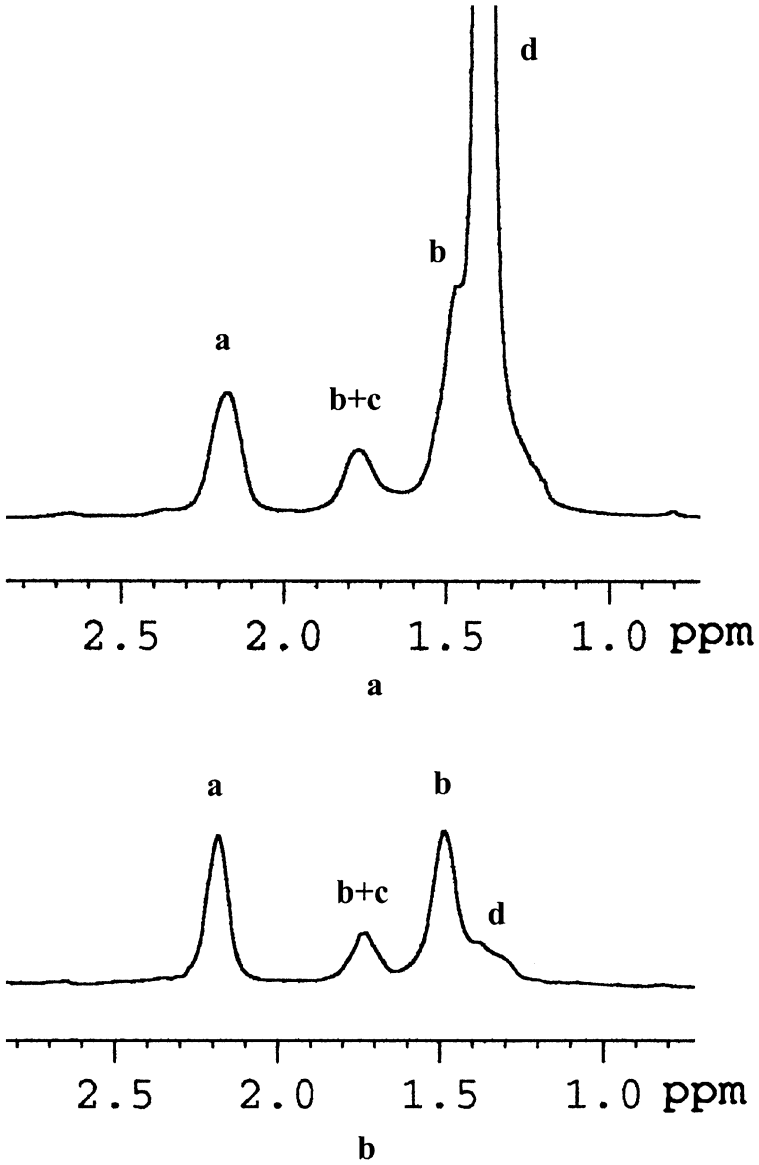


Figure 3. Comparison of (a) the ^{1}H-NMR of HPPtBA 7 with (b) the respective one of HPPAA 7. The letters a-d correspond to the same hydrogen atoms depicted in Fig. 1.

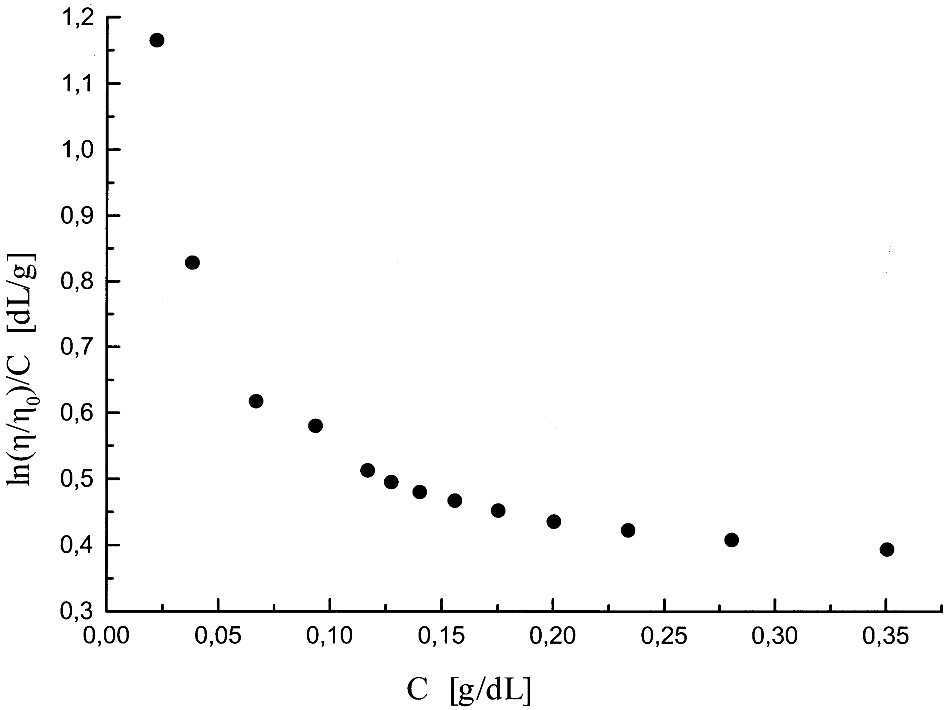


Figure 4. Inherent viscosity η_{inh} as a function of concentration of a QPPAA 1 water solution.

An interesting property of these water-soluble CRC copolymers is that they have the ability to emit light when excited with a UV radiation. This is due to the conjugation along the phenylene rings. In Fig. 5 the fluorescence spectra of a QPPAA sample in H_2O and DMF are displayed showing that there is no difference on their optical properties.

The ability of these amphiphilic CRC block copolymers to self-assemble in selective solvents was investigated using SLS. The systems examined are the copolymer QPPtBA 7 in MeOH and the same copolymer to its hydrolyzed form (QPPAA 7) in MeOH, EtOH 95% and water. In all cases, the solvents are selective for the flexible outer blocks. For the copolymer-organic solvent systems classical linear Zimm plots were obtained and apparent molecular weights were determined (see Table 2). Taking the polydispersity index for QPPtBA 7 into account (1.67), M_w values determined from can be easily converted to M_n ones. These M_n's are fairly close to those calculated by ^{1}H-NMR (i.e., $M_{n,\ \mathrm{QPPtBA}\ 7} = 8400$, $M_{n,\ \mathrm{QPPAA}\ 7} = 5500$), implying that association phenomena are absent. Provided that the solvent is a bad one for the middle rod-like block, monomolecular micelles seem to be formed. This means that the length of the flexible outer blocks is sufficient large to keep these copolymers in solution.

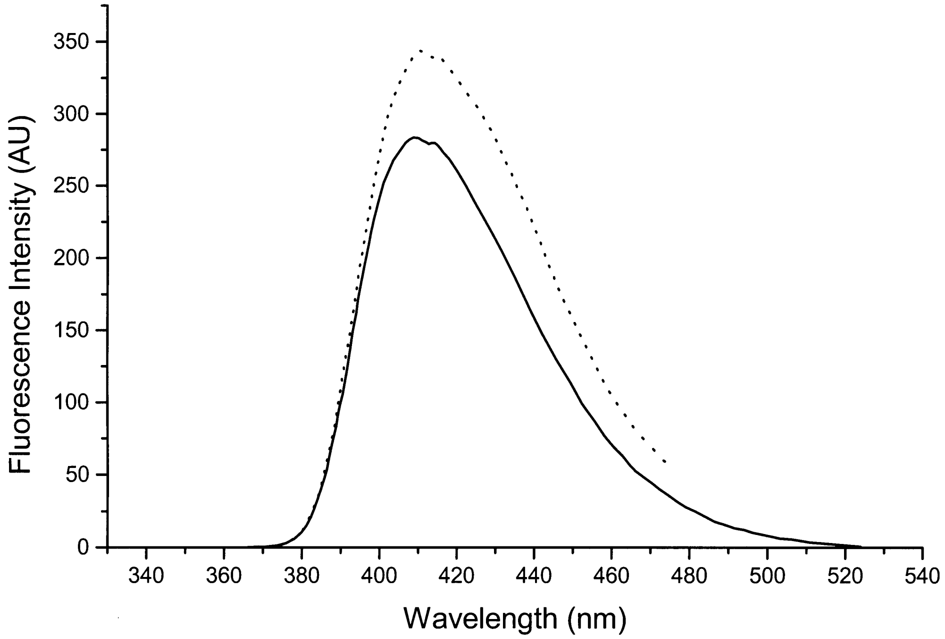


Figure 5. Emission spectra of QPPAA triblock copolymer in H_2O (—) and DMF (····).

On the other hand, by increasing solvent selectivity (i.e., passing to aqueous solutions) association phenomena take place. In Fig. 6 the inverse scattering intensity $Kc/(I\text{-}I_0)$ at 90° (where K is the optical constant and I, I_0 are the scattering intensities of the solution and the solvent respectively) has been plotted as a function of concentration c. In the same plot (inset) data from the QPPAA/MeOH system are also presented. As it can be observed, $Kc/(I\text{-}I_0)$ have been decreased several orders of magnitude with respect to the data obtained in MeOH. This implies that strong association phenomena are present in the aqueous system and large aggregates have been formed. At very low concentrations $Kc/(I\text{-}I_0)$ tend to increase. However, the critical aggregation concentration seems to be very small and cannot be detected by the present technique.

Table 2. Light Scattering Results and Refractive Index Increment Measurements of the Synthesized Quinquephenyl Triblock Copolymers

Polymer	Solvent	dn/dc	$\overline{M}_w$
QPPtBA 7	MeOH	0.109	12,150
QPPAA 7	MeOH	0.166	6300
QPPAA 7	EtOH 95%	0.135	8300

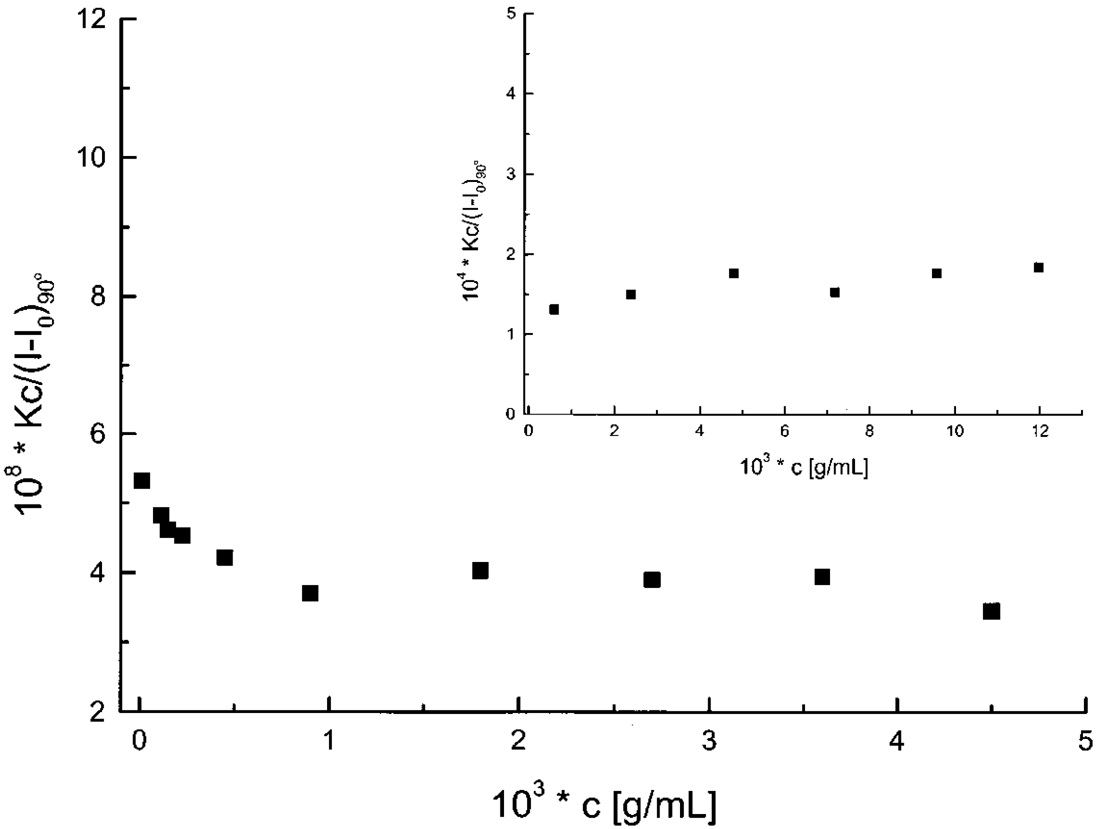


Figure 6. Inverse scattering intensity $Kc/(I\text{-}I_0)$ ($\theta = 90°$) plots as a function of concentration for solutions of QPPAA 7 in MeOH (inset) and in H_2O.

CONCLUSION

The synthesis of amphiphilic coil-rod-coil photoluminescent triblock copolymers via Atom Transfer Radical Polymerization has been presented. This method has been proved to be a sufficient one as to control the shape and the structure of the final copolymers. In some cases the size (molecular weight, polydispersity) was also controlled. Modified monodisperse rod blocks that emit blue light were used as ATRP macroinitiators, onto which flexible-coil acrylate chains were successfully developed. The solution behavior of these copolymers was explored in various selective solvents for the outer flexible blocks. Association phenomena seem to be absent in most of the cases, implying that monomolecular micelles have been formed. On the other hand, in the case of poly(acrylic acid) copolymers in water, association phenomena take place leading to the formation of large aggregates.

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