Synthesis of Conjugated−Acidic Block Copolymers by Atom Transfer Radical Polymerization

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ABSTRACT: A novel series of well-defined amphiphilic triblock copolymers containing conjugated polyfluorene (PF) and coillike poly(methacrylic acid) (PMAA) were successfully synthesized by vacuum thermolysis of the precursor block copolymers, poly(2-tetrahydropyranyl methacrylate)−PF−poly-(2-tetrahydropyranyl methacrylate) (PTHPMA−PF−PTHPMA) prepared by using atom transfer radical polymerization (ATRP) with a 2-bromoisobutyrate end-capped PF as the macroinitiator. Both the linear first-order kinetic plot and the linear dependence of the M_n vs conversion indicate the controlled nature of the polymerization of THPMA. The polydispersity indices of the PTHPMA−PF−PTHPMA triblock copolymers were essentially less than 1.3, demonstrating the well-defined structures of the obtained block copolymers. The chemical structures of the PTHPMA−PF−PTHPMA block copolymers were confirmed by ^{1}H NMR, ^{13}C NMR, and FTIR studies. Decomposition of the precursors at about 145 °C afforded the PMAA−PF−PMAA block copolymers, and the anhydride formed during the thermolysis could be successfully transformed to the corresponding acid by further hydrolysis in warm water. PMAA−PF−PMAA and PTHPMA−PF−PTHPMA presented almost identical photophysical behavior in diluted solutions, suggesting that similar excited species were essentially involved in their luminescent processes. Aggregation of PF segments was found to occur in the aqueous solution of the PMAA−PF−PMAA as revealed by spectroscopic studies. ^{1}H NMR results also substantiate the formation of PF aggregates stabilized by soluble PMAA.

Introduction

Amphiphilic block copolymers have been extensively investigated both theoretically and practically in the past few decades.[1] Traditional amphiphilic block copolymers containing chemically connected hydrophilic and hydrophobic coils provide a great variety of morphologies both in solid states and in selective solvents.[2−6] The micelles of these block copolymers formed in selective solvents, which consist of an inner core composed of insoluble segments surrounded by an outer shell of soluble segments swollen by the solvent, are potentially useful in nanotechnologies and biomedical fields. Recently, novel amphiphilic rod−coil block copolymers containing at least one conjugated segment for optoelectronic applications has received attention as an alternative strategy for fabrication of molecular electronic devices because the combination of the physical properties contributed by the component segments in the block copolymers may exhibit unique characteristics suitable for developing novel supramolecular structures.[7,8]

However, the preparation of well-defined rod−coil block copolymers has been synthetically challenging due to the distinct mechanisms involved in the respective polymerization processes of these chemically different segments.[8] Recent progress in controlled radical polymerization, especially nitroxide-mediated radical polymerization (NMRP)[9] and atom transfer radical polymerization (ATRP),[10] opens a new channel to prepare novel well-defined block copolymers comprising of widely different components. ATRP has proven powerful to develop novel well-defined macromolecular architectures with a wide selection of monomers and tolerant reaction conditions.

One of the widely studied conjugated polymers is polyfluorene, which is an excellent semiconducting materials for optoelectronic applications.[11,12] Several examples of polyfluorene-based block copolymers have been studied, appearing to be interesting supramolecular materials.[13,14] On the other hand, poly(acrylic acid) and poly(methacrylic acid) have been popularly chosen as the hydrophilic segments in synthesizing amphiphilic block copolymers due to their excellent hydrophility, and many fascinating morphologies involved in these block copolymers have been observed.[1−6] Unfortunately, since most of the living polymerization methods for preparing block copolymers developed so far are acid-sensitive, the polyacid-containing block copolymers often have to be synthesized by employing protected monomers with masked acid groups such as *tert*-butyl acrylate, trimethylsilyl methacrylate (TMSMA), benzyl methacrylate (BzMA), and 2-tetrahydropyranyl methacrylate (THPMA), followed by acid hydrolysis, thermolysis, or catalytic hydrogenolysis to liberate their original acid functionality.[15] The acid-labile THP group has been found to be useful in developing not only amphiphilic block copolymers but also chemically amplified photoresists in the area of photolithography.[16−19] PTHPMA and its block copolymers have been prepared by both

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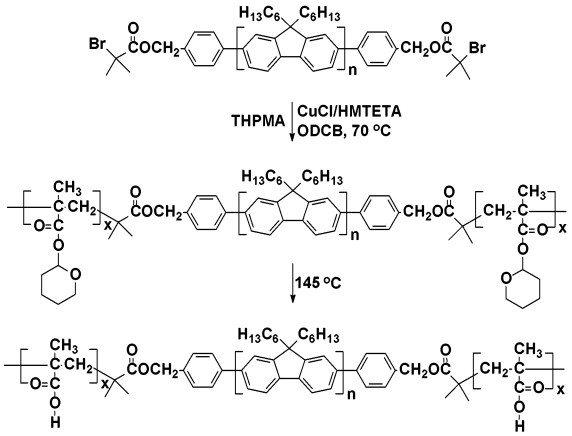
Scheme 1. Synthetic Route for the Conjugated−Acidic Triblock Copolymers



traditional radical polymerization and group transfer polymerization,[20−22] while they have never been obtained by ATRP so far. In this paper, we present the syntheses and characterization of novel well-defined rod−coil triblock copolymers containing polyfluorene (PF) and poly(methacrylic acid) (PMAA) through thermolysis of the precursors, PTHPMA−PF−PTHPMA, which were prepared by using the ATRP technique (Scheme 1). PMAA−PF−PMAA is, as far as we know, the first example of a conjugated−acidic block copolymer system.

Experimental Section

Materials. 2,7-Dibromofluorene, 1-bromohexane, 4-bromobenzyl alcohol, 1,1,4,7,10,10-hexamethyl triethylenetetramine (HMTETA), CuCl (99.995+%), 1,5-cycooctadiene, and bis(1,5-cyclooctadiene)nickel(0) were purchased from Aldrich Chemical Co. 3,4-Dihydro-2*H*-pyran and methacrylic acid (98%) were purchased from TCI. All reagents were used as received. *N*,*N*-dimethylformamide (DMF), dichloromethane, and *o*-dichlorobenzene (ODCB) were distilled from calcium hydride and stored under argon. Tetrahydrofuran and toluene were distilled from sodium/benzophenone. The synthesis of the end-capped polyfluorene macroinitiator (containing seven fluorene units according to end group analysis by ^{1}H NMR, PDI $\approx$ 1.5) has been described in our previous paper.[23] 2-Tetrahydropyranyl methacrylate (THPMA) was synthesized by the acid-catalyzed esterification of methacrylic acid (MAA) with 3,4-dihydro-2*H*-pyran according to the previously reported methods.[20] THPMA was purified by passing through a basic alumina column to remove traces of residual MAA. Two vacuum distillations from CaH_2 yielded THPMA of sufficient purity.

Synthesis of PTHPMA—PF—PTHPMA Triblock Copolymers by ATRP. The PTHPMA−PF−PTHPMA triblock copolymers were synthesized by solution polymerization in *o*-dichlorobenzene. In a typical experiment, a glass tube was charged with 0.03 g (0.01 mmol) of PF macroinitiator and 2.0 mg (0.02 mmol) of CuCl before it was sealed with a rubber septum. The tube was degassed with three vacuum−argon cycles to remove air and moisture. Then, 0.5 mL of *o*-dichlorobenzene and 5.4 μL of HMTETA (0.02 mmol) were introduced with syringes. After 0.4 mL of THPMA was added, the glass reactor was immersed in an oil bath at 70 °C and samples for ^{1}H NMR and SEC characterization were taken out from the reaction mixture at time intervals and passed through a column of neutral alumina to remove the catalysts. The progress of this reaction could be easily followed by the disappearance of the proton signal at 6.07 ppm and the appearance of the broad peak at 5.9 ppm in the ^{1}H NMR spectra, both of which are attributed to the protecting group. The monomer conversion was therefore calculated according to the following equation:

$$\text{conversion (\%)} = [I_{5.9}/(I_{5.9} + I_{6.07})] \times 100\%$$

The polymers were precipitated into excess hexane and dried in a vacuum at 40 °C. White powdery samples were obtained.

Preparation of PMAA—PF—PMAA Triblock Copolymers. The THP masking groups of the PTHPMA−PF−PTHPMA were removed by thermolysis under a vacuum at 145 °C for 5−6 h, followed by dispersing the powdery samples into warm water and stirring at 40 °C overnight. The solids were then collected and dried in a vacuum oven at 40 °C overnight.

Measurements. NMR spectra were collected on a Bruker Avance 400 spectrometer with tetramethylsilane as the internal standard. FTIR spectra were recorded on a Bio-Rad FTS 165 spectrometer by dispersing samples in KBr disks. UV−vis spectra were recorded on a Shimadzu 3101 spectrophotometer. Size exclusive chromatography (SEC) analysis was conducted with a Waters 2690 separation module equipped with a Waters 2410 differential refractometer HPLC system and 3 Waters Styragel columns (HR 4, 5, and 6) in series, using polystyrene as the standards and THF as the eluant at a flow rate of 1.0 mL/min. TGA measurements were performed on a TA Instruments Hi-Res TGA 2950 thermogravimetric analyzer at a heating rate of 10 °C/min under N_2.

Fluorescence measurement was carried out on a Perkin-Elmer LS 50B luminescence spectrometer with a xenon lamp as the light source.The fluorescence quantum yields (Φ_f) of the polymers in solutions were recorded by using a diluted quinoline solution in 0.1 N H_2SO_4 as the standard, assuming that the fluorescence quantum yield was 0.55 with the excitation wavelength of 365 nm. Φ_f was calculated according to[24]

$$\Phi_S = \Phi_R\left(\frac{A_R}{A_S}\right)\left(\frac{I_S}{I_R}\right)\left(\frac{{n_S}^2}{{n_R}^2}\right)$$

where Φ_R and Φ_S are the fluorescence quantum yields of quinoline and the polymers, respectively, A_R and A_S are the absorbances of quinoline and the polymers at the excitation wavelength, respectively, I_R and I_S are the integrated emission intensities of quinoline and the polymers, respectively, and n_R and n_S are refractive indices of the corresponding solvents of the solutions, respectively. In the cases of mixed solvents were employed, the refractive indices of the mixed solvents were calculated according to

$${n_{mix}}^2 = f_A{n_A}^2 + f_B{n_B}^2$$

where f_A and f_B are the fractions (vol/vol) of solvents A and B, respectively.

Results and Discussion

ATRP of THPMA Initiated by PF Macroinitiator. In our previous studies, we have demonstrated that the well-defined PF macroinitiator with 2-bromoisobutyrate groups in both ends could efficiently initiate the further ATRP of 2-(dimethylamino)ethyl methacrylate (DMAEMA) in preparing another class of conjugated−ionic triblock copolymers.[23] Therefore, in the current study, the same PF macroinitiator was employed, and ATRP of THPMA was performed at 60 °C or 70 °C in *o*-dicholobenzene solution with HMTETA as the ligand, both of which have been used in our ATRP reactions.[23] Since THPMA has been previously polymerized at 70−75 °C by traditional radical polymerization and 40 °C by group transfer polymerization,[15−17,21,25] the temperatures for the ATRP of THPMA were set to be no more than 70 °C. Note that the removal of THP masking

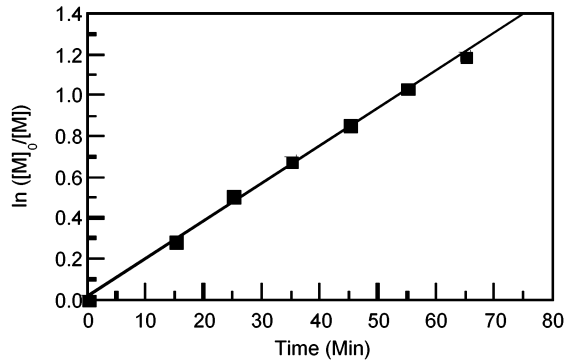


Figure 1. Kinetic plot for ATRP of THPMA in *o*-dichlorobenzene initiated by PF macroinitiator with HMTETA/CuCl as the catalytic system ([HMTETA]:[CuCl]:[PF] = 2:2:1). $[M]_0/[PF] = 279$; $V_{THPMA}/V_{ODCB} = 5:4$; 70 °C.

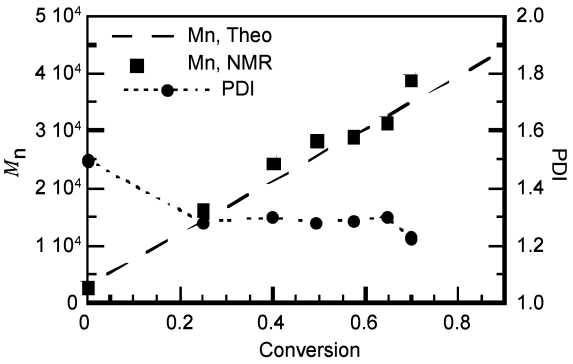


Figure 2. Dependence of molecular weight and molecular weight distribution on monomer conversion for ATRP of THPMA in *o*-dichlorobenzene at 70 °C initiated by PF macroinitiaor with CuCl/HMTETA as the catalytic system ([HMTETA]:[CuCl]:[PF] = 2:2:1; $[M]_0/[PF] = 279$; $V_{THPMA}/V_{ODCB} = 5:4$).

groups takes place at 70 °C in the presence of water,[21] so it is very important to keep the reaction mixture anhydrous during the ATRP reactions to suppress the unfavorable occurrence of deprotection that would be detrimental to the ATRP reaction because of the acid released. In addition, the halide catalyst used was CuCl during the polymerization in order to improve the ratio of the initiation vs propagation through the halogen exchange with the formation of more stable chlorine ends, which has proven beneficial to ATRP.[25] Figure 1 shows the kinetic plot of the ATRP of THPMA initiated by the PF macroinitiator at 70 °C. The $\ln([M]_0/[M])$ vs time plot was linear, indicating first-order kinetics with respect to monomer concentration and, therefore, a constant radical concentration during the polymerization. The dependence of the number-average molecular weight (M_n) on the THPMA conversion is illustrated in Figure 2. Because the different hydrodynamic volumes of the rod−coil block copolymers compared with the polystyrene standards used for calibration may lead to significant deviation of number-average molecular weights recorded by SEC, ^{1}H NMR spectra were employed to determine the composition of these copolymers. Note that there are in total $7 \times 6 + 8 = 50$ aromatic protons deriving from the PF segment, so the number of THPMA units in each PTHPMA−PF−PTHPMA chain can thus be calculated by the following equation: $DP_{THPMA} = 50I_{5.9}/I_{\text{aromatic protons}}$. It can be seen in Figure 2 that M_n increased linearly with the conversion of PTHPMA and were close to the theoretical values, suggesting that these block copolymers were essentially polymerized in a controlled fashion. In addition, all of the PTHPMA−PF−PTHPMA samples gave quite low polydispersity indices measured by SEC which were generally less than 1.3 as shown in Figure 2, implying that the preparation of well-defined PTHPMA−PF−PTHPMA block copolymers has been achieved. Table 1 summarizes some of the ATRP results of the PTHPMA−PF−PTHPMA block copolymers under different conditions. The high final conversions with good control of molecular weight and molecular weight distribution indicate that THPMA can be polymerized efficiently by ATRP.

It is well-known that SEC is very useful to detect the formation of the block structures during the preparation of block copolymers. The typical SEC profiles of the PTHPMA−PF−PTHPMA triblock copolymers developed by ATRP are shown in Figure 3. Compared with the SEC trace of the PF macroinitiator, those of the block copolymers clearly demonstrate the formation of the block copolymer structures in terms of the disappearance of the signals corresponding to the macroinitiator and the symmetrical shape without shoulders, which also indicate that all initiating groups in the PF macroinitiator were essentially involved in the initiation of the ATRP of THPMA.

The chemical structures of the PTHPMA−PF−PTHPMA triblock copolymers were confirmed by ^{1}H NMR, ^{13}C NMR and FTIR spectra (Figures 4, 5, and 6a respectively). The signals of those protons and carbons arising from the PF segments of the triblock copolymers in the ^{1}H NMR and ^{13}C NMR spectra, respectively, were almost identical with those from the PF macroinitiator, and the peaks for PTHPMA could be unambiguously assigned, indicating the successful integration of the PF structures into the block copolymers. The FTIR spectra of the block copolymers exhibited the characteristic features of ester and ether groups. Furthermore, no peak corresponding to an acid group was observed, suggesting the perfect intactness of the masking groups during both the ATRP and workup processes.

Preparation of PMAA—PF—PMAA Triblock Copolymers through Thermolysis. PTHPMA can be converted to PMAA through either acid hydrolysis or thermolysis, which has been used to prepare polyacid-based block copolymers. Unfortunately, in our current system, the acidic catalysts used for hydrolysis, such as hydrochloric acid, may result in chain scission or, as dopants, give rise to the change of the electronic structures of PF. Thermolysis of PTHPMA, however, can be easily conducted under mild conditions resulting in the release of the protecting reagent 3,4-dihydro-2*H*-pyran (DHP) to yield PMAA. The thermolysis approach has been found to be efficient in preparing some of amphiphilic block copolymers containing polyacid blocks with the removal of the masking groups.[6,19,20] Therefore, given the intactness of the block copolymer backbones during heating, thermolysis is very suitable for the present system.

The thermal stabilities of PTHPMA−PF−PTHPMA and the PF macroinitiator were investigated by TGA (Figure 7). It can be seen that the PTHPMA−PF−PTHPMA triblock copolymer gave expected different decomposition behavior compared with PF macroinitiator, as exhibited with the first weight loss at ca. 150 °C attributed to the release of DHP, which was very consistent with the reported values.[20,21] This temperature is much lower than that of the decomposition of

Table 1. ATRP Results of THPMA Initiated by PF Macroinitiator under Different Conditions[a]

entry	[M]/[I][b]	V_m/V_s[c]	time (min)	temp (°C)	convn (%)	$M_{n,theor}$	$M_{n,NMR}$	$M_{n,SEC}$	PDI
1	186	1:1	145	60	80	28 300	26 200	25 200	1.22
2	115	1:1	120	70	91	20 600	21 600	19 200	1.26
3	65	1:2	155	70	95	13 300	16 300	14 100	1.21
4	200	5:4	165	70	96	36 900	39 700	30 700	1.29

[a] [HMTETA]:[CuCl]:[I] = 2:2:1. [b] [I] is defined as the molar concentration of PF macroinitiator containing seven fluorene units and two benzene rings with initiating groups. [c] Ratio of monomer (THPMA) vs solvent (*o*-dichlorobenzene) in volume.

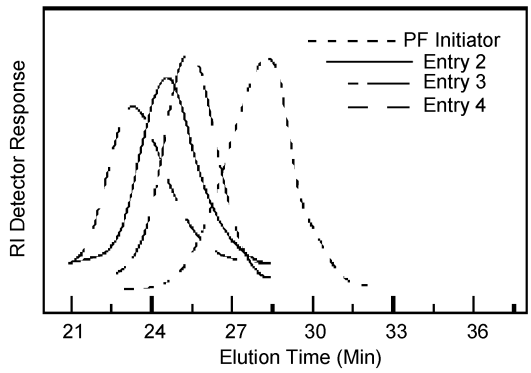


Figure 3. GPC traces of the PF macroinitiator and the PTHPMA−PF−PTHPMA block copolymers (see Table 1).

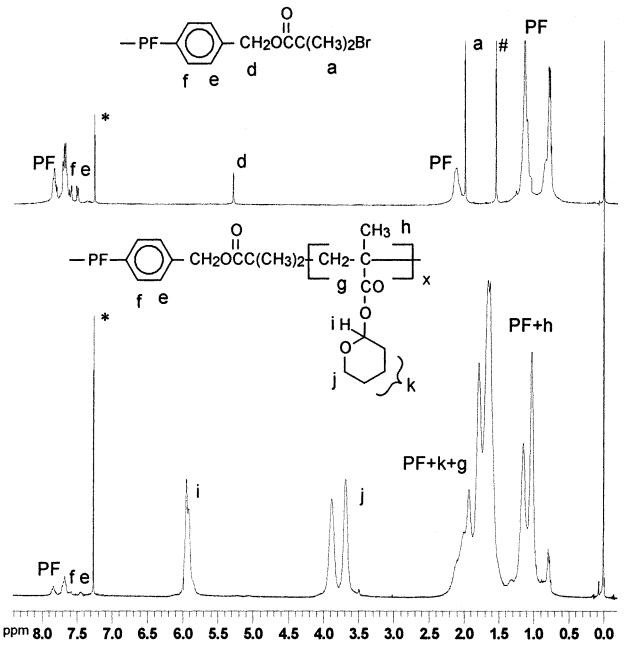


Figure 4. ^{1}H NMR spectra of the PF macroinitiator and a PTHPMA−PF−PTHPMA triblock copolymer (Sample: Entry 4) in $CDCl_3$ ((∗) $CHCl_3$; (#) H_2O).

the PF macroinitiator, indicating that the selective decomposition of the masking groups can be achieved without affecting the main chain of the block copolymers.

It was reported that THP groups could be quantitatively removed by thermolysis at 145 °C under a vacuum for 3−4 h.[20] In our studies, a prolonged period of heating (5−6 h) was employed aiming to thermolyze the copolymers more sufficiently. The thermolysis of the triblock copolymers was followed by ^{1}H NMR spectroscopy, and the gradual disappearance of the signals at 5.9 ppm deriving from the THP groups indicated the occurrence of the decomposition of PTHPMA. Generally, under the above decomposition conditions, more than 98% loss of THP groups could be achieved as confirmed by ^{1}H NMR spectroscopy, implying a relatively complete transformation of PTHPMA to PMAA. Figure 8a shows the typical ^{1}H NMR spectrum of the triblock copolymers that have been decomposed for 6 h. It can be seen that the signals at 5.9, 3.87, and 3.68 ppm attributed to the THP groups had almost thoroughly disappeared. Simultaneously, a peak at 12.7 ppm attributed to acidic protons could be clearly observed in the ^{1}H NMR spectrum, which also substantiated the formation of the carboxylic acid functionality.

The successful functional groups transformation through thermolysis could also be demonstrated by FTIR. Figure 6b shows the FTIR spectrum of a decomposed block copolymer sample which had been heated for 6 h at 145 °C. The very broad absorbance in the range of 2500−3600 cm^{-1} is attributed to the formation of the carboxylic acid functionality. Furthermore, FTIR also detected the presence of anhydride structures resulting from the interchain and intrachain dehydration of the PMAA residues. In Figure 6b, a weak peak at around 1802 cm^{-1} deriving from the C═O stretching vibration is clearly visible, which, together with the appearance of the stretching of C−O−C band at 1022 cm^{-1}, strongly demonstrates the existence of the anhydride structures. It was reported that the thermolysis of PTHPMA could result in the formation of anhydride, which was more serious under a longer heating period and gave rise to the decrease of the solubility of the final copolymers.[16,20] Similar dehydration was also observed during the thermolysis of the P^{t}BuMA-containing block copolymers, which seemed to be more prominent as more drastic thermolysis conditions (over 200 °C) were involved.[6] We believe that the cross-linking reaction under the above conditions had yet to affect the solubility of the final copolymers as they could still form clear solution in THF. To recover the carboxylic acid functionality of the PMAA segments completely, the decomposed samples were treated with warm water at 40 °C overnight. The FTIR spectrum of the resulting block copolymer (Figure 6c) is very similar to that of the block copolymer before hydrolysis except the disappearance of the peaks attributed to anhydride, indicating the complete conversion of the anhydride to the corresponding acid structure.

The final PMAA−PF−PMAA triblock copolymers were soluble in THF, DMSO and even MeOH with the formation of clear solutions, but could not be dissolved in $CHCl_3$ and water. It is noteworthy that the precursor copolymers, PTHPMA−PF−PTHPMA, were soluble in $CHCl_3$ but not MeOH, therefore, the clear solution of PMAA−PF−PMAA formed in MeOH indicated the essential intactness of the copolymer backbone without the formation of insoluble PF homopolymers due to the scissoring of the block copolymer main chains.

Aggregation Behavior Studies. Recently, the photophysical properties of amphiphilic polyquinoline-*block*-polystyrene (PPQ−PS) rod−coil block copolymers were studied, and the findings showed that the photophysical behavior featured the corresponding supramolecular

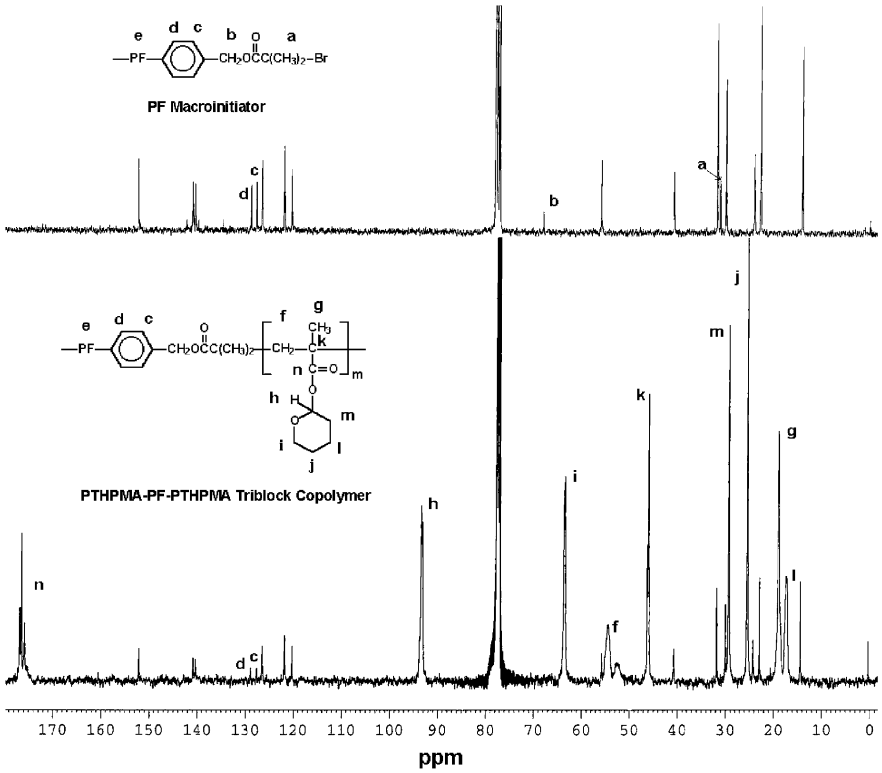


Figure 5. ^{13}C NMR spectra of the PF macroinitiator and a PTHPMA−PF−PTHPMA triblock copolymer in $CDCl_3$ (sample: entry 4).

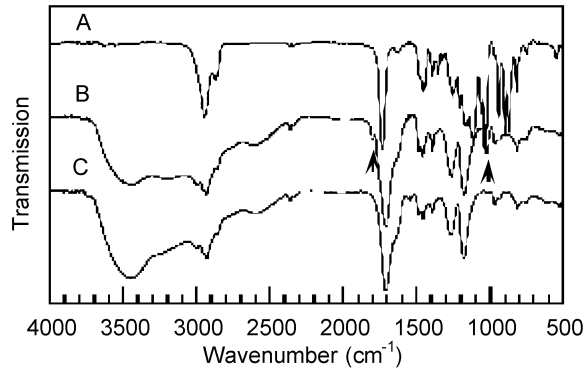


Figure 6. FTIR spectra: (A) of a PTHPMA−PF−PTHPMA triblock copolymer; (B) after thermolysis of a copolymer at 150 °C for 6 h under a vacuum; (C) after hydrolysis of the thermolysis product at 40 °C overnight (sample: entry 3).

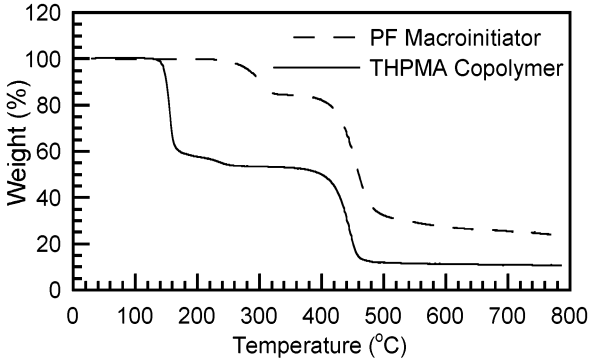


Figure 7. TGA profiles of the PF macroinitiator and a PTHPMA−PF−PTHPMA block copolymer (sample: entry 3).

morphologies of these polymers in solution, which could be explained by the existence of chromophore aggregation within the micelles according to the electronic spectra.[27] In our current rod−coil block system, the

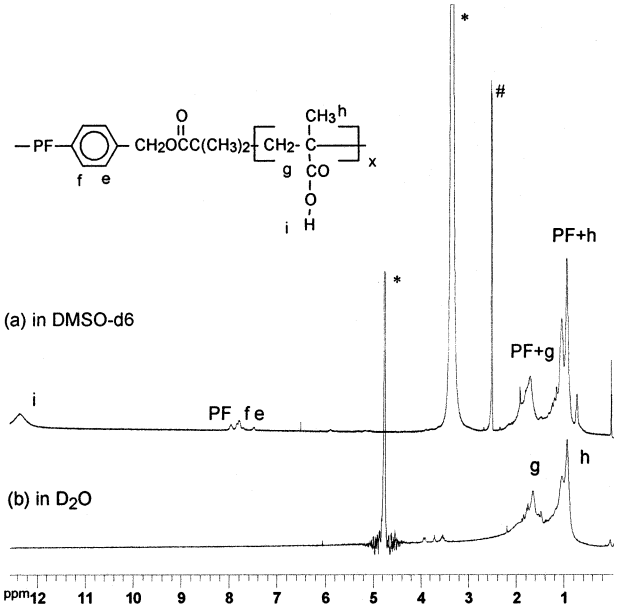


Figure 8. ^1H NMR spectra of a PMAA−PF−PMAA block copolymer (sample: entry 4) in DMSO-d_6 and D_2O ((∗) H_2O; (#) DMSO).

conjugated PF segments, as a chromophore, can contribute the characteristic luminescent properties to the final rod−coil block system, which is useful in examining the effect of the coils with different chemical functionalities on the photoluminescent behavior of PF segments. Furthermore, the photophysical characterization of the triblock copolymers is also helpful in understanding the solution behavior of the triblock copolymers.

The optical properties of PMAA−PF−PMAA and PTHPMA−PF−PTHPMA block copolymer were investigated by UV−vis and fluorescence spectroscopy (Fig-

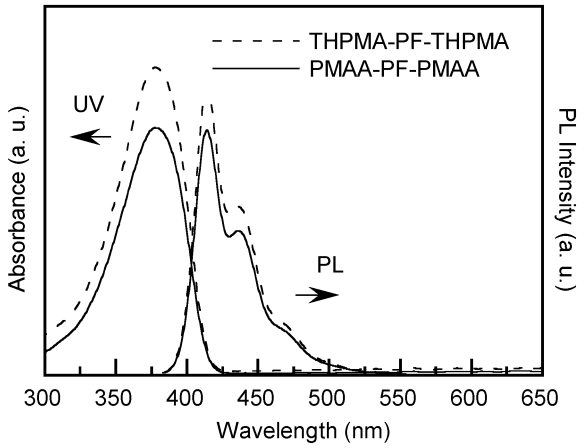


Figure 9. UV−vis and PL spectra of a PTHPMA−PF−PTHPMA and a PMAA−PF−PMAA in THF (sample: entry 4).

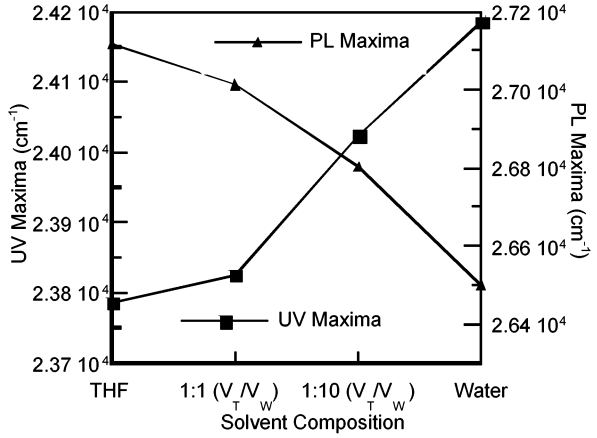


Figure 10. Dependence of the UV and PL maxima of a PMAA−PF−PMAA (sample: entry 4) on the solvent composition (V_T/V_W: volume of THF to water).

ure 9). The PMAA−PF−PMAA block copolymers exhibited a maximum absorption peak at 378 nm attributed to the $\pi-\pi^*$ transition derived from the PF segments which was almost identical with that of the PTHPMA−PF−PTHPMA, indicating the essentially identical electronic structures of the PF segments in the presence of either neutral or acidic coils in diluted solutions. The value is also very close to that of the reported PF oligomer with seven repeating units.[28] In the fluorescence spectra, both of the block copolymers gave strong emission peak located at 414 nm with two well-resolved vibronic shoulders, suggesting that similar radiational species are involved in their photoluminescence processes which is also supported by the extremely high values of the quantum efficiency of both cases ($\Phi_{PTHPMA} = 0.85$ and $\Phi_{PMAA} = 0.90$, as shown in Figure 11). Interestingly, the quantum efficiency of the PMAA−PF−PMAA solution was slightly higher than that of the PTHPMA−PF−PTHPMA, which may imply the suppression of the unfavorable radiationless transition by the telechelic PMAA coils.

As an amphiphilic triblock copolymer, PMAA−PF−PMAA presented interesting photophysical behavior in water. Although the triblock copolymers were insoluble in water, the aqueous solution of PMAA−PF−PMAA could be prepared by adding small amount of K_2CO_3 with stirring into the mixture to increase the solubility of the copolymer in water. The UV−vis and fluorescence

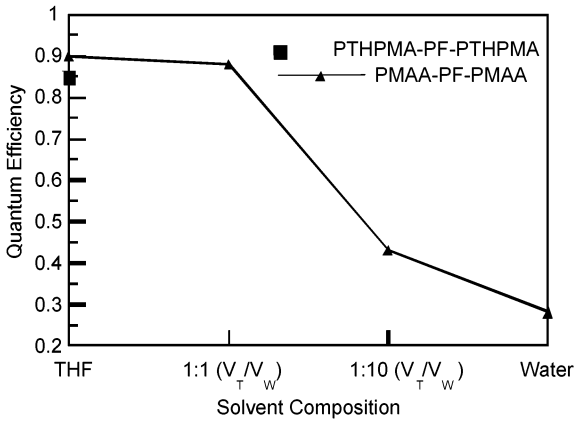


Figure 11. Dependence of the fluorescence quantum efficiency of a PMAA−PF−PMAA (sample: entry 4) on the solvent composition (V_T/V_W: volume of THF to water).

spectra of the PMAA−PF−PMAA in diluted solutions with different ratio of THF vs water are very similar in shape with different maxima of absorption and emission. Figure 10 shows the effect of the composition of the mixed solvents (THF and water) on the maxima of absorption and emission of a PMAA−PF−PMAA triblock copolymer. It can be seen that as more volume of water was introduced, a constant blue shift of the absorption maxima of the PMAA−PF−PMAA block copolymer was observed, suggesting the occurrence of the aggregation of the PF segments, which was found to be most prominent in the case of the pure water used as the solvent with a blue-shift up to 10 nm. On the contrary, as compared with the absorption spectra, the behavior of emission mixima showed the opposite behavior where a continuous bathochromic shift was detected, which may also derive from the formation of the aggregates of the PF segments. It should be noted that the changes in both absorption and emission spectra of the PMAA−PF−PMAA block copolymer in term of wavelength shifts due to the chromophore aggregation are not so prominent as the PPQ−PS systems, which may result from the less polarity of both ground and excited states of PF than those of PPQ−PS. However, such spectral modification would be more remarkable in polythiophene (PT) and poly(phenylene ethylene) (PPE) systems due to the stronger ground state and excited-state interactions, and the work is underway. In addition, the change of the emission species may also be reflected by measuring the fluorescence quantum efficiency (Φ_f). The calculated Φ_f values of a PMAA−PF−PMAA in the solutions are presented in Figure 11. A steady decrease of the Φ_f with the increase of the introduced water can be observed, which further demonstrates the presence of the aggregation. Such a behavior of these PMAA−PF−PMAA in water is very similar to that of our previously studied quaternized PDMAEMA−PF−PDMAEMA and can be readily explained by the dramatically different solubility of the PMAA and PF segments in water. We suggest that the PF aggregates may be stabilized by the PMAA that is solvated by water. The PF segments within the domain packed closely with each other, leading to a spectral modification

^{1}H NMR spectroscopy has been utilized to confirm the formation and structures of the amphiphilic block copolymers micelles. Because of the insoluble nature of the components within the micelle core, their NMR signals generally cannot be observed. Figure 8b presents

the ^{1}H NMR spectrum of a PMAA−PF−PMAA triblock copolymer in water. Only the peaks arising from the PMAA segment could be observed and those from the PF segment had totally disappeared, which strongly verifies the formation of the PF aggregates. Such a supramolecular assembly may be potentially useful to develop novel nanostructures with unique physicochemical and electronic properties in optioelectronic application.

Conclusion

In summary, amphiphilic PMAA−PF−PMAA triblock copolymers were successfully prepared by thermolysis of the precursor copolymers, PTHPMA−PF−PTHPMA prepared by atom transfer radical polymerization. The polymerization kinetics of the ATRP of THPMA was investigated, and both the first order kinetic plot and the dependence of the M_n on the monomer conversion were linear, indicating the polymerization of THPMA was generally controlled. The formation of the well-defined block structures was confirmed by SEC, ^{1}H NMR, ^{13}C NMR, and FTIR. The deprotection of the PTHPMA−PF−PTHPMA was successfully accomplished by thermolysis, and the PMAA−PF−PMAA triblock copolymers free of anhydride structures were obtained by further hydrolysis. The PF segments within the block copolymers were found to form aggregates in water as revealed by electronic spectroscopy and ^{1}H NMR studies.

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