Chemistry Letters Vol.38, No.8 (2009)

# Synthesis and Characterization of Functional ABA Block Polymer Containing Aniline Trimer

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An ABA block polymer, polyester-*b*-(aniline trimer)-*b*-polyester, was synthesized through the reaction of double amino-capped aniline trimer and 6-hexanolide, with stannous octoate as catalyst, via ring-opening polymerization in anhydrous toluene solution. The structure of the block polymer was characterized and verified by $^1$H NMR, FT-IR, and UV–vis spectroscopies, CV, and GPC. The molecular weight ($5.9 \times 10^3$ g mol$^{-1}$) calculated through $^1$H NMR was very close to the data collected by GPC ($M_n = 5.0 \times 10^3$, $M_w = 5.8 \times 10^3$, DMF as solvent). The polymer has good solubility in common organic solvents, such as THF and DMF. Both thermostability and electrostability of the block polymer are enhanced, compared to aniline trimer. Moreover, the polymer's sensitivity to pH value is superior to the stand-alone aniline trimer. The enhancement of both stability and sensitivity may give the block polymer more opportunities to be used as sensor material.

Polyaniline is a class of conducting polymer composed of nitrogen-connected benzenoid and quinoid units. It is one of the most extensively investigated conductive polymers because of its high conductivity, moderate stability, and inexpensive monomer resource. Polyaniline can be used as sensor material to detect many chemical substances at room temperature,[1] such as hydrochloric acid,[2] organic vapor,[3] and hydrazine,[4] because of its excellent electric conductivity performance. However, unmanageable and poor mechanical properties limit the practical applications of polyanilne seriously.

Oligoanilines, such as trimer, tetramer, and octamer have chemical structures similar to polyaniline and show chemical activity similar to polyaniline. The electrical conductivity of octamer aniline is very close to that of polyaniline.[5,6] Especially, oligoaniline can be obtained in pure state and without any structural defects. This is very important to clarify the relationship of the structure and properties.[7–9] However, the direct application of oligoaniline has some disadvantages: 1. because of low molecular weight, it can be dissolved in common solvents, and thus it would be slowly drained off in practical usage; 2. the lower molecular weight will also lower its stability. As a sensor material, response range, sensitivity and stability should be enhanced to guarantee the stability and repeatability of the sensor in practical applications.

In this letter, an ABA block polymer, polyester-*b*-(aniline trimer)-*b*-polyester, was synthesized via a ring-opening polymerization method. Compared to aniline trimer, both thermostability and electrostability of the block polymer are enhanced. Particularly, the sensitivity of a block polymer DMF solution to pH value is superior to the stand-alone aniline trimer. The color of the polymer solution can be changed from violet to cyan (from pH 7 to 5). When the pH value is adjusted from 7 to 8, the solution color is bleached greatly. However, the stand-alone aniline trimer responds only to acid solution, with the color from royal purple to turquoise.

The block polymer was synthesized through the following steps: double animo-capped aniline trimer (0.29 g, 1 mmol),[10] 6-hexanolide (3.42 g, 30 mmol), and stannous octoate (0.2 g) were put into a 50-mL round flask, followed by 20-mL anhydrous toluene. Then the reaction system was held at 120 °C for 24 h under argon. The product was precipitated from hexane and extracted with acetone for 24 h. The final block polymer, grey powder, was dried under vacuum for 24 h at room temperature with the yield about 80%.

$^1$H NMR of the block polymer was recorded on a Mercury-Plus 300 in DMSO-$d_6$ solvent. The proton ascription can be found in Figure 1. According to the integral area proportion of the proton 3 and 7, we can work out the molecular weight of the block polymer, ca. 5900 g mol$^{-1}$. The NMR result is very close to the data collected by GPC ($M_n = 5.0 \times 10^3$, $M_w = 5.8 \times 10^3$, single peak, DMF as eluent, see GPC graph in Supporting Informatino).[12] These results indicate that there is no free aniline trimer in the block polymer we synthesized.

In the infrared spectrum (Figure 2), aniline trimer has a broad peak at 3200–3400 cm$^{-1}$, representing its two end amino groups. After reaction with 6-hexanolide, the peak shape

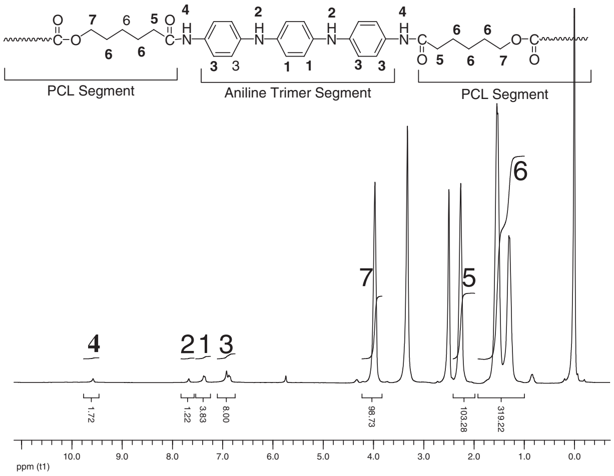

**Figure 1.** $^1$H NMR spectra for ABA block polymer, in DMSO-$d_6$.

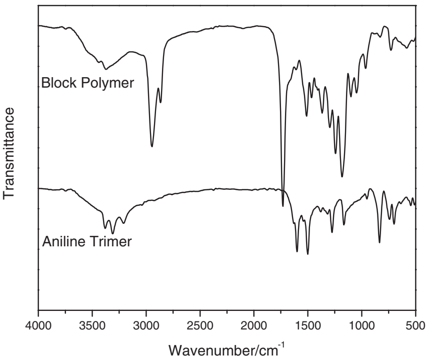

**Figure 2.** FT-IR spectra of aniline trimer and ABA block polymer, KBr plate.

changed, representing the change from amino to imino groups. The strong bands at ca. 2900 cm$^{-1}$ are attributed to the presence of aliphatic sp$^3$ (PCL segment) C–H stretching, while the bands at ca. 1090 cm$^{-1}$ for C–O stretching arise from PCL segment. The band at ca. 1730 cm$^{-1}$ represent the carbonyl groups. The typical quinoid and benzenoid ring stretching at ca. 1600 and 1500 cm$^{-1}$ as well as C–N stretching at 1310 and 1220 cm$^{-1}$ remain, indicating that the characteristics of the aromatic chain in the block polymer are completely analogous to those of aniline trimer.[11] These results show that the reaction only occurs at the end groups of aniline trimer.

The thermostability was tested by thermogravimetric analysis under nitrogen atmosphere with a heating rate at 20 °C min$^{-1}$. The aniline trimer lost weight gradually over 100–300 °C, maybe resulting from the instability of the end amino groups. Over the range of 300–500 °C, aniline trimer lost weight quickly, representing the decomposition of the aniline segments. The block polymer obtained was very stable up to 300 °C, indicating that thermal stability was enhanced by the aniline trimer protected by PCL segments.[12]

The electrical chemical stability was investigated by cyclic voltammetry (Figure 3). In 1.0 M $H_2SO_4$ with a scan rate at 100 mV s$^{-1}$, both aniline trimer and the block polymer were tested. They have similar electrical chemical properties, with similar redox potential, indicated both of them have similar chemical structure (conjugated segment and aniline segment). From the cumulative CV curves, we can see that the electrical chemical stability of the block polymer is much better than that of the stand-alone aniline trimer.

The most interesting thing is that the block polymer DMF solution can show different color at different pH value. The solution of the stand-alone aniline trimer was royal purple when pH value was 7 and 8. When the pH value was adjusted to 5, the color of its solution changed to turquoise. In its UV spectra (Figure 4), a new peak at 410 nm appeared and the peak 570 nm was shifted to 730 nm. As for the block polymer, the color of the solution can be changed to different color at pH 8 (the color bleached greatly compared to pH 7, violet) and pH 5 (cyan). These changes were reflected in polymer UV spectra. When the pH value changed from 7 to 8, the peak at 530 nm shifted to 672 nm and the intensity was enhanced greatly. When the pH value was adjusted from 7 to 5, the peak at 530 nm shifted to 570 nm with similar intensity, and a new peak at 420 nm appeared. What causes of these changes is still not clear. We speculate these changes could result from the amphipathicity of the block polymer (PCL segment vs. aniline trimer segment).

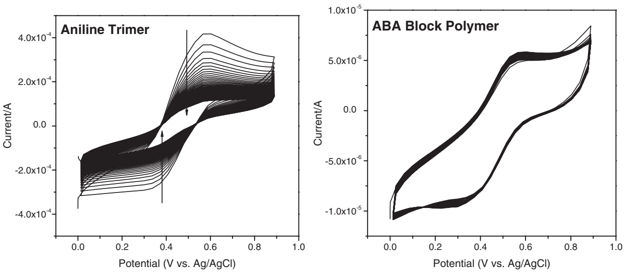

**Figure 3.** Cumulative CV curves of aniline trimer and ABA block polymer in 1 M $H_2SO_4$ with a scan rate of 100 mV s$^{-1}$.

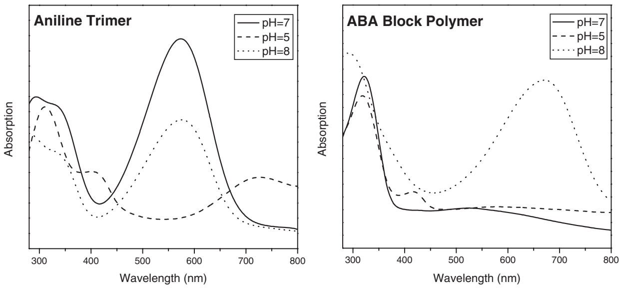

**Figure 4.** UV–vis spectra of aniline trimer and polymer obtain in DMF solution with different pH value.

In summary, an ABA block polymer, polyester-*b*-(aniline trimer)-*b*-polyester, has been synthesized successfully. The characteristics of aromatic chains in the block polymer are completely analogous to those of the stand-alone aniline trimer. After the aniline trimer is protected by polyester, both thermostability and electrostability are enhanced. Moreover, the sensitivity to pH value of the polymer is much better than that of aniline trimer.

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12 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

Published on the web (Advance View) July 25, 2009; doi:10.1246/cl.2009.840