Pyrene Functional Poly(vinyl alcohol) by "Click" Chemistry

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ABSTRACT: Side-chain pyrene functional poly(vinyl alcohol) (PVA) was synthesized by using "click chemistry" strategy. First, partial tosylation of PVA with *p*-toluene sulfonyl chloride were performed. The resulting PVA-*Ts* polymer was then quantitatively converted into poly(vinyl alcohol)-azide (PVA-N_3) in the presence of NaN_3/DMF at 60 °C. Propargyl *pyrene* was prepared independently as a photoactive click component. Finally, azido functionalized PVA was coupled to propargyl *pyrene* with high efficiency by click chemistry. Incorporation of pyrene functionality in the resulting polymer was confirmed by spectral analysis. It is also shown that pyrene functionalized PVA (PVA-*Py*) exhibited characteristic fluorescence properties and improved solubility in highly polar solvents such as water, DMSO, and DMF as well as less polar solvent such as THF compared with pristine PVA. © 2009 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 47: 1317–1326, 2009

Keywords: "click"; chemistry; fluorescence; functionalization of polymers; photoreactive effects; polymer modification; poly(vinyl alcohol); pyrene

INTRODUCTION

Poly(vinyl alcohol) (PVA), a polyhydroxy polymer, is the largest volume, synthetic water-soluble resin produced in the world. The excellent adhesion capacity of PVA to cellulosic materials makes it useful as an adhesive and coating material, highly resistant to solvents, oil, and grease. The excellent chemical resistance and physical properties of PVA resins have resulted in broad industrial use such as textile sizing, adhesives, protective colloids for emulsion polymerization, fibers, production of poly(vinyl butyral), and paper sizing.[1]

PVA can be comparatively easily derivatized via the hydroxyl groups in a manner similar to other secondary polyhydric alcohols. The most common PVA modifications reactions are esterification and etherification of the hydroxyl groups. Esterification of PVA with acid chlorides,[2–4] anhydrides,[5–9] and carboxylic acid active esters[10] has been widely used. The ester bond is, however, easily hydrolyzed, and chemical modification with ether linkages may be an alternative approach. More recently, Hilborn and coworkers[11] reported partial functionalization of the PVA hydroxyl groups via carbamate linkages which allowed introduction of azide groups to one PVA component as well as alkyne groups to the other one was further shown to yield transparent hydrogels upon mixing these components in the presence of the copper(I) catalyst via "click" chemistry.

The "click"-type reactions, mainly exemplified by Huisgen[12] 1,3-dipolar azide-alkyne, [3 + 2], or Diels-Alder cycloadditions,[13] [4 + 2], have attracted much attention because of their important features including high yields, high tolerance of functional groups, and selectivity.[14] Thiol-ene chemistry[15] has recently been introduced as an

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alternative click route that can be performed at moderately low temperatures by using photoinitiators. Huisgen 1,3-dipolar cycloaddition occurs between an alkyne and an organic azide to give 1,2,3-triazole ring. The reactions can be performed under mild experimental conditions[14,16] when catalyzed by copper (I). "Click" reactions have been extensively used in the synthesis of polymers with different composition and topology, ranging from linear (telechelic,[17] macromonomer,[18] and block copolymer[19]) to nonlinear macromolecular structures (graft,[20] Star,[21] miktoarm star,[22] H-type,[23] dendrimer,[24] dendronized linear polymer,[25] macrocyclic polymer,[26] self-curable polymers,[27] and network system[28]).The development and the application of "click" chemistry in polymer and material science have recently been reviewed extensively.[29]

Pyrene containing polymers received interest because of their potential use as semiconductors, photoresist materials, and fluorescent probes.[30] Various methods have been developed to attach pyrene moieties to polymers. For instance, living anionic[31–33] and conventional and atom transfer radical polymerization[34–36] processes were successfully applied to prepare polymers with pyrene termini.

We now report a versatile method to synthesize pyrene functional PVA directly from the bare PVA using "click" reaction. Previous works within this department have shown the suitability of this process for making thermally curable polystyrenes[27] and poly(vinyl chloride) (PVC)[37] starting from poly(styrene-*co*-chloromethylstyrene) and the bare PVC, respectively.

EXPERIMENTAL

Materials

Chloroform (≥99%, Sigma), dimethylformamide (DMF, ≥99%, Aldrich), ethanol (>99.5%, Aldrich), tetrahydrofuran (THF, 99.8%, J.T. Baker), diethylether (≥98%, Sigma-Aldrich), methanol (99%, Acros Organics), dimethyl sulfoxide (DMSO, ≥99%, J.T. Baker), PVA (BDH Chemicals, Ltd.) (Mn [1/4] 63,000, PDI [1/4] 2.17), anhydrous pyridine (99.5%, Lab-Scan), sodium azide (98.5%, Carlo-Erba Reagent), copper(II) sulfate ($CuSO_4.5H_2O$) (≥98%, Fluka), L-ascorbic acid sodium salt (99%, Acros), toluene-4-sulfonic acid monohydrate (PTSA, 99%, Fluka), sodium hydride (98%, Fluka), propargyl bromide (~80 vol % in toluene, Fluka), and 1-pyrene methanol (98%, Sigma-Aldrich) were used as received.

Characterization

^1H NMR spectra were recorded in DMSO-d_6 and $CDCl_3$ with $Si(CH_3)_4$ as internal standard, using a Bruker AC250 (250.133 MHz) instrument. Fourier transform infrared spectrometer (FTIR) spectra were recorded on a Perkin-Elmer FTIR Spectrum One spectrometer.

Fast transient fluorescence measurements were performed using Photon Technology International's Strobe Master System. During the fluorescence lifetime measurements, pyrene molecules were excited at 340 nm and fluorescence decay profiles were obtained at 390 nm for various temperature. Steady-state fluorescence measurements were carried out using a Perkin–Elmer Model LS-50 Spectroflurimeter. All measurements were made at 90° position and slit widths for excitation and emission were both kept at 15 nm. *In situ* experiments were performed in 1 cm × 1 cm quartz cell at various temperatures. During the fluorescence measurements, the wavelength of the excitation light was kept 340 nm and pyrene emission intensities at wavelength of 390 nm were monitored for several temperature. Thermal gravimetric analysis (TGA) was performed on Perkin-Elmer Diamond TA/TGA with a heating rate of 10 °C min under nitrogen flow.

Synthesis and Modification

Partial Tosylation of PVA

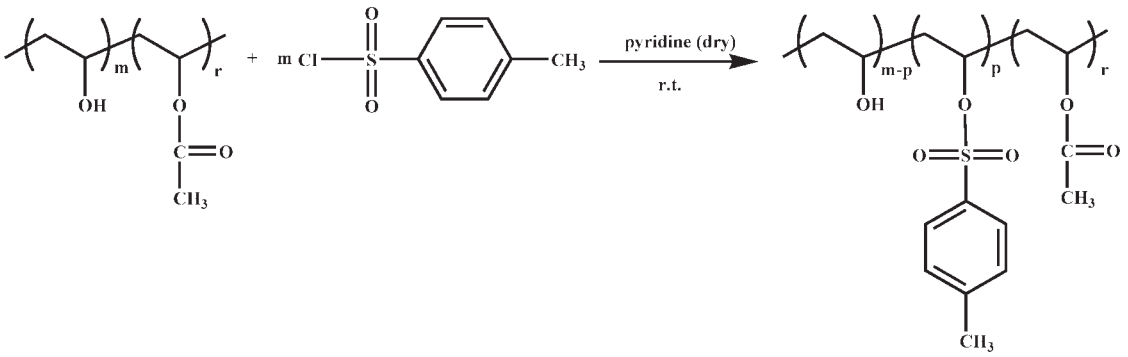
Partial tosylation of PVA (PVA-*Ts*) with *p*-toluene sulfonyl chloride (*p*-TsCl; 1:1; in terms of hydroxyl moieties) in the presence of anhydrous pyridine at room temperature[38] yielded 10% PVA-*Ts*.

Synthesis of PVA-N_3 Coploymer

PVA-*Ts* was dissolved in *N,N*-dimethylformamid (DMF), NaN_3 (two times excess to the mole of tosyl of PVA was added. The resulting solution was allowed to stir at 65 °C for 2 days and precipitated into diethylether (10 times excess).

Synthesis of Propargyl Pyrene

To a solution of pyrene methanol (1.0 g, 4.3051 mmol) in dry 20 mL of THF was added to sodium hydride (60 wt % dispersion in oil) (0.113 g, 4.7356 mmol) and the reaction mixture was



Scheme 1. Partial tosylation of PVA.

stirred at 0 °C under nitrogen for 30 min. A solution of propargyl bromide (0.5633 g, 4.7356 mmol) in toluene was added portion wise to the solution. The mixture was kept stirring at room temperature for 24 h. Then it was refluxed for 3 h in the dark. The resulting mixture cooled to room temperature and evaporated to half of its volume. The solution was extracted with ethyl acetate, and the organic layer was dried over anhydrous $MgSO_4$. Evaporating ethyl acetate afforded light yellow product. The crude product was dissolved in toluene and was passed through a column of basic silica gel to remove unreacted pyrene methanol. Toluene was removed by evaporating and the residue was dried in vacuum oven (Yield: 55%).

Synthesis of PVA Containing Pyrene Side-Group (PVA-Py)

In a flask, PVA-N_3 (0.10 g), propargyl *pyrene* (0.1231 g, 0.45 mmol) dissolved in 5 mL of DMSO. Freshly prepared aqueous solution of sodium ascorbate (0.068 g, 0.34 mmol) was added followed by aqueous solution of copper(II) sulfate pentahydrate (0.017 g, 0.068 mmol), so that the final concentrations of sodium ascorbate and copper(II) sulfate pentahydrate in the mixture 30 and 6 mM, respectively. The ratio of azide and alkyne groups was 1. The mixture stirred for 2 days of ambient temperature. Functionalized polymer precipitated in diethyl ether (10 times excess), filtered and dried under vacuum.

RESULTS AND DISCUSSION

Synthesis and Characterization of Tosyl Functional PVA

In the scope of this study, our main goal was to introduce "click" chemistry approach for the modification of PVA. As stated in the introduction section, previous reports on the introduction of azide groups to PVA as the major click component involves an indirect route in which hydroxyl antagonist molecule possessing azide group was prepared separately. However, this approach has some limitations such as involvement of several independent steps and explosive nature of the azidation particularly on low molar mass compounds.[39]

In this study, we report a versatile method which allows converting hydroxyl groups into azide functionality by a simple two-step reaction performed only on PVA. For this purpose, partial tosylation of PVA with *p*-toluene sulfonyl chloride (*p*-TsCl; 1:1; in terms of OH-moieties) were

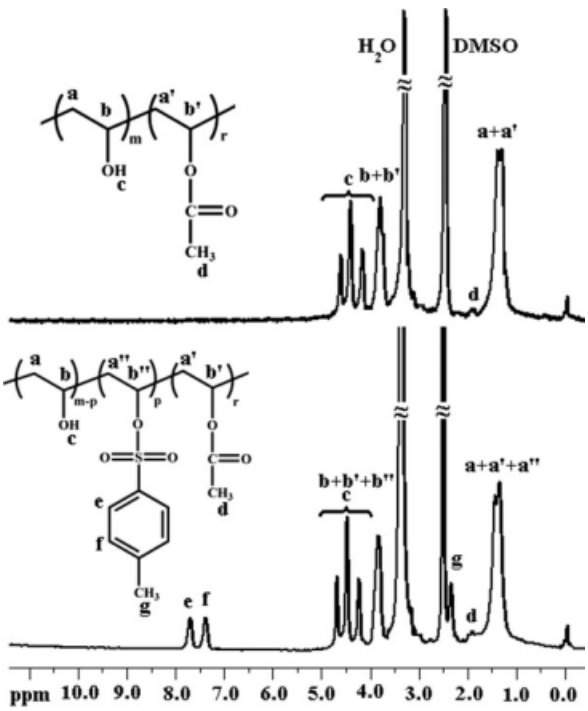
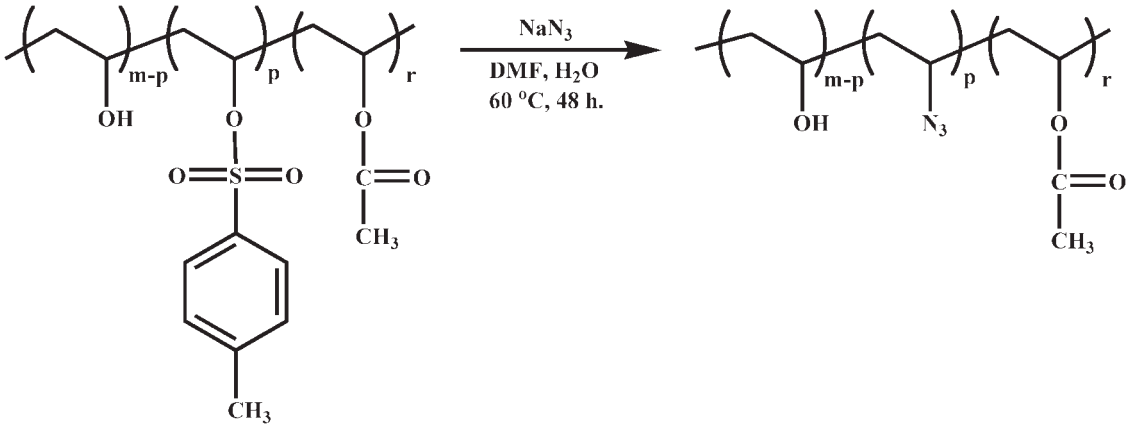


Figure 1. ^{1}H NMR of PVA and PVA-*Ts* in d_6-DMSO.



Scheme 2. Synthesis of azide functional PVA.

conducted as described in experimental section to obtain PVA with tosyl pendant groups (PVA-*Ts*) (Scheme 1).

Primarily, the extent of the modification was determined. In the ^{1}H NMR spectrum of PVA-*Ts*, the new signals corresponding to CH_3 protons adjacent to phenyl ring at 2.34 ppm and the aromatic protons of *p*-toluene sulfonyl group between 7.38 and 7.85 ppm were detected (Fig. 1). The signals at δ 3.69–4.00 and δ 1.19–1.78 ppm belong to resonances of the methine and metylene protons in the main chain. Protons corresponding to OCOCH_3 group from acetyl of pristine PVA appear at 1.8 ppm.

The composition of the polymers can be calculated by using the following equations:

$$\%\mathrm{Ts} = I\mathrm{Ar}100/4I\mathrm{CH} \text{ and}$$

$$\%\mathrm{OCH_3} = I\mathrm{OCH_3}100/3I\mathrm{CH}$$

where %Ts and %OCCH$_3$ represent the amount of units with tosyl and acetyl groups, respectively, and *I*Ar, *I*OCH$_3$, and *I*CH represent the intensities of the integrals corresponding to the *p*-toluene sulfonyl, the OCCH$_3$ and CH protons of the main chain, respectively. The content of acetyl units of the starting PVA is about 2.82%. After the tosylation, the content of tosyl groups is determined to be 10.03%.

Synthesis and Characterization of Azide Functional PVA

The resulting PVA-*Ts* polymer was then quantitatively converted into PVA-N_3 in the presence of NaN$_3$/DMF at 60 °C (Scheme 2). Functionalization was kept deliberately at low level so as to preserve PVA properties.

In the ^{1}H NMR spectrum, the disappearance of the signals at δ 7.38–7.85 and 2.34 ppm corresponding to aromatic and CH_3 protons of *p*-toluene sulfonyl side groups was indicative of quantitative conversion (Fig. 2). Successful azidation was further supported by the observation of the azide stretching band at 2094 cm^{-1} in the FTIR spectrum of PVA-N_3.

Synthesis and Characterization of Propargyl *Pyrene*

Propargyl *pyrene,* possessing both click functional group and chromophoric pyrene moiety, was prepared according to the following reaction (Scheme 3).

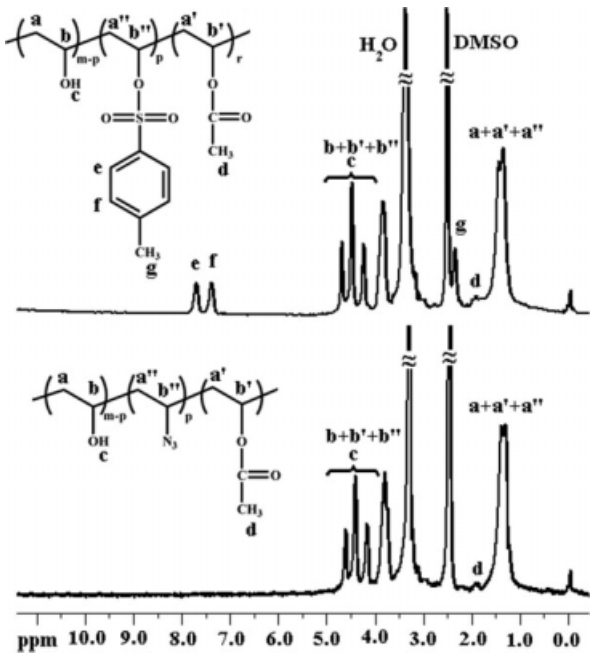
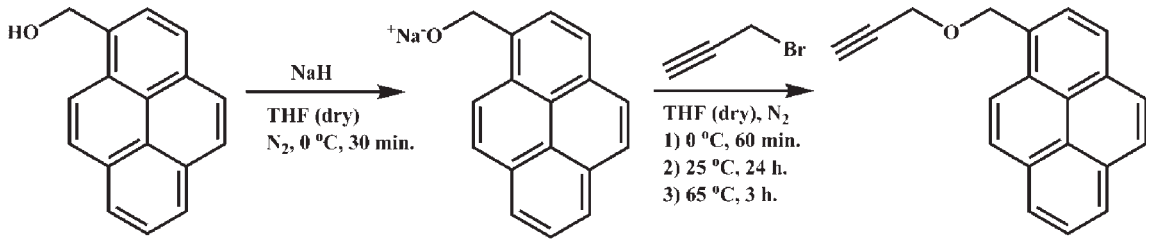


Figure 2. ^{1}H NMR of PVA-*Ts* and PVA-N_3 in d_6-DMSO.



Scheme 3. The synthesis of propargyl *pyrene*.

The chemical structure of propargyl *pyrene* was confirmed by both ^{1}H NMR and FTIR. The ^{1}H NMR spectrum of propargyl *pyrene* showed two signals at 4.34 and 5.25 ppm which are assigned to C*H*$_2$ protons adjacent to pyrene ring and propargyl moiety, respectively. Notably, *H*C≡C proton of propargyl moiety and DMSO overlap and appear at 2.50 ppm. Also, aromatic protons of pyrene were detectable at 7.04–8.42 ppm (Fig. 3). In the FTIR spectrum, propargyl group was evidenced by characteristic bands of H—C≡C and —C≡C— appeared at 3277 and 2121 cm^{-1}, respectively.

Synthesis and Characterization of Pyrene Functional PVA

For the desired click process, the PVC-*N*$_3$ was dissolved in DMSO and reacted with propargyl *pyrene* in the presence of aqueous solution of sodium ascorbate and copper(II) sulfate pentahydrate at room temperature (Scheme 4). The modified polymer was precipitated in diethyl ether and dried under vacuum.

Evidence for the occurrence of the "click" reaction is obtained from ^{1}H NMR and FTIR spectroscopy. The extent of conversion of the side azido moieties to triazoles was monitored by observing the appearance of the new methylene protons adjacent to the triazole and pyrene ring at 4.10 and 5.26 ppm (triazole-C*H*$_2$—O—C*H*$_2$-Py) and the triazole proton (*N*—CH=C—) at 7.56 ppm. The peaks between 8.12 and 8.42 ppm, characteristic for aromatic protons of pyrene were also noted (Fig. 4).

Moreover, in the IR spectrum, the band corresponding to -N$_3$ group at 2105 cm^{-1} completely disappeared (Fig. 5). These spectral characterizations clearly indicate that the side group click reaction was efficient, and near-quantitative functionalization was achieved.

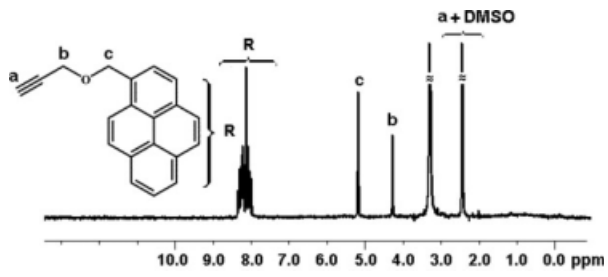


Figure 3. ^{1}H NMR of propargyl *pyrene* in d_6-DMSO.

Fluorescence Analysis

Playing the predominant role in labeling polymers, the fluorescence properties of the pyrene units incorporated to PVA side-chains are important and were also studied. The fluorescence spectrum of diluted solution of PVA-Py in DMSO excited at $\lambda_{exc} = 350$ nm showed vibrational structures of pyrene chromophore (Fig. 6). The observed emission property of PVA obtained this way is a striking advantage particularly for biomedical applications involving various polymer matrix-specific molecule interactions.

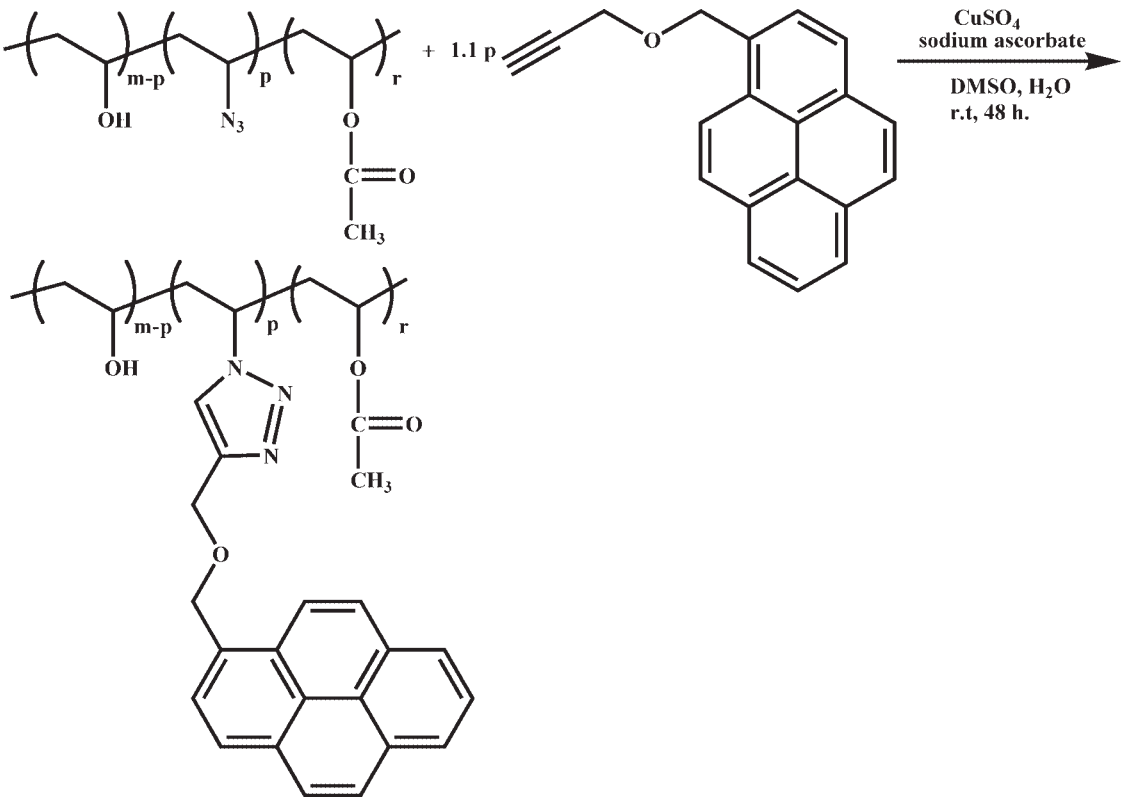
Fluorescence Lifetime Measurements

The typical temperature dependent fluorescence decay curves of PVA-*Py* in DMSO at several temperatures is presented in Figure 7. It is seen that PVA-*Py* decays faster as the temperature is increased. Fluorescence decay curves were fitted to a single exponential.

$$I_p = A \exp(-t/\tau)$$

where τ is pyrene lifetime and A is the corresponding amplitude of decay curves. Here, it has to be noted that lifetime of pyrene, τ corresponds to the mobility of the PVA-*Py* chains in DMSO. Figure 8 shows a decay curve and weighted residuals.

Measured lifetimes of propargyl *pyrene* and PVA-*Py* are presented in Figure 9, respectively. As seen in Figure 7, when the temperature increased the excited pyrenes decay faster and



Scheme 4. "Click" reaction of PVA-N_3 with propargyl *pyrene*.

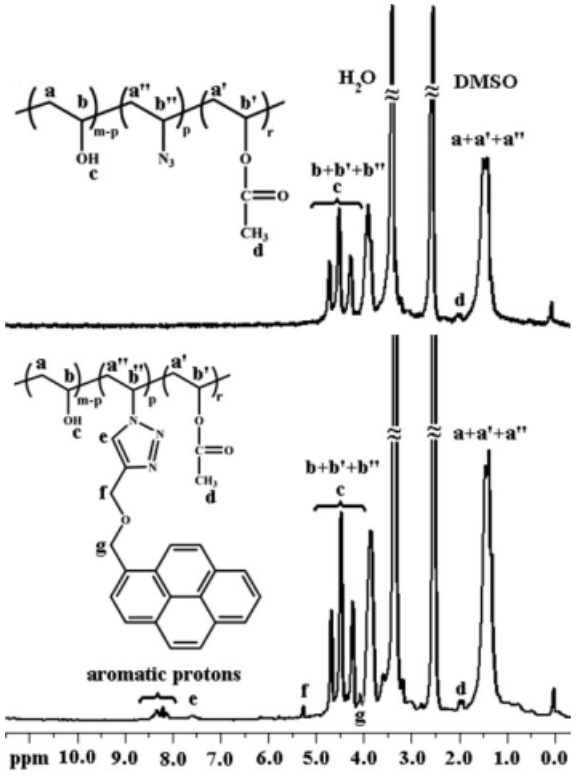


Figure 4. ^{1}H NMR of PVA-N_3 and PVA-*pyrene* in d_6-DMSO.

faster, indicating a probable collision between molecules which essentially results in fluorescence quenching. In another words, the DMSO acts as an energy sink for rapid vibrational relaxation which occurs after the rate-limiting transition from the initial state. An excellent linear relationship was observed between the lifetime

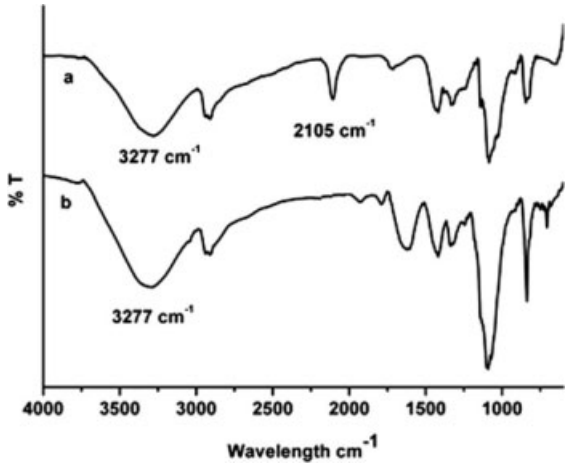


Figure 5. FTIR spectra of PVA-N_3 (a) and PVA-*Py* (b).

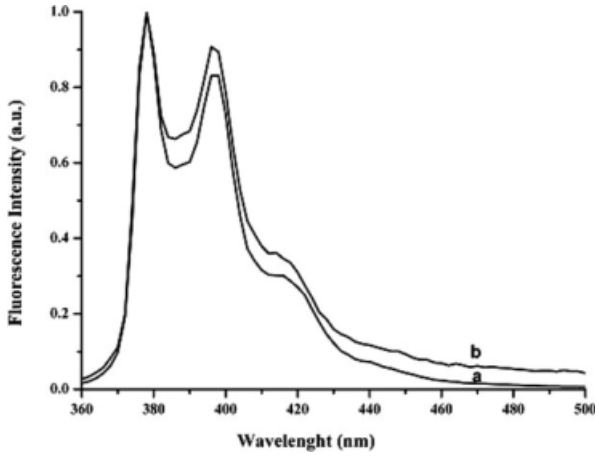


Figure 6. Emission spectra of propargyl *pyrene* and PVA-*Py*; $\lambda_{exc} = 350$ nm. The concentrations are 10^{-6} M in terms of pyrene moieties.

values of pyrene and temperature in the range of 22–75 °C. The linear regression equation of the calibration graphs and a linear regression correlation coefficients were found to be $\tau = 338.96 - 0.8237$ and $\tau = 347.98 - 0.856T$, and 1 and 0.975 for propargyl *pyrene* and PVA-*Py,* respectively. These findings clearly indicate that free pyrene (propargyl *pyrene*) is more (even if slightly) mobile than attached one as expected.

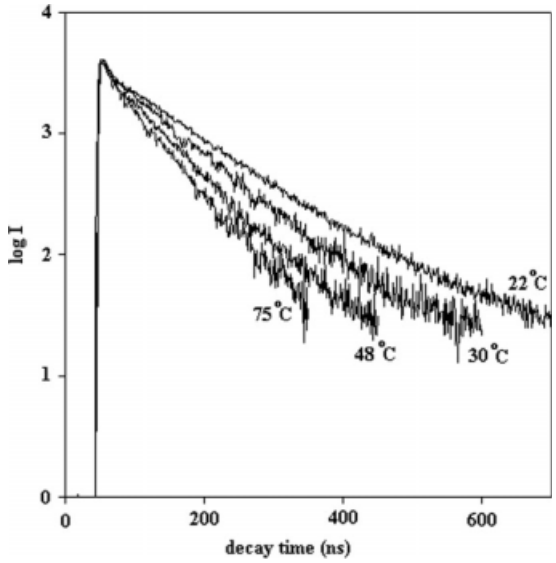


Figure 7. Fluorescence decay profiles of PVA-*Py* in DMSO. Number on each decay curve presents solution temperature.

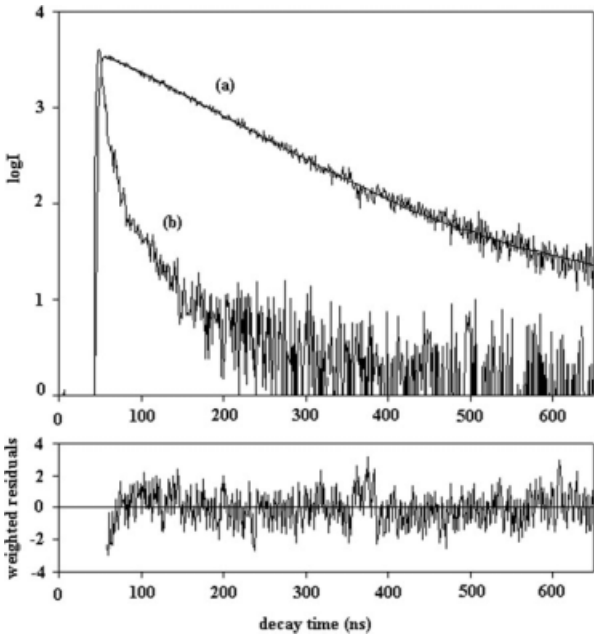


Figure 8. Fluorescence decay curve of PVA-*Py* (a) in DMSO and the incident light pulse (b).

Temperature Dependence of the Fluorescence Emission Intensity of PVA-Py

Figure 10(a,b) show typical temperature dependent fluorescence emission spectra of *PVA-Py* (2×10^{-5} M) in water and propargyl *pyrene* (1×10^{-5} M) in DMSO at several temperatures, respectively.

The fluorescence emission intensity of PVA-*Py* decreased as the temperature increased. This

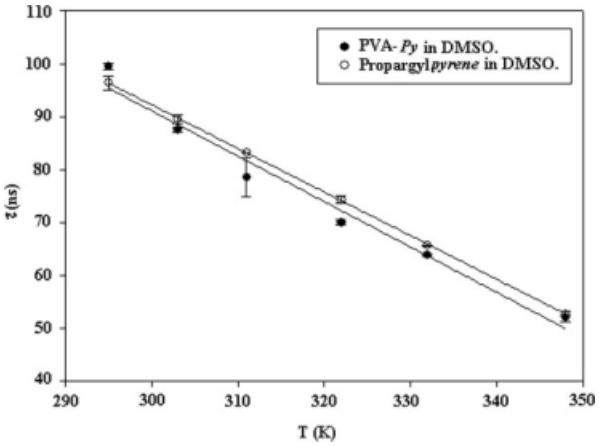


Figure 9. The plots of the measured pyrene lifetimes (propargyl *pyrene* and PVA-*Py*), τ versus temperature.

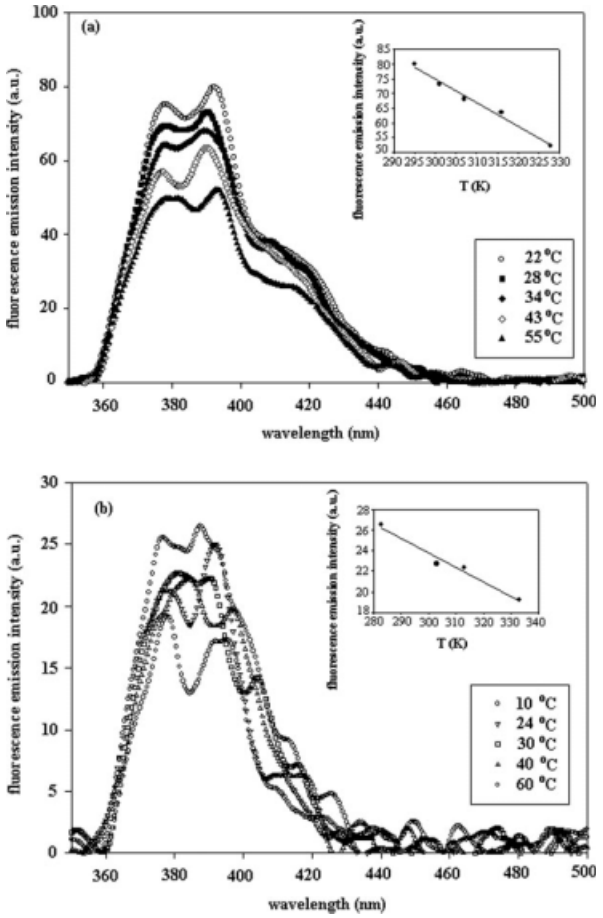


Figure 10. Fluorescence emission spectra of PVA-*Py* in water (a) and propargyl *pyrene* in DMSO (b) for various temperature. Linear dependency of fluorescence intensity versus temperature is also presented in inset.

behavior is mainly controlled by a radiationless temperature-dependent process. As the temperature increases, probable collision among molecules results in fluorescence quenching and intersystem crossing reinforced with increasing temperature. Decreasing the fluorescence emission intensity should be a result of a convolution among photophysical process dependent on concentration, bimolecular quenching, unimolecular rate process, and photochemical processes decreasing the chromophore concentration and mobility of polymer chains.[40] An excellent linear relationship between the fluorescence emission intensity and temperature was observed and calibration graph was obtained by linear regression process. Obtained calibration equation are Flu $= 314.53 - 0.798T$ with a linear regression correlation coefficients of 0.9885 and Flu $= 66.93 - 0.142T$ with a linear regression correlation coefficients of 0.975 for propargyl *pyrene* and PVA-*Py,* respectively, (*Flu* stands for relative fluorescence intensity).

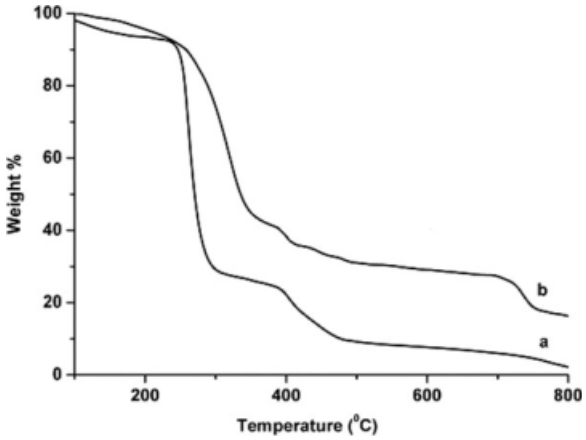


Figure 11. TGA curves of PVA (a) and PVA-*Py* (b) recorded under nitrogen at heating rate of 10 °C/min.

Thermal Analysis

Thermal stability of the PVA-*Py* was investigated by TGA and compared with pristine PVA. The TGA curves are presented in Figure 11 and weight loss behaviors of the species are tabulated at Table 1. TGA data showed that the degradation for the bare PVA and pyrene functionalized PVA begins at temperatures close to 210 °C indicating that the general thermal degradation pattern of PVA was not influenced by the incorporation of pyrene units. On the other hand, the thermal data also reveals that the char yield of the PVA-*Py* is enhanced approximately four folds compared to unreacted PVA because of the presence of more rigid and bulky pyrene group. Another noticeable feature is that the weight loss difference at 800 °C between the polymer before and after modification. Interestingly, this value corresponds to the pyrene content of the polymers.

Table 1. Thermal Properties of PVA-*Py* and PVA

Polymer	$T_{5\%}$[a] (°C)	$T_{10\%}$[b] (°C)	$T_{d\ max}$[c] (°C)	Y_c[d] at 800 °C (%)
PVA-*Py*	209.1	257.8	241.0	16.3
PVA	211.0	251.3	218.4	4.1

[a] $T_{5\%}$: The temperature for which the weight loss is 5%.
[b] $T_{10\%}$: The temperature for which the weight loss is 10%.
[c] $T_{d\ max}$: Maximum weight loss temperature.
[d] Y_c: Char yields.

Table 2. Solubility[a] of PVA, PVA-N_3, and PVA-*Py* in Solvents Ranked According to Dielectric Constants

Solvent Type	Dielectric Constants[b]	PVA	PVA-N_3	PVA-*Py*
Water	80	SS	S	S
DMSO	46	S	S	S
DMF	36	SS	S	S
THF	7.6	NS	SS	SS

[a] Three milligram of polymer in 4 ml of solvent; solubility observed after 5 h.
[b] At 20 °C.
S, soluble; SS, slightly soluble; NS, nonsoluble.

Solubility of Modified PVA

The modification drastically changes the solubility behavior of PVA as the process results in a decrease in the number of hydroxyl groups contributing to strong intra- and intermolecular hydrogen bonding. As can be seen from Table 2, the polymer with 10% modification is soluble in highly polar solvents such as water, DMSO, and DMF as well as in the less polar solvents such as THF.

CONCLUSIONS

In summary, we have demonstrated pyrene chromophoric groups can readily be incorporated to PVA. The process involves the synthesis of azide functionalized PVA and subsequent click reaction of these functional groups with propargyl *pyrene*. The strategy adopted in this study appears to be entirely satisfactory in terms of efficiency and simplicity. Successful functionalization was confirmed by FTIR, ^{1}H NMR and fluorescence spectroscopic analyses. Such functionalization has brought about improved solubility and functionalized PVA is highly soluble in a range of solvents with different polarity. Further studies to use pyrene labeled PVA in biomedical applications such as fluorescence monitoring of drug release process from PVA matrix, fluorescence temperature sensor are now in progress together with the efforts to expand this approach to other functionalities.

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