# Synthesis and Characterization of Poly(4-diphenylaminostyrene)-Poly(9-vinylanthracene) Binary Block Copolymer

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**ABSTRACT:** Block copolymerization of plural types of monomers offers a new opportunity for the preparation of a variety of multifunctional polymers. Poly(4-diphenylaminostyrene) (PDAS)-poly(9-vinylanthracene) (PVAN) binary block copolymer (PDAS-PVAN) was synthesized by (living) anionic polymerization using the benzyllithium/*N,N,N′,N′*-tetramethylethylenediamine system. The photoluminescence emission of PDAS-PVAN was enhanced by the fluorescence resonance energy transfer from PDAS block to PVAN block in PDAS-PVAN. The hole drift mobility of the copolymer was controllable by the amount of triphenylamino groups in the polymer chain. The optical and electrical properties of PDAS-PVAN were adjustable through the polymer chain structure. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 69–73, 2010

**Key words:** anionic polymerization; block copolymers; fluorescence; living polymerization; structure-property relations

## INTRODUCTION

Poly(4-diphenylaminostyrene) (PDAS), also known as poly(4-vinyltriphenylamine), has been recognized as an attractive hole-transport semiconducting polymer for optoelectronic applications.[1–11] However, the controlled polymerization of 4-diphenylaminostyrene (DAS), a monomer of PDAS, has been considerably difficult by all conventional methods, including anionic,[1,3] radical and living radical[1,2,4–11] polymerization. PDAS with a well-defined and controlled polymer chain structure was not obtained in previous studies.

Recently, we attempted the anionic polymerization of DAS to obtain PDAS with a well-defined and controlled polymer chain structure, and as a result, the first example of living anionic polymerization of DAS was successfully developed using the benzyllithium (BzLi)/*N,N,N′,N′*-tetramethylethylenediamine (TMEDA) system (Scheme 1).[12–14] Furthermore, the stereoregularity of the PDAS polymer chain was revealed.[12,14] Subsequently, it was found that the BzLi/TMEDA system could anionically polymerize 9-vinylanthracene (VAN) at moderate temperatures in hydrocarbon solvents, although the limitations of yield and the number average molecular weight ($M_n$) were around 90 wt % and 2000 (g/mol), respectively. The poly(9-vinylanthracene) (PVAN) obtained exhibited good luminescent properties.[15] Polymer chemists are well aware that living anionic polymerization offers good conditions for the preparation of block copolymers via step-by-step polymerization reactions with plural types of monomers. Therefore, it was suggested that PDAS-PVAN block copolymers could be prepared using the BzLi/TMEDA system in hydrocarbon solvents as new semiconducting polymer with good luminescent properties.

In this article, we report the first example of synthesis of the PDAS-PVAN binary block copolymer (PDAS-PVAN) with the BzLi/TMEDA system in a hydrocarbon solvent. The optical and electrical properties of the copolymer are also described.

## EXPERIMENTAL

### Materials

Toluene (≥99.8%), and TMEDA (≥99.5%) were refluxed over calcium hydride ($CaH_2$, 95%) and then distilled under dry argon. *tert*-Butyllithium (*t*-BuLi; 1.70 mol/L in pentane) and methanol (MeOH, ≥99.9%) were used without further purification. DAS was prepared via a previously reported standard Wittig reaction.[12] VAN (97%) was dried under reduced pressure. All reagents were purchased from Aldrich.

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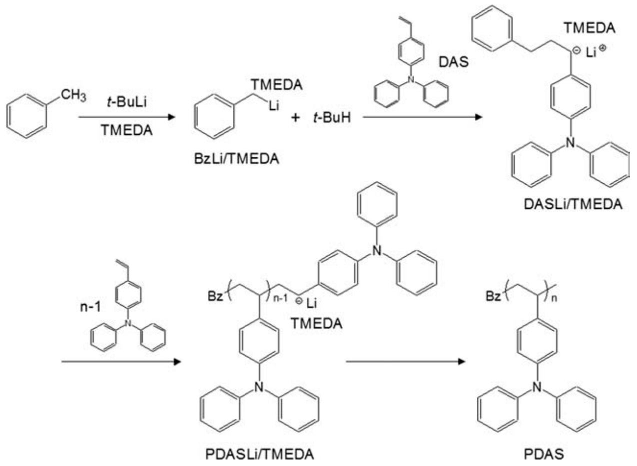


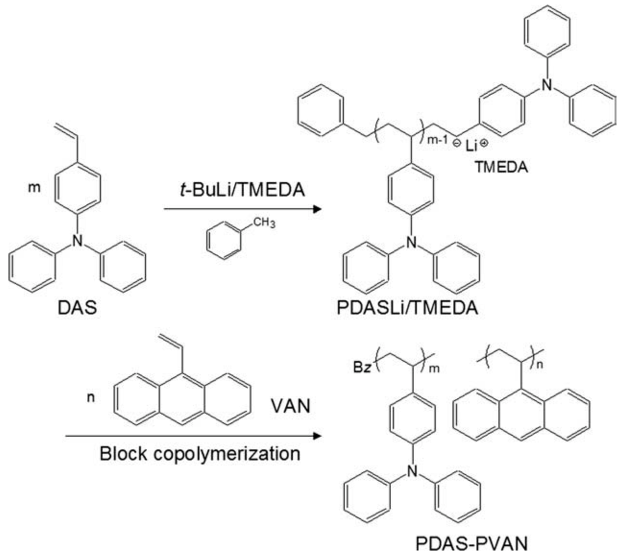
**Scheme 1** Living anionic polymerization of DAS using the BzLi/TMEDA (1.00/1.25) system.

## Polymerization

A well-dried 50 mL Schlenk tube was purged with dry argon and 5.0 mL of toluene was injected at room temperature (ca. 25°C) using a syringe. *t*-BuLi was supplied to the solution with a syringe and TMEDA was then added to the solution under dry argon, and the mixture was then stirred for 10 min to form the BzLi/TMEDA (1.00/1.25) system. DAS (0.185 mol/L solution in toluene) was added to this solution ($[\mathrm{DAS}]_0/[\mathrm{Li}]_0 = 7.40$), and the reaction mixture was magnetically stirred under dry argon at room temperature for 2 h. VAN (0.245 mol/L solution in toluene) was added to this solution ($[\mathrm{VAN}]_0/[\mathrm{Li}]_0 = 9.80$) and the reaction mixture was magnetically stirred under dry argon at room temperature for 24 h. After block copolymerization, dry methanol (MeOH) was added to the reaction mixture in an equimolar amount to the lithium (Li) atoms present in the reaction mixture to terminate the reaction. The polymerization mixture was then poured into a large volume of MeOH to precipitate the polymer, which was then separated by filtration. The product was dried under reduced pressure in dry argon at room temperature for 24 h, which resulted in a light yellow powdery polymer.

## Measurements

$M_n$, the weight average molecular weight ($M_w$), and polydispersity index (PDI; $M_w/M_n$) were determined using gel permeation chromatography (GPC) apparatus equipped with a differential refractive index (RI) detector (Shimadzu RID-6A), a UV detector (Shimadzu SPD-6A), and a Shimadzu Shim-pack GPC-80M column (column length: 300 mm, column diameter: 8 mm, effective molecular weight range of 100–4,000,000) at 40°C. THF was used as the eluent at a flow rate of 1.0 mL/min. A molecular weight calibration curve was obtained using polystyrene (PSt) standards. $^1$H-nuclear magnetic resonance (NMR) spectra of the polymers were measured in deuterated chloroform ($CDCl_3$) at 500 MHz using a Jeol ECA 500 spectrometer. UV/vis spectroscopic measurements were performed in THF using a Jasco V-570 UV/Vis/NIR spectrophotometer with quartz cells. Photoluminescence (PL) spectra of the samples were measured in THF using a Jasco FP-6500 spectrofluorometer with quartz cells. The drift mobility was determined using a time-of-flight (TOF) method with a device consisting of an Al/Ti-phthalocyanine/polymer film/Au cell, a xenon flash lamp (Hamamatsu Photonics, L2359), and a digitizing oscilloscope (Gould, DSO630). The polymer film thicknesses were determined using a profilometer (Dektak II, Solan).



**Scheme 2** Block copolymerization of DAS and VAN using the BzLi/TMEDA (1.00/1.25) system.

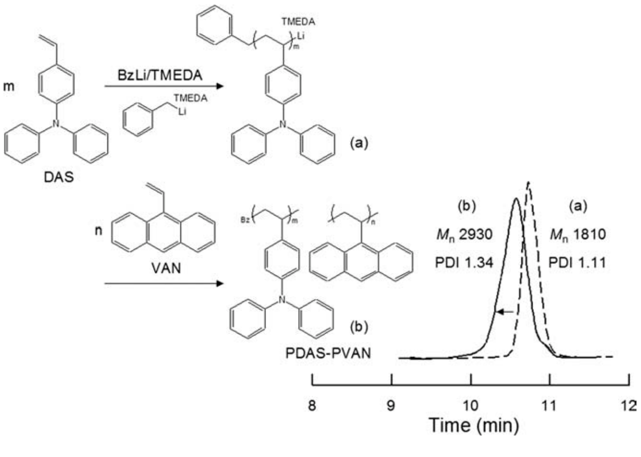


**Figure 1** GPC traces of (a) the PDAS prepolymer, and (b) PDAS-PVAN in THF at 40°C. Polymer/THF = 5.0 mg/5.0 mL.

**TABLE I**
**Polymers Prepared for Evaluation**

| Polymer type | $[DAS]_0/[VAN]_0/[Li]_0$ | Yield (wt %) (PDAS/PVAN) | $M_n$ (g/mol) (PDAS/PVAN) | PDI |
|---|---|---|---|---|
| PDAS-PVAN | 7.40/9.80/1.00 | 88 (100/75) | 2930 (1810/1120) | 1.34 |
| PDAS[a] | 7.40/0.00/1.00 | 100 | 1780 | 1.10 |
| PVAN[b] | 0.00/9.80/1.00 | 90 | 1860 | 1.40 |

[a] Polymerization was carried out in toluene under dry argon at room temperature for 2 h.
[b] Polymerization was carried out in toluene under dry argon at room temperature for 24 h.

## RESULTS AND DISCUSSION

### Synthesis of PDAS-PVAN

The synthesis of a binary block copolymer consisting of PDAS block and PVAN block was attempted according to Scheme 2. A toluene solution of DAS was added to a toluene solution of the BzLi/TMEDA (1.00/1.25) system ($[DAS]_0/[Li]_0 = 7.40$), and the polymerization was carried out under dry argon at room temperature for 2 h. 100% conversion of DAS to PDAS was achieved, and the $M_n$ and PDI of the PDAS prepolymer were 1810 (g/mol) and 1.11, respectively. Subsequently, a toluene solution of VAN ($[VAN]_0/[Li]_0 = 9.80$) was added to the reaction mixture containing poly(4-diphenylaminostyryl)lithium (PDASLi) and polymerization was continued under dry argon at room temperature for 24 h. Seventy-five percent conversion of VAN to PVAN block in PDAS-PVAN was achieved after 24 h, and the resulting polymer product obtained was a light yellow powder.

Figure 1 shows GPC chromatograms of the PDAS prepolymer [Fig. 1(a)] and PDAS-PVAN [Fig. 1(b)]. The $M_n$ of the polymer increased from 1810 (g/mol) to 2930 (g/mol), although with a broad PDI range of 1.34, due to some side reactions (e.g., transfer and termination reactions) of VAN during the anionic polymerization.[15] PDAS and PVAN homopolymers were then synthesized with the BzLi/TMEDA (1.00/1.25) system as comparison samples ($[DAS]_0/[Li]_0 = 7.40$, $[VAN]_0/[Li]_0 = 9.80$), according to previously reported procedures.[12,15] The results obtained are summarized in Table I.

Subsequently, $^1$H-NMR measurements were performed for each polymer to examine the polymer chain structure. Figure 2 shows the $^1$H-NMR spectra of PDAS [Fig. 2(a)], PVAN [Fig. 2(b)], and PDAS-PVAN [Fig. 2(c)]. With regard to the $^1$H-NMR spectrum of PDAS [Fig. 2(a)], aromatic (from 6.4 to 7.4 ppm), methine (around 2.3 ppm), and methylene proton signals (around 1.7 ppm) were observed, which are indicative of an isotactic-rich configuration.[12,14] In the case of the $^1$H-NMR spectrum of PVAN [Fig. 2(b)], very broad aromatic proton signals (from 6.5 to 8.5 ppm) were observed, and indicate an appreciable degree of shielding caused by the inter-ring interaction in the polymer chain.[15] For the $^1$H-NMR spectrum of PDAS-PVAN [Fig. 2(c)], broad aromatic proton signals from 6.4 to 8.5 ppm were observed due to overlapping of the aromatic proton signals of the PDAS [from 6.4 to 7.4 ppm, Fig. 2(a)] and PVAN blocks [from 6.5 to 8.5 ppm, Fig. 2(b)].

The results displayed in Figures 1 and 2 confirmed the formation of PDAS-PVAN via (living) anionic polymerization of DAS and VAN using the BzLi/TMEDA (1.00/1.25) system.

### Effects of polymer chain structure on the optical properties

To obtain fundamental information regarding the optical properties of PDAS-PVAN, UV/vis and PL analyses were performed.

Figure 3 shows the UV/vis spectra of PDAS, PVAN, and PDAS-PVAN. The UV/vis spectrum of PDAS [Fig. 3(a)] shows absorption bands in the region from 260 to 350 nm, and the maximum point ($\lambda^{ab}{}_{max}$) was at ~ 300 nm. Therefore, the absorption in the region from 260 to 350 nm can be considered to be caused by the triphenylamino (TPA) group in the polymer chain. The absorptions in the region around 260 nm and from 340 to 420 nm in the UV/vis spectrum of PVAN [Fig. 3(b)] are attributed to

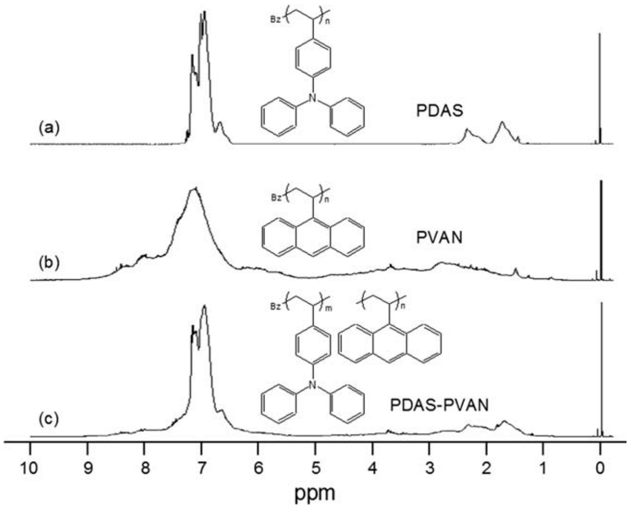


**Figure 2** $^1$H-NMR spectra of (a) PDAS, (b) PVAN, and (c) PDAS-PVAN in a 5.0 wt % solution of $CDCl_3$ at 50°C.

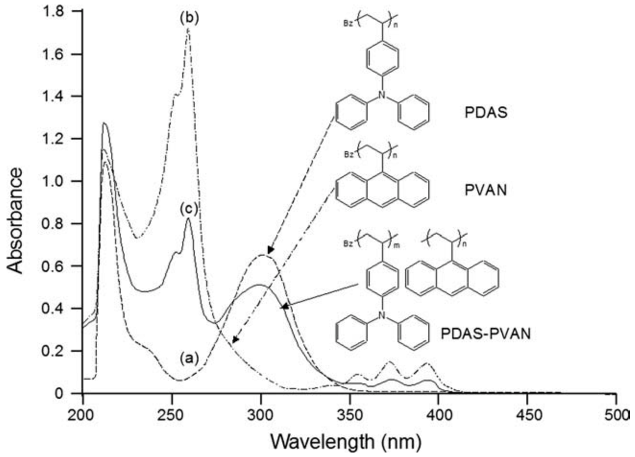


**Figure 3** UV/vis spectra of (a) PDAS, (b) PVAN, and (c) PDAS-PVAN. Polymer/THF = 0.10 mg/10.0 mL.

the anthracenyl (ATC) group in the polymer chain, and the maximum point ($\lambda_{\max}^{ab}$) is at ~ 260 nm. In the case of PDAS-PVAN [Fig. 3(c)], absorptions are observed in the region around 260 nm, from 260 to 350 nm, and from 340 to 420 nm. Thus, the spectrum clearly indicates the presence of TPA and ATC groups in the polymer chain.

The PL spectra of PDAS, PVAN, and PDAS-PVAN are given in Figure 4. The emission maximum ($\lambda_{\max}^{em}$) in the PL spectrum of PDAS is in the region from 360 to 380 nm [Fig. 4(a)]. A very strong PL emission from PVAN is observed in the region from 380 to 400 nm [Fig. 4(b)]. The PL emission from PDAS-PVAN [Fig. 4(c)] is close to that for PVAN [Fig. 4(b)], although the amount of ATC groups in PDAS-PVAN is considerably less than in the PVAN homopolymer of the same weight samples (Table I). In addition, the PL emission from PDAS block in PDAS-PVAN is disappeared. Therefore, fluorescence resonance energy transfer from PDAS block to PVAN block in PDAS-PVAN seems to occur.

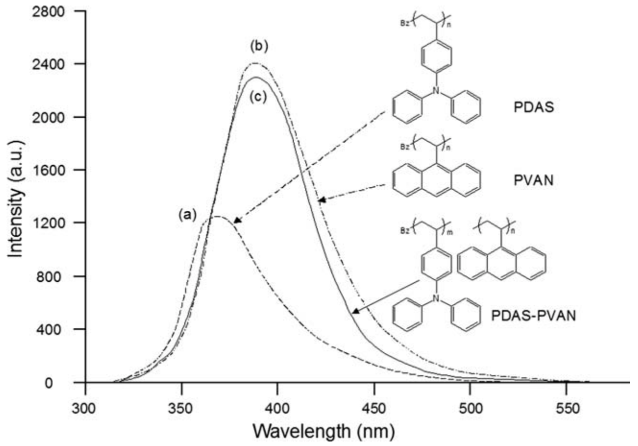


**Figure 4** PL spectra of (a) PDAS, (b) PVAN, and (c) PDAS-PVAN. Polymer/THF = 0.10 mg/10.0 mL. Excitation wavelength: (a) 300 nm; (b), (c) 255 nm.

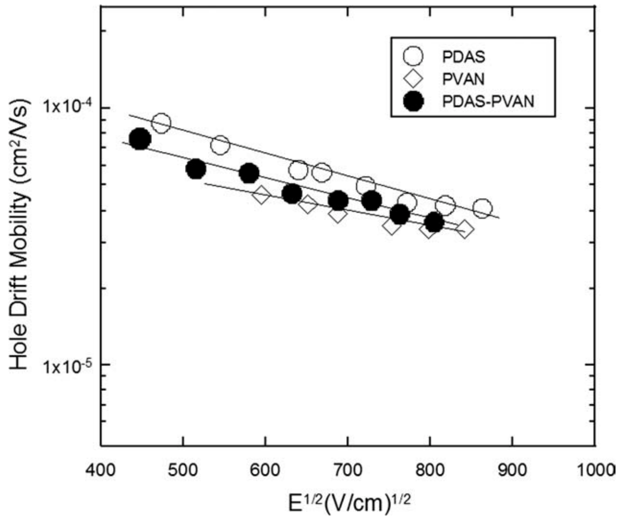


**Figure 5** Dependence of the hole drift mobility on the applied field for PDAS, PVAN, and PDAS-PVAN thin films.

### Effects of polymer chain structure on the electrical properties

The hole drift mobility of polymer films was examined as a typical electrical property of semiconducting polymers. Three different transparent polymer films with thicknesses in the order of 1.0−3.0 μm were prepared by the bar coating method using *o*-xylene solutions of PDAS, PVAN, and PDAS-PVAN (polymer/*o*-xylene = 0.03 g/1.0 g). The hole drift mobility μ, of the PDAS, PVAN, and PDAS-PVAN films were then determined using a standard TOF method, calculated according to the following equation:

$$\mu = L^2/t_T V;$$

where $L$ is the polymer film thickness, $t_T$ is the transit time, and $V$ is the applied voltage. The value for $t_T$ was determined from log $i$ (current) vs. log $t$ (time) plots. The logarithm of the hole drift mobilities for PDAS, PVAN, and PDAS-PVAN are plotted against the square root of the applied field [$E^{1/2}$(V/cm)$^{1/2}$] in Figure 5.

The polymer chain structure has a strong effect on the hole drift mobility of the polymer films. The hole drift mobilities for PDAS, PVAN, and PDAS-PVAN are in the order of $10^{-5}$ (cm$^2$/V s) with a negative slope. The hole drift mobility of PDAS is higher than that of PVAN, and that of PDAS-PVAN is increased compared with PVAN, due to the presence of the PDAS block in the polymer chain, although the hole drift mobility of this block copolymer is somewhat lower than that of the PDAS homopolymer. Therefore, the hole drift mobility of PDAS-PVAN is thought to be controllable by the amount of TPA groups in the polymer chain.

## CONCLUSIONS

The first successful example of the synthesis of PDAS-PVAN was achieved via (living) anionic polymerization with the BzLi/TMEDA system in a hydrocarbon solvent. The fluorescence resonance energy transfer from PDAS block to PVAN block in PDAS-PVAN occurred, so that the PL emission of PDAS-PVAN was considerably enhanced. The hole drift mobility of PDAS-PVAN was controllable by the amount of TPA groups in the polymer chain. PDAS-PVAN is regarded as new type of semiconducting polymer with controllable optical and electrical properties.

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