Synthesis and Study of a New Polyorganophosphazene

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Received 7 January 2000; accepted 21 March 2000

ABSTRACT: In this study, a new polyorganophosphazene with pendant carbazolyl groups was synthesized, and its structure was characterized by IR, ^{1}H-NMR, and ^{31}P-NMR spectroscopy. To understand its carrier photogeneration and transport property, we also studied fluorescence spectra and photovoltage spectra. Fluorescence spectra show that the polymer possesses properties dissimilar to those of PVK. There are only two emission peaks at $\approx$ 360 nm in its spectra, which coincides with that of the monomer model compound, 9-ethylcarbazole. This may be because of the influence of the spacer. The results of SPS shows that band–band transition mainly comes from electron π–π^* transition, and the polymer is a *p*-type semiconductor. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 1446–1451, 2001

Key words: polyorganophosphazene; carbazole; fluorescence; photovoltage; p-type semiconductor

INTRODUCTION

Well-characterized high-molecular-weight polymers based on inorganic elements are relatively rare but are attracting considerable attention because of their unique properties and potential application. Among them, polyphosphazene (PPPZ) is a broad class of inorganic polymers with a backbone consisting of alternating P and N atoms. Owing to the synthetic versatility of the precursor, poly(dichlorophosphazene) $(NPCl_2)_x$, a wide variety of different side groups can be attached to the polymer chain by nucleophilic reaction.[1–3] This leads to many important properties, such as polymer electrolytes,[3,4] unusual thermal properties,[5,6] biocompatibility,[7] and optical properties,[8,9] membrane,[10,11] some of which have commercial application. In particular, because of its photochemical stability and transparency of backbone, PPPZ may be useful in photonics technology.[9]

By contrast, charge carrier photogeneration and transport in polymer with aromatic chromophores as side groups or with the chromophores dispersed in insert polymers have been studied extensively during the past two decades. In this field, the carbazolyl group is one of the most widely used chromophores for charge photogeneration and transport and other potential applications. This is why polymers with pendant carbazolyl groups have received so much attention.[12–15]

In this study, carbazolyl groups were incorporated into the PPPZ as side groups; its structure was characterized by infrared (IR) spectra, ^{1}H-NMR spectra, ^{31}P-NMR spectra (Fig. 1), ultraviolet (UV) spectra, thermogravimetric analysis (TGA) differential thermal analysis (DTA) (Fig. 2), and wide-angle X-ray diffraction (XRD) (Fig. 3). We also studied its charge carrier photogeneration and transport property by fluorescence spectra and surface photovoltage spectra (SPS).

EXPERIMENTAL

Materials

Hexachlorocyclotriphosphazene (Fluka, >98%) and sodium hydride (with 20% paraffin oil; AR),

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Journal of Applied Polymer Science, Vol. 80, 1446–1451 (2001)
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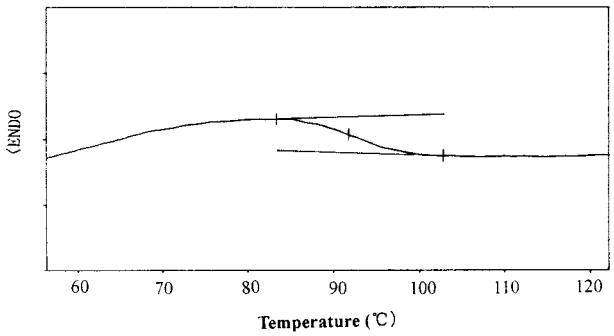


Figure 1 Differential thermal analysis (DTA) of the polymer.

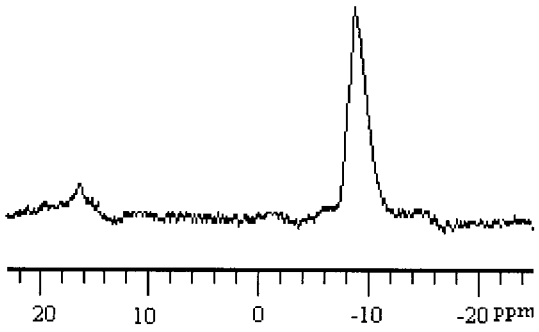


Figure 2 ^{31}P-NMR spectrum of the polymer.

were used as received. 9-(2-hydroxyethyl)Carbazole (HECz) was synthesized following the method described by Ho et al.[16] Other organic solvents were all analytic reagents and were treated according to standard methods before use.[17]

Synthesis

Polydichlorophosphazene (1.0 g, 8.5 mmol), prepared as described earlier,[1] was dissolved in dry THF (30 ml) added dropwise to the THF solution of HECz, which had been refluxed for 24 h with NaH (1.0 g). The mixture was refluxed under N_2 atmosphere for 24 h. After refluxing of most of the solvent from the mixture, the solution was poured into an excess of water to remove the salt. The insoluble material was dissolved in THF and precipitated by pouring into an excess of water, methanol, and cyclohexane three times, respectively. The product was dried in vacuum at 50°C for 2 days.

Measurement

^{1}H-NMR spectra were obtained on a Varian Unity 400 spectrometer operating at 400 MHz, using $CDCl_3$ as the solvent. The chemical shifts were detected with reference to TMS. ^{31}P-NMR spectrum was obtained on a Varian Unity 400 spectrometer operating at 161.9 MHz, using dimethyl sulfoxide (DMSO) as the solvent. The chemical shifts were detected with reference to H_3PO_4. IR spectra were recorded on a Nicolet Avatar-360 FTIR spectrometer. TGA was done on Perkin-Elmer TGA7 thermogravimetric analyzer. DTA was done on a Perkin-Elmer DTA1700 DTA. Wide-angle XRD data were obtained using a Shimadzu D/max-rA X-ray diffractometer operated at 12 kW with a nickel-filtered CuK_a X-ray beam. UV spectra were recorded on a Shimadzu UV-Vis

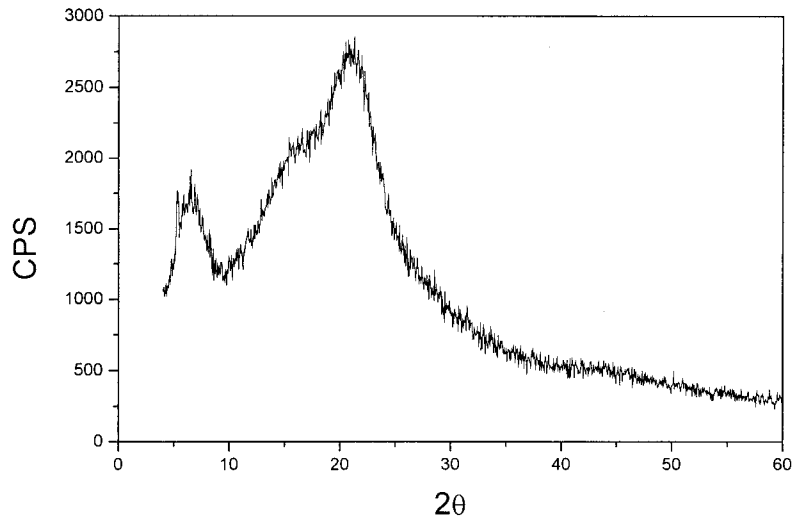
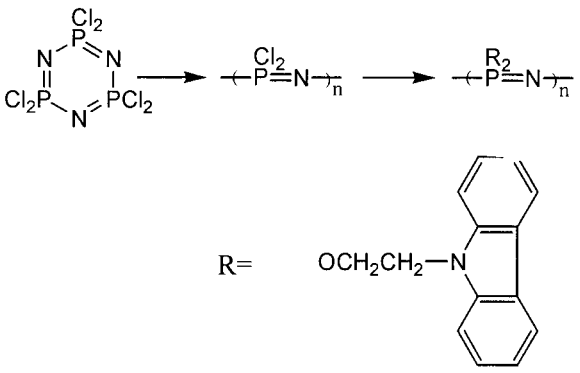


Figure 3 WAX diagram of the polymer.



Scheme 1 Synthetic route of the polymer.

UV-3100 spectrometer. Fluorescence spectra were measured with a Shimadzu RF-5301 PC spectrofluoriphotometer. Surface photovoltage spectra were measured with a surface photovoltage spectrometer. The electrode was made of ITO glass. The photovoltage cells consisted of an ITO/sample (solid)/ITO sandwich structure. Field-induced surface photovoltage spectra were obtained with the aid of a DC bias applied to the two sides of sample cell. When the external electric field was directed from the irradiated surface to the bulk, the applied bias was called positive.

RESULTS AND DISCUSSION

Synthesis of PPPZ with pendant carbazolyl groups was accomplished using a procedure similar to that previously described,[1] and the structure was confirmed by IR spectroscopy and ^{1}H-NMR spectroscopy, as illustrated in Scheme 1. The IR spectrum in Figure 4 shows the characteristic absorption for P═N (1231 cm^{-1}, 1327 cm^{-1}), P—N (722 cm^{-1}, 749 cm^{-1}), P—O—C (970 cm^{-1}, 1049 cm^{-1}), aryl groups (1457 cm^{-1}, 1486 cm^{-1}, 1597 cm^{-1}, 3048 cm^{-1}), alkyl group (2937 cm^{-1}). This indicates that the HECz group and phenoxide groups were covalently attached to the polymer main chain.

Figure 5 shows the ^{1}H-NMR spectrum of the polymer. The chemical shift peaks at 3.3 ppm and 3.85 ppm are attributed to hydrogen atoms of methylene groups, respectively, and the peak at 7.1 ppm belongs to hydrogen atoms at the *m*-position of the carbazolyl groups. Similarly, the chemical shift peaks at 7.24 ppm and 7.95 ppm are attributed to hydrogen atoms at the *o*-position and the *p*-position of the carbazolyl groups. There is only one chemical shift peak at −8.737 ppm in

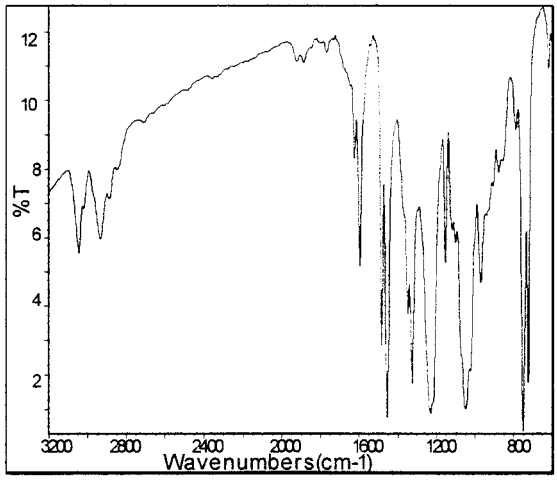


Figure 4 IR spectrum of the polymer.

^{31}P-NMR spectrum, which means that the chlorine atoms in polydichlorophosphazene were almost completely substituted by HECz groups.

Since polydichlorphosphazene possesses good thermal properties, it may contribute to the thermal stability of organic molecules that are attached to the main chain. As shown in the TGA diagram presented in Figure 6, the polymer began to decompose at 286°C, and HECz began to decompose at 166°C. T_d increased by 120°C, because of the influence of polydichlorophosphazene. Furthermore, the polymer decomposed by a

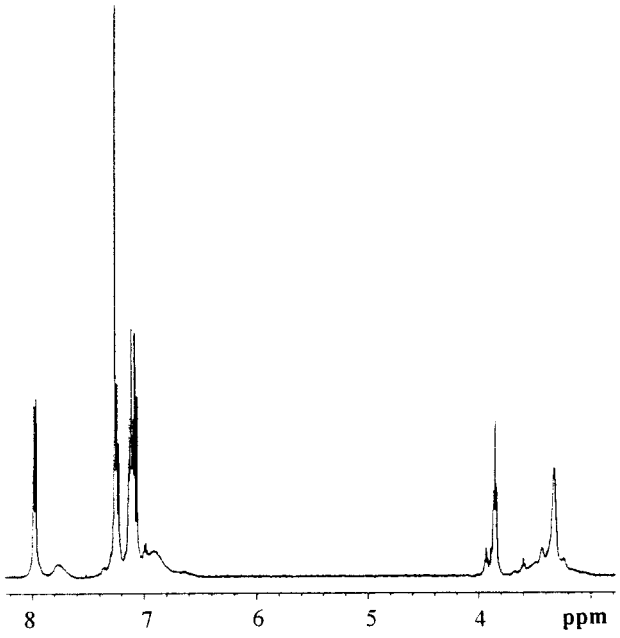


Figure 5 ^{1}H-NMR spectrum of the polymer in $CDCl_3$.

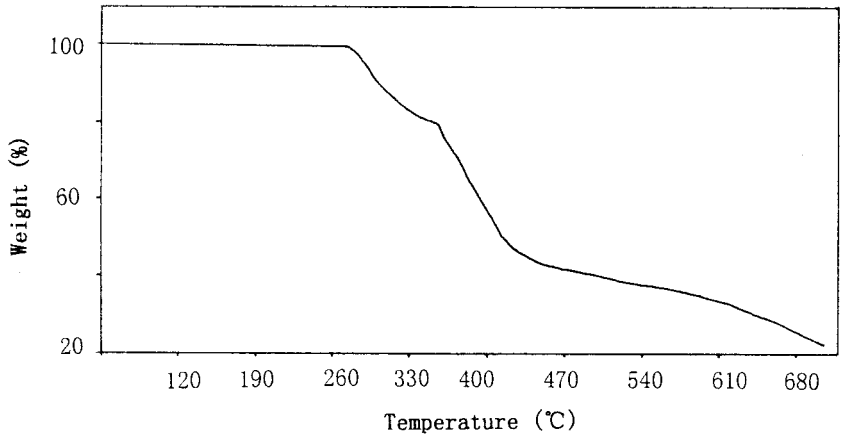


Figure 6 Thermogravimetric analysis diagram of the polymer.

three-step process, leaving a 20% remainder at 680°C, which is slower than HECz. However, in comparison with PVK, T_d of the polymer decreased by about 90°C, which may be attributable to the influence of the ethyl group in it. In addition, the glass transition temperature (T_g) is 91.6°C, and the wide-angle XRD result shows that the polymer is amorphous.

Figure 7 is the UV spectrum of the polymer. There are four maximum absorption peaks at 262, 290, 330, and 343 nm, respectively, consistent with the fluorescence excitation spectrum in Figure 8. The UV absorption comes mainly from the electron π–π^* transition of carbazolyl groups.[18,19]

Fluorescence Properties

The photophysical behavior of PVK is intriguing because its fluorescence is dominated by emission from two excimer species, except from the carbazole monomer at about 350 nm: emission centered at ~-420 nm originated from a conventional sandwichlike excited-state dimer, whereas the peak[6] at ~ 380 nm has been attributed to luminescence from a partially overlapped "second" excimer.[15] However, as shown in Figure 5, there are only two emission peaks at ≈ 360 nm. This spectrum is easily assigned to the monomer fluorescence of carbazole chromophores because the spectrum profile is similar to that of a monomer model compound, 9-ethylcarbazole. The disappearance of emission peaks of two excimers may be attributable to the influence of the spacer. Carbazole chromophores in the polymer are separated from the main chain by three atoms, —O—C—C—, making it difficult to take up structures with overlap of neighboring carbazole moieties.[20] Furthermore, the band gap E_g (3.53 eV) estimated from the onset position of the absorption is consistent with the emission band (3.54 eV).

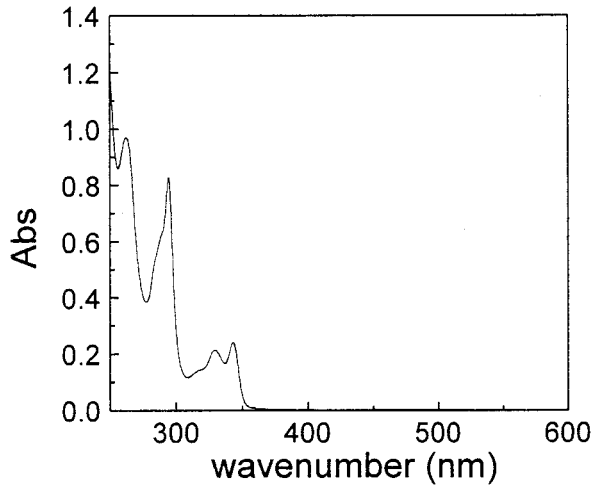


Figure 7 UV spectrum of the polymer in $CHCl_3$ solution.

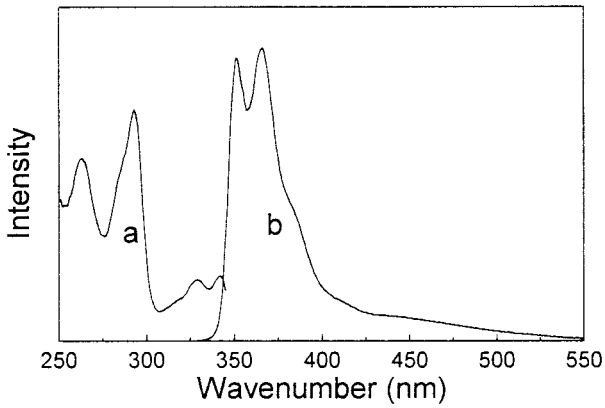


Figure 8 Fluorescence excitation and emission spectra of the polymer in $CHCl_3$ solution at a concentration of 0.037 mg mL^{-1}.

The result suggests that the fluorescence at 350.0 nm (3.54 eV) is attributed to the migration of electrons in the conduction band (CB) to the valence band (VB). Figure 9 is the emission spectra at different concentrations. With the increased concentration, the emission intensity is increased and is then decreased as a result of concentration quenching effect.[21]

SPS Measurement

SPV spectroscopy, as a surface-sensitive technique, has been proved a very powerful method for the study of photoinduced charge separation. SPV is caused by the separation of photoinduced electron-hole pairs, which results in the change population in space charge region (SCR).[22] For the type of system described in this article, the band–band transition is characterized as π–π^* transition in the 300–400-nm region. Under the built-in electric field, the minority carriers move toward the surface, and the majority carriers move toward bulk. For semiconductor materials, the application of the external field changes the strength of the built-in field, lifetime, diffusion length, and the separation efficiency of photoinduced electron-hole pairs, leading to the change of surface photovoltage. When the external field is in the direction of the built-in field, SPV is enhanced. By contrast, when the external field is in the direction opposite to the build-in field, the photovoltage is reduced.[23,24] Therefore, field-induced surface photovoltage can be used to determine the direction of the built-in field. The SPV response with different external electric field is given in Figure 10. When a positive bias was applied to the sample, the response strength of band increased; to the contrary, when the negative bias was applied, response strength decreased. This shows that the built-in field in SCR coincides with the direction of positive electric field, i.e., direction from surface to bulk. This indicates the polymer behaves as a *p*-type semiconducting polymer.

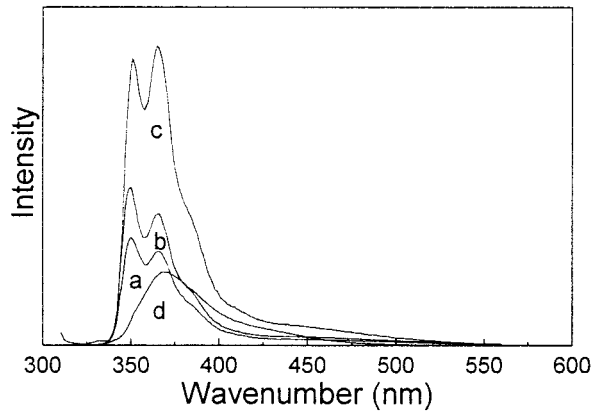


Figure 9 Fluorescence emission spectra of the polymer in $CHCl_3$ at different concentration: (a) 5.9×10^{-5} mg mL^{-1}; (b) 1.5×10^{-3} mg mL^{-1}; (c) 0.037 mg mL^{-1}; (d) 0.46 mg mL^{-1}.

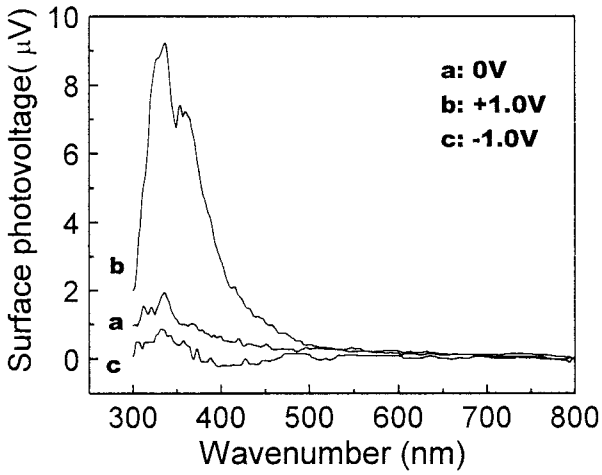


Figure 10 External field-induced surface photovoltage spectra of the polymer: (a) 0 V (b) +1.0 V (c) −1.0 V.

CONCLUSIONS

A new polyorganophosphazene with pendant carbazolyl groups was synthesized and its structure was characterized by IR, ^{1}H-NMR, and ^{31}P-NMR spectroscopy. As shown from the spectra, there are only two emission peaks at ≈ 360 nm, which coincide with that of the monomer model compound, 9-ethylcarbazole. This is because of the influence of the spacer, i.e., —O—C—C—. The results of SPS shows that band–band transition mainly comes from electron π–π^* transition, and the polymer is a *p*-type semiconductor.

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