

Unique UV Absorbance for Triphenylimidazole-Based Polymer

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ABSTRACT: In this study, a novel vinyl polymer containing 2,4,5-triphenylimidazole side groups was synthesized through conventional radical polymerization, which possesses the characteristic of temperature-dependent absorbance in the near-ultraviolet (UV) spectral region. The linear dependence of UV absorbance on temperature was confirmed for the

polymer both in solid state and in solution by experiment and also supported by the results of theoretical investigation. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: absorbance; temperature dependence; theoretical calculation; photophysics; polymer

INTRODUCTION

Materials exhibiting temperature-dependent ultraviolet–visible (UV–vis) absorbance have attracted much attention in recent years because of the prospects of their potential applications in areas such as temperature-indicating devices, temperature-sensitive light filters, and self-diagnostic labels for microchips. Temperature dependence of optical absorption for inorganic crystalline solids,¹ small organic dyes,^{2–4} and complexes^{5–7} has been studied extensively. The thermo-optical behavior, a reversible change in the UV–vis absorption of these materials when they are heated or cooled, can be the manifestation of different features, including changes in the crystalline phase as in the case of inorganic crystals,¹ in the dissociation and associa-

tion constants as in the case of organic dyes and charge transfer complexes, respectively,^{2–4,6} in the ligands geometry, and/or in the coordination number as in the case of metal complexes.^{5,7}

For the past few decades, there are, however, few reports demonstrating polymers with temperature-dependent UV–vis absorbances. This may be partly due to the fact that prediction of temperature-dependent absorption spectra from a given molecular structure remains infeasible. However, extensive investigations have been carried out on the dyed-polymer films.^{8–11} The unique mechanical properties and processability exhibited by polymers make them excellent candidates for the development of novel temperature-sensitive materials.^{12–15}

Here, we demonstrate a polymer based on triphenylimidazole possessing a characteristic of temperature-dependent absorbance in the near-UV spectral region (250–350 nm). As is well known, 2,4,5-triphenylimidazole is an attractive compound with excellent fluorescence and chemiluminescence properties for analytical applications.¹⁶ Additionally, 2,4,5-triphenylimidazole can undergo dimerization in the presence of potassium ferricyanide and potassium hydroxide in ethanol/water mixed solvents, leading to the formation of hexaphenylbiimidazole (HPBI) that exhibits photochromism, thermochromism, and piezochromism with irradiation, temperature change, and grinding.¹⁷ It has been found that the photochromism, thermochromism, and piezochromism of HPBI are

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due to reversible dissociation of the dimer into imidazolyl radicals, which is shown by the reversible reaction. Taking advantage of this transition, crosslinking and de-crosslinking of the polymer having a HPBI moiety in the crosslinkage moiety has been reported by Iwamura and Sakaguchi.¹⁸ However, they found that the homopolymerization of triphenylimidazole-based monomer cannot proceed under the usual radical polymerization conditions. In this work, a novel vinyl monomer with pendant triphenylimidazole groups was thus synthesized and homopolymerized to yield a homopolymer, of which temperature-dependent absorbance offers a remarkable opportunity to develop new temperature sensor.

EXPERIMENTAL

Materials and measurements

N,N-Dimethylformamide (DMF) was dehydrated and purified via vacuum distillation. 2,2'-Azobis(isobutyronitrile) (AIBN) was recrystallized from ethanol. The other solvents and reagents were of analytical grade and used as received. ¹H-NMR and ¹³C-NMR spectra were recorded with a 400-MHz Bruker AV-400 NMR spectrometer at 25°C. IR spectra in KBr pellets were recorded on a Perkin-Elmer Spectrum One FTIR spectrophotometer. Differential scanning calorimetry (DSC) was performed on a DSC Q10 instrument with a heating rate of 10°C min⁻¹ in flowing N₂. Thermogravimetric analysis (TGA) was carried out on a STA 449C instrument with a heating rate of 10°C min⁻¹ in flowing N₂. Gel permeation chromatography (GPC) measurements were performed on a Waters 1515 GPC setup equipped with a Waters 2414 differential refractive index detector in DMF at 45°C with a flow rate of 1.0 mL min⁻¹. Narrowly distributed polystyrene standards in the range of 0.5–1000 kDa were used for calibration. The thickness of polymer film was measured using a F20-UV thin-film measurement system. The UV-vis spectra were recorded on a PE Lambda 750 spectrophotometer combined with an Oxford C39535 Optistat DN.

Synthesis of 4-((4'-vinylbenzyl)oxyl)benzaldehyde

4-Vinylbenzyl chloride (1.52 g, 10.0 mmol), 4-hydroxybenzaldehyde (1.22 g, 10.0 mmol), and K₂CO₃ (2.5 g) were suspended in DMF (5.0 mL) and stirred at 56–60°C for 10 h. Then the mixture was poured into 120 mL of cold water and collected on a filter. The solid was washed by water and recrystallized from EtOH. The product was obtained in 56.7% yield. IR (KBr, cm⁻¹): 3427, 2980, 2933, 2821, 2726, 1924, 1697, 1629, 1600, 1577, 1506, 1464, 1425, 1407, 1381, 1323, 1307, 1251, 1212, 1183, 1160, 1110,

1007, 993, 955, 925, 877, 834, 798, 749, 732, 667, 648, 613, 552, 516, 500. ¹H-NMR (400 MHz, CDCl₃, δ, ppm): 5.29 (d, *J* = 10.9 Hz, 1H, CH₂CH), 5.78 (d, *J* = 17.6 Hz, 1H, CH₂CH), 6.75 (dd, *J* = 17.6 Hz, *J* = 10.9 Hz, 1H, CH₂CH), 5.16 (s, 2H, CH₂O), 9.91 (s, 1H, CHO), 7.07–7.86 (m, 8H, Ar-H).

Synthesis of 2-(4'-((4'-vinylbenzyl)oxyl)phenyl)-4,5-diphenylimidazole (VBPD)

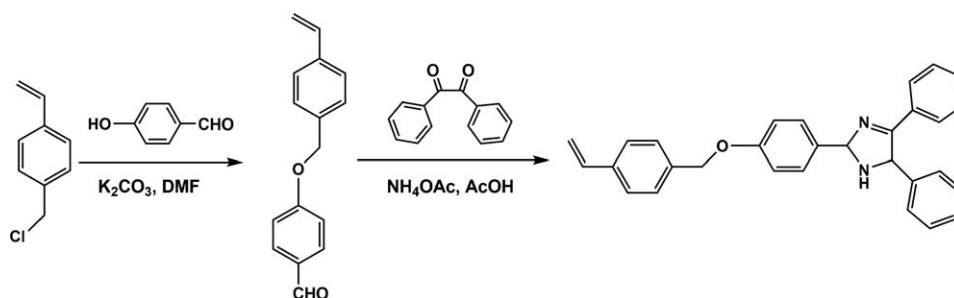
Benzil (2.10 g, 10.0 mmol), 4-((4'-vinylbenzyl)oxyl)benzaldehyde (2.38 g, 10.0 mmol), ammonium acetate (7.71 g, 0.100 mol), and a small amount of polymerization inhibitor were dissolved in glacial acetic acid (150 mL) and then refluxed. The reaction was monitored by thin layer chromatography. After cooling to room temperature, the reaction mixture was poured into cool water and collected on a filter. The solid was washed by cold water and recrystallized from CH₃OH/DMF (1/1, v/v). The product was obtained in 58.4% yield. m.p. 261–262°C. IR (KBr, cm⁻¹): 3425, 2984, 2858, 2794, 2726, 2635, 1816, 1610, 1578, 1543, 1506, 1492, 1451, 1440, 1407, 1388, 1324, 1311, 1263, 1232, 1210, 1181, 1155, 1133, 1114, 1070, 1026, 1015, 994, 968, 906, 852, 831, 776, 764, 740, 727, 695, 673, 648, 614, 516. ¹H-NMR (400 MHz, DMSO-*d*₆, δ, ppm): 5.27 (d, *J* = 11.0 Hz, 1H, CH₂CH), 5.85 (d, *J* = 17.6 Hz, 1H, CH₂CH), 6.75 (dd, *J* = 17.6 Hz, *J* = 11.0 Hz, 1H, CH₂CH), 12.52 (s, 1H, NH), 5.16 (s, 2H, CH₂O), 7.12–8.04 (m, 18H, Ar-H). ¹³C-NMR (100 MHz, DMSO-*d*₆, δ, ppm): 69.6, 114.9, 115.5, 123.9, 126.7, 127.2, 127.4, 128.2, 128.4, 128.8, 136.8, 137.1, 137.3, 146.1, 159.0.

Synthesis of polymer

VBPD (110 mg, 0.260 mmol) and AIBN (1.70 mg, 4.0 mol% to the monomer) were dissolved in DMF (2.0 mL) in a single-neck round-bottomed flask, which was then degassed and sealed *in vacuo*. After being stirred at 70°C for 24 h, the mixture was precipitated in methanol, and the precipitated polymer was dried *in vacuo*. IR (KBr, cm⁻¹): 3394, 3191, 3052, 2969, 2924, 1661, 1610, 1578, 1541, 1505, 1491, 1450, 1422, 1406, 1383, 1309, 1288, 1247, 1176, 1119, 1072, 1015, 971, 914, 872, 834, 765, 737, 723, 696, 673, 603, 524. ¹H-NMR (400 MHz, DMSO-*d*₆, δ, ppm): 1.18–1.99 (m, 3H, CH₂CH), 12.61 (s, 1H, NH), 5.14 (s, 2H, CH₂O), 6.79–8.52 (m, 18H, Ar-H).

UV-vis absorption measurement

Monomer and polymer solution samples for UV-vis measurements were prepared at concentrations of 2.4×10^{-5} M and 7.8×10^{-5} M, respectively, in DMF. Solutions were placed in a quartz cuvette (1 cm path), and baseline correction was done by



Scheme 1 Synthesis route of VBPD.

subtracting the signal for pure solvent. The polymer film was prepared by spin coating the polymer solution onto clear quartz slide at 2500 rpm. After being completely dried under vacuum at 100°C, a film with average thickness ~ 80 nm determined by a F20-UV thin-film measurement system was obtained. A baseline correction was executed in bare quartz slide not covered by the polymer film.

RESULTS AND DISCUSSION

Synthesis of monomer and polymer

Monomer having a 2,4,5-triphenylimidazole moiety, 2-(4'-((4'-vinylbenzyl)oxy)phenyl)-4,5-diphenylimidazole (VBPD), was synthesized by a one-step reaction from benzil, 4-(4'-vinylbenzyl)oxybenzaldehyde, and ammonium acetate in a moderate yield (Scheme 1).^{19,20} The monomer was well characterized by IR and NMR spectroscopy (Supporting Information Figs. S1–S3).

The radical polymerization of the obtained monomer was carried out at 70°C for 24 h by using AIBN as an initiator to give the polymer poly(2-(4'-((4'-vinylbenzyl)oxy)phenyl)-4,5-diphenylimidazole) (PVBPDP) in good yield. Polymers with number-average molecular weight (M_n) of 9300 and 27,500 g mol⁻¹ were separately prepared and characterized by IR and NMR spectroscopy (Fig. 1) as well as by GPC (Fig. 2). As determined by TGA (see Supporting Information Fig. S5), the thermal decomposition of polymer starts around 427°C. The amorphous nature of polymer is demonstrated by DSC analysis (Fig. 2), which shows a glass transition temperature at 173°C.

Experimental investigation of temperature-dependent absorbance for monomer

The aim of this study is to investigate the temperature dependence of UV-vis absorbance for triphenylimidazole-based polymers. For this purpose, we first study the influence of temperature variation on the absorption spectra of VBPD in DMF solution. In this study, the sample was maintained at the measurement temperature for at least 10 min prior to UV-vis spectroscopy investigation (*sic passim*).

The spectral changes for the monomer solution (2.4×10^{-5} M) are shown in Figure 3. The solution is pale yellow in color and shows an absorption band with a peak at 309 nm (λ_{max}). The absorbance of the solution is sensitive to temperature change. A plot of absorbance at 309 nm against temperature is also shown in Figure 3 (inset). Interestingly, the absorbance of monomer solution decreases linearly with increasing temperature in the range of 30–90°C. However, absorbance measurements at higher temperature (above 90°C) were not tried because of the limits of our experimental capabilities.

Experimental investigation of temperature-dependent absorbance for polymer

In an attempt to investigate the temperature-dependent UV-vis absorption spectra for the polymer with molecular weight of 27,500 g mol⁻¹ (PDI = 1.28), temperature was systematically altered between 30 and 85°C while the concentration of polymer solution in DMF was kept constant (7.8×10^{-5} M based on triphenylimidazole moieties), and their effect was evaluated by UV-vis measurements. As shown in Figure 4, the UV absorption spectra of polymer solution are very similar to those of

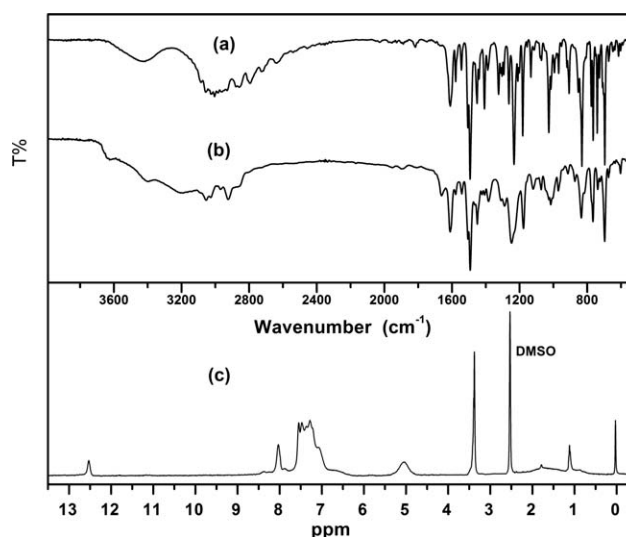


Figure 1 IR spectra of VBPD (a) and polymer (b), and ¹H-NMR spectrum of polymer (c, in DMSO-*d*₆).

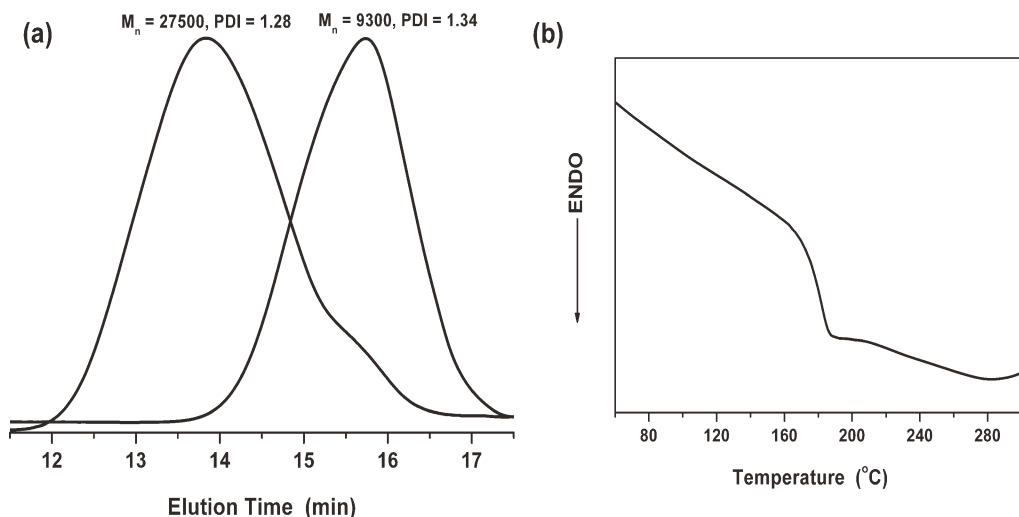


Figure 2 GPC (a) and DSC (b) curves of the polymer.

monomer solution, showing an absorption band with a peak at 307 nm. A plot of absorbance at 297, 307, and 317 nm (with an arbitrary selection), respectively, against temperature is also shown in Figure 4. Again, the absorbance of polymer solution decreases linearly with increasing temperature between 30 and 85°C. Moreover, the absorbance shifts observed in Figure 4 are reversible within that temperature range, that is, absorbances measured for three cycles by either increasing or lowering the temperature almost overlap as shown in the same figure. Additionally, absorbance decreases (increases) with increasing (decreasing) temperature reversibly between 30 and 85°C for polymer with molecular weight of 9300 g mol^{-1} ($PDI = 1.34$) at the same concentration.

PVBPD is substantially noncrystalline and forms a film that is excellent in transparency and gloss and that can maintain its transparency over a long period of time. Taking advantage of its film-forming ability, we next investigated the temperature-dependent absorption spectra of the polymer film. The sample was prepared by spin coating the polymer solution onto clear quartz slide at 2500 rpm. After being completely dried under vacuum at 100°C, a film with average thickness ~ 80 nm was obtained. Film studies have shown that polymer has a broader absorption band with a maximum absorbance at 302 nm (Fig. 5). In Figure 5, the absorption spectra show a “nearly” Gaussian distribution, indicating no other significant species (such as strong intermolecular interactions)

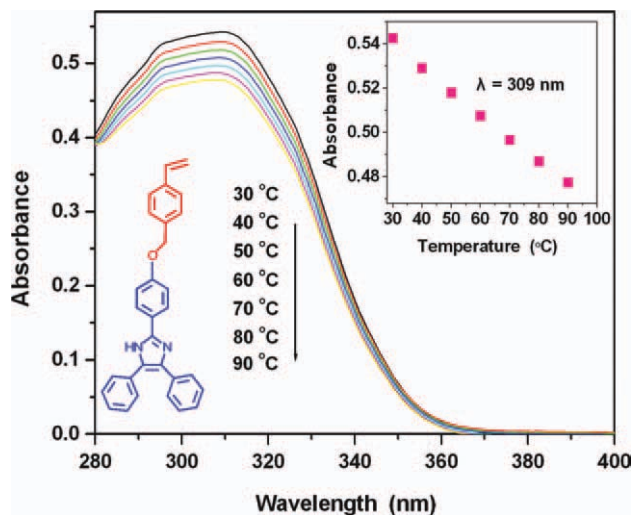


Figure 3 Absorption spectra of VBPDP in DMF solution (2.4×10^{-5} M) at different temperatures. The insets show the chemical structure of VBPDP as well as the temperature-dependent absorbance at 309 nm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

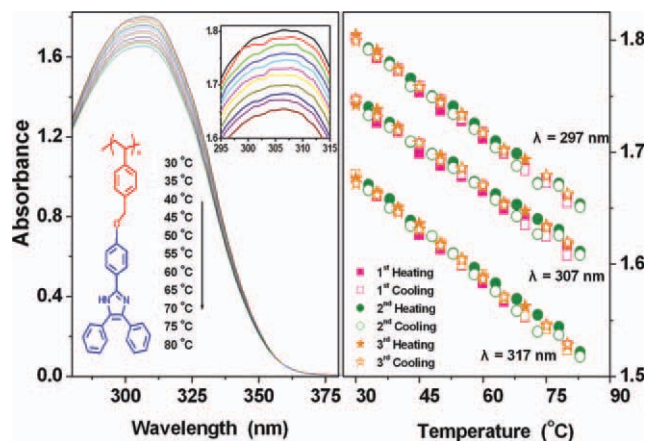


Figure 4 Absorption spectra of polymer in DMF solution (7.8×10^{-5} M based on triphenylimidazole moieties, $M_n = 27,500$ g mol^{-1}) at different temperatures (left), and a plot of absorbance at 297, 307, and 317 nm, respectively, against temperature during three heating and cooling cycles (right). The insets show the chemical structure of polymer as well as the magnified temperature-dependent absorption spectra. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

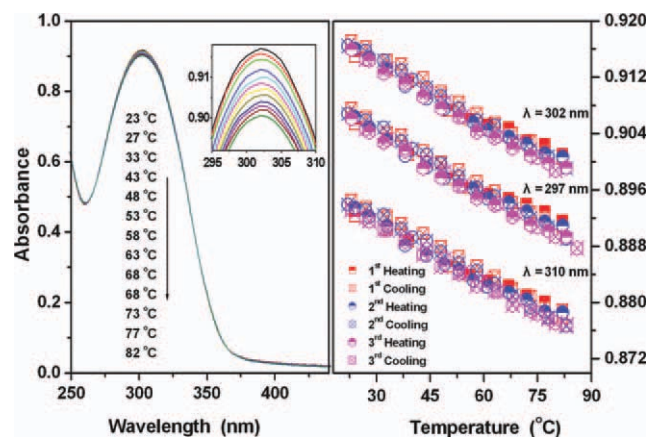


Figure 5 Absorption spectra of polymer film ($M_n = 27,500 \text{ g mol}^{-1}$) at different temperatures (left), and a plot of absorbance at 297, 302, and 310 nm, respectively, against temperature during three heating and cooling cycles (right). The insets show the magnified temperature-dependent absorption spectra. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

exist. When compared with the polymer solution, the broader absorption band of the film is the result of the distribution of different aggregate states of the polymer molecules.^{21,22} Similarly, absorbance measured for three cycles by either increasing or lowering the temperature almost overlap as shown in Figure 5. These results indicated that both polymer solution and film showed similar absorbance sensitivity to temperature changes. However, the absorbance change at λ_{max} between 30 and 85 °C is significantly different for polymer film and solution, which is found to be 0.013 and 0.15, respectively. The absorbance change of the polymer with temperature both in the solid state and in the solution offers us the opportunity to develop novel temperature sensor.

The experimental results presented above provide compelling evidence that it is the triphenylimidazole moiety that exhibits the temperature-dependent UV absorbance. Indeed, model compound, 2,4,5-triphenylimidazole, in DMF solution shows a linear relationship between UV absorbance and temperature (results are not shown). Of course, monomer or polymer concentration changes with the variation of temperature due to solvent extraction or expansion may cause this phenomenon. Considering the similar results for polymer film, however, the decrease in absorbance with increasing temperature cannot be attributed solely to the effect of dilution or concentration.

Theoretical investigation of temperature-dependent absorbance for monomer

To explain the most significant experimental observations of this work, we use the density functional

theory (DFT) combined with the time-dependent DFT (TD-DFT) in Gaussian 09 to simulate the electronic spectra at different temperatures by analyzing the conformational equilibrium shift with the temperature variation for the monomer solution.^{23,24} All the calculations are carried out using B3LYP method along with the 6-311+G* basis set. Considering the effect of solvent on electronic spectra, all the calculations in this study were performed in DMF solution, using the conductor-like polarized continuum model.

By geometries optimization and frequencies calculation, two stable conformations (Conformations A and B) of the monomer in DMF solution were substantiated (Fig. 6), which were characterized by the absence of imaginary frequencies. Their free energies at different temperatures are listed in Supporting Information (see Supporting Information Table S1).

TD-DFT calculation of the two stable conformations was therefore carried out. The calculation results indicate that the most intense theoretical absorption band resulted from the electronic transition from HOMO to LUMO+2 (their frontier orbitals from G09/B3LYP are represented in Supporting Information Fig. S9). The excitation energies, λ_{max} , and oscillator strengths are found to be 3.9344 and 3.9488 eV, 315.12 and 313.98 nm, and 0.7808 and 0.7942 for Conformations A and B, respectively. By combining with the DFT and the TD-DFT calculation, temperature-dependent oscillator strengths for the monomer solution were thus calculated and are shown in Figure 7. The experimental oscillator strength f was related to the molar absorptivities ϵ at

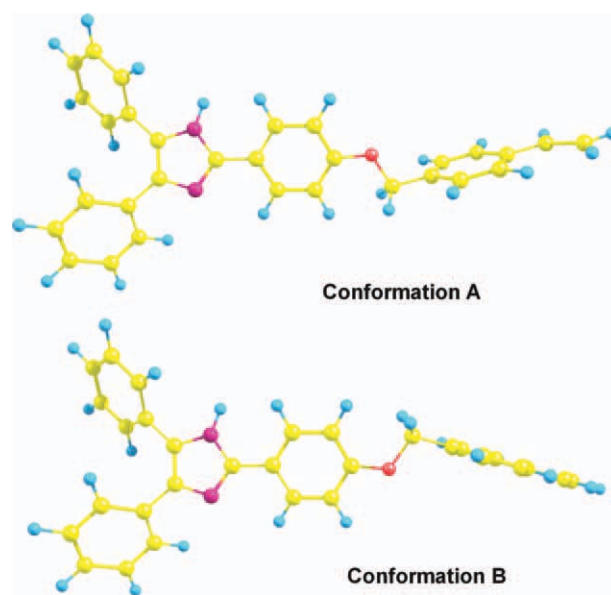


Figure 6 Optimized structures of VBPD in DMF solution (Conformations A and B). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

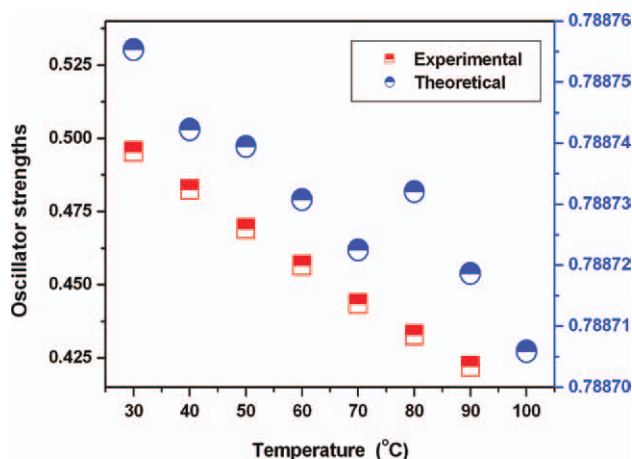


Figure 7 Theoretical and experimental oscillator strengths for VBPD in DMF solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

different temperatures (in $M^{-1} \text{ cm}^{-1}$) according to the literature.²⁵

$$f = 4.135 \times 10^{-9} \int_{-\infty}^{\infty} \epsilon d\bar{\nu},$$

where $\bar{\nu}$ is the transition energy in wavenumbers (cm^{-1}). The experimental results are also shown in Figure 7 for comparison. Clearly, both theoretical and experimental oscillator strengths decrease linearly with increasing temperature. However, there is an apparent bounce in theoretical calculation when the temperature is higher than 80°C. Possible sources of error considered include (1) an inadequate theoretical approach: TD-DFT calculations are defaulted for the system at 0 K, and therefore, we can only calculate the temperature-dependent oscillator strengths by an approximate method; (2) high temperature that may result in other conformers: high temperature may arouse other bond rotations that are restricted in low temperature; however, these have been ignored in theoretical calculation; and (3) neglect of numerous unstable conformational intermediates but could persist in reality. Nevertheless, we have theoretically demonstrated that the linear relationship between UV absorbance and temperature for the monomer can be attributed to the conformational equilibrium shift under different temperature circumstances.

CONCLUSIONS

Monomer having a 2,4,5-triphenylimidazole moiety was synthesized by a one-step reaction from benzil, 4-((4'-vinylbenzyl)oxyl)benzaldehyde, and ammonium acetate. Homopolymer of this monomer was prepared via conventional radical polymerization using AIBN as the initiator. The polymer exhibited a linear relationship between temperature and UV absorbance both in the solid state and in solution, which was verified by experimental and theoretical investigation.

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