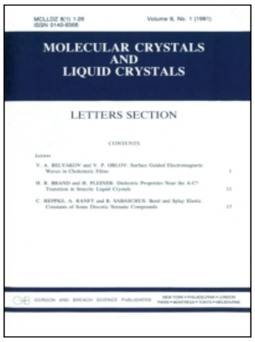

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Synthesis, properties and self-polymerization of 1,8-naphthalimide-based vinyl monomer

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ABSTRACT

1,8-Naphthalene imide with reactive vinyl group was synthesized by Suzuki reaction. Self-polymerization of the compound starts at 177°C as confirmed by differential scanning calorimetry. The electron affinity values of the monomer and the polymer were found to be −3.30 eV and −3.05 eV, respectively. The solid state ionization potential values of the monomer and the polymer were recorded to be 6.42 eV and 6.17 eV, respectively. The activation energy of the process was estimated using Ozawa method. It depends on the conversion degree and was found to be in the range of 136-195 kJ/mol. Pre-exponential factor values decrease during polymerization with decreasing chain mobility due to increasing molecular weight of the polymer.

KEYWORDS

1,8-Naphthalene imide; self-polymerization; activation energy; electron affinity; solid state ionization potential

1. Introduction

Organic low-molar-mass charge-transporting materials because of their good processability are attractive for the preparation of organic light emitting diodes and other optoelectronic devices. Such advantages are important when fabricating low cost, large area devices. [1]. The main difficulty in the preparation of such devices by solution processing is the solubility of the material which forms the bottom layer onto which the top layer has to be cast, because most organic semiconductors are soluble in the same solvents. One approach that was employed to circumvent this problem is the appliance of electro-active derivatives with reactive functional groups, which could be converted into polymers with lower solubility or even into insoluble networks by cross-linking reactions [2].

Self-polymerization which is also named as the thermal polymerization has several advantages over the other methods. The polymer layers obtained by the self-polymerization of electroactive monomers are free from the residual initiator and the side products which can act as traps for charge carriers. Moreover, thermally cured polymers exhibit good solvent resistance [3,4].

High electron-affinity of 1,8-naphthalimides determines the possibility of their use as electron-transporting media, and the imide nitrogen atom makes 1,8-naphthalimides easy to functionalize [5]. They exhibit good photochemical stability and high luminescence quantum yields [6]. The substitutions may change glass transition temperatures, shift photoluminescence wavelengths, change photoluminescence quantum yields, shift redox potentials and/or improve photoelectrical characteristics [7,8].

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In this work we report on the synthesis and properties of 1,8-naphthalimide-based vinyl monomer and demonstrate the possibility of its self-polymerization.

2. Experimental section

2.1. Materials and instrumentation

4-Bromo-1,8-naphthalic anhydride (Aldrich), dodecylamine (Aldrich), 4-vinylbenzeneboronic acid (Aldrich), and the required chemicals were purchased as reagent grade chemicals and used as received.

^{1}H and ^{13}C NMR spectra were recordered using Varrian Unity Inova (300 MHz (^{1}H), 75.4 MHz (^{13}C)) spectrometer at room temperature. Infrared (IR) spectra were recorded using Perkin Elmer Spectrum GX spectrometer. Mass (MS) spectra were obtained on a Waters ZQ 2000 (Milford, USA). Elemental analysis was performed with an Exeter Analytical CE-440 Elemental Analyzer. The molecular weights were determined by a gel permeation chromatography (GPC) system including GMHHR-M columns, which are designed for investigation of oligomers, and Bischoff LAMBDA 1000 detector. Polystyrene standards were used for calibration of the columns and THF was chosen as an eluent. Differential scanning calorimetry (DSC) measurements were performed using DSC Q2000, TA Instruments. Imide **2** (2.8 mg) was analyzed in aluminium pans under nitrogen atmosphere. Thermal polymerization reaction was investigated at heating rates (β) of 5, 10 and 20 C/min from 20°C to 220°C. Thermogravimetric analysis (TGA) was performed on TGA Q50 TA Instruments thermogravimeter at a heating rate of 20°C/min under nitrogen atmosphere. Melting points were recorded on Electrothermal MEL-TEMP melting point apparatus. UV absorption spectra were recorded on Perkin Elmer Lambda 35 spectrometer. Fluorescence (FL) spectra were recorded with a Perkin Elmer LS 55 spectromete. The cyclic voltammetry (CV) measurements were carried out by a three-electrode assembly cell from Bio-Logic SAS and a micro-AUTOLAB Type III potentiostat-galvanostat. The working electrode was a glassy carbon, the reference electrode and the counter electrode were Ag/Ag$^+$ 0.01 M and Pt wire, respectively. Argon-purged dichloromethane with tetrabutylammonium hexafluorophosphate (NBu_4PF_6) 0.1 M was used as electrolyte. The experiments were calibrated with the standard ferrocene/ferrocenium redox system [9].

2.2. Synthesis

4-Bromo-*N*-dodecyl-1,8-naphthalimide (1). A solution of 4-bromo-1,8-naphthalic anhydride (1 g, 3.61 mmol) in 25 ml of dimethylformamyde (DMF) was added to a 100 ml three neck round bottom flask equipped with a reflux condenser and a magnetic stirrer. Then dodecylamine (0.47 g, 3.61 mmol) was added drop-wise and the reaction mixture was heated up to 110°C and stirred under nitrogen for 1.5 h. The end of the reaction was detected by TLC (eluent: toluene/ diethyl ether, 6:1). The reaction mixture was concentrated using rotary evaporator and then the product was precipitated out into 1N HCl, filtered off and washed with 1N HCl. The crude product was purified by silica gel column chromatography using acetone and hexane mixture (vol. ratio 1:1.5) as an eluent. Yield: 0.86 g (62%) of white crystals. Mp = 62 – 63°C. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, δ, ppm): 8.70 (dd, 1H, $J_1 = 1.1$ Hz, $J_2 = 7.3$ Hz, $H_{Naphthalene}$), 8.61 (dd, 1H, $J_1 = 1.1$ Hz, $J_2 = 8.5$ Hz, $H_{Naphthalene}$), 8.45 (d, 1H, $J = 7.8$ Hz, $H_{Naphthalene}$), 8.08 (d, 1H, $J = 7.8$ Hz, $H_{Naphthalene}$), 7.89 (t, 1H, $J = 7.3$ Hz, $H_{Naphthalene}$), 4.18-4.11 (m, 2H, 2 × CH, $H_{aliphatic}$), 1.80-1.74 (m, 2H, CH_2, $H_{aliphatic}$), 1.45-1.32 (m, 18H, 9

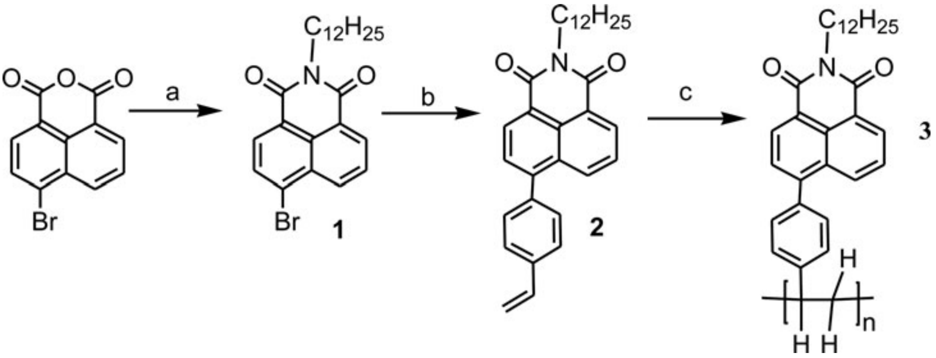
× CH_2, $H_{aliphatic}$), 0.99-0.90 (m, 3H, CH_3, $H_{aliphatic}$). IR, (in KBr), cm^{-1}: 3070 ν (CH_{ar}); 2959, 2926, 2871, 2855 ν ($CH_{aliphatic}$); 1702 ν ($C{=}O_{imide}$); 1653, 1590, 1504, 1459 ν ($C{=}C_{ar}$); 1344, 1231 ν (C–N); 783 γ (CH_{ar}); 664, 563 ν (C-Br). ^{13}C NMR spectrum (300 MHz, $CDCl_3$, δ, ppm): 164.2, 133.4, 132.3, 131.5, 131.3, 130.8, 130.3, 129.3, 128.3, 123.4, 122.5, 44.5, 38.1, 31.0, 28.9, 24.3, 23.3, 14.3, 10.9. MS ($APCI^+$, 20 V), m/z: 445 ($[M+H]^+$). Anal. Calcd. for $C_{24}H_{30}BrNO_2$: C, 64.86; H, 6.80; Br, 17.98; N, 3.15; O, 7.20%. Found: C, 64.79; H, 6.75; Br, 17.92; N, 3.18%.

4-(4-Vinylphenyl)-*N*-dodecyl-1,8-naphthalimide (2). To a degassed solution (N_2) of 4-bromo-*N*-dodecyl-1,8-naphthalimide (**1**) (0.5 g, 1.29 mmol) and $Pd(PPh_3)_2Cl_2$ catalyst (0.03 g, 0.04 mmol) in THF (15 mL), a solution of 4-vinylbenzeneboronic acid (0.42 g, 1.68 mmol) in THF (3 mL) and aqueous K_2CO_3 solution (1.79 g, 12.89 mmol) in water (2 mL) were added via a syringe. The reaction mixture was stirred at 80°C for 24 h. After cooling down, the product was extracted with CH_2Cl_2, washed with water and dried over $MgSO_4$. The solvent was evaporated and a crude product was subjected to column chromatography on silica gel using the mixture of ethyl acetate and hexane (1:8, *V*:*V*) as an eluent. Compound **2** was obtained as white crystals, yield 79%, m.p. 124 – 125°C; ^1H NMR (300 MHz, CDCl3, δ, ppm): 8.72 (d, 1H, $J = 1.1$ Hz, $H_{naphthalene}$), 8.69 (d, 1H, $J = 1.1$ Hz, $H_{naphthalene}$), 8.48 (d, 1H, $J = 2.1$ Hz, $H_{naphthalene}$), 8.46 (d, 1H, $J = 2.1$ Hz, $H_{naphthalene}$), 8.16 (dd, 1H, $J_1 = 1.1$ Hz, $J_2 = 8.5$ Hz, $H_{naphthalene}$), 6.76 (dd, 1H, AMX system $C\underline{H} = CH_2$ proton H^A), 5.81 (dd, 1H, AMX system $CH = C\underline{H}_2$ proton H^M trans $J_{AM} = 17.6$ Hz and gem $J_{MX} = 10.9$ Hz), 5.30 (dd, 1H, AMX system $CH = C\underline{H}_2$ proton H^X cis $J = 10.9$ Hz), 4.24-4.15 (m, 2H, CH_2, $H_{aliphatic}$), 2.03-1.95 (m, 1H, CH, $H_{aliphatic}$), 1.49-1.26 (m, 8H, 4 × CH_2, $H_{aliphatic}$), 1.02-0.89 (m, 3H, CH_3, $H_{aliphatic}$). ^{13}C NMR (75.4 MHz, CDCl3, δ, ppm): 163.8, 145.6, 145.3, 136.3, 132.2, 131.9, 131.6, 131.8, 131.7, 131.1, 131.0, 130.9, 128.2, 127.8, 124.2, 44.5, 38.3, 31.0, 28.5, 24.1, 23.4, 13.8, 10.9. IR, (in KBr), cm^{-1}: 3066 ν (CH_{ar}); 2960, 2923, 2876, 2857 ν ($CH_{aliphatic}$); 1698 ν ($C{=}O_{imide}$); 1655, 1589 ν ($C{=}C_{ar}$); 1524, 1506 ν (N–O); 1462; 1346, 1234 ν (C–N); 991, 911 ν (Alk. C=C); 786, 763, 750 γ (CH_{ar}). MS ($APCI^+$, 20 V), m/z: 468 ($[M+H]^+$). Anal. Calcd. for $C_{32}H_{37}NO_2$: C, 82.19; H, 7.97, N, 3.00; O, 6.84%; found C 72.77, H 6.24, N 6.62%.

Poly{4-(4-vinylphenyl)-*N*-dodecyl-1,8-naphthalimide} (3). Polymer **3** was obtained by self-polymerization of monomer **2** (2.8 mg) by differential scanning calorimetry method (DSC). $M_w = 4520$, $M_n = 2380$. ^1H NMR (300 MHz, $CDCl_3$, δ, ppm): 8.81-7.69 (m, 3H, Ar), 7.61-7.31 (m, 2H, Ar), 7.24-6.47 (m, 4H, Ar), 4.39-3.78 (m, 2H, $H_{aliphatic}$), 1.81-1.69 (m, 2H, $H_{aliphatic}$), 1.51-1.12 (m, 18H, $H_{aliphatic}$), 0.89 (s, 3H, $H_{aliphatic}$). IR, (in KBr), cm^{-1}: 3024 ν (CH_{ar}); 2923, 2852 ν ($CH_{aliphatic}$); 1661 ν ($C{=}O_{imide}$); 1590 ν ($C{=}C_{ar}$); 1507 ν (N–O); 1465; 1441, 1355 ν (C–N); 784, 759 γ (CH_{ar}).

3. Results and Discussion

Naphthalimide **2** was synthesized by two-step procedure. The first step was condensation of 4-bromo-1,8-naphthalic anhydride with dodecylamine. The target naphthalimide **2** was prepared by Suzuki cross-coupling reaction between compound **1** and 4-vinylbenzeneboronic acid. Polymer **3** was obtained by self-polymerization of monomer **2** (Scheme 1). The reaction was monitored by differential scanning calorimetry method (DSC). It is known that aromatic imides with high planarity and π-conjugation show a strong tendency to intermolecular interaction and therefore are often insoluble [10]. This problem can be overcome by introduction of longer alkyl chains. Monomer 2 and polymer 3 were found to be soluble in common organic solvents, such as chloroform, acetone, tetrahydrofuran (THF) etc. The thermal, optical,



Scheme 1. Synthesis of 1,8-naphthalimide-based vinyl monomer (**2**) and of the corresponding polymer (**3**). Reagents and conditions: (a) dodecylamine, DMF, 150°C, 1.5 h; (b) 4-vinylbenzeneboronic acid, $Pd(PPh_3)_2Cl_2$, THF, K_2CO_3, 24 h; (c) The reaction was monitored by DSC.

photophysical and electrochemical properties of imides are usually not affected by the length of alkyl chains [11]. However increase of the length of alkyl chains leads to the reduction the temperatures of morphological transitions such as melting points, glass transition temperatures [12]. The structure of compound **2** was confirmed by ^1H, ^{13}C NMR, IR- and mass spectrometry methods. The characteristic signal of vinyl group is observed in the ^1H NMR spectra of the monomer **2**. Three protons of vinyl group form three-spin AMX system. According to the coupling constants protons are assigned to the corresponding signals. The signals of H^A protons, which are near benzene ring, are observed at 6.76 ppm. The signals of H^X and H^M protons are observed at 5.30 ppm and 5.81 ppm respectively. The characteristic stretches of vinyl groups appear in the IR spectra of **2** at 991 cm^{-1} and 911 cm^{-1}.

The average molecular weight and polydispersity index of **3** were estimated by gel permeation chromatography. The weight average molecular weight of the polymerization product was found to be 4520 and polydispersity index of 1.9 (GPC, Fig. 1).

The behavior under heating of compound **2** was studied by DSC under a nitrogen atmosphere (Fig. 2a).

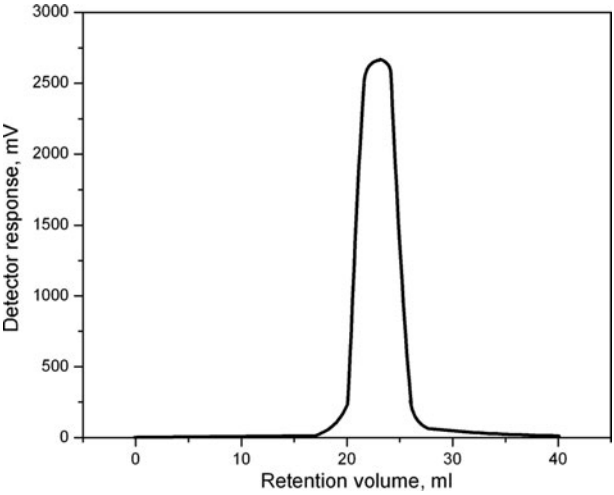


Figure 1. GPC of polymer **3**.

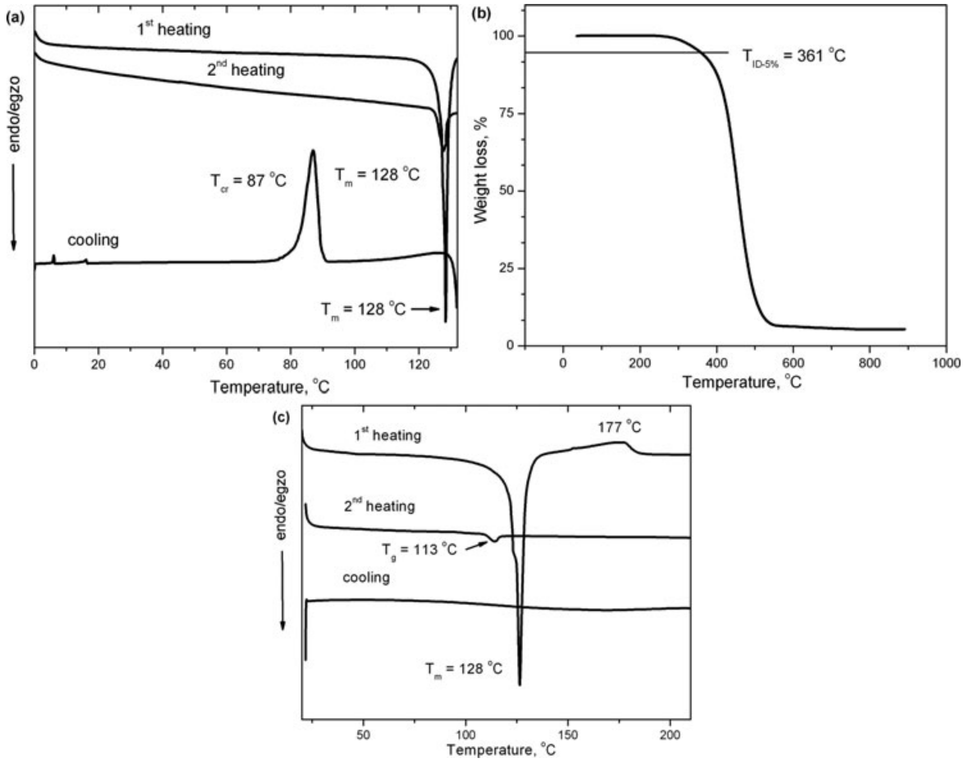


Figure 2. DSC curves of monomer **2** (a) and polymer **3** (c) at the heating/cooling rate of 10°C/min in N_2 atmosphere. TGA curve of **2** (b), heating scan rate 20°C/min, N_2 atmosphere.

In the first heating scan of the DSC experiment, compound **2** showed endothermic melting signal with the maximum at 128°C. Cooling from the melt revealed exothermal crystallization signal at 87°C. In the second heating scans compound **2** revealed only melting signal at 128°C. TGA revealed relatively high thermal stability of compound **2** which was similar to that of the earlier reported naphthalimides [13, 14, 15, 16]. The temperature of 5% weight loss (T_{ID}) of compound **2** was found to be 361°C (Fig. 2b).

Self-polymerization of the monomer (**2**) containing reactive vinyl group was studied by DSC. Melting peak appeared in the first DSC heating scan at 128°C. The exothermic signal starting at 145°C with the maximum at 177°C present in the curve of the first DSC heating scan can be assigned to polymerization of the monomer **2**. After the cooling the glass transition temperature of the product of polymerization of **2** was recorded at 113°C (Fig. 2c).

In the study of polymerization kinetics of compound **2** it was assumed that the degree of conversion was proportional to the heat of reaction. The area under the heat flux curve and above baseline was estimated as the heat of reaction. The values of the total reaction heat at 5, 10 and 20°C/min heating rate were found to be 22.58, 22.31 and 22.07 J/g, respectively. Only small differences in the total reaction heats were observed at the different heating rates. Thus the same degree of conversion of the monomer was reached at the different heating rates. By performing the DSC scans at the different heating rates, integrating exothermic peaks and measuring the temperature at the different degrees of conversion, the activation energy of the process was estimated using Ozawa method by the following equation (1) [17]:

$$E_a = \frac{-R}{1.052} \cdot \frac{\Delta \ln \beta}{\Delta \ln {}^{1}/_{T_i}} \tag{1}$$

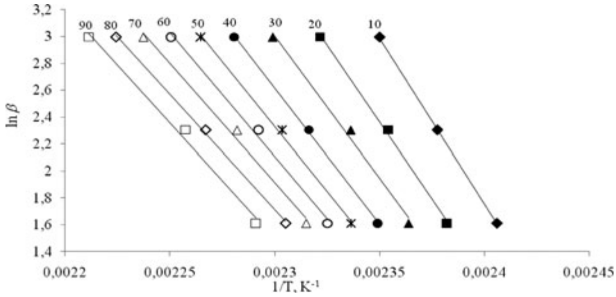


Figure 3. 1/T *vs* ln(β) at the different conversion degrees.

where, β is the heating rate; E_a is the activation energy; R is a gas constant; T_i is the temperature at the selected percentage of conversion i.

The Fig. 3 shows the slopes of lines of natural logarithm of heating rate *vs* $1/T_i$ from which activation energy was estimated. Very good linear relationship between the heating rate and the reversal of the exothermic peak temperature was observed ($R^2 > 0.991$).

The activation energy at each degree of conversion was calculated from the slope of isoconversional curves and plotted in Fig. 3. It was observed that E_a decrease 30% with the increase of conversion degree from 10 to 90%. The variation of activation energy with degree of conversion indicates the Trommsdorff effect [18]. The values of pre-exponential factor decreased with the increase of conversion degree due to reduced mobility of chain (Fig. 4).

UV-Vis absorption and fluorescence spectra of the dilute THF solution of monomer **2** and polymer **3** are shown in Fig. 5. Characteristic absorption maxima of imide chromophore at 357 nm is clearly recognized in UV absorption spectra of **2** and **3** derivatives. The estimated optical band gap was the same for both the derivatives (3.12 eV). The wavelengths of the absorption maxima of the spectra were found to be almost identical. The dilute THF solutions (10^{-5} M) of compounds **2** and **3** showed sky blue luminescence peaking at 441 nm after excitation with UV radiation with the wavelength of 360 nm.

To investigate the molecular structure and electron distribution of **2**, it was optimized using DFT calculations with Gaussian 09 program [19]. The calculations were performed with the B3LYP exchange correlation functional under 6-31G** (d) basis set. Fig. 6 shows the frontier molecular orbitals of **2** (containing methyl group instead of longer-chain alkyl group).

The highest occupied molecular orbital (HOMO) is delocalized over the vinylphenylnaphthalimide, while the lowest unoccupied molecular orbital (LUMO) mostly is centred on the naphthalimide moiety. The energies of HOMO and LUMO for **2** were found to be −6.1 eV and −2.4 eV, respectively.

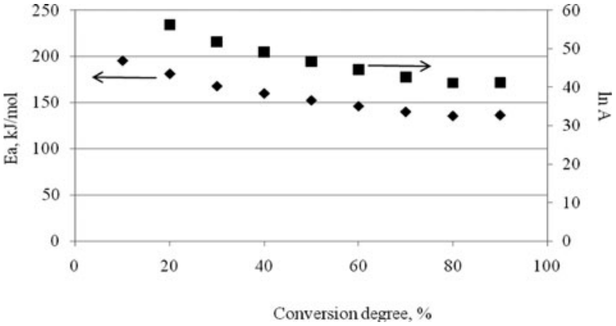


Figure 4. The activation energy and pre-exponential factor as a function of degree of conversion.

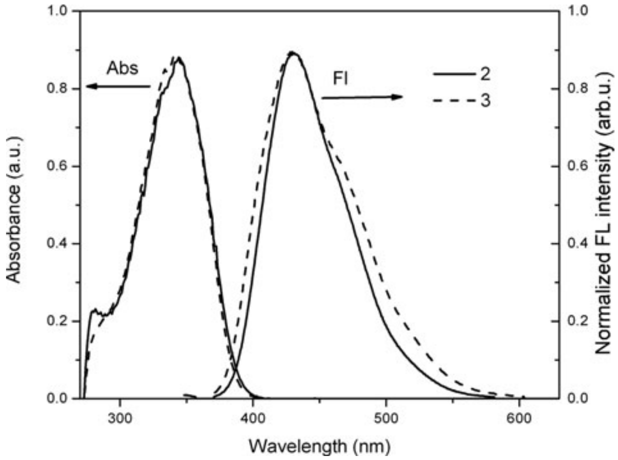


Figure 5. UV-Vis absorption and normalized fluorescence spectra ($\lambda_{ex} = 360$ nm) of the dilute THF solution (10^{-5} M) of compound **2** and polymer **3.**

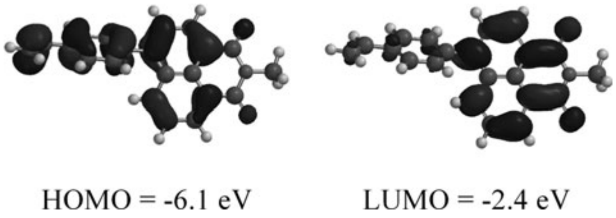


Figure 6. Molecular orbital distributions of **2.**

The electrochemical stability and the reversibility of the redox processes of the monomer and the product of its polymerization (**3**) was studied by cyclic voltammetry (CV). The cyclic voltammograms of **2** and **3** are shown in Fig. 7.

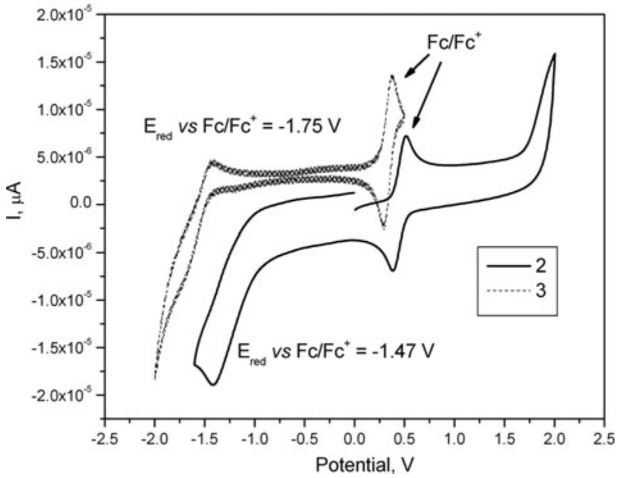


Figure 7. Cyclic voltammograms of **2** and **3** (scan rate = 100 mV/s, Ag/AgNO$_3$ reference electrode calibrated against Fc/Fc$^+$; 0.1 M NBu$_4$PF$_6$/dichloromethane electrolyte in argon-purged dichloromethane solution).

During the reductive scans, cathodic peaks were observed which can be attributed to the formation of anion radicals. Compounds **2** and **3** exhibited single irreversible reduction peaks in the negative potential range at −1.47 and −1.75 V, respectively due to the incorporated naphthalimide moieties [13]. The electron affinity values (EA_{CV}) of **2** and **3** were found to be −3.30 eV and −3.05 eV, respectively. The solid state ionization potential (IP_{CV}) values were calculated from EA_{CV} and optical band gap values. IP_{CV} of **2** and **3** were recorded to be 6.42 eV and 6.17 eV, respectively.

4. Conclusions

1,8-Naphthalimide-based vinyl monomer was obtained by Suzuki coupling, and its thermal, optical, photophysical, electrochemical properties were investigated. The monomer exhibited high thermal stability with the temperature of the onset of the thermal decomposition of 361°C. The possibility of self-polymerization of the synthesized monomer was demonstrated by differential scanning calorimetry. The differential scanning calorimetry heating scan of the monomer showed exothermic peak of self-polymerization at 177°C. The electrochemical stability of the monomer and of the product of its polymerization was studied by cyclic voltammetry. The electron affinity values of the monomer and the polymer were found to be −3.30 eV and −3.05 eV, respectively. The solid state ionization potentials of the monomer and the polymer were recorded to be 6.42 eV and 6.17 eV, respectively. The activation energy of the process of self-polymerization was estimated using Ozawa method. It was found to be dependent on the conversion degree and ranged from 136 to 195 kJ/mol.

Acknowledgments

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