

Poly (*N*-Isopropyl Acrylamide-*Co*-Vanillin Acrylate) Dual Responsive Functional Copolymers for Grafting Biomolecules by Schiff's Base Click Reaction

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Abstract

This article reports on the synthesis of acrylate monomer from renewable material. Vanillin was selected to be the start material to produce new monomer called vanillin acrylate and abbreviated by (VA). It has been successfully investigated by ¹H, ¹³C NMR, IR and UV and all results were in logic state. The next step was to synthesize three different thermo-responsive functional copolymers by incorporation of three different molar ratios of vanillin acrylate (10, 20, 30 mol%) with *N*-Isopropylacrylamide via free radical polymerization by AIBN as initiator in solution. All copolymers were deduced by ¹NMR and IR and all showed the presence of aldehyde group. The copolymer was used for grafting of tryptophan and β-alanine through the chemical link between amino group and the active aldehyde group by click reactions to form Schiff's base imine compounds. Moreover, polymers were also elucidated by ¹HNMR, IR and UV, Size Exclusion Chromatography (SEC) was used for the molecular weight determination, differential scanning calorimeter (DSC) for glass temperature of solid polymers, XRD for crystallinity. UV-vis Spectroscopy was used for the determination of phase separation or the lower critical solution temperature (*T*_c) of polymers solution not only in deionized water but in pH5 and pH11. The amount of conversation and linked amino acid was determined by UV-vis Spectroscopy.

Keywords

Dual Responsive Polymers, Functional Polymers, Grafting, Amino Acids, Schiff's Base, Click Reactions

1. Introduction

The applications of biomolecules and biomaterials have been recently developed. A new class has several identifications like, smart, intelligent, responsive, and environment. All definitions focused on the change in the physical properties of material with response to their surrounding environment [1]-[7]. On the basis of their response, they are pH, temperature, light, electrical or ionic strength [8]-[14]. The occurrence of such materials has been found in many natural products, like leaves of *Mimosa pudica* and Venus flytrap [15]. The environmental change can be detected in many kinds. One is the shape dimensions due to formation or removal of hydrogen bonding, which further effect in the hydrophilicity or hydrophobicity of the whole polymer chain and the electrostatic interaction such as osmotic pressure [16]. Temperature responsive polymer is the most familiar kind of responsive polymers. Polymer scientists have recently discovered two kinds of phase separation of polymer solution, one known as lower critical solution temperature (LCST) at which the transition occurred from an insoluble to a soluble state with raising temperature. On the other hand, the reversible process at which the transition occurred from a soluble to insoluble state with raising temperature and called upper critical solution temperature (UCST). Poly (*N*-Isopropylacrylamide) is the most popular temperature responsive polymer that exhibit LCST of 32°C [17] [18] [19] [20] [21]. The dual responsive Copolymers can be synthesized from T-responsive monomer or polymer such as NIPAAm with a pH-responsive with ionizable groups, such as poly (acrylic acid) PAA or poly (*N,N*-dimethylaminoethylmethacrylate) PDEAEMA [22] [23] [24]. They are widely applicable e.g. sensors, actuators, drug delivery, and bio-separation [25]-[31]. Green chemistry has an interested field for many chemists. New alternatives for styrene monomer were the target for several scientists for its disadvantages due to, hazardous air pollutants (HAPs), emitting during metering mixing process and curing; further the unreacted styrene continues to be released from composites during life cycle [32]. Renewable resources, like cellulose, starch, natural oil... etc., have been used as alternative to produce bio-based monomers [33]. The lignin produced from Vanillin becoming relatively easily accessible; still there are only a handful of reports on attempts to utilize vanillin as monomers for bio-based polymer synthesis [34] [35]. Several chemical modifications on vanillin have occurred due to the presence of both aldehyde and hydroxyl active groups [2] [36]. One recent article discussed the dimerization and the Polymerization of vanillin through electrochemical reductive with horseradish peroxidase [37].

Schiff's base has widely used as ligands in metal coordination chemistry and was found to be stable under oxidative and reductive conditions [37]. Further, epoxidation of vanillin was used to prepare Schiff bases [38]. The biological activity of Schiff's base polymers have been widely reported by several authors [40]-[45]. A review article has been published by Yuan *et al.*, covering the most interested articles used Schiff base as a stimuli-responsive linker in the polymer

chain [46]. The sensitivity of the imine linkage to pH value is responsible on the responsive feature of the polymer molecule [47] [48]. Moreover, the formation of complexes of the imine can also be used to expand the pH responsiveness of the linker [48]-[53]. Several publications have reported “click chemistry” as linkers for many bio-based molecules [54] [55] [56]. In the present work we prepared smart functional polymers from new monomer based on renewable material to use as linker for biological molecule.

2. Experimental

2.1. Materials

(AIBN Acrös) 2,2'-azobis(isobutyronitrile) was recrystallized from methanol, N-isopropylacrylamide (NIPAAm, Acrös) was recrystallized from distilled hexane. Vanillin (99% Acrös), triethylamine (Merck), acryloyl chloride (98% Merck), β -alanine and tryptophan (99% and 97% Acrös) were used as received. Buffer solutions pH 11 and pH5 used from (Aldrich). Dichloromethane, dioxane, tetrahydrofuran (THF), and diethylether were distilled over potassium hydroxide.

2.2. Instrumentations

Bruker AV 500 spectrometer was used to record ^1H and ^{13}C NMR spectra in DMSO d_6 or CDCl_3 at 500 MHz and 125 MHz, respectively. Vertex 70 Fourier transform infrared instrument for recording IR spectra. The samples were milled with dry potassium bromide KBr (Merck 99%) and pressed to pellets. The Molecular weights (M) and polydispersity (D) were analysed by size exclusion chromatography (SEC). Chloroform was used as eluent (containing of 0.1 vol% triethylamine) with a flow rate of 0.75 mL/min (Jasco 880-PU pump) with a Waters RI-Detector and toluene as internal standard at 30°C. The samples (15 mg/mL) were injected by hand via a 20 μL loop. PSS-SDV columns filled with 5 μm gel particles with a defined porosity of 106 Å (guard), 105 Å, 103 Å and 102 Å respectively were used. Molecular weight determination was based on narrow polystyrene standards. UV/vis spectrometer (Perkin Elmer Lambda 45) was used to determine the concentration of amino acid in grafted polymer. Further, Phase transition temperature (LCST) (T_c) were carried out by fixation with metal covet stand and water cycle injected from water bath (Julabo F12), with thermostat, and cooling system. Over manual thermostat (TEMPERATUR-MESSGERÄT MD 3040, BECKMANN + EGLE) was also used to adjust the actual temperature inside the solution at 2°C/min over the temperature range from 5°C - 80°C. The polymer solution was 1 wt% in water or pH solution. The DSC thermograms of the polymer solutions were recorded at a heating rate of 5°C/min. The polymer concentration was 50 mg/ml in deionized water and the onset value of the transition was taken as T_c . Perkin Elmer Differential Scanning Calorimeter (DSC) Pyris 1 was used for the determination of T_g of solid polymers. The thermogram was recorded at heating and cooling rate of 5°C/min. The morphology of the

polymer were examined by Scanning Electron Microscopy (SEM) using a Zeiss NEON 40 instrument (USA); 2 kV (30 μm aperture). Sputter coater is a Bal-Tec SCD 500 with a film thickness monitor QSG 100. We applied approx. 4 nm of gold-palladium (Au: Pd = 80:20).

2.3. Synthesis of 4-Formyl-2-methoxyphenylacrylate (VA) (I)

In 250 ml two neck flask fitted with argon balloon. 8 g of vanillin (0.052 mol) was dissolved in 100 mL dry CH_2Cl_2 and allowed to stir strongly and 10.52 g (0.1 mol) of TEA was added. The reaction mixture allowed cooling in ice bath to 0°C - 5°C . 5.4 g (0.059 mol) acryloyl chloride was added drop wise. The yellowish suspension was stirred at 5°C for 1h then, allowed to stir at RT overnight. The precipitate was filtered and solvent was evaporated under reduced pressure. The product was extracted by CH_2Cl_2 and washed three times with distilled water, one with sodium carbonate and one with 0.1 M HCl. The organic phase was dried with MgSO_4 overnight, then filtered and the product was distilled using oil pump and at 100°C . Yield %: 85%

Physical state: Colorless oil changed to white, slurrish solid after cooling overnight in refrigerator.

^1H NMR (500 MHz, CDCl_3): δ (ppm) = 3.73 (s, 3H, 11- CH_3), 5.93 (dd, 2J = 0.7 Hz, 3J = 10.5 Hz, 1H, 10a-CH), 6.23 (dd, 3J = 10.4 Hz, 3J = 17.3 Hz, 1 H, 9-CH), 6.47 (dd, 2J = 0.7 Hz, 3J = 17.3 Hz, 10b-CH), 7.12, (d, 2J = 7.9 Hz 1H, 5-Ar-CH), 7.36 (dd, 3J = 13.8 Hz, , 4J = 1.6, 1H, 3-Ar-CH, d, 4J = 1.2 HZ, 4-Ar-CH), 9.79 (s, 1H, 1-CHO).

^{13}C -NMR (125 MHz, CDCl_3): δ (ppm) = 55.91 (1C, 11- CH_3), 111.09 (1C, 4-Ar-CH), 123.36 (1C, 3-Ar-CH), 124.24 (1C, 5-Ar-CH), 127.08 (1C, 9-CH), 133.16 (1C, 10-CH), 135.26 (1C, 2-Ar-C), 144.62 (1C, 7-Ar-CH), 151.09 (1C, 6-Ar-C), 163.22 (1C, 8-C=O), 190.99 (1C, 1-C=O).

IR (KBr): ν (cm^{-1}): 2950 - 2970 (s) (CH_2 , CH_3), 2840 (m) (OCH_3), 1745 (s) (8-C=O, carbonyl), 1695 (s) (1-C=O, aldehyde), 1600 (s) (C=C), 784 - 885 (m) (Ar-CH).

2.4. Synthesis of Poly(N-isopropylacrylamide-Co-Vanillin acrylate) P(NIPAAm-Co-VA) with 5, 10 and 15 mol% of VA (II a-c)

In round bottom flask 10, 20 and 30 mol%, 0.544 g and 1.088 g, 1.632 respectively of 4-formyl-2-methoxyphenylacrylate was added to 2 g (0.0176 mol) NIPAAm in 40 mL 1,4-dioxane and AIBN was added as 10^{-3} mol% of total mole% of monomers. The reaction mixture was purged in argon for 20 min., and then heated in oil bath at 70°C for 8 h. After cooling at room temperature and also in refrigerator, the polymer was precipitated in diethylether, at -40°C , then dissolved in THF, and re-precipitated in diethylether to remove the unreacted monomers and impurities. Yield %: 88%, 82, and 76 for 10, 15 and 20 respectively, Physical state: Yellowish white solid.

^1H NMR (500 MHz, CDCl_3): δ (ppm) = 0.74 - 1.34 (m, 6H, 11- 2CH_3), 1.47 - 2.82 (m, 6H, 6- CH_2 , 7-CH), 3.60 - 3.73 (m, 3H, 12- OCH_3), 3.80 - 4.10 (br., 1H, 10-CH), 5.85 - 6.90 (br., 1H, 9-NH), 7.07 - 7.60 (m, 3H, 2-CH-Aromatic), 9.73 - 10.1 (br. (s), 1H, 1-CHO).

IR (KBr): ν (cm^{-1}): 2990(s) (6, 7-CH-Aliphatic), 1714 - 1743 (s) (5-C=O), 1640 - 1650 (s) (1-C=O), 1134 (s) (12- OCH_3).

2.5. Synthesis of Grafted 15 mol% P(NIPAAm-co-VA) with β -Alanine and Tryptophan (III-IV)

1.0 g of 10 mol% P(NIPAAm-Co-VA) and 1.0 g of (β -alanine, tryptophan) was dissolved in 50 mL ethanol-water 50/50 V/V %. NaOH was added till the solution becomes pH11. The mixtures were prepared in a 100 mL conical flask and stirred gently for 2 h at room temperature. Solvent was evaporated under reduced pressure. The precipitate was dissolved in THF and re-precipitate in diethylether at -40°C to remove impurities and unreacted molecules. Physical state: Brownish solid.

2.6. Synthesis of Grafted 15 mol% P(NIPAAm-Co-VA)-g-Tryptophan as a Function with Time

The same method discussed previously was repeated several times as a function with reaction time (5, 80, 230, 190, 1970, 2810, 5690 min). The products were separated off and purified. UV. vis spectroscopy was used for determination of reaction conversion for each reaction as the absorbance intensity measurement.

^1H NMR and IR of P(NIPAAm-co-VA)-g- β -alanine (III)

^1H NMR (500 MHz, DMSO): δ (ppm) = 0.78 - 1.24 (m, 6H, 12- 2CH_3), 1.25 - 1.70 (m, 4H, 8, 10- CH_2), 1.82 - 2.20 (m, 2H, 9, 11-CH), 2.62 - 2.75 (m, 2H, 2- CH_2), 3.14 - 3.25 (m, 2H, 3- CH_2), 3.70 - 3.98 (m, 4H, 6- OCH_3 , 13-CH), 7.00 - 7.85 (m, 3H, 5-CH, Aromatic), 8.8 - 8.13 (br. (s), 1H, 6-CH=N).

IR (KBr): ν (cm^{-1}): 2995 (m) (CH-Aliphatic), 1663 - 1650 (s) (7-C=O), 1570 - 1560 (s) (4-CH=N), 1026 - 1107 (s) (8- OCH_3).

^1H NMR and IR of P(NIPAAm-co-VA)-g-Tryptophan (IV)

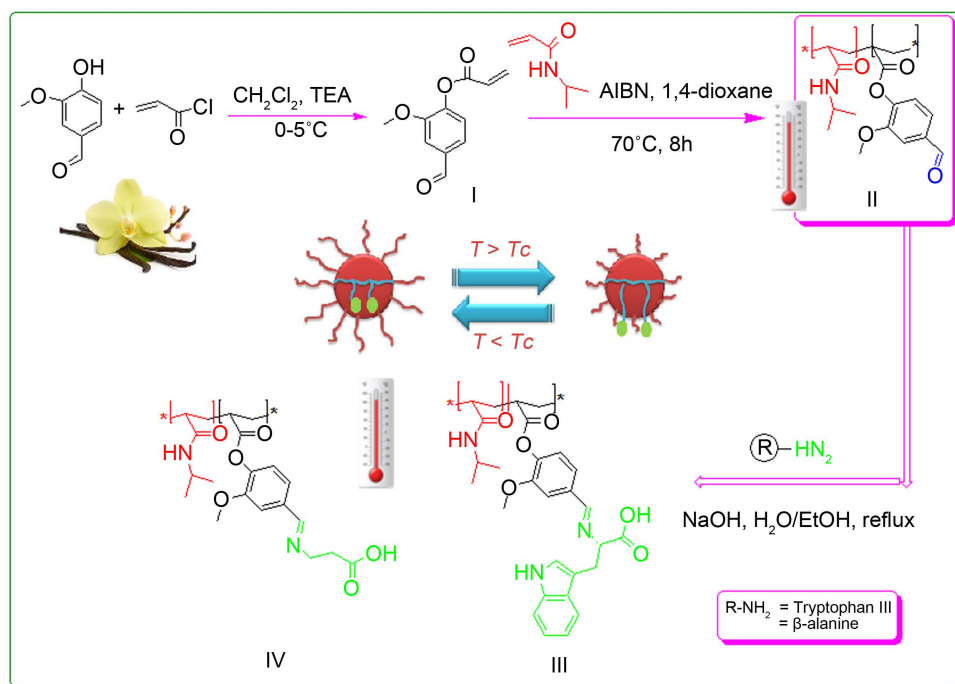
^1H NMR (500 MHz, DMSO): δ (ppm) = 0.75 - 1.26 (m, 6H, 17- 2CH_3), 1.28 - 1.64 (m, 4H, 13, 15- CH_2), 1.87 - 2.25 (m, 2H, 14, 16-CH), 2.95 - 3.05 (br.; t, 2H, 7- CH_2), 3.66 - 3.70 (m, 3H, 11- OCH_3), 6.08 - 6.29 (m, 1H, 8-CH), 6.65 - 6.74 (m, 1H, 6-CH), 6.80 - 7.72 (m, 7H, 1-4, 10-CH, Aromatic), 8.47 - 8.53 (br.; (s), 1H, 9-CH=N), 9.15 - 9.30 (s, 1H, 5NH).

IR (KBr): ν (cm^{-1}): 2993 (m) (CH-Aliphatic), 1663 - 1650 (s) (12-C=O), 1574 - 1563 (s) (9-CH=N), 1030 - 1107 (s) (11- OCH_3), 750 - 742 (s) (1-4-CH-aromatic).

3. Results and Discussions

3.1. Synthesis of Monomer, Copolymers and Grafted Copolymers

Monomer, copolymers and grafted copolymers were synthesized according to the chemical conditions described in **Scheme 1**.



Scheme 1. Synthesis of VA, copolymers and grafted polymers with NIPAAm.

Compound (I) or 4-formyl-2-methoxyphenylacrylate abbreviated by (VA) monomer was prepared in one step reaction between vanillin and acryloyl chloride in the presence of triethylamine or sodium as shown in **Scheme 1**. It has chemically evaluated by ¹H NMR and ¹³C and FT IR in **Figure 1**. All data was in logic state and proved the presence of active aldehyde group at 9.97 ppm and 196 ppm.

The lower critical solution temperature of poly(N-isopropylacrylamide) has influenced by introducing hydrophilic or hydrophobic moiety in polymer chain. Vanillin acrylate (I) act as the hydrophobic molecule which has copolymerized with NIPAAm in different mole ratios (5, 10 and 15 mol%) by random free radical polymerization as described in **Scheme 1**. The chemical structure of each polymer was evaluated by ¹H NMR and FT IR as shown in **Figure 2**. The ¹H NMR of copolymers II a-c showed specific broad multiples peaks at $\delta = 0.73 - 1.35$ ppm of 2CH₃ NIPAAm, at $\delta = 7.08 - 7.62$ ppm of Ar-H, and at $\delta = 9.74$ of H-CHO of VA monomer. FTIR showed the presence of (C=O stretch) ester at 1743 cm⁻¹ and (C=O stretch) amide at 1650 cm⁻¹. The actually composition of each monomer in the copolymer chain was calculated from ¹H NMR spectra by the ratio of the intensity of the signals at 4 ppm (for -CH isopropyl of NIPAAm), with signal at 9.74 ppm (for CHO of VA) as cleared in **Table 1**. Functionality with the aldehyde group in the polymer main chain was an interested to make grafting with any amino compound to produce Schiff's base which is familiar by click reaction **Scheme 1**. The grafting process has been done at room temperature in mixture of ethanol and H₂O 1:1 and pH11. Grafted copolymers were elucidated by ¹H NMR and FT IR. The ¹H NMR showed the disappearance

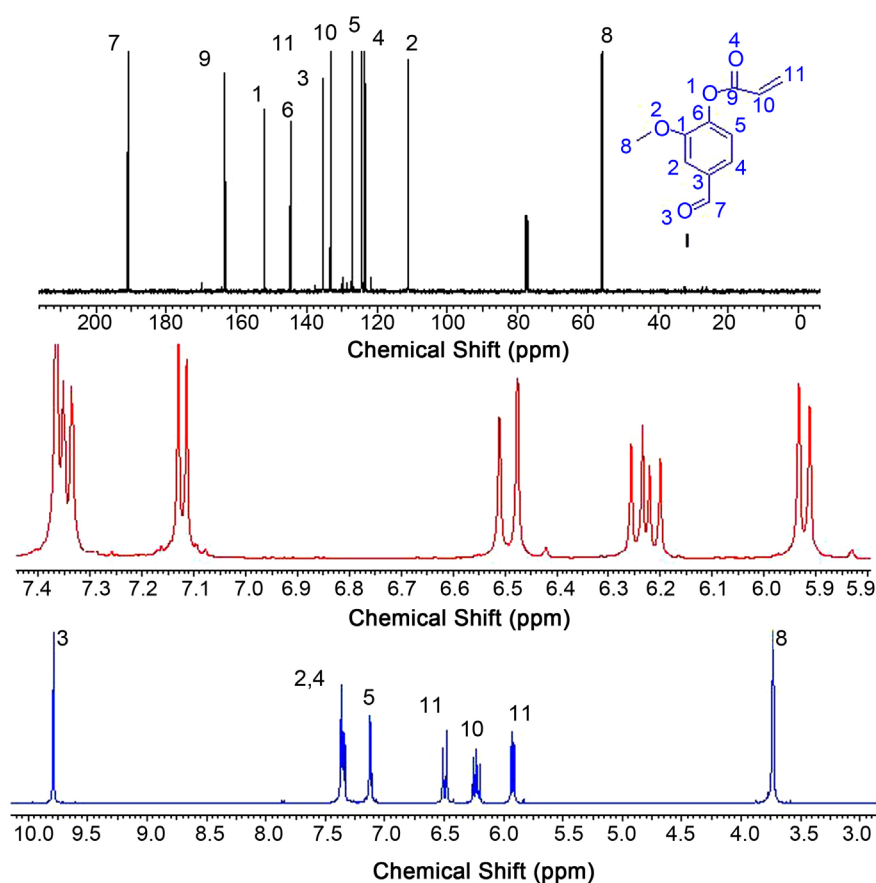


Figure 1. ^1H and ^{13}C NMR spectra (CDCl_3) of (VA).

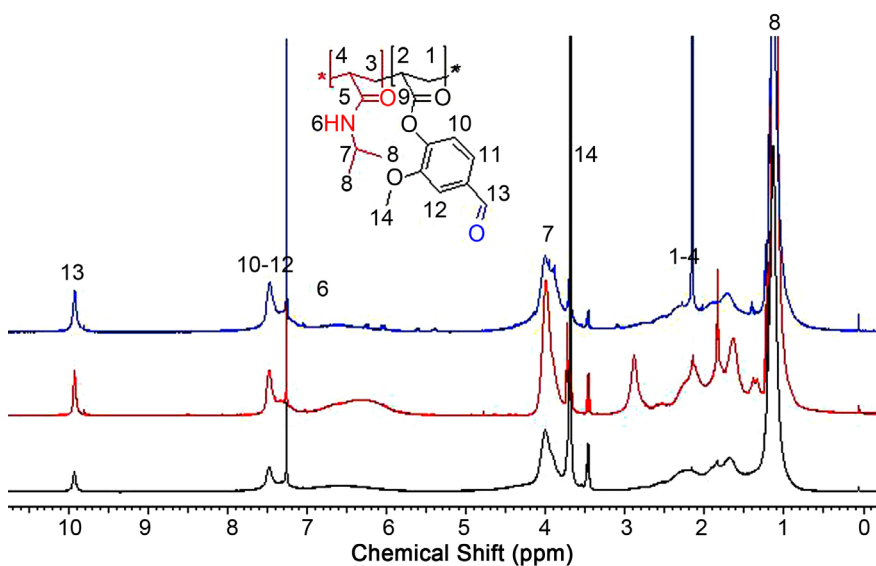


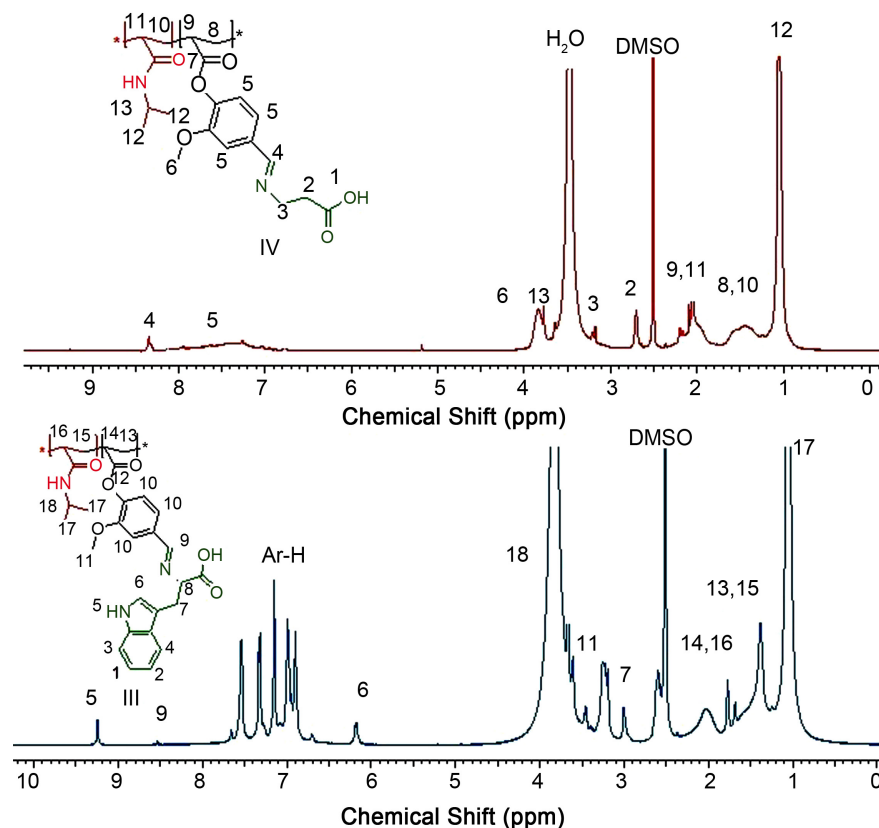
Figure 2. ^1H NMR spectra (CDCl_3) of $\text{P}(\text{NIPAAm-co-VA})$ 5, 10, 15 mole ratio of VA.

of aldehyde signal at 9.74 ppm and formation of imino ($\text{HC}=\text{N}$) signal at about 8.5 ppm as shown **Figure 3**. **Figure 4** showed FT IR spectra and proved the presence of ($\text{C}=\text{N}$ stretch) imine at about 1563 cm^{-1} .

Table 1. Yield, composition, conversion, number average molecular weight, polydispersity, and glass temperature of PVA, P(NIPAAm-co-VA) 10, 15, 20 mole ratio of VA and grafted P(NIPAAm-co-VA).

Polymer	Yield (%)	¹ HNMR VA (mol %)	Conversion (%)	Mn ^a (g/mol) 10 ⁴	PD ^b	T _g ^c (°C)	T _c ^d (°C)		
							H ₂ O	pH5	pH11
II a	92	8.93	-	45300	1.98	130	28	-	-
II b	89	15.42	-	16240	2.27	128	21	-	-
II c	85	25.38	-	13575	2.46	122	17	-	-
III	86	-	84	8990	1.87	138	-	39	-
IV	87	-	79	14530	2.12	132	-	44	-

^aNumber average molecular weight, ^bPolydispersity, ^cGlass transition temperature, ^dLower critical solution temperature.

**Figure 3.** ¹H NMR spectra (DMSO) of P(NIPAAm-co-VA)-g-Tryptophan or β-alanine.

3.2. Polymer Characterization

3.2.1. Molecular Weight

The molecular weight of polymers was determined by SEC with PS as standard in CHCl₃. The molecular weight of copolymers and grafted copolymers has summarized in Table. It shows one peak, that proofing the disappearance of low molecular weight like monomers or impurities as shown in **Figure 5(a)** and **Figure 5(b)**.

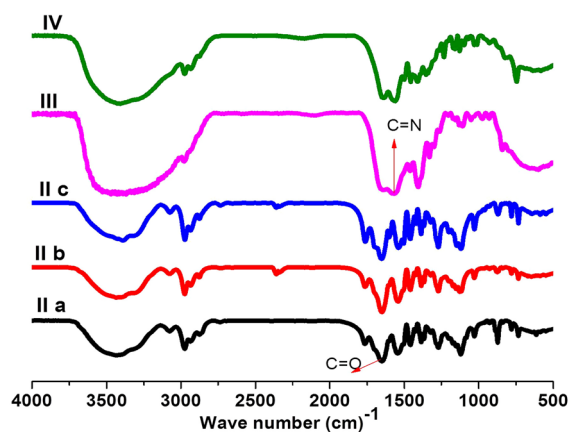
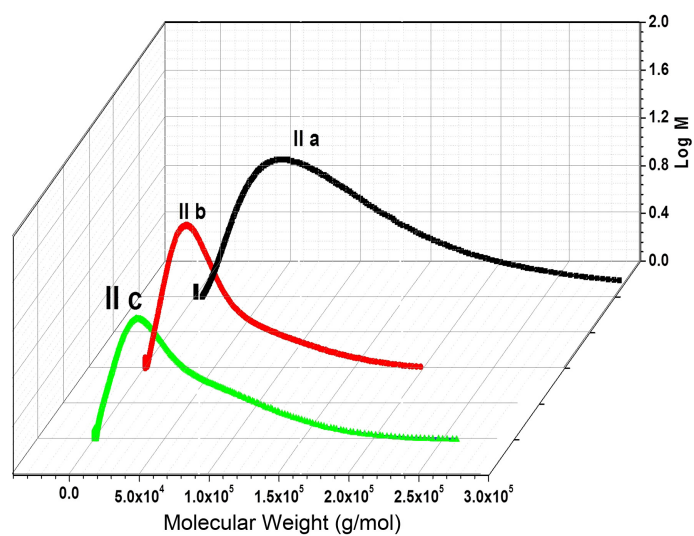
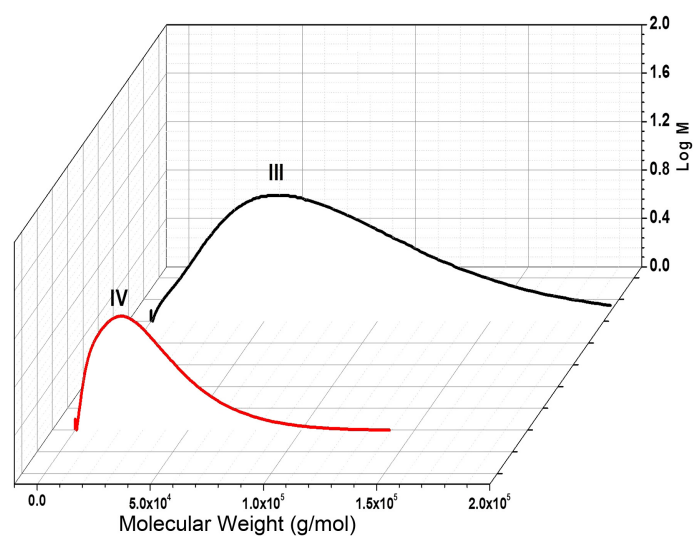


Figure 4. IR spectra and Poly(NIPAAm-co-VA) II a-c and grafted copolymers III-IV.



(a)



(b)

Figure 5. GPC molecular weight of copolymers.

3.2.2. The Phase Separation and Lower Critical Solution Temperature (LCST) of Copolymers and Grafted Copolymers Solution

The incorporation of vanillin acrylate in the polymer chain has a great interest to change the lower critical solution temperature. Decreased values of T_c with respect to VA molar concentrations in polymer chain were recorded. It demonstrated 28, 19, 16 for polymer II a, II b and II c respectively. This decreasing in the T_c values can be interpreted to the domination of hydrophobic moiety to hydrophilic in the polymer chains which logically increased by increasing VA monomer. The formation of Schiff's base with tryptophan and β -alanine amino acids was achieved for polymer III and IV. Generally, the stability of Schiff's base is occurred in alkaline solution and dissociated in highly acidic conditions, for this reason it characterizes as stimuli-responsive linker in polymer chemistry [46]. The presence of imine group in the copolymer change the hydrophobic effect to hydrophilic one and the chain dominates highly hydrophilicity and give the polymer dual response character to pH and temperature. The same technique was used for the determination of LCST of grafted copolymers in deionized water, pH5 and pH11 solutions. The pH responsive of the imine linkage has influenced on the value of the LCST of grafted copolymers. A sharp increase in the LCST was observed for all copolymers. However, the lowest value of LCST were assigned at pH5, this might be attributed to the instability of the imine linkage, which is going to decompose and again the hydrophobic feature being dominated in solution. When the solution became neutral or highly basic media, we could not see any turbidity in solution referring to the highly LCST value, indicating the strength of hydrophilic feature due to the hydrogen bonding between the amide group of NIPAAm with imine group in H_2O . The (T_c, s) values was summarized in Table 1, Figure 6 shows the relation between temperature and transmittance. The T_c for all copolymers was calculated as the inflected point; the cloud point was also calculated at 50% transmittance. The different T_c values detected by Uv-vis. Spectroscopy and DSC according to each specific definitions of the T_c (Figure 7).

3.2.3. Conversion of Poly(NIPAAm-Co-VA) to Poly(NIPAAm-Co-VA)-g-Tryptophan

In order to achieve the conversion of poly (NIPAAm-Co-VA) to poly (NIPAAm-Co-VA)-g-tryptophan through the chemical reaction, absorption has been measured as function with time. The polymer solution has diluted to 10-3 W/V for each measurement. Figure 8 shows the UV-vis. Spectroscopy of grafting reaction between poly(NIPAAm-Co-VA) with tryptophan. The relation between wavelength and absorbance proofed the disappearance of C=O aldehyde group at 250 - 270 nm and formation of new bond at 340 - 380 nm of C=N imine linkage. The formation of imino linkage has increased with time starting with 5 min which showed about zero absorbance and has been increased gradually till the highest value of absorbance 1.67 at 5690 min. Figure 9 shows the statistical clarification of absorbance intensity as a function with time per minutes.

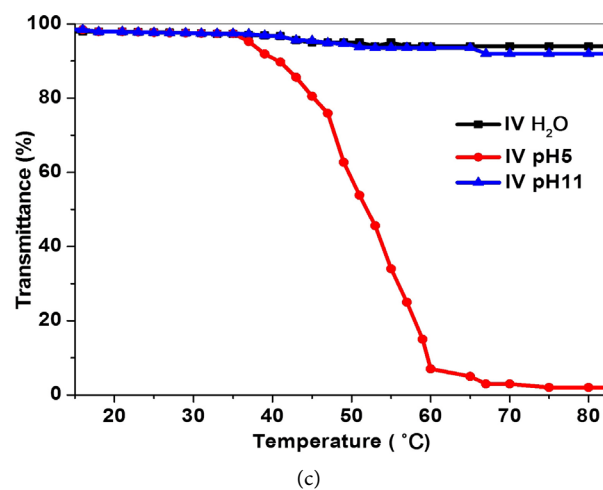
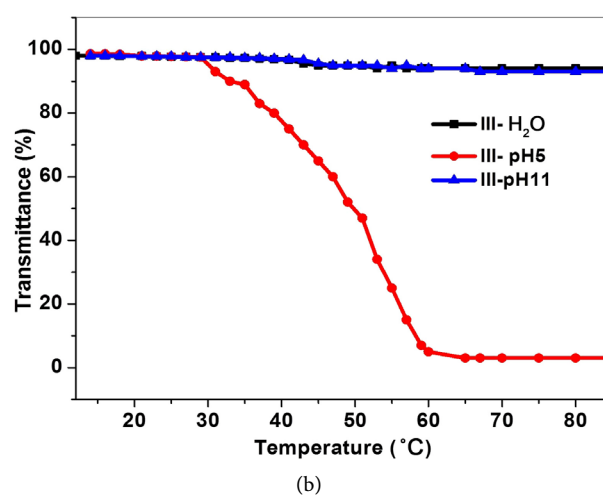
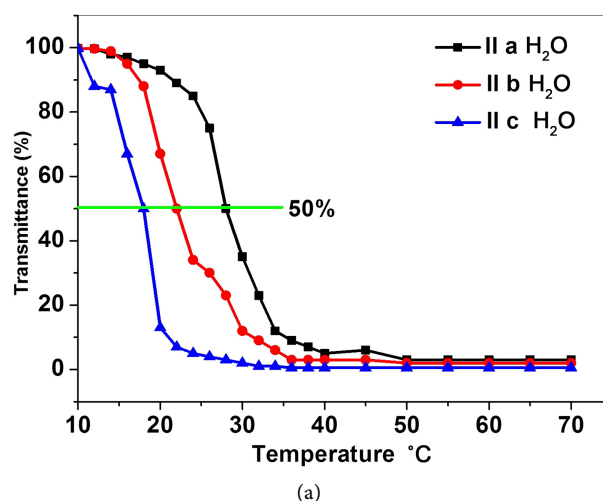


Figure 6. (a)-(c): The change in turbidity with temperature for determination the T_c of Poly(NIPAAm-Co-VA) with different mol% of VA (a), P (NIPAAm-Co-VA)-g-tryptophan with 15 mol% of VA (b), and P (NIPAAm-Co-VA)-g-β-alanine with 15 mol% of VA (c) using UV-vis. Spectroscopy for 1 wt% of polymer solution in H₂O (A) and H₂O, pH5 and pH11 ((b), (c)) respectively.

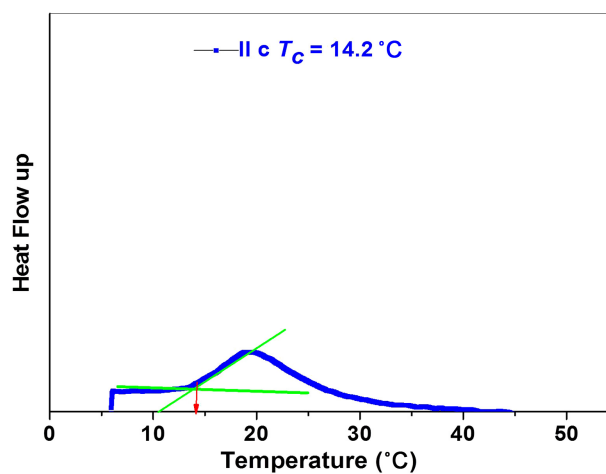


Figure 7. DSC of polymer solution (II c) for determination of LCST (T_g).

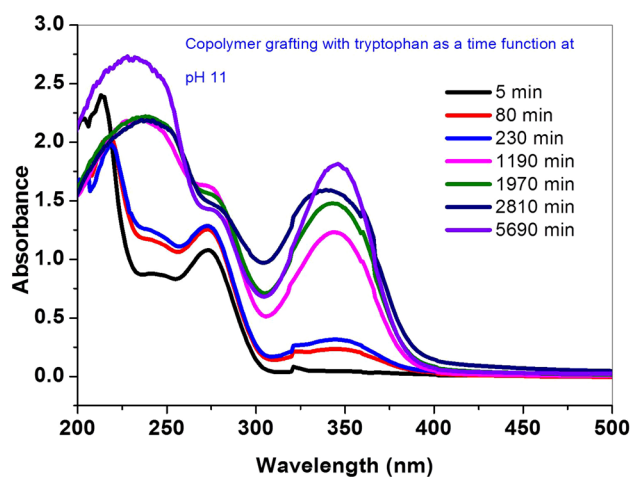


Figure 8. UV-vis. Spectroscopy for the formation of grafted poly (NIPAAm-Co-VA)-g-tryptophan as increasing in absorbance with time.

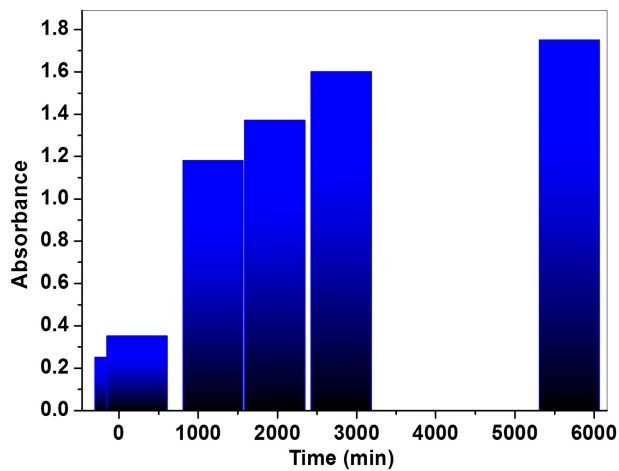


Figure 9. Statistical clarification of absorbance intensity with time.

3.2.4. Glass Transition Temperature

Differential Scanning Calorimeter was used to record the glass transition temperature (T_g) of dried samples at heating rate $5^\circ\text{C}/\text{min}$, and T_g was taken as the midpoint inflection. The (T_g ,s) values have been summarized in **Table 1** for homo-, copolymers and grafted copolymers. **Figure 10** showed a single T_g for each sample, which indicating the formation of random copolymers [56]. PNIAAm homopolymer showed T_g at 135°C . Incorporation of hydrophobic moieties in the copolymers chain resulted in decreased in T_g , which might be attributed to increase in the spacing and hence fewer interaction between polymer chains leading to more flexibility and T_g of the polymer decreased [56]. Introducing grafting molecule in copolymer III, IV main chain has directly effect in raising the T_g value due to increasing the hydrophilic moiety hence, increasing in hydrogen bonds. Further, the copolymer (III) grafted with tryptophan showed the highest value of T_g due to the steric hindrance of aromatic molecule.

3.2.5. Scanning Electron Microscope (SEM)

The micrographs in **Figure 11** is the SEM images obtained at a magnification of $1000\times$ for polymer II b before grafting and polymer III after grafting. Before grafted polymer surface appears compact and nonporous. After grafting the porosity of grafted polymer surface increases the whole surface looks like waxy with cross-linking referring to the imine linkage and grating of tryptophan.

4. Conclusion

In the present work, we synthesized new vanillin acrylate monomer in one step reaction. This monomer was used to prepare three different mole ratios of thermo-responsive functional polymers by copolymerization with N-isopropylacrylamide. The phase separation was our goal to achieve this work, the LCST of polymers was detected by UV-vis, spectroscopy, further micro-DSC for polymer solution. The Tcs exhibited lower temperature than PNIPAAm due

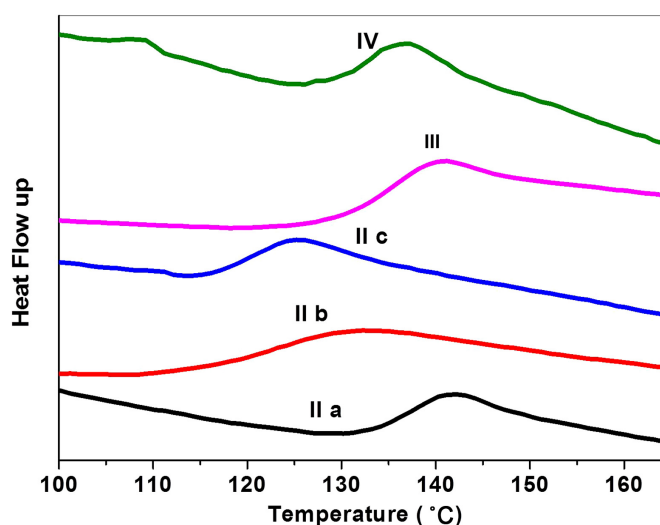


Figure 10. DSC shows the T_g of selective polymers.

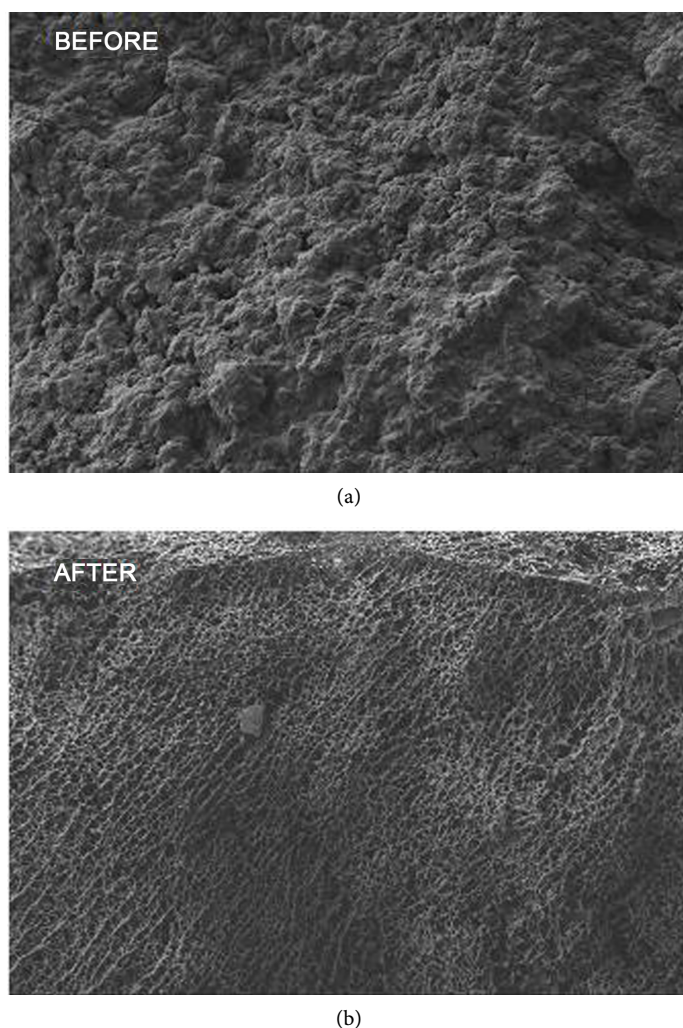


Figure 11. SEM of copolymer II b (before grafting) and grafted copolymer with tryptophan III at 1000× magnification.

to the domination of hydrophobic groups in VA. All monomer and polymers have completely been chemically and physically investigated. The presence of active aldehyde group in the polymer chain encouraged the formation of Schiff base with primary amine. For this we used tryptophan and β -alanine as a target for our linker. The grafted polymers were evaluated and characterized. The LCST showed higher temperature than non-grafted due to the highly hydrophilicity of polymers. Similarly, the T_g showed increase in the glass temperature for the same reason. The Scanning electron microscopy of polymers after grafting has exhibited pores and cross-linking indicating the formation of grafting imine linkers.

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