

Synthesis and Characterization of Poly(3,4-Diacetamidostyrene)

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Abstract

3,4-Diacetamidostyrene (DAAmS) was synthesized by two step reaction. The first step is the reduction of nitro group of 3-nitro-4-aminostyrene (NAS) to obtain 3,4-diaminostyrene (DAS) which is followed by acylation of amino groups with acetic anhydride as the second step. DAAmS monomer was polymerized by using AIBN as initiator in ethanol solution at 75°C, for 7 h to reach 87% conversion. Synthesized DAAmS was characterized by FT-IR, GC-MS and NMR (including ¹H- NMR, APT ¹³C NMR and HETCOR) studies. Poly(3,4-diacetamidostyrene) (PDAAmS) was characterized by FT-IR, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) studies. Disappearance of vinyl absorption peaks in H-NMR spectra of PDAAmS showed the polymerization. Glass transition temperature of polymer was observed to be 174°C from DSC thermogram.

INTRODUCTION

Reactive and functional polymers can be prepared by direct polymerization of functional group carrying monomers or chemical modification of polymers. Polystyrene has been widely used as a substrate material for a number of application requiring stability and inertness to various agents. Due to its ease of availability in various forms and shapes, chemical modification of polystyrene by introducing specific functional groups on the phenyl ring has long been considered as a versatile method for the synthesis of specialty polymers based on polystyrene and co-polymers with divinylbenzene [1,2]. A variety of functional groups have been

chemically substituted to PS for some specific end-uses such as immunologic assays [3], ion-exchange resins [4,5], catalysts [6], etc. There are a few studies reported in the literature on the di-reactive-substituted group carrying styrene derivatives and their polymers, such as; 3,4-diaminostyrene (DAS) and its derivatives and related polymers. The first synthesis of DAS was described by C. G. Overberger [7,8] in their attempt to the prepare 5(6)-vinylbenzimidazole. Manecke and Rotter 1969 [9] synthesized DAS and converted to the 2,3-diphenyl-6-vinyl-chinoxalin. In the last reported for the preparation of DAS, a new method was described for the preparation of poly(3,4-diaminostyrene) PDAS and additional reactions were carried on the polymer to obtain poly(5(6)-vinylbenzimidazole) (PBI) and poly(2-methyl-5(6)-vinyl benzimidazole) (PMAI) [10]. The polymers prepared from DAS were limited to PBI and PMBI in spite of good reactivity of

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diamino group for further reactions. The reason for the existence of a few polymers in the literature based on DAS monomer is clue to the instability of DAS coming from diamine groups [11] and brown colour of its homopolymer [10]. Therefore, in this study, stability of DAS was improved by the acylation of amine groups with acetic anhydride and a white monomer 3,4-diacetamidostyrene (DAAmS) was synthesized. Its homopolymer was prepared and characterized by FT-IR, NMR spectroscopy and thermal properties were studied by TGA and DSC.

EXPERIMENTAL

The reaction scheme for the synthesis of DAAmS monomer and PDAAmS homopolymer was given below. The starting molecule NAS was also prepared by following the recipe initially prepared by Brembilla (1982). Reduction of nitro groups of NAS to amine [10] was achieved by using Na_2S and reactive functional amine groups of DAS were acylated to obtain DAAmS monomer. Polymerization of DAAmS was carried out in ethanol solution by using AIBN initiator.

Synthesis of 3,4-diaminostyrene (DAS)

3-nitro-4-aminostyrene (0.5 g, 3.05 mmol) was added to hot Na_2S solution (100 mL water, 50 mL ethanol and 60 g Na_2S) and the temperature of the medium was kept at 90°C for 3 h. The mixture was cooled to room temperature, diluted with cold water and extracted with ethyl acetate. The colourless

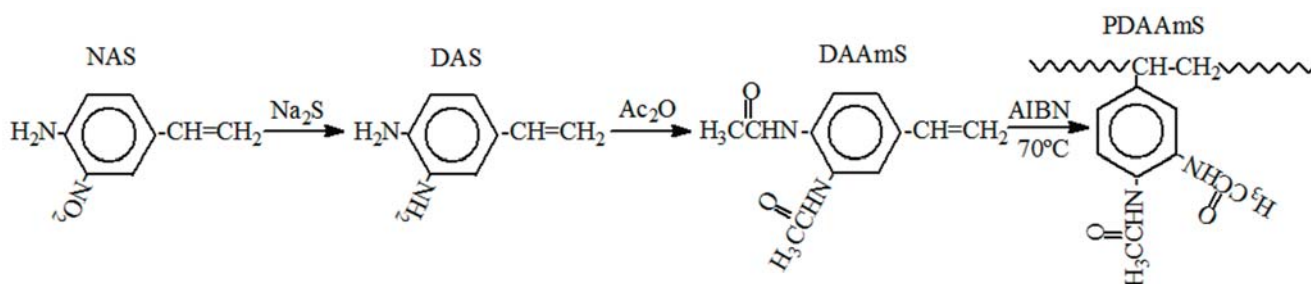
solution was washed three-times with water, dried with anhydrous sodium carbonate and filtered. Due to instability of DAS in the concentrated form, it was used in further reaction without additional purification. GC-MS characterization was made by direct injection of ethyl acetate into the system. A small amount of sample was isolated by rotary evaporation and dissolved in d₆-DMSO for NMR studies.

Synthesis of 3,4-diacetamidostyrene (DAAmS)

Excess acetic anhydride was added to the ethyl acetate solution of DAS in a separation funnel. The mixture was shaken for 5 minutes, washed with water, dried with anhydrous sodium carbonate, filtered and finally ethyl acetate was removed by rotary evaporation to dryness. The white precipitate was recrystallized from ether to give 0.56 g product with a m.p. of 202°C , (85% conversion, for two step reaction).

Polymerization of 3,4-diacetamidostyrene (PDAAmS)

1 g of DAAmS monomer was dissolved in 150 ml ethanol and 0.01g of AIBN was added as initiator. Polymerization was carried out in N_2 atm at 70°C for 7 h to reach 87% conversion. After cooling, ethyl acetate was added to precipitate the polymer, separated by filtration, dissolved in methanol and reprecipitated by adding ethyl acetate to remove unpolymerized monomer. Precipitated polymer, dried in a vacuum oven at 30°C to remove the solvent traces before characterization experiments.



Scheme 1. The reaction sequence for the synthesis of DAAmS and its polymerization.

Characterization of NAS, DAS, DAAMs and PDAAMs

DSC and TGA measurements were carried out by using Du Pont DSC-9100 and TGA-951 models respectively, with 9900 data processing system, under nitrogen atmosphere and at a heating rate of 10°C/min. For spectroscopic measurement Nicolet 520 FT-IR spectrometer was used. The $^1\text{H-NMR}$, APT $^{13}\text{C-NMR}$ and $^1\text{H-}^{13}\text{C}$ HETCOR spectra were recorded on AC400 Bruker spectrometer operating at 400 MHz in d_6 -DMSO, GC-MS measurements were made by using Agilent 6890N GC system and 5973 mass selective detector, with Agilent columns 122-5532 DB-5ms, (0.25 mm x 30 m x 0.25 μm).

RESULTS AND DISCUSSION

FT-IR Characterization of NAS, DAS, DAAMs and PDAAMs

The FT-IR spectra of starting material, intermediates and polymer are shown in Figure 1. In the spectrum of NAS Figure 1(a); the N-H stretching bands at

3468 and 3338 cm^{-1} , (Ar-NO₂) N=O stretching band 1336 cm^{-1} , C-N stretching of aromatic amine 1240 cm^{-1} and out of plane bending bands of vinyl group 986 and 904 cm^{-1} were observed. The spectrum of DAS is given in the same figure (b). This compound was obtained by the reduction of nitro group of NAS. The characteristic bands of DAS; N-H stretching band at 3400-3100 cm^{-1} , =C-H stretching band of vinyl at 3080 cm^{-1} , N-H bending of amine group at 1620 cm^{-1} , C=C ring stretching of aromatic group at 1518 cm^{-1} , the peak at 1290 cm^{-1} due to the C-N stretching of primary aromatic amine and out of plane C-H bending bands of vinyl group at 990 and 880 cm^{-1} were observed. When the spectra of DAS is compared with the NAS in Figure 1(a and b), it is observed that the band at 1336 cm^{-1} assigned to Ar-NO₂ group of NAS was disappeared, in the spectrum of DAS broad N-H stretching bands observed at the 3400-3100 cm^{-1} by the reduction of -NO₂ group of NAS. The spectra of DAAMs, synthesized by acylation of amine groups of DAS, can be seen in Figure 1c. The characteristic bands of 3260 cm^{-1} due to -NH- stretching of amide, the

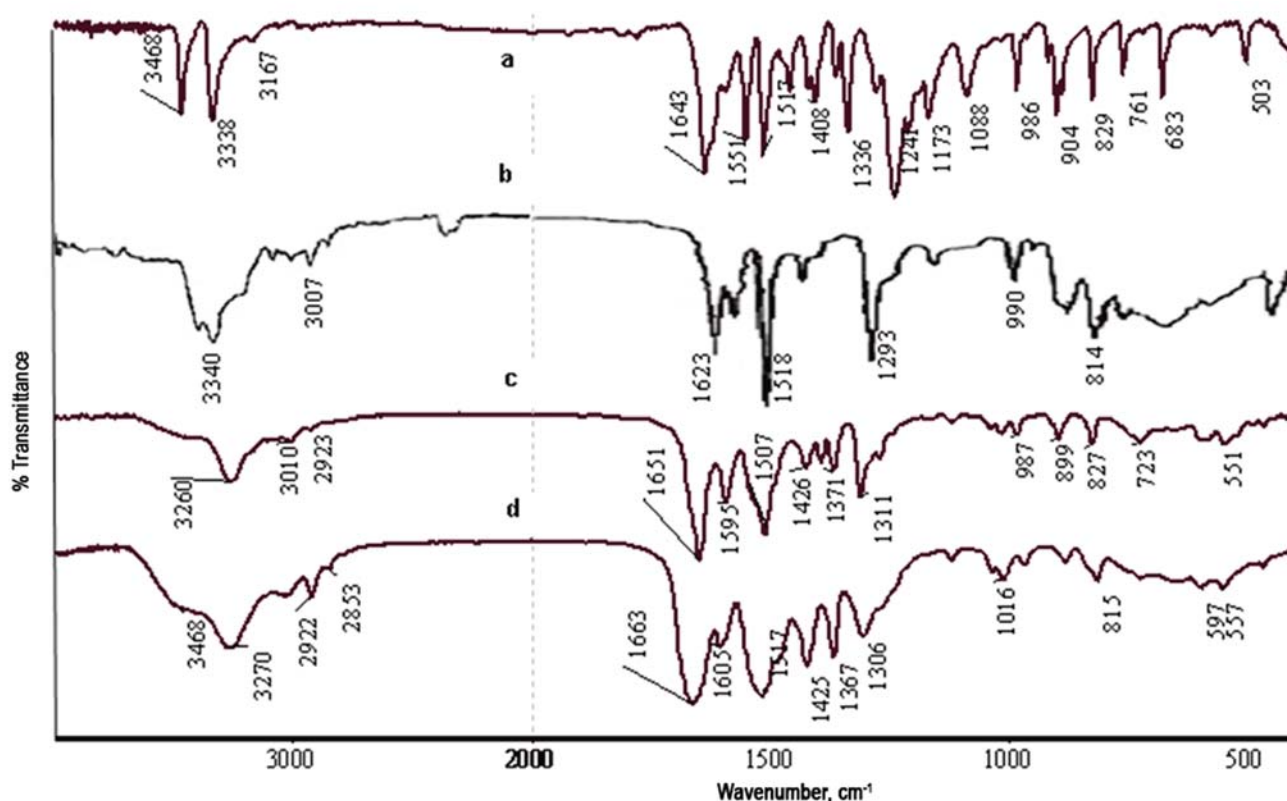


Figure 1. The FT-IR spectra of (a) NAS, (b) DAS, (c) DAAMs and (d) PDAAMs.

absorption band at 1650 cm^{-1} due to amide carbonyl $-\text{NHC}=\text{OCH}_3$, the peak at 1370 cm^{-1} due to bending of $-\text{CH}_3$, were observed. These bands are proof of synthesis of DAAMs by acylation of amine groups of DAS with acetic anhydride. The characteristic polymeric band broadening property was observed in the spectra of PDAAMs (Figure 1 d). The absorption bands of alkyl groups on the main chain of PDAAMs were observed 2922 and 2853 cm^{-1} . This is a full proof of free radical polymerization of DAAMs monomer.

GC-MS Characterization of DAAMs

GC-MS experiments were carried out to analyze DAAMs and its MS spectra is shown in Figure 2. The last positive ion peak observed in the MS spectra represents the corresponding molecular ion peak of DAAMs, which is 218 a.m.u. , and agreeing with the calculated molecular weight of this compound. The GC-MS studies of NAS and DAS were also studied and their molecular ion peaks were found as the same as the calculated molecular weights.

NMR Characterization of NAS, DAS and DAAMs

$^1\text{H-NMR}$, APT ^{13}C and HETCOR studies were carried out to elucidate the structure of NAS, DAS and DAAMs. The $^1\text{H-NMR}$ spectrum was presented

on vertical axis and decoupled APT $^{13}\text{C-NMR}$ spectrum was presented on horizontal axis of respective HETCOR spectra. Thus, they were not given separately. The HETCOR spectrum of the NAS is shown in Fig. 3. The signal observed at 5.12 (d) and 5.65 (d) ppm due to methylene protons of vinyl group and both correlated with the same peak of ^{13}C at 112 ppm in HETCOR spectrum. This indicates that methyl protons are not magnetically equivalent. The methyne proton ($-\text{CH}=\text{}$) of vinyl group is observed at 6.63 ppm (q) in $^1\text{H-NMR}$ which correlated with the peak of ^{13}C at 135 ppm . The broad signal of amine protons was observed at 7.57 ppm and not correlated with any peak of ^{13}C spectrum. The signals observed at 7.00 , 7.64 and 7.93 ppm are attributed to aromatic protons. They are correlated with the peaks of ^{13}C at 119.5 , 132.5 and 123.5 ppm , respectively. The number of protons of NAS, determined by integrating the area under absorption peaks in $^1\text{H-NMR}$, is eight which is equal to the theoretically calculated number of protons of NAS. FT-IR and NMR analysis of NAS confirmed its synthesis.

The HETCOR spectrum of DAS is shown in Figure 4 as it was previously mentioned, DAS was obtained by the reduction of nitro group of NAS. So, it is clear in the $^1\text{H-NMR}$ of DAS that all the proton peaks

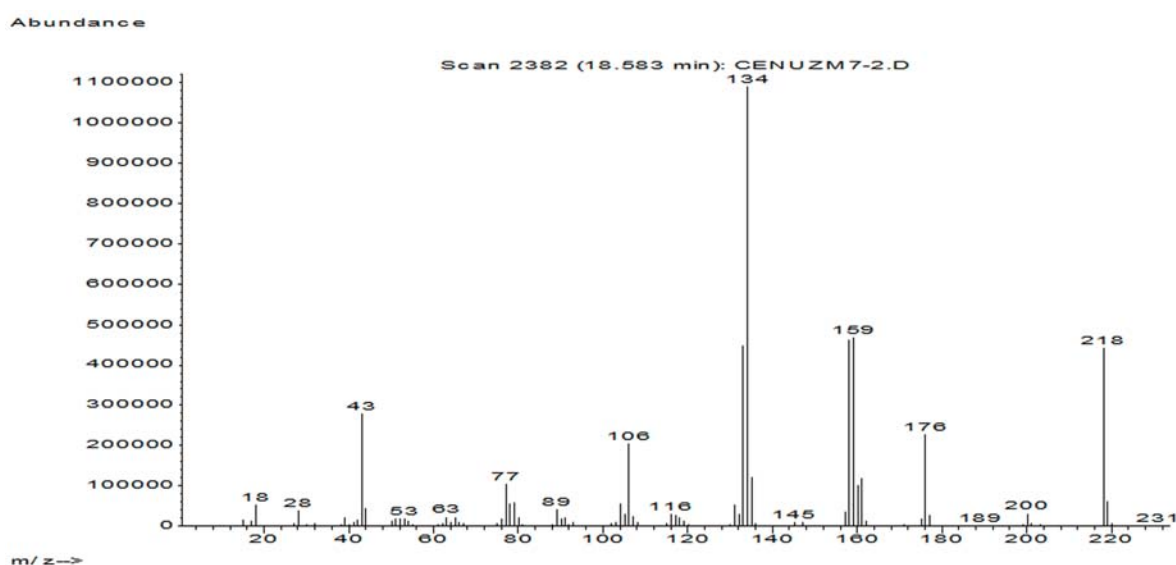


Figure 2. MS spectrum of DAAMs.

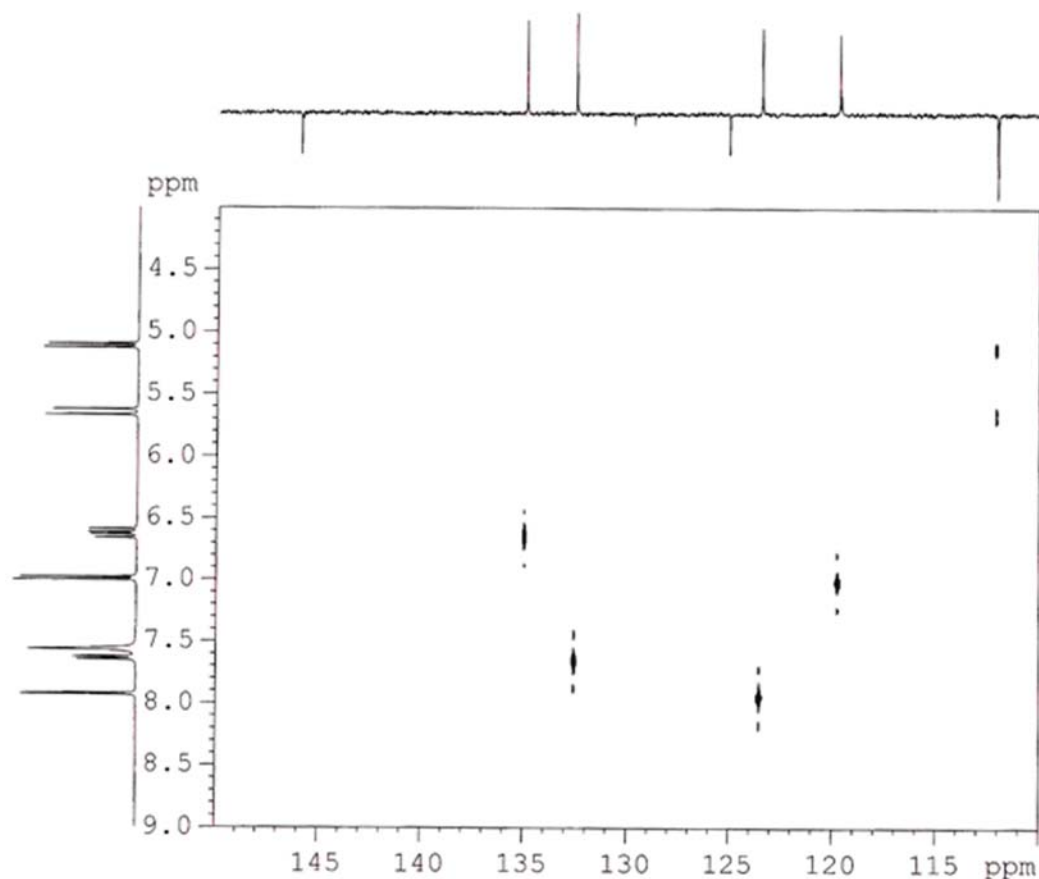


Figure 3. HETCOR spectrum of NAS.

shifted to upfield, because of the reduction of deshielding group $-\text{NO}_2$. Two double peaks seen in the region 4.85 (d) and 5.35 (d) ppm are due to methylene protons ($=\text{CH}_2$) of vinyl group which are correlated with the peak of a ^{13}C at 108.0 ppm. The broad signals of two amine group protons were observed at 4.60 and 4.46 (s) ppm.

The methyne proton of vinyl group and two aromatic protons overlapped in the region 6.50-6.40 ppm. The signals of this region are correlated with peaks of ^{13}C at 137.6, 116.7 and 114.0 ppm. The frequency difference between the two peaks, observed through high field in the overlapped region, is 10.82 Hz, which is equal to the spin coupling constant of methylene ($J_{\text{ax}}=10.85$ Hz) proton, observed at 4.85 ppm. This result proves the position of methyne proton of vinyl group. The signal observed at 6.49 ppm is attributed to aromatic proton. There are eight peaks in ^{13}C spectrum, four CH groups give up-peaks and three quarter C and one CH_2 group give down-peaks, which is equal to the number of

carbons of DAS. FT-IR and NMR analysis of NAS confirmed the synthesis of DAS.

The HETCOR spectrum of DAAMs is shown in Figure 5. As it was observed in the spectrum of NAS and DAS the methylene protons of vinyl group of DAAMs give two doublet peak in ^1H -NMR spectrum at 5.20 and 5.70 ppm with (J_{ax} and J_{bx}) 10.95 and 17.61 Hz, both peak correlated with the same peak of ^{13}C at 113.7 ppm in the HETCOR spectrum. This indicates that methylene protons are not magnetically equivalent. The methyne ($-\text{CH}=\text{}$) proton of vinyl group is observed at 6.66 (q) ppm and there are two spin coupling constants which are (J_{ax} and J_{bx}) 10.95 and 17.61 Hz due to spin-spin interaction with each protons of methylene separately. The peaks observed at 7.24, 7.55 and 7.58 ppm, are attributed to aromatic protons and they are correlated with the peaks of ^{13}C at 122.42, 124.49 and 122.71 ppm respectively. There are two amide ($-\text{NHCO}-$) groups on the DAAMs and the resonance signal is observed at 9.32-9.34 ppm in ^1H -NMR,

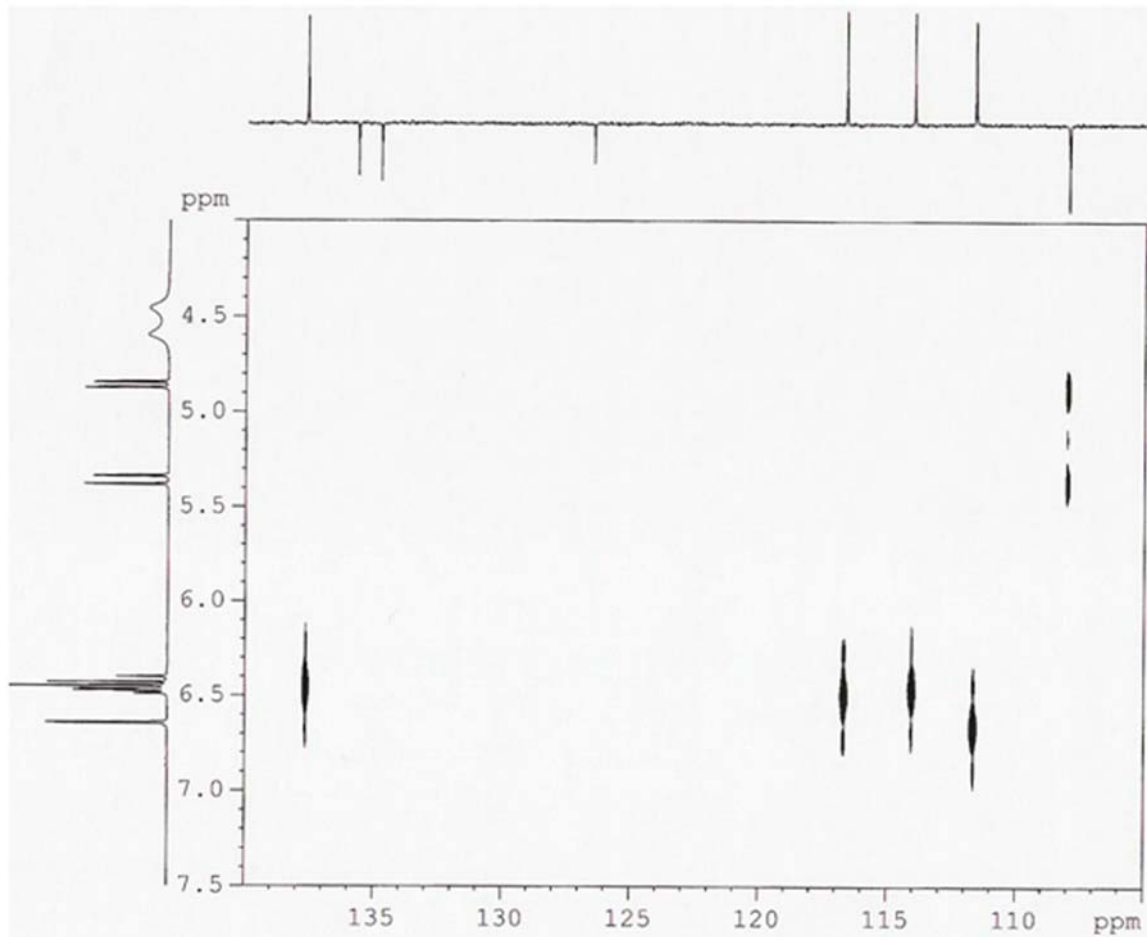


Figure 4. HETCOR spectrum of DAS.

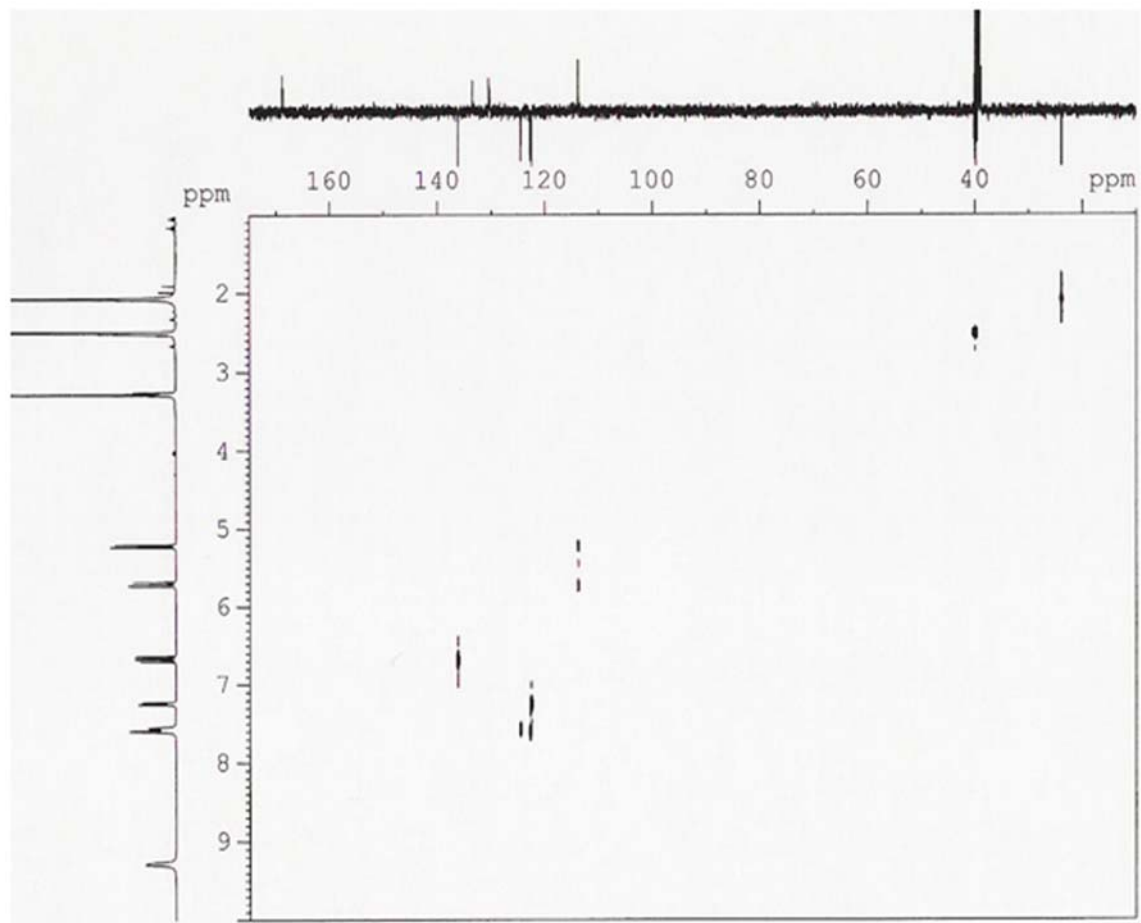


Figure 5. HETCOR spectrum of DAAMs.

which is sharp and looks like doublet peaks. The sharpness of the peak indicates that the rate of exchange of proton on the amide nitrogen is rapid. If the exchange is rapid, the NH proton is decoupled from N atom and from protons on adjacent atoms. Thus, it can be said that each peak of the doublet belongs to each amido group of DAAMs. The first three peaks which were observed at 2.10, 2.49 and 3.35 ppm in the $^1\text{H-NMR}$ spectrum, are due to methyl (NCOCH_3), residual protons of DMSO and dissolved water in DMSO, respectively.

NMR Characterization of PDAAMs

Deshielding effect of double bond on the hydrogen of vinyl group was observed in $^1\text{H-NMR}$ spectra of NAS, DAS and DAAMs (Figure 3-5). This effect is the main reason for the observation of proton peaks of vinyl groups at the low field. This effect can be used as a tool to check the free radical polymerization. The peaks were observed at 5.20, 5.70 and 6.66 ppm, Figure 5, due to vinyl hydrogens of DAAMs disappeared in the $^1\text{H-NMR}$ spectrum of PDAAMs (Figure 6.) after the polymerization reaction. This indicates that polymerization occurred by free radical polymerization. Resonance signals of amide hydrogens ($-\text{NHCO}-$) were observed at low field at 9.22 ppm. The same group was observed at 9.32-9.34 ppm in the spectrum of DAAMs. The peaks observed at 7.29 and 6.54 ppm, are due to aromatic protons. The region, in the range of 0.5-2.2 ppm, that formed by overlapping one sharp and broad peak include absorption peaks of main chain hydrogens of PDAAMs and side methyl groups. The peaks at 2.02 and 1.52 ppm are due to methyl (NCOCH_3) groups and methylene group of chain, respectively. It is very difficult to determine the chemical shift of the methyne (CH) group that belong to the main chain of polymer. It is most probably overlapped with peaks of methyl (NCOCH_3) and methylene groups.

The number of protons were determined for the repeating unit of PDAAMs by integrating the area under corresponding absorption peaks. As it is seen from the spectrum, in Fig. 6. the integrated value for the aromatic protons is 1.62 which is due to three hydrogen atoms present on the ring. According to this result, the number of the hydrogens under the area of the peaks 2.02 and 1.52 ppm were determined as 9.35. It is good agreement with theoretical number of hydrogens which is 9 actually. These results confirm the successful synthesis of PDAAMs.

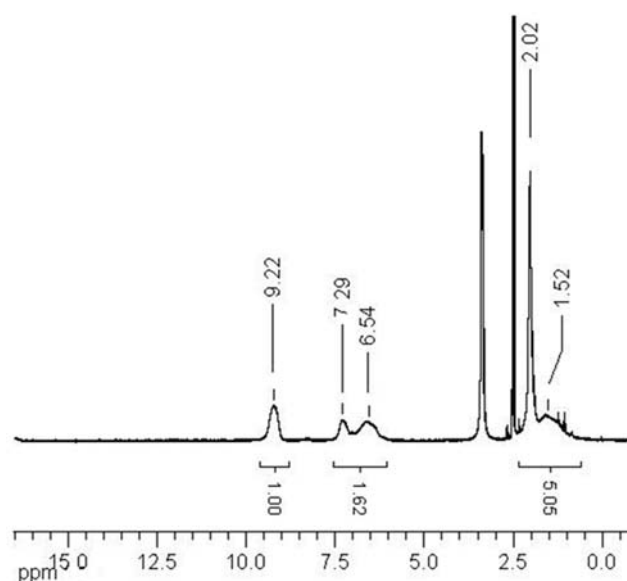


Figure 6. $^1\text{H-NMR}$ spectrum of PDAAMs.

Thermal Characterization of PDAAMs

DSC and TGA thermograms of PDAAMs were given in Figures 7 and 8. In the DSC thermogram, an endothermic shift from the baseline and an endothermic peak is observed. The endothermic shift gives the glass transition temperature (T_g) of PDAAMs which is 174°C . This glass transition temperature is higher than T_g of polystyrene, 100°C , due to polar acetamido groups on the aromatic ring.

The endothermic peak at 273°C in the DSC curve looks as if melting of PDAAMs. But, when the thermogram of DSC is compared with corresponding TGA curve, it was seen that the temperature interval ($237\text{-}320^\circ\text{C}$) of endothermic

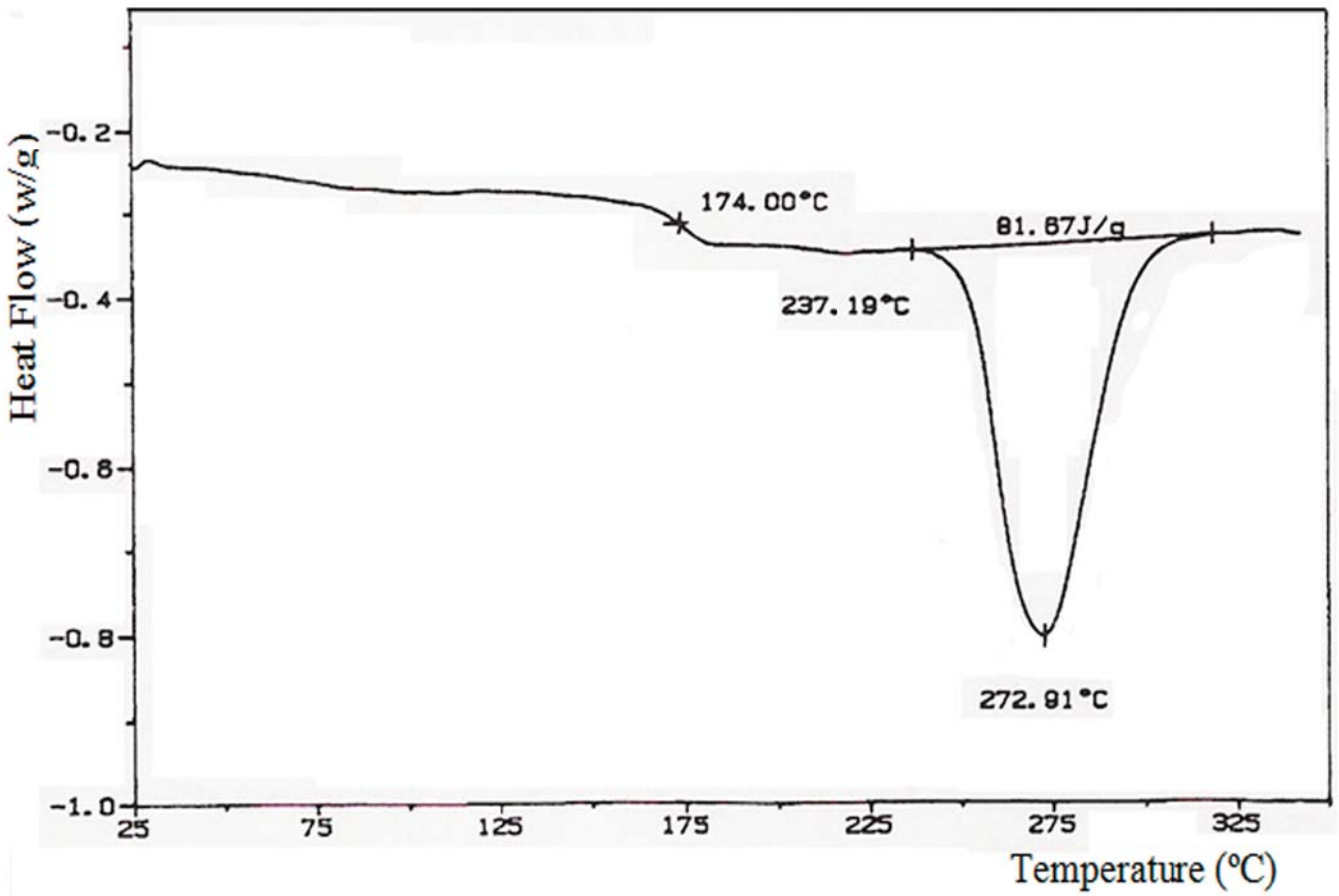


Figure 7. DSC thermogram of PDAAmS.

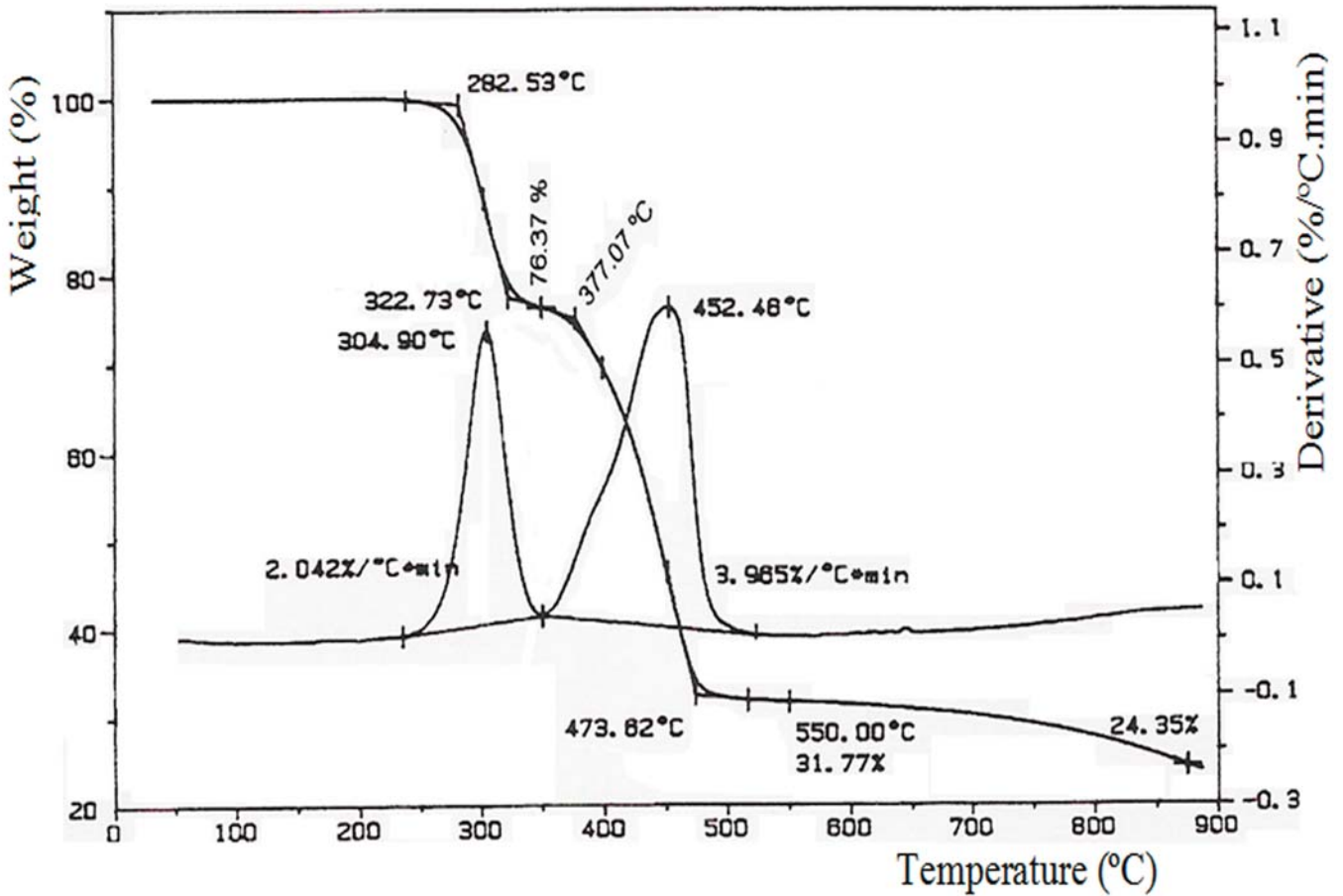


Figure 8. TGA thermogram of PDAAmS.

peak nearly overlaps with the temperature interval (278-320°C) of the first stage thermal decomposition process of PDAAmS in the TGA thermogram. The starting temperature of both events are little different. The starting temperature of endothermic peak is 237°C, on the other hand, the starting temperature of the first stage thermal decomposition process is 278°C. The starting temperature of endothermic peak is lower than the starting temperature of the first stage thermal decomposition process. It is clear that, all the energy requiring events can be observed in the DSC studies, either accompanied by weight loss or not. However, only weight change can be observed in the TGA studies. So the event, starting at 237°C in DSC curve may be melting or reorganization reaction of the groups of PDAAmS, which turns into weight loss reaction at the temperature 278°C. The details of this event will be given in the next study which will include the modification reactions on the side groups of PDAAmS. The second stage thermal decomposition starts at around 370°C and ends at 474°C by 70% weight loss. Thermolysis product of this stage is not determined yet to elucidate the thermal decomposition mechanism.

CONCLUSION

3,4-diacetamidostyrene (DAAmS) was synthesized by a two step reaction and characterized by FT-IR, GC-MS and NMR studies. The characteristic bands in FT-IR spectrum, 3260 cm⁻¹ due to -NH- stretching of amide, band at 1650 cm⁻¹ due to amid carbonyl and 1370 cm⁻¹ attributed to methyl bending (-CH₃), specified the monomer DAAmS. The molecular ion peak, 218 a.m.u., were found as the same as the calculated molecular weight of DAAmS in MS spectrum. The HETCOR spectrum, which includes ¹H-NMR, ATP ¹³C spectra, elucidated the structure of DAAmS. The peaks at 5.20, 5.70, and 6.66 ppm due to vinyl hydrogens of DAAmS disappeared in

the ¹H-NMR spectrum of PDAAmS after the polymerization reaction. This indicated that polymerization occurred by free radical polymerization. The observed endothermic shift in the DSC curve was given glass transition temperature of PDAAmS which is 174°C. The endothermic peak at 273°C in DSC curve was compared with TGA thermogram of PDAAmS and it was determined that the event, starting at 237°C in DSC curve may be melting or reorganization of the groups of PDAAmS, which turns into weight loss reaction at the temperature 278°C.

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