



Influence of Feed Ratio Variation on Structural and Thermal Properties of Pyrrole Aniline Copolymer

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ABSTRACT:

Pyrrole and aniline copolymers were chemically produced by changing the feed ratio of monomers at room temperature using FeCl₃ as an initiator. The prepared samples were characterized by employing FTIR, XRD and SEM techniques. The FTIR spectrum of copolymers indicates changes in the characteristic band positioning and the generation of additional bands. Similar type of results has been observed in X-ray diffractograms of prepared copolymers. This shifting or appearance of new bands can be attributed to feed variation of the monomers resulting in the random linkage of two units, as reactivity of each monomer in the feed is different. Also from the SEM analysis it is observed that the SEM images of prepared copolymers exhibit globular structure which varies with the feed ratio of two monomers. Further the thermal behaviour of prepared copolymers was studied by using DTA-TGA. From the DTA-TGA curves it is observed that prepared copolymers exhibit different values of T_g in the temperature range of 200°C to 270°C as compared to the parent polymers. Also it is observed that sample having higher aniline content is more thermally stable as compared to other copolymers or parent polymers.

Keywords: Pyrrole, Aniline, Copolymer, Feed ratio, SEM, DTA-TGA.

DOI Number: 10.48047/nq.2022.20.19.NQ99177

NeuroQuantology2022; 20(19): 2095-2106

1. Introduction:

Conducting polymers with improved properties are of prime importance due to their widespread applications ranging from display devices, photovoltaic cell, polymer batteries, diodes, dielectric, EMI shielding properties, electric and magnetic field applications [1-3]. These polymers can be transformed into composites or the copolymers to meet the specific requirement. However



extending the homopolymers to copolymer system; a better prospect of synthesizing various functional materials with characteristic features and structural arrangement can be achieved. Further the copolymerization offers an inbuilt heterogeneity to the polymer backbone and serves as a pathway to polymerize those monomers which are difficult to polymerize independently.[4] Thus, two entirely different monomers can be subjected to simultaneous polymerization in the common reaction medium and required chemical heterogeneity may be introduced. Hence copolymerization refers to the study of impact of complexation on copolymer chain origination and its propagation throughout the medium.

Pyrrole and aniline are most stable, environmentally safe and easily polymerizable monomers whose properties can be tailored effectively. Amid the mentioned advantages, these two have been extensively co-polymerized via electrochemical method (low yield) and to a lesser extent via chemical method with reference to literature. Hence, in the present work pyrrole and aniline have been subjected to chemical polymerization and the impact of feed ratio on copolymerization has been studied at room temperature and is reported. The influence of feed ratio on the structural and thermal properties of synthesized copolymers was also studied and the results are reported.

2. EXPERIMENTAL

2.1 Sample Preparation:

The basic monomers Pyrrole and aniline (SRL chemicals, Mumbai) were purified by distillation process. Further H_2SO_4 (Qualigen, Mumbai) was utilized to provide acidic medium and anhydrous $FeCl_3$ was used for origination of copolymerization. For sample synthesis the two monomers were taken in desired feed amount and were continuously stirred for about 15 – 20 minutes. To this feed, 30 ml sulphuric acid (0.5M) was added. This transparent solution was then uninterruptedly stirred till it became apparent and further anhydrous $FeCl_3$ (0.25M) was added. This copolymer base reaction mixture was rigorously mixed for around 1 hour at room temperature and was kept to polymerize for a period of 24 hours. In order to obtain the desired copolymer, the reaction mixture was filtered. The precipitate (sample) so obtained was washed with acetone and distilled water alternatively so as to eliminate impurities. The sample was further dried in the oven at $60^\circ C$ and weighed to establish a constant weight.

A solubility test was done to ensure the synthesis of pyrrole aniline copolymer during the above mentioned process, and not the physical combination of the two monomers. As DMF and DMSO, polypyrrole (PPy) and polyaniline (PANI) are completely insoluble, whereas the synthesized material is soluble in all three solvents [5]. In addition, the FTIR spectrum of a physical composition of aniline and pyrrole (1:1 weight ratio) was compared to that of the copolymer's. The bands formed in both instances are on different side of the spectrum. Consequently, it is conceivable to

establish the formation of copolymer. Table 1 gives the nomenclature of feed ratio employed for preparing copolymer samples.

Table 1: Feed ratio of monomers taken.

| Designation | Pyrrole : Aniline |
|-------------|-------------------|
| X | 1 : 1 |
| Y | 1 : 2 |
| Z | 2 : 1 |

2.2 Infrared Spectroscopy:

The FTIR investigation of the copolymers was then carried out in the 400-4000 cm^{-1} wave number range and transmission spectra were obtained with a Shimadzu IR spectrometer (FTIR-8101A).

2.3 Wide Angle X-Ray Diffraction:

The XRD results of the synthesized samples were obtained using the PANalytical Xpert Pro XRD apparatus. The copper k alpha1line from a sealed tube with a copper electrode was the source of radiation. The specimen sample was powdered and placed on an aluminium holder.

This holder was placed on the rotating diffractometer stage and in the reflection mode, sample was scanned from 5° to 40° across a spectrum of 2θ .

2.4 Scanning Electron Microscopy:

Scanning electron microscopy was utilized to investigate the morphology of the prepared copolymer samples. Using a sputtering process, the amorphous powder was coated with platinum metal. With the help of a JEOL 6380 A scanning electron microscope the scanning was completed at various magnifications.

2.5 Thermal Analysis:

The sample's thermal behavior was examined further in the temperature range of 305 – 873K. The DTA-TGA spectrum was acquired using a Thermo gravimetric / Differential Thermal Analyzer (PERKIN ELMER DIAMOND TG/ DTA).

3 RESULTS AND DISCUSSION:

In the present study, Chemical copolymerization was performed by applying FeCl_3 as an initiator and the feed ratio of monomers was varied. This procedure was adapted for 0.1M and 0.25M concentrations of the FeCl_3 (initiator). The percentage conversion of monomers to copolymers at synthesis temperature of 30°C (303K) is given in table-2. From table-2 it is clear that the percentage conversion of copolymers depends upon the feed ratio and the concentration of initiator. This may be attribute to the fact that FeCl_3 is a good initiator for pyrrole than aniline[5-7] hence sample having

high proportion of pyrrole gets polymerized to large extent. The FTIR spectra of the copolymers was studied and the characteristic bands obtained have been tabulated in table-3.

Table 2 : Percentage conversion of monomers to copolymer samples.

| Sample Designation | Initiator Concentration | Percentage Conversion |
|--------------------|-------------------------|-----------------------|
| X2 | 0.1M | 15.9116 % |
| Y2 | 0.1M | 6.1301% |
| Z2 | 0.1M | 28.9628% |
| X5 | 0.25M | 36.3988 % |
| Y5 | 0.25M | 13.2592% |
| Z5 | 0.25M | 54.5236% |

Table 3 : IR band positions of aniline, pyrrole, copolymer samples

| PANI | X2 | Y2 | Z2 | X5 | Y5 | Z5 | PPy |
|------|------|----------|------|------|----------|------|------|
| ---- | 450 | 435 | 414 | 416 | ---- | 418 | ---- |
| 618 | ---- | ---- | ---- | ---- | ---- | | 610 |
| ---- | ---- | 700, 760 | 750 | ---- | 700, 750 | 750 | ---- |
| ---- | ---- | ---- | 790 | 785 | ---- | ---- | 780 |
| 816 | 800 | ---- | ---- | ---- | ---- | 800 | ---- |
| ---- | ---- | ---- | ---- | ---- | ---- | ---- | 830 |
| ---- | ---- | ---- | ---- | ---- | ---- | ---- | 910 |
| ---- | 950 | ---- | 940 | 935 | 930 | 940 | ---- |
| | 1053 | 1049 | 1050 | 1049 | 1049 | 1050 | 1048 |
| 1114 | ---- | ---- | ---- | ---- | ---- | ---- | ---- |
| 1160 | ---- | ---- | ---- | ---- | ---- | ---- | ---- |



| | | | | | | | |
|-------|------|-------|------|------|------|------|------|
| ---- | ---- | ---- | ---- | ---- | ---- | ---- | 1185 |
| ---- | ---- | ---- | ---- | ---- | ---- | ---- | 1250 |
| ---- | ---- | ---- | ---- | ---- | ---- | ---- | 1290 |
| 1302 | ---- | ---- | ---- | ---- | ---- | ---- | ---- |
| 1385 | ---- | ---- | ---- | ---- | ---- | ---- | ---- |
| 1493 | 1400 | 1400 | 1400 | 1400 | 1400 | 1400 | 1451 |
| ---- | 1508 | ---- | ---- | ---- | ---- | ---- | 1510 |
| 1599 | 1600 | 1600 | ---- | 1647 | ---- | 1600 | ---- |
| 1706 | ---- | ---- | ---- | 1718 | ---- | ---- | ---- |
| ---- | 1830 | ---- | 1830 | 1860 | 1830 | ---- | ---- |
| ---- | 2350 | 2350 | 2350 | 2350 | 2360 | 2350 | ---- |
| ---- | | 2850 | ---- | ---- | ---- | ---- | 2843 |
| ---- | 2920 | 2926 | ---- | 2920 | 2920 | 2920 | 2906 |
| ---- | ---- | ----- | ---- | ---- | ---- | ---- | 2963 |
| ----- | ---- | ---- | ---- | ---- | ---- | ---- | 3441 |

According to the FTIR analysis, the IR spectra of the copolymers differs from that of the homopolymers, PANI and PPy. The comparison of the IR bands shows that many IR peaks appearing in homopolymers have either shifted to higher or lower wavenumber side or they are absent in the IR spectrum of the copolymers [8-9]. This relocation of the peaks to the low wavenumber side can be attributed to the chains that transform from coiled to stretched chains as a result of the action of hydrogen bonds and electrostatic interactions, hence increasing the degree of conjugation of the copolymer chains [10].

The subsequent shifts in these IR bands may be due to hetero association between the aniline and pyrrole units. The polymerization proceeds as soon as initiator is added to the solution leading to the beginning of polymer chain, which might be interrupted due to the presence/attachment of hetero unit, causing shifting of characteristic bands. As the feed ratio changes the quantity of comonomer in the feed also changes thereby resulting in several new bands amongst copolymer samples also. Due to the subsequent attachment of new side groups, the bond's composition and related vibrational frequency are also altered.

The new attachments results in the formation of new bonds causing shifting of original bond lengths. This may be due to the interactions between permanent and transient charges that resulted



from the copolymerization and caused the polar effects. It is noticed that the peaks of the copolymer of aniline and pyrrole have migrated to lower wavenumbers, indicating the presence of adjacent aniline and pyrrole constitutional units [11].

The x-ray diffractograms of the prepared copolymers are shown in figure 1 and the corresponding peaks are tabulated in table-4. From the close observation of 2θ values for all the copolymers, it can be seen that all six copolymers exhibit different peaks as compared to copolymers [12-13] and shows common peak at 24° and 32.8° . This suggests that these peaks must exhibit common bonding shared by all copolymers. Though there is variation in the feed ratio but still we get some common angular peak positions owing to common hetero linkage. This common bond can be understood as the attachment of pyrrole and aniline units at a certain point on the monomers (i.e. C-N or C-H or N-H). As the primary chain of the copolymer comprises of random attachment of two reactant units, this attachment must be retaining in all the copolymers.

Table 4 : 2θ peak positions for aniline, pyrrole, copolymer samples.

| PANI | X2 | Y2 | Z2 | X5 | Y5 | Z5 | PPy |
|-------------|-----------|-----------|-----------|-----------|-----------|-----------|------------|
| 9.5 | 13.2 | 6.8 | 7.8 | 10 | 6 | 12 | 23.6 |
| 14.7 | 21 | 16.8 | 15 | 22.5 | 11 | 24.5 | 25.8 |
| 20.4 | 24 | 22.1 | 22.3 | 24 | 24 | 26 | -- |
| 25.1 | 26 | 24.1 | 24 | 28 | 25.7 | 28.4 | -- |
| -- | 33 | 26 | 26 | 32.8 | 32.8 | 32.7 | -- |
| -- | 34 | 33 | 30 | 35.7 | 35 | 40.8 | -- |
| -- | 35.5 | 34 | 32.5 | -- | 39.5 | -- | -- |
| -- | -- | -- | 34.5 | -- | -- | -- | -- |
| -- | -- | -- | 40.3 | -- | -- | -- | -- |

Also due to hetero association small units with different crystal planes may get created hindering thereby the unit cell dimensions of the homopolymers. Thus the small crystallites may get created with a common lateral plane but varied diagonal plane. Depending upon the sequences of pyrrole and aniline units in the primary copolymer chain the dimensions of the unit cell are restricted subsequently influencing the interfacial angles. Thus varying the feed ratio even affects the geometry of the copolymers created.



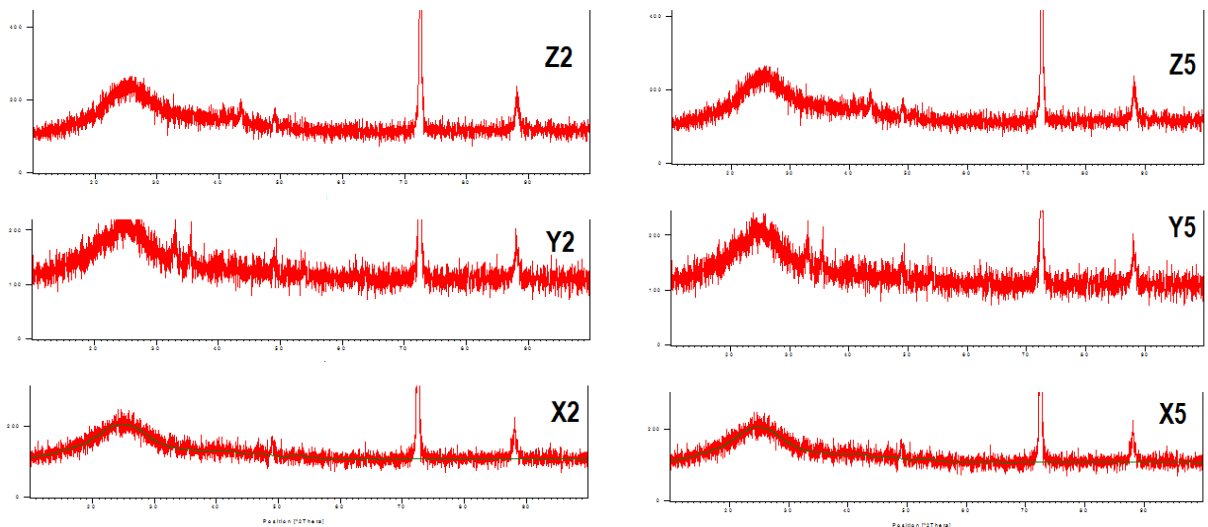


Figure. 1 : X-ray diffractograms of copolymer samples.

The scanning electron micrograph of prepared copolymers are shown in figure 2. SEM images show that agglomerated particles develop spherical shapes during aniline and pyrrole copolymerization. The spherical structures have sizes between 10 and 20 μ m. Few samples have flaky structure [14]. The feed monomers alter the copolymer's shape. The copolymer reveals uneven, disorganized (amorphous) spherical agglomerates. As feed is varied, the copolymerization proceeds with consumption of both units in random manner yielding thereby new structures [15].

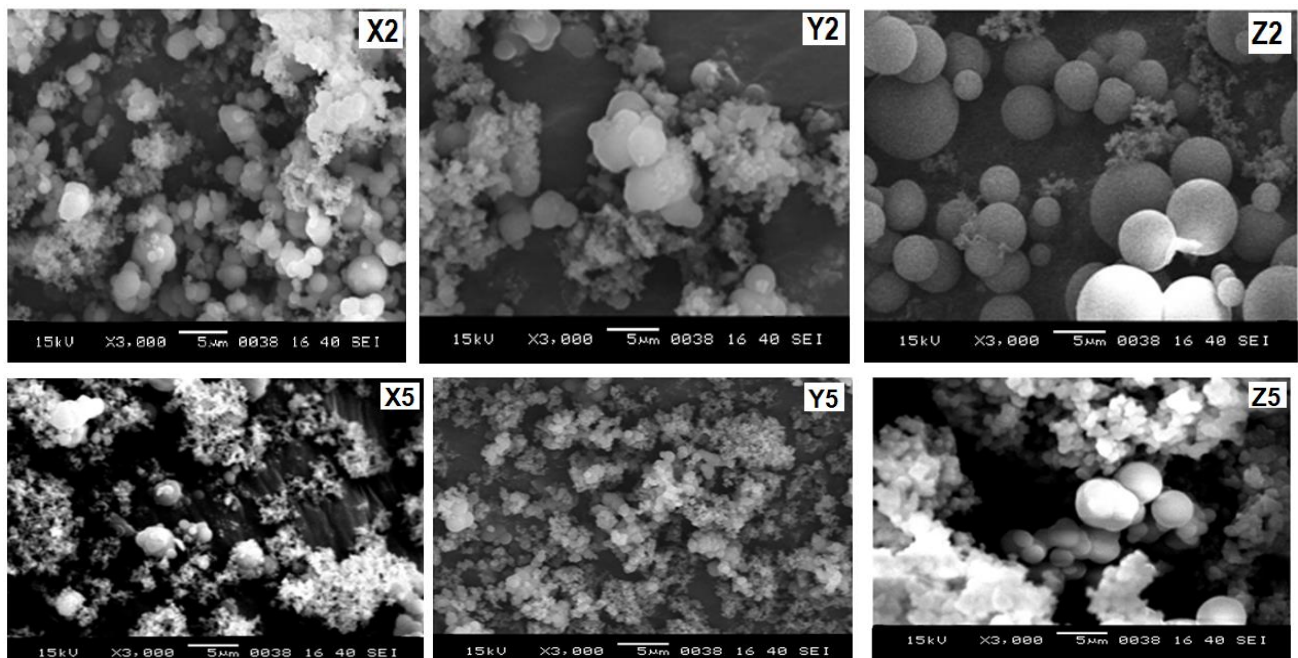


Figure 2 : SEM images of copolymer samples.

From the analysis of DTA curves, as shown in figure 3 , the T_g values for all the copolymers have been estimated in Table 5 which shows that all the copolymers exhibits T_g values in the temperature range 200°C to 270°C . The existence of these higher T_g values could be due to the dissociation of tiny crystallites scattered throughout the amorphous copolymer matrix. Through covalent connections, these crystallites are connected to the amorphous polymer areas. The rotational / vibrational motions of monomers composing crystallites increase as samples are heated to high temperatures. The relative motion of these crystallites increases with further increase in the thermal energy. Thus bonds between the neighboring polymer chains in a polymer crystallite are broken up and the chains become relatively free thereby making the polymer visco-elastic [16-18].

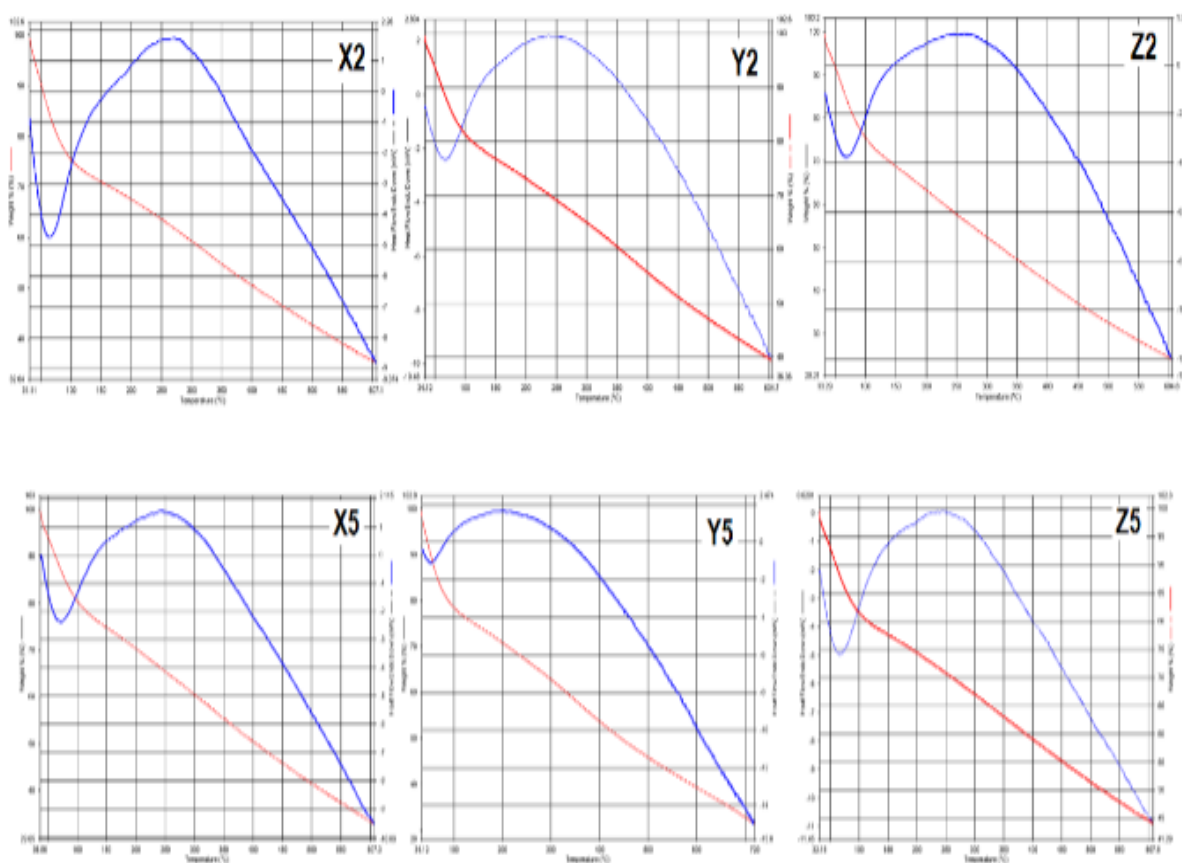


Figure 3 : DTA-TGA graphs of copolymer samples.

As a result, part of the connections that link the amorphous and crystallite regions are broken, and a thermal transition, arises. This could be revealed through the thermal degradation of the samples presented in Table 6.

Table 5 : Table showing Tg values of aniline, copolymer samples.

| Sample | Tg (°C) | Sample | Tg (°C) |
|--------|---------|--------|---------|
| UX2 | 262°C | UX5 | 240 °C |
| UY2 | 250°C | UY5 | 200 °C |
| UZ2 | 250°C | UZ5 | 235°C |

Table 6 : Table showing thermal degradation copolymer samples with temperature.

| Percentage Degradation | | | | | | |
|------------------------|---------|---------|---------|---------|---------|---------|
| Temp. (°C) | X2 | Y2 | Z2 | X5 | Y5 | Z5 |
| 50 | 9.0937 | 5.7416 | 7.5038 | 5.4929 | 8.6011 | 6.4314 |
| 100 | 24.0256 | 18.3213 | 24.0221 | 19.1595 | 20.9946 | 18.0005 |
| 150 | 28.4139 | 22.8518 | 30.6814 | 24.8493 | 25.0538 | 21.9616 |
| 200 | 31.8459 | 26.5247 | 36.1657 | 29.3111 | 28.7022 | 25.0924 |
| 250 | 35.7533 | 30.4794 | 41.7085 | 34.2185 | 32.4703 | 28.8041 |
| 300 | 40.0724 | 34.6017 | 47.0844 | 39.2678 | 36.5917 | 32.5364 |
| 350 | 44.5481 | 39.1854 | 52.3102 | 44.3488 | 41.2205 | 36.5646 |
| 400 | 48.7036 | 43.9130 | 57.3878 | 49.1332 | 45.7568 | 40.3318 |
| 450 | 52.8477 | 48.4879 | 62.4236 | 53.7347 | 49.9068 | 44.4194 |
| 500 | 56.6024 | 52.4739 | 66.8768 | 58.0948 | 53.5539 | 48.1448 |
| 550 | 60.2346 | 56.2891 | 71.0663 | 62.2043 | 56.9060 | 51.6552 |
| 600 | 63.5523 | 59.9024 | 74.9484 | 66.2083 | 60.1854 | 54.8625 |

The feed ratio affects the copolymer's thermal stability. The thermal degradation of polymers is likely caused by the evaporation of the solvent, the retention of monomers and oligomers within the polymers, and the presence of unbound dopant. The loss of bounded dopant can occur partly. The main weight loss occurs in the temperature range between 300°C and 600°C, Feed varies depending on the structure and nature of the copolymer.



At this temperature range, the primary chains of the copolymer and the dopant within the polymer decompose.

In addition, the weight loss as a function of temperature was investigated, as it is a key indicator of the thermal stability of polymers.

4. Conclusion:

Pyrrole and aniline have been copolymerized chemically using FeCl_3 as an initiator at room temperature successfully by varying the feed ratio and initiator concentration. It is noticed that samples having high initiator concentration and pyrrole content give better percentage conversion. From the FTIR, XRD and SEM analysis it can be inferred that copolymer structures are affected by feed composition. Similar kind of behaviour is noticed from the thermal analysis of the samples.

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