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OPTIMIZATION OF GRAFTING PARAMETERS OF NYLON6-GRAFT-ACRYLIC ACID COPOLYMER USING CERIC AMMONIUM NITRATE AS AN INITIATOR

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Abstract:

In the present work, the graft copolymerization of acrylic acid onto Nylon6 (N6) was carried out using ceric ammonium nitrate (CAN) as an initiator in aqueous nitric acid medium. Variation of synthetic parameters such as grafting percentage, grafting efficiency, percentage monomer conversion and grafting yield with initiator concentration, temperature, monomer concentration and polymer concentration were investigated for N6-g-AA graft copolymer. The optimum synthetic conditions obtained from the above results were given as follows: CANconcentration-0.8g; Temperature-70˚C; acrylic acid-2.0ml and nylon6 concentration-3g for N6-g-AA copolymer. The structures of the prepared N6-g-AA copolymers were characterized by Fourier Transform Infrared Spectroscopy (FT-IR) and X-ray diffraction (XRD) studies. The appearance of new peaks due to the presence of acid group in case of N6-g-AA copolymer from FT-IR measurements clearly suggest that acrylic acid monomer gets effectively grafted onto polyamide Nylon6 and the XRD pattern elucidates the changes in crystallinity of the grafted polymeric samples.

Key Words: Nylon-6, Acrylic Acid, Graft Copolymerization & Ceric Ammonium Nitrate

Introduction:

Biomaterials generally have a hydrophobic and chemically inert surface and hence great efforts have been made to the synthesis and manufacture of biomaterials with different properties according to the required application[1]. One of the widely used methods for modifying some of the properties of natural and synthetic polymers was the grafting[2.] The interface energy of matrix in the aqueous biological environment was decreased by grafting the hydrophilic monomer to hydrophobic matrix and in addition it also reduces the superficial driving force. This process allows the hydrophobic material to have a better affinity with water by the introduction of active functional groups onto a polymer backbone[3]. Graft copolymers are essential components of many materials, including chemically and thermally resistant plastics, thermoplastic elastomers, compatibilizers, and polymeric emulsifiers[4]. They are required widely in various application fields of polymer alloys (blends), compatibility improvements, surface modifications, and so on[5]. Graft copolymers has a wide range of applications deriving from the possibility to tailor their properties through the combination of monomers that form the backbone and the side chains. Considerable work on the graft copolymerization of natural, synthetic polymers and natural fibers with the vinyl monomers has been reported [6,7].

Graft copolymers can be mainly obtained by three methods: (a) “grafting from”, method in which the polymerization of second monomer is initiated by sites located on the main polymer chain; (b) “grafting onto” method in which the polymeric species reacts with functional groups located on the chain of another polymer; and (c) “grafting through” method in which the macro monomer is copolymerized with a small-molecule co monomer[8]**.** Graft copolymers are prepared by first generating free radicals on polymeric chains and then allowing these free radicals to serve as macro initiators for the vinyl or acrylic monomer polymerization[9]. In recent years, the graft copolymerization of various monomers was initiated by ceric ammonium nitrate[10,11,12], ammonium persulphate[13],potassium persulphate[14,15,16],ferric ion hydrogen peroxide[17] and gamma rays[18]. Among the chemical initiation methods, redox initiated grafting offers advantages since in the presence of redox system, grafting can be carried out under milder conditions and the side reactions are at a minimum. Of the redox systems initiated so far the tetravalent ceric ion has received considerable interest[19,20] because of its high grafting efficiency and very low homopolymer formation. Graft copolymerization by the free radical mechanism is an interesting method for the preparation of polymeric system with specific properties. Nylon-6 is a polyamide which possesses high quality of physicomechanical properties, chemical and thermal stability and hence it is commonly used for domestic and industrial applications. Graft copolymerization of nylon-6 can further enhance this property to meet the requirement of the specific application in respective field. The grafting of methyl methacrylate onto nylon6 initiated by irradiation in the presence of benzophenone as aphotosensitizer[21].

Many works were reported on the grafting of acrylic acid monomer onto various polymers using various free radical initiators[22]. The acrylic acid monomer diffuses and polymerizes easily into nylon and as a result forms grafts composed of long polymeric chains. Hence based on the literature review, in this paper the graft copolymerization of acrylic acid (AA) onto nylon6 was carried out using ceric ammonium nitrate as an as a redox initiator in aqueous nitric acid medium. The objective of the present work is to prepare the N6-g-AA graft copolymers, characterized by FT-IR, XRD studies and the tentative mechanism is proposed to explain the formation of graft copolymer. In addition the present investigation also describes the optimization of the reaction conditions of grafting of acrylic acid monomer onto nylon6 using ceric ammonium nitrate as an initiator. The results were investigated.

Materials and Methods:

Materials:

Nylon6 were purchased from Formulated Polymer Limited, Chennai. The monomer acrylic acid was purchased from Sisco Research Laboratory, Mumbai. Solvents such as formic acid and ethanol were obtained from SD Fine chemicals private Ltd. Nitric acid and ceric ammonium nitrate $Ce(NH_4)_2(NO_3)_6$ used were procured from Thomas Bakers Chemical and Company. All the reagents used in the present research work were of analytical grade.

Preparation of Ceric Ammonium Nitrate:

CAN in the presence of nitric acid have been used as an efficient initiator for graft copolymerization (Gupta et. al., 2002). The initiator solution was prepared by dissolving 0.5g of ceric ammonium nitrate in 10ml of 1N nitric acid solution.

Preparation of Graft Copolymer:

In a typical experiment, the graft copolymerization was carried out as follows; A required amount of Nylon6 (1g) taken in a 250 ml beaker was dissolved in formic acid (30ml) with constant stirring to form a homogeneous solution. About 1ml of the acrylic acid monomer dissolved in 60ml of water was then added to the above prepared homogeneous solution. Then to initiate the polymerization process, the initiator ceric ammonium nitrate prepared in the above manner (10ml) was then added.

The above mixture was then heated to 70˚C. Simultaneously, the stirring of that mixture was performed using a magnetic stirrer. After the required reaction time, the solution mixture was then poured into excess of (2N) sodium hydroxide solution to precipitate the graft copolymer. After the desired time the products were taken out and washed thoroughly with acetone to remove the homopolymer formed during the graft copolymerization completely. Finally the graft copolymer was then dried in an oven, cooled to a room temperature and weighed.

The grafting percentage, grafting efficiency, grafting yield and the monomer conversion percentage was calculated by weighing the original polyamide nylon6 and the grafted product. The synthetic grafting parameters including the grafting efficiency (GE), grafting yield (GY), grafting percentage (GP), and % conversion (%C) were systematically evaluated as a function of various initiator, temperature, monomer and nylon6 concentration[23,24,25].

$$GE(\%) = \frac{\text{Wt. of graft copolymer}}{\text{Wt. of graft copolymer + Wt. of homopolymer}} \times 100$$

$$GY(\%) = \frac{\text{Wt of graft copolymer – Wt of ungrafted polymer}}{\text{Wt of ungrafted polymer}} \times 100$$

$$GP(\%) = \frac{\text{Weight of graft copolymer}}{\text{Weight of substrate}} \times 100$$

$$\%C = \frac{\text{Weight of graft copolymer}}{\text{Weight of monomer}} \times 100$$

Characterization:

FT-IR Spectral Analysis:

The FT-IR spectra of grafted polyamide nylon6 was recorded by FT-IR Thermo Nicolet AVATAR 330 model Fourier transform infra-red spectrophotometer (FT-IR) in the wavenumber range of 500-4000 cm^{-1} during 64 scans, with 2 cm^{-1} resolution at 25°C.

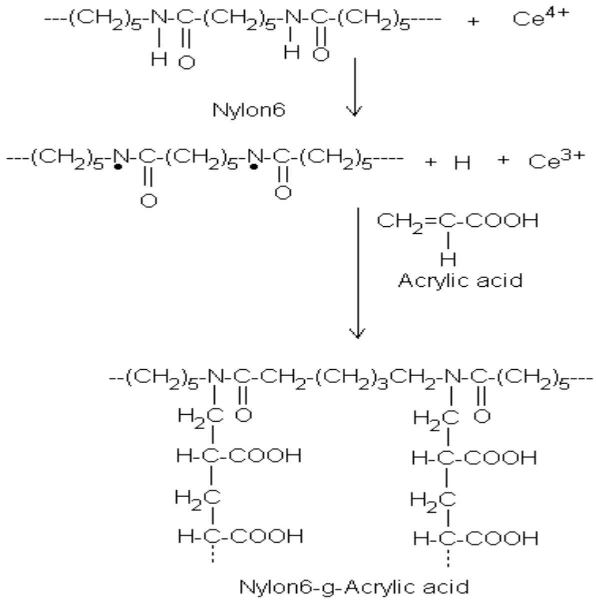
X-Ray Diffraction Analysis:

X-Ray diffraction patterns of the grafted copolymeric samples were carried out by scattering SHIMADZU XD-D1 diffractometer using Ni filter, Cu Kα radiation source (λ=0.154nm), set a scan rate = 10˚/min. The voltage and the current used were of 40kV and 30 mA. The XRD patterns were recorded with a step size of 0.020˚ between 10.000˚ and 79.993˚.

Results and Discussion:

The mechanism of the graft copolymerization of acrylic acid onto nylon6 was shown in Scheme-1.

Scheme 1:



The optimization of the various parameters such as concentration of initiator, temperature, concentration of monomer and concentration of nylon6 was obtained for graft copolymerization of acrylic acid onto nylon6.

Effect of Initiator Concentration:

The concentration of initiator has a decisive effect on the grafting. The effect of ceric ammonium concentration on the grafting parameters such as grafting efficiency, grafting yield, grafting percentage and percentage monomer conversion was studied in the range of 0.5g-0.9g for N6-g-AA graft copolymers at constant nylon6 concentration, monomer concentration and temperature. The observed result was shown in the Figure 1.

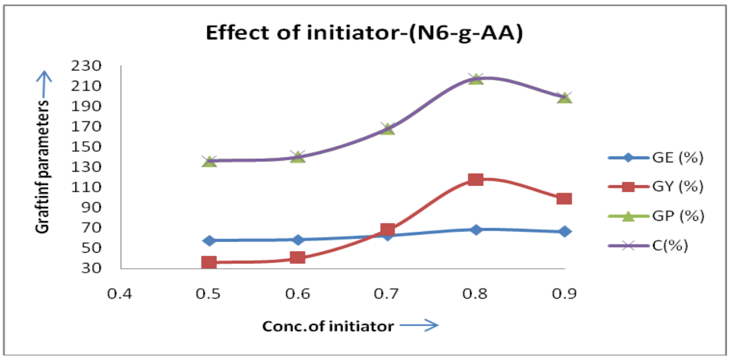


Figure 1: Effect of initiator concentration on the grafting parameters of N6-g-AA copolymer

From the results presented in the Figure-1, it was observed that with increasing initiator concentration upto 0.8g for N6-g-AA, the graft yield increases and thereafter it decreases. In a grafting point of view, in the initial stage with increasing the initiator concentration, the number of grafting sites on the backbone of the nylon6 increases by the interaction of the nylon6 with the initiator. This results in the increase in graft yield. But with further increasing of CAN over 0.8g, the initiator might interact with the monomer molecules producing homopolymer, thereby decreasing graft yield [26,27]. In other words we can say that at higher ceric ammonium nitrate concentration (>0.8g), since the initiator solution is used as dilute HNO_3, a more acidic pH probably causes partially termination of the macroradicals on nylon6 which will result in the compensation of increased free radicals by the partial termination of the macroradicals and hence it shows a decrease in the grafting parameters[28].

Effect of Temperature:

The temperature of grafting medium is one of the most important reaction parameters that has a strong effect on the grafting parameters. The grafting reaction was carried out at different temperatures ranging from 50-90°C under constant experimental conditions. The observed results were presented in Figure 2. With the increase in temperature from 50°C to 70°C, the grafting yield increased and maximum grafting yield was achieved at 70°C for N6-g-AA graft copolymers respectively, but thereafter it declines. The initial increase with the rise in temperature upto 70°C may be due to the increase of the initiation and propagation rates of graft copolymerization due to the increased mobility of AA monomer onto nylon6.

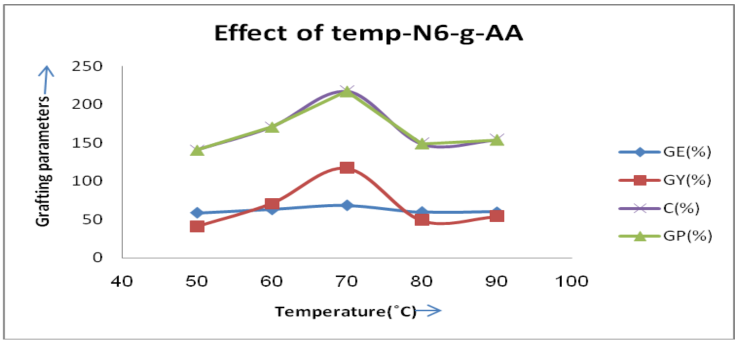


Figure 2: Effect of temperature on grafting parameters of N6-g-AA copolymer

Increase in the degree of grafting with increasing temperature is also due to increase in the decomposition of the initiator leading to the formation of more free radicals and the generation of active sites on the polymeric backbone. But beyond 70˚C, the grafting rate decreases. Probably this is because at higher temperature, higher combination rates of monomer are obtained increasing homopolymerization reactions, which results in a decreased grafting rate[29,30]. Decrease in percentage of grafting beyond optimum temperature was attributed to premature termination of the growing polymeric chains and to the occurrence of chain transfer reactions. Similar observations have been noted by Somanathan and his coworkers with grafting methacrylic acid onto PET using benzoyl peroxide as an initiator [31].

Effect of Monomer Concentration:

The effect of monomer concentration on the grafting parameters was studied within the range of 1-3g at constant nylon6, initiator and temperature and the observed results was presented in Figure-3. It can be seen from the Figure-3, that at first the grafting reaches a maximum value and after it reaches a certain monomer concentration it shows a decrease. With the increase in AA from 1-2g, the graft yield increased and then it decreases. The maximum graft yield was achieved at AA=2g. The observed initial increase in grafting parameters was due to the fact that most of the monomer is utilized by the available free radical sites on the nylon6 backbone using ceric ammonium nitrate. Moreover, at the lower concentration, the extent of homopolymerisation of the monomer is also smaller and hence it shows an increase in the grafting parameters [32].

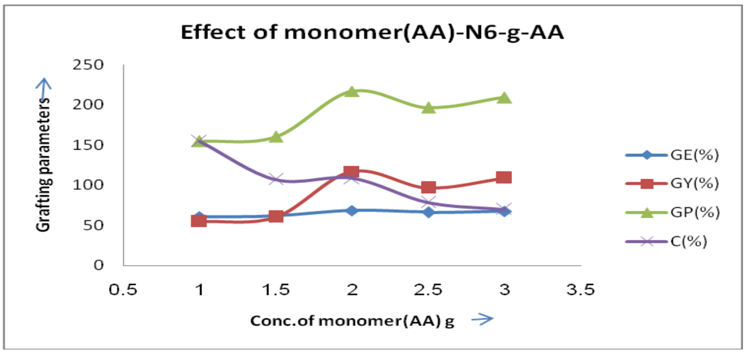


Figure 3: Effect of monomer concentration on the grafting parameters of N6-g-AA copolymer

With the further increase in AA, the gel effect was more pronounced. Due to this gel effect, the chain transfer from nyon6 macroradical onto monomer increased, leading to the lowering of graft yield and leads to preferential formation of homopolymer at higher concentrations. The degree of homopolymerization increases, and the grafting percentage decreases[33]. The growing polymeric radical at higher concentrations may terminate grafting process [34,35] leading to a decrease in grafting parameters.

Effect of Polymer Concentration:

The effect of concentration of nylon6 on the grafting parameters was studied within the range of 1-4g for N6-g-AA copolymer at constant initiator, monomer concentration, and temperature. The obtained results were presented in Figure 4. From the results presented in Figure 4, it was observed that the grafting parameters of N6-g-AA copolymer increased with the increase in concentration of nylon6 and reaches a maximum at Nylon 6=3g for N6-g-AA respectively. There exists an optimum nylon6 concentration at which the percent of grafting reaches maximum. It may be explained that an increase in backbone concentration can make more monomers and initiators easily approachable to the surface of nylon6 and produce more grafted side chains which cause grafting efficiency to increase. The observed initial rising in the grafting parameters with increasing N6 concentration is attributed to the availability of more grafting sites for initiation of graft copolymerization[36].

The decreasing trend of all the parameters after a certain Nylon 6 concentration may be explained as follows: firstly, the high viscosity of the reaction system makes the diffusion of monomer and CAN to nylon6 difficult, thus the rate of grafting will be hindered greatly. Besides, the difficulty of CAN diffusion leads to a higher local CAN concentration, which makes the rate of termination accelerate due to the reaction between the propagating chain radicals and primary radicals. Similar observations have also been reported in the case of ceric-induced grafting of ethyl acrylate onto sodium alginate [37].

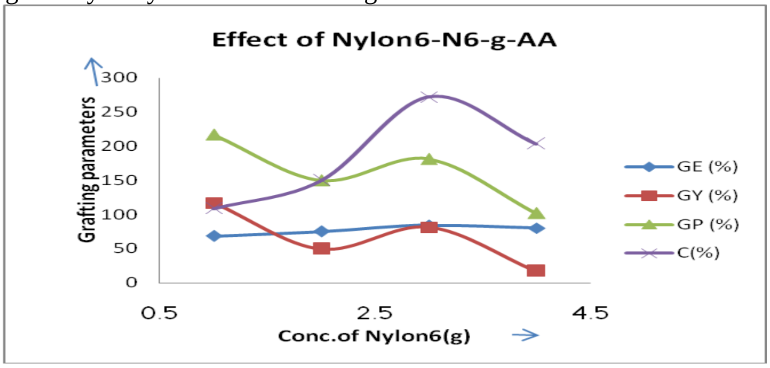


Figure 4: Effect of polymer concentration on the grafting parameters of N6-g-AA copolymer

FT-IR Spectral Analysis:

Evidence of Graft:

The formation of graft copolymer of nylon6 with acrylic acid monomer was confirmed through FT-IR analysis. The FT-IR spectrum of pure nylon6 and N6-g-AA prepared under optimum conditions was shown in the Figures:(5)-(6).The FT-IR spectrum of pure nylon6 (Figure-5) showed a broad peak at 3350 cm-1 due to hydrogen bonded N-H group[38] and at 2987 cm^{-1},1670cm^{-1} and 1200 cm^{-1} due to CH_2,C=O in secondary amide and C-C stretching respectively whereas in the spectrum of the graft copolymer(N6-g-AA) (Figure-6) besides retaining the above mentioned bands of pure nylon6, it shows an additional stronger absorption band at 1730.0 cm^{-1}, 1264 cm^{-1} corresponding to the characteristic carbonyl group in acid and C-O stretching of acid. The absence of the above peaks in the FT-IR spectrum of pure nylon6 confirms that the acrylic acid monomer have been grafted onto nylon6 effectively. In addition to the above bands, the graft copolymer shows a strong absorption at 1632 cm^{-1} corresponding to tertiary amide carbonyl group which is an evidence for grafting and these additional peaks confirm the formation of N6-g-AA copolymer.

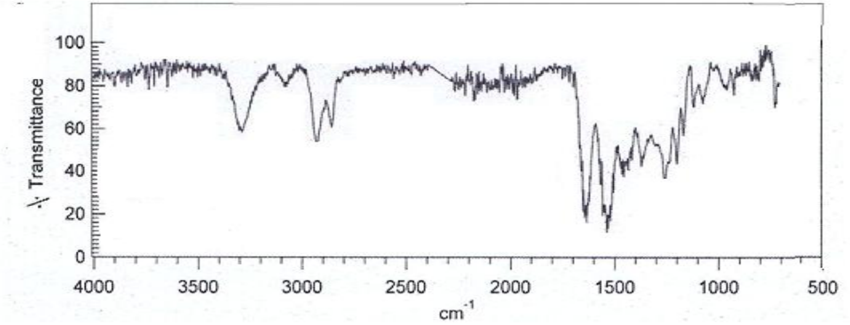


Figure 5: FT-IR spectrum of pure nylon6

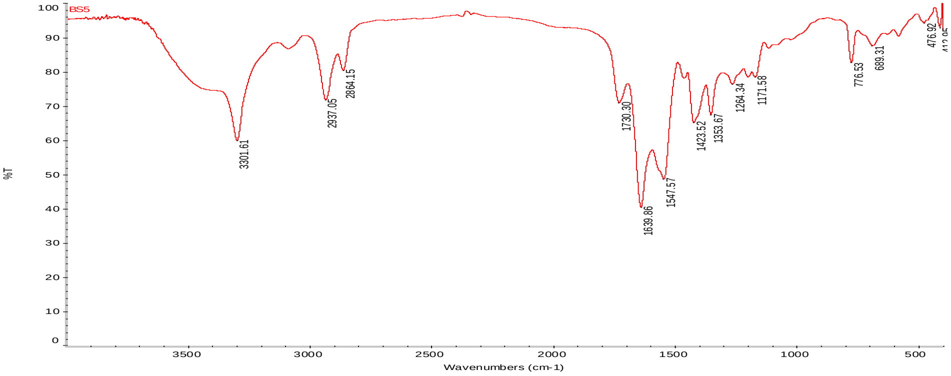


Figure 6: FT-IR spectrum of N6-g-AA copolymer

XRD Diffraction Studies:

X-ray diffraction (XRD) analysis is an important tool in determining the structure and crystallization of polymer matrices[39]. X-ray diffraction patterns of N6-g-AA copolymer were measured to investigate the change of crystalline nature of nylon6 after polymerization. The X-ray diffraction patterns of pure nylon 6 and N6-g-AA copolymer prepared under optimized conditions was shown in the Figures-(7)-(8).

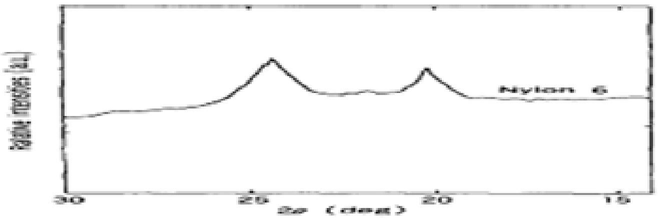


Figure 7: X-Ray diffractogram of pure nylon6

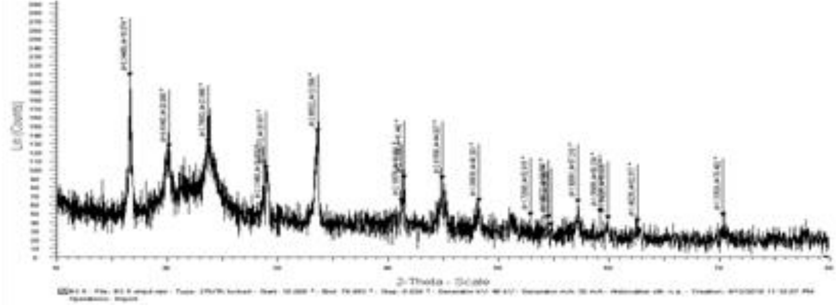


Figure 8: X-Ray diffractogram of N6-g-AA copolymer

The X-Ray diffractogram of pure nylon 6 show sharp peaks at 20˚ and 23.9˚ .Semi crystalline nature was indicated by these peaks[40]. In addition to the above peaks, the XRD spectrum of N6-g-AA copolymer shows sharp peaks at 16.5˚,20˚,23.6˚,28.9˚,33.5˚ 41.2˚.From the number of peaks obtained it was concluded that there is a change in the crystallinity of polyamide (nylon6) due to polymerization with acrylic acid monomer. The observed results indicate that the graft copolymers of nylon 6 has more number of crystalline forms when compared to the pure nylon6. The changes in the XRD patterns of these graft copolymers clearly indicate that there is a coordination between the nylon6 and the acrylic acid monomer.

Conclusion:

Based on the results presented in this paper, we conclude that ceric ammonium nitrate was found to be an efficient initiator for grafting of AA onto nylon6 under a wide range of experimental conditions. Only small amounts of PAA were extractable as homopolymer. Grafting parameters such as conversion of monomer to polymer, grafting yield can be varied substantially by varying the concentration ratio of initiator (Ce^{4+}) to nylon6 and monomer to nylon6. The optimum synthetic conditions obtained from the above results may be given as follows: CANconcentration-0.8g; Temperature-70˚C; acrylic acid-2.0ml and nylon6 concentration-3g for N6-g-AA copolymer. The proof of grafting was obtained from the FT-IR results. The changes in crystalline nature of the polyamide nylon6 due to polymerization were confirmed using X-ray diffraction patterns. This type of work could encourage the synthesis of new grafted membranes, where some functionality is required, for specific purposes.

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