Copolymer of Acrylonitrile/Acrylic acid Solid Surface Dendrigrafted with Citric Acid - Comparison between Film and Fiber

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Abstract

The synthesis of a dendritic polymer of citric acid(CA) on a solid-phase of acrylonitrile /acrylic acid copolymer P(AN/AA) core from zero(G0) through fourth step (G4) is described. Copolymer of P(AN/AA) was synthesized by suspension polymerization. The product was analyzed by elemental analysis technique and nuclear magnetic resonance (1H NMR) that showed 15 % of the copolymer was acrylic acid. The solution of P(AN/AA) in dimethylformamide (DMF) was cast into film with 350 μm thickness. Also the solution of P(AN/AA) in DMF was converted in to fiber by a laboratory wet spinning machine. The diameter of the filaments was 200±20 μm, after drying. Dendritic molecules were grown by a reaction between the carboxylic acid of acrylic acid and hydroxyl group of citric acid activated by dicyclohexylcarbodiimide (DCC) on fibers and films samples. Products were analyzed using Fourier transform infrared spectroscopy (FTIR) in transmission mode and 1H NMR. The analysis of the results indicates the formation of carboxylic acid of citric acid on the P(AN/AA) films and fibers. The percent of conversion of the reaction of copolymer with citric acid was calculated from the results of the measurement with NMR. The percent of conversion shows a gradual reduction with the increase in step numbers. Also it shows that the percent of conversions of the reactions on the fibers are higher than on the films. Reduction of the conversion with the step number and the differences in the conversion for the fibers and films seem to be very interesting and it is explained based on the established theories and the pertinent literature.

Keywords: Dendrigraft, Citric Acid, solid-phase, acrylonitrile /acrylic acid copolymer, dicyclohexylcarbodiimide (DCC), conversion

1. INTRODUCTION

During the past few decades new classes of macromolecular rs[10-10] have been introduced and a number of papers devoted to this subject[11]. For the sake of brevity a few are mentioned here[1-13]. Different monomer, chemicals and procedure were employed and a number of end uses were found for each product. Now dendrimers are used for applications such as drug delivery systems, bioactive macromolecules, catalysts and additives. Special structure and the location of the end groups determine their numerous applications[11-13].

Polymeric materials with a specific surface property can have some technological end uses[14-16]. An appropriate condition is required to modify the surface for any intended use. Dendritic structure has been used to modify the surface properties of polymeric materials. In this case it is expected that functional groups having specific structure concentrate on the surface and make properties of the surface different from the bulk[14-16]. Generally, due to the effect of the nature of growth of dendritic structure the expectations may not be fulfilled.

Dendritic molecules can be synthesized in solid or solution architecture including dendrimer[1-7], dendrigraft[8, 9] and random hyperbranched polyme

phase17-. Several investigators used solid–phase methodology. The preference of solid-phase polymerization over solution-phase is described by Wells et all. [17] It is stated that solution-phase synthesis is often time consuming and it requires significant purification. Reaction in solid-phase can be completed with a large amount of reagent with a small purification.

Among different type of polymers, acrylics are very common. Acrylics are made from monomeric acrylonitrile and a co-monomer and it can be polymerized by diverse methods. Emulsion, solution and suspension polymerization methods are often used. Preparation of acidic comonomers such as acrylic acid (AA) has been reported in the literature[18]. Acidic copolymer improves properties of the polymer for specific applications. It is expected that by increasing the number of acidic groups through the incorporation of dendritic units the properties would be improved further. Because of the possibility of incorporating acidic copolymer in to the main

chain of acrylic polymer film, it may become an interesting polymer for making changes on the surface. Acidic copolymer is required for further reaction with a multifunctional reagent such as citric acid. When citric acid is used as generations and DCC is used to activate the carboxylic acid functional groups on the surfaces, the number of carboxylic group increases considerably. For producing dendritic structure, citric acid has been used as the generation by several investigators[19-20].

To be specific to the acrylic copolymers, Hirt et al[21] studied the modification of ethylene–acrylic acid (EAA) copolymer film surface with amine. Dicyclohexylcarbodiimide (DCC) was used to activate the carboxylic acid functionality. It is believed[21] that in the case of the branched architecture the conversion of the reaction decreases with each successive step.

The present work describes a divergent synthetic route to the synthesis of a dendritic polymer on the surface of acrylonitrile/acrylic acid P(AN/AA) copolymer film. Copolymer of P(AN/AA) was synthesized by suspension polymerization and converted into film. Dendritic molecules are grown by a reaction between the carboxylic acid of acrylic acid and –OH group of citric acid activated by dicyclohexylcarbodiimide (DCC The reactions involve in the production of the third step (G3) with 100 % conversion is expected to be according to Figure 1.
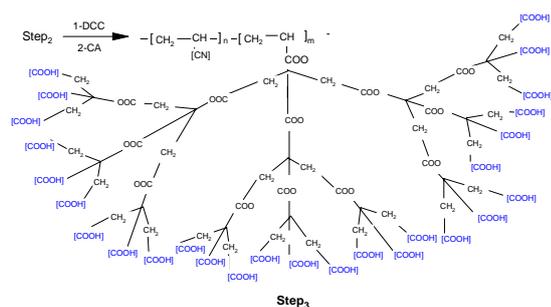

g. 1- The third step of citric acid on the P(AN/AA) copolymer.

2. EXPERIMENTAL

2-1. Materials
Acrylonitrile (AN) from Fluka was freed from inhibitor by washing with 0.1 N sodium hydroxide solution and then with water until completely freed from sodium hydroxide. Dimethylformamide (DMF) from Fluka and acrylic acid (AA) from Merck was purified by distillation before use. Sodium metabisulfate, sodium bicarbonate and dicyclohexylcarbodiimide (DCC) were purchased from Merck and used as received. Potassium persulfate was purified by re- crystallization in methanol. Citric acid was obtained from Merck and then purified with refluxing over NaOH for 2 h by subsequent distillation. 1, 4-Dioxane and tetrahydrofuran (THF) were purchased from Lab-Scan.1,4-Dioxane was dried by refluxing over calcium hydride and distilled under reduced pressure of nitrogen atmosphere. THF was purified by distillation under purified nitrogen atmosphere after being dried by refluxing with Na/benzophenone before use.

2-2. Analytical techniques
IR spectra of films were recorded between 400 and 4000 cm^{-1}

by Nicolet 670 FTIR spectrophotometers in transmission and ATR mode. Nominal resolution for all spectra was 4cm^{-1} , and there were 32 scans for each spectrum. The absorbed band in FTIR spectra are identified by several investigated[21-24]. In order to quantify the relative amount of chemicals species the peak area ratio (PA) of the characteristic peaks are divided by the peak area centered at 2240 cm^{-1} that is characteristic of stretching mode of –C≡N in acrylonitrile and it is served as an internal standard23-. The limits for PA integration are 2879-3100 cm^{-1} (for –OH), 2823-2879 cm^{-1} (for -CH$_2$ stretch), 1689-1826 cm^{-1} (for -C=O stretch) and 1282-1303 cm^{-1} (for –C-O bending of carboxylic acid). All of the reported PA values in the related figures are an average of at least three reading; the confidence intervals with 95% probability are shown.

^{1}H, ^{13}C NMR and 135-DEPT NMR were recorded in DMSO-d$_6$ on a Bruker AVANCE 300 MHz spectrometer.

Elemental analysis of the copolymer was carried out using a Vario 3 Elemental analyzer to determine the carbon, hydrogen and nitrogen content of G$_0$ products.

2-3. Synthesis
2-3-1.Synthesis of P(AN/AA) copolymer
Acrylonitrile 0.2 mol (10.612g) was copolymerized with 0.04 mol (2.882g) acrylic acid by the aqueous suspension method at 60±1°C with potassium persulfate and sodium metabisulfate as the redox initiator[22] in a four necked reactor. The reactor was fitted with a condenser and a stirrer and the third neck was used for purging nitrogen. The fourth neck was equipped with a sensor for measuring temperature. The reaction was carried out for 3 hours with good agitation. The copolymer was isolated by filtration and it was washed successively with water and methanol and dried under vacuum at 50°C. The %conversion was calculated by dividing the weight of dried powder products by the weight of monomer used. The conversion of P(AN/AA) copolymer was about 40%. The copolymers were then dissolved in DMF and re-precipitated in methanol and vacuum dried. The composition of the copolymers was ascertained by elemental analysis and ^{1}H NMR which was equal to 15%AA in copolymer. The dried P(AN/AA) powder was dissolved in DMF (20 %(w/v)) and filtered under vacuum. This solution was cast into film by a film casting device (Gardner). Also the solution of P(AN/AA) in DMF was converted in to fiber by a laboratory wet spinning machine. The diameter of the filaments was 200±20 μm, after drying.

2-3-2. Synthesis of dendrigraft
P(AN/AA) films were reacted with DCC. A flask equipped with a condenser, a glass perforated stool and a magnetic stirrer inside the flask were used. The P(AN/AA) film was placed over the perforated glass and the flask filled with the required solutions. This arrangement was used to keep the film inside the stirring solution and prevent it from creasing. Solution of DCC in the mixture of dioxane and THF (50:50 v/v) was added to the flask. The mol fraction of DCC was equal to the mol fraction of AA in P(AN/AA) film . The solution was stirred for 3 hours at room temperature by a magnetic stirrer. Then the film was removed from the solution and washed with pure dioxane to

remove any excess of DCC. The film was allowed to hang free at room temperature for another 1 h to remove the excess of dioxane by free evaporation. The product is called DCC activated film.

In the next step, the DCC activated film was placed in the prescribed reaction flask. A solution of CA was dissolved in dioxane/THF mixture (50:50 v/v) and the solution was added to the flask where the film was placed and the bath was stirred for 3 h at 60±1°C. Mol fraction of CA was equal to 3× mol fraction of AA that was equal to 15% of P(AN/AA). After three hours the film was taken out and washed with pure dioxane/THF to remove any excess of CA. Then the film was allowed free at room temperature for 24 h for evaporate the excess solvent. This product is designated by G_1. Choosing the temperature of 60 °C was based on a preliminary experiment.

In a preliminary experiment we compared the product of the above reaction at two different temperatures, namely the room and 60 °C with ^{1}H NMR and FTIR measurements. It was found that the %conversion at 60°C was more than that at room temperature. Then the dried film was used in the next step of synthesis and all the reactions were performed at 60±1°C.

In the succeeding reaction G_1 is used to prepare the next product that is designated by G_2. First the films were activated by DCC and then reacted with CA, in the same way that is used for the preparation of G_1. Then the successive compounds G_3 and G_4 were prepared. The procedure for the next steps, G_3 and G_4, was similar to preparation of G_1. These reactions were repeated to produce dendrigrafted fiber from G_0 to G_3.

3. RESULTS AND DISCUSSION

3-1. Analysis of FTIR results:

The preparation routes of a series of end-functionalized dendrimer are expected to be according to the figure 1. The polymerization process was confirmed by the results of FTIR and NMR. The representative FTIR spectra for the neat P(AN/AA) (G_0) film and G_1 through G_4 are shown in Figure 2.
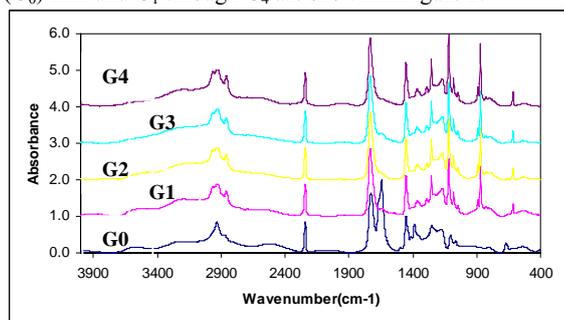
Fig. 2 Representative FTIR spectra of Gn(n=0-4) .

The absorbed bands in FTIR spectra[19 -24] for $G_{n (n=0-4)}$ are a broad and weak peak due to COOH at 2879-3100 cm^{-1}, a sharp peak due to -C=O stretch at 1727 cm^{-1} for G_0 and at 1733 cm^{-1} for $G_{n(n=1-4)}$, -C-O bending at 1290 cm^{-1}, 1050 cm^{-1} and CH$_2$ stretch at 2859 cm^{-1}. Figure 3 shows the PA of characteristic peaks for $G_{n (n=0-4)}$ films. The acid picks[21-24] at 2964 cm^{-1} (-OH stretching), -C=O stretching (at 1727 cm^{-1} for G_0 and at 1733 cm^{-1} for the other step), -C-O bending (at 1290 cm^{-1}, 1050 cm^{-1}) and –CH$_2$ stretching at 2859 cm^{-1} increases with the steps,
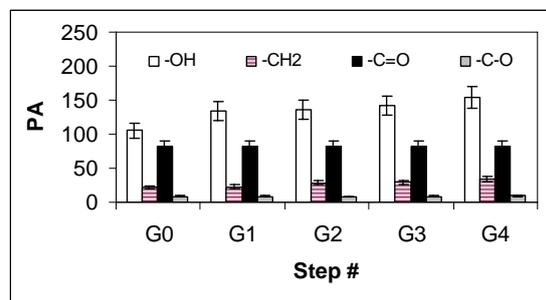
according to Figure1.

Figure 3. Peak area (PA) characteristic peaks for $G_{n (n=0-4)}$ films. The error bands represent 95% confidence intervals.

Figure 4 shows the PA of the –CH$_2$ stretching at 2859 cm^{-1} on the fibers and films. The results shows that the PA of the –CH$_2$ on the fibers are higher than on the films because surface area of the fibers is more than films.
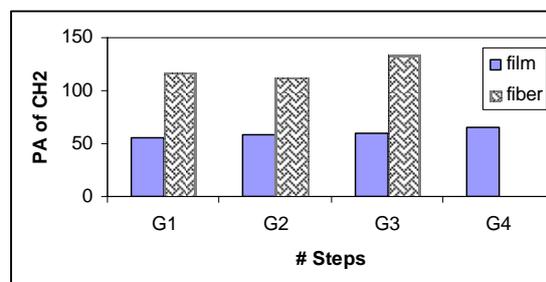
Fig. 4- The PA of the –CH$_2$ stretching at 2859 cm^{-1} on the films and fibers

3-2. Analysis of NMR results
3-2-1. ^{1}H NMR analysis

The results of NMR studies support the findings from FTIR The ^{1}H NMR spectra of G_0 (P(AN/AA) film) displayed a strong envelope between δ1.50 to 2.25 ppm with its peak at δ2.03ppm due to methylene protons and a triplet appeared between δ 3.13 ppm which was due to –CH protons. A broad down field peak at δ 12.64 ppm is related to proton of carboxylic acid (AA) [21-24]. The chemical shifts at δ 2.50 ppm are due to the solvent (DMSO). The resulting reaction of citric acid (CA) with P(AN/AA) film displayed methylene protons (-CH$_2$) resonances at 2.61-2.93 ppm in the H NMR spectra, which do not appear in G_0 spectra[19, 20].

The conversion (C %) was calculated using the Equation (1).

$$C\% = \frac{A}{2bB[1 + a(n-1)]} \times 100 \qquad (1)$$

Where, A is the integrated intensity due to –CH$_2$ of CA (dendritic units), n is the step number, B is the integrated intensity due to –CH$_2$ of P(AN/AA)(linear units of the chain). The values of A and B is determined from ^{1}H NMR spectra.

The parameter "a" is the functionality of component in each step which is a constant and it is equal to 3 for CA, b is the % active content of core which is equal to % AA in copolymer of P (AN/AA) measured by elemental analysis, that was obtained to be 15%. The expression $[1+a(n-1)]$ in the denominator is the general term of an arithmetic progression with the initial term of one and the common difference of successive members is "a". Frechet[25] determined the degree of branching by an equation expressing the number of dendritic units + number of terminal units to the total number of units. Figure 5 shows the percent conversion of the reactions of films that decreases with each successive step. A modified method would be required for achieving a higher conversion.
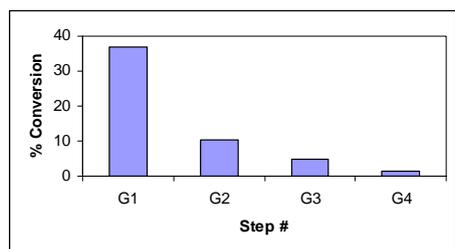

Fig. 5- % conversion of dendrigrafts films calculated using Equation 1 from the integrated intensities of ^{1}H NMR spectra.

Figure 6 shows the comparison of the % conversion of the reaction between films and fibers. The results show that the percent of conversions of the reactions on the fibers are higher than on the films because surface area of the fibers is more than films.
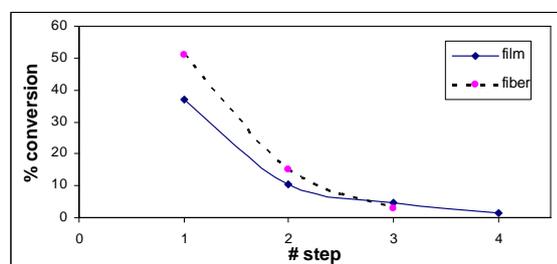

Fig.6- % conversion of dendrigrafts on the films and fibers

3-2-2. ^{13}C NMR, 135-DEPT analysis

The ^{13}C NMR spectra of P(AN/AA) film and fiber after different steps support the findings from FTIR and H NMR. Because of complexity of ^{13}C NMR spectra of dendrimer, the 135-DEPT NMR technique is used. Due to this technique, the –CH, -CH$_3$ groups have positive peak, -CH$_2$ group has negative peak and fourth –C (Carbonyl) do not have any peak in ^{13}C NMR spectra[24]. The results shows –CH$_2$ carbon of P(AN/AA) appear at δ 33.05 to 39.10 ppm with its peak at δ 36.23 ppm that is a negative peak, methine carbon (-CH, positive peak) gives rise a triplet peaks centered at δ 27.82ppm. Similarly, nitrile carbon (CN) resonance is mostly down field at δ 120.45ppm, carbonyl carbon (-C=O) display at δ 174.93 ppm21-[24]. The methyl carbon of CA (negative peak) display at δ

66.80 for G$_{n (n=1-4)}$, which do not appear in G$_0$. The 135-DEPT spectra of G$_0$ and G$_4$ on films are shown in Figure 7.
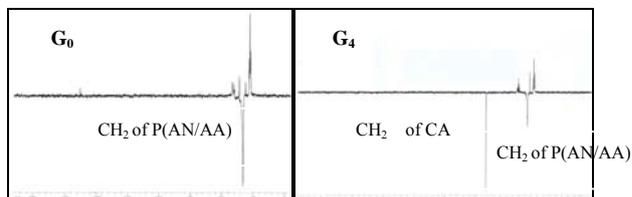

Fig.7- The 135 -DEPT Spectra of G$_0$ (left) and G$_4$ (right).

4. CONCLUSION

A divergent synthetic route to the synthesis of various step of a dendritic polymer from acrylonitrile /acrylic acid P(AN/AA) copolymer core and citric acid (CA) from zero (G$_0$) through fourth step (G$_4$) were examined. Products from G$_0$ through G$_4$ are analyzed using several analytical techniques. The results indicate formation of citric acid dendrigraft on the P(AN/AA) film and fiber in the heterogeneous system. NMR results showed that the %conversion decreased with each successive step. The results show that the percent of conversions of the reactions on the fibers are higher than the films because surface area of the fibers is more than films.

5. Acknowledgment

6. References

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