

Graft Copolymerization of Binary Monomer Mixtures with Acrylonitrile onto Cellulose using KMnO_4 /Citric Acid Redox System

Amany S. El-khouly^{*1,2}, Yoshiaki Takahashi¹

¹Institute for Materials Chemistry and Engineering, Kyushu University, Fukuoka 816-8580, Japan

²Department of Chemistry, Faculty of Science, Tanta University, Tanta 31527, Egypt

*Email: amanyelsawy@yahoo.com

Graft copolymerization of cellulose with binary vinyl monomer mixtures such as acrylonitrile (AN) / methylmethacrylate (MMA), AN / acrylic acid (AA), and AN / styrene (Sty.) was carried out by using KMnO_4 /citric acid redox system. Under the efficient conditions, maximum grafting yield (89.5 %) was found with AN/MMA binary monomer mixture. Synthesized graft copolymers were characterized with FT-IR spectroscopy, solid state NMR, X-ray diffraction, and TGA.

Desirable and targeted properties can be imparted to natural or synthetic polymers through graft copolymerization in order to meet the requirements of specialized applications. This has led to a new class of materials called specially polymers, which play an important role in many frontline technological applications. Graft copolymerization of vinyl monomers onto natural and synthetic polymers has advantages of adding properties of the monomers to them. A considerable numbers of the studies on graft copolymerization of single monomers onto cellulose using different methods of initiation has been reported¹⁻⁵. But graft copolymerization of binary mixtures of vinyl monomers has special importance in comparison with simple grafting of individual monomers. This technique of grafting of monomer mixtures has the advantage of creating grafted chains with tailor-made properties for specific applications. The synergistic effect of the comonomer in grafting mixture plays an important role in controlling the composition and the graft yield onto cellulose. Few reports are available about the grafting of vinyl monomers from their mixtures onto cellulose⁶.

In our previous studies, we prepared cellulose-*graft*-polyacrylonitrile (C-g-PAN) by using KMnO_4 /citric acid redox system⁷ and the most efficient conditions of the graft copolymerization were evaluated. The grafting of AN onto cellulose by using KMnO_4 /different acids as redox system had been also studied and their mechanical properties were investigated as a function of the crystallinity degree⁸, where the mechanical properties of the grafted samples prepared by using strong acids became more poor than those for samples prepared by weak acids, indicating that more chain rupture occurred when strong acids are used. Also, amidoximated grafted cellulose was prepared from C-g-PANs and their adsorption efficiency towards the metal ions was studied⁹. It was evaluated that the adsorption efficiencies of amidoximated grafted cellulose was improved through the grafting of AN onto cellulose by using KMnO_4 /citric acid redox initiation, where the adsorption metal ion values are about three times larger than the previous studies¹⁰⁻¹⁷.

Moreover, C-g-PAN was modified with ethylenediamine to produce aminated grafted cellulose. Aminated grafted cellulose was reacted with some aldehydic aromatics¹⁸.

Aminated grafted cellulose and their derivatives were characterized by solid state NMR and FT-IR and also their antimicrobial activities were studied. With low concentration of these modified grafted cellulose materials, the growth inhibition of the fungal species reached to 100% and almost 60% of the bacterial species. By increasing the concentration, the inhibition growth of bacterial species increases to be more than 80%. The mode of action was studied to evaluate that these derivatives have bactericidal effect against the bacterial species¹⁸.

In this study, we investigated the graft copolymerization of different vinyl monomers using AN as comonomer onto cellulose by a chemical initiation method. The grafting of these monomers led to the incorporation of well-defined graft chains. In this report, preliminary results of characterizations of the binary monomer mixture grafted samples are reported.

The individual grafting of some vinyl monomers have been studied by using KMnO_4 /citric acid redox system by using the efficient grafting reaction conditions as described before⁷. It was found that AA and Sty have poor grafting onto cellulose in the presence of the redox system in comparison to AN and MMA. According to these results, the grafting of AA and sty onto cellulose are not active enough to attach directly to cellulose backbone, see Figure 1a.

Figure 1b represents grafting of binary monomer mixtures with AN where the AN monomer used as principle and acceptor monomer. From the figure we can observe that in the case of AN/AA and AN/Sty binary mixtures, the percent graft yield increases with increasing the ratio of AN up to 60% of the total volume of the binary mixture. In addition, in the case of AN/MMA binary mixture, both have high activity towards grafting onto cellulose, which results in the formation of more free radical sites and hence an increased in the graft yield has been observed. The best ratio is 80:20 of AN/ MMA binary mixture.

Figure 2 shows the ¹³C Cp-MAS spectra of Un-C, C-g-PAN, C-g-PMMA, C-g-P(AN-co-AA), C-g-P(AN-MMA), and C-g-P(AN-co-Sty). As reported in the previous studies^{7,8}, the resonances belongs to the cellulose (60-110 ppm) are well observed in the all spectra. Also

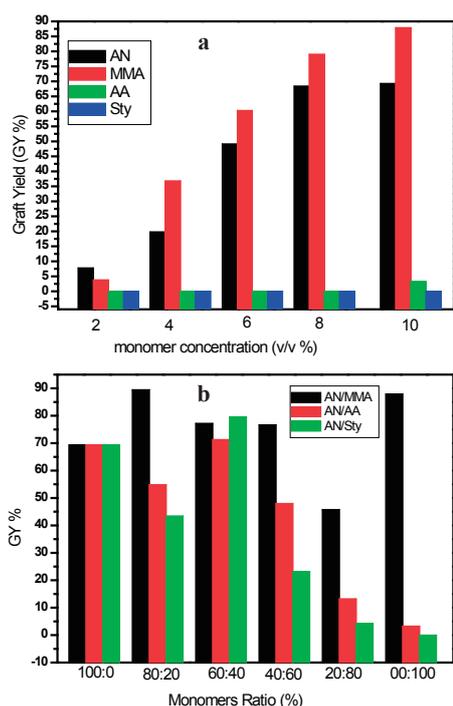


Fig. 1. Percent graft yield of a) different monomers with different concentration, b) different binary mixtures with 10 v/v% concentration.

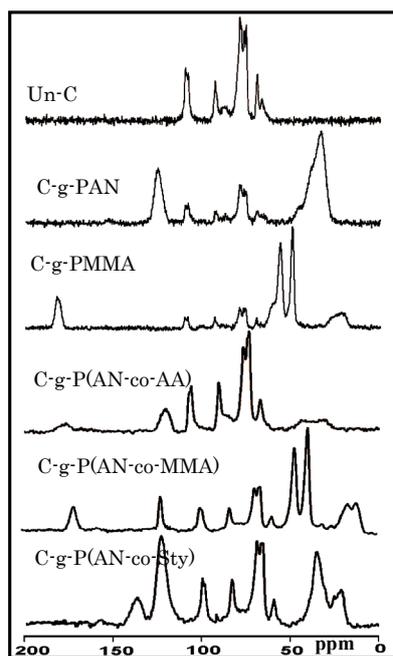


Fig. 2. ¹³C CP-MAS NMR spectra of Untreated cellulose (Un-C), and its grafted derivatives.

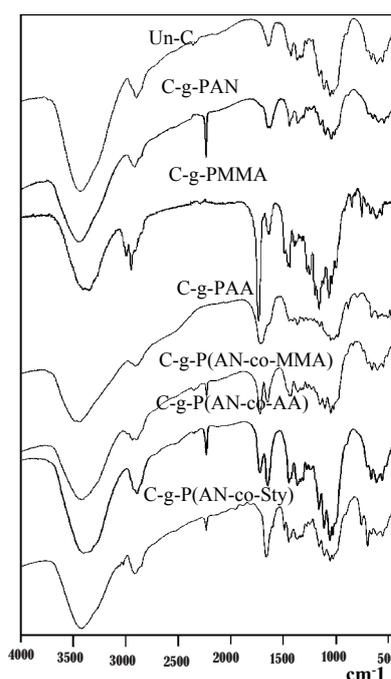


Fig. 3. IR spectra of Untreated cellulose (Un-C), and its grafted derivatives.

the resonance peak related to the grafted chain (40 pm) and resonance peak related CN group (125 ppm) in PAN chain are observed in the all grafted binary mixtures and C-g-PAN. The resonance peak at 180 ppm in C-g-PMMA is related to CO group in the grafted chain. Also this resonance peak is observed in C-g-P(AN-co-MMA) and C-g-P(AN-co-AA) related to the carbonyl group in PMMA and PAA grafted chains. In the spectrum of C-g-P(AN-co-Sty), the aromatic carbon resonate at the clear intense peak at 122 ppm and at 140 ppm. These results confirmed the evidence for the grafting of the binary monomer mixture onto cellulose backbone.

Figure 3 shows the IR spectra of untreated cellulose and the grafted cellulose with PAN, PMMA, and with the different binary mixture, all the grafted cellulose with the binary mixture have band at 2243 cm⁻¹ which is related to the CN group of the PAN grafted chain. Another bands at around 1750 cm⁻¹ in C-g-PMMA, C-g-P(AN-co-PMMA), and C-g-P(AN-co-PAA) related to the carbonyl group in the grafted chain of PMMA and PAA.

More characterizations such as, X-ray diffraction, SEM, TGA and mechanical properties, are in progress to compare the physical properties of the cellulose before and after grafting with different monomers and will be discussed in detail in the future.

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