

Synthesis and Characterization of a Novel Acrylonitrile Copolymer Containing Glucose Pendants

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Abstract: In this work, a novel sugar-containing copolymer was synthesized by the copolymerization of α -allyl glucoside (AG) with acrylonitrile (AN). The copolymers were characterized by NMR spectroscopy. It was found that acrylonitrile-based copolymers containing as high as 22wt.% of α -allyl glucoside can be synthesized by the free radical solution copolymerization of the two monomers in DMSO with AIBN as initiator.

Keywords: α -Allyl glucoside, acrylonitrile, copolymerization, sugar-containing copolymer.

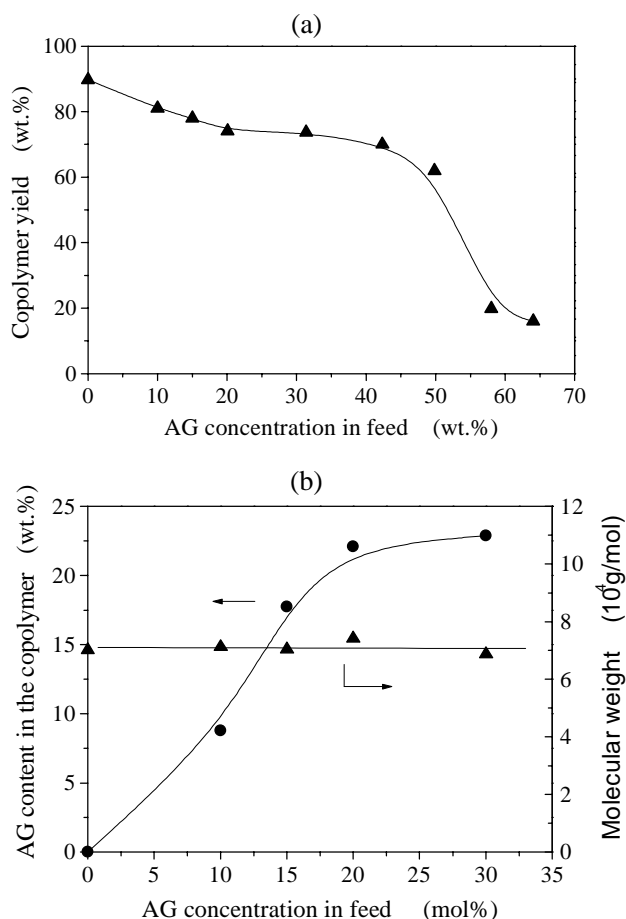
It is well known that carbohydrates exist in many forms and play important roles in living systems and have received considerable interest in recent years^{1,2,3,4}. Copolymerization of vinyl carbohydrates with acrylonitrile (AN) can also offer, in some degree, the intrinsic highly hydrophilic character as well as the compatibility with biomolecules to the acrylonitrile-based copolymers⁵. In this letter, therefore, the preliminary results of the copolymerization of α -allyl glucoside (AG) with acrylonitrile in DMSO using AIBN as the initiator were reported for the first time. The copolymers were characterized by ¹H-NMR and ¹³C-NMR spectroscopy.

α -Allyl glucoside was synthesized by Talley *et al.*⁶. Copolymerization of AG with AN initiated by AIBN was carried out in DMSO with stirring at 70°C. The resulting polymer was isolated by pouring the reaction mixture into anhydrous ethanol (AR) and then filtrated, washed three times with pure water and ethanol to remove the reaction residues. The obtained copolymer was dried at 50°C under vacuum for 24 h. NMR spectra were measured on a Bruker Advance DMX500 spectrometer. The solvent is d₆-dimethyl sulfoxide and three drops of D₂O were added to the solution for the deuterium exchange of the hydroxyl protons.

Typical results for the copolymerization of AN with AG are summarized in **Figure 1**. **Figure 1(a)** shows that the monomer feed ratio had great influence on the copolymerization. The yield of copolymer was lower than that of AN homopolymer. It decreased slightly with increasing the AG concentration from 0 to 45wt.% and then decreased sharply with increasing the AG concentration from 50 to 64wt.% in the monomer feed. This is reasonable that the C=C bond of AG is linked with alkoxy bond

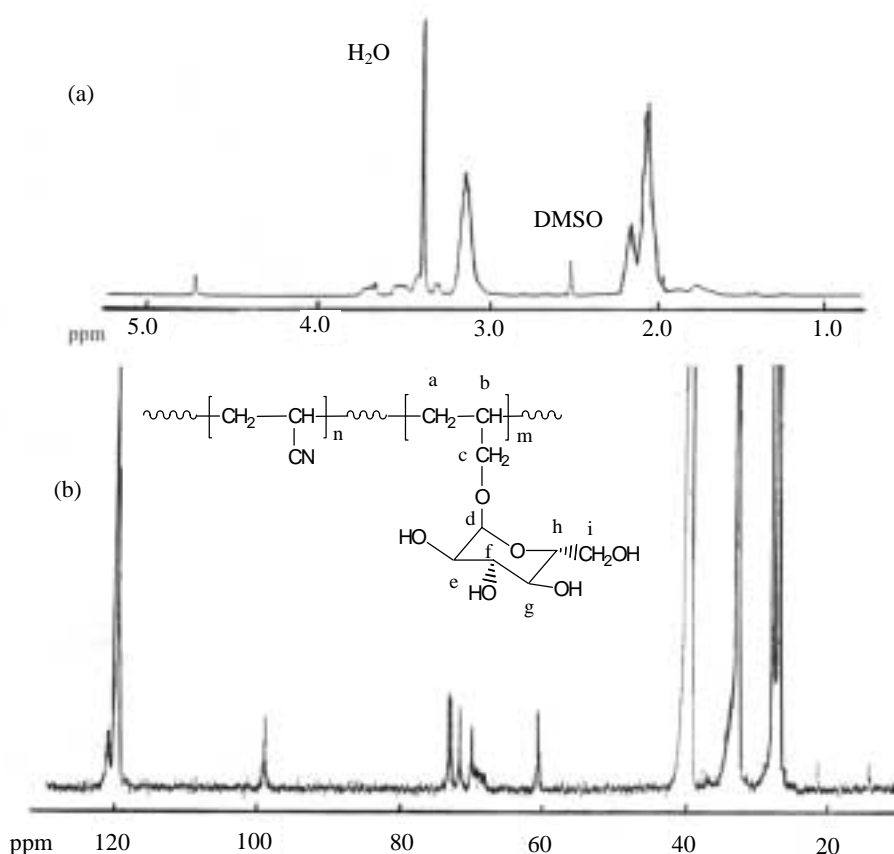
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Figure 1 Typical results of the copolymerization in DMSO at 70°C for 6h ([Initiator]/[Monomer] = 1/500): (a) Effects of AG content in monomer feed; (b) Relationship between the copolymer composition and the AG concentration in feed



which has a negative effect to the radical polymerization. **Figure 1(b)** shows the effect of monomer feed ratio on the composition and molecular weight of the resulted copolymer. It can be seen that increasing the monomer feed ratio of AG/AN principally increased the AG content in the copolymers. However, when the AG content in the copolymers was too high, the copolymers became fragile, degradable, and water-soluble due to the sugar moieties. Therefore, the behavior of copolymerization for [AG]/[AN] ratio above 30/70 was not studied here. And in the studied range, it seems that the monomer ratio had no obvious influence on the molecular weight of the resulted copolymer.

Figure 2 ^1H NMR (a) and ^{13}C NMR (b) spectra of the copolymer



The NMR technology was widely used to verify and measure the composition of copolymer in polymer chemistry. The copolymers were washed by pure water for three times to remove the unreacted monomers together with the water-soluble AG homopolymer before the NMR measurement. Therefore, the samples consist only with AN-AG copolymers. From **Figure 2** it can be seen that the ^1H NMR and the ^{13}C NMR all give the information of both AN and AG monomer unit in the samples, which confirms the samples are AN-AG copolymers. The ^1H NMR spectrum of the copolymer is presented in **Figure 2(a)**. Compared with the spectrum of the α -allyl glucoside monomer (^1H NMR: $\delta=3.27\text{-}3.31$ (t, HOCH<, 1H_f), $3.43\text{-}3.46$ (m, HOCH<, 1H_g), $3.58\text{-}3.60$ (bd, HOCH₂-, 2H_i), $3.62\text{-}3.66$ (m, -CH<, 1H_h), $3.73\text{-}3.76$ (m, HOCH<, 1H_e), $3.97\text{-}4.12$ (dq, -CH₂O-, 2H_c), $4.85\text{-}4.86$ (d, -OCHO-, 1H_d), $5.14\text{-}5.28$ (dd, CH₂=CH-, 2H_a), and $5.82\text{-}5.90$ (m, CH₂=CH-, 1H_b)), fine structures can not be observed for the corresponding copolymer. However, from this spectrum it was seen that the peaks at $3.12\text{-}3.15$ ppm and 4.70 ppm could provide the qualitative information about the AG content in the copolymer because the proton of >CH-CN showed a broad peak in the

range of 3.12-3.15 ppm while the d proton in the AG unit gave a single peak around 4.70 ppm. The composition of the copolymers can be calculated according to the following equation:

$$\text{AG (wt. \%)} = 220 I_{4.70} / (220 I_{4.70} + 53 I_{3.12-3.15}) \times 100$$

where I is the intensity of the peaks in the NMR spectrum. Other protons in the main chain gave broad peaks from 1.97 to 2.17 ppm. The ^{13}C NMR spectrum of the copolymer (**Figure 2(b)**) showed $\delta=60.72$ ($-\text{C}_c\text{H}_2\text{O}-$), 68.00-69.50 (HOC_iH_2-), 70.04 ($\text{HOC}_f\text{H}<$), 71.69 ($\text{HOC}_g\text{H}<$), 72.87 ($\text{HOC}_h\text{H}<$), 73.15 ($\text{HOC}_e\text{H}<$), and 98.92 ($-\text{OC}_d\text{HO}-$) for the glucose-carrying monomer in the copolymer. It seems that the $-\text{CH}_2\text{-CH}-$ of this monomer on the polymer chain were overlapped with those of acrylonitrile at 26.72 to 33.52 ppm.

From above results, it can be concluded that novel acrylonitrile-based copolymers containing glucose pendants could be synthesized by the free radical solution copolymerization of acrylonitrile and α -allyl glucoside in DMSO. Further work concerning the synthesis of the copolymers by precipitation polymerization in water and the membrane fabrication from the resulted copolymers has been carrying out in our lab.

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