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Copolymers

Preparation and Characterization of Poly(Vinyl Alcohol-co-Methyl Methacrylate) Copolymers

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Summary

An investigation is presented of the preparation and characterization of poly(vinyl alcohol-co-methyl methacrylate) copolymers which can be used for the preparation of novel membranes. These polymers were prepared by copolymerization of vinyl acetate and methyl methacrylate by γ-irradiation, followed by methanolysis of the produced copolymers. IR and ^{1}H-NMR studies established the structure of the copolymers.

Introduction

Poly(vinyl alcohol-co-methyl methacrylate), henceforth referred to as P(VA-co-MMA), copolymers may be excellent candidates as separation membranes because of the wide range of hydrophilicity exhibited by changing the ratio of the two monomers during the copolymerization reaction. It is well known that the thermodynamic partition coefficient of a solute between the membrane and the surrounding solution is an important parameter in the overall solute permeation through the membrane (PEPPAS and MEADOWS, 1983). Therefore, by adjusting the hydrophilicity of poly(vinyl alcohol) copolymers by copolymerization with a highly hydrophobic monomer, such as methyl methacrylate, one is able to control the partition coefficient.

Various P(VA-co-MMA) copolymers may be prepared by hydrolysis of the acetate groups of poly(vinyl acetate-co-methyl methacrylate) [P(VAc-co-MMA)], which in turn is produced by copolymerization of vinyl acetate (VAc) with methyl methacrylate (MMA). Previous studies of random copolymerization of VAc with MMA have been reported by various investigators (MAYO et al., 1948; HAM, 1964; SAKAGUCHI and FUNAYA, 1958; SENGUPTA et al., 1966; BLACK and WOYSFOLD, 1974; McNEILL et al., 1976). Most of these studies were conducted in bulk with chemical initiation. BLACK and WOYSFOLD (1974) studied the anionic, block copolymerization of the same monomers. SAKAGUCHI and FUNAYA (1958) investigated the conditions of hydrolysis for the production of P(VA-co-MMA). In general, the copolymerization of MMA and VAc is unfavorable, since the reactivity ratios are $r_1 = 20 \pm 3$ and $r_2 = 0.015 \pm 0.015$ (MAYO et al., 1948). To our knowledge no investigation has been reported of the preparation of membranes from these copolymers.

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Preparation of P(VAc-co-MMA)

Vinyl acetate (Aldrich Chem. 98% purity) was distilled and the fraction between 72.2 and 72.8°C was collected. Methyl methacrylate (reagent grade) was washed with a 10% aqueous solution of NaOH and a large quantity of water in order to remove the inhibitor; it was distilled under vacuum (b.p. 33 - 35°C, 60 mmHg).

Mixtures of VAc and MMA were prepared with molar fractions of MMA of f_1 = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5 and 1.0. They were placed in Petri dishes, sealed with Saran Wrap^R, and irradicated in a Co-60 source delivering 3,486 rads/min. Total γ-irradiation dose varying from 5.02 to 9.62 Mrads was used for the initiation of the copolymerization; the reaction temperature was kept constant at 27°C. The bulk-copolymerized products were received as transparent discs which were dissolved in acetone (100 ml), except for the sample with f_1 = 1.0. The copolymers were precipitated in diethyl ether at 0°C. The precipitate was suction-filtered and dried in the vacuum oven at 50°C for one day. The yield was 50%.

Preparation of P(VA-co-MMA)

Due to the poor solubility of certain P(VAc-co-MMA) copolymers, the methanolysis technique was carried out in a 60/40 v/v mixture of methanol and acetone which was found to be the best solvent for the copolymers. The concentration of NaOH used was set at 0.05 M in methanol to prevent degradation of the copolymers upon hydrolysis.

In a typical reaction, 2.5 g P(VAc-co-MMA) were placed in an Erlenmeyer flask and dissolved in 90 ml of the methanol-acetone mixture, to which there were added 10 ml of the methanol solution of NaOH (0.2 g NaOH). The reaction was carried out in a water bath at 30 ± 0.5°C for 3 days without agitation. A white gel-like precipate appeared after 10 minutes of reaction. The methanolysis reaction was terminated by neutralizing the system with a 1M aqueous solution of HCl. At the end of the reaction, the products were filtered and washed with a large quantity of methanol to remove the unreacted P(VAc-co-MMA) and by products such as sodium acetate, methyl acetate, acetic acid, etc.

The filtered product was dissolved in a 50/50 v/v ethanol and water mixture, and the solution was placed in a dialysis tubing (Spectrapor^R , M.W. cutoff point of 6,000). It was dialyzed in deionized water for 2 days to remove any additional byproducts or small molecular weight copolymer.

The dialyzed solution was distilled *in vacuo* at 60°C and the final polymer was precipitated from the solution in diethyl ether, and dried. The yield was 50%.

Polymer Characterization

The P(VA-co-MMA) samples were analyzed by elemental analysis, IR and NMR spectroscopy. Thin films for IR studies were prepared by casting an aqueous ethanolic solution of the copolymers on a glass plate and drying it at T = 70°C for 30 min.; this technique was used for the copolymers with f_1 = 0, 0.1 and 0.2. For the copolymer with f_1 = 0.3, 0.4 and 0.5 casting was done on mercury, followed by vacuum drying at 30°C. In all cases, the film had thickness less than 10 μm.

The IR spectra (Perkin Elmer, model 1420) of all the copolymers prepared are shown in Figure 1. All the spectra show that almost 100% of the VAc groups of the copolymer hydrolyzed. Indicative of this fact is the existence of absorption band characteristic of poly(vinyl alcohol), such as 3340 cm^{-1} (-OH), 1140 cm^{-1} (C-O) and 1085-1096 cm^{-1} and the disappearance of vinyl acetate sensitive bands, such as 1030 cm^{-1} (a strong C-O band) and 1740 cm^{-1}.

The 1030 cm^{-} strong C-O band may be used to distinguish the two kinds of esters present, i.e. acetates and carbonates, since it disappears in carbonate structures.

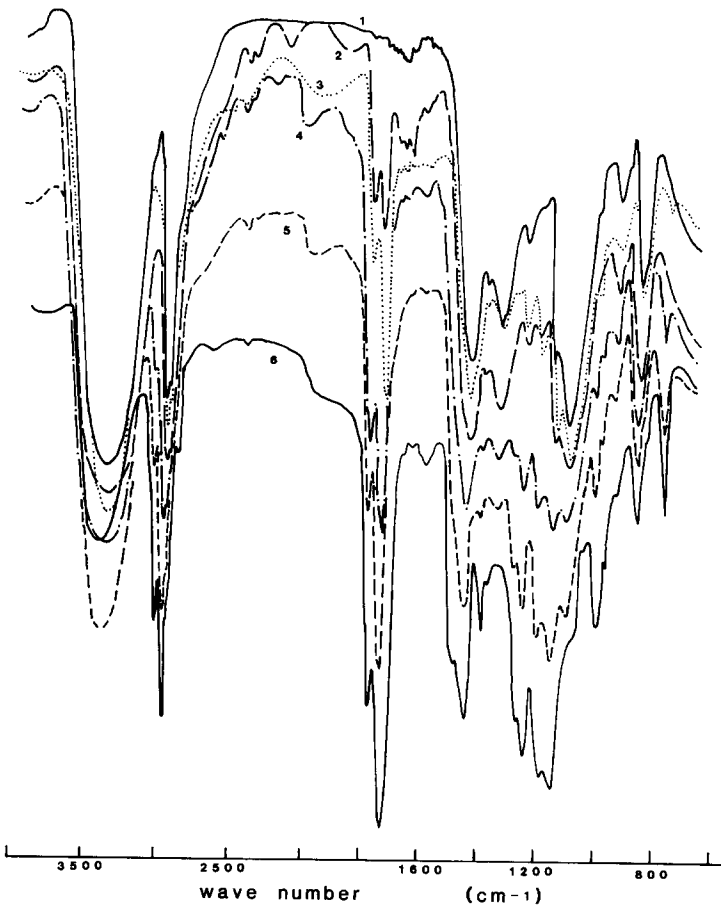

Figure 1: IR spectra of P(VA-co-MMA) copolymers. Spectra 1 through 6 are for copolymers with f_1 = 0 to 0.5 and increasing progressively by 0.1

As the amount of MMA increased in the copolymers, the characteristic ester peak increased, as indicated by the peaks at 1730 cm^{-1} (C = O), 1255 cm^{-1} (C - O), 1230, 1190, 1150 and 750 cm^{-1}. Quantitative analysis of these results is rather difficult.

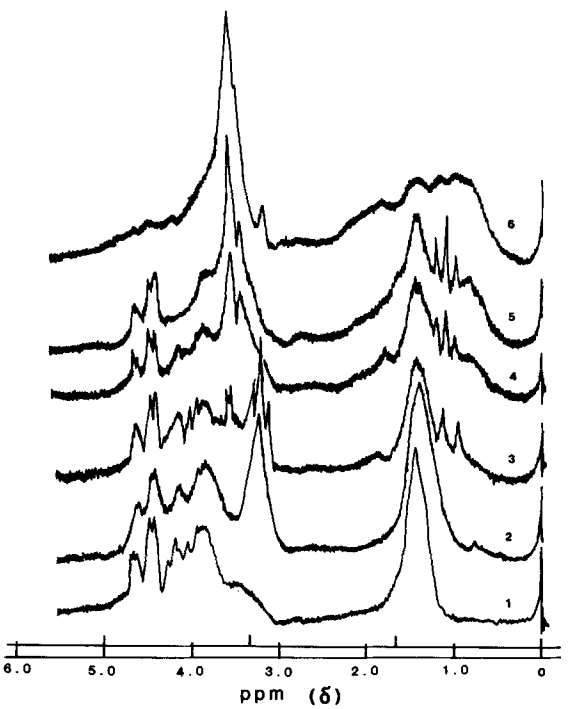

Figure 2: NMR spectra of P(VA-co-MMA) copolymers. Spectra 1 through 6 are for copolymers with f_1 = 0 to 0.5 and increasing progressively by 0.1

The ^{1}H-NMR spectra (Varian, model T - 60) were obtained at 60 MHz in a 15% solution of the copolymers in deuterated dimethyl sulfoxide. As the MMA content increased, the chemical shifts of $O=\underset{|}{C}-OCH_3$ and $C-CH_3$ appeared at about 3.5 and 1.0~1.5 δ respectively.

It is therefore concluded that it is possible to produce poly(vinyl alcohol) copolymers with varying degrees of hydroxylation by copolymerization with methy methacrylate. These copolymers, upon dissolution in water and crosslinking, can be transformed into membranes, suitable for a variety of separation processes as will be reported elsewhere.

Acknowledgements

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