Properties of Blend Polymers Composed of Phospholipid Polymer and Photocrosslinkable PVA

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1. Introduction

A methacrylate copolymers having the phospholipid polar group, 2-methacryloyloxyethyl phosphorylcholine (MPC) show excellent blood compatibility [1,2]. On the other hand, poly(vinyl alcohol) is employed in practical applications because of its excellent chemical resistance and physical properties, and because it is completely biodegradable [3].

In this work the behaviors of blend polymer chains in aqueous solutions were estimated by fluorescence and viscosity measurements. In addition, the retention and the protein adsorption-resistant properties of MPC copolymers were examined in the swelling film, which composed of poly(MPC-co-HEMA) with a photocrosslinkable PVA.

2. Experimental

MPC polymers used in this study listed in Table 1. They were supplied by NOF Corp.. Fig.1 shows the structure of poly(MPC). Poly(vinyl alcohol) was supplied by Kuraray Co., Ltd., Okayama, Japan. It had as a viscosity-average degree of polymerization of 1700 with a degree of saponification of 88 mol%. The blended polymer solutions were prepared from 2-methacryloyloxyethyl phosphorylcholine and 2-hydroxyethyl methacrylate (HEMA), poly (MPC-co-HEMA) with different PVA compositions. Sodium 8-anilino-naphthalene sulfonate (ANS-Na) used as received. The viscosity of polymer solutions was measured by a micro-viscometer at 30°C. Fluorescence emission was observed with an excitation maximum at 350 nm for ANS-Na ([C]=1 \times 10^{-5}M) in aqueous solutions. The photosensitive PVA was prepared by acetalization with formylstyrlypyridinium salt (FStbQ) according to the known method [4]. The 5wt% polymer solutions obtained were cast with a doctor blade, and then dried at 60°C. A high-pressure Hg lamp irradiated the films with a pyrex glass filter. The films were immersed in water to the equilibrium at 25°C. The swollen films were immersed in the solution of γ-globulin during 2 hours at 37°C. The amount of the adsorbed γ-globulin was measured by the method of a micro-BCA reagent.

<table>
<thead>
<tr>
<th>Code</th>
<th>MPC</th>
<th>HEMA</th>
<th>$M_w$*</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMPC</td>
<td>100</td>
<td>—</td>
<td>$1.1 \times 10^5$</td>
</tr>
<tr>
<td>PMH90</td>
<td>90</td>
<td>10</td>
<td>$1.2 \times 10^5$</td>
</tr>
<tr>
<td>PMH70</td>
<td>70</td>
<td>30</td>
<td>$5.3 \times 10^5$</td>
</tr>
<tr>
<td>PMH50</td>
<td>50</td>
<td>50</td>
<td>$5.1 \times 10^5$</td>
</tr>
</tbody>
</table>

* Determined by gel-permeation chromatography with polyoxyethylene standards for the MPC polymers.

![Structure of poly(MPC)](image_url)

Fig. 1. Structure of poly(MPC).

3. Results and Discussion

Fig. 2 shows the relationship between the maximum intensity of fluorescence spectra and the viscosity of various polymer solutions ranging in
concentration from 0.10 to 5.0 wt%. The fluorescence intensity increased with increasing MPC component in a poly (MPC-co-HEMA), and increased more rapidly than 90 mol%MPC. The increase in fluorescence intensity is due to the strong hydrophobic interaction around the polymer chain. On the other hand, the viscosity of polymer solutions decreased. As the concentration of the polymer solution is increased, the deviation from a straight line is gradually increased with increasing composition of the HEMA in a copolymer. This behavior is responsible for the large dimension of polymer chains due to the water molecules interacting with the HEMA.

Fig.3 shows the dependence of reduced viscosity on the PVA content in a blend solution at 1.0wt%. The reduced viscosity increased slowly with increasing PVA composition in blend solutions, and changed in viscosity of polymer solutions in the vicinity of 80 wt% PVA. The changes in reduced viscosity are attributable to miscibility in blends of high PVA contents with more MPC component.

The conformation of MPC polymers in aqueous solutions is little affected by the addition of a PVA. The hydration state of water molecules on the MPC coil is quite different from that of polymers such as a poly(HEMA) and a PVA. The characteristics of the MPC polymer system are closely related to the state of water molecules around the polymer chain.

Fig. 4 shows the amount of the γ-globulin adsorbed on the swollen films of PVA-SbQ, poly (MPC-co-HEMA) and poly (MPC) containing 20wt% PVA-SbQ. The presence in the MPC moiety is effective in reducing the amount of γ-globulin adsorption. In general, the amount of adsorbed protein is small and decreased with an increase in the MPC moiety [5]. However, on the surface of the poly(MPC-co-HEMA) with HEMA 10mol%, the amount of adsorbed γ-globulin was less than that of the poly(MPC).

For MPC polymers with PVA-SbQ, a peculiar change in conformation of polymer chains was observed at HEMA 10 mol%. The miscibility of polymer chains is partially governed by the presence of SbQ groups. Thus, it is considered that the conformation of a poly (MPC-co-HEMA) chains with HEMA 10 mol% is different from that of a poly (MPC).

References