



Structure of water at zwitterionic copolymer film–liquid water interfaces as examined by the sum frequency generation method

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ABSTRACT

A copolymer film composed of zwitterionic carboxymethylbetaine (CMB) and *n*-butyl methacrylate (BMA), Poly(CMB-*r*-BMA), was cast on a flat plane of an octadecyltrichlorosilane (ODS)-modified fused quartz prism with a semi-cylindrical shape. C–H stretching of the polymer film and O–H stretching of water at the surface of the film were examined using the sum frequency generation (SFG) technique. The C–H stretching band of the cast film, indicating a *gauche* defect of the film, was affected by the contact medium including dry nitrogen, water vapor-saturated nitrogen and liquid water. In contrast, the C–H stretching of an octadecyl group introduced onto the quartz prism for stable attachment of the cast film was not significantly changed by the contact medium. The O–H stretching band indicated that water molecules at the surface of the Poly(CMB-*r*-BMA) film in contact with liquid water were not greatly oriented in comparison with those at the surfaces of a bare prism, an ODS SAM-modified prism, and a prism covered with a PolyBMA film or a copolymer film of BMA and methacrylic acid or 2-(dimethylamino)ethyl methacrylate. A similar small perturbation of the structure of water was previously observed in the vicinity of water-soluble zwitterionic polymers and zwitterionic copolymer films using Raman and attenuated total reflection infrared spectroscopies, respectively. A distinct effect of charge neutralization to diminish the perturbation of the structure of interfacial water around polymer materials was suggested.

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1. Introduction

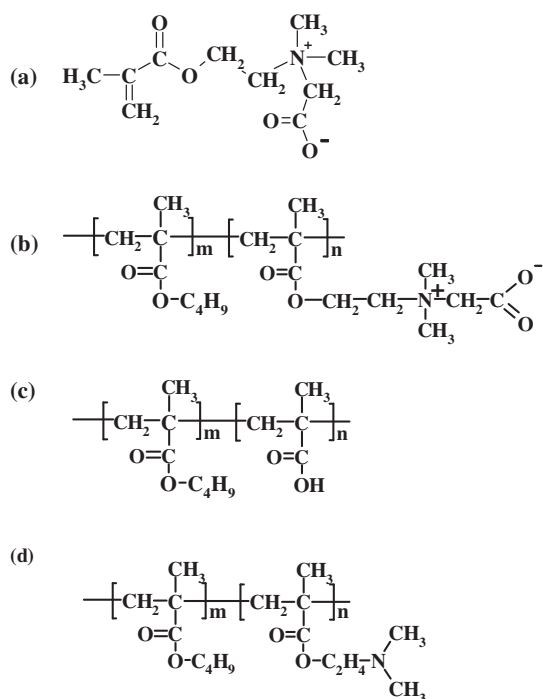
“Zwitterionic polymer” is the general term for an ampholytic polymer containing identical numbers of cationic and anionic species, commonly on the same monomer units [1]. Zwitterionic polymers have been designed to mimic phosphatidylcholine (lecithin), which is abundant in cell membranes [2–5], and their applicability to bio-medical fields has been extensively investigated. For example, polymer films composed of apolar monomers such as *n*-butyl methacrylate (BMA) and zwitterionic monomers such as 2-methacryloyloxyethyl phosphorylcholine (MPC, phosphobetaine), 3-sulfo-*N,N*-dimethyl-*N*-(3'-methacrylamidopropyl)propanaminium inner salt (SPB, sulfopropylbetaine) and 1-carboxy-*N,N*-dimethyl-*N*-(2'-methacryloyloxyethyl)methanaminium inner salt (CMB, caboxymethylbetaine, Scheme 1(a)) [6–13] were found to be highly

biocompatible [6,7,10–19]. The amount of proteins adsorbed and the number of platelets adhered onto a film of a random copolymer of CMB and BMA were found to be much less than those onto a PolyBMA film [11,12]. The usefulness of a CMB-BMA copolymer as a dressing for wound healing has also been reported [13].

Meanwhile, chemical and physical properties of polymer materials greatly affect the processes of water sorption and the structure of adsorbed water [20]. The sorbing processes of water to polymeric materials or distinction of the water sorbed to the polymers from that incorporated within the polymer matrix have been examined with difference spectra obtained by attenuated total reflection (ATR) infrared spectroscopy [21].

Using this method, it was found that the structure of water incorporated in the matrix of poly(2-methoxyethyl acrylate) (PMEA), which has been reported to have excellent blood compatibility (high anti-thrombogenicity) [22,23], was similar to that of bulk water [24,25]. The presence of water showing a so-called “cold crystallization” phenomenon (upon rapid cooling and subsequent gradual heating, devitrification of some of the water at about –45 °C) inside the PMEA hydrogel has been suggested by DSC

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Scheme 1. Chemical structure of (a) 1-carboxy-*N,N*-dimethyl-*N*-(2'-methacryloyloxyethyl)-methanaminium inner salt (CMB), (b) a copolymer of CMB and *n*-butyl methacrylate (BMA) (Poly(CMB-*r*-BMA)), (c) a copolymer of methacrylic acid (MA) and BMA (Poly(MA-*r*-BMA)), and (d) a copolymer of 2-(dimethylamino)ethyl methacrylate (DMAEMA) and BMA (Poly(DMAEMA-*r*-BMA)).

measurements [23]. Precise temperature-dependent infrared spectroscopic measurements of PMEA films, however, clearly indicated that the amount of water molecules showing the “cold crystallization” phenomenon was largely dependent on the cooling rate of the sample [26], and the amount of so-called “intermediate water” therefore cannot univocally be determined.

The cold crystallization phenomenon was also observed for various nonionic polymers such as polystyrene [27], poly(*n*-butyl methacrylate) and poly(2-ethoxyethyl acrylate) [28]. Most of these polymers are neither blood-compatible nor bio-compatible (anti-biofouling: very small adsorption and adhesion of proteins and cells, respectively). Among the polymers examined, only poly(tetrahydrofurfuryl acrylate) (PTHFA) and PMEA showed both blood compatibility and cold crystallization phenomenon. However, PMEA adhered to cells such as fibroblasts to a large extent, and PMEA therefore cannot universally be considered “bio-compatible”. Based on these findings, we suggested that the cold-crystallization phenomenon is not directly correlated with the biocompatibility and blood compatibility of the polymer materials [28].

In a manner similar to that for PMEA, inert properties to the vicinal water were observed for polymer films composed of BMA and zwitterionic monomers such as MPC, SPB and CMB [11–13]. Raman and infrared spectroscopies indicated that the hydrogen-bonded network structure of water in the vicinity of zwitterionic polymers and copolymers is not largely disturbed, in contrast to the electrostatic hydration by ordinary polyelectrolytes [29–31]. In addition, the solution behavior of zwitterionic polymers has received much attention due to unique properties toward typical polyelectrolytes (so-called “anti-polyelectrolyte effect”) [1]. Based on these findings, we have been insisting that the small perturbation effect of zwitterionic polymers on the structure of water at polymer–water interfaces is one of the important factors for their excellent bio-compatibility. The structure of water at water–polymer interfaces

is definitely one of the most central subjects in the field of surface chemistry.

In this study, a thin film of a zwitterionic copolymer, Poly(CMB-*r*-BMA), was prepared on the surface of a fused quartz prism with a semi-cylindrical shape by the cast method, and the structure of water at the surface of the copolymer film was observed using the sum frequency generation (SFG) technique. Both Raman and infrared measurements are very useful for investigating the structure of water in polymer solutions and polymer thin films, respectively [11–13,24–31]. However, the structure of “interfacial” water cannot directly be observed by these methods, and we cannot examine whether the materials that are inert to the interfacial water are biocompatible or not. Since the SFG method can detect molecules that lose centro-symmetry [32], it would be possible to examine the signals reflecting O–H stretching of water at polymer–water interfaces. In this work, water molecules at the interfaces with polymer materials were not precisely limited to those just directly in contact with the polymers, because the detection range of SFG cannot be a single water molecule from the polymer surface. Moreover, the polymers in contact with liquid water affect surrounding water molecules gradually with the distance. Therefore, we presume that the interfacial water molecules detected by SFG are similar to water molecules in the “vicinity” of polymer materials.

2. Materials and methods

2.1. Materials

A carboxymethylbetaine monomer (CMB) was prepared by the coupling of 2-(dimethylamino)ethyl methacrylate (DMAEMA) with potassium chloroacetate in aqueous media and subsequent electric dialysis [33,34]. 2,2'-Azobisisobutyronitrile (AIBN) from Wako Pure Chemicals, Osaka, Japan, was purified by recrystallization from ethanol. *n*-Butyl methacrylate (BMA), methacrylic acid (MA) and DMAEMA from Wako Pure Chemicals were distilled at low pressure. Other reagents used were commercially available. A fused quartz prism with a semi-cylindrical shape (flat face, 25 mm × 25 mm) was from Daiko, Kyoto, Japan. For the deposition of copolymer films, a fused quartz semi-cylindrical prism pretreated with a UV/ozone cleaner was modified with octadecyltrichlorosilane (ODS, 50 μL/500 mL anhydrous chloroform) at room temperature for 24 h. All aqueous solutions were prepared with Ultrapure water (18 MΩ cm, Millipore System).

2.2. Preparation of copolymers

To ethanol (75 mL) in a sample vial were added CMB, BMA and AIBN (molar ratio, 30:70:0.05, [monomer] = 1.15 M). After replacing the atmosphere with N₂ gas, the vial was tightly sealed and incubated at 70 °C for 24 h. After evaporation, the copolymer was dialyzed against methanol for several days (MWCO, 3500; Spectra/Por[®] dialysis membrane; Spectrum Laboratories, Inc., Rancho Dominguez, CA). After evaporation, the copolymer was dissolved in a small amount of ethanol again and precipitated in *n*-hexane (yield: 12.4 g). A similar procedure was used for preparation of Poly(MA-*r*-BMA) and Poly(DMAEMA-*r*-BMA) (feeding ratio, MA:BMA = 30:70 and DMAEMA:BMA = 35:65). The composition of copolymers was determined by using ¹H NMR (Table 1). The molecular weight and polydispersity (*M_w*/*M_n*) of the copolymers were determined by gel permeation chromatography (standards, PMMA; mobile phase, Poly(CMB-*r*-BMA), 0.1 M LiCl MeOH:CHCl₃ = 3:2; Poly(MA-*r*-BMA), THF; Poly(DMAEMA-*r*-BMA), 0.2 M LiCl MeOH:CHCl₃ = 1:1).

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