

Surface and Interfacial Energetic Analysis of Amphiphilic Copolymers

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A Series of hydrophilic-hydrophobic copolymeric surfaces of 2-hydroxyethyl methacrylate (HEMA) and various alkyl methacrylate (RMA) have been prepared by in-situ solution copolymerization using a redox radical initiator. Contact angles of various probing fluids on the polymeric surfaces were determined in air (hydrophobic environment) and under water (hydrophilic environment). From contact angle data, the dispersive interaction contribution (γ^d) and the polar contribution (γ^p) to the total surface free energy (γ^t) and interfacial energetic quantities (e.g., water-polymer, liquid-polymer interface, etc.) were estimated by surface and interface physicochemical theory. From the comparison of surface energetic components between hydrophobic and hydrophilic media, it is found that surface and interface energetic components of polymeric surface as a representative low-energy surface are highly dependent on environmental fluids. Also, from the correlation between interfacial energetic results and surface energetic criterion of biocompatibility, we found that HEMA/BMA, HEMA/HMA copolymer systems are in the region of biocompatibility.

Introduction

Some of the most important and extensive applications of surface chemistry and physics are concerned with solid-liquid interface, for example, adhesion and adsorption, paints and coatings, wettability and biocompatibility and so forth.^{1,2} Particularly, surface free energy of polymeric materials is a very important characteristic with respect to the interfacial phenomenon from both a theoretical and practical standpoint. However, there is no direct method of measuring surface free energy of polymeric solids due to the poor fluidity. Several indirect methods of estimating the energy have been proposed so far, the contact angle study is one of the most available ones.^{3,4}

Surfaces of polymeric solids are distinctly different from those of more rigid materials, such as metals, ceramics and glassy solids because of their surface mobility. This means implicitly that polymer surfaces can adopt different surface configurations in different environments so as to increase their interfacial interactions with the environmental fluid and thereby minimize the total free energy of the system like fluid phase system. Recently, for the biomedically applicable polymers, a number of researchers have suggested that the important factors for biocompatibility are the surface energetic components (e.g., γ_s^d , γ_s^p or γ_s^d/γ_s^p) and moreover its relationship to the interfacial interactions with the bio-fluids.⁵⁻⁶ Although a number of investigations on solid surfaces such as polymers, monolayers, crystals and so forth have been performed by various approaches,^{7,9} however, the polymeric surface properties have not yet been fully and widely characterized in a systematic fashion, particularly using model surfaces gradually changing the surface properties from hydrophilic to hydrophobic by varying the size of alkyl group and the structure of monomers for the comonomer recipe.

We investigated that the environmentally induced microscopic molecular restructuring of mobile polymer surfaces and its influences on their macroscopic physical properties such as surface and interfacial energetic characteristics in the new perturbed environment are closely correlated with each other effects. Here, a series of copolymeric solid surfaces of HEMA and various RMA have been prepared and used as

model surface systems.

Theoretical

We utilized the following thermodynamic wetting equations from Young-Dupre relation using the extended Firifalco-Good-Fowkes equation and other theoretical interfacial approximations and assuming that the equilibrium spreading pressure is negligible (i.e. $\pi_e = 0$).¹⁰⁻¹² For measurements in the air, the wetting equation is as follows.

$$W_{SL}/2 = \gamma_L/2(1 + \cos\theta_{SLV}) = (\gamma_s^d \cdot \gamma_L^d)^{1/2} + (\gamma_s^p \cdot \gamma_L^p)^{1/2} \quad (1)$$

where W_{SL} is the solid/liquid interfacial work of adhesion and γ_s , γ_s^d and γ_s^p are the total, dispersion and polar components of the surface free energy, respectively and θ_{SLV} is equilibrium contact angle for which Young-Dupre relation holds. $W_{SL}/2$ can be computed from the observed contact angles and γ_L^d and γ_L^p are known parameters given in the literature, otherwise, independently determinable from surface and interfacial tension data. Eq.(1) can be rearranged in a linear form as follows,

$$\frac{\gamma_L(1 + \cos\theta_{SLV})}{2(\gamma_L^d)^{1/2}} = (\gamma_s^d)^{1/2} + (\gamma_s^p)^{1/2} \left(\frac{\gamma_L^p}{\gamma_L^d}\right)^{1/2} \quad (2)$$

From $(\gamma_L^p/\gamma_L^d)^{1/2}$ vs. $\frac{\gamma_L(1 + \cos\theta_{SLV})}{2(\gamma_L^d)^{1/2}}$ plot, the intercept and the slope from which γ_s^p and γ_s^d can be computed, respectively, are obtained.

For under-water measurements, the wetting equation is expressed as

$$\gamma_w - \gamma_L - \gamma_{wL} \cos\theta = (I_{SW}^d - I_{SL}^d) + (I_{SW}^p - I_{SL}^p) \quad (3)$$

where γ_{wL} is the liquid/water interfacial tension, I_{SW}^d and I_{SW}^p (or I_{SL}^d and I_{SL}^p) are the dispersion and polar interaction energy at the S-W (or S-L) interfaces, and θ is the equilibrium contact angle. In general, for two phases (A, B), I_{AB} is as follows,

$$I_{AB} = I_{AB}^d + I_{AB}^p = f(\gamma_A^d, \gamma_B^d) + g(\gamma_A^p, \gamma_B^p) \quad (4)$$

where f and g are either the geometric or the harmonic mean function according to the choice of theoretical approximations. This wetting equation can be solved for γ_s^d and γ_s^p by

Table 1. Copolymeric Model Surfaces Utilized in This Study 2-Hydroxyethyl Methacrylate(HEMA) based Alkyl Methacrylate (RMA) Copolymers
General System:

R	Name	Abbreviations for R
-CH ₃	Methyl	M
-CH ₂ CH ₃	Ethyl	E
-CH(CH ₃) ₂	Isopropyl	I
-CH ₂ CH ₂ CH ₂ CH ₃	Butyl	B
-CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃	Hexyl	H
C = O	Benzoyl	BE
-CH ₂ CH ₂ OCH ₂ CH ₂ OCH ₃	Methoxyethoxyethyl	MEE
-CH ₂ CH ₂ OCH ₃	Methoxyethyl	ME

^aVolume ratio: HEMA:RMA = 7:3.

Table 2. Water Content of Various Copolymeric Model Surfaces

Model Surface	Water Content(%)
M	28.5
E	25.2
I	20.2
B	16.8
H	12.4
BE	20.0
MEE	52.5
ME	38.5

the Hamilton's method for the captive air-octane case and graphically for the water-immiscible fluid series.¹⁴⁻¹⁷

Experimental

Copolymeric Model Surfaces. Highly pure (98-99%) 2-hydroxyethyl methacrylate (HEMA), methoxyethyl methacrylate (MEMA), methoxyethoxyethyl methacrylate (MEEMA) and alkyl methacrylate (RMA) monomers were obtained from polysciences Inc. and Tokyo Kasei Company. Benzoyl ethyl methacrylate (BEMA) was synthesized in our laboratory.¹⁸⁻¹⁹ HEMA, MEMA, MEEMA, RMA and BEMA monomers were purified by distillation under reduced pressure and RMA monomer series were used after extraction of stabilizers or inhibitors with dilute NaOH aqueous solution. Also, highly pure reagent grade solvents and chemicals were used. The in-situ solution copolymerization technique was used to make copolymeric model surfaces between two clean glass plates using a redox radical initiator (12%(NH₄)₂S₂O₈/6%Na₂S₂O₅) according to the chemical formulation listed in Table 1. The copolymerization systems were retained for 24 hours at room temperature, then were put into an oven at 60°C for 25 minutes in order to assure complete polymerization. The formed polymeric surfaces after completion were allowed to equilibrate with distilled water to remove organic and inorganic reaction residues for one week frequently refreshing the water. The equilibrium water content of the copolymer was determined approximately by gravimetric method.

Table 3. Surface and Interfacial Energetic Properties of Probe Fluids at 20°C (ergs / cm²)

Fluids	γ_{LV}	γ_{LV}^d	γ_{LV}^p
n-Propanol	23.87	20.80	3.07
Diacetone alcohol	30.30	23.30	7.00
1-Bromonaphthalene	44.60	31.70	12.90
Ethylene glycol	48.20	17.50	30.70
Methylene iodide	50.80	46.60	4.20
Formamide	58.40	18.10	40.30
Glycerol	63.40	37.00	26.40
Water	72.60	21.80	50.80
(in air)			
Water immiscible Fluids	γ_{LV}	γ_{LW}	γ_{LW}^d
n-Hexane	18.40	51.10	21.63
iso-Octane	18.90	49.70	23.11
n-Heptane	20.40	50.20	22.45
n-Octane	21.80	50.80	21.80
Cyclohexane	25.00	50.30	22.37
Dodecane	25.40	51.70	21.10
Air Bubble	0.00	72.60	21.80
(under water)			

Probe Liquids. For measurements in the air, highly pure reagent grade n-propanol, 1-bromonaphthalene, ethylene glycol, methylene iodide, formamide, glycerol, water(triply distilled) were selected as a probe liquid series to ensure accomodation of widely spread wettability spectrum.

Under water measurement, n-hexane, iso-octane, n-heptane, n-octane, cyclohexane, n-dodecane and air bubbles were used as probe fluids. The surface and interfacial tensions of probe fluids were measured by the Fisher Tensiometer, otherwise obtained from literatures¹⁸⁻¹⁹ (see Table 3).

Contact Angle Measurements. For measurements in the air, the equilibrium contact angles of each probe liquid on model copolymeric solid surfaces were directly measured with a goniometer(NRL Contact Angle Goniometer, Model A100, Rame-Hart Inc). At least, 15 measurements of the contact angle were performed and averaged for each surface in order to obtain reliable experimental data.

For under-water measurements, the equilibrium contact angles of probe fluids were measured on a same goniometer using the environmental chamber by two-liquid contact angle technique. The mutually saturated water and hydrocarbon phases were used for contact angle measurements. The water-immiscible probe fluid bubbles were introduced by a microsyringe onto a model copolymer surface previously immersed in a distilled water in order to assure complete hydration. Very small(0.2-0.3 μ l) bubbles were used in order to minimize gravitational effects. Angles on both sides of each bubble edge were measured to ensure the symmetry and generally eight or more bubbles were measured on several parts of each surface and averaged.

Results and Discussion

Characterization. A series of hydrophilic-hydrophobic

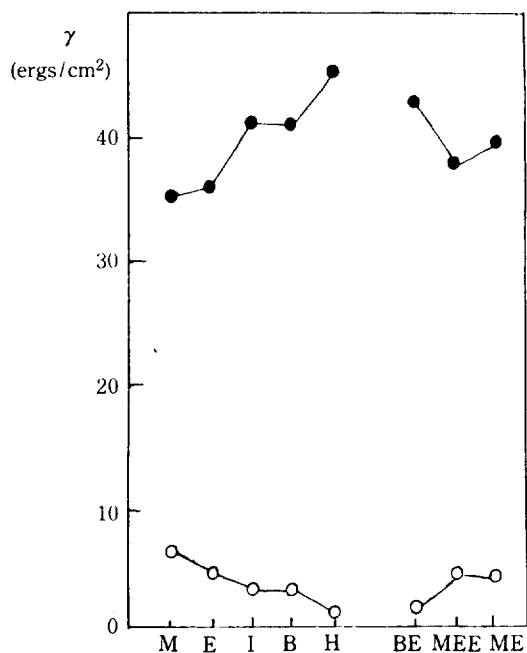


Figure 1. Surface free energy measured by contact angle in air. (Hydrophobic medium). ○: polar component of surface free energy. ●: dispersive component of surface free energy.

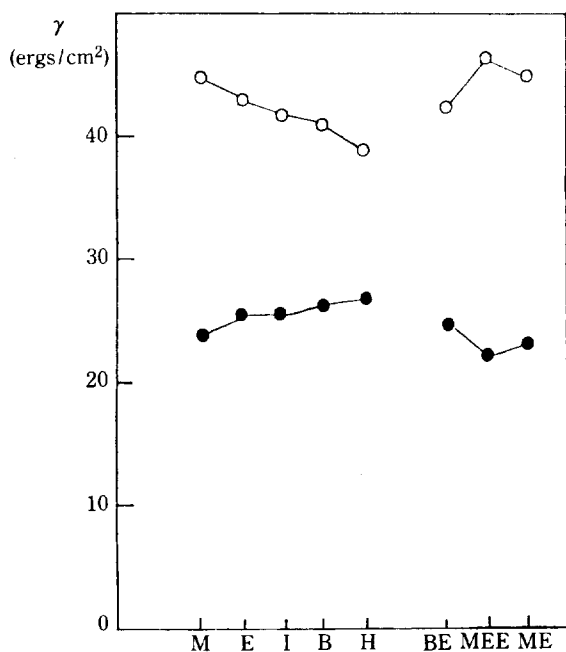


Figure 2. Surface free energy measured by contact angle under water. (Hydrophilic medium). ○: polar component of surface free energy. ●: dispersive component of surface free energy.

copolymers of HEMA and RMA have been prepared as model surface systems for studying the environmental dependence of surface and interfacial energetic components and semiempirical prediction of biocompatibility in terms of interface energetic criterion.

A series of chemically related surfaces, increasing the pendent alkyl group of the copolymer in a systematic fashion, can be ideal for such a model. The rationale behind

the HEMA/RMA copolymer series is that gradually modifying surface properties by changing the alkyl group of alkyl methacrylate comonomer from methyl (M) to hexyl (H) along with branched alkyl (I), ether-linkaged alkyl (ME, MEE) and aromatic ring (BE) should exhibit the surface and interfacial energetic components variation. The chemical formulations and related informations of copolymers are summarized in Tables 1 and 2. Indeed these chemically modified comonomer variations have been consistently reflected in physical properties such as water contents and gradual changes in measured contact angles for each probe liquid and its relation to surface and interface energetics. Probably, the expected changes of other surface properties (e.g., morphology, surface composition etc.) can be observed by other instrumental means such as SEM, ESCA, ATR-IR and so forth.²²⁻²³

From Table 2, the water contents in the model polymer systems seems to decrease with increasing the size of the alkyl group of the comonomer due to the increased hydrophobic interaction.

Environmental Dependence. As shown in Figures 1 and 2, it is found clearly that the copolymers in air dominantly have much larger dispersion component (γ^d) than polar term (γ^p) while the same copolymers under water have larger polar component than dispersion one. Although the surrounding water has a role as composite for copolymers under water, it is reasonable that these phenomena are qualitatively interpretable by environmentally induced surface molecular restructuring, that is, upon changing the environment of surfaces from hydrophobic (or nonpolar) medium to hydrophilic (polar) one. The environment impact produces driving forces which can initiate the time dependent reorientation or rearrangement (i.e., relaxation process) of the buried polar group (e.g., OH, CO₂, -O-) in copolymers from its bulk to its surface for minimizing the substrates-environment interfacial free energy and attaining the optimum thermodynamic condition. While, upon changing the environment of polymeric surfaces from hydrophilic (polar) medium to hydrophobic (nonpolar) one, the buried nonpolar groups (e.g., -CH₃, -R, -Ar, polymer backbone etc.) in the copolymers are also undergone kinetically dependent rearrangement from its bulk to its surface by the environmentally initiated driving of minimizing the interfacial free energy in a similar mechanistic view. Since polymer chain reorientation occurred due to the presence of an orientating environment and those microscopic molecular phenomena are reflected in macroscopic physical properties, the surface and interfacial energetic components of low energy surfaces such as polymers are highly dependent upon its environmental fluids (i.e., relaxation of surface and interface free energy of low energy surface). Probably, these restructuring or reorientation phenomena will be also detected by other approaches such as contact angle hysteresis or ESCA study.

Consequently, the surface and interfacial energetic components of polymers as a representative low energy surface can not be considered as independent intrinsic physical quantities and be named as the environment-dependent quantities. Holly and Refojo²⁴ also asserted that the polymer chains at the gel surface appear to have sufficient mobility to reorient and the type of interface resulting from these conformational changes depends on the nature of the adjacent

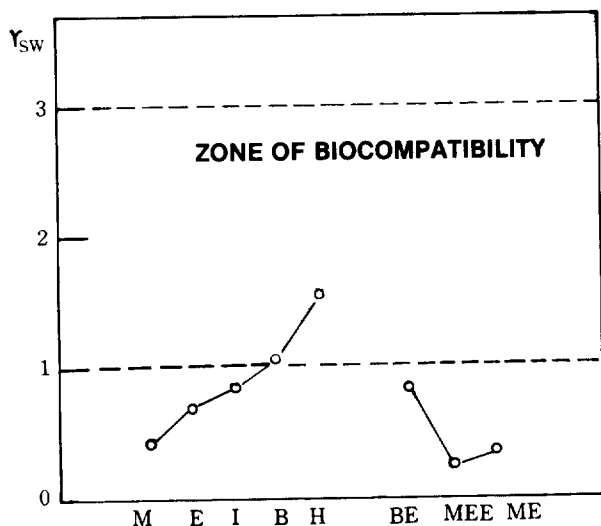


Figure 3. Polymer-water interfacial free energy.

phase

Consideration of Biocompatibility. In the recent article,²⁵ it has been suggested that a low interfacial free energy between blood and foreign materials is required to obtain good blood compatibility of the latter. Also, it was proposed that a range of desirable interfacial free energies is $\gamma_{SW} = 1-3 \text{ erg/cm}^2$, based on the twin requirements of minimizing the thermodynamic driving force for the adsorption of blood components and maintaining a mechanically stable blood-biomaterial interface.

From the comparison between our estimated polymer-water interfacial free energy in Figure 3 and the interfacial energetic criterion of biocompatibility, we also found that HEMA/BMA and HEMA/HMA copolymers are within the range of biocompatibility.

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