ISSN 0027-1314, Moscow University Chemistry Bulletin, 2008, Vol. 63, No. 5, pp. 265–268. © Allerton Press, Inc., 2008.
Original Russian Text © Yu.G. Bogdanova, V.D. Dolzhikova, G.P. Belov, O.N. Golodkov, A.E. Chalykh, 2008, published in Vestnik Moskovskogo Universiteta. Khimiya, 2008, No. 5, pp. 319–322.

Prediction of Biocompatibility of Olefin–Carbon Monoxide Alternating Copolymers from Their Surface Energy Parameters

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Received November 12, 2007

Abstract—Contact angle measurements were used to determine the surface energy characteristics at polymer–air and polymer–water interfaces for olefin–carbon monoxide alternating copolymers (polyolefinketones), a new class of polymers: propylene–CO (PCO; a binary copolymer) and propylene–CO–ethylene–CO (PECO; a ternary copolymer). Introduction of ethylene–CO comonomers into PCO increases its surface energy. Comparison of copolymer interfacial energies at copolymer–water interfaces with criterion values for blood-compatible materials showed that PECO can be recommended for medical and biological testing for blood compatibility.

DOI: 10.3103/S0027131408050064

It is well known that biomedical materials should be biologically inert and nontoxic and that their mechanical and adhesion characteristics should be stable in exploitation. The combination of these factors is conventionally referred to by the term *biocompatibility* of a polymer material, which means the possibility of its existence in a living organism or in contact with living systems without negative consequences [1–4].

In this study, we consider the biocompatibility of materials in the aspect of their blood compatibility, meaning the low adhesion of blood proteins to the surface in long-term contact with blood. This factor is of paramount importance to choose materials for implants: for example, adsorption of fibrinogen on their surfaces enhances thrombosis [5]. Before beginning comprehensive medical and biological studies of the biocompatibility of a material, one can ascertain its potential medical utility using simple, rapid physicochemical tests, for example, contact angle measurements [3, 6, 7].

Studies pertaining to development of blood compatibility criteria demonstrated that the behavior of a material in a biological medium is dictated by the interfacial energy of the polymer at the water interface [3]. In the Ruckenstein concept for blood-compatible materials, the interfacial energy at the polymer–water interface ($\sigma_{S(W)/W}$) should be close to the cell/blood plasma interfacial energy: for blood-compatible materials, the criterion value $\sigma_{S(W)/W}$ = 1–3 mJ/m^2 [3]. For polymer materials used in medical practice, however, $\sigma_{S(W)/W}$ has a wider value corridor. For silicon elastomer, for example, $\sigma_{S(W)/W}$ = 5.8 mJ/m^2 [6]. However, $\sigma_{S(W)/W}$ < 1 mJ/m^2 does not exclude the utility of the polymer as a blood-compatible material with the provision that its mechanical strength is not noticeably deteriorated in contact with a biological medium [7].

The interfacial energy of a polymer at the water interface can be derived from contact angle measurements in the advancing, receding, and preferred wetting modes using equations of the molecular theory of wetting [8]. Thus, contact angle measurements open a possibility of predicting blood compatibility for polymer materials. Biocompatible polymers are exemplified by diphilic block-copolymers of poly(propylene oxide), poly(ethylene oxide), poly(vinylpyrrolidone), poly(hydroxybutyrate), poly(caprolactone), polyurethanes, and others [9–13].

Polyolefinketones, a new class of strictly alternating copolymers of carbon monoxide CO and olefins [14], are potential biocompatible materials [14]. Studies of the surface properties of polyolefinketones and determinations of their energy characteristics at various interfaces are of paramount importance for optimizing polymer materials design for medicine and bioengineering.

Whether polyolefinketones are blood-compatible is still an open question. Here, we determine the interfacial energy in polyolefinketone–water system, $\sigma_{S(W)/W}$, and ascertain the possibility of using polyolefinketones as blood-compatible materials.

We studied two new copolymers (Fig. 1): propylene–CO (PCO; a binary copolymer) and propylene–

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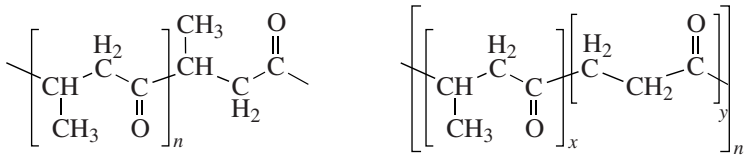

PCO PECO

Fig. 1. Structural formulas for monomer units of propylene–CO (PCO) and propylene–CO–ethylene–CO (PECO) copolymers.

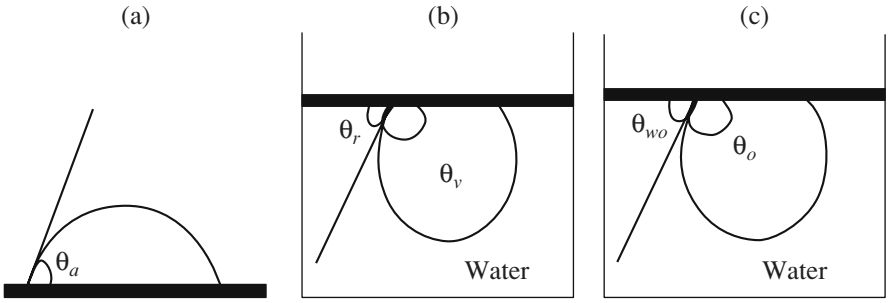

Fig. 2. Scheme of contact angle measurements: (a) advancing, (b) receding, and (3) preferred contact angles. Contact angles are designated in accordance with [3].

CO–ethylene–CO (PECO; a ternary copolymer) [14]. The weight-average molecular mass M_w was 4.8×10^4 for PCO and 25.5×10^4 for PECO.

Polymer films were applied to aluminum plates 1 × 1.5 cm from 3% PCO solution in methylene chloride and 3% PECO solution in chloroform. Then, the films were dried for 24 h at room temperature.

Contact angles were measured on an MG horizontal microscope equipped with a goniometer attachment in the advancing mode (θ_a) with drops 0.01–0.02 mL in volume applied to a solid surface (Fig. 2a), in the receding mode (θ_r) with an air bubble brought to the surface of a sample in a liquid (Fig. 2b), and in the preferred wetting mode (θ_{WO}) with an octane drop brought to the surface of the sample in water (Fig. 2c). Contact angles were measured 3 min after the drop was brought into contact with the surface (after the bubble was anchored to the surface). The contact angle measurement accuracy was ±1°. For each sample, contact angles were measured for six to nine drops. The root mean square deviation ranged from ±1° to ±2°. All measurements were carried at 20°C.

Table 1. Surface tension σ_L and dispersive (σ_L^d) and polar (σ_L^p) components for test liquids

Liquid	σ_L^p, mJ/m^2	σ_L^d, mJ/m^2	σ_L, mJ/m^2
Water (W)	50.8	21.8	72.6
Ethylene glycol (EG)	19.0	29.3	48.3
Octane (O) [6]	0	21.8	21.8

To determine the specific free surface energy of polymer films, we used test liquids whose surface tension is known (Table 1) [6, 15]. The surface energy of polymers σ_S and its polar σ_S^p and dispersive σ_S^d components were derived from measurements of water and ethylene glycol contact angles by solving the following simultaneous equations [16]:

$$(1 + \cos\theta_{L1})\sigma_{L1} = 2(\sigma_{L1}^d\sigma_S^d)^{1/2} + 2(\sigma_{L1}^p\sigma_S^p)^{1/2}, \quad (1)$$

$$(1 + \cos\theta_{L2})\sigma_{L2} = 2(\sigma_{L2}^d\sigma_S^d)^{1/2} + 2(\sigma_{L2}^p\sigma_S^p)^{1/2}. \quad (2)$$

Here, θ_{L1} and θ_{L2} are the advancing contact angles for the test liquids; and σ_{L1}^p, σ_{L2}^p, σ_{L1}^d, and σ_{L2}^d are the polar and dispersive components of surface tension for the test liquids; $\sigma_S = \sigma_S^p + \sigma_S^d$. Water and ethylene glycol surface tensions were determined by the Wilhelmy technique ($\Delta\sigma_L = \pm 0.5$ mJ/m^2). The polar and dispersive components of σ_L were derived from the advancing contact angles of liquids on Teflon-4 (σ_S = 18 mJ/m^2) using the Girifalco–Good–Fowkes–Young relationship [17]. The uncertainty in σ_S is $\Delta\sigma_S = \pm(0.5–0.7)$ mJ/m^2.

The interfacial energy at the polymer–water interface σ_{SW} was calculated from

$$\sigma_{SW} = \sigma_S + \sigma_W - 2(\sigma_S^d\sigma_W^d)^{1/2} - 2(\sigma_S^p\sigma_W^p)^{1/2}, \quad (3)$$

where σ_W, σ_W^d, and σ_W^p are the water surface tension and its dispersive and polar components, respectively [8]. The σ_W, σ_W^d, and σ_W^p (Table 1) and σ_S, σ_S^d, and σ_S^p (Table 2) used in these calculations were derived from the experimentally measured contact angles of test liquids using Eqs. (1) and (2), respectively.

The interfacial energy for water-equilibrated polymers at the water interface, $\sigma_{S(W)/W}$, was determined by the Ruckenstein method [3], as follows: polymer films were exposed to water for 24 h; then, contact angles were measured for octane drops (θ_O) and air bubbles (θ_V) brought to the surface of samples in water. These measurements were used (according to [3]) to calculate equilibrium values of the polar $\sigma_{S(W)}^p$ and dispersive $\sigma_{S(W)}^d$ components of the surface energy of water-equilibrated polymers. $\sigma_{S(W)/W}$ was calculated from

$$\sigma_{S(W)/W} = \{(\sigma_{S(W)}^p)^{1/2} - (\sigma_W^p)^{1/2}\}^2 + \{(\sigma_{S(W)}^d)^{1/2} - (\sigma_W^d)^{1/2}\}^2. \quad (4)$$

$\sigma_{S(W)}^p$ and $\sigma_{S(W)}^d$ were, respectively, calculated from

$$\sigma_{S(W)}^p = (-\sigma_{OW}\cos\theta_O + \sigma_W - \sigma_O)^2/4\sigma_W^p, \quad (5)$$

where σ_{OW} is the interfacial tension at the octane–water interface and σ_W and σ_O are the water and octane surface tensions, respectively; and from

$$\sigma_{S(W)}^d = (\sigma_{OW}\cos\theta_O - \sigma_W\cos\theta_V + \sigma_O)^2/4\sigma_O. \quad (6)$$

The data compiled in Table 2 demonstrate that both polymers are wetted by water ($\theta < 90°$); the PECO surface is more hydrophilic because of the existence of fragments containing (ethylene–CO–)$_n$ blocks in the backbone of this copolymer.

The surface energies $\sigma_{S(W)/W}$ of PECO at the water interface determined by the Ruckenstein method (Table 3) coincide, within the determination errors, with σ_{SW} calculated from Eq. (3). For PCO, σ_{SW} calculated from Eq. (3) is higher than $\sigma_{S(W)/W}$ determined using the Ruckenstein method. This can be interpreted as follows: as a result of equilibration of a polymer with water, surface carbonyl groups are reoriented, which is hindered for PCO because of the synchronous reorientation of its methyl and carbonyl groups (Fig. 3).

Table 2. Advancing contact angles for test liquids (θ_W, θ_{EG}, and θ_{GL}) on polymers and specific free surface energies of polymers

Polymer	PCO	PECO
θ_W, deg	81	62
θ_{EG}, deg	63	50
θ_{GL}, deg	77	64
σ_S^p, mJ/m^2	11.5	30.4
σ_S^d, mJ/m^2	15.7	8.4
σ_S, mJ/m^2	27.2	38.8

Table 3. Energy characteristics of water-equilibrated polymers at the water interface

Polymer	PCO	PECO
θ_V, deg	43	43
θ_O, deg	89	63
$\sigma_{S(W)}^p$, mJ/m^2	22.8	26.8
$\sigma_{S(W)}^d$, mJ/m^2	43.8	31.8
$\sigma_{S(W)/W}$, mJ/m^2 as in [3]	8.9	3.6
$\sigma_{S(W)/W}$, mJ/m^2 calcd. from (3)	14.5	3.9

Calculations from Eqs. (3) and (4) show that PECO can be recommended for medical and biological testing for blood compatibility: its $\sigma_{S(W)/W}$ is close to the criterion value.

To summarize, the surface energy characteristics of polyolefinketones determined in this work signify that a polymer containing considerable proportion of hydrophilic groups in the backbone is a potential blood-compatible material. The incorporation of ethylene–CO fragments into the backbone of PCO copolymers not only offers a means for controlling the mechanical properties of polyolefinketones [18], but also opens a way to synthesizing blood-compatible polymer materials based on them.

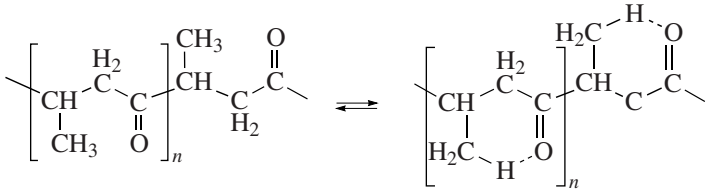

Fig. 3. Rearrangement of the PCO surface layer upon equilibration with water.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project no. 07-03-00363a).

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