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PREPARATION AND SURFACE PROPERTIES OF ACRYLIC COPOLYMERS CONTAINING FLUORINATED MONOMERS*

Tai-jiang Gui[a,c], Hao Wei[b], Ying Zhao[b], Xiu-lin Wang[a], Du-jin Wang[b**] and Duan-fu Xu[b]

[a]*Chemistry and Chemical Engineering College, Ocean University of China, Qingdao 266003, China*

[b]*State Key Laboratory of Polymer Physics and Chemistry, Joint Laboratory of Polymer Science and Materials, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China*

[c]*Marine Research Institute of Chemical Industry, Qingdao 266071, China*

Abstract A series of copolymers comprising butylmethacrylate, styrene, butylacrylate, hydroxypropyl acrylate and perfluoroalkyl methacrylate were synthesized by the free radical polymerization using BPO as an initiator. The surface property of the copolymer films was subsequently characterized. The contact angle measurements and energy dispersive analysis of X-ray (EDAX) show that the length and content of perfluoroalkyl side chains in the copolymers are crucial for the preparation of the film with low surface energy. At a given content of fluorinated monomers in the copolymers, the longer the perfluoroalkyl side chain, the larger the water contact angle of the copolymer films will be. On the other hand, the higher the content of fluorinated monomers, the lower the surface energy is. The water contact angle increases with the increase of the fluorinated monomer content and reaches a plateau at 3 wt% of fluorinated monomer content.

Keywords: Acrylate copolymers; Fluorinated monomers; Surface property; Contact angle; X-ray energy dispersive analysis.

INTRODUCTION

Antifouling coatings are used on the ship hulls to prevent the attachment of marine organisms. Fouling decreases the speed, maneuverability and range of ship, and raises propulsive fuel consumption by as much as 30 wt%. When a coating fails, the ship must be hauled out from the water and mechanically cleaned to remove fouling. Although poisonous chemicals were used to keep marine creatures off the hulls, the environmental authorities in most of the countries are now pressuring the marine industry to discontinue the use of toxic coatings, and the developed nations have already banned the use of poisonous coatings on most ships[1, 2].

Brady's study[3] showed that the polymer coatings with low surface energy are useful in preventing the adherence of marine organisms. Fluorocarbon polymers have been widely studied as materials for low surface energy coatings and for nonwetting biological applications[4–7]. One of the most popular and successful strategies for lowering the surface tension of films is incorporation of fluorine into the polymer molecule. Some reports[8–14] indicated that the surface energy of copolymer films can be reduced by grafting perfluoroalkyl groups onto polymer main chains.

However, previous studies have focused mainly on polymers with relatively large weight fractions of fluorinated components[15, 16]. The current work will demonstrate that large weight fractions of fluorinated materials are necessary to achieve low surface tension, and the side chain length of perfluoroalkyl methacrylate monomer also plays an important role for reducing surface tension. A series of acrylate copolymers were synthesized by free radical polymerization, the structures of which are shown in Fig. 1. Three fluorinated

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** Corresponding author: Du-jin Wang (王笃金), E-mail: djwang@iccas.ac.cn

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monomers were chosen for the comparative investigation of the surface energy of the copolymer films. The surface morphology and elemental compositions of the solution-casting films on Teflon surface were examined by using SEM, contact angle measurements and EDAX.

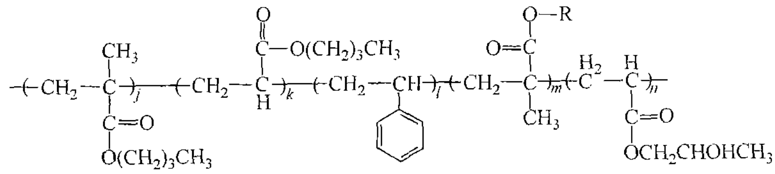

Fig. 1 Schematic illustration of the copolymers with different lengths of perfluoroalkyl side chains
R: $-CH_2CF_3$ (**1**); $-CH_2C_2F_5$ (**2**); $-(CH_2)_2(CF_2)_8F$ (**3**)

EXPERIMENTAL

Preparation of Copolymers

2,2,2-trifluoroethyl methacrylate ($H_2C{=}C(CH_3)CO_2CH_2CF_3$ (**1**), 99 wt%) was obtained from ACROS. 2,2,3,3,3-Pentafluoro-*n*-propyl methacrylate ($H_2C{=}C(CH_3)CO_2CH_2C_2F_5$ (**2**), 99 wt%) and 1H,1H,2H,2H-perfluorodecyl methacrylate ($H_2C = C(CH_3)CO_2(CH_2)_2C_8F_{16}$ (**3**), 99 wt%) were purchased from Alfa Aesar. Styrene (S, 99.6 wt%), butyl acrylate (BA, 99.5 wt%), butyl methacrylate (BMA, 99.2 wt%) and hydroxypropyl acrylate (HPA, 99.5 wt%) were all obtained from Beijing Chemical Reagent Co. Butanone was used as solvent. Benzoyl peroxide (BPO) was used as initiator. The isocyanate cross-linking agent (99.8 wt%) was obtained from Bayer Co. and is composed of isocyanurate trimer of hexamethylene diisocyanate.

The copolymers with different lengths of perfluoroalkyl side chains were synthesized by charging a vessel with the solution consisting of butanone, perfluoroalkyl methacrylate monomer, BA, HPA, S and BMA, and blanketing with nitrogen. In the reaction, the weights of BA, HPA, S and BMA were fixed at 20 g, 10 g, 30 g, and 40 g, respectively. The content of perfluoroalkyl side chain in copolymers was controlled by changing the feed weight of perfluoroalkyl methacrylate monomer (Table 1). When the solution was heated to reflux, another solution containing butanone and BPO was added over a period of 4 h to ensure complete conversion of monomers. The ratios of different elements in the copolymers are shown in Table 1. In all the addition of isocyanate, the $-OH$ (from hydroxypropyl acrylate)/NCO ratio was maintained at 1:1.

Table 1. EDAX data and theoretical values for various copolymers

Copolymers	Comonomer content (wt%)	Weight (%)					
		Experimental			Theoretical		
		F	C	O	F	C	O
Control	0	0	91.96	8.04	0	75.0	25.0
1c	3	1.28	85.01	13.71	1.23	74.49	24.28
2c	3	2.16	84.33	13.51	1.46	74.50	23.95
3a	1	0.75	89.42	9.83	0.683	74.38	24.937
3b	2.5	2.32	80.65	17.03	1.74	73.64	24.62
3c	3	2.75	82.52	14.73	2.04	73.43	24.52
3d	4	3.21	84.49	12.30	2.697	72.97	24.32
3e	7	3.36	81.64	15.00	4.71	71.55	23.73

Characterization

Contact angle measurements were performed using a VCA-2500 contact angle goniometer from AST Products. The device used a CCD camera, frame grabber and software to capture the contact angle image. Typically, the measurements were collected for four drops across the surface. The standard deviations are shown in the contact angle figures. Contact angles were determined by expanding the droplet until its base was contacted and an equilibrium angle was seen.

EDAX and scanning electron microscope (SEM) measurements were performed on a Hitachi S-4300 scanning electron microscope with a Kevex Quantum 3600-0388 energy-dispersive X-ray analyzer. The accelerating potential of the microscope was fixed to 15 kV.

RESULTS AND DISCUSSION

The conditions used to make the perfluoroalkyl methacrylate-containing acrylic polymers are typical. The standard polymer system was prepared from the free radical polymerization (using BPO as initiator) of butyl methacrylate, styrene, butyl acrylate, hydroxypropyl acrylate and perfluoroalkyl methacrylate with different lengths of side chain in methyl amyl ketone solvent using semibatch, monomer-starved conditions. The pure copolymer systems will have a low T_g, so crosslinking is necessary to provide the desired mechanical properties. The cross-linker employed in the current study is the isocyanurate trimer of hexamethylene diisocyanate. Synthetically, the parameters varied including the amount and kinds of fluorinated methacrylate monomer.

Contact Angle Measurements

Our works will focus on three types of fluorinated methacylate monomer with different lengths of fluorinated side chain, CH_2CF_3 (**1**), $CH_2C_2F_5$ (**2**) and $(CH_2)_2C_8F_{16}$ (**3**), respectively. The content variation of the fluorinated methacrylate monomer is also considered for all the copolymers. Figure 2 shows the water contact angles on the surfaces of copolymers. Obviously, the water contact angles greatly depend on the type and amount of fluorinated methacrylate monomers. The data for varying the amounts of fluorinated methacrylate monomer **1** in copolymer (0.5–7 wt%) do not show any obvious advantage upon increasing the water contact angles, and the biggest water contact angle is about 90°. The increase of the alkyl side chain length of the fluorinated side chain greatly affects the water contact angle. It is obvious that almost at all the same weight fraction of fluorinated monomers, copolymer **3** shows the largest water contact angles. At the given weight percent of the fluorinated monomers 3 wt% in the copolymer, the water contact angles for copolymers **2** and **3** are 97° and 115°, respectively.

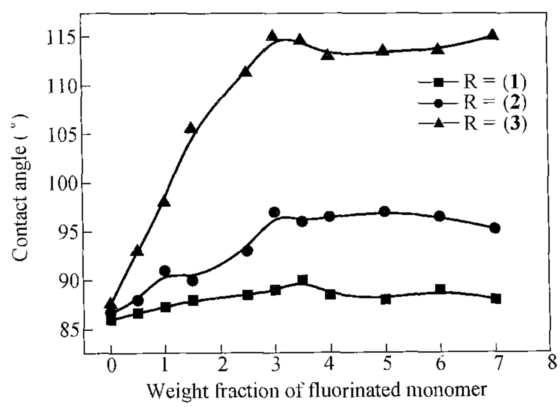

Fig. 2 Water contact angles on the copolymer films with different contents and lengths of perfluoroalkyl methacrylate-modified side chains

On the other hand, the amount of fluorinated methacrylate monomers shows great effects on the water contact angle. Take copolymer **3** for an example, as the comonomer content is below 3 wt%, the water contact angle increases with increasing the comonomer content, and the maximum angle is 115°, close to the theoretical maximum value for $-CF_3$ dominated surfaces (*ca.* 125°)[17, 18]. Over the 3 wt% value in copolymer **3**, the further increase of the fluorinated comonomer content has no obvious benefit to the higher water contact angle. It is easily observed that the water contact angle is still 115° as the fluorinated comonomer content reaches as high as 7 wt%. Similar trend can be found for the other two copolymers containing fluorinated comonomers (Fig. 2).

The Composition and Morphologies of Films

EDAX analysis of the copolymer film surface containing the fluorinated monomers clearly demonstrates that the surface is enriched in fluorine well above theoretical levels (Table 1). A comparison of the experimental EDAX composition data of the copolymers with the theoretical values demonstrates that the surface is dominated by the fluorinated side chains. This finding is in good agreement with the water contact angle data of polymer films, *i.e.*, the surface of which is mainly occupied by the fluorinated moieties.

Shown in Fig. 3 are the SEM images of the copolymer films surface containing various weight percent of fluorinated methacrylate monomer (**3**). When the amount of fluorinated monomer is zero, the surface is very smooth (Fig. 3a), indicating that there is no self-assembled structure of the copolymers on the Teflon surface. The addition of fluorinated monomers leads to the formation of a rougher surface. It is clear that the protuberance appears and becomes bigger with the increase of fluorinated monomers below 2.5%. Further increasing the content leads to the reduction of protuberance, which can be easily observed by comparing Figs. 3(c) and 3(d). These crimple phenomena are attributed to the aggregation of fluorine on the surface, resulting in different surface tensions at different regions.

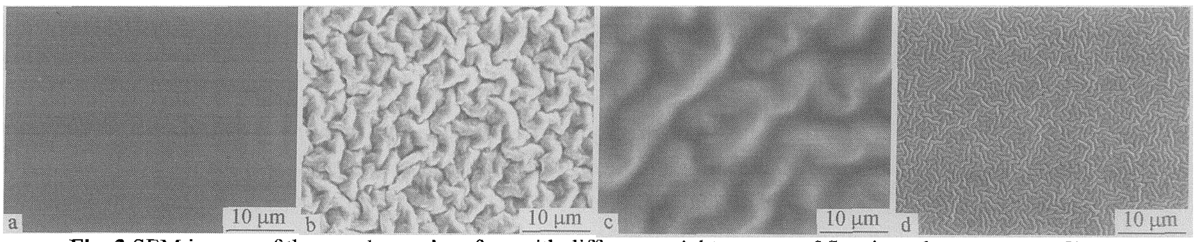

Fig. 3 SEM images of the copolymers' surface with different weight percent of fluorinated comonomer (**3**)
(a) 0; (b) 1%; (c) 2.5%; (d) 3%

A conclusion can be drawn that two factors, the length and content of perfluoroalkyl side chains in the copolymers, are crucial in the preparation of copolymer films with low surface tension, and the water contact angle attains its maximum volume at the weight content of 3% for all the three (perfluoroalky)ethyl methacrylate copolymers studied.

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