Photocurable Fluorinated Methacrylates: Synthesis and Polymerization

Sang-Yeon Shim, Eei Seok Kim*

Summary: A series of hydroxy fluoroalkyl methacrylates were synthesized in 50% yields by the esterification reaction of the methacryloyl chloride with fluoroalkyl diol. These fluorinated methacrylates undergo rapid photopolymerization using Igacure651 as a photoinitiator. Hydrogels were prepared from various molar ratios of 2-hydroxyethylmethacrylate (HEMA), ethylene glycol dimethacrylate and fluorine containing monomers with a photoinitiator. Analyzing the water contents and contact angles of the hydrogels, we found that the content of fluorinate monomers increased, water contents decreased and contact angles increased.

Keywords: HEMA; hydrogels; hydroxyfluoroalkyl methacrylates; photoinitiator; photopolymerization

Introduction

Hydrogels are cross-linked polymers that absorb many times their weight in water that exhibit good compatibility with the human body without stimulating the tissue or mucous membranes. They are composed of hydrophilic polymers and rendered insoluble due to the presence of chemical cross-links. These cross-links provide the network structure. Therefore they have attracted attention as biomedical materials for applications such as artificial tissues, drug delivery system, and soft contact lenses.[1–3]

Protein deposition on biomaterials is an important problem which is especially serious in hydrogels. Therefore, there is the need for deposit-resistant materials. Of special interest are polymers obtained from fluorinated monomers(F-monomers), which typically possess high thermal stability, excellent chemical resistance, low refractive index, high oxygen permeability and resistance to protein deposition.[4,5] For this reason, they are finding various uses in high performance coatings and films.

Photoinitiated polymerization is one of the most effective curing methods in thin film applications such as inks, coatings, and adhesives.[6,7] This technique is ecologically as well as industrially attractive because of the rapid cured speed, the low energies which are required, and the free of polluting solvents. Most of the UV-curable resins used are made of acrylic type monomers, due to their high reactivity, low cost, and excellent mechanical and physical properties of cured films produced from these monomers. In this article, we prepared hydroxy fluoroalkyl methacrylates and determine the relative order of reactivity in photopolymerization. We also applied these hydroxy fluorinated monomers to the hydrogel formulations and then evaluated physical properties such as water contents and contact angels.

Experimental Part

Materials

All reagents were used as purchased from the Aldrich Chemical Co. without addi-

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Dept. of Environmental & Appl. Chem. Eng., Kangnung National University, 120 Gangneungdaehakro, Gangneung, Korea
Fax: (+82) 33 641 2410;
E-mail: syshim@kangnung.ac.kr

tional purification.; Methacryloyl chloride, 2,2,3,3,4,4,5,5- octafluoro-1,6-hexanediol(HO), 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,-hexadecafluoro-1,10-decanediol(HH), 2-hydroxyethyl methacrylate(HEMA), ethylene glycol dimethacrylate(EGDM), triethyl amine, anhydrous sodium sulfate. Diethyl ether was freshly distilled over calcium hydride. Irgacure651 and 2,2-dimethoxy-2-phenylacetophenone(DMPA) were used as received.

Instrumentation

^{1}H-NMR data were recorded with a Jeol Lamda 300 spectrometer using $CDCl_3$ as a solvent. Routine infrared spectra were obtained using a Jasco Corp. Model 460 Fourier transform infrared spectrometer. Elemental analyses were performed by CE instruments, EA1110.

Preparation of 6-hydroxy-2,2,3,3,4,4,5,5-octafluorohexane methacrylate[HOM]

Into a 100 mL round-bottom flask fitted with a magnetic stirrer, a reflux condenser, and a nitrogen inlet were placed HO (2 g, 7.63 mmol) and triethyl amine (2.32 g, 22.89 mmol) with 50 mL diethyl ether. To this stirring mixture methacryloyl chloride (0.87 g, 8.39 mmol) was added dropwise in an ice bath since the reaction is slightly exothermic. After 1 hr reaction, the reaction mixture was poured onto 30 mL distilled water and extract with 3x30 mL diethyl ether. The organic layer was separated, dried with sodium sulfate, filtered and the excess of solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography (silica gel, 99/1 methylene chloride: methanol) to give 0.76 g pure product (yield: 50.9%).

^{1}H-NMR($CDCl_3$) δ 6.5-5.5(d, 2H, CH_2=), 4.7(t, 2H, –CH_2O–), 4.2(m, 2H, –CH_2OH), 2.0(s, 3H, CH_3)

FT-IR(NaCl) $\nu = 3450$(OH stretching), 1740(–O–C=O stretching), 1650(C=C stretching) cm^{-1}

Elemental analysis $C_{10}H_{10}F_8O_3$ Calcd C: 36.38% H: 3.03% Found C: 37.69% H: 2.91%

Preparation of 6-hydroxy-2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,-hexadecafluorodecane methacrylate[HHM]

Into a 100 mL round-bottom flask fitted with a magnetic stirrer, a reflux condenser, and a nitrogen inlet were placed HH (2 g, 4.33 mmol) and triethyl amine (21.31 g, 13 mmol) with 50 mL diethyl ether. To this stirring mixture methacryloyl chloride (0.5 g, 4.76 mmol) was added dropwise in an ice bath since the reaction is slightly exothermic. After 1 hr reaction, the reaction mixture was poured onto 30 mL distilled water and extract with 3 × 30 mL diethyl ether. The organic layer was separated, dried with sodium sulfate, filtered and the excess of solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography (silica gel, 99/1 methylene chloride: methanol) to give 1.16 g pure product (yield: 50.6%).

^{1}H-NMR($CDCl_3$) δ 6.5-5.5(d, 2H, CH_2=), 4.7(t, 2H, –CH_2O–), 4.2(m, 2H, –CH_2OH), 2.0(s, 3H, CH_3)

FT-IR(NaCl) $\nu = 3450$(OH stretching), 1740(–O–C=O stretching), 1650(C=C stretching) cm^{-1}

Elemental analysis $C_{14}H_{10}F_{16}O_3$ Calcd C: 31.71% H: 1.90% Found C: 32.95% H: 1.89%

The Photopolymerization and Fourier Transform Real-Time Infrared(FT-RTIR) Measurement

Photoinitiated radical polymerization was studied by real-time infrared spectroscopy using the method described by Decker.[8]

Samples were prepared by placing liquid monomers with 0.5–1 mol% Irgacure651 between two 14 μm polyethylene films, which were then sandwich-like mounted in 5 × 5 cm slide frames. The RTIR measurements were performed on a Jasco Corp. Model 460 Fourier transform infrared spectrometer equipped with a Spectral Energy Co. LPS251SR 200W Hg-Xe lamp. All studies were conducted using a broad band and unfiltered UV light at an intensity of 15 mJ/cm^2 min. Light intensity measurements were made with an International Light Co. Model L290 Radiometer. The progress of polymerization was quantita-

Table 1.
Formulation for hydrogels of the fluorine-containing copolymer.

ID	R (g)	CF4-0.2 (g)	CF4-1 (g)	CF8-0.2 (g)	CF8-1 (g)
HEMA	9.9	9.9	9.8	9.9	9.8
EGDM	0.1	0.1	0.1	0.1	0.1
HOM		0.02	0.1	0.02	0.1
HHM					
DMPA	0.5	0.5	0.5	0.5	0.5

tively determined by monitoring the decrease of the double bond absorption of an 1650–1700 cm^{-1} (acrylic group).

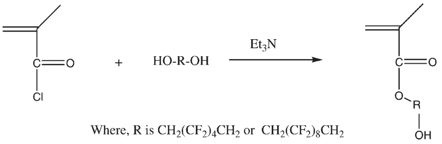
Hydrogels Preparation

Bulk-polymerized hydrogels were prepared by mixing monomers in the stated weight ratio (Table 1) with photoinitiator(DMPA) at 0.5%w/w. The resulting solutions were coated onto the slide glass with a thickness of about 0.2 mm. The curing reaction was performed for 2 min at 400 W Hg-Xe lamp.

Results and Discussion

Synthesis and Photopolymerization

We prepared series of hydroxy fluoroalkyl methacrylates in 50% yields by the esterification reaction of the methacryloyl chloride with fluoroalkyl diol. The reaction scheme is as follows.



Where, R is $CH_2(CF_2)_4CH_2$ or $CH_2(CF_2)_8CH_2$

All the hydroxyfluoroalkyl methacrylates were characterized by ^{1}H-NMR. Typical ^{1}H-NMR spectra are shown in Figure 1. The peaks at 6.5–5.5 ppm are assigned to the protons of methacrylate double bond in the spectrum.

Photoinitiated radical polymerization of F-monomers (HOM, HHM) was performed using photoinitiator, Igacure651 at a concentration 0.5~1 mol% to the monomers. The rate of polymerization and conversions to polymer increased with the concentration of the photoinitiator (Figure 2). In Figure 3, the RTIR curves for the

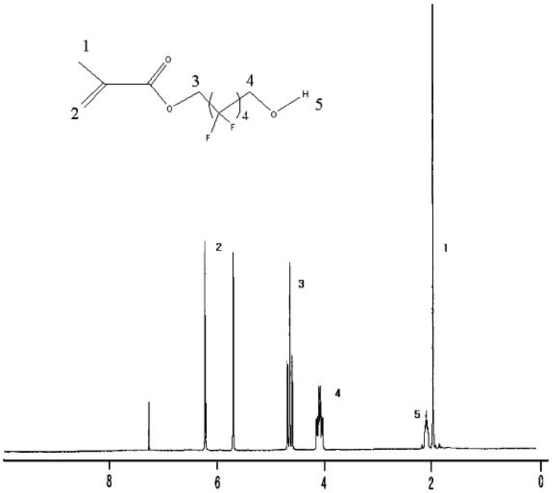


Figure 1.
^{1}H-NMR spectra of HOM.

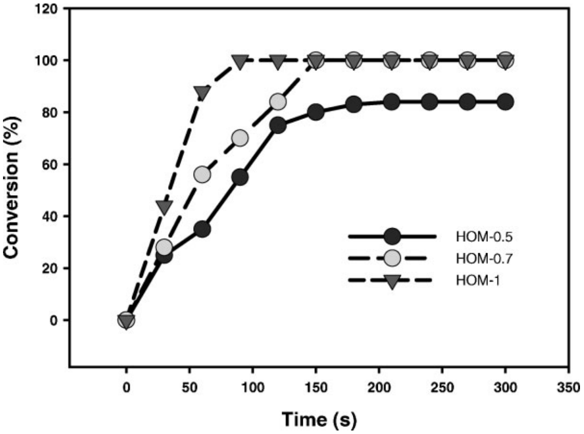


Figure 2.
RTIR curves for the photopolymerization of HOM in the presence of 0.5, 0.7, and 1 mol% Igacure651.

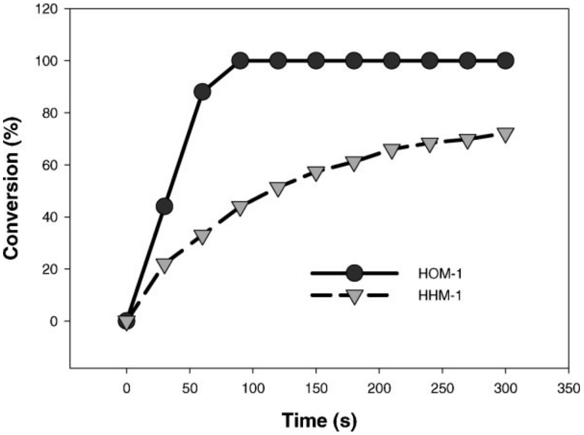


Figure 3.
RTIR curves for the radical polymerization of HOM and HHM in the presence of 1 mol% Igacure651.

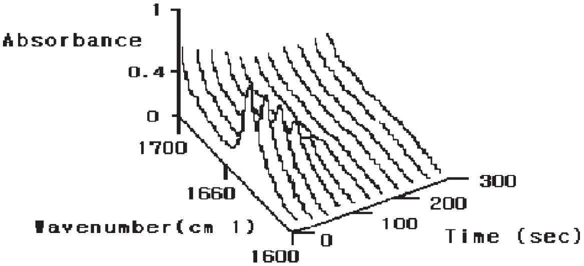


Figure 4.
FTIR study of the radical polymerization of HOM.

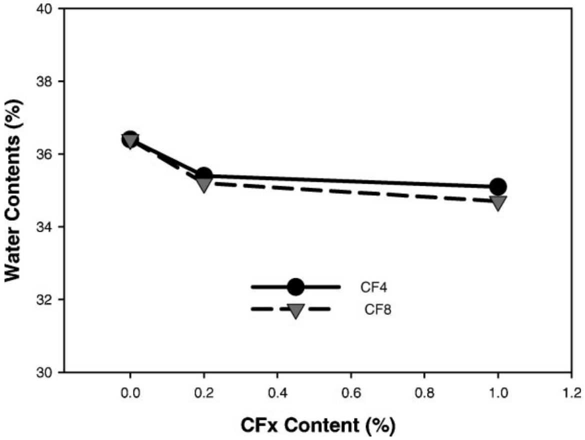


Figure 5.
Water contents as a function of weight% for F-monomers.

polymerization of [HHM] shows lower reactivity than [HOM] probably due to the long fluoroalkyl group in the side chain. Figure 4 depicts a three-dimentional spectral profile of decrease of the methacrylate absorption band (1650 cm^{-1}) of monomer [HOM] in the presence of 0.7 mol% Igacure651. This Figure shows a rapid decrease in the methacrylate band, indicating that this monomer is highly reactive toward photoinitiated radical polymerization.

Preparation of Hydrogels

Hydrogels were prepared with F-monomers varying from about 0.02 to 0.1 wt% by varying the amount of HOM, HHM used in the copolymers. The photopolymerization was carried out by 400 W Hg-Xe lamp for 2 min. All the monomer compositions shown in Table 1 undergo polymerization within 2 min. The monomer designation used is CFx-y, where x is the number of CF_2 group and y is the wt% of F-monomers in the formulation.

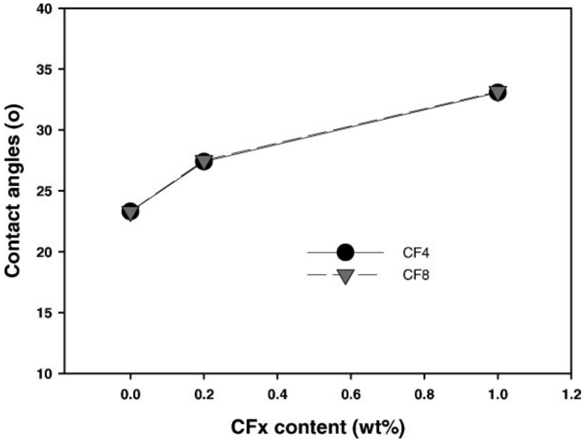


Figure 6.
Contact angles as a function of weight% for F-monomers at 25 °C.

Figure 7.
Water contact angles profiles of cured films R(23°), CF4-0.2(27°), CF4-1 (33°).

Measurements of Physical Properties

We measured water contents and contact angles of hydrogels. Water content in hydrogels is one of the key determinants of biocompatibility characteristic. Water content was determined by the weight comparison of wet and dry film as shown in the following equation.

$$\begin{aligned}&\text{Water content}(\%) = 100\\&\times [\text{weight of wet film}\\&- \text{weight of dry film}]/[\text{weight of wet film}]\end{aligned}$$

As shown in Figure 5, the water content of the hydrogel without F-monomers was about 36.4%. Water contents slightly decreased with the increase of the amount of HOM or HHM in the copolymer.

Another important factor to consider is the wettability on surface. The wettability is characterized by the contact angle. Contact angles can range from 0° (complete wetting) to 180° (non-wetting). The lower the angle is, the better wettable is the surface. Either of hydrogels containing CFx-y show higher contact angles than that of HEMA based hydrogel (R) (Figure 6, 7).

Conclusion

A new series of hydroxyfluoroalkyl methacrylates were prepared in 50% yields by straightforward methods using methacryloyl chloride with fluoroalkyl diol. These monomers exhibit excellent reactivity in radical photopolymerization in the presence of photoinitiators. The rate of polymerization and conversions to polymer increased with the concentration of the photoinitiator. [HHM] shows lower reactivity than [HOM] probably due to the long fluoroalkyl group in the side chain. Physical properties of hydrogels containing these fluorinated monomers such as water contents and contact angles were evaluated. The water contents of the CFx-0.2 and CFx-1 had a little lower values than that of HEMA based hydrogel (R). Contact angles were increased from 23 to 33° with the increase of the content of F-monomers.

Acknowledgements: We thanks the Regional Technology Innovation Program [grant no. RTI05-01-02] of the Ministry of Commerce, Industry and Energy(MOCIE) for financial support.

[1] P. Ulanski, I. Janik, S. Kadlubowski, M. Kozicki, P. Kujawa, M. Pietrzak, P. Stasica, J. M. Rosiak, *Polym. Adv. Technol.* **2002**, *13*, 951.
[2] R. Langer, N. A. Peppas, *AIChE J.* **2003**, *49*(12) 2990.
[3] G. Miquelard-Garnier, C. Creton, D. Hourdet, *Macromol. Symp.* **2007**, *256*, 189.
[4] S.-Y. Shim, D. H. Suh, in: *Photo. Poly., ACS symp. Series* 847, **2003**, Chap 24, p. 277.
[5] A. Matsuda, T. Kaneko, J. Gong, Y. Osada, *Macromolecules* **2000**, *33*, 2535.
[6] J. V. Crivello, U. Bulut, *Macromolecules* **2005**, *38*, 3584.
[7] J. V. Crivello, B. Falk, *Chem. Mater.* **2004**, *16*, 5033.
[8] C. J. Decker, *J. Polym. Sci. Poly. Chem.* **1992**, *30*, 913.