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Surface Modification of Polymethyl Methacrylate by Graft Copolymers

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Summary

Graft copolymers composed of poly(methyl methacrylate) branches and different backbones of poly(fluoroalkyl acrylate(FA)-co-methyl methacrylate(MMA)), poly (hydroxyethyl methacrylate(HEMA)-co-MMA), and poly(FA-co-HEMA) were prepared by macromonomer technique to study their application as a surface modifier for PMMA films. Contact angle of water droplet on PMMA film specimens containing various amounts of these graft copolymers cast on glass slides from THF solution was found to change considerably with the graft copolymer concentration, depending on their backbone component. And there was considerable difference in contact angle between air and glass side of the film surfaces. These results were considered in terms of the surface accumulation of graft copolymers during the solvent evaporation.

Introduction

There has recently been a great deal of interest in studies of the structure and properties of polymer surfaces because of the practical importance of their modification for a particular usage and of understanding their nature(LEE,1977; CLARK et al.,1978). In surface modification technique, to control the surface properties by the surface accumulation of the desired functional segments of tailor made graft copolymers is a most interesting and important for any particular application.

In the previous paper, we have reported on the surface activity of the graft copolymers prepared by radical copolymerization of methy methacrylate macromonomers with fluoroalkyl acrylate in PMMA films and indicated that a small amount of these graft copolymers sufficiently improved the wettability of PMMA film specimens to hydrophobic fluoropolymer like surfaces (YAMASHITA et al.,1981). In this paper, we will report on the wettability variation in the case of graft copolymers containing hydrophilic HEMA units.

Our studies of this kind give an example of the

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application of well-defined graft copolymers which are easily prepared by macromonomer technique.

Experimental

Preparation of graft copolymers

Graft copolymers were prepared by radical copolymerization using MMA macromonomers (ITO et al., 1980). Carboxyl terminated MMA prepolymers at one end were obtained by radical polymerization of MMA monomer with AIBN and TGA(thioglycolic acid) as a chain transfer agent at 60°C. MMA macromonomers having methacrylgroup at one end were obtained by the reaction of the carboxyl group of the prepolymer with GMA(glycidyl methacrylate) (50 mol% excess) in xylene at 140°C with small amounts of hydroquinone and N,N-dimethyllaurylamine. Extent of the reaction of prepolymers with GMA estimated from the titration of unreacted carboxyl group was more than 90%. Table 1 gives the details of the preparation of macromonomers.

The MMA macromonomers thus obtained were copolymerized with HEMA(hydroxyethyl methacrylate), with FA(fluoroalkyl acrylate) $CH_2{=}CHCOOCH_2CH_2C_nF_{2n+1}$ ($\bar{n}=6.0$), and with MMA in the polymerization solvent with AIBN at 60°C in ampules degassed and sealed under vacuum to give the graft copolymers having PMMA branches. HEMA and MMA monomers were commercially available and FA monomer was kindly supplied from Asahi Glass Co., Ltd., Japan. And these monomers were distilled in vacuum over $CuCl_2$. Polymerization solvents were selected so as to obtain homogeneous reaction condition. The graft copolymers were precipitated into methanol and purified by repeated extraction with diethyl ether and methanol to remove unreacted macromonomer and oligomer. Table 2 and 3 give the details of preparation and characterization of graft copolymers, respectively. PMMA having the number average molecular weight of 5.2×10^4 g/mol was prepared by radical polymerization and was used.

TABLE 1

Preparation of Macromonomers[a)]

run	$[S]_o/[M]_o$ ($\times 10^{-2}$)	$[M]_o/[Bz]$	time (hr)	Mn x10^{-3}			Mw/Mn	C_s[b)]	R[c)]
				VPO	tit	GPC			
1	1.66	0.53	2.3	6.0	8.0	2.8	2.8	0.69	93.6
2	2.66	0.51	2.3	4.6	5.5	1.8	2.8	0.63	92.8
3	5.84	0.52	2.0	3.0	2.3	1.9	1.9	0.75	99.6

a) reactions were carried out at 60°C in benzene with 0.5 mol% of AIBN, [S]=[TGA], [M]=[MMA]

b) chain transfer const. calculated by $C_s=\log(1- [M]_o/n[S]_o)/\log(1-)$, ;conversion, n;degree of polymerization c) conversion to macromonomer determined from end group titration

Contact angle measurements on PMMA film specimens containing graft copolymers

PMMA film specimens containing various amounts of the graft copolymers were cast into thin films of about 0.1 mm thickness by pouring dilute solutions of ca. 5 w/v% concentration in THF(tetrahydrofuran) onto clean glass slides and evaporating the solvent gradually at about 30°C. The films thus formed were further dried under vacuum for a few days before use.

Contact angle of water droplet on the specimen was measured at 20°C with CA-A type goniometer of Kyowa Co., Ltd., Japan using twice distilled water. The advancing contact angle were measured by gently placing a droplet on the specimens and adding small increments of water to the droplet until the advancing contact angle reached a reproducible value. The film specimens were carefully peeled from each glass slide just before measuring the contact angle on the glass side of the films.

TABLE 2

Preparation of Graft Copolymers[a)]

Sample	Mn x 10^{-3} b)	feed (wt%)				Solvent(wt%)			yield
Code	of MM	HEMA	FA	MMA	MM[c)]	BF[d)]	EtOH	THF	(%)
GH	6.0	40.0	-	40.0	20.0	-	23.0	77.0	68.5
GHF	4.6	40.0	40.3	-	19.7	24.7	39.2	36.1	63.0
GF	3.0	-	21.0	49.0	30.0	100.0	-	-	64.8

a) reactions were carried out at 60°C with 0.5 mol% of AIBN for 3 days. b) determined with Vapor Pressure Osmometer c) MM; MMA macromonomer d) BF; Benzotrifluoride

TABLE 3

Characterization of Graft Copolymers

Sample	Composition[a)]			no. of	Mn x 10^{-3} b)	type
Code	HEMA	FA	MMA	branches	total	
GH	51.7	-	48.3	1.0[c)]	39.0	G(HEMA/MMA-PMMA)
GHF	47.4	34.7	17.9	1.2	30.0	G(HEMA/FA-PMMA)
GF	-	18.3	81.7	5.0[c)]	50.0	G(MMA/FA-PMMA)

a) calculated from Elementary Analysis and ^{1}H-NMR b) calculated from GPC using the calibration curve for polystyrene c) calculated from feed ratios

Results and Discussion

The results of the wettability variations with the graft copolymer concentration are shown in Fig.1-3, including both air side and glass side of film specimens. It can be seen in Fig. 1 that cosine of contact angle (cosθ) on the air side of PMMA film specimens decreases considerably with the amount of GF (Table 3) which contains 18.3% of FA component and 0.5 wt% of GF is enough to change sufficiently to the hydrophobic surface of fluoropolymers (cosθ=-0.3), whereas on the glass side of the film surfaces, cosθ is almost constant except in the higher concentration region where cosθ is slightly lower. On the other hand, in the case of the GH (Table 3) containing PMMA specimens, as shown in Fig. 2, cosθ on the air side has an almost constant value of about 0.24 which is the value of the pure PMMA films, whereas on the glass side cosθ increases gradualy up to the value of 0.4 with GH graft concentration. Fig. 3 shows the cosθ variations in the case of specimens containing GHF (Table 3), the backbone of which contains both hydrophilic HEMA and hydrophobic FA components. On the air side of the specimens cosθ decreases with GHF concentration as on the same side of GF containing specimens but the hydrophobicity of GHF containing films decreases to a great extent, whereas on the glass side cosθ decreases much more than in the case of GF.

It can be seen from Fig. 1 that the graft copolymer GF shows pronounced surface activity at the air side surface, however at the glass side, the enrichment of GF is strongly suppressed in the whole concentration range. In Fig. 2, graft copolymer GH has no surface activity at the air side, whereas on the glass side noticeable effect on the enrichment of GH occurs. It should be noted that it was not easy to peel off the specimen containing GH from the glass slide as in the case of GF. Fig. 3 shows that the added graft copolymers GHF have the tendency to accumulate on both sides of the film surface, and this can be explained by the coexistence of the hydrophilic HEMA and hydrophobic FA components in the same chain which can introduce both preferential affinity to the glass surface and surface activity. We can ascribe the interfacial accumulation of the graft copolymers of GH and GHF to the specific interaction between the HEMA and polar glass surface and also to the interfacial segregation which may arise from the repulsive interaction between the backbone components and PMMA matrix and the PMMA branches is effective to disperse the graft copolymers in the PMMA matrix and to hold them on the PMMA films as the anchor segment. Above results indicate that the graft copolymers containing not only surface active FA component but also polar HEMA component, which may have higher surface energy than that of PMMA, can modify surface properties of PMMA such as wettability toward water. Further details are being studied and will appear elsewhere.

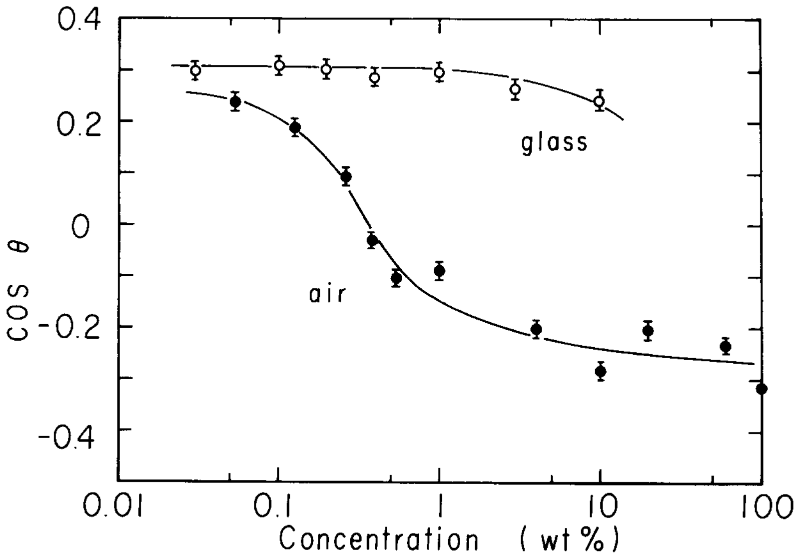

Fig.1 Contact angle variations for water on PMMA film specimens containing GF graft copolymer

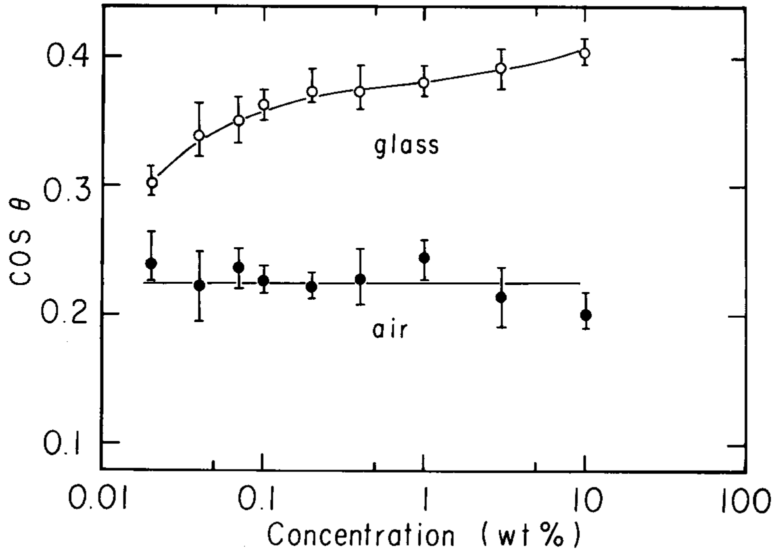

Fig.2 Contact angle variations for water on PMMA film specimens containing GH graft copolymer

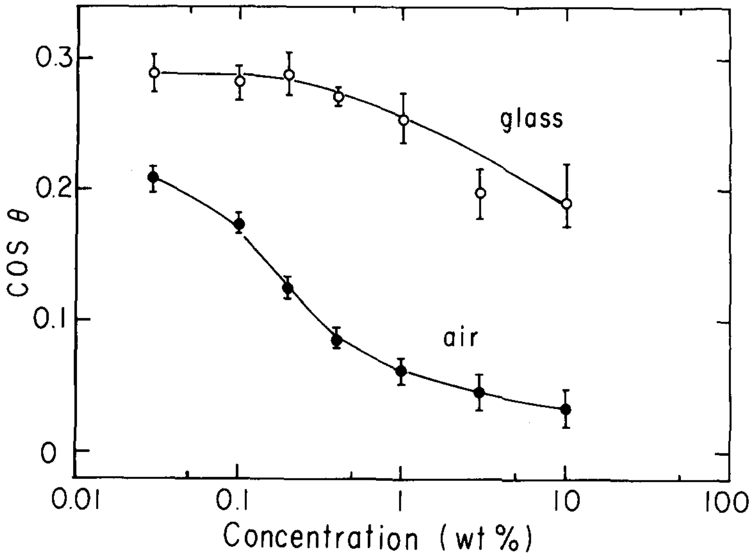

Fig.3 Contact angle variations for water on PMMA film specimens containing GHF graft copolymer

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