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Surface molecular mobility for copolymers having perfluorooctyl and/or polyether side chains via dynamic contact angle

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It is well known that a segment of a multicomponent polymeric system such as copolymer selectively adsorb and orient to the surface of the system so as to minimize interfacial free energy in response to an environmental media. Surface molecular mobility of perfluorooctyl (PFO) group of acrylic copolymers, having PFO as a side chain, was investigated via dynamic contact angle and X.p.s. For all copolymers, more fluorine was detected than calculated amount from composition via X.p.s. In addition, the shallower sampling depth of X.p.s., the more fluorine was detected. These sample polymers exhibited a relatively large contact angle hysteresis. Advancing contact angle θ_A for copolymers increased with an increase in PFO content. Receding contact angles were largely influenced by polar group of copolymers. © 1997 Elsevier Science Ltd.

(Keywords: acrylic copolymer; perfluorooctyl group; dynamic contact angle)

INTRODUCTION

It is well known that a segment of a multicomponent polymeric system such as copolymer selectively adsorb and orient to the surface of the system so as to minimize interfacial free energy in response to an environmental media. We have already reported on the effect of side chain of polymers on this behaviour via dynamic contact angle (DCA) measurement. It was shown that poly(vinyl alkylate)s (PVA1) having alkyl side chain length from 6 to 12 carbon atoms showed very large molecular mobility[1]. We found that copolymers composed of methylmethcrylate (MMA) and methoxypolyethyleneglycolmethacrylate (MPEGMA) showed an interesting behaviour that advancing contact angles of the second cycle in DCA measurement were larger than those of the first cycle[2]. This behaviour was explained by reorientation of hydrophilic polyethyleneglycol side chain to polymer surface in water and formation of hydrophobic ultrathin layer of methoxy group after dipping out of water. In addition, we also measured DCA for copolymers having both hydrophobic polydimethylsiloxane (PDMS) and methoxypolyethyleneglycol (MPEG) side chains[3]. It was clear that the composition dependence of DCA was affected by the balancing of the contribution of hydrophobic and hydrophilic side chains.

In this paper, we took up the effect of perfluorooctyl (PFO) group introduced in polymer on DCA. Perfluoroalkyl group was very interesting material in the field of polymer surface science, since it had extremely low surface free energy and showed very strong hydrophobicity. We[4] reported that when some terpolymers composed of MMA, perfluorooctyl ethyl methacrylate (PFOM) and glycidyloxyethylmethacrylate (GMA) were blended in epoxy resin, the resin surface was covered with PFO layer and showed excellent water and oil repellency. We prepared some copolymers and terpolymers composed of MMA, PFOM, perfluorooctyl-N-methylsulfonamide ethyl methacrylate (PFOSAM), and/or MPEGMA, having different compositions and discussed surface molecular mobility of hydrophobic PFO and hydrophilic MPEG side chains. The following results were hypothesized: a low surface free energy PFO segment would be predominant at the surface of these copolymers; in aqueous environment, a PEG segment would reorient to the surface to lower interfacial free energy between copolymer and water; and dipping in water would reduce the receding contact angle. In addition to measure the DCA of these copolymer surfaces, a X.p.s. spectrum was conducted.

EXPERIMENTAL

Materials

We synthesized two types of copolymers and a terpolymer composed of MMA, PFOM, PFOSAM, and/or MPEGMA, having different compositions. The molecular structures of these monomers are shown in *Scheme 1*.

Copolymers MMA/PFOM and MMA/PFOSAM and terpolymers MMA/MPEGMA/PFOM were synthesized by living radical polymerization under irradiation with a u.v. light source. Photopolymerization was carried out in benzene or mixed solvent of benzene/chloroform at 30°C for 8–15 h with a sealed bottle using benzyl

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MMA : $CH_2{=}C(CH_3)COOCH_3$
PFOM : $CH_2{=}C(CH_3)COOCH_2CH_2(CF_2)_8F$
PFOSAM : $CH_2{=}C(CH_3)COOCH_2CH_2N(CH_3)SO_2(CF_2)_8F$
MPEGMA : $CH_2{=}C(CH_3)COO(CH_2CH_2O)_{23}CH_3$

Scheme 1

BDC : $C_6H_5CH_2S_2CN(C_2H_5)_2$
XDC : $C_6H_4(CH_2S_2CN(C_2H_5)_2)_2$

Scheme 2

N,*N*-diethyldithiocarbamate (BDC) or *p*-xylylene-bis(*N*,*N*-diethyldithiocarbamate) (XDC) as photoinifeter. The molecular structures of these photoinifeter are shown in *Scheme 2*.

Characterization details of the copolymers and terpolymers synthesized are shown in *Table 1*. We denoted these copolymers with such nomenclature as MMA/PFOM (30), MMA/PFOSAM(30) or MMA/MPEGMA/PFOM(30). The figure in parentheses showed wt% of fluorine containing monomer. Here, we used nomenclature PFO for perfluorooctyl group SA for sulfonamide group and MPEG as methoxypolyethyleneglycol group. Terpolymers MMA/MPEGMA/PFOM had a fixed MMA content (50 wt%) but differed in PFOM and MPEGMA content.

Preparation of sample specimen

The specimens for dynamic contact angle (DCA) measurement were prepared as follows: aluminium plates (20 mm wide, 50 mm length, 0.3 mm thickness) were dipped in a MEK solution (20 wt% of copolymer) of the copolymers and then were dried in a vacuum oven at 90°C for 20 h.

Dynamic contact angle measurement

For DCA measurement, we employed an instrument made by Orientec Corporation (DCA20), applying the Wilhelmy plate technique used for measuring the surface tension of a liquid. The principles of the Wilhelmy method are shown elsewhere[2]. A sample plate (about 20 mm wide, 50 mm length and 1 mm thickness) hanging onto a load cell is dipped into and out of a standard liquid giving the contact angle. By this method, adhesion tension ($\gamma_L \cos\theta = \gamma_S - \gamma_{SL}$) was measured and contact angle was calculated with surface tension of water. The contact angles in the dipping in and out processes are called the advancing contact angle (θ_A) and receding contact angle (θ_R), respectively.

X.p.s. spectrum measurement

X.p.s. spectra were measured by a Shimadzu Manufacturing Ltd. ESCA 850 X-ray photoelectron spectrometer using a Mg $K\alpha$ X-ray source. The X-ray gun was operated at 8 kV and 30 mA, and the analyzer chamber pressure was less than 1×10^{-6} Pa. Two types of sample holders having take-off angle (ϕ) 15 and 90°C were used to obtain depth profile and the sampling depths were 2.5 nm and 10 nm, respectively.

RESULTS AND DISCUSSION

X.p.s. measurement

Table 2 shows X.p.s. data for MMA/PFOMA, MMA/PFOSAM and homopolymers obtained with sample holders with take-off angles of 15 and 90°. In *Table 2*, atomic ratios of O_{1s}, F_{1s}, N_{1s} and S_{2p} to C_{1s} were shown.

Table 1 Characterization for copolymers and terpolymers composed of MMA, PFOM, PFOSAM and/or MPEGMA, synthesized

Polymer	Time[c] (h)	Feed wt ratio	Molecular weight			Composition wt ratio[d]
			M_n ($\times 10^{-4}$)	M_w ($\times 10^{-4}$)	M_w/M_n	
PFOM (100)[a]	8	/			–	/
PFOSAM (100)	15	/	–	–	–	/
MMA/PFOM (10)	15	90/10	4.92	6.81	1.39	90.6/9.4
MMA/PFOM (30)	15	70/30	6.86	9.51	1.39	70.2/29.8
MMA/PFOM (50)	15	50/50	3.94	5.48	1.39	50.2/49.8
MMA/PFOM (70)	15	30/70		–	–	28.5/71.5
MMA/PFOM (90)	15	10/90		–	–	
MMA/PFOSAM (10)	12	90/10	5.26	7.16	1.36	88.5/11.5
MMA/PFOSAM (30)	12	70/30	3.10	4.82	1.56	64.2/35.8
MMA/PFOSAM (50)	12	50/50	2.83	4.04	1.43	44.6/55.4
MMA/PFOSAM (70)	12	30/70	1.69	2.24	1.33	25.3/74.7
MMA/PFOSAM (90)	12	10/90	–			10.2/89.8
MMA/MPEGMA/PFOM (5)[b]	12	50/45/5	4.78	7.37	1.54	49.8/41.1/9.1
MMA/MPEGMA/PFOM (15)	12	50/35/15	4.74	7.82	1.65	49.8/34.0/16.2
MMA/MPEGMA/PFOM (25)	12	50/25/25	3.98	5.99	1.51	54.5/21.6/23.9
MMA/MPEGMA/PFOM (35)	12	50/15/35	4.37	6.44	1.47	48.6/16.7/34.7
MMA/MPEGMA/PFOM (45)	12	50/5/45	3.93	5.51	1.40	49.7/6.2/44.1

[a] Values in parentheses indicate content of fluorine containing monomer
[b] Number of PEG side chains in MPEGMA; 23
[c] Time of irradiation with u.v. light source
[d] Determined by n.m.r.

Table 2 Atomic ratio of O_{1s}, F_{1s}, N_{1s} and S_{2p} to C_{1s} for MMA/PFOM, MMA/PFOSAM copolymers and those homopolymers, via X.p.s. measurements

		O_{1s}/C_{1s}			F_{1s}/C_{1s}			N_s/C_{1s}			S_{2p}/C_{1s}		
Polymer	Φ^b	Calc.	Meas.	Meas./Calc.	Calc.	Meas.	Meas./Calc.	Calc.	Meas.	Meas./Calc.	Calc.	Meas.	Meas./Calc.
PFOM (100)[a]	90	0.14	0.17	1.17	1.21	1.45	1.20						
	15		0.13	0.89		1.79	1.48						
MMA/PFOM (90)	90	0.19	0.18	0.96	1.00	1.43	1.43						
	15		0.16	0.85		1.75	1.75						
MMA/PFOM (30)	90	0.35	0.35	1.00	0.22	0.44	1.98						
	15		0.27	0.76		0.90	4.06						
PFOSAM (100)	90	0.27	0.25	0.92	1.13	1.27	1.12	0.07	0.08	1.15	0.07	0.05	0.69
	15		0.22	0.81		1.50	1.33		0.05	0.81		0.05	0.69
MMA/PFOSAM (90)	90	0.29	0.29	1.00	0.92	1.16	1.27	0.05	0.07	1.28	0.05	0.04	0.78
	15		0.24	0.82		1.43	1.56		0.07	1.37		0.06	1.06
MMA/PFOSAM (30)	90	0.37	0.39	1.04	0.24	0.27	1.13	0.01	0.02	1.29	0.01	0.010	0.71
	15		0.38	1.02		0.54	2.23		0.03	1.93		0.02	1.29

[a] Values in parentheses indicate content of PFOM
[b] Take-off angle for photoelectron

For all copolymers, more fluorine was detected than calculated from composition. In addition, the shallower sampling depth of X.p.s., the more fluorine was detected. It was clear that PFO group adsorbed and oriented to copolymer surfaces. Almost same amounts of oxygen atom were obtained with the 90° sample holder as calculated from molecular composition but the amounts with the 15° holder were less than them. This was due to the adsorption of PFO group to outermost layer and the arrangement of ester group under its subsurface. For lower PFO content copolymers [MMA/PFOMA(30) and MMA/PFOSAM (30)], the detected amounts of fluorine obtained with 15° sample holder were twice of 90° while for high content region, this ratios were about 1.2. This fact suggested that surfaces were composed of very thin PFO layer < 2 nm. For MMA/PFOSAM, nitrogen and sulfur introduced with SA group were detected and also increased with a shallowing in sampling depth but oxygen decreased. This fact suggested that nitrogen and sulfur arranged within sampling depth with PFO but oxygen which was bonded to SA by $-CH_2-CH_2-$, was excluded from the depth. In addition, the rate of the increase of F, N and S with the decrease in sampling depth for lower PFOSAM content copolymers were much larger than for higher content. From these X.p.s. data, we could consider the following: for lower PFO content copolymer, PFO groups were isolated and could lie on the surface to make a thin PFO layer, while for high PFO content copolymers, they could orient perpendicular to the surface to make a relatively thick condensed monolayer of PFO by using the very strong cohesive energy of the SA group.

Table 3 shows X.p.s. data for MMA/MPEGMA/PFOM, obtained with sample holders of take-off angle of 15 and 90°. In *Table 3*, atomic ratios of O_{1s} and F_{1s} to C_{1s} are shown. For all terpolymers, more fluorine was detected than the calculated amount from composition. In addition, for the 15° sample holder, more than twice the amounts of fluorine of 90° were detected. It was clear that the PFO group adsorbed and oriented to copolymer surfaces. Almost the same amounts of oxygen atom as calculated were detected with 90° sample holder but less than those with 15°. This was due to the adsorption of PFO group to the outermost layer and the arrangement of the polyether group under its subsurface.

Dynamic contact angle measurement

As shown, the copolymers used in this work exhibited a relatively large contact angle hysteresis ($\Delta\theta = \theta_A - \theta_R$). Such factors responsible for contact angle hysteresis of a polymer include: (1) surface contamination; (2) surface roughness; (3) heterogeneity of the surface structure; (4) reorientation or mobility of the surface segment; (5) swelling; (6) deformation, and so on. The relatively

Table 3 Atomic ratios of O_{1s}, F_{1s} to C_{1s} for MMA/MPEGMA/PFOM copolymers having fixed MMA content (50 wt%), via X.p.s.

			O_{1s}/C_{1s}			F_{1s}/C_{1s}		
Polymer	n^b	ϕ^c	Calc.	Meas.	Meas./Calc.	Calc.	Meas.	Meas./Calc.
MMA/MPEGMA/PFOM (5)[a]	23	90	0.42	0.44	1.05	0.062	0.26	4.19
		15		0.41	0.98		0.59	9.52
MMA/MPEGMA/PFOM (25)	23	90	0.38	0.40	1.05	0.18	0.52	2.89
		15		0.29	0.76		1.07	5.94
MMA/MPEGMA/PFOM (45)	23	90	0.33	0.44	1.33	0.36	0.63	1.75
		15		0.23	0.70		1.18	3.28

[a] Values in parentheses indicate content of PFOM
[b] Number of oxyethylene units
[c] Take-off angle for photoelectron

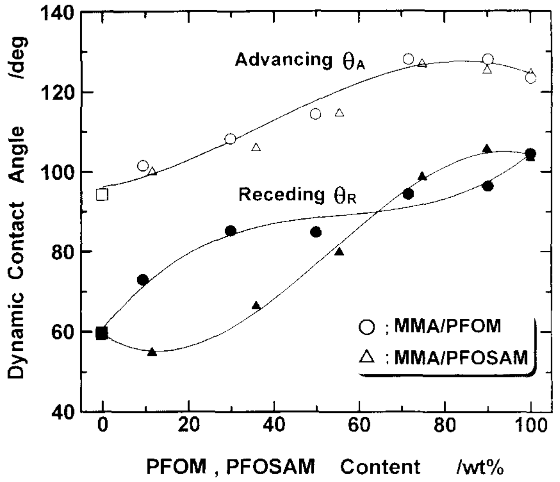

Figure 1 Dynamic contact angles for MMA/PFOM and MMA/PFOSAM copolymers as a function of fluorine containing monomer content (squares indicate values of PMMA)

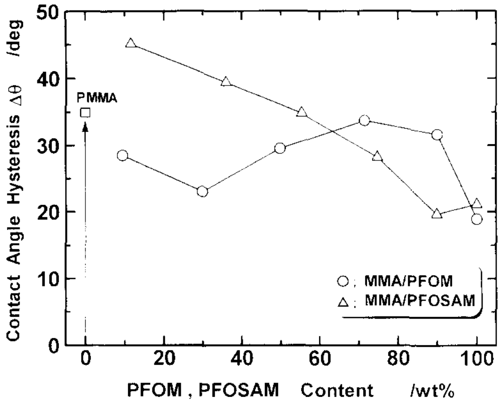

Figure 2 Contact angle hysteresis ($\Delta\theta = \theta_A - \theta_R$) for MMA/PFOM and MMA/PFOSAM copolymers as a function of PFOM or PFOSAM content

important factors in this study were the heterogeneity of the surface structure and the reorientation or mobility of the segment of the polymer surface. Johnson and Dettre[5,6] showed that at a heterogeneous surface, a hydrophobic component predominantly contributed to advancing contact angle (θ_A) and a hydrophilic one to receding contact angle (θ_R).

Figure 1 showed the composition dependence of DCA for MMA/PFOM and MMA/PFOSAM copolymers. We have already measured θ_A and θ_R for a few fluororesins, and obtained 109.6 and 89.2° for tetrafluoroethylene/hexafluoropropylene copolymer (FEP), 116 and 92° for polytetrafluoroethylene (PTFE) and 94 and 60 for polyvinylidene fluoride (PVDF), respectively. DCAs for homopolymers of PFOM and PFOSAM were comparable to these values. θ_A for copolymers used increased with an increase in PFOM or PFOSAM content and showed an almost similar value for both copolymers of the same composition, while θ_R showed different behaviour. As shown by fluororesins, perfluorocarbon showed very high contact angle because it had extremely low surface free energy. It was expected that this fluorinated segment adsorbed and oriented to the surface of the systems so as to decrease surface tension, when it was combined in a multicomponent polymeric system such as a copolymer. Therefore, θ_A increased with an increase in PFOM or PFOSAM content of copolymer. Especially, in the region of PFO content > 70 wt%, θ_As were very large > 120°. In this region, a surface layer of copolymer could be made of PFO as shown by X.p.s. measurement described above. In addition, the PFO groups could orient perpendicular to the surface to make a surface layer and the outermost layer could consist of terminal $-CF_3$ group which had lower surface free energy than the $-CF_2-$ group. Therefore, θ_As were very large.

θ_R for MMA/PFOM initially increased rapidly with an increase in the PFOM content and in the region of PFOM content > 50 wt% increased slowly. It was shown that θ_R was increased by the introduction of a small amount of PFOM. On the other hand, for MMA/PFOSAM, θ_R initially decreased and increased after minimum at 10 wt% of PFOSAM content. This was an effect of hydrophilic SA group of PFOSAM. In this copolymer, ester group bonded to SA group by means of flexible ethylene group. These strong polar groups could easily reorient to a water/copolymer interface in the water. At the low PFOSAM content copolymer surface, each side chain was isolated and could individually move. Therefore, as SA groups at the surface could take a role to decrease interfacial free energy, θ_R showed low value. At the high PFOSAM content copolymer surface, PFO groups were crowded and, therefore, could be oriented perpendicular to the copolymer surface to make a surface layer of them by strong intermolecular force of polar groups, since they, especially SA, had strong intermolecular cohesion energy. In the region of the content > 70 wt%, θ_R for MMA/PFOSAM were larger than for MMA/PFOM. PFO, itself, had very weak intermolecular cohesion energy as shown by its extremely low surface free energy. Therefore, for MMA/PFOM, a few ester groups arranged under the PFO layer could reorient to the water/copolymer interface through this layer. On the other hand, for MMA/PFOSAM, the foot of PFO groups could bind tight to each other by the SA group, which had strong intermolecular force, to make a relatively thick PFO layer. Since this layer could act as a barrier to contact of the SA group to water through this layer, θ_R for this copolymer was larger than for MMA/PFOM. This was the reason that θ_R for MMA/PFOSAM showed low values in low PFO content region, and had higher values than that for MMA/PFOM in high PFO content region.

Figure 2 showed the composition dependence of $\Delta\theta$ for MMA/PFOM and MMA/PFOSAM copolymers. $\Delta\theta$ for MMA/PFOM initially decreased with an increase in PFOM content and after minimum at 30 wt%, it increased. This was due to the relative large θ_R as shown in *Figure 1*. $\Delta\theta$ for MMA/PFOSAM showed large value at 10 wt% and decreased with an increase in PFOSAM content. It was also clear that the SA group contributed to θ_R in the low content region.

Figure 3 shows the composition dependence of dynamic contact angle for MMA/MPEGMA/PFOM terpolymers. In *Figure 3*, DCAs for MMA/MPEGMA and MMA/PFOM are plotted at 0 and 50 wt% respectively. θ_A increased with an increase in PFOM content. θ_R showed a very low value up to 25 wt% and then increased. The high value of θ_A was responsible for the hydrophobic PFO group adsorbed to surface. θ_As were comparable to MMA/PFOM or MMA/PFOSAM

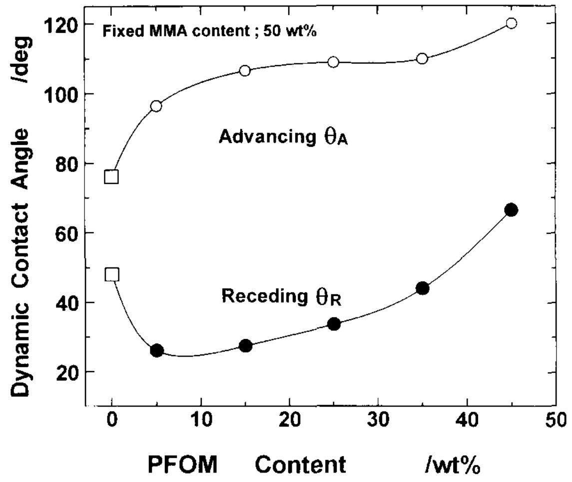

Figure 3 Dynamic contact angles for MMA/MPEGMA/PFOM copolymers, having fixed MMA content (50 wt%) as a function of PFOM content

with the same content of PFOM or PFOSAM. Especially, we must note that the introduction of a small amount of PFOM greatly increases θ_A. Hydrophobic PFO segment, having extremely low surface free energy, selectively adsorbed and oriented to polymer surface when it was cast from solvent in the air and became predominant. Since the hydrophilic polyether group reoriented to water/polymer interface so as to minimize interfacial free energy when sample plates were dipped into water, θ_Rs showed very low values in the region of PFOM content from 5 to 25. Here, θ_Rs for terpolymers in low PFOM content region showed low values than those for MMA/MPEGMA. We have already reported on the DCA and X.p.s. for MMA/MPEGMA cast from various solvents having different solubility parameter (SP). It was shown in the work that surface layer of the copolymer cast from MEK solution was composed of MMA segment which migrated with evaporation of the solvent having the same SP as the MMA and MPEG segment which was oriented to the surface to make the outermost ultrathin layer of methoxy group having very low surface free energy. Then the mobility of MPEG was restricted by the coexisting MMA segment. As a result of this, θ_R was 48° as shown in *Figure 3*. If the surface was composed of only PEG segment, θ_R might be 0° because it was soluble in water. For MMA/MPEGMA/PFOM, extremely low surface free energy PFO segment disturbed the migration of MMA segment to surface. Moreover, since the cohesion energy of the PFO segment was very weak, PEG side chain arranged under methoxy group adsorbed to surface could move easily. Therefore more PEG segment for this terpolymer than that for MMA/MPEGMA was at the water/terpolymer interface. This is for the reason that θ_Rs for terpolymers in low PFOM content region showed lower values than those for MMA/MPEGMA.

CONCLUSIONS

Two types of copolymers and a terpolymer composed of MMA, PFOM, PFOSAM, and/or MPEGMA, having different compositions were synthesized and surface molecular mobility of perfluorooctyl group was investigated via DCA and X.p.s. For all copolymers, more fluorine was detected than calculated amount from composition via X.p.s. In addition, the shallower sampling depth of X.p.s., the more fluorine was detected. These sample polymers exhibited a relatively large contact angle hysteresis. θ_A for copolymers increased with an increase in PFOM or PFOSAM content and showed an almost similar value for both copolymers of the same composition. θ_R for MMA/PFOM initially increased rapidly with an increase in the PFOM content and increased slowly in the region of PFOM content > 50 wt%. It was shown that θ_R was increased by the introduction of a small amount of PFOM. On the other hand, for MMA/PFOSAM, θ_R initially decreased and increased after minimum at 10 wt% of PFOSAM content. For MMA/MPEGMA/PFOM terpolymers, θ_A increased with an increase in PFOM content and θ_R showed a very low value up to 25 wt% and then increased.

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