

## Anionic Polymerizations of Perfluoroalkyl Methacrylates and Synthesis of Well-Defined ABC Triblock Copolymers of Methacrylates Containing Hydrophilic, Hydrophobic, and Perfluoroalkyl Groups

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**ABSTRACT:** Anionic polymerizations of three perfluoroalkyl methacrylates, 2,2,2-trifluoroethyl- (1), 2-(perfluorobutyl)ethyl- (2), and 2-(perfluorooctyl)ethyl methacrylates (3), were carried out in THF at  $-78^{\circ}\text{C}$  for 1 h with 1,1-diphenyl-3-methylpentyllithium in the presence of 5-fold lithium chloride. Poly(1) and poly(2) were obtained in quantitative yields and those possessed predicted molecular weights based on the molar ratios of monomers and initiator and narrow molecular weight distributions (MWD,  $M_w/M_n < 1.15$ ). Polymerization of 3 also proceeded quantitatively to give poly(3) showing very limited solubility. Sequential anionic copolymerizations of 2, *tert*-butyl methacrylate (tBMA), and 2-(trimethylsilyloxy)ethyl methacrylate and the subsequent deprotection of trimethylsilyl group afforded a series of well-defined ABC triblock copolymers by changing the additional order of three comonomers.  $^1\text{H}$  NMR spectra of the resulting triblock copolymers suggested the formation of their micelles in the selective solvents. Contact angle and X-ray photoelectron spectroscopic measurements of the triblock copolymer films confirmed the enrichment of the poly(2) segment at the film surface in dry state and the surface rearrangement in respect to changing the environmental conditions. It was suggested that segmental sequence in the triblock copolymers affected the structure in solution and at surface.

**KEY WORDS** Anionic Living Polymerization / ABC Triblock Copolymer / Segmental Sequence / Perfluoroalkyl Methacrylate / *tert*-Butyl Methacrylate / 2-Hydroxyethyl Methacrylate / Surface Structure /

Block copolymers constituted with hydrophilic and hydrophobic segments have been intensely studied on their interesting structures and properties in solution, in bulk, and at surface.<sup>1</sup> Syntheses of hydrophilic/hydrophobic block copolymers via anionic living sequential polymerizations have been restricted to the termination reaction with hydrophilic moiety, such as hydroxy group, and the inherent difference in the monomer reactivity. However, the recent developments of the new living polymerization reactions open the routes for the novel block copolymers having hydrophilic groups, predictable segment length and composition, and narrow molecular weight distribution (MWD).<sup>2</sup> We have succeeded in the tailored synthesis of a series of block copolymers containing hydrophilic segment by means of the anionic living polymerization of the protected functional monomers followed by complete removal of the protecting groups.<sup>3</sup> The hydrophilic monomers employed involve styrenes substituted with hydroxy,<sup>4</sup> amino,<sup>5</sup> and carboxyl groups,<sup>6</sup> 2-hydroxyethyl methacrylate (HEMA),<sup>7</sup> and 2,3-dihydroxypropyl methacrylate (DIMA).<sup>8</sup> For example, the diblock copolymers, poly[styrene-*block*-HEMA],<sup>7b</sup> poly[styrene-*block*-DIMA],<sup>8</sup> poly[isoprene-*block*-HEMA],<sup>7b</sup> poly[isoprene-*block*-DIMA],<sup>9</sup> and poly[(4-octenylstyrene)-*block*-HEMA]<sup>10</sup>, with precisely controlled chain structures have been synthesized by the anionic living polymerization. The top-surface of these block copolymer films under dry and wet conditions were monitored by the transmission electron microscopic (TEM) observation and contact angle and X-ray photoelectron spectroscopic (XPS) measurements. It is demonstrated that the characteristic morphological restructuring at the outermost surface takes place in respect to the environmental change.

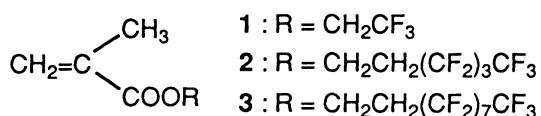
Although the synthesis, structure, and properties have been investigated on a variety of block copolymers, such as

AB diblock, ABA triblock, and  $(\text{AB})_n$  multiblock copolymers,<sup>11</sup> most of them consist of two segmental units.<sup>12</sup> Very recently, the study of ternary ABC triblock copolymers has been started and particularly their unique and complicated microphase separated structures have attracted great attentions.<sup>13-17</sup> Stadler *et al.* synthesized poly(styrene-*block*-butadiene-*block*-methyl methacrylate)s by anionic living block copolymerization and characterized their various interesting microphase separated structures depending upon the content of each segment.<sup>14</sup> The segmental sequence in these triblock copolymers is expected to play an important role in morphology<sup>13,15</sup> and solution property<sup>16</sup> along with the influence of molecular weight, composition, and incompatibility of the segments. However, the triblock copolymer with special segmental sequence, poly(styrene-*block*-methyl methacrylate-*block*-butadiene) could not be prepared by sequential block copolymerization, because of the lower reactivity of the anionic propagating species of methyl methacrylate. Thus, the effect of segmental sequence of ABC triblock copolymer has not been clarified yet in the previous studies due to the synthetic difficulties.

In this study, we introduce a third incompatible component into the conventional hydrophilic-lipophilic amphiphilic block copolymer and synthesize a series of novel triblock copolymer having different sequences such as ABC, ACB, and BAC to investigate the effect of segmental sequence on the structures in the solution and at the surface. Fluorine-containing polymers are suitable candidates for this purpose, since they are well known to show the unique hydrophobic and lipophobic characters and very low surface free energy in the dry solid state. In fact, a number of studies of fluorine-containing polymers are dedicated to understand their surface chemistry.<sup>18-20</sup> Interestingly, a diblock copolymer containing poly(perfluoroalkyl (Rf) acrylate) segment acts as a stabilizer of the dispersion polymerization in supercritical carbon dioxide.<sup>21</sup>

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We herein select Rf methacrylates, *tert*-butyl methacrylate (tBMA), and 2-hydroxyethyl methacrylate (HEMA) as the monomers for the synthesis of ABC triblock copolymers, since they are expected to have the comparable polymerizability. Needless to say, the polymerizability of monomers and the living character of the polymerization are essential to synthesize a series of above-mentioned ABC triblock copolymers via the sequential copolymerization of three comonomers in any addition order. The formation of anionic living polymers of tBMA and 2-(trimethylsilyloxy)-ethyl methacrylate (a protected form of HEMA) has been known.<sup>7</sup> The aim of this study is to demonstrate the controlled anionic polymerizations of three Rf methacrylates, 2,2,2-trifluoroethyl- (1), 2-(perfluorobutyl)ethyl- (2), and 2-(perfluorooctyl)ethyl methacrylates (3), and the tailored synthesis of novel ABC triblock copolymers including poly(Rf methacrylate) with different segmental sequences.



## RESULTS AND DISCUSSION

Although free-radical polymerization of Rf methacrylates was reported to undergo readily,<sup>18-20</sup> their anionic polymerization behaviors were not clarified in detail. Narita and his co-workers attempted to polymerize Rf acrylates and methacrylates in THF or toluene with various initiators such as zincate complexes, Grignard reagents, and organolithiums.<sup>22</sup> Exploring a variety of polymerization conditions, the yields of the polymers were far from quantitative in most cases and the formation of the living polymer was ambiguous. Therefore, we again examine the anionic polymerization of a series of Rf methacrylate, 1-3, to achieve quantitative conversions and accurate molecular weight control, and to confirm the living nature of the propagating species using the typical anionic initiators. The length of Rf chain in 1-3 may also affect the polymerization behavior owing to the solubility of the resulting polymer.

Recently, we have successfully introduced Rf groups at the chain end of the anionic living polystyrene through the nucleophilic substitution reaction of the living polymers with alkyl halides containing Rf groups.<sup>23</sup> In this case, the terminal carbanions of the living polymers exclusively react with the C-Br or C-I bonding of the Rf-alkyl halides not with the C-F bond. This indicates that the considerable stability of Rf group toward the nucleophilic anionic species and prompts us to investigate the anionic polymerization of Rf methacrylates, 1-3. Furthermore, since the propagating enolate-anions of methacrylates are known to be less nucleophilic and less basic than the benzyl carbanion of living polystyrene, the anionic polymerizations of 1-3 are expected to proceed without serious chain termination.

### Anionic Polymerization of 1-3

The anionic polymerization of 1 was carried out in THF at  $-78^\circ\text{C}$  with 1,1-diphenyl-3-methylpentyllithium in the absence or in the presence of 3 fold LiCl.<sup>24</sup> The polymerization was completed within 1 h to give the poly(1) quantitatively in each case, as shown in Table I. The molecular weights of the resulting poly(1)s, which were determined by

the end-group analysis using the  $^1\text{H}$  NMR,<sup>25</sup> agreed with the calculated values based on the molar ratio of monomer to initiator. The SEC of poly(1) produced in the absence of LiCl showed unimodal and relatively broad molecular weight distribution (MWD,  $M_w/M_n = 1.39$ ). The addition of LiCl effectively narrowed a MWD as was seen in the previous reports,<sup>7b,24,26</sup> although MWD was again broadened ( $M_w/M_n = 1.37$ ) when a feed  $[\text{M}]/[\text{I}]$  ratio was increased. Thus, it is demonstrated that the anionic polymerization of 1 proceeds quantitatively to afford a polymer having a predicted molecular weight and a narrow MWD.

Under the similar condition, 2 was allowed to polymerize with triphenylmethyl lithium, -potassium, and -cesium, and diphenylmethylpotassium in addition to 1,1-diphenyl-3-methylpentyllithium (Table I). Upon addition of 2 to the initiator solution, the rapid color change of the reaction system was observed from red to colorless and the white precipitate immediately appeared in the reaction mixture. This indicates the rapid initiation and propagation reactions of 2 and the low solubility of the poly(2) in THF at  $-78^\circ\text{C}$ , although the isolated polymer was readily dissolved in THF at room temperature. The poly(2)s were obtained in quantitative yield within 10 min and possessed the predictable molecular weights based on the feeding molar ratio of initiator and monomer, except for the case initiated with  $\text{Ph}_3\text{CLi}$ . It should be noted that the  $M_n$  values estimated by SEC in THF were underestimated compared with those measured by NMR, probably due to the relatively small hydrodynamic volume of poly(2) compared with that of PMMA standards. Interestingly, the MWDs of the polymers produced with the organolithium initiators were quite narrow ( $M_w/M_n < 1.15$ ), particularly when LiCl was added to the initiator system. Even at a higher polymerization temperature, at  $-30^\circ\text{C}$ , fine control of  $M_n$  value and narrow MWD were successfully attained. The poly(2) of a narrow MWD and a predicted  $M_n$  value was also obtained with the bulky organopotassium and organocesium initiators. Addition of 5 fold weak Lewis acid,  $\text{Et}_2\text{Zn}$ , may reduce the propagation reaction rate to result in controlled molecular weight and narrow MWD (Run 10), as was observed in the anionic polymerizations of methyl methacrylate,<sup>27</sup> *tert*-butyl acrylate,<sup>28</sup> and *N,N*-dialkylacrylamides.<sup>29</sup> Thus, it is clearly shown that the various anionic initiators induce the controlled anionic polymerization of 2 under the wide range of conditions.

Persistency of the propagating carbanion of poly(2) was investigated by the sequential block copolymerization of 2 and tBMA. The first-stage polymerization of 2 was carried out with *s*-BuLi/DPE/LiCl in THF at  $-78^\circ\text{C}$  for 10 min to give a milky solution. The polymerization of 2 proceeded rapidly at  $-78^\circ\text{C}$  and the monomer was consumed completely within 10 min. After withdrawing an aliquot of polymerization system, tBMA was added to the reaction mixture at  $-78^\circ\text{C}$ . The second-stage polymerization of tBMA was continued for 2 h and the reaction mixture turned clear probably due to the enhanced solubility of the resulting block copolymer in THF. The polymer was obtained quantitatively after terminating with methanol. The SEC curve of copolymer is unimodal and clearly shifts from that of homopolymer of 2 toward the higher molecular weight region, as shown in Figure 1. The molecular weight of the block copolymer estimated by  $^1\text{H}$  NMR is close to the calculated value (Table II). Thus, sequential copoly-

**Table I.** Anionic Polymerizations of **1**, **2**, and **3** in THF at  $-78\text{ }^{\circ}\text{C}$ 

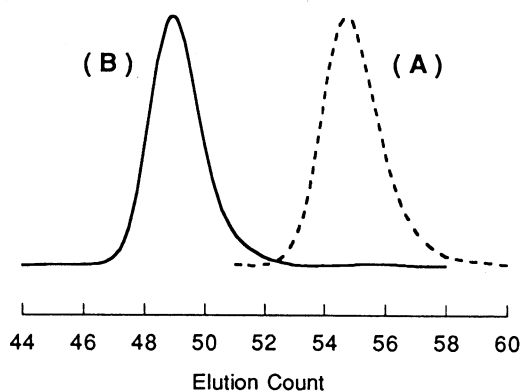
Run	Monomer mmol	Initiator mmol	DPE <sup>a</sup> mmol	LiCl mmol	Time h	$M_n \times 10^{-3}$			$M_w/M_n^c$
						Calcd <sup>b</sup>	SEC <sup>c</sup>	NMR <sup>d</sup>	
1	1, 5.51	<i>s</i> -BuLi, 0.105	0.287	-	20	10	12	11	1.39
2	1, 6.16	<i>s</i> -BuLi, 0.0974	0.234	0.302	20	11	10	9.0	1.12
3	1, 8.39	<i>s</i> -BuLi, 0.0741	0.192	0.270	20	19	23	21	1.37
4	1, 5.51	<i>s</i> -BuLi, 0.105	0.234	0.302	1	9.0	11	10	1.15
5	2, 2.15	Ph <sub>3</sub> CLi, <sup>e</sup> 0.0630	-	-	1	12	11	18	1.19
6	2, 3.61	<i>s</i> -BuLi, 0.120	0.230	0.356	1	10	7.1	9.9	1.11
7	2, 3.64	<i>s</i> -BuLi, 0.0666	0.137	0.183	1	18	11	20	1.15
8 <sup>f</sup>	2, 2.14	<i>s</i> -BuLi, 0.0790	0.136	0.236	1	9.2	7.2	10	1.09
9	2, 2.21	<i>s</i> -BuLi, 0.0767	0.116	0.287	10 min	9.5	7.9	10	1.05
10	2, 3.34	Ph <sub>2</sub> CHK, 0.113	-	0.567 <sup>h</sup>	1	9.8	6.8	11	1.21
11	2, 1.55	Ph <sub>3</sub> CK, <sup>i</sup> 0.0505	-	-	1	10	7.1	11	1.11
12	2, 2.26	Ph <sub>3</sub> CK, 0.0367	-	-	2	21	13	21	1.16
13	2, 1.30	Ph <sub>3</sub> CCs, <sup>j</sup> 0.0400	-	-	1	11	7.8	10	1.11
14	3, 1.37	<i>s</i> -BuLi, 0.0515	0.115	0.267	0.5	14	k	-	-
15	3, 1.40	PSLi, <sup>l</sup> 0.0971	0.303	0.276	0.5	18	13	18	1.06

Yields of polymers were quantitative in all cases. <sup>a</sup> 1,1-Diphenylethylene. <sup>b</sup>  $M_n(\text{calcd}) = (\text{MW of monomer}) \times [\text{monomer}]/[\text{initiator}] + \text{MW of monomer}$ . <sup>c</sup>  $M_n(\text{SEC})$  and  $M_w/M_n$  were determined by the SEC measurement using poly(methyl methacrylate) standards in THF. <sup>d</sup>  $M_n(\text{NMR})$  was determined by end group analysis using the initiator residue by <sup>1</sup>H NMR. <sup>e</sup> Triphenylmethyl lithium. <sup>f</sup> At  $-30\text{ }^{\circ}\text{C}$ . <sup>g</sup> Diphenylmethylpotassium. <sup>h</sup> Diethylzinc was used as an additive. <sup>i</sup> Triphenylmethyl lithium. <sup>j</sup> Triphenylmethyl cesium. <sup>k</sup> The resulting poly(**3**) was insoluble in THF. <sup>l</sup> Anionic living polystyrene was prepared with *s*-BuLi in THF at  $-78\text{ }^{\circ}\text{C}$ . The propagating chain end was capped with DPE to reduce the reactivity before the addition of **3**.

merization of **2** and tBMA afforded the diblock copolymer having narrow MWD in quantitative initiation efficiency, indicating the living character of the propagating carbanion of poly(**2**) at  $-78\text{ }^{\circ}\text{C}$  for 10 min. The stability and the sufficient nucleophilicity of the active chain end of poly(**2**) enable us to synthesize block copolymers including poly(**2**) segments by means of the sequential copolymerization in any additional order of monomers.

The polymerization of **3** was finally attempted in THF at  $-78\text{ }^{\circ}\text{C}$  with 1,1-diphenyl-3-methylpentyl lithium in the presence of LiCl. The white precipitate was formed as soon as **3** was added to the initiator system. The poly(**3**) was obtained in quantitative yield within 0.5 h, although the polymerization proceeded heterogeneously. The resulting poly(**3**) was only soluble in hexafluoropropan-2-ol and was insoluble in most organic solvents, as shown later. Long Rf chain of poly(**3**) apparently provides the limited solubility, which is observed in common for the polymers containing Rf chain. We then employed an anionic living polystyrene ( $M_n = 9600$ ,  $M_w/M_n = 1.05$ ) prepared with *s*-BuLi as a macroinitiator of **3** in order to overcome the poor solubility of the poly(**3**). The polymerization of **3** with the living polystyrene proceeded without precipitation at  $-78\text{ }^{\circ}\text{C}$  in THF to give a well-defined block copolymer having a predicted segment composition and a very narrow MWD as shown in Table I (Run 15). The resulting poly(styrene-*block*-**3**) was soluble in a variety of solvents such as CHCl<sub>3</sub> and THF, as expected. This strongly indicates that the polymerization of **3** also proceeds in a controlled fashion without serious side reactions as well as those of **1** and **2**.

In summary, we have thus succeeded in the controlled anionic polymerizations of three Rf methacrylates, **1-3**, and demonstrated that the anionic polymerizability of **1-3** is comparable to those of alkyl methacrylates such as MMA and tBMA.

**Figure 1.** SEC curves of poly(**2**) (A) and poly(**2**-*block*-tBMA) (B).

#### Synthesis of ABC Triblock Copolymers of **2**, tBMA, and 2-(Trimethylsilyloxy)ethyl Methacrylate

Synthesis of a series of ABC triblock copolymers containing the Rf, lipophilic, and hydrophilic side chains in the respective segments was examined by means of a sequential anionic copolymerization. We chose **2** as a monomer having Rf chain, because of the living nature of the anionic propagating poly(**2**), homogeneity of the polymerization mixture, and the characteristic solubility of poly(**2**), as discussed later. As the lipophilic and hydrophilic monomers, tBMA and HEMA were employed, respectively. Before the polymerization of HEMA, the hydroxy group was purposefully protected with the trimethylsilyl group as a form of 2-(trimethylsilyloxy)ethyl methacrylate (HEMA-TMS).<sup>7</sup> The anionic polymerizations of tBMA and HEMA-TMS are known to proceed quantitatively to give their stable living polymers.<sup>7</sup>

We then attempted to synthesize a series of ABC triblock copolymers by the sequential copolymerizations of **2**, tBMA, and HEMA-TMS. After the polymerization, trimethylsilyl protecting group in the poly(HEMA-TMS)

segment was deprotected to give the hydrophilic poly-(HEMA) segment.<sup>7</sup> The total molecular weights of the copolymers after the deprotection are designed to be around 20 000 and  $M_n$  value of each segment is controlled to be equal. For example, a triblock copolymer of poly-(HEMA-*block*-tBMA-*block*-2) (H-T-F) was synthesized by the initiation of HEMA-TMS with *s*-BuLi/DPE/LiCl followed by the sequential additions of tBMA and 2 in THF at -78 °C and subsequently by treating with 2N HCl to remove the trimethylsilyl protecting group from the poly-(HEMA-TMS) segment, as shown in Scheme 1. The yield of the product was quantitative by assuming the complete conversions of three comonomers. The SEC curve of the copolymer showed a unimodal peak with a narrow distribution ( $M_w/M_n = 1.07$ ). The observed molecular weight and the segmental composition, which were determined by <sup>1</sup>H NMR, showed in good agreements with the values calculated from the molar ratios of three comonomers and initiator (Table II). These results strongly indicate a synthetic achievement of ABC triblock copolymer having a well-defined chain structures. Similar tailored ABC triblock copolymers, H-F-T and T-H-F, possessing narrow MWDs and predicted segment lengths could be successfully synthesized by changing the additional order of the comonomers, as shown in Table II.

#### Solubility of the Triblock Copolymers in Methanol and in Chloroform

Table III shows the solubility of the polymers obtained in this study. The polymers included poly(1), poly(2), poly(3), poly(tBMA), poly(HEMA), and three triblock copolymers. Although poly(1) is soluble in a variety of organic solvents, poly(2) is insoluble in both nonpolar solvents such as benzene and polar solvents such as DMF and methanol, indicating the lipophobic and hydrophobic character of the longer R<sub>f</sub> pendant group. This tendency is clearer in the solubility of poly(3) having longer (perfluorooctyl)ethyl group. It is only soluble in hexafluoropropan-2-ol but insoluble in most of common organic solvents. Compared with the limited solubility of poly(2), poly-(tBMA) is soluble in a wide range of solvents including non-

polar and polar ones. On the other hand, poly(HEMA) is only soluble in polar solvents such as DMF and methanol, showing its strong polarity and high hydrophilicity. Interestingly, three triblock copolymers show the similar solubilities regardless of the difference in the segmental sequence. Although chloroform and methanol are non-solvents for poly(HEMA) and poly(2), respectively, all the triblock copolymers are apparently soluble in both solvents. They are considered to be the typical selective solvents for our triblock copolymers, since the third component of triblock copolymer, poly(tBMA), is soluble in the both solvents. Therefore, aggregation behavior of the triblock copolymers in the selective solvents are of interest, because it might be more complicated than those of diblock copolymers.

A series of <sup>1</sup>H NMR spectra of the triblock copolymer having H-T-F sequence in CDCl<sub>3</sub>, CD<sub>3</sub>OD, and a mixed solvent (CDCl<sub>3</sub>/CD<sub>3</sub>OD = 5/1) are shown in Figure 2. The characteristic NMR signals due to three polymethacrylate segments are clearly observed in the mixed solvent. The signals at 3.7 and 4.0 ppm are corresponding to the methylene protons of poly(HEMA) segment. For the poly(2) segment, CH<sub>2</sub> protons adjacent to the CF<sub>2</sub> group and COOCH<sub>2</sub> protons are observed at 2.4 and 4.2 ppm, respectively. The strong singlet signal at 1.35 ppm is due to the *tert*-butyl proton of poly(tBMA) segment. In the mixed solvent, the relative signal intensities of three segments agree with molar ratio of three comonomers in the feed. By contrast, in the selective solvents, the signals due to the corresponding insoluble segments disappear or broaden seriously. In CDCl<sub>3</sub>, the side chain signals for poly-(HEMA) and poly(tBMA) segments are certainly present. It is thus evident that insoluble segments in either CDCl<sub>3</sub> or CD<sub>3</sub>OD are not observable because of the restricted mobility of the ester side chain in the selective solvents. This suggests that the H-T-F triblock copolymer associates to form the micelle in the both selective solvents. In CDCl<sub>3</sub>, H-F-T triblock copolymer also showed the <sup>1</sup>H NMR spectrum similar to that of H-T-F, suggesting formation of the aggregate in chloroform. However, whole proton signals were observed with the reasonable intensities in the <sup>1</sup>H NMR spectra of T-H-F and T-F-H in CD<sub>3</sub>OD and T-H-F in CDCl<sub>3</sub>, indicating that these triblock copolymers were dissolved as a unimer and do not associate in the solvents. In methanol, connective of F-H may make the poly(2) segment soluble, although homopolymer of 2 is insoluble in methanol. The central poly(HEMA) segment becomes soluble in CDCl<sub>3</sub> by linking to poly(2) and poly(tBMA) at



Scheme 1.

**Table II.** Block Copolymerization of 2, tBMA (T), and HEMA-TMS (H) in THF at -78 °C<sup>a</sup>

1st monomer	2nd monomer	3rd monomer	$M_n \times 10^{-3}$ total (1st-2nd-3rd) <sup>b</sup>		$M_w/M_n$
			calcd	obsd	
2	T	-	12 (5.0-7.0)	16 (4.3-11.7)	1.06
H	T	2	18 (5.8-6.2-6.0)	19 (6.0-5.4-7.7)	1.07
H	2	T	19 (6.7-6.3-6.0)	20 (6.9-7.8-5.3)	1.07
T	H	2	21 (8.7-6.3-6.0)	21 (7.4-6.1-7.4)	1.07

<sup>a</sup> Yields of polymers were quantitative in each case. The polymerizations of 2, HEMA-TMS, and tBMA were respectively carried out for 10, 10, and 120 min to achieve the complete conversions. <sup>b</sup>  $M_n$  values of poly(HEMA) segments in  $M_n$  total and  $M_n$  (1st-2nd-3rd) showed the calculated values from the feed amount of HEMA-TMS and the value determined by <sup>1</sup>H NMR spectroscopy after deprotection of trimethylsilyl group of poly(HEMA-TMS) segment.

**Table III.** Solubility of Polymers

Solvent	Monomer Unit of Polymer							
	1	2	3	tBMA	HEMA	H-T-F <sup>a</sup>	H-F-T <sup>b</sup>	T-H-F <sup>c</sup>
hexane	I	I	I	I	I	I	I	I
benzene	S	I	I	S	I	I	I	I
chloroform	S	S	I	S	I	S	S	S
diethyl ether	S	S	I	S	I	I	I	I
1,4-dioxane	S	S	I	S	I	I	I	I
THF	S	S	I	S	I	S	S	S
DMF	S	I	I	S	S	S	S	S
methanol	S	I	I	S	S	S	S	S
water	I	I	I	I	I	I	I	I
(CF <sub>3</sub> ) <sub>2</sub> CHOH	S	I	S	I	I	I	I	I

<sup>a</sup> Poly(HEMA-*b*-tBMA-*b*-2). <sup>b</sup> Poly(HEMA-*b*-2-*b*-tBMA).

<sup>c</sup> Poly(tBMA-*b*-HEMA-*b*-2).

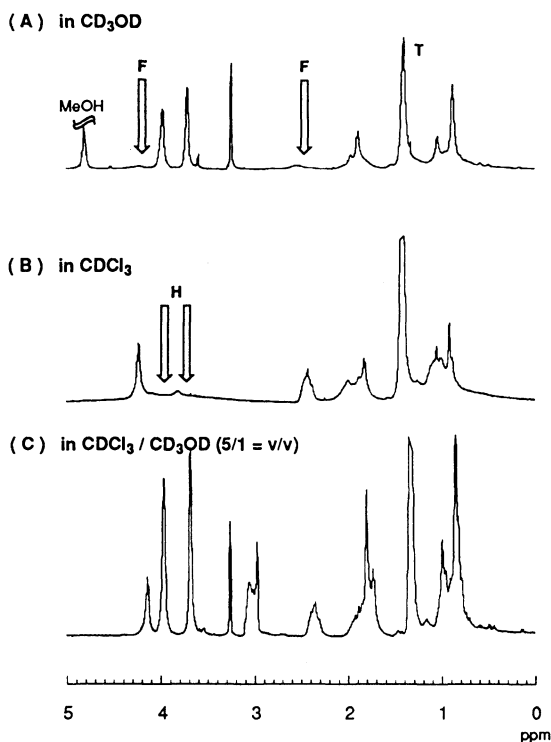


Figure 2.  $^1\text{H}$  NMR spectra of H-T-F in  $\text{CD}_3\text{OD}$  (A),  $\text{CDCl}_3$  (B), and mixed solvent (C).

the both ends. These results mean that the segmental sequence of the ABC triblock copolymer plays an important role in terms of their solubilities and formation of aggregates in the selective solvents. A similar observation was recently reported by Patrickios *et al.* in the micellization of an ABC triblock copolymer in water.<sup>16</sup> The light scattering study of our ABC triblock copolymers is now in progress to discuss the aggregation behavior in detail.

#### Surface Characterization of the Triblock Copolymer Films

We have already confirmed that the hydrophilic/hydrophobic diblock copolymer films cause a so-called surface restructuring in respect to environmental change.<sup>9,10</sup> The dynamic changes of the polymer surface could be successfully acquired by contact angle, XPS, and TEM measurements. In our previous report, the remarkable enrichment of the Rf group attached to polystyrene chain terminal was clearly observed under dry condition, indicating the strong hydrophobic nature of the Rf group.<sup>23</sup> Such hydrophobic poly(2) is linked as a terminal segment for H-T-F and T-H-F, and as a central segment for T-F-H. The hydrophobicity and the connectivity of poly(2) in the triblock copolymer may interestingly affect the outermost surface structure of the polymer film under dry condition.

The surface of the triblock copolymer film was characterized by the XPS and contact angle measurements. The results of the XPS measurement are summarized in Table IV. For the H-T-F triblock copolymer, the annealed film (condition A) showed a high fluorine atomic percent (42.9%,  $10^\circ$  takeoff angle). This is exactly the same value for homopoly(2) indicating that the top surface is predominantly covered with the terminal poly(2) segment in the H-T-F triblock copolymer. After soaking the annealed film in water at room temperature (condition B), the fluorine atomic content diminished to 17.7%. By soaking the sample in water at  $80^\circ\text{C}$  (condition C), the fluorine atomic percent was

Table IV. Contact Angle and XPS Atomic Surface Composition of Polymer Films

Polymer Code	Condition <sup>a</sup>	C.A. <sup>b</sup> deg	Atomic % <sup>c</sup>		
			C	O	F
H-T-F <sup>d</sup>	A	106	47.4 (54.1)	9.7 (15.2)	42.9 (30.7)
	B	98	60.2 (59.0)	22.1 (21.0)	17.7 (20.0)
	C	53	69.5 (68.6)	29.4 (25.6)	1.1 (5.8)
	D	107	48.5 (56.9)	10.7 (15.9)	40.8 (27.1)
	bulk(calcd)	-	63.7	20.6	15.8
H-F-T <sup>d</sup>	A	80	50.2 (56.3)	11.7 (16.8)	38.1 (26.9)
	C	49	67.3 (61.0)	26.4 (31.8)	6.3 (7.2)
	D	81	49.7 (52.6)	11.1 (23.3)	39.2 (24.2)
	bulk(calcd)	-	63.7	21.1	15.2
T-H-F <sup>d</sup>	A	104	48.6 (58.1)	10.9 (16.9)	40.6 (25.0)
	C	59	61.1 (64.0)	26.9 (20.6)	12.1 (15.4)
	D	104	48.4 (57.8)	12.2 (18.5)	39.4 (23.7)
	bulk(calcd)	-	65.5	20.7	13.8
Poly(2)	-	111	47.6 <sup>e</sup>	9.5 <sup>e</sup>	42.9 <sup>e</sup>
Poly(HEMA)	-	30	66.7 <sup>f</sup>	33.3 <sup>f</sup>	0.0 <sup>f</sup>
Poly(tBMA)	-	91	80.0 <sup>g</sup>	20.0 <sup>g</sup>	0.0 <sup>g</sup>

<sup>a</sup> A: the as-cast film was annealed at  $80^\circ\text{C}$  for 2 h under vacuum. B: the annealed film was soaked in water at room temperature for 30 min and air-dried. C: the annealed film was soaked in water at  $80^\circ\text{C}$  for 30 min and air-dried. D: the soaked film was again annealed at  $80^\circ\text{C}$  for 2 h under vacuum. <sup>b</sup> Contact angle of a water droplet on the polymer film. <sup>c</sup> Atomic percent was obtained at  $10^\circ$  takeoff angle and the value in parentheses was obtained at  $80^\circ$  takeoff angle. <sup>d</sup> The film was cast from a polymer solution of THF/MeOH (5/1 = v/v). <sup>e</sup> Calculated value for poly(2). <sup>f</sup> Calculated value for poly(HEMA). <sup>g</sup> Calculated value for poly(tBMA).

drastically decreased to be 1.1% meaning the disappearance of the poly(2) segment from the top surface. It is suggested from the atomic percent of carbon and oxygen that the concentration of poly(HEMA) segment occurs at the surface under the wet condition. Not only an aqueous environment but also high temperature are required for the effective restructuring of the triblock copolymer surface. By annealing the hydrated film under the dry condition (condition D), the poly(2) segment having low surface energy again reverts to the outermost surface. The similar surface restructuring in response to the environmental change was also observed for the films of H-F-T and T-H-F type triblock copolymers.

These surface dynamics can be well followed by the results on the contact angle of water droplet on the polymer films, as shown in Table IV. The H-T-F triblock copolymer film under condition A showed a contact angle of 106 degree. This is a little bit lower than the contact angle on the poly(2) film (111 degree), but shows that the top-surface of the film consists mostly of poly(2) under condition A. By soaking in water at room temperature (condition B) and at  $80^\circ\text{C}$  (condition C), the contact angles decreased to 98 and 53 degrees, indicating that the hydrophobic surface changed to the hydrophilic one under the wet condition at the elevated temperature. After annealing again in vacuo, the contact angle returned to 107 degree due to the reversion to hydrophobic surface. These results of the contact angle measurement for the H-T-F film exactly correspond to those of XPS measurement described above. The other triblock copolymers also showed the similar behaviors in the contact angle measurement.

Comparing with the XPS data and the corresponding contact angles in more detail, interesting tendency has been found. The H-F-T triblock copolymer film showed

relatively lower contact angle around 80 degree even under the dry conditions. This is also supported by the lower fluorine atomic percent under the dry conditions of H-F-T film. We now consider that the film surface is not completely covered with the poly(2) segment of H-F-T triblock copolymer, because such enrichment of the central block is to some extent restricted by the foreign terminal segments from the geometrical requirement. The similar situation is observed in the case of the T-H-F triblock copolymer under the wet condition. The surface concentration of the central hydrophilic poly(HEMA) segment is partially prevented, resulting in the relatively high contact angle (59 degree) and higher fluorine atomic percent even under the wet conditions. Depth profile of fluorine atom (15.4% at 80° takeoff angle) suggests that the poly(2) segment is located in the shallow wet surface of the T-H-F film. In the case of H-T-F copolymer, the most hydrophobic poly(2) and most hydrophilic poly(HEMA) segments attached to the both terminals induce the ideal surface enrichment under dry and wet conditions, respectively, as was typically observed for the hydrophilic/hydrophobic diblock copolymers.

## EXPERIMENTAL

### Anionic Polymerization

A series of three ABC triblock copolymers were synthesized by the sequential anionic polymerization of 2, HEMA-TMS, and tBMA in THF at -78 °C with 1,1-diphenyl-3-methylpentyllithium/LiCl by changing the additional order of the comonomers. The polymerization of 2, HEMA-TMS, and tBMA was respectively carried out for 10, 10, and 120 min to attain the complete conversion of the monomers.

### Measurements

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker DPX300. SEC were obtained in THF (1.0 mL min<sup>-1</sup>) at 40 °C with a TOSOH HLC-8020 (TOSOH G5000H<sub>XL</sub>, G4000H<sub>XL</sub>, and G3000H<sub>XL</sub>). The polymer films for contact angle and XPS measurements were prepared by centrifugal casting (4000 rpm, 20 s) of the triblock copolymer solutions (3wt% in THF/MeOH = 5/1, v/v) onto a glass disk. Contact angle of the polymer film was measured with a Kyowa Interface Science CA-A contact angle meter. Contact angle measurements were carried out within 30 s after placing a water droplet on the polymer film surface and repeated at least 10 times on the other positions of the same specimen. XPS measurement was performed by a Perkin-Elmer 5500 MT X-ray photoelectron spectrometer with a monochromatic Al K $\alpha$  X-ray source. A series of takeoff angles of 10 and 80 ° were measured.

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