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Effects of High Side Chain Densities of Hydrophobic Poly(substituted methylene)s on Surface Free Energies

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ABSTRACT

All the carbon atoms in main chains of poly(substituted methylene) possess side chains. The densities and chemical structure of the side chains drastically change the polymers' thermal, mechanical and surface properties. Herein, we focused on the surface properties and structures of poly(substituted methylene)s with hydrophobic side chains of ethyl and perfluoroalkyl groups and evaluated the effects of their side chain densities. The surface free energies of poly(substituted methylene) with ethyl groups, C1-PEA, was lower than that of poly(ethyl acrylate) because the high density of side chains in C1-PEA decreased its chain mobility and the dispersion component of surface free energy was also suppressed. The surface free energy of poly(substituted methylene) with perfluoroalkyl groups including only six carbon atoms in the fluoroalkyl groups, C1-PF, achieved less than 10 mJ/m^2. In addition, the surface segregation of perfluoroalkyl groups in *block-like* copolymer and its more hydrophobic properties were observed, compared with its *random* copolymer. C1-PEA showed the dependence of the surface free energy and structure on the preparation methods. It is revealed that the high-dense side chains provided the restriction of molecular chains and more hydrophobic surface properties.

Introduction

Conventional vinyl polymers were widely accepted as food package contents, frame works of vehicles, inside components and paints in buildings, and so on. These polymers are synthesized from vinyl monomers, where one side chain was possessed every two carbon atoms in their main chains. Therefore, the main chains of conventional vinyl polymers were alternately composed of flexible CH_2 units and side chain units. In addition, the polar or rigid functional groups in side chains and the steric hinderance of the side chains decided their glass temperature, thermal properties, mechanical properties, and optical indexes of vinyl polymer. The densities of the side chains have large effects on main chain behaviors and gyration radii of the polymer. However, the side chain densities were up to 50% in conventional vinyl polymers. This upper limit of the side chain densities restricts the control of the polymer chain behaviors. In contrast, the polymers with side chains in every carbon atom of the main chains were designed and attempted to be synthesized. Although several polymers with side chains in every carbon atom of the main chains were synthesized, their molecular weights were insufficient or the chemical structures of monomers were restricted.[1–3] Recently, the development of organo transition metallic catalysts provided the synthesis of polymers with side chains in every carbon atom of the main chains, "poly(substituted methylene)".[4–8] Bruin and co-authors reported on the synthesis of *syndiotactic* poly(substituted methylene) with high molecular weight, more than 100k.[4,5,7] Ihara and others also achieved to the control of stereoregularity of poly(substituted methylene) and the syntheses of poly(substituted methylene) with various functional side chains with palladium catalysts.[9–11] Furthermore, various functional groups were introduced to the side chains of poly(substituted methylene)s and the functional properties based on their side chains with high density were revealed.[5,7,12–16]

Surface properties of the polymers, which attract much attention in the fields of biomaterials, painting, adhesion, anti-fouling and others, receive large effects from the polar groups in their chemical structure as well as the molecular dynamics of polymer chains at the surface. The surface properties are evaluated through their surface free energies. Moreover, the surface free energy is separated into the polar component and dispersion component, γ^p and γ^d, respectively.[17] The polar component γ^p depends on the polarity of the functional groups of polymers, whereas the dispersion component γ^d is attributed to van der Waals (dispersion) interaction as well as molecular dynamics at the surface. For examples, the perfluoroalkyl groups well-aligned at the surface possessed the "lowest" surface free energy[18–24] but the surface free energy was increased when the assembly structure of the perfluoroalkyl groups were disordered even slightly.[25–28] In polyacrylate with alkyl or perfluoroalkyl side chain, the surface of the polymer with longer side chains was more hydrophobic than that with shorter side chains. This reason was not only the larger fraction of hydrophobic segments but also the tightly packing and prevention of bending of the longer alkyl or perfluoroalkyl side chains by their self-assembly, compared with shorter ones[26–28] In this way, the surface properties have been also controlled by the side chain of the polymers.

Herein, we focused on the surface properties of poly(substituted methylene)s with alkyl and perfluoroalkyl side chains and their dependence on their side chain densities and the preparation methods. In addition, we synthesized *block-like* poly(substituted methylene) copolymer with perfluoroalkyl side chains and evaluated the effect of surface segregation of perfluoroalkyl side chain segments on their hydrophobic properties.

Experimental

Materials

All the chemicals for syntheses and measurements were purchased from chemical companies. Their purchased chemicals were used without any further purification. Deionized water was obtained with Elix Essential UV3 (merck Millipore Co. Ltd.). Rhodium catalyst [(*L*-prolinate)Rh(I)(1,5-dimethyl-1,5-cyclooctadiene)] for synthesis of poly(substituted methylene) was synthesized in the same methods as the reported literature.[5]

Synthesis of polymer C1-PEA

The polymerization for synthesis of C1-PEA was performed in the reported methods.[4,5] [(*L*-prolinate)Rh(I)(1,5-dimethyl-1,5-cyclooctadiene)] 200 mg (0.60 mmol) as a catalyst was added into ethyl diazoacetate 3.27 g (25.0 mmol, including 13 wt% dichrolomethane) and chloroform 60 mL under nitrogen atmosphere. After the solution was stirred at room temperature for 14 h, the solvent was removed with evaporation and the crude was obtained. After the crude was solved into chloroform, the solution was poured into methanol. The yellowish white powder 0.67 g was obtained as 31% yield through three times of centrifugation at 7000 rpm and 10 °C and vacuum drying. The obtained NMR spectra of C1-PEA corresponded to the literature.[4,5]

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ(ppm)= 4.27-3.95 (br, 2H, CH_2), 3.38-3.12 (br, 1H, C*H*), 1.43-1.22 (br, 3H, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$, 298 K): δ(ppm)= 170.9, 60.7, 45.5, 14.1 M_n = 160,000, M_w = 330,000, M_w /M_n = 2.1.

Synthesis of 2-perfluorohexylethyl diazoacetate monomer (1)

Into 50 mL of acetonitrile, 1*H*,1*H*,2*H*,2*H*-perfluoro-1-octanol 800 mg (2.20 mmol), and sodium hydrogen carbonate 527 mg (6.59 mmol) was added under nitrogen atmosphere and bromoacetyl bromide 886 mg (4.39 mmol) was dropped into the solution after cooled down in an ice bath. After stirring the solution at room temperature for 3 h, the reaction was quenched by adding of 50 mL

water. Then, washed with brine and evaporated to remove solvent, the crude was purified by silica gel column chromatography (hexane/chloroform = 2 : 1) to give a white solid (691 mg).

Followed by the above procedure, the obtained white solid, *N*,*N*′-bis(*p*-toluenesulfonyl) hydrazine 1.12 g (3.29 mmol), and 1,8-diazabicyclo[5.4.0]-7-undecene 667 mg (4.39 mmol) were added into tetrahydrofuran (THF) 50 mL at 0 °C. After 2 h stirring at room temperature, the solution was washed with saturated sodium hydrogen carbonate aqueous solution and brine. The crude was obtained by evaporation of solvent and was purified with neutralized silica gel column chromatography (hexane/chloroform = 2 : 1) to give a yellow liquid (359 mg, 37%). The obtained NMR spectra of monomer **1** corresponded to the literature.[29]

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ(ppm)= 4.77 (s, 1H, C*H*), 4.46 (t, 2H, J =6.4 Hz, O-CH_2-CH_2), 2.56-2.40 (m, 2H, CH_2-CH_2-CF_2). ^{19}F NMR (375 MHz, $CDCl_3$ including C_6F_6 as a standard, 298K): δ(ppm)= -82.1 (s, 3F), -114.9 (s, 2F), -123.2 (s, 2F), -124.2 (s, 2F), -125.3 (s, 2F), -127.3 (s, 2F). HRMS $[M+H]^+$ (DART-ESI$^+$): *m/z* 433.0872.

Synthesis of polymer C1-PF

[(*L*-prolinate)Rh(I)(1,5-dimethyl-1,5-cyclooctadiene)] 7.55 mg (0.02 mmol) as a catalyst was added into monomer **1** 500 mg (1.16 mmol) and chloroform 50 mL under nitrogen atmosphere. After the solution was stirred at room temperature for 14 h, the solvent was removed with evaporation and the crude was obtained. After the crude was solved into trifluoroacetic acid, the solution was poured into methanol. The white powder 230 mg was obtained as 48% yield through three times of centrifugation at 7000 rpm and 10 °C and vacuum drying.

^{1}H NMR (400 MHz, TFA-*d*, 298 K): δ(ppm)= 5.15-4.82 (br, 2H, O-CH_2-CH_2), 4.14-3.82 (br, 1H, CH), 3.18-2.95 (br, 3H, CH_2-CH_2-CF_2). ^{19}F NMR (375 MHz, TFA-*d* including C_6F_6 as a

standard, 333K): δ(ppm)= -80.1 (s, 3F), -111.5 (s, 2F), -119.7 (s, 2F), -120.8 (s, 2F), -121.4 (s, 2F), -124.4 (s, 2F).

Synthesis of polymer C2-PEA

Ethyl acrylate 200 mg (1.99 mmol) as a monomer, and 2,2'-azobis(isobutyronitrile) (AIBN) 2 mg (0.01 mmol) as an initiator were added into THF 50 mL, and the solution was stirred at 70 °C for 24 h. the crude was obtained with evaporation to remove solvent. After the crude was solved into acetone, the solution was poured into deionized water. The white powder 86 mg was obtained as 43% yield through three times centrifugation at 7000 rpm and 10 °C and vacuum drying.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ(ppm)= 4.16-3.99 (br, 2H, O-C*H*$_2$-CH_3), 2.38-2.22 (br, 2H, CH-C*H*$_2$-CH), 1.98-1.36 (br, 1H, CH_2-C*H*-CH_2), 1.31-1.18 (br, 3H, C*H*$_3$). M_n = 36,000, M_w = 106,000, M_w /M_n = 2.9.

Synthesis of polymer C2-PF

Into 50 mL of THF, 1*H*,1*H*,2*H*,2*H*-perfluorooctyl acrylate 250 mg (0.60 mmol) as a monomer, and AIBN 2 mg (0.01 mmol) as an initiator were added, and the solution was stirred at 70 °C for 24 h. the crude was obtained with evaporation to remove solvent. After the crude was solved into chloroform, the solution was poured into methanol. The white powder 83 mg was obtained as 33% yield through three times centrifugation at 7000 rpm and 10 °C and vacuum drying.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ(ppm)= 4.42-4.19 (br, 2H, O-C*H*$_2$-CH_2), 2.57-2.23 (br, 3H, CH_2-C*H*-CH_2, CH_2-C*H*$_2$-CF_2), 2.18-1.34 (br, 2H, CH-C*H*$_2$-CH). ^{19}F NMR (375 MHz, $CDCl_3$ including C_6F_6 as a standard, 298K): δ(ppm)= -82.3 (s, 3F), -115.2 (s, 2F), -123.4 (s, 2F), -124.4 (s, 2F), -125.1 (s, 2F), -127.7 (s, 2F). M_n = 19,000, M_w = 60,000, M_w /M_n = 2.9.

Synthesis of *random* copolymer C1-PEA-*r*-PF

Into 50 mL of chloroform, ethyl diazoacetate 482 mg (3.68 mmol, including 13 wt% dichrolomethane), 2-perfluorohexylethyl diazoacetate 120 mg (0.37 mmol) and [(*L*-prolinate)Rh(I)(1,5-dimethyl-1,5-cyclooctadiene)] 30 mg (0.08 mmol) were added under nitrogen atmosphere. After the solution was stirred at room temperature for 14 h, the solvent was removed with evaporation and the crude was obtained. After the crude was solved into chloroform, the solution was poured into methanol. The white powder 361 mg was obtained as 68% yield through three times centrifugation at 7000 rpm and 10 °C and vacuum drying.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ(ppm)= 4.35-3.91 (br, 1.97H, O-CH_2-CH_2, O-CH_2-CH_3), 3.32-2.92 (br, 1H, CH-C*H*-CH), 2.61-2.40 (br, 0.29H, CH_2-CH_2-CF_2), 1.26-1.14 (br, 2.61H, O-CH_2-CH_3). ^{13}C NMR (150 MHz, $CDCl_3$, 298 K): δ(ppm)= 170.8, 169.7, 118.7, 115.8, 113.1, 111.1, 108.4, 69.1, 60.8, 56.8, 45.4, 30.1, 16.7, 13.8. ^{19}F NMR (375 MHz, $CDCl_3$ including C_6F_6 as a standard, 298K): δ(ppm)= -82.3 (s, 3F), -115.1 (s, 2F), -123.4 (s, 2F), -124.3 (s, 2F), -124.8 (s, 2F), -127.6 (s, 2F). M_n = 100,000, M_w = 170,000, M_w /M_n = 1.7.

Synthesis of *block-like* copolymer C1-PEA-*bl*-PF

Into 50 mL of chloroform including ethyl diazoacetate 482 mg (3.68 mmol, including 13 wt% dichrolomethane), [(*L*-prolinate)Rh(I)(1,5-dimethyl-1,5-cyclooctadiene)] 30 mg (0.08 mmol) as a catalyst was added under nitrogen atmosphere. After the solution was stirred at room temperature for 4 h, 2-perfluorohexylethyl diazoacetate 215 mg (0.48 mmol) was added into the solution. When the solution was stirred for another 10 h, the solvent was removed with evaporation and the crude was obtained. After the crude was solved into trifluoroacetic acid, the solution was poured into methanol. The white powder 343 mg was obtained as 63% yield through three times centrifugation at 7000 rpm and 10 °C and vacuum drying.

^{1}H NMR (400 MHz, TFA-*d*, 298 K): δ(ppm)= 4.92-3.85 (br, 1.99H, O-C*H*$_2$-CH$_2$, O-C*H*$_2$-CH$_3$), 3.62-2.95 (br, 1H, CH-C*H*-CH), 2.68-2.35 (br, 0.24H, CH$_2$-C*H*$_2$-CF$_2$), 1.69-1.02 (br, 2.73H, O-CH$_2$-C*H*$_3$). ^{13}C NMR (150 MHz, CDCl$_3$, 298 K): δ(ppm)= 172.8, 171.9, 172.8, 149.5, 147.3, 139.4, 125.7, 124.1, 118.0, 111.9, 111.5, 111.2, 63.6, 58.5, 46.5, 34.8, 34.3, 33.9, 31.8, 30.2, 29.7, 29.5, 29.2, 28.9, 24.7, 22.4, 18.9, 12.8. ^{19}F NMR (375 MHz, TFA-*d*, 298K): δ(ppm)= -80.9 (s, 3F), -112.8 (s, 2F), -120.9 (s, 2F), -122.0 (s, 2F), -122.6 (s, 2F), -125.6 (s, 2F).

Preparation of cast films of the synthesized polymers

To evaluate the surface properties of the synthesized polymers, the films were prepared on silicon wafers using the casting methods. Solutions of the obtained polymers with 0.5 wt% concentration were prepared. The combinations of the polymers and solvents were summarized in Table S1 in the Supplemental Material. The polymer solutions were dropped on the 30 mm × 30 mm squared silicon wafers and dried slowly under saturated vapor pressure of the solvents.

For investigation of the dependence of the surface on the preparation methods, C1-PEA films were prepared using the melt-press method and spin-coating method.

In the melt-press method, C1-PEA powder was pressed at 150 °C under 5 MPa and quenched into the ice-water bath. Then, the obtained film was annealed at 90 °C. The self-standing C1-PEA film was obtained with 170 μm thickness.

Thin film of C1-PEA on a silicon wafer was prepared from 0.5 wt% C1-PEA in chloroform solution through spin-coating at 3000 rpm for 40 s, and then annealed at 90 °C.

Nuclear Magnetic Resonance (NMR) measurements

^{1}H, ^{13}C and ^{19}F NMR measurements of the obtained polymers were performed with NMR spectrometer (JEOL Ltd., JNS ECZS). NMR samples were prepared in CDCl$_3$ or CD$_3$COOD. The frequencies of ^{1}H, ^{13}C, and ^{19}F NMR measurements were 400 MHz, 150 MHz, and 375 MHz.

High-resolution mass spectrometer (HRMS) measurements

HRMS were measured by JEOL JMS-T100LP AccuTOF LC-Plus (ESI) with a JEOL MS-5414DART attachment.

Molecular weight measurements

Gel permeation chromatography (GPC) measurements of the synthesized polymers C1-PEA, C2-PEA, C2-PF, and C1-PEA-*r*-PF, were performed with Prominence CBM-20Alite (Simadzu Co. Ltd.) using a RI detector RID-20A (Simadzu Co. Ltd.). The eluent solvent was chloroform, the columns were HXR-H and TSK-gel GMHHR-M (Tosoh Co. Ltd.) and polystyrenes were used as standards.

Measurements of differential scanning calorimetry (DSC)

Melting temperatures (T_m) of the synthesized polymers were measured by DSC. DSC profiles were recorded on Rigaku DSC8230 with the sample weight of 5 mg, the scan rate of 10 °C/min under dried N_2.

Measurements of surface roughness of the prepared films

Atomic force microscopic measurements of the prepared films on silicon wafers were performed with Nano Navi II E-sweep (SII Co. Ltd.) with a dynamic force mode. SI-DF20 (SII Co. Ltd.) with 15 N/m of spring constant and 10 nm of tip radius was employed as a cantilever. The surface roughness was presented by the root-mean-square (RMS) values as follows;

$$\mathrm{RMS(nm)} = \sqrt{\frac{1}{X_{max}Y_{max}}\int_0^{Y_{max}}\int_0^{X_{max}}\{F(X,Y)-Z_0\}^2 dXdY}$$

where X_{max}, Y_{max} were 20 μm, F(X,Y) was height at the pixel (X,Y) and Z_0 is the average of the height.

Measurements of dynamic contact angles and surface free energies

For the evaluation of surface properties of the synthesized polymers, advancing and receding contact angles (θ_a and θ_r) of water and methylene iodide droplets on surface of the prepared polymer films were observed with optical microscopy OL-35 (HIROX). The measurements of dynamic contact angles were performed within 10 seconds, and the diameters of droplets on the polymer thin films were less than 1 mm. From their dynamic contact angles, the averaged contact angles θ were calculated as follows;

$$\cos\theta_{av} = \frac{\cos\theta_a + \cos\theta_r}{2}$$

In addition, $\Delta\theta$ was the hysteresis between advancing and receding contact angles.

Surface free energies γ_S of their polymers were calculated using the following Young-Owens equation.[17,30]

$$\frac{(1+\cos\theta)\gamma_L}{2} = \sqrt{{\gamma_S}^d {\gamma_L}^d} + \sqrt{{\gamma_S}^p {\gamma_L}^p}$$

$$\gamma_X = {\gamma_X}^d + {\gamma_X}^p$$

(X = S or L)

where γ_L was surface free energies of droplet liquid, and ${\gamma_X}^d$ and ${\gamma_X}^p$ were dispersion and polar components of the surface free energies of substrate polymer (X = S) or liquid solvent (X = L). In addition, ${\gamma_L}^d$ and ${\gamma_L}^p$ of water and methylene iodide were ${\gamma_{water}}^d$ = 21.8 mJ/m^2 and ${\gamma_{water}}^p$ = 51.8 mJ/m^2, and ${\gamma_{CH2I2}}^d$ = 48.5 mJ/m^2 and ${\gamma_{CH2I2}}^p$ = 2.3 mJ/m^2, respectively.[17,31]

X-ray diffraction measurements

For the investigation of structure of C1-PEA prepared in various methods, small angle incidence X-ray diffraction measurements were performed with SmartLab (Rigaku Co.) with 30 mA and 40 kV. The CuKα X-ray beam (wavelength of 1.5418 Å) was irradiated on the surface with the incident angle of 0.20°, which is larger than the critical angle (α_c = 0.143°) of C1-PEA. The

detector of X-ray beam was a scintillation counter. The detector scanned in the out-of-plane direction. The small angle incidence X-ray diffraction measurements were performed with larger incident angle of X-ray beam than the critical angle. Therefore, the bulk structures of the casting films were investigated with large footprints.

Results and discussion

The chemical structures of the synthesized polymers were shown in Figure 1. C1-PEA was synthesized from ethyl diazoacetate with rhodium catalyst in the method reported by Bruin and co-workers.[4,5,7] The number-averaged molecular weight M_n of the obtained C1-PEA was more than 150k, which was sufficient for the evaluation of the surface properties as a thin film. In addition, its NMR chart also corresponded to the reported one. In ^{1}H NMR spectrum, the single peak originated from proton of methine groups in the main chain suggested that the synthesized C1-PEA possessed highly syndiotactic stereoregularity.[4,5,13,14,16] C1-PF was also synthesized in the similar method to one of C1-PEA. In the NMR chart of C1-PF, the broaden peaks originated from the polymer were observed. C1-PF also was highly syndiotactic because of the single peak of proton of methine groups in the main chain in ^{1}H NMR spectrum.[16] Unfortunately, C1-PF was insoluble in chloroform and THF which were conventional solvents for GPC measurements. Therefore, the molecular weight of C1-PF was unrevealed. However, smooth thin films for the evaluation of surface properties were prepared from the synthesized C1-PF. In order to compare their surface properties from the viewpoint of side chain densities, C2-PEA and C2-PF were synthesized through free-radical polymerization. These obtained C2 polymers were characterized with NMR and GPC measurements.

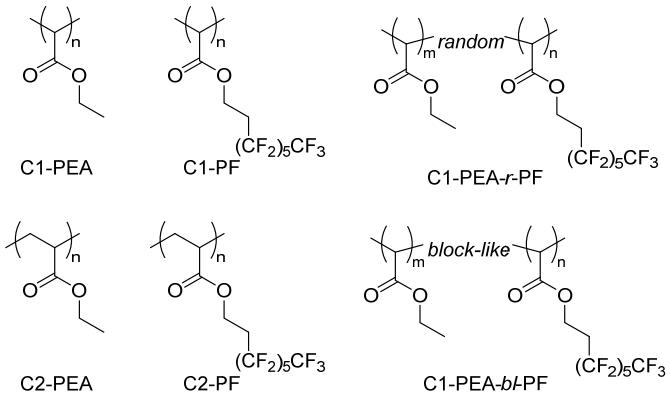

Figure 1. Chemical structures of the synthesized polymers C1-PEA, C1-PF, C2-PEA, C2-PF, C1-PEA-*r*-PF, and C1-PEA-*bl*-PF.

Copolymers of C1-PEA and C1-PF were also synthesized, and random copolymer C1-PEA-*r*-PF and *block-like* copolymer C1-PEA-*bl*-PF were obtained. The molar fraction ratios of PF units in the copolymers C1-PEA-*r*-PF and C1-PEA-*bl*-PF were 15 mol% and 12 mol% from their ^{1}H NMR charts, respectively. The weight-averaged molecular weight M_w of the obtained C1-PEA-*r*-PF was calculated from its GPC measurement but the molecular weight of C1-PEA-*bl*-PF was unavailable because of low solubility into conventional GPC solvents such as chloroform and THF. For the investigation of the distribution of component fractions, the molecular weights of C1-PEA-*r*-PF and C1-PEA-*bl*-PF, the amounts of unreacted perfluoroalkyl monomer **1** in solution and the fraction ratio of the perfluorooctyl units in the copolymers were traced under polymerization, using the peaks of methine groups in monomer **1** at 4.77 ppm. The results were shown in Figures S9-S12 in Supplemental Material. The random polymerization of C1-PEA-*r*-PF was progressed using the mixture solution of ethyl diazoacetate monomer and perfluorooctyl diazoacetate monomer **1**. In the first of polymerization, the molar fraction ratio of the perfluorooctyl units in C1-PEA-*r*-PF was lower than 5 mol%, but until 4 hours polymerization, the fraction ratio of the perfluorooctyl

units achieved to around 0.09 and was slightly increased after 4 hours polymerization. The change of weight-averaged molecular weight M_w was saturated after 4 hours polymerization. The decrease of monomer **1** in reaction solution corresponded to the change of M_w and the molar fraction ratio of monomer **1** in C1-PEA-*r*-PF. In the polymerization of C1-PEA-*bl*-PF, 4 hours after polymerization of only ethyl diazoacetate monomer, perfluorooctyl diazoacetate monomer **1** was added into the reaction solution. After addition of perfluorooctyl diazoacetate monomer, the molar fraction ratio of monomer **1** in C1-PEA-*bl*-PF and this molecular weight were increased gradually. Thus, it is concluded that the "*block-like*" copolymer C1-PEA-*bl*-PF was obtained.

In the DCS thermograms, C2-PEA show only glass transition temperature at -23 °C, whereas C1-PEA possessed melting temperature at 122 °C. The melting temperature of C2-PF was observed at -15°C, which corresponded to the melting of side chain. The melting temperature of C1-PF was at 77 °C. In addition, both the synthesized copolymers, C1-PEA-*r*-PF and C1-PEA-*bl*-PF showed the two endothermic peaks. The two peaks of C1-PEA-*r*-PF at 70 °C and 104 °C broadened, while those of C1-PEA-*bl*-PF were observed at 49 °C and 114 °C more clearly than C1-PEA-*r*-PF. These results supported that C1-PEA-*bl*-PF possessed *block-like* seguments.

Before the evaluation of surface properties, the roughness of the films prepared in the casting method was investigated with AFM measurements as shown in Table S2 in the Supplemental Material. The roughness of all the prepared thin films was less than 160 nm enough to evaluate their surface properties.

Figure 2 shows water droplets on the thin films of the synthesized polymers and their static contact angles. The hydrophobicity of C1-PEA with a larger contact angle was increased relative to C2-PEA. In addition, C1-PF also showed a larger contact angle 114° and more hydrophobic property, compared with C2-PF. These results suggested that the restriction of molecular chain

dynamics with high-dense hydrophobic side chains of poly(substituted methylene)s provided more hydrophobicity to their surface. In the case of copolymers of poly(substituted methylene)s, *block-like* copolymer C1-PEA-*bl*-PF showed a larger contact angle than *random* copolymer C1-PEA-*r*-PF.

To investigate the surface properties of the synthesized poly(substituted methylene)s, the measurements of their dynamic contact angles and the evaluation of their surface free energies were performed. Table 1 and Table S1 in the Supplemental Material shows dynamic contact angles of water and diiodomethane droplets on their thin films and the calculated surface free energies of the synthesized polymers. C1-PEA possessed larger contact angles of both the water and diiodomethane droplets and lower surface free energies, relative to C2-PEA. The polar component of C1-PEA was similar to that of C2-PEA, while the dispersion component of C1-PEA was lower than that of C2-PEA. This reason is that the C1-PEA possessed the same ester groups as the C2-PEA, while the side chains of C1-PEA restricted polymer chain dynamics.

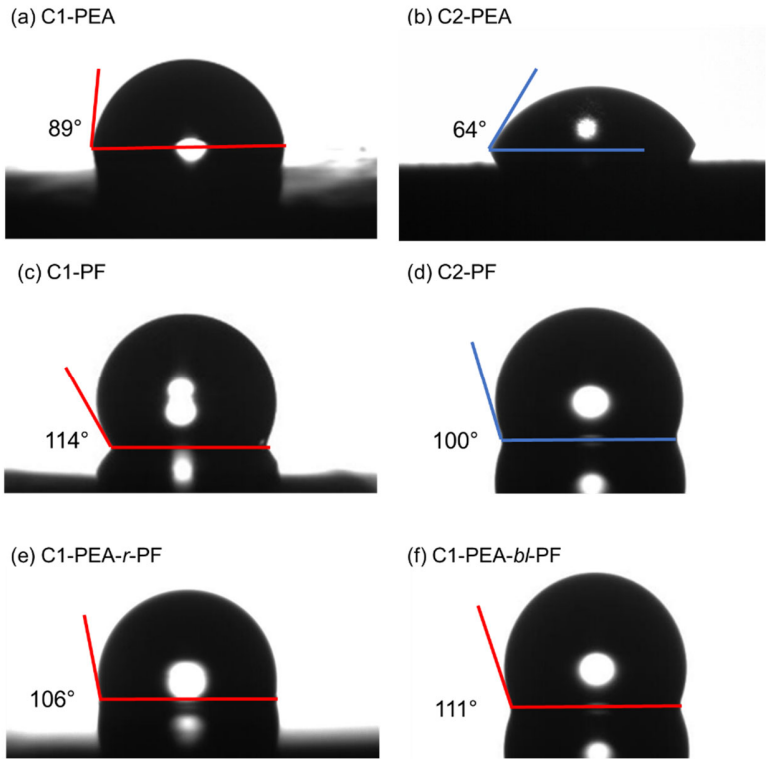

Figure 2. Static contact angles of water droplets on the synthesized polymers.

Table 1. Surface free energies γ, dispersion (γ^d), and polar (γ^p) components of the synthesized polymers.

	Surface free energy		
	γ	γ^d	γ^p
	mJ/m^2		
C1-PEA	28.2	24.6	3.6
C2-PEA	37.9	32.7	5.2
C1-PF	9.0	7.9	1.1
C2-PF	15.4	13.4	2.0
C1-PEA-*r*-PF	20.7	14.4	6.4
C1-PEA-*bl*-PF	13.2	6.7	6.5

C1-PF possessed a low surface free energy, 9.0 mJ/m^2. In contrast, C2-PF showed 15.4 mJ/m^2, a larger surface free energy. In the C2-PF, this perfluoroalkyl side chains would buckle at the surface and some parts of perfluoroalkyl side chains would burrow inside the bulk because the number of carbon atoms in perfluoroalkyl side chains of C2-PF was less than 8.[27] Therefore, the surface free energies was larger than 10.0 mJ/m^2. The well-aligned perfluoroalkyl groups at the surface possessed lower surface free energies than 10.0 mJ/m^2.[25,26] Since C1-PF possesses high density of side chains, bending and burrowing of perfluoroalkyl side chains of C1-PF was prevented. Therefore, the perfluoroalkyl side chains of C1-PF effectively performed for the hydrophobic surface property, relative to C2-PF. This result was coincided to that of measurements of static contact angles.

The copolymers C1-PEA-*r*-PF and C1-PEA-*bl*-PF with the similar molar fraction ratios of ethyl side chain units and perfluoroalkyl side chain units possessed different surface free energies. The *block-like* copolymers C1-PEA-*bl*-PF showed lower surface energy 13.2 mJ/m^2, than 20.7 mJ/m^2 of the *random* copolymer C1-PEA-*r*-PF, as shown in Table 1. This reason is that perfluoroalkyl-rich segments in C1-PEA-*bl*-PF would be segregated at the surface of the films, whereas perfluoroalkyl side chain was homogeneously introduced into the polymer chains of C1-PEA-*r*-PF and the prepared films of C1-PEA-*r*-PF possessed structure without any local segregation. Actually, from the below the equation and their surface free energies, the apparent fraction ratios of the alkyl and perfluoroalkyl segmentsat the film surface of C1-PEA-*r*-PF and C1-PEA-*bl*-PF, $X_{C1\text{-}PEA}$ and $X_{C1\text{-}PF}$, were estimated.

$$\gamma_Y = \gamma_{C1\text{-}PEA} \times X_{C1\text{-}PEA} + \gamma_{C1\text{-}PF} \times X_{C1\text{-}PF} \quad (Y : \text{C1-PEA-}r\text{-PF or C1-PEA-}bl\text{-PF})$$

$$X_{C1\text{-}PEA} + X_{C1\text{-}PF} = 1$$

where γ_Y was the surface free energy of the copolymer, and $\gamma_{C1\text{-}PEA/C1\text{-}PF}$ was the surface free energy of C1-PEA or C1-PF, 28.2 mJ/m^2 and 9.0 mJ/m^2, respectively. The values of $X_{C1\text{-}PF}$ of C1-PEA-*r*-PF and C1-PEA-*bl*-PF were 0.39 and 0.78, respectively. These results suggested that larger fraction of the perfluoroalkyl chains in C1-PEA-*bl*-PF would segregate at the surface, compared to C1-PEA-*r*-PF.[23,24,28,32,33]

We investigated on the dependence of structure in C1-PEA films on their surface free energies. We prepared C1-PEA films in casting, melt-pressing, and spin-coating methods. Their structures evaluated with small-angle incidence X-ray diffraction. In the X-ray diffraction profiles of all the C1-PEA films in Figure 3, the diffraction peaks were observed at around 9°. The diffraction peaks at around 9° would be originated from intermolecular distances between polymer main chains. This result means that C1-PEA polymer chains in these films possessed periodic structures aligned in the parallel direction to the film surface. Moreover, the diffraction of intermolecular distances was shifted to the lower angle sides in the order of spin-coating, melt-pressing and casting films and another peak was also observed at around 7° in C1-PEA films prepared in the casting method. These results suggested that, because the casting film possessed most thermodynamically stable states relative to the others, another periodic structure with larger intermolecular distance would be formed in the casted film. In the X-ray diffraction profiles of C1-PF, no diffraction peak observed, as shown in Figure S17 in Supplemental Material. From the endothermic peak in the DCS measurements and no diffraction peak in X-ray diffraction profile, it is suggested that the periodic structure of C1-PF would be slightly disordered.

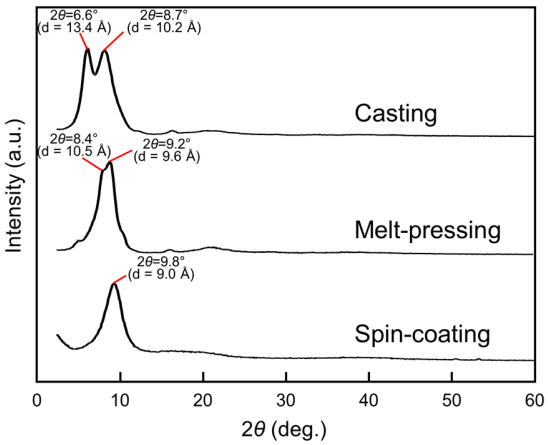

Figure 3. Small angle incidence X-ray diffraction profiles of C1-PEA films prepared in casting, melt-pressing and spin-coating methods.

Table 2. Surface free energies γ, dispersion (γ^d), and polar (γ^p) components of C1-PEA films prepared in casting, melt-pressing and spin-coating methods.

	Surface free energy		
	γ	γ^d	γ^p
	mJ/m^2		
casting	28.2	24.6	3.6
melt-pressing	29.6	24.1	5.4
spin-coating	30.9	25.7	5.2

In addition, the hydrophobicities of C1-PEA films were increased and these surface free energies were decreased in the order of films prepared with spin-coating, melt-pressing and casting, as shown in Table 2. This reason is that the surface of C1-PEA film in the casting would be most stable and the disordered structure of polymer chains at this surface would be decreased. They corresponded to the difference in crystalline structures between their prepared films. These

structural difference and would be provided by the rigid polymer structure of C1-PEA with high dense side chains.

The X-ray diffraction profiles of copolymers were shown in Figure 4. The diffraction peaks originated from crystalline structure of C1-PEA were observed at around 9° in the both profiles of C1-PEA-*r*-PF and C1-PEA-*bl*-PF, but C1-PEA-*bl*-PF, not C1-PEA-*r*-PF, possessed extra diffraction peak at lower angle 8.7°. In addition, the X-ray profiles of C1-PEA-*r*-PF and C1-PEA-*bl*-PF resembled those of C1-PEA prepared in spin-coating and melt-pressing methods, respectively. These results mean that the effective surface segregation of the PF segments of C1-PEA-*bl*-PF led to the lower surface energy of C1-PEA-*bl*-PF, relative to C1-PEA-*r*-PF.[23,24,28,32,33] Moreover, the intermolecular chain distances of both the copolymers were decreased relative to C1-PEA. This means that only the PEA segments in these copolymers might aggregate partially.

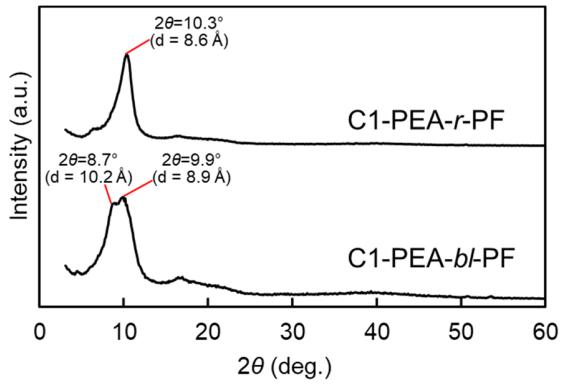

Figure 4. Small angle incidence X-ray diffraction profiles of C1-PEA-*r*-PF and C1-PEA-*bl*-PF.

Conclusions

We focused on poly(substituted methylene), which possessed side chains with all the carbon atoms in the polymer main chain, and investigated on the dependence of surface properties on the densities of polymer side chain. C1-PEA with ethyl side chains showed lower surface energy than C2-PEA because of the restriction of polymer chain dynamics. The surface free energies of C1-PF including perfluoroalkyl $–(CF_2)_5CF_3$ side chains was 9.0 mJ/m^2, much lower than that of C2-PF. This reason is that the high side-chain-densities in C1-PF, not C2-PF, would provide the prevention of bending and burrowing of perfluoroalklyl side chains. In C1-PEA-*bl*-PF *block-like* copolymers, the more effective surface segregation of PF units and lower surface free energies were observed, relative to the *random* copolymers. In addition, it was revealed that the surface free energies and structures of C1-PEA films depended on the preparation methods of the films. The casting films of C1-PEA with thermodynamic stability possessed the lowest surface free energy in the C1-PEA films. We revealed that the high side-chain-densities of polymers have large impacts on the structure and the surface free energies.

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Notes

The authors declare no competing financial interest.

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