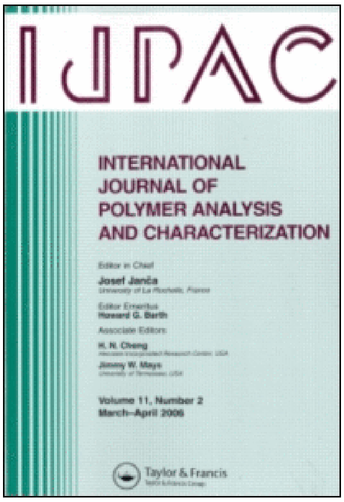

International Journal of Polymer Analysis and Characterization
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646643

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To cite this Article Isemura, T. , Sato, T. , Kawahara, K. and Otsuka, K.(2008) 'Determination of Chemical Composition Distribution and Molecular Weight Distribution of Poly(2-(perfluoroalkyl)ethyl acrylate-*co*-alkyl acrylate) by High Performance Liquid Chromatography and Size Exclusion Chromatography', International Journal of Polymer Analysis and Characterization, 13: 2, 119 — 135

To link to this Article: DOI: 10.1080/10236660801905718

URL: http://dx.doi.org/10.1080/10236660801905718

International Journal of Polymer Anal. Charact., 13: 119–135, 2008

ISSN: 1023-666X print
DOI: 10.1080/10236660801905718

Determination of Chemical Composition Distribution and Molecular Weight Distribution of Poly(2-(perfluoroalkyl)ethyl acrylate-*co*-alkyl acrylate) by High Performance Liquid Chromatography and Size Exclusion Chromatography

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Abstract: The molecular weight distribution (MWD) of poly(2-(perfluoroalkyl) ethyl acrylate-*co*-alkyl acrylate) can be determined by size exclusion chromatography (SEC) using an appropriate mobile phase such as a mixture of HCFC225 and THF; however, the chemical composition distribution (CCD) of the copolymer has not been elucidated. We developed an HPLC method for determining the CCD by using a silica-based column modified by polyfluorinated groups, a devised mobile phase gradient system, and an evaporative light scattering detector. In this system, polymers having perfluoroalkyl units are retained on the column through interaction between fluorinated groups and elute at longer retention times. It has become apparent that the copolymer has a broad and characteristic CCD of three components, consisting of fluorinated and non-fluorinated forms and their copolymer. Two-dimensional development of MWD and CCD of the copolymer, called cross-fractionation, is also examined and discussed.

Submitted 4 December 2007; accepted 9 January 2008.

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Keywords: 2-(Perfluoroalkyl)ethyl acrylate; Chemical composition distribution; Cross-fractionation; HCFC225; HPLC; Molecular weight distribution; SEC

INTRODUCTION

Polyacrylates having polyfluorinated groups in their side chains are widely used as protective coatings and surface modifiers in, among other uses, textile finishes, carpets, paper, and upholstery. In particular, copolymers of polyfluorinated acrylate, such as 2-(perfluoroalkyl)ethyl acrylate, and non-fluorinated alkyl acrylate and/or vinyl monomers, such as vinyl chloride, are in wide commercial use as coating agents with water-oil repellency. In industrial applications, relatively small amounts (1–5 mol%) of hydrophilic monomers having functional groups such as OH are used together with poly- and non-fluorinated monomers to improve practical performance, for example, durability, texture of the articles, and soil-release property during laundering.

Detailed characterization of these homo- and copolymers having perfluoroalkyl group has considerable importance for the R&D and manufacturing of such products or explaining their properties. The practical system used in industrial applications is complex. However, studies of such aspects as ordered structure of perfluoroalkyl chains on a film surface and its relationship with the chain length distribution, molecular weight distribution (MWD), and chemical composition distribution (CCD) help to understand the unique system.

In the case of homopolymers of polyfluorinated acrylates, surface structure such as degree of ordering has been investigated by X-ray analysis and calorimetry.[1] The number of CF_2 groups in the side chain of the polymer and the difference among acrylate, methacrylate, and α-fluoroacrylate plays an essential role in the water-oil repellency of the surface of its coating film. The repellency, evaluated by dynamic contact angle, is closely related to the crystallinity of fluoroalkyl chains and lamellar structure of fluorinated and non-fluorinated layers.[2–5] This ordered structure is formed through the intermolecular interaction among fluoroalkyl chains. On the other hand, in the case of copolymer, it is essential to consider CCD in order to understand the mechanism of water-oil repellency. It is more likely to form an ordered structure if the copolymer has a broader CCD or contains more fluoroalkyl-rich as well as non-fluoroalkyl-rich acrylate components.

In addition, the chain length of the perfluoroalkyl group and its distribution also affect the character of the polymer. In industrial applications, the group is prepared by a telomerization process based on tetrafluoroethylene addition, which brings about a group having a broad chain length distribution. In the case of 2-(perfluoroalkyl)ethyl acrylate, the carbon number of perfluoroalkyl group is required to be no less than 8 to develop a practical repellency.[4,5] Therefore, in general, the practical distribution of carbon number is set to 6–18, with 8–10 maximum to show the best performance.

Furthermore, the most common method to evaluate an MWD is by size exclusion chromatography (SEC). Tetrahydrofuran (THF) is the most frequently used solvent, provided the sample is completely soluble. As examples of its application to polyfluorinated polymers, two-dimensional gel permeation chromatography (2D-GPC) has been proposed to evaluate a sol-gel polymerization process of 1H,1H,2H,2H-perfluorooctyltriethoxysilane[6] and poly(ethylene oxide) and poly(perfluorohexylethyl methacrylate) containing triblock copolymers,[7] both employing THF as SEC mobile phase. However, it is often the case that polyfluorinated polymers are not soluble in non-fluorinated solvents. In that case, a popular fluorinated solvent is 1,1,2-trichloro-1,2,2-trifluoroethane (CFC113).[8,9] In the extreme case of perfluoropolymers, the range of applicable solvents is significantly restricted. As an example, perfluoro(2-butyltetrafluorofuran) is used for poly[perfluoro(4-vinyloxyl-1-butene)].[10] In addition, a mixed solvent containing 90% Vertrel XF (1,1,1,2,2,4,4,5,5-decafluoropentane) is used to analyze perfluoropolyethers,[11] and trifluoromethybenzene, hexa-fluorobenzene are used with fluorinated gels.[12] Recently, we proposed a superior solvent system using dichloropentafluoropropane (HCFC225).[13] One of the unique advantages of using HCFC225 is that polymethylmethacrylate (PMMA) is soluble in the solvent and commercial narrow polydispersity polymer standards can be employed for molecular weight calibration.

Meanwhile, recent advances in high-performance liquid chromatography (HPLC) and lively discussions allowed and generalized the evaluation of the CCD of various copolymers. CCD is usually evaluated by non-exclusion liquid chromatography (NELC), which is classified into several categories,[14] liquid adsorption chromatography (LAC), liquid precipitation chromatography (LPC), normal and reversed phase liquid chromatography (NPLC and RPLC), orthogonal chromatography (OC), and liquid chromatography at critical adsorption point (LC-CAP). Although these classifications of separation principles are in practice mixed and complex, copolymers can be separated by the combination of influences from both solubility and adsorption.[15]

Moreover, OC has been developed into cross-fractionation or two-dimensional chromatography,[16] that is, a combination of two separation systems of SEC and HPLC. For example, styrene-methylmethacrylate copolymer[17] and poly(styrene-vinyl acetate) block copolymers[18] have been fractionated by both SEC and LAC. LAC uses a silica gel column and chloroform/ethanol or a 1,2-dichloroethane (DCE)/ethanol gradient system. In a similar way, styrene-2-methoxyethyl methacrylate copolymer has been fractionated by SEC and subsequent gradient HPLC or LPC.[19] In this case, the initial mobile phase composition of the gradient HPLC is a non-solvent of the copolymer so it precipitates at the top of the column, followed by the elution by mixtures containing an increased percentage of a good solvent. The products of the grafting reaction of methyl methacrylate onto ethylene-propene-diene rubber (EPDM) have been characterized by SEC and gradient HPLC.[15] The researchers used an evaporative light scattering detector (ELSD) and showed the advantages of this detector for the gradient elution of polymers. LC-CAP[20,21] is an alternative choice for HPLC separation based on a combination of exclusion and adsorption separation mechanisms in a special isocratic mobile phase composition at the critical adsorption point. Therefore, it is suitable for separation of polymers having similar structures and is often combined SEC to characterize two-dimensional distribution of CCD and MWD.

However, none of the above HPLC studies involved polyfluorinated polymers, except for several reports on SEC[6–13] and another one on HPLC. The latter used liquefied carbon dioxide (CO_2).[22] It is difficult to find an appropriate solvent even for SEC and even more so to determine the CCD for polyfluorinated polymers because of the complexity caused by the need to consider the consequences of additional fluorine content to polarity and solubility. In this work, an excellent system that can evaluate the MWD and CCD of copolymer of poly and non-fluorinated acrylate is proposed and their combination, cross-fractionation, is discussed.

EXPERIMENTAL SECTION

Materials and Reagents

1,3-Dichloro-1,1,2,2,3-pentafluoropropane (HCFC225cb)[13] was selected as the primary component of the mobile phase to make use of its solubility of polyfluorinated polymers and PMMA for both SEC and HPLC. Asahiklin AK-225G® (Asahi Glass Co., Ltd., Tokyo), consisting of about 99.8% HCFC225cb and 0.2% HCFC225ca ($CF_3CF_2CHCl_2$), was directly used as the HCFC225cb. Asahiklin AK-225® (Asahi Glass), containing both HCFC225cb and HCFC225ca as main components, was also used. 2,2,3,3-Tetrafluoropropanol (TFPO) was prepared by Asahi Glass, and THF, chloroform, and methanol was purchased from Kanto Chemical Co., Inc. (Tokyo) and used without further purification. Narrow polydispersity PMMA mixtures (Easi-Cal PM-1, molecular weight: a mixture of 10 standards from 1,020 to 1,577,000 Da) were purchased from Polymer Laboratories Ltd. (UK).

2-(Perfluoroalkyl)ethyl acrylate (FA) with a wide perfluoroalkyl chain length distribution (6–20, mainly 8–10) was prepared by Asahi Glass Co., Ltd. Stearyl acrylate (StA), another primary constituent of the copolymer, was industrial grade, containing some different chain length components. Several percent of hydrophilic acrylate termonomer (X) was also contained in the copolymer to exploit its better performance in practical use.

Sample Preparation

FA/StA/X copolymers were prepared in five different molar ratios, 100/0/x, 68/32/x, 57/43/x, 47/53/x, and 0/100/x, by a conventional emulsion polymerization technique. Although these ratios are based on the amount of monomers in the feed, the resulting copolymers are expected to have corresponding composition because the extent of polymerization is sufficiently high.

Meanwhile, it is difficult in practice to predict the CCD from copolymerization reactivity constants of each monomer because the FA and StA monomers are immiscible and mechanical stirring has a strong influence on the feed of monomers to the micelle, resulting in a broad CCD. The resulting copolymers were extracted by addition of methanol and dried after removing the emulsifier by rinsing.

Three homopolymers of 2-(perfluorobutyl)ethyl acrylates (homo-C4FAs) having different molecular weights and a homopolymer of 2-(perfluorohexyl)ethyl acrylate (homo-C6FA) were prepared also by emulsion polymerization. The molecular weight was evaluated by SEC using HCFC225cb/hexafluoroisopropanol (HFIP) = 99/1 (vol.) mobile phase as described elsewhere.[13] PMMA equivalent number-average molecular weights (M_n) were 4700 g/mol, 12500 g/mol, and 19000 g/mol for homo-C4FAs, and 40900 g/mol for the homo-C6FA.

Instrumental Conditions

Size Exclusion Chromatography

The copolymers to be measured were dissolved in a sample solvent (HCFC225cb/THF = 1.5/1 (vol.)) by shaking for several minutes and then standing until the solute was no longer visible (usually overnight). The sample concentration was 0.2 or 0.5 wt.%. After filtration through a 0.45 μm pore polytetrafluoroethylene (PTFE) membrane (Titan® Filtration Systems, SUN-SRi, N.C., USA), 50 μL of each solution was introduced into an HLC-8020 or HLC-8220 size exclusion chromatograph

(Tosoh, Tokyo) using an auto injector. Besides a differential refractive index (RI) detector, an ultraviolet (UV) detector UV-8010 set at 230 nm was also used. For some analyses, an evaporative light scattering detector (ELSD; Alltech ELSD 500, Alltech Associates, Inc., Ill., USA) was also used instead of an RI or UV detector for better sensitivity. The ELSD drift tube and exhaust temperatures were set at 63°C and 38°C, respectively, and the nitrogen gas flow rate was set at 1.67 dm^3/min. Two 30 cm × (0.75–0.8 cm) columns, PLgel mixed-C (Polymer Laboratories) or TSKgel GMH_{HR}-M (Tosoh) were combined in series with or without a pre-column. The column oven was set at 37°C, and the mobile phase flow rate was 1 mL/min.

Narrow polydispersity PMMA mixtures were used for molecular weight calibration. The concentration and injection volume of the standard PMMA was not strictly stipulated, but they were in the range of ca. 0.2% (solvent: HCFC225cb/THF = 1.5/1 (vol.)) and 50 μL.

Non-exclusion Liquid Chromatography

Sample solutions dissolved in the same way as for SEC measurement were introduced into an HPLC system adjusted as follows. An HLC-8010 HPLC system (Tosoh) with an auto injector and ELSD detector set to the same conditions as in the SEC measurements was used. As the common conditions for non-exclusion modes, 20–50 μL of the solution was injected onto the column, the flow rate was 0.8–1 mL/min, and the column temperature was maintained at 35°C.

In the case of separation using a silica gel column, YMC SIL A-303 4.6 mm × 250 mm (YMC, Kyoto, Japan) was used. The mobile phase consisted of A (5 wt.% TFPO/AK-225®) and B (20 wt.% TFPO/$CHCl_3$). The following gradient condition was employed: 100% A at 0 min, to 40% B (linear) at 10 min, to 100% B (linear) at 20 min, hold 100% B until 24 min, to 0% B at 25 min.

The conditions when using the octadecylsilica (ODS) column were as follows: flow rate: 0.8 mL/min, column: YMC ODS AM-303 4.6 mm × 250 mm (YMC), mobile phase A: AK-225®, mobile phase B: dicloroethane/$CHCl_3$ = 98/2 (vol.). The following gradient conditions were employed: 100% A at 0 min, to 40% B (linear) at 10 min, to 100% B (linear) at 20 min, hold 100% B until 24 min, to 0% B at 25 min.

As an application of a fluorinated column to this work, Fluofix® INW425 4.6 mm × 250 mm (Neos, Japan) was used. According to the column manufacturer, the stationary phase of this column is composed of silica gel modified by a fluorinated alkyl ($CF_3CF_2CF_2C(CF_3)_2(CH_2)_3Si(CH_3)_2O$-) group. Initial gradient conditions were 100% mobile phase A (methanol/tetrahydrofuran = 3/7 (vol.)). A linear gradient to 100% mobile phase B (HCFC225cb) over 10 min was run and maintained for 5 min. The gradient was returned to initial conditions at 16 min.

FT-IR of Dried Fractions from SEC and NELC

Preparative isolation was conducted for specific peaks eluted by SEC and NELC to determine the chemical composition of the fraction. Fractions were air dried on a clean bench and Fourier transform-infrared (FT-IR) measurement was conducted for the dried solid. An FT-IR (Nicolet 760; Thermo Fisher Scientific, Mass., USA) spectrometer fitted with an infrared microscope was used in the transmission mode.

Cross-Fractionation

In this study, SEC preparation was conducted prior to NELC analysis. The retention time range of the fractionation was determined in advance by ELSD detector. First, 500 µL of 1 wt.% solution of FA/StA/X = 57/43/x copolymer was introduced to an HPLC (equipment described above) conditioned for SEC as described above. Six fractions of retention time from 9.8 to 18.8 min, 1.5 min each, were collected by a fraction collector FC-8010 (Tosoh). The preparation was repeated 10 times, and each collection was combined and air dried. After the collections were redissolved by the sample solvent (HCFC225cb/THF = 1.5/1 (vol.)), 50 µL fraction was injected into an HPLC conditioned as described above. In this case, Fluofix® column condition was employed because it was suitable to evaluate the CCD of the copolymer.

RESULTS AND DISCUSSION

Solubility of Copolymers in Mixtures of HCFC225cb and THF

Solubility tests were conducted at a concentration of 0.5 wt.% copolymers in the mixture of HCFC225cb and THF. The results are shown in Table I. As for the FA homopolymer, it should be emphasized that there are practically no good solvents other than HCFC225s. According to visual examination, FA/StA/X = 57/43/x copolymer dissolved in these compositions. However, the copolymers consisting primarily of FA were not dissolved in THF and those consisting primarily of StA were not dissolved in HCFC225cb. As the sample copolymers are expected to have broad CCDs, it is necessary to use a solvent that allows a better solubility of each component. In addition, as refractive indices of copolymers are higher than that of HCFC225cb and close to that of THF, an HCFC225cb-rich composition is preferable for better sensitivity when the refractive index detector is used. For these reasons, we employed HCFC225cb/THF of 1.5/1 (vol.) composition for both SEC mobile phase and sample solvent except for FA homo- and FA-rich polymers,

Table I. Solubility test at a concentration of 0.5 wt.% FA/StA/x copolymers to the mixtures of HCFC225cb/THF

HCFC225cb/THF (vol.)	FA/StA/X = 100/0/x	FA/StA/X = 0/100/x
0.571/1	P	S
0.857/1	P	S
1.141/1	S′	S
1.5/1	S′	S
2/1	S′	I
1/0	S	I

S: soluble; S′: soluble but the solution was slightly hazy; P: partially soluble (some residue remained); I: insoluble.

where HCFC225cb was used. FA/StA/X = 100/0/x copolymer was not perfectly soluble in this co-solvent, presumably because of the insolubility of polar component containing the monomer X.

Size Exclusion Chromatography

The SEC system was calibrated by narrow polydispersity PMMA mixtures. As was the case with the HCFC225cb/HFIP = 99/1 (vol.) mobile phase,[13] the correlation coefficient of the PMMA calibration curve was high enough in combination with good reproducibility for HCFC225cb/THF = 1.5/1 (vol.).

Size exclusion chromatograms of samples obtained by using the mixture of HCFC225 and THF mobile phase and RI and UV (230 nm) detection are shown in Figure 1. Copolymers having greater StA content showed stronger signals, especially for RI detection, because the higher refractive index of StA leads to a greater difference in the indices. The RI detection peak of a copolymer consisting primarily of FA disappeared behind the baseline or was rather detected on the negative (lower refractive index) side. The refractive index of the FA-rich polymer was very similar to that of the HCFC225cb/THF = 1.5/1 (vol.) mobile phase. For better detection of FA-rich polymers by RI, mobile phases having different refractive indices, such as HCFC225cb/1% HFIP (lower refractive index than HCFC225cb/THF = 1.5/1 (vol.)), can be selected,[13] or alternatively, a UV detector or ELSD can be employed.

We assume that these copolymers have broad MWD except for the FA-rich copolymer (only for the 100/0/x copolymer), which has a lower molecular weight and narrower MWD. The PMMA equivalent molecular weight of these polymers can easily be calculated on the following assumptions: each copolymer has a negligible end group effect on the

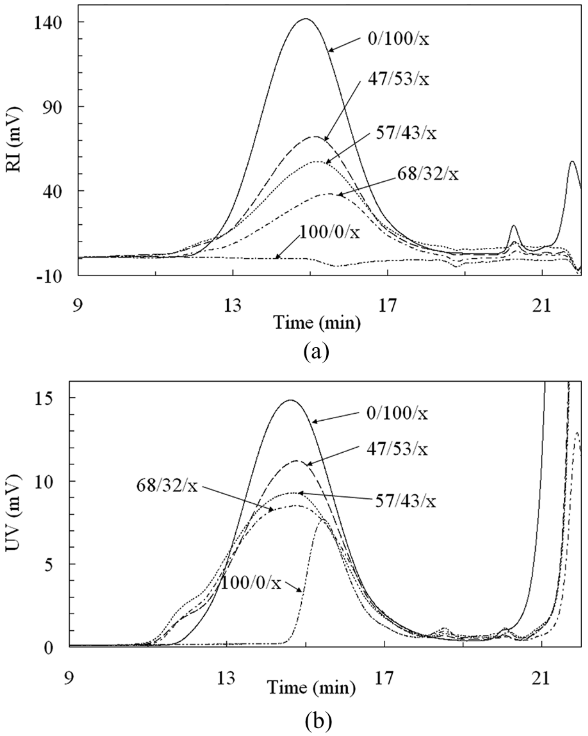

Figure 1. Size exclusion chromatograms of FA/StA/x copolymers having various FA/StA compositions using two TSKgel GMHHR-M columns in HCFC225cb/THF = 1.5/1 (vol.) mobile phase: (a) RI detection; (b) UV 230 nm detection.

detection, each copolymer has a narrow CCD, and the molecular size is proportional to molecular weight. Although it is obvious that these assumptions are not wholly effective, the PMMA equivalent number-average molecular weight (M_n) calculated for reference by RI chromatogram for the FA/StA/X = 57/43/x copolymer was 45,694 Da, and the area fraction of the component having the PMMA equivalent molecular weight less than 10^4 Da was 2.1%.

To simply check the homogeneity of the copolymer, higher, middle, and lower molecular weight fractions on the chromatogram of FA/StA/X = 57/43/x copolymer were collected, and their chemical compositions were determined by infrared spectroscopy. The higher molecular weight fraction was found to possess an FA-rich composition and the opposite for lower molecular weight fraction. In addition, the IR spectra of different sampling positions in the same dried fraction differed greatly. Therefore, the copolymer was shown to have, at least, a broad CCD.

HPLC Using Silica Gel and ODS Column

The FA/StA/X copolymers employed here contain additional contributing factors making the CCD analysis more difficult in addition to broad MWD and CCD, that is, the confinement of sample solvent and the existence of polar termonomer X. Therefore, initially, the application of HPLC using a silica gel column by effectively utilizing the difference of sample solubility in fluorinated and non-fluorinated solvents was attempted.

Figure 2 shows the chromatograms of copolymers by using silica gel column in decreasing fluorinated solvent and ELSD detection. This detector has been shown to be suitable for fluorinated polymers,[13] and here it was shown to be advantageous in terms of sensitivity, baseline stability when using gradient elution, and selectivity of detection of polymer in HPLC conditions. FA/StA/X = 100/0/x and 0/100/x polymers showed two major peaks each, and IR spectra of each fraction indicated

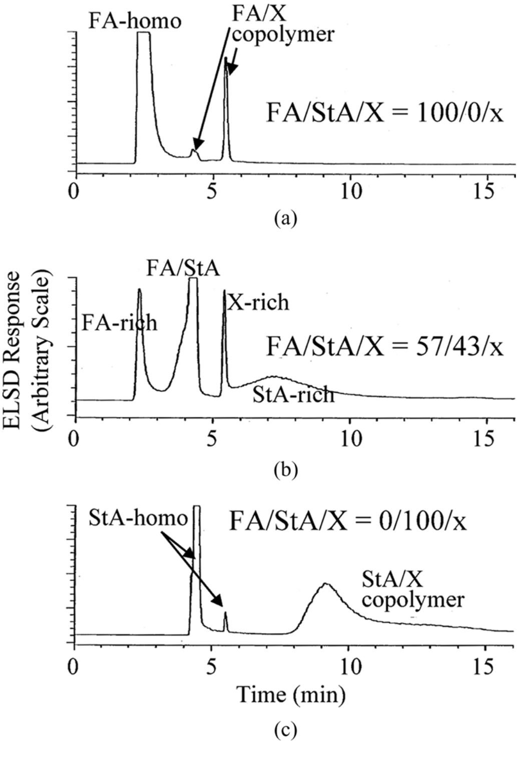

Figure 2. NELC chromatograms of three FA/StA/x copolymers, (a) 100/0/x; (b) 57/43/x, (c) 0/100/x, using a silica gel column and 5 wt.% TFPO/AK-225® to 20 wt.% TFPO/$CHCl_3$ mobile phase.

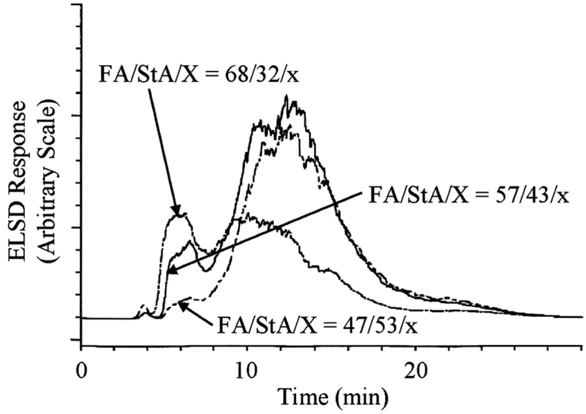

Figure 3. NELC chromatograms of three FA/StA/x copolymers, 68/32/x, 57/43/x, and 47/53/x, using an ODS column and HCFC225cb to dichloroethylene/2% chloroform mobile phase.

that these separations were based on their difference in polarity derived from the X composition distribution of the polymer. Although separation based on CCD was attained for FA/StA/X = 57/43/x polymer, the significance of this system is lessened because of the concomitant separation based on the polarity and of the narrow range of the retention times between the FA-rich and StA-rich components.

Second, an ODS column and a fluorinated solvent were used with the aim of interaction between StA component and ODS moiety, which delays the StA elution. Figure 3 shows the chromatograms of three copolymers using the ODS column, HCFC225cb to dichloroethylene/2% chloroform mobile phase, and ELSD detector. Although a partial separation based on FA/StA composition was attained, the resolution was unsatisfactory.

HPLC Using Fluorinated Column

The above-described conditions were not successful for the separation based on the CCD of FA/StA. An entirely new separation concept was required and the interaction of a fluorinated column and perfluoroalkyl group was selected. Recent trends in "fluorous chemistry" utilize this interaction effectively,[23] which seems to be more prevalent in synthetic chemistry than in analytical chemistry. As far as we know, there are two principal perfluoroalkyl types available commercially, perfluorooctyl group from Fluorous Technologies (Pittsburgh, Penn., USA) and perfluoro(1,1-dimethylbutyl) group from Neos Company (Kobe, Japan). The latter was used in this experiment, although the former is also expected to be successful.

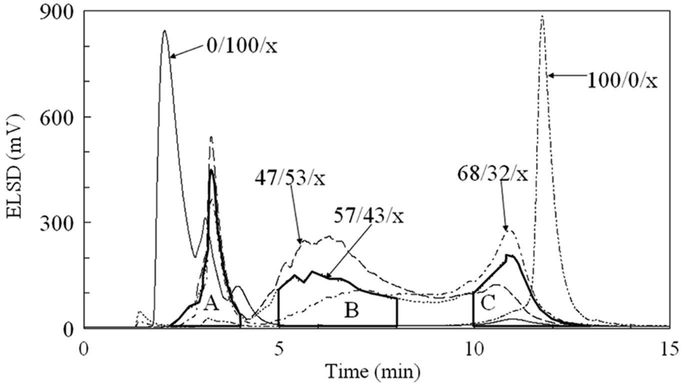

Figure 4. NELC chromatograms of FA/StA/x copolymers using Fluofix® INW425 and methanol/tetrahydrofuran = 3/7 (vol.) to HCFC225cb mobile phase.

The mobile phase gradient condition, described in the experimental section, was applied as follows. First, a fluorinated component is attached to the stationary phase of the column under the initial solvent conditions, followed by the elution by fluorinated solvent. Second, an StA-rich component is eluted without delay, and, finally, adsorption or precipitation of polar component to the column is suppressed by the addition of methanol to the initial mobile phase. Although the sample solvent, HCFC225cb/THF of 1.5/1 (vol.), is a good solvent for the entire copolymer CCD, the initial mobile phase, methanol/THF of 3/7 (vol.), is a poor solvent, especially for FA-rich components. Thus, the injected sample may be attached to the top of the column not only by fluorinated interaction but also by precipitation.

Figure 4 shows the chromatograms of the sample copolymers having various compositions. StA primary copolymer eluted at t_0, as we expected, without interaction, and the FA primary copolymer eluted within a sharp band after a sufficient interaction and retention in the column. Three FA/StA/X copolymers, 47/53/x, 57/43/x, and 68/32/x, showed broad and characteristic CCDs of three components consisting of FA-rich, StA-rich, and their copolymer component. This was also confirmed by IR spectra after preparation of the eluted component (Fraction A, B, C) from the column as shown in Figure 5. After normalization to the acrylic C=O group (1735 cm^{-1}), fraction A has more C-H group and less C-F group, and fraction C, vice versa. Consequently, a CCD analysis method was established using a fluorinated column and careful selection of the mobile phase.

Meanwhile, it was necessary to evaluate the influence of molecular weight of the copolymer on the CCD analysis in this fluorinated system. According to general information for non-fluorinated copolymers, if the

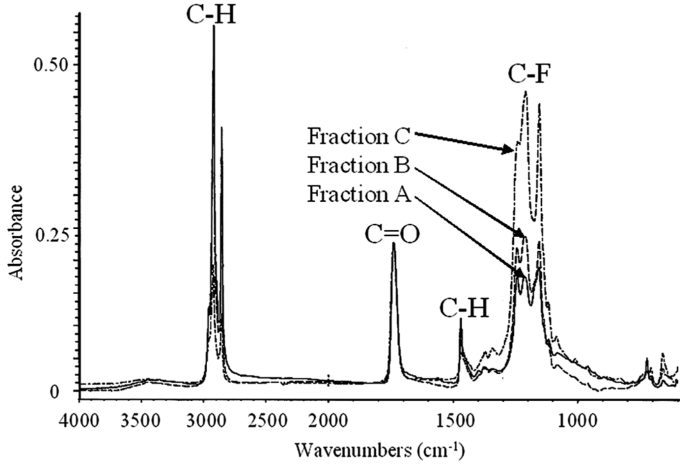

Figure 5. IR spectra of three dried fractions of an FA/StA/x = 57/43/x copolymer prepared by NELC as shown in Figure 4.

separation is based on the size exclusion mechanism, polymers having higher molecular weights elute earlier, while if based on the absorption chromatography mechanism, they elute later.[20–21] LC-CAP is a successful example of balancing these mechanisms, resulting in the elimination of the influence of the molecular weight. Figure 6 shows the NELC chromatograms of three homo-C4FAs and a homo-C6FA using the aforementioned

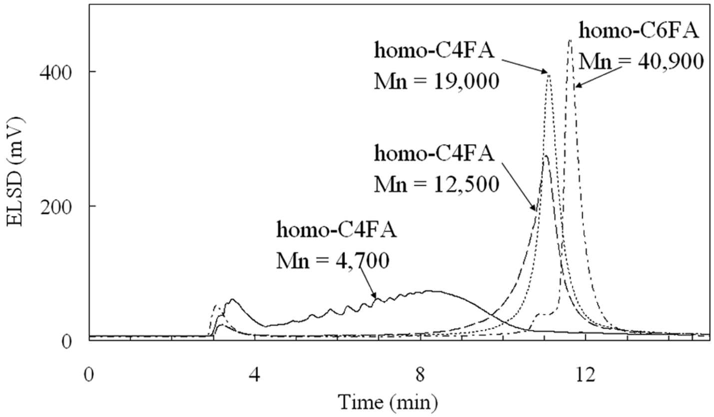

Figure 6. NELC chromatograms of three homo-C4FAs with different molecular weights and a homo-C6FA using Fluofix® INW425 and methanol/tetrahydrofuran = 3/7 (vol.) to HCFC225cb mobile phase.

conditions. Homo-C4FA ($M_n = 19000\,g/mol$) showed a relatively sharp and symmetric peak, while homo-C4FA ($M_n = 4700\,g/mol$) showed a leading pattern, and homo-C6FA ($M_n = 40900\,g/mol$) eluted just after the homo-C4FA peak in a sharp band. The leading of the lower molecular weight polymer would be caused by the lack of the interaction between the C_4F_9 group and the fluorinated surface of the column packing; therefore, the absorption chromatography mechanism appears to be dominant in this case. The stronger interaction of homo-C6FA than homo-C4FA is also explained by this mechanism. Consequently, the leading of low molecular weight component of the FA/StA/X copolymers used in this experiment is expected to be suppressed because their dominant component has a longer Rf group than C_6F_{13} and larger PMMA equivalent molecular weight than $10^4\,g/mol$.

Finally, to obtain a practical CCD from the chromatograms, correction for the detection sensitivity of various copolymer compositions is required. Known concentrations of FA/StA/X = 100/0/x and 0/100/x polymers were injected under the same HPLC conditions. Calculation of detection sensitivity was based on two assumptions: the ELSD signal has a linear correlation with the FA/(FA + StA) ratio (either mol or weight), and the FA/(FA + StA) ratio has a linear correlation with the retention time between the retention times of two samples, 0% FA (0/100/x) and 100% FA (100/0/x). As a result, the detection sensitivity was 3.1 times better (per weight) for 0/100/x polymer. This can be partially attributed to the molar ratio (1.6) of the same weight of StA and FA. The practical distribution obtained here was also applied to the cross-fractionation described in the following section.

Cross-Fractionation

The development of successful methods to evaluate both MWD and CCD for these types of copolymers made cross-fractionation a real possibility. Three-dimensional distribution can be displayed, and the information can shed light on the correlation between the distributions and the property of the copolymer.

Theoretically, it is desirable to conduct preparation by NELC first, followed by SEC analysis of the fractions because SEC separates with respect to hydrodynamic volume and not to molecular weight; therefore the copolymer could not be quantified with respect to MWD if SEC is conducted before separation by NELC.[16] However, as the loading mass in general NELC analysis is less than that of SEC analysis, the more practical and more prevalent order is to conduct SEC first, followed by NELC of the fractions. In addition, as shown previously, the copolymer shows a characteristic and rather sharp CCD pattern; NELC preparation

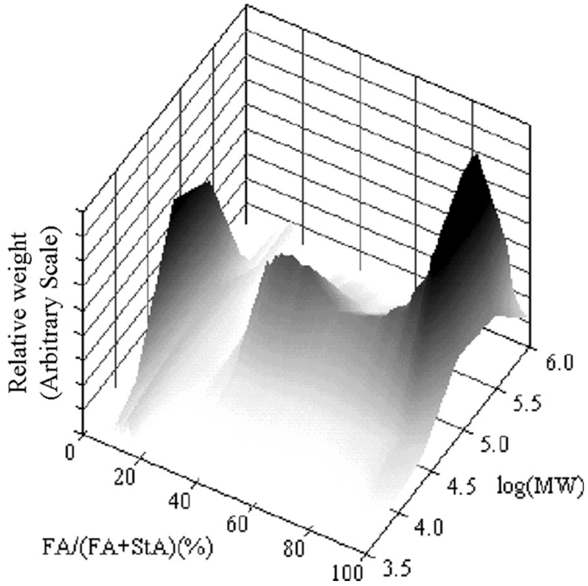

Figure 7. Contour plot of the NELC vs. SEC separation of an FA/StA/X = 57/43/x copolymer.

is expected to undermine the CCD resolution unless preparative isolation is conducted in many fractions.

In this study, SEC preparation was conducted first as described in the experimental section. Figure 7 shows a contour map of the three-dimensional distribution for FA/StA/X = 57/43/x copolymer. Here, MWD was expressed by PMMA equivalent molecular weight, and CCD, expressed by FA/(FA + StA), was presumed to be proportional to the retention time, and difference of detection sensitivity by the copolymer composition is corrected as shown previously.

As a result, the correlation between MWD and CCD became visible for this copolymer. An StA-homopolymer-like component was revealed to have lower molecular weight, and the FA-homopolymer-like component to have higher molecular weight.

The application of this method to copolymers having practical composition opens up new possibilities for obtaining information regarding the correlation between the structure and performance, such as water-oil repellency, and provides additional measures to find minor differences of structurally similar copolymers. For example, we studied the effect of the difference in polymerization conditions on the water-oil repellency and found that the two copolymers had almost identical MWD and different CCD.

CONCLUSIONS

A method to evaluate the MWD and CCD of poly(2-(perfluoroalkyl)ethyl acrylate-*co*-alkyl acrylate) was proposed and their combined two-dimensional development, cross-fractionation, was successfully conducted. By employing a mixed solvent of HCFC225cb and THF that dissolves a copolymer having a broad CCD, a PMMA equivalent MWD was successfully determined. In addition, a CCD was demonstrated by employing a silica-based column modified by polyfluorinated groups that retains polymers having perfluoroalkyl units in an appropriate gradient mobile phase system. ELSD was shown to be an optimal detector for these systems, especially for gradient HPLC. The contour map obtained by the cross-fractionation made an examination of the correlation between structure and performance a real possibility.

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