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GPC−MALS Characterization of Fluoropolymers in a α,α,α-Trifluorotoluene Mobile Phase: An Enabling Step in the Syntheses of Well-Defined Fluoropolymer-Based Self-Assembling Materials

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ABSTRACT: GPC−MALS in α,α,α-trifluorotoluene mobile phase has been employed successfully to determine molecular weight and molecular weight distribution for highly fluorinated (hydrocarbon insoluble) polymers. This technique was used to characterize several fluoroalkyl acrylic and fluorolkyl methacrylic polymers, perfluoropolyethers, hydrocarbon polymers such as polystyrene and poly(*n*-butyl acrylate), and their block copolymers with excellent results. The current report is focused on characterization of poly(1,1,2,2-tetrahydroperfluorodecyl acrylate) and polystyrene as representative materials of interest. Results for samples ranging from 1000 to 1 600 000 g/mol were in excellent agreement with independent measurements determined by ^{1}H NMR end group analysis, GPC in hydrocarbon solvents, and those provided by the supplier, as applicable.

Macromolecules with precisely defined fluorocarbon segments have tremendous potential as building blocks for advanced applications.[1−5] Fluorocarbon-based materials exhibit very low dielectric constants, surface tensions, and refractive indices.[6] Fluorocarbons are also unique in their extreme solvophobicity relative to hydrocarbon and aqueous media, and have a substantial impact on surface properties and supramolecular order even at very low levels of incorporation ($\leq$100 ppm).[7,8] Self-assembled materials based on fluoropolymers and their block copolymers offer potential access to materials with sharp gradients in dielectric constant and refractive index. This combination of large refractive index contrast and strong phase segregation will ultimately enable the design of increasingly complex materials with optical properties of substantial technological importance—such as photonic band gap materials with substantially larger refractive index contrast than is possible with currently available polymeric materials, and increasingly complex materials capable of self-organization on the 5−100 nm size scale.[1,3,9−13] Considering the substantial potential impact of fluoropolymer-based block polymers with narrow molecular weight distributions, why are there only a handful of reports for such materials in emerging fields of nanotechnology and others? Currently available synthetic and analytical techniques are simply not adequate to prepare materials with the degree of control needed for such applications. Our first priority has been to develop appropriate analytical techniques.

Effective methods for product characterization are essential to any successful synthetic effort. This issue has long been a major hurdle in the synthesis of well-defined fluorocarbon-based macromolecules. Techniques that provide a representative assessment of molecular weight and molecular weight distribution are of primary importance—especially in the synthesis of well-defined block copolymers where individual block molecular weight distributions dictate the chemical composition distribution for final materials. Although fluoroalkyl acrylate and methacrylate based polymers may eventually be phased out due to potential environmental concerns, they currently remain the most accessible and most widely reported building blocks employed in the pursuit of narrow molecular weight distribution materials.[14] Investigators have previously reported molecular weight determination for fluoroalkyl acrylic polymers using light scattering,[15] small-angle X-ray scattering,[16] ^{1}H NMR spectroscopy,[8] small-angle neutron scattering,[17] elemental analysis[18] and attempts to employ gel permeation chromatography.[19,20] We recently reported the catalytic chain transfer syntheses of fluoroalkyl methacrylate macromonomers, with molar mass and molar mass distribution determined using GPC−MALS.[21] To out knowledge, there are no previous reports of reliable, reproducible separation and characterization methods for this general class of materials.

In order to address this issue, we have investigated gel permeation chromatography with multiangle laser light scattering online detection (GPC−MALS) in α,α,α-trifluorotoluene mobile phase as a general technique for the characterization of molecular weight and molecular weight distribution for highly fluorinated amorphous polymers and their block copolymers. This approach was found to be useful in the characterization of fluoropolymers and hydrocarbon polymers and will be particularly useful for detailed characterization of block copolymers incorporating both fluorocarbon and hydrocarbon segments. We have successfully characterized poly(1,1,2,2-tetrahydroperfluorodecyl acyrlate), poly(1,1-dihydroperfluorooctyl acrylate), poly(1,1,2,2-tetrahydro-perfluoroalkyl methacrylate)s, perfluoropolyethers, polystyrene, poly(*n*-butyl acrylate) and others. The current report is focused primarily on poly(1,1,2,2-tetrahydroperfluorodecyl acrylate) and polystyrene as representative materials.

Traditional gel permeation chromatography (GPC), often termed size exclusion chromatography (SEC), relies on size-based chromatographic separation combined with a calibration curve constructed using narrow molecular weight distribution samples. It is the mainstay technique for determination of

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molecular weight and molecular weight distribution of synthetic polymers.[22] GPC can yield accurate and reliable assessment of molecular weight and molecular weight distribution weight if the following conditions are met: (1) the calibration curve is constructed with narrow distribution standards of a similar or identical polymer; (2) the molecular weight of the standards encompass the molecular weight range of the analyte polymer; (3) the analyte polymer is well solvated and exhibits no polar interactions with the column stationary phase. The larger the deviation from these ideal conditions the larger will be the error in the molecular weights thus determined. There are no narrow distribution standards available for fluorinated polymers, and even though polystyrene dissolves in α,α,α-trifluorotoluene, the use of a polystyrene-constructed calibration curve for fluoropolymer molecular weight distribution could hardly be expected to yield reasonable results.[23,24] Several comprehensive reviews of GPC and the associated calibration methods are available which highlight these and related issues.[25−27]

The use of multiangle light scattering (MALS) detection combined with a suitable concentration detector has been established as an effective method for the direct determination of molecular weight.[25,28,29] To yield accurate results the concentration detector must be carefully calibrated and it is essential that the refractive index increment (d*n*/d*c*) be known for the polymer being analyzed—in the mobile phase employed. It is best if d*n*/d*c* is determined at the same wavelength employed by the light scattering detector and that it is relatively constant across the sample being characterized. There is a significant potential for error in the characterization of copolymers that are not uniform in composition. There are promising methods that overcome this difficulty for samples having significant distribution in composition so long as the degree of chromatographic separation is such that molecular weight distribution and composition distribution are monodisperse for each slice of data analyzed.[30]

Refractive index increments (d*n*/d*c*) were measured in α,α,α-trifluorotoluene for each type of polymer characterized and for different molecular weight samples within each series to ensure uniformity over the molecular weight range of the samples. Representative d*n*/d*c* values determined in α,α,α-trifluorotoluene are as follows: poly(1,1,2,2-tetrahydroperfluorodecyl acrylate) = −0.061 mL/g, polystyrene = 0.175 mL/g, perfluoropolyether (Fomblin Y HVAC) = −0.078. Determinations were made using static measurements for a concentration series introduced to the refractometer using a syringe pump. To avoid wavelength related error, the incandescent light source in the Waters R-401 refractometer was replaced with a light emitting diode having an emission wavelength of approximately 660 nm. After modification the detector was calibrated and linearity was verified using a series of sodium chloride solutions. The light source in the Wyatt Minidawn employed is approximately 680 nm.

An overlay of representative chromatograms for a series of bromine-terminated poly(1,1,2,2-tetrahydroperfluorodecyl acrylate) samples with systematically increasing molecular weight is shown in Figure 1. Corresponding number-average molecular weight (M_n, g/mol) and polydispersity index (M_w/M_n) are provided in Table 1. Molecular weights obtained using the ratio of integrated ^{1}H NMR resonances for end groups and backbone are provided for comparison and agree well with GPC−MALS for the molecular weight range of 700−6000 g/mol. The chromatographic overlay clearly shows an increasing retention time with decreasing molecular weight. Plots of log molar mass vs elution volume were linear for individual samples and across the series presented in Figure 1. The apparent increase in intensity with increasing molecular weight for the overlay in Figure 1 is due to gradually increasing concentration of the injections, a consequence of the method by which the samples were originally isolated. The minimum signal to noiseratio for chromatograms included in the current report was 90:1 (peak height/baseline noise). The perfluoroalkyl acrylic polymer samples represented in Figure 1 materials were synthesized using atom transfer radical polymerization. Detailed syntheses for these and related macromolecules will be described in a forthcoming report.

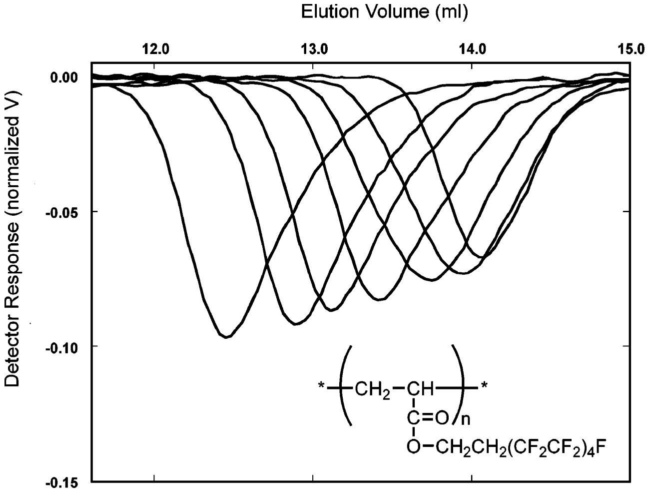

Figure 1. GPC−MALS data for a representative series of poly(1,1,2,2-tetrahydroperfluorodecyl acrylate) macroinitiators made using ATRP.

Table 1. GPC−MALS Data for a Series of Poly(1,1,2,2-tetrahydroperfluorodecyl acrylate) Macroinitiators Made using ATRP

GPC−MALS (TFT)			^{1}H NMR	
M_n (g/mol)	M_w (g/mol)	M_w/M_n	M_n (g/mol)	M_w/M_n
740	960	1.30	790	N/A
1400	1540	1.10	1600	N/A
1600	1920	1.20	1800	N/A
2000	2220	1.11	2000	N/A
3300	4100	1.24	3200	N/A
4300	5200	1.21	3900	N/A
4600	5700	1.24	4300	N/A
5700	6900	1.21	5600	N/A

GPC−MALS (TFT)		^{1}H NMR	
M_n (g/mol)	M_w/M_n	M_n (g/mol)	M_w/M_n
740	1.30	790	N/A
1400	1.10	1600	N/A
1600	1.20	1800	N/A
2000	1.11	2000	N/A
3300	1.24	3200	N/A
4300	1.21	3900	N/A
4600	1.24	4300	N/A
5700	1.21	5600	N/A

An important consideration for the characterization of materials incorporating fluoroalkyl moieties lies in the source of the fluoroalkyl segments. Fluoroalkyl chain length, distribution in chain length, and distribution and branching can each have a significant effect on the solution properties of the corresponding polymers. Even subtle differences in the distribution of fluoroalyl chains present in a polymer can have a substantial impact on solution and aggregation properties. For telomer products, all fluorocarbon side chains are linear, and typically include distribution of lengths ranging from 2 to as many as 16 fluorinated carbons or more (based on distributions provided

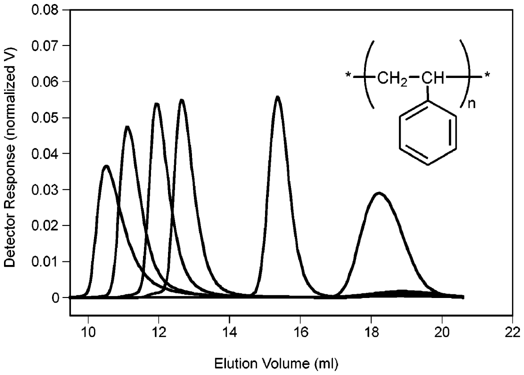

Figure 2. GPC−MALS data for a representative series of poly(1,1,2,2-tetrahydroperfluorodecyl acrylate) macroinitiators made using ATRP.

in DuPont Zonyl product literature and GC analyses of representative monomer samples). As the length of the fluoroalkyl chains increases, solubility decreases and aggregation is more prominent in solution. Fluoroalkyl moieties produced using electrochemical fluorination processes do not show a distribution in fluoroalkyl chains length, but some of the chains, 5−20%, contain trifluoromethyl branches which disrupt crystallinity and generally increasing solubility of the resulting products.[6]

The onset of aggregation (when observed) for samples analyzed in our lab was typically evident from the light scattering chromatograms which showed relatively small concentrations of very high molecular weight structures (aggregates) and was a function of both molecular weight and the length of fluoroalkyl side chains for the sample. Over the limited temperature range of 20−40 °C accessible using our current equipment, it appears that fluoroalkyl chain length is more important than molecular weight in determining aggregation. Even at 40 °C aggregation is a problem for telomer products when fluoroalkyl chains having 10 or more fluorinated carbon atoms are present. It is highly likely that this is a strong function of temperature and that by increasing the temperature beyond out current limit of 40 °C would overcome the attractive forces/insolubility for longer fluoralkyl chains. At 20 °C some aggregation for 8-carbon fluoroalkyl chain polymers, but this is not observed at temperatures of 30 °C or higher for the samples we've examined to date. Fluoroalkyl acrylic and methacrylic polymers having primarily 8-carbon and shorter fluoroalkyl side chains and perfluoropolyethers showed no aggregation at 40 °C. These trends have been evident in samples prepared in our labs and those received from other sources. We have successfully characterized fluoroalkyl acrylic samples with molecular weights (M_n) in excess of 1 000 000 g/mol.

An important issue in the synthesis of well-defined block copolymers and more complex architectures is the use of GPC to verify the overall molecular weight and molecular weight distribution and to verify the absence of homopolymer or bimodal molecular weight distributions (that may for example occur due to incomplete reinitiation or inefficient crossover during synthesis). An overlay of elution chromatograms for an extended series of primary polystyrene standards ranging from 1100 g/mol to 1 600 000 g/mol is shown in Figure 2. Corresponding number-average molecular weight (M_n, g/mol) and polydispersity index (M_w/M_n) are provided in Table 2. The values obtained using GPC−MALS in TFT are in excellent agreement with those supplied by the manufacturer, and also with determinations made in house using GPC in THF. Representative data for block copolymers is also given in Table 2 for comparison. For these samples d*n*/d*c* was estimated using the weighted average of d*n*/d*c* for individual blocks as based on the composition by ^{1}H NMR characterization. The molecular weights reported for these materials in Table 2 should be regarding as estimates due to the complexity of accurately estimating d*n*/d*c* for block copolymers. They correspond well to estimates of molecular weight made using integrated ^{1}H NMR spectra and known molecular weight of the individual starting blocks used in syntheses. Detailed syntheses of these and related materials will be the subject of a forthcoming report.

Table 2. GPC−MALS Data for Polystyrene and a Representative Series of Block Copolymers

GPC−MALS (TFT)			reference[a]		
M_n (g/mol)	M_w (g/mol)	M_w/M_n	M_n (g/mol)	M_w (g/mol)	M_w/M_n
1 610 000	2,061,00	1.28	1 540 000	2 000 000	1.30
831 000	950 000	1.14	820 000	900 000	1.10
184 000	191 000	1.04	190 000	200 000	1.06
34 200	35 600	1.04	38 000	40 000	1.06
28 800	30 200	1.05	28 000	30 000	1.06
3660	4060	1.10	3800	4000	1.06
poly(HFA-*b*-Sty) block copolymer (2000 g/mol PHFA block)					
6090	6760	1.11			
8500	9600	1.13			
9880	10 770	1.09			
11 000	12 650	1.15			

[a] Primary light scattering standards from Wyatt Technologies, Inc.; reference values represent manufacturer supplied values and correspond well with those determined by GPC and GPC−MALS in THF.

GPC−MALS was carried out using a Waters 510 HPLC pump (fitted with pulse dampener made in house) and equipped with a Waters 717$_{\text{plus}}$ Autosampler, Polymer Labs PLGel Mixed C and Mixed D mixed bed size exclusion columns (one each in series), Waters R-401 differential refractometer fitted with a 660 nm light source, Waters 486 tunable absorbance detector, and Wyatt Technologies MiniDawn MALS detector slightly modified in house to provide temperature control up to 40 °C. Mobile phase employed was TFT (1.0 mL/min) at 40 °C. Samples were prepared well in advance, and maintained at 40 °C in the autosampler for several hours prior to injection. This step was required to ensure uniform sample dissolution and was necessary to achieve reproducible results. Wyatt Technologies Astra software package was used for data collection and analysis. Toluene was added to each run to serve as a flow rate marker. Initial studies were carried out using a Waters Alliance 2690 with 2410 refractive index detector, but significant problems were encountered with seal materials in the solvent proportioning valve. Trifluorotoluene (99%) was purchased from Aldrich, distilled over sodium carbonate, and recycled by subsequent distillations. Polystyrene primary light scattering standards were used as received from Wyatt Technologies.

In conclusion, GPC−MALS in α,α,α-trifluorotoluene mobile phase has been employed successfully to determine molecular weight and molecular weight distribution for highly fluorinated (hydrocarbon insoluble) fluoroalkyl acrylic polymers and hydrocarbon polymers. This technique was used to characterize, hydrocarbon polymers such as polystyrene and poly(*n*-butyl acrylate); perfluoropolyethers; and several fluoroalkyl acrylic and fluorolkyl methacrylic polymers and their block copolymers with excellent results. Molecular weight and molecular weight distributions determined for samples ranging from 1000 to 1 600 000 g/mol were in excellent agreement with independent measurements using ^{1}H NMR end group analysis, GPC in hydrocarbon solvents, when possible, and values provided by suppliers for narrow distribution polystyrene standards.

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