

# Laser Light-Scattering Molecular Weight Analysis of a Poly(fluoro acrylate)

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**ABSTRACT:** Two leading macromolecular characterization techniques were employed for analysis of a unique, difficult to dissolve fluorinated polymer system (PFA), Poly(*N*-methyl perfluorooctyl sulfonamido ethyl acrylate). Multiangle Laser Light Scattering (MALLS) and Viscosity-Right Angle Laser Light Scattering (RALLS) were used to measure the weight-average molecular weight and molecular size-radius using the solvent HFIP, 1,1,1,3,3,3-hexafluoroisopropanol. HFIP is shown to be an excellent solvent for light scattering measurements on the PFA as well as on

Polyamide-11 and Polymethyl methacrylate. It is shown that the Viscosity-RALLS approach gives results that differ from the MALLS system due to the assumptions used. It is also shown that the addition of salt does affect the molecular weight dependence of the radius of gyration but not the value of  $M_w$ . © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3447–3454, 2004

**Key words:** light-scattering; molecular weight; polyamides; fluorinated polymers

## INTRODUCTION

A unique series of poly(fluoro acrylates) were synthesized and characterized using laser light-scattering techniques. The polymers, referred to as PFA, are of potential industrial importance as water repellants, and were synthesized and characterized for the first time in this study. Development and use of techniques to measure molecular size and conformation in solution remains an essential but often difficult step in characterizing new polymer systems. The appropriate choice and implementation of solvent, measurement technique, and test conditions is a challenging task, given the lack of information available when characterizing a new polymer for the first time.

The objective of this study is to identify the molecular weight, and the conformational behavior of this PFA polymer in hexafluoroisopropanol HFIP. Two different detectors are used with size-exclusion chromatography. One uses viscosity and a single-angle laser light-scattering detector RALLS. The second uses a multiangle laser light-scattering detector, MALLS. In addition, the role of an additive salt to electrically balance the solvated polymer and potentially reduce solvent chain expansion behavior of the polymer in solution is examined.

## EXPERIMENTAL

The poly(fluoro acrylates) were polymerized and provided by the 3M Corp. Figure 1 displays the chemical structure of the monomer unit.

The polymerization chemistry was carefully controlled and designed to produce a set of samples of varying molecular weights. The level of initiator was kept constant for samples 1 through 5, and a decreasing amount of chain transfer agent was used for each sample in the set, with sample 1 having the most chain transfer agent and sample 5 having none. Samples 6 and 8 were polymerized with varying amounts of initiator and no chain transfer agent. Sample 9 was polymerized using an emulsion polymerization and no chain transfer agent.

Because the fluoro acrylates are not soluble in most conventional solvents but are soluble at room temperature in hexafluoroisopropanol, HFIP, background studies were carried out on two types of polyamide-11, PA-11, and one poly(methylmethacrylate), PMMA, standards to verify the compatibility of the HFIP-SEC macromolecular characterization technique. These include commercial samples of Atochem's Besno P40TL, a plasticized PA-11, extruded into pipe. In addition, unplasticized PA-11 made in our laboratory by polymerization of 11-aminoundecanoic acid was characterized. Three samples of varying molecular weight were made. These samples were made in an oven flushed with Argon gas and held at 190°C and under a reduced pressure of 380 Torr. To control the molecular weight, reaction times were varied: 12 h for the high molecular weight sample ( $M_w \approx 53,000$ ) and 1.5 and

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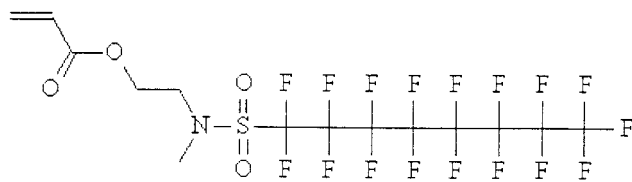


Figure 1 Chemical formula for PFA monomer unit.

0.75 h for lower molecular weight samples ( $M_w \approx 25,000$  and  $15,000$ ), where  $M_w$  is the weight-average molecular weight. PMMA narrow molecular weight standards were purchased from Polymer Laboratories, Inc.

### Multiangle laser light scattering

Size-exclusion chromatography (SEC) was conducted with 1,1,1,3,3,3-hexafluoroisopropanol as the mobile phase at a flow rate of 0.6 mL/min with a JordiGel DVB Mixed Bed HPLC column at 40°C. To obtain absolute measurements<sup>1-3</sup> of weight-average molecular weight  $M_w$  and root-mean-square radius  $R_g$  by light scattering, a Wyatt Multiangle Laser Light Scattering Instrument (MALLS) with a Wyatt Optilab 903 Interferometric Refractometer was used. The detectors used light at 690 nm, from a diode laser in the MALLS mini-Dawn and from a filtered light source in the Optilab. This system was operated both with and without salt present in the mobile phase. Each sample was run in the system with no salt present, then the set was run with 0.02 M Sodium trifluoroacetate salt (NaTFA) in the HFIP mobile phase and finally in 0.05 M potassium trifluoroacetate (KTFA). It is well known that for polymers such as polyamides, polyesters, and fluoropolymers in highly polar solvents, the addition of salt can help with disaggregation of the polymer molecules.<sup>4,5</sup> Solutions of PA-11, PMMA, and PFA were made at roughly 5.0 mg/mL concentration. This relatively high concentration was chosen so that viscosity measurements could be made on the same solution in an earlier study on characterizing PA-11.<sup>6,7</sup> The highest molecular weight PFA sample was run at 1/3 concentration to determine the effect of concentration. The results indicated that there was no discernible concentration effect as seen in Tables III and IV. *m*-Cresol was used as the solvent for PA-11 and PMMA solutions, and HFIP was used for PFA solutions.

### Right-angle laser light scattering

A second SEC system with HFIP mobile phase and 0.05 M Potassium trifluoroacetate salt (KTFA) at a flow rate of 1.0 mL/min with one Polymer Laboratories HFIPGel column at ambient temperature was

used to characterize the PFA. Solutions of PFA in HFIP were made at roughly 2.5 mg/mL concentration. Using this salt-solvent SEC system measurements of  $M_w$  and  $R_g$  were taken with a Viscotek Triple Detector system: differential refractive index detection, viscosity, and Single-Angle 90° Laser Light Scattering (RALLS). The RALLS detector used light at 670 nm.

## RESULTS AND DISCUSSION

### Poly(methylmethacrylate)

The PMMA results shown in Figure 2 and Table I illustrate the typical unimodal peak obtained and the resultant accuracy of the HFIP system with a MALLS light scattering detector.

As seen in Table I, the measured  $M_w$  values are quite close to those provided with the known standards. These results verify that MALLS is capable of absolute measurement of PMMA molecular weight in HFIP over a range of roughly  $10^3$  to  $10^6$  Daltons. Use of a salt such as KTFA or NaTFA in the mobile phase is clearly not necessary for accurate determination of  $M_w$  in this case for PMMA in HFIP.

### PA-11

Figure 3 illustrates a representative unimodal peak typical in the MALLS and RI output for PA-11 in our system. As is the case with PMMA, there is good separation using the JordiGel DVB column. There is no evidence of distortion in the shape of SEC chromatogram as has been reported in some studies of polyamides in HFIP due to a "polyelectrolyte" effect, and there is no reason, therefore, to expect error in the  $M_w$  calculations because of distortion in the chromatogram. As seen in Table II, MALLS measurements of PA-11, both synthesized in our laboratory and commercial samples, show the same value of  $M_w$  in 0.05 M KFTA salt and without salt in the HFIP mobile phase. Even when there is chain extension as will be discussed later, it is relevant to note the MALLS measurement of  $M_w$  is an absolute measurement, regardless of the shape that the dissolved PA-11 molecule assumes in the mobile phase as seen in Table II.

Veith and Cohen<sup>8</sup> report a bimodal peak for PA-6 in HFIP without salt due to a "polyelectrolyte" effect. This is not seen for PA-11 in our HFIP system, as demonstrated in Figure 3. In fact, HFIP without salt has been previously demonstrated to be an effective and reliable solvent for PA-11.<sup>9,10</sup> We suggest that the reason for the effect in PA-6 and not in PA-11 is due to the higher number of amide bonds per unit length along the chain backbone in PA-6. The relatively close proximity of the amide linkages in PA-6 gives rise to heightened repulsive forces and the resultant physical

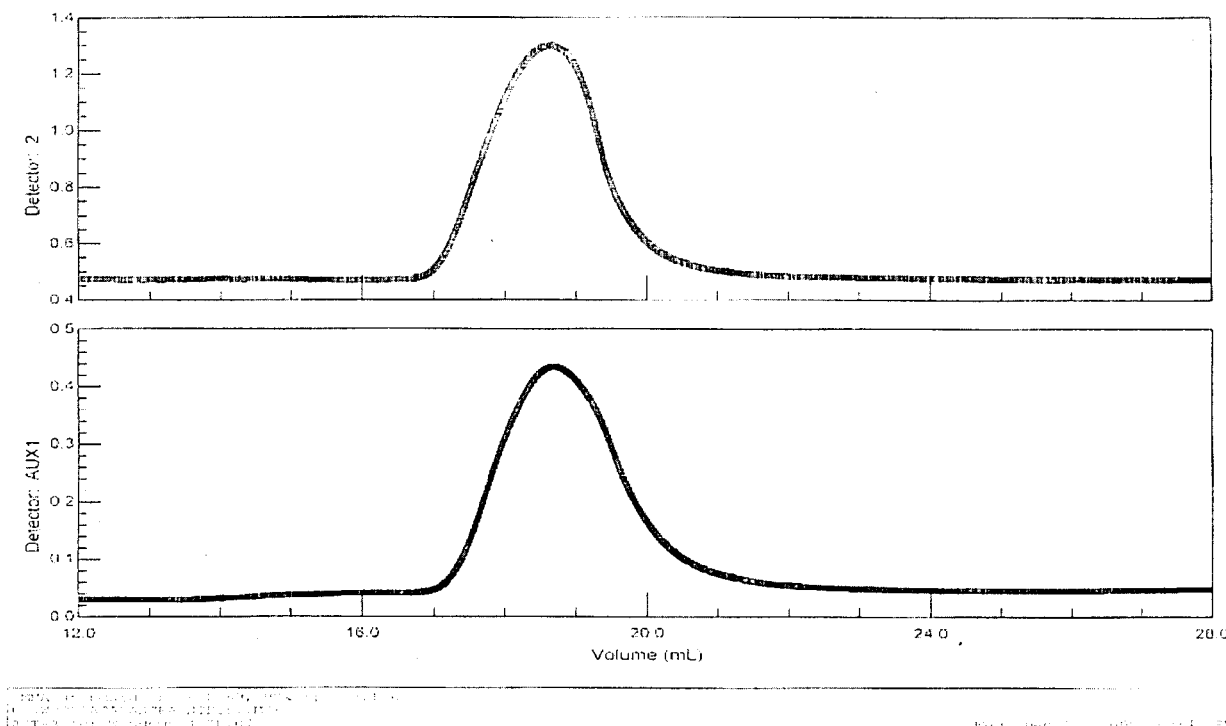


Figure 2 Representative MALLS (light scattering) and RI (concentration) output for PMMA in the HFIP no-salt system.

expansion of the chain from a relaxed coil to a more expanded form in solution.

Figure 4 shows a representative PA-11 molecular weight data, measured by the SEC-MALLS/HFIP system without salt. As seen in Figure 4, MALLS detection calculates  $M_w$  slice by slice as the polymer elutes from chromatography, and has a lower limit of approximately 7500 Daltons for PA-11.

In addition to calculating molecular weights using light scattering measurements, a conventional plot of  $M_w$  vs the retention volume peak using refractive index data from size exclusion chromatography can be constructed. The accuracy of a calibration using this technique is severely limited by an assumption that the hydrodynamic radii for all of the polymers, both

the standards and analytes, are consistent for all given values of  $M_w$ . Nevertheless, this technique can be useful in comparing the molecular weight of polydisperse samples, especially those with appreciable amounts of low molecular weight polymer near or below the lower limit of detection by light scattering.

A plot of molecular weight vs retention volume for the PMMA and PA-11 samples is provided in Figure 5. This plot shows a similar linear trend for PMMA and PA-11 retention volumes that are closely related, again suggesting there is not more than the expected expansion for the PA-11 in HFIP without salt.

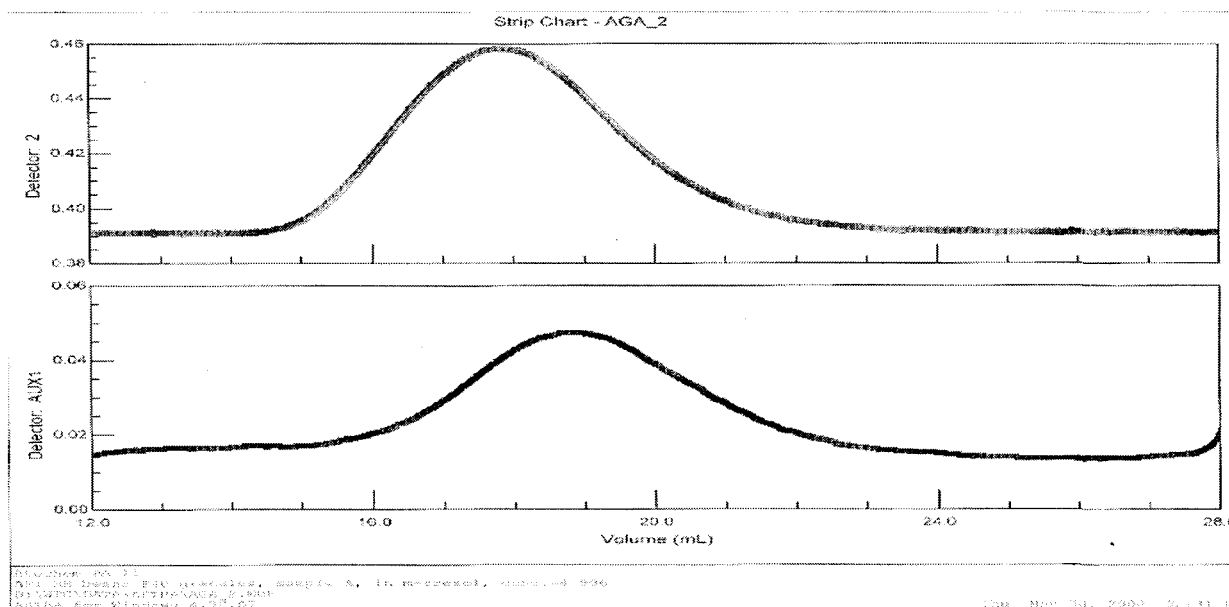
A universal calibration can be used to estimate molecular weights based on a combination of viscosity measurements and retention volumes. However, in HFIP, it has been previously and rather conclusively demonstrated that the universal calibration is not an improvement, and does not work well for polymers such as polyamides and PMMA in HFIP.<sup>6,10</sup>

TABLE I  
PMMA Analysis in HFIP No Salt System  
Multi Angle Light Scattering

Sample (MW)	$M_w$	$R_g$
2400	2080	—
4910	4100	—
6900	6150	—
10,000	9744	—
28,900	30,660	12 + 4
69,000	70,180	13 + 4
212,000	232,400	15 + 4
910,500	913,500	49 + 1

#### PFA

The poly(fluoro acrylate) or PFA, the focus of this study, has a unique structure compared to the PMMA and PA-11. To understand the behavior of the HFIP-solvated PFA molecules and the effect of the detection method, the samples were studied in two detection systems and both with and without salt. Light-scattering results from the multiangle (MALLS) under no



**Figure 3** Representative MALLS (light scattering) and RI (concentration) output for unaged PA-11 in the HFIP no-salt system.

salt, 0.05 M KTFA salt and 0.02 M NaTFA salt conditions and the single-angle (RALLS) light-scattering system with 0.05 M KTFA salt are reported in Tables III and IV.

As seen in the tables, there are noticeable differences between the data sets, salt vs no salt, a 0.02 M sodium salt vs a 0.05 M potassium salt and the MALLS vs RALLS detection systems. Overall, the calculated values for  $M_w$  and  $R_g$  from the SEC-MALLS system are consistently higher than the Viscosity-RALLS system. The values differ by a factor of up to nearly 2 for the PFA homopolymer set.

First, some notes on the data collection. In the first stage of this experimental work, data was taken with the MALLS system *without* salt and on the RALLS system *with* salt. It was postulated that the difference in calculated  $M_w$  values was due to an unexpected

polyelectrolyte effect; an "aggregation" resulting in higher mw values seen in the MALLS salt-free system but not in the RALLS salt system. It is known that localized charges on the polymer side groups can cause the polymer chains to become extended in solution. In a traditional SEC salt effect experiment, dissolved salt can counteract a polyelectrolyte effect, allowing the solvated polymer chains to relax into a near random coil state.

Without exhaustive salt *and* no salt data for both detector systems, the difference between the RALLS and MALLS data sets was postulated to be a result of this unexpected aggregation effect, due to attractive interactions between the large fluorinated hydrophobic side groups. It was hypothesized that these hydrophobic side groups are attracted to each other in the HFIP solution, resulting in chain pairs where the ends of each chain extend beyond each other due to partial chain overlap. In this working hypothesis the salt present in the RALLS system induces the chains to separate, resulting in the lower calculated molecular weights and corresponding values of  $R_g$  of the single chain. This hypothesis was disproved after additional consideration of the two data sets as well as with the acquisition of additional data in two MALLS salt studies.

First 0.02 M sodium trifluoroacetate was added to the solvent. The addition of this salt into the HFIP mobile phase of the MALLS system caused an increase in baseline noise for light scattering. Although this noise decreased the overall signal-to-noise ratio in the MALLS measurements, only in the two low molecular weight samples was this issue of serious concern. For

**TABLE II**  
MALLS Characterization of PA-11 in HFIP  
with and without Salt

Sample	No salt		0.05 M KTFA salted HFIP	
	$M_w$	$R_g$	$M_w$	$R_g$
Unplasticized PA-11 made 6/28/99	17,100	12 ± 4	14,700	8 ± 4
Unplasticized PA-11 made 6/17/99	26,010	15 ± 3	24,200	17 ± 3
Unplasticized PA-11 made 6/3/99	53,760	19 ± 2	53,300	20 ± 2
Commercial PA-11 Asg B	62,360	26 ± 2	61,400	18 ± 2

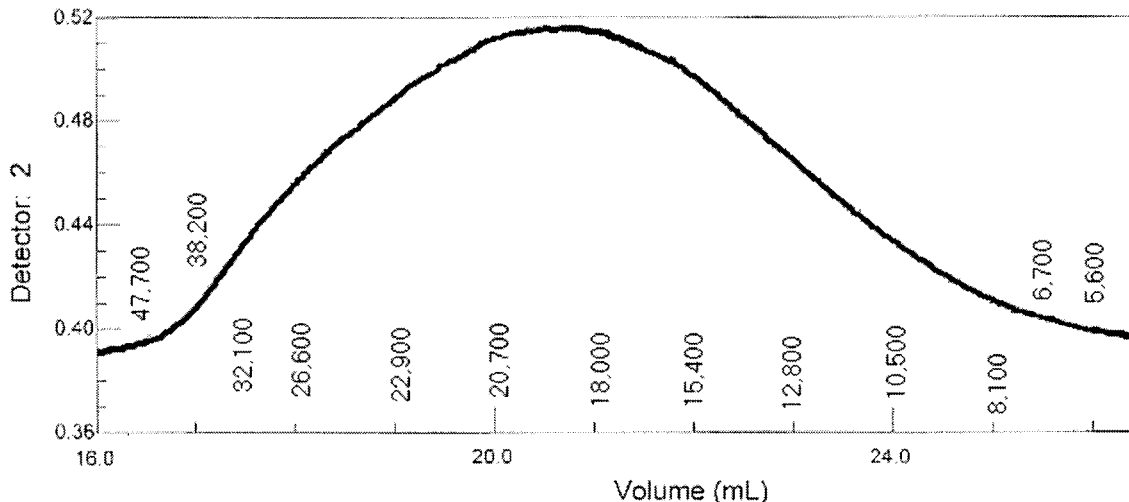


Figure 4 The 90° light-scattering signal trace and the molecular weight distribution for PA-11,  $M_w \sim 15,000$  Daltons.

the other samples, which have a much larger  $M_w$  and thus scatter light with greater intensity, the large response of the polymer light-scattering signal was much larger than the noise level in the baseline. Then, to have a direct comparison of the two detector systems 0.05 M potassium trifluoroacetate was added to the HFIP. The  $M_w$  values are close to the expected uncertainty. But slightly higher values for  $M_w$  are seen in the MALLS-salt testing vs the MALLS-no salt testing. We believe they result from additional noise in the overall light-scattering signal for the salt systems.

The presence of trace amounts of water and the decreasing sensitivity of the MALLS detector to characterize molecular weights below 7500, made a complete characterization of the molecular weight distribution difficult. Further, the runs using one column plus a guard column approached 2 h in length. Thus,

the focus of this work was on measuring  $M_w$ . Nevertheless, values of  $M_z/M_w$  do provide insight into the molecular weight distribution. For the PFA polymers the  $M_z/M_w$  ratios were  $1.4 \pm 0.1$ . We believe this value to be on the low side, because the  $M_z/M_w$  value for the PA-11 was  $1.35 \pm 0.05$  and the expected value for this condensation polymer is 1.5.

Discussion of  $R_g$

The MALLS system directly measures  $R_g$  using the angular dependence,  $P_\theta$ , of scattered light from the dissolved polymer. This technique is limited to molecules with  $R_g$  of more than about 10 nm for reasonable resolution,<sup>11</sup> but the measurement requires no assumption about the shape or conformation of the polymer in solution or its relation to the hydrodynamic volume. Only knowledge of the exact wavelength of light,  $\lambda$ , and the scattering intensity at each

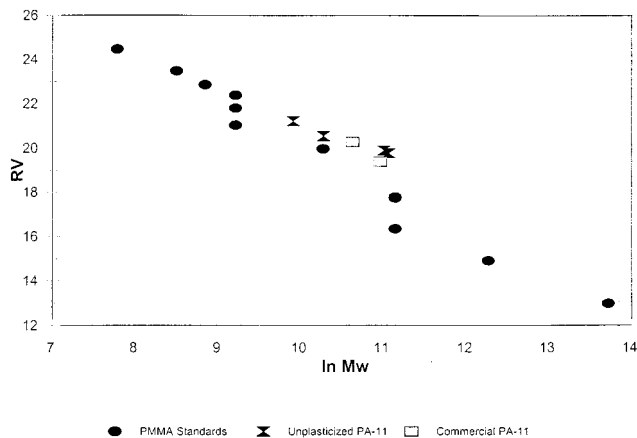


Figure 5 A plot of molecular weight vs retention volume for the PMMA and PA-11, without salt, showing a similar linear trend for PMMA and PA-11 retention volumes, suggesting there is not a major distortion in shape due to a polyelectrolyte effect for either polymer in HFIP.

TABLE III  
MALLS and RALLS Characterization of PFA  $M_w$

Sample	MALLS			Viscosity-rAlls
	No salt	0.02 M NaTFA	0.05 M KTFA	0.05 M KTFA
	$M_w$	$M_w$	$M_w$	$M_w$
2	29,000	—	27,740	17,850
3	104,000	—	101,100	72,920
4	201,000	228,000	236,000	164,600
5	696,000	849,000	835,000	506,300
6	929,000	1,011,000	1,041,000	577,700
8	1,126,000	1,128,000	1,290,000	734,100
9	1,072,000	1,101,000	1,050,000	641,400
9 (1/3) <sup>a</sup>	1,057,000	—	—	—

<sup>a</sup>Sample run at 1/3 concentration to show that concentration is not a *facto*.

TABLE IV  
MALLS and RALLS Characterization of  $R_g$  in PFA

Sample	MALLS			Viscosity-ralls
	No salt	0.02 M NaTFA	0.05 M KTFA	0.05 M KTFA
	$R_g$	$R_g$	$R_g$	$R_g$
2	—	—	—	2.9
3	16 ± 4	—	11 ± 4	5.7
4	19 ± 3	25 ± 3	18 ± 3	9.0
5	46 ± 2	49 ± 2	32 ± 2	17.9
6	50 ± 2	52 ± 2	33 ± 2	19.6
8	56 ± 2	57 ± 2	37 ± 2	22.9
9	57 ± 2	57 ± 2	36 ± 2	20.2
9 (1/3) <sup>a</sup>	52 ± 2	—	—	—

<sup>a</sup> Sample run at 1/3 concentration to show that concentration is not *a facto*.

angle  $\theta$  is used. The relationship between  $P_\theta$ ,  $\lambda$ , and mean square radius is:<sup>12</sup>

$$1/P_\theta = 1 + (16\Pi^2/3\lambda^2) \langle r_g^2 \rangle \sin^2(\theta/2) \quad (1)$$

Thus, because MALLS measures light scattering at multiple angles simultaneously, this method is exact and preferable in cases where the conformation in solution is unknown.

For measurement of  $R_g$ , the RALLS system employs measurements of viscosity, which are related to the hydrodynamic volume of the polymer in solution. This viscosity data is then used to estimate  $R_g$  via a series of assumptions, equations, and a combination with data from light scattering at one angle.

The light-scattering equation relates polymer scattering through the excess Rayleigh Rati,  $R_\theta$ ; sample concentration,  $c$ ; the second virial coefficient,  $A_2$ ;  $M_w$ ; and  $P_\theta$  as:<sup>12</sup>

$$Kc/R_\theta = (M_w P_\theta)^{-1} + 2A_2c \quad (2)$$

where  $K$  is the traditional optical constant, which includes the wavelength of light used:  $\lambda$ , the refractive index of the solvent,  $\eta$ , and the specific refractive index increment,  $d\eta/dc$ .

The first assumption for this model is that the polymer is at infinite dilution in solution. This is a reasonable and practical assumption that allows the  $2A_2c$  term to be dropped from the light scattering equation.

$$Kc/R_\theta = (M_w P_\theta)^{-1} \quad (3)$$

Then a calculation of molecular weight can be made by assigning  $P_\theta$  an initial iterative value of 1 and solving for  $M_w$ . Given that  $P_\theta$  approaches unity for molecules with an  $R_g$  of  $\lambda/20$  or less, this is a reasonable assumption for small molecules. Particles of a size on the order of  $\lambda/20$  or less scatter light in all direc-

tions equally. However, the angular dependency of light scattering for larger particles is significant. Thus, the  $P_\theta = 1$  estimate is a significant source of uncertainty for this study, considering that many of the samples have an  $R_g$  greater than  $\lambda/20$ .

The next assumption is that the polymer is in a random coil state in solution. This assumption is necessary to determine the angular dependency term  $P_\theta$ , as  $P_\theta$  cannot be measured directly with only a right-angle light-scattering measurement. Assuming the random coil conformation in solution permits an estimate of the Mark-Houwink constant "a." But the conformation in solution is an unknown characteristic for the poly(fluoro acrylate) under study. The "a" term is, in fact, unknown. As such the assumption of a shape of the dissolved polymer molecule in solution is a source of uncertainty.

Nevertheless, with this estimate of the Mark-Houwink constant, the Flory-Fox and Ptitsyn-Eizner formalisms<sup>13,14</sup> can be used to estimate the value of  $R_g$ . This approach uses the experimentally measured viscosity,  $\eta$  and the first estimate of  $M_w$  from the modified light scattering equation (3):

$$Rg = 1/6^{0.5*}([\eta]M_w/F)^{1/3} \quad (4)$$

where

$$F = 2.86 \times 10^{21}(1 - 2.63\varepsilon + 2.86\varepsilon^2) \quad (5)$$

and

$$\varepsilon = (2a - 1)/3 \quad (6)$$

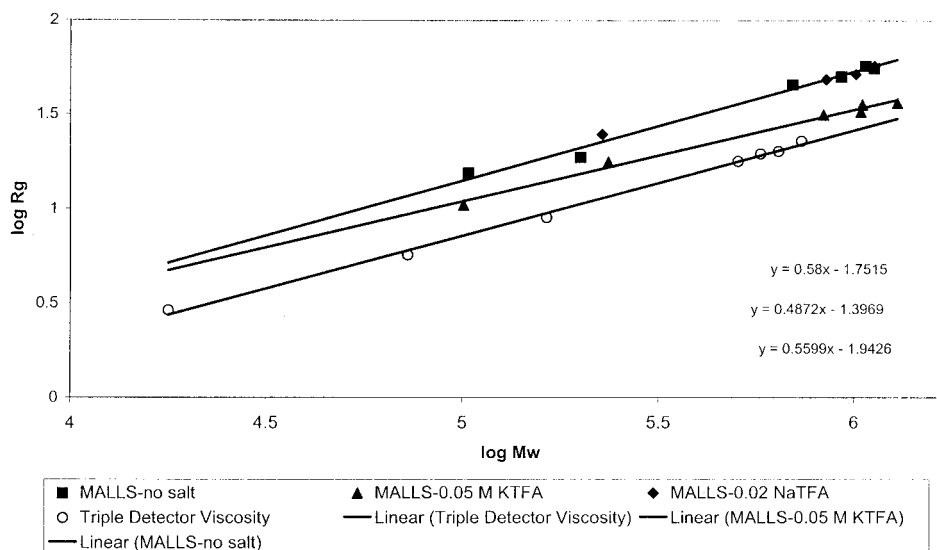
The use of eqs. (4), (5), and (6) introduces additional uncertainty in this approach. Equation (5) is susceptible to errors derived from these empirically determined universal constants that are not necessarily applicable to every polymer such as the PFA under study.

With an estimate of  $R_g$  and still assuming the random coil conformation, the angular dependence  $P_\theta$  can be back-calculated. The following relation is used:

$$P(\theta)_{\text{est}} = [2^*(e^{-x} + x - 1)]/x^2 \quad (7)$$

$$x = 4\Pi n_o/\lambda_o R_g \quad (8)$$

and  $n_o$  is the refractive index of the solvent. Now this estimate of  $P_\theta$  is inserted into eq. (3) for recalculation of  $M_w$ , and the cycle is iterated until  $M_w$  and  $R_g$  no longer change. Thus,  $R_g$  and  $M_w$  in this approach are not directly measured but rather are based on a single-angle light-scattering measurement, an assumption of conformation and the applicability of the Flory-Fox and Ptitsyn-Eizner equations.



**Figure 6** A plot of  $\log R_g$  vs  $\log M_w$  for PFA measured using MALLS without salt, with 0.05 M KTFA salt and using RALLS-viscosity with 0.05 M KTFA salt.

### SUMMARY OF RESULTS

The PFA molecules in samples 1, 2, and 3 are beyond the limit of detection for meaningful MALLS measurement of  $R_g$ . Nevertheless, both the MALLS and RALLS systems report clear trends in  $M_w$  and  $R_g$ , which match changes in polymerization chemistry over the sample set. Samples 1 through 4 show increasing values for  $M_w$  and  $R_g$ , indicative of the decreasing amounts of chain transfer agent used in each polymerization. Much higher  $M_w$  and  $R_g$  values are reported for samples 5, 6, 8, and 9, the samples polymerized without chain transfer agent.

Again, looking at Tables III and IV, there are differences in calculated values of  $M_w$  and  $R_g$  for each sample in the RALLS system with salt vs the MALLS system with salt. The MALLS salt and no-salt data reflect the extent of the chain expansion due to a polyelectrolyte effect in HFIP mobile phase without salt. A plot of  $\log R_g$  vs  $\log M_w$  (Fig. 6) suggests that roughly the excluded volume expansion factor 0.6 vs the excluded volume expansion factor 0.5 relationship between  $R_g$  and  $M_w$  holds for samples in the pure HFIP vs HFIP with 0.05 M KTFA salt. That is, the random coil shape of the PFA is extended in HFIP, but not in 0.05 M KTFA. The 0.02 M sodium salt is not strong enough to remove the polyelectrolyte excluded volume effect and the dependence of  $R_g$  on  $M_w$  is closer to the no-salt case.

The triple detector viscosity determined  $R_g$  slope in HFIP with 0.05 M KTFA is 0.56, lower than that observed from light scattering.

The variation of 3 to 15% for  $M_w$  in the results between MALLS with and without salt is evidence enough that the polyelectrolyte effect does not effect the MALLS calculation of  $M_w$  in HFIP (ref Table III).

Yet, the RALLS-calculated molecular weights are lower by a factor of 2 and  $R_g$  is 50% smaller than the value calculated by MALLS, strongly suggesting the method and assumptions used to calculate  $M_w$  using a single right-angle detector coupled with viscosity and the Flory-Fox, Pititsyn-Eizner formalism are not valid for this PFA polymer system. On the other hand, the viscosity detector can measure the relative size of the polymer with better precision at very low molecular weights.

### CONCLUSIONS

The results for PMMA and PA-11 demonstrate that HFIP is an excellent room temperature solvent for use in Multiangle Laser Light-Scattering measurements of molecular weight for those polymers, with evidence of no need for salt in solution to characterize  $M_w$  by MALLS. There is no effect of the presence of salt vs no salt on the measurement of  $M_w$  for the PFA in HFIP using MALLS. This behavior is evidenced by the linearity of the plot of  $\log R_g$  vs  $\log M_w$  for both the no-salt and salt systems and by the agreement within experimental uncertainty between measured values of  $M_w$  by the MALLS detector in conditions with and without salt in the mobile phase. Overall, the PFA polymer is observed to be a random coil experiencing excluded volume to no excluded volume conditions depending on salt concentrations. Differences in calculated values of  $M_w$  and  $R_g$  for PFA by Multiangle Laser Light Scattering (MALLS) vs Right-Angle Laser Light Scattering (RALLS) are a function of the assumptions used in the RALLS method for these high molecular weight fluorinated polymers.

Overall, MALLS depends only on normal light scattering and the assumption of a low concentration while

RALLS with a one-point detector uses polymer theory, which is particularly weak for highly polar polymers.

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