

Morphology of Perfluoroalkylacrylate/Stearyl Methacrylate Polymers and Their Effect on Water/Oil Repellency

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ABSTRACT: The small-angle X-ray scattering technique was applied to study the morphology of a series of water-repellent terpolymers polymerized from a fluoro-component, a hydrocarbon-component and a crosslinking agent. The intraparticle homogeneity of the terpolymers was semiquantitatively determined from the small-angle X-ray spectra using a proposed structural model. The X-ray results were correlated to the water repellency test data using the AATCC test method 22-1989. The consistency of the polymerization reaction process as a function of the weight ratio of the fluoro-components is discussed. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 903–909, 1997

Key words: oil repellency; small angle x-ray scattering

INTRODUCTION

Fluorochemicals have been known to exhibit both water and oil repellency since the late 1950s and 60s.^{1–5} Nowadays, varieties of water- and oil-repellent polymers are available in the market. The fluorinated compounds remain the most common active ingredients for water- and/or oil-repellent purposes.^{6,7} As far as water or oil repellency is concerned, the efficiency increases when the weight ratio of the fluoro-components in the polymer increases. However, the relatively high market prices of the fluorinated monomers limit their use, unless their weight ratios can be minimized while maintaining reasonable water/oil repellency. One alternative to resolve this dilemma is to enhance the homogeneity of the monomers during the polymerization reaction. Thus, a randomly polymerized form becomes the ideal intra-

molecular distribution from the water- and/or oil-repellency point of view.

In this work we performed a polymerization reaction using perfluoroalkylacrylate (Zonyl TA-N, the fluoro-component) and stearyl methacrylate (SMA, the hydrocarbon-component) as the monomers and *N*-methylolacrylamide (*N*-MAM) as the crosslinking agent. Four TA-N to SMA weight ratios were used to make the terpolymers. The resulting terpolymers had molecular weights ranging from approximately 150,000 to 200,000. We then characterized the morphology of these polymers using the small angle X-ray scattering (SAXS) technique. SAXS measurements allowed us to semiquantitatively determine the morphology of the terpolymer, the structure of the monomers in the terpolymer, and the intraparticle homogeneity. From the intraparticle homogeneity, the consistency of the polymerization process, as a function of the TA-N/SMA ratio, can be evaluated. The intraparticle homogeneity was characterized by analyzing the intensity of the scatter-

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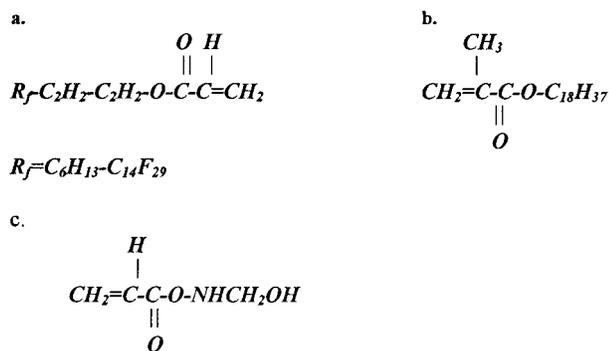


Figure 1 Chemical structures of TA-N (a), SMA (b), and *N*-methylolacrylamide (c).

ing peaks with increasing TA-N/SMA ratios. The structure of the monomers in the terpolymer was determined by fitting the SAXS data with a structural model we proposed. Information extracted from this analysis can be compared to the water repellency test (the AATCC test method).

The next section describes the chemical structure of the components used in the polymerization reaction, the sample preparation processes, the polymerization reaction, the SANS set up and measurement, and the AATCC water-repellency test. In the third section the scattering intensity is briefly introduced and the structural model used for SAXS data analysis is derived. The fourth section discusses the experimental results and data analysis, and results from model-independent analyses and model fitting are given. This is followed by a discussion of the results in the fifth section and conclusion in the sixth section.

EXPERIMENTAL

Samples

The perfluoro alkyl acrylate (PFA) monomer (referred to as Zonyl TA-N) was from DuPont with >95% purity. It was used for the polymerization reaction directly without further purification. The hydrocarbon-component used was the industrial grade stearyl methacrylate (SMA). It was from the Eternal Chemical Corporation, Ltd., Taiwan. Their respective structures are depicted in Figure 1. The crosslinking agent, *N*-methylolacrylamide (45% aqueous solution), was also from the Eternal Chemical Corporation, Ltd., Taiwan. *N*-methylolacrylamide was kept at 2 wt % for all samples studied.

Polymerization Reactions

The polymerization reaction was a typical emulsion polymerization method. The monomers and the crosslinking agent were first pre-emulsified in a dilute aqueous solution containing ITRI-A mixed surfactant (a proprietary synergistic formulation containing two nonionic surfactants and a cationic surfactant). The mixed surfactants served as dispersant of the hydrophobic monomers. The pre-emulsified monomers-surfactant mixture was homogenized at 13000 rpm for 20 minutes with a starting temperature of 25°C and an ending temperature at 50°C. The resulting emulsion was then fed dropwise into an aqueous nonionic/cationic mixed surfactant solution at room temperature. The feeding process lasted for approximately 3 hours. The system was agitated for another hour after feeding was completed. The surfactant amount used in the reaction was far less than the monomer amount. Therefore, it had no essential effect on the intraparticle homogeneity of the terpolymers, nor on their water repellency.

The polymerization reaction was initiated by adding 0.5% ammonium persulfate. The reaction temperature was kept at 75°C. When the reaction was completed, the reactor was cooled to room temperature. The resulting latex solution was then filtered by a 127 μm pore size filter to obtain the final products for SAXS study. The solid content of the final product was about 20%.

SAXS Experiment

The SAXS experiment was performed on the 10-meter small-angle spectrometer at Oak Ridge National Laboratory. A rotating anode with a copper target operated at 4 kW to generate photons at various wave lengths, λ . The $\lambda = 1.54 \text{ \AA}$ (i.e., copper K_{α}) photons were selected using a graphite monochromator. The selected photons then passed through a series of pin-hole collimators before impinging onto the sample cell made of aluminum with two Kapton windows. The path length of the cell was 1 mm. Besides measuring the terpolymer samples, the transmission, empty cell spectrum, and background were also measured for data reduction and intensity correction. The detector used was a 20 × 20 cm two-dimensional continuous wire detector. The sample-to-detector distance was kept at 2 meters which resulted in a momentum transfer range $Q = [4\pi/\lambda \sin(\theta/2)]$, $\theta =$ scattering angle] of 0.01 to 0.35 \AA^{-1} .⁸

Water Repellency Spray Test (The AATCC Test Method)

The latex solution from the polymerization reaction was first diluted with water 20 times in volume. The diluted solution contained approximately 1 wt % solid. The tested cloth was dipped into this diluted latex solution, then passed through a padder to remove the excess water. The cloth was then dried at 170°C for a 90 second period, followed by a four-hour setting period before we performed the water repellency test (AATCC test method 22-1989). This process loaded approximately 0.1 wt % polymer to the test cloth.

SAXS INTENSITY DISTRIBUTION

The scattering intensity distribution function, $I(Q)$, for a dispersed system consists of two major factors, namely, the interparticle structure factor and the intraparticle structure factor. The former describes the correlation between scattering centers and the latter provides the information about the shape and the size of the scattering centers.^{9,10}

It is anticipated that a fraction of the TA-N and SMA will be well dispersed so that only intraparticle structure factors are observed in the scattering. In the meantime, other fractions of TA-N and SMA maintain their original forms and exhibit their respective structures. The experimental spectra do exhibit pronounced small-angle scattering (single particle scattering), as well as the characteristic peaks (the interparticle scattering) indicative of a mixing of these two modes.

To model the scattering intensity $I(Q)$ of such a mixing mode system, one writes $I(Q)$ as

$$I(Q) = \alpha[P_T(Q) + P_T(Q)S_T(Q)] + \beta[P_S(Q) + P_S(Q)S_S(Q)] \quad (1)$$

where α is the weight ratio of the TA-N, $P_T(Q)$ is the intraparticle structure factor of TA-N, and $S_T(Q)$ is the interparticle structure factor of the TA-N. β , $P_S(Q)$, and $S_S(Q)$ have the same meaning for SMA. If we assume both TA-N and SMA are spherical and their correlation peaks are describable by a power law, then, P_T , P_S , S_T and S_S can be rigorously formulated.

In order to calculate the intraparticle structure factor accurately, particle polydispersity is included in the formalism. For this particular case,

the Schultz distribution function is used to describe the polydispersity. Taking the mean radius of the particles as R_i and the width parameter of the Schultz distribution as z_i , one can quantify the polydispersity by¹¹⁻¹⁴

$$P_i = \frac{\sqrt{\langle R_i^2 \rangle - \langle R_i \rangle^2}}{\langle R_i \rangle} = \frac{1}{\sqrt{z_i + 1}} \quad (2)$$

For a system containing particles with sizes according to the Schultz distribution, the intraparticle structure factor can be derived explicitly^{14,15}

$$P_i(Q) = 8\pi^2 \left[\frac{R_i}{z_{ij} + 1} \right]^6 (\omega_i^6 - \xi_1 + \xi_2 + \xi_3 + \xi_4) \quad (3)$$

where $i = T, S$; $z_{ij} = z_i + j$; $\omega_i = z_{ij}/QR_i$ $\mu_{ij} = z_{ij} \cdot \tan^{-1}(2/\omega_i)$.

$$\xi_1 = \cos(\mu_{i1}) \times \exp \left[\frac{z_{i1}}{2} \log(4 + \omega_i^2) + z_{i7} \log(\omega_i) \right] \quad (4)$$

$$\xi_2 = z_{i1}z_{i2}\omega_i^4 \quad (5)$$

$$\xi_3 = \cos(\mu_{i3})z_{i1}z_{i2} \times \exp \left[-\frac{z_{i3}}{2} \log(4 + \omega_i^2) + z_{i7} \log(\omega_i) \right] \quad (6)$$

$$\xi_4 = -2 \sin(\mu_{i2})z_{i1} \times \exp \left[-\frac{z_{i2}}{2} \log(4 + \omega_i^2) + z_{i7} \log(\omega_i) \right] \quad (7)$$

The structure factor $S_i(Q)$ describes the morphology of the intercorrelated monomers. Although the structures of the monomers remain intact, their intercorrelation is re-established upon the polymerization reaction. As a result, no rigorous mathematical form can be derived *a priori*. We thus chose a convenient power law form for the structure factor^{16,17}

$$S_i(Q) = \exp \left[-\frac{|Q - Q_i|^{\eta_i} R_i^{\eta_i}}{\sigma_i} \right] \quad (8)$$

where Q_i is the peak position of the i th species, σ_i is the standard deviation, and η the power law exponent. Equations (1)–(8) are used to fit the

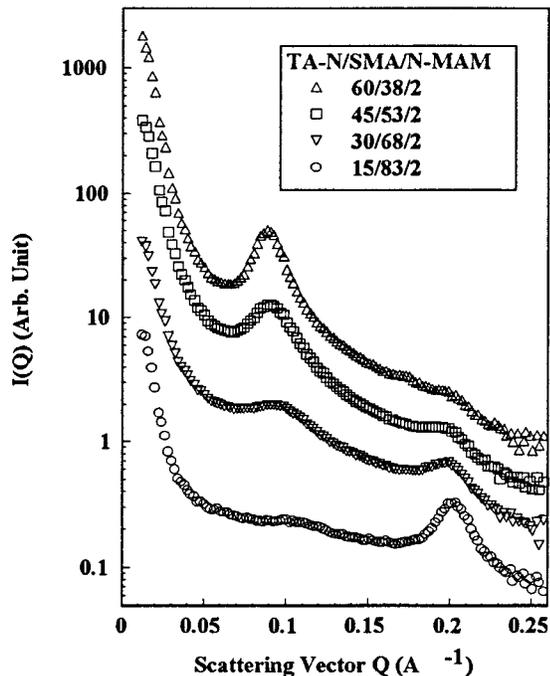


Figure 2 $I(Q)$ for TA-N/SMA/N-MAM. The curves are shifted for better presentation.

experimental data with eight parameters: the particle radii R_T and R_S , width parameters z_T and z_S , power law exponents η_T and η_S , and standard deviations σ_T and σ_S .

RESULTS AND ANALYSIS

Scattering and Structure

Figure 2 shows the scattering intensity distribution function $I(Q)$ for four TA-N/SMA mixed systems. The scattering spectra are shifted for better presentation.

There are two characteristic peaks observed in each curve. From the growth of the peaks as a function of the TA-N/SMA weight ratio, one sees the small Q peaks (referred to as the T peak in the text that follows) correspond to TA-N, while the large Q peaks (referred to as the S peak) correspond to SMA. One also sees that the T -peak position, Q_T , increases when the TA-N content decreases. This can be understood from the coupling of $P_T(Q)$ and $S_T(Q)$. When the TA-N weight ratio decreases, the number of large particles in the terpolymer decreases. The $P_T(Q)$ thus extends out to high Q and results in the positive shift of the TA-N peak position. On the other hand, the S -peak position, Q_S , is more or less independent

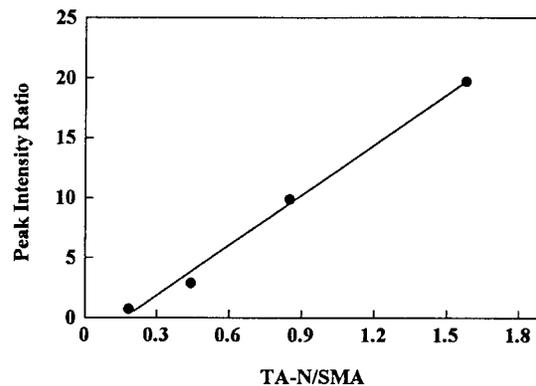


Figure 3 $I_T(Q_T)/I_S(Q_S)$ as a function of TA-N/SMA weight ratio.

of the SMA content, since both $P_T(Q)$ and $P_S(Q)$ level off at $Q = \sim 0.2 \text{ \AA}^{-1}$.

Figure 3 shows the relative intensity of the T peak to the S peak [i.e., $I_T(Q)/I_S(Q)$] as a function of their weight ratio. It increases linearly, indicating that the homogeneity (or miscibility) is independent of TA-N/SMA weight ratio. It also indicates that the polymerization process we used to make TA-N/SMA copolymer is consistent, regardless of their mixing ratios.

Before the $P_i(Q)$ - $S_i(Q)$ model (eqs. (1)–(8)) is introduced, the scattering data at a sufficiently small Q range can be analyzed using the Guinier theory.¹⁸ It is a model-independent method. It can provide a rough sketch of the structure, even in a multicomponent system. The Guinier analysis approximates the scattering intensity by

$$I(Q) \sim \exp\left(-\frac{Q^2 R_g^2}{3}\right) \quad (9)$$

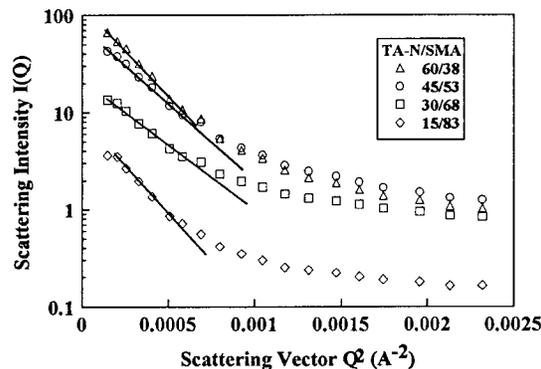


Figure 4 The Guinier analysis for the TA-N/SMA system of various TA-N/SMA ratios.

Table I The Extracted Parameter Values from the Model Analysis

TA-N/SMA	R_g (Å)	R_T (Å)	R_S (Å)	P_T (%)	P_S (%)	η_T	η_S	σ_T ($Q \cdot R_T$)	σ_S ($Q \cdot R_S$)
60/38	109.9	105.8	31.5	21.1	20.3	1.21	.31*	1.29	5.98
45/53	99.9	96.1	34.5	24.6	24.9	1.11	.73*	1.67	1.31
30/68	94.3	94.3	27.2	23.2	23.2	.18	1.49	3.50	0.30
15/83	106.6	113.1	30.4	22.0	21.9	.77*	1.23	5.72	0.31

* The data may not have sufficient statistics for accurate extraction of the parameters.

where R_g is the radius of gyration. Equation (1) is applicable for the Q range where $QR_g < 1$.

Figure 4 shows the Guinier analysis for the four samples investigated. The R_g values obtained are tabulated in Table I. In the small Q range the scattering intensity $I(Q)$ is dominated by the form factor. From eq. (3) one easily sees that the large particles would contribute to the scattering intensity more than the small particles in this Q range. In our systems, the large particles are the TA-N molecules. The R_g values extracted from the Guinier analysis for all four systems are around 100 Å. This means that the size of the TA-N particles should be around 100 Å. R_g varies slightly when the TA-N weight ratio decreases. This is partly due to the coupling effect from the increasing SMA particles, which have smaller sizes.

If we treat the TA-N particles as the dispersed phase immersed in the SMA "solvent," then the intensity at $Q = 0$, $I(Q)$, should show a simple linear relation as a function of TA-N/SMA weight ratio. $I(0)$ can be estimated by extrapolating the Guinier analysis to $Q = 0$. This can be done by taking the exponential of the constants obtained from the linear regression analysis. In Figure 5 we show $I(0)$ as a function of the TA-N/SMA

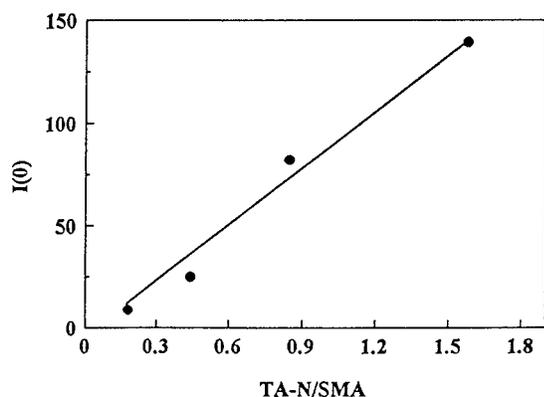


Figure 5 $I(0)$ as a function of TA-N/SMA weight ratio.

weight ratio. As expected, the intensity correlates very well with the weight ratio of the TA-N. This indicates that the large particles are indeed TA-N monomers and they can be treated as the dispersed phase immersed in SMA. Structurally, it appears that the TA-N particles form the disperse phases and are coated with the crosslinking agent *N*-methylolacrylamid.

In the following we present an analysis using the model developed [see eqs. (1)–(8)] to quantify the equations' respective contributions to the scattering intensity spectrum. Figures 6–9 show the model fitting using eqs. (1)–(8). The symbols are experimental data and the solid line is the fit. The agreement is excellent for all four samples. Because eight adjustable parameters were used in the fitting process, non-unique convergence may occur. To avoid it, we restricted some of the parameter values to be within certain physical ranges. For example, the particle radii were restricted to be around the values extracted from the Guinier analysis and the standard deviations around the full-width half maximum of the scattering peaks. Additionally, we checked the convergence with different starting parameter values. With the constraints imposed, we used various

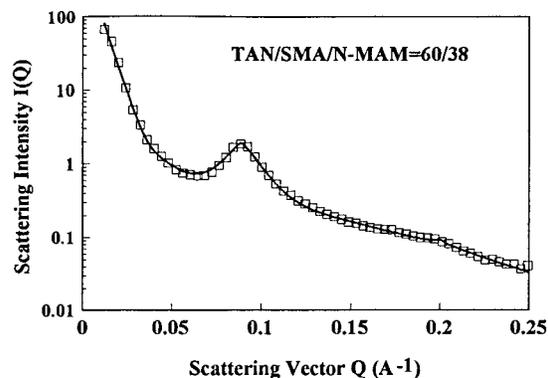


Figure 6 $I(Q)$ for TA-N/SMA = 60/38 (symbol) and the model fitting (solid line).

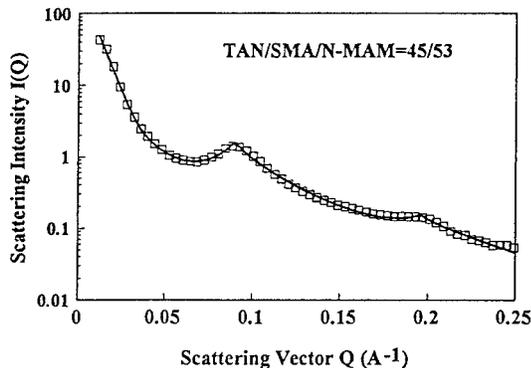


Figure 7 $I(Q)$ for TA-N/SMA = 45/53 (symbol) and the model fitting (solid line).

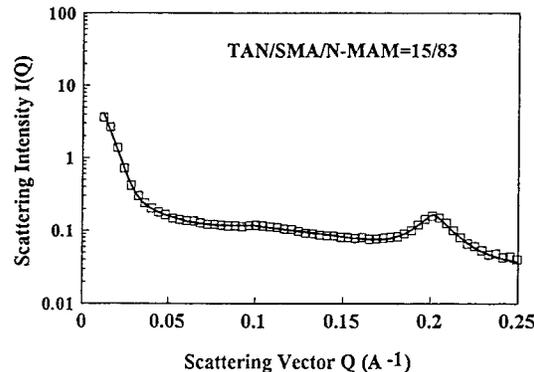


Figure 9 $I(Q)$ for TA-N/SMA = 15/83 (symbol) and the model fitting (solid line).

starting parameter values and found the convergence is unique, at least for the data we analyzed. The parameter values extracted from these fittings are given in Table I.

R_T and R_S extracted are about 100 and 30 Å, respectively. The polydispersities for both TA-N and SMA are between 20 and 30% which is considered low. Since the sizes of TA-N and SMA remain unchanged upon changing their weight ratios, it is reasonable to conclude that the homogeneity is independent or weakly independent of the TA-N/SMA ratio. This point is further justified by comparing with Figure 3 where the scattering intensities of TA-N and SMA are linearly proportional to their relative ratios.

Water/Oil Repellency Test

Figure 10 shows the water repellency of the TA-N/SMA samples according to the AATCC test method 22-1989. In the test, the cloth coated with TA-N/SMA was tilted 45° and washed by water

with a constant flow. The water repellency was defined as the amount of water recovered after running through this tilted cloth. As one can see from Fig. 10, the TA-N amount appears to be the sole factor of its water repellency, even though SMA also shows water repellency capability. As indicated in Figure 10, water repellency reaches 80% as the TA-N weight ratio goes beyond 15% (TA-N/SMA = 15/83) and reaches 100% at TA-N/SMA = 30/68. Thus, 15% of TA-N appears to be the critical weight ratio. In fact, after five washes its water repellency is only 10% lower than that of the one with the highest TA-N content (i.e., TA-N/SMA = 60/38).

DISCUSSION

From the data extracted from the model analysis, the dependence of R_g and R_T on the TAN-N/SMA ratio is similar. The difference is that the Guinier analysis gives only the features of the large parti-

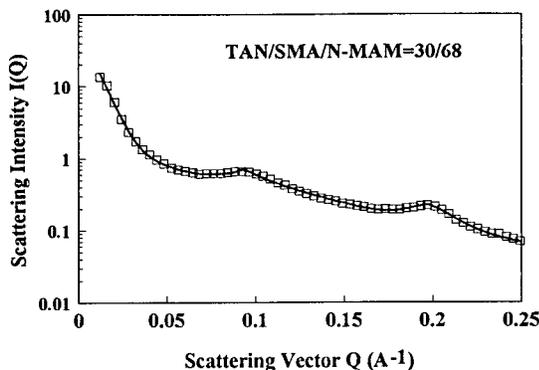


Figure 8 $I(Q)$ for TA-N/SMA = 30/68 (symbol) and the model fitting (solid line).

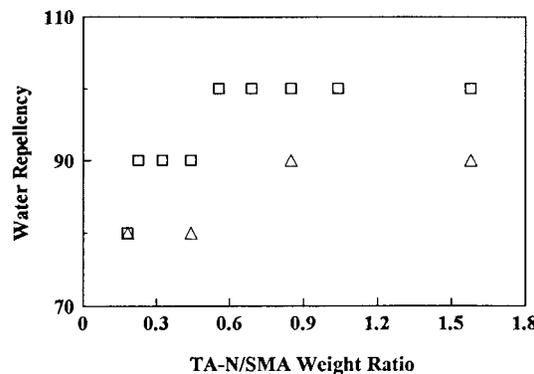


Figure 10 The water repellency test: (□) before wash and (△) after five washes.

cles. In this case, it is the TA-N particle (around 100 Å). SMA particles are smaller (around 30 Å) and can only be determined through model analysis. The sudden increase of R_g and R_T in the TA-N/SMA = 15/83 sample is due to its low TA-N content which reduces the counting statistics. Even so, the deviation is still within 15%. This is because the particle size depends on the peak position rather than the scattering intensity.

The polydispersities of both polymers are between 20 and 25%. This is considered low, which means that the polymerization process we used is plausible. Another interesting point is the power law exponents. Both polymers show power of ~ 1.2 – 1.4 , indicating a relatively weak interparticle correlation when compared with crystals or liquid crystals. The 0.77, 0.31 and 0.73 powers shown in Table I should not be taken seriously, because the counting statistics were not good enough. Power law $S(Q)$ is very sensitive to the peak shape and intensity; therefore, it requires good counting statistics before any concrete conclusion can be drawn from the fitting.

CONCLUSION

We performed a simple polymerization reaction using perfluoroalkylacrylate (Zonyl TA-N) as the fluoro-component, stearyl methacrylate (SMA) as the hydrocarbon-component and *N*-methylolacrylamide as the crosslinking agent. The resulting terpolymer morphology was characterized by small-angle X-ray scattering (SAXS). Its water repellency was tested using the standard AATCC test method 22-1989. The SAXS study and the water repellency test suggest: 1) the reaction process we used is effective and consistent in forming an appropriate morphology of the TA-N/SMA complex, as far as the water repellency is concerned; 2) TA-N forms much larger particles and can be viewed as the dispersed phase in SMA with *N*-methylolacrylamide serving as the crosslinking, as well as the surface active agent; 3) this reaction process is able to produce small enough TA-N and SMA particles (~ 100 and ~ 30 Å respectively), making TA-N/SMA thermodynamically equivalent to a miscible polymer blend; 4)

the water repellency is proportional to the Zonyl TA-N weight ratio and saturated when Zonyl TA-N weight exceeds 30% (or TA-N/SMA > 0.5); and 5) SAXS is an appropriate technique for characterizing the morphology of such systems.

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