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Dynamic Scaling and Growth Kinetics of 3-Glycidoxypropyltrimethoxysilane-Derived Organic/Silica Hybrids

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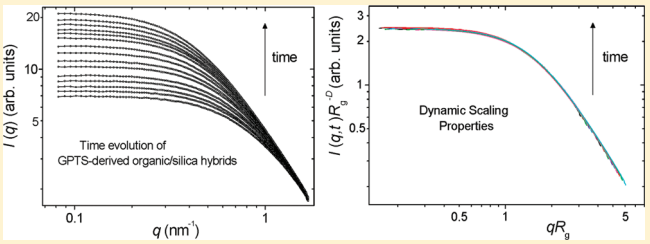
ABSTRACT: Structural evolution and dynamic scaling properties have been probed by small-angle X-ray scattering (SAXS) in the growth kinetics of 3-glycidoxypropyltrimethoxysilane (GPTS)-derived organic/silica hybrids in basic solution. The SAXS intensity curves were found to be well described by a particle form factor valid for polydisperse coils of linear chains and for particular cases of random and nonrandom polycondensates in solution together with an interference factor accounting for very weak correlations of particles. The SAXS data are consistent with formation and growth of GPTS-derived organic/silica hybrids in solution with polydispersity increasing with time. The following properties have been found: (i) The SAXS intensities $I(q,t)$ corresponding to different times t are given by a time-independent function $F(qR_g) = I(q,t)R_g^{\ D}$, R_g being the average radius of gyration of the hybrid particles; (ii) the average radius of gyration grows in a power-law with time t as $R_g \propto t^{\alpha}$, with $\alpha = 0.307 \pm 0.009$, suggesting growth of domains by a diffusion-controlled mechanism; (iii) the SAXS intensity $I(0)$ extrapolated to $q = 0$ increases in a power-law with time t as $I(0) \propto t^{\beta}$, with $\beta = 0.547 \pm 0.020$, so $\beta/\alpha = 1.78 \pm 0.12$; (iv) the extrapolated intensity $I(0)$ scales with R_g as $I(0) \propto R_g^{\ D}$, with $D = 1.69 \pm 0.01$, which is in good agreement with the value β/α and suggests that the macromolecules grow in a dimensionality ≈ 1.7, typical of macromolecules in good-solvent conditions in diluted or semidiluted solution. This set of findings is in notable agreement with the dynamic scaling properties. Dynamic scaling properties are important to confront phase-separation theories through the remarkable characteristics of the structure function associated. New insights on the development of the structural heterogeneities in hybrid materials are apprehended from the present dynamics of the sol—gel process probed by SAXS.



INTRODUCTION

Organic—inorganic hybrid materials have attracted much attention since they can be tailored to combine the advantages of organic polymers, like toughness and flexibility, with those of inorganic components yielding materials which possess enhanced mechanical properties, chemical resistance, optical quality, and other useful properties which arise from the synergistic interaction of the individual organic and inorganic constituents. Up until now, organically modified silicas (ORMOSIL) are the most studied and important class of hybrids due to their high applicability in several fields such as optics, microelectronics, energy, and medicine.[1,2] ORMOSIL synthesized via sol—gel yield nanoscale growth of inorganic domains into the organic polymeric matrix, consisting of a highly dispersed and homogeneous system achieved by molecular interactions and covalent linkages during hydrolysis and polycondensation reactions of alkoxysilane precursors.

Tetraethoxysilane (TEOS) is a tetralkoxysilane largely used in the sol—gel process due to its remarkable property of easily converting into silicon dioxide at low temperatures, by formation of Si—O—Si linkages by hydrolysis, and polycondensation reactions. Polycondensation reaction of alkoxysilane can results in a variety of structures, ranging from monodisperse silica particles to polymeric silica networks, depending on the conditions involved in synthesis.[3] The fast reaction rate of tetraethoxysilane (TEOS) during the sol—gel process and severe shrinkage during the drying process made it difficult to obtain flexible and crack free bulks.

3-Glicidoxypropyltrimethoxysilane (GPTS) is an important trialkoxysilane precursor because it possesses the functionality of both silicon and a terminal epoxy group in its molecule. GPTS is commonly employed as a coupling agent to strengthen the interaction between organic and inorganic domains because the epoxy ring can be chemically or UV-light opened and activated for molecular bonding.[4] GPTS has applications in a variety of areas like proton conducting membranes, corrosion and scratch resistant coatings, and optical applications, mainly due to its cross-linking capacity through the epoxy group. Liu et al.[5] and Peng et al.[6] introduced GPTS into chitosan and PVA matrix, respectively, and found that the moderate condensation rate of silanol in the sol—gel process effectively prevented macrophase separation during membrane formation.

ORMOSIL films are outstanding materials because through the sol—gel synthesis parameters it is possible to control the porosity, refractive index, and thickness of the coating and to improve the mechanical properties and transparency of the film

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without heat treatment.[7] When organic groups are incorporated in glasses, the shrinkage is low because the bulky organic components fill the pores between the inorganic oxide chains. The material reaches its final density at low temperature, especially if the organic groups can be cross-linked by epoxy polymerization, as is the case of GPTS.

In the sol−gel processing of the system with mixed tetra and trialkoxysilane precursors, the difference in rates of hydrolysis and polycondensation reactions of the alkoxysilanes can lead to prolonged gelation times. The study of mixed TEOS-GPTS systems is of high interest, once the resulting ORMOSIL can be tailored to possess the optimal properties and characteristics of each alkoxysilane precursors by varying sol−gel processing parameters. The sol−gel chemistry of silicon alkoxide precursors is highly complex and a great deal of investigation has gone into their hydrolysis and condensation reactions. The important feature of the organic-functionalized alkoxides polymerization is competition between the ongoing processes of hydrolysis, condensation, and phase separations, which are strongly dependent on the pH value and determine the final properties of the hybrid.[8,9]

In this work, the growth kinetics of organic/silica hybrids prepared from acid hydrolysis of mixtures of GPTS and TEOS was studied *in situ* by small-angle X-ray scattering (SAXS). The evolution of the SAXS intensity was considered in terms of a particle scattering factor which is valid for polydisperse coils of linear chains, for randomly branched f-functional polycondensates in solution,[10] and also for particular cases of nonrandomly branched polycondensates in solution.[10] We also consider a factor to account for weak correlations between the particles scattering. The data were analyzed for the structural evolution of the scattering domains and for dynamic scaling properties of the system. The time evolution of phase separation in the organic/silica hybrid systems is naturally of interest to several researchers in order to confront different phase-separation theories and associated mechanisms. For instance, one could distinguish phase separation controlled by spinodal decomposition from the growth of domains controlled by coarsening mechanisms by probing the characteristics of the growth kinetics and the dynamic scaling properties of the system.[11,12] The present results bring new insights on the understanding of transient hybrid structures apprehended from the dynamics of the sol−gel process probed in situ by SAXS.

EXPERIMENTAL SECTION

Samples of organic/silica hybrid species sols were obtained by acid hydrolysis of solutions of glycidoxypropyltrimethoxysilane (GPTS) (Aldrich 98%, 48.0 mL) and tetraethoxysilane (TEOS) (Aldrich 98%, 97.0 mL) in ethanol (Aldrich PA, 92.0 mL). A 4.0 M HCl solution (40 mL) was slowly dropped into the alkoxides solutions (HCl as a catalyst and water as a source for the hydrolysis), and the reactant mixtures were refluxed at 343 K for 2 h under mechanical stirring to produce very stable sols at such a strongly acidic condition. For the SAXS experiments, the condensation reactions were accelerated by addition of 0.1 mL of a 0.5 M NH_4OH solution under magnetic stirring into a separated 10 mL volume of the sols, so the final base concentration in the aggregating sample was approximately 0.005 M. The kinetics of the aggregation was studied in situ by small-angle X-ray scattering (SAXS) at 298 K up to beyond the gel point. The SAXS spectra of the sample were collected as a time function just after the base addition.

The SAXS experiments were carried out using synchrotron radiation with a wavelength $\lambda = 0.1608$ nm at the SAXS beamline of the LNLS synchrotron radiation facility, Campinas, Brazil. The beam was monochromatized by a silicon monochromator and collimated by a set of slits defining a pinhole geometry. A 2D position-sensitive X-ray detector was used to obtain SAXS intensity from isotropic systems as a function of the modulus of the scattering vector $q = (4\pi/\lambda)\sin(\theta/2)$, where θ is the scattering angle. The experimental setup allowed us to obtain SAXS data from $q_0 = 0.069\ \mathrm{nm}^{-1}$ up to $q_m = 1.68\ \mathrm{nm}^{-1}$ in intervals of $\Delta q = 6.52 \times 10^{-3}\ \mathrm{nm}^{-1}$. The data were corrected by sample attenuation and parasitic scattering and normalized with respect to the beam intensity.

SAXS from Polycondensates in Solution. The SAXS scattering intensity $I(q)$ from a diluted set of polydisperse coils of linear chains or of particular cases of random and nonrandom branched polycondensates in solution[10] can be expressed by the Zimm equation[10] as

$$I(q) = I(0)/(1 + R_g^2 q^2/3) \quad (1)$$

where R_g is the average of the radius of gyration of the macromolecule and $I(0)$ accounts for the intensity at $q = 0$. Equation 1 incorporates the Guinier law[13] behavior at very low q since $(1 + R_g^2 q^2/3)^{-1} \cong \exp(-R_g^2 q^2/3)$ for $q \to 0$, so

$$I(q \to 0) = I(0)\exp(-R_g^2 q^2/3) \quad (2)$$

The mass M of polymeric macromolecules in solution often exhibits a power-law dependence on their radius of gyration[13] as $M \propto R_g^D$, where the exponent D provides information of the geometry of the aggregates and on the mechanisms of growth in solutions.[14] For mass-fractal structures the exponent D have values within the interval $1 < D < 3$. The SAXS intensity extrapolated to $q = 0$, $I(0)$, is proportional to the mass M of the macromolecule in solution,[13] so one can write

$$I(0) \propto R_g^D \quad (3)$$

Mass-fractal systems with fractal dimension D and the correlation length proportional to R_g may exhibit dynamic scaling properties.[14−17] The following properties are expected to hold for such systems:[15] (i) the SAXS intensities $I(q, t)$ at different times t obey a time-independent universal function given by $F(qR_g) = I(q, t)R_g^{-D}/Q$, where Q is the invariant;[13] (ii) R_g exhibits a power-law behavior with time as $R_g \propto t^{\alpha}$, the exponent α depending on the mechanism of growth; (iii) The SAXS intensities $I(R_g^{-1}, t)$ at $q = R_g^{-1}$ and different times t, in an analogy to the maxima in the SAXS intensity at a given $q = q_{max}$ in classical dynamic scaling system,[17] exhibit a time dependence given by $I(R_g^{-1}, t) \propto t^{\beta}$, with $\beta/\alpha = D$.

The polymerization reaction of alkoxysilanes may result in a variety of structures depending on the functionalities of the alkoxyde and on the reaction conditions. In general, the tetralkoxysilanes form the densely cross-linked silica structure SiO_2 while organofunctional trialkoxysilanes polymerize to branched polysilsesquioxanes of general formula $RSiO_{3/2}$. In particular, the organic/inorganic hybrids resulting from mixing TEOS and GPTS present structural microheterogeneities that are a result from interphase interactions between the inorganic domains and organic medium that determine the size and the size distribution of the domains and the final properties of the material. Important aspects about the particle growth kinetics and the associated mechanisms together with the structural properties of the hybrid domains are expected to be evinced from the present SAXS study.

RESULTS AND DISCUSSION

Figure 1 shows the time evolution of the SAXS intensity in a log−log scale during the growth process of GPTS-derived organic/silica hybrids in basic medium with NH_4OH at a concentration of 0.005 M. The time t of the kinetic study was set to zero just after the base addition to the sol. The kinetic study was surely extended far beyond the gel point. The sol−gel threshold was studied separately by determining when the

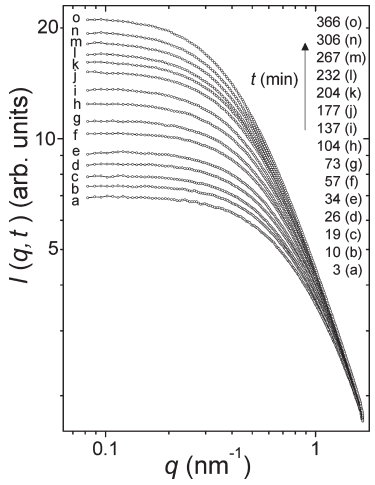

Figure 1. Time evolution of the SAXS intensity in the growth of GPTS-derived organic/silica hybrids in solution with a NH_4OH concentration of 0.005 M.

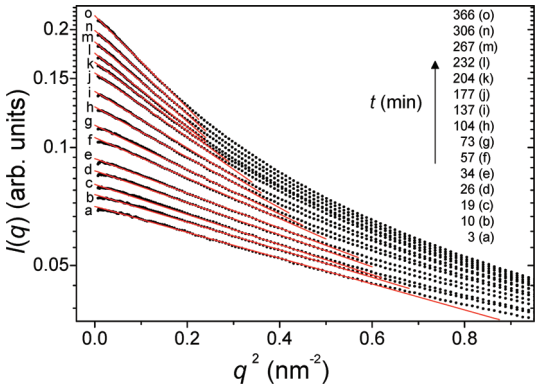

Figure 2. Time evolution of Guinier's plots (points) in the growth of GPTS-derived organic/silica hybrids in solution with NH_4OH concentration of 0.005 M. Full lines (red) are linear fittings of Guinier's law at low-q.

solution left in a closed flask, after filling the SAXS cell, no longer flowed when it was tilted. The gel point was found to occur at about the first third of the total time elapsed in the kinetic study. No particular event could be assigned to the gel point in the SAXS curves of Figure 1.

The SAXS curves in Figure 1 shows an apparent plateau at low-q; the plateau rising in the intensity scale and shortening in the low-q range, apparently shifting toward the low-q region with time. At high-q, the SAXS curves apparently exhibit a single crossover point around a value of q, which is very close to $q_m \sim 1.7\ nm^{-1}$, the maximum value for q probed in the present study. This set of experimental data is compatible with growth with time of particles in solution at the expense of smaller ones, probably increasing the polydispersity with time.

The polydispersity can be inferred from Guinier's law (eq 2) behavior at low-q. Figure 2 shows the time evolution of $\log I(q)$ versus q^2 plots together with the corresponding linear fittings of eq 2 to the experimental data at very low-q. From the linear fitting, the average radius of gyration R_g and the extrapolated intensity $I(0)$ have been determined. The low-q interval for Guinier's law application was found diminishing while the average radius of gyration was found increasing with time. This behavior in the Guinier law at low-q together with that isosbestic point in the intensity found at high-q suggest that the particles grow in solution at the expense of smaller ones, with an increase of polydispersity.[15]

The mechanism of growth of particles in solution at the expense of smaller ones yielding randomly branched polycondensates in solution were observed in the pure TEOS-derived gelling system.[17] It was concluded that the aggregation process occurs by a mechanism of phase separation by coarsening which was found strong enough to be associated with hydrodynamic forces[18] rather than the pure diffusion controlled cluster−cluster aggregation mechanism. In the case of the mixed TEOS−GPTS aggregating system, the interphase interactions between the inorganic domains and organic medium are expected to yield a minor rate of particle growth and likely minor polydispersity with respect to the pure TEOS-system. Minor particles and minor particle polydispersity often improve the properties of the material.

Since Guinier's law is restricted to low-q and it applies only fairly to polydisperse systems, we considered the possibility of the entire scattering curves be described by a form factor valid typically for diluted polydisperse polymeric molecules in solution, such as polydisperse coils of linear chains or particular cases of random and nonrandom branched polycondensates in solution,[10] which in all cases could be described at the low- and intermediate-q range by a typical Zimm's equation (eq 1). We have found that eq 1 fits well to all the SAXS curves in the entire measured q-range with values for the average radius of gyration R_g and $I(0)$ which are comparable but a few larger than those provided by Guiner's law. We have also noted that the fitting process of eq 1 to the experimental data is largely improved if a factor accounting for weak correlations of particles is considered. Weak correlations of particles have been considered by simply multiplying the particle scattering factor by an interference function $S(q\zeta)$ on the basis of a hard sphere model that can be cast as[19]

$$S(q\zeta) = 1/[1 + k\Phi(q\zeta)] \quad (4)$$

where

$$\Phi(q\zeta) = 3[\sin(q\zeta) - q\zeta\cos(q\zeta)]/(q\zeta)^3 \quad (5)$$

is a form factor for weak correlations of particles occurring at an average radial distance ζ and k is a packing factor.[19]

The data were then fitted by the equation

$$I(q) = I(0)[1/(1 + R_g^2 q^2/3)]S(q\zeta) \quad (6)$$

using a nonlinear least-squares routine (Levenberg−Marquardt algorithm) to obtain the parameters $I(0)$, R_g, ζ, and k as a function of time. Figure 3 shows eq 6 fitting very well to the experimental data in the entire q-range for all time in the interval of the present study. Figure 4 shows the time evolution of fitted parameters $I(0)$, R_g, ζ, and k.

As expected, the values for R_g and $I(0)$ obtained by taking into account weak correlations of particles were found to be about 20% larger than those obtained from Guiner's law without particle interference. The average radius of gyration R_g was found to change from about 1.8 nm up to 3.6 nm (Figure 4B) in the time interval studied, practically doubling its initial value, while the intensity $I(0)$ increased up to a few more than 3 times its initial value in the same time interval. These relative variations in

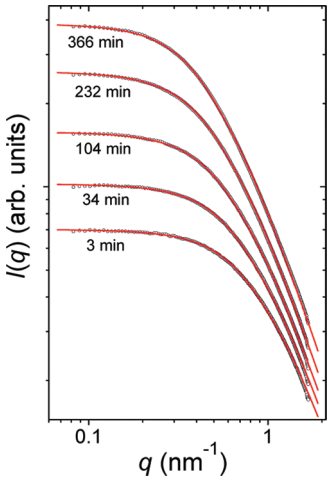

Figure 3. Linear fitting (full line) of Zimm's equation with a factor accounting for weak correlations of particles to the experimental data (points) at times along the entire period of study. The curves are vertically shifted for the sake of clarity.

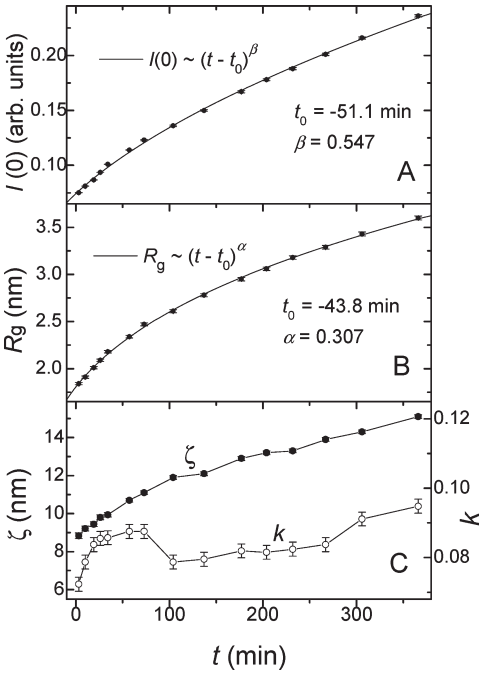

Figure 4. Time evolution of the structural parameters evaluated from Zimm's equation with very weak correlation of particles based on the rigid sphere model. Full lines in $I(0)$ (Figure 4A) and R_g (Figure 4B) plots are power-law nonlinear fittings to the experimental data as $I(0) \propto (t - t_0)^{\beta}$ and $R_g \propto (t - t_0)^{\alpha}$. The full lines in Figure 4C were drawn just to guide the eyes.

R_g and $I(0)$ found for the present TEOS/GPTS system are lower and apparently slower than those typical variations that have been observed in pure TEOS gelling systems.[17] This suggests that the organic glycidoxypropyl group incorporated to the organic/inorganic domains acts as a true interphase interaction between inorganic domains and the organic medium, retarding the particle growth and the aggregation kinetics. The reduction of the size of inorganic domains and the minor polydispersity with respect to the pure TEOS-derived system improve the properties of the material.

The values for the packing factor k were found typically in the range between 0.07 and 0.09 (Figure 4C), which are very small values compatible with just very weak correlations of particles. The average interparticle radial distance ζ was found increasing slightly with time from about 9 to 15 nm (Figure 4C), approximately accompanying the increase of R_g. The increase of the interparticle distance ζ is in agreement with the mechanism of particle growth at the expense of the smaller ones. In this process, the particles grow at the expense of smaller ones so that the number of domains in the volume sample is diminished, increasing the average interparticle distance ζ. The cluster−cluster aggregation process occurs because the proportion TEOS/GPTS $\approx$ 2 used in the present study is great enough to allow several active SiOH terminals, besides the energetically favorable glycidoxypropil terminal, be present at the interphase of the organic/inorganic hybrid to promote cluster−cluster aggregation. We do not think that the cluster−cluster aggregation by curing of the epoxy group associated with the GPTS could be significant under these experimental conditions.

A rough estimate of the ratio φ between of the average-volume v_0 of the particles, which is proportional to R_g^3, and the average-volume v_1 available to the particles, which is proportional to ζ^3, could be carried out. For spherical particles and simple cubic packing, one would have $\varphi = (4\pi/3)(5/3)^{3/2}R_g^3/\zeta^3$. The data for R_g and ζ from Figure 4B,C yield values for φ which are in the range between 0.09 and 0.12, the values increasing slightly with time. We have estimated that the volume fraction of the equivalent in silica (SiO_2) in our samples is about 0.064. Thus, the higher values found for the volume fraction of the scattering domains with respect to the equivalent volume of the silica in the samples are in agreement with formation and growth of organic/silica hybrids domains, since it is reasonable to suppose that φ should be greater than 0.064 for the incorporation of a fraction of organic groups in the hybrid domains. The slight increase found in φ with time may mean that the organic content in the domains, and so the average electronic density contrast $\Delta\rho$ with respect to the matrix, could be changing slightly with the growth process.

The typical values obtained for the packing factor k were apparently not in agreement with the values estimated or expected for the volume fraction φ, since $k = 8\varphi$ in the hard sphere interference model.[19] Indeed, a typical value of $\varphi = 0.10$, as estimated in the previous paragraph, should yield $k = 0.8$, which is too large when compared with the typical experimental 0.08 obtained for k (Figure 4C). A value of $k = 0.8$ is enough to display a fairly maximum in the SAXS curve at some $q_{max} \approx 2\pi/\zeta$, which was never observed in the present system. Then the lack of maxima in the SAXS curves together with the apparently too small values found by fitting k were attributed to the polydispersity of both: the particle size R_g and the interparticle average distance ζ. For instance, the scattering from a set of particles with $\varphi = 0.064$, then $k = 8\varphi \approx 0.5$, containing 80% volume of a class with $R_{g1} = 1.5$ nm, $\zeta_1 = 5$ nm, $k_1 = 0.4$ ($\approx 8 \times 0.80\varphi$), and 20% volume of another class with $R_{g2} = 3.3$ nm, $\zeta_2 = 10$ nm, $k_2 = 0.1$ ($\approx 8 \times 0.20\varphi$) could be excellently fitted by eq 6 yielding $\langle R_g \rangle$ = 3.0 nm, $\langle \zeta \rangle$= 11 nm, and $\langle k \rangle = 0.04$ as average values, the last being substantially smaller than k_2 and much smaller than either k or k_1, if we assume a reasonable particle size distribution number as $\propto 1/R_g^2$, for instance.

The time evolution of both $I(0)$ and R_g (Figure 4A,B) were found to be well described by a power-law with time t as $I(0) \propto (t - t_0)^{\beta}$ and $R_g \propto (t - t_0)^{\alpha}$, with $\beta = 0.547 \pm 0.020$ and

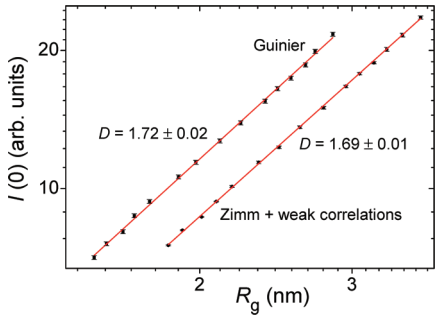

Figure 5. Probing dynamic scaling through the relationship $I(0) \propto R_g^D$ for the growth process of GPTS/silica hybrids in basic medium. Data were plotted with the parameters as obtained from fitting the Zimm equation with weak correlations of particles and from fitting Gunier's law without correlations of particles. Full lines are linear fittings of the power-law $I(0) \propto R_g^D$ to the experimental data.

$\alpha = 0.307 \pm 0.009$, being $t_0 = (-51.1 \pm 5.3)$ min from $I(0)$ and $t_0 = (-43.8 \pm 3.6)$ min from R_g. The parameter t_0 was interpreted as an offset time to account for all cumulative formation and growth eventually occurred in the early acid step of the process, before the NH_4OH addition for the SAXS study. So we can write $I(0) \propto t_c^{\beta}$ and $R_g \propto t_c^{\alpha}$ with the time scale $t_c = t + |t_0|$ corrected by the offset time t_0.

The value of 0.307 found for the exponent α in the power-law $R_g \propto t_c^{\alpha}$ (Figure 4B) is close to the value $^1/_3$, which is characteristic of the domain growth by a diffusion-controlled mechanism.[20] This result is very significant since the diffusion-controlled mechanism of growth is relatively less severe than that typical phase separation by coarsening controlled by hydrodynamic forces, as observed in pure TEOS-derived systems.[17,18] Retarding the domains growth and diminishing the polydispersity often improve the properties of the material.

The value of 0.547 found for the exponent β (Figure 4A) should be analyzed in connection with the value of the exponent α. For the system described by eq 1, the intensity at $q = R_g^{-1}$ and time t is given by $I(R_g^{-1}, t) = I(0)/(1 + {}^1/_3) = ({}^3/_4)I(0)$ or simply proportional to $I(0)$. So $I(0) \propto t_c^{\beta}$ means $I(R_g^{-1}, t) \propto t_c^{\beta}$ and $I(R_g^{-1}, t) \propto R_g^{\beta/\alpha}$, suggesting that the system obeys a dynamic scaling property with $\beta/\alpha = 1.78 \pm 0.12$.

Dynamic scale properties can be probed alternatively by analyzing the dependency of $I(0)$ on the average radius of gyration R_g. Figure 5 shows $I(0)$ versus R_g in a log−log scale with the experimental data as obtained either from fitting the Zimm equation with weak correlations of particles or from fitting Gunier's law, naturally without correlations of particles. Although the values for R_g from Guinier's law were about 20% smaller than those from Zimm's equation with weak correlation, as mentioned, the data could be fitted very well, in both the cases, by a power-law $I(0) \propto R_g^D$, giving very similar values for the exponent D, which are 1.69 ± 0.01 from Zimm's equation and 1.72 ± 0.02 from Guinier's law. These values for D are in good agreement with the value $\beta/\alpha = 1.78 \pm 0.12$ as obtained from the kinetics study, since from both the kinetics law $I(0) \propto t_c^{\beta}$ and $R_g \propto t_c^{\alpha}$ it follows directly $I(0) \propto R_g^{\beta/\alpha}$.

The dependency in power-law of $I(0)$ on the average radius of gyration R_g found for the present system is in agreement with the structural characteristics of the macromolecules described by eq 3. Equation 3 has been shown to be held even for a set of nonidentical macromolecules, since the macromolecule mass distribution could be described by a dynamic scaling[14] and R_g could be interpreted as the average radius of gyration, which is often strongly biased toward the largest macromolecules. The value of about 1.7 found for D in the present system is close to the mass-fractal dimension $D \approx {}^5/_3$ expected for macromolecules in good-solvent conditions in a dilute or semidilute solution.[21] Because the precursor species are very soluble, it is expected that the interactions with the solvent would be energetically favorable causing the polymer sections to expand due to the excluded volume associated, diminishing the value of the mass-fractal dimension D with respect to the value $D \approx 2$, often observed for the pure TEOS gelling system.[17,18] Thus, the good-solvent conditions seem to be propitiated by the 3-glycidoxypropyl functional group present in the hybrid, while the particle growth and the cluster−cluster aggregation are caused mainly by the TEOS-derived silica content. As a matter of fact, simulations carried out in idealized systems derived from pure GPTS did not show a clear tendency for particle segregation or coarsening.[22]

To exhibit dynamic scaling properties, such a mass-fractal system should exhibit a time-independent universal scaling function $F(qR_g) = I(q, t)R_g^{-D}/Q$, where Q is the invariant given by[13]

$$Q = \int_0^{\infty} q^2 I(q)\, dq = 2\pi^2(\Delta\rho)^2\varphi(1-\varphi)V \qquad (7)$$

where V is the irradiated volume of the sample. The invariant Q could not be obtained with certainty from our experimental data for the lack of a wider measured range at high-q, which could allow us to extrapolate the integration of eq 7 up to infinity, typically through a Porod's law.[13] However, it could be argued that Q should be essentially constant in the process of particles growth at the expense of smaller ones, which would be corroborated by the isosbestic point apparently settled with time at around $q_m \approx 1.7\ nm^{-1}$. Under this condition, the gain with time in the integration of $q^2I(q)$ below q_m, because $I(q)$ increases with time at low- and intermediate-q, would be counterbalanced by the loss with time in the integration above q_m, because $I(q)$ would diminish there with time for the isosbestic point. According to eq 7, the constancy of Q implies in the constancy of the factor $(\Delta\rho)^2\varphi(1-\varphi)$. We have suggested that φ could be varying with time from about 0.09 to about 0.12, which would cause an increase of about 20% in the factor $\varphi(1-\varphi)$, but as a counter effect, the increase of the organic content in the hybrid with time, as suggested too, should diminish the average electronic density $\Delta\rho$ of the domains. So, the assumption of constant Q seems consistent with all experimental results, and the time-independent universal scaling function could be probed just as $F(qR_g) = I(q, t)R_g^{-D}$.

Figure 6 shows the plots of the function $F(qR_g) = I(q, t)R_g^{-D}$ versus qR_g with $D = 1.69$ (as determined from the plots of Figure 5) for every time t in the growth process of GPTS-derived organic/silica hybrids. All curves impressively coincide becoming a time-independent function under this dynamic scaling transformation, demonstrating the dynamic scaling properties of the system.

The time-independent scaling function $F(qR_g)$ as obtained in Figure 6 does not exhibit a maximum at a certain value $q = q_{max}$, as expected for classical dynamic scaling systems. We have suggested that the lack of maxima should be due to the polydispersity and the diluted character of the system in the case of the pure

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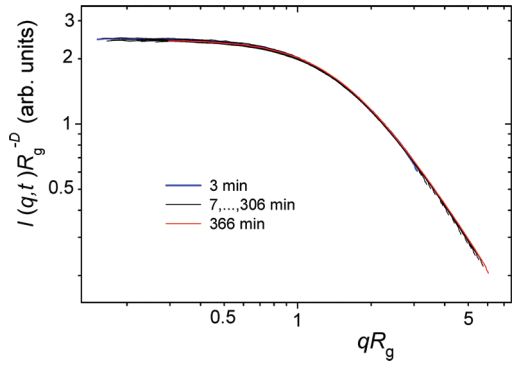

Figure 6. Plots of the function $F(qR_g) = I(q, t)R_g^{-D}$ versus qR_g with $D = 1.69$ (Figure 5) for every time in the growth process of GPTS/silica hybrids, demonstrating the dynamical scaling properties of the system since all curves coincide with an unique time-independent function when scaled.

TEOS-derived system.[17] This seems to be also the case of the present GPTS/TEOS-derived system. The scaling function approximates to a power-law behavior with an exponent close to the mass-fractal dimension $D \approx 1.7$ at high values of the scaling variable qR_g. As mentioned, the value $D \approx 1.7$ is expected for macromolecules in good-solvent conditions in dilute or semidilute solution,[21] which causes the macromolecules to expand due to energetically favorable interactions with the solvent. This causes a diminution of D with respect to the value ≈ 2 often observed for the pure TEOS-derived system.[17,18] The good-solvent conditions should be due to the 3-glycidoxypropyl functional group present preferentially at the interphase between the hybrid domains and the organic solvent. The dimensionality of the system seems not to change with the growth process, so there could be some structural reorganizing in the cluster aggregation to match the same fractal dimension as the particles grow.

The presence of a maximum in the dynamical SAXS intensity $I(q,t)$ at a fixed value $q = q_{max}$ would be indicative of a mechanism of phase-separation in which a wave of composition fluctuation with wavelength $\approx 2\pi/q_{max}$, eventually appearing at the first stages of the process, would grow in amplitude by a spinodal decomposition mechanism.[11,12,15] The lack of maxima in the dynamical SAXS intensity $I(q,t)$ suggests strongly that no simple wave of composition sets at the beginning of the process so the spinodal decomposition could be discarded and it could be assumed that the separation of the phase should occur by a coarsening mechanism. This picture is corroborated by the increase in a power-law with time of the correlation distance of the system, which could be considered as proportional to the radius of gyration R_g in the coarsening process. Furthermore, the exponent of the power-law with time in the increase of the radius of gyration is indicative of a diffusion-controlled mechanism of phase-separation by coarsening, which seems not to be completely the case of the coarsening process observed in the pure TEOS-derived system.[18] The interphase interactions between the inorganic domains and organic solvent in the TEOS/GPTS-derived system prevent great rates of particles growth and yield likely minor polydispersity with respect to the pure TEOS-system. Minor particles and minor particle polydispersity often improve the properties of the material.

Finally, we should emphasize the importance of understanding the development of transient hybrid structures that the present scattering analyses provide. These new insights allowed us (i) to accompany the evolution of the size, polydispersity, and the internal mass-fractal structure of the hybrid domains; (ii) to infer about the diffusion-controlled mechanisms of phase separation by coarsening accompanying the growth of macromolecules; (iii) to suggest that the growth is mainly due to the TEOS-derived polycondensation while the epoxy groups originated from GPTS retard the growth; and (iv) especially to establish the dynamic properties of the growing system. The description of such dynamic systems has been a challenge in several fields, so the present insights open new perspectives to be applied to analogous dynamics of hybrid systems.

CONCLUSIONS

The growth kinetics of GPTS-derived organic/silica hybrids in solution under basic conditions has been studied by small-angle X-ray scattering (SAXS). The SAXS intensity curves were found to be well described by a particle form factor valid for polydisperse coils of linear chains and for particular cases of random and nonrandom polycondensates in solution together with an interference factor accounting for very weak correlations of particles. The SAXS data are consistent with formation and growth of GPTS/silica hybrids in solution with polydispersity increasing with time.

The average radius of gyration R_g of the polycondensates was found growing in a power-law with time t as $R_g \propto t^{\alpha}$, with $\alpha = 0.307 \pm 0.009$; the exponent α being very close to the value $\alpha = {}^1/_3$ expected for domain growth by the diffusion-controlled mechanism. The SAXS intensity $I(0)$ extrapolated to $q = 0$ was found increasing in a power-law with time t as $I(0) \propto t^{\beta}$, with $\beta = 0.547 \pm 0.020$. From both kinetics laws, it follows directly $I(0) \propto R_g^{\beta/\alpha}$, with $\beta/\alpha = 1.78 \pm 0.12$. This suggests that the system obeys a dynamic scaling property with $\beta/\alpha = D$, where D is the mass-fractal dimension of the polycondensates.

The power-law $I(0) \propto R_g^{D}$ was confirmed directly by plotting $I(0)$ versus R_g in a log−log scale from data obtained by fitting the SAXS intensity curves with time. It was found $D = 1.69 \pm 0.01$, which is in good agreement with $\beta/\alpha = 1.78 \pm 0.12$. The value $D \approx 1.7$ is expected for macromolecules in good-solvent conditions in a dilute or semidilute solution. The good-solvent conditions should be due to the 3-glycidoxypropyl functional group present preferentially at the interphase between the hybrid domains and the organic solvent.

The SAXS intensities $I(q, t)$ corresponding to different times t were found to impressively coincide with an unique time-independent function given by $F(qR_g) = I(q, t)R_g^{-D}$. This set of findings is in notable agreement with the dynamic scaling properties by the present system. The dimensionality of the system seems not to change with the growth process. The general results are compatible with a phase separation by a diffusion-controlled coarsening mechanism. The interphase interactions between the inorganic domains and organic solvent in the TEOS/GPTS-derived system prevent great rates for particles growth and yield likely minor polydispersity with respect to the pure TEOS-derived system.

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