Electrorheological Effects of Synthesized Octacyanopropylsilsesquioxane Cage Structure

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Supporting Information

ABSTRACT: This article introduces a new electrorheological (ER) fluid. A molecular cage structure for electrorheological applications has been synthesized, and the ER behavior of the octa-functionalized polyhedral oligomeric silsesquioxane (POSS) variant in silicone oil (PDMS) has been shown. The hydrolyzation route has been used in the synthesis, the microstructure has been displayed using scanning electron microscopy, the yield has been ascertained, and the compound has been characterized. The rheological properties are demonstrated on the ER fluid through steady flow and oscillatory tests to investigate the effects of change in concentration on the functional group attached to the inorganic silicon–oxygen core structure of the POSS compound. The electrorheological efficiency was analyzed, and dielectric characterization was done. The flow curve was described by the Herschel–Bulkley model, and yield stress values were derived from the model. The octa-cyanoPOSS/PDMS electrorheological fluid has been shown to have ER activity.

INTRODUCTION

Polyhedral oligomeric silsesquioxane (POSS) compounds are silicon–oxygen compounds that have a \((\text{SiO}_{1.5})_n\) nucleus in a perfect geometrical arrangement with organic fragments attached at some or all of the apex Si atoms. POSS compounds are also called spherioloxanes because of their geometry. Geometries of the Si–O arrangement have \(n\) ranging from 6 to 8, 10, 12, 14, and 16. The spherical core of these POSS cages is assigned the symbol \(T_n\) (i.e., the \((\text{SiO}_{1.5})_n\) nucleus).

Each of the Si center is bonded to three o xo groups in all the cases, which, in turn, is linked to other Si centers. The fourth group that is linked to the Si center is usually an alkyl, halide, hydride, or alkoxide group.

Depending on the reaction conditions, which includes temperature, pH, type of catalyst used, and concentration of starting material or monomer, different silsesquioxane structures are formed, which include random polymeric networks without long-range order; ladder-shaped, incompletely condensed polyhedral species; and fully condensed polyhedral species. Having high symmetry and multiple functionalities is one of the attractions of POSS compounds, having high symmetry and multiple functionalities enable formation of multiple bonds with other components to form new materials.

The most important group of POSS compounds is the octa-functionalized group of \(T_nR_8\) with a core of 12 O atoms and 8 apical Si atoms. Most of the industrial interest and research in POSS are concentrated on the octameric variants such as octavinylsilsesquioxanes, because of their applicational properties and use in dielectric films for integrated circuits and as a resist for electron lithographic manufacture of semiconductor microreliefs, and octaphenylsilsesquioxanes, which have thermal stability and application as binders for ceramic materials. Octahydridosilsesquioxanes have been identified as a precursor and starting material to many other octasilsesquioxane structures and elaborate derivatives.

There are several distinct routes for the synthesis of octameric POSS structures, but the most commonly used routes are (i) hydrolytic condensation of organotrihalosilanes or trialkoxysilanes in the presence of amberlite and FeCl3 catalysts and (ii) hydrosilylation of octahydridosilsesquioxanes with functionalized allyl compounds in the presence of a Karstedt or Speier’s catalyst. In the latter route, the hydridot\(T_8\) will have to be synthesized first before the target octameric derivative is synthesized.

Route 1 involves the hydrolysis and condensation of trifunctional silanes of the type RSiX₃, where X is normally a halide or alkoxide group, and R is a chemically stable substituent group. Most commonly used silanes are trialkoxysilanes (where R = H) as in \([\text{HSi(OR)}_3]\) or...
trichlorosilanes (HSiCl₃) in the presence of an acid or base catalyst and organic solvents.¹

\[ \text{RSiX}_3 + 3\text{H}_2\text{O} \rightarrow \text{RSi(OH)}_3 + 3\text{HX} \]

\[ 8\text{RSi(OH)}_3 \rightarrow (\text{RSiO})_3/\text{H}_2\text{O} + 12\text{H}_2\text{O} \]

Route 2 involves the hydrolysis of octahydridosilsesquioxane with functionalized allyl compounds²,¹¹ in the form of the reaction

\[ \text{H}_2\text{T}_8 + 8\text{CH}_2=\text{CH}+\text{CH}_2=X \xrightarrow{\text{H}_2\text{PtCl}_6} (\text{X}−\text{Pr})\text{T}_8 \]

where \( X = −\text{SiMe}_3, −\text{Ph}, \) or \( −\text{C}_8\text{F}_5 \) for the weak electron-withdrawing group.

\[ \text{H}_2\text{T}_8 + 8\text{CH}_2=\text{CH}+\text{CH}_2=X \xrightarrow{\text{Pt(COD)}\text{Cl}_2} (\text{X}−\text{Pr})\text{T}_8 \]

where \( X = −\text{OPh} \) or \( −\text{CN} \) for the electron-withdrawing group.

When \( X \) is a weak electron-withdrawing group, the reaction undergoes full condensation, and there are no side products when using a hexachloroplatinic acid catalyst (Speier’s catalyst). However, when facing an electron-withdrawing group, such as \( −\text{CN} \) or \( −\text{OPh} \), as shown in the reaction above, the use of \( \text{H}_2\text{PtCl}_6 \) yields a large amount of polymer side products, and the reaction has no significant yield. To prevent these side reactions, the use of large amounts of an allylic compound along with a very small amount of platinum catalyst \( \text{Pt(COD)}\text{Cl}_2 \) is reported to give yields as high as 95% at 70 °C.²,¹¹

The aforementioned routes of octasilsesquioxane synthesis can be tuned, and the experimental factors are selectively adjusted to generate a high-yield procedure. Some of these factors include the pH type of catalyst used (acid or base), nature of the solvent, rate of water addition, temperature of reaction, initial monomer concentration, and identity of the X and R constituents (in the hydrolytic condensation).²⁴ For the purposes of this work, we will lay emphasis on the hydrolytic condensation method.

Dare et al.⁶ modified already established hydrolytic condensation procedures for improved synthesis of octavinylsilsequioxane, octaphenylsilsequioxane, and octabenzyldilsequioxane structures. For example, the octabenzyldilsequioxane (octabenzyldilT₈) structure was synthesized by the hydrolytic condensation of vinyltrichlorosilane in methanol using an acid amberlite catalyst. This reaction yielded 23.9% of octabenzyldilT₈ in the first cycle of acid amberlite use. This was an improvement in the 6% yield earlier derived by Andrianov et al.¹² Repetitive use of the solid acid amberlite was done for eight cycles by having it regenerated with HCl and methanol. The yield increased until the third cycle (41%) and started dropping from the fourth cycle onward with some xerogel side product formation. It is worthy to note that the yield profile, however, changes for the same octabenzyldilT₈ when the chloro group (X-group in the hydrolytic condensation reaction) is replaced with a methoxy or ethoxy group. The substitution of the −Cl group with −OMe and −OEt yielded maximum values of 26.12 and 22.93% of octabenzyldilT₈, respectively, in the third cycle of amberlite reuse. This helps explain the earlier point made where the identity of the X-group in the cage structure can affect the yield derived from the synthesis.⁶

It was also reported by Dare et al.⁶ that the octabenzyldilT₈ synthesized (74% yield) was done with solid base amberlite instead of solid acid amberlite that was used for octabenzyldilT₈. The reason is because the reaction failed in the presence of an acid amberlite. The reaction was done with phenyltrichlorosilane in the presence of ethanol as a solvent and stabilizer of the large percentage of completely condensed octaphenylT₈. OctabenzyldilT₈ was also synthesized following the same reaction conditions of octaphenylT₈ with a 68% yield.⁵

Thus, the acid and base types of the amberlite ion exchange resin create the optimum pH condition for different silsesquioxane end products. The amberlites are chemically modified gel-type polystyrene beads stored in Na⁺ form (acid amberlite) and Cl⁻ form (base amberlite). The acid and base forms are converted to the active H⁺ and OH⁻ versions by treating with a homogeneous acid or base, which are used for the complete condensation of the reaction to yield the silsesquioxane.⁶

Several base-catalyzed reactions produce nearly quantitative yields of a single polyhedral framework, although in most cases, product mixtures resulting from base-catalyzed hydrolytic condensation of RSiX₃ are complex and time-consuming to separate on a multigram scale. Precipitation of a very poorly soluble or insoluble product is usually the driving force for these base-catalyzed reactions.⁶

Intermediates are formed during the hydrolytic condensation of RSiX₃ monomers to fully condensed POSS structures. These intermediates can be present in small or large amounts and are unstable under the reaction conditions. It is therefore imperative to select the reaction conditions that will yield an optimal amount of the end product and a minimal amount of side products or intermediates. These intermediate compounds, however, are useful and have a wide range of applications. For example, the hydrolytic condensation of PhSiCl₃ in aqueous acetone gives a good yield of tetrasilanol, which has many applications as a precursor to a more elaborate framework and is highly prone to self-condensation and decomposition. Incompletely condensed silsesquioxanes can also be produced through controlled partial hydrolysis of POSS.⁴

Rheological properties such as viscosity and shear modulus of electrorheological (ER) fluids undergo instantaneous and reversible change when an electric field is applied. Previous research on the electrorheology of POSS structures is limited.¹³

One of the main drawbacks in ER application is particle sedimentation. It is important to identify and design a particle−fluid combination that would exhibit a large ER effect and overcome sedimentation problems. POSS structures have been used by Li et al.¹⁹ to adjust the hydrophilicity of graphene oxide (GO) nanosheets so that it can be compatible with silicone oil and overcome phase separation or sedimentation. This has been achieved by decorating the active amine groups of octameric aminopropylisobutyl POSS with the oxygen-containing groups of GO, thereby preventing the reaggregation of GO and reducing the total thickness of the final POSS-GO structure.¹⁹

McIntyre et al.⁵ discovered that less than 10 wt % (7%) sulfonated polyhedral silsesquioxane cage structures (s-POSS or TSae-POSS, which means the tri-sulfonic acid ethyl POSS) in polydimethylsiloxane (PDMS) gave an increase in viscosity by a factor of \( 1 \times 10^7 \) on an electric field strength of 2 kV/mm. This was in contrast to another POSS particle known as isotropic octa-isobutyl POSS, which exhibited virtually no electrorheological behavior at that weight percentage. Even when increased to 10 wt %, the octa-isobutyl POSS particles still showed no ER effect. Upon investigating the dielectric

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properties, it was discovered that the octa-isobutyl POSS/PDMS system is not dielectrically active, while that of TSAE-POSS is, and it was concluded that the presence of the sulfonated groups is responsible for the dipolar behavior.

Another study was done by McIntyre et al., which was an improvement on the previous work. The study showed that, when mixed with a small (1 wt %) amount of nanocage sulfonated POSS (s-POSS), 10 wt % micrometer-sized polystyrene (PS) particles in PDMS (89 wt %) liquid gave a significant ER effect. They associated this improved behavior to the formation of a thin adsorbed layer of s-POSS onto the PS surfaces to give a new core/shell particle with improved dielectric and conductive properties. The s-POSS/PS/PDMS suspension exhibited an increase in ER activity by an order of magnitude beyond that of s-POSS/PDMS suspension.

In this work, the aim is to octa-functionalize the POSS cage structure by introducing the cyano functional group and investigate the electrorheology. ER suspensions containing high concentrations of particles that possess permanent dipoles show larger ER effects in suspensions than conventional ER fluids. It has been stated that the octamer variant of POSS offers a high 3D symmetry, low density, and multiple functionalities. This allows for a relatively easier application compared to other POSS structures for addition of a cyanopropyl functional group on the POSS framework to generate a structure with more dipoles that show an appreciable ER effect. We synthesized the cyanopropylT8, investigated its shape and size by SEM, characterized it using Fourier transform infrared spectra (FTIR) studies, prepared the suspensions, and then carried out rheological and dielectric tests with the application of an electric field.

**RESULTS AND DISCUSSION**

**Dielectric Properties.** The dielectric test was done to determine the polarizability of the compound synthesized. Systems that possess high dielectric constants give enhanced particle polarization, and this results in strong and stable mesostructure formation within the suspension spanning the electrodes. The mechanism of the ER effect had earlier been investigated and understood to be governed by slow polarization processes. The interfacial polarization rather than the debye polarization was found to be the determinant to the ER effect. Interfacial polarization is defined by the dielectric constants and conductivities of the components of the ER fluid.

In Figure 1, as the electric field-induced charge separation occurs in the material, the relative permittivity ascends in the low-frequency region, while the dielectric loss show a descent from its maximum value in the low-frequency region. This is an unusual occurrence. There is no obvious dielectric relaxation observed between the $1 \times 10^2$ Hz and $1 \times 10^5$ Hz frequency regions at the concentration tested, as recommended in the work done by Hao et al.

The height of the $\varepsilon'$ curve reflects the size of the induced dipole moment, which indicates the presence of polarization and that the synthesized compound is dielectrically active. The introduction of the cyano group to the POSS cage structure is believed to have provided particles with higher polarity, polarizability, and dielectric activity.

**Shear Thinning.** The shear thinning or thickening behavior of the suspension was investigated for the microstructural changes that occur during shearing. In Figure 2, it is shown that the cyanopropylT8 suspension undergo shear thinning even without the application of the electric field. The broken chains of the solid network continuously reform at low shear rate regions, and it is unable to match up the speed of rotation at higher shear rates. At low shear rates, the particles are loosely held and form a porous particle network by van der Waals interactions, and this results in a solid-like behavior for the flocculated suspension.

This can be understood better on a macroscopic scale by considering the fact that, at lower shear rates, the upper plate spins slowly and the liquid between the plates flows slowly. As the shear rate increases, the plate spins faster and the liquid between the plates flows quickly and therefore increases the hydrodynamic drag on the solid cyanopropylT8 particles. On a microscopic scale, the resistance to flow is controlled by the solid particle network. At low shear rates, the loosely held porous structures span the plate, remain intact, and are not affected by the slowly flowing liquid around it. As the shear rate increases, the hydrodynamic forces become stronger and break apart the solid network of particles and the resistance to flow is transferred from the solid network to the fluid containing the particles. It is this breakup of the solid network and transfer of stress from the solid network to the fluid that lead to shear thinning.

To investigate the temperature effect on the suspension of cyanopropylT8, the temperature was ramped up at increments of 20 °C from 25 to 85 °C. The increase in temperature affects...
both the particle–particle interactions and the Brownian motion of the particles. As the temperature increases, the viscosity of the suspension drops in order of the temperature values. For systems where an electric field has been applied with temperature changes, it has been reported that the Brownian motion is intensified at higher temperatures and becomes strong enough to compete and weaken the ER effect.9

Electrorheological Analysis. The steady-state flow curves were measured with and without applying an electric field to show the ER activity of cyanopropylT8. At the off state, the data can be seen as noisy, and the stress profiles of all concentrations are lumped together and are hard to differentiate. The non-Newtonian behavior of the concentrations with no applied electric field in Figure 3a is unusual, especially for the lowest concentration of 1%. A previous work of Liu et al.23 showed a Newtonian behavior for silica microspheres and for a particle concentration that was as high as 10% by volume. Conversely, an optically transparent ER fluid of urea-modified silica nanoparticles, which has been fabricated by Liu et al.,24 has been found to behave like a non-Newtonian fluid but at a higher concentration of 10% by volume with no electric field applied. They attributed this behavior to the dispersion state of the particles and their wettability to the dispersing oil medium.

The electric field was applied in increments of 1 kV/mm, but for representation, an increment of 4 kV/mm was shown. At 4 kV/mm shown on Figure 3b, the ER effect was evident in the increase in shear stress and ultimately yield stress. The higher particle concentration in the suspensions led to a significant increase in the ER effect of these suspensions. The higher particle concentrations were able to form a stiffer and stronger chain-like structure than the suspensions with lower particle loading. Thus, the increased amount of polarizable particles in the suspension leads to the formation of a stiffer solid network and a higher ER effect. The 8 wt % concentration showed a greater ER response at the 4 kV/mm electric field strength at higher shear rates.

It is worthy to note the sharp decrease in the stress of the higher concentrations especially the 8 wt % concentration in the lower shear rate region of <2 (1/s). This occurrence may be associated to electric saturation of the suspension. The dielectric particles within the suspension break down as the electric field is increased beyond its breakdown voltage, and it acts as an electrical conductor with electrostatic discharge. This happens mainly in the lower shear rate region where the hydrodynamic forces are weak and there is sufficient particle–particle interaction and contact for electrostatic discharge to occur. Thus, the yield stresses for the suspensions go through a maximum at 3 kV/mm and show a breakdown at 4 kV/mm.

The dynamic yield stresses of 4, 6, and 8% concentrations are shown for 1 to 3 kV/mm electric fields in Figure 5a. The yield stress is the stress required to initiate flow, and it typically depicts the strength of the solid network of particles in the suspension. The yield stress has been calculated from the flow curves of the cyanopropylT8 suspensions of different concentrations and electric field strengths. The 1 wt % concentration was fl at and displayed no apparent ER effect as the electric field increased, as shown in Figure 3, and was therefore excluded from the Herschel–Bulkley yield stress plot in Figure 5a. The yield stress was calculated using the Herschel–Bulkley model. Higher yield stress values are obtained as the particle volume fraction goes up. As shown in Figure 5a, the Herschel–Bulkley model fits the data for all concentrations and the electric fields of up to 3 kV/mm except for the 4 kV/mm electric field (not shown in Figure 5a).

The log–log dependence of the yield stress on the electric field strength obeys the power law from the conduction and polarization models.
where $q$ is the rigidity of the internal structures formed when the electric field is applied, and the value $\alpha$ should be within the range of 1.5–2 for well-developed structures for the conduction model and 2 for the polarization model. The polarization model relates the material parameters such as the dielectric constants of the liquid and solid particles to the rheological properties using an idealized ER system of uniform, hard dielectric spheres dispersed in a Newtonian fluid medium, and the yield stress is found to be proportional to the square of the applied electric field (i.e., $\alpha = 2$). The conduction model, on the other hand, considers particle interaction only as the factor for the ER effect when the gap between the conducting particles in the fluid decreases and the $\alpha$ value approaches 1.5. In Figure 5a, $\tau_y$ scales as $\sim E^{\alpha - 2}$ for both 6 and 8% concentrations and $E^{\alpha - 5.5}$ for 4% concentration.

As previously discussed, at 4 kV/mm, the electric field applied exceeds the breakdown voltage of the dielectric particles, and this causes a drop in the shear stress values at lower shear rates. The yield stress, which is an extrapolation of the shear stress using applicable yield stress models, ultimately drops with this phenomenon. This occurrence is visible at increasing concentrations and becomes more pronounced at the highest concentration of 8%. The yield stress values at 4 kV/mm are shown in Table 1.

Table 1. Yield Stress Values of the Herschel–Bulkley Model at 4 kV/mm for Concentrations of 4, 6, and 8%

| Concentration (%) | Yield Stress (Pa) |
|-------------------|-------------------|
| 4                 | 10.6              |
| 6                 | 22.4              |
| 8                 | 24.2              |

The ER efficiency measures the electroviscosity difference between the off state with no electric field applied and the on state with an electric field applied. It is given as efficiency

$$e = (\eta_0 - \eta)/\eta_0$$

This parameter is of high importance because it gives vital information of how well the ER fluid performed across the shear rate band. Figure 5b shows the ER efficiency dependence on concentration at shear rates of 10 (1/s) and 100 (1/s). In this case, the data presented is the difference in viscosity at 0 kV/mm when no field was applied and at 4 kV/mm. The ER efficiency is lowest for the lowest concentration of 1% and highest for the highest concentration of 8%. The efficiency is higher at shear rates in the mid-region of 1 (1/s) and 10 (1/s) than the higher shear rates. The increase in viscosity at high shear rates of, for instance, 100 (1/s) when the electric field is on is not as great as the lower shear rates because the structures at high shear rates have been broken apart. The difference between the 10 (1/s) and 100 (1/s) ER efficiency values increases as the concentration increases from 1 to 8%.

Oscillatory measurements were carried out to determine the viscoelastic properties of the ER suspensions. This gives a better understanding of the microstructural changes in the linear and nonlinear viscoelastic regions. Applying the electric field creates a transition in the fluid from viscous behavior to linear viscoelastic (LVE) behavior to nonlinear viscoplastic behavior. This means that increasing the electric field not only increases the viscosity but also changes the rheological mechanism by which we can model the materials.

The complex shear moduli $G'$ and $G''$ were measured with and without the electric field, as seen in Figure 6 (top and bottom). These measurements allow for comparisons of the structure within the suspension with and without the electric field. At 0 kV/mm, the $G'$ values for all concentrations appear to be similar and are all clustered together like the flow curves in Figure 3a. Upon application of an electric field at 4 kV/mm, the 1% concentration remained the same, while the higher concentrations showed a marked increase in the modulus, with 8% concentration being the highest. It can be seen from the 4 kV/mm plot for $G''$ that, as the concentration increases, the plateau that represents the LVE region shrinks.

The critical strain where the storage modulus crosses the loss modulus is shown in Table 2. The critical strain varied with concentration but showed no trend with increasing concentration.

Figure 7 shows the increasing trend of $G'$ and $G''$ as the electric field strength is increased on the suspension. The highest modulus can be seen to be at the highest electric field of 4 kV/mm.

Figure 5. (a) Increase in Herschel–Bulkley yield stress for 4, 6, and 8% concentrations as the electric field strength increases from 1 to 3 kV/mm. (b) ER efficiency of cyanopropylT8 suspensions at shear rates of 10 (1/s) and 100 (1/s).
Figure 8 shows the frequency sweep of the ER fluid with both the storage and loss moduli at 1% fixed strain. The frequency sweep was used to investigate the time-dependent deformation behavior of the suspension in the linear viscoelastic region. Both the storage and loss moduli showed an increase as the strength of the applied electric field is increased, indicating that the ER fluids show a solid behavior.\textsuperscript{21} There is an increase in storage modulus at higher frequencies. At higher frequencies, the structures in the suspension exhibit less flexibility and higher rigidity at a faster motion, and the

Table 2. Critical Strain Amplitude for Different CyanopropylT\textsubscript{8} Concentrations at All Electric Fields

| concentration (%) | 1 kV/mm | 2 kV/mm | 3 kV/mm | 4 kV/mm |
|-------------------|---------|---------|---------|---------|
| 1                 | 5.01    | 5.01    | 5.01    | 6.31    |
| 4                 | 7.94    | 6.31    | 6.31    | 6.31    |
| 6                 | 7.94    | 7.94    | 7.94    | 6.31    |
| 8                 | 6.31    | 6.31    | 5.01    | 3.98    |

Figure 7. (a) Storage modulus versus strain at all electric fields for 8 wt % concentration. (b) Loss modulus versus strain at all electric fields for 8 wt % concentration.
storage modulus values could increase up to 5 to 10 times higher than the plateau region at a low frequency.22

CONCLUSIONS

A new ER particle has been synthesized using the hydrolyzation route and characterized. The addition of the cyano group into the inorganic POSS structure has been found to respond to an applied electric field. The yield can be improved by exploring the possibility of using other catalysts, changing reaction conditions, or using other routes. An ER fluid of cyanopropylT8/PDMS suspension was prepared and characterized dielectrically and electrorheologically. These suspensions have been found to be dielectrically active and show a shear thinning behavior. The change in the rheological properties of the ER fluid upon application of an electric field has been demonstrated through steady flow and oscillatory tests. The flow curves have been used to show the effects of increasing viscosity and shear stress as the concentration and electric field are increased. The yield stress has been derived by using the Herschel−Bulkley model to fit the flow curves, and the yield stress has been found to increase up to 3 kV/mm and drops at 4 kV/mm due to dielectric breakdown. The power law with respect to conduction and polarization models has been used to describe the ER effect. The electrorheological efficiency was also analyzed. The viscoelastic analysis for amplitude and frequency sweeps suggests that the strength and formation of the cyanopropylT8 structures in PDMS are augmented by increasing the magnitude of the electric field. The 1% concentration showed no apparent ER response in both flow and oscillatory tests.

EXPERIMENTAL SECTION

Synthesis of Octa-cyanopropylsilsesquioxane. The hydrolyzation route used in ref 6 was adopted. The RSiX₃ was replaced with a trihalosilane (cyanopropyltrichlorosilane, CH₂CH₂CH₂-CNSiCl₃) purchased from Sigma-Aldrich.

The reaction was carried out in an inert atmosphere. The acid amberlite (strongly acidic and hydrogen form, IR-120) was weighed (40 g) into a small beaker. Concentrated HCl (25 mL) was measured with a graduated cylinder and used to wash the acid amberlite twice. Each washing period lasted 10 min on top of a magnetic stirrer. The acid was decanted after the two-time washing of 20 min. Deionized water (50 mL) was used to wash the amberlite with the same procedure and timing. The water was decanted, and methanol (25 mL) was also used to wash the amberlite with the same procedure and timing. The methanol was decanted, and the acid amberlite was ready for use. The amberlite was charged into a 500 mL flat-bottom flask, which has 150 mL of methanol in it, and this was stirred at 30 ºC. The temperature was monitored by a thermometer. Cyanopropyltrichlorosilane (0.04 mol or 6.23 mL) was added dropwise and stirred into the amberlite methanolic solution at 30 ºC. Stirring was carried out at room temperature for 10 h, after which the methanol was decanted and dichloromethane was added to dissolve the microparticles that formed. The amberlite was filtered out for reuse. The resulting solvent was poured into a round-bottom flask and concentrated with a rotary evaporator, and the resultant residues are the cyanopropylT8 crystals (Figure 9). The crystals were removed from the walls and bottom of the flask, and the resultant yield (2.03%) was calculated and ready for characterization.

Characterization of Prepared CyanopropylT8. The microstructure and morphology of the synthesized cyanopropylT8 particles were observed by SEM.

SEM images in Figure 10 show that particles are micrometer-sized. They are well dispersed in size and ranges from 1 to 200 μm.

The attenuated total reflectance FTIR method via a Cary 630 instrument was used to identify the absorption bands and assign them to the bonds within the compound. In accordance with the literature, the typical FTIR characteristic data...
obtained include stretching vibrations at 2245.8 cm\(^{-1}\) for the
−CN group, stretching vibration at 2939.8 cm\(^{-1}\) (C−H), and
bending vibration at 1406.0 cm\(^{-1}\) (C−H). Also, vibration at
747.4 cm\(^{-1}\) corresponds to Si−C, while that at 1096 cm\(^{-1}\)
corresponds to Si−O stretch.

**Preparation of Electrorheological Suspensions.** The
required quantities of cyanopropylT\(_8\) and silicone oil of 500
cSt viscosity that were purchased from Sigma-Aldrich were
weighed out and vacuum-dried at 130 \(^\circ\)C for 24 h to ensure
that traces of moisture, which could influence the outcome of
the results, were eliminated. After drying, the POSS compound
was crushed to ensure a uniform particle size distribution.
Contact with air was minimized by capping the containers, and
concentrations of 1, 4, 6, and 8 wt % were prepared in separate
vials. A homogeneous mixture between the particles and the
silicone oil was obtained by using a vortex mixer.

**Electrorheological Measurements.** Rheological prop-
erties were measured using a strain-controlled Anton Paar MCR
302 parallel plate rheometer with a plate size of 25 mm and 0.3
mm spacing between plates in such a way that, to get a 1 kV/
mm electric field strength, a setting of 0.3 kV will have to be
entered. An electric field was applied using the FuG DC power
supply HCP 14-12500. The sample from the vial is slowly and
uniformly dispersed on the top of the bottom plate, and the
required experimental settings are entered in the PC Rheoplus
software before the start of each test is activated. Each test
(rotational and oscillatory tests) were carried out with fresh
samples because, once a sample is used, the structure is broken
down and takes time to rebuild; therefore, the chances of
having an accurate result with the same sample reduces. A shear
rate sweep of 0.1 to 100 s\(^{-1}\) was done at fields of 0 to 4
kV/mm in 1 kV/mm incremental steps for all four
concentrations prepared. This was done at a constant
temperature (25 \(^\circ\)C) to measure the flow curves. The yield
stress of the suspensions was ascertained by using the
Herschel−Bulkley model. Oscillatory tests for strain amplitude
were conducted at variable strain from a low to higher strain
while the frequency is held constant. Amplitude sweep was
done from 0.01 to 1000% at a constant frequency of 10 rad/s
while the frequency is held constant. Amplitude sweep was
recorded remotely on the PC. The parallel plate capacitor
equation
\[
C = \varepsilon \varepsilon_0 A/d
\]
was used to calculate the dielectric constant, and the dielectric
loss was also calculated.

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**ASSOCIATED CONTENT**

Supporting Information
The Supporting Information is available free of charge at
https://pubs.acs.org/doi/10.1021/acsomega.9b02105.

Attenuated total reflectance Fourier transform infrared
spectra (FTIR) for cyanopropylT\(_8\) (PDF)

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Notes
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Figure 10. SEM images of cyanopropylT\(_8\) particles in increasing order of magnification.
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