From single molecules to aggregates to gels in dilute solution: Self-organization of nanoscale rodlike molecules

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A transition from a fluid to a constrained phase, in dilute solutions of a rodlike molecule, poly(2,5-dinonyl*para*phenylene ethynylene)s (PPE) in toluene has been studied, exploring the dynamics and the structure of the PPE molecules and the solvent in both phases. The transition is characterized by visual changes in the viscosity of the system and in its color, where a transparent liquid transforms into a yellow glassy phase. Nuclear magnetic resonance relaxation measurements indicated that significant restriction of motion of the solvent and of the polymeric molecule take place as the gel-like phase is formed. Small angle neutron scattering studies have shown that in the liquid phase, PPE forms molecular solutions where the molecules are fully extended. Upon transition into the constrained phase, aggregation of PPE molecules into large flat clusters occurs. When the aggregates are too large to freely move in the solution, a transition into a constrained phase takes place. The interaction between the highly conjugated PPE molecules and the solvent results in constraint of the motion of the solvent as well. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1486215]

I. INTRODUCTION

A wide range of soft materials such as colloids, emulsions and foams undergo constraint of their motion at low temperatures or high volume fractions.[1–8] The constrained gel-like phase, or "jammed" phase, is characterized by a solidlike rheological response while the local dynamics is often rather fast in comparison with that of molecules in a solid.[1–5] In contrast to solids, in this type of fragile matter, changing the direction of applied stress will release the constraint.[4] These characteristics are typical to numerous systems, from macroscopic granular systems to microscopic molecular clusters.[2] In colloidal systems (rigid particles with no electrostatic interaction), the balance between the thermal energy of a system at a given temperature, $\sim kT$ (where k is the Boltzmann constant and T is the temperature), and the attractive interaction between particles determines the state of the system, i.e., fluid or constrained. The same phenomena have been observed in solutions of some polymeric micelles and star polymers, where cooling or heating leads to formation of gel-like phases.[5–8] Similarly to colloidal systems, the energy balance in complex fluids that consist of clusters of molecules and solvents, controls the state of the system. However, changing the temperature in a complex system, which consists of aggregates, is not merely changing the interparticle interactions and kT. Temperature changes over relatively small intervals may be accompanied by significant changes in the microstructure of the system, thus the formation of a constrained phase is a combination of multiple factors.[7]

The assembling of particles, in particular, polymeric chains into aggregates and the dynamics of the entire aggregate define the overall properties of the complex fluid. The association of macromolecules is strongly affected by their conformation. For flexible polymers the conformation of the chains is governed by its degree of polymerization and their interaction with the immediate surrounding, including solvents or other polymers. With increasing of the persistence length of the polymers, their rigidity becomes a significant factor in their collective behavior. The stiffness affects the viscosity of a polymeric solution, and may induce phase separation, gelation and liquid crystallinity.[9,10]

The present study utilizes rodlike oligomers of dinonyl poly(*para*phenyleneethynylene)s (PPE), in toluene to study the formation of constrained phases in complex fluids. The molecular structure of the PPE under consideration is shown as an inset in Fig. 1. Dilute solutions of PPE in toluene exhibit fluid rheological characteristics above room temperature. When cooled down a glass-like transparent phase, which does not flow, is formed, referred to herein as a gel-like phase. In contrast to most physical gels, a gentle shear is sufficient to break the gel-like phase and form a liquid.

PPE molecules are neutral, long, linear objects. They are highly conjugated, thus attractive $\pi–\pi$ interaction contributes to the interparticle interaction. The strength of $\pi–\pi$ interaction varies from $\sim 2–6$ KCal/mole, depending on the overlap between the aromatic groups.[11] At high concentration solutions as well as in melts, phenylene–ethynylenes (PE), depending on their topology, show multiple modes of fine-tuned association. Helical, tubular, and lamellar nanostructures have been observed.[12–18] The manner in which the
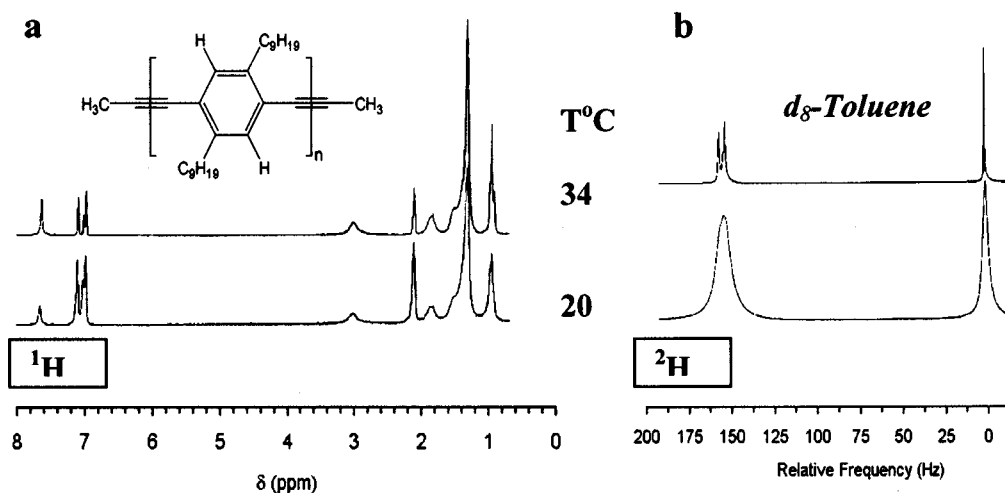
FIG. 1. (a) ^{1}H NMR spectra of a solution of a 2.13 wt. % PPE in d_8 toluene, measured on a Bruker AC-200 operating at 200 MHz upon heating, starting with samples which were cooled to 5 °C for 10 min prior to the first measurement; (b) ^{2}H NMR of d_8 toluene in the same solution, measured upon heating.

PE units are joined (i.e., *para, ortho, meta*) and the nature of the substituents on the aromatic ring, determines the structure and the association of PEs. Introduction of polar groups for example, such as oligoethyleneglycol substituents to drive self-assembly of *meta*-phenylene–ethynylenes into helical structures.[13] The tendency of PE molecules to associate and form regular structures has been further demonstrated at the solid air interface. Surface studies[14] have shown that PPE molecules spontaneously arrange in periodic array of single molecule wirelike structures on a single crystal carbon support (HOPG). When cast from toluene solution, PPE forms nanometer length cablelike aggregates.[16] These large organized features may either preform in solution, or PPE molecules self-assemble during the casting process onto the surface, similar to the process that occurs upon crystallization of polymers from solution. The structure of dilute PPE solutions is addressed in the present study by small angle neutron scattering (SANS) and the dynamics of the solvent and the molecule are studied by nuclear magnetic resonance (NMR). These measurements have been accompanied by differential scanning calorimetry (DSC) studies across the temperature range in which a transition from a liquid to a constrained phase, takes place.

II. EXPERIMENT

PPE molecules with a polymerization number Pn=82, and $M_w/M_n=2$,[18] have been dissolved in d_8 toluene (Cambridge Isotope Laboratories). The polymerization number has been determined by gel permeation chromatography (GPC), using a saturated analog of the conjugated molecule.[19] ^{2}H and ^{1}H NMR measurements have been carried out on a Bruker AC200 spectrometer at 30 and 200 MHz, respectively, using one pulse with $\pi/2=15$ μs for protons and $\pi/2=45$ μs for deuterium. NMR relaxation time measurements were carried out on a Joel500, at 500 MHz, using $\pi-\tau-\pi/2-echo$, sequence and a $\pi/2=12.7$ μs. The temperature was controlled to ±0.5 °C. Differential scanning calorimetry measurements were carried out on a Mettler–Toledo DSC820 system. Small angle neutron scattering ex-

periments were carried out at NIST on NG3 at $\lambda=6$ Å. One-dimensional patterns were obtained by integrating over the detector area. The over all q range was attained by combining the scattering from two configurations, where the detector was placed at 3 and 13 m from the samples. The patterns presented are normalized to the scattering of the solvent. The samples were encapsulated in a 2 mm thick, 1 cm diameter, quartz cells. The temperature was controlled using a water bath to ± 0.5 °C.

III. RESULTS AND DISCUSSION

The formation of a gel-like phase in dilute solutions of PPEs was first observed on a phenomenological level for short oligomers (30–100 monomers) in toluene, at concentrations as low as 0.1 wt. %. A clear transition from a fully liquidlike solution into a gel-like phase, which does not flow on the time scale of weeks, has been observed when the solutions are cooled below room temperature. Further manifestation has been attained from shifts in UV–VIS spectra of PPE solutions. With increasing viscosity, a transformation from a colorless solution to a yellow gel-like phase takes place. It has been suggested that following aggregation of the PPE molecules, the rotational motion around the aryl-ethynyl–single bond is hindered. This allows further coupling of electronic states, resulting in emission of yellow light.[17] The yellow gel-like phase becomes a transparent fluid upon either increase in temperature or vibration of the sample. The nature of the phase transition and the dynamics of the molecules in both phases have been studied by NMR, DSC, and SANS.

A. NMR and DSC studies

The ^{1}H NMR spectra of dinonyl-PPE ($P_n=82$) and the ^{2}H NMR spectra of d_8 toluene, used as a solvent, have been measured between 5 °C and 45 °C in a 1.06 wt. % and 2.13 wt. % PPE solutions. Representative spectra for a 2.13 wt .% solution, of the high (34 °C) and low temperature phases (20 °C) are shown in Figs. 1(a) and 1(b) for the PPE (^{1}H) and for d_8 toluene (^{2}H), respectively. The linewidth of the PPE
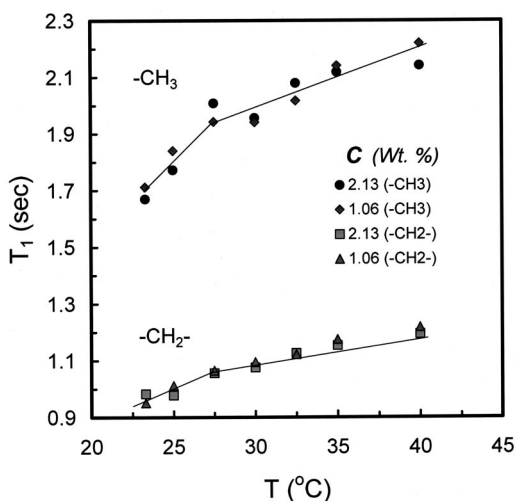
FIG. 2. Temperature dependence of T_1 of CH_3 end group and CH_2 of the nonyl side group of PPE in solutions of 1.06 and 2.13 wt. % of PPE in d_8 toluene, measured upon heating. Samples were cooled down to 5 °C for ~10 min prior to the first measurement. The solid lines describe trends.

and the solvent increase as the system forms a gel-like phase. The NMR linewidth is inversely proportional to the molecular relaxation times, which are dependent on the rotational and transnational motion of the molecules. The increase of the width with decreasing temperature indicates slowing down of the motion of the molecules.[20] While the motion has been hindered, beyond the changes expected from decrease in kinetic effects [see measurements of the solvent in Fig. 3(a)] as the temperature is reduced, the line width and shape between 5 °C and 45 °C, remained consistent with those of viscous liquids.[20–22] No evidence of liquid crystallinity or any anisotropy expressed as quadrupole splitting or powder characteristics, have been detected in the ^2H spectra.[19] Polarized optical microscopy further confirmed that the gel phase is isotropic.[23]

The spin lattice relaxation times T_1 of the nonyl side chain and the solvent have been measured as a function of temperature for two concentrations. The temperature dependence of T_1 of the protons of the CH_2 and CH_3 groups of the nonyl side chains is presented in Fig. 2 and that of residual protonated solvent in d_8 toluene is shown in Figs. 3(a) and 3(b) at concentrations as indicated in the figures. The relaxation time of the nonyl side chain of the PPE is of the order of 1 to 2 seconds in the liquid phase and decreases in the gel-like phase. T_1 of the aromatic component of the PPE molecule was undetectable on the time scale of the NMR measurement. The short relaxation times are consistent with a rather rigid molecule even in the liquid phase. T_1 of both CH_3 and the CH_2 groups increases with temperature. The rate of the change, which corresponds to the slope of the line, changes discontinuously upon transition from the gel-like to the liquid phase. We note that the change is more pronounced for the CH_3 group than the CH_2. Both curves display a discontinuity in the relaxation time at the transition. Being the terminal group, CH_3 is less constrained in the liquid state than CH_2. Therefore constraining effects are more pronounced.[20,22]
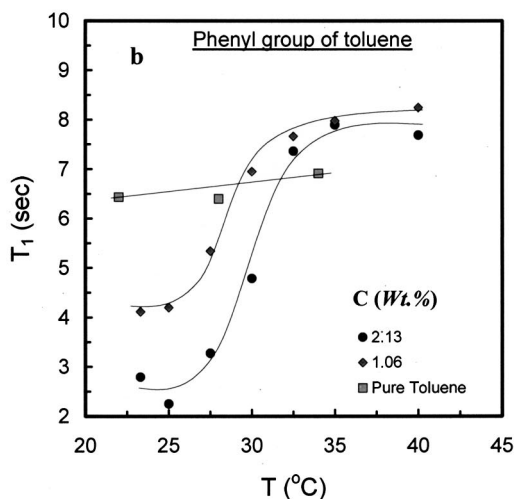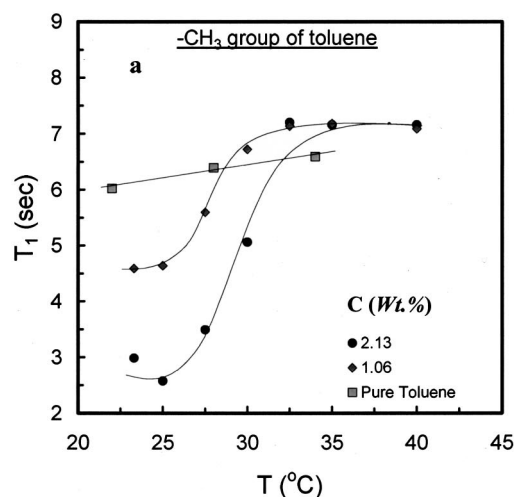

FIG. 3. Temperature dependence of T_1 of residual protonated toluene in the deuterated solvent in the PPE solutions shown in Fig. 2. (a) T_1 of the CH_3 group; (b) of the phenyl group. Samples were cooled down to 5 °C for ~10 min prior to the first measurement. The lines represent trends. The dependence of the same groups in pure toluene is shown for comparison for both groups.

The relaxation time of the solvent is of the order of 7–8 seconds in the liquid phase and it drops to 1–2 seconds below room temperature, as a phase transition into the gel-like phase takes place. Comparison with the value of the relaxation time in pure toluene suggest that at high temperatures, in the liquid phase limited association takes place between the solvent and the PPE molecules. While the change in the slope of the relaxation time of the nonyl side chain is discontinuous, the change in T_1 of the solvent takes place over a temperature range of ~8 °C. The concentration of the PPE molecules has no effect on the relaxation time of the side chains of the PPE molecules while the relaxation time of the solvent is invariant to concentration, in the liquid phase and inversely proportional to the concentration of the PPE molecules, in the gel-like phase. The concentration dependence of the relaxation time indicate that increasing concentration increases the area of contact between the PPE molecules and the toluene, thus increasing the confinement of the solvent.

The NMR measurements have shown that the motion of

the solvent as well of the PPE molecules has been constrained as the transition into the gel-like phase takes place. The solvent, which is rather free to move in the liquid phase, similarly to the motion of the molecules in pure toluene is significantly confined in the gel-like phase. The rheological response of the system suggests that the translation motion is constrained in the gel-like phase. The NMR lines of both the aromatic and aliphatic parts of the PPE as well as that of the solvent are relatively narrow. The relaxation times for the side chains as well as the solvent are in the range expected for a liquid suggesting that while some coupling between the aromatic parts takes place as the gel-like is formed, significant rotational freedom is retained. The slow down of the motion to a higher degree than expected from a decrease of kinetic energy due to cooling indicate that further constraint occurs. The decrease in relaxation time is consistent with the formation of larger clusters that limit the motion of the PPE molecules. When the clusters are sufficiently large they can no longer move freely, resulting in a transition to a constrained phase.

DSC measurements have shown that the transition is characterized by a broad line centered about 28 °C, corresponding to enthalpy changes of ~31 and 70 ($\pm$3) J/mole for 1.06 and 2.13 wt. % solutions, respectively. The change in enthalpy, which accompanies the significant changes in the magnetic relaxation times of the PPE molecule and the solvent, indicates that further microstructural changes take place, resulting in a transition to a constrained phase.

B. SANS studies

The structure of the PPE molecules in the fluid and gel-like phases have been further explored by small angle neutron scattering.[21–25] Neutron scattering allows the direct study of the dimensions of the molecule without including any associated solvent molecules or being affected by the florescence observed upon association of the molecules. Measurements have been carried out as a function of temperature for 1.06 and 2.13 wt. % PPE in d_8 toluene. Patterns for the three different regimes, the isotropic liquid (40 °C), the transition regime (30 °C) and the gel-like phase (25 °C) for 2.13 wt. % are shown in Fig. 4(a) for a 2.13 wt. % solutions of PPE in d_8 toluene at different temperatures. At 40 °C, the solution is clear and fluid. At this temperature, the scattering profile is consistent with a cylindrical form factor.[21,24,25] For cylindrical objects, with no interparticle interaction, the scattered intensity as a function of q is given by $I(q) = L(\pi/q)I_c(q)$ where L is the length of the cylinder, $I_c(q) = (\Delta\rho^2)A\int 2\pi r\, dr\, \gamma_{co}(r)J_0(qr)$. $I_c(q)$ is the intensity related to the cross section; $\Delta\rho$ is the scattering contrast; A is the cross-section area; $\gamma_{co}(r)$ is the correlation function of the cross-section geometry; J_0 is the zero order Bessel function.[24–27] The scattering length density for PPE molecule is 3.97×10^{-7} Å^{-2}, and for d_8 toluene is 5.64×10^{-6} Å^{-2}. $\Delta\rho$, the difference between the density of PPE and toluene, has been fitted to allow the presence of solvent in the vicinity of the PPE molecule. This was followed by fitting the dimensions of the cylinders. This yields cylindrical objects with characteristic dimensions of $L\sim641$ Å, and a radius ~11 Å. These dimensions are consistent with the size of a stretched
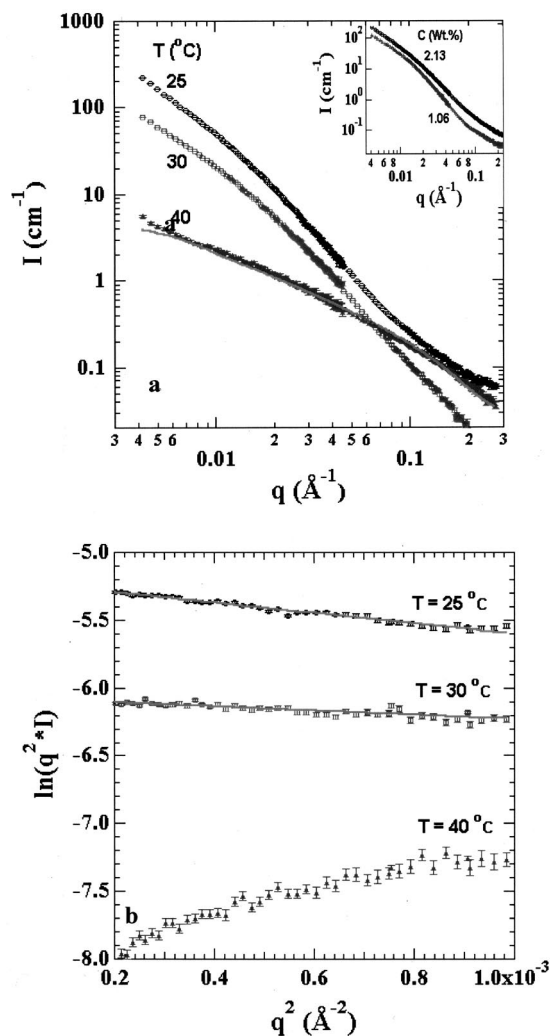

FIG. 4. (a) Neutron scattering intensity (I), normalized to the scattering of the solvent, as function of momentum transfer q (where $q=4\pi/\lambda \sin\theta$; λ is the neutron wavelength and θ is the incident angle) for a 2.13 wt. % at the indicated temperatures. The patterns were obtained by combining the scattering from two configurations where the detector was placed at 3 and 13 m from the samples. The symbols correspond to experimental data, and the solid lines represent different fittings. The insert corresponds to comparison between 1.06 and 2.13 wt. % at 25 °C. (b) A plot of the low q range of the patterns presented in Fig. 4(a), showing the linear line obtained at 30 °C and 25 °C characteristics of flat large objects. Cylindrical characteristics are observed at 40 °C.

PPE molecule of ~80 repeating units. This result is rather surprising since in absence of strong electrostatic interactions, even rodlike polymeric molecules are known to fold or bend in solution.[9] It is consistent however with the short relaxation times observed by NMR. It is also in agreement with the STM images of rodlike PPE molecules when they are captured from solution onto a carbon substrate.[14] A careful analysis of the small q region, at 40 °C show that some longer cylindrical objects are present in the liquid phase (~1000 Å long and ~17 Å in diameter). No changes take place in this regime with increasing temperature, indicating that this contribution arises from longer oligomers in the solution (note that the polydispersity of the polymer is 2).

The dimensions of the PPE molecules in solution provide further insight into the nature of the phases, formed by

the molecules. While at higher concentrations, most of the PEs and numerous other rodlike molecules and micelles form liquid crystalline phases, the concentrations of PPEs addressed in this study are below the threshold concentration for a mesophase formation. An estimate of the threshold concentration for liquid crystallinity can be obtained from mean field approach as described by Onsager Theory.[28] The liquid crystallinity threshold concentration for rigid rods is given by $\phi_a = 4.49 d/L$, where d corresponds to the diameter of the rod and L to its length. Based on the dimensions obtained from neutron scattering $\phi_a = 0.155$ for the specific PPE molecule under consideration. Therefore rods with dimensions of the PPE molecules should occupy at least 15.5% of the volume of the solution to form a liquid crystalline phase, concentrations which are an order of magnitude higher than the concentrations in this study.

Cooling down below 40 °C, the line shape changes as can be seen in the pattern measured at 30 °C. Although the solution still flows, this pattern cannot be fit with the cylindrical form factor. Further cooling leads to a formation of a phase, which macroscopically does not flow exhibiting a neutron pattern similar to that obtained at 30 °C. In the gel-like phase, the scattering intensity increases significantly and the line shape changes. While the system appears like a gel, the neutron patterns cannot be fit to a simple physical thermoreversible gel, in which single chains form a network. Based on the viscous nature of the sample, the layered structure[29] reported in the solid sate of PPE in absence of solvent in the bulk, and ribbonlike micron-length clusters has been observed by AFM,[16] a network of large flat aggregates has been considered.

For thin, flat aggregates, where the length and width of the cluster are much larger than its thickness, the scattering function is given by $I(q) = A(2\pi/q^2)(\Delta\rho)^2 T^2 \exp(-q^2 R_t^2)$, where $R_t = T/\sqrt{12}$ and T is the thickness of flat particle.[25,30] Plotting $\ln(q^2 I)$ as a function of q^2, shown in Fig. 4(b) provides the thickness of the aggregate. At 40 °C, no defined aggregate is observed. Cooling down to 30 °C, well defined aggregates, with a thickness of 46.1 Å are observed. At this temperature, NMR and DSC data show that some aggregation takes place, however the system is macroscopically fluid. Further cooling leads to the formation of the gel-like phase revealing aggregates of $T \sim 62.9$ Å, as shown at 25 °C. The thickness does not change as the temperature is further decreased. Similar patterns have been observed for the 1.06 wt. % as shown in the insert in Fig. 4(a) at 25 °C.[24,25] Extrapolating to $I(q=0)$ shows that I_0 increases linearly with concentration, suggesting that the volume of the scattering objects increases linearly with concentration. It may correspond to either growth in the number or size of the aggregates. This is consistent with the dependence of T_1 of the solvent molecules, as measured by NMR.

In their solid state, PPEs form a lamellar phase where the molecules are aligned on top of each other at a distance of 3.8 Å and aromatic rings are staggered, to allow optimal packing of the aliphatic chains.[29] If these aggregate in solution would constitute a perfect stacking, similar to their solid-state configuration, an aggregate would constitute 15–18 molecules. X-ray studies however did not show a well

distinct line, suggesting that when a flat sheet is formed the molecules within are randomly displaced. We note that from this analysis the length and width of the aggregate cannot be obtained.

The data obtained from SANS, NMR and calorimetric studies suggest that the liquid phase consists of mostly single noninteracting molecules. The solvent molecules are as free to move as in pure toluene. As the temperature decreases, aggregation sets in over a temperature range of ~ 8 °C, accompanied by changes in enthalpy. The association results in large flat aggregates, where the stacking of the aromatic rings defines the direction of association of the molecules. When these aggregates become large enough their motion is constrained due to their size. According to the NMR studies, the motion of the solvent becomes highly constrained at this stage as well. This may be explained by π–π interactions between the increasing restricted highly conjugated surface areas of the aggregates, which induce further arrest of the motion of the toluene.

IV. CONCLUSIONS

This study has shown that the dialkyl-PPEs form molecular solutions of fully extended dimensions in toluene and self-assemble into large flat structures at lower temperatures. These structures are large enough to result in a gel-like phase at relatively high temperatures and low concentrations. A very light shear of the sample is sufficient to destroy its fragile texture. This fragility of the phase is rather distinctive.

The translational diffusion of the aggregates is restricted but rotational motion of individual solvent molecules and the side chains of the PPE molecules are maintained, allowing the detection of NMR signals using high-resolution NMR methods. The aggregates are large enough to induce arrest of the solvent most probably via π–π interactions, the mechanism that drives aggregations in such systems. This is a rather unique behavior for a polymeric organic molecule, where fully extended chains and aggregates of these dimensions are found only in highly charged systems. Further studies of the mechanism of the aggregation and the factors that affect the overall microstructure of both phases, are currently on the way.

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