SUPRAMOLECULAR SELF-ASSEMBLY OF MONOCARBOXYDECYL-TERMINATED DIMETHYLSILOXANE OLIGOMER

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Abstract

The supramolecular self-assembly of monocarboxydecyl-terminated dimethylsiloxane oligomer is investigated and characterized by combining different experimental methods. Thermodynamic properties were accessed by temperature modulated differential scanning calorimetry and two sub-ambient phase transitions were identified. Fourier transform infrared spectroscopy gave access to the main molecular entities involved in these phase transitions. Diffraction experiments using small angle X-ray scattering and wide angle X-ray scattering evidenced the development of two distinct well ordered sub-10 nm structures, each associated with one of the thermal transitions,

without any indication of long-range atomic order. All the results point to the self-assembly of the oligomeric dimers below 230 K giving rise to supramolecular structures involving new H-bonding interactions. A further structure is developed below 205 K by the assembly of the alkane part of the molecules in an arrangement of hexagonally packed cylinders. Dielectric relaxation experiments evidenced both the pronounced effect of the lowest temperature transition on the H-bond network fluctuations, and the very effective segregation of dimethylsiloxane at lower temperatures. Moreover, we found that the structured liquid presents a rubber-like mechanical behavior in the temperature range 150-200 K, where dimethylsiloxane phase remains amorphous, and at lower temperatures a glassy nanostructured material is found.

Introduction

Molecular self-assembly is a convenient way for the bottom-up approach in nanotechnology (see Ref. 1 and references therein). Particularly, block copolymers are well-known by their ability to self-assemble into a wide variety of morphologies either in bulk (lamellae, gyroids, cylinders, spheres, etc.) or in solution (spherical micelles, vesicles, cylinders, etc.).^{2,3} The shape and size of self-organized morphologies can be suitably controlled through a number of variables. In bulk, the geometries and structural lengths are mainly determined by block sizes and the interaction parameter,⁴ although other factors such as conformational asymmetry and polydispersity also play a significant role.⁵⁻⁷ Thus, block copolymers form a collection of elementary building blocks for the precise construction of advanced materials.⁸ Following this route, it has been possible to obtain a high variety of well segregated and ordered nanostructures with periodicities in the range 10 to 100 nanometers. The limit for smaller sizes comes because the entropic contributions to the free energy unfavors segregation and the spontaneous thermal fluctuations give rise to interfaces with a typical width of a few nanometers.⁹ Nevertheless, ordered structures with sub-10 nm features have been achieved by significantly increasing the value of the effective interaction parameter.^{6,7,10}

On the other hand, there is a relatively new class of materials where supramolecular structures are developed due to highly directional and reversible non-covalent interactions.^{11,12} The structural reversibility caused by the transient nature of secondary interactions renders supramolecular systems as promising materials with unique properties. Self-assembly of supramolecular structures can be favored by the specific interactions present in these systems, which when combined with short polymer chains could help in the development of structures with shorter periodicity than those accessible using block copolymers alone.^{13,14} Amongst different chemical groups giving rise to supramolecular structures, the carboxyl end-group is a rather simple one. Carboxyl group is endowed of self-complementary hydrogen bonding ability, which is responsible for the usual formation of dimers in aliphatic acids, resulting from the planar and cyclic intermolecular connection between two carboxyl end-groups.¹⁵ This is a very directional and quite strong interaction with a rather high energy of about 60 kJ/mol. Moreover, dimers can further interact to each other giving rise to tetramers.¹⁶ Taking into account the hydrogen bonding energy, small block copolymers in combination with functional carboxyl end-groups could provide a way of achieving well ordered sub-10nm structures.

In this work we show that, nanostructures with typical periodicity of a few nanometers are developed in monocarboxydecyl-terminated dimethylsiloxane oligomer when cooled below 230 K, without indication of long-range atomic order,. Particularly, by decreasing temperature the disordered liquid develops first a well ordered regular mesostructure with 6.3 nm periodicity by the self-assembly of the oligomeric-dimers generated by directional interactions of the carboxyl end-groups. At lower temperature, this mesostructure remains and a new regular arrangement arises below 200 K, which consists of hexagonally packed cylinders of 2.4 nm diameter with a lattice constant of 5.5 nm. This new structure, which provides rubber-like properties to the material, does not involve significant changes in the dimethylsiloxane part of the molecule. Moreover, our data show that the dimethylsiloxane oligomer phase remains always fully amorphous and reaches the glassy state at 150

K. All these features change dramatically when the intermolecular H-bond interactions are suppressed by methyl esterification of carboxyl end-group, which proves the key role of H-bonding interactions in the observed structures.

Experimental

Samples

Monocarboxydecyl terminated dimethylsiloxane oligomer (o-DMS-DCOOH) prepared by living anionic polymerization of hexamethyl cyclotrisiloxane was purchased from Polymer Source, Inc. and used as received. This functionalized oligomer (see Scheme 1) has a weight average molecular weight (M_w) of 1300 g/mol and polydispersity index (M_w/M_n) of 1.3. This corresponds to around 14 dimethylsiloxane monomeric units per molecule. Thus, it can be viewed as a block-co-oligomer with a DMS block and an aliphatic one with a carboxylic acid ending group. For comparison purpose, a similar material was prepared in our laboratory by substituting the carboxyl end group by a methylcarboxylate one (o-DMS-DCOOCH₃) following the commonly reported route.¹⁷ In short, the procedure started dissolving 1.33 g (1.04 mmol) of o-DMS-DCOOH with 64 ml of a mixture toluene : methanol (9 : 1 volume : volume) and 2.56 ml of a 2.0 M solution of trimethylsilyldiazomethane (5.12 mmol) was added. The mixture was allowed to react in a loosely capped vial for 30 minutes at room temperature, allowing the nitrogen gas formed during the reaction to escape. Excess reagent was eliminated by adding approximately 320 microliters ($\approx$ 5.6 mmol) of acetic acid and allowing the mixture to stand for 30 minutes at room temperature. The sample compound was purified by rotary evaporation of the solvents at 330 K. The so obtained material is a color-less liquid at room temperature as it was o-DMS-DCOOH. When preparing the samples for different experimental setups, they were first stored at 350 K in a vacuum oven for twelve hours. After this period of time the samples were allowed to cool-down to room temperature in the vacuum oven before being placed into the corresponding sample holders.

Scheme 1: Schematic formula of the monocarboxydecyl terminated dimethylsiloxane oligomer investigated in this work.

Differential Scanning Calorimetry (DSC)

Differential scanning calorimetric measurements were carried out using a Q2000 calorimeter from TA Instruments. The samples were prepared by encapsulating about 10 mg of the liquid material in hermetic aluminum pans. Most of the calorimetric results were obtained by temperature modulated experiments (TMDSC) while cooling from 300 K to 100 K and heating back to 300 K. In this experimental protocol we used an average heating/cooling rate of 3 K/min, with 60 s period oscillation and 0.5 K temperature amplitude.

Small Angle X-ray Scattering (SAXS)

SAXS diffraction experiments were performed on the Rigaku PSAXS-L equipment consisting of a MM002+ micro focus source, a 2D-200X gas detector, and a three pinhole collimation. The 2D intensity data were azimuthally averaged assuming isotropic scattering. The so obtained scattered intensities are represented as a function of the momentum transfer q to obtain the 1D scattering pattern. Reciprocal space calibration was done using silver behenate as a standard. The sample was placed in a sealed boron-rich capillary, with an outside diameter of 1 mm and wall thickness of 0.01 mm, at 2 and 0.5 m from the detector, which allowed covering a q range from 0.008 - 0.8 $\text{\AA}^{-1}$. The measurements as a function of temperature were performed by means of a Linkam Scientific Instruments THMS600 temperature controller. The measuring time was 1 hr at each temperature.

Wide Angle X-ray Scattering (WAXS)

WAXS diffraction experiments were performed on a Bruker D8 discover diffractometer (Cu-K radiation), working in reflection and parallel beam geometry free of K_β radiation. Varying the scattering angle 2θ from 5 - 30° with a step of 0.05°, the scattering vector q ranges between 0.4 and 2.2 Å⁻¹. The counting time was 5 s/point. The sample was placed on a flat Si-111 wafer mounted on an Anton Paar TTK 450 low-temperature chamber under vacuum conditions.

Attenuated Total Reflectance Fourier Transform Infrared spectroscopy (ATR-FTIR)

Temperature dependent ATR-FTIR measurements were carried out with a Jasco 6300 spectrometer in combination with a low-temperature diamond ATR system (Golden Gate-Specac) purged with nitrogen gas. The spectra were obtained after 120 accumulations with 4 cm⁻¹ resolution.

Rheology

Rheological experiments were performed by using an ARES rheometer (TAI rheometrics series) with a parallel plate geometry. The sample was filling the 1 mm gap in between the two 25 mm plates (invar tools). A sinusoidal torsional deformation of low amplitude, to avoid non-linear effects, was applied with the lower plate and the resulting torque was detected by a transducer attached to the upper tool. The temperature was controlled with the environmental test chamber using liquid nitrogen as the gas source.

Broadband Dielectric Spectroscopy (BDS)

Broadband Dielectric Spectroscopy experiments were performed over a broad range of frequencies and temperatures. Data were acquired using two different instruments. For the

low-medium frequency region a Broadband Dielectric Spectrometer (BDS) Alpha-A Novo-control was used, covering the range from 10^{-1} up to 10^6 Hz. Higher frequency data were collected using an Agilent 4291B Impedance analyzer exploring a frequency range from 10^6 up to 10^9 Hz. In all cases the sample preparation was carried out by adding (by drop) about 50-100 mg of sample over a gold plated electrode disk of 10 mm (high frequencies) and 30 mm (low-medium frequencies) diameter. An upper electrode of 10 mm and 20 mm (high/low-medium frequencies respectively) was placed on the previously prepared film, maintaining a separation of 0.1 mm between both electrodes by means a cross-shaped teflon spacer of small area. The sample cells were set in a cryostat, and the temperature was controlled via nitrogen gas jet stream coupled with the Novocontrol quattro controller. Dielectric measurements of the samples were obtained isothermally in the range 120 K - 300 K in steps of 5 K with ± 0.01 K stability. Dielectric experiments at a few selected frequencies during continuous temperature variation at 3 K/min were also conducted.

In the analysis of the isothermal BDS data the measured dielectric losses are commonly fitted according to the empirical Havriliak-Negami (HN) equation:¹⁸

$$\epsilon_{HN}^*(\omega) = \epsilon_{\infty} + \frac{\Delta\epsilon}{[1 + (i\omega\tau_{HN})^{\alpha}]^{\beta}} \quad (1)$$

In this equation, $\omega = 2\pi f$, α and β denote respectively the symmetric and asymmetric broadening of the relaxation loss peak ($0 < \alpha, \alpha \cdot \beta \leq 1$), $\Delta\epsilon$ is the relaxation strength, ϵ_{∞} is the high frequency limiting permittivity, and τ_{HN} (the HN relaxation time) is related to the loss peak relaxation time, $\tau = 1/(2\pi f_{max})$, by the equation:

$$\tau = \tau_{HN} \left[\sin \left(\frac{\alpha\pi}{2\beta + 2} \right) \right]^{1/\alpha} \left[\sin \left(\frac{\beta\alpha\pi}{2\beta + 2} \right) \right]^{-1/\alpha} \quad (2)$$

Figure 1: a) TMDSC experiments on o-DMS-DCOOH using average rate of 3 K/min. (cooling dashed lines, heating solid lines), modulation period of 60 s and temperature amplitude 0.5 K. The results of a similar experiment performed by heating an initially amorphous PDMS (long-dashed and dotted lines) is shown at the bottom for comparison. b) Expanded view of the reversing heat capacity (solid line) and non-reversing heat-flow (dashed line) of o-DMS-DCOOH as determined by means of quasi-static TMDSC using an average rate of 0.2 K/min., a modulation period of 60 s, and a temperature amplitude 0.5 K.

Results

Figure 1 shows the results of TMDSC experiments on monocarboxydecyl terminated dimethylsiloxane oligomer (o-DMS-DCOOH). The thermal behavior of this material evidences the occurrence of phase transitions at around 230 K and 205 K, in addition to a clear jump in heat flow (HF) at around 150 K. The latter compares well with the usual glass transition range of polydimethylsiloxane (PDMS) (see bottom part of the figure). When comparing the measured HF jump (17 mW/g) with the value corresponding to the glass transition jump of amorphous PDMS measured in the same conditions (20 mW/g) it is found that the ratio between both values is close to the weight fraction of DMS segments in the sample (≈ 80 wt%). This result suggests that PDMS crystallization is inhibited in this material, which is also confirmed by the absence of any crystallization/melting signature similar to those observed in PDMS. The exothermic peak detected on cooling at about 230 K shows no appreciable changes in the corresponding reversing HF signal, which indicates a kinetic process. On heating, a weak peak (2 kJ/mol) is detected at slightly higher temperatures, mainly contributing to the reversing HF signal. These features resemble those of a first order transition. Contrarily, the more prominent transition occurring at around 205 K shows quite distinctive characteristics. First, most of the detectable HF on cooling occurs in the reversing HF part with only a very weak non-reversing HF signal. The observation of a nearly identical behavior of the reversing HF on heating, with again very low values of the non-reversing HF signal, could be indicative of the occurrence of a continuous phase transition with negligible latent heat. To further corroborate this finding, the heat capacity behavior was determined by quasi-static TMDSC experiments, i.e. using 0.2 K cooling rate (see Figure 1 b). Here we found that around the transition range the specific heat capacity increases sharply in a factor of nearly 2 with a maximum at 205.9 K. This behavior of the specific heat capacity resembles that of a continuous order-disorder transition, as for instance an isotropic-to-nematic phase transition, showing cusp-like divergence.¹⁹

Trying to find out the molecular entities responsible of the thermal transitions observed by

DSC, FTIR experiments at temperatures around the thermal transitions were performed. Figures 2a-c show the most relevant ranges where the IR absorption bands of o-DMS-DCOOH occur. The measurements at different temperatures are compared with the IR absorption bands of PDMS at room temperature. For the comparison, the data have been scaled to match the peak intensity of the prominent band associated to the Si-O bond stretching at around 1020 cm^{-1} . Frames (a), (b) and (c) correspond respectively to absorption bands dominated by Si related bonds, C=O stretching, and C-H stretching. In this way it is quite evident that the Si related bands change with temperature smoothly and therefore they are not significantly affected by the occurrence of the transitions detected by DSC. This result is also in agreement with the already commented inhibition of DMS crystallization, since it has been found that crystallization of DMS gives rise to quite clear changes in the double band located in the range $1100\text{-}1000\text{ cm}^{-1}$.²⁰ Contrarily to the monotonous behavior of the Si related bands, the other ranges shown in frame (b) and (c) are to some extent affected by the occurrence of the thermal transitions. The bands in the range $3000\text{-}2800\text{ cm}^{-1}$, associated to the C-H stretching, are not much affected by the high temperature transition, but when cooling below 205 K they change clearly in intensity and a new band becomes quite apparent at around 2860 cm^{-1} . According to the previous results concerning Si-related bands, the prominent band attributed to C-H stretching of methyl groups at 2960 cm^{-1} is not changing much but the bands that are not present in PDMS (related with C-H stretching of ethylene groups) become quite stronger at low temperature. This evidences that the monocarboxydecyl functional group is actually involved in the thermally most prominent transition. On the other hand, the band more clearly affected by both thermal transitions is that attributed to C=O stretching (Figure 2b). The single peak detected at temperatures above the transitions develops a prominent shoulder at lower wavenumbers, and shifts slightly, on cooling below 230 K. When cooling further below 205 K, the shoulder becomes a visible distinct peak and the whole band shifts clearly to lower wavenumbers. The position of the C=O vibration at room temperature matches well that commonly found in n-alkylcarboxylic acids and

it is originated from dimers formed through association by H-bonds between two carboxyl end-groups of distinct molecules.^{21,22} As a comparison, the C=O absorption band peak in *o*-DMS-DCOOCH₃ is observed at 1744 cm⁻¹ (see Figure S1 in the Supporting Information), i.e. close to that expected for a C=O group not involved in H-bonds. The behavior of the C=O stretching band shifting towards lower frequencies and the emergence of a lower frequency sub-band are both in agreement with the arising of new H-bonds interactions among the carboxyl dimers which would reinforce dimer forming associations. This seems to occur already below 230 K but further develops below 205 K, where the bands associated to the rest of the monocarboxydecyl moiety are also clearly altered.

The above results evidence the occurrence of two thermal transitions in *o*-DMS-DCOOH that mainly involve the monocarboxydecyl functional group. Looking for structural features related with these thermal transitions, X-ray diffraction experiments covering both wide angles (WAXS) and small angles (SAXS) were performed in the relevant temperature ranges. The obtained results are summarized in Figures 3 and 4. At temperatures above 230 K both WAXS and SAXS diffraction patterns correspond to a typical liquid with no specific features in SAXS and a main broad diffraction halo at around 0.9 Å⁻¹ with a shoulder at 1.5 Å⁻¹ in WAXS. As could be expected, these WAXS features are quite similar to those of liquid PDMS²⁰ (note that DMS amounts ≈80 wt%). However, below 230 K, whereas the WAXS pattern remains nearly unchanged, clear features are evidenced in SAXS with visible diffraction peaks appearing at 0.1, 0.2, 0.3 and 0.4 Å⁻¹. Cooling further below 205 K, SAXS results show the appearance of a pronounced new diffraction peak at 0.13 Å⁻¹ superimposed on the nearly unchanged intensity profile determined at 220 K. This new feature in the SAXS diffraction pattern is accompanied by modest concomitant changes in the WAXS range. Particularly, the WAXS pattern evidences the development of a more structured shoulder, with increased intensity at 1.7 Å⁻¹. Nevertheless, the main WAXS diffraction halo shows just a minor narrowing. The X-ray diffraction results evidence that none of the two transitions detected by DSC gives rise to a well developed atomic long range order typical of

Figure 2: IR absorption bands of o-DMS-DCOOH measured by ATR-FTIR at several temperatures (black: 250 K, blue: 220 K, green: 180 K) as compared with the absorption in PDMS at room temperature (red curves). For the comparison the raw data have been normalized to the peak intensity of the Si-O related band at 1020 cm^{-1} .

a (semi-)crystalline material. However, the shoulder developed at $1.7 \text{ \AA}^{-1}$ could suggest the presence of some short range intra-chain atomic correlations that could be connected with the changes affecting the alkyl part below 205 K.

Contrarily to WAXS results, both transitions manifest in rather well defined features in the SAXS pattern giving evidence of well ordered mesostructures. The detailed analysis of the SAXS features was done after subtraction of a background signal. To account for the background of the low temperature SAXS data, the SAXS pattern at 250 K has been described by a simple mathematical function, particularly $a+bq^{-3}+cq^3$, and a similar functional form has been used at lower temperatures to describe the SAXS intensities out of the relevant range, i.e. below $0.08 \text{ \AA}^{-1}$ and above $0.5 \text{ \AA}^{-1}$. The intensity profile resulting from the subtraction of such a background from the measured data is shown as empty triangles in the figures. The so obtained data at 220 K present very well defined diffraction peaks nearly equally spaced. This is a common characteristic of lamellar-like structures. Actually, the line fitting the data in Figure 4 was obtained with a model consisting of a lamellar arrangement of thin layers, of $\approx 4 \text{ \AA}$ thickness, equally spaced from each other with an overall periodicity of $63 \text{ \AA}$. For these calculations we used the "scatter" software²³ available at <http://www.esrf.eu/UsersAndScience/Experiments/CRG/BM26/SaxsWaxs/DataAnalysis/Scatter>.

The lower temperature SAXS data (180 K) show the coexistence of the above described structure with a new one, without any detectable interference. As a prove, the background-free data at 220 K were subtracted from the background-free data at 180 K, which resulted in a rather simple pattern (filled inverted triangles in Figure 4b). As can be seen, the scattered intensity determined in this way presents minor peaks at $0.22 \text{ \AA}^{-1}$ and $0.26 \text{ \AA}^{-1}$, in addition to the main peak located at $0.13 \text{ \AA}^{-1}$. These scattering features can be well described (see solid line in Figure 4b) by an arrangement of hexagonally packed cylinders of $24 \text{ \AA}$ diameter with $55 \text{ \AA}$ lattice constant. According to the previous results, these cylindrical structures would not involve DMS and consequently they have to be formed by the aliphatic part of the molecules.

Figure 3: Wide angle X-ray diffraction patterns of o-DMS-DCOOH at two temperatures (solid blue: 180 K, dotted green: 220 K) as compared with that of PDMS melted (long-dashed orange) and crystallized (dashed red).

To find the impact of the structures developed in o-DMS-DCOOH on the mechanical properties, we conducted rheological experiments during a continuous heating at a rate of 2 K/min from 170 K. The results so obtained for the complex shear modulus, $G^* = G' + iG''$, evidence dramatic changes around 205 K (see Figure 5). At low temperatures the experimental data correspond to a viscoelastic rubber like material (G' , $G'' \sim 20$ kPa at 200 K) but G' drops in more than 5 orders of magnitude above 205 K and the material transforms in to a viscous liquid ($\eta \sim 50$ Pa $\cdot$ s at 220 K and $\eta \sim 6$ Pa $\cdot$ s at 240 K).

As a final part of this investigation we used BDS to prove molecular mobility as an additional tool for characterizing the different structural states of o-DMS-DCOOH. BDS experiments are sensitive to molecular motions involving dipolar entities.¹⁸ Note that there are two main distinct molecular dipoles in o-DMS-DCOOH, those associated to DMS monomeric units (the majority) and that related specifically with the carboxyl end-group, being the

Figure 4: SAXS patterns of o-DMS-DCOOH at 250 K (empty circles) and at lower temperatures (filled circles) (a) 220 K and (b) 180 K. The open triangles correspond to background free values obtained by subtracting an "isotropic liquid-like background" (see text). The inverted triangles in (b) were obtained by further subtracting the background free signal at 220 K from the background free data at 180 K. The lines correspond to the scattering profiles calculated with simple structural models (see text).

Figure 5: Temperature dependence of the complex shear modulus (G' : filled squares, G'' : empty circles) of o-DMS-DCOOH determined at 1 Hz. Vertical dashed arrows indicate the thermal transition temperatures.

contribution of the alkyl part to the orientational electric polarization negligible. Figure 6 shows the temperature dependence of the complex dielectric permittivity of o-DMS-DCOOH as determined at relatively low frequencies (1, 10 and 100 Hz) during heating at a rate of 1 K/min.

As can be seen in Figure 6, the most relevant dielectric features are detected in the low temperature range (below 205 K). In this range, the imaginary part shows the presence of two main relaxation peaks related with the molecular dynamics, the dominant one around 150 K attributed to the DMS segmental mobility (with characteristics close to those found in PDMS²⁴), and the other around 180 K most likely related with fluctuations involving the carboxyl end-group dipole moment. In addition, a rapid increase of the dielectric losses at the highest temperatures is detected, which is originated from the d.c. conductivity, σ , ($\epsilon''_{\sigma}(T, \omega) = \frac{\sigma(T)}{\epsilon_0 \omega}$).

Figure 6: Temperature dependence of the complex dielectric permittivity of o-DMS-DCOOH determined at three distinct frequencies. Inset shows the temperature dependence of the dc-conductivity. Vertical dashed arrows indicate the thermal transition temperatures.

The lower temperature relaxation phenomenon is also very apparent in the real part (Figure 6a) as a clear step in the temperature dependence of $\epsilon'(T)$, whereas the dispersion associated to the weaker relaxation at higher temperatures is barely detectable. However, a clear increase in the real part is detectable in $\epsilon'(T)$ at around 205 K. The fact that this increase occurs simultaneously for the three frequencies is a clear signature that it is related with a sudden change in the material dielectric properties (it has not a pure dynamical origin). On the contrary, no change can be detected in $\epsilon'(T)$ at around 230 K where the higher temperature transition occurs. Despite of that, when crossing this temperature range we found a change in the temperature dependence of the d.c. conductivity as determined from the loss data at very low frequencies (0.01-1 Hz). As can be seen in the inset of Figure 6a, the apparent activation energy ($\propto \frac{d[\ln\sigma(T)]}{d(1/T)}$) shows abrupt changes when crossing the two thermal transitions. Particularly, what is observed is an overall monotonous increase of the apparent activation energy on cooling, with a clear peak at around 235 K and another more

prominent peak at around 205 K (note the logarithm vertical scale).

The present dielectric results show that the molecular dipole fluctuations as well as the diffusion of ion impurities originating the conductivity in this type of materials both feel to some extent the structural developments occurring in o-DMS-DCOOH. In agreement with the DSC results, the changes in the higher temperature transition are tiny, but the lower temperature transition produces very evident effects on the BDS results. Interestingly, as can be seen in Figure 6, when measured at 100 Hz the relaxation related with the carboxyl end-group dipole actually presents significant losses at temperatures above 205 K. This means that it is possible analyzing the impact of the low temperature thermal transition on the carboxyl molecular motions by means of a detailed evaluation of this relaxation process over the broad frequency interval from 10^{-1} to 10^6 Hz. For this end, the frequency dependent dielectric losses measured isothermally in the range 170 to 250 K were fitted. These data are shown in Figure 7, where for clarity the d.c. conductivity contribution at low frequencies ($\epsilon''_{\sigma}(\omega)$) has been subtracted from the whole measured dielectric losses. In this isothermal representation the weak loss peak related to carboxyl dipole fluctuations is superimposed on the low-frequency tail of the most prominent dielectric relaxation related with the DMS segmental dynamics. Thus, to describe the data we used the sum of a Cole-Cole function (eq. 1 with $\beta=1$), to account for the relaxation loss peak, and a power law with a fixed exponent 0.28, to account for the high frequency increase due to DMS segmental relaxation. The lines in Figure 7 show that in this way the data are very well described. The resulting parameter values characterizing the carboxyl-related dielectric relaxation at different temperatures are plotted in Figure 8. This plot shows that the 3 parameters present a non-monotonous temperature variation when crossing the transition at around 205 K. Above the transition, the relaxation time follows an Arrhenius temperature dependence with an activation energy of about 37 kJ/mol (0.36 eV) and a pre-exponential factor of $1.6 \cdot 10^{-14}$ s, which is of the order of the reciprocal of a typical vibrational frequency. Also above 205 K, the α parameter is close to unity as would correspond to a purely exponential

(Debye-like) relaxation. Both results suggest a single jump between two equivalent energy minima as a suitable model for the carboxyl dipole fluctuations. In addition, in this high temperature range the relaxation strength diminishes rapidly as temperature increases. All these characteristics, observed above 230 K, i.e. before any thermal transition occurs, allow attributing this dielectric relaxation of o-DMS-DCOOH as originated from the fluctuations of the H-bonds among carboxyl units. This assignment is supported by the fact that a Debye-like relaxation shape and a rapidly decreasing relaxation strength are typically found for the slowest dielectric relaxation of simple mono-alcohols, a relaxation that is commonly attributed to the fluctuations of the H-bond network.²⁵

Figure 7: Frequency dependence of the conductivity-free dielectric losses of o-DMS-DCOOH in the temperature range where structural transitions take place. Lines correspond to fitting functions as described in the text.

Clear changes in the behavior of the 3 parameters occur below the transition range. The most dramatic one is a fast increase of the dielectric relaxation strength, the product $T\Delta\epsilon$ reaching a plateau-like behavior below 190 K. The value of $T\Delta\epsilon$ is a quantity directly related with both number-density and orientation-correlations of the molecular dipoles participating

in the relaxation process. So, the fast increase of $T\Delta\epsilon$ when crossing the transition temperature supports the idea that the structural arrangements occurring when cooling below 205 K reinforce the H-bond network. The reinforcement of the H-bond system could also explain the faster increase on decreasing temperature of the main relaxation time (the apparent activation energy is nearly double below the transition). Furthermore, this transition seems to provoke a rather heterogeneous dynamics as indicated by the decreasing trend of the shape parameter α , from values of nearly 1 above the transition to values as low as 0.6 at the lowest accessible temperature.

Figure 8: Temperature dependence of the parameters characterizing the dielectric relaxation of o-DMS-DCOOH associated to the H-bond fluctuations ($T\Delta\epsilon$: circles, α : squares, τ : triangles). Dashed lines represent Arrhenius-like description of the relaxation time. The dotted line correspond to the value of α for a Debye relaxation. Vertical dashed arrows indicate the thermal transition temperatures.

As afore commented, the most prominent dielectric relaxation of o-DMS-DCOOH is related to the DMS segmental dynamics, which also determines the glass transition detected by DSC. At low-middle frequencies this relaxation occurs at temperatures well below the two structural/thermal transitions. Nevertheless, the clear jump in the temperature behavior of

the real dielectric permittivity observed at around 205 K (see Fig. 6) suggests some effect of the lower temperature transition on the DMS segmental behavior. The DMS relaxation becomes too fast above 170 K to be well characterized in the frequency range below 1 MHz, where the dielectric experiments provide the best accuracy. Thus, new experiments at higher frequencies were required to analyze how the DMS dynamics behaves on crossing the transition around 205 K. Due to accuracy limitations of the dielectric loss measurements at high frequency, we have analyzed the high frequency data in the isochronal representation (as that used in Fig. 6).²⁶ From these data we have evaluated the temperature dependence of the DMS relaxation time by calculating the temperature T_{max} of the relative maximum of the corresponding $\epsilon''(T)$ curve for various frequencies. The results are shown in Figure 9. As can be seen in Figure 9, the data obtained below 205 K follow the typical non-Arrhenius temperature dependence characteristic of molecular motions in viscous liquids.²⁷⁻²⁹ However, the extrapolation of the so obtained behavior to temperatures above 205 K yields temperature/frequency values markedly lower/higher than those determined by the experiments at the highest frequencies. This would indicate that when cooling across the low temperature transition range the DMS segmental dynamics becomes accelerated. To exclude artifacts related with the used experimental approach we have performed similar experiments on the methylcarboxylatedecyl terminated dimehtylsiloxane oligomer (o-DMS-DCOOCH₃), where the single difference is that the carboxyl group is replaced by the methylcarboxylate one. This liquid material can be measured without any transformation down to 195 K (see Figure S2 in the Supporting Information). The results obtained on o-DMS-DCOOCH₃ are also included in Figure 9 (empty triangles). We found nearly indistinguishable loss peak temperatures than those in o-DMS-DCOOH above 205 K, but the DMS dynamics in o-DMS-DCOOH is about a factor of 2 faster than that in o-DMS-DCOOCH₃ below the transition range. These new experiments, showing a good agreement between the data of o-DMS-DCOOH and o-DMS-DCOOCH₃ above 205 K, also indicates that the higher temperature transition in o-DMS-DCOOH at around 230 K must have a negligible effect on the DMS dynamics,

since which, o-DMS-DCOOCH₃ does not suffer any transition when cooling from room temperature down to 195 K,

Figure 9: Relationship between frequency and peak temperature of the isochronal dielectric losses. Filled circles correspond to o-DMS-DCOOH and empty triangles to o-DMS-DCOOCH₃. Lines are guides to the eye obtained by using VFT like equations (see text). The horizontal arrow line marks the thermal transition temperature.

Discussion

The above results demonstrate that o-DMS-DCOOH self-assembles below room temperature giving rise to highly regular nano-structures without any significant long-range atomic order. The first transformation, from a disordered liquid to a nanostructured phase, manifests as a weak thermal transition accompanied by the emergence of clear diffraction peaks in the SAXS range. According to the FTIR results the carboxyl end-groups are the molecular entities directly involved in this transition. These characteristics clearly suggest that arrangements involving H-bond formation are responsible of the first emerging nanostructures. In fact, it

is well documented that dimers formed by intermolecular associations connecting the end acid groups exist in carboxylic acids.²¹ The strong FTIR absorption band corresponding to the C=O stretching observed at around 1715 cm^{-1} indicates that already at room temperature dimer association is also well established in o-DMS-DCOOH. This is confirmed when comparing the position of the C=O stretching absorption in o-DMS-DCOOH with that in o-DMS-DCOOCH₃, which occurs at a frequency much closer to that expected for a free C=O stretching vibrations ($\sim 1760\text{ cm}^{-1}$). Consequently, the origin of the first nanostructure detected below 230 K has to be related with association of the carboxyl group dimers arising by the double H-bonded carboxyl groups (R22(8) motifs), which are planar entities.³⁰ The planarity of the ring is essential for the optimal interaction between monomers to produce excellent R22(8) motifs with a large interaction energy of 20-26 kcal/mol. Calculations show that the formation of tetramers by direct interaction of dimers through additional carboxyl H-bonds is energetically preferred when compared with trimer formation.²¹ The setting up of new interactions would explain both the arising of a new C=O sub-band in the IR absorption and also the overall shift of the band towards lower frequencies. Moreover, these new H-bond interactions would introduce correlations in the orientation of the carboxyl dipole moments explaining the fast increase of the strength of the dielectric relaxation attributed to H-bond fluctuations below 230 K, which is very weak above 230 K and rapidly increases as the temperature decreases below 230 K, as can be seen in Figure 7.

Concerning structural characteristics, we note that the identified lamellae are formed by thin layers ($\sim 4\text{ Å}$ thick), a size that roughly matches with that of the carboxylic R22(8) motifs. The planar nature of these entities could promote stacking, which would be also favored by the self-association of the carboxylic acid dimers into tetramers.²¹ Taking these facts into account, a possible origin of the lamellae developed below 230 K could be connected with the self-assembly of the planar R22(8) entities. SAXS results show a lamellae long range periodicity of 6.3 nm, a value that is only slightly larger than twice the end-to-end distance of the molecule in a random coil conformation.

When considering the structures generated at lower temperatures, FTIR results showed that they involve the aliphatic part of o-DMS-DCOOH but not the DMS part. Moreover, the volume fraction corresponding to the identified cylinders is $\sim 18\%$, which is close to the non-DMS weight fraction in the o-DMS-DCOOH molecule. Despite that the transition occurs in a temperature range where PDMS usually crystallizes,²⁴ in the present case DMS crystallization is fully prevented, as confirmed by WAXS and FTIR, and further corroborated by BDS and DSC results. Moreover, the usual tendency of alkane strands to develop a crystalline-like long range atomic order is not clearly found here. Thus, it seems that a well developed long-range atomic ordering becomes impeded by the preexisting structures. This is further confirmed when comparing the results for o-DMS-DCOOH with those found for o-DMS-DCOOCH₃. o-DMS-DCOOCH₃ shows no transitions above 190K, but below this temperature there are clear signatures of crystallization involving separately both DMS and aliphatic parts as deduced from the presence of sharp diffraction peaks in the WAXS experiments (see Figure S3 in the Supporting Information). Therefore, the first structures arising below 230 K in o-DMS-DCOOH have a strong impact on the lower temperature behavior. Particularly, below 205 K SAXS results clearly evidence the emergence of a nanoscopic long-range order but without noticeably altering the preexisting one. FTIR results show that this nanostructure must involve the aliphatic part of the oligomer and not the DMS one. On the other hand, the peak of the heat capacity around 205 K (see Figure 1b) resembles the behavior expected around an isotropic-nematic transition.¹² This suggests that the alkane part of the molecules could develop nematic-like orientational correlations, likely forming bundles, instead of developing the usual long-range atomic order. The presence of hexagonally packed regular arrangements of cylinders would be responsible of the rubber like mechanical behavior of the oligomer observed below 205 K, i.e. at temperatures far above the glass transition temperature.

After this part of the discussion, it becomes clear that finding the precise molecular picture of the structures generated in o-DMS-DCOOH below 230 K would require intensive

molecular modeling, which is beyond the scope of the present work. However, the structures above proposed would also explain the behavior of the DMS part of the oligomer, which according to FTIR and X-ray diffraction results does not participate in the self-assembly events arising in *o*-DMS-DCOOH below 230 K. Dielectric results show that the high temperature transition has no effect on the dielectric permittivity (largely determined by the DMS dipole moments), neither on the DMS segmental dynamics, since *o*-DMS-DCOOH and *o*-DMS-DCOOCH₃ show nearly indistinguishable relaxation times. Nevertheless, a minor effect of the high temperature transition on the sample conductivity was found in the dielectric experiments, which can be explained by the interference of the lamella structures with the diffusion of the ionic impurities. Contrarily, at temperatures below 205 K both the low frequency permittivity and the rate of segmental DMS dynamics are found to clearly change. Both changes can be accounted for by the above proposed self-assembly involving the aliphatic part. On one hand, the DMS segregation would be promoted below the transition yielding a faster dynamics of DMS segments, as confirmed by the comparison of the dielectric results in *o*-DMS-DCOOH with those in *o*-DMS-DCOOCH₃ (thermal fluctuations prevents significant DMS segregation in this oligomer). Moreover, the rigid alkane structures would restrict the re-orientation ability of dipole moments from DMS segments in the neighborhood (mainly those tethered to the alkane part), which would account for the sudden change of the static (low frequency) dielectric permittivity observed at 205 K. Moreover, the anchoring effect would also explain the significant contributions of the DMS dynamics at relatively low frequencies, which are larger than those found in fully amorphous PDMS. This result is similar to that found in well segregated block PDMS copolymers with a rigid block, i.e. a situation where PDMS remained mobile whereas the other block segments were frozen.^{20,31,32} (see for example BDS data at 170 K in Figure 7 compared with Figure 4 in ref³¹). Interestingly, also in some of these block copolymers DMS crystallization is inhibited, a fact attributed to presence of a relatively rigid nanostructure.

Conclusions

By combining thermal, structural, spectroscopic and dynamic characterization techniques over a broad temperature range, in this work we have shown that a monocarboxydecylterminated dimethyl oligomer self-assembles in sub-10nm well ordered nanostructures. Below 230 K lamella-like structures made of thin layers about 4 Å thick and 63 Å periodicity are developed. We identify the H-bonding between carboxyl groups dimers as first responsible of this sub-nanometer structures. Furthermore, below 205 K a new nanostructure is developed. This new nanostructure, that do not alter the structural characteristics of the preexisting one, can be well described by a regular arrangement of hexagonally packed cylindrical objects of 21 Å diameter with a 55 Å lattice constant. Our results suggest that the cylinders are perpendicular to the lamella plane and consist of elongated orientationally-ordered aliphatic entities. Also likely because the presence of these mesostructures, DMS becomes segregated and its crystallization results completely inhibited. Once the two nanostructures are developed the oligomeric material presents a rubber-like behavior down to the glass transition temperature. Interestingly, the glass-transition event in the oligomer containing about 20 wt% aliphatic part occurs at about 150 K, a temperature similar to that of fully amorphous high molecular mass PDMS.

Summarizing, the presence of functional (carboxyl) end-groups in the oligomer has an utmost important effect on its properties below room temperature giving rise to small size regular nanostructures and simultaneously preventing the development of long-range atomic order.

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Supporting Information Available

The following files are available free of charge.

- Supporting Information: FT-IR, DSC and WAXS results on o-DMSCOOCH₃.

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