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Rheology of Phenylpropylsilsesquioxane in the Fiber-Spinning Regime

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ABSTRACT: A potential ceramic precursor, phenylpropylsilsesquioxane (Petpps) has been studied under conditions where fibers are typically spun. The rheology of the polymer in this regime is studied by using dynamic mechanical analysis, as well as step shear, step strain, and steady shear. The polymer exhibited an unusual elasticity dependence on temperature. It is shown that the changes in elasticity are caused by changes in the morphology of the melt.

Introduction

Phenylpropylsilsesquioxane, one of the polymeric precursors for SiC fibers, exhibits unusual rheological activity which is driven by its microstructure. It is these fundamental structure to property relationships that this paper attempts to elucidate. It will be shown that reversible changes in microstructure account for the reversible changes in rheological elasticity. The relationships between microstructure and rheology are of general interest, although the material is specifically targeted as a silicon carbide precursor. Therefore, at this point a brief review of ceramic precursors is relevant.

Silicon carbide fibers maintain good mechanical properties at a very high temperature,[1] and the high thermal conductivity and low coefficient of thermal expansion allow for impressive thermal shock resistance. They also have a high modulus and show exceptional chemical resistance due to the formation of an oxide layer on the surface.[2,3] Fiber formation using conventional SiC processing involving powder sintering is perhaps only possible with appropriate binders and laser heating, and production involving chemical vapor deposition (CVD) onto a carbon core is expensive, time consuming, and difficult. CVD fibers are also limited to large diameters, approximately 100 μm, which are unsuitable for forming complex shapes.[4]

In recent years, ceramic materials have been produced from the thermal decomposition of some organometallic polymers. Yajima et al. were the first to report the production of continuous SiC fibers from an organometallic polymer.[5] They started with a dimethyldichlorosilane and dechlorinated with lithium. The resulting polymer was spun into a fiber and then heat treated in a vacuum to a primarily amorphous SiC fiber with small domains of β-SiC.

Another class of materials that may form SiC are polysiloxanes. Silicon alkoxides have long been used as precursors for silicates; however, an alkyl group may be bonded to the silicon, and it is possible to obtain a suitable silicon to carbon ratio for the formation of SiC. The gelling process for these materials involves the hydrolysis of the alkoxy groups and the subsequent condensation polymerization. Frequently, trialkoxysilanes are used because they can cross-link and avoid vaporization during subsequent heat treatments. Since these polymers have an idealized formula $(RSiO_{1.5})_n$, they are therefore termed silsesquioxanes. The precursor melt flows around 100 °C, depending slightly on the R group. Also around this temperature the –OH groups begin to condense. Fibers may be formed at this stage.[6] Exposure to UV results in cross-linking, and exposure to temperatures above 200 °C allows the core to undergo cross-linking. Upon pyrolysis, an intimate mixture of free carbon, silicon carbide, and silicon oxycarbide is formed.[7–9] Generally, the use of polymeric precursors allows tailoring of the structure to take advantage of low-temperature processing and still obtain high char yield ceramics.

Sol–gel processing of these polymeric precursors has recently become an area of increased interest due to its inherent advantages over conventional processing techniques.[10] It allows mixing on the molecular level, low-temperature processing, convenient shaping, and high purity. The term sol usually refers to a colloidal suspension of solid particles. However, the ceramic community has expanded sol–gel to a broader category, which includes low molecular weight organometallic alkoxide precursors.

The rheology of sols and its relation to fiber drawing has been studied to some extent by Sakka et al.[11] They report spinnability from Newtonian organometallic alkoxides in the viscosity range of 1–10 Pa·s (10–100 P). Also shown are examples of structural viscosity, thixotropy, which are unable to be drawn into fibers even in the prescribed viscosity range. They therefore concluded that linear molecules were preferred since they would be the least likely to form some type of structure that could cause non-Newtonian behavior.

The purpose of this project is to study the rheology of a polymeric hydrolyzate of a trifunctional silane, which is a potential ceramic precursor, and to relate this information to fiber spinnability. The focus of this study is on the relationships between morphology and rheological behavior of the polysiloxane material up to its gel point. Phenylpropylsilsesquioxane (Petpps) was chosen because it was commercially available and showed good fiber-spinning properties, as well as being a potential precursor to SiC and silicon oxycarbide ceramic fibers. Therefore, the rheology of this material at various temperatures is of keen interest to a study of the spinnability of the polymer precursors. The kinetics of the condensation reaction, that is, the irreversible changes that occur primarily through the formation of covalent bonds, has been studied in a previous paper.[12] This paper will focus on reversible rheological changes that Petpps undergoes as a function of temperature under a complement of experimental testing conditions.

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Experimental Section

The phenylpropylsilsesquioxane was purchased from Petrarch Systems, Inc., and was used as received. The material was a co-oligomer formed by hydrolyzing phenyltrichlorosilane ($PhSiCl_3$) and propyltrichlorosilane ($CH_3CH_2CH_2SiCl_3$) and then allowing them to undergo a condensation reaction, forming a siloxane backbone oligomer. Poly(dimethylsiloxane) (trimethylsiloxy terminated), PDMS, nominally having a viscosity of 1 Pa·s (10 P) and 1,3,5-trimethyl-1,3,5-triphenylcyclotrisiloxane also were purchased from Petrarch Systems, Inc., and were used as received.

The rheological study was done by using a dynamic mechanical spectrometer, a Rheometrics RMS-800, equipped with a 2000 g·cm force rebalance transducer. The dynamic experiments were performed with an oscillatory shear rate of 1 Hz, in a parallel-plate geometry with strains between 10 and 30%. The plates had a 50-mm diameter, and the gap used was typically between 1 and 1.5 mm. The steady shear thixotropic loops were done by using the same instrument with a cone and plate geometry. The plate was 50 mm in diameter, and the cone angle was 0.039 rad. Shear rates were varied between 0.1 and 10 s^{-1} over a period of 2 min. The transient stress overshoot experiments again made use of the cone and plate geometry. Here, a steady shear of 10 s^{-1} was imposed at time zero, and the stress was monitored as a function of time. Stress relaxation measurements were made by using the 50-mm parallel-plate geometry. At time zero a step strain was introduced, and the stress decay was monitored as a function of time.

Samples in powder form were placed on the lower plate and allowed to flow at the desired temperature for typically 15 min. Following this equilibration procedure, the upper plate or cone was lowered to the desired height. Excess sample was removed, and the fixture was again allowed to equilibrate for another 10 min at the desired temperature. On the basis of a previous paper,[12] very little condensation occurs in the bulk during this time period. The desired rheological test was then performed.

X-ray diffraction measurements were performed on both a Phillips diffractometer and a Rigaku Θ–Θ diffractometer equipped with a high-temperature attachment. Both powder and melt samples were measured.

Gel permeation chromatography (GPC) was used to help elucidate the nature of the phase-separated material observed in the Petpps. The GPC samples were prepared at concentrations of 5 mg/mL in tetrahydrofuran (THF) and filtered through a 0.45-μm Teflon filter, and then 0.1 mL was injected. A flow rate of 1 mL/min was maintained by using non-UV-stabilized HPLC-grade THF as the eluent. Separation was achieved by using Ultrastyragel with 50-, 100-, and 1000-nm pore size columns. The columns were calibrated based on polystyrene standards. A refractive index detector (Waters 410) and an ultraviolet detector (Waters 484) were employed.

Results and Discussion

From the rheological point of view, fiber-forming melts can be grouped into one of three categories:[13] (i) inorganic materials (glasses, metals), (ii) linear polycondensates (polyesters, polyamides) with rather low molecular weights (MW = 10 000–30 000), and (iii) linear polyolefins and vinyl polymers, (polyethylene, polypropylene, polyvinylidene chloride) with high molecular weights (MW = 50 000–1 000 000). It was determined in a previous paper[12] that the Petpps was comprised of primarily 16 repeat unit oligomers, corresponding to a molecular weight of approximately 2200. Therefore, melt spinning of this material is essentially spinning of a glass. Fibers may be drawn from the melt by immersing a glass rod and then withdrawing it. On the basis of these data, it was determined empirically that fibers may be formed from Petpps between 100 and 140 °C. This data may be somewhat subjective; however, it does provide a reasonable estimate of the temperature range available for fiber spinning.

In order to study quantitatively the properties of the melt during fiber spinning, thixotropic loops were performed over the temperature range of interest, as shown in Figure 1. It can be seen that the spinnable range corresponds to a viscosity range between 5 and 100 Pa·s. The loops in this range are very linear, indicating Newtonian behavior in the shear rate range of 0.1–10 s^{-1}. This information corresponds reasonably well with the data of Sakka et al.[14,15] They found that spinnability was observed in tetrafunctional alkoxides for a viscosity range between 1 and 10 Pa·s. They also concluded that Newtonian behavior at high viscosity was an additional spinning requirement.

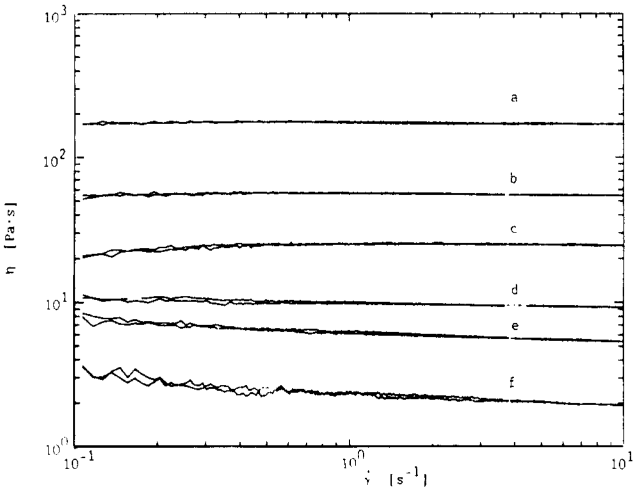

Figure 1. Thixotropic loop of Petpps at 100 (a), 110 (b), 120 (c), 130 (d), 140 (e), and 150 °C (f).

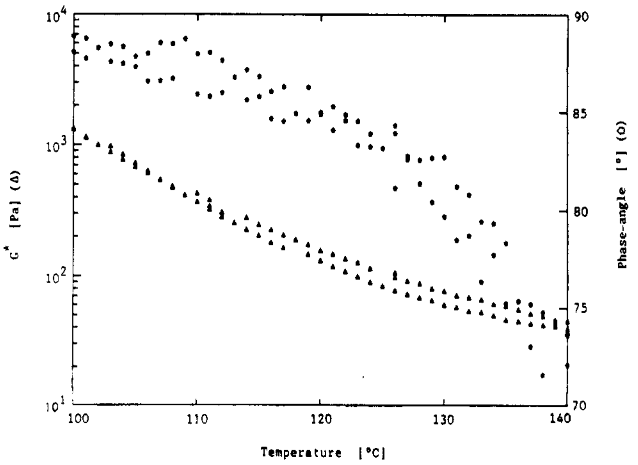

Figure 2. Dynamic analysis of Petpps between 100 and 140 °C showing G^* and phase angle.

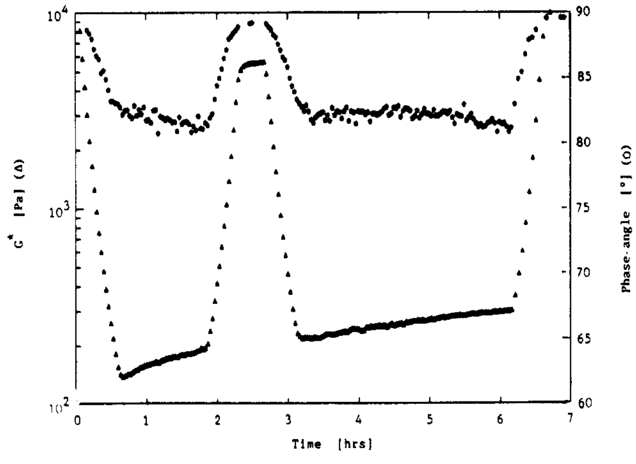

Figure 3. Dynamic analysis of Petpps heating and cooling between 100 and 125 °C showing G^* and phase angle.

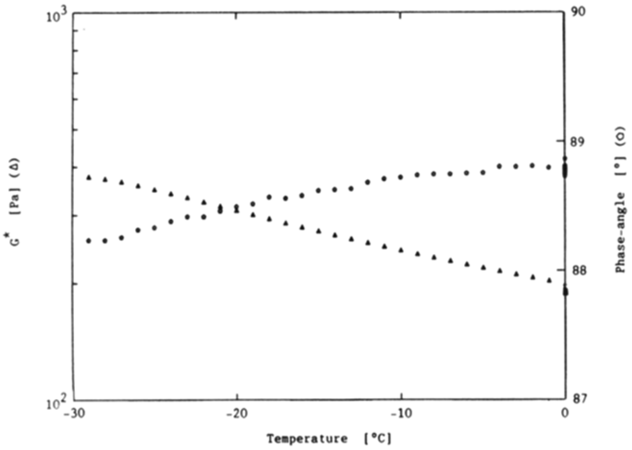

Figure 4. Dynamic analysis of PDMS between −30 and 0 °C showing G^* and phase angle.

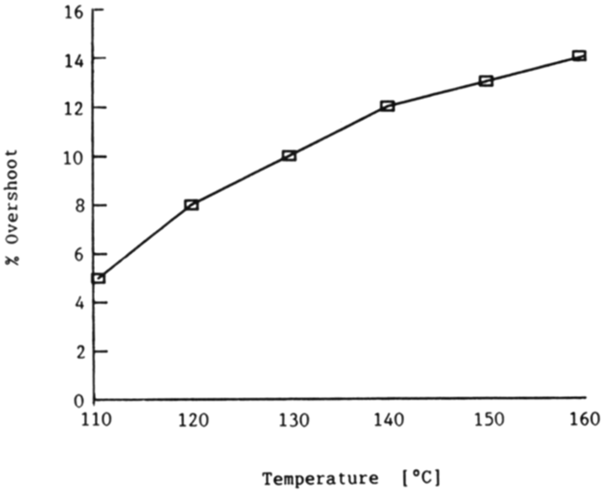

Figure 5. Petpps percent stress overshoot between 100 and 160 °C.

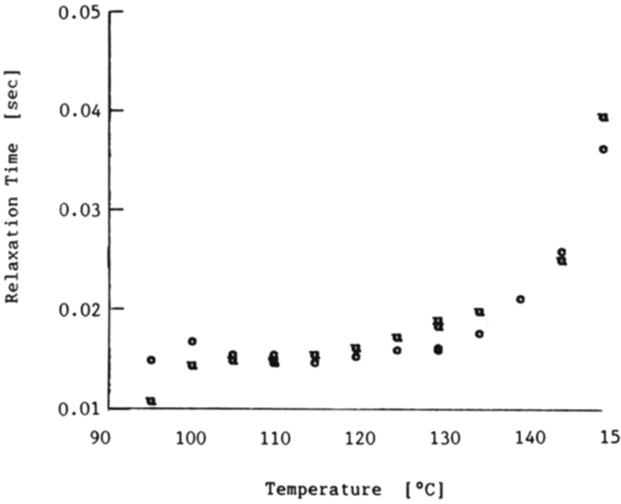

Figure 6. Petpps characteristic relaxation times: u, heating; c, cooling.

Figure 7. Photograph at nominally 95× showing the Petpps as received.

A dynamic measurement was performed over the temperature range of interest using parallel-plate geometry. The temperature was increased from 100 to 140 °C and then decreased back to 100 °C. The rate of temperature change was 1 °C/min. Changes in modulus and phase angle with temperature are shown in Figure 2. One can see that as the temperature is increased the modulus drops, as expected, but most unexpected is the drop in phase angle, indicating increased elasticity. One should note that this is completely reversible, as seen by comparing the heating and cooling curves. This is supported by the thixotropic loop observations, which also suggest increased elasticity at higher temperatures because of shear thinning behavior.

This unusual behavior is seen more clearly in a similar experiment where the temperature is raised from 90 to 125 °C, then cooled back to 100 °C, and again raised to 125 °C. The results of this experiment are shown in Figure 3. Here the data are plotted as a function of time. As the temperature is raised at the beginning one can see the rapid fall in modulus, accompanied by a fall in phase angle, indicating more elastic behavior. When the temperature is held at 125 °C, one can see the slow increase in modulus and the expected slow decrease in phage angle due to reaction. When the temperature is again dropped to 100 °C, both the modulus and the phase angle increase. When the temperature is increased back to 125 °C, both the modulus and the phase angle again fall. This shows very clearly the full reversibility of this phenomenon under the same conditions where one can observe normal reaction behavior in both modulus and phase angle. An ordinary material that is not undergoing a reaction and does show signs of elasticity should show opposite tendencies in the modulus and phase angle. This type of ordinary behavior is shown for PDMS in Figure 4. The PDMS was heated at 1 °C/min from −30 to 0 °C. Note that the modulus is in the same range as that measured for the Petpps; therefore, the instrument conditions are similar, which excludes the possibility of a machine artifact. One can see for PDMS that, as the modulus decreases, the phase angle

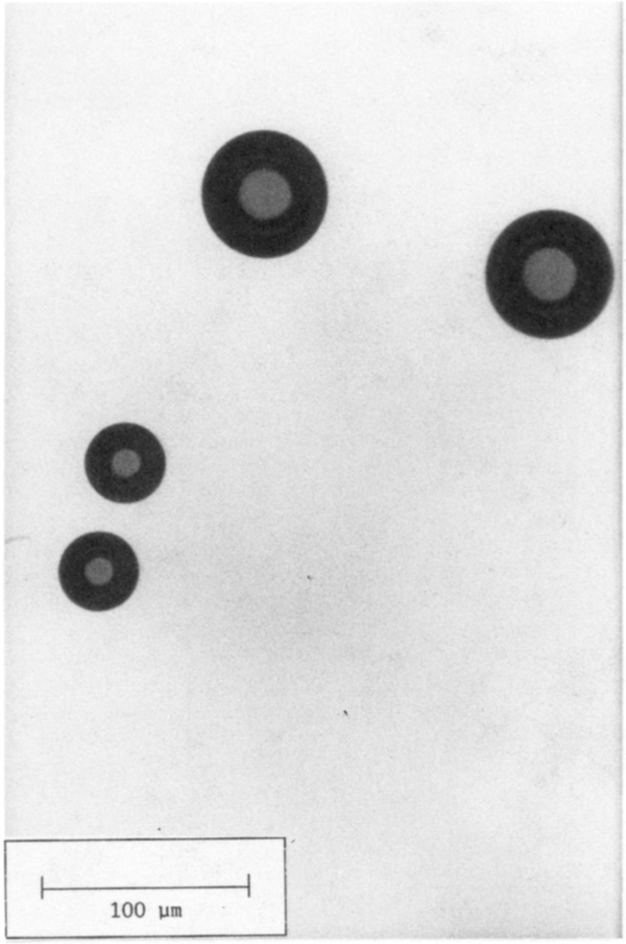

Figure 8. Photograph at nominally 95× showing the Petpps slightly beyond the melt temperature (taken at 90 °C).

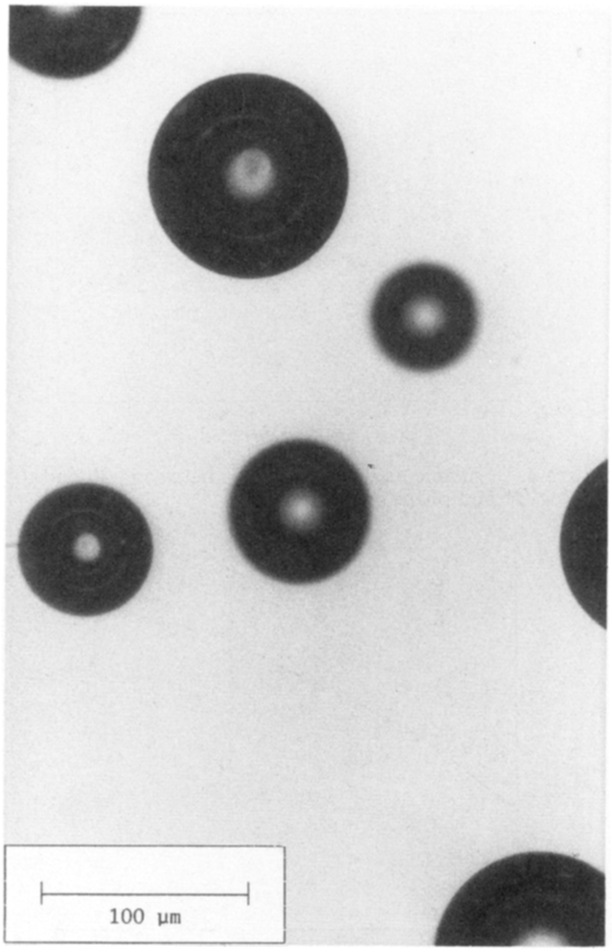

Figure 9. Photograph at nominally 95× showing the Petpps at 120 °C.

increases, indicating reduced elasticity, and then levels off. This is an example of ordinary behavior and is opposite of that observed for the Petpps. Petpps and PDMS are both silicon based, having siloxane bonds, yet they behave contradictorily. Petpps is trifunctional, but the unusual rheological behavior is not due to silanol condensation reaction; rather it is some sort of reversible, physical phenomenon. The other main difference is the presence of phenyl rings in the Petpps. The rheological behavior of another silicon compound, 1,3,5-trimethyl-1,3,5-triphenylcyclotrisiloxane, was measured between 0 and 25 °C. This cyclic siloxane also behaves as an ordinary material; that is, as the modulus falls, the phase angle increases.

Both the thixotropic loops and the dynamic analysis probe steady-state viscoelastic structure. Further insight may be gained by looking at transient measurements, such as "stress-overshoot" measurements. These measurements are somewhat contested; yet they have a long history in the literature.[16-25] The exact mechanism is not known; however, it is generally accepted that the yield stress obtained, the overshoot, is due to the break up of structure or association, the exact nature of which is sample dependent. These curves are often used when dealing with filled systems such as suspensions or foams. A Newtonian material should not show any stress overshoot. At room temperature, PDMS is virtually Newtonian, and there is no noticeable stress overshoot. This indicates that the instrument is functioning properly. The step shear rate experiment was performed for the Petpps between 110 and 160 °C at 10 s^{-1}. A stress overshoot is clearly evident, and the peak can be normalized by the steady-state stress to obtain a percent stress overshoot, as shown in Figure 5; here, one can see the increase of the relative stress overshoot as the temperature increases. Again, this is counterintuitive and indicates that the effects of structure are increasing as the temperature is increased. This again supports the behavior observed both by dynamic analysis and from steady shear thixotropic loops.

Another transient measurement that can be used to probe structure is stress relaxation. Here a step strain is introduced and the stress decay is monitored. The characteristic relaxation times, the time taken to drop to $1/e$ of the peak value, as a function of temperature, both in heating from 95 to 150 °C and in cooling back down are shown in Figure 6. Here it can be seen that as the temperature increases the relaxation time increases and that this is a completely reversible phenomenon. There is some subjectivity in defining a characteristic response time; however, the same method was used for all relaxation curves so they could be compared directly. It should be noted that the response times range from 0.01 to around 0.05 s. This is a very rapid relaxation, typical of near-Newtonian fluid. These measurements also support the observation of increased elasticity at higher temperatures, since an increase in elasticity should increase the relaxation time. This experiment also supports the reversible nature of the elasticity change.

These rheological experiments show an unexpected trend, that is, a reversible increase in relative elasticity as the temperature is increased. There is also rheological evidence for some type of transition around 130 °C, for which higher temperatures exhibit the same trends but become much more pronounced. The different rheolog-

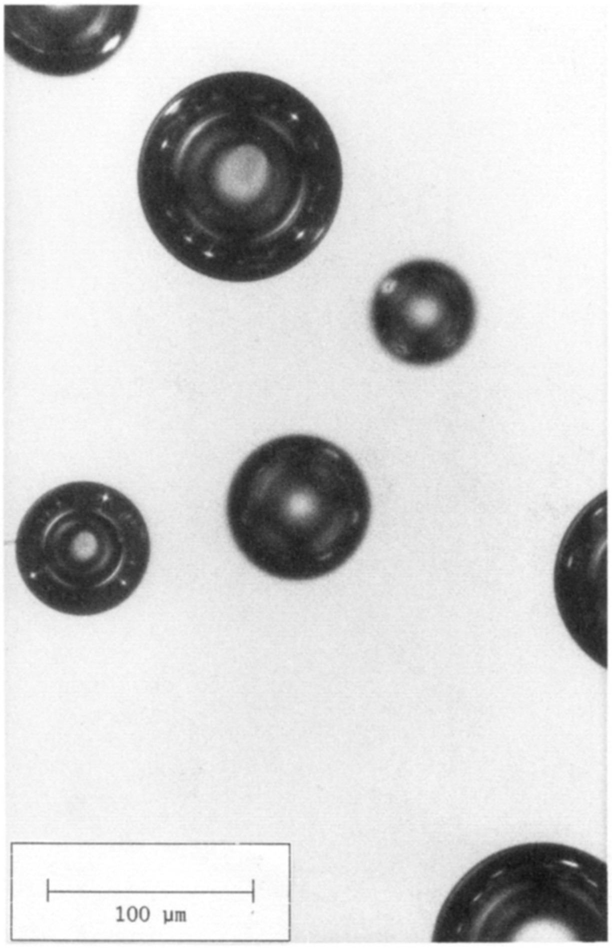

Figure 10. Photograph at nominally 95× showing the Petpps at 120 °C viewed with cross-polarized light.

ical experiments each challenge different aspects of the rheometer capability, and in concert they illuminate behavior typical of the material. The thixotropic loop has limitations in shear rate range due to transducer sensitivity. The dynamic experiments require very accurate phase-angle determination. The stress overshoot measurements require very precise motor control, and the stress relaxation measurements require very fast transducer response times.

Light microscopy, in conjunction with a hot stage, can help elucidate the morphology of the material. A photograph of the as-received starting material at 95× is shown in Figure 7. There is evidence for small crystals in a primarily amorphous bulk. As the temperature is raised, melting behavior is observed around 80 °C. At this point the crystallites form small phase-separated spherical regions as shown in Figure 8. As the temperature is further increased, these phase-separated regions grow in size. For example Figure 9 shows the typical morphology seen at 120 °C. These regions continue to grow in size and begin to contact each other above 130 °C. With microscopy, one can also see that the size decreases if the samples are cooled. There are some differences between what is seen on a microscope slide and in the bulk due to the cover slide in microscopy, which limits film thicknesses to about 0.1 mm. This difference can be observed by taking note of the number of focal planes. At first there are two distinct focal planes, which are reduced to a single plane above 125 °C. This means that the two layers are crowded into one. By looking at dimensions of the sphere at this point, one can get an approximate measure of the gap between slide cover and slide. Above this point, it can no longer be assumed that the regions remain spherical. By looking at these phase-separated regions while in the melt state with cross-polarized light, it is clearly evident that there is some degree of order, as shown in Figure 10. If the sample is cooled back to room temperature where it is a solid, the morphology remains basically the same as that in the melt state, as shown in Figure 11.

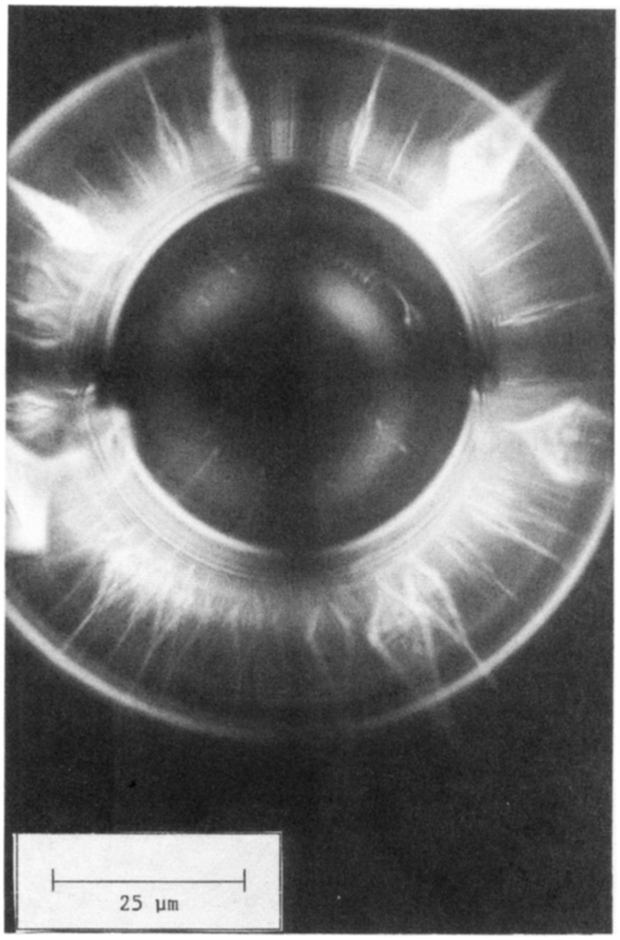

Figure 11. Photograph at nominally 300× showing the Petpps cooled from 120 °C to room temperature viewed with cross-polarized light.

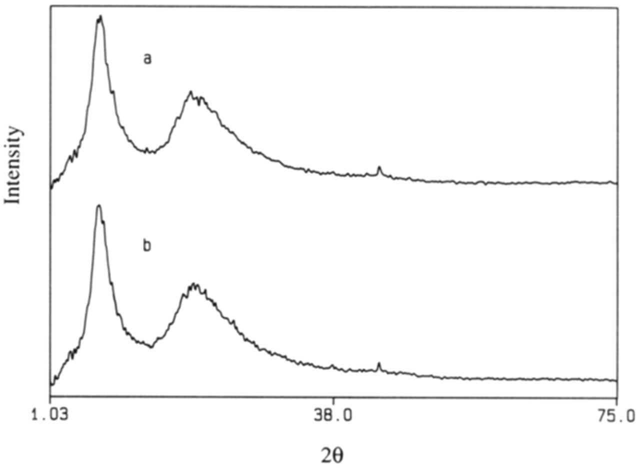

Figure 12. X-ray diffraction of neat Petpps (a) and Petpps heated to 130 °C and then cooled to room temperature in the sample holder (b).

Even though microscopy shows a different morphology for the cooled material as compared to the starting material, the X-ray information is the same for the two bulk samples, as shown in Figure 12. This suggests that the degree of order is approximately the same. By use of a heated stage,

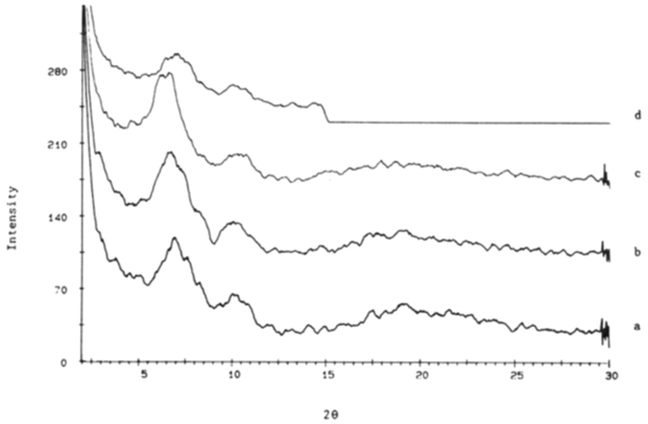

Figure 13. X-ray diffraction of Petpps at 25 (a), 100 (b), and 150 °C (c) and cooled back to 25 °C from 150 °C (d).

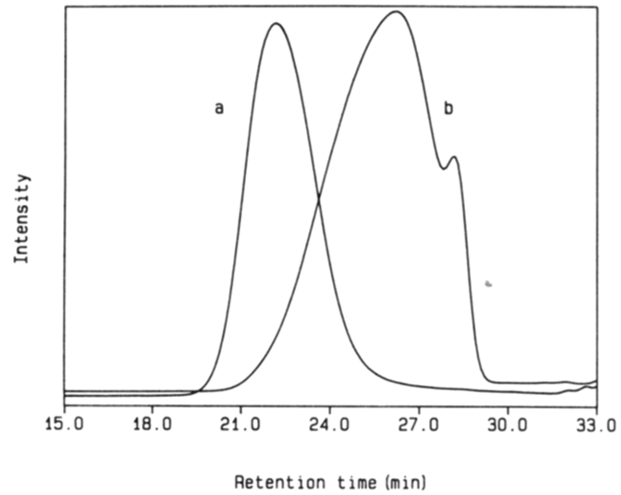

Figure 14. GPC of gel-separated (a) and neat (b) Petpps.

it was possible to collect X-ray information while the material was in the melt state. Figure 13 shows the X-ray information for the neat material which was then heated to 100, 120, and 150 °C; finally the sample was cooled back to room temperature. Here, it is possible to see that as the material melts the diffraction peaks intensify and shift to slightly lower angle, indicating increased order. It is satisfying the observe that when the sample is cooled, the X-ray intensity is quite similar to the starting material; however, the peak has shifted to slightly lower angle. This means that, for the thin film examined, while mostly reversible, complete recovery under these conditions was not possible.

Qualitatively, the microscopy and X-ray information both support and explain the rheological behavior. As the ordered, phase-separated regions expand with increasing temperature, their likelihood of interaction increases, so the relative elasticity increases. However, these regions are held within an amorphous bulk whose viscosity shows a normal temperature dependence, so the overall modulus (or viscosity) decreaseas as temperature is increased. The transition seen in all of the rheological experiments around 130 °C corresponds to that where the phase-separated regions begin touching. Of course the thickness of the rheological samples was at least 10 times greater than that in the microscopy, but the relatively close agreement in the transition temperature suggests that the behavior is not substantially different. Certainly, the mechanism causing the trend of increased elasticity is elucidated. The reversible nature of the size of these spheres and the large range that they span would suggest that the center is filled with a gas, either air or water vapor. The average diameter of the phase-separated regions, as found by microscopy, increases by almost 1 order of magnitude with a 50 °C increase. As the size of the regions in Petpps increased, the thickness of the outer ring decreased, thereby constraining the freedom of molecular packing. This constraint would explain the increased order seen by X-ray in the melt state.

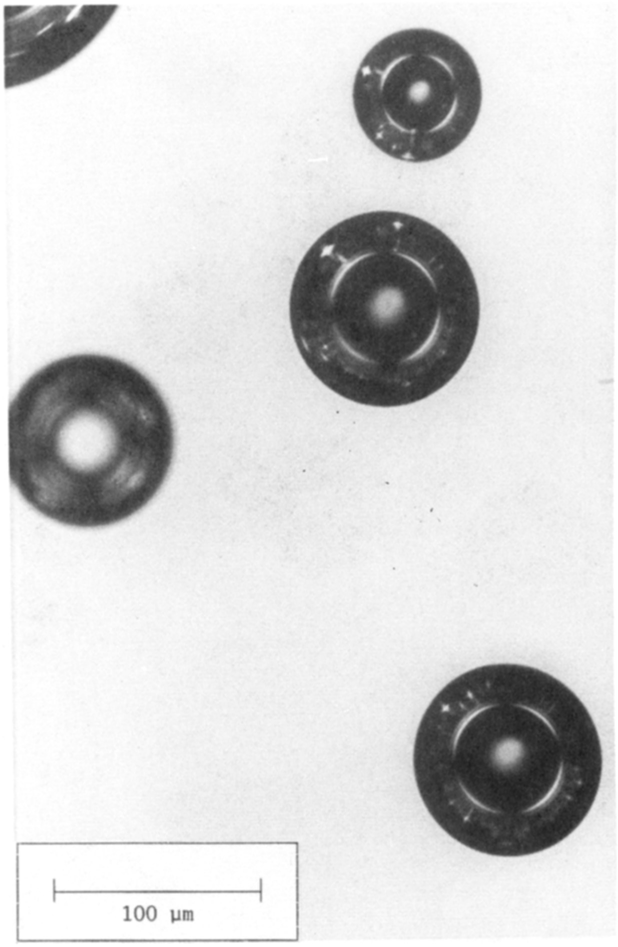

Figure 15. Photograph at nominally 95× showing the silylated Petpps viewed with cross-polarized light at 50 °C.

Both microscopy and X-ray showed that the phase-separated material possessed a degree of order in the melt state. The size of the spheres is on the order of 50 μm; therefore, the two most likely explanations are a type of vesicle formation or liquid crystallinity. As for the cause, it could be due to a particular molecular weight component, arise from the hydrophobic effect,[26] be a result of the incompatibility of the phenyl and propyl constituents, or be due to specific chain configurations.

The Petpps is quite soluble in acetone; when a nonsolvent such as *n*-hexane was added, it was possible to emulsify some of the components that could then be separated by centrifugation. When this type of separation is done twice, it was possible to obtain a relatively narrow molecular weight distribution, which did not contain significant concentrations of the molecular weights found in the starting material, as shown in Figure 14. This material still showed similar phase-separated structures under microscopy, although the melting point was elevated. Therefore, it seems that particular molecular weight components are not responsible for the structures.

The hydrophobic effect, on a cursory inspection, would seem a likely candidate due to the amphiphilic nature of the molecules, but the separation between hydrophobic and hydrophilic ends is unusually small, just a silicon atom. In addition, the silylated Petpps, described previously, also exhibited similar structures without any hydrophilic groups present, as shown in Figure 15. Therefore, it seems that either incompatibility of the phenyl and propyl substituents or specific chain configurations is the cause for the observed behavior. A requirement for the incompatibility mechanism is that the constituents be able to phase separate. The results from the HPLC done in a previous paper[12] support this mechanism because it suggests that a significant portion of the phenyl and propyl constituents are only a physical mixture and are not covalently bonded. However, it has also been observed that pure phenylsilsesquioxanes and pure methylsilsesquioxanes also show similar phase-separated domains, although to a lesser extent.[27] This tends to support that specific chain configurations are causing these domains. It is very difficult to test this hypothesis directly. Component incompatibility may promote certain chain configurations, such as a ladder conformation; so it is not contradictory that one observes an increase in these phase-separated domains in a mostly incompatible blend. The exact nature of these regions is elusive and will be the subject of future research.

Conclusions

There is interest in Petpps as a precursor to ceramic fiber. The material was determined to be Newtonian at high viscosity, which had been reported as a requirement for spinnability. The specific viscosity range for spinning was determined to be between 5 and 100 Pa·s. The material also showed shear thinning behavior at higher temperatures. This was most unexpected as it suggested an increase in structure, or at least the effects of structure, at elevated temperatures. It was determined that this phenomenon was reversible. These qualitative statements were reinforced by dynamic measurements, stress-overshoot measurements, and stress relaxation measurements. All four rheological techniques supported an increase in elasticity at increased temperature, which was reversible if the temperature was again lowered. The origin of this behavior is due to phase-separated regions, which expand, reversibly, upon heating. Domain expansion increases the likelihood of interaction, thereby increasing the relative elasticity while allowing the overall modulus to decrease. The driving force behind this phase-separated region is most likely packing considerations for specific chain configurations, although incompatibility between the phenyl and propyl constituents is also likely to have some effect. It was postulated that the expansion of these ordered regions was driven by vapor expansion from the center.

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