The Preparation and Characterization of New Polyether Ketone-Tetraethylorthosilicate Hybrid Glasses by the Sol-Gel Method

JOHN LEE W. NOELL, GARTH L. WILKES, DILLIP K. MOHANTY,* and JAMES E. McGRATH, *Departments of Chemical Engineering and Chemistry, Polymer Materials and Interfaces Laboratory, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061-6496*

Synopsis

In recent years, tetraethyl orthosilicate (TEOS) has been used as a precursor in preparing inorganic glasses. The technique, known as the sol-gel process involves a two step poly(hydrolysis-condensation) reaction sequence. The work presented here is concerned with the utilization of a suitably functionalized oligomeric "glassy" organic polymeric component in this two step sequence. In particular, an amine terminated amorphous poly(arylene ether) ketone, (PEK), end capped with isocyanatopropyl triethoxy silane was used to synthesize a hybrid network with TEOS. Low incorporation of the PEK oligomers into the network caused by early vitrification can be eliminated by carrying out reactions at elevated temperatures. A systematic change in mechanical and physical properties of the hybrid glass has been found with TEOS content and the annealing temperatures. A model for the network has been proposed based on structural and morphological evidence.

INTRODUCTION

In general, the worlds of ceramic and polymer science have grown and developed independently from one another with little overlap between the two areas. Generally, the field of ceramics concerns itself with the preparation of inorganic matrix glass materials through a sintering or firing process while the area of polymers relates to the synthesis, characterization, and processing of linear, nonlinear, and network forming organic high molecular weight molecules. Products of both areas have similar and dissimilar features, but on the whole, ceramic materials strongly differ in chemistry and mechanical properties from that of organic polymers. Even though this fact remains evident, advancing science and technology has sought to combine the beneficial physical properties of polymeric and ceramic systems to invent a new class of materials for futuristic applications. Thus, by incorporating the hardness of an inorganic glass and the higher extensibility of a polymer into one material, the resulting hybrid inorganic-organic network may display a number of the beneficial properties of both sciences. For instance, a polymeric glass might be prepared that has good impact resistance, a characteristic of certain polymers, and the transparency and scratch resistance approaching that of an inorganic glass. Materials of this nature could be much lighter and stronger than the traditional silicate

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* Present Address: Department of Chemistry, Michigan Polymer Consortium, Central Michigan University, Mt. Pleasant, MI 48859.

bulk glasses which could be very important in the future of the coatings industry as just one example.

The major short coming of this idea is that to produce an inorganic glass with structural integrity, a high temperature sintering process (i.e., $\sim 1200°C$) is generally required. Temperatures of this magnitude would, realistically degrade any organic component in a hybrid glass, and consequently would rule out any hopes of developing an inorganic-organic network material. However, one new area of research, which was spawned in the ceramics field, has emerged as a viable technique for developing these hybrid systems. This relatively new method has been termed the sol-gel process, and its name refers to the evolution of a network glass from solution.

The general reaction mechanism is a two step poly(hydrolysis-condensation) process in which first a metal (M) or silicon alkoxide, $(M(OR)_4$ e.g., $Si(OR)_4)$, is hydrolyzed to form a $\equiv M-OH$ functionality that can subsequently condense in the second step to form a metal oxide network site $(\equiv M-O-M\equiv)$. In the ceramics area, this technique has generated considerable enthusiasm because of the potential for making multicomponent homogeneous glasses of solution at low temperatures. Considering the addition of an organic species, if an oligomer or polymer can be functionally modified to have sol-gel reactive components located in at least two positions (preferably terminal placement) on the polymer chain, then the organic material can be used as a precursor in the poly(hydrolysis-condensation) reaction. Of course, the relative solubilities of the inorganic and organic species would also need be considered. Therefore, this last development offers one possible avenue of systematically obtaining polymer modified inorganic glasses. The chief advantage and objective of this experimental procedure is that the hybrid materials produced, in principle, could be tailor made with specific physical properties depending on the nature of the moieties employed.

Typically, the preparation of organically modified sol-gel glasses have been primarily synthesized with elastomeric components such as hydroxyl terminated polydimethyl siloxane (PDMS) and triethoxy silane endcapped polytetramethylene oxide (PTMO) studied by Wilkes et al.[1-3] At the present time, only Schmidt and Philipp have attempted to incorporate a glassy component (below the T_g) in a sol-gel inorganic network.[4-7] Their experimental method combines a sol-gel mechanism with an independent free radical reaction sequentially that requires a somewhat tedious and complex reaction procedure. It is our intention to simplify this approach by developing a synthetic route that only necessitates the use of the sol-gel mechanism to incorporate the glassy oligomeric species. Thus, both the inorganic and organic multicomponent mixture can be reacted simultaneously to promote an efficiently intermixed inorganic-organic network in one simple step. By thermal treatment, sufficient network structure can be developed which will hopefully lead to new and useful material properties.

Wilkes and co-workers and Mark and co-workers have used the basic approach described above in the preparation of elastomer modified sol-gel systems.[1,2,8-11] In order to make a hybrid material by this method, the organic or oligomeric species to be incorporated in the network must be functionally reactive with the silicon alkoxide precursor during the course of the sol-gel reaction. Two ways have been investigated in the literature[3,10] with both involving some form of an endcapping procedure to place silicon alkoxide functional

groups on the ends of the oligomer chains. The first method deals with the addition of trialkoxysilane to vinyl terminal groups located on at least two positions of the oligomer through a hydrosilylation reaction using a platinum based catalyst. Typically, the hydrosilylation reaction's yields are lower than 75%, and this may ultimately have a deleterious effect on the physical properties of the sol-gel derived product.[12] Another possible endcapping scheme relies on the principles of traditional polyurethane chemistry. Specifically, the reaction of an isocyanate functional group with an amine or hydroxyl terminated species to form either urea or urethane linkages. This reaction normally proceeds very rapidly at room temperature to extents much greater than 95% with primary amines in the absence of a catalyst.[13] Since isocyanate functionalized trialkoxy silanes are commercially available, this latter endcapping procedure offers a distinct advantage over the hydrosilylation reaction as long as the organic or oligomeric species can be amine or hydroxyl terminated. However, this linkage does have notable disadvantages which include relatively low thermal stability and a potential susceptibility to urea or urethane hydrolysis during the sol-gel reaction.

Even though the urea and urethane endcapping procedures have some potential weaknesses it still provides a very systematic approach to developing the sol-gel reactive organic precursors. All that is required is to find a sol-gel compatible amine or hydroxyl terminated oligomer of a manageable molecular weight. After a thorough inspection of several classes of glassy polymers, the amine terminated bisphenol-A functional poly(arylene ether) (PEK) ketone oligomers of controlled molecular weight were selected to demonstrate our approach. This polymer, which was first synthesized by McGrath et al., meets all criteria specified for the endcapping and sol-gel reactions.[14] In general, PEK is an amorphous engineering thermoplastic material with mechanical properties, good thermal stability, and a relatively high T_g of ca. 150°C. This material is a member of the poly(arylene-ether-ether)ketone family of polymers which are marketed by ICI. A major difference is that the PEK discussed here has a bisphenol-A linkage in the repeat units which prevents the crystallization of the polymer in contrast to a hydroquinone functionality in the repeat unit of PEEK. Furthermore, the primary amine terminal groups of the PEK can easily undergo the isocyanate addition to form urea linkages which are more thermally stable than the urethane linkages due to greater hydrogen bonding capabilities. With this information in mind, we now address the preparation and characterization of PEK/TEOS hybrid materials.

EXPERIMENTAL

Preparation of PEK Oligomers

The synthesis of controlled oligomeric molecular weight amine terminated PEK (Mn = 3900) was accomplished by controlling the ratio of bisphenol-A to p-amino-bisphenol-A and holding the amount of the 4,4'-difluorobenzenophenone constant (see Scheme I). One example of a starting reaction recipe consisted of 0.0922 moles of bisphenol-A, 0.016 moles of p-amino bisphenol-A, and 0.1 moles of 4,4'-difluorobenzophenone in 175 ml of NMP (n-Methyl pyrrolidone). These materials were placed in a specially designed reaction apparatus
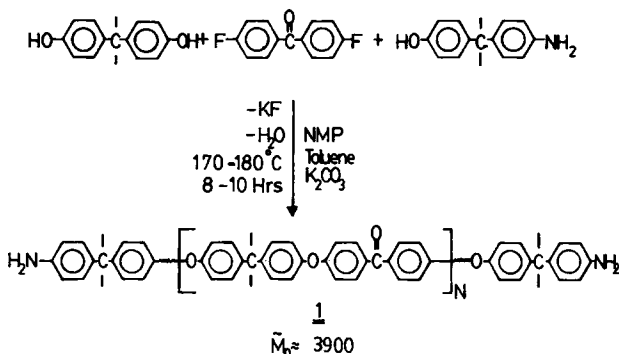
Scheme I.   Reaction scheme for the synthesis of amine terminal PEK.[14]

with 20.0 g of anhydrous K_2CO_3 and 75 mL of toluene (an azeotroping agent) while under a constant nitrogen purge. Since the basic procedural details for synthesizing controlled molecular weight amine terminated PEK materials has been described elsewhere it will therefore not be presented here.[14]

Preparation of the Triethoxysilane Endcapped PEK

The synthesized amine terminated PEK, ($Mn \approx 3900$), was endcapped with isocyanatopropyltriethoxysilane that was purchased from Petrach, Inc. and used without further purification—see Scheme II. The amine end groups of the PEK were reacted with the isocyanate functional grouping of the endcapping material to form urea linkages. This reaction was carried out in dry tetrahydrofuran (THF) under a nitrogen atmosphere without the presence of a catalyst for a period of 3 h. The isocyanatopropylytriethoxysilane and PEK amine groups were present in the reaction solution at a stochiometric ratio of 1.25 : 1.0 (i.e., 25% excess endcapping agent). The final recovered product contained a 10 wt. % content of PEK in a THF based solution which was used as the organic starting material in the subsequent preparation of PEK/TEOS sol-gel derived glasses. However, before the sol-gel reaction was performed, infrared spectroscopy was utilized to qualitatively analyze the extent of the endcapping reaction.

Preparation of the PEK/TEOS Glasses

The sol-gel technique was used to produce thin film samples with several different PEK/TEOS compositions. Samples were synthesized with the purified
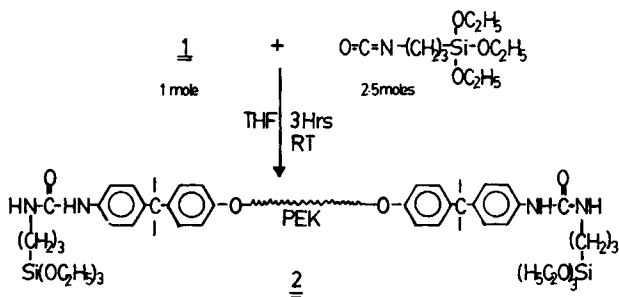
Scheme II.   Endcapping reaction of amine terminated PEK with isocyanatopropyltriethoxysilane.

triethoxysilane endcapped PEK, and TEOS starting materials to form the glass compositions of 100/0% *PEK/TEOS* (PETE) 75/25% PETE, 50/50% PETE, and 25/75% PETE by weight (see Scheme III). (*Note that these compositions are based on the initial weight percent of the starting materials and are not truly representative of the actual composition of the final glasses due to major mass loss of the by product (ethanol) from the TEOS species during the sol gel reaction.*) With the exception of the 100/0 PETE samples, where an excess of water was employed, the hydrolysis conditions were as follows: 6 moles of water per mole of endcapped PEK plus two moles of water per mole of TEOS; 10 mL of THF per gram of PEK; and a pH of approximately 2.0, adjusted with addition of 10 N HCl dropwise. The reaction solution was refluxed for one half hour at 80°C (Scheme III). The entire reaction mixture was allowed to react further within Teflon molds. After solidification and vacuum drying to remove the residual solvent, portions of the finished bulk product were subjected to selected thermal treatments (25°C (control), 100°C, and 200°C) for 6 h in air prior to characterization.

CHARACTERIZATION METHODS

Dynamic Mechanical Studies

The dynamic mechanical properties of the PEK/TEOS glasses were analyzed by a Toyo Baldwin DD-II-C Rheovibron Dynamic Viscoelastometer automated with a Hewlett Packard 9000 Series Model 216 computer and data station. The samples were temperature scanned at 2–3°C/min and probed with 11 Hz to monitor the storage (E′), loss (E″) modulus, and tan δ behavior. The temperature range investigated was between 0–200°C, but for a few runs the range was expanded to −130–200°C to investigate subambient transitions. Since no significant behavior was observed at the subzero temperatures, only the data collected over the 0–200°C region will be presented within this paper.

Differential Scanning Calorimetry

The T_g and the endothermic/exothermic behavior of the PETE glasses were monitored using a Perkin-Elmer DSC-4 Thermal Analyzer with a Model 3600

$$(x)\ Si(OC_2H_5)_4\ +\ (y)\ \underline{\underline{2}}\ +\ (2x+6y)\ H_2O$$
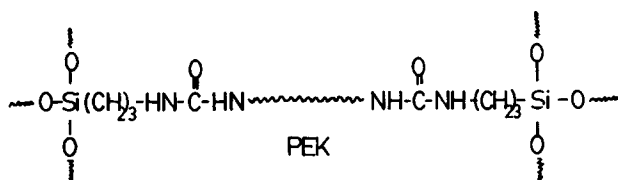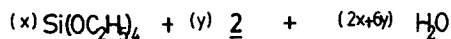
Scheme III. The endcapped PEK/TEOS Hydrolysis Condensation Reaction where R = $(CH_2)_3$.

Data Station. Three sets of experimental conditions were employed. The first set involved the running of two consecutive DSC scans on a single sample from 25–300°C with heating and cooling rates of 20°C/min and 320°C/min, respectively. For the second set, stepwise DSC measurements were begun initially within the range of 25–100°C range, and the maximum scan temperature (Tmax) was incremented at 30°C intervals with each successive sample scan until a "Tmax" of 300°C was reached. In the final set of experiments, samples cured at 25°C were subjected to isothermal treatments at the temperatures of 100, 130, 160, and 190°C for holding times of 5, 10, 20, and 30 min. After the sample received its specified thermal pretreatment, the material was then scanned from 25–300°C with the earlier prescribed heating and cooling rates to gather information on the effect of the prior thermal history.

Infrared Analysis

IR analysis was performed using a Nicolet 5DXB FTIR Spectrometer with a 1 mW HeNe laser. Sample preparation of the PETE glasses were carried out using the KBr pellet technique while the sol residue samples and other starting materials were analyzed as thin films cast on a KBr window.

Mechanical Experiments

The mechanical experiments were conducted with an Instron Model 1122 Mechanical Tester to determine the Young's modulus and maximum extensibility of the PETE glasses as a function of the curing temperature. Micro-dumbells 10 mm in length were the designated sample size, and a 20%/min initial extension rate was utilized.

Small Angle X-ray Scattering (SAXS) Studies

SAXS was carried out to study structural features of the PETE materials. A standard Kratky X-ray camera was utilized with a Siemens Ag Cu 40/2 X-ray source operated at 40 kV and 20 mA by a GE XRD-6 generator. The scattered intensity was monitored with a M. Braun position detector (Innovative Technology, Inc.).

Soxhlet Extraction Experiments

The soxhlet extraction experiments were performed to provide a qualitative indication of the degree of network information achieved through the sol-gel reaction and following the post thermal treatments. Sample preparation of the PETE materials consisted of first a removal of all the dissolved solvents under vacuum, and then finely "chopping" the samples to increase the extractable surface area. All of the analyses were run in a standard soxhlet extraction apparatus using THF or methylene chloride as solvents for a minimum of 24 h. The final weights of the PETE materials were measured to determine the sol fraction removed.

Thermogravimetric Analysis

The TGA measurements were made with a Perkin-Elmer TGA-2 Thermogravimetric Analyzer over the temperature range of 50–750°C with a 10°C/

min scan rate in air. The purpose of these experiments was to provide a secondary confirmation of the continued thermal curing phenomena at the elevated thermal treatments.

End Group Analysis of Amine Terminated PEK

The exact number average molecular weight of the amine terminated oligomer was obtained by titration. The procedure has been discussed elsewhere in detail.[14]

Analytical Characterization of the Sol Gel Network

IR Analysis of the amino capped PEK and the triethoxysilane endcapped product indicate qualitatively that indeed the urea linkage was formed in the latter—recall Scheme III. This was determined by inspecting the 3450 cm^{-1} region of the IR spectrum of both the reactant and product materials. The reactant PEK has a primary amine terminal group which produces two sharp and one weak N-H stretching bands in the 3450 cm^{-1} region while in the triethoxysilane endcapped PEK, the newly formed urea linkage results in the development of secondary amine functionalities. The secondary amine groups, located adjacent to the potentially strong electron withdrawing carbonyl, gives rise to only one broad and weak intensity N-H stretching band in the same region. Cursory survey of the IR spectrum of the reactant and product PEK's support the occurrence of the endcapping reaction. Little information on the extent of reaction, however, could be gained since both the primary and secondary amines absorb in the 3450 cm^{-1} region and tend to overlap. Nevertheless, the absence of the two primary amine bands and the strong presence of the secondary amine stretch clearly indicated that the endcapping reaction's extent was relatively high (> 95%) which was expected.[13]

A second question addressed was whether the sol-gel reaction of the PEK/TEOS component had any deleterious effects on the urea linkages. For example, if the urea linkage becomes hydrolyzed during the sol-gel reaction, the triethoxysilane endcapped PEK reverts back to the amine terminal form and would become only a "filler" in the final network. Thus, after the preparation of the 100/-%, 75/25%, 50/50%, and 25/75% PETE glasses, samples of the materials were subjected to soxhlet extraction to remove any free PEK, if any, which underwent subsequent IR analysis to check for the presence of primary amine functional groups. The occurrence of the two primary N-H stretches in the 3450 cm^{-1} region should provide a good indication of urea degradation and/or the unsuccessfulness of the endcapping reaction.

The initial soxhlet extraction experiments of the different composition PETE samples indeed revealed that only a low degree of network formation was achieved by the sol-gel reaction *when carried out at 25°C*—see Table I. However, the IR spectrum of both the extraction residue and the endcapped PEK starting material are very nearly identical which suggests that the incomplete network formation is *not likely a degradation and/or endcapping problem*. The last finding is further confirmed by the soxhlet extraction results for the 25°C cured samples which displayed a notable trend (see Table I). That is, as the glass content of the PETE system is increased, the sol-fraction percentage drops accordingly. This phenomena is attributed to a greater degree of network formation occurring

TABLE I
Soxhlet Extraction Results for PETE Glasses

Sample	Mw PEK	Wt. % extracted
100% PEK		
25°C Cure	4000	25.80
100°C Cure*	4000	4.40
200°C Cure*	4000	−13.02
75/25% PETE		
25°C Cure	4000	—
100°C Cure*	4000	0.58
200°C Cure*	4000	−15.15
50/50% PETE		
25°C Cure	4000	17.60
100°C Cure*	4000	2.62
200°C Cure*	4000	−9.33
25/75% PETE		
25°C Cure	4000	2.44
100°C Cure*	4000	1.23
200°C Cure*	4000	0.43

* For the cure temperatures of 100°C and 200°C, all samples were cured for 6 h in air.

in the higher TEOS content mixtures. This is to be expected since the addition of the TEOS precursor adds four more potential network sites per "monomer" which in turn enhances the probability of the trialkyloxysilane terminated PEK being incorporated into the network before vitrification occurs as the network develops.

In the lower trialkoxy silane containing materials, it is believed that the lower degree of network formation results from an earlier vitrification. Specifically, as the sol-gel reaction continues, the T_g of the entire system increases due to an overall molecular weight buildup and finally approaches the temperature of cure where vitrification occurs—a concept that has been well discussed and proven by Gillham and coworkers for network developing systems.[15] As a result, the local mobility of the chain is severely restricted. This restricted mobility reduces the probability of the trialkoxysilane endgroups finding a functional reactive partner to form the inorganic bridges necessary to produce the network. For this reason, thermal treatments were employed to overcome the diffusional and/or kinetic limitations developed during the vitrification process. By heating the PETE samples at the prescribed temperatures of 100 and 200°C for 6 h, a remarkable decrease in the sol-fraction is noted (see Table I). For example, the 100°C cured samples sol-fraction dropped dramatically to lower than 5.0% for all the PETE compositions. It is, however, more difficult to explain the slight weight gain observed with some of the samples (e.g., 100% PEU, 75/25% PETE, and 50/50% PETE) cured at 200°C. This may be due to the incomplete removal of water (reaction product) or possibly insufficient drying to remove the extracting solvent from the network structure.

In addition to the reduction of the sol fraction with the 100°C and 200°C thermal treatments, the physical appearance and physical properties reveal a

substantial change. First, the physical nature of the sol gel derived glasses that have not been thermally treated are crack free and monolithic in form and can be shown to form a hard and rather scratch resistant coating when cast on wood, metal, or glass substrates—a potential area of application for these systems. They possess a yellow-gold color similar to that of the pure PEK oligomer and are transparent with the exception of the 25/75% PETE system which displayed turbidity caused apparently by poor miscibility at this high TEOS concentration. As expected, as the amount of the TEOS content is increased in the PETE material, the sample brittleness increases along with the sample shrinkage during gelation. The 100/0% PETE hybrid glass has no notable sample shrinkage, a fairly flexible nature, and a smooth texture while the 25/75% PETE glass experiences large sample shrinkage, brittleness, and a more inorganic glasslike behavior as would be expected.

After the thermal treatment at 100 and 200°C, the appearance of these materials is significantly altered in comparison with the 25°C controls. In all cases, the added curing results in a color darkening. The 100°C systems develop a slightly darker shade of yellow-gold whereas the 200°C materials exhibit a vivid auburn color. Also with increasing temperature treatments, the samples experience greater shrinkage which is associated due to the densification caused by the continuation of the sol gel reaction. In the 100/0% PETE system, the volume is reduced by about 6% and 10% for the 100 and 200°C treatments while for the 25/75% system, the volume is reduced even more so. Besides these observations, a distinct difference in the mechanical properties are noted. Interestingly, the 100° treated samples tend to be tougher than the 25°C cured control materials. The 200°C systems generally are more brittle due to the higher level of enhanced crosslinking of the TEOS components—particularly for the higher TEOS containing systems. Restated, the 25°C cured materials display a poor network formation and hence are poorer mechanically while the 100°C cured intermediate group has obtained a sufficient level of crosslinking where the mechanical properties become more suitable due to higher network connectivity. However, after a 200° thermal treatment, the enhanced crosslinking begins to promote a more brittle system—common of more highly crosslinked systems.

It is worthy to mention the significant weight loss occurring during the removal of the ethoxy functional groups during the hydrolysis condensation reaction. Up to this point, the sol gel glasses have been referred to as having the compositions of 100/0%, etc. which are based on the initial weight percent of the added PEK and TEOS in the starting reaction mixture. Truly these compositions do not accurately represent the final values formed as a result of the sol gel reaction. If the hydrolysis condensation mechanism were carried out to the extent of 100%, the alkoxy endcapped PEK would undergo a 3.4% weight loss while the TEOS would lose about 71% of its initial weight. This would change the beginning PETE glass compositions from 100/0%, 75/25%, 50/50%, and 25/75% to 100/0%, 91/9%, 77/23%, 53/47% PEK/TEOS, respectively. In the real situation, the composition lies somewhere between these two extremes depending upon the extent of the sol gel reaction.

Thermal Analysis Investigations

Based on the above observations, it is clear that the initial level of reaction is limited by vitrification. This vitrification process limits the further reactivity

by placing diffusivity limitations on the reactants. As stated earlier, this concept has been well discussed by Gillham and coworkers[15] through their utilization of the time-temperature transformation behavior of network curing materials. In short, and using their terminology, a system is limited in terms of achieving complete reaction if the build-up and molecular weight leads to a sufficient rise in the glass transition temperature of the network promoting vitrification before full extent of reaction can occur. Hence, to offset this limitation, one must cure above what Gillham refers to as Tg_∞. Here, Tg_∞ represents the highest glass transition possible for a given network with a specific composition.

To further verify, if it is vitrification that limits the initial extent of reaction, further DSC studies were carried out to inspect how the glass transition of the systems varied with curing conditions as well as composition ratio. Figure 1A illustrates the DSC scans (obtained at 20°C per minute) on the various PETE compositions that had been cured at 25°C—note that the scans were terminated at ca. 280°C. Figure 1B provides the *immediate rescans* of these same materials following their initial cooling to ambient. Clearly, the results are as anticipated as based on previous consideration of the time/temperature transformation concept. Specifically, it is obvious that for those materials cured at 25°C, upon heating, the glass transition temperature appears just above room temperature and for those systems containing higher TEOS contents, exothermic behavior is denoted due to continuation of the crosslinking reaction. However, the rescans illustrate that the glass transition temperature for all of the materials has reached nearly 200°C although it is somewhat less distinct a transition in the higher TEOS containing materials as might be expected due to the lower content of the PEK oligomer. Hence, it appears that the value of 200°C is near the
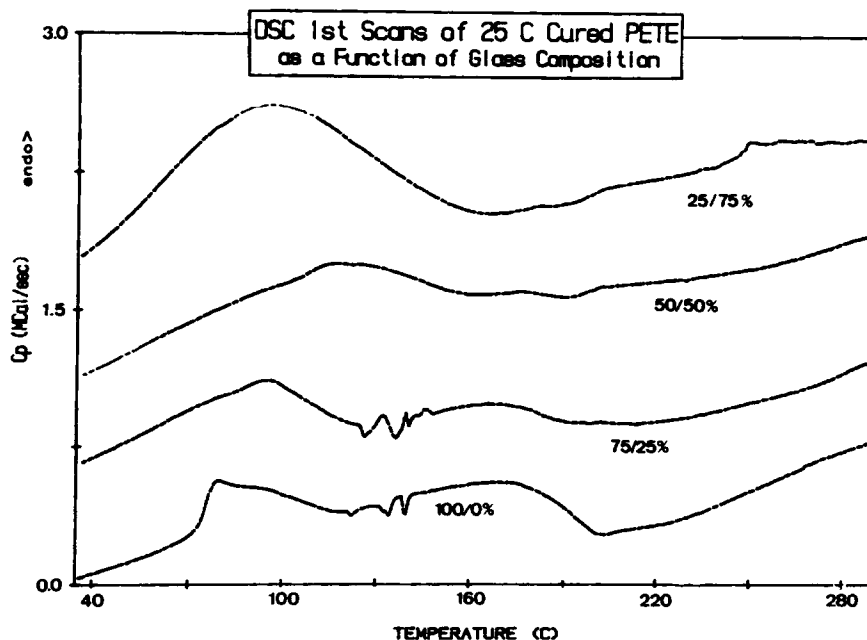

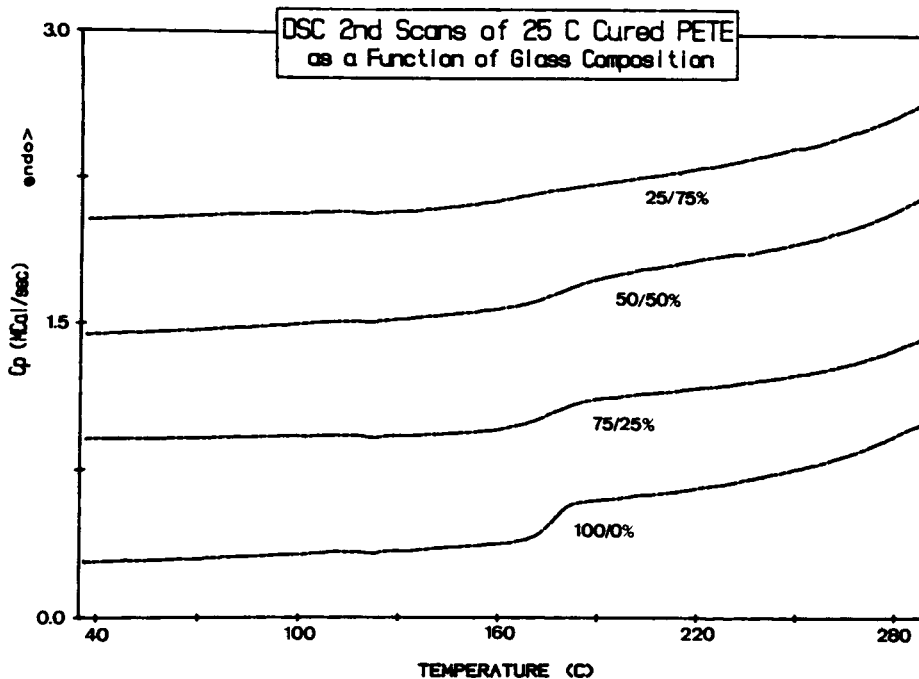Fig. 1A.   Initial DSC scans of 25°C cured PETE as a function of glass composition.

Fig. 1B.   DSC scans of 25°C cured PETE as a function of glass composition.

vicinity of Tg_∞. Further confirmation of these latter statements are provided with the results shown in Figure 2 which indicate a systematic series of DSC scans obtained on PETE 100/0% but where now each subsequent scan achieved a somewhat higher temperature than the preceding one. The results clearly show that the glass transition temperature is systematically shifted to higher values with each subsequent scan thereby indicating that vitrification had limited the Tg of the previous scan up to the order of the temperature 200°C after which no further extent of reaction was developed.

Dynamic mechanical experiments revealed a similar pattern of behavior as observed by the DSC results. In particular, monitoring E' and tanδ of these systems following the 25° cure and subsequent cures show that the drop in E' at the glass transition and the corresponding dispersion tanδ region associated with that transition were systematically shifted upwards with further annealing treatment, but above 200°C, no further change was observed—see Figures 3A and 3B.

Qualitative information regarding the extent of the reaction with varying cure temperature was obtained from IR analysis of the PETE samples. Figure 4 illustrates one such finding for the 50/50 PETE glass. The absorption intensities of the band due to Si-O-Si stretch at 1100–1000 cm^{-1} were used to qualitatively monitor the reaction with increasing cure temperature. The ratio, R, of the Si-O-Si and carbonyl (present in the PEK backbone) band intensities were used for comparison purposes in order to avoid discrepancies arising out of differences in film thickness. An examination of Fig. 4 indicates that R increases from 3.11 to a value of 6.06 for samples cured at 25°C and 200°C,

Stepwise DSC Scans
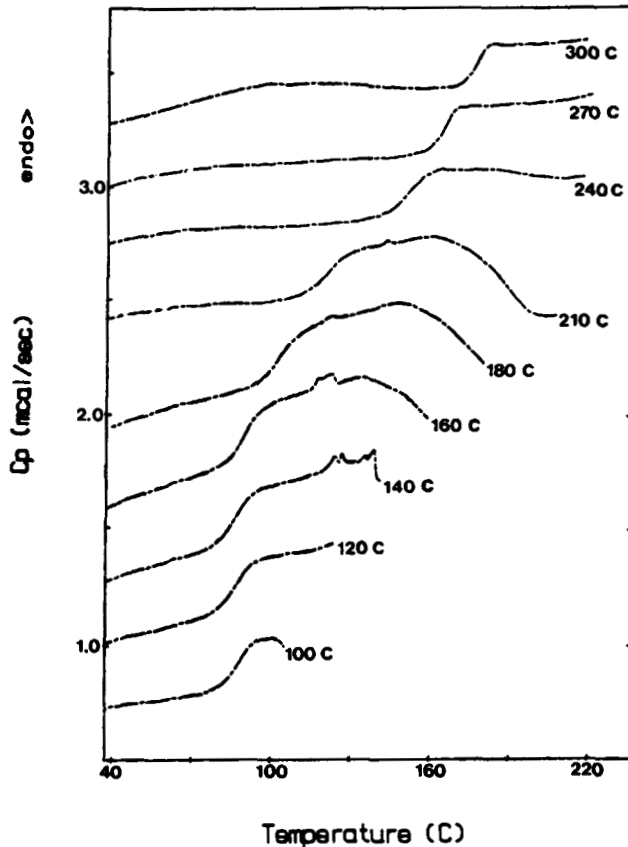## for 100/0% PETE

Fig. 2. DSC scans of 100/0% PETE cured at different temperatures (as indicated).

respectively. This further confirms our contention that increasing the cure temperature allows far better mobility and further condensation of the unreacted silanol functionalities.

Structural Investigations

In an attempt to obtain additional information on the morphological/structural features of this material, both scanning electron microscopy and small angle x-ray scattering (SAXS) methods were applied. In particular, only those systems were investigated that retained optical clarity since any others which displayed turbidity implied poor compatibility of the PEK oligomer and clearly some macrophase separation had occurred at a sufficient length scale as to promote light scattering accordingly. Applying SEM on fracture surfaces of the various transparent films provided no direct observation of multiphase behavior. However, very distinct signs of local phase separation did exist as can be clearly
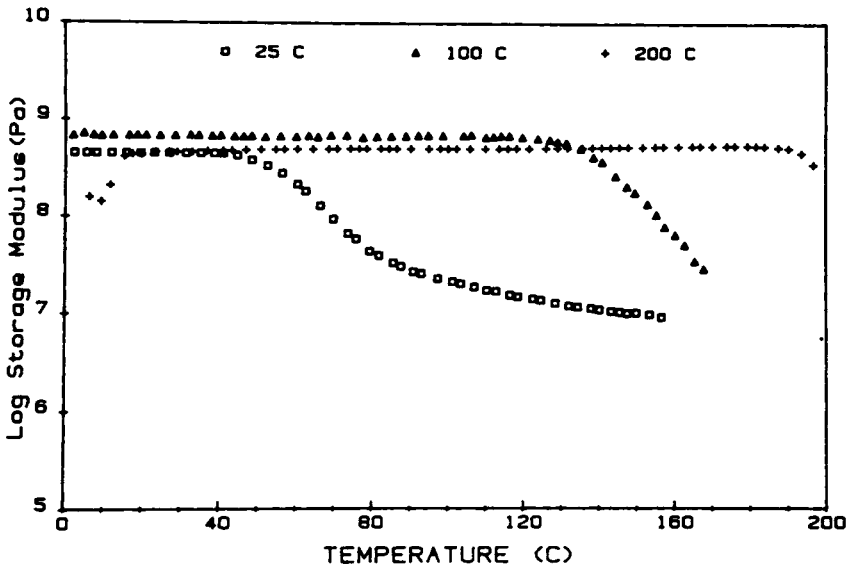
Fig. 3A. Storage modulus of 100/0% PETE as a function of initial cure temperature.

discerned from the SAXS results. Figures 5A, B, and C illustrate the slit smeared intensities obtained from the PEK/TEOS materials as cured at the specified temperatures. There is a distinct single order peak observed in these plots which are presented in the form of $I(S)$ vs. S where S is equal to $(2 \sin(\theta/2)/\lambda)$ with λ being the x-ray wavelength (1.54 Å) and θ represents the radial scattering angle. In essence, if a shoulder appears in the intensity plot provided in this form, the results indicate the presence of a correlation length in the
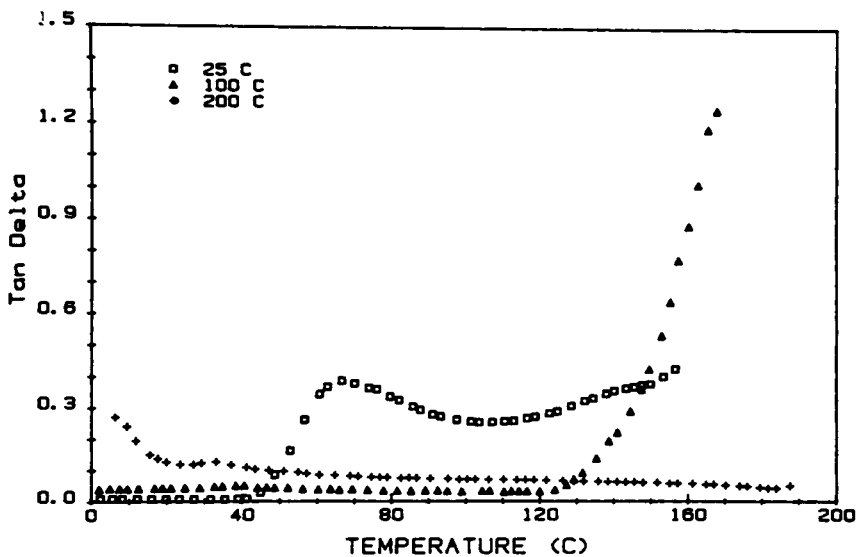
Fig. 3B. Tanδ spectrum of 100/0% PETE as a function of initial cure temperature.
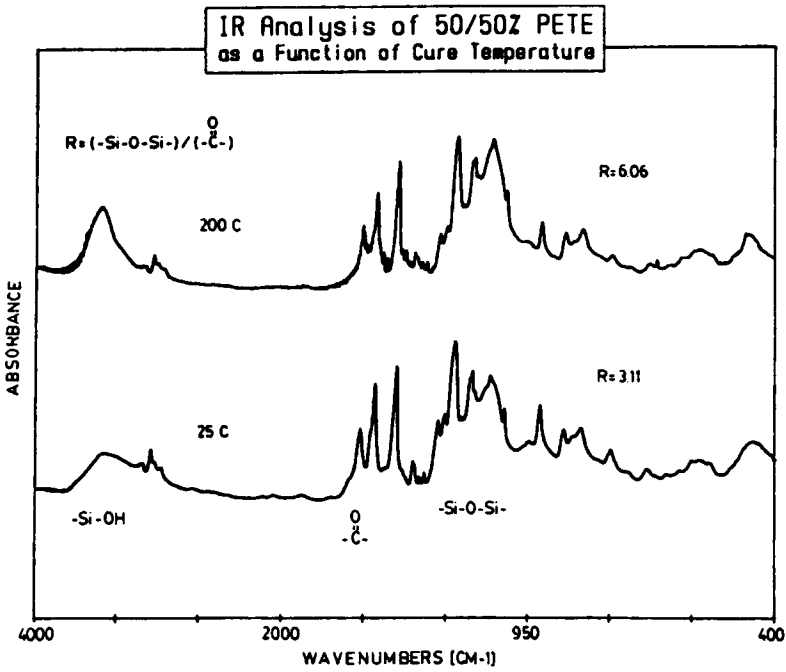
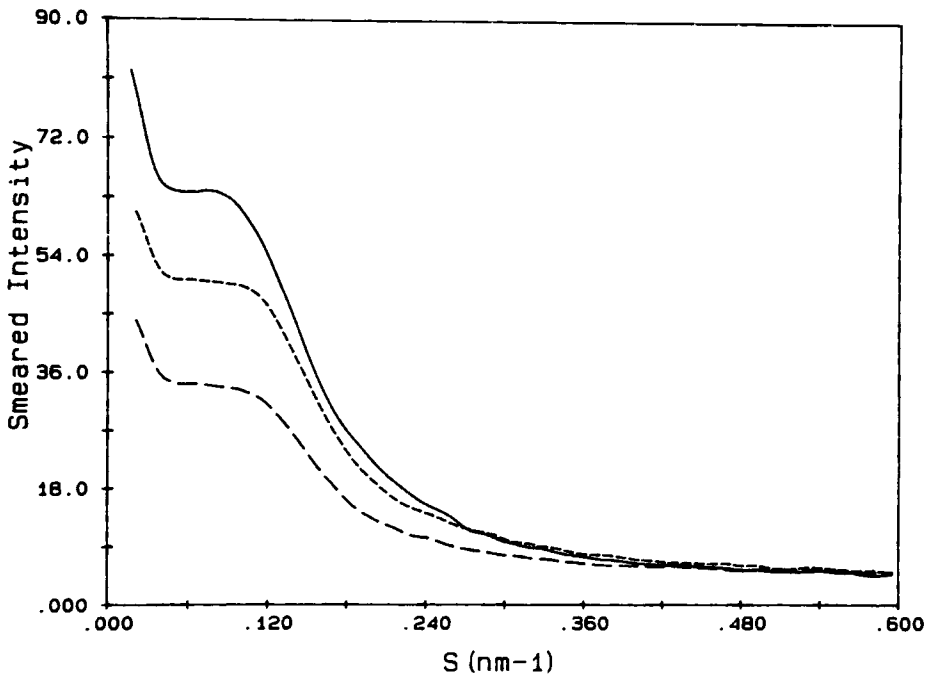Fig. 4. Infrared spectra of the 50/50 PETE hybrid system following two different cure temperatures.

Fig. 5A. SAXS scans of 75/25% PETE as a function of cure temperature: (– – –) 25°C cured, (---) 100°C cured, and (——) 200°C cured.
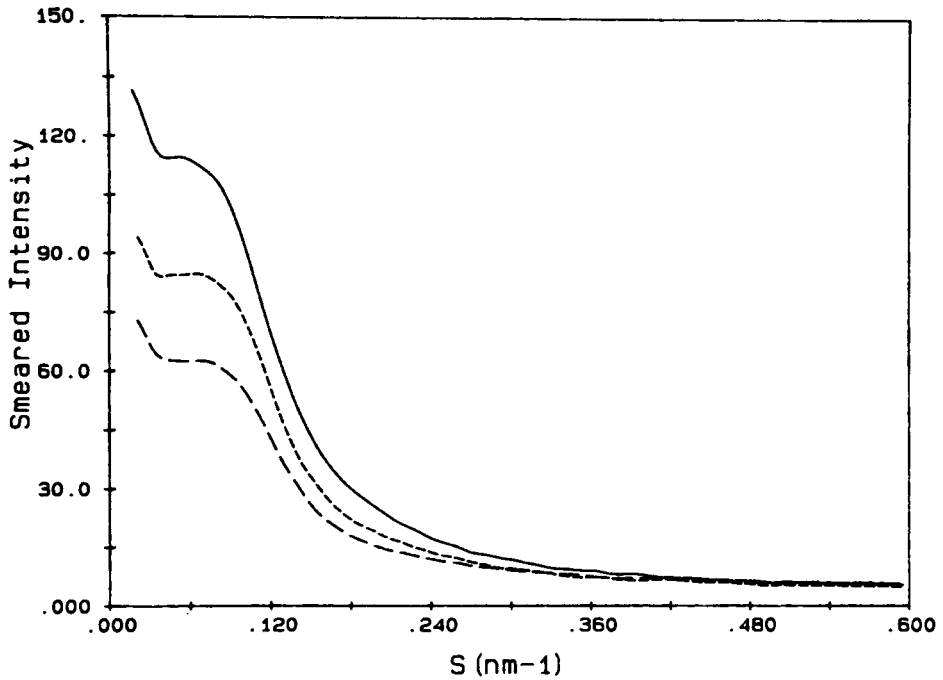
Fig. 5B.   SAXS scans of 50/50% PETE as a function of cure temperature: (– – –) 25°C cured, (---) 100°C cured, and (———) 200°C cured.
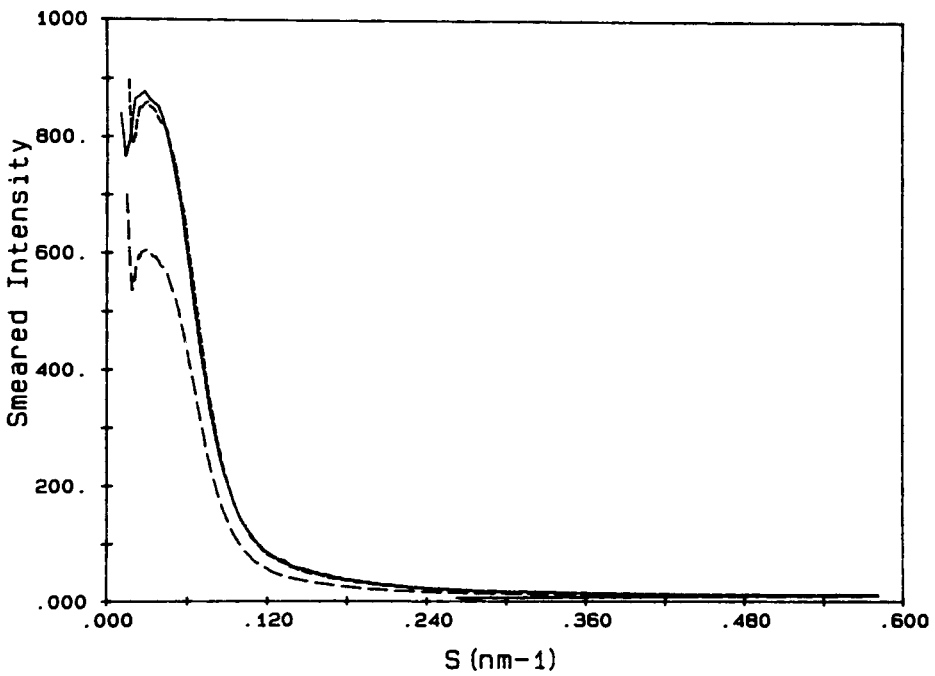

Fig. 5C.   SAXS scans of 25/75% PETE as a function of cure temperature: (– – –) 25°C cured, (---) 100°C cured, and (———) 200°C cured.

system over which a rather periodic fluctuation in electron density occurs which serves as the basis for the x-ray scattering. In particular, a single shoulder or peak in this intensity trace provides a clear suggestion that microphase separation has occurred between the TEOS and PEK components arising from the higher compatibility of the end groups of the alkoxy endcapped PEK with that of TEOS in contrast to the backbone of the PEK itself. To obtain an estimate of this correlation distance a first approximation is simply to invert the value of S at the scattering peak, i.e., this correlation length can be estimated as 1/ S (by Bragg's law), but it must be recognized that without further details of what the exact morphological texture is, i.e., lamella, spherical domains, etc. it is difficult to provide additional details. As shown in Fig. 5, a distinct shoulder occurs in all of the PETE materials and each provides a correlation length that is of the order of 10 nm. The exact "d" spacing or correlation length systematically varies with the amount of TEOS as shown in Figure 6 for a given curing temperature. These data strongly suggest (but do not absolutely confirm) that the nature of the phase separation is likely along the lines sketched in the simplified model provided in Figure 7. Here it is illustrated that a richer TEOS phase develops in the chain end regions of the PEK leaving a richer PEK matrix—at least for those compositions of higher PEK content. As the TEOS content increases, the relative size of the TEOS phase also should be expected to increase whereas the PEK chain length is still maintained—these latter two features together would promote a greater correlation length as indeed is observed—recall Fig. 5a–c. It should be pointed out that this basic morphological model that is presented here has also received support from other structural studies on related ceramer materials prepared with functionalized oligomers, other than PEK, that have been reacted with TEOS.[16]
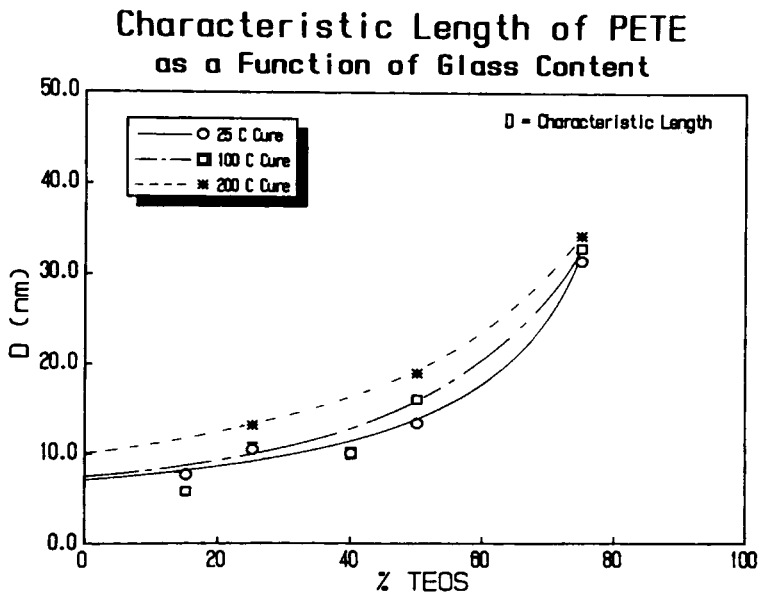

Fig. 6. Correlation length, D, of the PETE glasses as a function of TEOS content and cure temperature.
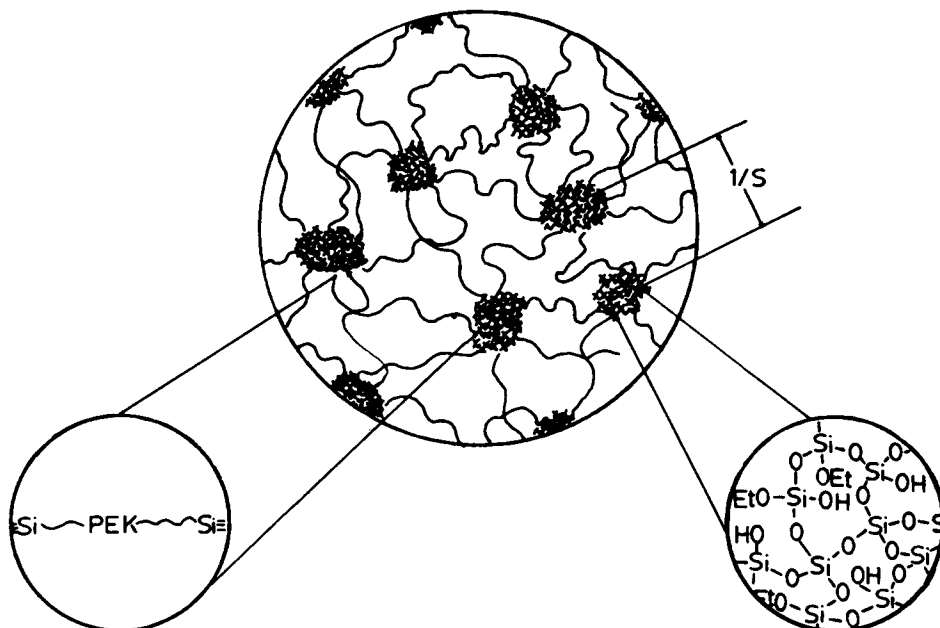
Fig. 7. Postulated structural model of PETE glasses based on structural, mechanical, and thermal studies.

In line with our earlier observations that increasing the cure temperature also promotes a greater curing of the TEOS component, at least until the temperature of nearly 200°C is obtained, one would anticipate that the SAXS results would also reflect this difference in extent of cure. This statement follows from the fact that the electron density of the PEK would still be maintained following higher extent of cure but that the electron density of the TEOS rich phase would be further decreased as the system approaches more of SiO_2 glass phase. This result would enhance the relative magnitude of the fluctuation in electron density between the two phases which directly enhances the degree of scattered intensity at a given angle. Indeed, as shown in Fig. 5a–c, the scattered intensity curves for PETE materials at any composition clearly illustrate this feature in that the scattered intensity is distinctly increased as the degree of cure is increased. In addition, it is noted that the peak or shoulder change very little in position, thereby suggesting that it is principally only the level of curing that is promoted but no major change in morphology occurs as a result of this enhanced network growth. This certainly is the expected result in view of our earlier discussions based on DSC, dynamic mechanical and related information.

SUMMARY

In conclusion, we have demonstrated the development of a new hybrid material based on the incorporation of organic functionalized oligomers into a sol gel reaction with inorganic alkoxides. A major difference in the system discussed here relative to our earlier papers concerned with oligomers whose T_g is well

below room temperature during the curing reaction, is that for the PEK system presented here, its higher glass transition temperature limits the extent of cure caused by vitrification as gelation and network buildup occurs—at least at the lower cure temperatures. However, further network development can be promoted and in fact completed as far as glass transition behavior is concerned by utilizing thermal post cure treatments. The final materials can maintain transparency in the optical frequency range but do illustrate that *local microphase* separation may well occur. This microphase texture develops due to the network formation regions that possess a greater affinity for the alkoxy end-capped peak components—hence leading to a proposed model—recall Fig. 7.

The result of this work demonstrates that any functionalized oligomer that can display reactivity with inorganic alkoxides and whose miscibility exists at the time of the sol gel reaction can promote interesting hybrid network materials that might display potential applications in the area of coatings, spun fibers, encapsulants, and related applications. In particular, there are many high temperature polymers today that do not easily lend themselves to coating operations due to their insolubility or lack of melt processability, e.g., many of the polyimides, polysulphones, etc. By using lower molecular weight oligomers functionalized as discussed within this work, they may be made more suitable for protective coating applications. Work in this regard is continuing in our laboratories and will be reported at a later date.

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