

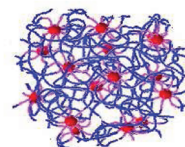
Kinetics of Polymerization of a Liquid with Nanosize Structural Heterogeneities

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ABSTRACT: We report the effects of chemically reacting, nanometer-size structural heterogeneity on a polymerization process. Heterogeneity is introduced by adding 2 nm size molecules of polyhedral oligomeric silsesquioxane with multipoxide groups (POSS) while maintaining stoichiometry of a polymerizing triamine–diepoxide mixture. Calorimetric studies show that POSS addition first increases the polymerization rate and then decreases it progressively more. In the presence of nanometer-scale structural heterogeneity, diffusion-controlled kinetics begins sooner in time. The enthalpy of polymerization decreases with the amount of POSS heterogeneity according to the mixture rule; the glass–liquid transition endotherm of the partially polymerized state becomes broader, and the enthalpy of post polymerization decreases. The POSS-alone mixture polymerizes relatively slower, and the glass–liquid transition exotherm of the polymerized state is indistinguishably broad. Both are attributed to the distribution of diffusion rates or dispersive kinetics, and the development of dynamic heterogeneity more rapidly for the POSS-only mixture than for others. Increase in the polymerization rate on initial addition of nanometer-size POSS and then decrease on further addition is explained in terms of decoupling of diffusion from viscous flow, that is, when the diffusion rate decreases less rapidly with the polymerization time than the viscosity increases.

**Triamine + Diepoxide +
Polyhedral Oligomeric Silsesquioxane
(2-nm structural heterogeneity) to form:**



INTRODUCTION

Kinetics of polymerization reactions is mass-controlled in low viscosity liquids. The viscosity, η , and the average diffusion coefficient, D_{av} , have no role in determining the reaction kinetics, and a liquid's composition controls the polymerization rate. As polymerization progresses, η increases and, over a narrow range of high viscosity and higher density, the reaction rate becomes affected by increasing η and decreasing D_{av} , and the polymerization kinetics becomes diffusion-controlled. It was suggested that this sets up a process of negative feedback between the chemical reaction and molecular diffusion.¹ Briefly, addition reactions cause a molecular entity to grow in size, and, as that occurs, η increases and D_{av} decreases. This in turn decreases the rate at which two molecules or its reacting groups can diffuse to reach a proximity needed for their chemical reaction, thereby slowing the rate of reaction itself. As the occurrence of one slows the other, polymerization and diffusion occur at a progressively slower rate until neither reaction nor diffusion can occur over an experiment's time and the liquid vitrifies. This negative feedback between diffusion and polymerization reactions has been studied by changing the temperature,² pressure,^{3–5} and composition,⁶ by allowing phase separation,⁷ and by investigating gelation prior to vitrification.⁸ Experimental techniques of dielectric,^{1–7,9–15} mechanical,^{16,17} specific heat,^{18–20} and ultrasonic^{21,22} relaxations, of Brillouin^{23–27} and Raman scattering,^{28–30} of infrared spectroscopy,³¹ of thermal conductivity,³² and density,³³ have been used for studying polymerization in real time with a focus on its physical chemistry. Some of the thermokinetic properties measured have also been modeled.^{34–36}

Distribution of relaxation times, which is characteristic of an ultraviscous liquid's dynamics, was considered in terms of a sum of Debye type single relaxation times in 1971 by Majumdar,³⁷ and a similar summation was used by Schmidt-Rohr and Speiss.³⁸ They also developed the concept of dynamic heterogeneity in supercooled liquids for explaining why the relaxation time and η vary with temperature in a non-Arrhenius manner, that is, more sensitively than the Arrhenius equation requires, and why ultraviscous liquids show non-Arrhenius and nonexponential behavior of their dynamics. Here, the term dynamic refers to the fact that the heterogeneity, although at nanometer scale, has not been observed in structural features of a liquid. Because the relaxation time is related to the diffusion coefficient, D , it follows that D would also show a distribution of times. Accordingly, there would be a distribution of reaction rate constants in diffusion-controlled reactions in ultraviscous liquids, and the average value of the rate constant would show a non-Arrhenius temperature variation. Calorimetric studies have shown these effects when isothermally occurring polymerization changes from mass-controlled to diffusion-controlled regime.^{39–41}

It is however possible to introduce a structural or static heterogeneity at the nanometer scale by using nanoparticles of metals or ceramics in a liquid. These may hinder diffusion but would produce a non-Newtonian viscosity of a solid–liquid suspension, and they themselves would not participate in a

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polymerization reaction. Phase separation of the mixture's components may also occur by spinodal decomposition before polymerization is complete,^{7,42,43} and thus have the effect of changing the polymerization rate. We consider an alternative to these two, that is, to introduce relatively rigid molecules that participate in the chemical reaction and become a dynamic part of the liquid's structure, while remaining unobservable in structural features. Here, we report an investigation of the effects of such nanometer-scale heterogeneities on the polymerization kinetics. We use a member of the polysiloxane family known as polyhedral oligomeric silsesquioxane (POSS), which has a general formula of $R(SiO_{1.5})_n$. It is comprised of a Si–O cage-like core with functional groups attached at the Si-vertices of the cage.

Nanocomposites of POSS-containing polymers have been studied by a number of groups. These were reviewed by Li et al.⁴⁴ in 2001. Since then, Win et al.⁴⁵ have shown that addition of 10 wt % POSS reduces the thermal pressure coefficient of an epoxy-diamine thermoset, thereby improving its mechanical properties on thermal cycling, and others have shown that incorporation of small amounts of POSS into epoxy-amine/anhydride mixtures, either as pendant groups or as reactants, improves flame retardancy,^{46,47} elasticity,^{48,49} dielectric,^{50,51} physical aging,⁵² and related properties. It has been found that in some cases POSS increases the glass–liquid transition temperature of the nanocomposites,^{52–54} and decreases it for others.^{50,55,56} Kinetics of polymerization of POSS-containing mixtures has also been studied. We will refer to these in the relevant discussion. Our study is focused on the changes in the overall kinetics of polymerization of a triamine with varying concentration of POSS and a diepoxide, ranging from POSS-free to diepoxide-free mixtures. Polymerization has been performed (i) by heating at a fixed rate and (ii) isothermally at 323 K. Effects of addition of 2 nm size POSS molecules on the polymerization kinetics are interpreted in terms of decoupling of the decrease in D_{av} from increase in η with time; that is, D_{av} is no longer proportional to $1/\eta$, and the Stokes–Einstein equation ceases to be valid, after the polymerization reactions become diffusion-controlled. The effect is analogous to that envisaged for supercooling of a liquid in which, as described in the Discussion, the temperature dependence of D_{av} decouples from that of η .

EXPERIMENTAL METHODS

Diethylenetriamine (DETA) was purchased from Sigma-Aldrich Chemicals, and diglycidyl ether of bisphenol A (DGEBA) was supplied by Miller-Stephenson, Mississauga, Ontario, Canada. The specified number of repeat units, n , in DGEBA is 0.14. For preparing mixtures, we used an average mol wt of 380 g/mol after LeMay et al.⁵⁷ The glycidyl–POSS compound EP0409 (POSS) was purchased from Hybrid Plastics in Hattiesburg, MS. According to the manufacturer, it contains water (<1% wt) in dissolved and/or suspension state. DETA is a very low viscosity liquid at room temperature, and both DGEBA and POSS are high viscosity liquids. Other relevant properties and the structures of DETA, DGEBA (commercial name EPON-828), and the glycidyl–POSS compound EP0409 (POSS) are listed in Table 1. Here, f refers to the functionality in terms of chemical reactive groups, that is, the amine protons in DETA and the epoxide groups in the DGEBA and POSS molecules, and EEW denotes the epoxide equivalent weight, the mass of the sample that contains 1 mol of the epoxide group.

The POSS liquid has a distribution of molecular sizes. Its molecule typically has 8–12 vertices and a glycidyl ether-bearing group attached to each vertex. The manufacturer and others⁵³ have stated this distribution as approximately 60% T10, 18% T12, 4% T8, where T refers to the vertices, and the remainder consists of larger sized silsesquioxanes, which may or may not be shaped as cages. To estimate the average mol wt and the average f , that is, the average number of epoxide groups per molecule, we assumed that the “larger sized, less defined silsesquioxanes” are also cage-structure molecules comprised of 9% T14 and 9% T16. Thus, the average mol wt is 1867 g/mol, and f is 11.2. The same value of f was found from measurements of rubbery modulus for the same POSS by Li et al.⁵³ They noted that the value of 11.2 for the effective f of POSS is slightly lower than the value of 11.8 expected on the basis of the functionality and distribution of the POSS cages in the mixture. In their calculation of $f = 11.2$, all of the increase in the rubbery modulus was attributed to an increase in cross-link density, and it was assumed that the rubber density changes with nanoparticle concentration in a way similar to the change measured in the glass density.

By using the average mol wt of 1867 g/mol and the manufacturer-specified density of 1.25 g/mL at 298 K, we determine the average diameter of the POSS molecule as 1.7 nm and refer to it as 2 nm size. By using the bond lengths and molecular model for POSS, we estimated this size as ~ 2 nm. At 298 K, the viscosity of the as-received POSS containing <1% water is stated as 48 P and that of DGEBA (Epon 828) as 110–150 P. Because the amount of ~ 1 wt % correspond to ~ 0.5 mol fraction of water in POSS and the viscosity of water is ~ 1 cP at 298 K, it would have lowered the viscosity considerably even if one assumes the solution to be ideal and the viscosity an additive property. Therefore, we deduce that removal of water from POSS would raise the viscosity significantly higher than 48 P.

A mixture of stoichiometric composition contains one epoxide group for every amine proton. Because 1 mol of DGEBA contains two epoxide groups and 1 mol of DETA contains five amine protons (2 with each NH_2 group and 1 with one NH group), a stoichiometric ratio for complete reaction for DGEBA:DETA is 1:0.40 (mol:mol). Because one POSS molecule contains on average 11.2 epoxide groups, 1 mol of POSS is equivalent to 5.6 mol of DGEBA in terms of the epoxides (0.1786 mol of POSS is chemically equivalent to 1 mol of DGEBA). For maintaining the stoichiometry, therefore, we vary the POSS mole fraction from 0 to 1 by replacing DGEBA by POSS. These compositions are listed in Table 2, in both wt % POSS (w_{POSS}) with respect to epoxide-containing compounds, and in mol % POSS (x_{POSS}), while maintaining stoichiometry of the epoxide groups to amine proton.

$$x_{POSS} = \frac{n_{POSS}}{n_{POSS} + n_{DGEBA}} \times 100\% \quad (1)$$

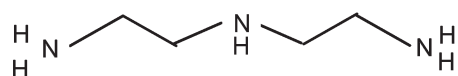
where n_{POSS} is the moles of POSS and n_{DGEBA} is the moles of DGEBA, and one may thus determine the wt % of POSS in the total wt of the mixture.

A differential scanning calorimeter model Q100 DSC manufactured by Thermal Analysis instruments was used for the study. It was calibrated by using sapphire and indium. Experiments were performed with uncovered pans, and 99.9% purity dry nitrogen was used as the purge gas. For preparing the mixture, DGEBA and POSS were weighed first, and then an appropriate (weighed) amount of DETA was added. The mixture was stirred by hand for several minutes until the solution appeared homogeneous. The sample mass was accurately determined to within 0.01 mg.

Table 1. Chemical Structure and Properties of the Three Components Used for Polymerization Studies^a

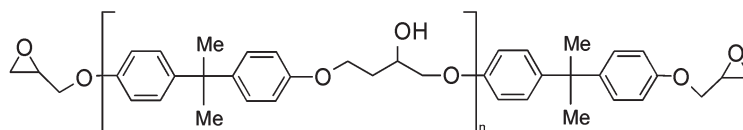
Diethylene triamine

DETA

density = 0.955 g/mL, mol wt = 103.2, $f = 5$ 

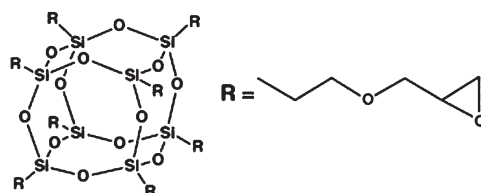
Diglycidyl ether of Bisphenol A

DGEBA

density = 1.16 g/mL, EEW = 186-192, $f = 2$ 

Oxirane, 2-[[3-(trimethoxysilyl)propoxy] methyl] – hydrolyzed

EP0409 (POSS)

density = 1.25 g/mL, EEW = 167, $f = 11.2$ ^a The density is at 298 K.Table 2. Compositions of the Polymerizing Mixtures in mole % and weight % of POSS and the Enthalpy of Polymerization Determined by Heating and That Obtained by Scaling^a

x_{POSS} (mol %)	w_{POSS} (wt %)	$\Delta H_{q,\text{average}}$ (kJ/mol epoxide)	ΔH_{scaled} (kJ/mol epoxide)	E_a ($\alpha = 0.4$) [kJ/mol]	E_a ($\alpha = 0.6$) [kJ/mol]	E_a ($\alpha = 0.8$) [kJ/mol]
0	0	109.7		60.3	63	69.6
2.0	8.9	103.8	109.2	59	59.5	53.4*
4.3	18.1	101.2	108.5	58.4	59.4	60.5
5.6	22.7	100.8	108.1	59.6	60.3	64.7
10.7	37.1	100.9	106.9	59.5	59.5	65.6
21.2	57.0	97.5	104.2	61.9	64.7	66.1
100	100	83.9		70.4	72	76

^a The epoxide groups are in stoichiometric ratio to amine protons for all compositions. (The fitting of the data in set marked with “*” was poor.)

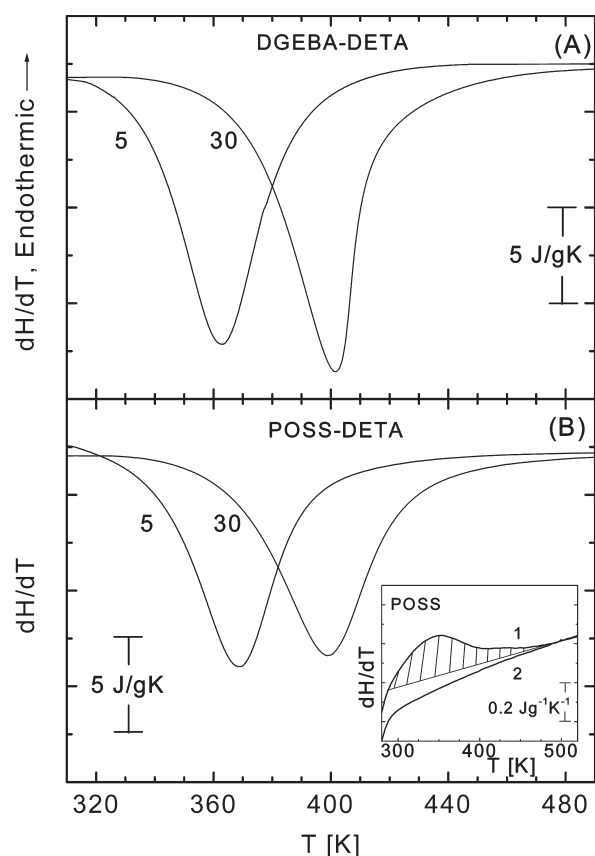


Figure 1. (A) The dH/dT plotted against the temperature for stoichiometric DGEBA-DETA mixture heated at rates of 5 and 30 K/min. (B) The corresponding plots for stoichiometric POSS-DETA mixture. Numbers next to the curves indicate heating rate. The inset in (B) is for POSS heated at 10 K/min (curve 1), cooled at the same rate to 273 K, and reheated at 10 K/min (curve 2).

For our study of polymerization kinetics during heating, the samples (from a mixture of a given composition) were heated from 303 K until a temperature was reached where the change in heat flow became negligible or undetectable. The heating rate q for each sample was 5, 10, 15, 20, and 30 K/min. The stock mixture was stored in a refrigerator at 278 K during the period over which these experiments were performed, which was less than 1 h. A freshly made mixture was used for studying the polymerization kinetics at a fixed T .

In addition to errors due to impurities present, the error in the compositions of the sample is at most $\pm 2\%$, which is due to weighing. The usual errors in the DSC measurements are 1–2%.

RESULTS

First, we describe the calorimetric features of the as-received POSS. A sample was cooled to 273 K and then heated at a rate q of 10 K/min to 525 K. The dH/dT plot obtained from the DSC scan is shown as curve 1 in Figure 1B (inset). There is a broad peak in dH/dT at 350 K, indicating an endothermic effect due to evaporation, melting, and/or molecular disaggregation occurring over a broad temperature range. The sample was thereafter cooled back to 273 K at 10 K/min and reheated at the same rate. Its dH/dT plot is shown as curve 2 in Figure 1B (inset). The enthalpy increase determined from the area between the

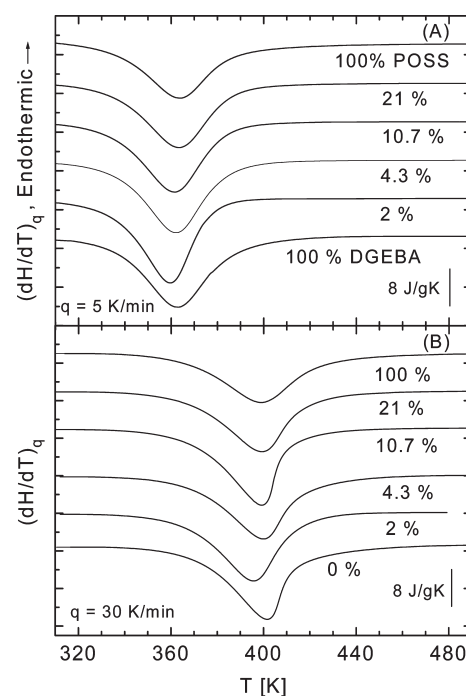


Figure 2. (A) The dH/dT plotted against the temperature for six stoichiometric [DGEBA-POSS]-DETA mixtures of varying compositions during their heating at 5 K/min. (B) The corresponding plots during heating at 30 K/min. The lowest curve is for DGEBA-DETA, and the highest curve is for POSS-DETA.

baseline and curve 1 is 16 J/g, and it was found that there is a weight loss of <0.3 mg per 15 mg of the sample. This loss was not taken into account for obtaining curve 2, and, partly for this reason, curve 2 lies below curve 1. The enthalpy of evaporation of water is 2.26 kJ/g (40.65 kJ/mol) at 373 K, and impurities dissolved in water decrease its vapor pressure and raise the boiling point. If attributed entirely to the evaporation of water, 16 J/g would correspond to 1 g of water in 142 g of POSS or $\sim 0.7\%$, which is within the specified amount of $<1\%$ water. Therefore, we attribute the endothermic peak to loss of (dispersed and/or dissolved) water from the sample. We will consider its effect on thermodynamics and kinetics of polymerization of the POSS-containing mixtures later here.

The plots of dH/dT against T for stoichiometric compositions of DGEBA-DETA (0% mol POSS) mixture heated at rates of 5 and 30 K/min are shown in Figure 1A, and the corresponding scans for the equivalent POSS-DETA (DGEBA-free) mixture are shown in Figure 1B. These plots show the thermodynamic effects of the change in the amounts of the reactants and products with time plus the effect of increase in the reaction rate constant with continuously increasing temperature. Therefore, both the profile of the curves and the net calorimetric effects observed differ for different heating rates. To investigate how thermodynamics and kinetics of polymerization change with the amount of POSS by replacing the equivalent amount of DGEBA, dH/dT of six mixtures measured for q of 5 K/min is plotted against T in Figure 2A and for q of 30 K/min in Figure 2B. The plots have been shifted vertically for clarity, and the curves are labeled by the mol % of POSS, x_{POSS} , in the polymerizing mixture. Because of their similarity with other plots, the plots for $q = 10, 15$ and 20 K/min of the six mixtures and all plots of 5.6% are excluded. Analysis of those data is included in the Discussion.

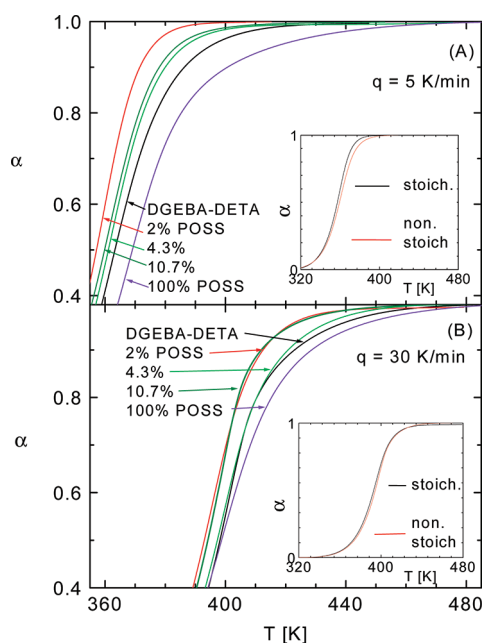


Figure 3. (A) The extent of polymerization, α , is plotted against the temperature for six stoichiometric [DGEBA-POSS]-DETA mixtures of varying compositions during their heating at 5 K/min. To show clearly the difference between the rate of increase in α , only the portion of the plots between $0.4 < \alpha < 1.0$ is shown. (The plots at $\alpha < 0.4$ showed differences in the slopes in a systematic manner and no crossover.) (B) The corresponding plots of the extent of polymerization during heating at 30 K/min. The insets in (A) and (B) are for the extent of polymerization of the nonstoichiometric mixture and its analogous stoichiometric mixture (2% POSS mixture) for the same heating rates of 5 and 30 K/min.

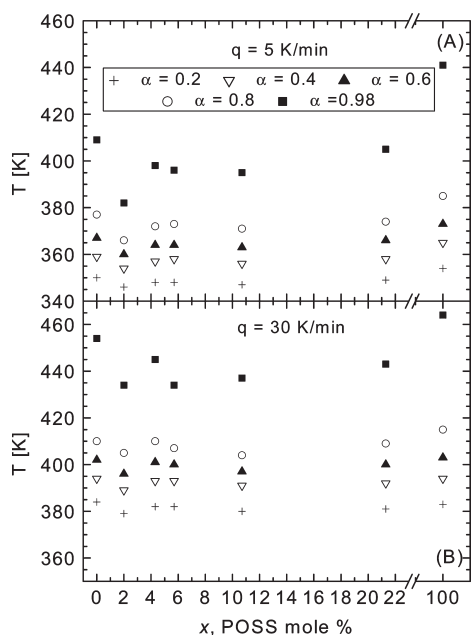


Figure 4. (A) The temperature at which the extent of polymerization equal to 0.2, 0.4, 0.6, 0.8, and 0.98 is reached during heating at 5 K/min is plotted against x_{POSS} , the mole % of POSS. (B) The corresponding plots by heating at 30 K/min.

The extent of polymerization, α , was determined from the partial integral of the dH/dT plot divided by the total area of a

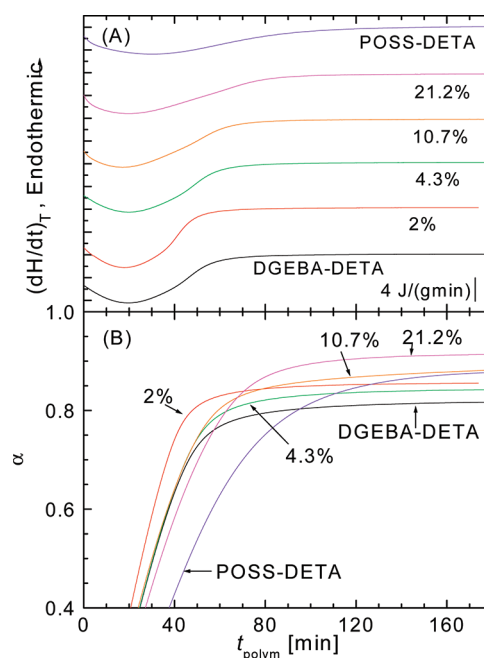


Figure 5. (A) The rate of heat released dH/dt during polymerization of stoichiometric [DGEBA-POSS]-DETA mixtures at a fixed temperature of 323 K is plotted against the elapsed time of polymerization, t_{polym} . (B) The corresponding plots of the extent of polymerization, α , against t_{polym} determined by taking into account the heat evolved on post polymerization by heating the partially polymerized samples at 10 K/min (data shown in Figure 6).

polymerization exotherm. The magnitude of dH/dT from the beginning of the plot to the postpeak plateau was used as a baseline. For all mixtures, the calculated value of α is plotted against T for q of 5 K/min in Figure 3A, and for q of 30 K/min in Figure 3B. To show clearly the difference between the rate of increase in α , only the portion of the plots between $0.4 < \alpha < 1.0$ is included. (The plots at $\alpha < 0.4$ showed differences in the slopes in a systematic manner and showed no significant crossover.) To elaborate the effect of POSS-content on the kinetics of polymerization, the temperature at which α reaches values of 0.2, 0.4, 0.6, 0.8, and 0.98 on heating at 5 K/min is plotted against the mol % of POSS-content in the mixtures in Figure 4A, and the corresponding values for heating at 30 K/min are plotted in Figure 4B. These data contain errors from two sources: (i) the small extent of polymerization during the time interval between mixing the sample and beginning the DSC scan, (ii) loss from evaporation and convection effects from using open pans, and (iii) estimating the partial and full integral of the dH/dT against T plots needed to determine α .

Here, the 2% POSS mixture shows the fastest polymerization kinetics. The kinetics is slower for the 4.3% POSS mixture, but is still faster than that of the (POSS-free, stoichiometric) DGEBA-DETA mixture. Further addition of POSS makes the kinetics faster up to 10% POSS composition, and thereafter it begins to decrease. It is slowest for the POSS-alone, that is, stoichiometric POSS-DETA mixture. Thus, a small amount of POSS makes polymerization occur faster, and a larger amount makes it occur slower.

After we became aware of the effects of POSS addition on polymerization kinetics, we performed a study of a nonstoichiometric DGEBA and DETA mixture by heating at 5 and 30 K/min rate.

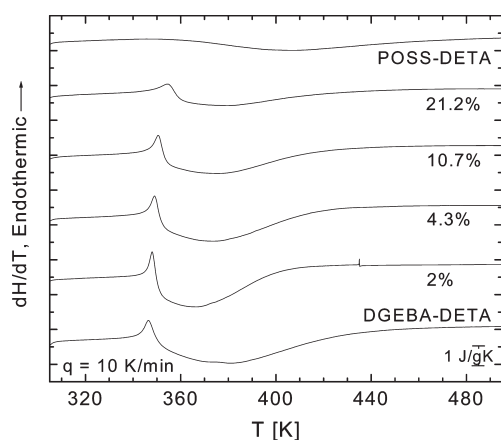


Figure 6. The dH/dT measured during postpolymerization of stoichiometric [DGEBA–POSS]–DETA mixtures on heating at 10 K/min. The samples were in the state obtained after polymerization at 323 K for which the data are given in Figure 5A. The sharp endothermic rise found for all compositions except for POSS–DETA indicates the onset of glass-softening; the peak appears when the rate of enthalpy gain due to physical process of structural recovery is equal to the rate of enthalpy loss due to polymerization reaction. The broad minimum after the peak is due to the heat released on further polymerization.

It contained the same molar amounts of DGEBA and DETA as the (stoichiometric) 2% POSS mixture, but without the POSS and thus less than the stoichiometric amount of the epoxide groups. The plots of α against T for stoichiometric 2% POSS mixture and nonstoichiometric DGEBA–DETA mixture for heating at 5 and 30 K/min are shown as insets in Figure 3A and B, respectively.

Figure 5A shows the plots of dH/dt against the polymerization time, t_{polym} obtained for the six mixtures kept at a fixed polymerization temperature T_{polym} of 323.2 K. In the classical description of chemical kinetics, polymerization occurs at a fixed rate constant, and the data show thermodynamic effects of the change in the amounts of the reactants and products with t_{polym} . In most polymerization studies, chemical reactions do not reach completion under isothermal conditions, and the heat evolved is less than the expected total value, ΔH_{total} . To determine ΔH_{total} after t_{polym} of 180 min, as indicated for each plot in Figure 5A, each sample was quenched to 303.2 K and was then heated from 303.2 to 523.2 K at 10 K/min, a process known as postpolymerization. These dH/dT plots are shown in Figure 6. The sharp endothermic rise present in the plots for all compositions, except the POSS-only mixture, is due to the onset of glass-softening to an ultraviscous liquid, the subsequent peak is due to the onset (or predominance) of further polymerization reactions in the ultraviscous liquid, and the broad minimum appearing after the peak is due to the heat released on further polymerization as the rate constant increases with increasing T . This feature is highly broadened in the POSS–DETA mixture. Also, the temperature range of postpolymerization for the POSS-free sample appears broader than the others, and it decreases on initial addition of POSS and thereafter increases. This indicates that addition of POSS nanosize molecules initially increases the postpolymerization rate and its sensitivity to T and further that the magnitude of both effects decreases after a certain fractional amount of POSS is present. This aspect will be discussed later here. The heat evolved on postpolymerization at 10 K/min heating of the partially polymerized samples (shown in Figure 6) was determined and added to the heat evolved on isothermal

polymerization in Figure 5A. The extent of polymerization α was determined by using this sum, and its value is plotted against t_{polym} in Figure 5B.

Because our interest is in the physical chemistry of polymerization, we do not fit the various empirical relations for the kinetics of the diepoxide–amine polymerization^{58,59} to our data. These formalisms are generally based on classical reaction kinetics that include in some cases parameters referring to a change in the order of chemical reaction, but in all cases the formalism ignored the findings that classical kinetics equation do not apply when a chemical reaction in viscous liquids becomes diffusion-controlled. Recently, Corezzi et al.⁶⁰ have described the diepoxide–amine network polymerization rate in terms of a power law between the diffusion coefficient and the inverse of relaxation time. They combined together the diffusion rate constant k_D and chemical rate constant as in earlier studies, and related k_D to an empirical equation between the dielectric relaxation time and α , thus relating k_D to α .⁶⁰ Because of the empirical nature of their model, we do not use it. It is possible also to qualitatively interpret the results in terms of steric effects on chemical reactions, in which case rotational and translational diffusion of reacting groups can release the steric effects.

We now consider the extent to which our estimate for the enthalpy of polymerization would be affected by the heat absorbed on heating pure POSS. This is seen as an endotherm in Figure 1B, inset, of 16 J/g. It amounts to 4% of the total exotherm of the 450 J/g for the POSS–DETA mixtures, and its inclusion would decrease the enthalpy estimate by that amount. Yet, as part of this endotherm appears before the temperature of 303 K is reached, that is, before the onset of the dH/dT exotherm, an amount much smaller than 16 J/g should be included. Because preparation of the nanocomposites takes several minutes, it is likely that a portion of the contaminate will have evaporated prior to the DSC measurements. This would reduce the error in the enthalpy estimate to $\sim 2\%$. Correction to the α values is even smaller. Therefore, neglecting the effect due to heating POSS has little consequence for our interpretation.

We also estimate the activation energy for isoconversional condition, that is, by plotting the $\ln(q)$ against $1/T$ according to the equation:

$$\ln(q) \Big|_{\alpha} = \ln(q_0) - \frac{E_a}{RT} \Big|_{\alpha} \quad (2)$$

for a fixed value of conversion, that is, fixed α . Here, $\ln(q_0)$ is a constant in the high-temperature limit, E_a is the activation energy (per mole of the reactant), and T is the temperature. Development of this model-free equation has been discussed by Budrugeac et al.⁶¹ Their comparison of the isoconversion differential and integral methods showed that the values of E_a obtained by the two methods differ. These values were obtained for three values of α , 0.4, 0.6, and 0.8, using the differential method and are listed in Table 2. These show that E_a initially decreases with increase in the amount of POSS for a fixed α and then increases, and it also increases with increase in α , except for $x_{\text{POSS}} = 0.2$ at $\alpha = 0.8$, which is attributed to the poor fit to the scatter in the limited data.

DISCUSSION

Growth of a macromolecule in the amine–epoxide mixtures occurs by consecutive reactions in the following sequence: One

H atom of the —NH_2 group of the diamine combines with the —O— of the epoxide (cyclic ether) ring, thus forming an —OH group and opening the terminal epoxide ring. The N atom thus becomes covalently bonded to the terminal C atom of the epoxide group attached to a molecule. Next the second H atom of the now more sterically hindered —NH— group in the $\text{R—NH—(CH}_2\text{)}_n\text{—NH}_2$ of the diamine reacts similarly with the terminal epoxide group of another molecule, producing a network structure. Thus, by losing its amine protons, a multiamine molecule forms a cross-linked molecule with several epoxide group-bearing molecules according to the number of N atoms present. The number of —OH groups formed with the O atom of the epoxide group is equal to the number of covalent bonds formed between the N and C atoms in the macromolecule. This is the usual polymerization mechanism in a stoichiometric composition. A further reaction called etherification is also occasionally considered.⁶² It is found to be significant when the epoxide amount is in excess, or when polymerization is performed at elevated temperatures.^{62,63} At low temperatures, the liquid may vitrify before the reaction has reached completion; at high temperatures, it may remain fluid even though the reaction may reach completion.

In physical terms, as chemical reactions occur to form larger covalently bonded entities with time, molecular diffusion becomes slower and η increases. The reaction gradually becomes diffusion-controlled, and thereafter any further decrease in the diffusion coefficient slows the polymerization rate, whose albeit slower occurrence leads to a further decrease in the diffusion coefficient. Thus, negative feedback is established between polymerization reactions and molecular diffusion; that is, occurrence of one slows the other and the liquid vitrifies isothermally, and polymerization becomes unobservable on the experiment's time scale. If the vitrified state is heated, the diffusion coefficient increases and polymerization occurs further and continues until a temperature is reached at which a chemical equilibrium between the unreacted and reacted species is established. The equilibrium constant of polymerization reactions is extremely large, and as only a negligibly small number of epoxide and amine groups of the molecules remain unreacted, the network structure is said to be almost complete. Although the majority of epoxy–amine–silsesquioxane nanocomposites studies have focused on mechanical and thermal properties, there have been sufficient studies on polymerization kinetics of mixtures similar to ours, and we will consider their relevance.

First, we discuss the reactivity of pure POSS–triamine mixture, which shows slower kinetics than pure DGEBA–triamine mixture according to the plots shown in Figures 3 and 5B. The so-called lower reactivity of mono- and polyfunctional POSS with diamines has been attributed to increased steric hindrance.⁶⁴ On the basis of their calorimetric studies, Teo et al.⁵⁴ reported that the kinetics of polymerization of mixtures of octakis(dimethylsiloxybutyl epoxide)–POSS with hexahydrophthalic anhydride is significantly slower than the kinetics of the corresponding mixtures of epoxy resin N,N,N',N' -tetraglycidyl-4,4'-diaminodiphenyl methane. While they did not indicate variation of polymerization kinetics with the fractional amount of POSS, they did report that premixing POSS with the anhydride before adding their epoxy resin improved homogeneity as well as the physical properties of the nanocomposite formed. Li et al.⁵³ observed that addition of 10% POSS in a DGEBA–tetrafunctional amine mixture decreased the polymerization rate, and further postcuring at a higher temperature was necessary to achieve complete cross-linking. We also note Zhang et al.'s⁶⁵ finding

that amine-terminated POSS in a DGEBA–diamino-sulfone system decreased the polymerization rate. This is contrary to our results for the epoxide–POSS with DGEBA–DETA mixture and indicates that different reactant groups on POSS and different amines have different effects on the polymerization kinetics.

Ramirez et al.⁶⁶ studied the kinetics of DGEBA and diamine (4,4'-(1,3-phenylenediisopropylidene) bis aniline) with octa-epoxy-cyclohexyldimethylsilyl–POSS, whose functional groups are not only slightly bulkier than the POSS used in this study, but also the epoxides are attached to cycloaliphatic rings as opposed to an aliphatic chain of EP0409. By using ATR-FTIR to analyze the relative reactions of POSS and DGEBA, they found that 5 wt % POSS accelerates the rate at which the DGEBA glycidyl epoxy rings open, thus accelerating the reaction. They concluded that POSS itself does not participate in the polymerization reactions; that is, it behaves as a catalyst even though it contains epoxide groups that can react with the amine proton. Although they did not describe why or how the epoxy-cyclohexyl–POSS catalyzes the opening of DGEBA glycidyl rings, they were able to model the kinetic process. Our calorimetric experiments do show an increase in the polymerization rate on initial addition of POSS. By using a variety of techniques, Strachota et al.⁶⁴ have studied polymerization of mixtures of glycidylexypropyl-heptaphenyl POSS and of three other POSS molecules of different chain lengths with poly(oxypropylene) diamines and DGEBA. They concluded that POSS molecules are less reactive with the amines than the DGEBA molecules; that is, the reaction with POSS is slower than that with DGEBA. It is evident that polymerization kinetics changes differently with different POSS composition and phase separation may occur for different types of POSS. Studies of different silsesquioxane mixtures and its substituents have shown phase separation.^{64,67,68}

It has been known since the 1950s^{69,70} that hydroxyl and other groups capable of forming H-bonds increase the polymerization rate, presumably by creating a dipole that favors the reaction by acting as an electrophile that donates a proton to the terminal epoxide —O— group. The kinetics of the third-order-catalyzed reaction being faster seemed to dominate autocatalysis, and autocatalysis being even slower than that would in turn dominate the kinetics of noncatalytic reactions. Because the silsesquioxane nucleus is inert, any catalytic behavior would be due to the functional groups. In this respect, Perrin et al.⁷¹ found, by using calorimetry, that quaternary ammonium salt functionalized POSS acts as a catalyst in DGEBA–poly(oxypropylene)-amine mixtures. Ghaemy et al.⁶³ concluded that the —OH groups from nanosilica particles accelerated the rate of reaction between DGEBA and DDA (4,4'-diaminophenylamino, a triamine that resembles DETA in molecular architecture), and similar effects were observed by Fu et al.,⁷² which they related to the silanol groups of the phenyl-trisilanol POSS they used. Ragosta et al.⁵⁶ used Fourier transform near-infrared spectra to study the kinetics of DGEBA with diamino disulfone (DDS) and found that the reactivity of 20 wt % octa glycidyl–POSS mixture is comparable with that of the DGEBA-containing mixtures. Moreover, the postcuring kinetics, performed isothermally, of 20 wt % POSS-containing samples was slower than that of the POSS-free samples, and they attributed this to the increased steric hindrance induced by the silsesquioxanes. The decrease in reactivity for isothermal postcuring (at a higher temperature) is the opposite of the increased reactivity observed in our postcuring studies performed by heating.

In contrast to the above reviewed studies, we discuss the physical chemistry of the effects of POSS as a substituent for DGEBA, in particular, (i) of the change in the total enthalpy loss on polymerization, (ii) of the kinetics of postpolymerization, and (iii) of the effects of nm size static heterogeneities on the kinetics of polymerization.

i. Effects of POSS on Thermodynamics of Polymerization.

First, we consider the enthalpy decrease on polymerization, ΔH_q , which was obtained by heating experiments at different q . The net error in these values is at most 4%. The data showed that for 100 mol % DGEBA mixture, ΔH_q is 109.7 ± 2.5 kJ/(mol epoxide group), and it decreases with an increase in the mol % of the substituent POSS. (Because the mixtures are stoichiometric with respect to the epoxide group and amine hydrogen, ΔH_q per mole of epoxide group is the same as per mole of amine hydrogen.) For less than 21 mol % POSS-mixture, it was found that ΔH_q did not change with q in the range 5–30 K/min, within the experimental error. For the 100 mol % POSS mixture, ΔH_q was 83.9 ± 3.5 kJ/mol of epoxide. It varied with q without a systematic trend but remained within ± 4 kJ. (The fluctuation would seem more pronounced if ΔH_q were expressed in units of J/g of the mixture, which shows that per mole units are to be used.) Nevertheless, the results showed that ΔH_q decreases when DGEBA is substituted by POSS.

The data showed a similar effect in the enthalpy decrease, ΔH_{iso} , measured during isothermal polymerization at 323 K. ΔH_{iso} remains constant at 84.6 ± 2.9 kJ/(mol epoxide group) in the 0–21 mol % POSS range, and thereafter ΔH_{iso} decreased to 65.5 kJ/(mol epoxide group) for 100 mol % POSS. Over this composition range, the enthalpy released on post polymerization, ΔH_{post} , remained in the range of 16.1 ± 5.5 kJ/mol, but decreased slightly with POSS content. The total heat evolved, $\Delta H_{\text{total}} = \Delta H_{\text{iso}} + \Delta H_{\text{post}}$ was less than ΔH_q for 0, 10.7, 21, and 100 mol % POSS mixtures but was about the same for the other three compositions.

It is evident that substitution of DGEBA by POSS in stoichiometric mixtures with DETA decreases the enthalpy of polymerization, ΔH_{polym} . The decrease is unlikely to be attributed to some of the epoxy groups in POSS not reacting with the amine protons because ΔH_{polym} includes ΔH_{post} and post polymerization is expected to allow complete reaction. For a full reaction, FTIR studies would show no peak associated with (cyclic ether of) the epoxy group, but as the study requires calibration of the peak height against the extent of reaction by using other methods, it was not performed. The maximum number of covalent bonds that can form on polymerization in these mixtures is $5N_A$, where N_A is the Avogadro number. If the enthalpy change on bond formation did not depend upon the number of covalent bonds already formed, the decrease in ΔH_{polym} would indicate that the enthalpy loss per bond formation is less with the POSS–epoxide groups than with the DGEBA–epoxide groups. To investigate this, we determined whether ΔH_{polym} values of the mixtures scale with the POSS concentration in mole fraction by using the relation, $\Delta H_{\text{scaled}} = [x_{\text{DGEBA}} \times (\text{the average } \Delta H_q \text{ for DGEBA–DETA}) + x_{\text{POSS}} \times (\text{the average } \Delta H_q \text{ for POSS–DETA})]/100$. In kJ/(mol of epoxide group), the values obtained by scaling and the values measured from heating experiments are listed in Table 2. The difference between the two sets of values is within experimental errors. We conclude that the enthalpy of polymerization of the mixture is additive; that is, the enthalpy loss per covalent bond formation does not depend upon the bonds already present.

In general, the enthalpy of covalent bond formation is expected to vary with the size and electrical characteristics of the molecule to which the epoxide group is attached and to which the amine proton is attached. Because this enthalpy is observed to be less for the POSS than for the DGEBA mixture here, it indicates that the energy of formation of the covalent bond between the epoxide terminal C and the amine nitrogen is less (i.e., the bond formation is less exothermic) for POSS than for the DGEBA. This means that if the energies of the unreacted states of POSS–DETA mixture and the DGEBA–DETA mixtures were the same, the energy of the polymerized state with POSS would be higher than that of the polymerized state with DGEBA. If the energies of the unreacted mixtures differed, the energy of the polymerized states would be such that the decrease is less for the polymerized state with POSS than that with the diepoxide. This can be verified by specific heat measurements of the reactants and products.

ii. Effect of POSS-Nanoheterogeneity on Polymerization

Kinetics. As mentioned earlier here, POSS containing $\sim 1\%$ water is reported to be less viscous ($\eta = 48$ P) than DGEBA ($\eta = 110$ P) at 298 K, and it is much more viscous than DETA. According to the activated complex theory for reaction kinetics, chemical reactions occur when two entities come within a certain distance to form the activated complex. When the probability of reaching such a distance is high or the time taken is less, the reaction is expected to occur faster. Therefore, if the additivity rule for an ideal solution were to be valid for η of a hydrogen-bonded ternary mixture, η of the unreacted mixture would decrease on increasing x_{POSS} , and one would expect that the η -related diffusion times of the DGEBA, DETA, and POSS molecules in the mixture would all decrease. Accordingly, in a viscosity-controlled mechanism, all POSS-containing mixtures would be expected to polymerize more rapidly than the (POSS-free) DGEBA–DETA mixture, and the POSS–DETA mixture to polymerize most rapidly. However, the plots of α in Figure 5 show that only the 2–10.7% POSS mixture polymerizes more rapidly than DGEBA–DETA mixture, the POSS–DETA mixture polymerizes at the slowest rate, and there is a crossover of the plots for the 21% POSS-mixtures. This is also evident from the plots of α against T in Figure 3.

As noted earlier, the 2 nm size POSS molecule contains on average 11.2 epoxide groups, about 6 times as many as the 1 nm diameter DGEBA molecule. Therefore, one 2 nm size POSS molecule replaces about six, 1 nm size DGEBA molecules to maintain stoichiometry. (The 1 nm size of DGEBA was estimated by using mol wt of 380 and density of 1.16 g/mL, assuming that the molecule is folded into a sphere.) The above-noted amount of ~ 1 wt % water corresponds to ~ 0.5 mol fraction of water in POSS. Because η of water is ~ 1 cP at 298 K, it would have lowered the viscosity of POSS considerably. Therefore, loss of this water from POSS during the heating to the polymerization temperature in our experiments would have raised the viscosity to a value higher than that of DGEBA such that η of the mixture increases on increasing x_{POSS} . Moreover, nonideal solutions do not obey the mixture rules of transport properties, particularly when hydrogen bonding occurs. For these reasons also, it is not surprising that the behavior of α observed in Figures 3 and 5 is inconsistent with the monotonic decrease in η on addition of POSS to the DGEBA–DETA mixture. We also point out that dielectric studies^{3–6} on the effect of pressure on the rate of polymerization have shown that the polymerization becomes faster as η increases on application of a hydrostatic pressure.

Therefore, it does not seem appropriate to consider that decrease in η on initial addition of POSS increases the polymerization rate.

In estimating the average size of a POSS molecule as 2 nm, we assumed that the long-chain functional groups in POSS are folded such as to envelop the siloxane cage. In their unfolded state, the distance of approach for chemical reaction would vary from site to site, and it is not certain how the three types of molecules are distributed in either their pure or the mixed liquid states. Therefore, we need to restrict our discussion to the phenomenology of polymerization. Ramirez et al.⁶⁶ found that epoxycyclohexyl–POSS did not react in their polymerizing mixtures. Further to our findings from post-polymerization we investigate whether all epoxy–POSS groups in our mixtures chemically react. For this purpose, we prepared a nonstoichiometric mixture by reducing the amount of epoxide groups by 10% below stoichiometric amount (i.e., the amount of DETA is greater than that needed by stoichiometry). This mixture is the nonstoichiometric DGEBA–DETA. It contains the same number of moles of DGEBA as in the 2% POSS mixture but without POSS. We expect that both ΔH_q and the shape of the α against T plots for this mixture would provide information on the effects of POSS epoxide groups in polymerization. The ΔH_q obtained for the nonstoichiometric DGEBA–DETA is 107.9 kJ/(mol epoxide groups) and is comparable with its scaled estimate value of 109.7 but is slightly more than $\Delta H_q = 103.8$ kJ/(mol epoxide groups) for 2% mixture ($\Delta H_{\text{scaled}} = 109.1$). The difference between ΔH_q and ΔH_{scaled} for the nonstoichiometric mixture is 1.6%, while that for 2% POSS mixture is 5%. Therefore, when scaling is done with the enthalpy of polymerization with 100% POSS and with 100% DGEBA, the scaled and measured values for all mixtures agree within 5–7%.

For convenience of discussion, the plot of α against T for the nonstoichiometric mixture is added as the red line in the insets of Figure 3A and B. It shows that when the mixture contains less amount of epoxide (or greater amount of DETA) than stoichiometric, polymerization is faster than for DGEBA–DETA but slightly slower than the 2% mixture. This is consistent with the earlier finding by calorimetry⁷³ and dielectric measurements^{74,75} that when the amount of DGEBA is less than (or the amount of the amine is more than) the stoichiometric requirement, polymerization becomes faster, although some partially reacted diamine persists in the polymerized mixture. The proximity of the plots for stoichiometric compositions and for the nonstoichiometric compositions shown in the Figure 3 inset increases when q is increased from 5 to 30 K/min. This indicates that when the POSS concentration in a stoichiometric mixture is extremely low, its effect is similar to the effect of starving the mixture in epoxide groups or saturating in the amine.^{73–75} The water present as impurity in the POSS liquid may contribute to polymerization kinetics, but as some of the water evaporates on heating, its role in polymerization kinetics is uncertain.

Studies have shown that multifunctional glycidyl POSS molecules are less likely to form aggregates in epoxy solutions as compared to those with inert molecules or those with monofunctional groups.^{48,64} This is also evident from our finding that there is a systematic trend in the change in the reaction rate kinetics with increase in the amount of POSS, suggesting that any nanoaggregation that might have occurred is insignificant. The nucleus of a POSS molecule, the silsesquioxane of which consists of Si–O bonds, is enveloped by the C–C chains containing the epoxide groups at their ends and which makes it multifunctional. Therefore, POSS is not expected to form aggregates in a solution

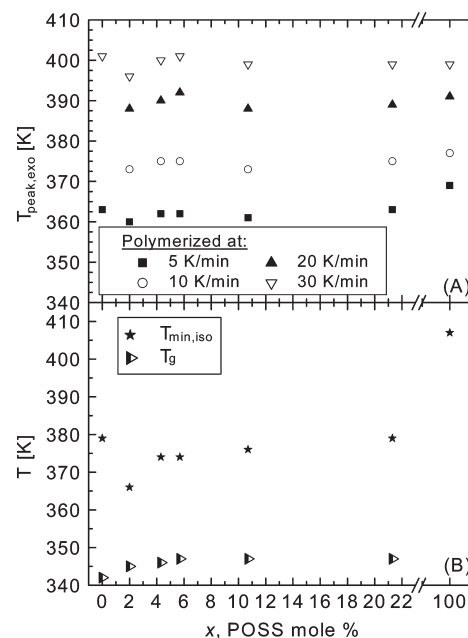


Figure 7. (A) The plots of the temperature of exothermic minimum, $T_{\text{min,exo}}$, observed on heating at 5, 10, 20, and 30 K/min rate against x_{POSS} , the mol % amount of POSS in the mixtures. (B) The corresponding plots of the onset temperature of glass-softening, T_g , and of the peak temperature, $T_{\text{peak,iso}}$, observed during heating the isothermally polymerized sample at 10 K/min.

of DGEBA and DETA. Moreover, studies by using SEM techniques by Mariani et al.⁷⁶ have shown that a similar POSS (octa epoxy-cyclohexyl) compound in a DGEBA–DETA mixture did not show aggregation. They note, however, that X-ray diffraction⁷⁶ has shown minor amounts of Si crystal-like aggregation in the solution of an 8% wt POSS mixture.

The exothermic part of the dH/dT plots in Figure 6 is due to polymerization of the ultraviscous liquid obtained on heating the glassy state, a process also known as postcuring or postpolymerization. It is done to achieve full or the maximum polymerization. The plots show how POSS addition effects postpolymerization on heating the glassy state obtained after polymerization at 323 K. As mentioned earlier, the exotherm begins after the sample has been heated through the temperature range of its glass–liquid transition, as made evident by an endothermic peak of varying sharpness (Figure 7). The height of this peak is determined by (i) the broadness of the T_g endotherm, (ii) any structural relaxation of the polymerized state during heating and the consequent overshoot in the specific heat due to enthalpy recovery, and (iii) growth of the macromolecule and the consequent loss of enthalpy immediately after η of the liquid has decreased on heating. Processes (i) and (ii) are physical in nature, reversible, and are observed for all chemically stable glasses. Process (iii) is chemical in nature, irreversible, and is observed when chemical reactions occur. The plots show that this peak height increases on initial addition of POSS substitution for DGEBA. It then decreases and vanishes when POSS has replaced all DGEBA.

Concomitantly, the postpolymerization exotherm first becomes narrower and then broadens to almost beyond recognition for POSS–DETA, and the exothermic minimum shifts first to a lower T and thereafter gradually to higher T . ΔH for postpolymerization decreases with increasing amounts of POSS,

and this indicates that the POSS-containing samples achieve a higher extent of reaction (Figure 5B) in comparison to the DGEBA–DETA mixture; that is, it is easier to form an almost infinitely connected covalent bond network with POSS-containing mixtures than with POSS-free mixture.

iii. Static Heterogeneity of Nanoscopic POSS and Dynamic Heterogeneity. We now consider how physical consequences of polymerization, increase in η and decrease in the average diffusion coefficient, D_{av} , bear upon the kinetics of a macromolecule's growth. It is well-known that the reaction rate kinetics in low-viscosity liquids is mass-controlled and is described by the laws of classical reaction kinetics. Yet in polymerization reactions, the growth of a macromolecule results in a continuous increase in viscosity, for which the classical laws would not be applicable. Such chemical reactions have been mathematically treated as Brownian diffusion in which the diffusing particles coalesce when they come within a certain distance of mutual approach, with the consequence that the particle size increases and D_{av} decreases with time. (For a brief review of the subject, ref 1 and 60 may be consulted.) Accordingly, it is accepted that a chemical reaction becomes diffusion-controlled when E_D^* , the activation energy for the diffusion of the relevant molecules, A and B, exceeds E^* , the activation energy for the chemical reaction. Here, the absolute values of E_D^* and E^* are not required, only that $(E_D^* - E^*)$ change from negative to positive at a certain value of α or t_{polym} . As macromolecules grow and η increases, the rate of diffusion, instead of the mass of the reactants, begins to control the rate at which polymerization reactions may occur. As long as the reaction is mass-controlled in the beginning of the reaction at low viscosity, increase in η at fixed T has little effect on the reaction kinetics. When T is already low and η of the polymerizing mixture is high, polymerization reactions would be diffusion-controlled from the beginning; as T is increased at a fixed rate, the reactions would become mass-controlled when η has decreased to a relatively small value at high temperatures.

Smoluchowski⁷⁷ showed that the rate constant, k_{diff} for a diffusion-controlled reaction of spherical solute molecules of radii R_A and R_B undergoing Brownian motions in a viscous liquid is related to their respective diffusivities D_A and D_B by:

$$k_{diff} = 4\pi(D_A + D_B)(R_A + R_B) \quad (3)$$

Others, especially Waite,⁷⁸ have further developed Smoluchowski's equation. Calef and Deutch⁷⁹ have reviewed these developments, replaced D by the viscosity of the solvent, η_s , according to the Stokes–Einstein equation, and rewrote eq 3, which we adapt for the case of polymerization as,

$$k_{diff}(t_{polym}) = \frac{2RT}{3\eta_s(t_{polym})} \left[\frac{[R_A(t_{polym}) + R_B(t_{polym})]^2}{R_A(t_{polym})R_B(t_{polym})} \right] \quad (4)$$

where R is the gas constant and the variables change with time, t_{polym} . The η_s and size of reacting solute molecules increase with time. According to eq 3, k_{diff} is proportional to $[(R_A + R_B)^2 / \eta_s R_A R_B]$. In a polymerization process, $(R_A + R_B)^2$ increases more rapidly with t_{polym} than does $R_A R_B$. Therefore, for k_{diff} to decrease with t_{polym} , it is required that η_s increase more rapidly than the term $[(R_A + R_B)^2 / R_A R_B]$. When the reacting site of a molecule is enveloped by the nonreacting part of the remaining molecule, the reaction rate is additionally determined by the internal motions of that part of the molecule that shields the active site from

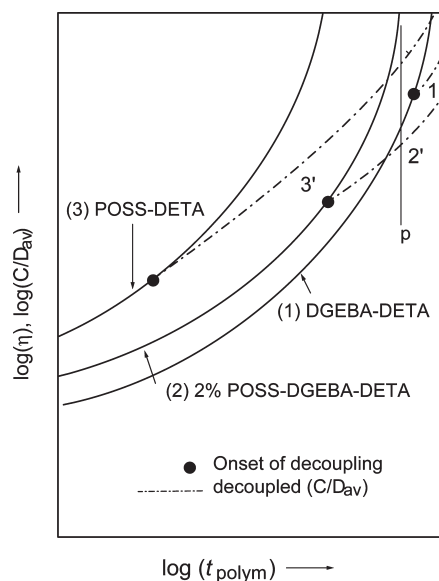


Figure 8. Depiction of the decoupling of the inverse of average diffusion coefficient (— · — · —) from viscosity (—) as the polymerization time increases. The dot indicates the condition at which decoupling is suggested to occur. At the time denoted by vertical line at p , polymerization occurs in the viscosity controlled zone for the DGEBA–DETA mixture, but in the decoupled diffusion-controlled zone for the 2% POSS–DGEBA–DETA mixture, where it is faster, and still in the decoupled diffusion-controlled zone for the POSS–DETA mixture, where it is slower.

reaction, and it becomes difficult to establish a direct relation between the diffusion coefficients, η_s and k_{diff} .

In a recent monograph, Ngai⁸⁰ has described, in comprehensive detail, the changes in the dynamics of ultraviscous liquids and glasses with changes in T , pressure, and composition, and their molecular interpretations, which one may consult for details. The gradual change from Arrhenius variation of η with T to a non-Arrhenius variation on supercooling a liquid has also been explained by postulating that a heterogeneity develops in the dynamic properties of liquids;^{81–90} that is, the molecular diffusion coefficient in the bulk of liquid varies from site to site, and this variation can be several orders of magnitude different in two regions only a few tens of nanometers distant from each other.⁸⁵ This is then related to the distribution of relaxation times,^{81–90} and it has also been argued that when the behavior changes from Arrhenius to non-Arrhenius, not only departure from exponential relaxation (related to diffusion coefficient) occurs but molecular diffusion coefficient becomes decoupled from viscosity.^{81–90} The decoupling refers to the finding that the product ηD_{av} ceases to remain constant with changing T on supercooling a liquid as η increases. The measured diffusion coefficient differs by as much as 2 orders of magnitude⁹⁰ from the value obtained from viscosity by using the Stokes–Einstein equation. The finding is attributed to the increasing difference between translational and rotational diffusion coefficients as dynamic heterogeneity develops. It has a lesser effect on translational motions than either on the rotation motions or on the motions that determine η .^{81–86} The heterogeneity measured on a length scale corresponds to about 2 nm, and it represents the size of domains in which molecules move slowly than in the intervening domains.

The progressive (reversible) increase in the relaxation time (and η) observed on supercooling a liquid has been shown to be

qualitatively similar to the (irreversible) increase in the dielectric relaxation time (and η) with t_{polym} .⁹¹ Therefore, we extend the notion of the development of dynamic heterogeneity as η increases on supercooling a liquid to the development of dynamic heterogeneity as η increases (irreversibly) on isothermally polymerizing a liquid, recognizing the fact that relaxation features of polymers are qualitatively indistinguishable from those of molecular liquids.^{92,93} Both the dynamic heterogeneity and the added nanometer-size static POSS heterogeneity are expected to increase η with t_{polym} , as the reaction mechanism changes from mass-controlled to diffusion-controlled, and both would have an effect on k_{diff} .

According to the view of heterogeneous dynamics, the plots of $\log \eta$ and $\log(C/D_{\text{av}})$ against $1/T$, where C is the constant of proportionality in the Stokes–Einstein relation ($\eta = C/D_{\text{av}}$), show that η and C/D_{av} increase along the same curve initially on supercooling. Gradually, the increase in C/D_{av} becomes slower than the increase in η , and the two increase along different curves. Similarly, the plots of $\log \eta$ and $\log(C/D_{\text{av}})$ against t_{polym} would show that η and C/D_{av} increase along the same curve initially, and then, gradually, the increase in C/D_{av} (decrease in D_{av} and in k_{diff}) becomes slower, C/D_{av} decouples from η , and the two quantities increase along different curves. This is depicted in Figure 8 where the “●” indicates the onset of decoupling or of deviation from the Stokes–Einstein equation. The viscosity-controlled zone of polymerization on a given plot is before this onset, and the diffusion-controlled zone is after it. The $\log(C/D_{\text{av}})$ plot against t_{polym} for one mixture crosses the $\log(\eta)$ plot of the other mixture, but neither the plots of $\log(C/D_{\text{av}})$ for different compositions cross each other nor the plots of their $\log(\eta)$. For the DGEBA–DETA mixture ($x_{\text{POSS}} = 0$), decoupling is depicted to occur at a higher η because in this case dynamic heterogeneity develops intrinsically as η increases and most of the polymerization would occur in the viscosity-controlled zone. When POSS is first added, η of the 2% mixture is already slightly higher than that of the POSS-free mixture from the beginning of the reaction. (As described here earlier, the ternary mixture is taken as a nonideal solution, and removal of ~ 1 wt % water from the as-received POSS during heating to the polymerization temperature is assumed to have raised its viscosity to a value higher than that of DGEBA, albeit by a small amount.) In the presence of static heterogeneity of POSS molecules, decoupling occurs at a lower η value. Thus, the plot of C/D_{av} against t_{polym} for the 2% POSS mixture crosses the plot of η for the DGEBA–DETA mixture (Figure 8). In the decoupled zone, C/D_{av} of the 2% mixture is less than η of the DGEBA–DETA mixture.

Because k_{diff} varies as D_{av} (higher k_{diff} for lower C/D_{av}), polymerization in the decoupled diffusion-controlled zone for the 2% POSS mixture would be faster than polymerization in the viscosity-controlled zone for the DGEBA–DETA (POSS-free) mixture. Further increase in structural heterogeneity by adding POSS would cause decoupling to occur sooner. The diffusion time in the decoupled zone increases, and polymerization kinetics of the (POSS-alone) POSS–DETA mixture occurring in this zone at a given time is the slowest. This is indicated by the vertical line labeled “p” in Figure 8. Here, polymerization occurs in the η -controlled zone for the DGEBA–DETA mixture, in the decoupled diffusion-controlled zone for 2% POSS–DGEBA–DETA mixture where it is faster, and still in the decoupled zone for POSS–DETA mixture, where it is the slowest. Addition of the static heterogeneity in the polymerization process may be treated in the same manner as the development of dynamic

heterogeneity. This conclusion may be tested by measuring the relaxation time, diffusion coefficient, or viscosity of polymerizing liquids, or by investigating the effect of POSS on the dynamic behavior of a nonpolymerizing, preferably of a rigid molecular, liquid.^{92–94}

In a series of papers^{95,96} and in a monograph,⁹⁷ Plonka has shown that dynamic processes in a condensed phase are dispersive in nature in which many time scales of diffusion and reaction coexist. Accordingly, k depends on time. This is rationalized by the fact that chemical reactions disturb reactivity distributions of the reactants in condensed media, as the more reactive species are the first ones to disappear from the system. The ratio of the reactions rates to the rate of internal rearrangements (mixing) in the system restores the initial distribution of reactivity. When the extent of disturbance is negligible, the rate follows approximately the classical reaction kinetics. Yet when the rates of chemical reactions exceed the rates of internal rearrangements, the initial distributions in reactant reactivity are not preserved during the course of reactions and the k depends on time. This is equivalent to a distribution of both the reaction and the relaxation rates. He has discussed the dependence of reaction rates on viscosity in detail.^{95–97}

CONCLUSIONS

The presence of a small amount of chemically reacting, structural, or static heterogeneity of 2 nm size polyhedral oligomeric silsesquioxanes (POSS) in an otherwise homogeneous polymerizing mixture of diepoxide and triamine initially increases the rate of polymerization. Larger amounts of POSS cause the polymerization to become progressively slower. When POSS alone is used for polymerization with triamine, the kinetics of a macromolecule’s growth becomes too slow, and for the same polymerizing conditions and it takes unusually long time for the liquid to reach vitrification. Addition of POSS decreases the enthalpy of polymerization and broadens the glass–liquid transition endotherm of the partially polymerized state. It is argued that the kinetics of polymerization, like that of other chemical reactions,^{95–97} and of molecular relaxation processes, is dispersive.

In an interpretation based on decoupling of molecular diffusion from viscosity, polymerization of a mixture occurs initially in the viscosity-controlled zone and later in the decoupled diffusion-controlled zone. It is suggested that decoupling occurs at a lower viscosity or sooner in time during isothermal polymerization of (water-free) POSS-containing mixtures. In the POSS-free mixture with only dynamic heterogeneity, most of the polymerization occurs in the viscosity-controlled zone. Addition of 2% structural heterogeneity causes decoupling to occur sooner, polymerization occurs mostly in the decoupled diffusion-controlled zone, and the kinetics is faster. Further increase in structural heterogeneity by adding POSS increases the diffusion time in the decoupled zone such that, ultimately, polymerization is slowest for the POSS-alone mixture.

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