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Hydrolysis and Condensation Coupling of (Trimethoxysilyl)phenyl-Terminated Polystyrene Macromonomers

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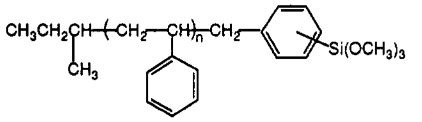
ABSTRACT: Anionically grown monofunctional polystyrene macromonomers are coupled through the hydrolysis and condensation of trimethoxysilyl end groups. Hydrolysis is initiated by adding acidified water to a tetrahydrofuran solution of the macromonomer. Condensation is facilitated by evaporating the solvent and heating the polymer under vacuum above the glass transition temperature. The macromonomers couple to form high molecular weight polymers and reach a finite size, beyond which further growth is inhibited. The final products are completely soluble star-shaped polymers, which are characterized by size-exclusion chromatography with molecular weight sensitive detectors. The molecular weight distributions of the stars are surprisingly narrow, although there are definitely mixtures of stars with different numbers of arms. The average number of arms in a star decreases as the molecular weight of the macromonomer increases. The final, limiting structures of the stars can be explained by the free energy changes associated with the number and length of arms. The results strongly suggest that the prevalent mode of growth at later stages of condensation becomes addition of macromonomer to stars, rather than addition of stars to stars. Studying the condensation coupling of the macromonomers provides understanding for more complicated network-forming systems; the technique also provides a unique method for synthesizing star-shaped polymers that has several advantages over other synthetic methods.

Introduction

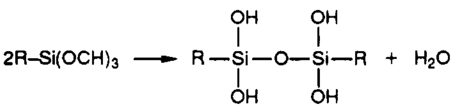
Coupling reactions between preformed polymer chains are an important part of polymer science and technology. Network-forming coupling reactions, such as the vulcanization of natural rubber, are some of the earliest examples.[1] More recently, coupling of reactive end groups on macromonomers has been used in the formation of many novel architectures, including networks,[2,3] stars,[4,5] and block and graft[6–8] polymers. Recently, we disclosed the synthesis and subsequent condensation of trimethoxysilyl-terminated polystyrene:[9,10]



(I)

This macromonomer is made by termination of a "living" anionic styrene polymerization with [*p*-(chloromethyl)-phenyl]trimethoxysilane, resulting in a single reactive terminal group on each chain. Predictable molecular weights are achieved by changing the ratio of initiator to monomer. The macromonomers are capable of reaction with each other by conventional sol-gel pathways.[11,12] Coupling proceeds in two steps: hydrolysis of the silicon alkoxide bond, followed by condensation of the resulting silanol to form siloxane linkages. The reactions can occur

$$\mathrm{R{-}Si(OCH_3)_3 + 3H_2O \rightleftarrows R{-}Si(OH)_3 + 3CH_3OH} \qquad \text{(II)}$$



$$\mathrm{2R{-}Si(OCH)_3 \longrightarrow R{-}\underset{OH}{\overset{OH}{Si}}{-}O{-}\underset{OH}{\overset{OH}{Si}}{-}R + H_2O} \qquad \text{(III)}$$

concurrently, depending on experimental conditions, although details are incompletely understood for tetraalkoxysilanes,[11,12] and the effects of an attached organic polymer chain on hydrolysis and condensation have only recently received attention.[13–19] The formation of materials by reaction of alkoxysilyl-functionalized polymers with tetralkoxysilyl monomers[13,16] is one potential application of this coupling chemistry. All of these studies are based on the formation of hybrid materials, frequently referred to as "ceramers",[20] which become completely insoluble upon formation of networks. Hence, most ceramers can be studied only by solid-state techniques, and only limited information can be obtained about the cross-link sites. Monofunctionalized polystyrene is a potentially useful model for understanding ceramer chemistries, because coupling reactions lead to completely soluble products which may be characterized by a broad array of solution techniques.

Another unique application of this macromonomer chemistry is the formation of star-shaped macromolecules. Star polymers are generally synthesized by two popular arm-first strategies. The first process involves coupling of "living" anionic polymers with divinylbenzene (DVB).[21–25] After complete polymerization of the linear arms, the sequential polymerization of DVB generates a networklike hub. The number of arms in the star polymer is controlled by varying the molar ratio of DVB to "living" anion, and star polymers containing as many as 56 weight average arms have been prepared.[24,26] Arms with predictable molecular weights and stars with narrow molecular weight distributions are possible by this technique. The second process has been pioneered by Fetters et al.[27,28] This process, in a similar fashion to DVB coupling, involves direct reaction of the "living" polymeric arms. A molecule with a plurality of silyl chloride functionalities is added to an excess of the polymeric arm. In favorable cases, the number of arms in the final star polymer is equivalent to the number of silyl chloride functionalities in the coupling

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Table I
Polystyrene Macromonomers

designation	$\bar{M}_n$	$\bar{M}_p$	$\bar{M}_w$	$[\eta]$,[b] dL/g
	molecular weight averages[a]			
2.1 K	2 100	2 140	2 500	0.046
4.5 K	3 850	4 470	4 790	0.063
10.1 K	9 400	10 100	10 000	0.099
45.8 K	46 100	45 800	52 500	0.303

[a] Polystyrene narrow standard calibration SEC. [b] SEC viscosity detection.

reagent. The preparations of these multifunctional coupling reagents generally involves multiple steps, and the compounds are difficult to isolate, characterize, and store for long periods of time. In addition, the excess homopolymer arm must be extracted in order to generate a well-defined star polymer. Condensation coupling of trimethoxysilyl-terminated macromonomers offers advantages over both procedures.

Experimental Section

Condensation Conditions. The macromonomers were prepared by anionic polymerization as described previously.[9,10] Each was dissolved individually at a concentration of 10% (wt/vol) in uninhibited HPLC-grade tetrahydrofuran (THF). Hydrolysis and condensation of the alkoxysilyl end group was initiated by adding a measured quantity of aqueous 0.15 N HCl. The acidified water was added at either of two levels: near stoichiometric (approximately 4:1 water:Si) or large excess (0.4 mL of H_2O/g of polymer, which corresponds to a water:Si ratio of >10:1, depending on the molecular weight of the macromonomer). The solutions remained clear, or cleared immediately with gentle stirring, after the addition of acidified water. After reacting in solution, typically for 24 h, the solutions were poured into aluminum weighing pans and allowed to slowly evaporate to dryness. After several days, sample appearances ranged from white powders (low molecular weight macromonomers) to clear films (high molecular weight macromonomers). Samples were then placed under vacuum and brought to their final cure temperature, in steps, over the course of ~2 h.

Size-Exclusion Chromatography. The size-exclusion chromatography (SEC) system using differential viscometry (DV), low-angle laser light scattering (LALLS), and differential refractive index (DRI) detectors has been described in detail.[29] The LALLS and DV detectors were connected in parallel after three 5-μm PLgel mixed-bed columns (Polymer Laboratories, Amherst, MA). The DRI was connected in series after the LALLS detector. Samples were injected at a concentration of 1.5 mg/mL or less in a volume of 100 μL. The nominal flow rate was 1.00 mL/min; actual flow rates were measured with a thermal pulse flow meter (M-Tek, Pittsburgh, PA).[30]

Results

Characterization of Macromonomers. The molecular weight of each macromonomer must be accurately known to calculate the number of arms in the polymer condensates. Practically, it is difficult to measure the true molecular weights of trimethoxysilyl-terminated polystyrenes directly because small amounts of material condense through the reactive end groups during or immediately after isolation of the macromonomer. To simplify characterization of the starting macromonomers, a small fraction of each living polystyrene was separated and terminated with a proton by addition to methanol. The remaining material was then terminated with (trimethoxysilyl)phenyl groups. The proton-terminated polystyrenes are not contaminated with coupled macromonomer, and the data of Table I should most accurately approximate the true macromonomer molecular weights.

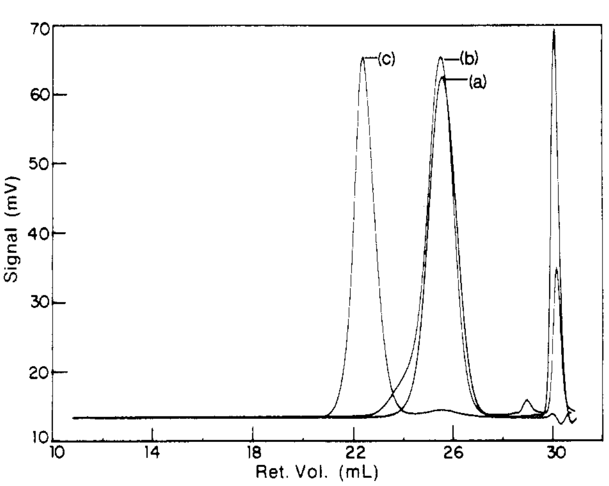

Figure 1. Size-exclusion chromatograms (DRI signals) of (a) 2.1 K proton-terminated macromonomer, (b) 2.1 K macromonomer after reaction in solution for 60 days, and (c) after evaporation of solvent and heating under vacuum at 120 °C for 10 days.

SEC and ^1H NMR confirmed that residual [*p*-(chloromethyl)phenyl]trimethoxysilane terminating reagent and related, small-molecule alkoxysilanes were not present in the macromonomers. NMR confirmed nearly complete functionalization of all but the largest macromonomer, which contained on the order of 25% unfunctionalized material. The accuracy of NMR in the determination of the degree of functionalization in high molecular weight macromonomers can be questioned. It is only important to recognize in the following discussion, that small amounts of unreactive, unfunctionalized material are present in *all* samples. No attempt was made to remove this unfunctionalized polymer, and we have assumed that it does not affect the chemistry of reactions I and II.

Evolution of Star Structures. The hydrolysis and condensation of alkoxysilanes has been studied extensively, particularly with near-stoichiometric addition of water.[9-11] It is not known how the attachment of the trialkoxysilyl group to polystyrene chains of different lengths affects hydrolysis and condensation. Upon addition of acidified water to THF solutions of these macromonomers, we observe only small increases in molecular weight and size over a period of several months. However, upon evaporation of the solvent, followed by heating under vacuum, molecular sizes increase markedly, as shown in Figure 1 (size increases from right to left in raw chromatograms) for the lowest molecular weight macromonomer and in Figure 2 for the highest molecular weight macromonomer. In both examples, uncondensed material is present and is presumed to be a result of small amounts of unfunctionalized polystyrene. It is of note that heating below the glass transition temperature of the macromonomers under vacuum (e.g. 70 °C) results in only slightly more condensation than obtained from air drying. Additionally, there is no further increase in molecular size when samples are heated for times between 2 and 10 days at 120 °C or at temperatures up to 150 °C. Consistently, a limiting molecular size is reached, beyond which further condensation is inhibited. In all cases, *completely soluble* polymeric products are obtained.

Effects of Reaction Conditions on Star Formation. Hydrolysis and condensation of alkoxysilanes are dependent upon a number of experimental variables, notably water concentration, hydrolysis time, pH, and cure conditions.[11] Predictably, we observe effects of these variables on the hydrolysis and condensation of trimethoxysilyl-terminated polystyrenes.

For example, the initial concentration of acidified water added to THF solutions affects both hydrolysis and

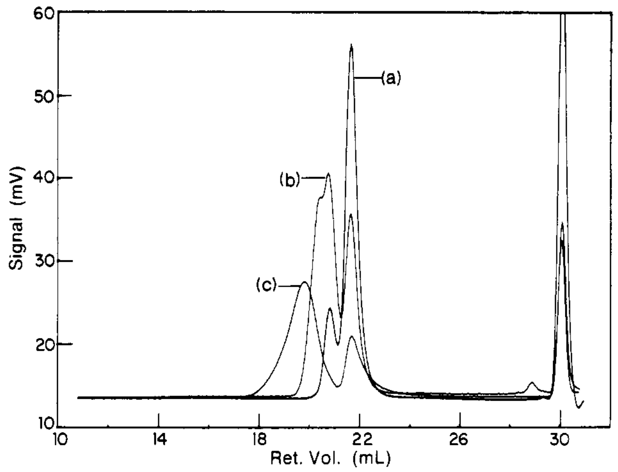

Figure 2. Size-exclusion chromatograms (DRI signals) of (a) 45.8 K proton-terminated macromonomer, (b) 45.8 K macromonomer after reaction in solution for 60 days, and (c) after evaporation of solvent and heating under vacuum at 120 °C for 10 days.

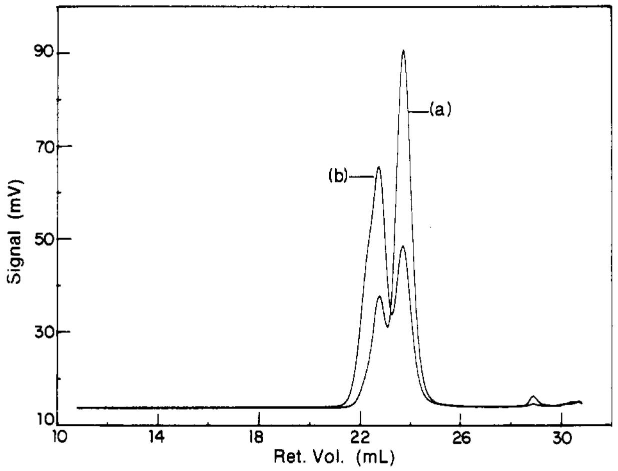

Figure 3. Effects of initial acidified water concentration on the formation of stars from 10.1 K macromonomer by air drying: (a) stoichiometric water and (b) excess water.

condensation. The molecular size of polymer condensates at the air-dried stage is noticeably larger when a large excess of acidified water is used (Figure 3). However, with heating and drying under vacuum, macromonomer treated with a stoichiometric amount of water consistently grows to a slightly larger size than samples treated with excess water (Figure 4). Also, the final, cured material was unaffected by hydrolysis times longer than 2 h, regardless of water content.

It is known that hydrolysis of tetralkoxysilanes is fastest in the presence of acid, while condensation is fastest under basic conditions. We might expect to reach the maximum extent of reaction by hydrolyzing in acid and adjusting to basic conditions with ammonium hydroxide for condensation. An example shown in Figure 4c shows that there is no significant difference between a final, cured sample of our trialkoxysilane using this procedure and one that has been treated with acid alone.

The effects of water concentration are more clearly understood by examining the evolution of structures in solution. The macromonomers condense slowly in the presence of excess acidified water, showing significant changes in molecular size only after several months (e.g., curves b and c, Figure 5). A mixture of uncondensed macromonomer and condensed polymer containing 2–4 arms is present. Upon addition of molecular sieves to the solution on day 164, we observe additional growth (curve d). Further growth is obtained when the molecular sieves are replaced a second time on day 170 and then examined 6 days later (curve e). As we have noted, even larger structures are obtained when the solutions are taken to dryness and heated under vacuum. All of the examples show that removal of water by sieves or in the most extreme case, by evaporation (drying), increases coupling.

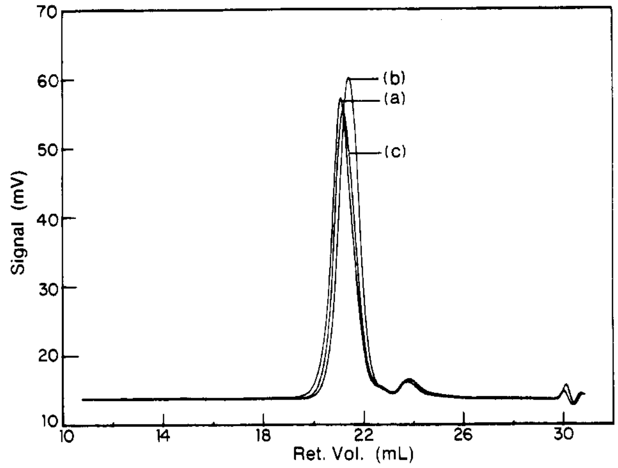

Figure 4. Effects of initial acidified water concentration on the formation of stars from 10.1 K macromonomer by drying under vacuum at 120 °C for 10 days: (a) stoichiometric water, (b) excess water, and (c) acid–base swap.

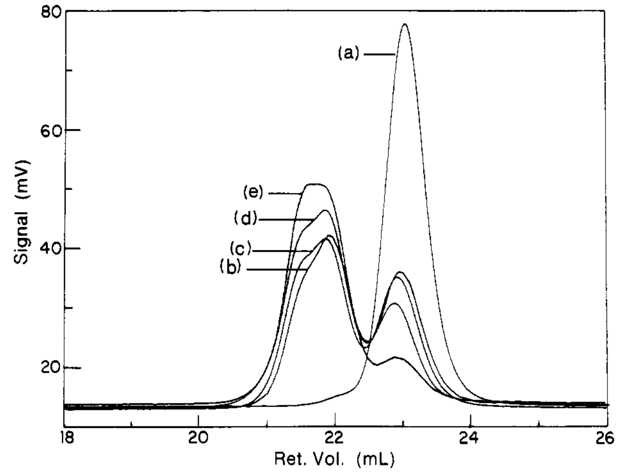

Figure 5. Effects of acidified water concentration on the formation of stars from 10.1 K macromonomer in THF solution: (a) starting macromonomer, (b) day 92 after reaction with stoichiometric water, (c) day 163, (d) day 170, after molecular sieves added on day 164, and (e) day 176, after fresh molecular sieves added on day 170.

Although it might seem apparent that removal of water increases coupling, several factors confound the explanation of this increase. The degree of substitution and the concentration of cyclic siloxanes species may differ at different water concentrations. This may invoke different steric arguments for condensation around the structurally different siloxane sites, in addition to simple removal of a reaction product (water). In addition, water was added as a 0.15 N HCl solution in both stoichiometric and excess water examples, resulting in an approximately 2.5 excess acid concentration in the excess water case. It is unknown whether the accompanying small difference in hydrogen ion concentration will affect the hydrolysis and condensation reactions significantly. These complications exemplify the complexity of interpreting sol-gel reactions; however, all of the results are consistent with one general conclusion: a limiting size is reached after which additional growth is hindered, regardless of reaction conditions.

Table II
Characterization Data for Polystyrene Stars

designation	molecular weight averages[a] $\bar{M}_n$	$\bar{M}_p$	$\bar{M}_w$[b]	$[\bar{\eta}]$,[c] dL/g	f
2.1 K	24 000	44 000	45 900	0.087	20.6
4.5 K	24 150	55 000	52 200	0.113	12.3
10.1 K	47 700	120 000	131 000	0.180	11.9
45.8 K	65 200	270 000	315 000	0.484	6.1

[a] SEC-LALLS. [b] Equation 2. [c] SEC-DV, eq 1.

Quantitative Characterization of Polystyrene Stars. SEC coupled with molecular weight sensitive detectors can provide characterization data of nonlinear polymers regardless of chromatographic complications, provided the entire sample elutes from the SEC column. The bulk intrinsic viscosity $[\bar{\eta}]$ of the sample is obtained by integration of the DV detector (specific viscosity, $\eta_{sp}(v)$, at each retention volume v) and the total mass of sample injected, m. The value obtained in this manner is

$$[\bar{\eta}] = 1/m\int_0^\infty \eta_{sp}(v)\, dv \qquad (1)$$

independent of axial dispersion caused by imperfect resolution in the chromatographic system. Likewise, the absolute weight-average molecular weight, $\bar{M}_w$, is obtained by intergration of the excess Rayleigh scattering $R_\theta(v)$ obtained by LALLS:

$$\bar{M}_w = 1/(mK)\int_0^\infty R_\theta(v)\, dv \qquad (2)$$

where K is an optical constant. These values are given in Table II for each star obtained from addition of stoichiometric amounts of water followed by evaporation and drying at 120 °C under vacuum for 250 h. Other molecular weight averages must be obtained by summation, after correcting both the molecular weight sensitive and concentration detector signals for axial dispersion.[31]

The molecular weights of the stars may also be calculated from the intrinsic viscosity at each eluting slice and a calibration curve generated from narrow standards of known molecular weights and intrinsic viscosities, provided the principle of universal calibration (eq 3) applies, where

$$M_s[\eta]_s = M_u[\eta]_u \qquad (3)$$

subscripts s and u designate the narrow standard and unknown polymers, respectively. However, the product of axial dispersion corrected, peak-average molecular weights and peak-average intrinsic viscosities of all except the highest molecular weight stars do not superimpose on a universal calibration curve of narrow standard polystyrenes (Figure 6). The differences in $M[\eta]$ in (Figure 6) between narrow distribution, linear polystyrene standards and the polystyrene stars may appear small on a logarithmic scale, but they actually result in overestimation of molecular weights by as much as 30%.

There are several reasons why universal calibration fails in size-exclusion chromatography;[32] however, the limited amount of data presented in Figure 6 do not allow us to determine the source of this failure conclusively. The data do provide an example, however, of why viscometry detection and methods that calculate molecular weights by universal calibration should be used cautiously on these and other highly branched or condensed polymers. The SEC of these materials is best verified using multiple, molecular weight sensitive detection schemes.

The number of arms, f, in a star is properly calculated from the number-average molecular weights of the star and its arms (macromonomer). In some instances, the molecular weight distributions of the stars are surprisingly narrow, although they are clearly a mixture of stars with different numbers of arms (Figure 7). It can be seen that the number-average molecular weight of the entire polymer may be inappropriate for calculating the number of arms in a star because it is heavily biased by the low molecular weight tails observed in the distributions. When superimposing local intrinsic viscosities obtained by DV (Figure 8) and weight-average molecular weights obtained by LALLS (Figure 9) on polystyrene narrow standard calibration curves, we find that the low molecular weight regions (longest retention volumes) of these curves converge with linear polystyrene calibration standards. We thus assume that this low molecular weight material is linear or nearly linear polystyrene which has not condensed to form stars. A more appropriate calculation is

$$f = \bar{M}_{p(star)}/\bar{M}_{p(arm)} \qquad (4)$$

where $\bar{M}_{p(star)}$ and $\bar{M}_{p(arm)}$ are the peak-average molecular weights of the star and macromonomer, respectively. From this calculation, we show that the number of arms decreases with increasing arm molecular weight (Table II).

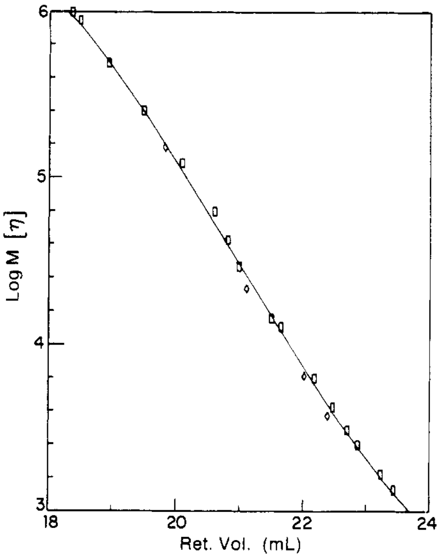

Figure 6. Universal calibration curve: polystyrene narrow standards (□) and stars obtained from macromonomers by drying under vacuum for 10 days (◇).

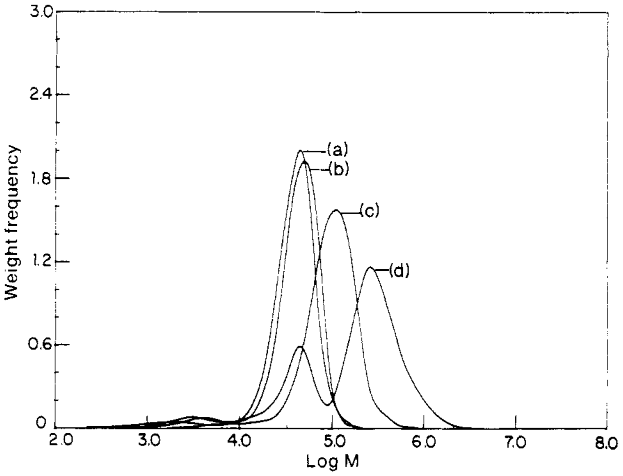

Figure 7. Molecular weight distributions obtained by SEC-LALLS of stars obtained from vacuum-curing 10 days at 120 °C. Derived from macromonomers (a) 2.1 K, (b) 4.5 K, (c) 10.1 K, and (d) 45.8 K.

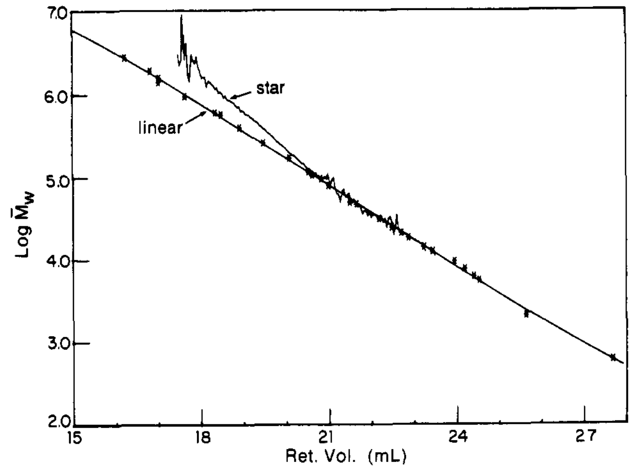

Figure 8. log M_w vs retention volume obtained from SEC-LALLS of star derived from 45.8 K macromonomer cured at 120 °C under vacuum for 10 days.

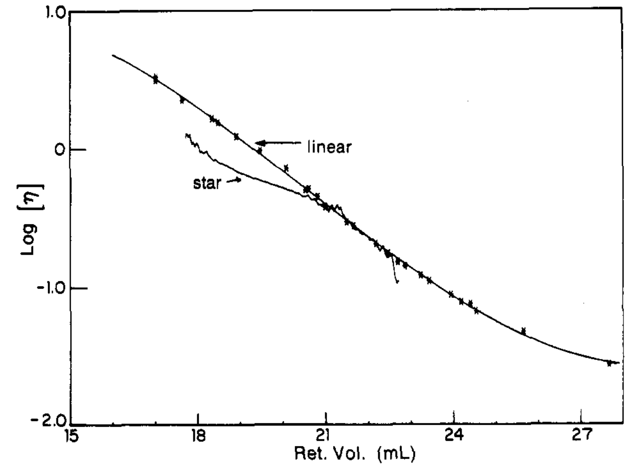

Figure 9. log [η] vs retention volume obtained from SEC-DV of star derived from 45.8 K macromonomer cured at 120 °C under vacuum for 10 days.

Table III
Hydrodynamic Data for Polystyrene Stars

designation	peak: [η], dL/g	star $\bar{\rho}_{seg}$, g/cm	equiv MW linear polystyrene: $\bar{\rho}_{seg}$, g/cm	g'
2.1 K	0.085	0.294	0.096	0.328
4.5 K	0.118	0.212	0.082	0.388
10.1 K	0.180	0.139	0.047	0.340
45.8 K	0.540	0.046	0.026	0.573

We may approximate the average density of polymer within the hydrodynamic sphere, $\bar{\rho}_{seg}$, from the intrinsic viscosity obtained from the SEC differential viscometry detector:

$$\bar{\rho}_{seg} = 2.5/[\eta] \tag{5}$$

To again avoid the complications of multimodal distributions, we choose the peak intrinsic viscosity, $[\eta]_{peak}$. Results are compared with average densities of linear polystyrenes of equivalent molecular weights in Table III. The calculations show that the stars are several times more dense than linear polystyrenes of equivalent molecular weights.

One common method of comparing branched (in our case star) and linear polymers at equivalent molecular weights is through so-called "g" factors based on radii of gyration or intrinsic viscosities. Only the latter are directly measured by DV detection in this SEC experiment:

$$g' = [[\eta]_{star}/[\eta]_l]_M \tag{6}$$

where $[\eta]_l$ is the intrinsic viscosity of linear polystyrene of molecular weight (M). Values of g' (included in Table III) less than 1.0 indicate that the star-shaped polymers are smaller than linear polymers of equivalent molecular weights. Small values of g' have traditionally been related to the highest degrees of branching or compactness through structurally dependent models. It is worth noting that the values of g' are dependent upon both the number and molecular weight of the arms hence there may not be a systematic change in g' with arm molecular weight, as shown by the data in Table III.

Discussion

The solubility of the condensed macromonomers in this study raises interesting questions about the structure of these materials, regardless of their use as models for ceramer systems. It is presumed that the reaction proceeds in a fashion similar to other sol-gel reactions under acid conditions, and in some ways resembles a step-growth polymerization.[33] The inorganic portion of the structure should be highly branched, with a distribution of 1–3 siloxane linkages to each silicon atom. A 2.1 K macromonomer cured at 120 °C under vacuum for 10 days contains 16% silicon atoms with one siloxane linkage, 49% with two, and 35% with three siloxane linkages (data obtained from Si NMR integrals). Because of this branching, we might visualize the condensed structures as compact inorganic cores from which radiate linear polystyrene chains. We thus make an analogy between the polystyrene macromonomer condensates and star molecules.

Assuming star geometry, we may calculate an expansion factor, α:

$$\alpha = \frac{R_{h(star)}}{D_{h(arm)}} \tag{7}$$

where $R_{h(star)}$ and $D_{h(arm)}$ are hydrodynamic radius and diameter, respectively. Values greater than unity indicate that the radiating arms are extended relative to their random coil configuration. The extension is caused by crowding of adjacent arms. Values of $R_{h(arm)}$ may be calculated for linear polystyrene, using the data of Table I, from

$$R_{h(arm)} = \left[\frac{3[\eta]M}{10\pi N_a}\right]^{1/3} \tag{8}$$

where N_a is Avogadro's number. $R_{h(star)}$ may be estimated from SEC retention volumes. To do so, we first assume that the elution of the stars is a function of hydrodynamic size, as is generally accepted in SEC. This assumption is not invalidated by the demonstrated failure of universal calibration for some of the stars; the latter only indicates that the hydrodynamic size measured by SEC of some stars may not be well approximated by the product $M[\eta]$. We then assign values of R_h to each elution volume spanned by this column set using eq 8 and the intrinsic viscosities and molecular weights of narrow-standard polystyrenes. Values calculated in this manner (given in Table IV) indicate increasing arm expansion with decreasing arm molecular weight.

The characteristics of our star-shaped polystyrene may also be compared with polystyrene stars made by other means. Extensive characterization in toluene and cyclohexane of polystyrene stars made by addition of "living", anionic polymers to chlorosilanes has been presented.[34,35]

Table IV
Polystyrene Star Expansion Factors

designation	arm: R_h, nm	star: R_h, nm	α
2.1 K	1.07	4.41	2.05
4.5 K	1.60	5.15	1.61
10.1 K	2.53	7.64	1.51
45.8 K	5.82	13.23	1.14

Values of g' for 12 and 18 arm stars in toluene are comparable to those in Table III. Values of g' in THF for stars produced by coupling living polystyrene through divinylbenzene molecules range between 0.2 and 0.6 for a variety of arm lengths and numbers.[36] Although data for stars with identical arm lengths and numbers as ours are not available, these comparisons indicate that the hydrodynamic properties of stars made by condensation coupling are similar to stars made by other means.

We would like to understand why the reaction apparently stops after a finite number of coupling reactions, leading to fully soluble products. Related to this is a dependence of the number of arms per star on the macromonomer molecular weight. Using free energy calculations from models which calculate the stability of star geometries, we may estimate the importance of kinetic versus thermodynamic issues in stabilizing the star products.

Most recent theories of star molecules are variants of the Daoud–Cotton model.[37] The model describes the configuration of a single chain (arm) in the star by considering effects of other chains emanating from the same core. In the region closest to the core, the local segment density is largest. Density decreases proceeding outward from the core as the volume of the annular shell increases. Interpenetration of chains is entropically unfavorable, due to the loss of configurational degrees of freedom, and packing requirements make the problem most severe in the core region of the molecule. Since each chain is terminally attached to the core, all chains must expand radially outward to obtain their minimum free energy. Following scaling arguments, these chains are divided into concentration blobs, which form because of screening effects of adjacent chains. The blob size increases progressively outward from the core, due to the reduced concentration of neighboring chains. This basic construct has also been applied to problems of colloidal stabilization[38] and block copolymer micelle formation.[39] Some details described in these applications are useful for our purposes.

The important considerations for understanding the growth process of the stars formed from these macromonomers are those involving the loss of entropy in the system when increasing the number of arms, f. This loss in entropy must be balanced by an enthalpic gain in the system resulting from chemical bonds formed in the sol-gel condensation reaction given by III. The key question is a simple one. Does the reaction stop because of kinetic limitations or does it reach a thermodynamic limit?

By a kinetic limitation, we mean that continued reaction would further lower the free energy of the system, but at some point these reactions become too slow for us to observe. In this case, the macromonomer and small aggregate (dimer, trimer) populations are depleted, and the steric barrier to larger stars interpenetrating sufficiently to allow core–core reactions becomes large compared to the thermal energy gained from siloxane bond formation, e.g., star–star coupling is unfavorable. In contrast, the thermodynamic limit is the state where the entropy barrier to addition of but one more macromonomer to the star is larger than the enthalpy gain from an additional Si–O–Si reaction.

First, we consider the enthalpic contributions. In this reaction, the exact heats of formation of the various silicate structures are not known. We may, however, approximate the net change in enthalpy of the system from the bond energies of reactants and products in reaction III. In the reactants, one Si–OH bond and one SiO–H bond must be broken. One SiO–Si bond and one HO–H bond are formed in the products. Assuming that the Si–OH and SiO–Si bonds have approximately equal bond energies, the net reaction is the loss of an SiO–H bond (approximately 105 ± 5 kcal/mol) and the formation of an HO–H bond (119 kcal/mol). The net enthalpy gain for the reaction is then approximately 14 kcal/mol. Including the uncertainty in bond energies, this corresponds to approximately 18 ± 6 units of kT for the 120 °C curing temperature.

Next, we must compare this gain in enthalpy with the loss in configurational energy caused by condensation of macromonomers and larger structures. Witten and Pincus[38] have derived a form for the configurational free energy of a star, which in their case is a core of finite dimensions with polymer chains attached to the surface at a particular packing density. The essential elements of their treatment that should also apply to these polystyrene stars are that the free energy, F, of a star varies according to

$$F \sim kT(f^{3/2}) \ln N \qquad (9)$$

where f is the number of polymer chains per star and N is the number of monomers per chain. The theory is written for the limit of long chains and assumes a loss of about kT of entropy for each blob that is formed. The increase in free energy, ΔF, to bring the cores of two such stars in contact is of the order of F for one of the original stars. This represents the kinetic or aggregation limit of the reaction.

The thermodynamic limit requires evaluation of the increase in free energy for the addition of a single arm to a star:

$$\Delta F \sim kT[(f+1)^{3/2} \ln N - f^{3/2} \ln N] \qquad (10)$$

As f becomes large, eq 10 approximates the derivative of F with respect to f, which reduces the problem to the scaling form

$$\Delta F \sim kTf^{1/2} \ln N \qquad (11)$$

This form contains a much weaker dependence of the change in free energy on f than the kinetic form given by eq 9, i.e., as we would expect, since adding a single chain to a star results in a smaller perturbation in the configurational energy of the system than does adding a star to a star.

The number of blobs per chain, n_s, is proportional to the entropy loss per chain resulting from incorporation into a star, in units of kT, according to[39]

$$n_s \sim f^{1/2} \ln (R/R_{\mathrm{core}}) \qquad (12)$$

where R is the radius of the star and R_{core} is the radius of the core. In a good solvent, $R \simeq af^{1/5}N^{3/5}$, where a is the monomer length. For our system, we expect R_{core} to be of the order of a, or by substitution into eq 12,

$$n_s \sim f^{1/2} \ln (f^{1/5}N^{3/5}) \qquad (13)$$

We thus can evaluate n_s regardless of whether growth is kinetically or thermodynamically limited. The number of blobs per arm should correspond roughly to the energy barrier to further macromonomer addition as described by eq 10.

Table V
Calculated Free Energy Changes for Polystyrene Stars

		ΔF (units of kT)			
designation	f	star–star coupling	macromonomer addition	blobs/chain	range $f_{\max}$
2.1 K	20.6	283	20.8	11.0	6.6–27.5
4.5 K	12.3	162	20.2	9.7	4.1–17.7
10.1 K	11.9	188	24.2	11.2	2.6–11.8
45.8 K	6.1	92	23.5	9.9	1.3–6.4

In the present example, each macromonomer reached a different value of f before the reaction no longer proceeded perceptibly. A calculation of the increase in free energy for the next coupling reaction should then be a constant as a function of ln N according to eq 9 if the growth is kinetically limited, or eq 10 if it is thermodynamically limited. The calculated free energy changes by both formulae are listed in Table V. The average number of blobs per chain are also tabulated. Changes in free energy calculated by the kinetic or aggregation limit model show a strong dependence on molecular weight, whereas the monomer growth or thermodynamic limit is virtually independent of molecular weight. This result suggests that the reaction is reaching (or has reached) the thermodynamic limit for star size for each macromonomer examined. The prevalent mode of growth at later stages of condensation must therefore become addition of macromonomer to stars, rather than addition of stars to stars.

The magnitude of the entropic barrier is also significant. The Witten and Pincus arguments give an approximate form for the free energy function applicable to this system, expected to be correct within a constant with a value of the order of 1. Therefore, a value for the entropic loss that is much in excess of the 18 ± 6 kT units available from enthalpic energy gains through a condensation reaction would lead to a thermodynamically unfavorable reaction. The kinetic or star–star coupling model falls in this category, while the monomer growth model is very close to the limit. The calculated values of n_s, which are numerically similar to monomer growth entropy losses, also support this conclusion.

The theoretical maximum number of arms per star, $f_{\max}$, can be calculated in a straightforward manner from eq 10, using an enthalpic gain of 18 ± 6 kT as the limiting ΔF value for each molecular weight. The ranges of $f_{\max}$ calculated in this manner are also listed in Table V. The ranges include the measured functionality of stars formed after heating under vacuum at 120 °C for 10 days, although little more can be inferred because of the breadth of the ranges resulting from the large uncertainty in the magnitude of bond energies (±6 kT).

The results of this study suggest that we are approaching the thermodynamic limit for growth in these reactions. However, we must be cautious in the application of this theory to the macromonomers in this study, because the samples approach the limit of "long chains" for only the highest molecular weights studied and the scaling arguments may be inappropriate for the lower members of the series. According to Daoud and Cotton,[37] the long-chain limit applies for N much greater than $f^{1/2}\nu^{-2}$. For $\nu = 0.5$ (a θ solvent), our smallest chain is very close to the limit, so its configuration is probably best described by the relationship for intermediate molecular weights. We are also unable to treat the variation in f within a given sample in any simple form, so we have proceeded using the values of f listed in Table II, based on the peak of the distribution of stars.

Conclusion

The polymerization of a new macromonomer system has been described, and we find that it leads to the formation of well-defined, soluble macromolecules, despite the possibility for the chemistry involved to lead to gel formation. The structures formed resemble star molecules, and the number of arms depends strongly on molecular weight of the macromonomers. Coupling is expected to follow a step-growth mechanism, except that the reactivity of higher order stars decreases rapidly due to steric stabilization of the reactive site with respect to approach by other reactive species. As a result, gelation is not observed. Based on theories for star polymers, it appears that these stars are growing very close to their thermodynamic limiting aggregation number. The effects due to changes in reaction conditions are readily observable in this system and should be useful in optimizing conditions required for network-forming (ceramer) reactions. The molecular weight dependence on the number of arms in a star may also provide clues to varying the functionality of network junctions in ceramer systems.

Although the number of arms attainable is limited by the molecular weight of the macromonomer, and the molecular weight distributions are broader than obtained by some methods, preparation of star polymers via a sol-gel process, as described herein and in detail earlier,[11-13] offers many advantages over existing techniques. It is not necessary to synthesize complicated coupling reagents. Also, the reactive arm can be isolated, stored, and easily characterized. Coupling occurs readily and efficiently by simply adding acidified water to a solution of macromonomer, followed by evaporating to dryness and curing. Finally, the functionalized arms react quantitatively in most cases to from stable, star polymers. Consequently, residual linear arm is not present and tedious extraction processes are not necessary.

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References and Notes

(1) Rodriquez, F. *Principles of Polymer Systems*; McGraw-Hill: New York, 1970; Chapter 1.
(2) Jurek, M. J.; Geier, D. T.; McGrath, B. E.; McGrath, J. E. *Polym. Prepr.* **1986**, *27* (1), 315.
(3) Hergenrother, P. M. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 3131.
(4) Hadjichristidis, N.; Fetters, L. J. *Macromolecules* **1980**, *13*, 191.
(5) Meunier, J. C.; Van Leemput, R. *Makromol. Chem.* **1971**, *142*, 1.
(6) Lutz, P.; Masson, P.; Beinert, G.; Rempp, P. *Polym. Bull.* **1984**, *12*, 79.
(7) Rempp, P.; Lutz, P.; Masson, P.; Frantz, E. *Makromol. Chem. Suppl.* **1984**, *8*, 3.
(8) Ito, K.; Tsuchida, H.; Kitano, T. *Polym. Bull.* **1986**, *15*, 425.
(9) Long, T. E.; Kelts, L. W.; Turner, S. R.; Wesson, J. A.; Mourey, T. H. *Polym. Prepr.* **1990**, *31* (2), 490.
(10) Long, T. E.; Kelts, L. W.; Turner, S. R.; Wesson, J. A.; Mourey, T. H. *Macromolecules* **1991**, *24*, 1431.
(11) Brinker, C. J. *J. Non-Cryst. Solids* **1988**, *100*, 31.
(12) Klein, L. C. *Ann. Rev. Sci.* **1985**, *15*, 227.
(13) Noell, J. L.; Wilkes, G. L.; Moharty, D. K.; McGrath, J. E. *J. Appl. Polym. Sci.* **1990**, *40*, 1177.
(14) Huang, H.-H.; Orler, B.; Wilkes, G. L. *Macromolecules* **1987**, *20* (6), 1322.
(15) Huang, H.-H.; Glaser, R. H.; Wilkes, G. L. *Inorganic and Organometallic Polymers*; Zeldin, M., Wynne, K. J., Allcock, H. R., Eds.; ACS Symposium Series 360; American Chemical Society: Washington, DC, 1988; p 354.
(16) Schmidt, H. *Mat. Res. Symp. Proc.* **1984**, *32*, 327.

(17) Mark, J. E. *Brit. Polym. J.* **1985**, *17*, 144.
(18) Clarson, S. J.; Mark, J. E. *Polym. Commun.* **1987**, *28*, 249.
(19) Sur, G. S.; Mark, J. E. *Eur. Polym. J.* **1985**, *21*, 1051.
(20) Glasser, R. H.; Wilkes, G. L. *Polym. Bull.* **1989**, *22*, 527.
(21) Mikovich, R. Canadian Patent 712245, Aug 24, 1965.
(22) Martin, M. K.; Ward, T. C.; McGrath, J. E. In *Anionic Polymerization: Kinetics, Mechanisms, and Synthesis*; McGrath, J. E., Ed.; ACS Symposium Series 166; American Chemical Society: Washington, DC, 1981.
(23) Worsfold, D. J.; Zillox, J. G.; Rempp, P. *Can. J. Chem.* **1969**, *47*, 3379.
(24) Quack, G.; Fetters, L. J.; Hadjichristidis, N.; Young, R. N. *Ind. Eng. Chem. Prod. Res. Dev.* **1980**, *19*, 587.
(25) Sheridan, M. M.; Hoover, J. M.; Ward, T. C.; McGrath, J. E. *Polym. Prepr.* **1984**, *25* (2), 102.
(26) Quack, G.; Fetters, L. J. *Polym. Prepr.* **1977**, *18* (2), 558.
(27) Hadjichristidis, N.; Guyot, A.; Fetters, L. J. *Macromolecules* **1978**, *11*, 668.
(28) Hadjichristidis, N.; Fetters, L. J. *Macromolecules* **1980**, *13*, 191.
(29) Mourey, T. H.; Miller, S. M.; Balke, S. T. *J. Liq. Chromatogr.* **1990**, *13*, 435.
(30) Lew, R.; Ho, M.; Balke, S. T.; Mourey, T. H. *J. Liq. Chromatogr.* **1990**, *13*, 453.
(31) Hamielec, A. E. *J. Liq. Chromatogr.* **1981**, *4*, 1697.
(32) Janca, J. *Steric Exclusion Liquid Chromatography*; Marcel Dekker, Inc.: New York, 1984.
(33) Winter, R.; Hua, D. W.; Song, X.; Mantulin, W.; Jonas, J. *J. Phys. Chem.* **1990**, *94*, 2706.
(34) Roovers, J.; Hadjichristidis, N.; Fetters, L. J. *Macromolecules* **1983**, *16*, 214.
(35) Khasat, N.; Pennisi, R. W.; Hadjichristidis, N.; Fetters, L. J. *Macromolecules* **1988**, *21*, 1100.
(36) Taromi, F. A.; Grubisic-Gallot, Z.; Rempp, P. *Eur. Polym. J.* **1989**, *25*, 1183.
(37) Daoud, M.; Cotton, J. P. *J. Phys.* (les Ulis) **1982**, *43*, 531.
(38) Witten, T. A.; Pincus, P. A. *Macromolecules* **1986**, *19*, 2509.
(39) Halperin, A. *Macromolecules* **1987**, *20*, 2942.