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Rheokinetic investigations on the thermal polymerization of benzoxazine monomer

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Abstract

The thermal cross-linking polymerization of bisphenol-A based benzoxazine was monitored at different isothermal curing temperatures by rheological analysis. An autocatalytic kinetic model was proposed for the curing of benzoxazine monomer. Gel point (t_{gel}) was determined from tan δ maximum and also from intercept of storage and loss modulus and the corresponding activation energy was estimated. All kinetic parameters including reaction orders and kinetic constants were determined. The autocatalytic effect was very significant. A master equation for the cure rate was generated from the kinetic data that was numerically integrated to predict the cure-profile. The theoretical cure prediction matched reasonably well with the experimental results. The high autocatalytic effect was attributed to the presence of phenolic ─OH groups generated by the ring-opening polymerization; which aids further ring-opening polymerization.

Keywords: Benzoxazine; Curing; Rheokinetics; Kinetic modeling

1. Introduction

Polybenzoxazine is a new generation of thermoset polymer possessing many salient properties such as low volumetric shrinkage or expansion upon curing [1], low moisture absorption, excellent resistance to chemicals and UV light [2,3], high Tg, all of which makes it an attractive candidate for many engineering applications. These properties have been attributed to the unique H-bonding structure found in these materials. In addition, polybenzoxazine can be cured without strong acid or base catalyst and does not release by-products during polymerization [4,5]. 3-Substituted-3,4-dihydro-2*H*-1,3-benzoxazines have been shown to polymerize via a thermally induced ring-opening reaction to form a phenolic structure characterized by a Mannich base bridge (–CH_2–NR–CH_2–) instead of the methylene bridge associated with the traditional phenolic resins [6–9]. Benzoxazine monomers can provide linear or cross-linked polymers, depending on the reaction occurring at the *ortho* and additional *para* positions. It has been demonstrated that the preferred reaction site is the position *ortho* to the hydroxyl functionality on the aromatic ring [7,9,10]. Recently, materials with useful mechanical and thermal properties based on benzoxazine chemistry have been reported. Benzoxazine monomers cure, by ring-opening polymerization and the extent of curing has a bearing on the polymer properties.

Ring-opening polymerization occupy a unique place in polymer chemistry since this reaction provides an important methodology for resin processing. Generally, the functionality contained in the cyclic starting material as well as the ring size has decisive effects on the polymerization reaction. Cure characterization and kinetics have significance in this context. The control over the cure of the thermosetting material requires an accurate knowledge of the polymerization kinetics as a function of the applied conditions for optimization of the process. Curing rheokinetics of various thermosetting resins have been explored [11,12]. There have been many qualitative studies on rheokinetics of benzoxazine curing [5,6]. However, quantitative treatment of the cure kinetics by using DSC has been reported [13]. Thus, in the present work, we report the kinetics of the ring-opening polymerization of bisphenol-based benzoxazine monomer, monitored by rheological analysis; also the factors governing enhanced autocatalysis will be examined.

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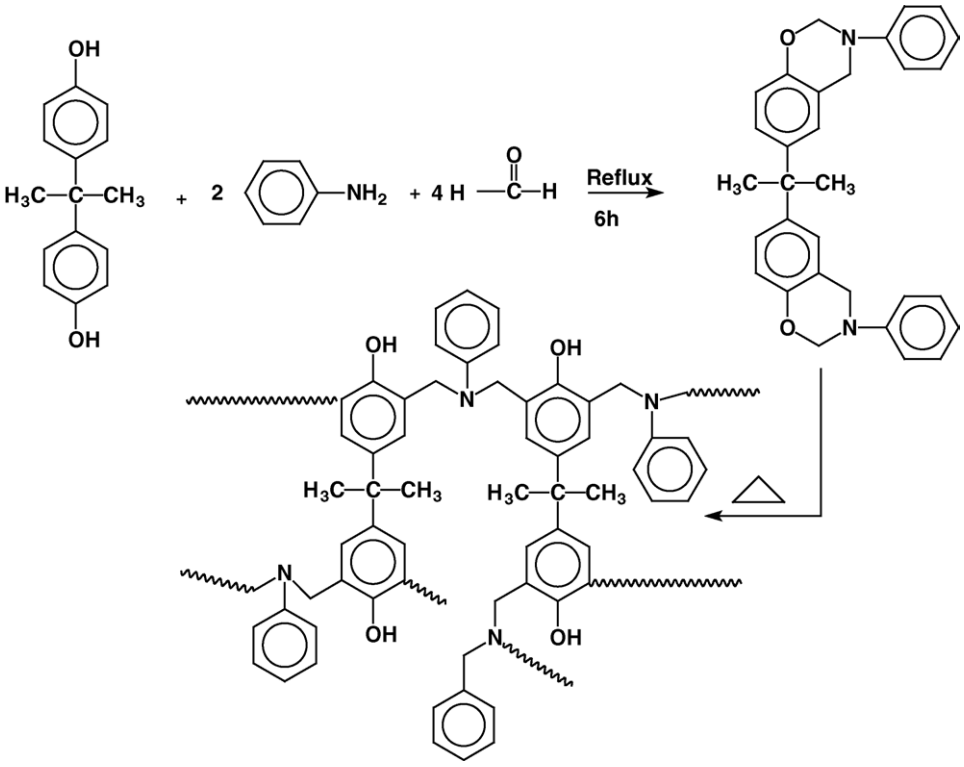


Scheme 1. Synthesis and polymerization of benzoxazine monomer.

2. Experimental

2.1. Materials

The bifunctional benzoxazine monomer 6,6′-bis(3-phenyl-3,4-dihydro-2*H*-1,3-benzoxazinyl) isopropane (BZ-a) was synthesized from 4,4′-isopropylidenediphenol (bisphenol A) (SD's Chemicals, India). Aniline, formaldehyde (37%) (Merck Chemicals), 1,4 Dioxane (Spectrochem Chemicals, Mumbai, India) and diethyl ether (Nice Chemicals) were used as received except aniline, which was used after vacuum distillation.

2.2. Characterization

Proton nuclear magnetic resonance spectroscopy (^{1}H NMR) was performed by using a 300 MHz Bruker Avance spectrometer. The size exclusion chromatography was carried out with a Waters Alliance 2690 separation module in conjunction with Waters 410 differential refractive index detectors. The columns were Waters HR 1 and HR 2 Styragel columns. FTIR spectra were executed on a Perkin-Elmer spectrum GXA at a resolution of 4 cm^{-1}.

2.3. Synthesis of benzoxazine monomer 6,6′-bis(3-phenyl-3,4-dihydro-2H-1,3-benzoxazinyl) isopropane (BZ-a)

6,6′-Bis(3-phenyl-3, 4-dihydro-2*H*-1,3-benzoxazinyl) isopropane (BZ-a) from aniline and bisphenol A was synthesized according to the reported procedure [14]. Aniline (0.50 mol) was added slowly to formaldehyde (0.1 mol, 37%) in 80 ml dioxane, keeping the temperature below 10 °C. While stirring, bisphenol A (0.25 mol in 100 ml dioxane) was added to the mixture and was refluxed for 6 h. The solvent was removed and the viscous fluid was dissolved in diethyl ether. It was washed with 3N NaOH followed by distilled water. The monomer was dried for 24 h under vacuum at 40 °C and the material was kept at −5 °C. Scheme 1 shows the reported synthetic route for benzoxazine monomer.

^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ 4.59 ppm (Ar–CH_2–N–), δ 5.33 ppm (–O–CH_2–N–), δ 6.6–7.3 ppm (Ar–H), δ 1.56 ppm (–C–CH_3). FTIR ($CHCl_3$): ν 947 cm^{-1} (oxazine ring); ν 754 cm^{-1} and 694 cm^{-1} (monosubstituted benzene); ν 1030 cm^{-1} (–C–O str aromatic ether), ν 1232 cm^{-1} (Ar–O–C asym str). SEC: monomer purity >98%.

2.4. Rheological analysis

Rheological characterization was done with a Reologica Stresstech Rheometer, model Reologica Viscotech QC, using a 20 mm parallel plate assembly in oscillation mode at a frequency of 1 Hz and a controlled strain of 0.01. The benzoxazine monomer was melted and degassed for 30 min at 110 °C under vacuum before loading on the plate. The gap between the plates was maintained at 0.5 mm. The samples were loaded onto the plates at 120 °C. The data analysis was done with the instrumental software.

3. Results and discussions

3.1. Cure kinetics

Fig. 1 depicts the isothermal reaction storage modulus curves as a function of time at temperatures 190, 195, 205, and 210 °C.

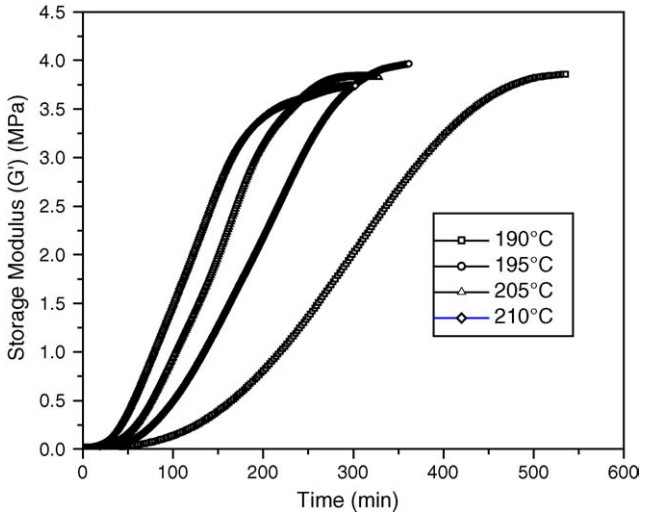


Fig. 1. Evolution of storage modulus as a function of time at different isothermal temperatures.

The storage modulus attains a maximum and follows a plateau after certain time intervals, which is considered as the time for complete cure. The plateau of storage modulus is more or less in the same region at all temperatures. The modulus increases with temperature and shifts to a lower time scale. The rheological fractional conversion at any time was calculated from the equation.

$$\alpha = \frac{G'(t)}{G'(\infty)} \tag{1}$$

where $G'(t)$ is the storage modulus at time t, $G'(\infty)$ is the maximum modulus at each temperature. The resultant time-conversion plots are shown in Fig. 2. At all temperatures, fractional conversion showed a rapid increase immediately after the reaction is triggered. The steep rate increase is indicative of the high autocatalytic nature of the cure mechanism. Rate of reaction versus time graphs shown in Fig. 3 imply an autocatalytic mechanism for the reaction. The conversion at $G'(\infty)$ has been

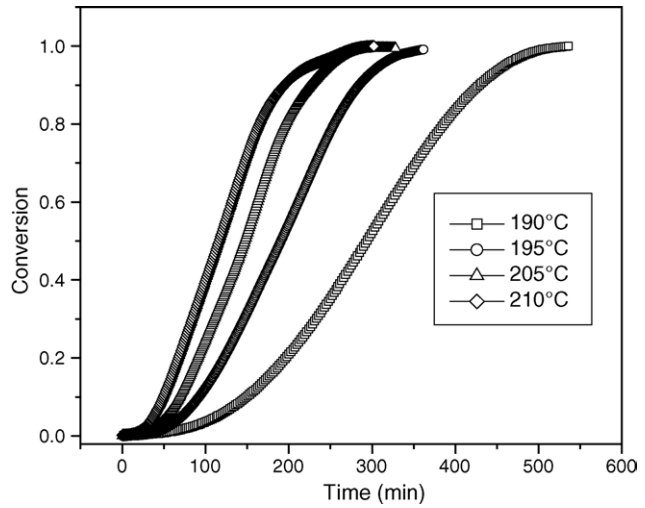


Fig. 2. Isothermal fractional conversion as a function of time for BZ-a.

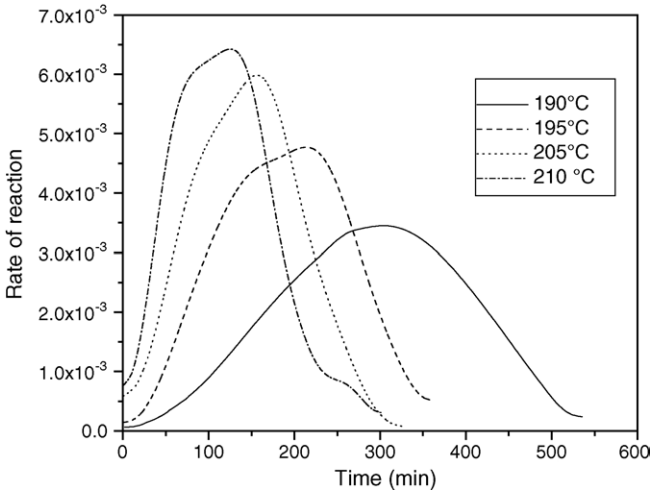


Fig. 3. Conversion rate as a function of time at several isothermal temperatures of benzoxazine monomer.

experimentally found by FTIR to be 100%. This has been done by following the evolution of peaks corresponding to oxazine ring at 946 $cm^{-1}$and –OH group at 3439 cm^{-1}. The comparative spectrum of the monomer and polymer at $G'(\infty)$ of the 190 °C cured polymer are included in Fig. 4. This shows that the reaction goes to completion in the horizontal plateau region of G'-time plots irrespective of the cure temperature.

To take into account the autocatalytic reaction where initial reaction rate is not zero, a generalized expression can be used as [15]

$$\frac{d\alpha}{dt} = (k_1 + k_2\,\alpha^m)(1-\alpha)^n \tag{2}$$

where k_1 and k_2 are the first order and autocatalytic reaction rate constants, respectively. The kinetic rate constants are assumed to be constant at a given temperature and follow Arrhenius temperature dependence.

$$K_i = A_i e^{(-E_i/RT)}, \quad i = 1, 2 \tag{3}$$

where A_i is the pre-exponential constant, E_i the activation energy; R the gas constant and T, the temperature in Kelvin. In this study, k_1 was calculated graphically as the initial reaction

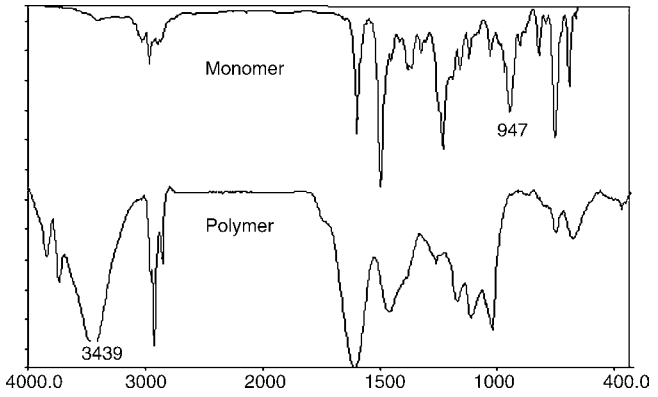


Fig. 4. Comparative IR spectrum of monomer and the 190 °C cured polymer showing the completion of polymerization.

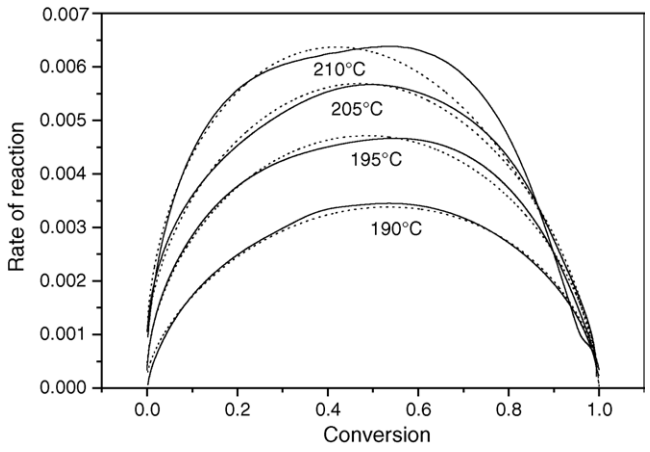


Fig. 5. Curve fitting using Eq. (2). Fitted curve (dots) and experimental data points (bold) at various temperatures.

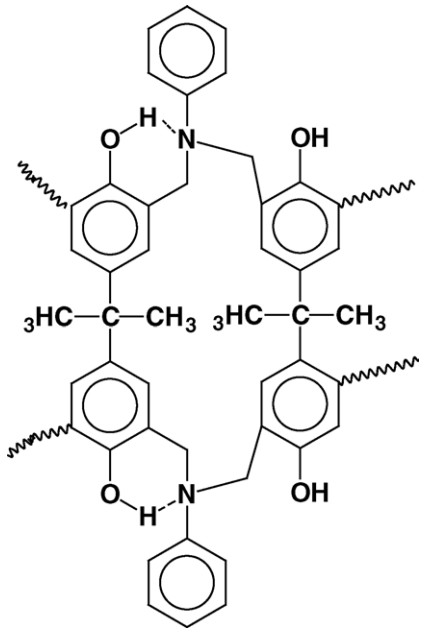
rate at $t = 0$ given by the intercept in the reaction rate versus time curve. The other kinetic parameters k_2, m and n were calculated by fitting the experimental data to the Eq. (2) by multiple regression analysis using a computer software. The best fit gave the values of m and n for each temperature. This was done for all four temperatures and the average of m, n were found. Typical curve fitting for each temperature are shown in Fig. 5.The kinetic parameters obtained are shown in Table 1.

3.2. Enhanced autocatalysis

The important cause for the enhanced autocatalysis must be the availability of huge volume of highly catalyzing –OH groups in the products, unlike in other autocatalytic systems like polyacrylonitrile [16], Alder-ene systems [17] and so on. From the results of monofunctional benzoxazines study [18], a number of possible network structures can be envisioned. If the benzoxazine polymerize only at the *ortho* phenolic sites, a phenolic Mannich bridge network structure would develop. In addition, a network structure, in which all of the oxazine rings cleave during cure, could produce a fully bisphenolic methylene bridge network. Russel et al. showed through N^{15} solid-state NMR that indeed some sites on the aryl amine ring does react. Russel et al. [19] showed that the bisphenolic methylene linkage is generated at longer cure times above 200 °C. GC/MS analysis of the degraded materials indicates that from BZ-a, the network structure consist of largely phenolic Mannich base structure with small amount of the aryl amine rings, being cross-linked by Mannich bridges as evident in the studies of Ishida's group [19]. Both the structures constitute collectively for the high autocatalysis. It can be concluded that both the structures catalyses the polymerization, resulting in a synergetic effect. Due to the presence of intra-molecular H-bonding in polymeric architecture of benzoxazine as a part of chelate ring as shown in Scheme 2 [20], this polymer is very stable. Hence after a very fast initial increase in reaction, the rate slows down and takes more time for completion. Thus, a large volume of catalyzing groups could be the major factor governing the kinetics of benzoxazine cure.

Table 1
Kinetic parameters for curing of benzoxazine at different temperatures

Temperature (°C)	$k_1 \times 10^4$ (min^{-1})	$k_2 \times 10^3$ (min^{-1})	m	n
190	2.0	7.64	0.68	0.57
195	3.2	10.20	0.61	0.58
205	11.0	12.67	0.71	0.63
210	15.4	15.71	0.71	0.78



Scheme 2. H-bonding and chelation in polybenzoxazine.

It is obvious that for any chemical reaction to occur, the reactive centers should be in close proximity to each other and also properly oriented so that a product is formed. For the cure of benzoxazines, prior to gelation and vitrification, the reaction occurs in the liquid state and the rate of cure is chemically controlled. However, for all thermosetting polymers when the viscosity increases, the rate of cure depends also on diffusion of reactants to reactive site, so that the reaction could become diffusion controlled. This may also due to the high cross-linking nature apparently enhanced by the extensive H-bonding. Even in a dimer, the free –OH groups can form a six-membered chelate ring via intra-molecular H-bonding. When monomer breaks and free –OH groups are formed, immediately the inter- and intra-molecular H-bonding possibility arises and strong H-bonding favors stability of polymer.

3.3. Activation energy for gelation

According to gelation theory, a material reaches its gel point at a critical extent of reaction. Thus, the critical gel is the iso-conversion property of any given thermosetting system and will occur at the same conversion regardless of cure temperature if the polymerization proceeds with a single mechanism. Times to gelation (t_{gel}) for benzoxazine cure at different isothermal temperatures were measured. Gelation time was determined at the onset of storage modulus or peak of phase angle (loss factor)

Table 2
Gelation times for benzoxazine at several isothermal temperatures by different methods

Temperature (°C)	t_{gel} (min) (tan δ peak)	α_{gel} (%)	t_{gel} (min) (crossover method)	α_{gel} (%)
190	52.3	0.9	112.8	4.9
195	33.8	0.6	59.6	2.9
205	31.0	1.0	49.6	4.0
210	21.0	1.2	32.7	3.4

[21] where the material began to develop mechanical properties characteristics of the elastic solids. Gelation time was also determined by the intersection of storage modulus and loss modulus. Gelation times obtained from both methods and their respective conversion at gelation are compiled in Table 2. It is known that the second method is not too dependable as on changing the frequency (frequency sweep method) the gelation time also varies, hence first method is accepted. The related activation energy was calculated by plotting ln t_{gel} against $1/T$. For gelation, the activation energy was found to be 71 kJ mol^{-1}. This early gelation also indicates rapidity of the reaction.

3.4. Generalization of cure kinetic model

The model represented by Eq. (2) has been successfully applied to the autocatalytic polymerization reactions of benzoxazine monomers. The rate constants in Eq. (2) were represented as functions of temperature. The average orders m and n were computed as 0.70 and 0.59, respectively. The activation energies corresponding to the two kinetic constants k_1 and k_2 were obtained by plotting ln k_1 and ln k_2, respectively against $1/T$. The activation energies were 198 and 62 kJ mol^{-}, respectively. The low activation energy for autocatalysis implies the prominence of this phenomenon in the overall kinetics. The various relations deduced are:

$$k_1 = \exp\left(42.85 - \frac{23790}{T}\right) \quad (4)$$

$$k_2 = \exp\left(11.20 - \frac{7423.6}{T}\right) \quad (5)$$

Substitution of these expressions in Eq. (2) led to a master differential equation, describing the conversion rate as function of T and α as

$$\frac{d\alpha}{dt} = \left[\left(\exp\left(42.85 - \left(\frac{2.3790 \times 10^4}{T}\right)\right)\right) + \left(\exp\left(11.2 - \frac{7.423 \times 10^3}{T}\right)\right)\alpha^{0.70}\right] \times (1-\alpha)^{0.59} \quad (6)$$

This master equation enables prediction of the reaction rate for polymerization of benzoxazine at any desirable temperature. Since an analytical integration was difficult for Eq. (6) the time-conversion profile was obtained from equation by its numerical integration using small time-intervals. The predicted and experimental conversion values are shown in Fig. 6, where the comparatively close match between the two validates kinetic model proposed.

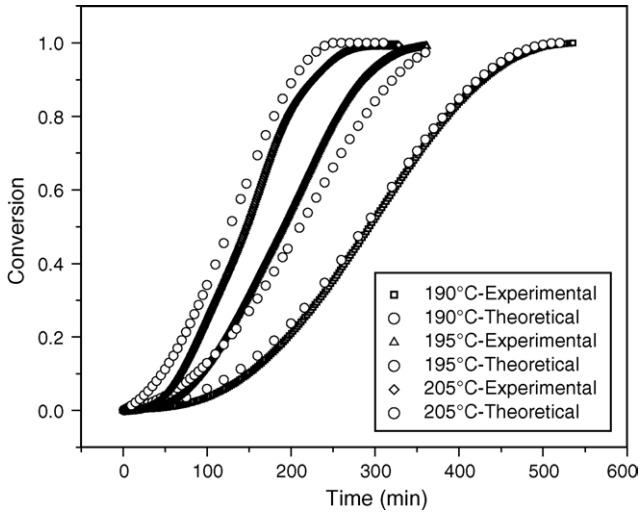


Fig. 6. Comparison between the experimental values of conversion with the values obtained from the generalized Eq. (6) at three typical isothermal temperatures.

4. Conclusions

A quantitative study on the curing of benzoxazine monomer is reported. Curing of benzoxazine (BZ-a) exhibited an enhanced autocatalysis owing to the generation of catalyzing –OH groups and the interaction of the ring-opened structures with the monomers. The curing of benzoxazine followed an autocatalytic kinetics, which was empirically modeled. The proposed empirical model conformed to the experimental time-conversion profile. The kinetic model is in league with the proposed mechanism for ring-opening polymerization of benzoxazine wherein the –OH bonding of the polymer with the monomer has greater bearing on the autocatalysis while the –OH bonding in the network accounts for the early gelation and vitrification of the system.

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