Polymer Bulletin 13, 499–503 (1985)

Polymer Bulletin

Networks

Stopping of Crosslinking Reaction in a PDMS Polymer at the Gel Point

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SUMMARY

A method has been developed to stop the crosslinking reaction of a polydimethylsiloxane system without disturbing the state of the sample. Oscillatory shear experiments on samples just before and just beyond the gelation point demonstrated the transition of the material from a viscoelastic liquid to a viscoelastic solid. At the gel point the loss modulus and the storage modulus were found to be **identical** over several decades of frequency and for temperatures ranging between $-50^{\circ}C$ and $+180^{\circ}C$. Both moduli were proportional to the square root of the frequency.

INTRODUCTION

Very little is known about the transient states of a molecular network during its crosslinking reaction. Measurements can readily be taken before onset or after completion of the reaction but intermediate states are passed by too quickly to allow detailed physical characterization. A method is needed for conserving transient states of the network by stopping the reaction without disturbing the state of the molecular structure already formed. The evolving crosslinking process is then representable by a discrete set of samples with increasing extent of reaction. Measurements on these samples can answer questions such as:

- How do viscoelastic properties change with the extent of reaction?
- How does molecular network structure develop?
- Is there a single transition state between liquid and solid?
- If so, what are the properties of the transition state?

In this study, a method is proposed for stopping the crosslinking reaction of a model network polymer. The technique is based on very rapid poisoning of the catalyst at chosen degrees of conversion. Initial rheological experiments reveal unexpected properties at the transition state.

Several other methods for stopping the reaction were considered: thermal quenching of the system while crosslinking, changes of the stoichiometric ratio of the reactants, end-capping of all the functional groups. These methods are not employed since the first one does not allow the use of time-temperature superposition, and the latter two will strongly disturb the state of the structure formed and hence would only barely approximate the stages of partial conversion.

Further rheological experiments and measurements of the extent of reaction will be presented in a later publication. The long term objective of this research is a correlation of rheological properties with extent of reaction (1) and with branching theory (2-4).

EXPERIMENTAL

Poly(dimethylsiloxane) (PDMS) networks were prepared by the hydrosilation reaction of tetrakis(dimethylsiloxy)silane and α, ω divinyl-terminated linear PDMS prepolymer in the presence of cis-dichlorobis (diethylsulfide)platinum(II) catalyst. This system was suggested by the previous work of Valles and Macosko (1). It was chosen for its well defined chemical nature, the need of catalysis, the availability of prepolymers with different molecular weights, and the elastomeric nature of the samples after crosslinking.

The PDMS prepolymer was purchased from Petrarch System Inc.. Low molecular weight volatiles (1.1% by weight) were removed by stirring the materials for 12 hours at 140°C under high vacuum. The number average molecular weight was measured by vapor pressure osmometry and was found to be Mn=10300. The tetrafunctional crosslinker was distilled in a Perkin Elmer spinning band column. The purity obtained was higher than 99.99% as measured by gas-liquid chromatography (using a 10% OV101 column). The purified crosslinker was stored under nitrogen atmosphere. The platinum catalyst was synthesized following the procedure of Kauffman & Cowan (5). The cis isomer was made very pure after successive recrystallizations (m.p. 105°C). The catalyst was prepared in the form of a $1.8X10^{-3}$ molal solution of platinum in dry toluene and was stored under nitrogen.

The samples were prepared at room temperature and under nitrogen atmosphere by first mixing the PDMS prepolymer with the catalyst for one hour. Then the crosslinker was added in stoichiometric amounts, and the mixture was stirred for 15 minutes and degassed. The platinum concentration in the sample was $8.6X10^{-5}$ mole of Pt per mole of prepolymer, and the amount of toluene (from the catalyst) incorporated into the reactants was less than 0.4% by weight. After mixing the reactants, the preparation was placed into several small containers which were stored in liquid nitrogen.

Prior to use, all the samples were removed from liquid nitrogen and reacted isothermally at 34°C. Some samples were used to continuously record the evolution of the storage (G') and loss (G") moduli during the crosslinking reaction. The mechanical measurements were performed with a Rheometrics Dynamic Mechanical Spectrometer using 25mm diameter parallel disks. All the measurements were carried out within the range of linear viscoelasticity. The other samples were poured on the bottom plate of the rheometer and allowed to react. At chosen extents of conversion the reaction was stopped by spraying a toluene solution of elemental sulfur on top of the sample. Elemental sulfur even in trace amounts is known to destroy the catalyst instantaneously (1). The molar ratio of sulfur to platinum employed was less than 1000, and the amount of toluene introduced into the samples was less than 1.5% by weight. Just after spraying the poison solution, the upper plate of the rheometer was positioned, and the storage and loss moduli were recorded during the process of catalyst poisoning. After the reaction was completely stopped, master curves of G' and G" versus frequency were obtained by applying time-temperature superposition (7).

RESULTS AND DISCUSSION

Figure 1 shows the evolution of the dynamic storage G' and loss G"

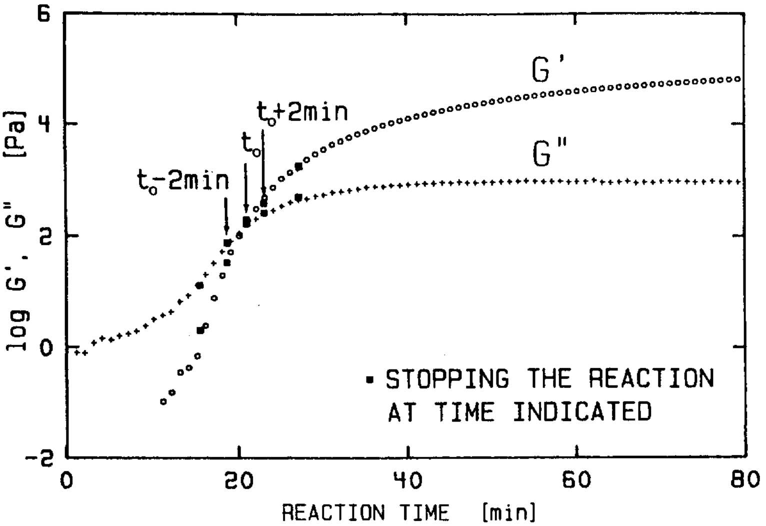

Figure 1. Evolution of the complex shear modulus, G' and G" during crosslinking of PDMS at 34°C, ω = 0.5rad/s

moduli during the isothermal crosslinking process. By continuously decreasing the shear strain amplitude from 3.0 to 0.005 the increase of the linear viscoelastic material properties is accurately followed over 6 decades in modulus. Samples from the same batch have the same history, thus the curing curve is extremely reproducible. Because of the well defined procedure employed during the sample preparation, and because of the high purity of the reactants, a very high reproducibility from batch to batch is obtained.

At any conversion, the reaction is stopped within 2 to 3 minutes of poisoning which is short compared to the total reaction time of 180 minutes. A sample thickness of 0.7 to 0.8mm is used in order to minimize the diffusion time of the sulfur into the sample. Complete evaporation of the slight amount of toluene introduced into the sample during the spraying of the sulfur solution is obtained by drying the material for 2 hours at 120°C. The partially reacted samples are stable beyond 180°C, but an increase of both moduli attributed to oxidation is observed above 200°C.

As represented by the dark squares on the curing curve, Figure 1, the dynamic and loss moduli of the partially reacted samples superimpose very well upon the data measured on the continuously curing samples. The temperature stability allows the use of time-temperature equivalence in order to obtain master curves of G' and G" versus frequency at different stages of the crosslinking process, Figure 2. This study requires the use of parallel disk geometry since gap corrections must be made to compensate for variations in sample volume during the temperature changes.

Before reaching the gel point, G" is higher than G' within the frequency range investigated, Figure 2a. Hence more energy is dissipated than stored during one cycle of deformation. Both moduli decrease to zero at low frequencies or long times. Beyond the gel point, Figure 2b, the viscoelastic behavior is reversed since G' is higher than G". A plateau value of G' is observed at low frequencies which indicates that the material possesses a permanent elasticity.

The transition state at the gel point is characterized by equal

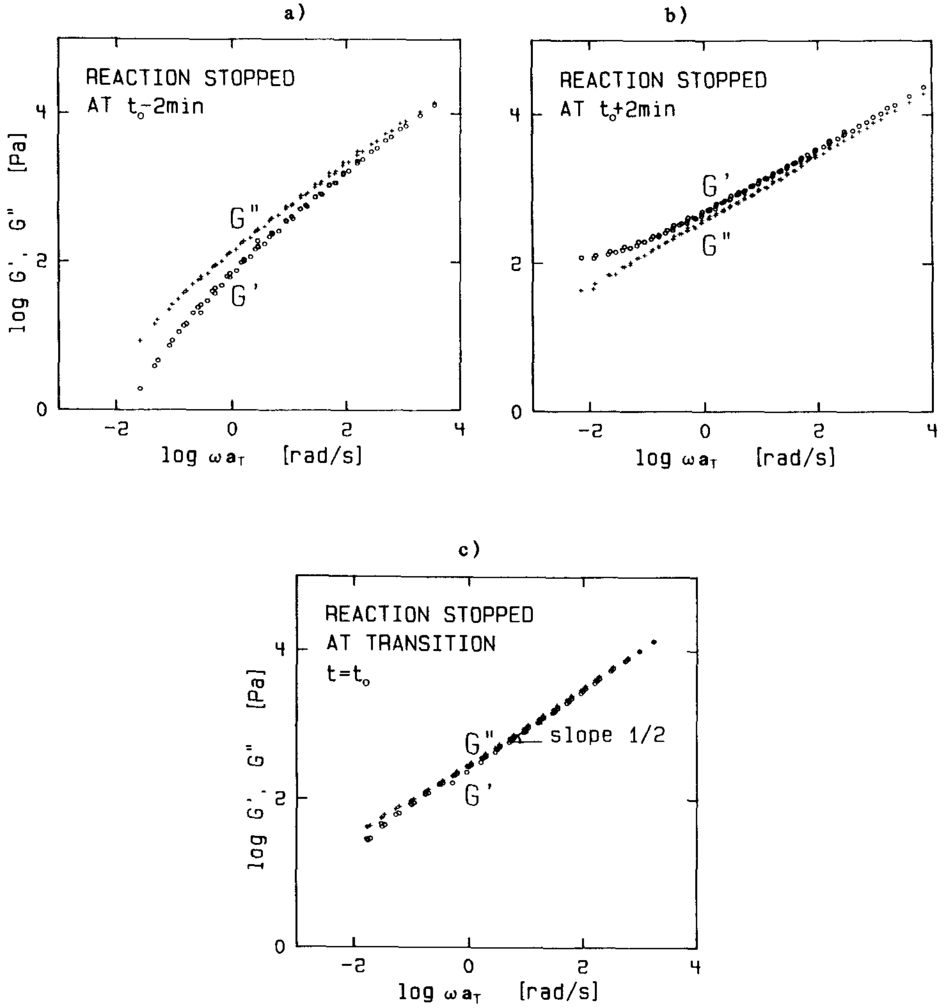

Figure 2. Evolution of the storge G' and loss G" moduli. Master curves reduced at 34°C
a) 2 minutes before the transition state
b) 2 minutes after the transition state
c) the transition state (very slightly before)

storage and loss moduli for nearly all the frequencies investigated, Figure 2c. This state corresponds to the transition from a material without permanent elasticity to a material with permanent elasticity. This transition from liquid-like to solid-like behavior is defined as gelation in non-linear polymerizations (2). This result confirms the speculation of Tung et al. (6) that the crossover of the storage and loss moduli measured during isothermal curing occurs at the gel point.

The storage and loss moduli are defined by the theory of linear viscoelasticity (7) as:

$$G' = \omega \int_0^\infty G(t)\sin(\omega t)dt \qquad \text{and} \qquad G'' = \omega \int_0^\infty G(t)\cos(\omega t)dt$$

with a relaxation modulus G(t). At the transition state, the experiments shown in Figure 2c indicate that:

$$G' = G'' = A\ \omega^{1/2}$$

where A is a material constant. A possible solution for G' equal to G'' at all the frequencies is obtained for a relaxation modulus:

$$G(t) = g\ \sqrt{\lambda/t}$$

where g is a modulus and λ is a relaxation time. A decay of the relaxation modulus proportional to $t^{-1/2}$ is predicted at the transition state which confirms the liquid-like nature of the material as observed in Figure 2c. However, it must be noted that the proposed solution presents a singularity at short times and hence the behavior described by this solution is only applicable at large times ($t > \lambda$). The zero shear viscosity predicted from this relaxation function is infinite. Therefore at the transition state the material is predicted to have an infinite viscosity but is not yet a solid since it cannot support a stress for an infinitely long time without flowing.

In conclusion, the crosslinking reaction of a PDMS system has been stopped at intermediate states. No disturbance prior to stopping the reaction has been observed. The time required for stopping the reaction is small compared to the overall reaction time, and the samples obtained are stable over a wide range of temperatures. The crossover point of the storage and loss moduli measured during isothermal curing is shown to correspond to a transition state from a liquid-like to a solid-like material. Stress relaxation and steady state viscosity of the network at the transition state are predicted from oscillatory shear data. Rheological experiments to verify these predictions are in progress and will be reported in a follow-up article.

ACKNOWLEDGEMENTS

Financial support from the Center for UMass Industry Research in Polymers (CUMIRP) is acknowledged. We are also grateful to Professor S. Kantor for helpful discussions about PDMS chemistry and to Professor T. McCarthy for the use of his laboratory.

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Accepted June 10, 1985

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