Relaxation patterns of endlinking polydimethylsiloxane near the gel point

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Summary

While the theological behavior at the gel point (GP) itself is well known, many questions remain about the approach to the gel point (from either side). For studying this phenomenon, rhelogical experiments were performed on crosslinked polydimethylsiloxanes (PDMS) and characteristic patterns in the relaxation behavior were abstracted into a phenomenological model for the relaxation time spectrum. The well known power law with slope -n and cutoff at the longest relaxation time λ_{max} governs the relaxation near the gel point. Beyond the gel point, an additional box-like contribution appears in the spectrum. The relaxation exponent n decreases with increasing extent of crosslinking. The longest relaxation time λ_{max} and equilibrium modulus G_e show power-law scaling with the distance from the get point, $|p - p_c|$. For samples with imbalanced stoichiometric ratios $r \geq 1$, the function $n(p-p_c)$ is independent of r. Samples with strong crosslinker deficiency (r=0.5) exhibit a different functional form for $n(p- p_c)$ from those with $r \geq 1$. The power law relaxation with decreasing n in the terminal zone was found previously for a different crosslinking system. It seems to be a common pattern for partially crosslinked materials from polymeric precursors.

Introduction

Crosslinking polymeric materials can form molecular clusters which are held together by covalent bonds. The gel point (GP) is reached at a critical degree of crosslinking, p_c, when the largest cluster diverges and spans the entire sample as a three-dimensional network. The material is at an intermediate state between liquid and solid. The relaxation behavior at GP shows a selfsimilar pattern which was first observed by Chambon and Winter (1-3) on the same PDMS materials that we use in the present study. The GP relaxation modulus at long times follows a power law

$$G(t) = S\, t^{-n} \qquad\qquad \lambda_0 < t < \infty \qquad\qquad (1)$$

where S is known as the get stiffness and n is the relaxation exponent. The corresponding relaxation time spectrum also shows power law behavior

$$H(\lambda) = \frac{S}{\Gamma(n)} \lambda^{-n} \qquad\qquad \lambda_0 < \lambda < \infty \qquad\qquad (2)$$

where $\Gamma(n)$ is the gamma function. The power law relaxation at GP results in a simple criterion for GP: The loss tangent at GP is independent of frequency in the terminal relaxation regime and directly related to the relaxation exponent n:

$$\tan\delta = \tan\frac{n\pi}{2} \qquad (3)$$

This criterion is conveniently used to experimentally determine GP.

While the relaxation directly at GP follows this simple pattern, the rheology in the vicinity of GP is more complex (4,5). Using a system of partially crosslinked polybutadienes (PBD) from nearly monodisperse precursors with $M_w > M_e$, we have expressed rheological data a phenomenological model (4) that reproduced the G', G'' data before and after GP. The relaxation pattern consisted of a superposition of three power laws, two resulting from the BSW-spectrum (6) describing the precursor relaxation and a third one containing the information of additional longer relaxation times due to the crosslinking reaction. Rather surprisingly, a box-like contribution had to be added beyond GP to be able to describe the experimental G'' data. In addition, the value for the equilibrium modulus, G_e, had to be specified after GP. All important parameters (n, λ_{max}, G_e) are functions of the extent of crosslinking.

The objective of the present study is to evaluate the model on a different system, built from a polydisperse precursor with a molecular weight below the entanglement molecular weight. Such a precursor does not show BSW relaxation behavior. It is known for one of those systems that the relaxation exponent at GP takes on different values depending on the stoichiometric ratio (r=ratio of concentration of functional groups of the crosslinker and concentration of vinyl groups of the polymer precursor) of the crosslinking mixture (3). In the present study we address the question whether and how the stoichiometric ratio influences other model parameters. Furthermore, this study concerns endlinking molecules while the PBD of the previous study was vulcanized.

Our general goal is to use modeling as a tool for analyzing experimental observations on crosslinking PDMS and for detecting characteristic relaxation patterns in the vicinity of GP. The model can then be interrogated to gain further insight into the gelation phenomenon. Such study is needed in light of the unusual findings with crosslinking PBD (4).

Experimental results and discussion

The precursor polymer (7) is an α,ω-divinylterminated polydimethylsiloxane (PDMS) with number average molecular weight of approximately 10^3 and polydispersity index of about 2. The molecular weight is well below the entanglement molecular weight, M_e. The polymer can be endlinked with a four-functional crosslinker, tetrakis-(dimethylsiloxy)silane. The crosslinker, after vacuum distillation, was determined (by chromatography) to be at least 99.2 % pure. The platinum catalyst of the crosslinking reaction, cis-dichlorobis(diethylsulfide)platinum(II), is applied in a $1.8*10^{-3}$-molar solution in toluene. It is easy and convenient to prepare several samples with exactly the same initial conditions. 15 g of PDMS are mixed in a flask with 0.1 ml of the catalyst solution. The mixture is stirred for one hour at room temperature and then degassed for 10 minutes using a vacuum pump. The stoichiometrically needed amount of crosslinker is added and the mixture is stirred for another 20 minutes including 2 minutes for degassing. The mixture is subsequently poured into several small glass vials and then stored in liquid nitrogen to effectively stop the crosslinking reaction. If a sample is needed for an experiment, one vial is allowed to thaw for 5 minutes at room temperature.

Rheological studies were performed both during the reaction and after having stopped the reaction at intermediate conversions. Reacting samples were investigated at 30 °C using a time-resolved rheometry technique (8) in a Rheometrics™ Mechanical Spectometer, RMS 800, equipped with parallel plates (diameter 25 mm). Cyclic frequency sweeps (CFS) probed the samples in a frequency window of 1 rad/s to 200 rad/s. Stopped samples were prepared as follows: The reacting mixture was poured into a mold (formed by a bottom rheometer plate, an aluminum ring to prevent the liquid from flowing off the plate, and a peroxide cured rubber O-ring to seal the gap between plate and ring) with a diameter of 25 mm and a depth of about 0.8 mm. At the desired reaction time, the catalyst was poisoned by spraying a 0.33-molar solution of sulfur in toluene on top of the sample. This effectively stopped the crosslinking reaction. The average diffusion time of the catalyst poison of 1 to 2 mm is considerably smaller than the overall reaction time to reach GP (approximately 1 hour). The aluminum ring was then removed, and the sample was placed into the rheometer. The dynamic mechanical response of a variety of stopped samples at stoichiometric ratios of r=0.5, r=1.0, and r=1.5 was measured at temperatures between -50 °C and 150 °C.
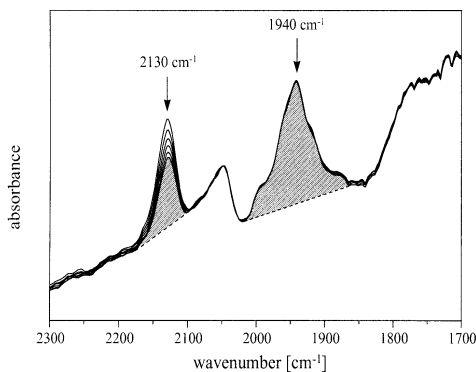

Fig. 1: Infrared absorption spectra of crosslinking PDMS (stoichiometric ration r=1.0). The absorbance band at 2130 cm^{-1} corresponds to the silane, group of the crosslinker, the band at 1940 cm^{-1} does not change during crosslinking and is used as a reference

The chemical extent of reaction during crosslinking was monitored by FTIR spectroscopy. The reacting mixture was poured between two KBr plates (using 0.25 mm spacers) in a Harrick liquid cell which was set to a temperature of 30 °C. This assembly was then placed into an IBM IR/32 infrared spectrometer which took a spectrum every 3 min at a resolution of 4 cm^{-1}. The absorbance at around 2130 cm^{-1}, which is linearly proportional to the depletion of the crosslinker's silane group, reflects the extent of reaction (7). The validity of Beer's law (linearity between absorbance and concentration) was tested with a set of well defined samples of different crosslinker concentrations. Figure 1 shows the evolution of the infrared absorption spectrum during crosslinking of the PDMS sample with a stoichiometric ratio of r=1.0. The extent of reaction was calculated by

$$p(t) = \frac{A(t_0) - A(t)}{A(t_0)} \qquad (4)$$

where $A(t)$ and $A(t_0)$ are the normalized areas of the silane peak at time t and initial time t=0 (taken from the calibration curve), respectively. For normalization the peak areas were divided by the area of the reference peak at 1940 cm^{-1}. The area of the these peaks are shown for the last spectrum in the series.

A direct correlation between rheological data and extent of reaction was possible by simultaneously performing rheological and infrared experiments on the same sample. The

temperatures of rheometer and IR liquid cellwere calibrated prior to the experiments to agree within ±0.3 K.

This evolution of the dynamic storage and loss moduli, G' and G'', during the crosslinking of a sample with r=1.0 is shown in Figure 2 for three different frequencies.
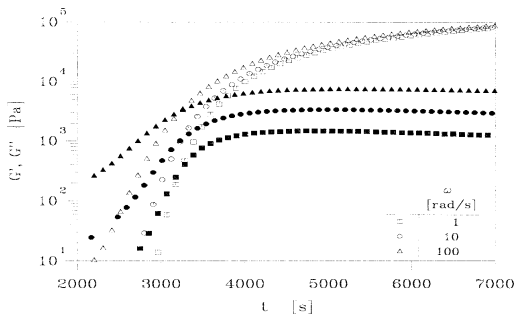

Fig. 2: Evolution of dynamic moduli during crosslinking (r=1.0) at 30 °C. Data at three different frequencies are shown. (open symbols: G', filled symbols: G'').
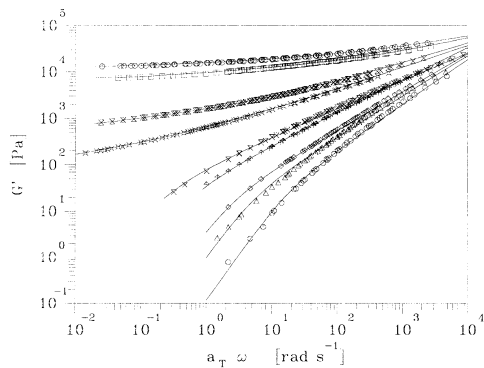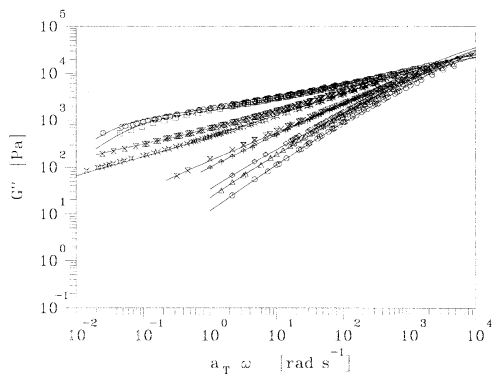

Fig. 3: storage modulus G' (tcp), loss modulus G'' (bottom) data compared to model (lines) of stopped samples (r=1.0) at different extents of reaction (T_{ref}=30 °C). The model is defined in eq.5 below.

The FTIR data yields the necessary p(t)-relation to convert this time dependence into a dependence on extent of reaction. Frequency dependent data can then be interpolated at any given time (or extent of reaction) of the experiment, i.e. at any stage of crosslinking, resulting in an instantaneous rheological picture of the material.

Stopped sample data at different temperatures were shifted onto master curves. The G' and G" master curves of a variety of stopped sample with r=1.0 are displayed in Figure 3. The reference temperature for all master curves equals the reaction temperature during the CFS experiment, i.e., T_{ref}=30 °C. The extent of reaction of these stopped-sample data sets can be determined by matching stopped-sample data and interpolated data from the CFS experiment for which the extent of reaction is known. This matching procedure is described in more detail in a previous paper (4).
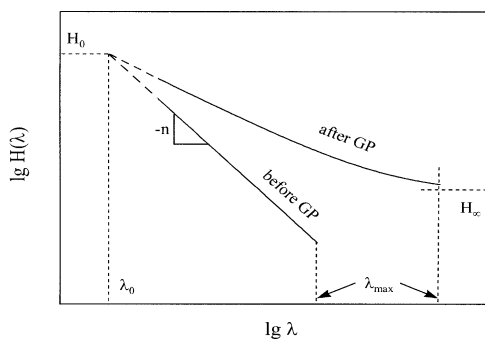
Fig. 4: Schematic of the model relaxation time spectrum before and after the gel point.

Model Relaxation Time Spectrum

When describing the relaxation patterns of partially crosslinked polybutadienes with an initial molecular weight above the entanglement molecular weight we developed a relaxation time spectrum that consists of a combination of several power laws (4). The crosslinking mainly influenced the terminal relaxation regime. Therefore, the BSW-spectrum (6), which describes the relaxation behavior of the nearly monodisperse precursor, still described (with minor modifications) the relaxation behavior in the entanglement and glass transition regimes. The additional longer relaxation times that were introduced by the crosslinking reaction followed a power law relaxation pattern with a variable exponent (-n). After GP, a further box-like contribution to the spectrum (which we termed H_∞) was needed to satisfactorily describe the data. This spectrum with its characteristic pattern was able to describe all rheological observations near GP including the master curves, the time evolution of the dynamic moduli, the divergence of zero-shear viscosity and equilibrium compliance at GP, the functional dependence of the gel stiffness, and the frequency dependence of the rates of change of the dynamic moduli at GP.

The PDMS used in this study does not exhibit any entanglement relaxation since the molecular weight is below the entanglement molecular weight. Hence, the model spectrum for the partially crosslinked PDMS samples can not contain the BSW-part. The relaxation can be modeled by a single power law spectrum before GP which is modified by the box H_∞ after GP (Figure 4):

$$H(\lambda) = \left(H_0 - H_\infty\right)\left(\frac{\lambda}{\lambda_0}\right)^{-n} + H_\infty \quad \text{for } \lambda_0 < \lambda < \lambda_{max} \tag{5}$$

with H_∞ equal to zero before GP. Additionally, a value for the equilibrium modulus, G_e, has to be specified after GP to characterize the solid-like behavior of the material. The parameters H_0 and λ_0 are coupled. One of them can be chosen freely, which in turn fixes the value of the second parameter. All spectra for samples of the same stoichiometric ratio could be modeled with almost the same pair of (H_0, λ_0). This, however, is not a strict requirement and cannot be necessarily deducted from the experimental data. A tendency towards a single fix point can be seen in the calculated spectra although outside the experimental time window. An example for the evolution of the model spectra is depicted in Figure-5 (r=1.0).
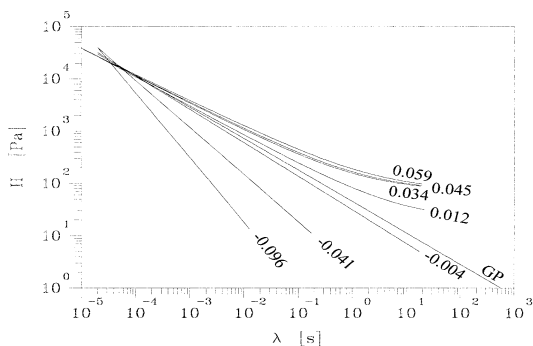

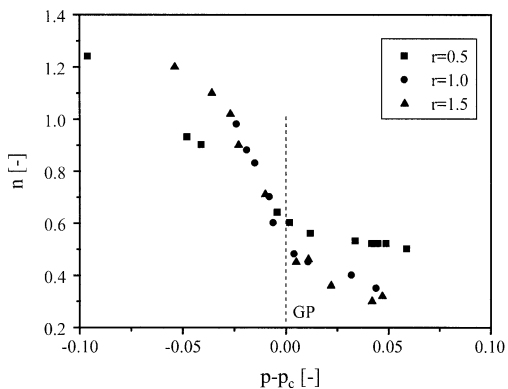Fig. 5: Relaxation spectra used for modeling the dynamic data of stopped PDMS samples (r=0.5).

Fig. 6: Evolution of the relaxation exponent n with extent of reaction for all stoichiometric ratios. The relaxation exponent at the gel point equals 0.61 for r=0.5 and 0.5 for r=1 and r=1.5.

The relaxation exponent at GP can be determined from the crossover of the loss tangent (eq 3). For the material with crosslinker deficiency (r=0.5) n equals 0.61 at GP while the materials with r=1.0 and r=1.5 show a relaxation exponent of 0.5 at GP. Initially, we believed that the dependence of n on the extent of reaction is the same for all samples with r≥1.0 and simply shifted to higher values of p-p$_c$ for the sample with r=0.5. Figure 6 shows the result from modeling the experimental data. The dependence of n on p near

GP is the same for the samples with r≥1.0 as expected but the functional form for the (r=0.5) sample is completely different. It is decays much less than for samples with higher stoichiometric ratios.

Several physical models for nearly critical gels that are given in the literature, such as dynamic scaling (9, 10) and time-cure superposition (11), appear to result in a constant value for n. They might be applicable to crosslinking of <u>small</u> molecules. However, they need to be altered to include the functional dependence of n on p of polymeric systems.

The longest relaxation time, λ_{max}, scales characteristically in some power law with the distance from GP, $|p - p_c|$, as does the equilibrium modulus, G_e, and the box contribution, H_∞. These parameters are shown in Figure 7. Scaling exponents for λ_{max}, before GP and G_e and H_∞ after GP were determined by linear regression. However, because of the insufficiency of the low frequency data, the values for λ_{max} after GP could only be determined accurately for the samples with r=1. For the other samples, only a lower limit can be given. This was already explained in more detail in our previous paper (4). Hence, the assumption of symmetric scaling of the longest relaxation time around GP (12) can not be tested for the partially crosslinked PDMS samples except at r=1. Here, symmetry does not occur. It is interesting to note that α_-, the scaling exponent of the longest relaxation time before GP, shows a strong increase with increasing stoichiometric ratio.

The scaling exponents for the equilibrium modulus are similar for all studied three stoichiometric ratios. They are also in the same range as the values determined for the high molecular weight PBD samples previously studied (4). Furthermore, although the value of ξ at balanced stoichiometric ratio deviates significantly from the samples at imbalanced stoichiometric ratio, the values in general are similar to those found for PBD.
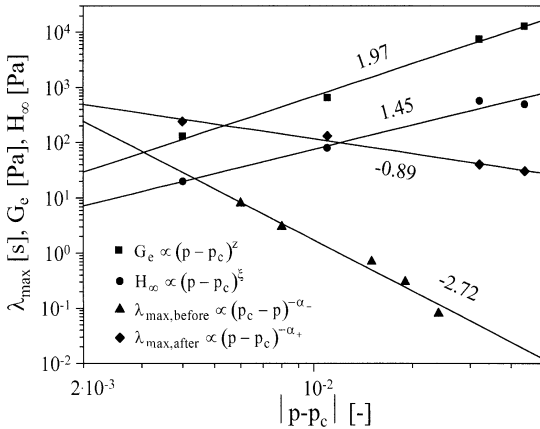

Fig. 7: Scaling of parameters λ_{max}, G_e, and H_∞ with distance from the gel point, $|p - p_c|$, for PDMS (r=1.0). Symbols depict the values extracted from modeling the stopped sample master curves, lines represent the corresponding fit by linear regression. The scaling exponent for each parameter is displayed as well.

Conclusions

Nearly critical gels of the PDMS samples exhibit the same relaxation patterns in the terminal zone as the polybutadienes (PBD) of ref. (4). This is in spite the fact that they not only have different chemical building blocks but also lower molecular weight (below entanglement limit), polydispersity, and connectivity by endlinking. The model parameters of the relaxation pattern are n and λ_{max} before and n, λ_{max}, H_∞, and G_e after GP. in addi-

tion, we use material inherent values for H_0 and λ_0 which only depend on the specific stoichiometric ratio of a sample.

The relaxation exponent, n, of the PDMS, strongly decreases with increasing extent of reaction, as was found with the PBD. Interestingly, the dependence of n on the extent of reaction is the same for samples with stoichiometric ratios of r≥1. These samples also have the same relaxation exponent at GP (n=0.5). The sample with crosslinker deficiency, r=0.5, however, exhibits a completely different dependence of n(p) near GP. Also, the value of n at GP is higher for this sample (n=0.61). Because of the change of the relaxation exponent with extent of reaction, dynamic scaling and time-cure superposition does not apply to our system. Both principles require constant n.

The box-like contribution to the spectrum, H_∞, is needed to express the rising G" beyond GP. This is further evidence for lack of symmetry between the relaxation time spectrum before and after GP.

Over all, the differences in the precursor relaxation between PDMS and PBD do not seem to influence the spectrum in the terminal zone where most of the changes take place during the crosslinking. Power law relaxation with decreasing relaxation exponent, n, and the appearance of a box-like contribution to the spectrum, H_∞, seems to be a common pattern for partially crosslinked polymers near GP.

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