

RHEOLOGY OF CROSSLINKING POLYMERS AT THE GEL POINT

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Very little has been known about the transient states of network polymers during the crosslinking reaction. Measurements could be readily taken during early stages or near completion of the reaction. Intermediate states near the gel point were passed by too quickly to allow detailed physical characterization. Chambon and Winter (1) therefore developed a method for conserving intermediate states of a crosslinking polydimethylsiloxane (PDMS) (2). Stopping the reaction did not disturb the preceding network formation process. The continuous crosslinking reaction was thus represented by a discrete set of stable samples with increasing extent of reaction. Rheological measurements on these stable samples showed clearly how the gel point was approached and passed during network formation. The linear viscoelastic behavior at the gel point was found to follow a surprisingly simple constitutive relation (3)

$$\tau(t) = S \int_{-\infty}^t (t - t')^{-n} \dot{\gamma}(t') dt'$$

where τ and $\dot{\gamma}$ are the stress and the rate of deformation. Stress relaxation of the gel follows a power law with an exponent

$$n \begin{cases} = 1/2 & \text{stoichiometrically balanced (3)} \\ > 1/2 & \text{stoichiometrically imbalanced (4)} \end{cases}$$

which depends on the stoichiometry of the polymer system. The gel-strength S depends on the molecular parameters of the network. For completeness, it should be mentioned that the constitutive equation can easily be rewritten for finite viscoelasticity (3).

The experiments suggest fractal behavior of the gel with a fractal dimension of 2 for the stoichiometrically balanced network (5). The network with imbalanced stoichiometry has a fractal dimension of

$$d_f = \frac{2n}{n-1}$$

The fractal dimension is not expected to exceed the value 3. This indicates an upper bound for the power law exponent $n_{\max} = 3/5$.

The rheological constitutive equation describes the classical attributes of the gel (6): infinite steady shear viscosity and zero equilibrium modulus. The instant of gelation can also be detected by the occurrence of the power law relaxation behavior. This makes it now possible to accurately measure the instant of gelation.

The simplicity and clarity of the constitutive law for the PDMS gel suggest universal validity for network polymers at the gel point. Chambon

et al. (7) therefore measured the linear viscoelastic behavior of a stoichiometrically balanced model polyurethane (PU) (8) during crosslinking and found exactly the same constitutive relation as for the PDMS. This is a rather remarkable result since not only is the chemistry of the two networks different but the crosslink functionality was chosen to be different (4-functional for the PDMS and 3-functional for the PU).

The networks under investigation were all formed by endlinking reaction. They were studied much above the glass transition, except for one sample which indicated that closeness to glass transition may mask the rheology of the gel. Physical entanglements are assumed to be of no importance in this study since the molecular weight of the prepolymers was chosen below the entanglement limit.

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References

1. F. Chambon and H. H. Winter, *Polym. Bull.*, 13, 499 (1985).
2. E. M. Valles and C. W. Macosko, *Macromolecules*, 12, 521 (1979).
3. H. H. Winter and F. Chambon, *J. Rheol.*, 30, xxxx (1986).
4. F. Chambon and H. H. Winter, *J. Rheol.*, (1986), submitted for publication.
5. M. Muthukumar and H. H. Winter, *Macromolecules*, 19, xxxx (1986).
6. P. J. Flory, 'Principles of Polymer Chemistry', Cornell Univ. Press, Ithaca, NY, 1953.
7. F. Chambon, Z. S. Petrovic, W. J. Macknight, H. H. Winter, *Macromolecules*, (1986), submitted for publication.
8. C. Feger, S. E. Molis, S. L. Hsu, W. J. Macknight, *Macromolecules*, 17, 1830 (1984).