

Organising Committee

Prof. J. W. Goodwin (*Chairman*)
Dr. R. Audebert
Dr. R. Buscall
Prof. M. Djabourov
Dr. A. M. Howe
Prof. J. Livage
Prof. J. Lyklema
Prof. S. B. Ross-Murphy

ISBN: 0-85404-878-2

ISSN: 0301-7249

Typeset by Santype International Ltd., Netherhampton Road, Salisbury, Wiltshire and
printed and bound in Great Britain by Whitstable Litho Printers Ltd.

Rheological Expression of Physical Gelation in Polymers

Claudius Schwittay, Marian Mours and H. Henning Winter

Department of Chemical Engineering, University of Massachusetts, Amherst, MA 01003, USA

Polymeric materials at the liquid–solid transition exhibit unusual simplicity and regularity in their relaxation pattern. This expresses itself in a self-similar relaxation modulus $G(t) = St^{-n}$ at long times $\lambda_0 < t < \infty$, where λ_0 is the characteristic time for the crossover to a different relaxation regime (*e.g.* crossover to glass transition or entanglement region). Rheological features of liquid–solid transitions are very similar for chemical and physical gelation: (1) broadening of the relaxation time spectrum, (2) divergence of the longest relaxation time (with an upper cut-off for physical gels) and (3) self-similar relaxation patterns. We have borrowed terminology from chemical gelation and applied it to an example of physical gelation: the isothermal crystallization of isotactic polypropylene. The transition through the gel point has been investigated by dynamic mechanical experiments. The influence of temperature and crystallization rate have been studied. The degree of crystallinity (estimated by the Avrami equation) at the gel point was very low (6–15% depending on the crystallization temperature).

Introduction

A cross-linking material is able to form molecular clusters which grow in size. A transition from a liquid to a solid state occurs when the largest cluster diverges in size at a sufficiently high degree of cross-linking, p_c . The material at this transition [gel point (GP)] is known as a critical gel. The long-range connectivity in the material can be arrived at by different mechanisms: (1) during chemical gelation permanent covalent bonds connect molecular strands into a three dimensional network while (2) in physical gelation the 'bonds' are of a temporary reversible nature (*e.g.* crystalline regions, hydrogen bonding, ionic clusters, phase separated microdomains) and the average lifetime of such a bond is long compared with the observation time. The molecular weight distribution diverges at the GP in chemically cross-linking systems but remains finite in physically cross-linking materials. The difference between chemical and physical bonds can be clearly seen in a solvent extraction experiment: it works well for identifying the GP of a chemically cross-linking system which before the GP (called 'sol') can be completely dissolved in suitable solvents and after the GP ('gel') cannot be completely dissolved because of the permanent network structure. This is different for a physical gel which can still be dissolved in suitable solvents, even beyond the physical GP. This makes it difficult to define the physical gel point.

Rheologically, the GP (in chemically cross-linking systems) is defined as the instance during cross-linking at which the zero shear viscosity, η_0 , diverges and the equilibrium modulus, G_e , is still zero. Before the GP, the zero shear viscosity may be measured in a constant rate experiment at low shear rates, while the equilibrium modulus after the GP is usually extrapolated from the long time response of a step strain experiment. The closer the material is to the GP the longer the stress needs to reach its steady state. Constant-rate experiments for measuring η_0 necessarily impose large strain, even at low

shear rates, which tends to interfere with the growth of the three dimensional structure. This is especially true for physical gelation since the bonds are reversible. Also, very near the GP the time to reach steady shear flow might be similar or longer than the lifetime of the physical bond, therefore the zero shear viscosity might remain finite at the GP because the material can still completely relax. Furthermore, transient experiments by which the zero shear viscosity before, and the equilibrium modulus after, the GP can be measured are not possible very near to the GP due to instrument limitations and can therefore only yield an approximate gel time. The viscosity measurement is therefore quite inconclusive.

Critical gels exhibit an unusually simple and regular relaxation behaviour which expresses itself in a self-similar relaxation modulus which was experimentally discovered by Chambon and Winter:¹

$$G(t) = St^{-n} \quad (1)$$

where S is the gel stiffness and n the critical relaxation exponent. The self-similar relaxation behaviour is valid in the terminal zone at long times, $\lambda_0 < t < \infty$. The lower limit corresponds to some relaxation time that characterizes the crossover to a different relaxation mechanism. This can be the glass transition or entanglement behaviour depending on the molecular weight of the precursor.² Since the longest relaxation time diverges at the chemical gel point, the self-similar relaxation is valid to infinite time. The self-similar relaxation behaviour can also be expressed by a power-law relaxation time spectrum, known as a Chambon–Winter spectrum:

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

The relaxation exponent may have values $0 < n < 1$. Relaxation exponents < 0 would lead to an unphysical increase in the relaxation modulus with time and the upper limit of $n < 1$ guarantees the divergence of the viscosity at the GP. Consequently, the dynamic storage and loss moduli, G' and G'' , scale with frequency, ω , at the GP:

$$G' = \frac{G''}{\tan \delta} = S\Gamma(1-n)\cos \frac{n\pi}{2} \omega^n; \quad 1/\lambda_0 > \omega > 0 \quad (3)$$

This leads to a loss tangent which is independent of frequency at the GP and closely related to the relaxation exponent n :

$$\tan \delta = \tan \frac{n\pi}{2} \quad (4)$$

The gel stiffness S was found to follow a simple power law equation^{3,4}

$$S = G_0 \lambda_0^n \quad (5)$$

where G_0 is close to the equilibrium modulus of the fully cured material and $G_0 \lambda_0$ takes values in the order of the zero shear viscosity of the precursor.

The frequency independence of the loss tangent is most easily and reliably used to determine the gel point.⁵ Dynamic mechanical experiments can be performed during the transition from liquid to solid. These experiments do not disturb the ongoing cross-linking process since usually only small strains are imposed on the materials. Many researchers use the crossover of G' and G'' as an indicator for the GP⁶ which is wrong in general. The only exception in which the true GP and this crossover coincide is the critical gel for which the relaxation exponent $n = 0.5$.⁷ The independence of the loss tangent of frequency therefore provides the most reliable and generally valid method to determine the gel time. The method has been widely tested on chemically (*e.g.* PDMS,^{1,8}

PU,⁹ epoxies¹⁰) and physically (*e.g.* PVC,¹¹ thermoplastic elastomeric PP¹²) cross-linking systems. Depending on the nature of these systems relaxation exponents spanning almost the entire possible interval of $0 < n < 1$ were found.

The importance of physical gelation (particularly crystallization) is, for instance, evident when considering the fact that many polymers solidify into a semicrystalline morphology. Their crystallization process, driven by thermodynamic forces, is hindered due to entanglements of the macromolecules and the crystallization kinetics is restricted by the molecular diffusion of the polymers. Therefore, crystalline lamellae and amorphous regions coexist in semicrystalline polymers. The formation of crystals during the crystallization process results in a decrease of molecular mobility since the crystalline regions act as cross-links which connect the molecules into a sample-spanning network. Dynamic mechanical experiments are known to be a sensitive measure of these processes.²³

Injection moulding of semi-crystalline polymers is an example of a process which is dominated by crystallization. Particularly, the rate of crystallization is important. During injection of the molten polymer into the mould, a layer of polymer gets deposited at the cold walls of the mould where it starts solidifying while exposed to high shear stress due to ongoing injection. This is an important part of the process since the wall region later forms the surface of the manufactured product. A high shear stress during this crystallization might rupture the already solidified surface layers resulting in surface defects. This could be avoided if the crystallization behaviour were known together with its effect on the developing strength of the material. The polymer could be modified to adjust its crystallization behaviour or a different polymer could be used or developed. A suitable tool to monitor the time dependence of crystallization processes and thus to select the best material and processing conditions is rheology. The characteristic crystallization time for each material can be tailored to the given moulding circumstances. The stretching and shearing during the injection moulding have a large effect on crystallization.²² This will not be addressed in the following which is solely concerned with crystallization under static conditions.

Objective

The rheological analogy between physical and chemical gelation has been shown previously for certain crystallizing polymers.^{11,12} It is interesting to study the crystallization behaviour of a commercially important isotactic polypropylene to confirm this analogy. If the GP can be clearly defined and measured in rheological experiments it can be taken as a reference state for the development of the properties of the material. The gel time has to be measured and related to important crystallization conditions, *e.g.* temperature. Furthermore, the material stiffness at and after the gel point has to be studied and compared with structural parameters (crystal size, degree of crystallinity). It is important to show how rheology can be a powerful tool to study and monitor the crystallization behaviour of semi-crystalline polymers.

Experimental

The material used in this study was a commercial capacitor-grade isotactic polypropylene (iPP). Polypropylene was selected not only because of its practical importance but also because it is known to exhibit slow crystallization kinetics (which makes it accessible to observation). iPP may achieve a high degree of crystallinity (Cook¹³ reported degrees of crystallinity up to 65–75%). The iPP used had the following charac-

teristics:¹⁴ melt flow index (MFI) 4.3 g (10 min)⁻¹ at 230 °C, $M_n = 79\,300$, $M_w = 476\,000$. The glass transition temperature and the melting peak temperature were measured using a Perkin Elmer differential scanning calorimeter (DSC-7). For this, the DSC sample was melted for 20 min at 200 °C and then quenched in liquid nitrogen. The calorimetric scan was conducted at a heating rate of 15 K min⁻¹.

Experiments under the rapid crystallization conditions applied in industrial processes are extremely difficult to study.^{14,22} We therefore slowed down the crystallization process by setting the supercooling conditions accordingly. The rheological experiments were performed in a Rheometrics mechanical spectrometer RMS800 using parallel discs with a diameter of 25 mm. Samples were prepared by moulding the iPP pellets for 10 min at 200 °C under vacuum in a Carver laboratory press. The samples were then allowed to cool slowly, still under vacuum. Moulded samples were stored in a vacuum oven at about 120 °C to prevent moisture absorption. Utilizing disposable fixtures on the RMS800, the sample was heated to 180 °C. At this temperature the iPP is already molten. The sample disc was squeezed by *ca.* 30 μm in order to smooth the surface of the sample and the edge was carefully cut off. Then the samples were melted in the rheometer at 210 °C for 20 min under nitrogen. iPP is thermally stable, with respect to molecular weight, up to 230 °C and the breakdown to volatile products is insignificant below 300 °C in the absence of oxygen.¹⁵ The melting temperature in this study was well below these temperatures. After melting, the samples were cooled to the experimental temperature, still in a nitrogen atmosphere. The cooling took *ca.* 10–15 min since a temperature undershoot below the experimental temperature had to be avoided. Otherwise crystals would have formed faster than at the intended temperature,¹⁶ thus shortening the crystallization time considerably. The actual rheological experiment was started as soon as the experimental temperature was reached. This instance was taken to be the beginning of the crystallization ($t = 0$). The cooling time was not taken into account since a few min at a temperature some degrees higher than the actual testing temperature caused only negligible crystallization as will be shown below. For the same reason the experiment had to be started at the testing temperature and not several degrees higher. To avoid the slow and inaccurate response to programmed temperatures and temperature changes of the instrument's heating system, the temperature was controlled manually during the melting and cooling process. The gap setting was adjusted to accommodate the density changes during crystallization.

Cyclic frequency sweeps were performed once the experimental temperature was reached. The frequency window between 0.01 rad s⁻¹ (at $T = 146$ °C) or 0.1 rad s⁻¹ (at all other temperatures) and 200 rad s⁻¹ was repeatedly scanned taking 3–6 data points per decade depending on the temperature. The experimental temperatures were $T = 130, 135, 139, 146$ and 151 °C. The experiment was stopped by the instrument as soon as the torque imposed on the transducer became too large due to the ongoing crystallization. The initial strain of *ca.* 10% (ensuring sufficiently high torque values) was manually decreased during the experiment to stay within the linear viscoelastic region and below the maximum torque of the instrument.

The experimental data was analysed using IRIS¹⁷ and GELPRO¹⁸ software.

Experimental Results

The DSC results are shown in Fig. 1. The peak in the thermogram was used to estimate the melting temperature, $T_m = 163$ °C. A closer look at the temperature region between -50 and +50 °C revealed a glass transition temperature of $T_g = -13$ °C.

The master curves of the storage and loss moduli for the investigated polypropylene were determined at a reference temperature of $T_{ref} = 140$ °C using time-temperature superposition¹⁹ as shown in Fig. 2. Two frequency sweeps were performed above the

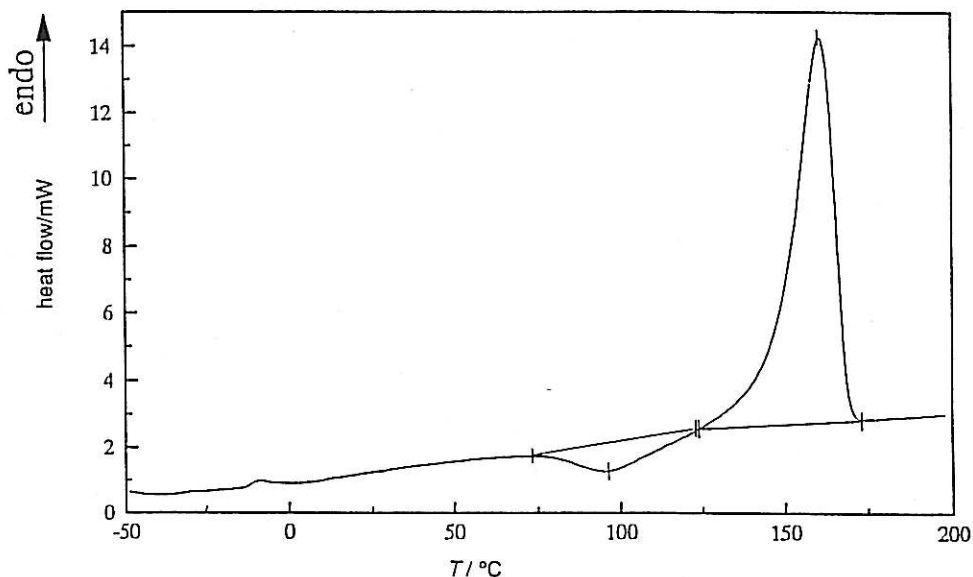


Fig. 1 DSC thermogram of a 9.5 mg iPP sample, conducted at a heating rate of 15 K min^{-1} after quenching in liquid nitrogen. The melting peak can be clearly seen around $T_m = 163^\circ\text{C}$. $x_1 = 124.7^\circ\text{C}$, $x_2 = 173.7^\circ\text{C}$, peak = 162.7°C , area = 703.4 m .

melting temperature at $T = 171$ and 181°C , all others were taken below T_m . The first frequency sweep of the CFS experiments after quenching to a temperature $T_{\text{exp}} < T_m$ approximately characterizes the melt behaviour since the crystallization process has not started to a substantial extent.

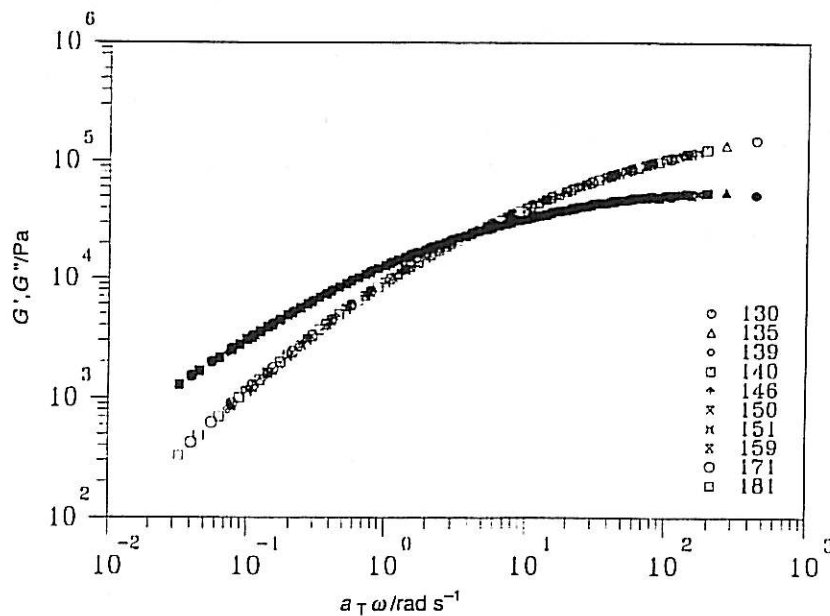


Fig. 2 Master curve of isotactic polypropylene at $T_{\text{ref}} = 140^\circ\text{C}$. G' is represented by open symbols and G'' by filled symbols. The frequency sweep data from different temperatures, given in the figure, are depicted by different symbols.

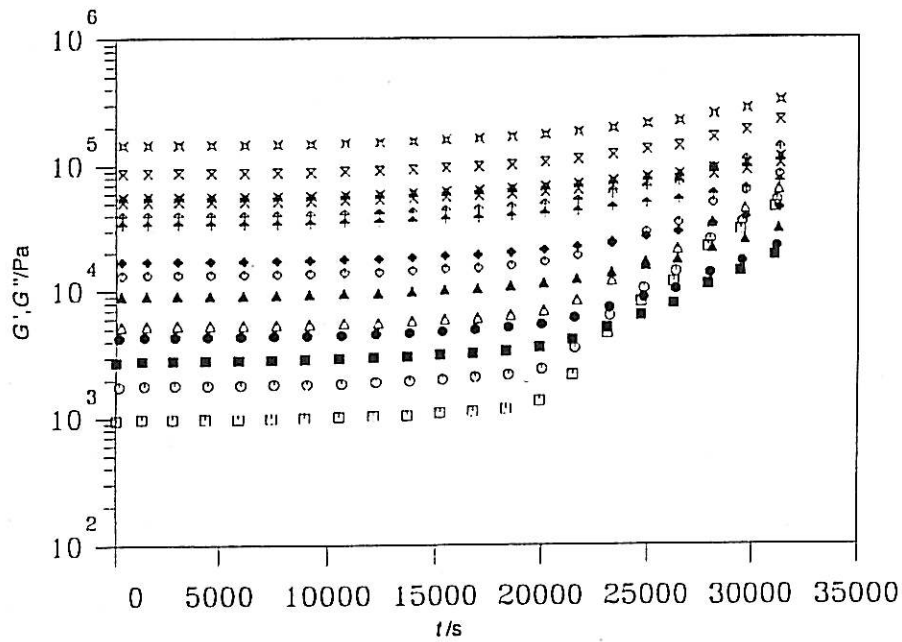


Fig. 3 Cyclic frequency sweep data at a crystallization temperature of 146°C. Different frequencies are depicted by different symbols. Open symbols represented G' , filled symbols represent G'' .

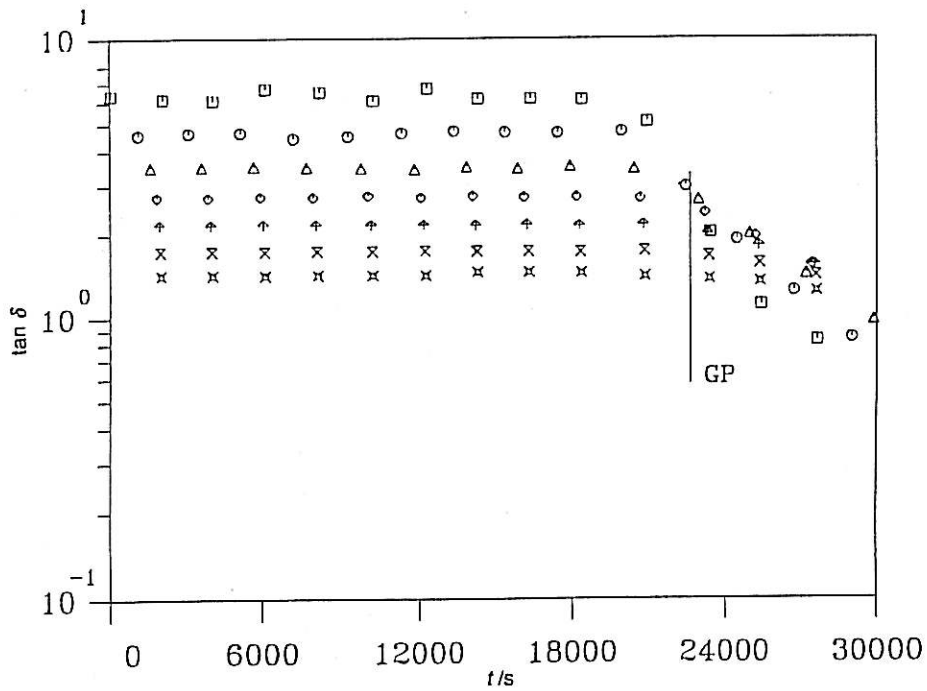


Fig. 4 Loss tangent, $\tan \delta$, vs. time during crystallization at $T_{\text{exp}} = 146^\circ\text{C}$. Different symbols depict different frequencies. The gel time can be estimated from the crossover of the lowest frequency data.

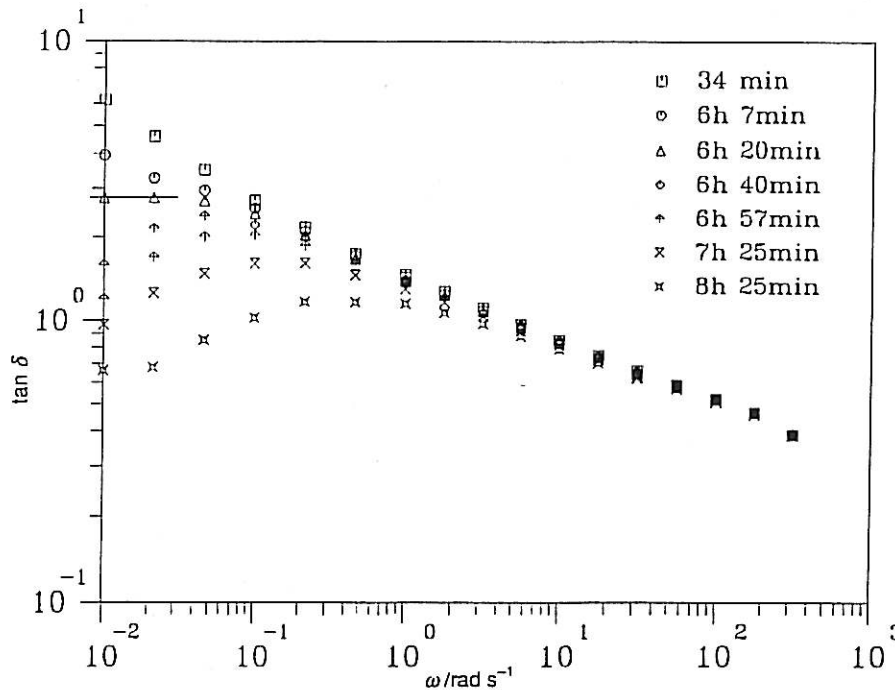


Fig. 5 Interpolated $\tan \delta$ vs. frequency at different instances during the crystallization process ($T_{\text{exp}} = 146^\circ\text{C}$). The estimated gel time is marked by the horizontal line. The relaxation exponent n is found to be equal to 0.78.

A typical data set from the dynamic mechanical experiments is shown in Fig. 3 ($T_{\text{exp}} = 146^\circ\text{C}$). The plot shows the evolution of storage and loss modulus data at different frequencies with crystallization time. A long induction period is evident before the moduli start to rise sharply. At the beginning of the experiment, the low frequency storage modulus, G' , is smaller than the corresponding loss modulus, G'' . As the crystallization proceeds, both moduli grow. Initially, G' and G'' increase in a nearly parallel manner but after some time the storage modulus starts to grow faster than the loss modulus. Eventually, G' exceeds G'' and, at the end, G' dominates the experiment. The GP can be extracted by replotting the data in terms of the loss tangent $\tan \delta$, Fig. 4, to look for frequency independence. As the master curve reveals, the entanglement zone of this broadly distributed iPP extends to frequencies of about $\omega = 1 \text{ rad s}^{-1}$. This is nearly true throughout the entire investigated temperature range due to values of a_T near unity. Since the loss angle at GP is independent of the frequency only in the terminal zone, the frequency independence will show only in the range of $\omega < 1 \text{ rad s}^{-1}$. The experimental frequency range is restricted by the equipment available and the experimental time in relation to the rate of change. Therefore the terminal frequency is about $0.1 < \omega < 1 \text{ rad s}^{-1}$ for all temperatures except $T = 146^\circ\text{C}$. In Fig. 4, the GP is taken as the instance at which the $\tan \delta$ curves of the three lowest frequencies cross. The loss tangent could also be plotted vs. frequency at interpolated times, Fig. 5. The time at which $\tan \delta$ is independent of the frequency at the low end of the frequency window is marked by a horizontal line. The gel times at the other crystallization temperatures were estimated in a similar way.

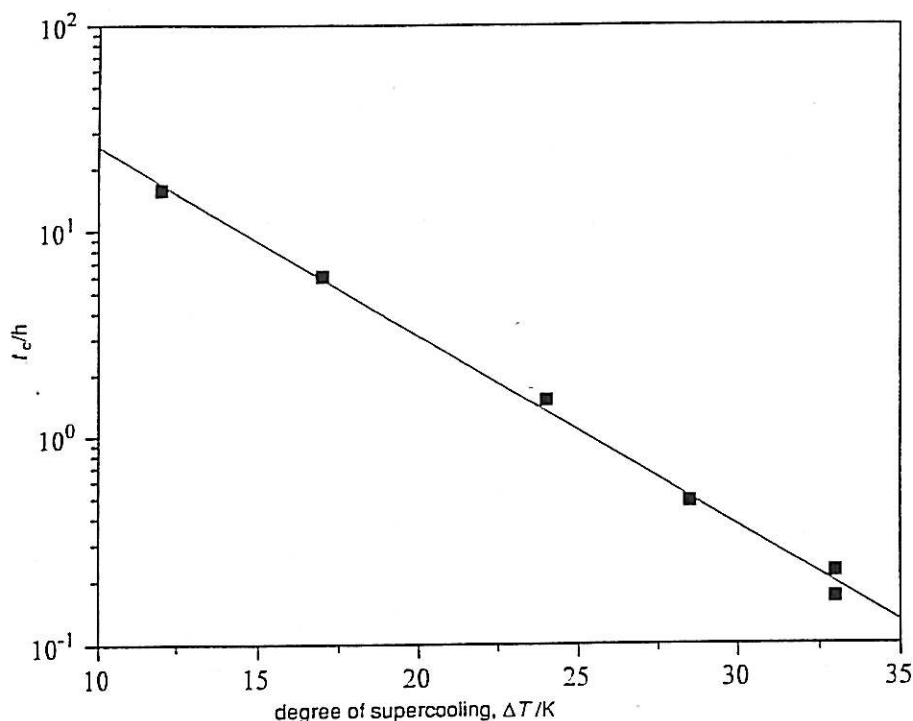


Fig. 6 Semi-logarithmic plot of critical gel time vs. degree of supercooling. The line represents an apparent linear fit of the data points. Data at 130°C ($\Delta T = 33$ K) are estimated.

Analysis and Discussion

The logarithm of the critical gel time (estimated from the conditions $\tan \delta = \text{constant}$) vs. the degree of supercooling, $\Delta T = T_m - T_{\text{exp}}$, is depicted in Fig. 6. For $T_{\text{exp}} = 130^\circ\text{C}$, the possible range of the critical gel time is shown since an exact value could not be obtained due to the fast crystallization rate. The data points can be fitted by an apparent linear function resulting in

$$t_c = A \exp\left(-\frac{\Delta T}{B}\right) \quad (6)$$

The fit results in parameter values of $A = 215.6$ h and $B = 4.71$ K. Thermodynamically, ΔT may be interpreted as the driving force of crystallization, large values resulting in a short crystallization time. B is an energy, normalized by the universal gas constant.

The temperature range for which this equation is valid could not be manifested. It is evidently valid in the investigated temperature range of $130 \leq (T_{\text{exp}}/^\circ\text{C}) \leq 151$. Obviously it does not apply to temperatures above T_m where no gel can be formed. At temperatures significantly lower than 100°C the influence of the glass transition will increase. The diffusion of the macromolecules is hindered and spherulites are not able to form. Another uncertainty is the degree of supercooling itself. The thermodynamic equilibrium melting temperature, T_m^0 , is not the same as the measured melting temperature, T_m . T_m^0 can be extrapolated using DSC data of melting peaks from material that crystallized at different temperatures.^{20,21} Practically, the difference between T_m^0 and T_m is of little importance. The thermodynamic melting point describes the melting temperature of an ideal infinite crystal without any defects. Polymers however are never able to form

an ideal crystal due to entanglements, chain defects, *etc.* Furthermore, a different melting temperature would result in a purely horizontal shift in Fig. 6 not affecting the important parameter B .

The degree of crystallinity at the GP can be estimated using the Avrami equation

$$1 - V_c = \exp(-Kt^{n_A}) \quad (7)$$

It combines the relative crystallinity by volume V_c with a rate constant K and the crystallization time. The rate constant depends on crystallization temperature and the Avrami exponent is related to the crystal growth dimension.^{15,22} The temperature dependence of polypropylene crystallization was studied by Kim *et al.*¹⁶ They measured V_c of neat iPP at distinct temperatures as a function of the crystallization time. At a temperature of 129.7°C they found the relative crystallinity to be zero after 1.5 min and 0.02 after 5 min. At a temperature of 136.1°C, V_c remained nearly zero for more than 10 min. They evaluated an isothermal rate constant K for their calculated values of the Avrami exponent, n_A , for n_A between 2.45 and 2.74. A parameter set for K was extrapolated in this study using linear extrapolation fits in a $\log K$ vs. T plot which lead to a simple equation for the temperature dependence of the rate constant K

$$\log K = A + BT_{exp} \quad (8)$$

with $A = 96.99$ and $B = 0.25 \text{ K}^{-1}$. The Avrami exponent n_A was set to be $n_A = 2.5 = \text{const}$. The gel time was taken from eqn. (6). The result is a nearly linear decreasing degree of crystallinity with increasing crystallization temperature as shown in Fig. 7. The error bars correspond to an error in the gel time of ± 1 min. The degree of crystallinity at the gel point is remarkably low and lies between 6 and 15%.

The critical gel time was determined by plotting the loss angle vs. frequency at interpolated times. The time at which $\tan \delta$ is frequency independent in the terminal zone

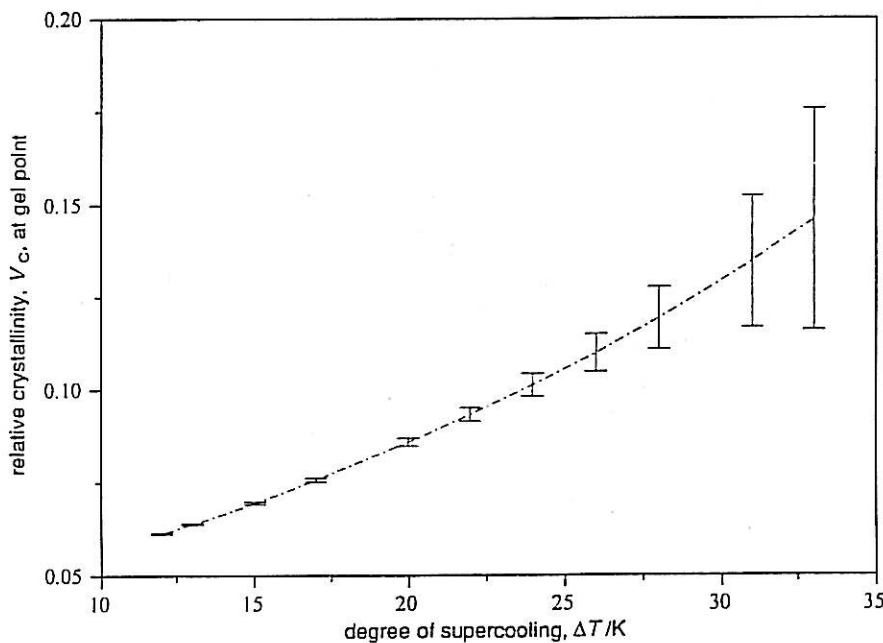


Fig. 7 Degree of crystallinity at the gel point vs. degree of supercooling. Data calculated from eqn. (8).

was taken as the critical gel time. The frequencies were varied between 0.01 rad s^{-1} (for $T_{\text{exp}} = 146^\circ\text{C}$) or 0.1 rad s^{-1} (for all other temperatures) and 200 rad s^{-1} . Only a small part of the terminal zone is covered by this frequency range. Therefore the determination of t_c might lead to a systematic error since the real critical loss tangent might actually be found at shorter times and higher values of n . The effect of such an error is shown in Fig. 8. For $T = 146^\circ\text{C}$ the critical gel time when using a frequency range from $\omega = 0.1 \text{ rad s}^{-1}$ upwards is 417 min, when using the extended frequency range from $\omega = 0.01 \text{ rad s}^{-1}$, $t_c = 380 \text{ min}$. Consequently the 'real' value of n is 0.78 ($\omega > 0.01 \text{ rad s}^{-1}$) instead of 0.65 ($\omega > 0.1 \text{ rad s}^{-1}$). Measuring at lower frequencies, however, increases the experimental time further since Δt is approximately inversely proportional to ω . This also increases the mutation number⁹

$$N_{\text{mu}} = \Delta t \frac{1}{g} \frac{\partial g}{\partial t} \quad (9)$$

which is a measure for the total change of the measured property g during a single experiment of duration Δt . Long experimental times and high rates of change (here rates of crystallization) result in high mutation numbers. Rheological experiments usually require stable samples since the determination of dynamic properties are not instantaneous. Recently it has become more and more common to examine materials with a changing structure such as polymers during gelation, phase transition, decomposition, polymerization, etc. since these materials have very distinct properties. A condition was developed^{9,18} that allowed measurements on samples with sufficiently slow mutation.

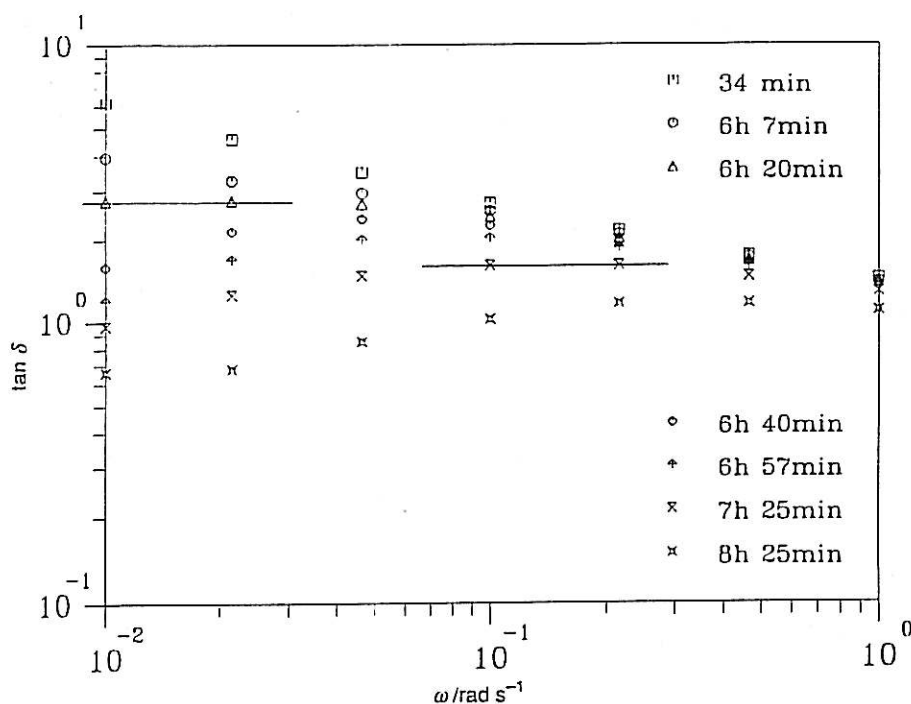


Fig. 8 Loss tangent, $\tan \delta$, vs. frequency during crystallization at $T_{\text{exp}} = 146^\circ\text{C}$. Different symbols depict the interpolation times given in the figure. The effect of a truncated frequency window on the estimation of t_c is demonstrated with the two different lines (using $\omega_{\text{min}} > 0.01 \text{ rad s}^{-1}$ and $\omega_{\text{min}} > 0.1 \text{ rad s}^{-1}$, respectively, to determine t_c).

Such experiments can be considered to be quasi-stable and therefore the mutation can be neglected. If this condition (small N_{mu}) is not satisfied, the rheometer may deliver false data or no data at all.

The condition was checked for the dynamic experiments in this study. At the gel point, values for N_{mu} were calculated (for G' at $\omega = 0.1 \text{ rad s}^{-1}$) to lie between 0.0045 for $T_{\text{exp}} = 151^\circ\text{C}$ and 0.6565 for $T_{\text{exp}} = 135^\circ\text{C}$. The mutation numbers for the loss modulus were less than half of the values determined for the corresponding storage modulus. Since the computed mutation numbers are smaller than one, it is safe to assume that the samples were quasi-stable.

Dynamics data at crystallization temperatures below 135°C are not reliable, especially at low frequencies, since the crystallization rate is too high. Unfortunately, it is also impossible to measure at frequencies below 0.1 rad s^{-1} for temperature below 140°C (this would result in $N_{\text{mu}} > 2$). Therefore, the critical gel times determined from the $\tan \delta$ data at $\omega > 0.1 \text{ rad s}^{-1}$ cannot be proven or possibly improved by measuring at frequencies further into the terminal region. It has to be assumed that the estimated gel times are too long (see Fig. 8). However since this is supposedly a systematic error it has no direct effect on the trends found in this study.

Conclusions

Cross-linking materials exhibit a self-similar relaxation pattern at the liquid–solid transition which expresses itself in a power-law relaxation spectrum and modulus. The isothermal physical gelation (crystallization) of a semicrystalline polypropylene was found to behave similarly to chemical gelation. The dynamic moduli exhibited the same growth characteristics while changing from a viscous ($G' < G''$) to an elastic ($G' > G''$) dominated phase. The dynamic moduli were followed at different crystallization temperatures over a wide range of frequencies. The time at which the material passes the gel point was found to decrease exponentially with the degree of supercooling below the equilibrium melting temperature.

The degree of crystallinity at the gel point was estimated using the Avrami equation. It increases exponentially with the degree of supercooling. Very low relative crystallinities between 6 and 15% were found at the liquid–solid transition. This means that only a few physical cross-links are necessary to form a network that spans ('percolates') the entire sample.

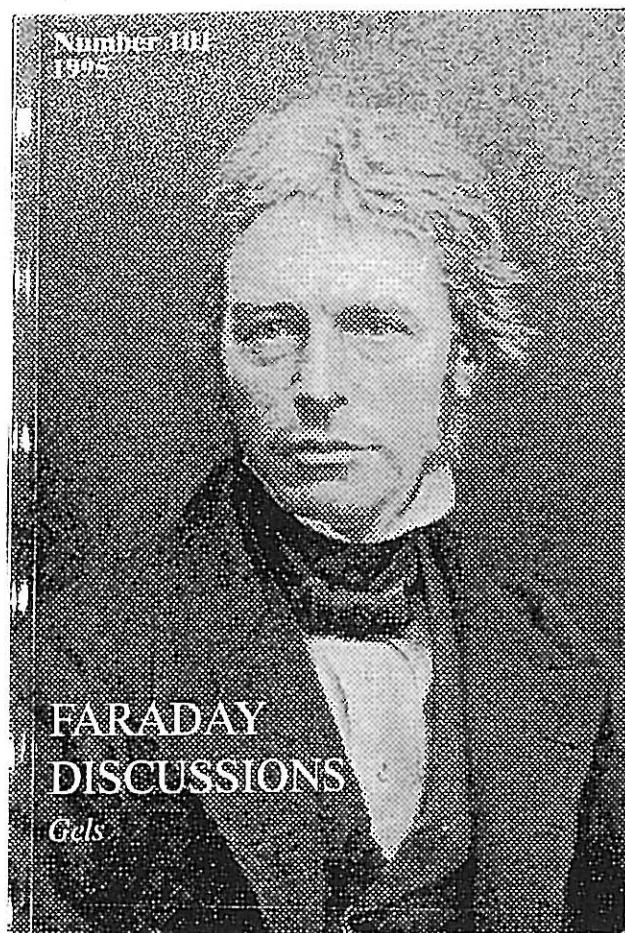
The crystallization rate greatly influences the rheological experiment. Low crystallization temperatures (below $\Delta T \approx 30 \text{ K}$) could not be investigated since the crystallization rate is too fast and the total change of investigated property is too large for reliable data to be obtained. However, rheology is shown to be a powerful tool to inspect and monitor crystallization processes.

The project was supported by a grant from Raychem. M.M. gratefully acknowledges financial support of the German Academic Exchange Service (DAAD-Doktorandenstipendium aus Mitteln des zweiten Hochschulsonderprogramms). The phenomenon of gel fracture as a reason for the occurrence of surface defects in injection moulding was introduced to us by Dr. Ye-Gang Lin.

References

- 1 F. Chambon and H. H. Winter, *Polym. Bull.*, 1985, 13, 499.
- 2 M. E. DeRosa and H. H. Winter, *Rheol. Acta*, 1994, 33, 220.
- 3 J. C. Scanlan and H. H. Winter, *Macromolecules*, 1991, 24, 47.
- 4 A. Izuka, H. H. Winter and T. Hashimoto, *Macromolecules*, 1992, 25, 2422.
- 5 E. E. Holly, S. Venkataraman, F. Chambon and H. H. Winter, *J. Non-Newt. Fluid Mech.*, 1988, 27, 17.
- 6 C. Y. M. Tung and P. J. Dynes, *J. Appl. Polym. Sci.*, 1982, 27, 569.
- 7 H. H. Winter, *Polym. Eng. Sci.*, 1987, 27, 22.

- 8 F. Chambon and H. H. Winter, *J. Rheol.*, 1987, 31, 683.
- 9 H. H. Winter, P. Morganelli and F. Chambon, *Macromolecules*, 1988, 21, 532.
- 10 A. Apicella, P. Masi and L. Nicolais, *Rheol. Acta*, 1984, 23, 291.
- 11 K. te Nijenhuis and H. H. Winter, *Macromolecules*, 1989, 22, 411.
- 12 Y. G. Lin, D. T. Mallin, J. C. W. Chien and H. H. Winter, *Macromolecules*, 1991, 24, 850.
- 13 J. G. Cook, *Handbook of Polyolefin Fibres*, Merrow Publishing, England, 1967.
- 14 S. Piccarolo, *J. Macromol. Sci., Phys.*, 1992, 31, 501.
- 15 H. P. Frank, *Polypropylene*, Gordon and Breach Science, New York, 1968.
- 16 C. Y. Kim, Y. C. Kim and S. C. Kim, *Polym. Eng. Sci.*, 1993, 33, 1445.
- 17 H. H. Winter, M. Baumgärtel and P. R. Soskey, in *Techniques in Rheological Measurement*, Chapman and Hall, London, 1993, ch. 5.
- 18 M. Mours, H. H. Winter, *Rheol. Acta*, 1994, 33, 385.
- 19 J. D. Ferry, *Viscoelastic Properties of Polymers*, Wiley, New York, 1980.
- 20 J. I. Lauritzen and J. D. Hoffman, *J. Res. Nat. Bur. Std. Sect. A*, 1960, 64, 73.
- 21 J. D. Hoffman and J. J. Weeks, *J. Res. Nat. Bur. Std. Sect. A*, 1962, 66, 13.
- 22 G. Eder, H. Janeschitz-Kriegl and S. Liedauer, *Prog. Polym. Sci.*, 1990, 15, 629.
- 23 R. Hingmann, J. Rieger and M. Kersting, *Macromolecules*, 1995, 28, 3801.



Organising Committee

Prof. J. W. Goodwin (*Chairman*)
Dr. R. Audebert
Dr. R. Buscall
Prof. M. Djabourov
Dr. A. M. Howe
Prof. J. Livage
Prof. J. Lyklema
Prof. S. B. Ross-Murphy

ISBN: 0-85404-878-2

ISSN: 0301-7249

Typeset by Santype International Ltd., Netherhampton Road, Salisbury, Wiltshire and printed and bound in Great Britain by Whitstable Litho Printers Ltd.

Prof. Dušek opened the discussion of Prof. Winter's paper: Structureless polymer solutions (like atactic polystyrene of high molecular weight in a good solvent) undergo a transition from a state of viscous liquid to an elastic solid (gel) when the concentration increases. Can a gel point be defined and determined or is the transition continuous?

Prof. Winter said in reply: The liquid–solid transitions which we have studied so far, and there are quite a variety, have always exhibited a gradual increase of the longest relaxation time, divergence at the gel point, and a reduction again beyond the gel point. Samples at the gel point (critical gels) always relaxed with a power law spectrum at long times. I expect that this will also happen with the atactic polystyrene solution as the concentration, c , is increased. This argument is entirely based on the analogy between physical and chemical gelation. Physical gels developed the same relaxation patterns as were observed universally for chemical gels. If the analogy between physical and chemical gels holds, then the atactic polystyrene sample with power law relaxation denotes the gel point concentration.

To explore this in detail, it would be good to perform dynamic mechanical experiments on atactic polystyrene solutions if this has not already been done. The transition through the gel point is continuous as far as the dynamic mechanical data are concerned. At the gel point one can expect a power law relaxation time spectrum and use this for defining the gel point. An easy way of detecting the critical concentration would be repeated frequency sweeps on samples with increasing concentrations. The critical concentration c_c for the gel point would be found (by interpolation) as the intersect of the $\tan \delta(\omega, c)$ vs. c curves when plotted for discrete frequencies $\omega_1, \omega_2, \omega_3, \omega_4$ etc. in the terminal frequency range. The resulting figure should look similar to Fig. 8 (later); however, the independent variable would be the concentration c (instead of the reaction time, t).

Dr. In said: In the introduction of your paper you mention that the mass distribution in physically gelling systems does not diverge at the critical point. Why do you expect a power law for the relaxation? In other words, are you sure that the constancy of $\tan \delta$ that you observe on a very narrow range of frequency, holds at low frequency?

This could be proved if you showed that $\tan \delta = \tan(n\pi/2)$, but it is not clear whether you could determine the gel exponent n .

Prof. Winter replied: The molecules do not change during physical gelation and the divergence of the mass distribution (which one is used to seeing in chemical gelation) does not occur. This takes away the classical definition of the gel point as the instant at which the largest molecular cluster diverges. However, if one neglects the type of connection mechanism and focuses on the developing network structure, then physical gels look very similar to chemical gels. Rheology is probing this developing network connectivity and the liquid–solid transition in physically gelling systems is marked by the same power law relaxation which we are used to seeing in chemical gelation.

Concerning your second question/comment, it is important to note that the power law relaxation occurs at low frequencies only. At higher frequencies, additional relaxation mechanisms enter and the spectrum might adopt appropriate forms which are unaffected by the liquid–solid transition. The question remains of how low in frequency we have to go to observe the liquid–solid transition behaviour. In our study on PP, we barely make it into the terminal region, and it would be more convincing if the data would extend by one or two decades lower in frequency. Our result gives an upper possible value for the gel time. The solidification could have occurred earlier, but I do not think that this is possible since the degree of crystallinity is already extremely low at our proposed gel point. The relation which you would like to have tested, $\tan \delta = \tan(n\pi/2)$, is satisfied by our data. One can see this when comparing the spacing of G' and G'' with the slope in the terminal region. If we were to do this study again, I would prefer a lower molecular weight PP since its low frequency behaviour would be easier to observe with our instruments.

Prof. Ross-Murphy said: Your paper and other contributions at this meeting have demonstrated how improvements in instrumentation over the last 15 years have enabled small deformation rheological measurements to be made through the gel point. However, one limitation of such measurements is that measurements can only be made within the linear viscoelastic region, *i.e.* where G^* , the complex storage modulus, and/or G' and G'' respectively, its in-phase and out-of-phase components, are independent of the applied strain. Have you considered the effect of the strain dependence for physical gels close to the gel point? It can be argued that this linear viscoelastic strain γ_{lin} must be dependent on the proximity to the gel point, making the validity of such measurements very difficult to assess. Fig. 7 illustrates this tendency. The question that really needs to

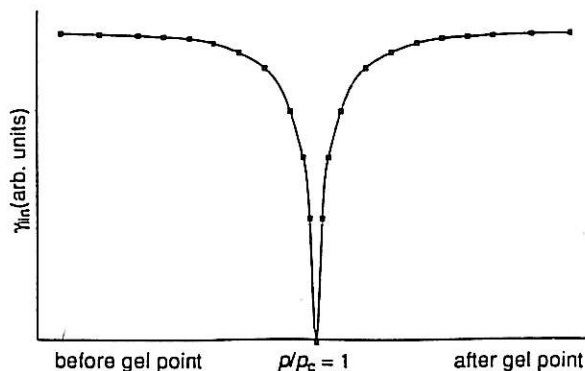


Fig. 7 Linear viscoelastic strain (in arbitrary units) plotted against p/p_c (arbitrary scale), where p_c is the gel point conversion (percolation threshold)

be answered is 'what is the linear viscoelastic strain at the gel point'? As Fig. 7 developed on the very reasonable hypothesis that γ_{lin} depends upon the reciprocal molecular weight of the sol fraction before gelation, and on the (amount of) gel fraction afterwards shows, this may be vanishingly small. It may be that the region illustrated is so minute that it is of no practical significance. However, we believe this is not so for physical gels, since the structure of these is necessarily more tenuous than that for covalently cross-linked systems. Such materials close to gelation are often closer to colloidal and particulate systems. In these, the linear viscoelastic strain can be <0.001 , rather than the values $>ca. 0.1$ found for covalent polymer networks.

Prof. Winter said in reply: The question is difficult to investigate experimentally since the sample undergoes changes in time due to the physical gelation process. Chemical gelation is more informative here, at least for systems in which the cross-linking reaction can be arrested near the gel point and strain effects can be tested. We produced stable polydimethylsiloxane critical gels in this fashion and studied the onset of non-linearity: strain levels up to two ($\gamma < 2$) gave a linear viscoelastic response.¹ In stable samples, the range of linear viscoelasticity is easy to measure even if it is very difficult to predict. One simply repeats shear (or extension) experiments at increasing strain levels and reduces the data according to the linear viscoelastic framework as described in the textbook by Ferry² (for instance). Deviations from linearity show up at a characteristic strain or stress level at which the data cannot be collapsed any more. Physical gels, as you point out, are often less flexible and have a smaller range of linear viscoelasticity. To answer your question, one would have to repeat the gelation experiments at a set of discrete strain levels and then normalize with the strain. What we do instead is to run the gelation experiment under oscillatory shear once and then repeat it without flow until roughly the gel point so that gelation cannot be affected. Then we start the oscillatory shear and compare the data from the two types of probing. This needs to be done for each individual system since strain effects are hard to predict.

1 S. K. Venkataramen and H. H. Winter, *Rheol. Acta*, 1990, 29, 423.

2 J. D. Ferry, *Viscoelastic Properties of Polymers*, Wiley, New York, 1980.

Prof. Keller said: You determine the gel point, or in general perform rheology during the initial stages of crystallization while crystallization is still in progress. Are you not concerned that strain-induced orientation is affecting the crystallization itself?

Prof. Winter replied: We keep the strain levels very small for our experiments. This is possible since PP is fairly viscous and the required torque level for our transducer is small. We did not expect an effect of small amplitude shear on the crystallization process but did not study this phenomenon. Our method would be ideal for exploring this effect of shear. When subjecting the sample to large strain, we would expect drastic increase in crystallization rate as has been reported in the literature by Janeschitz-Kriegl,¹ for instance. This phenomenon is especially important in our injection moulding example.

1 G. Eder, H. Janeschitz-Kriegl and S. Liedauer, *Prog. Polym. Sci.*, 1990, 15, 629.

Prof. Keller said: It does not follow that larger crystals formed at lower supercooling have larger 'functionalities'. Normally, under those circumstances the chains will be crystalline to a larger extent by chain folding which being 'intra' molecular will reduce the functionality hence the gelation tendency.

Prof. Winter replied: Let us look at the crystallization process at a low degree of supercooling where the crystal sizes are known to be largest. Here, we observe a long gel time t_c , but the gel point is reached at a low degree of crystallinity (from applying Kim's

crystallization data¹). The low degree of crystallinity at the gel point suggests that the few available crystals (per volume) are very effective in forming a network. By analogy to chemical gelation, we know that the gel point is reached at a lower extent of cross-linking when the functionality of the cross-links is increased. The PP crystals seem to be able to attach many tie chains and are, because of this, considered as cross-links of high functionality. A direct proof of this speculative argument is still needed. The proposed formation of large crystals of low functionality does not seem to occur here, but it certainly is an interesting phenomenon which should affect the rheology very strongly.

1 C. Y. Kim, Y. C. Kim and S. C. Kim, *Polym. Eng. Sci.*, 1993, 33, 1445.

Prof. Keller asked: At what stage did you measure the degree of crystallinity? The final degree of crystallinity (at which normally such measurements are—or can be—made) may be quite different from that which pertains to the time when the rheological measurements were made.

Prof. Winter responded: The degree of crystallinity is so low at the gel point that it was not possible for us to measure it. We simply took crystallization data from the literature (as reported in the paper) and extrapolated to the early times at which the gelation occurred. It would be most interesting to learn more about these early stages of crystallization. Rheology is very powerful in showing the existence of a sample spanning cluster very early in the crystallization process but the clusters' structure is still unknown.

Prof. Djabourov said: You have investigated the crystallization of polypropylene in a supercooled state, using a commercial sample. In the supercooled state the nucleation is governed by the presence of impurities (even the walls of the vessels). You compared your data to the measurements of Kim *et al.*¹ to derive the degree of crystallinity. How can you justify the comparison with the data obtained on a different sample?

1 C. Y. Kim, Y. C. Kim and S. C. Kim, *Polym. Eng. Sci.*, 1993, 33, 1445.

Prof. Winter replied: We cannot exclude the effects from the walls of the sample holders, but the samples had been cleaned from nucleating additives. This was also true for Kim *et al.* so that we expect similar crystallization behaviour. We tried to exclude effects of prehistory as much as possible by preheating the sample to a relatively high temperature before supercooling it.

Prof. Djabourov said: In Fig. 7 of your paper you show that the degree of crystallinity at the gel point increases with the degree of supercooling. What is the physical meaning of this behaviour

Prof. Winter responded: Our study's focus was really on the rheological patterns of the solidification process. This gave us timescales and rates of change without revealing the underlying crystalline structure. A high degree of crystallinity at the gel point (see Fig. 7) tells us that the crystals are not very effective in connecting the flexible molecular strands into a network. This can be attributed to a relatively low functionality of the crystals, *i.e.* a small average number of tie chains per crystal.

Dr. Howe communicated: What is the best method of measuring the gel point? Are there significant systematic differences between apparent gel times determined from (a) constant $\tan \delta$, (b) the $G' = G''$ crossover and (c) the onset of growth in G' ?

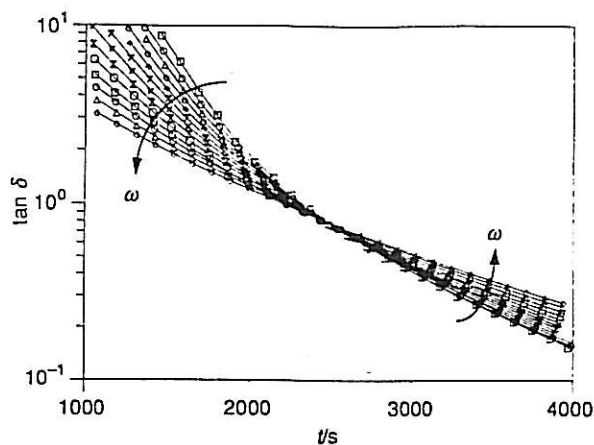


Fig. 8 Evolution of loss tangent at several frequencies during cross-linking of PBD38 ($T = 28^\circ\text{C}$). The $\tan \delta(\omega)$ intersect is the gel point. PBD38 is a nearly monodisperse polybutadiene with $M_w = 38\,000$ and 7.7 wt.% vinyl content. The polymer is cross-linked at these vinyl groups with *p*-bis(dimethylsilyl)benzene as cross-linking agent. The reaction is catalysed by *cis*-dichlorobis(diethylsulphide)platinum(II). The experimental frequencies range from 1 s^{-1} to 100 s^{-1} , with six frequencies per decade.

Prof. Winter communicated in reply: There are many good methods for determining the gel point. They can be divided into two groups: (1) very well established are extrapolation methods in which the measured quantity diverges at the gel point. They allow us to narrow down the region of gelation from both sides of the gel point, but they fail in the immediate vicinity of the gel point. The most widely used extrapolation methods are the following: (i) solvent exposure of chemically cross-linking samples which dissolve before the gel point but merely swell beyond the gel point; very near to the gel point measurements fail since the swelling is strong enough to fracture the very fragile gel structure. (ii) Detection of the largest cluster with light scattering; the divergence of the largest cluster cannot be detected any more when its size becomes too large. Beyond the gel point, light scattering could be used to monitor the holes in the network. The determination of the gel point through steady-state rheological properties, namely the steady shear viscosity and the equilibrium modulus, has been used to home in on the region of gelation: the main problem is the breakage of the molecular structure in these experiments which only allows detection of a liquid–solid transition on broken gels. (2) Direct measurement of the gel point: up to now we know only of one such method. It is based on the observation that the long time tail of the relaxation time spectrum adopts power law format at the gel point.¹ This results in plots in which $\log G'(\omega)$ and $\log G''(\omega)$ vs. $\log \omega$ are straight parallel lines at low frequencies. The gel point can be detected by a flat $\tan \delta(\omega)$ or a $\tan \delta(\omega)$ intersect when plotted against conversion or reaction time.² A newer example for such $\tan \delta$ -intersect is shown in Fig. 8.

With apparent gel times you probably mean some approximations to the gel point but not the real gel point. There have been many proposals and you mentioned some of them. (a) The constant $\tan \delta(\omega)$ should not be called apparent since it gives the real gel point (see above) when measured appropriately. (b) The $G' = G''$ crossover is far off in many gelation processes.³ Deviations are especially large for cross-linking of small molecules and for most physical gels. (c) The growth of G' cannot be used to determine the gel point since it starts much before the gel point. It also depends on the sensitivity of

the instrument. This is evident from the many experimental data on chemical and physical gels.

- 1 F. Chambon and H. H. Winter, *Polym. Bull.*, 1985, 13, 499.
- 2 E. E. Holly, S. K. Venkataraman, F. Chambon and H. H. Winter, *J. Non-Newtonian Fluid Mech.*, 1988, 27, 17.
- 3 H. H. Winter, *Polym. Eng. Sci.*, 1987, 27, 1698.

Dr. Howe communicated: What do you regard as the minimum practical frequency to be used when using the condition of constant $\tan \delta$ to determine the gel point?

Prof. Winter communicated in reply: The choice of frequency is essential for the success of the experiment. Both, the lower and upper limit are important. You raised the question of the minimum frequency which is dictated by the reaction rate of the sample since the experimental time increases with $1/\omega$. During this experimental time, the sample keeps changing and the overall change during an experiment should not exceed a tolerance level. One might set this tolerance level at 10% change of the measured quantity during the taking of a single data point. This is manifested in the mutation number.¹

On the other hand, the experiments have to be performed at sufficiently low frequency. As an example, cross-linking polybutadienes of high molecular weight respond strongly when probed at frequencies below $\omega = 1/\lambda_p$, where λ_p is the longest relaxation time of the polybutadiene precursor. Little response to the cross-linking is seen at higher frequencies. This has direct implication for the $\tan \delta$ method which should only include the low frequency data.

- 1 H. H. Winter, P. Morganelli and F. Chambon, *Macromolecules*, 1988, 21, 532.

Dr. Howe communicated: Do you think that a material should have an equilibrium modulus to be correctly classified as a 'gel'? If not, what is the minimum value of the longest relaxation time that would be sufficient for this classification?

Prof. Winter communicated in response: A soft material with an equilibrium modulus satisfies the mechanical criteria for being a 'gel' (sometimes, other non-mechanical criteria are added). The existence of the equilibrium modulus implies that the connectivity of the gel is permanent. The gel might be sensitive to strain so that it is very difficult to determine its equilibrium modulus without breaking it. However, this does not interfere with its classification as a gel.

More disputable is the definition of a soft material in which the network connectivity relaxes with a finite time. Many physical gels belong to this category. I suggest identifying physical gels by the gelation process by which they assemble. Physical gelation can be recognized by the increased connectivity and the long timescales which start to dominate the relaxation processes. The characteristic of (physical) gelation is this inherent increase of the longest relaxation time.