Gelation behaviour during chainwise crosslinking polymerisation of methacrylate resins

Jakob Lange[a,*], Mats Johansson[a], Camilla T. Kelly[b], Peter J. Halley[b]

[a]*Department of Chemical Engineering, University Queensland, QLD 4072, Australia*
[b]*Department of Polymer Technology, Royal Institute of Technology, S-100 44 Stockholm, Sweden*

Abstract

The gelation process in chainwise crosslinking polymerisation of methacrylate resins with average functionalities of 2.1–50 (1.05–25 methacrylate groups/molecule) was investigated using dynamic mechanical analysis. For all systems a crossover in tan δ (tan δ independent of frequency) was observed at gelation. The gel time was found to decrease with increasing functionality of the system. Within the measured frequency ranges, power law behaviour for the dynamic modulus was observed at the gel point in all systems. A value of the power law exponent n of 0.4 ± 0.2 to 0.6 ± 0.1 (increasing with increasing functionality of the system) was determined for gelation during reactions at $T \geq T_{g\infty}$. This trend suggests that the differences in screening between the systems dominate over the difference in fractal dimension. For reaction temperatures below $T_{g\infty}$ a value of $n = 0.3 \pm 01$ was obtained, which was attributed to the influence of micro-vitrification. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Gelation; Power law behaviour; Chainwise polymerisation

1. Introduction

The phenomenon of gelation in crosslinking polymerisation and the properties of materials in the critical gel state have attracted lot of attention in the literature [1–11]. The experimental determination and prediction of gelation is important for the processing of crosslinking polymer systems [7], whereas the criticality of the phenomenon and the universality of the properties on the gelation threshold make gelation interesting from a fundamental point of view [5,12]. Although many aspects of the gelation process have been investigated, there are still some questions, such as the influence of polymerisation mechanism, that have received limited attention.

It is widely accepted that gelation is well described by the theory of percolation [13,14]. This theory has been extended to also include predictions for how the dynamic properties are expected to scale with time or frequency [11,15–17]. Thus at the gel point the frequency dependence of the dynamic shear modulus, G^*, and the elastic (G') and loss (G'') moduli, are expected to obey a power law over a large

frequency range.

$$G^* \sim G' \sim G'' \sim \omega^n, \tag{1}$$

where the loss angle, δ, (defined from tan $\delta = G'/G''$) is related to the power law exponent n as

$$\delta = \frac{n\pi}{2}. \tag{2}$$

Further, the steady state viscosity η_s and the equilibrium elastic modulus G_s are expected to scale with the reduced extent of reaction ϵ as

$$\eta_s = \eta_o \epsilon^s \tag{3}$$

and

$$G_s = G_0 \epsilon^t, \tag{4}$$

where η_{0s} and G_0 are linked to the microscopic properties of the system and the exponents s and t relate to n as $n = t/s + t$. Prior to gelation the system is expected to behave as Newtonian liquid (with $G' \sim \omega^2$ and $G'' \sim \omega$) and after gelation as Hookean solid ($G' \sim \omega^0$ and $G'' \sim \omega$). Experimentally, Eqs. (1) and (2) were verified for a large number of systems [1,3,18] whereas fewer results have been reported for the relations described by Eqs. (3) and (4). This reflects the experimental difficulties involved in determining the zero-time viscosity and modulus for reacting

* Corresponding author. Corresponding address. Nestlé Research Centre, Vers-chez-les-Blanc, CH-1000, Lausanne 26, Switzerland. Tel.: +41 21 785 8071; fax: +41 21 785 8553.

systems. The long measurement times required means that such experiments are practical only for quenched systems, i.e. systems where the crosslinking reaction has been halted, or model networks, as in other systems the continuing reaction modifies the properties as they are being measured. Recently, it has been suggested that the limited availability of data confirming Eqs. (3) and (4) and the approach commonly used to verify the relationship between the exponents, provide insufficient proof of scaling [11]. Therefore, it is argued that percolation theory cannot be directly applied to dynamic properties of gelling systems, and experimental data should be considered to provide only apparent exponents for the power laws [11]. Further work will be required to confirm or refute this hypothesis.

Percolation theory is based on self-similarity (or a fractal nature), and the absence of any characteristic length scale except the size of the largest cluster and of the monomer building block [3]. The fractal dimension, D_f, of molecular cluster is related to the radius of gyration, R, and molecular weight, M, by the following expression:

$$R \sim M^{1/D_f}. \tag{5}$$

The fractal dimension at the gel point depends on the theory used, but varies from $D_f = 4$ (Zimm–Stockmayer theory [19,20]). $D_f = 2.5$ (percolation theory [21]) and $D_f = 2$ (Muthukumar and Winter's theory [22]). For a system obeying Rouse dynamics and without considering screening of the excluded volume effect, D_f and the power law exponent n are related through

$$n = \frac{D}{(D_f + 2)}, \tag{6}$$

where D is the space dimension [22,23]. For the case of complete screening, this expression turns into [24,25]

$$n = \frac{D(D + 2 - 2D_f)}{2(D + 2 - D_f)}. \tag{7}$$

The fact that power law behaviour for the dynamic modulus is observed experimentally confirms that the structure of the critical gel is self-similar over a wide length scale [2]. The limits of the length scale are reflected in the limiting values of frequency between which the power law is valid; ω_0 and ω^* which correspond to the highest frequency/shortest length scale and lowest frequency/longest length scale, respectively. At the gel point, ω^* tends to zero as the size of the largest cluster approaches infinity, i.e. the macroscopic dimensions of the system. In the experimental observation of this behaviour the higher frequencies are typically outside the accessible range, and the results are dominated by the low frequency/long time behaviour [3,5].

Different theoretical models have predicted values of the power law exponent n, ranging from 0.5 for a simple electrical analogy [5], over 2/3 for the Rouse model [15] to 0.7 for percolation theory with electrical analogy [26]. It has

also been shown that n is expected to decrease as the crosslink density or molecular weight of the precursor of the system is increased, whereas an increase in n is expected when the system is diluted with low molecular weight species [23,18]. Experimentally, n has been investigated for a variety of systems such as end-linking networks, epoxies, urethanes, and as function of stoichiometric ratio as well as molecular weight of the precursors [1–3,5,8,18]. Many systems have shown n values of 0.66–0.7, which thus supports the percolation and Rouse models, but lower values, 0.5–0.25, have also been reported [8,27]. However, recent work notes that rheological determination of n may not be sufficient to distinguish between popular theories of gelation, and stresses the importance of additional determination of fractal dimension and molecular weights in providing a more in-depth characterisation of the gelled network [18].

Most of the systems in which gelation during crosslinking polymerisation was investigated were of the step-wise reacting type. Polymer networks may be formed by two principally different mechanisms; step-wise and chain-wise reaction [28,29]. Chain-wise crosslinking polymerisation reactions have a number of features that set them apart from their simpler and more easily understood step-wise counterparts [30,31]. Chain-wise reacting systems generally have high functionality and reactivities that change as the reaction proceeds, which in combination with the localised initiation of the polymerisation leads to highly heterogeneous systems and low gel point conversions [30,32,33]. It has been shown that densely crosslinked micro-gel particles are formed prior to the macroscopic gel point in free-radical polymerisation of diacrylates [34,35]. The low overall degree of conversion at the gel point in combination with the high crosslink density of the micro-gel particles implies that the gelling structure is at the same time both loosely and densely crosslinked, which suggests that this structure might be less self-similar than step-wise type networks [30].

At present, only limited rheological work on the gelling behaviour of chain-wise crosslinking systems has been reported. A study on cationic polymerisation of a diepoxide found that gelation occurred when $G' = G''$ or $\tan \delta = 1$ as measured at 1 Hz, which leads to $n = 0.5$ [36]. However, as measurements were only performed at one frequency, the presence of a power law behaviour was not confirmed. Work on free-radical UV polymerisation of high molecular weight urethane-based thiols found a power law behaviour at gelation with a value of $\tan \delta = 2–3$, which gives $n = 0.7–0.8$ [37].

Although the rheological measurement of the relationships described in Eqs. (1) and (2) i.e. power law behaviour of G' and G'' and $\tan \delta$ independent of frequency, is the most precise method of experimentally determining the gel point, a number of other criteria and tests have been suggested and used in the literature [38]. These test are often employed in more practical, application-oriented situations where the

Fig. 1. Schematic representation of the tetra-ethoxylated bisphenol A dimethacrylate (**1**), isobornyl methacrylate (**2**) and hyperbranched methacrylate (**3**) monomers.

focus is on simplicity and a moderate degree of precision is sufficient. Measurement of the increase in steady shear or dynamic viscosity and the onset of a negative normal force in rheological experiments are examples of such alternative tests [7,38].

In the present work the gelation behaviour during isothermal crosslinking polymerisation of three methacrylate systems with different structures and number of functional groups is investigated using a torsional dynamic mechanical analyser. G' and G'' and tan δ are measured as a function of reaction time at several frequencies simultaneously, and the evolution of viscoelastic properties as the system gels is described. Criteria for gel point determination such as tan δ independent of frequency, rise in viscosity and onset of negative normal force are applied, and the results compared for the different systems.

2. Materials

Tetra-ethoxylated bisphenol A dimethacrylate (**1**), 540 g/mol, isobornyl methacrylate (**2**), 222 g/mol, azobisisobutyronitrile (AIBN) and tert butyl hydroperoxide were obtained from Aldrich. The hyperbranched methacrylate (**3**), is a resin based on a hydroxyfunctional hyperbranched aliphatic polyester which has been partly methacrylated via a base catalysed esterification with methacrylic anhydride. **3** has an average molar mass of $\approx$ 9000 g/mol and an average of 25 $\pm$ 5 methacrylate groups per molecule. The preparation and properties of the hyperbranched base polymer as well as of acrylated/methacrylated derivatives has been described elsewhere [39–41]. All chemicals were used without further purification. The monomers are presented in Fig. 1.

Three different sample compositions were investigated.

Table 1
Properties of the acrylate systems measured by DMA on samples cured at 160°C

System	T_g[°C] (tan δ peak)	G' at 25°C [Mpa]	G' $T \gg T_g$ [Mpa]	M_c (from Eq. (9)) [g/mol]
5% dimethacrylate	140 ± 5	1400 ± 100	2 ± 0.5	⌣ 2500
100% dimethacrylate	110 ± 5	1500 ± 100	25 ± 3	⌣ 150
Hyperbranched dimethacrylate	100 ± 5	1300 ± 100	26 ± 3	⌣ 140

The mixture of 1 and 2 in a 5 : 95 molar ratio has an average functionality of 2.1 (each methacrylate group is considered to have a functionality of two) and will be referred to as 5% dimethacrylate. Pure 1 is called 100% dimethacrylate and has a functionality of 4, whereas 3 is referred to as hyper-branched methacrylate and has an average functionality of 50 ± 10 [39]. To all samples 1.5% by weight of initiator was added. To obtain reasonable rates of reaction, the hydroper-oxide was used for cure at 130°C whereas AIBN was used at 70°C.

3. Methods

Dynamic mechanical analysis was performed in a Rheo-metrics RDS 2, using parallel plates of 25 or 50 mm diameter and sample thickness of 0.5–1 mm. Samples were placed in the instrument at ambient temperature, and brought to the cure temperature as fast as the instrument allowed which was about 50°C/min. The complex modulus was measured at regular intervals throughout the heating up and cure process using a multi-wave technique involving superposition and decomposition of the signal, which permitted data at several frequencies to be collected simul-taneously. Compared to the strain sweep method, the multi-wave technique offers similar information but with signifi-cantly shorter measurement times [9]. However, the techni-que imposes some limitations. Thus the strain has to be constant throughout the experiment, which makes it difficult to obtain good readings both before and after gelation, and the base frequency, on which higher harmonics is overlaid, has to be ≤0.25 Hz. Since the polymerisation reaction proceeds as each measurement is performed, it is important that the frequency should not be too low as this would mean that the properties changed significantly during the measure-ment. The condition that has been used to verify this is [4,42]

$$\left(\frac{1}{G^*}\right)\left(\frac{\partial G^*}{\partial t}\right)\left(\frac{1}{\omega}\right) \leq 0.1, \tag{8}$$

where a 10% change in properties during measurement thus is considered acceptable. It was found that the change in properties during measurement at 0.25 Hz was of the order of 20% for the hyperbranched system and below 10% for the two other systems. The frequencies used were 0.25, 0.5, 1, 2 and 4 Hz. The strain was 2%, which was checked to be in the linear viscoelastic region. Data was collected as often as possible, which was every 15 s. The normal force was kept at zero throughout the experiment, and the change in plate

distance required to maintain a constant normal force regis-tered. Steady shear experiments were run in the same instru-ment using the same conditions as for the dynamic tests, and a shear rate of 0.5 s^{-1}.

4. Results and discussion

The properties after complete reaction of the three sample compositions that were investigated are presented in Table 1. An estimated molecular weight between crosslinks, M_c, was calculated for each system from G' above T_g according to rubber elastic theory:

$$M_c = \frac{\rho RT}{G} \tag{9}$$

where ρ is the density and R the gas constant [43]. Eq. (9) is strictly valid only for lightly crosslinked, entropy-elastic networks and is used here only to provide a relative compar-ison between the materials. As Table 1 shows, all systems have comparable T_g : s and glassy moduli, but the 5% dimethacrylate system exhibits a significantly lower rubbery modulus and crosslink density than the other two systems. This can be explained by the low average functionality of this system. The fact that the hyperbranched system and the 100% dimethacrylate system have similar crosslink densi-ties is simply a reflection of the average molecular weight per methacrylate group of the corresponding monomers, which is similar for the two systems. Regarding the func-tionality of the systems, it is reminded that the term func-tionality is used to describe the bond-forming capacity per molecule in the same manner as commonly done for step-wise reacting systems, i.e. each methacrylate group is considered to have a functionality of two.

It is worth mentioning that chain-wise polymerisations in most cases are very fast, which means that the experimental investigation of these processes either requires very rapid data sampling or the use of model systems where the reac-tion has been halted prematurely [29]. The present work attempts to follow the process in real time, with the difficul-ties regarding data sampling this entails. As will be further discussed in the following sections, the stiffness of the criti-cal gels of the systems in this investigation is quite low, which renders the quantification of their properties difficult.

4.1. Gel time determination

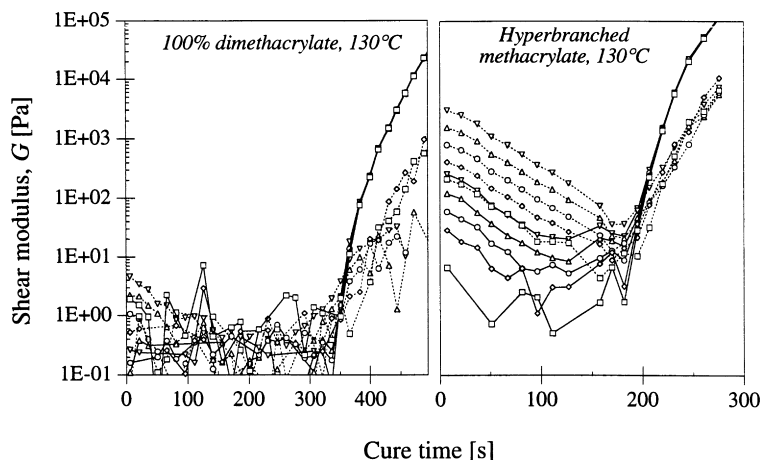Examples of experimental curves of G' and G''during isothermal reaction of the three different systems at 130°C

Fig. 2. G' (solid lines) and G'' (dashed lines) measured at 0.25 Hz (∇), 0.5 Hz ($\triangle$), 1 Hz ($\bigcirc$), 2 Hz ($\diamond$) and 4 Hz ($\square$) during isothermal polymerisation at 130°C.

and 70°C are given in Figs. 2 and 3. Earlier in the experiment, during the heating-up, the materials are liquid and show Newtonian behaviour ($G'' \sim \omega$) in the cases where the viscosity is high enough to be detected. For the 5% dimethacrylate sample and the 100% dimethacrylate sample at 130°C, the viscosity is low, and significant scatter is observed during the initial part of the run. As the samples gel there is a rapid increase in G' which also becomes independent of frequency, and a gradual increase in G'. The fact that G'' is independent of frequency and G'' remains fairly low in all cases means that no sign of vitrification in the vicinity of the gel point is seen in any of the experiments, even when the cure temperature is below the ultimate T_g of the system. Of course, on cure below the ultimate T_g vitrification will always be observed eventually. Tan δ as a function of reaction time for the same samples and conditions are presented in Figs. 4 and 5. The low viscosity of the monomer mixtures is reflected in the initial scatter observed for all but the hyperbranched sample. As the polymerisation reaction proceeds, the values of tan δ decrease. Allowing

for some scatter, a point (indicated in Figs. 4 and 5) where a crossover in tan δ measured at different frequencies occurs, and tan δ consequently is independent of frequency, is observed in all cases. This point coincides with the rise in G' (Figs. 2 and 3) and is the point of gelation [1,4,7]. After gelation tan δ continues to decrease as the materials enter the rubber elastic state. Steady shear tests for the systems reacted at 130°C, presented in Fig. 6, indicate the low initial viscosity of the 5% and 100% dimethacrylate systems. For all systems the rapid increase in viscosity on gelation can be observed.

Table 2 presents the gel times for all systems and compositions determined through dynamic and steady tests. As can be seen there is reasonable agreement between the gel times from tan δ crossover and rise in steady shear viscosity, although the rise in viscosity always occurs somewhat later. Similar delays in gel time as determined in steady shear tests have been reported previously [3], and been attributed to the shear-induced breakdown of the incipient gel [7]. The onset of a negative normal force during a dynamic test occurs as the sample solidifies and the shrinkage caused by the polymerisation reaction is conveyed to the plates of the instrument. This phenomenon has previously been used to determine the gel point [44,45]. As Table 2 shows, the onset of a negative normal force correlates well with gelation as determined by tan δ crossover for the 100% dimethacrylate system. However, for the hyperbranched and 5% dimethacrylate systems the negative normal force is observed respectively before and after the tan δ crossover. In the case of the hyperbranched system the explanation for the discrepancy is believed to be the high viscosity of the system prior to gelation restricting the flow of material. Regarding the 5% dimethacrylate, it is suspected that the stiffness of the incipient gel is too low to permit enough force to be conveyed between the plates of the instrument, and it is not until later when a sufficient stiffness has been built up that a detectable force arises.

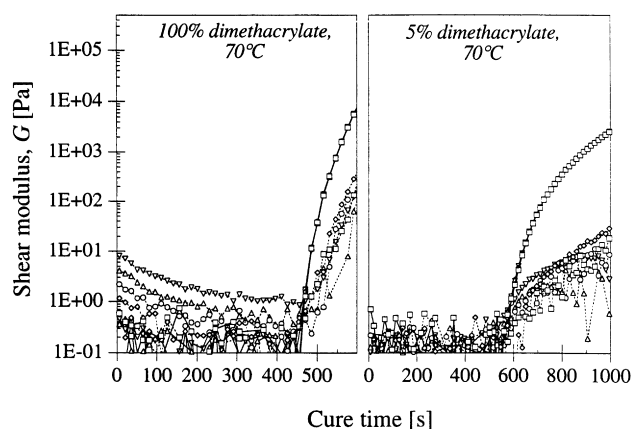Table 2 shows a clear trend of decreasing gel time with

Fig. 3. G' (solid lines) and G'' (dashed lines measured at 0.25 Hz (∇), 0.5 Hz ($\triangle$), 1 Hz ($\bigcirc$), 2 Hz ($\diamond$) and 4 Hz ($\square$) during isothermal polymerisation at 70°C.
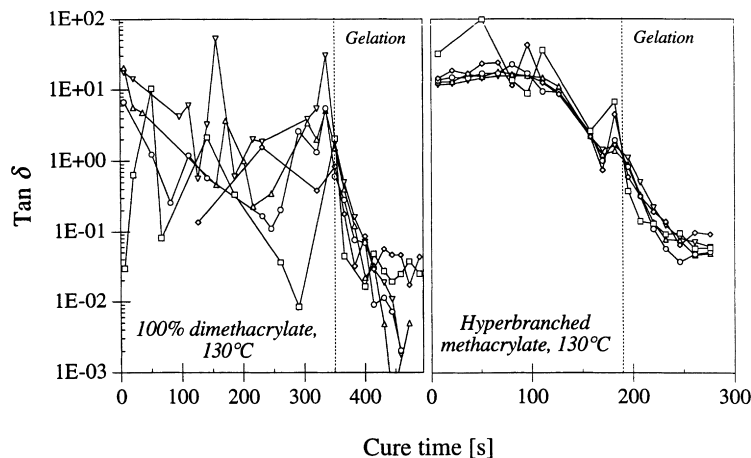
Fig. 4. Tan δ measured at 0.25 Hz ($\triangledown$), 0.5 Hz ($\triangle$), 1 Hz ($\bigcirc$), 2 Hz ($\diamondsuit$) and 4 Hz ($\square$) during isothermal polymerisation at 130°C. The point at which tan δ is independent of frequency is indicated.

increasing average functionality of the system at each reaction temperature, reflecting the decrease in gel point conversion with increasing number of functional groups. Regarding the influence of temperature on gel time, it is reminded that different initiators were used at the two temperatures, which means that a comparison has little relevance.

4.2. Viscoelastic behaviour

As discussed in the introduction, there are several ways of characterising the viscoelastic behaviour at the gel point and determining the characteristic exponents. The first condition that has to be fulfilled if the theories illustrated in Eqs. (1)–(7) are to be applicable is that the system obeys a power law behaviour. It is reminded that the validations of the zero-time properties, i.e. Eqs. (3) and (4), is beyond the scope of the present work. If tan δ really is independent of frequency, as indicated by the data in Figs. 4 and 5, a power law behaviour of G' and G'' should be observed at the same

time. Figs. 7 and 8 present G' and G'' as functions of frequency at times close to the gel point for all systems. As can be seen the moduli of the critical gels are only of the order of 1 Pa for the 5% and 100% dimethacrylate systems and 10 Pa for the hyperbranched material. The values reported for other critical gels of e.g. epoxy/amine systems, urethanes and end-linking networks are generally orders of magnitude higher [1,2,4,8,42]. This difference is believed to be related to the degree of conversion at gelation, which determines the fraction of monomer units attached to the emerging network. For step-wise reactions the gel point conversion is typically 30%–70% depending on the functionality, whereas it is only 1%–15% in chain-wise crosslinking polymerisations. The reason why the hyperbranched system, which has the lowest gel point conversion, exhibits the highest modulus at gelation is believed to be the high viscosity of the sol fraction. Allowing for some scatter, Figs. 7 and 8 show that G' and G'' appear to obey a power law behaviour at the gel point for all systems over the frequency range investigated. However,
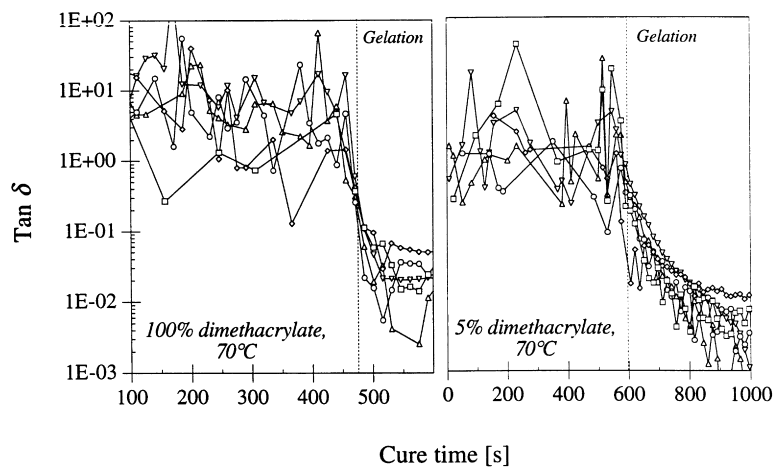

Fig. 5. Tan δ measured at 0.25 Hz ($\triangledown$), 0.5 Hz ($\triangle$), 1 Hz ($\bigcirc$), 2 Hz ($\diamondsuit$) and 4 Hz ($\square$) during isothermal polymerisation at 70°C. The point at which tan δ is independent of frequency is indicated.
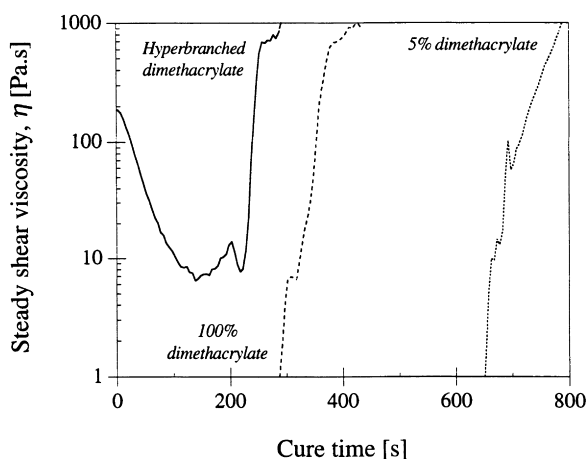
Fig. 6. Steady shear viscosity during isothermal polymerisation of the different systems at 130°C.

the slope of log G vs. log ω, i.e. n, which is supposed to be the same for both G' and G'' in each case, exhibits some variation. This is attributed to the difficulty in finding the exact point of gelation in combination with the low stiffness of the systems at the gel point. It can also be seen in Figs. 7 and 8 that after gelation, all systems exhibit Hookean behaviour ($G' \sim \omega^{\circ}$), with no apparent signs of vitrification.

Table 3 presents values of n obtained from the slope of log G vs. log ω as well as from the value of tan δ at gelation (Eq. (2)). In spite of the uncertainties in the values, some trends can be distinguished. The values of n determined from the slope of log G vs. log ω are generally lower and exhibit more scatter than the ones calculated from tan δ. It is not known why the values derived from G' and G'' at the gel point are lower, it could well be an artifact as a result of the scatter in the data. As the determination of tan δ at gelation involves averaging over several data points, the n values calculated from tan δ are believed to be more accurate, and will be used in the following. Comparing the three systems reacted at 130°C reveals that n appears to increase as the functionality and molecular weight of the system is increased, from 0.4 ± 0.2 for the 5% dimethacrylate to 0.6 ± 0.1 for the hyperbranched system. At 70°C, no clear difference in n between the 5% and 100% dimethacrylate systems can be seen, but n seems to decrease with decreasing temperature (0.3 ± 0.2 at 70°C compared to 0.4–0.5 ± 0.2 at 130°C). n is not expected to depend on the reaction temperature [42]. However, it is reminded that 70°C is

below the ultimate T_g of the systems. Studies on an epoxy/amine system found a similar decrease in n as the reaction temperature was lowered below T_g, which was explained in terms of vitrification [4]. Thus, although no signs of vitrification are present until well after gelation (see Figs. 3 and 8), the vitrification process still appears to influence the behaviour at the gel point. This apparent contradiction is believed to be related to the heterogeneous structure of chain-wise reacting systems. The formation of micro-gel particles earlier in the reaction has already been mentioned, and recent work has shown that these particles probably vitrify instantly as they are formed, well before macroscopic vitrification occurs [46]. Vitrification thus appears to be a complex process in these systems, and the definition of the actual point of vitrification will depend on if it is macro- or microscopic properties that are referred to.

The dependence of n on the functionality of the system can be discussed in terms of the fractal dimension, D_f, and the degree of screening of the excluded volume effect at the gel point. As the functionality of the system is increased, it can be argued that two effects should be observed. A higher functionality will lead to a higher degree of branching and thus to more compact clusters, resulting in an increase in D_f. As the functionality is increased, the gel point conversion decreases which leads to the clusters becoming more diluted with unreacted monomer molecules at the gel point. This should result in a decrease in screening. The dependence of n on D_f for completely unscreened and screened cases (Eqs. (6) and (7), respectively), assuming $D = 3$, is outlined in Fig. 9 (adapted from Muthukumar [23]). As can be seen, an increase in D_f is expected to produce a decrease in n independent of the degree of screening, whereas a decrease in screening should result in an increase in n. The fact that n is observed to increase as the functionality of the system increases suggests that the decrease in screening is the dominating effect. However, this does not exclude the possibility of changes in D_f. If it is assumed that the 5% dimethacrylate system with $n = 0.3$ is completely screened, Eq. (7) and Fig. 6 give $D_f = 2.2$. Assuming the hyperbranched material to be unscreened, inspection of the corresponding curve in Fig. 9 shows that for $n = 0.6$, D_f is > 3. As the real behaviour will be intermediate between the limits depicted by the completely screened and unscreened cases, the change in D_f would have to be smaller than in this theoretical example. However, it does illustrate that as long as the decrease in screening is sufficient, significant increases in D_f

Table 2
Gel times for the different systems and cure temperatures in seconds

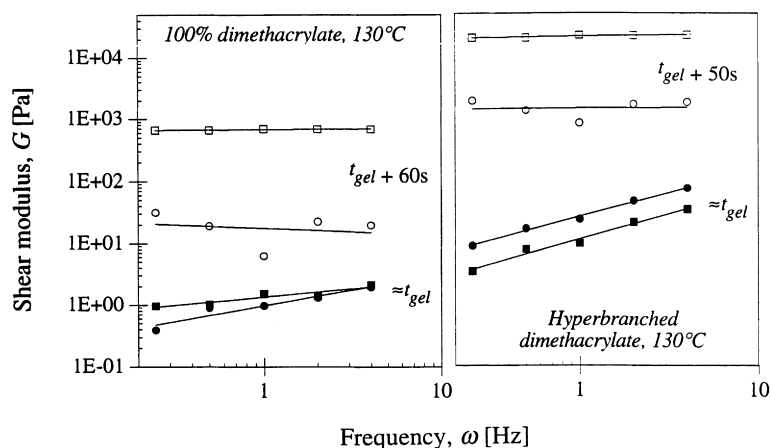| Cure temp. [°C]	System	Tan δ independent of frequency	Onset of negative normal force	Viscosity rise, $\eta = 500$ Pa.s
130	5% dimethacrylate	650 ± 30	750 ± 30	750 ± 30
	100% dimethacrylate	350 ± 30	350 ± 30	380 ± 30
	Hyperbranched	190 ± 15	100 ± 30	250 ± 15
70	5% dimethacrylate	600 ± 30	800 ± 30	–
	100% dimethacrylate	470 ± 30	500 ± 60	–

Fig. 7. G' (squares) and G'' (circles) near the gel point and after gelation as a function of measurement frequency for polymerisation at 130°C.
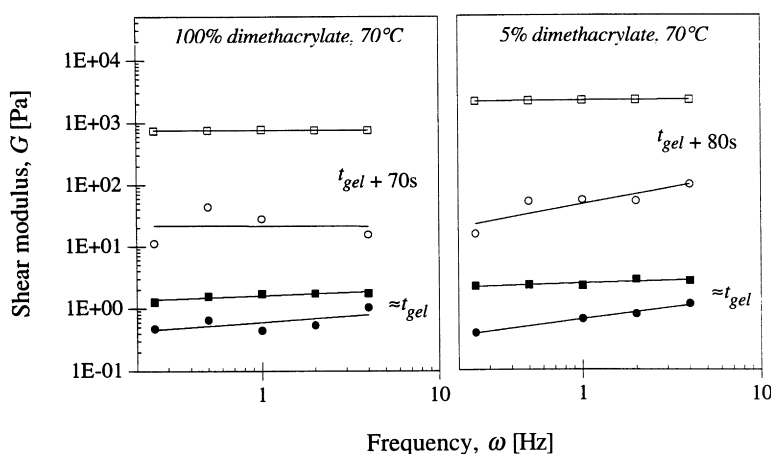

Fig. 8. G' (squares) and G'' (circles) near the gel point and after gelation as a function of measurement frequency for polymerisation at 70°C.

could occur and the net result still be an increase in n. Further work, e.g. characterisation of the fractal dimensions of the systems and/or investigation of the influence of dilution on the behaviour, will be required to quantify the relative influence of the two effects.

5. Conclusions

Examination of the gelation process in chainwise cross-linking polymerisation of methacrylate resins with different functionalities has shown that all systems exhibit similar gelation behaviour in terms of rheological data. A crossover in tan δ (tan δ independent of frequency) was observed, and the time at which this occurred correlated well with the time at which an increase in steady shear viscosity occurred. An onset of a negative normal force was observed before, at the same time as or after the tan δ crossover, depending on the viscosity of the system. The gel time was found to decrease with increasing functionality of the system.

Table 3
Values of the power law exponent n for the different systems and cure temperatures

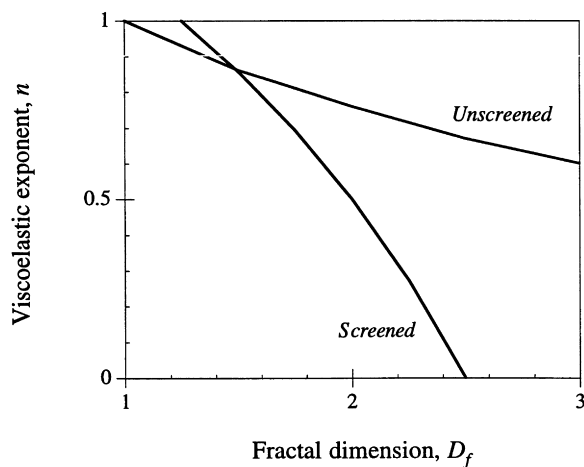| Cure temp. [°C]	System	Tan δ at gelation	n_1 (from tan δ)	n_2 (from G')	n_3 (from G'')
130	5% dimethacrylate	0.7 ± 0.3	0.4 ± 0.2	0.1 ± 0.2	0.2 ± 0.2
	100% dimethacrylate	1.0 ± 0.5	0.5 ± 0.2	0.3 ± 0.2	0.3 ± 0.2
	Hyperbranched	1.4 ± 0.6	0.6 ± 0.1	0.5 ± 0.1	0.5 ± 0.1
70	5% dimethacrylate	0.5 ± 0.3	0.3 ± 0.2	0.1 ± 0.1	0.4 ± 0.2
	100% dimethacrylate	0.5 ± 0.2	0.3 ± 0.1	0.1 ± 0.2	0.2 ± 0.2

Fig. 9. Schematic representation of the relationship between n and D_f for the completely unscreened and screened cases (Eqs. (4) and (5), with $D = 3$). Adapted from Muthukumar [23].

Within the measured frequency range, a power law behaviour for the dynamic modulus was observed at the gel point in all systems. The stiffness of the critical gel was found to be of the order of 1 Pa for all systems, which is low compared to other types of systems investigated in the literature. A value of the power law exponent n of 0.4 ± 0.2 to 0.6 ± 0.1 was determined for gelation during reactions at $T \geq T_{g\infty}$. n was found to increase with increasing functionality of the system. This trend suggests that the differences in screening between the systems dominate over the difference in fractal dimension. For reaction temperatures below $T_{g\infty}$ a value of $n = 0.3 \pm 0.1$ was obtained, which is believed to be related to micro-vitrification.

Acknowledgements

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