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Macrogels, Microgels and Reversible Gels – What is the Difference?

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Summary

The state of knowledge of permanently crosslinked makro- and microgels is considered. Experimentally observed deviations from predicted critical behavior were disclosed. The observed dependence on the reaction vessel size remained unsettled. Reversible gels and networks show two main differences to permanent networks i.e. bundle formation which establish junction zones and influence of thermodynamic interactions. The dynamics of constrained chains remained not well understood.

Introduction

In the past 30 years almost all types of polymer gels and networks have intensely been studied in various laboratories. Interest was focussed mainly to the technically important property of stress-strain behavior and viscoelasticity. Little comparative work was done with regards to other properties and the different types of gels. The present contribution makes an attempt of such comparison and is based on structures which could be elucidated by light scattering. A number of unexpected details will be disclosed, and may give new insight in the structure of networks.

Macrogels

Macrogels are known to polymer scientists as long as polymers could be synthesized from monomers. Best known is the free radical copolymerization of styrene with divinyl benzene [1]which is easily performed but even after all the years the structure formation of this system escaped a reliable description by theory [2]. A real step forward was achieved by Flory [3] with the experimental work on the polycondensation of *f*-functional monomers to branched and gelled polyesters. He discovered growing clusters preceding the gelation which led him to the famous gel condition [4]. The derivation of the cluster size as a function of monomer conversion turned out to be extremely complex. Stockmayer [5] solved the statistical problem.

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He derived the molar mass distribution and found a rather simple relationship for the weight average degree of polymerization. The Flory-Stockmayer (FS) theory became the basis for our understanding of networks. In the 1980s [6] when computers easily became available physicists started simulations of network formation by placing units on the sites of special lattices and followed the clustering via attached sites. At a critical occupation density a percolation threshold was obtained equivalent to the gel point. More seriously, a molar mass distribution was found that differed from Stockmayer's distribution. Noticing that in this FS-theory the radius of gyration of monodisperse clusters only weakly increases with molar mass 4-dimensional objects were concluded being derived which appeared physically senseless. Therefore, the Flory-Stockmayer theory was discarded as basically wrong. To prove this statement we started a number of different experiments and compared the results with predictions from both theories. This comparison gave us new insight.

Molar mass distribution and critical behavior

Percolation theory could make predictions on behavior but not on absolute values. No reliable predictions on the position of the gel point was possible. The weight average distribution of cluster sizes (x = degree of polymerization) was found to follow power law behavior with a cutoff function f(x/x*) that describes a sharp decrease of the weight fraction to zero.

$$w(x) \propto x^{1-\tau} f(x/x^*) \qquad \mathbf{(1)}$$

An exponent $\tau_{\mathrm{perc}} = 2.2$ was obtained [6]. The shape of the cutoff function could not be defined, but was found to scale with a cutoff degree of polymerization x^* in a critical domain with respect to the position of the gel point. Later, by size exclusion chromatography (SEC), x^* could be assigned to the z-average degree of polymerization. The power law behavior of randomly formed clusters is significantly different from the most probable distribution for linear chains which has a maximum near the number average degree of polymerization, in contrast eq.1 which continuously decreases with the *x*. The weight average degree of polymerization x_w could not quantitatively be estimated but showed critical behavior as given by

$$x_w \propto \frac{1}{|\alpha_c - \alpha|^{\gamma}} \qquad \mathbf{(2)}$$

with $\gamma_{\mathrm{perc}} = 1.8$ and α denotes the occupation probability of lattice sites.
After the gel point the mass fraction m_{gel} of lattice sites which establish the network was evaluated and the amount of extractable clusters representing the sol fraction. The clusters from this sol were expected to followed the same behavior of eq. 2 where now $\alpha > \alpha_c$.The gel fraction also showed critical behavior and increased with en exponent of $\beta_{\mathrm{perc}} = 0.48$

$$m_g \propto (\alpha - \alpha_c)^{\beta} \qquad \mathbf{(3)}$$

Another critical exponent was obtained for the radius of gyration $R_g \equiv [\langle S^2 \rangle_z]^{0.5}$. The various critical exponents are related to each other. Whenever two exponents have been determined the other can be expressed by these two exponents. Details are found in the book by Stauffer [6].

The *Stockmayer distribution* is an analytical function and consists of enthalpic and entropic contributions, and is given by the equation [5]

$$w(x) = \frac{(1-\alpha)^2}{\alpha} f \frac{[(f-1)x]!}{(x-1)![(f-2)x+2]!} b^x \qquad (\mathbf{4})$$

with

$$b = \alpha(1-\alpha)^{f-2} \qquad (\mathbf{5})$$

The members containing the extent of reaction α constitute the enthalpy contribution and the combinatory expression the entropy. The corresponding weight average has the simple form

$$w_x = \frac{1+\alpha}{1-(f-1)\alpha} \qquad (\mathbf{6})$$

and w_x diverges at

$$\alpha_c = \frac{1}{f-1} \qquad (\mathbf{7})$$

which is Flory's gel condition. The gel fraction was analytically derived by Flory. The critical exponent in eq.3 was $\beta_{FS} = 1.0$. In the form of eq.4 the Stockmayer distribution is not easily compared with the percolation result of eq.1. Stockmayer considered the limit of large degrees of polymerization, and making use of Flory's gel condition he obtained

$$w(x) = \frac{(1-\alpha)^2}{\alpha} fx \frac{\exp[-(b/b_c)x]}{2\pi^{0.5}(f-1)^{2.5} x^{2.5}} \qquad (\mathbf{8})$$

This equation agrees with the general percolation prediction but with an exponent $\tau = 2.5$ instead of $\tau = 2.2$. Moreover, an analytic cutoff function was derived. The difference in the exponent τ is small and was difficult to determine experimentally, but the distribution up to the gel point covers a very broad range in x, and within this range the difference in the distribution becomes noticeable. Figure 1 shows this effect.

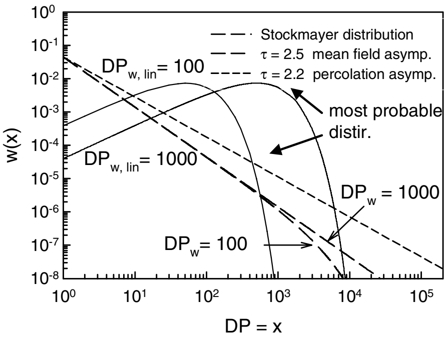

Figure 1. Molar mass distributions of randomly branched clusters according to Stockmayer and percolation theory. The most probably ditributions show a maximum at the number average x_n.

Experimentally determined molar mass distributions [7] gave good agreement with the Stockmayer prediction but with increasing x_w the percolation limit is approached and reached at $x_w > 100$. In summary both competitive treatments led to the same type of equation, but with different values for the critical exponents. Experimentally a transition was observed from the Stockmayer distribution at small extent of reaction to percolation prediction at large α. The conclusion of four dimensional clusters drawn by the physicists required a closer inspection.

Experimental test for critical behavior

The test was made in our laboratory and by several other groups. The following outline will be confined to our systems. In the first case an ionic copolymerization of a monogylcidylether with a diglycidylether as crosslinker was carried out [8]. The other system consisted of 3-arm polystyrene star molecules with OH-groups at the end of the arms and were crosslinked via their ends by toluene diisocyanate [9]. Crosslinking was performed by adding a well defined amount of the crosslinker which reacted to full conversion. Only the results of the epoxide crosslinking will be considered.

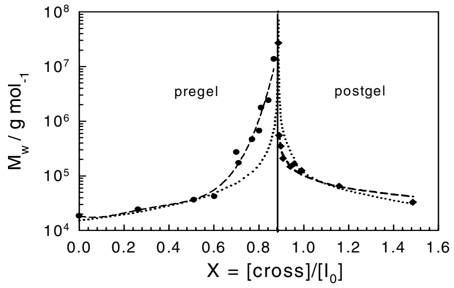

Figure 2. Molar mass dependence of clusters from the pre-and post-gel as a function of the crosslinkers to initiator ratio (number of crosslinks per living chain). The dotted lines describe the Stockmayer theory, the dashed ones the experimental scaling behavior [8].

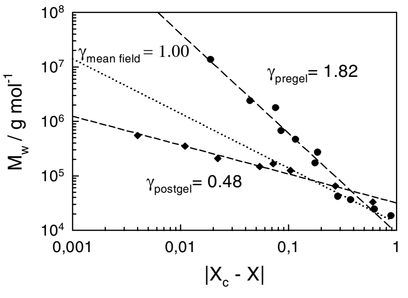

Figure 3. Plot for critical behavior of molar mass. Exponents of $\gamma_{FS} = 1.0$ and $\gamma_{perc}=1.80$ were predicted for both regimes [8].

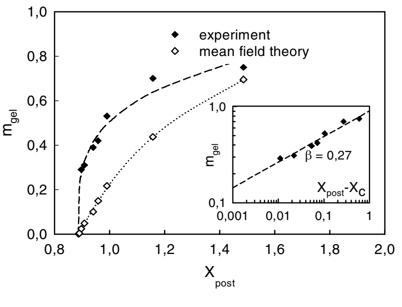

Figure 4. Gel fraction as a function of X =[BADGE]/[I] and (inset) plot for critical behavior of m_{gel} [8].

Figure 2 shows the dependence of the molar mass as a function of the ratio X = [BADGE]/[I], which represents the number of crosslinked per living chain and is related to the extent of reaction α in the original Stockmayer theory (BADGE =

bisphenol-A-diglycidylether, I = initiator). The symbols represent the experimental data, the dotted lines correspond to the Flory-Stockmayer (FS) theory, and the dashed lines resulted from the critical behavior. The data after the gel point refer to the values from the extracted sol fractions. Figure 3 shows the same data but now plotted against $|X-X_c|$ in a log-log scale. Evidently, the percolation theory gave a good description of the behavior in the pre-gel state, but the critical exponent of the clusters from the sol fractions drastically deviated from both, the percolation and the FS predictions. Also the critical behavior of the gel fraction deviated strongly from predictions by both theories (Figure 4). Off lattice simulations [10] gave critical exponents of $\gamma = 1.77 \pm 0.16$ and $\beta = 0.300 \pm 0.024$ in better agreement with experiments.

Global conformational properties

Figure 5 shows the molar mass dependencies of the viscosity of the clusters from the pre- and post-gel states in comparison to that of linear chain analogues. Near the gel point the clusters from both regimes show the same property. However, at low molar mass the clusters from the sol fraction have a significantly lower intrinsic viscosity. Consulting the Flory-Fox equation [11]

$$[\eta] = \Phi \frac{R_g^3}{M} \propto \frac{1}{d_{segment}} \tag{9}$$

one finds a higher segment density of the clusters from the sol fraction than of those from the pre-gel state of the same molar mass. This indicates mean excessive intramolecular reaction within the clusters. Similar heterogeneity may well be present in the gel. In fact, already during branching in the pre-gel state ring formation takes place. This ring formation reduces the number of functionalities which now no longer are available for attachment to the gel.

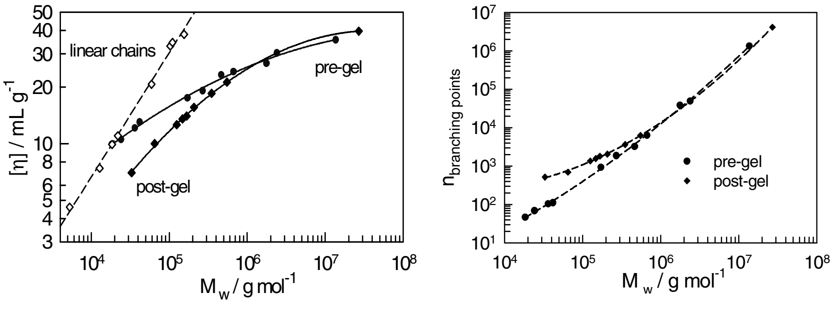

Figure 5. Left: Molar mass dependence of the intrinsic viscosity for linear polyesters and the branched cluster in the pre- and post-gel regimes. Right: Number of branching points in the clusters from both regimes, which were derived with the Zimm-Stockmayer equation [12] from the shrinking factors g and g' assuming $g = g'^{0.6}$.

Angular dependence of scattered light

As already mentioned Zimm and Stockmayer [12] found for the monodisperse clusters a molar mass dependence of $R_g \propto M^{0.25}$. Assuming self-similarity a fractal dimension of $d_f = 1/\ 0.25 = 4$ is obtained. The question of self similarity can be tested by considering the angular dependence of the scattered light. In a log-log plot of the scattering intensity as a function of the scattering vector $q = (4\pi n/\lambda)\sin(\theta/2)$ a power law should be observed with an exponent of $-d_f$. In 1971 Kajiwara [13] derived the angular dependence of such monodisperse fractions which gave a particle scattering factor *P(q)* of

$$P(q) = \frac{1}{x}\sum_{n-1}^{x-1}\exp(-l^2q^2/6)\frac{\left[(f-2)n+f\right]}{f-1}\left\{\left[1-\frac{n}{(f-1)x}\right]^{(f-1)x-n} / \left[1-\frac{n}{x}\right]^{x-n}\right\} \qquad \mathbf{(10)}$$

where x is the degree of polymerization. For $f = 4$ the angular dependencies are shown in Figure 6**,** represented as log-log Kratky plot. The slope at large q-values approaches asymptotically an exponent of –2.5 in agreement with percolation predictions for clusters in the unperturbed state. The asymptote is continuously shifted towards larger q-values as x increases which corresponds to smaller segment domains. Evidently the clusters possess a *structural heterogeneity* composed of a dense core and much smaller branched segment domains in the unperturbed state. The low exponent in eq. 9 arises from a mass that increases considerably stronger than that of the particle volume. Not every power law behavior means self similarity.

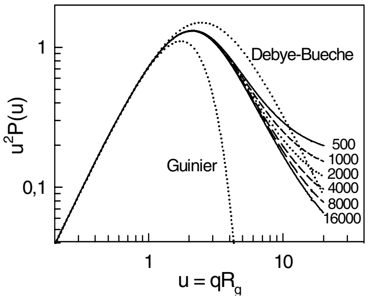

Figure 6. Angular dependence of scattered light from monodisperse randomly branched chusters of different DP [13], presented in a normalized log-log Kratky plot.

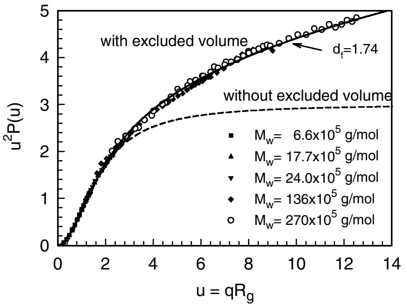

Figure 7. Experimental angular dependence of scattered light from non-fractionated polyester clusters of various molar masses including one from the sol fraction [14].

Unsolved questions

It remained the question why the critical behavior in percolation deviates from the FS theory. Ring formation or excluded volume interactions are considered as possible reasons. Ring formation causes a shift of the gel-point but its influence on branched structures remained unsolved. An effect of excluded volume interaction was found, indeed, experimentally from the angular dependence of scattered light. In the Kratky plots we found marked deviation from the well-known Debye function which also was derived for randomly branched clusters. These deviations turned out being caused by excluded volume interaction. A good description of the curves became possible with the approximation $P(q) = [1+a(qR_g)^2]^{-d_f}$ with $ad_f = 1/3$. An even better description became possible by the more fundamental theory of Feltoft et al. [15] (equation not shown) as demonstrated [14] by the solid curve in Figure 7. When Flory, Stockmayer and Zimm developed the early branching theories it was fully out of imagination that excluded volume effects could influence structure formation. In fact, it never can occur with low molar mass compounds. However, intramolecular interaction among chain segments, which corresponds short-time ring formation, influences the probability of chemical clustering of large branched chain molecules. The extent of reaction α of a functionality is not solely determined by the reaction among two i*ndependent* functional groups but also contains a contribution from the chain conformation at the time of reaction.

Microgels

A macrogel has two significant properties: The system must have passed a gel point and after the gel point the systems should have disproportionated into a gel- and a sol-fraction. We wondered how the system behaved if gelation was carried out in a confined space and the boundaries were removed after the crosslinking reaction. We checked these questions by carrying out a free radical crosslinking polymerization of vinylacetate with divinylether as crosslinker in latex particles of uniform size [16]. Both the crosslinker fraction and the reaction temperature were varied and the reaction was carried out for monomer conversions from a few % to 100%. The monomer droplets quickly disappeared as was followed by static light scattering (LS). After the reaction the latex stabilizing surfactant was removed and the molar mass, radius of gyration and the angular dependence of the scattered light were measured in methanol.

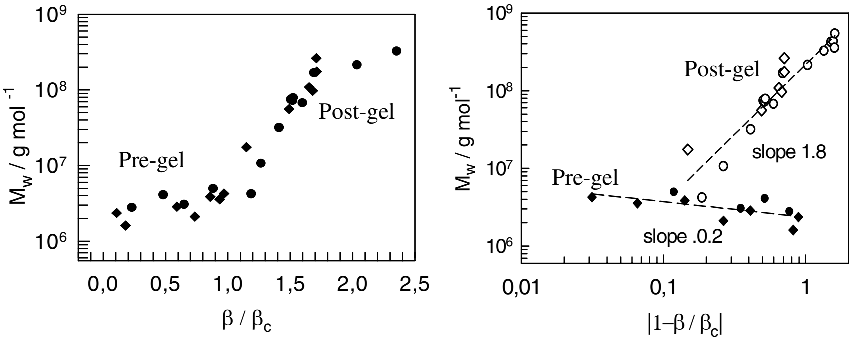

Figure 8. Left: Molar mass dependence of vinylacetate polymerization in monodisperse latex particles as a function of monomer conversion β normalized by gel point conversion β_c [17]. Right: Plot for critical behavior of the clusters in the pre-gel state and for the molar mass of the gels. The exponents significantly deviate from those for macrogels.

Figure 8 shows as one example the result for two series as a function of conversion. A common growth of R_g with M_w was found until some clusters had reached the size of the latex particles. After this point the radius of gyration remained almost constant while the molar mass further increased. Critical scaling behavior was observed for the clusters before gelation but also for the gel fraction with critical exponents, not predicted so far by any theory. Size exclusion chromatography (SEC) made a sol fraction apparent as is shown in Figure 9. After gel formation a high molar mass became visible. The clusters in the pre-gel state showed a bimodal distribution which probably arose from branching due to chain transfer of radicals by the polymer. Sol- and gel-fractions could separately collected by preparative SEC, and were measured by static LS.

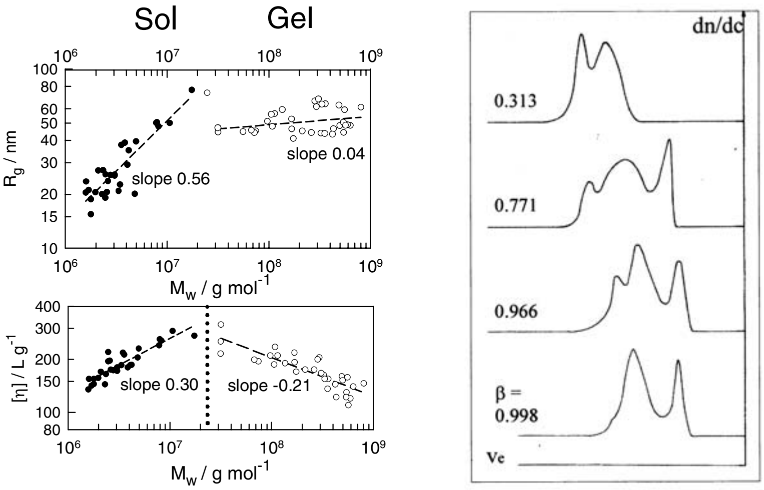

Figure 9. Left: Molar mass dependence of the intrinsic viscosity [η] of the samples from the pre-and post-gel states [16]. The change in behavior occurs at the gel-point and is explained by the Floy-Fox equation eq. 8 [16]. Right: SEC diagrams from samples before and after gel point. Arround $\beta = 0.77$ a high molar mass component appeared which represents the gel fraction. The two peaks from the sol fraction arise from branching via chain transfer of polyvinylacetate.

Figure 10 shows the angular dependence from two gels, one shortly after the gel point, the other of high cosslinking density. The sol fractions from both samples form a common angular dependence but the gel fractions developed increasingly globular behavior. Again structural heterogeneity was observed that resembled that of monodisperse clusters in Figure 6.

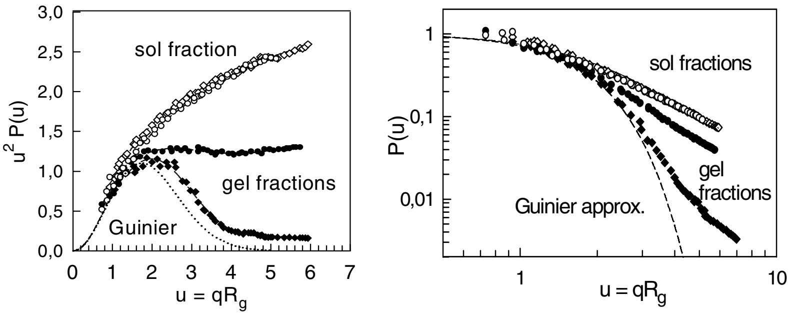

Figure 10. Left: Kratky plots of the scattering intensity from two gel fractions and the corresponding sol fractions. Right. Log-log plot of the same data as shown left. Note the coinciding sol fractions and the asymptotic power law for the large gel. The scattering curve revealed [17] structural heterogeneity with a dense core and a fraction dimension of approximately $d_f = 2.5$.

Another type of microgels is obtained when the monomer concentration remained considerably smaller than the overlap concentration of the clusters. Then no connected clusters can be formed which would expand through the whole reaction vessel. In such cases not reacted crosslinkers can only react further *intra*molecularly. It remains the question whether these microgels ever passed a critical gel point. Very likely these microgels have no sol-fraction. It would be of interest whether two well separated peaks of different segment density could be detected by SEC combined with online multi angle LS and viscometry. It also would be of interest to measure the viscoelasticity and the stress-strain behavior of such microgels. The elasticity of microgels is of special interest in medical application when used as drug carrier. Similar to red blood cells deformable microgels could passe narrow blood vessels without breaking.

Reversible networks and gels

This field has many different faces and was considered in a book [18] and two review articles[19,20]. Similar to permanent networks a number of soluble polymers undergo a sol/gel transition, which can be caused by changes in temperature, concentration, pH, added salts or other low molar mass compounds. Evidently the sol/gel transition is controlled by thermodynamic interactions and not alone by conditions of connectivity. This fact establishes the main difference to permanent networks. Gelation can take place in good and poor solvents, because special interactions between functional groups only little contribute to the chemical potential.

The second striking difference to permanent gels is the discover by Rees in the late 1960s that a helix/coil transition had to precede the gelation. Rees [21] concluded from his study with carrageenans double helix formation. This suggestion was corrected by Smidsrod et al. [22] by the observation that association of two chains had the same effect. Mostly, such structure formation of helices or laterally aligned chains is followed by further aggregation to larger bundles. Only sections of chains can be incorporated into such bundles, but it is essential that further chain sections from one bundle become incorporated into other bundles. In this way the bundle domains form *junction zones* which take the charge of point like crosslinks in permanent networks.

This discover was made with polysaccharides but has a much broader impact and remains valid also for synthetic polymers of high tacticity. The discover was possible with polysaccharides with their optically active monosaccharides as repeat units. A helically wound chain significantly contributes to the optical rotation and permitted a quantitative study of the helix coil transition. Most iso- and syndiotactic chains are not optical active, but helix formation could be detected by FTIR spectroscopy [23]. Iso- and syndiotactic chains often crystallize in a helical morphology. Several examples were carefully studied by Berghmans and his coworkers [23] and were shown to be non-crystalline structures. Figure 11 shows the temperature dependence of the helix coil transition on heating and the reversible process on cooling for sPMMA in toluene [24]. The transition from helix to coil appeared as an equilibrium process, but on cooling the formation is significantly delayed by metastable states of coils. This was revealed when the still amorphous system was annealed as a function of time. Slowly the equilibrium state was reached. Such aging is a common feature of many systems which show histeresis. The structure formation was detected by recording the storage shear modulus G'. The open symbols in Figure 11 indicate the helix content and the filled ones G'. Following the heating process one notices that a flexible network remained effective over a broad temperature interval. From 34°C to 43°C the helix content decreased already to 30%, but rapidly broke down when the temperature was further increased. On cooling the opposite behavior occurred. Until 34°C the system

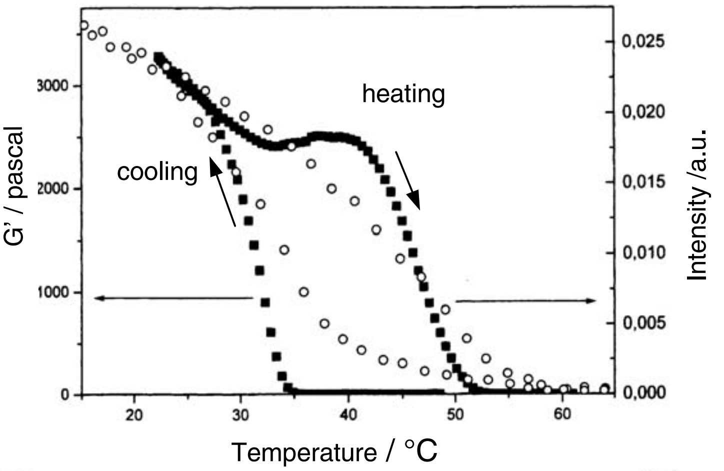

Figure 11. Helix-coil transition on heating and cooling as detected by FTIR (open symbols) and structure formation detected by the elastic shear modulus G' (filled symbols) [24].

developed no macroscopic structure formation, although 30% of the helix has been rebuilt. On further cooling the network formation proceeded abruptly. Evidently, only if the helix had reached a critical length, gel formation became possible.

Effect of life-time

So far the structure formation was considered as static process. However, as long as only short helix segments were formed the system comprises significant fluctuations between shorter and longer helix sections which also include association/dissociation fluctuations. Apparently the structure forming element (the helix in this example) requires a certain length before the associate has reached a sufficiently long *life-time*. We checked this conjecture by comparing the process of end-linking 3-arm PS star molecules via covalent [25] and associative [26] bonds. For covalently linked stars the gel point occurred as expected, but via a bifunctional coupler gelation could not be observed. We came to the conclusion that network formation will be not possible via association if only pointlike bonds are formed. Several bonds in a row have to react cooperatively before a a sufficiently long life-time is attained.

Influence of branching on chain dynamics

The dynamics in networks has been largely neglected in the study of networks. Commonly rheological measurements were carried out to find the point when G' becomes larger than the loss modulus G'', or when both moduli in their frequency dependence become parallel to each other. Little attempts have been made to measure the relaxation spectrum. However, in the pre-gel state dynamic light scattering makes such studies possible. The behavior of flexible chains is well known and was found in good agreement [27] with the Zimm-Rouse [28,29] relaxation spectrum. Also the effect of chain stiffness [30,31] is partially well understood. However, with branched samples new effects were obtained. In dynamic light scattering a time correlation function is measured which at short delay times decays as a single exponential. The decay constant is called first cumulant Γ(q) and has the dimension of a. reciprocal time. The first cumulant has a strong dependence on the scattering angle, i.e. on values of the scattering vector q. For small qR_g one universally finds an increase with q^2 which is caused by the mutual diffusion coefficient of the center of mass [32]. At larger values ($qR_g > 4$) LS probes the internal structure and the corresponding mobility. For flexible chains the motions under hydrodynamic interaction follow the Zimm-Rouse relaxation spectra which in dynamic LS is responded by a q^3 dependence [27-29.]. Such behavior was found for polystyrene and polyisoprene [27]. Everybody was sure that gels and crosslinked clusters prepared from flexible chains would show the same Zimm-Rouse relaxation behavior. This conjecture was based on the low branching density and the fact that at large qR_g values only linear chain sections are probed which connect two crosslinking points. However, a considerably weaker increase (decrease in Γ/q^3) was found as shown in Figure 12 in which Γ/q^3 is plotted against qR_h using a log-log representation [33,34]. First thoughts that polydispersity would be the cause for the deviations from the expected plateau had to be discarded, because the deviations approached more and more the behavior of hard spheres as the branching density increased. At present no theory is available which would describe these effects. Another point of concern is that we cannot distinguish between relaxation and internal structural fluctuation times i.e. the life time of physical bonds.

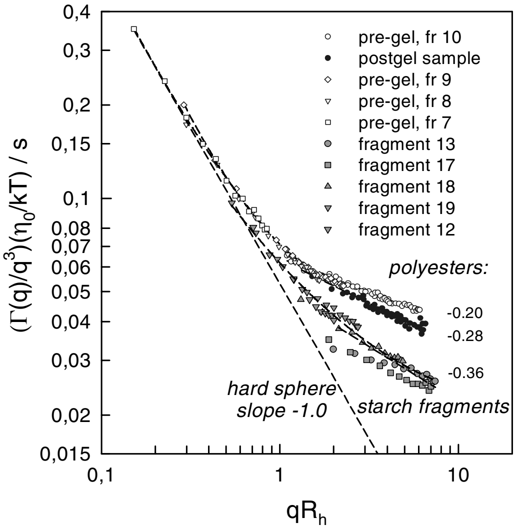

Figure 12. Log-log plot of the reduced first cumulant Γ/q^3 as a function of qR_h, (R_h hydrodynamic radius of the branched macromole-cules). The polyesters are randomly branched, the starch fragments hyper-branched. The clusters from the post gels are higher branched than those from the pre-gel domain. For flexible linear chains a plateau of 0.071 is reached. The devia-tions turn more and more towards hard sphere behavior.

Conclusions

A good understanding of structure and mechanical properties of permanently branched or crosslinked clusters has been attained. The internal structure and the chain dynamics in networks remained insufficiently explored. Conclusions on the dynamics were solely based on analogues from linear chains and are misleading. The understanding of reversible gels remained unsatisfactory. Length and thickness of the junction zones could not determined. A theory on structural fluctuations, and dynamics of tethered chains, is missing.

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