research currently in progress throughout the world required a new journal. Such a journal would highlight the role of chemistry as a source of new materials and processes for materials technology and bring together work now widely scattered throughout the literature. The recommendation that a new journal be established was subsequently approved by the ACS and the first issue is scheduled for publication in January, 1989.

From the beginning *Chemistry of Materials* was envisioned as a primary research journal which would emphasize the more chemical and fundamental aspects of materials science which underlie current and future materials technology. This journal seeks to publish the results of forefront research efforts with a molecular-level perspective at the interface of chemistry, chemical engineering and materials science. Preliminary communications and full papers, in addition to selected short reviews highlighting particular topics in materials chemistry, will be featured in its bimonthly issues.

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[1] As evidence of this increasing interest in establishing better connections between chemistry, chemical engineering and materials science in the USA, several granting agencies have recently established special initiatives such as the National Science Foundation's "Materials Chemistry" initiative which are specifically directed at encouraging research at the interface between these disciplines.

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Microgels—Polymers with a Special Molecular Architecture

Polymer Networks
Cross-linking
High-impact Polymers

By Markus Antonietti*

1. Introduction

The development of new polymeric systems and the improvement of their physical properties for technological applications can be brought about by two main directions of research. On the one hand, polymer properties can be adjusted by developing new monomer units: the resulting changes in local molecular properties such as rotation barriers, polarity or anisotropy are reflected in bulk polymer properties such as stiffness or flexibility, solubility, or properties associated with crystallinity. However, for obvious reasons, the scope for inventing useful "new" monomers is limited. Consequently this strategy increasingly leads to "low quantity" polymers with very special properties.

On the other hand, the properties of polymeric materials are also determined by the geometrical parameters of their macromolecules. For instance, short and long chain linear polymers have completely different properties; branched and cross-linked systems again show different behavior. Here the microscopic topology of the polymer chains and the resulting geometrical interactions, such as entanglements or even knots, are reflected in the product properties. An understanding of the relationships between these microscopic parameters and macroscopic properties helps to improve existing materials by controlling the topological structure without necessarily changing the chemical composition of the macromolecular system. These types of approaches have just started to yield quantitative relationships in polymer science. Thus, the possibilities for obtaining "new" materials (or better still, old materials with new properties) are most promising. Often small changes in reaction conditions result in different topologies and create or improve the desired property.

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This article is concerned with the second approach to improving the properties of polymeric materials; a group of polymers with a very special topology will be discussed: synthetic microgels ("μ-gels") or μ-networks. We will also focus on some of their unconventional properties and potential applications. Defining the term "μ-gel" is not a straightforward matter. It can be illustrated by means of Figure 1.

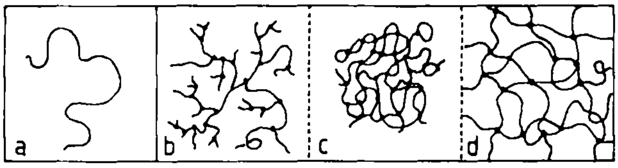

Fig. 1. Sketch showing polymer systems with different topologies: a) linear and b) branched macromolecules, c) μ-gel and d) macroscopic network.

Most commercial polymers, such as polystyrene, polyethylene or polycarbonate, have linear or slightly branched chains. Highly branched structures appear more often in the field of biopolymers, e.g. amylopectins. Networks are the oldest known "synthetic" materials: we are familiar with the properties of vulcanized "natural" rubber in daily life. μ-Gels represent structures that are intermediate between branched and macroscopically cross-linked systems. Their overall dimensions are still comparable with those of high molecular weight linear polymers. However, the internal structure of μ-gels resembles a typical network. Of course, the transition to the neighboring structures is continuous, and the definition is to some extent arbitrary. In the field of synthetic materials, μ-networks have not been extensively studied, but they are well known in biochemistry: most enzymes are linear chains cross-linked to each other by S_2 bridges or by secondary valences. Here again, special properties result from a combination of a particular geometrical arrangement with chemical functionality.

μ-Gels interestingly combine characteristics of both: being molecular structures they dissolve (networks only swell) but their conformation is nearly fixed. They can be processed like linear polymers but the final product still shows characteristic network behavior. Their solubility allows one to use the classical methods of polymer analysis in solution, enabling typical network characteristics to be identified. Therefore the objectives in studying μ-networks are twofold. First, one can study networks by modeling them with μ-gels, taking advantage of the convenience of solution characterization to examine network properties. Second, one hopes to develop a completely new group of materials with special properties. Both aspects will be illustrated in the following sections.

2. Synthesis of μ-Networks

Compared to the natural synthesis of enzymes, the possibilities available to a polymer chemist are limited. Only two routes to μ-networks are known:

1) Type A μ-gels: The addition of cross-linking agents to polymers or of multifunctional monomers to a polymerizing system usually leads to networks. According to the Ziegler dilution law, diluting the systems increases the probability of intramolecular cross-linking. This can be forced up to a threshold where no more macroscopic gelation occurs and only μ-gels are formed.[1-3]

This transition has the character of a phase transition where the critical concentration c_{crit} is given by the Flory argument:[4] internal cyclization reduces the average number of bonds to other chains below the critical value of two. Slightly below the critical concentration, structures with molecular masses $> 10^8$ g mol^{-1} are easily obtained.[1] At concentrations low compared to c_{crit} the μ-gels become smaller, until at very low concentrations only the elementary structures[3] or the "self cross-linked" molecule are formed[2,5] (molecular mass does not change upon cross-linking).

2) Type B μ-gels: μ-Gels are also obtained when the cross-linking reaction is carried out in a restricted volume, for instance in the small micelles of an emulsion,[6] or in μ-emulsion polymerization[7] of lipophilic monomers in water. Although such reaction conditions would result in macroscopic networks, the absolute molecular mass of the μ-networks is determined by the maximum micelle size, which can easily be controlled to be between 10 nm and 500 nm. This corresponds to molecular masses between 10^6 and 10^{11} g mol^{-1}.

3. Static and Dynamic Properties of μ-Gels

Type A and B μ-gels exhibit completely different properties. Cross-linking in dilution produces a lot of small loops, and, under suitable experimental conditions, a controllable proportion of dangling ends.[1,3] At the critical concentration of cross-links, type A μ-networks show an internal structure which is "self-similar". Geometrically this can be described as a "fractal", a geometrical body with a broken dimensionality. It has been proved by small angle neutron scattering measurements that this theoretical treatment fits the experimental data; a spatial dimension of $d_f = 2.5$ in the unperturbed state is obtained.[3] One can visualize a structure where the local fine structure repeats itself on a larger linear scale within the μ-network. Because type A μ-gels are still embedded in the "usual" three-dimensional space, they have a rather dense center and open up continuously towards the outer regions.

In contrast μ-networks of type B exhibit an internal structure comparable to that of macroscopic networks, except that close to the surface of the particles a higher concentration of loops is formed to ensure the molecular character. The characterization of these particles with static and dynamic light scattering reveals that the μ-gels in solution behave like nearly homogeneous swollen spheres, if the amount of cross-linking is moderate or high.[7] Where the amount of cross-linking is small, a transition to branched structures is observed, as mentioned above.[8] For these reasons, µ-networks of type B can be used to model the behavior of macroscopic networks. Possible perturbations due to surface contributions can be estimated by changing the absolute size of the µ-networks and thus the surface to volume ratio.

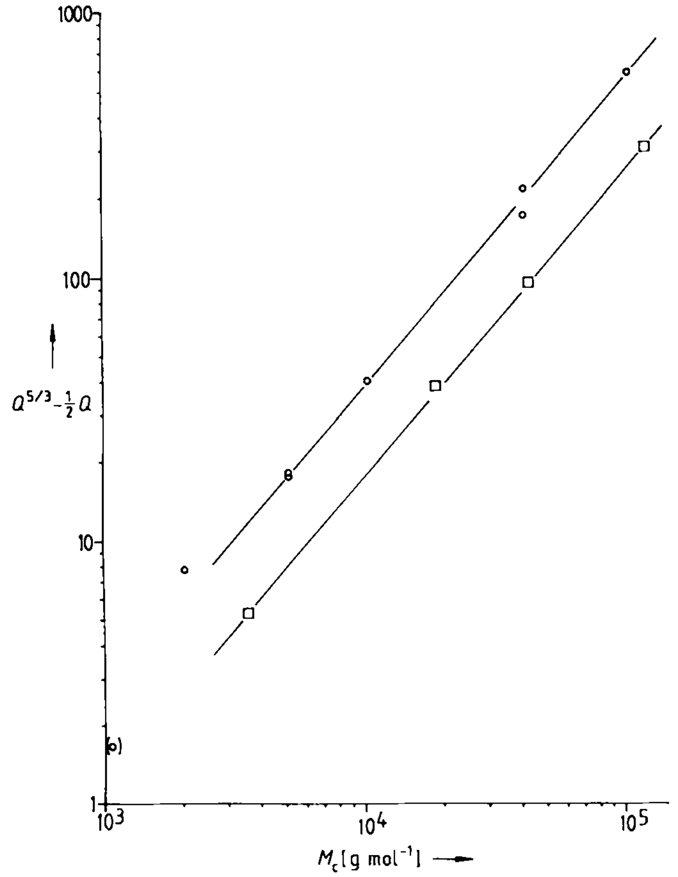

Fig. 2. Flory plot of the swelling ratio Q as a function of the chain length between two cross-links M_c; circles: styrene/*m*-diisopropenylbenzene µ-gels in toluene [7]; squares: styrene/divinylbenzene µ-gels in DMF [6].

The study of networks by substituting experiments on µ-gels is illustrated by the determination of the swelling ratio Q. Here, simple viscosity measurements replace the ambiguous swelling measurements on networks. The intrinsic viscosity $[\eta]$, a typical solution property of polymers, measures the relative increase of the viscosity of a solution per gram added polymer extrapolated to infinitesimally small polymer concentrations. According to *Einstein*, for spherical particles $[\eta]$ yields directly the average density of the swollen polymer within the sphere.[9] Since the degree of swelling of a network depends on the number of cross-links, *Flory* has derived an exact relationship between these two properties using the equations of entropy elasticity.[4] Figure 2 shows data obtained for two different network systems consisting of µ-gels.

The straight lines indicate the theoretical behavior of macroscopic networks for two different types of solvents. These measurements clearly show that type B µ-networks model the situation for all cross-linked systems. Measurements of the swelling ratio as a function of the density of cross-links, determined by intrinsic viscosity measurements, were also performed for the smallest possible µ-gels, the self-cross-linked molecules.[2] Although the treatment of the data is more complicated, the results are qualitatively in good agreement.

The situation in the case of type A µ-gels is more complicated: due to their fractal structure the swelling ratio depends only slightly on the density of cross-links, but is a function of the absolute molecular mass.[3] Although the fractal nature of type A µ-gels is more a matter for academic discussion, there are interesting implications for "real" systems. From these studies it seems likely that one can deduce certain topological knotting rules, which will lead to the understanding of internal cyclization, a typical network defect. Moreover, µ-gels offer a new way of easily determining the topological structures that result from different polymerization techniques, with regard to the degree of internal cyclization.

For characterizing the dynamic behavior of µ-gels, dynamic mechanical experiments provide the most detailed information. Here, information about both the internal, intramolecular modes of mobility and the dynamic quantities relating to the complete molecule can be obtained. In dynamic shear experiments the real and complex parts of the elastic constants (G' and G'') of the polymer are measured as a function of shear stress and frequency ω. G' describes the energy which is stored during the deformation (comparable to a spring constant) whereas G'' accounts for the viscous contribution and the energy which has been lost. From these two quantities, the complex viscosity η^* which describes the flow resistance at a certain frequency can be easily calculated.

Since we observe the response of small chain segments at high frequencies and of larger structures on a longer time scale, the data can also be interpreted as a measure of the molecular visco-elasticity as a function of a correlation

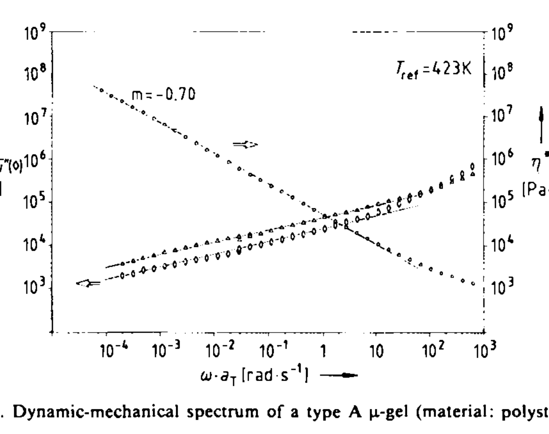

Fig. 3. Dynamic-mechanical spectrum of a type A µ-gel (material: polystyrene).

length. This length is of the same order as typical molecular substructures. For these reasons, the dynamic responses of different parts of the same polymer molecule become separated in the frequency domain.

Figure 3 shows the dynamic mechanical spectrum of a "fractal" type A μ-gel above the glass transition at a reference temperature of 150°C. In this double logarithmic plot, the elasticity varies over three orders of magnitude, while the frequency covers six decades. The resulting plots are strictly linear, with a spring constant which depends on the time scale of the mechanical perturbation.[10] Independently of frequency, a certain amount of energy is always lost (G' parallels G'').

The opposite is observed for type B μ-networks, as seen in Figure 4. Here, G' is nearly independent of frequency, as theoretically expected for an ideal macroscopic network. This is due to the fact that in the ideal case the cross-link density is uniform throughout. The plateau value in this specific sample exceeds that of linear polystyrene by a factor of two, and the mechanical loss at low frequencies is extraordinarily low for polymers. Here 98% of the stored energy can be recovered.[11]

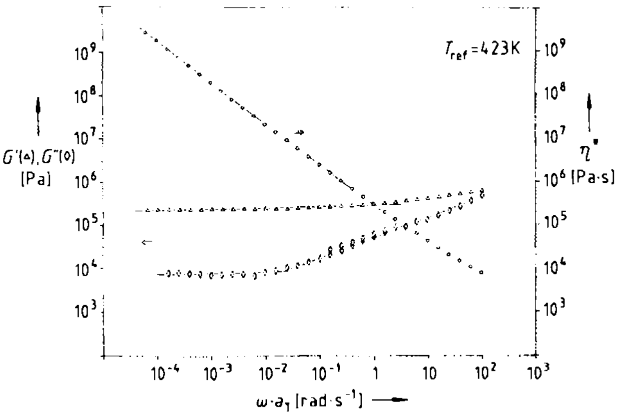

Fig. 4. Dynamic-mechanical spectrum of a type B μ-gel (material: polystyrene).

A potential application for these systems is their use as fillers for optically transparent "high impact" polymers. Here, μ-gels embedded in a matrix of linear polymer chains stabilize the whole structure by distributing the mechanical tension. Similar structuring techniques are already known, although the chemical pathway to them does not involve μ-gels.

In addition to that, one can construct composites consisting of two topologies of the same polymer. This represents a simple method of improving already existing products. Comparing Figures 3 and 4 one clearly recognizes the importance of topology in determining polymer properties: although both systems consists of the same chemical components (even molecular mass and chemical cross-linking density could be the same), a completely different macroscopic behavior can result for different topologies. Therefore, topologically structured μ-gels and networks will play a role of increasing importance since in that way the properties of any polymeric material can be varied over a wide range to fulfil the technological demands for special applications.

4. Complex Structured μ-Gels

Up to this point we have dealt with homogeneous μ-networks made of one kind of monomer and cross-linking agent. More complex molecules with μ-gel structure can easily be synthesized, and these cover a much wider range of properties and applications.

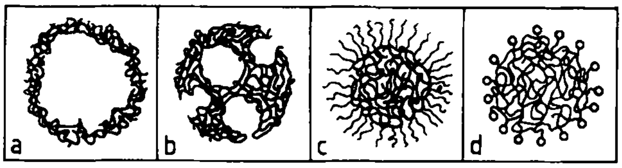

Fig. 5. Sketch showing various more complex μ-networks: a) hollow sphere μ-gel, b) macroporous μ-network, c) core-shell μ-gel, d) functionalized μ-gel where the circles indicate the centers of functionality.

Varying only structural parameters but preserving the molecular chemistry, it is possible to construct special porosities within the μ-networks (Fig. 5). The simplest case is given by the geometry of a hollow sphere, where the surface consists of cross-linked material of a controllable thickness (see Fig. 5a). Although this structure is reminiscent of vesicles prepared from special amphiphilic monomers,[13] fundamental differences exist. The hollow sphere μ-gels can be synthesized from most monomers on a larger scale, but the surface structure and the porosity are certainly far less defined. However, from a technical point of view, hollow sphere μ-gels can be used for some chemical applications which have been extensively discussed in the case of synthetic vesicles.

The second type to be discussed are macroreticular μ-networks. In simple terms, these are μ-gels with pores of different sizes. The polymerization of type B μ-gels in the presence of an ambident non-solvent leads directly to porous structures,[7] in analogy to the already known case of macroreticular networks.[14] The distinctive geometry, which is stabilized by the cross-links, results from the spinodal decomposition of the polymer and the non-solvent during the polymerization process. Materials with a continuum of pore sizes and macroscopic stability are the basis of all size exclusion chromatography techniques.[14] A study of these μ-gels by the techniques developed for simpler systems could help to provide a relationship between reaction conditions during network synthesis and the chromatographic separation properties. Such a relationship would help in designing column packings, which have hitherto been chosen more or less empirically. In this case, the step from research to a final product is small: by increasing the size of the network particles from the nm-region to approximatey 10 μm, they can immediately be used as column packings.

In addition to these two geometrical strategies for the construction of complex μ-networks, many other possibilities exist based on varying the chemical composition of μ-gels. Just two of the most important should be mentioned. *Burchard* et al. have examined μ-gels made of two incompatible polymers, where a cross-linked core of one polymer is surrounded by a shell of grafted linear chains of the other type.[15] Light scattering techniques can be used to determine the structures of these systems, which model inner surfaces in polymer blends. Another course is being followed by *Obrecht, Seitz* and *Funke*, who have examined[15] different possibilities for synthesizing "reactive" or functionalized μ-gels. For instance, some properties of μ-networks containing vinyl, sulfate or hydroxy groups have been described.

Although the strategies applied for μ-network synthesis are still relatively crude (compared to nature), some possible goals of all these efforts are worth mentioning. The combination of a fixed, soluble structure of nanometer dimensions with a specific functionality is one possible starting point for the construction of tailor-made polymeric catalysts, mediators or phase transfer reagents. The term "artificial enzyme" in the context of this kind of research is certainly presumptuous, but functionalized μ-gels are already used as catalysts in non-aqueous media and as stabilizers in complex coatings, and that is just the beginning. Nature's concepts will increasingly be applied to synthetic materials. The development and examination of structured polymers is just one field where the patterns of nature are imitated; μ-gels are one component within this strategy.

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New Organic Superconductors

BEDT-TTF Salts
2D (Super)Conductors
Charge-Transfer Complexes

By Hiroo Inokuchi*

1. Introduction

The first report of the discovery of an organic superconductor, $(TMTSF)_2PF_6$, a tetramethyltetraselenafulvalenium cation radical salt, appeared in 1980.[1] Since then, thirty different types of charge transfer complexes have been reported as organic superconductors, as summarized in Table I.

Of the seven kinds of $(TMTSF)_2X$ superconductors, the so called Bechgaard salts, only the $ClO_4^\ominus$ salt becomes superconducting at ambient pressure. Though TMTSF contains selenium atoms, after the discovery of superconductivity in $(BEDT\text{-}TTF)_2ReO_4$, the first sulfur-based organic superconductor, a large part of the research into organic superconductors was devoted to the BEDT-TTF salts. The most important BEDT-TTF superconductor was β-$(BEDT\text{-}TTF)_2I_3$.[23] It was the first ambient-pressure BEDT-TTF superconductor, in addition its T_c could be increased greatly to 8 K by the application of moderate pressure; this value was the highest T_c of organic superconductors before the discovery of $(BEDT\text{-}TTF)_2Cu(NCS)_2$. Following β-$(BEDT\text{-}TTF)_2I_3$, several other BEDT-TTF iodine salts with different crystal structures, designated by the Greek letters β, γ, θ, and κ, were found to be ambient-pressure superconductors. The β-$(BEDT\text{-}TTF)_2I_3$ salt also stimulated research into salts with other linear anions, from which it has been found that $IBr_2^\ominus$ and $AuI_2^\ominus$ salts[26,27] can become superconducting.

One should also mention the unique $[M(dmit)_2]$ series; these salts are the only acceptor-based organic supercon-

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