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ORIGINAL CONTRIBUTION

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Structure of W/O-microemulsion templated polymer networks

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Abstract The droplet phase of a water-in-oil microemulsion is used as a matrix to create amphiphilic polymer network structures from a poly(oxyethylene)-poly(isoprene)-poly(oxyethylene) triblock copolymer bearing polymerizable methacrylate end groups. Conductivity measurements and freeze fracture electron microscopy are used to obtain information about the structure of these gels. The droplet structure of the underlying microemulsion is only preserved for low droplet and polymer concentration. For higher concentrations the crosslinking reaction can induce the formation of a bicontinuous structure.

Key words Microemulsion – block copolymer – polymer network – bicontinuous structure

Introduction

Microemulsions are thermodynamically stable mixtures of oil, water and surfactant. They exhibit a well-defined structure which is characterized by typical correlation lengths in the nanometer scale. Their underlying compartmentalized structure of individual hydrophobic and hydrophilic domains finds increasing interest as a medium for polymerizations [1]. One chief goal in this area is to imprint the characteristic structural features of the microemulsion on the resulting polymer. This may lead to ultrafine lattices (mimicking the droplet phase of the microemulsion) [2], mesoporous solids (mimicking a bicontinuous microemulsion) [3] or, as recently shown, to structured amphiphilic elastomers (mimicking the complete three-dimensional structure of the colloidal matrix) [4].

Amphiphilic elastomers can be prepared, for example, by crosslinking end-group functionalized triblock copolymers in the respective phase structure of the underlying complex solvent [4]. The individual parts of polymers consisting of water- and oil-soluble segments can be selectively dissolved in the corresponding domains of, for example, a microemulsion or lyotropic liquid crystalline phase [4b, 5]. It is well-known that these polymers are able to bridge different domains of the same type thus leading to a three-dimensional polymer network structure [6]. The formation of chemical bonds between reactive chain ends of different triblock copolymers can be achieved in the interior of the domains without changing the structural parameters (e.g. droplet radii) of the system [4].

The resulting covalently crosslinked polymer gels ("microemulsion elastomers") combine solid-state properties like elasticity or stability of shape with the structure and the phase behavior of the underlying microemulsions (for a sketch see Fig. 1). The polymer network and the phase structure of the system, however, mutually influence each other. While, for example, the average droplet–droplet distance in the microemulsion determines the efficiency of the crosslinking reaction [4b], the formation of a three-dimensional polymer network leads to a considerable extension of the one-phase domain of the underlying microemulsion due to an elastic stabilization [4].

Beyond this, in microemulsion elastomers the nanodroplets serve as crosslinks and should therefore no longer be able to perform translational motions.

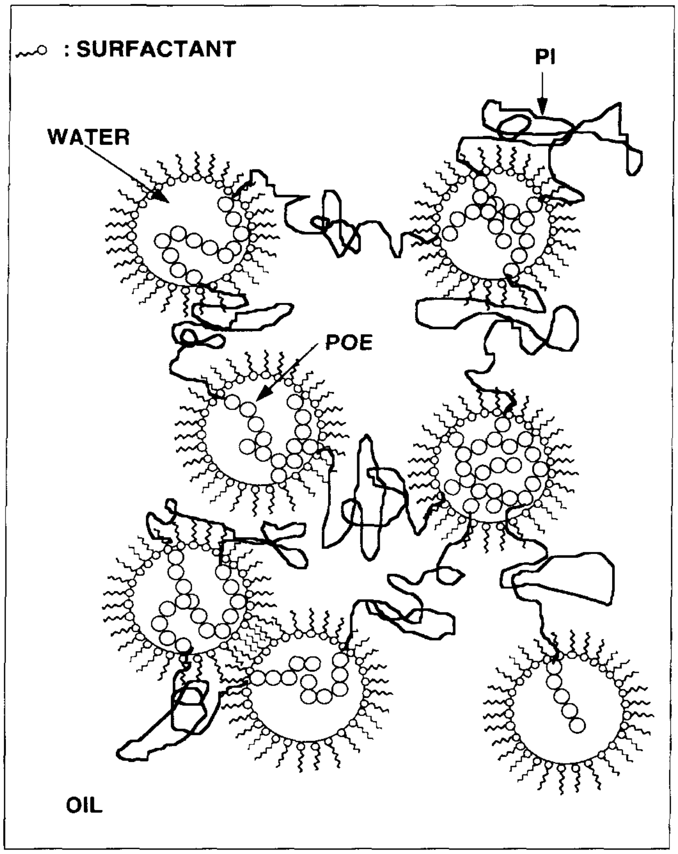


Fig. 1 Schematic representation of a microemulsion-templated amphiphilic polymer network

Such migration of charged droplets in the electric field, however, is the main conductivity mechanism in dilute w/o-microemulsions according to the charge fluctuation theory [7, 8]. The excess charges of the droplets arise from spontaneous thermal composition fluctuations of the water droplets. Consequently, the formation of a covalent, three-dimensional polymer network structure in a w/o-microemulsion must be expected to be of significant influence on the conductivity behavior of the whole system.

Therefore, temperature- and composition-dependent conductivity measurements are performed on a series of microemulsion elastomers. To interpret the results, structural changes in the system are proposed, which are supported by cryo-electron microscopic investigations.

Experimental

Materials

Microemulsions were prepared by mixing weighed amounts of the individual components. Mass fractions of the droplets are given by $c_w = (m_w + m_s)/(m_w + m_s + m_o)$ with m_i the mass fraction of water (i = w), surfactant (i = s) and oil (i = o). The droplet size is determined by $r_w = m_w/m_s$ with $r_w = 2.5$ = const. for the whole series of samples. This corresponds to a 20 nm diameter of the water core of the droplets. The anionic surfactant sodium bis (2-ethylhexyl)sulfosuccinate (AOT) and *i*-octane were obtained from Fluka in the highest grade available and used without further purification. Water was deionized with an Alpha-Q reagent grade system from Millipore.

The amount of the functionalized *triblock copolymer* in the microemulsions is given by the number ratio R = (triblock copolymer molecules/nanodroplet). The methacrylate end-groups bearing poly(oxyethylene)-b-poly(isoprene)-b-poly(oxyethylene) triblock copolymer (M-POE-PI-POE-M) was synthesized via anionic polymerization [4a]. The molecular weights of the individual blocks of the polymer were $M_w(\mathrm{PI}) = 50\,000\ \mathrm{g\,mol^{-1}}$, $M_w(\mathrm{POE}) = 5000\ \mathrm{g\,mol^{-1}}$ and $M_w/M_n = 1.02$ [4a]. The degree of conversion for the methacrylate end-groups was found to be larger than 95% by ^{1}H-NMR.

The *amphiphilic polymer networks* in the microemulsions were prepared using a light-induced free radical polymerization of the methacrylate groups in the interior of the water droplets. The detailed procedure is described in Ref. [4].

Measurements

Determination of the phase diagrams required thermostating of the samples in a water bath to within 0.02 K. Phase boundary temperatures were determined by visual inspection in transmitted light, in scattered light, and between crossed polarizers. The kinetics of phase separation and the reverse process, solubilization, was very slow (in the order of days) in the covalently crosslinked samples. The lower phase boundary for the microemulsion elastomers was always below 0 °C and the upper phase boundary >80 °C (for $R \geq 10$!) (see Ref. [4a]).

Conductivity measurements were carried out with a plate condenser type glass cell with two rectangular Pt electrodes of 5 × 10 mm and a gap of 2 mm. Conductance was determined by an autobalancing conductance bridge (Radiometer Copenhagen instrument type CDM 83) to be between 1.3 and 2×10^{-8} S (between 73 Hz and 50 kHz).

Freeze-fracture replication transmission electron microscopy was carried out following the procedure described previously [4b]. The sample was shadowed with W/Ta under an angle of 30° and the replica examined with a Hitachi H-8000 electron microscope operating at 100 kV.

Results and discussion

Electric conductivity is a structure-sensitive property and, therefore, can be used to get information about the structure and structural changes in colloidal systems. As already mentioned, in w/o-microemulsions consisting of nanometer-sized water droplets dispersed in a continuous-oil-phase charge transport occurs via migrating charged droplets. The electric conductivity is, therefore, usually low, in the order of 10^{-8}–10^{-6} $\mathrm{S\,m^{-1}}$ (for pure alkanes, however, 10^{-18}–10^{-14} $\mathrm{S\,m^{-1}}$! [9]).

By varying temperature or composition the formation of droplet clusters up to an infinite (system-spanning) droplet cluster or even bicontinuous structures can frequently be observed [10–12]. This transition is usually accompanied by an increase of the electric conductivity by several orders of magnitude due to a possible intra-cluster charge transport through a water-rich structure [10–12]. Cluster formation occurs in microemulsions derived from anionic surfactants (like e.g. AOT) with rising temperature and is, for example, monitored in Fig. 2: The electric conductivity σ is plotted as a function of temperature for several covalently crosslinked microemulsions. It is obvious that despite the three-dimensional polymer network structure the temperature-induced droplet cluster formation is possible. The transition is, however, considerably shifted towards higher temperature with increasing concentration R of the bridging polymer. This shift can be explained by steric constraints which are also responsible for the stabilization of the droplet phase, already mentioned above. The network chains inhibit singly dispersed nanodroplets approaching each other, and can, therefore, be regarded as a polymer spacer [13] acting against cluster formation or coalescence.

In the temperature region below this transition, where the system should mainly consist of isolated droplets another effect can be observed. The electric conductivity increases at constant temperature with increasing polymer content (see Fig. 3). This seems at a first sight to be rather surprising, since one intuitively would expect the mobility of the water droplets to be drastically reduced due to their incorporation into the polymer network structure and consequently σ should decrease as it can be, for example, observed for transient networks formed by solutions of unmodified triblock copolymers in w/o-microemulsions [14].

One possible explanation would be that during the crosslinking process the formation of droplet clusters or even open water channels coexisting with free droplets may be induced. As already mentioned the crosslinking occurs by a free radical polymerization and individual droplets may collide during the lifetime of the active center at the end of the growing polymer chain. Consequently, in the course of the polymerization the polymer chain should be able grow through more than one water droplet. This possibly leads to rod-like aggregates composed of long chains of interconnected poly(oxyethylene) blocks of the triblock copolymers surrounded by a water/surfactant shell, in equilibrium with singly dispersed (but also triblock copolymer containing) water droplets (for a sketch of the structure see Fig. 4). A similar structure has been proposed for the so-called gelatin-based organogels [15] where a three-dimensional gelatin network builds the backbone of open water channels.

Basically, such droplet coalescence is also believed to be the origin of particle growth in microemulsion

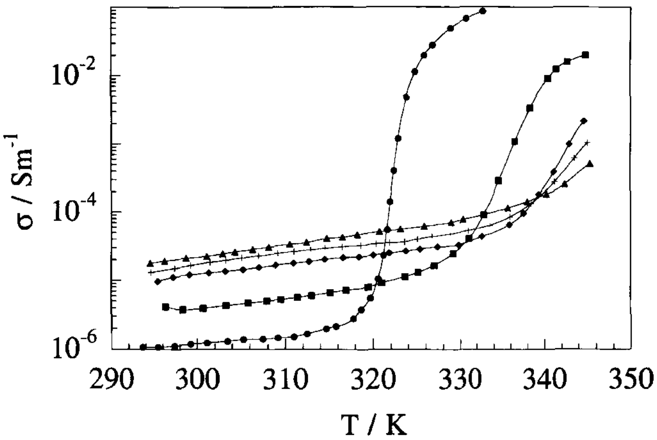


Fig. 2 Electric conductivity σ as a function of temperature for several concentrations R (= number of triblock copolymer molecules per water droplet) of the bridging triblock copolymer: ●: $R = 8$; ■: $R = 10$; ◆: $R = 14.5$; +: $R = 16.5$; ▲: $R = 19.5$

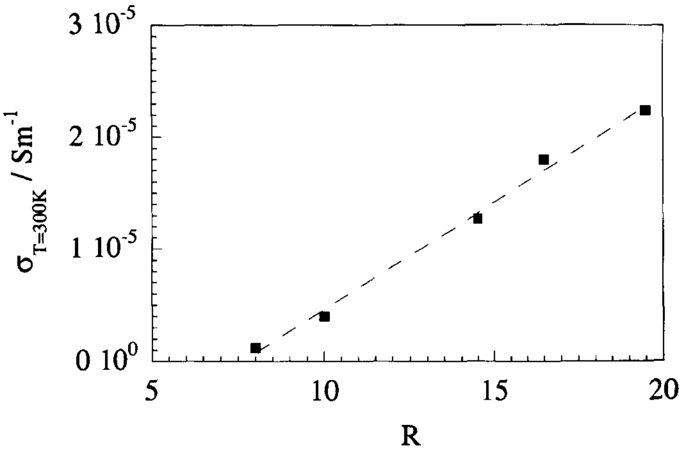


Fig. 3 Isothermal electric conductivity σ at $T = 300$ K as a function of triblock copolymer concentration R. Dotted line serves as a guide to the eyes

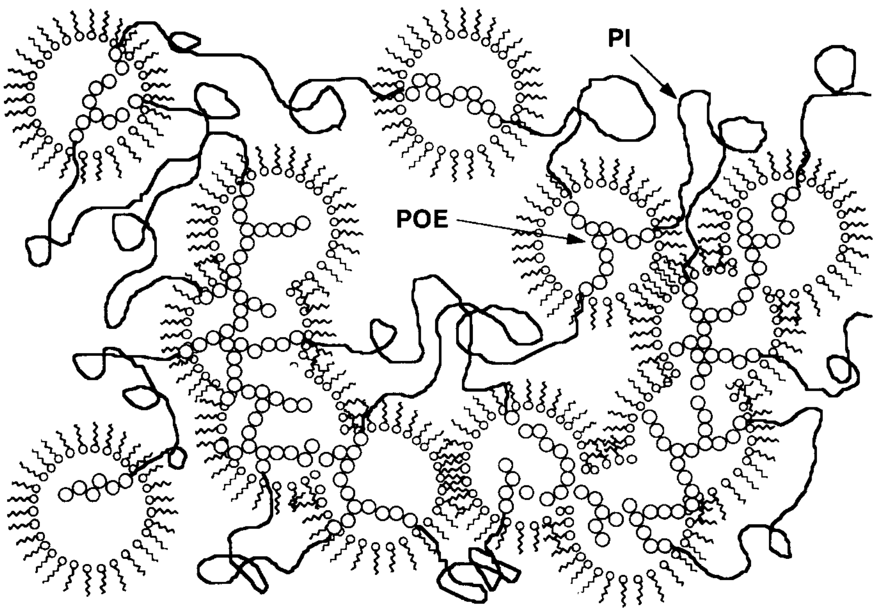


Fig. 4 Schematic representation of polymerization-induced droplet cluster formation in w/o-microemulsions

polymerization where generally polymer lattices larger than the original microemulsion droplets are obtained [1]. This would be plausible, especially in our case, where attractive interactions exist between the methacrylate-terminated poly(oxyethylene)-blocks of the triblock copolymer and the anionic surfactant AOT [16, 17]. The active end of the growing polymer chain is, therefore, expected to be located near the oil/water interface or can even be solubilized in the oil phase by the surfactant [16] so that chain growth through more than one droplet should be simplified. With increasing concentration of the triblock copolymer, i.e. polymerizable groups in the system, the probability increases for such droplet coalescence. Then, the fraction of polymerization-induced droplet clusters increases at the cost of singly dispersed droplets. An increasing number of water channels (with very low resistance compared to isolated droplets) are now available for charge transport and the electric conductivity increases (see Fig. 3), thus diminishing the difference in conductivity below and above the thermally induced infinite cluster formation (see Fig. 2). The observed shift of the temperature-induced cluster formation to higher temperature with increasing polymer concentration (Fig. 2) reflects the already above-mentioned steric stabilization of the fraction of free droplets [13], not belonging to the polymerization-induced cluster.

This concept of a polymerization-induced cluster formation is in good agreement with results of quasielastic light-scattering investigations on these microemulsion elastomers, which indicate the formation of large long-living droplets clusters with increasing polymer concentration [4a]. Another hint supporting our picture arises from the temperature dependence of the electric conductivity below the infinite cluster formation: σ increases monotonously with increasing temperature in contrast to the negative temperature coefficient of the conductivity in the underlying pure microemulsion or the non-crosslinked triblock copolymer solution [18, 19]. Here the decrease of σ reflects the hindered mobility of the charged droplets due to a gradual clustering.

Charge transport in the open water channels probably occurs via migrating Na^+ counterions of the anionic surfactant. The mobility of ions in the water channels is, however, only controlled by the viscosity of water. Ion migration in the clusters of a microemulsion can, therefore, be described as an activated process analogous to ionic conduction in bulk water. The activation energy E_a for charge transport can be derived from an Arrhenius plot of the electric conductivity σ (inset Fig. 5). Within experimental accuracy, E_a increases linearly with increasing triblock copolymer concentration (Fig. 5). This probably reflects the increasingly hindered ion migration caused by the rising POE-block concentration in the water. Extrapolation of the straight line to zero polymer concentration ($R = 0$) yields $E_a = 16\,\mathrm{kJ\,mol^{-1}}$ which is in reasonable agreement with the value for bulk water $E_a = 17.5\,\mathrm{kJ\,mol^{-1}}$ determined from the temperature dependent conductivity of a 1 M NaCl.

The probability that a polymer chain has the chance to grow through more than one water droplet should not only depend on the polymer concentration but also on the droplet concentration. Only for very low droplet concentrations the collision rate of the droplets should be lower than the lifetime of the active sites at the end of the

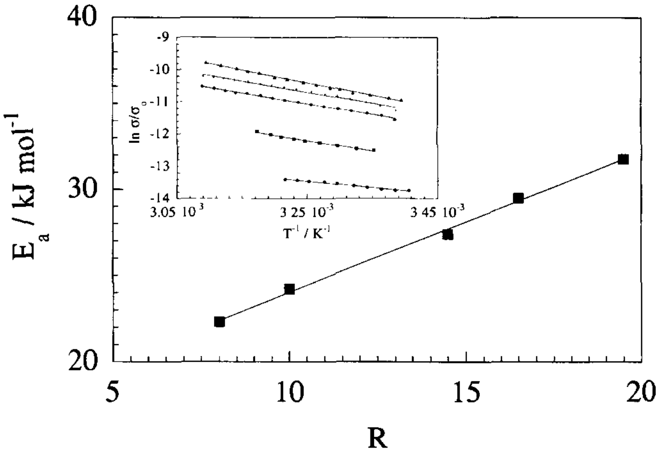


Fig. 5 Activation energy E_a for charge transport in microemulsion elastomers as a function of triblock copolymer concentration R. Inset shows plot of $\ln(\sigma/\sigma_0)$ (with $\sigma_0 = 1\ \mathrm{S\,m^{-1}}$) as a function of reciprocal temperature T^{-1}: ●: $R = 8$; ■: $R = 10$; ◆: $R = 14.5$; +: $R = 16.5$; ▲: $R = 19.5$

growing polymer chains, so that polymerization should be confined to one single droplet.

This is directly reflected in Fig. 6 where the electric conductivity behavior of microemulsion elastomers with different weight fractions of water droplets c_w is shown. Only for the two lowest droplet concentrations the conductivity corresponds to that of the singly dispersed droplets in the underlying pure microemulsion. Obviously, charge transport in the crosslinked system is possible to approximately the same extend as in the pure microemulsion despite the fact that now the droplets are part of the polymer network and therefore translational motions can be excluded. One possible mechanism able to explain this experimental fact would be a charge transport via harmonic network vibrations of the nanodroplets. In how far this picture holds will be subject of a forthcoming paper.

For higher droplet concentrations ($c_w \geq 0.2$) always the temperature-induced infinite cluster formation can be clearly identified although the crosslinking reaction freezes in an increasing fraction of a bicontinuous structure, thus assimilating the structure below and above the thermally induced cluster formation. The isothermal conductivity in the temperature region below the cluster formation increases sigmoidally with increasing weight fraction of droplets (see Fig. 7) reflecting the transition from a covalently crosslinked microemulsion network mainly consisting of singly dispersed droplets at small c_w to a form-stable gel with a bicontinuous structure at higher c_w.

This can be visualized, for example, by freeze fracture replication electron microscopy of such systems. Figure 8a shows a micrograph of a covalently crosslinked water-in-oil microemulsion system with a mass fraction of water droplets of $c_w = 0.1$. In agreement with previous observations on oil-in-water microemulsion networks [4b] the droplet structure of the microemulsion is preserved despite the crosslinking reaction. The average droplet diameter can be directly measured from the micrograph yielding 20 ± 4 nm in good agreement with the data for the underlying pure microemulsion [20]. The micrograph displays a slightly inhomogeneous distribution of the nanodroplets: Regions of closer packed "droplet-clusters" with an average (intra-cluster) center-to-center distance of the droplets of 39 ± 6 nm are separated by nearly droplet free oil islands. This is probably caused by the polymer network formation in the system. The poly(isoprene) middle block of the polymer is only able to bridge different water droplets without loss of entropy when the average

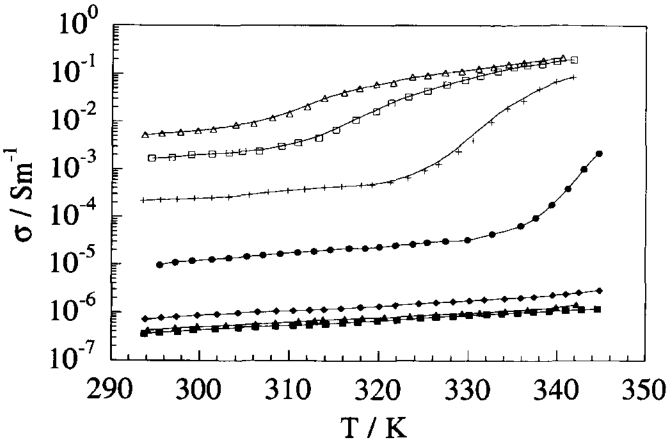


Fig. 6 Electric conductivity σ as a function of temperature for different weight fractions of water droplets c_w: ■: $c_w = 0.05$; ▲: $c_w = 0.1$; ◆: $c_w = 0.15$; ●: $c_w = 0.2$; +: $c_w = 0.25$; □: $c_w = 0.3$; △: $c_w = 0.35$

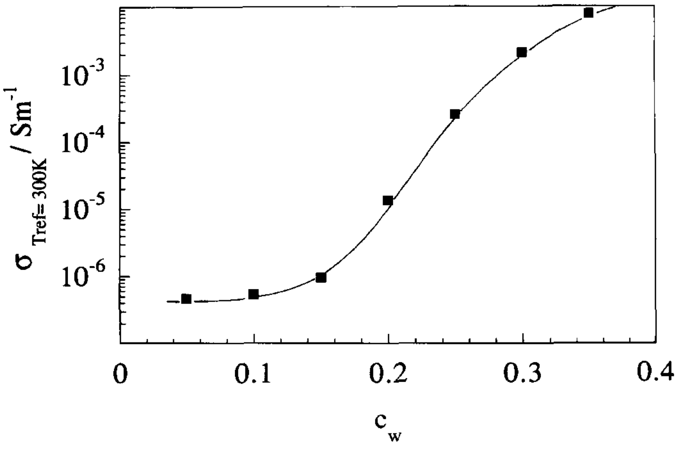
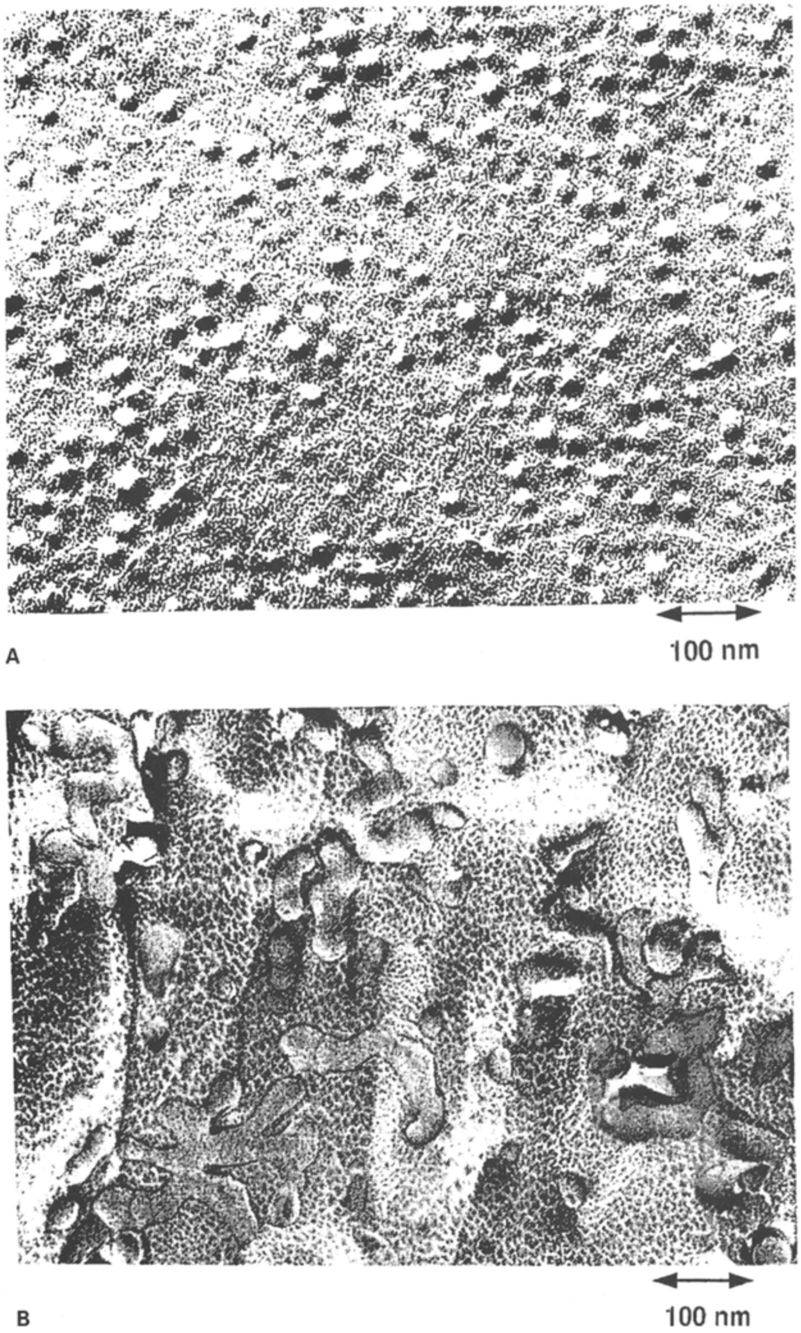


Fig. 7 Isothermal electric conductivity σ at $T = 300$ K as a function of the weight fraction of water droplets c_w. Dotted line serves as a guide to the eyes

Fig. 8A Micrograph of a microemulsion elastomer with a weight fraction of water droplets $c_w = 0.1$ (polymer concentration $R = 14.5$)
B Micrograph of a microemulsion elastomer with a weight fraction of water droplets $c_w = 0.3$ (polymer concentration $R = 14.5$)



droplet–droplet distance is compatible with the natural random coil conformation of the polymer chain. For deviations from this preferred distance the network chains in our covalently crosslinked system have to be deformed. This leads to an elastic force acting on the droplets which forces them to relax into a favored equilibrium distance. For low droplet concentrations, as in our example, where the average droplet shell-to-shell distance (= center-to-center distance-2(droplet radius), here ≈ 35 nm, assuming a homogeneous distribution of the droplets) can be calculated to be larger than the mean square end-to-end distance of the network chains, i.e. the poly(isoprene) middle block (27 nm, see Ref. [21]), this results in the observed inhomogeneous droplet distribution.

In contrast to that a sample with a higher droplet concentration ($c_w = 0.35$), as shown in Fig. 8b, displays a completely different appearance. Instead of individual spherical droplets now the sample mainly consists of elongated aggregates and/or water and oil domains which are mutually interwoven. This is typical for an at least partially bicontinuous structure [22] as already proposed above. The underlying pure microemulsion and even the not covalently crosslinked triblock copolymer solution of the corresponding composition, however, consist of individual nanodroplets [6d, 20, 23, 24]. Consequently, this structural transition observed in the covalently crosslinked sample must be the result of the crosslinking reaction. This agrees well with the conductivity measurements and strongly supports a polymerization induced formation of water channels in the hydrophobic matrix of these systems.

Conclusions

Poly(oxyethylene)-poly(isoprene)-poly(oxyethylene) triblock copolymers bearing additional reactive end-groups can be covalently crosslinked in w/o-microemulsions thus yielding form stable, transparent gels. Due to a possible material exchange and/or droplet coalescence during the crosslinking reaction the structure of individual water droplets dispersed in a hydrophobic matrix is only preserved for low droplet and/or polymer concentrations. With rising droplet and/or polymer concentration the crosslinking reaction obviously induces the formation of an increasingly bicontinuous structure, probably similar to that reported for gelatin based organogels.

Similar to the organogels these microemulsion networks are potentially useful as carrier materials to entrap and immobilize enzymes in the interior of the water domains or to prepare selective membranes for a variety of separation and purification processes. The structure of the resulting microemulsion elastomer can be controlled to a certain degree by the composition of the system. Nevertheless, the gels still possess a high "internal mobility" which enables them to undergo temperature or possibly also external field induced structural changes. In particular, this would allow the preparation of a switchable hydrophilic/hydrophobic membrane with a controlled permeability.

Although investigations on these new microemulsion based polymer networks are still in the very beginning it is obvious that these gels are an intriguing new material for which many applications can be foreseen in the near future.

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