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ORIGINAL CONTRIBUTION

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Microemulsion elastomers

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Dedicated to Prof. Dr. Hans-Friedrich Eicke on the occassion of his 65th birthday

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Abstract ABA-triblock copolymers bearing polymerizable methacrylate end-groups are covalently crosslinked in the droplet phase of W/O- and O/W-microemulsions. The resulting microemulsion elastomers combine the structure and the phase behavior of microemulsions with solid state properties such as elasticity or stability of shape. These new materials are characterized with the help of conductivity, dynamic-mechanical and dynamic light-scattering investigations. The influence of the chemical crosslinking process on the phase behavior and the dynamics of the underlying microemulsion is discussed.

Key words Microemulsion – ABA-triblock copolymer – polymer network – elastomer

Introduction

Thermodynamically stable microemulsions consist of individual water and oil domains. Due to this compartmental structure microemulsions have attracted increasing interest as model systems for the study of colloid–polymer interactions [1]. Especially polymerization in microemulsions has developed to a broad field due to the possibility of generating ultrafine latices [2] as well as nanoporous polymeric materials [3].

In a certain range of the phase diagram microemulsions are composed of nanometer-sized droplets of the minor phase which are stabilized by the surfactant and dispersed in the major phase. This structure makes them preeminently suitable as a solvent for block copolymers. Especially ABA-triblock copolymers with A blocks soluble in the minor phase and a B block soluble in the major phase can lead to interesting new materials: these polymers are able to bridge different domains of the same type [4]. Increasing concentration leads to the formation of a three dimensional network structure which has been shown to be a convenient route to modify the mechanical properties of microemulsions [5–7]. An essential feature of these materials is that the phase behavior of the underlying microemulsion and the network structure mutually influence each other in a unique way [6].

However, the network junctions of these microemulsion networks are always able to exchange network chains. As a consequence they have a finite lifetime and the resulting material can be described in the theoretical framework of transient networks [6]. In other words the resulting gel-like material is able to react elastically to dynamical stress but can flow on a long time scale. Nevertheless, for many applications, for example in the paint-industry or pharmaceutical technology this fluid character is not desired. To freeze in the underlying polymer exchange of the nanodroplets (here the crosslinks of the network structure) the ends of the triblock copolymer molecules have to be covalently linked within the droplets (see Fig. 1). Since rather high local concentration of chain ends in the droplets (about 0.05 to 0.1 molar) can be easily obtained, one would expect that reaction of the polymerizable end-groups can be achieved by common polymerization techniques.

In this paper we describe the synthesis and characterization of new elastomeric materials from microemulsions

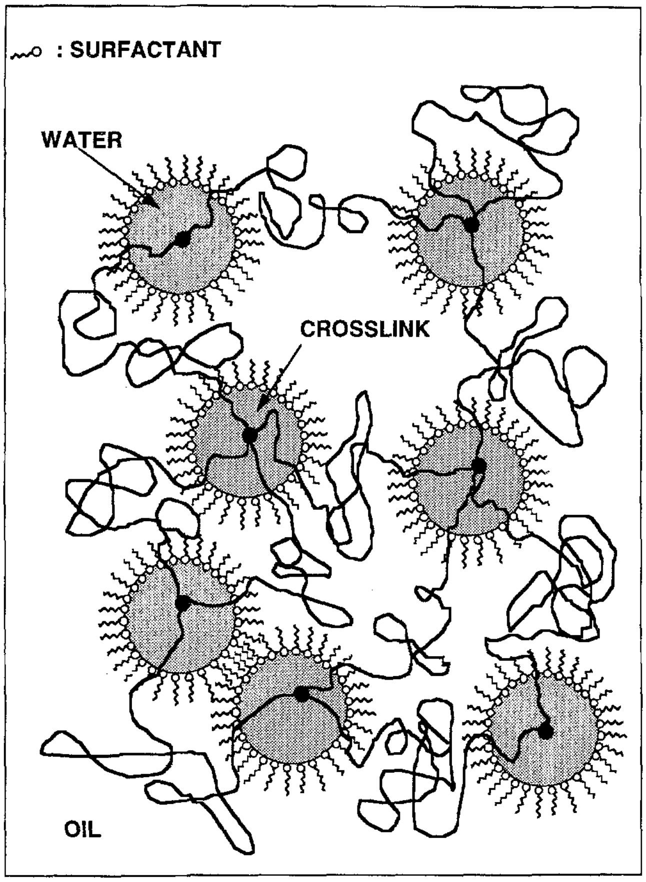


Fig. 1 Covalently crosslinked polymer network in a water-in-oil microemulsion

and end-group functionalized ABA – triblock copolymers by radical polymerization techniques. The resulting microemulsion elastomers are expected to combine in a unique manner typical elastomer properties such as stability of shape and rubber elasticity with the compartmental structure and the phase behavior of microemulsions.

Experimental Section

Materials

Scheme 1 shows the end-group functionalized triblock copolymers used. The syntheses are described in the following:

Polymer 1

Isoprene was purified by stirring with CaH_2 for 12 h, then distilled under *Ar* and stored at $-20\,°C$ prior to use. A last purification step, carried out immediately before the polymerization, used high vacuum techniques with phenylmagnesium chloride as a drying agent. The purified monomer was recondensed into an ampoule, which was then filled with a slight overpressure of dry *Ar*. Ethylene oxide was purified by the same procedure. The polymerization was carried out in a stirred glass reactor under *Ar* atmosphere. Tetrahydrofuran, used as solvent for the polymerization, was purified by refluxing and distilling over sodium benzophenone adduct. The polymerization of isoprene was initiated with potassium naphthalide at $-40\,°C$. After 3 h, a sample was removed from the reactor to characterize the polyisoprene middle block. Ethylene oxide was then added, resulting in a considerable increase in the viscosity of the solution. After 2 h, the temperature was gradually increased to 60 °C, and the ethylene oxide was left to polymerize overnight. The reaction was then terminated with an excess of methacryloyl chloride doubly distilled over CaH_2. The polymer was purified by repeated precipitation from methanol and finally dried under high vacuum for 3 days. The molecular weights of the individual blocks of the triblock copolymer were determined (light scattering and gel permeation chromatography) as $M_w(\mathrm{PI}) = 50\,000\ \mathrm{gmol}^{-1}$, $M_w(\mathrm{PEO}) = 5000\ \mathrm{gmol}^{-1}$ and $M_w/M_n = 1.02$. ^{1}H-NMR (Varian VXR-400MHz) confirmed the presence of the methacryloyl-end-groups (resonance at 5.6 and 6.1 ppm) with a conversion rate larger 90%. However, the small molecular weight of the polymerizable end-groups compared to the whole polymer molecule prevents the exact determination of the degree of conversion.

Polymer 2

12-Methacryloyl stearic acid

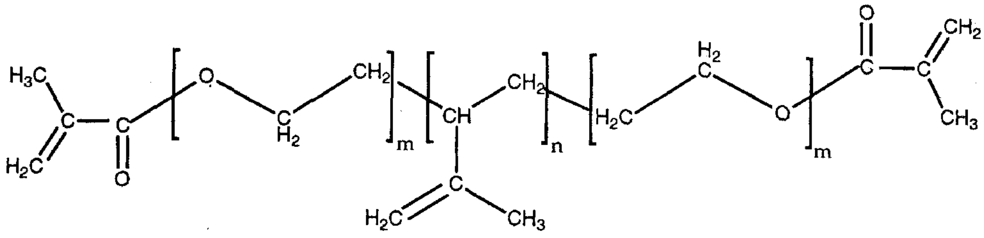
The methacrylic acid derivative of 12-hydroxy stearic acid was prepared by azeotropic esterification [8] using $CHCl_3$ as solvent. The crude product was purified by repeated recrystallisation from acetone. Yield: 51% ^{1}H-NMR: $\delta = 1.0$–$2.2(m, 36\ \mathrm{H})$, $5.0(m, 1\ \mathrm{H})$, $5.55(s, 1\ \mathrm{H})$, $6.05(s, 1\ \mathrm{H})$, $8.9(s, 1\ \mathrm{H})$

The product was heated for 2 h under reflux with 50 ml $SOCl_2$. Excess $SOCl_2$ was removed by distillation and the residue dried under oil vacuum. The resulting acid chloride was used without further purification.

Preparation of Polymer 2

20 g (0.57 mmol) anionically polymerized polyoxyethylene ($M_w = 35000\ \mathrm{gmol}^{-1}$; $M_w/M_n = 1.09$) bearing hydroxy

Scheme 1 Structure of the end-group functionalized ABA-triblock copolymers. For polymer 1: $n \approx 750$; $m \approx 110$; and for polymer 2: $p \approx 800$



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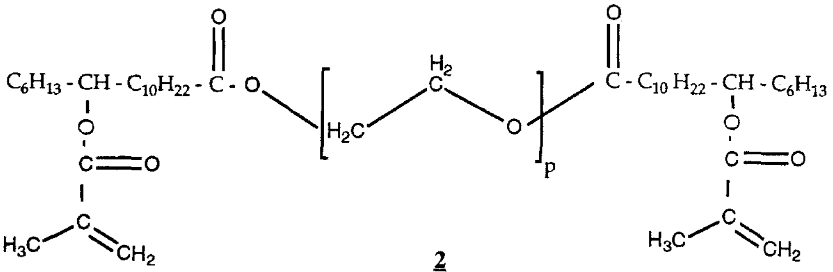


2

end groups was twice freeze dried from benzene to remove water traces. The polymer was dissolved in 75 ml CH_2Cl_2 freshly distilled over P_2O_5. Under an *Ar* atmosphere 3 ml of absolute pyridine and 3 g (7.8 mmol) of the acid chloride were added. After 3 h stirring at room temperature the reaction was complete. The resulting polymer was purified by repeated precipitation from diethyl ether and finally freeze dried from benzene (^{1}H-NMR indicated conversion of > 95% of the hydroxy end-groups of the polymer).

Microemulsions were prepared by mixing weighed amounts of the individual components. Mass fractions of the droplets are given by $c_w = (m_s + m_w)/(m_s + m_w + m_o)$ or $c_o = (m_s + m_o)/(m_s + m_o + m_w)$, respectively, with m_x the mass fraction of surfactant ($x = s$), water ($x = w$) and oil ($x = 0$). The droplet size is determined by $r_w = m_w/m_s$ or $r_o = m_o/m_s$. For the W/O-microemulsions $c_w = 0.2$ and $r_w = 2.5$ and for the O/W-microemulsion $c_o = 0.2$ and $r_o = 1$. The amount of polymer is given by the number ratio R = (triblock copolymer molecules/droplet). The number of the nanodroplets was calculated to be $n = 3 \times 10^{16}\,\mathrm{cm}^{-3}$ for the water-in-oil and $n = 6 \times 10^{17}\,\mathrm{cm}^{-3}$ for the oil-in-water microemulsions.

Determination of the phase diagrams required thermostating of the samples in a water bath to within 0.02 K.

Microemulsion Elastomers

Preparation of W/O-Systems

The end-group modified polymer 1 was dissolved in a mixture of *i*-octane, the surfactant and 20% of the total amount of water. After dissolution of the polymer, the rest of the water and the initiator (AIBN) were added and the reaction mixture was degassed. Polymerization to a three-dimensional polymer network could be achieved by 3 h irradiation with a 300 W mercury lamp at room temperature.

Preparation of the O/W-System

1.6 g of the end-group modified polymer 2 was dissolved in a mixture of 8 g water and 1 g $C_{12}E_5$. Afterwards 1 g decane and 3 mg initiator (AIBN) were added. Due to the high viscosity of these transient O/W-microemulsion networks only a polymer concentration of $R = 8$ was experimentally accessible (i.e., 16 polymerizable methacrylate groups per nanodroplet). To achieve covalent crosslinking of the polymer network additionally 18.7 mg cyclohexyl

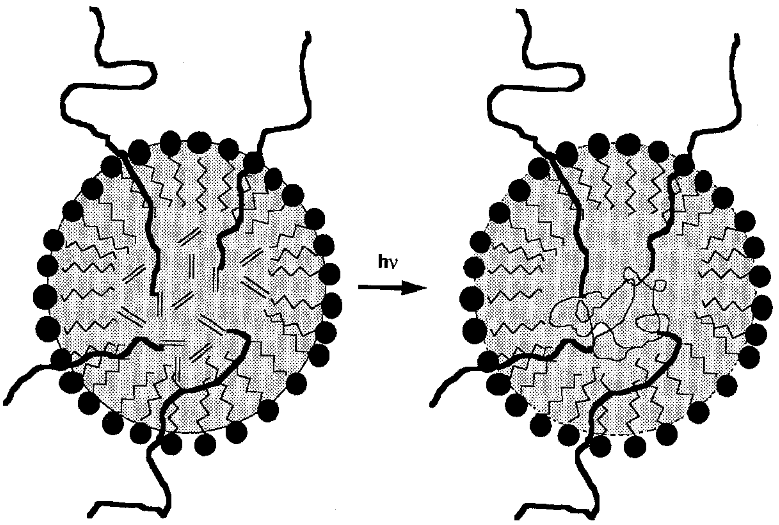


Fig. 2 Schematic representation of the crosslinking reaction in oil-in-water microemulsions in the presence of oil-soluble comonomers

Table 1 Sample characterization

Sample	R	$C_p/g\,l^{-1}$	Remarks
W/O-0	0	0	
W/O-8*	8	22.7	
W/O-8	8	22.7	
W/O-10	10	28.4	
W/O-14.5	14.5	41.2	
W/O-20*	20	55.4	
W/O-20	20	55.4	
O/W-0	0	0	1Φ: 23–31 °C
O/W-8*	8	77.0	1Φ: 16–31 °C
O/W-8	8	77.0	1Φ: 15–45 °C

* Polymer without polymerizable groups

methacrylate and 3.6 mg diisopropenyl benzene as comonomers had to be dissolved within the oil phase (see Fig. 2). The reaction mixture was degassed and polymerization to a three-dimensional network occurred as described above.

Comparable treatment of microemulsion networks (as well W/O as O/W-systems) containing triblock copolymers without polymerizable end-groups did not result in the formation of a covalently crosslinked polymer network structure. These samples were always able to flow.

The triblock copolymer concentration, expressed as the number ratio of copolymers per nanodroplet R, varied in the samples investigated between 0 and 20. The corresponding weight per volume concentrations are listed in Table 1.

Measurements

Mechanical properties of the microemulsion networks were studied by rheological measurements using a Carrimed CRSH 100 controlled stress rheometer combined with a laboratory made cone-cone geometry and a thermostatable cap. For details see refs. [5] and [6].

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

QELS: The dynamic light scattering was performed on a commercial goniometer (ALV-Langen) at scattering angles between 30° and 150° using a frequency doubled NdYAg-laser at 532 nm. An ALV-5000/E correlator was used to obtain the photon intensity autocorrelation function. The fluid samples were prepared for measurement by filtering with a Millipore filter (FGS, 0.2 μm) into 10 mm o.d. quartz cuvettes. The covalently crosslinked samples were measured directly in the reaction vessel. During measurement the samples were kept in a cylindrical vat under optical matching conditions and thermal stability was better than ± 0.02 K. Repetitive measurements at the same angle ensured reproducibility and a satisfactory signal-to-noise ratio. Data analysis was performed with the normalized intensity autocorrelation function using a non-linear regularization method performed by the ALV-800 Transputer.

Results and discussions

Using light-induced radical polymerization of the end-group functionalized triblock copolymers for the first time the formation of a covalently crosslinked polymer network structure within a microemulsion (a "microemulsion elastomer") could be achieved. In contrast to the transient networks formed by ABA-triblock copolymers in microemulsions, the resulting transparent gel-like material is no longer to flow (for polymer concentrations $R \geq 10$): irregularly formed samples retain their shape (over months) if they are kept in a closed vessel to prevent evaporation of the solvent.

The polymer concentration necessary for the formation of a system-spanning covalently crosslinked polymer network was found to be about $R \approx 10$ corresponding to a functionality of the crosslinks of about 20. Since gelation is expected to start for a functionality being slightly larger than 2 [9] this indicates a rather low efficiency of crosslinking (only about 10%). The triblock copolymers in this system predominantly form loops and dangling ends instead of bridging different droplets [see ref. 10]. According to ref. [11] the number of polymer molecules forming bridges between neighboring droplets can be roughly estimated to be $n = (2R)^{0.3}$, i.e. $20^{0.3}$ or $n \approx 2.5$ in rather good agreement with the expected value of 2. Samples with $R < 10$ were always able to flow, because only isolated covalently crosslinked network clusters are formed.

Due to the high viscosity, in case of O/W-microemulsion systems homogenous samples could be obtained only for $R \leq 8$. To enable the crosslinking reaction cyclohexyl-methacrylate and diisopropenyl benzene were used as comonomers within the oil droplets. As a result the crosslinks (here the oil droplets) of the system-spanning network are oil-swollen polymer networks themselves. Consequently, these systems might be described as "structured interpenetrating networks" for which interesting mechanical behavior can be expected.

Exposing samples containing non-functionalized triblock copolymers to the same polymerization conditions as the ones containing methacrylate end-groups (i.e. irradiation in the presence of initiator) does not lead to the formation of a covalently crosslinked network. These samples are always able to flow and the phase behavior is not affected. This confirms that the crosslinks of the microemulsion elastomers are indeed formed by the polymerized end-groups within the droplets (see Fig. 1) and no middle blocks of the triblock copolymers (polyisoprene for W/O- and polyoxyethylene for W/O-systems) are involved.

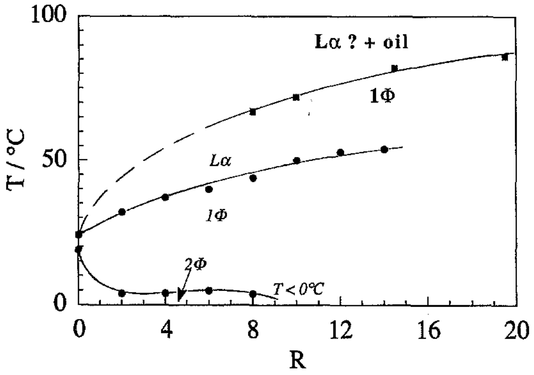


Fig. 3 Phase diagram of chemically (■) and physically (●) crosslinked W/O-microemulsions ($c_w = 0.2$; $r_w = 2.5$) as a function of polymer concentration R = number of copolymers / droplet

Phase Behavior: As was to be expected, crosslinking of the microemulsions affects considerably their phase behavior: a remarkable extension of the one phase domain is observed (Fig. 3; Table 1). As can be seen from Fig. 3 for the W/O-microemulsion networks (for O/W-systems see Table 1) for the transient ABA-triblock copolymer networks the same trend is observed [12]. However the overall effect is much smaller compared to the covalently crosslinked microemulsions. For the W/O-microemulsion elastomers the lower phase boundary was always below 0 °C. To assure that these crosslinked structures exhibit a thermodynamically stable one-phase domain the samples were heated above the upper phase boundary, where phase separation into a gel (*Lα*-phase ?) and an upper oil-phase occurred. The lower gel swelled upon subsequent equilibration at room temperature and the samples became homogenous within 3–5 days.

The observed extension of the one-phase domain of microemulsion elastomers is due to steric constraints. The network chains inhibit the nanodroplets approaching each other (acting as a polymer spacer) [13]. It is evident that fixing the network chains within the droplets by covalently crosslinking leads to a stronger coupling between polymer and droplet. Consequently, the one-phase domain for microemulsion elastomers is significantly more extended than for physically crosslinked transient triblock copolymer systems. This effect is, for example, also reflected in the temperature dependence of the electric conductivity of W/O-microemulsion systems. Due to weak interactions between the nanodroplets in W/O-microemulsions temperature variation may cause cluster formation up to an infinite system-spanning droplet cluster. The formation of the infinite droplet cluster is usually evidenced by an increase of electric conductivity by several orders of magnitude due to intra-cluster charge transport [14]. Figure 4 shows plots of the electric conductivity σ as

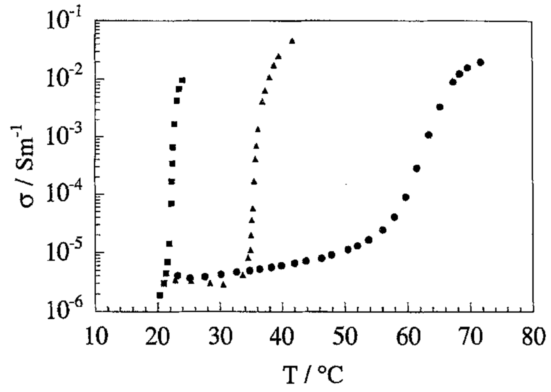


Fig. 4 Electric conductivity σ as a function of temperature. ■: pure microemulsion ($R = 0$); ▲: physically crosslinked microemulsion network ($R = 10$); ●: chemically crosslinked microemulsion network ($R = 10$)

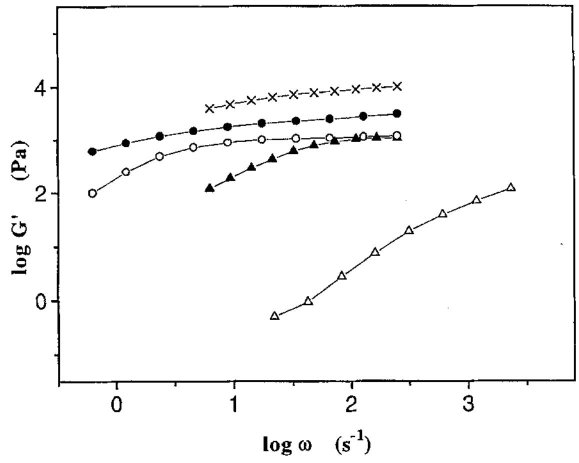


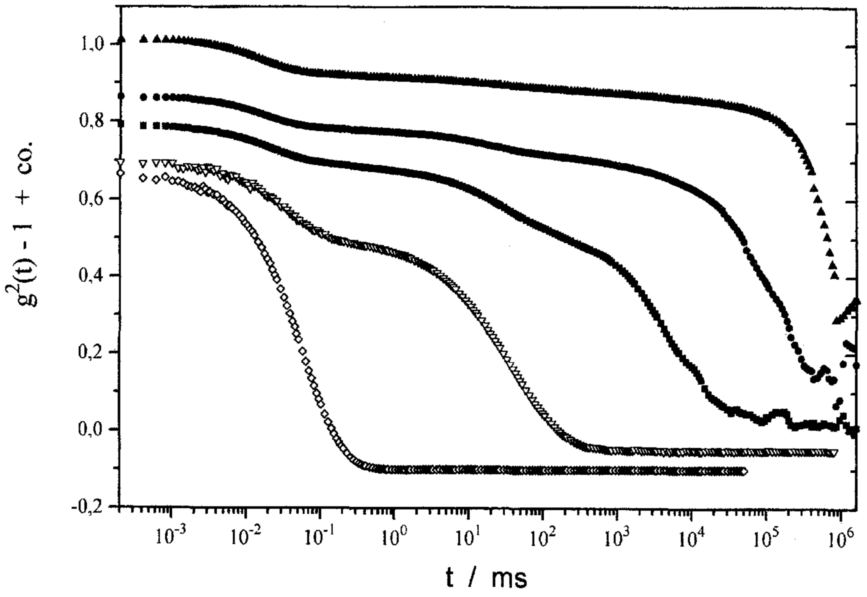
Fig. 5 Storage moduli G' as a function of frequency for several microemulsion networks ($T = 18\,°C$); physically crosslinked samples: △: W/O-8*; ○: W/O-20*; chemically crosslinked samples: ▲: W/O-8; ●: W/O-20; X: O/W-8; the isotherm of sample W/O-8* could be measured for technical reasons only at $T = 13\,°C$ (see ref. [6]). Applying the temperature-frequency superposition it was shifted to $T = 18\,°C$

a function of temperature for samples W/O-0 (pure microemulsion), W/O-8* (physically crosslinked) and W/O-8 (chemically crosslinked). The increasing steric constraint is directly reflected in the shift of the temperature T_c of infinite droplet cluster formation. Also in the temperature region below T_c a remarkable conductivity behavior of the microemulsion elastomer is observed. In this temperature region electric conductivity of pure W/O-microemulsions and physically crosslinked systems is determined by "Stokes transport" of charged nanodroplets [15]. Due to the increasing mass of the gradually growing droplet clusters, a negative temperature coefficient of the conductivity is usually observed [15, 16] (see also Fig. 4). In microemulsion elastomers a translational motion of the nanodroplets (which are simultaneously the crosslinks of the polymer network) over distances large compared to the interdroplet distance can be excluded. Therefore, a change in the charge transport mechanism has to be assumed. This is already reflected in the positive temperature coefficient of the conductivity in these systems. Here, the charge transport can probably be described in terms of harmonic network vibrations of the nanodroplets [17].

Mechanical Properties: The mechanical properties of the materials should be strongly influenced by covalently crosslinking the polymer network structure in the microemulsion. Therefore oscillatory shear measurements were performed on physically and chemically crosslinked microemulsion networks. The results are shown in Fig. 5, where typical plots of the isothermal ($T_{ref} = 18\,°C$) dynamic storage moduli $G'(\omega)$ are shown. In the following we will restrict ourselves only to a qualitative discussion of the high frequency relaxation process and its characteristic relaxation time (τ_{m1}) and the plateau modulus (G_{p1}). A detailed rheological study on the new microemulsion elastomers is in progress [18]. Comparing physically (e.g. samples W/O-8*, W/O-20*) with chemically (e.g. samples W/O-8, W/O-20) crosslinked samples, it is apparent that $G'(\omega)$ at fixed frequency increases considerably upon the crosslinking reaction (see Fig. 5). This is the result of converting crosslinks with a finite life-time (physically crosslinked) into permanent ones. As a consequence, for microemulsion elastomers with $R \geq 10$, where a system-spanning covalently crosslinked network structure exists, no high frequency relaxation process was observed (Fig. 5). Already for samples with $R \leq 10$ the formation of covalent crosslinks shifts the characteristic relaxation τ_{m1} to considerably larger times. Within the experimentally accessible frequency range, for samples with $R \geq 10$ (and also for the W/O-system) only a plateau in $G'(\omega)$, corresponding to the shear modulus of the sample, is found. The relative narrow frequency range had to be chosen because of the limited sample stability due to solvent evaporation in the rheometer (see also ref. [6]). Nevertheless, the results are consistent with the observation that samples with $R \geq 10$ do not flow any more under the influence of gravity, although the materials are highly swollen gels with a polymer content of about 5 wt%.

Dynamic Light Scattering: Quasielastic light scattering has been shown to be a powerful tool to monitor the dynamic changes in microemulsions upon addition of ABA-triblock copolymers forming physically crosslinked network structures [12]. In general for triblock copolymer microemulsion systems only light scattered from the nanodroplets is

Fig. 6 Intensity autocorrelation function obtained at 90° and 23 °C. ◇: pure microemulsion ($R = 0$); V: physically crosslinked reference sample ($R = 12$); ■: W/O-8; ●: W/O-14.5; ▲: W/O-20



observed due to their high molecular weight compared to that of the polymer. The measurements revealed that addition of triblock copolymers leads to a modification of the dynamics of the nanodroplets [12]. At low polymer concentration a slow diffusive process is found which was attributed to the polymer self-diffusion monitored by the nanodroplet motion. At higher concentrations additionally a third very slow process occurs which indicates the formation of large long living droplet cluster being probably a precursor of gelation. In microemulsion elastomers, additional effects on the dynamics of the nanodroplets are to be expected due to the covalent crosslinks within the droplets.

Figure 6 shows the intensity autocorrelation function for several covalently crosslinked microemulsion elastomers with different polymer concentrations R. The correlation curves were obtained at 90°. The scattering intensity averaged over a few milliseconds shows strong, very slow fluctuations of a factor of about 10 to 50. In contrast, in the physically crosslinked systems the fluctuations are much faster and about two orders of magnitude lower. This behavior is similar to non-ergodic systems [19]; in the systems under investigation it is the result of the very slow dynamics of the microemulsion elastomers. Consequently, the samples were measured 15 times over a period of 10000 s. The single runs were averaged using the non-ergodic normalization mode of the ALV-5000 software. Applying this procedure the averaged correlation curve reached the theoretically expected intercept for our optical setup to within ± 0.05.

Comparing the correlation functions of the chemically crosslinked samples with that obtained for a physical network (see Fig. 6), clearly two effects can be observed: i) a new correlation process appears as was to be expected from the behavior of the averaged intensity at very long times and ii) the intermediate process in the time range of a few milliseconds, which is also found in the physically crosslinked systems, vanishes with increasing polymer concentration. Instead, the correlation function shows a power-law behavior at long times which is typical for gelating systems [19]. The vanishing intermediate process indicates the freezing in of the PI-chain self-diffusion due to the covalent crosslinking. Therefore concentration fluctuation of the polymer chains and coupled concentration fluctuations of the nanodroplets cannot decay by self-diffusion. Nevertheless, despite the chemical crosslinks the nanodroplets preserve a local mobility because of the long flexible polymer spacers between the droplets. This leads to strong fluctuations in the averaged scattering intensity and a very slow decay of the correlation function. In Fig. 7 the initial decay rates obtained by the nonlinear regularisation method are plotted as a function of the square of the scattering vector. For all samples the observed process is diffusive within the accessible range of q-vectors, i.e. in a spatial range of 30 to 120 nm. The inset shows the ratio of the fast diffusion coefficient of the physically and chemically crosslinked systems to that of the pure microemulsion without polymer. For the chemically crosslinked microemulsion elastomers this ratio is larger by about a factor 2 compared to the physically crosslinked systems, indicating the significantly stronger repulsion between the droplets. This is the result of the polymer spacers acting like springs between the droplets: local motions may lead to a decreasing droplet-droplet distance and therefore

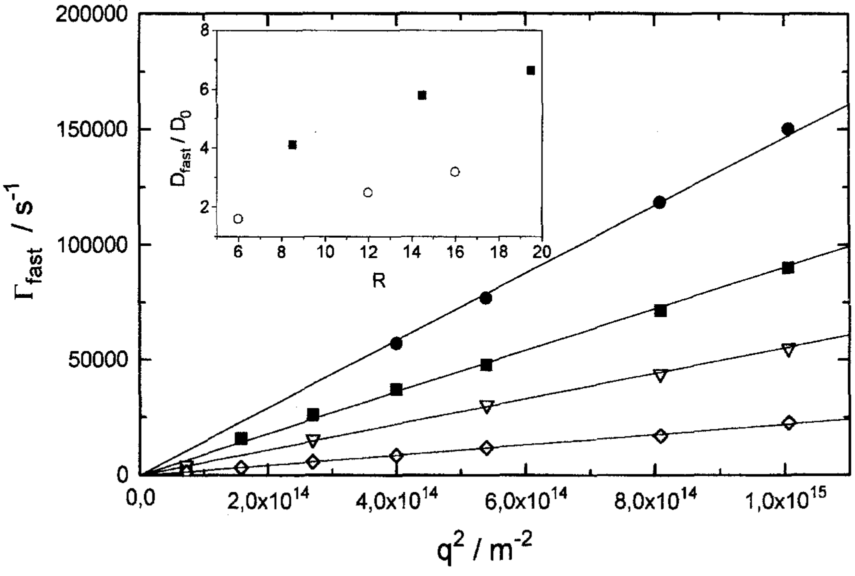


Fig. 7 Initial decay rate vs. q^2 obtained by a nonlinear regularisation method from the intensity autocorrelation function (◇: pure microemulsion; ▽: physically crosslinked reference sample (R = 12); ■: W/O-8; ▲: W/O-20). Inset shows the ratio of the fast diffusion coefficient of microemulsion networks to that of the pure microemulsion as a function of R; ●: physically crosslinked; ■: chemically crosslinked

a deviation of the network chains (i.e., the PI middle block) from their natural random coil conformation. Due to the covalent crosslinks within the droplet, the PI-chains cannot be exchanged from droplet to droplet to relax into their equilibrium end-to-end distance as it is possible in physically crosslinked systems. Hence the end-to-end distance of the PI-chains is decreased, leading to an entropic repulsive force between the droplets.

Conclusions

End-group functionalized ABA-triblock copolymers can be covalently crosslinked within the nanodroplets of microemulsions to a material exhibiting solid state properties as elasticity or stability of shape. For example, this allows for the first time the production of membranes with the compartmental structure of microemulsions. Nevertheless, the long flexible polymer spacers in these microemulsion elastomers still allow local motions of the nanodroplets. As a result the phase behavior of the underlying microemulsion is, at least qualitatively, preserved. For example temperature variations may cause droplet cluster formation up to an infinite nanodroplet cluster. This is analogous to the formation of water channels (in W/O-systems) through an otherwise hydrophobic material (or vice versa in case of O/W-systems) and allows for example the realization of a "switchable" hydrophilic-hydrophobic membrane, for which great potential for gas separation and probably also in desalination can be expected. Nevertheless, we are still in the state of a first description of these new complex materials and a multitude of further investigations is necessary for their complete characterization.

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