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ORIGINAL CONTRIBUTION

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Phase transitions and phase separations in aqueous polyether systems

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Abstract Detailed investigations on the structural and macroscopic properties of a hydrogel based on a polyether/water/LiCl system as a function of composition and temperature are reported. The investigations include the determination of the types of water by differential scanning calorimetry (DSC) measurements, the characterization of the polymorphism by microscopic observations in combination with DSC measurements as well as the determination of the optical and viscoelastic properties by spectroscopic and rheological measurements. The influence of the addition of salts on the water binding properties of the polyether are reported and the results are discussed on a molecular level. For the optical properties it was found that the transmission–temperature curves reflect the polymorphism of the samples. Two-phase regions at a phase transition or regions of coexisting phases (phase separation or mixing gaps) lead to the appearance of light scattering states, whereas homogeneous phase regions are highly transparent. The rheological measurements indicate the formation of hydrogels by cross-linking with LiCl, whereby in different phases the gelation occurs at different LiCl concentration ranges.

Key words Aqueous polymer systems · Types of water · Polymorphism · Optical transmission · Viscoelasticity

Introduction

In recent years, aqueous polymer systems have attracted considerable interest from both a theoretical as well as a practical point of view. The interaction between water and polymer is the main driving force for the structure formation in such systems. Depending on the composition and the temperature the distribution of water within aqueous polymer systems can vary and cause phase changes or phase-separation processes which are often accompanied by drastic changes in the macroscopic properties. In the majority of reports three different types of water are distinguished [1–5]. These types are nonfreezing bound water, which is strongly bound to the polymer, freezing bound water, which is weakly associated with the polymer, and free water, which forms a separate phase. Nonfreezing bound water is interpreted as water associated with polar groups of the macromolecular chains by hydrogen bonding or by polar interactions and freezing bound water is interpreted as water attached to the more hydrophobic groups of the polymer chains [1, and references therein]. The water binding properties of hydrogels do not only depend on the molecular structure but they also depend on the microstructure of the polymer. Thus, an analysis of the water binding properties of a polymer might provide useful information on its microstructure [5].

It is well known that electrolytes have a strong influence on the structure of aqueous polymer systems [6–10]. The addition of electrolytes often leads to a physical cross-linking of the polymer, whereby a three-dimensional polymeric network is built up and a hydrogel is formed [6–8]. Moreover, in thermotropic hydrogels a shift of the phase-separation temperature takes place by the addition of electrolytes [9, 10]. The formation of polymer–ion complexes and the influence of the electrolytes on the water structure are discussed to explain these effects.

In this article detailed investigations on the distribution of water, the phase behavior and the optical and rheological properties of a polyether/water/LiCl system are presented. The organization of the article is as follows. Differential scanning calorimetry (DSC) investigations to determin the water binding properties of the pure polyether and the effect of the addition of various amounts of LiCl on these properties are presented first. Then, results of microscopic observations and DSC measurements on the polymorphism and phase-transition temperatures of the polyether/water/LiCl system are reported. Finally, the temperature dependences of the optical transmission as well as of the rheological properties are presented and the complex temperature dependence of these macroscopic properties are discussed on the basis of the polymorphism of the samples.

Experimental

Materials

The polyether glycerol propoxylate-*b*-ethoxylate ($M_n \sim 4000$) was purchased from Aldrich and was used for the preparation of the aqueous polymer systems without further purification.

The aqueous polymer systems investigated were prepared as follows. Glycerol propoxylate-*b*-ethoxylate was added to aqueous LiCl solution or pure water, respectively. Then, the mixture was stirred for about 1 h and afterwards twice a day for about 15 min over a period of 4–5 days.

Differential scanning calorimetry

DSC measurements were carried out using a Perkin-Elmer DSC 7. The weight of the samples ranged between 5 and 20 mg. For the determination of the different types of water the samples were cooled from room temperature to −50 °C with a cooling rate of 5 °C/min and held at this temperature for about 30 min. Afterwards, the frozen mixtures were heated at a rate of 1 °C/min to 5 °C. In order to detect phase transitions and phase-separation processes in the temperature region above 0 °C the samples were heated from 5 to 90 °C at a rate of 5 °C/min. The heat of fusion was calculated from the peak area using indium as a standard.

Polarizing microscopy

A polarizing microscope (Olympus BH-2) fitted with a Linkam THMS 600 heating stage was used to study the phase behavior of the samples optically. Textural observations were performed with parallel as well as with crossed polarizers.

Optical transmission

The temperature dependence of the optical transmission of the samples was measured at a wavelength of 600 nm in 1-cm cuvettes against air in the reference beam by using a Perkin-Elmer UV/vis spectrometer (Lambda 18). The samples were kept at each temperature for about 20 min in order to achieve an equilibrium state.

Rheological properties

The rheological properties of the samples were studied by using an SR-200 dynamic stress rheometer (Rheometric Scientific) fitted with a Peltier heating stage. Samples of a thickness between 0.5 and 1.5 mm were placed between parallel plates (25-mm diameter) and covered with a solvent trap. A dynamic test mode was chosen to characterize the rheological properties of the samples (frequency 1 rad/s and an autostress adjustment to keep the strain in a range between 1.5 and 2%). The samples were heated from 0 to 90 °C at a heating rate of 0.5 °C/min and data were collected every 10 s.

Results and discussion

Determination of the water binding properties by DSC measurements

DSC measurements were performed in order to determine the melting enthalpy of frozen water of the polyether/water systems. For binary mixtures of polyether and water no water melting peak could be detected up to a water content of 15 wt%. In the region between 20 and 65 wt% water content a single water melting peak is observed. Above 70 wt% water content a second water melting peak occurs at higher temperature in comparison with the first one. With increasing water content the enthalpy of the higher-temperature water peak increases, while the enthalpy of the lower-temperature water peak decreases and finally disappears at a water content of 100 wt%. These results are in agreement with the existence of three different types of water [1–5]. At low water contents all water is strongly bound to the polymer and cannot be frozen (nonfreezing bound water). Above a certain content the additionally added water is only weakly bound to the polymer; thus, it can be frozen (freezing bound water). However, its melting point and melting enthalpy is lowered in comparison to bulk water. At high water contents the polymer is saturated with water and the additional added water builds a separate phase of free water. The different regions can also be clearly observed in a plot of the water melting enthalpy (or sum of the two enthalpies, respectively) as a function of the water content of the polyether/water system (Fig. 1). Within each region the data can be fitted linearly. The points of intersection between the different regions correspond to the compositions where the maximum amount of nonfreezing bound water or the maximum amount of (freezing plus nonfreezing) bound water, respectively, is reached. Using these data the total amounts of the three different types of water can be calculated for each composition (Table 1). Moreover, from the amount of freezing

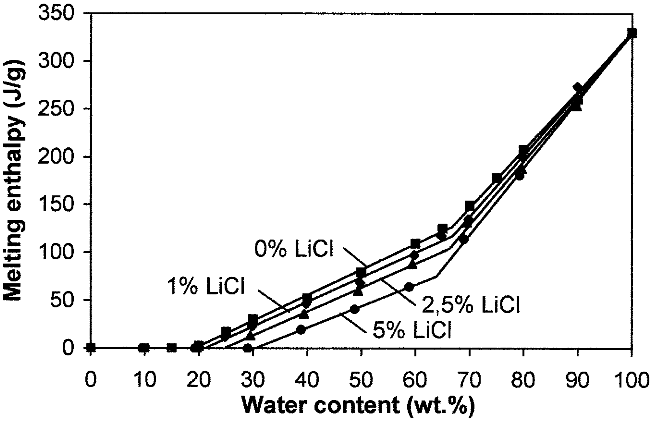

Fig. 1 Water melting enthalpy as a function of water content of the polyether/LiCl/water systems

bound water and the enthalpy of the corresponding DSC peak, the melting enthalpy of the freezing bound water and the binding enthalpy for its association with the polymer, which is the difference between the melting enthalpy of the freezing bound water and the melting enthalpy of free water, can be calculated. The results of these calculations are summarized in Table 2.

The nonfreezing bound water of aqueous polyether systems is interpreted as the water of the primary hydration shell of the ether groups. Investigations on polyether oligomers show that the ether group tends to build dihydrates [11]. However, for hydrogels based on polymers with a much higher degree of polymerization the ratio between the maximum amount of nonfreezing bound water and the number of polymer repeating units was often found to be significantly lower than expected from the hydration number(s) of the hydrophilic group(s). Moreover, it could be shown that the ratio between the maximum amount of nonfreezing bound water and the number of polymer repeating units not only depends on the molecular structure but that it also depends on the degree of polymerization, on the preparation method and on the storage time [1, 5]. According to Ref. [5] these effects can be explained by microcrystallites in the polymer structure, which cannot be hydrolyzed by water and, therefore, do not contribute to the water binding properties of the polymer.

The polyether/water system exhibits a saturation value of 0.74 mol nonfreezing bound water per polyether repeating unit, indicating thereby that only about one-third of the polyether groups can be hydrolyzed in this system.

Table 1 Measured water melting enthalpies, calculated amount and distribution of water and calculated melting enthalpy of the freezing bound water for different mixing ratios of the polyether/water system

Mixing ratio (wt%)		Measured enthalpy (J/g mixture)			Calculated composition of 1 g mixture (g)				Melting enthalpy (J/g)
Polyether	Water	1st peak	2nd peak	Sum of both peaks	Polyether	Nonfreezing bound water	Freezing bound water	Free water	Freezing bound water
100	0	–	–	0.00	1.000	0.000	0.000	0.000	–
90	10	–	–	0.00	0.900	0.100	0.000	0.000	–
85	15	–	–	0.00	0.850	0.150	0.000	0.000	–
80	20	2.67	–	2.67	0.800	0.190	0.010	0.000	256.73
75	25	16.96	–	16.96	0.750	0.178	0.072	0.000	234.74
70	30	30.40	–	30.40	0.700	0.166	0.134	0.000	226.70
60	40	52.40	–	52.40	0.600	0.142	0.258	0.000	203.26
50	50	79.25	–	79.25	0.500	0.119	0.382	0.000	207.73
40	60	109.20	–	109.20	0.400	0.095	0.505	0.000	216.15
35	65	125.20	–	125.20	0.350	0.083	0.567	0.000	220.79
30	70	107.71	41.39	149.10	0.300	0.071	0.528	0.101	203.88
25	75	99.06	79.33	178.39	0.250	0.059	0.440	0.251	225.01
20	80	74.90	132.70	207.60	0.200	0.047	0.352	0.400	212.67
10	90	33.60	226.90	260.50	0.100	0.024	0.176	0.700	190.83
0	100	–	330.49	330.49	0.000	0.000	0.000	11000	–

Table 2 Results of the differential scanning calorimetry (*DSC*) investigations on the water binding properties of the polyether

Maximum amount of nonfreezing bound water	0.237 g per gram dry polyether 0.74 mol per polyether repeating unit
Maximum amount of freezing bound water	1.761 g per gram dry polyether 5.48 mol per polyether repeating unit
Melting enthalpy of the freezing bound water	216.3 J/g
Binding enthalpy of the freezing bound water	−114.2 J/g

In order to study the influence of the addition of LiCl on the water binding properties of the polyether, various amounts of LiCl were added to the polyether/water system. Within each series the mixing ratio between LiCl and polyether was kept constant and the water content was varied. Three series containing a LiCl amount of 1, 2.5 and 5% of the polyether mass were prepared. A plot of the water melting enthalpy as a function of the water content of these three series as well as of the system without LiCl is given in Fig. 1. Similar to the procedure described previously for the binary polyether/water system the maximum amount of nonfreezing bound water, the maximum amount of freezing bound water as well as the melting enthalpy and the binding enthalpy of the freezing bound water were calculated (Table 3). With increasing LiCl concentration an increase in the maximum amount of nonfreezing bound water and a decrease in the melting enthalpy of the freezing bound water is observed, whereby both parameters show a linear dependence on the LiCl content. Independent on the starting concentration, the addition of 1 mmol LiCl leads to an increase in the maximum amount of nonfreezing bound water of about 9 ± 1 mmol and to a decrease in the melting enthalpy of the freezing bound water of about 49.3 J/g (calculated from a linear regression of the parameters plotted against the LiCl content).

How can these results be interpreted? First, let us assume that the increase in the maximum amount of nonfreezing bound water corresponds to the amount of water which builds the primary hydration shell of the Li^+ and Cl^- ions. The hydration number for a lithium ion is 5–6 and for a chloride ion it is 1 [12]. Thus, the addition of 1 mol LiCl should cause an increase in the maximum amount of nonfreezing bound water of 6–7 mol, which is in quite good agreement with the experimental result of 9 ± 1 mol. To test this model we investigated how the water binding properties of the same polyether are affected by the addition of 1% NaCl or 1% KCl, respectively. The hydration number for a sodium ion is 4–5 and for a potassium ion it is 3–4. For NaCl we obtained an increase in the maximum amount of nonfreezing bound water of 0.049 g/(1 g dry polymer + 0.01 g NaCl), which corresponds to 15.9 mol/mol NaCl and for KCl we obtained a decrease in the maximum amount of nonfreezing bound water of 0.009 g/(1 g dry polymer + 0.01 g KCl), which corresponds to 3.7 mol/mol KCl. For both salts the experimental results are far away from the results expected according to the model discussed. Thus, the change in the maximum amount of nonfreezing bound water clearly does not correspond with the amount of water bound in the primary hydration shell of the ions.

Another explanation for the change in the maximum amount of nonfreezing bound water by the addition of salts is to assume an influence of the salt ions on the microstructure of the polyether.

As a further result a decreasing melting enthalpy of the freezing bound water with increasing LiCl concentration was found for the polyether/water/LiCl system. This result clearly indicates that the polyether–water interaction becomes stronger with increasing LiCl concentration. The same effect was observed with the addition of 1% NaCl or 1% KCl, respectively, whereby NaCl has the smallest and LiCl the largest effect of these three salts. An influence of the ions on the water structure, a closer package of the polymer chains or a more rigid polymer structure are possible explanations for this result.

Phase behavior of the polyether/water/LiCl system

The phase behaviors of the polymeric systems were studied by microscopic observations and DSC measurements. On the basis of microscopic observations on the polyether/water system the following polymorphisms were detected. Mixtures with a low water content (up to 15 wt%) form one homogeneous (isotropic liquid) phase at room temperature. On heating this phase separates into two (isotropic liquid) phases, whereby one of these phases is a pure water phase. The phase-separation temperature decreases with increasing water content. At a water content between 15 and 25 wt% the polymorphism of the polyether/water system changes. For a mixture with 25 wt% water content a separation into two coexisting phases (mixing gap) is observed below about 30 °C. On heating above 30 °C the two coexisting phases transform into a homogeneous phase. As microscopic observations between crossed polarizers show, this phase possess an optical anisotropy, indicating thereby the presence of a supermolecular structure of the polyether/water system. On further heating, first a transition into a homogeneous isotropic phase (between 33 and 43 °C) and then a phase-separation process, starting at about 48 °C, takes place. With increasing

Table 3 Results of the DSC investigations on the water binding properties of the polyether with various LiCl content

Added amount of LiCl (% of the polyether mass)	0	1	2.5	5
Maximum amount (g) of nonfreezing bound water per gram dry polyether	0.237	0.269	0.334	0.458
Maximum amount (g) of freezing bound water per gram dry polyether	1.761	1.767	1.646	1.383
Melting enthalpy (J/g) of the freezing bound water	216.3	201.4	186.2	157.1
Binding enthalpy (J/g) of the freezing bound water	−114.2	−129.1	−144.3	−173.4

water content a decrease in the phase-separation temperature is observed, while the other transition temperatures are only slightly shifted. Thus, at about 50 wt% water content the phase separation occurs from the anisotropic phase and at about 60 wt% water content from the two coexisting phases, whereby the phase separation is observed in both the coexisting phases at slightly different temperatures. Above about 65 wt% water content the polyether is saturated with water and a separate water phase can be observed in all samples. In this concentration range the addition of water just leads to an increase in the amount of the separate water phase and does not affect the properties of the polyether/water phase any more. All these phase transitions and phase-separation processes of the polyether/water system are also detected by DSC measurements. As an example, the DSC curves of samples with polyether/water mixing ratios of 5:1, 4:1 and 3:1 are shown in Fig. 2. The change in the polymorphism at about 20 wt% water content from samples showing no other transition besides the phase separation process (e.g. mixing ratio 5:1) to samples exhibiting three different states below the phase-separation temperature (e.g. mixing ratio 3:1) can be observed by the appearance of two additional DSC signals. In the case of a polyether/water mixing ratio of 3:1 these signals are a double peak at around 28 °C, which corresponds to the occurrence of two coexisting phases below this temperature, and a broad peak between 33 °C and 43 °C, which corresponds to the occurrence of a homogeneous anisotropic phase between the two coexisting phases and the homogeneous isotropic phase. Besides the phase-separation process no other transition could be observed for the sample with a polyether/water mixing ratio of 4:1 (20 wt% water content); however, the rheological and optical measurements presented later indicate that at least one additional phase is already present in this mixture.

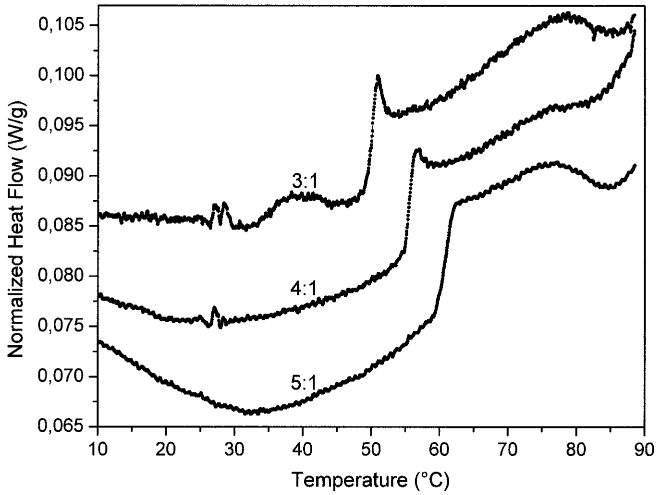

Fig. 2 Differential scanning calorimetry (*DSC*) curves of aqueous polyether samples with polyether/water mixing ratios of 5:1, 4:1 and 3:1

It is interesting to compare the polymorphism as a function of water content with the water binding properties of the polyether/water system (Fig. 1, Table 1). As can be seen, the presence of freezing bound water and the appearance of two additional states (two coexisting phases and a homogeneous phase with anisotropic properties) takes place at about the same water content. Moreover, the observation of a separate water phase above a concentration of about 65 wt% water content (saturation point) is in good agreement with the calculated maximum amount of (freezing plus nonfreezing) bound water.

Samples with a fixed polyether/water mixing ratio of 4:1 and a step-by-step increasing LiCl content of up to 6 wt% were prepared in order to study the influence of the LiCl concentration on the polymorphism and the macroscopic properties of the aqueous polymer system. Microscopic observations show that a phase-separation process takes place in all these samples. With increasing LiCl content the phase-separation temperature decreases until at about 4 wt% LiCl content a minimum is reached and then it slightly increases again. Furthermore, up to two other phases are observed, which are similar to the phases that occur by increasing the water content. At 0.5 wt% LiCl content a homogeneous anisotropic phase appears below about 30 °C and a separation into two coexisting phases takes place below about 0 °C. With increasing LiCl content the temperature of the transition from two coexisting phases into a homogeneous anisotropic phase increases and the temperature of the transition from a homogeneous anisotropic into a homogeneous isotropic phase decreases. Thus, above about 4.5 wt% LiCl content a direct transition from two coexisting phases into a homogeneous isotropic phase occurs. The DSC curves of these mixtures are displayed in Fig. 3. The phase-separation process, but not the other two phase transitions, is detected by this method. Above about 2 wt% LiCl some stepwise changes of the heat capacity are observed in the temperature range 15–30 °C. As shown by the rheological investigations presented later these steps display hydrogel formation or disaggregation processes. In agreement with the results of the microscopic investigations a minimum of the phase-separation temperature is observed at a LiCl content of about 4 wt%. Another interesting result is that the temperature range of the phase-separation process (broadness of the peak) becomes much smaller with the addition of LiCl. In opposition to the results of the variation of the water content (Fig. 2), not only the beginning of the phase separation process but also the temperature at which the phase separation is completed shifts depending on the LiCl content.

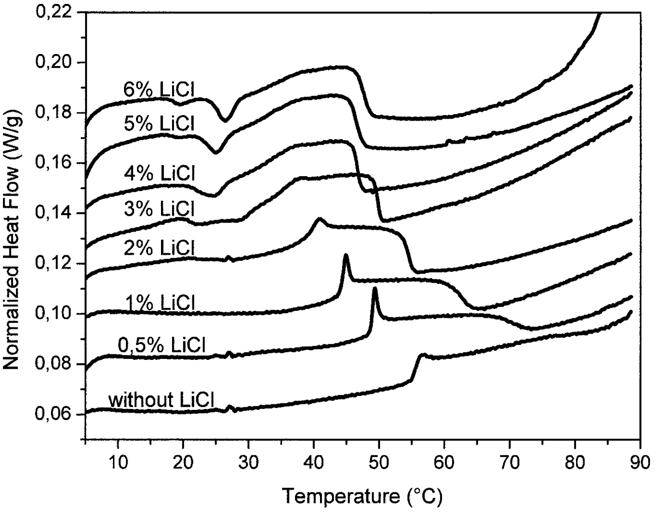

Fig. 3 DSC curves of LiCl containing aqueous polyether samples with a fixed polyether water mixing ratio of 4:1 and various LiCl contents ranging from 0 to 6 wt%

Optical transmission

The optical properties of aqueous polymer systems are mainly determined by the homogeneity of the mixtures. Whereas homogeneous mixtures are often highly transparent, phase-separation processes, two-phase regions and mixing gaps lead to a fine distribution of one phase into another and, as a consequence, to the appearance of a light scattering state. The optical properties of such states depend on the size and the distribution of the light scattering particles or droplets. The temperature dependence of the transmission at 600 nm of samples with polyether/water mixing ratios of 5:1, 4:1 and 3:1 is shown in Fig. 4. At phase-separation temperatures of about 48, 53 or 58 °C, respectively, all three samples transform from an optically highly transparent (transmission > 91%) into a light scattering opaque state (transmission < 0.1%). For comparison it should be mentioned that a transmission of about 92% was obtained for a water-filled cuvette under the same conditions. With increasing water content up to two additional phase transitions occur in the polyether/water system. The two-phase regions of these transitions lead to transmission minima in the transmission–temperature curves. As an example for such behavior the transmission–temperature curve of a sample with a polyether/water mixing ratio of 3:1 is displayed in Fig. 4. The transmission minimum between about 35 and 42 °C belongs to the two-phase region of the transition from the homogeneous anisotropic into the homogeneous isotropic phase and the one between about 26 and 32 °C to the transition from two coexisting phases into the homogeneous anisotropic phase. Below about 26 °C and above about 48 °C states with two coexisting phases appear. Accordingly, in these states the transmission is strongly reduced. In the two-phase regions and states of two coexisting phases the measured transmission values depend slightly on the thermal history of the samples and on the waiting time at the measuring temperature; therefore, these parts of the transmission–temperature curves are qualitatively but not exactly quantitatively reproducible.

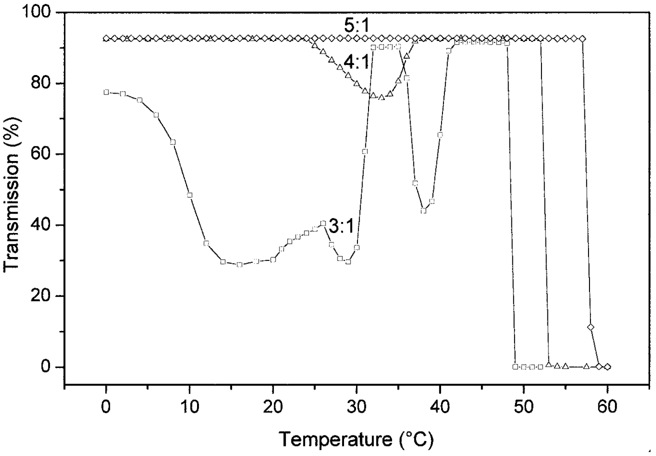

Fig. 4 Temperature dependence of the optical transmission at 600 nm of aqueous polyether samples with polyether/water mixing ratios of 5:1, 4:1 and 3:1

The temperature dependence of the transmission at 600 nm of samples with a polyether/water mixing ratio of 4:1 and a varying LiCl content of up to 6 wt% is shown in Fig. 5. Again, the optical transmission–temperature curves reflect the polymorphism of the samples. Depending on the LiCl content up to four different states occur, which are similar to the states of the sample with a polyether/water mixing ratio of 3:1; hence, similar transmission–temperature curves are obtained. The observed shifts of the transmission changes as a function of the LiCl content are in good agreement with the shifts of the transition temperatures which were determined by microscopic observations.

Rheological properties

Phase-transition, phase-separation and gelling processes of aqueous polymer systems are often accompanied by dramatic changes in the viscoelastic properties; therefore, rheological measurements can be used to detect such processes. The temperature dependence of the dynamic viscosity of samples with polyether/water mixing ratios of 5:1, 4:1 and 3:1 is shown in Fig. 6. For all three samples the beginning of the phase-separation process at about 48, 53 or 58 °C, respectively, is detected by an abrupt change in the slope of the curves. For a polyether/water mixing ratio of 3:1, an increase in the dynamic viscosity by more than 2 orders of magnitude is observed

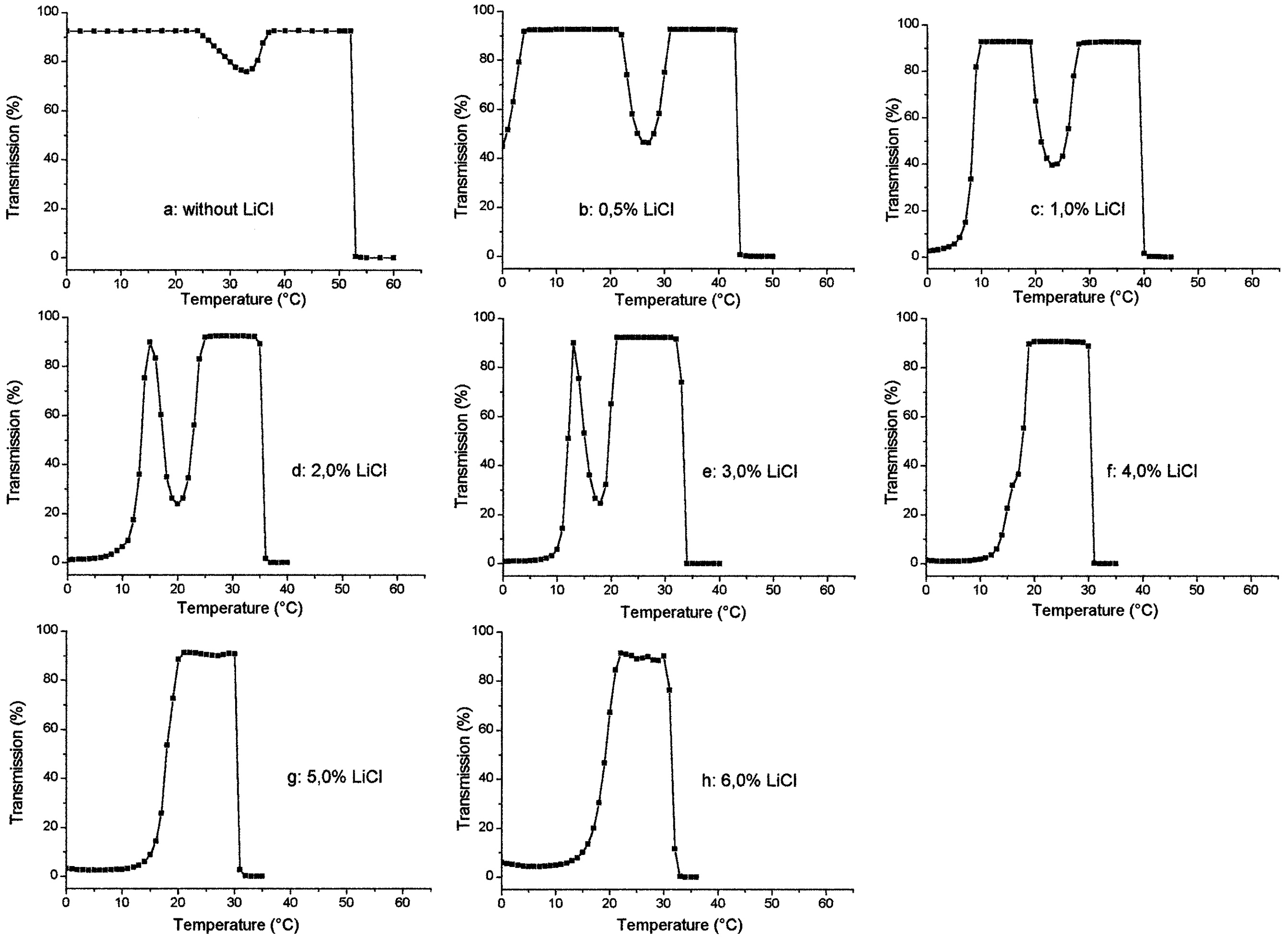

Fig. 5a–h Temperature dependence of the optical transmission at 600 nm of LiCl containing aqueous polyether samples with a fixed polyether/water mixing ratio of 4:1 and various LiCl contents ranging from 0 to 6 wt%

in the temperature range between about 27 and 32 °C. This peak of the dynamic viscosity–temperature curve has a shoulder, until passing 42 °C. Note that microscopic observations on this mixture have revealed the existence of a homogeneous phase with an anisotropic structure in this temperature range, whereby the temperature range of the shoulder corresponds to the two-phase region of the transition into the (isotropic) phase above. A separation of the dynamic viscosity into a viscous (loss modulus, *G″*) and an elastic portion (storage modulus, *G′*) shows that in this phase the elastic properties prevail, indicating thereby the presence of a three-dimensional inner structure (gel structure).

The temperature dependence of the dynamic viscosity of samples with a polyether/water mixing ratio of 4:1 and a varying LiCl content of up to 6 wt% is shown in Fig. 7. A complex dependence of the dynamic viscosity on temperature and LiCl content becomes obvious. In

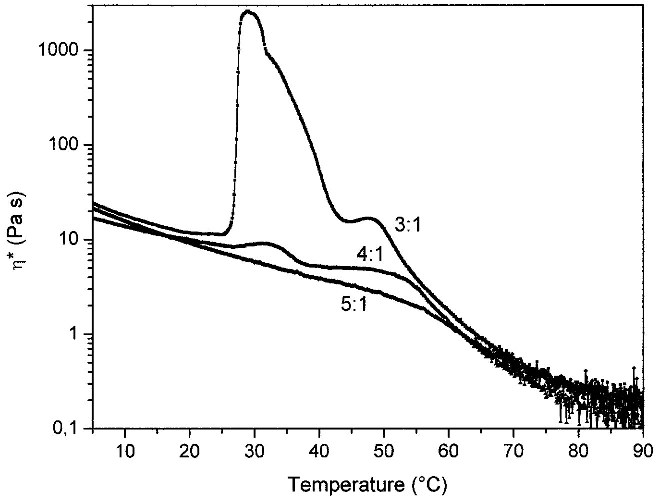

Fig. 6 Temperature dependence of the dynamic viscosity of aqueous polyether samples with polyether/water mixing ratios of 5:1, 4:1 and 3:1

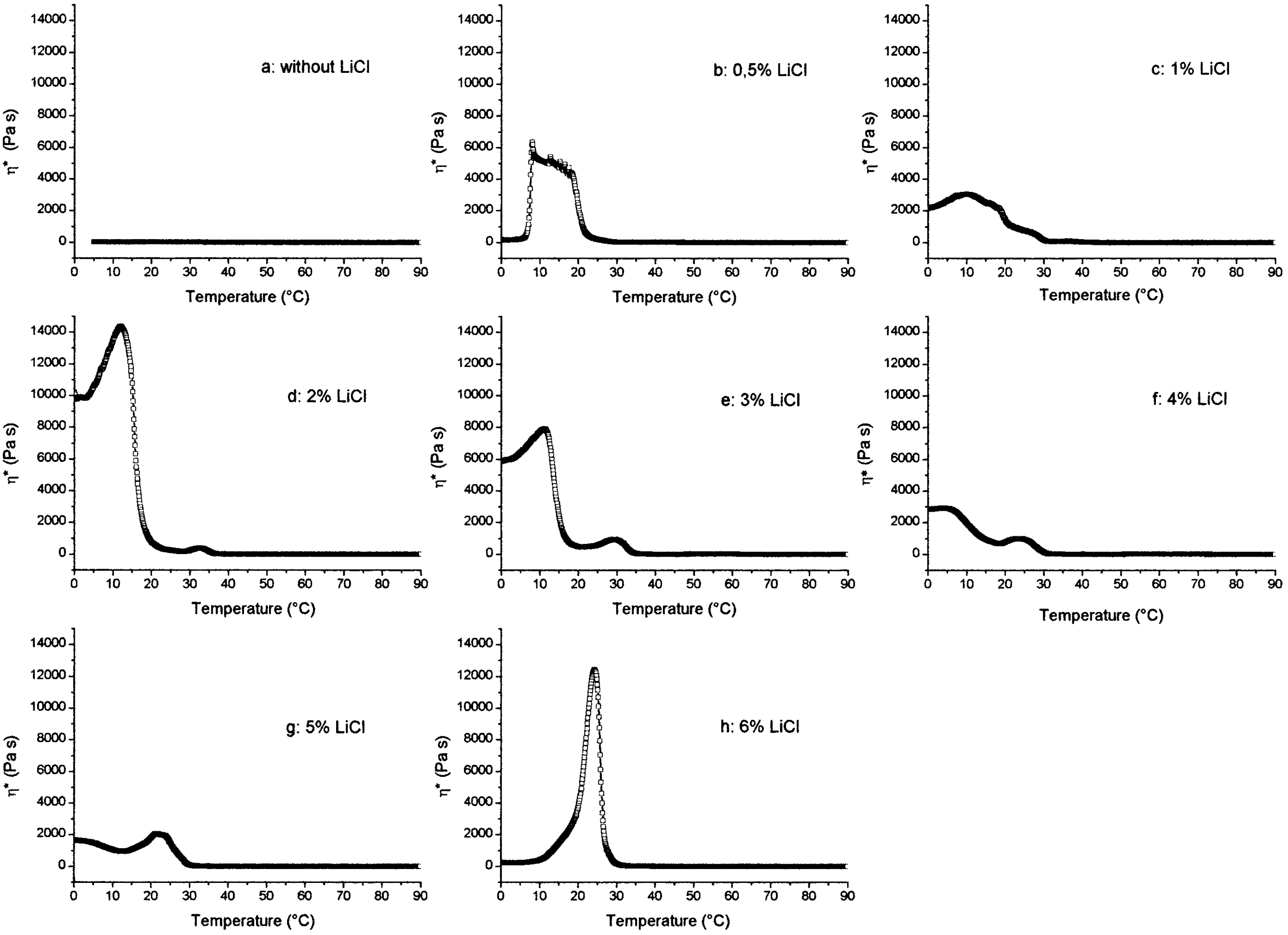

Fig. 7a–h Temperature dependence of the dynamic viscosity of LiCl containing aqueous polyether samples with a fixed polyether/water mixing ratio of 4:1 and various LiCl contents ranging from 0 to 6 wt%. Measuring conditions: parallel plates of 25-mm diameter, frequency: 1 rad/s

the different phases, structure formation and disaggregation processes are observed at different LiCl concentrations. At 0.5 wt% LiCl content a strong increase in the dynamic viscosity in the temperature range of the homogeneous anisotropic phase is observed. A more detailed analysis of the data (separation into G' and G'') shows that in this phase the elastic portion of the dynamic viscosity prevails, indicating thereby the presents of a hydrogel structure. With further increasing LiCl content a maximum value of the dynamic viscosity of the hydrogel is observed at about 2 wt% LiCl, whereby the results obtained at 1 wt% LiCl seem to indicate a discontinuous increase in the dynamic viscosity as a function of the LiCl content. However, stress and frequency ramps which were measured in the respective temperature ranges of the hydrogel show that the magnitude of the dynamic viscosity strongly depends on the measuring conditions (stress as well as frequency). This result shows that in all these samples the structure of the hydrogel is already influenced by the small applied mechanical stress during the measurement. Thus, the data obtained are not conclusive enough for a more detailed discussion. In the range between about 3 and 4 wt% LiCl content the homogeneous anisotropic phase only appears in a two- (or more) phase region in coexistence with the states above or below, respectively, and above this concentration range the homogeneous anisotropic phase does not occur anymore. Accordingly, a destabilization and finally a disappearance of the hydrogel state is observed by a decrease and finally vanishing of the corresponding peak of the dynamic viscosity as a function of temperature in the LiCl concentration range between about 3 to 4 wt% (Fig. 7). In the two coexisting phases (lowest temperature phase) the dynamic viscosity starts to increase at about 1 wt% LiCl content, reaches a maximum at about 2 wt% and then decreases again. Another structure formation is observed in the homogeneous isotropic phase between about 5 and 6 wt% LiCl content. Again, a more detailed analysis of the data shows that the elastic portion of the dynamic viscosity prevail, indicating thereby the presence of a hydrogel structure.

Conclusions

The interaction between water and polymer is the driving force for the formation of different phase structures in aqueous polymer systems. The data presented for the water binding properties and the polymorphism of a polyether/water system may indicate a relationship between the presence of different types of water and changes in the polymorphism. At the same water concentration at which the polymer is saturated with nonfreezing bound water and the presence of freezing bound water is detected, the appearance of two additional phases is observed in the aqueous polymer system investigated. One of these phases possesses a supermolecular structure as indicated by its optical anisotropy. The availability of a more mobile type of water seems to be necessary for the formation of the anisotropic structure.

The addition of LiCl, which acts as a physical cross-linker, leads to a stronger interaction between water and polymer. A linear increase in the maximum amount of nonfreezing bound water and also of the binding enthalpy of the freezing bound water is observed with increasing LiCl concentration. Although the polymer–water interaction becomes stronger with increasing LiCl concentration, the polymorphism of the system is not affected very much. Similar phase types are observed and an increase in the LiCl content influences the phase sequences nearly in the same way as a further increase in the water content. As the rheological measurements show, a cross-linking of the aqueous polymer system takes place with the addition of LiCl, whereby in different phases gelation occurs in different LiCl concentration ranges.

The results clearly show the strong influence of the structural features and the phase behavior on the macroscopic properties of aqueous polymer systems. Hence, a better knowledge of the structural and thermodynamic properties of such systems might contribute to more effective material development.

References

1. McCrystal CB, Ford JL, Rajabi-Siahboomi AR (1997) Thermochim Acta 294:91
2. Ahmad MB, Huglin MB (1994) Polym Int 33:273
3. Yoshida H, Hatakeyama T, Hatakeyama H (1992) J Therm Anal 40:483
4. Pissis P, Kyritsis A, Konsta AA, Daoukaki D (1999) Colloids Surf A 149:253
5. Cha W-I, Hyon S-H, Ikada Y (1993) Makromol Chem 194:2433
6. Shibayama M, Ikkai F, Moriwaki R, Nomura S (1994) Macromolecules 27:1738
7. Kurokowa H, Shibayama M, Ishimaru T, Nomura S, Wu W (1992) Polymer 33:2182
8. Deuel H, Neukom A (1949) Makromol Chem 3:113
9. Alexandridis P, Holzwarth JF (1997) Langmuir 13:6074
10. Fischer T, Holzbauer H-R, Seeboth A (1999) Mat-wiss U Werkstofftech 30:473
11. Kleeberg H, Klein D, Luck WAP (1987) Chem-Ing-Tech 59:440
12. Israelachvili JN (1985) Intermolecular and surface forces. Academic, London, p 43