Solar Energy Materials & Solar Cells 60 (2000) 263–277

Solar Energy Materials & Solar Cells

www.elsevier.com/locate/solmat

Materials for intelligent sun protecting glazing

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Abstract

The aim of this review is to present the last 10 years of development in sun protection by use of electrochromic devices, thermotropic gels and polymer dispersed liquid crystalline systems. Furthermore, the properties of new lyotropic liquid crystalline and thermotropic hydrogels are discussed. Thermochromic hydrogels, which change their colour by changes in the temperature, also are presented. The relationship between gel composition, optical behaviour and thermodynamic properties as investigated by differential scanning calorimetry (DSC) is also demonstrated. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Sun protection; Electrochromic devices; Thermotropic and thermochromic systems; Liquid crystalline gels; DSC

1. Introduction

Electrochromic and thermotropic organic materials form systems, which react accordingly to different external influences with a reversible colour modification or clouding. Granqvist reviews the development of these materials in the years before 1990 in detail [1]. In the past decade this topic has gained further significance. The motivation for all efforts to develop chromogenic materials is their potential technical application as electrically adjustable or thermally self-adjusting light and heat filters in the external glazing of buildings. These glazing items are frequently called "intelligent" or "smart" windows. Further potential applications are large area displays for information and traffic engineering, as well as temperature sensoring applications in medical technology.

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PII: S0927-0248(99)00087-2

2. Electrochromic materials and polymer dispersed liquid crystalline systems

The development and the application of electrochromic systems (ECD = ElectroChromic Devices) strongly increased in the last years. Over 2000 patents are already announced in this technology. The advantages of electrochromic materials are:

- Electric energy consumption only appears during the switching process and with a low switching voltage (1–5 V).
- ECDs have a grey scale and low polarisation.
- ECDs are always transparent-typical ECDs has an coverage transmissions of $T_{\text{colourless}} = 70\text{–}50\%$ and in the fully coloured state of $T_{\text{coloured}} = 25\text{–}10\%$ in the region of visible light.

A glass slide coated with electrochromic materials modifies its optical parameters in response to an electrical field. It recovers the original characteristics, if the field polarity is reversed. Monk, Mortimer and Rosseinsky described all aspects of electrochromic systems and materials in detail in their monograph from 1995 [2]. For application in the external glazing of buildings only transparent and non-reflecting electrochromic devices are useful. In a typical transparent ECD with five layers, the outside layers are transparent electrodes. The following layers are the optically switchable layer, electrochromic film, and an ion-storing layer. The internal layer is formed by the electrolyte or ion conductor, which has a high conductivity for small ions such as H^+ or Li^+ but low conductivity for electrons [3]. The most promising ion conductors are certain immobile solvent polymer systems, ionic glasses and *open channel* metal oxide structures such as perovskites [4]. Applying a DC voltage causes ion migration into the electrochromic layer and leads to its colouring (Fig. 1). On

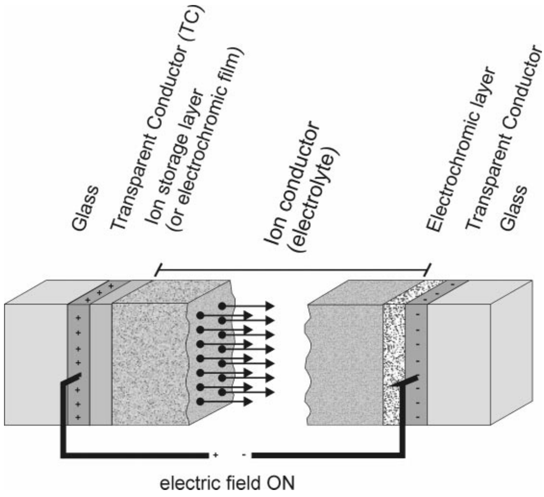

Fig. 1. Schematic diagram of an ECD with five layers in transmittance mode. With electrical field feed of cations or protons takes place into the electrochromic layer.

reversing the polarity the film delivers the ions under simultaneous clarification again. The voltage must be kept low in order to prevent the initiation of electrolytic processes or reducing mechanisms in the electrolyte layer.

The best-known material commonly used for the transparent electron conductor is indium-tin-oxide ($In_2O_3 : Sn$; ITO). For the electrochromic film the transparent tungsten oxide WO_3 is particularly suitable. If both electrodes bear an electrochromic layer like in a typical five-layered ECD, one oxide layer is present in its reduced form while the other is oxidised. During the storage of small ions into the crystalline lattice the frequently blue coloured mixed oxide M_xWO_3 is formed by a typical cathodic reaction (reduction process):

$$WO_3(\text{pale yellow/colourless}) + xM^+ + ye^- \rightharpoonup M_xWO_3(\text{blue}).$$

The complementary anodic reaction (oxidation process), eg. for the formation of the coloured vanadium pentoxide:

$$M_xV_2O_5(\text{pale blue}) - xM^+ - ye^- \rightharpoonup V_2O_5(\text{brown}).$$

Thus the complete redox reaction is

$$\underset{\text{bleached}}{WO_3(\text{pale yellow/colourless}) + M_xV_2O_5(\text{pale blue})} \rightleftharpoons$$

$$\underset{\text{coloured}}{M_xWO_3(\text{blue}) + V_2O_5(\text{brown})}.$$

Beside WO_3 the metaloxides NiO, MoO_3 and IrO_x have gained the most research interest in the last years.

Four typical kinds of ECD can be differentiated:

- ECDs with liquid electrolytes (e.g. $LiClO_4$ + propylene carbonate + 2% H_2O, limited by a primary film of WO_3 and an ion-storing iridium oxide layer, five layers between two glass slides) [5].
- ECDs with solid inorganic ion conductors of high volume.
- ECDs with solid inorganic ion conductors in the form of thin films (e.g. glass coated on one side with ITO, WO_3, $LiNbO_3$ as an ion conductor and V_2O_5 as ion memory layer) [6].
- ECDs with solid polymer electrolytes [7] (e.g. poly(propylenglycol) poly(methyl methacrylate) (PMMA)–$LiClO_4$ as electrolyte in a five-layered structure between two glass slides) [8].

ECDs of the latter type are of particular interest for their use in intelligent windows. In these electrochromic windows the high viscose polymer electrolyte makes it more difficult to flow out if the glass breaks. By Mani and Stevens [9] in the presence of a poly(propylene glycol)/$LiCF_3SO_3$ mixture methylmethacrylate was polymerised to a network in order to increase the mechanical stability of the electrolyte. This system showed no phase separation. All redox active and electrically conductive polymers are potentially electrochromic in thin-film form. Most of them are aromatic systems like polyaniline. Polyaniline and some other conductive polymers, are so-called *organic metals* and might be understood as real metals, which have some limitations due to their mesoscopic properties. The *organic metal* films of polyaniline are transparent (green) and highly conductive even at thickness of only 1 μm. The application of conducting-polymers as electrochromics has been reviewed by Mastragostino [10] and by Hyodo [11]. Jelle et al. [12] used poly (2-acrylamido-2-methylpropane sulfonic acid) as solid polymer electrolytes. The two ITO coated glass slides, when coated with polyaniline on the side directed to the light and with WO_3 on the other side, blue colouration occurred by complexation of polyaniline with formed H_2SO_4. More than 50% of the incident solar radiation could be held back by a further improvement of this system [13]. Likewise polymer electrolytes with complementary electrochromic films of polyaniline and WO_3 are investigated by Panero et al. [14].

The most studied organic electrochromics are the viologens or bipyridiliums. For short alkyl chain length 1,1-dialkyl-4,4-bipyridiliums, both the dication and radical cation states are soluble in water and any electrochromic device (ECD) using such bipyridiliums would have the limitation of a low colouring–decolouring efficiency. One solution to this problem involves electrostatic binding of bipyridilium dications into anionic polyelectrolyte films [15] and the additional use of longer alkyl chains (e.g.: 1,1′-diheptyl-4,4′-bipyridilium, heptyl viologen, HV) lowers the solubility in water. E.g. one approach is to incorporate bipyridiliums into films of the sulphonated perfluorinated polyether Nafion® [16,17].

Goldner et al. [18] examined glass substrates coated only on one side. They also used crystalline WO_3 as cathodic electrochromic layer, amorphous $LiNbO_3$ as an ion conductor, for the second electrochromic layer In_2O_3, Nb_2O_5 or $LiCoO_2$ and as limiting transparent electrodes ITO or In_2O_3. Frand et al. [19] used a mixture from $LiClO_4$ solved in propylene carbonate with 50% PMMA. The formed solid electrolytes were highly transparent and thermally stable up to 160°C. A switching time of only 20 s between 20% transmission (dark blue) and 80% transmission (clear) was obtained by Andrei et al. [20] with a polymer electrolyte based on polyepoxide, complexed with $LiClO_4$. Passerini et al. [21]. examined proton or lithium-cations conducting gel-like electrolytes with two different electrochromic layers of WO_3 and NiO_x. Beside WO_3 as electrochromic layer Lampert and Ozer [22] examined the cathodic oxides TiO_2 and Nb_2O_5, the anodic hydroxides $Ni(OH)_2$ and $Co(OH)_2$ as well as the oxides V_2O_5 and CuO_x. With these compounds different colouring can be produced. $Ni(OH)_2$ shows, e.g. a colour change from transparent to bronze/brown. By withdrawal of y Li^+ ions the pale-yellow $Li_yV_2O_5$ shows a transition to the blue V_2O_5 [23].

The utilisation of photochromic effects can also be used in ECDs. Gregg [24] describes a photoelectrochromic system that was build up by combination of a colour sensitive solar cell with an electrochromic electrode. A further advancement of Bechinger and Gregg [25] possesses the typical five-layered structure. In place of the ion memory they use a colour sensitive TiO_2 layer, which serves as semiconducting electrode for the production of a photoelectric voltage, whereby the discolouration of the WO_3-film is caused. The electrical voltage needed for switching the window is thus produced only by influence of light. With very thin electrolyte layer homogeneous discolouration can also be attained if only one part of the cell is exposed to light.

ECDs are investigated by many research institutes and companies around the world. The commercial application of electrochromic systems is not limited for the glazing of buildings. Also in the future automotive manufacture (windows, glass roofs and mirrors) and for the aeroplane technology (e.g. cockpit window in aeroplanes) applications are possible. In fact, mirrors are the most commercially electrochromic products. In 1991, the Gentex Co. was the first to market with a driver side flat exterior — NVS Night Vision Safety™ (NVS®) mirror. Further details of the market situation for ECDs and commercialised chromogenic products are reported by Lampert [26].

Likewise it is possible to use a polymer matrix with stored liquid crystalline droplets (Polymer-dispersed liquid crystals — so-called PDLCs) as the optically active layer. At first in the cloudy layer the liquid crystalline molecules are not aligned. By applying an electric field the molecules are aligned parallel and the PDLC layer becomes transparent (Fig. 2).

Crawford and Doane [27] examined 10 μm thick polymer layers with LC-Droplets of < 1 μm diameter. These could be reoriented in a light-transmittance status by a voltage of 40 V. For chiral PDLCs with large cholesteric pitch and negative dielectric anisotropy it was observed that in the centre of the LC droplets uniformly

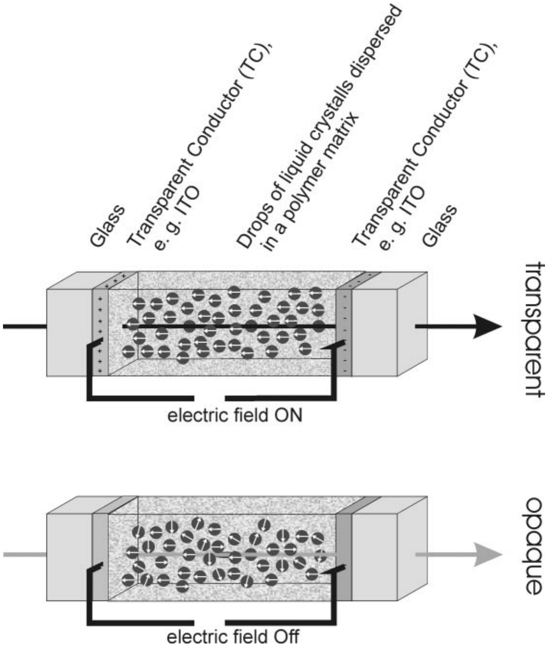

Fig. 2. Orientation of PDLCs in the electrical field. In the case of orientation toward the field the system posses high transparency.

aligned regions were developed if an electric field is switched on. Their radius rises exponentially with increasing field strength. On the other hand the threshold voltage decreases with an increase of droplet diameter and pitch [28].

Seeboth [29] determined threshold voltage and absorption of PDLC films under influence of an electrical field on lyophilised peptide layers with formerly embedded liquid crystals. For a film with layer thickness of 30 μm a threshold voltage around 35 V was determined. Hydrogels are likewise applicable as a polymer matrix in PDLC systems. Liquid crystals embedded in a hydrogel of poly (vinyl alcohol) crosslinked with borax was electrically controllable. That PDLC was stable against electrolytic decomposition, but the required threshold voltage was too high [30].

3. Thermotropic materials

3.1. Hydrogels and polymer blends

These materials are usually organic compounds and show, in a system depending temperature range, a reversible and more or less sharp transition from transparent to cloudy. Glazing based on these materials will be applicable in areas of buildings, which do not require constant transparency of the glazing, as for instance roof glazing, glazing in shopping centres or industrial buildings.

The use of thermotropic polymerfoils consisting of polymer blends [31] coated directly onto the glazing or the use of double glazing filled with a thermotropic substance are practicable ways of realisation (Fig. 3).

From our point of view the latter one is the more promising system. A glazing filled with thermotropic gel shows a better, well-defined transmission-temperature behaviour and is more resistant to exposure than polymerblends. A set of restrictions arise, without fulfilment an industrial application using this kind of sun filter must fail:

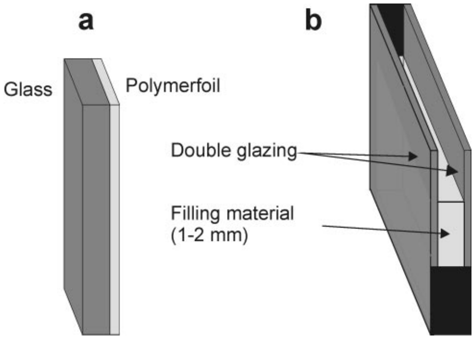

Fig. 3. Possible Smart windows: (a) polymerblend (∼ 0.2 mm) coated directly onto the glazing. (b) glazing filled with a thermotropic polymer gel, thickness of the layer is 1–2 mm.

- The used substances and systems should be stable against UV-radiation, biologically degradable, inexpensive, available in large quantities, innocuously, with low or non-flammability, free of organic solvents, safely manageably and non-freezing.
- The systems should possess a high viscosity in order to distribute the internal hydrostatic pressure evenly on the glazing and not to run out of the glazing.
- The temperature-dependent transitions of the glazing should take place between a status of high transparency with a transmission $> 85\%$ and a clouded, scattering status (paper white) with a transmission $< 15\%$.
- The turbidity should be distributed over the whole area of the glazing items, without appearance of streaks and with an acceptable rate for the human eye.
- The temperature, at which these transitions occur, should range between 30°C and 80°C.
- Furthermore, these transitions must be highly reversible and reproducible during a long period.

Promising systems are polymer-hydrogels [32] which are proved to fulfil not only most of, but also the most important of these requirements. Polymer-hydrogels are to date extensively used in pharmaceutical [33] and medical technology [34,35]. Hydrogels are interlaced macromolecules, in which at least one part of the network consists of hydrophilic groups. These polymer networks can be poured with the appropriate water content [36]. The swelling of the hydrogel results from cooperation of molecular interactions in aqueous, partial ionic polymer solutions on the one hand, and flexible characteristics of polymer networks on the other hand. At low temperatures the macromolecules are mixed as a homogeneous aqueous solution. During the rise in temperature an aggregation of the polymers or separation of water from the polymer network occurs. If the phases possess different refractive indices, the consequence is scattering of light and a visible clouding of the system. Layer thickness within the range of 1–5 mm commonly applicable for industrial production of filled glazing. Even for layer thickness of 1 mm extensive scattering of the incident light with a large proportion of reflection occurs [37]. Investigations of gelation [38,39] and of the swelling behaviour [40] were again strengthened in the last years. This particularly applies to the phase transitions in non-ionic hydrogels discovered by Tanaka in 1984 [41]. As suitable thermotropic polymer systems mainly water-soluble mixtures or copolymers from poly(acrylic acid) derivatives as well as systems based on poly (vinyl alcohol), cellulose ester, polyglycol, poly (vinyl acetal)-resins and polyether are examined. In the years 1991/1993 partially crosslinked copolymers from *N*, *N*-dimethylacrylamide and C_1–C_4 alkyl and alkoxyethyl acrylate were developed by Mueller [42–44] (Ciba-Geigy). These hydrogels showed sharp clear-cloudily transitions between 30°C and 80°C, which were accompanied by shrinking of the gel. In the year 1977 a thermotropic compound of acrylamide polymers and poly (vinyl alcohol) or poly (vinyl caprolactame) was already developed as a thermotropic component for the filling of double glazing by Rullier [45] (Saint Gobain Industries). The earliest attempt of this type took place between 1950 and 1960 in Germany in the residence of Munich zoo. A mixture of 5% poly (vinyl methylether) in agar–agar was used for the filling of a double glazing. This system however, reduced the transmission insufficiently and is therefore not of practical use. In 1995, a thermotropic system on the basis of poly (methyl vinylether) solved in water and crosslinked with methylenebisacrylamide was developed by Chahroudi [46,47] (Suntec Corp.). By addition of divinylspirodioxan this hydrogel is able to stick well to the filled materials from poly (vinyl acetate) or polypropylene. This thermotropic hydrogel is already commercially available as Cloud Gel™, however with limited success. Investigations on the thermotropic optical behaviour of this system were initiated by Wilson [48] and by Wittwer et al. [49]. In a layer with a thickness of 1 mm a change in transmission by 65% was observed (Fig. 4).

Polymerised ethylenic unsaturated *N*-substituted lactame, *N*-vinylsuccinimide as well as vinylethers and copolymers of these monomers with crosslinking comonomers were also developed 1995 by Kröner and Jahns [50] (BASF) for application as thermotropic gels. The influence of different crosslinkers on the homogeneity of hydrogels on the basis of poly (acrylic acid) was examined in 1997 by Oppermann et al. [51]. In order to prevent the irreversible sedimentation of polymer units often accompanying the phase separations and to implement the turbidity of the gel by a phase transition, Watanabe [52,53] added the amphiphilic poly (oxy propylene-2-ether-2-hydroxymethyl-1,3-propanediol) (MW = 400) to a gel made from hydroxypropylcellulose and water. The non-ionic amphiphile thereby acts as spacer preventing a complete phase separation. Meinhardt already tested the use of nonionics in thermotropic systems in 1987 [54]. The basic polymer of his system was a water-soluble polyether with ethylene-oxide functions mixed with poly (acrylic acid) and a base. The addition of nonylphenol as a wetting agent also caused here an improved reversibility of clear-cloudily transitions. The content of wetting agents controlled the temperature range of these transitions. The gelation achieved by the complexation or

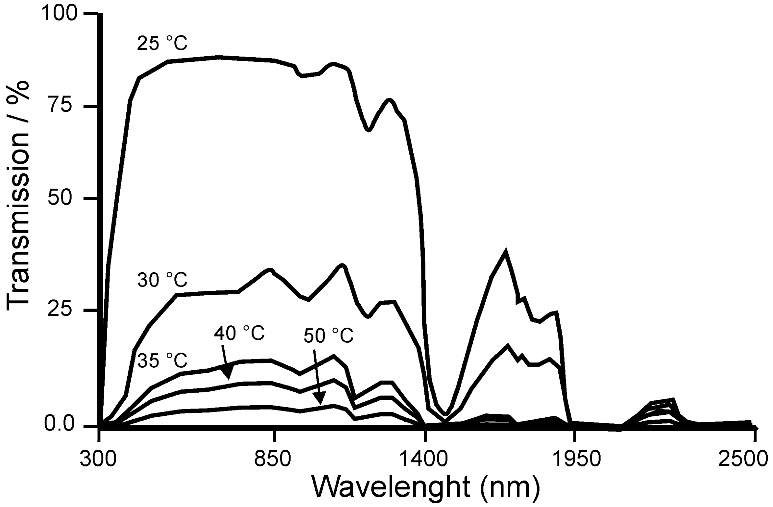

Fig. 4. Spectral transmittance of a *Cloud-Gel*™ sample at different temperatures [49,50].

crosslinking of aqueous poly (vinyl alcohol) (PVA) with borax is also a well examined system [55,56], which can be used as a gel basis for the production of thermotropic systems.

Non-aqueous, thermotropic polymer blends are likewise examined beside the hydrogels for their applicability as light and heat filters. Polymer blends are poured mostly as a film from an organic solvent on a glass or polymer substrate or made as foils. In 1993 Siol et al. [57] (Roehm GmbH) developed an applicable polymer blend made from chlorinated rubber and polymethacrylates. This polymer blend showed sharp cloud points between 60°C and 140°C depending on the polymer composition.

In the same year Eck et al. [58] developed a thermotropic polymerblend from poly (propylene oxide), a styrene-hydroxyethyl acrylate copolymer and a trifunctional cyclic isocyanate as crosslinker. The toluene solution of the polymer blend was poured to a thermotropic film. The temperature range, in which the turbidity occurred, also was controlled by the degree of crosslinking. By crosslinking the copolymer in the presence of propylene oxide a semi-interpenetrating network was obtained. A likewise crosslinked thermotropic polymer network was developed by BASF [59] in 1995. The dried films, formed from a styrene hydroxymethacrylate copolymer and a poly (propylene oxide) by radical polymerisation, showed reversible turbidity transitions between 40°C and 130°C. The combination of a non-thermotropic polymer matrix and a higher alkane as a thermotropic component was presented in 1996 by Meinhardt et al. [60]. The polymer matrix was based on a resin from phthalic anhydride, soy oil, pentaerythrit and a solvent. The films obtained after drying clouded themselves between 30°C and 40°C reversibly.

3.2. Lyotropic liquid crystalline hydrogels

Synthetic lyotropic LC polymers are well examined since the first observation of this phase formation in poly (benzyl glutamate) [61,62] (PBLG), hydroxypropyl cellulose [63,64] (HPC) and full-aromatic polyamides [65]. Common properties of these polymers are their good solubility in water and the structural feature of a more or less rigid polymer backbone (stiff chain of polymer) which enable the formation of liquid crystalline phases [66]. With an increase in the polymer concentration in the solvent, e.g. water, these polymers undergo a transition from an isotropic phase to a polymer solvent system with pronounced long-range order [67].

Our interest applies on the investigation of lyotropic LC-polymer gels, which are stable over a temperature range as large as possible in the gelled state. We could implement this, e.g. by a PEG/PVA borax system [68]. PEG forms liquid crystalline domains in a PVA-borax network, which is to be detected by the formed *schlieren* (Fig. 5a) and *radial-droplet* (Fig. 5b) structures using polarised optical microscopy.

The temperature-induced transition from the optically anisotropic LC-phase into the isotropic phase could be effected in this system without destroying the gel network. Both the optical and the gel characteristics are strongly dependent on the molecular weight and the molecular weight distribution of the polymers used here, the weight ratio of the individual polymers, the total concentration of the polymers and the degree of crosslinking. The temperature-dependent optical behaviour is well

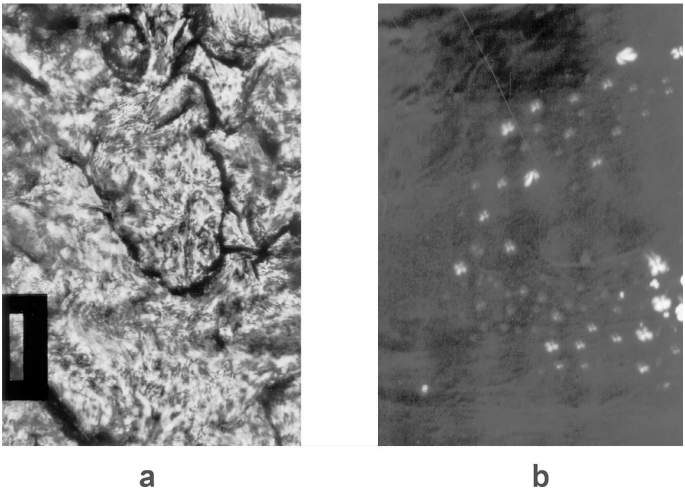

Fig. 5. Schlieren texture (a) und droplet texture (b), observed in the liquid crystalline phase between crossed polarisers.

adapted to the human eye. This is achieved by the fact that transmission modifications up to 85% take place not suddenly but in a quite broad temperature range of 5–15 K. Thus temperature gradients occurring at the warming up or cooling of large glazings do not cause abrupt differences of the transmission. It is particularly interesting, that lyotropic gels can posses several maxima and minima of transparency over a wide temperature range. Thus for an aqueous lyotropic gel of ethoxylized poly (dimethyl siloxane) (ePS)/PVA-borax [69,70], a transition from cloudy to clear and again too cloudy can be observed on heating up (Fig. 6). These thermotropic systems can protect interiors against overheating at elevated temperature and against cooling down at low temperatures. The reasons for the different optical states are phase transitions in the lyotropic LC system as well as phase separation at usually higher temperatures.

A further important point is the systematic investigation of the influence of salts on the transmission behaviour of thermotropic hydrogels. In certain polyether/water mixtures the formation of an anisotropic phase is induced by the addition of salts [71]. With addition of 1 wt% alkali chloride the polyether/water gel forms an anisotropic LC-phase between 20°C and 28°C. This anisotropic phase is detected as low turbidity of the former transparent gel. On warming up phase separation occurs. It is well known that the addition of alkali halides and particularly alkali chlorides lowers the temperature at which the phase separation occurs [72]. In the process of phase separation salt extracts free water from the polymer network by hydration of the ions and polar interactions of hydrates with polar molecule fragments occur. These polar fragments are usually oxygen or nitrogen atoms. We used alkali halides for our investigations, in order to study their influence on the phase separation and on the formation of the lyotropic LC-phase systematically. We observed that all salts strongly lower the temperature of the phase separating clear–cloudy transition. With

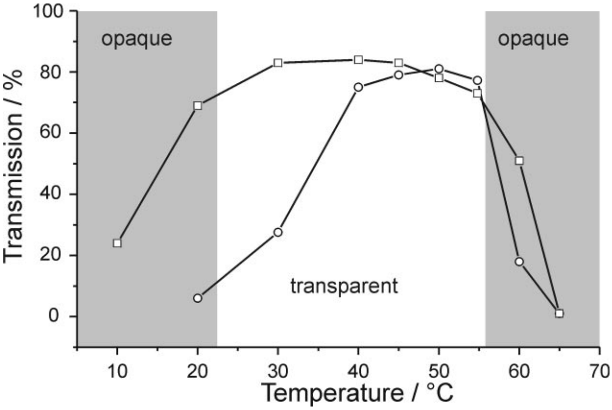

Fig. 6. Temperature/transmittance plot for ePS/PVA gels [70]. (□) ePS/PVA 70T 1 : 3 (15% polymer, 1,6% borax), (○) ePS/PVA 70T 1 : 3 (20% polymer, 1,6% borax).

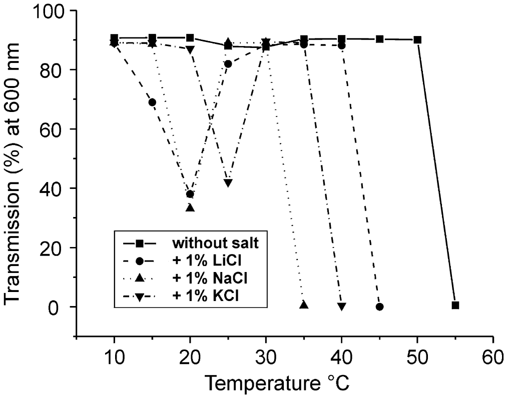

Fig. 7. Salt induced lyotropic LC-phases in polyether/water system [71].

alkali-bromides and -iodides a reduction of this effect in the order K > Na > Li was observed, which correlates with the decrease of the ion radii. On the other hand, the chlorides show a gradation in the order NaCl > LiCl > KCl, which does not obey this pattern. In comparison to NaCl and LiCl the LC phase shifts even with KCl addition from about 21°C around 5 K to higher temperatures (Fig. 7). With an increase in the water content from 20% to 30% an anisotropic LC-phase is formed without addition of salt, formation of which can be observed in a temperature range between 17°C and 32°C.

This temperature range also is maintained with salt addition. Additionally, the increase of the water content degrades the temperature of the phase separation by 11 K to 44°C. This effect is even still strengthened by salt addition. In addition to alkali halides also the effect of carbonates, nitrates and phosphates was examined. We understand however, predicting the influences of salts on the optical behaviour of the gels are only possible with difficulty.

Phase separations and phase transitions in hydrogels can be followed well by transmission spectroscopy and also differential scanning calorimetry (DSC). Investigations in this direction are however rather the exception [73] but the different types of water in hydrogels are examined well [74,75]. Due to different heating and cooling rates a direct comparison of the DSC measurements with the transmission spectra is only possible conditionally. By the example of the salt-free polyether/water system with a water content of 30 wt% the occurrence of the anisotropic phase was first observed at 27°C [76]. In the DSC appears a quite sharp endothermic peak with a maximum at 27°C (Fig. 8). The two isotropic phases that are present at lower temperatures could easily be detected in the light microscope under polarised light. The anisotropic phase begins to rearrange at 36°C into an isotropic phase. This temperature correlates approximately with the temperature range of highest transmission in the UV/VIS spectrum. By further heating to 44°C phase separation occurs. At this temperature a strong decrease of around approximately 90% of the transmission in the UV/VIS-spectrum is observed. Only the 40 K broad, endothermic rise of the DSC curve shows, that the phase separation process runs over a large temperature range and is completed by 84°C (T_d).

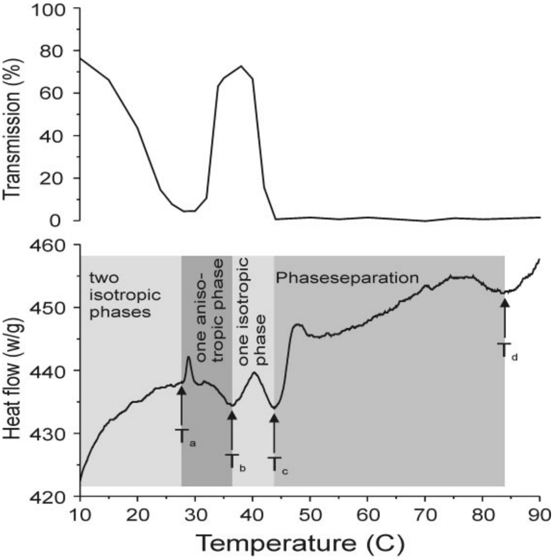

Fig. 8. UV/VIS-spectra and DSC plot of polyether/water system. T_a start of formation of the anisotropic phase, T_b begin of formation of the isotropic phase, T_c begin of phase separation, T_d end of phase separation.

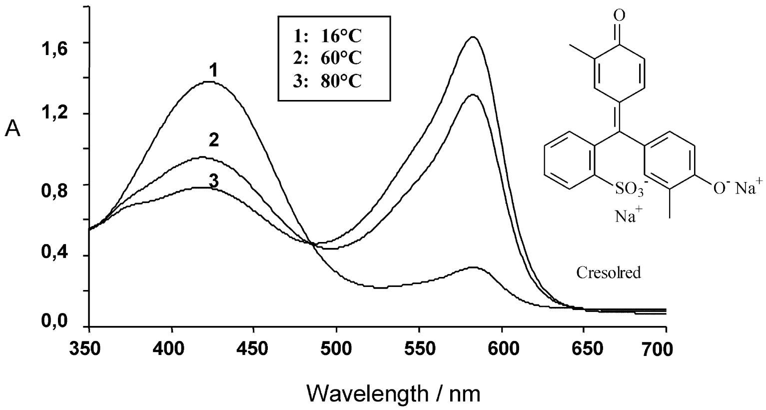

Fig. 9. Thermochromic behaviour of cresolol red embedded in a PVA/borax network at pH 8.5. UV/VIS-spektra ($d = 1$ cm) at different temperatures.

4. Thermochromic hydrogels

Gels with reversible colour changes, e.g. thermochromic gels are rarely described [77,78]. For many applications, e.g. dye sensors [79], large area displays with higher information density or intelligent windows, it is interesting to produce transparent hydrogels which in closed systems exhibit thermochromic behaviour in the practical relevant temperature range of 10–80°C. Recently we have found [80], that pH-sensitive dyes, like the Reichardt-dye $E_T(30)$, [81,82] or cresol red, embedded in an aqueous polyvinyl alcohol/borax/surfactant gel network can reversibly change their colour. The novel hydrogels are fully transparent at the investigated temperature range of 10–80°C. In case of $E_T(30)$ at pH = 8.5 the colour changes gradually from colourless at 10°C to a deep violet at 80°C. Similarly for cresol red a change from yellow to wine-red was observed. The corresponding UV/VIS-absorption for cresol red show an increase of the absorption maximum intensity at $\lambda = 581$ nm while the intensity of the second maximum at $\lambda = 419$ nm is reduced with raising temperature (Fig. 9). An explanation for the observed reversible colour changes in the closed hydrogel systems is given by a temperature-induced shift of the equilibrium between the phenolate and the phenol form of the dye molecules in the micro-environment of the gel network.

Acknowledgements

This work was supported by the Federal Ministry of Education, Science, Research and Technology (BMBF), Germany - Projekt No. 0329820B.

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