Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Optical and Electro-Optical Properties of Poly(2-hydroxyethylmethacrylate)/5CB Systems

F. Z. Elouali [a b], D. Aïnad Tabet [b] & U. Maschke [a]

[a] Laboratoire de Chimie Macromoléculaire (UMR CNRS 8009), Bâtiment C6, Université des Sciences et Technologies de Lille, Villeneuve d'Ascq, Cedex, France

[b] Laboratoire de Chimie Organique Physique et Macromoléculaire, Université Djillali Liabès, Sidi Bel Abbès, Algeria

Version of record first published: 01 Jun 2009

To cite this article: F. Z. Elouali, D. Aïnad Tabet & U. Maschke (2009): Optical and Electro-Optical Properties of Poly(2-hydroxyethylmethacrylate)/5CB Systems, Molecular Crystals and Liquid Crystals, 502:1, 77-86

To link to this article: http://dx.doi.org/10.1080/15421400902815746

Mol. Cryst. Liq. Cryst., Vol. 502, pp. 77–86, 2009

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400902815746

Taylor & Francis
Taylor & Francis Group

Optical and Electro-Optical Properties of Poly (2-hydroxyethylmethacrylate)/5CB Systems

F. Z. Elouali[1,2], D. Aïnad Tabet[2], and U. Maschke[1]
[1]Laboratoire de Chimie Macromoléculaire (UMR CNRS 8009), Bâtiment C6, Université des Sciences et Technologies de Lille, Villeneuve d'Ascq, Cedex, France
[2]Laboratoire de Chimie Organique Physique et Macromoléculaire, Université Djillali Liabès, Sidi Bel Abbès, Algeria

This paper reports on the phase behaviour of photochemically polymerized 2-hydroxyethyl methacrylate in a nematic liquid crystalline solvent. Samples were prepared via polymerization by ultraviolet (UV) radiation of initial solutions made of the reactive monomer 2-hydroxyethylmethacrylate (HEMA) and a photoinitiator (Darocur 1173). The swelling and deswelling properties were studied by polarized optical microscopy in a wide range of temperature for the low molecular weight liquid crystal 4-cyano-4′-pentylbiphenyl (5CB). Immersion of polymerized HEMA in an excess of 5CB did not exhibit any significant change of sample size and showed only limited dependence on temperature, indicating strong polymer/liquid crystal interactions.

Polymer/liquid crystal films were prepared by polymerization-induced phase separation of HEMA/Darocur 1173/5CB blends using UV radiation. The electro-optical behaviour of the films obtained was investigated as function of the initial composition and applied voltage. Strong memory effects have been observed in the case of samples prepared from 60 weight% 5CB/40 weight% HEMA.

Keywords: electro-optical properties; hydrogels; liquid crystals; memory effect; photopolymerization; swelling

The authors gratefully acknowledge financial support from Algerian and French governments allowing the stay of the first author (F.Z. Elouali) at the laboratory of Lille.

Address correspondence to U. Maschke, Laboratoire de Chimie Macromoléculaire UMR, CNRS N°8009, Université des Sciences et Technologies de Lille, 59655 Villeneuve d'Ascq, Cedex, France. E-mail: ulrich.maschke@univ-lille1.fr

1. INTRODUCTION

Hydrogels are hydrophilic polymer networks which may absorb from 10–20% (an arbitrary lower limit) up to thousands of times their dry weight in water [1,2]. Hydrogels may be chemically stable or they may degrade and eventually disintegrate and dissolve. They are called "reversible," or "physical" gels when the networks are held together by molecular entanglements, and/or secondary forces including ionic, H-bonding or hydrophobic forces. The manifest interest in hydrogels derives from their characteristics, particularly biocompatibility and non-toxicity [3,4]. Hydrogels based on Poly (2-hydroxyethylmethacrylate) (PHEMA) have been effective in ophthalmology field, due to their mechanical stability, high refractive index at room temperature ($n = 1.512$), and oxygen permeability. Interestingly, swollen PHEMA possess high light transmission capability in the visible and near-visible region, and PHEMA swelling behaviour greatly depends on temperature and penetrating solution. The extent of swelling is also determined by the balance between hydrophilic/hydrophobic groups, the length between links, and the architecture of the polymer.

The phase behaviour, swelling and deswelling properties of selected well defined PHEMA samples in a low molecular weight nematic LC will be discussed. A survey of the literature reveals a large number of theoretical and experimental reports mainly based on the swelling behaviour of isotropic polymer networks in isotropic solvents [5,6]. Only a limited number of reports are known combining synthetic polymeric hydrogels with opto-electronic materials [7–12]. The confinement of electro-optical materials in polymeric matrices has raised special interest due to their technological applications. It is part of systematic studies undertaken in our laboratory to explore the physical properties of composite materials made of polymers and low molecular weight LCs [13,14]. They are promising devices of light control and electrooptical applications because they can be switched electrically from a light-scattering "off state" to a highly transparent "on state."

In this work, PHEMA samples were immersed in a LC solvent and the swelling behavior was investigated as a function of temperature. Changes in the sample sizes from dry to swollen states were measured via optical microscopy for samples in the sub-millimeter size. To understand opto-electrical properties of synthesized polymer/LC films based on HEMA and 5CB, their transmission-voltage dependence has been studied in detail.

2. EXPERIMENTAL PART

2.1. Materials

The monofunctional monomer 2-hydroxyethyl methacrylate (HEMA) was purchased from Sigma-Aldrich and used without further purification. To initiate the reaction of free radical photopolymerization, 2-hydroxy-2-methyl-1-phenyl-propane-1 (commercial designation Darocur 1173, from Ciba-Geigy) was employed. The nematic LC used in this work was 4-cyano-4′-pentylbiphenyl (5CB), and was obtained from Synthon Chemicals GmbH (Wolfen, Germany).

5CB exhibits a crystalline to nematic transition temperature at $T_{CrN} = 23°C$, and a nematic to isotropic transition temperature at $T_{NI} = 35.5°C$. The chemical structures of the different components are given in Figure 1.

2.2. Polymer Gel Preparation

A blend of HEMA/Darocur 1173 was prepared in a ratio 99.5 weight% (wt.%)/0.5 (wt.%). This initial mixture was stirred mechanically at room temperature during several hours to become homogeneous, before it was cast in small flat sample holders. The samples were exposed to UV radiation under nitrogen atmosphere, using Philips TL08 UV lamps with a wavelength $\lambda = 365\,nm$ and an intensity $I_0 = 1.5 mW/cm^2$. The exposure time was fixed at 10 min although 5 min were sufficient to achieve complete conversion of monomer.

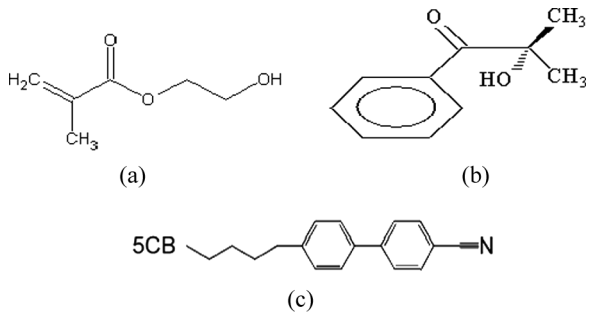

FIGURE 1 Chemical structures of the components of the initial mixtures prior to UV radiation exposure: (a) the monomer 2-hydroxyethyl methacrylate, (b) the photoinitiator Darocur 1173, and (c) the LC 5CB.

2.3. Swelling Measurements

Small specimens with nearly rectangular shapes of approximately 245 μm × 245 μm and thicknesses of roughly 60 μm, cut out from the dry PHEMA film, were used for swelling experiments to shorten the time required for equilibration (see Fig. 2 for an example). These samples were immersed in the LC solvent at room temperature and characterization was performed by observations via a polarized optical microscope in a wide range of temperatures. Micrographs were taken in intervals of 1°C using temperature increasing and decreasing ramps of 0.2°C/min, allowing the polymer samples to reach the thermodynamic equilibrium state at each temperature. A heating stage (Linkam LTS 350), a cooling unit (Linkam LNP 94/2), and a temperature controlling unit (Linkam TMS 94) were used together with a Olympus BX-41 polarized optical microscope, equipped with a Q-Imaging numerical camera (3.3MB). Measurements of length, width, and diagonals of the samples were collected as a function of temperature. Several duplicate samples were considered systematically to check reproducibility and averaged values of the results were used in data analysis.

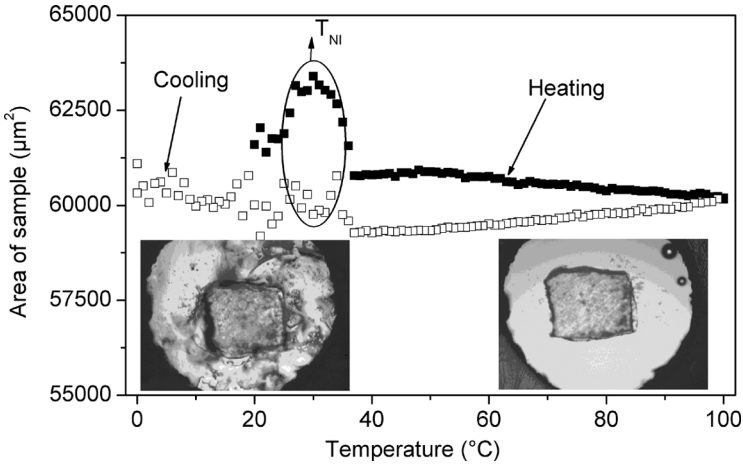

FIGURE 2 Swelling behavior of a PHEMA sample in the LC solvent 5CB as a function of temperature (heating cycle starting from room temperature to $T = 100°C$ and subsequent cooling cycle to $T = 0°C$). The two pictures were taken by polarized optical microscopy on the same sample at $T < T_{NI}$ (micrograph on the left side) and $T > T_{NI}$ (micrograph on the right side).

2.4. Polymer/LC Sample Preparation

Polymer/LC samples were prepared using the polymerization induced phase separation technique, starting from blends where the LC to monomer ratio was taken as 70 wt.%/30 wt.% and 60 wt.%/40 wt.%. A small amount of Darocur 1173 (2 wt.% compared to HEMA) was added to the initial blends. The homogeneous mixtures were sandwiched between Indium-Tin-Oxide (ITO) coated glass substrates so that the monomer/LC mixtures were in contact with both transparent conducting ITO layers. The sample thickness was about 15 μm.

2.5. Electro-Optical Measurements

Electro-optical experiments were performed at room temperature by measuring the transmission of an unpolarized HeNe laser light at a wavelength of $\lambda = 632.8$ nm orienting the films normal to the incident laser beam. The distance between the sample cell and the detector (silicon photodiode) was approximately 30 cm. The collection angle of the transmitted intensity was about ± 2. The uncorrected intensity of transmitted light was recorded on a micro-computer using an interface card (DAS 1600-2).

For electro-optical measurements, an external electric field was applied across the PDLC film. The output of a frequency generator was amplified and used to drive the shutter device. Starting from the electrical off-state, the applied sinusoidal voltage of frequency 145 Hz was increased continuously up to a desired maximum value V_{max}. It was subsequently decreased in the same way. The whole scan up and down ramp took 120 s with an additional measuring time of 60 s allowing to follow the relaxation behaviour of the transmittance in the off-state. The maxima of the voltage of the scan up/down cycles, V_{max}, were chosen in the following consecutive order: 10 V, 20 V, 30 V, 40 V,....

3. RESULTS AND DISCUSSION

The swelling behavior of PHEMA in LC solvent 5CB was investigated using polarized optical microscopy. This method is appropriate to small samples of sub-millimeter size which is particularly relevant to the case of low molecular weight LCs as solvent. Generally, the amount of solvent absorbed from polymeric samples increases with temperature and depends on polymer/solvent interactions. Chain stretching is high in a good solvent and low in a non-solvent. Depending on polymer/solvent interactions, the amount of solvent admitted in the polymer undergoes large changes.

The insets of Figure 2 exhibit two micrographs obtained by polarized optical microscopy observations showing the influence of temperature on a PHEMA sample. Both micrographs show the same sample immersed in 5CB at thermodynamic equilibrium. The micrograph on the left side of Figure 2 was taken below the nematic-isotropic transition temperature in the nematic phase of 5CB, whereas the photo on the right side was obtained in the isotropic phase of 5CB. The size variations in both x and y directions were taken into account by measuring the change of the sample area as a function of temperature.

Figure 2 displays the evolution of the area of PHEMA samples in 5CB as function of temperature. Only a weak effect of swelling and deswelling was found in the whole range of temperature explored, from 0°C to 100°C. A small swelling effect was observed around T_{NI} during the heating cycle and further temperature increase yields a slight size reduction of the sample. These results are in strong contrast with earlier investigations on chemically crosslinked Polybutylacrylate networks, where a strong increase of the degree of swelling was found around T_{NI} [15].

Kinetic swelling experiments from PHEMA, conducted in aqueous environnements at room temperature, revealed solvent uptake in the range of 50–60%. Since PHEMA samples were prepared in the absence of any added crosslinking agent, the obtained polymer was only loosely crosslinked, probably due to the presence of small amount of difunctional impurities. From these findings it can be assumed that the PHEMA/5CB interactions were rather strong. Following these lines, it would be interesting to investigate in-situ polymerized HEMA/5CB systems since LC will be forced to phase separate to a great extent from the formed PHEMA. Indeed, rather strong light scattering polymer/LC samples were obtained after UV-exposure of HEMA/5CB mixtures and the electro-optical response of these heterogeneous films was investigated as a function of applied electrical field.

Figure 3a illustrates transmittance versus voltage curves of UV-irradiated polymer/LC films obtained from initial mixture 60 wt.% 5CB/40 wt.% HEMA. The inset of Figure 3a shows that transmittance increases with applied voltage. At 10 V, the achieved transmittance was about 16%, whereas for films obtained from initial 70 wt.% 5CB/30 wt.% HEMA mixture, a transmittance at 10 V lower than 2% was observed (see inset of Fig. 3b).

If the voltage will be subsequently removed in both cases, transmittance in the electrical off-states will be identical to the initial T_{off} values. By successive increase of the electrical field, it was found that the transmittance of 60 wt.% 5CB/40 wt.% HEMA samples reached a horizontal plateau at about 80% in the on-state by applying voltages

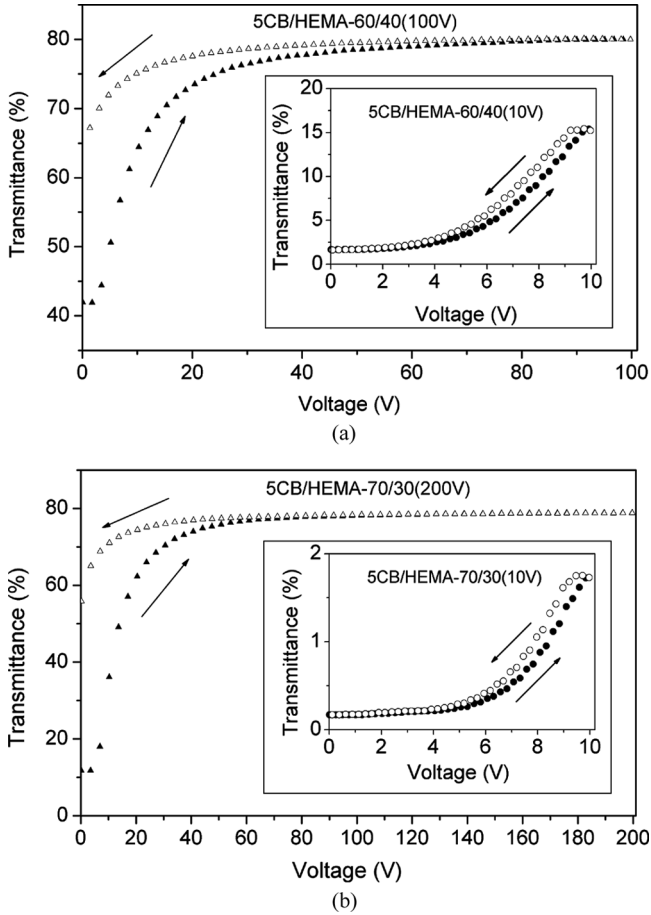

FIGURE 3 (a) Electro-optical response of 15 μm thick UV-irradiated polymer/LC films prepared using initial composition 60 wt.% 5CB/40 wt.% HEMA. (b) Transmission properties as function of applied voltage for UV-exposed polymer/LC films for initial composition 70 wt.% 5CB/30 wt.% HEMA.

above 40 V. When the voltage was removed, the transmittance did not return back to the initial level, but remained at a level of about $T_{off} = 65\%$, as shown in Figure 3a. This transparent state is preserved over a period of days.

Figure 3b shows that transmittance in the on-state of polymer/LC films prepared with initial composition of 70 wt.% 5CB/30 wt.% HEMA was 80% at voltages above 80 V. When the voltage was removed, the transmittance decreased only to approximately 55%, but

returned back to the initial off-state level during the following 60 s as will be discussed below.

Figure 4a shows the evolution of the transmittance as a function of time measured immediately after scan up and down voltage cycles with maxima of 100 and 200 V for polymerized 60 wt.% 5CB/40 wt.% HEMA and 70 wt.% 5CB/30 wt.% HEMA films, respectively. It can

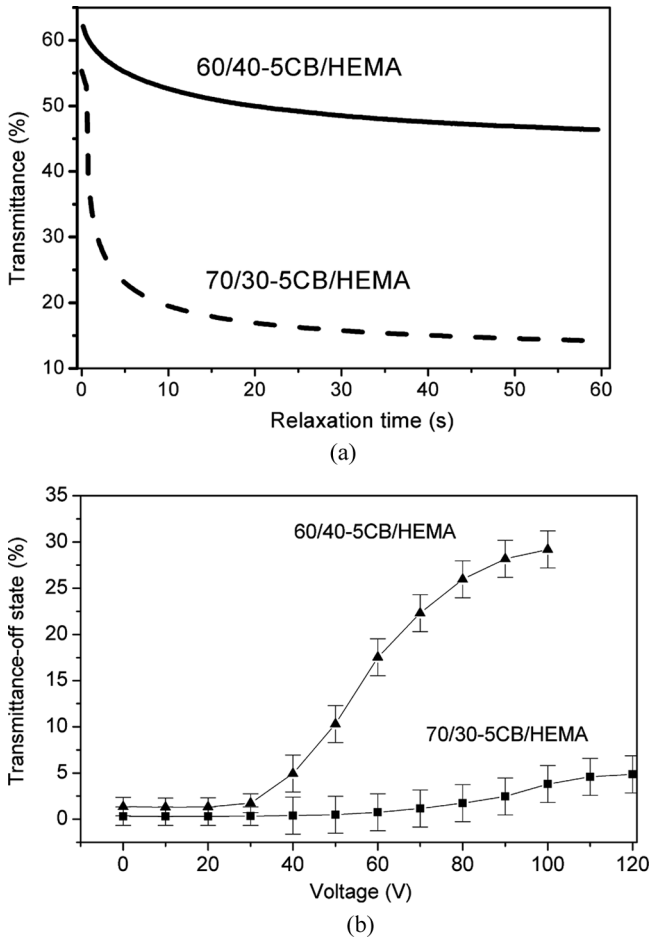

FIGURE 4 UV-irradiated 70 wt.%/30 wt.% and 60 wt.%/40 wt.% 5CB/HEMA films: (a) Transmittance as a function of time after removal of the applied electrical field. The transmission values at 60 s correspond roughly to the plateau values on Figure 4b, as expected. (b) Memory effect: dependence of the transmission values in the off states (T_{off}) on the maxima of the applied voltage scan up and down cycles. The continuous lines are guides for the eye.

be clearly seen that the transmittance decreases drastically from an initial value of 55% to 14% at $t = 60$ s for the sample prepared with initial composition 70 wt.% 5CB/30 wt.% HEMA. For the system with initial composition 60 wt.% 5CB/40 wt.% HEMA, the decrease of transmittance was less important, from 62% to 46%.

In relation with Figure 4a, Figure 4b illustrates the variation of the transmittance in the off state as function of the initial composition of PHEMA/5CB films and voltage maxima applied. In our electro-optical experiments, the maxima of the voltage of the scan up/down cycles V_{max} were chosen in the following consecutive order: 10 V, 20 V, 30 V, 40 V, ... until a plateau value of the transmittance was obtained.

The values of T_{off} in Figure 4b were taken at the beginning of the application of the different voltage scan up/down cycles. This figure shows two different regions. Below a voltage maximum value of approximately 30 V, the same transmittance values before and after applying the electrical field were obtained, for a given film, and these data were identical compared with the initial T_{off} values. Above $V_{max} = 30$ V, the films with initial composition 60 wt.% 5CB/40 wt.% HEMA exhibit continuously increasing T_{off} values in the field off state by further increasing the maxima of the voltage cycles applied. The transmission values T_{off} of the samples increased from 2% at 30 V to 40% at 110 V before reaching a plateau. This behavior is known as memory effect and has been investigated by some authors [7–12]. The memory effect is generally interpreted using the fact that the LC molecules do not completely relax back to their initial scattering off-state, if a sufficiently high electrical field has been applied. They remain partially aligned in the direction of the applied field even after it is removed. In this case, it can be assumed that the effective refractive index of this portion of the LC molecules is still close to the refractive index of the polymer matrix. The polymer/LC film prepared from initial mixture 60 wt.% 5CB/40 wt.% HEMA conserves, therefore, its transparent state to some extent.

Strong interactions between PHEMA and LC molecules might be the reason for the observed memory effect. Furthermore, it cannot be excluded that these UV-cured systems do not reach a chemically stable state under the given radiation conditions.

Only a weak memory effect was observed for samples with initial composition 70 wt.% 5CB/30 wt.% HEMA (see Fig. 4b).

4. CONCLUSION

By analyzing the swelling of photochemically polymerized HEMA in an excess of a low molecular weight LC solvent (5CB), only small

changes of sample size were observed upon application of heating and cooling cycles. It can be concluded that 5CB is a non-solvent of UV-exposed HEMA, probably due to the strong polymer/LC interactions.

The electro-optical responses of UV-polymerized HEMA/5CB films were investigated as function of composition and voltage. The transmission versus voltage curves show considerable differences between samples prepared from 60 wt.% 5CB/40 wt.% HEMA and 70 wt.% 5CB/30 wt.% HEMA. In particular, a strong memory effect was observed for the 60 wt.% 5CB/40 wt.% HEMA–based system.

REFERENCES

[1] Peppas, N. A. & Sahlin, J. (1996). *J. Biomaterials*, *17*, 1553.
[2] Ruel-Gariépy, E. & Leroux, J.-C. (2004). *Eur. J. Pharm. Biopharm.*, *58*, 409.
[3] Sershen, S. & West, J. (2002). *Adv. Drug Del. Rev.*, *54*, 1225.
[4] Lee, K. Y. & Mooney, D. J. (2001). *Chem. Rev.*, *101*, 1869.
[5] (a) Dusek, K. (Ed.) (1993) Responsive gels: Volume transitions I, *Adv. Polym. Sci.*, 109.
(b) Dusek, K. (Ed.) (1993). Responsive gels: Volume transitions II, *Adv. Polym. Sci.*, 110.
[6] Erman, B. & Mark, J. E. (1997). *Structure and Properties of Rubber-like Networks*, Oxford University Press: New York.
[7] Yamaguchi, R., Sudo, N., & Sato, S. (1995). *Mol. Cryst. Liq. Cryst.*, *262*, 119.
[8] (a) Yamaguchi, R. & Sato, S. (1992). *Jpn. J. Appl. Phys.*, *31*, 254.
(b) Yamaguchi, R. & Sato, S. (1991). *Jpn. J. Appl. Phys.*, *30*, 616.
[9] Yamaguchi, R. & Sato, S. (1993). *Liq. Cryst.*, *14*, 929.
[10] Yamaguchi, R., Ookawara, H., & Sato, S. (1992). *Jpn. J. Appl. Phys.*, *31*, 1093.
[11] Chang, S. J., Yin, Y. C., Lin, C. M., & Fuh, A. Y. G. (1996). *Liq. Cryst.*, *21*, 707.
[12] Chang, S. J., Lin, C. M., & Fuh, A. Y. G. (1996). *Liq. Cryst.*, *21*, 19.
[13] Gyselinck, F., Maschke, U., Traisnel, A., & Coqueret, X. (2000). *Liq. Cryst.*, *27*, 421.
[14] Maschke, U., Coqueret, X., & Benmouna, M. (2002). *Macromol. Rapid Commun.*, *23*, 159.
[15] Vendamme, R., Bouchaour, T., Pakula, T., Coqueret, X., Benmouna, M., & Maschke, U. (2004). *Macromol. Mat. Eng.*, *289*, 153.