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Hydroxypropyl–cellulose derivatives: phase behaviour of hydroxypropylcellulose methacrylate

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Abstract

Peculiar effects on the phase behaviour of hydroxypropylcellulose (HPC), obtained by the introduction of few methacrylic groups along the main chain, are discussed. In particular, the increase of mesophase stability in water, lowering the value of polymer concentration at which the anisotropic phase first appears with respect to underivatized HPC, as well as the decrease of stability of the anisotropic phase for neat polymers is illustrated and discussed in terms of substituent hydrophobicity.

Keywords: Hydroxypropylcellulose; Hydroxypropylcellulose methacrylate; Phase behaviour

1. Introduction

The first report concerning the mesogenic behaviour of hydroxypropylcellulose (HPC) is due to Werbowyj and Gray [1,2]. They noticed that aqueous solutions of HPC samples are birefringent at room temperature and show cholesteric texture when the volume fraction v_p of the polymer is higher than 0.37. Similar behaviour was successively found in other solvents, such as acetic acid [3], dichloroacetic acid [4], pyridine [5], dimethylacetamide [6]. However, the system more extensively investigated is the original HPC–H_2O. The phase diagram in the v_p range between 0 (pure water) and 1 (pure HPC) and at temperatures between 0 and 50°C, was determined by different authors [6–10]. All of them agree on the existence of a narrow biphasic region at low T and relatively high v_p, followed (at $T \cong 40°$) by a wide biphasic region, showing extensive turbidity. However, some important details, such as the presence of a thermotropic effect in the narrow region (i.e. the shift of the biphasic gap towards higher v_p values as T increases), as well as the shape of the wide region, are experimentally different for the various studies. This may be due to the experimental approach used by each author, but also the differences in chemical composition of the samples may not play a negligible role. In this respect, it is useful to remind that HPC is a rather heterogeneous polymer, due both to the polydispersity of the raw cellulose and to the number and distribution of propylene oxide residues along the chain. As a first consequence, only the average number of propylene oxide moles per mole of anhydroglucose unit is generally known. A method based on NMR spectra was suggested by Lee and Perlin [11] to determine both the total molar substitution (MS) and the substituent distribution on the different groups of cellulose repeat unit. In particular, they found that, although the reactivity of the three hydroxyl groups of the D-glucosyl residue differ notably with each other, in the chain extension reaction with propylene oxide such differences are not transferred to the OH residue of the propylene oxide substituent. Consequently, the hydroxypropyl residues are statistically distributed on all the reactive OH groups of the glucosidic ring. A fractionation procedure based on the extraction of a HPC sample with ethanol/*n*-heptane mixtures is described in Ref. [12] and allows us to obtain samples with different molecular weight. However, Fortin et al. [8], by applying the above method to a sample having MS = 6, found that MS increases as MW decreases. Therefore, although it is, in principle, possible to know MS and MW for a specific sample, the preparation of a series of samples having the same MW of the main chain and different MS or, vice versa, the same MS and different MW, is quite problematic. In the latter case, the trend of the limit volume fraction, v_p', for the appearance of the anisotropic phase as a function of MW may be supposed to be analogous to that observed for several semirigid lyotropic systems [4,13–15] (v_p' decreases to an asymptotic value as MW increases), while the effect of MS, that affects flexibility and diameter of the chain, as well as interactions with the

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Table 1
Synthetic conditions for HPC methacrylate samples

Sample	Acyl chloride/HPC_u (mol/mol)	DS	Temperature (°C)
HPCM1	0.39	0.05	5
HPCM2	0.40	0.05	5
HPCM3	0.43	0.06	5
HPCM4	0.60	0.08	5
HPCM5	0.77	0.10	5
HPCM6	0.79	0.09	5
HPCM7	1.35	0.19	5
HPCM8	1.35	0.20	5
HPCM9	3.00	0.50	5
HPCM10	4.49	0.70	5
HPCM11	5.41	0.88	5
HPCM12	0.09	0.01	0
HPCM13	0.32	0.02	0
HPCM14	0.53	0.03	0
HPCM15	0.83	0.05	0
HPCM16	1.38	0.09	0
HPCM17	1.95	0.13	0
HPCM18	2.55	0.19	0

solvent, is hardly valuable. Similar problems due to the heterogeneousness of commercial cellulosic samples were underlined in a recent paper by Rinaudo et al. [16], who suggested that the lack of samples with a well defined distribution of side substituents may be responsible for the only partial agreement of the experimental results by different authors.

Recently, we prepared some cellulose–polyolefin copolymers [17,18] and some hydrogels [19], starting from cellulose derivatives obtained by the reaction of cellulose with unsaturated acyl chlorides. The method proved to be useful even for HPC, not only for the aim previously described, but also in order to vary the polymer hydrophobicity. The results obtained by using methacryloyl chloride (MACl) are given in the following and, in our opinion, should contribute to clarify the role of hydrophobicity on the phase behaviour.

2. Experimental

2.1. Materials

HPC sample, supplied by Hercules Inc., analogous to that used in a previous work [6] was utilized for all syntheses. Its M_w and MS were 150 000 and 4 ± 0.5, respectively. The sample was dissolved in water at the polymer concentration $C_p = 5\%$ w/w, centrifuged at 10 000 rpm for 30 min to eliminate suspended particles, and freeze dried.

Dimethylacetamide (DMAc) was supplied by Fluka, distilled under vacuum and kept on molecular sieves.

Methacryloyl chloride (MACl) (Fluka) was used as received and stored at low temperature under dry nitrogen.

Doubly distilled water was used to prepare HPC and solution of its derivatives.

2.2. Methods

Synthesis of hydroxypropylcellulose methacrylate (HPCM) was performed by dissolving HPC in DMAc at $C_p = 3\%$ w/w; a suitable amount of MACl was added at constant temperature, under nitrogen flow and left to react for 22 h. The product was precipitated with ether, filtered, dissolved in water and freeze dried.

FTIR spectra measurements were performed by using a Bruker (Karlsruhe) IFS66 FT/IR spectrometer. Thin films ($\cong 50\ \mu$), obtained by evaporation of HPCM solutions in ethyl alcohol, were analysed. Comparison of the absorbance at 3450 cm^{-1} (–OH) and at 1720 cm^{-1} (–C=O) allows the evaluation of the substitution degree (DS), i.e. the moles of acyl residues per mole of HPC repeat unit (HPC_u). The molecular weight of HPC repeat unit was calculated considering the average MS value = 4. Hydroxyethylacrylate was used as standard, according to the method suggested by Mitchell et al. [20].

Optical microscopy: the HPCM critical concentration C'_p (easily correlated to v'_p [6]) at which anisotropy may be first observed for a sample put between crossed polarizers, at room temperature, was determined by using a Polyvar Pol Reichert polarizing microscope.

Thermal analysis: softening temperature T_s and isotropization temperature T_i of samples, previously dried in a vacuum oven at 40°C for 48 h, were determined by using a polarising microscope equipped with a Mettler FP82 hot stage. T_i was also measured by means of a Mettler DSC 30 differential scanning calorimeter. Sample amount of 10–12 mg was pre-treated in a nitrogen atmosphere at 150°C for 10 min and rapidly cooled in liquid nitrogen before measurement. The scan was carried out on films at 20°C/min from −20 to 300°C.

The cloud point T_c of isotropic solutions, 5% w/w, of HPC and HPCM samples was estimated by measurement of the turbidity of the solutions as the temperature increases. Quartz thin cells, 1 mm thick, were held between two heated plates that permit to control the heating rate. Direct measurement of the solution temperature was possible by using a thermocouple put inside the cell. A photometer was used to measure the variation of the intensity of a laser beam going straight through the cell.

CD spectra were recorded at room temperature by a Jasco J-500A spectropolarimeter, using a quartz cell having a thickness of 0.01 mm, sealed with Teflon film.

3. Results and discussion

Table 1 presents DS values of HPCM samples as a function of the molar ratio between MACl and HPC_u at 0 and 5°C. Fig. 1 shows their respective trends. As previously observed for other systems [17,18], the reaction temperature

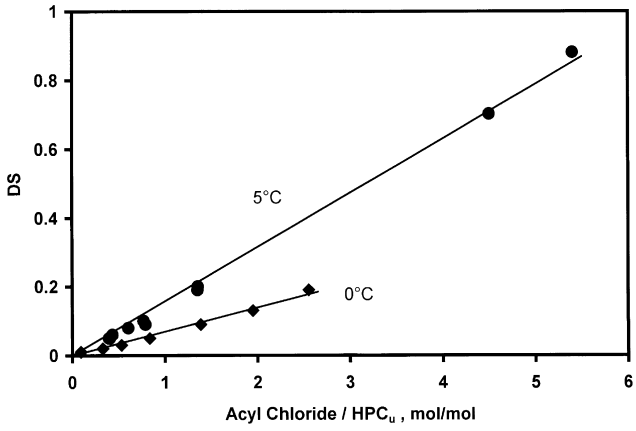


Fig. 1. DS as a function of the acyl chloride/HPC_u molar ratio at two temperatures: 0°C (◆) and 5°C (●).

strongly affects DS, at the same ratio MACl/HPC_u. This result puts in evidence the need for an accurate thermostatation of the system during the reaction. When the above condition is fulfilled, the data reproducibility is sufficiently good and DS fluctuation may be estimated as ±10%.

Aqueous solutions of some samples of Table 1 were prepared to test the existence of a lyotropic phase at suitable concentrations. The lack of good solubility in water when DS > 0.2 limits the mesophase formation in this solvent to samples having lower DS values, while in DMAc it was possible to explore the lyotropic behaviour up to DS = 0.5. The limited solubility of HPCM in aqueous solutions is reasonably related to the increase of hydrophobicity of the polymer when DS increases. A parameter, already used by other authors to discuss the increase of HPC hydrophobicity with MS [7], is the ratio C/O of the molecule. Therefore, we assumed this ratio as a crude index of hydrophobicity extensible to the series cellulose–HPC–HPCM. Table 2 gives the atomic contents of C and O and their ratio calculated per repeat unit of HPC and HPCM chains. Obviously, C/O ratio increases by increasing MS and DS, but this does not seem sufficient to explain the observed behaviours. In fact, a HPC sample having as an example MS = 4 and C/O = 2 is completely soluble in water [6,10], while a HPCM sample having MS = 4, DS = 0.25 and C/O = 2.03 is practically insoluble.

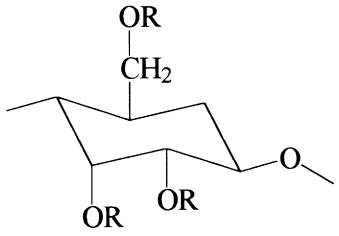
Table 2
Number of C and O atoms per repeat unit of CE, HPC at different MS and HPCM at different DS

Compound	C	O	C/O
Cellulose	6.0	5.0	1.20
HPC/MS1	9.0	6.0	1.50
HPC/MS2	12.0	7.0	1.71
HPC/MS3	15.0	8.0	1.88
HPC/MS4	18.0	9.0	2.00
HPCM(MS4/DS 0.1)	18.4	9.1	2.02
HPCM(MS4/DS 0.2)	18.8	9.2	2.04
HPCM(MS4/DS 0.25)	19.0	9.25	2.05

Consequently, the specific effect of $-OC-C(CH_3)=CH_2$ groups, grafted to HPCM chain, have to be taken in proper account. Namely, it is the water structuring around these groups that causes the improvement of hydrophobic interactions among HPCM macromolecules and determines the decrease of solubility.

A confirmation of this hypothesis is based on the good solubility of HPCM samples at DS up to ≅ 1 in DMAc and ethanol, as specifically verified in our laboratory.

From a chemical point of view, a repeat unit of our derivative may be represented as follows:



where R = H or $[(CH_2-CH(CH_3)O)_x-(OC-C(CH_3)=CH_2)_y]$: x may be 0 or a multiple of 1, while y 0 or 1. When $y = 0$, the group $[-(OC-C(CH_3)=CH_2)_y]$ is replaced by H. For our sample and referring to the glucosidic unit, the average value of isopropyl residue (MS) is 4, while that of methacrylic residue (DS) varies between 0.01 and 0.88.

The mesogenic behaviour of some of the samples listed in Table 1 was studied determining C'_p in water and DMAc, T_c in water (the demixing process was never observed in DMAc [6]) and T_i the transition temperature between anisotropic to isotropic phase of the neat sample.

The first determination refers to C'_p of the original (underivatized) HPC. At room temperature we found $C'_p = 40.5\%$ in aqueous solution and 41.5% in DMAc. The results in water well agree with literature data: in particular Werbowyj et al. [1,2] found $C'_p = 41\%$, unaffected by the molecular weight in the range 60×10^3–100×10^3. Other values for samples having different MS and MW are 43% [9] and 44% [10]. C'_p in DMAc is a little higher than in water and agree with previous results [6]. Fig. 2 gives the

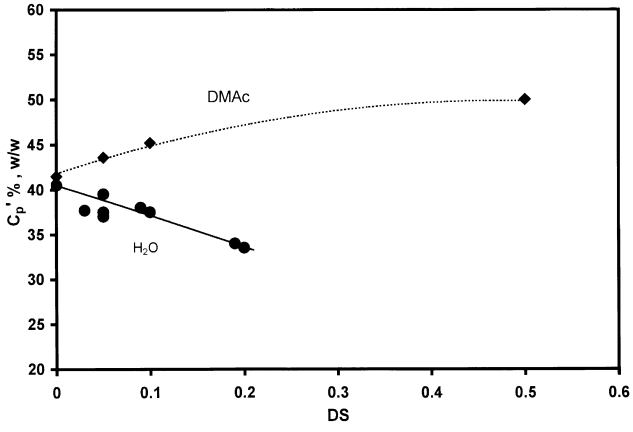


Fig. 2. Threshold concentration C'_p for the appearance of the anisotropic phase vs. DS in water (●) and DMAc (◆).

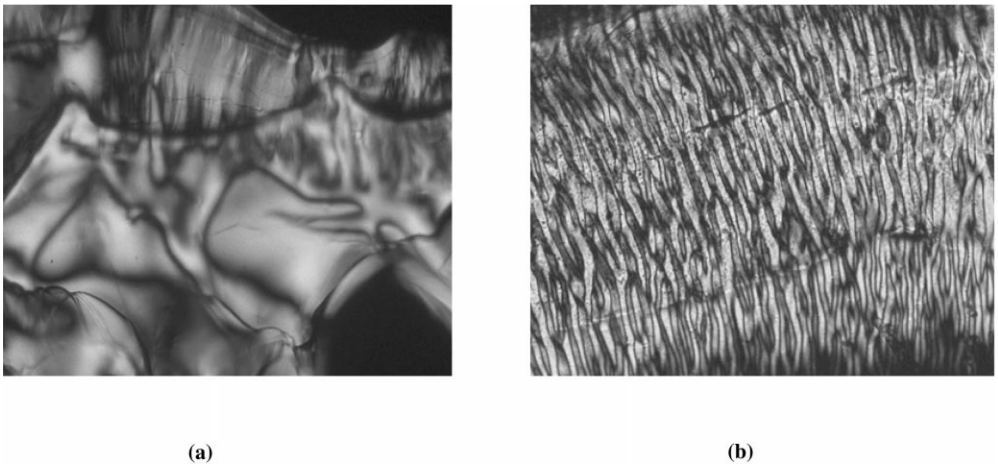


Fig. 3. Photographs of HMCM15/water solution, $C_p = 42\%$, under polarizing microscope: (a) solution at rest and (b) banded texture induced by a moderate external shear.

trends of C'_p vs. DS in both the solvents. First of all we would like to underline the decrease of C'_p in water as DS increases. The sample at DS = 0.2 shows anisotropy when the concentration is 33.5%, seven points lower than the value of neat HPC. A different behaviour in DMAc is evident and will be discussed in the following.

The anisotropic phase observed by optical microscopy at $C_p \gg C'_p$ was identified as a cholesteric one by circular dichroism spectra which showed a deep band of ellipticity vs. λ for all samples.

Fig. 3 shows the pictures of an aqueous solution of sample HPCM 5 at $C_p = 42\%$ at rest (a) and after shear (b). Brightness of the sample under cross-polarized light reveals the presence of an anisotropic phase (a), while the banded structure in (b) is common to nematic or cholesteric mesophase, when relaxed after a linear shear [21,22].

The cloud temperature, T_c, of 12 samples dissolved in water at $C_p = 5\%$ (isotropic region), is shown as a function of DS on Fig. 4. T_c decreases from ~40°C (unsubstituted HPC) to $T_c \sim 30$°C (HPCM having DS = 0.2).

The above trend agrees with the results reported in Ref. [8] for HPC fractions at different MS. In fact, the authors observed that the phase separation temperature of a 2% aqueous solution varies from $T_c = 65$°C at MS = 2 to $T_c = 40$°C at MS = 5. The demixing process was interpreted as due to the substitution of most polymer–water contacts by polymer–polymer and water–water contacts (concentrated and diluted phase, respectively), and related to the melting of water molecules in the hydrophobic regions specific of the polymeric molecular structure under examination. The lack of a similar biphasic region in DMAc [6], whose structuring is surely different from that of water, indirectly supports these results.

Moreover the mentioned T_c decrease of about 10°C, when DS increases from 0 to 0.2, confirms the strong hydrophobic effect due to the introduction of (–OC–C(CH_3)=CH_2) residue, especially if compared to a decrease of 25°C when MS varies by 3 units.

Determination of the transition temperature T_i between ordered and isotropic phases of neat HPCM samples was performed by using thin films ($\cong 50\ \mu$) obtained as reported in Section 2. All samples, when observed under cross-polarized light, are birefringent at room temperature and convert to a fluid liquid crystalline phase as T reaches the softening temperature T_s, whose value depends on DS. A further increase of T up to a specific value T_i causes the isotropization of the sample, i.e. the anisotropy disappearance. Similar behaviour has been also observed for underivatized HPC [23]: in particular, T_s was associated to the presence of microcrystallites which, dispersed in the liquid crystalline phase, hamper the system to flow. By increasing T their melting causes the transition to isotropic state at T_i. Values of T_s and T_i of our samples are collected in Table 3 and reported in Fig. 5 as functions of DS. Neither the thermal pre-treatment nor the heating cycle at the optical microscope cause crosslinking of the samples up to DS ≅ 0.2, as demonstrated by their total solubility in DMAc after the treatment. However, if DSC analysis is used, the pre-heating at 150°C starts up double bond reactions when DS > 0.1. T_i values evaluated by DSC

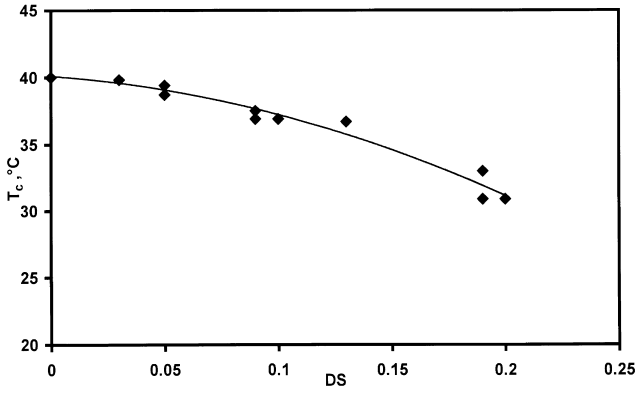


Fig. 4. Trend of the cloud temperature T_c vs. DS.

Table 3
Softening and isotropization temperatures of HPCM samples

Sample	DS	T_s (°C)[a]	T_i (°C)[a]	T_i (°C)[b]	T_g °C[b]
HPC	0	130	190	199	7
HPCM13	0.02	115	190		
HPCM14	0.03	115	190	195	3
HPCM2	0.05	115	182	182	− 1
HPCM15	0.05	115	178	188	1
HPCM6	0.09	110	176	176	− 6
HPCM5	0.10	105	172	183	− 5
HPCM18	0.19	55	136		
HPCM8	0.20	50	131	–	− 17[c]

[a] From optical microscopy.
[b] From DSC analysis.
[c] Measured after a milder pre-treatment.

measurements are given in the same figure and agree well with those obtained by optical observations.

It is interesting to observe that an increase of DS from 0 to 0.2 causes T_s and T_i to decrease from 130 to 50°C and from 190 to 131°C, respectively. The strong effect on T_s and T_i of methacrylate substituents can be related to the volume increase of side groups, which reduces the attractive interchain interactions and the hydrogen bonds.

The last column of Table 3 gives T_g values measured by DSC analysis. The determination was performed after a thermal pre-treatment, as reported in Section 2, in order to make uniform the initial state and to dry the samples. Considerations previously reported on the lack of crosslinking are obviously valid also in this case and only if DS increases over 0.1 a milder pre-treatment must be used (5 min at 105°C). According to what was observed by Rusing et al. [24] for HPC esters, T_g decreases as the esterification degree increases. By comparing $\Delta T_g/\Delta DS$ values of our samples and of their HPC butyl esters the values $\cong 120$ and 35, respectively, were found. These values confirm the strong effect of the methacrylic group on the polymer

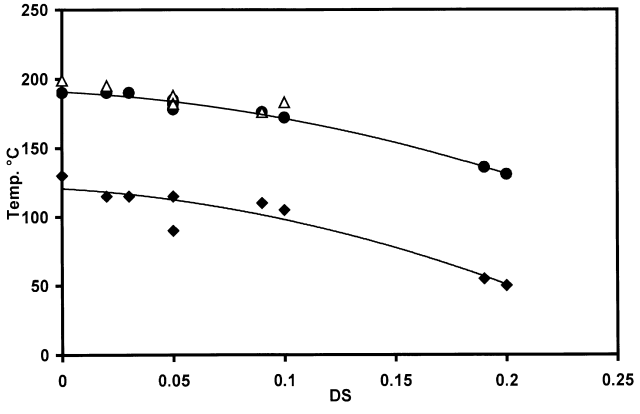


Fig. 5. Trend of the softening temperature T_s (◆) and isotropization temperature T_i vs. DS: (●) T_i from optical microscopy and (△) T_i from differential scanning calorimetry.

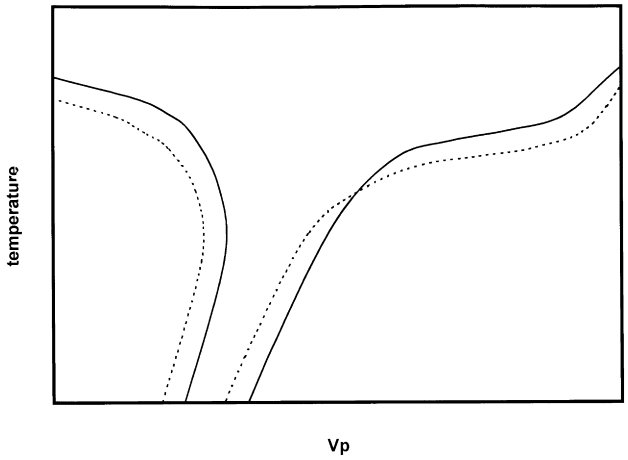


Fig. 6. Hypothetical phase diagram for HPCM having DS = 0 (full line) and DS > 0 (dashed line).

behaviour. A final observation concerning our derivatives is that T_g is always quite lower than T_s, indicating two widely different phenomena.

4. Conclusions

If we consider the whole set of C_p', T_c and T_i data, it is clear that they are consistent with a progressive shift of the phase diagram towards the origin of the axes (C_p,T), as DS increases. Fig. 6 gives a qualitative representation of the phenomenon for two hypothetical samples having DS = 0 (pure HPC) and DS > 0: the narrow chimney was purposely inclined to take into account the thermotropic effect observed for HPC in DMAc [6], and more recently, in water [10]. According to Flory's theory [25] the shift of the narrow biphasic gap towards lower C_p' values may be attributed to two different reasons: the variation of chain rigidity and (or) the presence of intermolecular anisotropic interactions. However, in real systems, other phenomena, such as inhomogeneous repeat units, intermolecular aggregation, polydispersity and so on, may influence the phase diagram. In our case it is hard to distinguish among the various possibilities; however, the increased structuring of water molecules around the hydrophobic residues, surely promotes a kind of hydrophobic bond among the polymer chains. Consequently, association phenomena, not considered by the theory, may not play a negligible role to determine the phase properties. A further confirmation of the specific role of hydrophobic interactions may be found, when considering the behaviour in dimethylacetamide where C_p' is quite higher than in water and increases with DS (see Fig. 2).

Similar considerations are valid to explain the decrease of T_c as DS increases, while in the case of T_i are the intermolecular interactions which become weaker as DS increases.

The main conclusion of this work is that the increase of hydrophobicity for HPC, due to the introduction of specific

side groups, allows to increase the stability of the anisotropic phase in aqueous solutions, while the mesophase stability for the neat polymer decreases. Application of these results to finely tune the swelling behaviour of hydrogels is in progress.

Acknowledgements

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