# Mesomorphic transitions in a mixture of a flexible and a semi-rigid polymer

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Phase studies on a mixture of two polymers are presented, one of which is mesomorphic. We have systematically examined the influence of the molecular weight of the flexible polymer (including the oligomers) and of the semi-flexible polymer. In addition to the effect of the molecular weight, specific interactions are important for compatibility and formation of a homogeneous mesomorphic phase. The nature of this phase is demonstrated to be cholesteric and the pitch is determined.

**(Keywords: liquid crystals; polymer; phase transitions; phase diagrams; mixtures; cholesteric; gel)**

## INTRODUCTION

This paper is a continuation of the systematic study of liquid crystalline polymer mixtures. We wish to identify the mechanisms leading to miscibility and to the formation of a homogenous mesomorphic phase. Systems of increasing complexity have been investigated: the pure thermotropic polymer[1], the polymer in a simple solvent[1] or in mixtures of solvents[2], mixtures of two polymers with a solvent[3-5].

Here we present results on phase diagrams in a binary mixture of two polymers, one of which is a semi-rigid thermotropic polymer, and the other, a flexible polymer. Two areas of active research and extensive industrial interest are involved: polymer blends[6-8] and liquid crystalline polymers[9,10].

In addition to the synthesis of new chain structures, a recent trend in polymer technology is the use of synergy to design new polymer blends for specific applications. As an example, mechanical strength of a blend can be enhanced by addition of a mesomorphic component. Cellulosics are often used in commercial blends[7,8] but in many cases, the evidence for miscibility is insufficient, and further data is required.

The system chosen for the present study is hydroxypropyl cellulose (HPC), well-known to be a thermotropic cholesteric gel[11]. For the non-mesomorphic component, we selected polyethylene glycol (PEG) with chemical structure $H{-}O{-}(CH_2{-}CH_2{-}O)_n{-}H$. Ethylene glycol ($n=1$) and diethylene glycol ($n=2$) are good solvents for methyl cellulose[12] and cellulose tricarbanilate and hydrogen bonds could occur between the PEG monomer and the hydroxyls of HPC. The molecular conformation of PEG is helical in the crystal[13-17] and possibly also in water[18] but a flexible coil conformation is manifest in the melt[19].

In the absence of specific attractive interactions or chemical and sterical similarity, miscibility is not general for polymers[6] and liquid crystalline polymer systems are no exception. In mixtures with flexible polymers[3,20] and with small molecule liquid crystals[21] aggregation and phase separation are observed. Indeed, in the extreme case of a bad solvent, local crystalline order can be destroyed by the presence of a flexible chain[22] and mean field theory[23,24] is no longer applicable. This was investigated in small molecule liquid crystal and flexible polymer mixtures[25-28]. However, a liquid crystal and a mesomorphic polymer of similar chemical structure (and generally of low molecular weight) can be dissolved over a wide range of concentrations[29-32].

It is therefore of interest to study the phase separation and phase transition of a mesomorphic polymer in a good monomeric solvent and then in a polymeric solvent of increasing molecular weight. Further information is obtained by variation of the molecular weight of the semi-rigid component for a fixed degree of polymerization of the flexible polymer. This allows one to test the relative importance of the different contributions to the heat of mixing and to obtain information on chain length dependence. In rigid rod systems[33], theoretical considerations predict a decrease in the entropy leading to immiscibility and destruction of the homogenous ordered phase. In semi-flexible systems, the specific (excluded volume, H-bonds) and orientational (Van der Waals, steric) are dependent not only on chemical composition but on the conformation also[34-36].

The purpose of the present paper is to study phase diagrams of mixtures of hydroxypropyl cellulose and polyethylene glycol using a polarizing microscope. We have endeavoured to specify, by experimental means, the influence of the molecular weight of the mesomorphic polymer and the maximum molecular weight of the flexible polymer in obtaining miscibility. Observations on liquid crystalline textures and measurement of the cholesteric pitch of the polymer blends lend further support to our conclusions.

## EXPERIMENTAL

The HPC samples (Aldrich) had molecular weights

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$M_w = 100\,000$, $300\,000$ and $1\,000\,000$. The $M_w = 60\,000$ sample was obtained from Polysciences. The ethylene glycol, diethylene glycol and PEG ($M_w$: 300, 600, 1000 and 6800) are synthesized by Aldrich and were used without further treatment. The concentrations of the polymer mixtures are given in weight % (g HPC/g solution).

Although it is advisable to form the mixtures in the isotropic phase, we have preferred to avoid the risk of decomposition of the thermotropic polymer. The solutions were therefore heated for several hours at 110°C and PEG was dissolved in the cholesteric phase of HPC. Homogeneous solutions were obtained 2–7 days after mixing, depending on the viscosity of the resulting solution.

A polarizing microscope was used to study the anisotropy of the mixtures. The solutions were placed between glass plates and temperature dependence investigated with help of a heat stage. The intensity of light transmitted by the anisotropic sample between crossed polarizers was measured with a photomultiplier, connected to a graphic plotter. The temperature corresponding to complete disappearance of birefringence and the appearance of a black field determines the transition from anisotropic to isotropic phase. The microscope was equipped with a camera which allows simultaneous photography of sample textures during heating and cooling cycles.

An automatic spectrophotometer was used to study the optical transmission of the samples for unpolarized light between 400 and 2500 nm wavelengths.

## RESULTS AND DISCUSSION

In the present experiments, two transition temperatures were accessible for each concentration of HPC/PEG.

(1) $T_c$, the temperature at which the anisotropic phase disappears on heating.

(2) $T_c^*$, the temperature at which the anisotropic phase appears on cooling.

These temperatures coincide within experimental error at the cholesteric–isotropic transition temperature $T_0$ of pure thermotropic HPC. The thermal cycles are reproducible and the width narrows on increasing the molecular weight of the mesomorphic polymer (*Figure 1*).

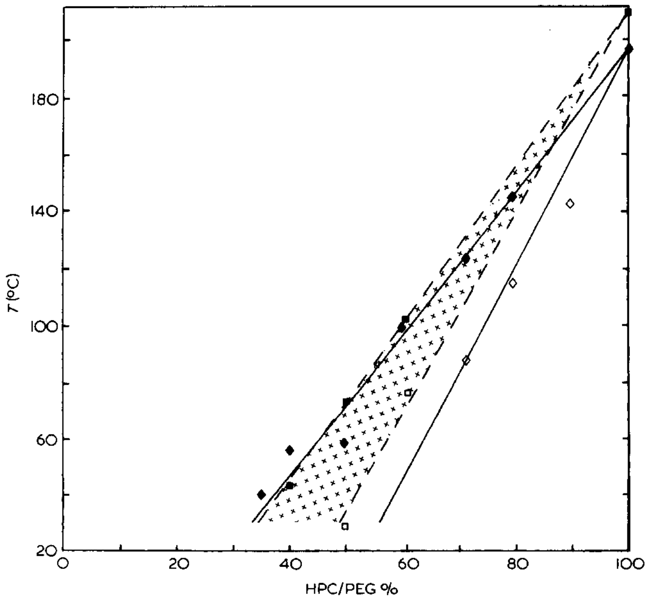

Figure 1 Phase diagrams of solutions: Transition temperature as a function of wt% HPC: HPC 60000/PEG 300 (—◆—) $T_c$ on heating; (—◇—) $T_c^*$ on cooling. HPC 100000/PEG 300 (—■—) $T_c$ on heating; (—□—) $T_c^*$ on cooling

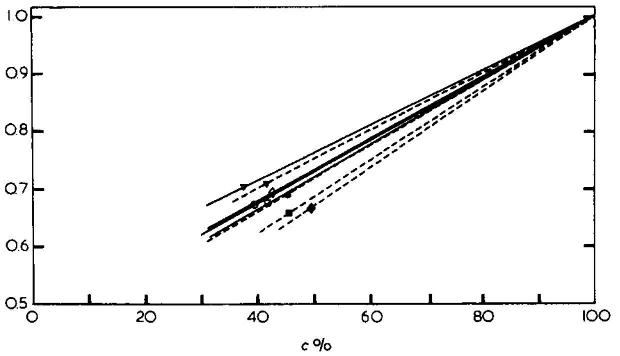

Figure 2 Reduced transition temperatures $T^* = T/T_0$ (K) as function of the concentration c% g/g (HPC) for solutions: (—◆—) HPC 60000/DMAC; (—◇—) HPC 60000/PEG 300; (—■—) HPC 100000/DMAC; (—□—) HPC 100000/PEG 300; (—●—) HPC 300000/DMAC; (—○—) HPC 300000/PEG 300; (—▲—) HPC 1000000/DMAC; (—△—) HPC 1000000/PEG 300. For clarity, only the low concentration point is marked on the experimental curve

Biphase separation was clearly observed only for high PEG molecular weights ($M_w \geqslant 1000$). As in previous experiments[1], the exact boundaries of the phase separated regions eluded specification and only $T_c$, less sensitive to experimental error (relaxation times, flow, surface effects), was plotted.

### *Influence of molecular weight of the mesomorphic polymer*

The PEG 300 molecule, with a degree of polymerization of 6 and a length (for zig-zag conformation) of ~20 Å is significantly shorter than the HPC molecule for the given range of molecular weights. We expect PEG 300 to act as a simple solvent with behaviour similar to the quasi-spherical solvent dimethylacetamide (DMAC) investigated previously[1].

*Figure 2* shows the results for the reduced phase transition temperature $T^* = T_c/T_0$ as a function of HPC concentration for four molecular weights of the mesomorphic component ($M_w = 60\,000$, $100\,000$, $300\,000$, $1\,000\,000$).

The variation with $M_w$ (HPC) is weaker in PEG than in DMAC but depends markedly on the degree of substitution of the HPC molecule and therefore on the origin of the HPC sample. The larger the $M_w$ (HPC), the smaller the difference in $T^*$ between PEG and DMAC solutions. However, it should be noted that the mixtures obtained with HPC (1 000 000) are elastic gels and extremely difficult to study with any accuracy. The values given should be understood as being indicative only.

In *Figure 3*, the critical concentration for the transition to the isotropic phase at 25°C are plotted as a function of $M_w$ (HPC). The values lie somewhat below the critical concentration for the HPC/DMAC system. The structure of the anisotropic phase is also similar, and *Figure 4* shows the typical anisotropic texture.

### *Influence of the molecular weight of the flexible polymer*

In the HPC 60 000 samples, the existence of blends was investigated for PEG of $M_w$ 300 ($DP = 6$), 600, 1000 and 6800 ($DP = 153$).

Due to the flexibility of the chain, PEG appears to have no effect on the orientation of the mesomorphic polymer.

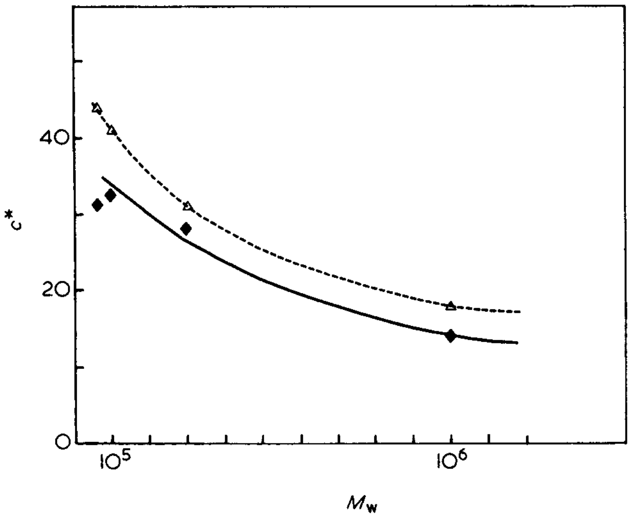

**Figure 3** Critical concentration $c^*$ as function of molecular weight of HPC in solution with: $c^*$:wt% HPC in (—△—) DMAC; (—◆—) PEG 300

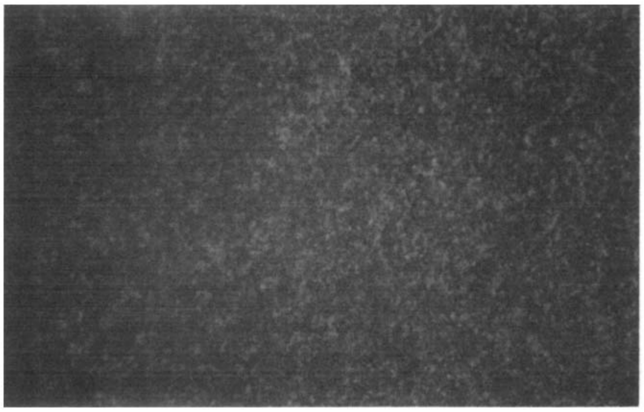

**Figure 4** Structure of anisotropic phase: polygonal texture of solution HPC 60000 Polysciences/PEG 300 70.97% (magnification = 680)

The flexible chains simply insert between the HPC molecules and dilute the anisotropic interactions. Increasing the length of the flexible chain should therefore not result in a variation of the anisotropy of the mixture. However, demixing could be expected to occur.

In *Figure 5* we show the resulting phase diagrams for the PEG/HPC 60 000 mixtures. In PEG 300 and 600, the transition temperatures $T_c$ virtually coincide, as well as in PEG 1000 above 80%. Clearly defined biphasic separation occurs for the first time in PEG 1000 at low HPC concentrations. The dotted line in *Figure 5* corresponds to the disappearance of anisotropy in the HPC-rich globules present in the wide biphasic zone. Demixing in the isotropic phase above this temperature may persist, but cannot be demonstrated by this method. Visual observation of the samples outside the microscope does not indicate visible isotropic liquid–liquid phase separation.

At higher $M_w$ (PEG), complete immiscibility occurs in the temperature range investigated and the transition temperature change for pure HPC can be observed in the polarizing microscope. This is supported by the ternary system HPC (60 000)/PEG (3400)/water which is inhomogeneous and forms white threads in suspension.

To test for specific interactions between the monomers of the flexible and rigid chains, we have also investigated phase diagrams of HPC in the monomer (ethylene glycol EG) and dimer (diethylene glycol DEG) of PEG. The solutions obtained are clear and extremely viscous. In contrast to previous experiments, on heating, the plotted birefringence does not decay continuously at the transition to isotropy but shows an initial decrease followed by an increase in anisotropy and then rapid total extinction. The anomalous shape of these curves could be due to crosslinking (gel) or relaxation phenomena.

The extinction temperatures are given in *Figure 6* as a function of HPC concentration. The behaviour of the monomer and dimer are quite different from the PEG chain at the same concentration of ethylene glycol monomers. Strong polymer/solvent interactions seem to occur in the short molecules which are not possible with the longer PEG chains. Intermolecular hydrogen bonding is of importance in these systems and could be weakened by the flexibility and curved conformations of the PEG

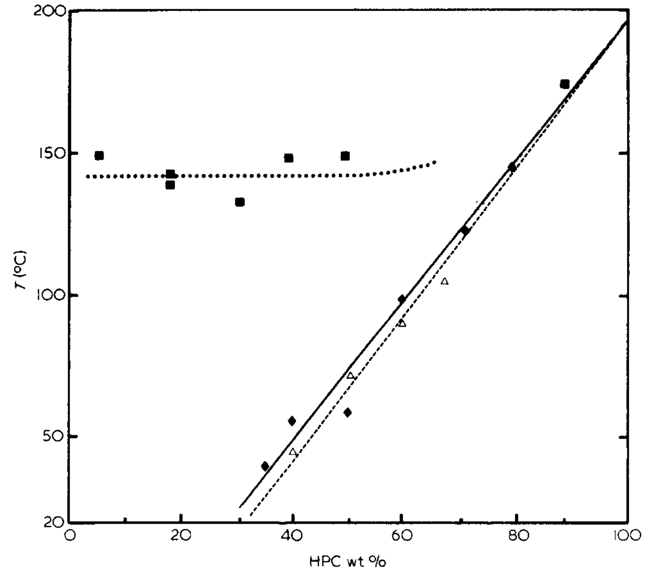

**Figure 5** Phase diagrams of solutions: $T_c$ as function of HPC wt%: (—◆—) HPC 60000/PEG 300; (—△—) HPC 60000/PEG 600; (··■··) HPC 60000/PEG 1000

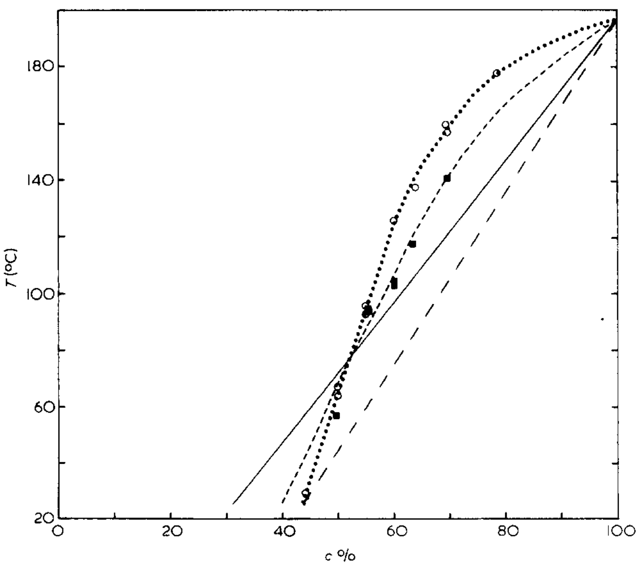

**Figure 6** Phase diagrams of solutions: $T_c$ as a function of HPC wt%: (– – –) HPC 60000/DMAC; (———) HPC 60000/PEG 300; (—■—) HPC 60000/diethylene glycol; (·····) HPC 60000/ethylene glycol

chain. Ethylene glycol and diethylene glycol could also bond to two HPC chains forming crosslinked ladder-like structures, not feasible for longer chains of PEG.

### *Nature of the mesomorphic phase*

The mesomorphic phase of HPC is cholesteric in nature and the anisotropic mixtures with PEG show focal conic textures. The ethylene and diethylene glycol mixtures are iridescent with dominant green or violet colouring.

The pitch of the cholesteric phase of the mixtures has been determined by optical measurements. The peak of the optical transmission spectra displays the cholesteric nature and the maximum spectrophotometric reflection in thin samples occurs at wavelength $\lambda = \bar{n}p$, where $\bar{n}$ is the average refractive index of the mixture[37,38]. This peak is superposed on the vibrational spectra of the molecules so that the method is limited to wavelengths between 0.4 to 1.5 µm. At room temperature (25°C) the flexible polymer blend HPC 60 000/PEG 300 (concentration 79.24%) shows a peak of weak intensity around 650 nm.

In *Figure 7*, the concentration dependence of $\bar{n}p$ is given for EG and DEG. Only a weak variation is observed compared with DMAC[38] or even water[3]. At 70% HPC, the pitch is estimated around 300 nm, using approximate values for the average refractive index (HPC (film)[39]: $\bar{n} = 1484$, EG at 20°C: $\bar{n} = 1431$, DEG at 20°C: $\bar{n} = 1446$).

A weak relation between the molar volume and the cholesteric pitch is found within a family of the same chemical type[38]. Along with water, EG and DEG seem to form a family of H-bound solvents, with symmetric OH groups at each end. Creation of strong crosslinkings and 'frozen in' gel-like structures would explain the weak variation of the cholesteric pitch with concentration and is consistent with the measured phase diagrams.

## CONCLUSIONS

Polymer compatibility is the exception rather than the rule and this is confirmed by present studies on HPC/PEG systems. At low molecular weights, PEG is compatible with HPC in the concentration range and temperature interval investigated. This is due to specific attractive, intermolecular interactions (H-bonds). As the chain length of the flexible polymer is increased, these interactions are weakened due to chain flexibility and demixing occurs over a wide range of concentrations and temperatures in high molecular weight PEG/HPC mixtures.

The anisotropic phase transition is shifted to higher temperatures as the molecular weight of the semi-rigid polymer is increased. No effect on increasing the molecular weight of the flexible polymer is found (apart from demixing which simply destroys the homogeneous anisotropic phase) but, in the monomer and dimer of PEG, there is a possibility of crosslinked structures occurring.

Light scattering studies of these systems would be of interest for further investigation of gel formation[6] and demixing.

Existence of crosslinking bonds between the polymer components in these mesomorphic polymer mixtures makes these systems candidates for ordered polymer gels[40] or even solid materials with liquid crystalline organization[41,42].

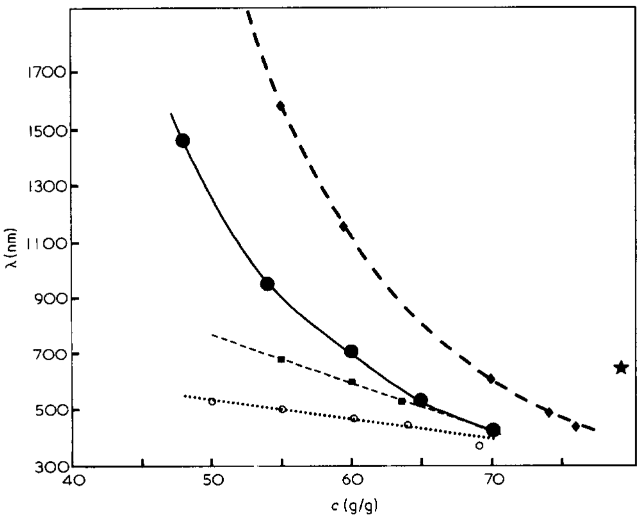

**Figure 7** Wavelength for transmission peak $\lambda$ (nm) in cholesteric HPC solutions as function of concentration wt% HPC for: (·····) HPC 60000/ethylene glycol; (—■—) HPC 60000/diethylene glycol; (—◆—) HPC 100000/DMAC; (—●—) HPC 60000/water; (★) HPC 60000/PEG 300

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