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Temperature-Concentration Phase Diagram of PEO-Urea

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Summary: The present paper reports on the phase diagram of the system PEO/Urea as established by differential scanning calorimetry. From this phase diagram one PEO/Urea compound is indentified with a stoichiometry 1/2. This value is in agreement with results derived from X-ray diffraction.

Keywords: compounds; phase diagram; poly[ethylene oxide]; urea

Introduction

Poly[oxyethylene] (PEO) forms compounds with a large variety or organic and inorganic molecules, such as urea and thiourea.[1-4] The phase diagrams in many systems, particularly with *para*-dihalogeno-benzene molecules,[1] have been reported. From these diagrams the number and the stoichiometry of the compounds have been obtained. While many investigations have been carried out with urea, which was the first PEO/solvent compound ever observed, the temperature-concentration phase diagram is still missing. This paper presents this phase diagram as obtained from differential scanning calorimetry. The results are discussed in light of the molecular structure derived from X-ray diffraction experiments.[5]

Experimental

The PEO samples were purchased from Aldrich. Two samples were used: one with a weight-averaged molecular weight of M_w= 3 10^5 g/mol with and polydispersity M_w/ M_n= 2 for the high urea contents, and one M_w= 6 10^3 g/mol for PEO contents above C_{PEO}= 0.8 (w/w). Urea was also purchased from Aldrich and use without further purification.

The PEO/urea samples were first prepared in test tubes by heating above the melting temperature of urea and by applying a vigorous stirring in order to obtain homogeneous solutions. They were then cooled down to room temperature. About 10 mg were taken out

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from the test tubes, and then placed into DSC sample pans that were hermetically sealed. Before taking any data, the samples were melted well above the melting temperature of urea and of the compound (namely at 160°C) and cooled down to room temperature. Differential calorimetry measurements were performed on a DSC4 from PERKIN-ELMER at a heating rate of 5°C/min.

The optical micrographs were obtained on a NIKON OPTIPHOT-2 equipped with a digital camera DXm1200, and using LCIA software for image processing and analysis.

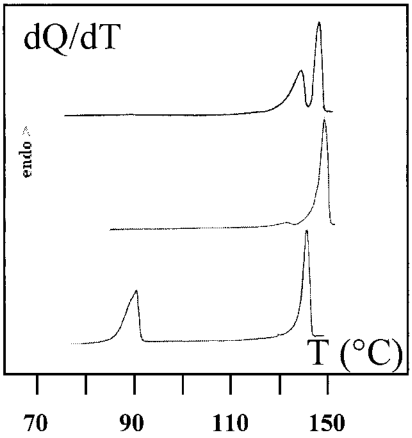

Figure 1. Typical thermograms obtained by differential scanning calorimetry at a heating rate of 5°C/m. Upper C_{PEO}= 0.1 (w/w), middle C_{PEO}= 0.25 (w/w), lower C_{PEO}= 0.6 (w/w).

Results and Discussion

As can be seen in figure 1, three types of endotherms can be observed. For *low PEO* contents two endotherms are seen at high temperature, that are close to the urea melting point. Close to what will be identified as the stoichiometric composition of the PEO/urea compound, only one endotherm is essentially observed, while for *high PEO* contents a second endotherm appears at lower temperature, that turns out to be actually close to pure PEO melting temperature.

The corresponding temperature-concentration phase diagram is plotted in figure 2, together with the corresponding Tamman's diagram (latent heats ΔH associated with all the 1st order thermal events as a function of the polymer concentration in w/w).

This phase diagram clearly evidences the formation of a PEO/urea complex whose stoichiometric composition is C= 0.26±0.03, and which displays congruent melting. The stoichiometric composition is derived both from the temperature-concentration phase diagram and from the Tamman's diagram. As a matter of fact, the enthalpy associated with the terminal melting goes, as expected, through a maximum at this composition. Also, the enthalpies associated with the eutectic events (invariance of temperatures at T= 135°C for C< 0.26 and T= 60°C for C> 0.26) become zero at the stoichiometric composition. The value C= 0.26 yields a stoichiometry of about *1 PEO monomer/2 urea molecules*. This value is in excellent agreement with what has been computed from the cristalline lattice derived from X-ray data [5].

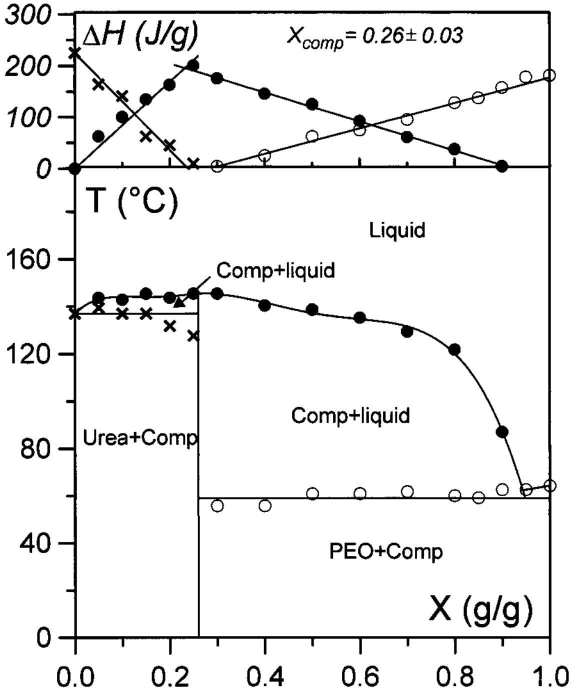

Figure 2. Temperature-concentration phase diagram PEO/Urea. On top Tamman's diagram representing the melting enthalpies ΔH (Joules per gramme of material) associated with the different thermal events (symbols correspond in both diagrams).

The morphology of the compound is shown in figure 3 from an optical micrograph obtained after quenching to room temperature a PEO/Urea sample whose concentration is close to the stoichiometric composition. As can be seen large spherulitic stuctures are obtained. Note that no such structures exist for the pure urea, unlike what is seen for pure PEO.

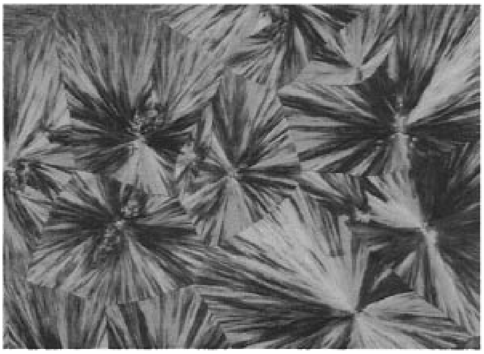

Figure 3. Optical micrograph obtained from a 0.3 g/g PEO/Urea, namely close to the stoichiometric composition.

Concluding remarks

The temperature-concentration phase diagram PEO/Urea is now available, and can thus be compared to previous diagrams obtained for PEO/dihalogenobenzenes. The compound formed with urea is a congruently-melting compound as with most of the PEO/dihalogenobenzenes. The stoichiometric with urea reaches, however, its highest value ever found for PEO complexes.

It is worth emphasizing that the stoichiometry is straightforwardly obtained from the Tamman's diagram, namely from the variation of the enthalpies associated with the different thermal events. This again emphasizes that this type of diagram is highly relevant [6], and thus very helpful for determining the stoichiometric composition with great accuracy.

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[1] M. Dosiere, *Macromol. Symp.* **1997**, *114,* 63
[2] J. Parrod, A. Kohler, G.Hild, *Compt. Rend. Acad. Sci.* **1958**, *246,* 1046
[3] J. Parrod, A. Kohler, G. Hild, *Makromol. Chem.* **1964**, *75,* 52
[4] H. Tadokoro, T. Yoshihara, Y. Chatani, S. Murahashi, *J. Polym. Sci.* **1964**, *B2,* 363
[5] A. Chenite, F. Brisse, *Macromolecules* **1991**, *24*, 2221
[6] J.M. Guenet, *Macromol. Symp.* **2003**, *203* 1