

A preparation of high-molecular poly(ethylene-oxide)-urea complexes from a solution and their structural changes on heating

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The preparation of high-molecular poly(ethylene oxide)-urea molecular complex by mixing their benzene and methanol solutions had been studied. The composition of the soluble and insoluble solid dispersed phase in benzene-methanol mixture had been investigated by means of X-ray and calorimetric analyses. It is shown that at molar ratio between poly(ethylene oxide) and urea of 1:2, which corresponds to the molecular complex composition, the yield of solid dispersed phase increases in a non-linear mode with an extension of the interaction time to 50 hours and after that it doesn't change any more.

The structural changes of poly(ethylene oxide)-urea molecular complex on heating from room temperature up to 147.5 °C had been studied using high-temperature X-ray analyses. It was shown that improvement processes of the molecular complex crystal structure were carried out in the temperature range before melting.

Key words: poly(ethylene-oxide), urea, complexes, preparation, structure.

INTRODUCTION

It is known that poly(ethylene oxide) (PEO) and urea form crystal molecular complex (MC) by mixing [1–5]. The molar ratio of PEO and urea in the molecular complex is 1:2. It has been established that the MC crystal structure is different from the crystal structure of the initial components [4, 5]. Its melting temperature ($T_m=144.5$ °C) is higher than the melting temperature of PEO (65 °C) and urea (132 °C).

Till now there are no references available concerning investigation of the structural changes in PEO-urea MC on heating and cooling. Wide-angle X-ray is an useful method for this purpose. The structure and the structural transformations of high-molecular PEO-urea molecular complex on heating and its mixtures with the initial components have been studied by means of this method. The results obtained are the subject discussed in the present paper.

EXPERIMENTAL

High-molecular PEO “Badimol”, produced industrially by “Chemist plant” at Dimitrovgrad with a molecular weight, determined viscosimetrically $M_v=2.7 \times 10^6$ was used for the preparation of PEO-urea molecular complex and their binary mixtures with the initial components. The urea is chem. pure for analysis, supplied by “Riedel de Hoen-Germany”. The PEO content in its urea mixtures was changed from 15 to 90 wt.%, which corresponds to the change of PEO-urea molar ratio from 1:3.5 to 1:0.1.

PEO-urea binary mixtures were prepared by mixing a 1% solution of PEO in benzene with methanol solutions of urea (10 wt.%) at 20 °C and benzene:methanol ratio of 1:0.27 volume parts. After some time in the range from 1 to 200 hours, the resulting insoluble precipitate was separated by a decantation and it was washed out with benzene. The decanted solution was evaporated under vacuum at 50 °C. The resulting solid residuum and the washed precipitate were dried at 50 °C under vacuum to a constant weight.

The X-ray investigations were carried out at room and elevated temperature by an apparatus “Dron-3” – Russia and “Tur-M 611” – Germany with Ni-filtered $\text{CuK}\alpha$ radiation under a reflection

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condition in the angular range (2θ) from 8 to 44° . A differential scanning calorimeter "DSC-111", a product of Setaram, France, was also used.

RESULTS AND DISCUSSION

A heterophase system of a solid dispersed phase and a liquid continuous phase is obtained by mixing monophased PEO solutions in benzene and a methanol solution of urea at a temperature of 20°C . The content and the composition of the insoluble solid dispersed phase depend on the initial ratio of the components PEO and urea and on the interaction period. At PEO-urea ratio of 1:2 molar fractions, corresponding to the molecular complex composition, the solid dispersed phase yield, which is insoluble in a benzene-methanol mixture increases in a non-linear mode with an extension of the interaction period 50 hours, it reaches 75–80 wt.% towards PEO-urea mixture and it doesn't change any more (Fig. 1, curve 1).

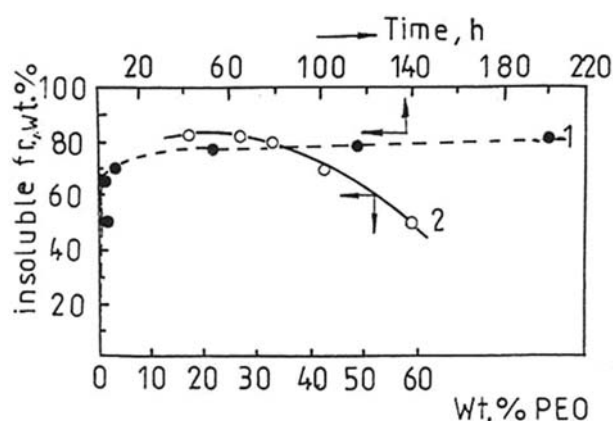


Fig. 1. Dependence of production of insoluble fraction in PEO-urea mixtures on the PEO content in the initial mixture (curve 2) and on the interaction period at PEO-urea ratio of 1:2 molar fractions (curve 1)

It has been established by means of X-ray and calorimetry, that the liquid phase and the solid fraction, dissolved in it and separated after the evaporation of a benzene-methanol mixture, represents PEO-urea molecular complex (Fig. 2, curve 4; Fig. 3, curve 2; Fig. 4, curve 3, 4).

The PEO-urea interaction at a ratio of 1:2 molar fractions and the formation of a molecular complex are carried out relatively quickly at the conditions investigated. Almost a complete (100%) association in a molecular complex has been observed. After 50 hours equilibrium between the soluble and insolu-

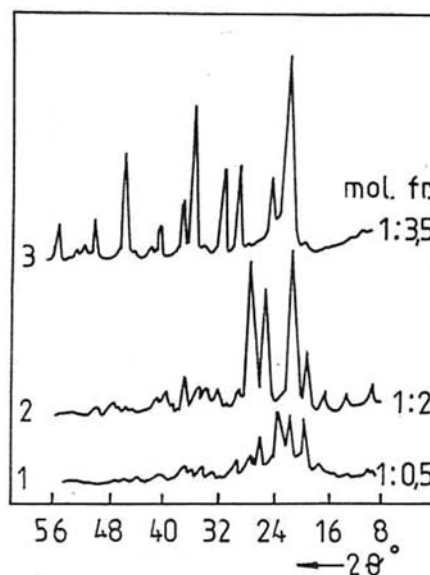


Fig. 2. Wide-angle X-ray diffractograms of PEO-urea mixtures, prepared from a solution (insoluble fraction). PEO - urea ratio, molar fractions: curve 1 - 0:1; curve 2 - 1:0; curve 3 - 1:0.5; curve 4 - 1:2; curve 5 - 1:3.5

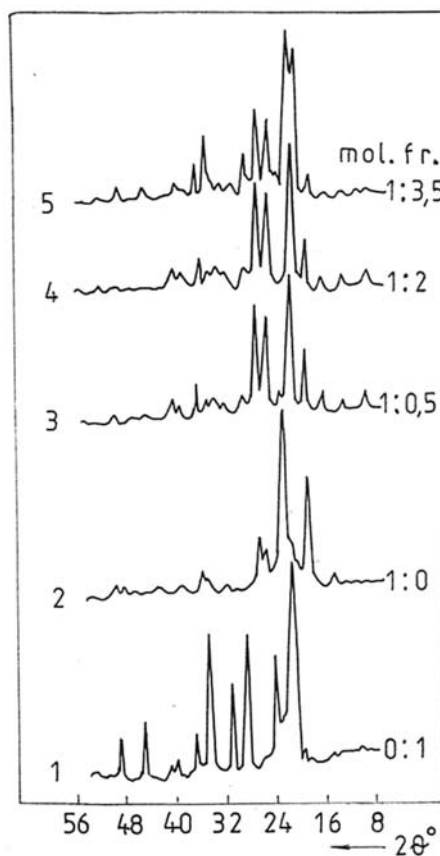


Fig. 3. Wide-angle X-ray diffractograms of PEO-urea mixtures, prepared from a solution (soluble fraction). PEO-urea ratio, molar fractions: curve 1 - 1:0.5; curve 2 - 1:2; curve 3 - 1:3.5.

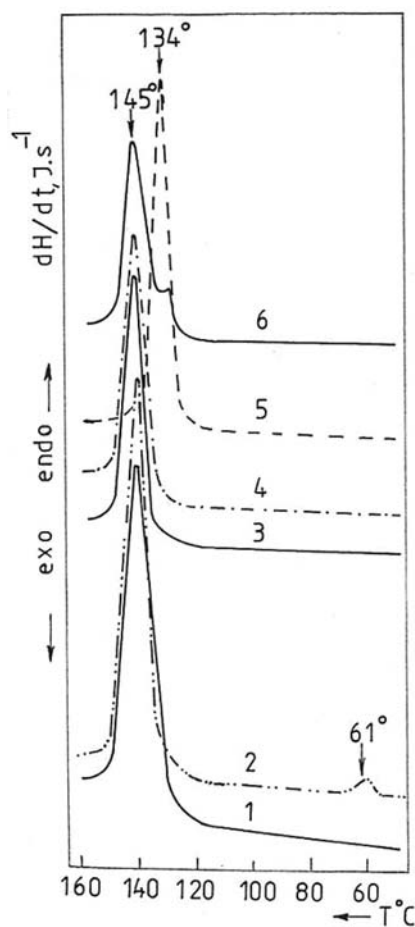


Fig. 4. DSC curves on heating of insoluble (1, 3, 6) and soluble (2, 4, 5) fractions in a benzene-methanol mixture of PEO-urea binary system. Molar fractions of PEO and urea: curves 1, 2 – 1:0; curves 3, 4 – 1:2 and curves 5, 6 – 1:3.5

ble fraction of the molecular complex in a benzene-methanol mixtures is established (Fig. 1, curve 1).

PEO-urea mixtures with a content of the first component from 17.3 to 59.5 wt.% in a benzene-methanol solution at an interaction period of 50 hours and at identical other conditions are prepared. The dependence of the insoluble fraction yield on the proportion between the two components is presented in Fig. 1, curve 2. It has been established by means of X-ray and calorimetry, that the insoluble fraction represents PEO-urea molecular complex at an urea content in the initial mixture from 0.5 to 2 molar fractions per ethylene oxide unit (Fig. 2, curves 3, 4; Fig. 4, curves 1, 3). The insoluble fraction represents PEO-urea molecular complex and traces of free urea at an urea content higher than 2 molar fractions per ethylene oxide unit (Fig. 2, curve 5; Fig. 4, curve 6).

It has been established as it was expected from the results obtained that the soluble fraction in

a benzene-methanol mixture differ in a composition from the insoluble solid dispersed phase, when the initial PEO-urea ratio is different from the complex composition. At a PEO content higher than 26.8 wt.% towards its urea mixture (less than 2 moles of urea per one monomeric unit), the soluble fraction in solid state represents molecular complex and free PE mixture, which form separate crystal phases (Fig. 3, curve 1; Fig. 4, curve 2). When the urea content in the initial mixture is above 73.2 wt.% towards its PEO mixture (above 2 moles of urea per ethylene oxide unit), the soluble fraction in solid state contains mainly free urea (Fig. 3, curve 3; Fig. 4, curve 5).

The structural changes on heating of PEO-urea molecular complex from room temperature to 147.5 °C have been investigated using high-temperature X-ray (Fig. 5).

It has been established that on first heating in the range about 120 to 135 °C, a slight but measurable increase of the integral intensity of the reflexes is observed, due to MC, 002 ($2\theta = 19.42^\circ$), 202 ($2\theta = 27.35^\circ$) and 102 ($2\theta = 21.64^\circ$) and also decrease of their half-width is observed (Fig. 6, 7).

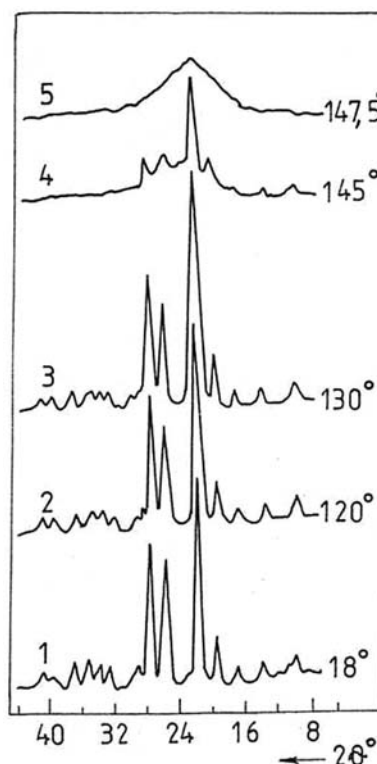


Fig. 5. Wide-angle X-ray diffractograms of PEO-urea MC, prepared from a solution (1:2 molar fractions) at different temperatures. First heating temperature, °C: curve 1–18; curve 2–120; curve 3–130; curve 4–145; curve 5–147.5

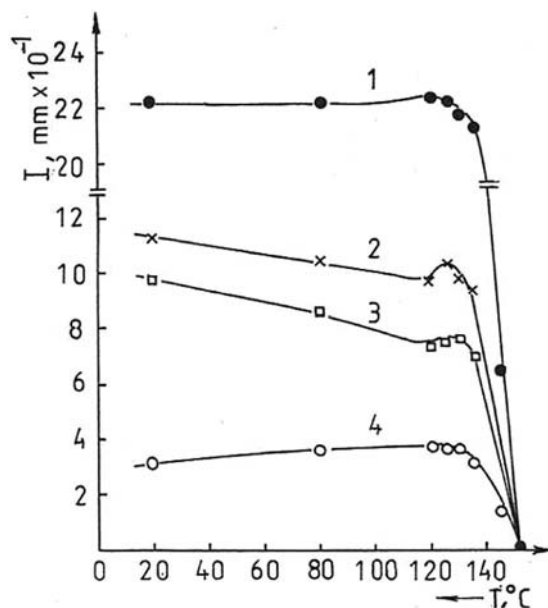


Fig. 6. Dependence of intensity of crystal reflexes in the wide-angle X-ray diffractograms of PEO-urea MC (1:2 molar fractions) (prepared from a solution), on the heating temperature, 20: 1–25.5°; 2–21.64°; 3–27.35°; 4–19.42°

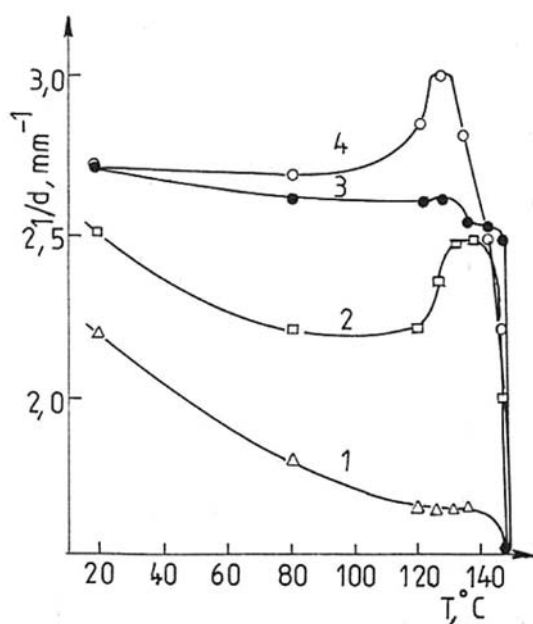


Fig. 7. Dependence of integral half-width of crystal reflexes in the wide-angle X-ray diffractograms of PEO-urea MC (1:2 molar fractions), prepared from a solution, on the heating temperature, 20: 1–25.5°; 2–27.35°; 3–21.64°; 4–19.42°

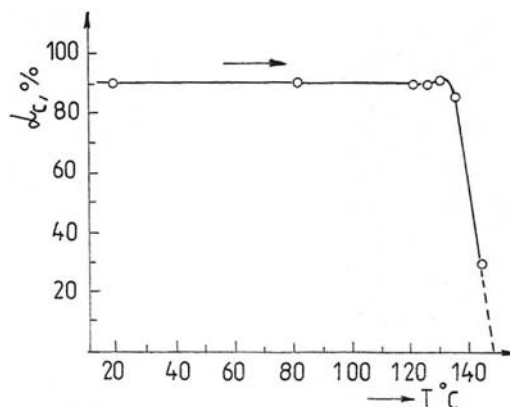


Fig. 8. Dependence of X-ray degree of crystallinity (α_c) of PEO-urea MC (1:2 molar fractions), prepared from a solution, on the temperature

Above 135 °C the intensity of the diffraction maximums of the molecular complex crystal phase (Fig. 6) and the degree of crystallinity (Fig. 8) abruptly decrease.

This temperature coincides with the initial melting temperature of the molecular complex determined calorimetrically. Consequently, improvement processes of the molecular complex crystal structure are carried out on heating in the temperature range before melting. Similar effects have been observed earlier (Fig. 6, 7) for high-molecular PEO and they are explained with the structural changes of the crystal phase into plastic state.

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ПОЛУЧАВАНЕ НА КОМПЛЕКСИ НА ВИСОКОМОЛЕКУЛЕН
ПОЛИЕТИЛЕНОКСИД И КАРБАМИД ОТ РАЗТВОР И СТРУКТУРНИТЕ
ИМ ПРОМЕНИ ПРИ НАГРЯВАНЕ

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(Резюме)

Получен бе молекулен комплекс от високомолекулен полиетиленоксид и карбамид чрез смесване на техни бензенови и метанолни разтвори. Композицията на разтворимата и неразтворимата твърда дисперсна фаза в бензен–метанолната смес беше изследвана рентгеноструктурно и калориметрично. Беше показано, че при молно съотношение между полиетиленоксида и карбамида 1:2, съответстващо на молекуления комплекс, количеството на твърдата дисперсна фаза нараства нелинейно с увеличаване на реакционното време до 50 часа и след това не се изменя повече.

Структурните изменения на молекуления комплекс между полиетиленоксида и карбамида при нагряване от стайна температура до 147.5 °С бяха изследвани с помощта високотемпературна прахова рентгенова дифрактометрия. Показано беше, че в температурния интервал преди топене се усъвършенства кристалната структура на молекуления комплекс.