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NANOSCALE EFFECTS IN TEMPERATURE INDUCED POLYMER COATINGS

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Abstract. In this paper the results of recent studies on the application of lower critical solution temperature (LCST) phenomena of polymer solutions to the surface modification of flat and spherical substrates are reported. It has been found that controlled polymer deposition can be achieved at temperatures exceeding LCST. The obtained polymer coating exhibits a peculiar surface morphology and, if particles are introduced, can be highly effective in pigment dispersions stabilizing. It has been established that the temperature induced polymer deposition can be carried out as the finely dispersed component precipitation on the substrate surface that goes along with the polymer deposition at temperatures exceeding LCST, which in its turn allows to modify the pigments surface when finely dispersed additives are incorporated into the surface modifying coating.

Keywords: polymer coatings, nanotechnology, temperature control, surface modification, lower critical solution temperature.

1. Introduction

The coating of the substrate with an organic polymer film is often required for application technology reasons. In the light of nanotechnology, coatings exhibiting features on the nanoscale are of increasing interest: this includes both coatings on more or less extended flat surfaces as well as surface modification of particles.

As to the technologies of film formation, besides conventional casting from solution (or dispersion) by solvent removal, a novel variant is to take advantage of temperature induced critical phenomena of polymer solutions. Polymer deposition on a substrate upon exceeding the lower critical solution temperature (LCST) or by cooling beyond the upper critical solution temperature (UCST) is particularly promising for the fabrication of coatings with novel surface properties [1-4].

2. Experimental

Materials employed for coating experiments were in most cases commercially available poly(oxyethylene-boxypropylene-b-oxyethylene) 3-block copolymers (P(EO-b-POb-EO) without and with polymerizable end-functionalities [2] and for selected comparative studies polystyrene and hydrophobically modified poly(oxyethylene)urethane model systems were taken [3]. Si-wafers were used as substrates for film deposition and surface topology studies, and particle surface modification was investigated with commercially available pigments. Turbidity measurements were carried out with a photometer TP 1 from Tepper Instruments. Previously published data were used to obtain information regarding the methodology of polymer deposition and coatings analysis [2].

3. Results and Discussion

In order to further explore the effect of the polymer concentration on the change in the surface topology of LCST deposited P(EO-b-PO-b-EO), a phase diagram was first established. Surprisingly, the turbidity measurements revealed two LCSTs in a semi-diluted concentration regime in a polymer weight fraction w2 between about $0.05 \le w2 \le 0.2$, whereas only one LCST was observed for both lower and higher concentrations (Fig. 1). The complete phase diagram is depicted in Fig. 2.

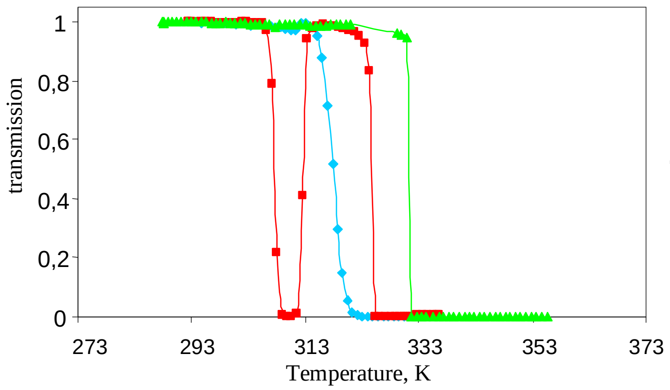


Fig. 1. Cloud point curves of the binary $H_2O/P(EO_7\text{-b-}PO_{20}\text{-b-}EO_7)$ system for low ($w_2=0.01$), intermediate ($w_2=0.08$) and high ($w_2=0.3$) polymer weight fractions w_2

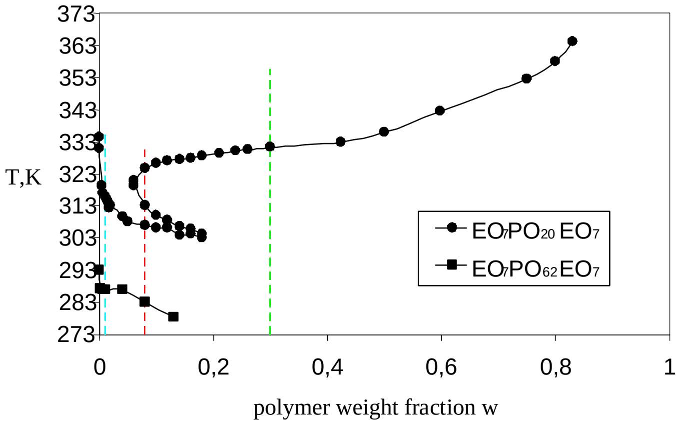
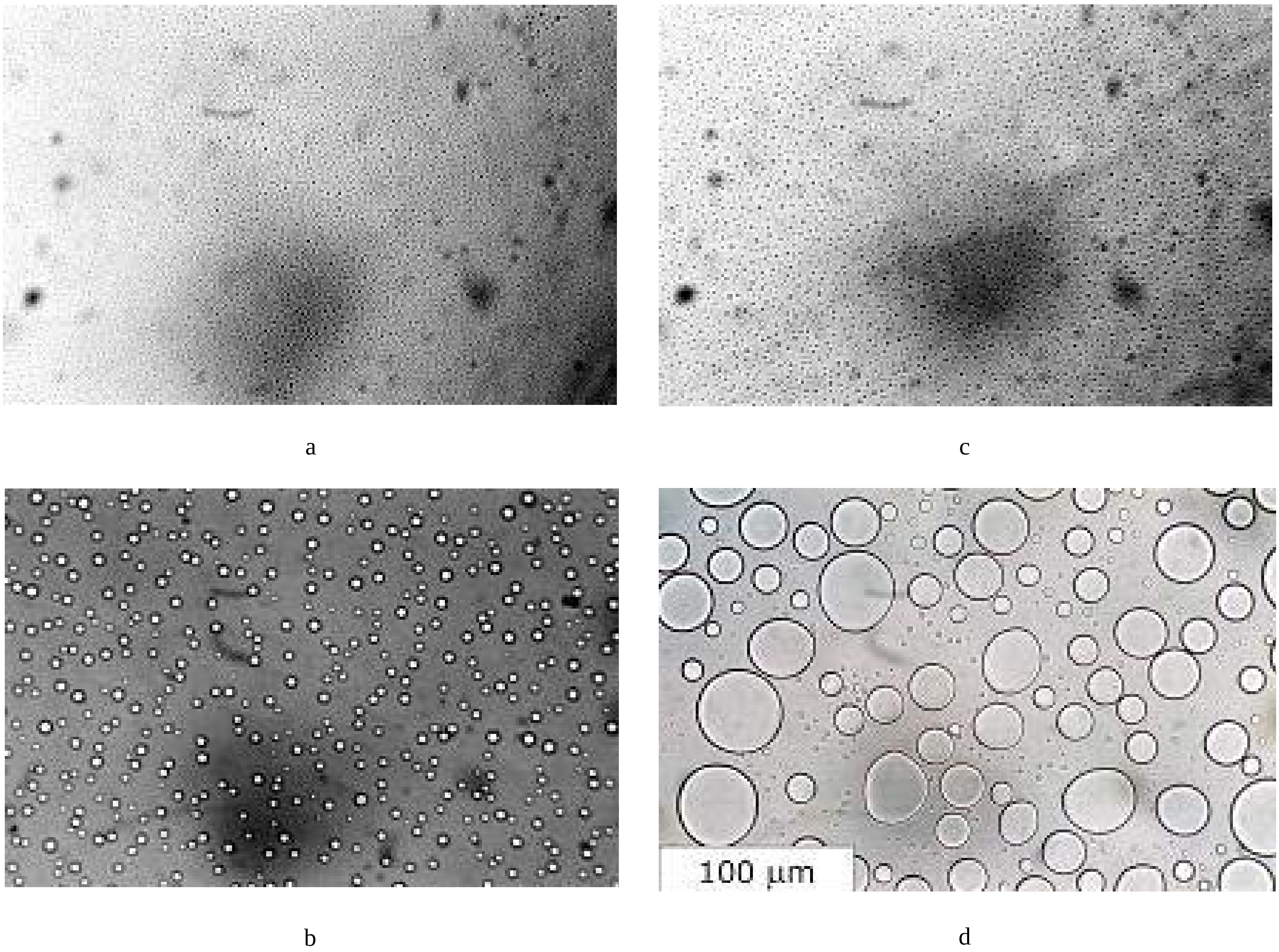


Fig. 2. Phase diagram of the binary $H_2O/P(EO_7\text{-b-}PO_{20}\text{-b-}EO_7)$ system (%) and $P(EO_7\text{-b-}PO_{62}\text{-b-}EO_7)$ (%) at normal pressure



a

c

b

d

Fig. 3. Light microscopy pictures of the binary $H_2O/P(EO_7\text{-b-}PO_{20}\text{-b-}EO_7)$ system ($w_2 = 0.08$) taken at 310 and 335 K at the onset of the demixing (a and c) and after completion of demixing (b and d, respectively)

It is evident that in an intermediate concentration range, upon temperature increase, a 2-phase regime is passed followed by a single-phase window until finally a second LCST is surpassed. The effect of the constitution, *e.g.*, the block length ratio on the phase behaviour is also evident from the data depicted in Fig. 2. The demixing of the two component water/copolymer system was also followed by light microscopy. All the systems studied so far showed the features characteristic for nucleation and growth mechanism (Fig. 3) and no indications for spinodal decomposition was obtained.

However, differences in the onset and course of demixing as well as in the finally found phase picture were observed depending on the chosen temperature in the two-phase regimes; this was particularly distinct in the intermediate concentration regime (compare Figs. 3a/c and Figs. 3b/d). The characteristics of the polymer films deposited on the substrate upon exceeding the LCST were studied by AFM. In general, the surface topology exhibited similar island-like relief structures which can be permanently fixed by subsequent crosslinking via the end group functionalities as already reported [1, 2, 4-8]. The comparison of the AFM pictures in Fig. 4 further reveals that the surface topology also depends from which point in the phase diagram the coating experiment was started: different results are obtained for the same polymer concentration in the two separated 2-phase regimes.

The LCST induced polymer deposition can also be used for the surface modification of particles: a coating layer around the particle is formed when the dispersion of the particles in a polymer solution is heated above the LCST of the respective polymer/solvent system [2]. Dispersion of such modified particles are extremely stable as demonstrated, *e.g*, with carbon black.

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Another aspect of the temperature induced polymer deposition is the coprecipitation of a finely dispersed component on the substrate surface that goes along with the polymer deposition after exceeding of the LCST. This opens new perspectives for the tailored surface modification of pigments since particulate additives can be incorporated into the surface modifying coating; as illustrated in Fig. 5 for a platelet-like pigment, an encapsulation with a nanoscopic polymer layer containing nanoparticles is possible.

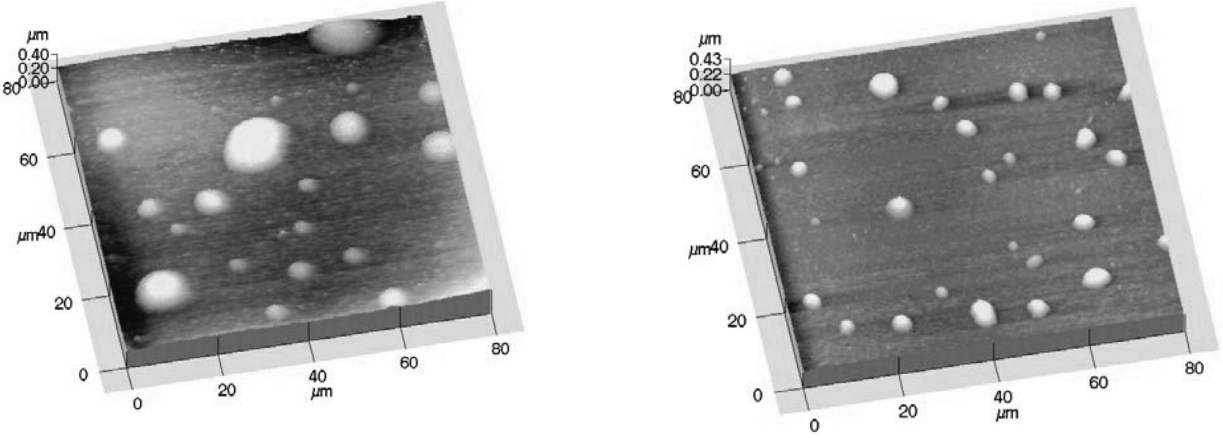

Fig. 4. AFM image of the P(EO$_7$-b-PO$_{20}$-b-EO$_7$) film on a silicon wafer as obtained from a 8 wt % aq. solution at 310 (a) and 335 K (b)

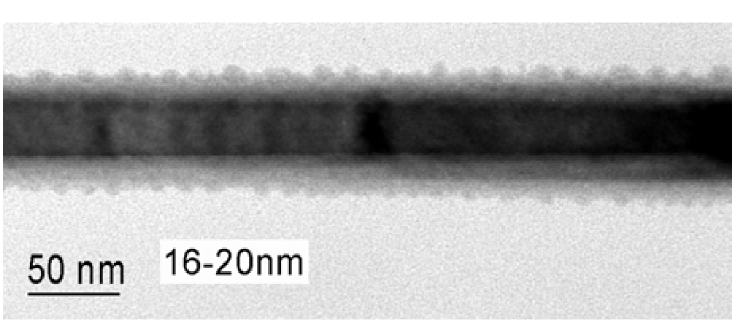

Fig. 5. EM picture of the surface coating (cross section) on a platelet-like pigment as achieved by exceeding the LCST of the polymer solution containing additional nano particles

4. Conclusions

The above studies have shown that the application of the critical phenomena of polymer/solvent systems to the modification of the surface of extended planar substrates as well as of the particles leads to novel surface characteristics. Ongoing work will explore aspects of the LCST technique application in coatings technology.

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НАНОРОЗМІРНІ ЕФЕКТИ В ТЕМПЕРАТУРО-ІНДУКОВАНИХ ПОЛІМЕРНИХ ПОКРИТТЯХ

Анотація*. Наведені результати досліджень можливості застосування нижньої критичної температури розчинності (НКТР) в полімерних розчинах для модифікації поверхні пласких і сферичних підкладок. Визначено, що можна досягти контрольованого осадження полімерів при температурі, вищій за НКТР. Одержані при цьому полімерні покриття мають специфічну морфологію поверхні, а при введені частинок дозволяють ефективно стабілізувати пігментні дисперсії. Встановлено, що температуро-індуковане осаджування полімерів може здійснюватись як нанесення тонкодиспергованого компоненту на поверхню підкладки, яке відбувається одночасно з осадженням полімеру при температурі, вищій за НКТР. Це, в свою чергу, дозволяє проводити контрольовану модифікацію поверхні пігментів, при якій тонкодисперговані присадки розподілені в шарі модифікуючого покриття на поверхні.*

Ключові слова: *полімерні покриття, нанотехнологія, температурний контроль, модифікація поверхні, нижня критична температура розчинності.*