

Creation of Coatings by Temperature-Controlled Polymer Deposition

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Abstract

In this paper, the results of the recent studies on application of lower critical solution temperature (LCST) phenomena of polymer solutions to the surface modification of flat and spherical substrates are reported. It was found that a controlled polymer deposition can be achieved upon prevailing of the LCST, a peculiar surface topology of polymer coating and particles those remarkably effective in stabilizing pigment dispersions. Second, the finding is that the temperature induces polymer deposition as the coprecipitation of a finely dispersed component on the substrate surface. That goes along with the polymer deposition after exceeding of the LCST which in turn allows for the tailored surface modification of pigments in that particulate additives can be incorporated into the surface modifying coating.

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 the surface modification of particles.

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

Experimental

Materials employed for coating experiments were in most cases commercially available poly(o-

xyethylene-boxypropylene-b-oxyethylene) 3-block copolymers (P(EO-b-PO-b-EO)) without and with polymerizable end-functionalities (cf. [2]), and for selected comparative studies polystyrene and hydrophobically modified poly(oxyethylene) urethane model systems (cf. [3]). Si-wafers were used as substrates for film deposition and surface topology studies by atomic force microscopy (AFM), and particle surface modification was investigated with commercially available pigments. Turbidity measurements were carried out with a photometer TP 1 from Tepper Instruments. Instrumental uncertainties have not exceeded 1%. For information regarding the methodology of polymer deposition and coatings analysis it is referred to previously published data [2].

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), first the phase diagram was established. Surprisingly, the turbidity measurements revealed two LCSTs in a semi-diluted concentration regime in a polymer weight fraction w_2 between about $0,05 \leq w_2 \leq 0,2$, whereas only one LCST was observed for lower as well as higher concentrations (Fig. 1). The complete phase diagram is depicted in Fig. 2.

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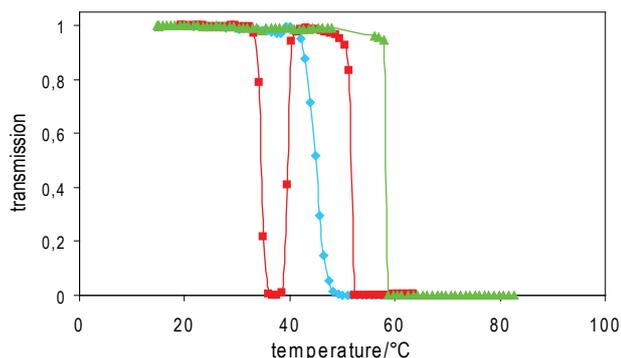


Fig. 1. Cloud point curves of the binary $\text{H}_2\text{O}/\text{P}(\text{EO}_7\text{-b-PO}_{20}\text{-b-EO}_7)$ system for low ($w_2=0,01$), intermediate ($w_2=0,08$) and high ($w_2=0,3$) polymer weight fractions w_2 .

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 behavior is also evident from the data depicted in Fig. 2. The separation of the two component water/copolymer system was also followed by a light microscopy.

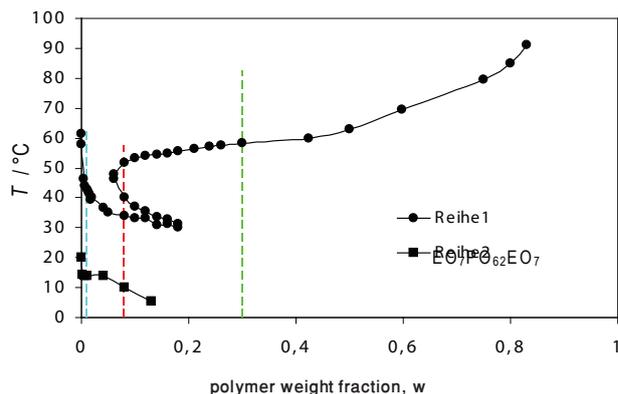


Fig. 2. Phase diagram of the binary $\text{H}_2\text{O}/\text{P}(\text{EO}_7\text{-b-PO}_{20}\text{-b-EO}_7)$ system (\blacktriangledown) and $\text{P}(\text{EO}_7\text{-b-PO}_{62}\text{-b-EO}_7)$ (\blacksquare) at normal pressure.

mechanism (Fig. 3), and no indications for spinodal decomposition were obtained.

However, differences in the onset and course of separation as well as in the finally found phase picture was 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

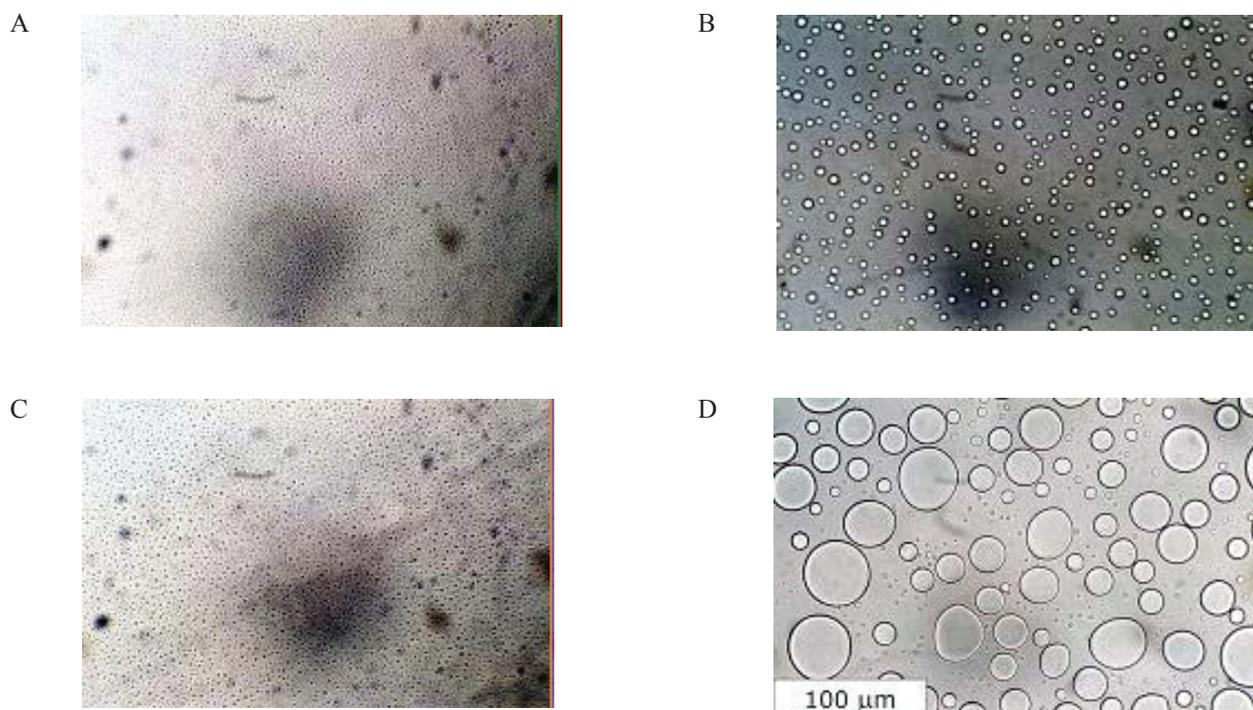


Fig. 3. Light microscopy pictures of the binary $\text{H}_2\text{O}/\text{P}(\text{EO}_7\text{-b-PO}_{20}\text{-b-EO}_7)$ system ($w_2 = 0,08$) taken at 37°C and 62°C at the onset of the separation (A and C) and after completion of separation (B and D, respectively).

general, the surface topology exhibited similar island-like relief structures which could 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 on which point in the phase diagram the coating experiment could be started. Different results are obtained for the same polymer concentration in the two separated 2-phase regimes.

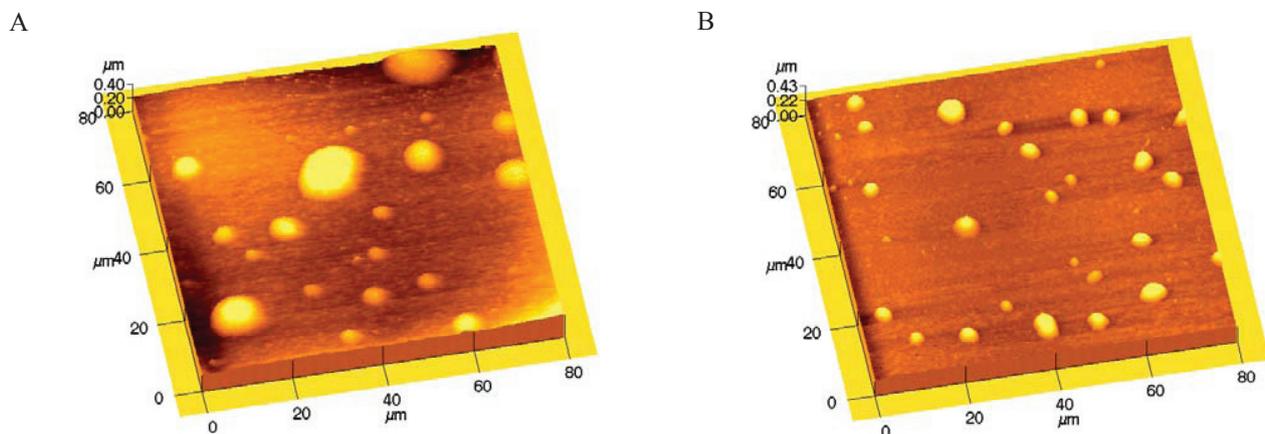


Fig. 4. AFM image of the P(EO₇-b-PO₂₀-b-EO₇) film on a silicon wafer as obtained from a 8 wt.-% aq. solution at 37 °C (A) and 62 °C (B).

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 (cf. [2]). Dispersion of such modified particles are extremely stable as demonstrated, e.g., with carbon black.

Another aspect of the temperature induced polym-

er 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. Those 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 also possible.

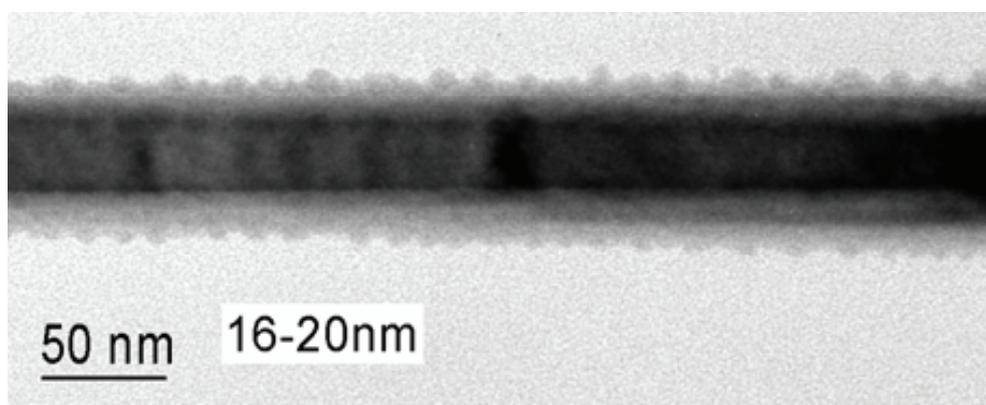


Fig. 5. EM picture of the surface coating (cross section) on a platelet-like pigment as achieved by exceeding the LCST of the polymer solution containing additional nano particles.

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 particles leads to novel surface characteristics. Ongoing work further explores aspects of the LCST technique for application in coatings technology.

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