Contents lists available at ScienceDirect

Polymer

Phase behavior of LiClO$_4$-doped poly(ε-caprolactone)-*b*-poly(ethylene oxide) hybrids in the presence of competitive interactions

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ABSTRACT

The phase behavior of a series of LiClO$_4$-doped poly(ε-caprolactone)-*b*-poly(ethylene oxide) (PCL-*b*-PEO) was studied as a function of PEO volume fraction (f_{PEO}), doping ratio (r) and temperature (T). It is found that the morphology of the hybrids changes from disordered structure (DIS) to hexagonally packed cylindrical (HEX) structure and then to lamellar (LAM) structure as the volume fraction of the PEO/salt phase ($f_{PEO/salt}$) increases at $f_{PEO/salt} < 0.5$. Order−order transitions are observed upon heating some hybrids. An approximate phase diagram of the PCL-*b*-PEO/LiClO$_4$ hybrids with $f_{PEO/salt} < 0.5$ was constructed in terms of $f_{PEO/salt}$ and the segregation strength ($\chi_{eff}N$). As compared with the phase diagram of the weakly segregated diblock copolymers, the phase diagram of the hybrids has two features: the boundaries of the LAM and HEX structures shifts to lower $f_{PEO/salt}$ and body-centered cubic spherical (BCC) structure is not observed for the samples studied. This can be attributed to the weaker ability of the salt inducing microphase separation at low f_{PEO} and the conformational change of the PEO block induced by the salt. Some unexpected phase behaviors were observed for the hybrids with $f_{PEO/salt} > 0.5$, including the hexagonally perforated layers (HPL) to LAM transition upon heating the same hybrid and HEX to gyroid (GYR) transition with the increase of doping ratio at the same temperature. These unexpected phase behaviors are qualitatively interpreted based on the competitive association of the PCL block with Li$^+$ ions at elevated temperatures and higher doping ratios, which leads to re-distribution of the Li$^+$ ions in different phases and the inconsistency between the calculated $f_{PEO/salt}$ and the real volume fraction of the PEO/salt phase.

1. Introduction

Block copolymers (BCPs) can self-assemble into various ordered nano-structures, such as body-centered cubic spherical (BCC), hexagonally packed cylindrical (HEX), gyroid (GYR), lamellar (LAM), and hexagonally perforated layers (HPL), when the segregation strength between different blocks is high enough [1−3]. Composite materials comprising BCP and inorganic salt have received great attention in the past decade because of their potential applications in lithium batteries, fuel cells and high density templates. Since this kind of hybrid system can combine both inorganic and organic characteristics, many studies have been carried out on the self-assembly behavior and properties of ion-doped BCPs [4−29].

In the reported BCP/inorganic salt hybrids, the inorganic salt is usually selectively incorporated into the microdomain of one

component, leading to the change of volume fraction and a different morphology from the neat BCP [30−39]. Balsara et al. observed that, as the salt-doping ratio increased, the polystyrene-*b*-poly(ethylene oxide) (PS-*b*-PEO)/LiTFSI hybrids could exhibit HEX, GYR and LAM structures, respectively [33]. The addition of inorganic salt may also alter the interaction between different components in BCPs [40−42]. The "effective" Flory−Huggins interaction parameter (χ_{eff}) is frequently used to describe the interaction between different blocks with consideration of the effect of inorganic salt [43]. It is reported that χ_{eff} usually increases with the salt-doping ratio, i.e. the blocks in BCPs become more repulsive in the presence of inorganic salt. As a result, the order−disorder transition temperature (T_{ODT}) of the hybrids increases with the salt-doping ratio [6,31,34]. Sometimes inorganic salt can even induce disordered or homogeneous BCPs to undergo microphase separation and produce ordered nano-structures [5,32]. It should be noted that χ_{eff} depends on both cation and anion in the organic salt. Therefore, the segregation strengths are different at the same salt-doping ratio for various inorganic salts [6,15]. Since

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the microdomain spacing of BCPs is related to the Flory–Huggins interaction parameter (χ) [44], the microdomain spacing of BCP/inorganic hybrids also varies with the salt-doping ratio. Increase of the microdomain spacing with salt-doping ratio is frequently reported [17,32,45]. In addition, the ionic conductivity of the BCP/inorganic hybrids is mainly determined by the salt-doping ratio and the ordered structure of the hybrids. Cho et al. reported that the ionic conductivity varied with the microphase-separated morphology and observed remarkable discontinuous changes in the ionic conductivity around order–order transition (OOT) in Li^+ ions-doped PEO-containing amphiphilic dendrons [23,46]. However, Naidu et al. demonstrated that the ionic conductivity increased with increasing ion salt concentration but was morphology-independent [32].

Since the properties of the BCP/inorganic hybrids is dependent on the microphase-separated structure, understanding the phase diagram of the BCP/inorganic hybrids is of great importance, because it can be used as guidance to regulate the morphology and properties of the hybrids [21,47,48]. However, so far only the phase diagrams of the BCP/inorganic hybrids for single BCP at a specific composition or in a narrow composition range but different salt-doping ratios are reported [31,32,49,50]. To our knowledge, there is no systematic study of the phase behavior of the BCP/inorganic hybrids both in a broad composition range of BCP and at various salt-doping ratios. Moreover, in most of the reported BCP/inorganic hybrid systems inorganic salt only selectively interacts with one of the components of BCP [6–9,32,33], leading to quite simple phase behavior of the salt-doped BCP hybrids. Although Ruzette et al. found that $LiCF_3SO_3$ could induce microphase separation in poly(methyl methacrylate)-b-poly(oligo oxyethylene methacrylate) (PMMA-b-POEM), the possible competitive interactions of Li^+ ions with both blocks were not investigated [5]. When inorganic salt can interact with both components of a BCP, the phase behavior of such a hybrid system may become more complex. It is also expected that the regulation of the structure and properties of the hybrid can be realized via adjusting the competitive interactions of the salt with different components.

Previously we studied the phase behavior of a poly(ε-caprolactone)-b-poly(ethylene oxide) (PCL-b-PEO) BCP doped with different amounts of $LiClO_4$ and observed that $LiClO_4$ could induce microphase separation of the miscible PCL-b-PEO in the melt [51]. The competitive interactions of Li^+ ions with both PCL and PEO were confirmed by Chiu's and our work [19,51]. In the present work, a series of PCL-b-PEO BCPs with different compositions were doped with $LiClO_4$ at various doping ratios. The phase behavior of the PCL-b-PEO/$LiClO_4$ hybrids was studied and an approximate phase diagram was constructed.

2. Experimental

2.1. Materials

The PCL-b-PEO BCPs with a narrow molecular weight distribution were synthesized according to our previous work [52]. The number-average molecular weights of the PCL-b-PEO BCPs and the polymerization degrees of the PCL and PEO blocks are calculated from ^1H NMR spectra. The molecular weight distribution (M_w/M_n) was determined by gel permeation chromatography (GPC). The PCL-b-PEO BCPs are also denoted as PCL_m-b-PEO_n, where the subscripts m and n are the polymerization degrees of the PCL and PEO blocks, respectively. The molecular weight, molecular weight distribution, volume fraction of the PEO block and polymerization degrees of the PCL and PEO blocks for all the PCL-b-PEO BCPs used in the present work are listed in Table 1. The inorganic salt lithium perchlorate ($LiClO_4$) was purchased from Acros-Organics. Before

Table 1
The data of PCL-b-PEO BCPs with different compositions.

PCL-b-PEO	f_{PEO}	M_n	M_w/M_n
PCL_{183}-b-PEO_{44}	0.085	22,860	1.14
PCL_{119}-b-PEO_{44}	0.124	15,570	1.15
PCL_{78}-b-PEO_{44}	0.178	10,900	1.16
PCL_{50}-b-PEO_{44}	0.253	7700	1.20
PCL_{76}-b-PEO_{113}	0.357	13,660	1.04
PCL_{46}-b-PEO_{113}	0.479	10,240	1.16

preparing the $LiClO_4$-doped PCL-b-PEO samples, all the materials were dried for 24 h under dynamic vacuum. $LiClO_4$ was used as-received without further purification. Tetrahydrofuran (THF) was refluxed with sodium flakes and distilled prior to use.

2.2. Preparation of PCL-b-PEO/$LiClO_4$ hybrids

Pre-described amount of $LiClO_4$ and PCL-b-PEO was dissolved in THF, and stirred for 24 h. All the operations including weighing and mixing were conducted in a glove-box under N_2 atmosphere to avoid the possible effect of humidity. The solution was dried under dynamic vacuum for 24 h at 70 °C to remove the THF completely. After drying, the hybrids were stored in a glove-box. The doping ratio, r, which is defined as the molar ratio of Li^+ ion to EO unit ($r = [Li^+]/[EO]$), was used to describe the relative content of $LiClO_4$ in the hybrids.

2.3. Small angle X-ray scattering

Temperature-variable small angle X-ray scattering (SAXS) experiments were performed at BL16B1 beamline in Shanghai Synchrotron Radiation Facility (SSRF) and 1W2A beamline in Beijing Synchrotron Radiation Facility (BSRF), China. The wavelengths of X-ray at SSRF and BSRF are 1.24 Å and 1.54 Å, respectively. The sample-to-detector distance was set as 2000 mm. Two-dimensional (2D) SAXS patterns were recorded by time-resolved mode. The average exposure time was 300 s for each scan. The bull tendon was used as standard material for calibrating the scattering vector. The 2D SAXS patterns were converted into one-dimensional (1D) SAXS profiles using Fit2D software. A Linkam hot-stage was used to heat the samples.

2.4. Differential scanning calorimetry

The thermal behavior of salt-doped PCL-b-PEO samples was characterized by differential scanning calorimetry (DSC) on a TA Q200 instrument. About 3–4 mg of the sample was sealed in an aluminum pan. The samples were first heated from 40 °C to 100 °C, and kept for 5 min to eliminate the thermal history, then cooled to −40 °C to obtain the non-isothermal crystallization DSC curves. Subsequently the samples were heated to 100 °C to acquire the melting traces. Both the heating and cooling rates are 10 °C/min.

3. Results and discussion

3.1. Phase behavior at $f_{PEO/salt} < 0.5$

In our previous work we reported that $LiClO_4$ could induce microphase separation of PCL_{50}-b-PEO_{44} in the melt [51]. In this study, we prepared a series of PCL-b-PEO BCPs with f_{PEO} ranging from 0.085 to 0.479 (Table 1). $LiClO_4$ was hybridized with PCL-b-PEO at various doping ratios (r). The morphology of the hybrids was investigated with temperature-variable SAXS. Since PCL-b-PEO BCPs can crystallize at room temperature, the morphology of the hybrids in the