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Short communication

Synthesis and solid-state properties of thermotropic liquid crystalline polypeptide bearing imidazolium and *p*-tolyl groups

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ABSTRACT

Polypeptides bearing imidazolium and *p*-tolyl groups have been synthesized by click chemistry between poly(γ-3-azidopropyl-L-glutamate) (PAPLG) and 3-butyl-1-propargyl imidazolium bromide (BPIB) and 1-methyl-4-prop-2-ynyloxybenzene (MPB). The FTIR results revealed α-helical conformation of all resulting polypeptides in the solid-state. POM and WAXS study revealed that polypeptides with high *p*-tolyl contents (molar percentage ⩾54%) possessed nematic liquid crystalline phases and hexagonal packing in the solid-state. DSC analysis revealed the solid to liquid crystalline transitions in the temperature range of 35–42 °C.

Polymeric ionic liquids (PILs) are a class of polyelectrolytes with ionic liquid moieties (e.g., imidazolium, pyridinium, hexafluorophosphate and triflates) in the main-chain and side-chain [1,2]. They possess both intrinsic polymer properties (e.g., viscoelastic properties) and properties of ionic liquids (ILs), such as ionic conductivity, thermal, and chemical stability. PILs have gained increasing attention for their potential applications in electrochemical devices [3,4], nanocomposites [5–7], smart materials [8–10], catalysts [11,12], and biomaterials [13,14]. Diverse types of PILs with polyimide [15], polyolefin [16,17], and conjugated polymer main-chains [18,19] have been prepared by chain-growth or step-growth polymerizations for versatile uses.

Polymers bearing imidazolium moieties are the most widely studied PILs due to their high ionic conductivity [20,21], good biocompatibility for biomedical applications (e.g., gene delivery) [13], versatile functional substitutes with tuneable material properties, and capability of dispersing carbon nanotubes by π–π stacking interactions [22,23]. The physical properties, especially the ionic conductivity of these polymers depend strongly on polymer primary and secondary structures, nature of the counter-ions and mesophase morphologies [24,25]. Yet, most polymers bearing imidazolium moieties are non-crystalline amorphous polymers likely due to the mobile nature of the counter-ions which suppressed their crystallization. Evidence indicates that ionic liquid moieties packed in highly ordered structures can significantly improve the materials' performances [26,27]. While several strategies have been attempted to spatially control the imidazolium moieties in the ordered structure, liquid crystalline materials have showed diverse mesophase for the spatial control of ionic species in a long-range order [27,28].

Liquid crystalline polypeptides [e.g., poly(γ-benzyl-L-glutamate), PBLG] with rigid main-chains are known to adopt α-helical conformations due to their intramolecular H-bonds [29–31]. They are able to form lyotropic and/or thermotropic liquid crystalline phases with different molecular packing (e.g., nematic, smectic, and cholesteric

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phase) [32–34]. Among them, liquid crystalline polypeptides bearing ionic side-chains, specifically ionic liquid moieties have been rarely investigated. For example, polypeptide–surfactant complexes prepared by mixing poly(L-lysine hydrobromide) with dodecylbenzenesulfonic acid sodium salt or phosphodiester surfactants exhibited thermotropic liquid crystalline phases [35,36]. In this contribution, we provide a new strategy to prepare liquid crystalline polypeptides bearing ionic liquid moieties.

Recently, we demonstrated that α-helical polypeptides bearing ionic liquid moieties can be prepared by a copper-mediated 1,3-dipolar cycloaddition with quantitative grafting densities [37]. They showed superior single-walled carbon nanotube dispersibility in water. Nevertheless, they are amorphous materials with no highly ordered structures in the solid-state. Given that charge repulsion and mobility of the counter-ions probably suppressed the crystallization, we reason that highly ordered polypeptides bearing ionic liquid moieties can be achieved by incorporating non-ionic aromatic groups in the side-chain to decrease the charge repulsion.

Here, we report the design and synthesis of a series of polypeptide bearing imidazolium and *p*-tolyl side-chains and evaluation of their solid-state properties. The resulting polymers adopt α-helical conformations and form crystalline and nematic liquid crystalline phases with hexagonal packing in the solid-state. To our knowledge, this is the first example of thermotropic liquid crystalline polypeptides bearing ionic liquid moieties.

1-Methyl-4-prop-2-ynyloxybenzene (MPB, Fig. S1) was synthesized by etherification of 4-methylphenyl with 3-bromopropyne in the presence of potassium carbonate. Poly(γ-3-azidopropyl-L-glutamate) (PAPLG), 3-butyl-1-propargyl imidazolium bromide (BPIB) and poly(γ-propyl-L-glutamate)-graft-(*N*-butyl imidazolium bromide) (PPLG-*g*-BIB) were synthesized by reported procedures [37,38]. Polypeptides bearing imidazolium and *p*-tolyl moieties with different molar ratios (P2-P4) were prepared by copper-mediated [2 + 3] alkyne-azide 1,3-dipolar cycloaddition (i.e., click chemistry) using PAPLG, BPIB, and MPB (Scheme 1). The samples were purified by dialysis against deionized water at pH = 5–7 to remove the copper ions and excess BPIB, and washing with diethyl ether to remove excess MPB. For comparison, sample P5, functionalized exclusively with *p*-tolyl side-chains, was also synthesized via the click chemistry between PAPLG and MPB. It was purified by neutral alumina chromatography to remove the copper ions and precipitation from diethyl ether.

The molecular structures and molecular weights of the resulting polypeptides (P1–P5) were confirmed by ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy (Fig. 1, S2–S6), Fourier transform infrared spectrometer (FTIR) spectroscopy (Fig. 2), and gel-permeation chromatography (GPC, Fig. S7). The ^{1}H NMR resonances were consistent with the polymer structures. For instance, the chemical shifts at 6.86–7.03 ppm and 7.79 ppm corresponded to the characteristic resonances of *p*-tolyl (H_q and H_r) and imidazolium groups (H_i and H_j), respectively. The chemical shifts at 8.33 and 8.21 ppm were attributed to the triazole groups (H_{g1} and H_{g2}) next to the imidazolium and *p*-tolyl groups, respectively. Additionally, the integrations of resonances at 5.54 (H_h) and 5.03 (H_p) ppm were used to calculate the molar ratio of imidazolium and *p*-tolyl groups existing in the samples, which are summarized in Table 1. In the FTIR spectra (Fig. 2a), BPIB and MPB showed characteristic bands at 2122 cm^{-1} corresponding to the vibration modes of alkynes (ν_{alkyne}). Furthermore, BPIB showed the vibration mode ($\nu_{imidazolium}$) and the C—H deformation mode (δ_{C-H}) of imidazolium at 1558 and 748 cm^{-1} while MPB showed those modes of phenyl rings at 1508 and 806 cm^{-1}, respectively. PAPLG with a degree of polymerization of 110 (i.e., $PAPLG_{110}$) exhibited amide I and amide II bands at 1651 and 1545 cm^{-1}, respectively, indicating the α-helical conformation in the solid-state [39]. In comparison, the polypeptides containing ionic liquid moieties (P1–P4) or exclusively *p*-tolyl groups showed characteristic bands at around 3288 (ν_{N-H}), 2954 (ν_{C-H}), 2728 ($\nu_{C=O}$ of ester), 1650 (amide I), 1546 (amide II), 1508 (ν_{phenyl}), 808 (δ_{C-H} of *p*-tolyl), and 748 cm^{-1} (δ_{C-H} of imidiazolium), suggesting the successful preparation and the α-helical conformation of the resulting polypeptides. The absence of $\nu_{N=N=N}$ and ν_{alkyne} in the FTIR spectra of P1–P5 suggested a quantitative grafting efficiency and high purity. In the GPC chromatographs (Fig. S5), P5 showed higher molecular weight than $PAPLG_{110}$ indicating the successful grafting of *p*-tolyl side-chains. Yet, the GPC curves of P1–P4 bearing imidazolium groups were featureless due to the strong absorption between the imidazolium groups and the stationary phase of GPC.

The solubility of the resulting polypeptides (P1–P5) was measured by directly mixing them with room temperature solvents (Table S1). All samples were readily soluble in dipolar aprotic solvents (e.g., DMF and DMSO). Furthermore, polypeptides with high imidazolium contents (P1–P3) were soluble in polar solvents, such as methanol and water. Polypeptides with high *p*-tolyl contents (P4 and P5) tended to dissolve in less polar solvents including dichloromethane and chloroform.

The solid-state properties of the polypeptide samples were firstly investigated by polarized optical microscopy (POM, Fig. 3). Polypeptides with high imidazolium contents (P1 and P2) were amorphous polymers with no birefringence under POM observation, which resulted from the charge repulsion between adjacent polymer chains. In comparison, polypeptides with high *p*-tolyl contents (P3 and P4) exhibited strong birefringence, suggesting that ordered molecular packing has been achieved by incorporating of *p*-tolyl groups which decreased the charge repulsion and consequently promoted the ordered structures. Additionally, the liquid crystal to isotropic phase transitions of P3 and P4 were also revealed by POM. The liquid crystal clear points of P3 and P4 were at around 110 and 170 °C, respectively and increased with increasing *p*-tolyl content. The crystalline textures appeared in the cooling cycle, suggesting a reversible liquid crystalline behavior. P5 with no imidazolium groups also showed birefringence in the temperature range between room temperature and its decomposition temperature (T_d), which was similar to most thermotropic liquid crystalline polypeptides, such as poly(γ-benzyl-L-glutamate) (PBLG) [31] and poly(γ-chloropropyl-L-glutamate) (PCPLG) [38], due to the rigid polypeptide main-chain and consequent poor chain mobility.