Synthesis and Characterization of Poly(4-vinyl pyridine)-*b*-Poly(2,2,2-trifluoroethyl methacrylate) for Hierarchical Nanostructures

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Abstract
Block copolymers (BCPs) containing poly(4-vinyl pyridine) (P4VP) are expected to exhibit unique hierarchical microphase-separated structures owing to relatively strong intermolecular interaction with other molecules by the pyridyl group. This study investigates the effects of the molecular weight, volume fraction (f_{P4VP}), and interaction via the pyridyl groups on the resulting higher-order structures of poly(4-vinyl pyridine)-*b*-poly(2,2,2-trifluoroethyl methacrylate) (P4VP-*b*-PTFEMA).

1. Introduction
Numerous BCPs are known to form well-ordered nanostructures with various morphologies by the microphase separation and are expected to be applied in a wide range of fields such as porous materials, lithography, drug delivery systems, and batteries. Among porous materials, hierarchical porous materials with different length scales of pore diameters require precise control of the ordered morphology, and BCPs modified with side chains are considered to be suitable for obtaining such materials. In addition, polymers exhibiting adsorption ability by lone pair, such as pyridyl groups, have another advantage of selective separation by molecular adsorption. This study aims to create a porous material with different pore diameter length scales and molecular adsorption capabilities based on hierarchical polymer nanostructures. We selected P4VP, which can interact with detachable small molecules via the pyridyl groups, and PTFEMA, which can be easily etched for the mesoscale porosity, as the two blocks of a BCP. Herein, we synthesized the BCPs of P4VP-*b*-PTFEMA and investigated the formation of hierarchical nanostructures based on microphase separation.

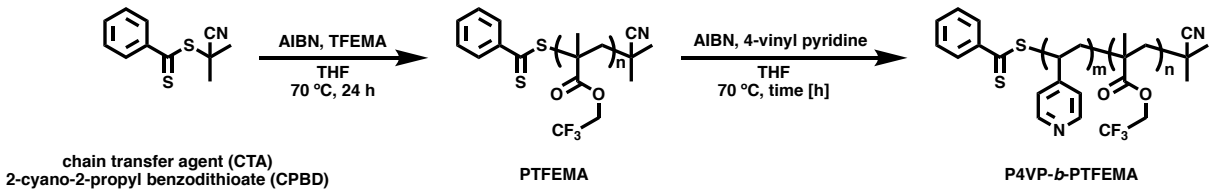
2. Experiment


Fig. 1 Synthetic scheme of PTFEMA and P4VP-*b*-PTFEMA.

A typical PTFEMA and P4VP-*b*-PTFEMA were synthesized via RAFT polymerization (Fig. 1). $PTFEMA_{128}$ was yielded as a pale pink powder (1.95 g; 97% yield). The number-average molecular weight (M_n) was calculated to be 13,000 and M_w/M_n of 1.12 by SEC analysis based on polystyrene (PS) standards. $P4VP_{252}$-*b*-$PTFEMA_{128}$ was yielded as a light pink powder (0.61 g). The SEC analysis yielded M_w/M_n of 1.07. The M_n and volume fraction of P4VP (f_{P4VP}) were determined to be 27,000 and 0.57, respectively, by ^{1}H NMR.

3. Results and discussion

3.1 Synthesis and Bulk studies for PTFEMA and P4VP-*b*-PTFEMA.

A series of the BCP, P4VP-*b*-PTFEMA, was synthesized using the synthesized PTFEMA as the macro-CTA (Table I). By changing the reaction time, temperature, and solvents, various BCPs with different volume fractions (f_{P4VP}) were obtained. Bulk samples for small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM) analyses were prepared by slow evaporation of the polymer solutions in chloroform, followed by thermal annealing *in vacuo* at 473 K.

Table I Characterization of PTFEMA and P4VP-*b*-PTFEMA.

polymer	temp. [°C]	time [h]	M_n [g mol^{-1}]^a	M_w/M_n^{a}	f_{P4VP}^{b}	Morphology^c
$PTFEMA_{128}$	70	24	21,000	1.18	–	–
$P4VP_{49}$-*b*-$PTFEMA_{128}$	70	1.5	27,000	1.12	0.24	HEX
$P4VP_{252}$-*b*-$PTFEMA_{128}$	70	12	48,000	1.13	0.61	LAM

^{a}Determined by SEC based on PS standards. ^{b}Determined by ^{1}H NMR (solvent: $CDCl_3$) and density of PTFEMA (1.45 g/cm^3)[1], P4VP (1.11 g/cm^3)[2]. ^{c}Determined by SAXS and TEM.

3.2 Self-Assembly of P4VP-*b*-PTFEMA with 4-Dodecylphenol (4DP).

P4VP(4DP)-*b*-PTFEMA was prepared by mixing with a stoichiometric amount of 4DP, which is expected to form hierarchical microphase-separated nanostructures via hydrogen bonds with P4VP. According to SAXS (Fig. 2a-b) and wide-angle X-ray diffraction, it was suggested that the addition of 4DP induced a morphological change from lamellae (d = 43.5 nm) to cylinders (d = 41.8 nm). Besides, another order of structure (d = 3.4 nm) is also observed in $P4VP_{252}$(4DP)-*b*-$PTFEMA_{128}$.

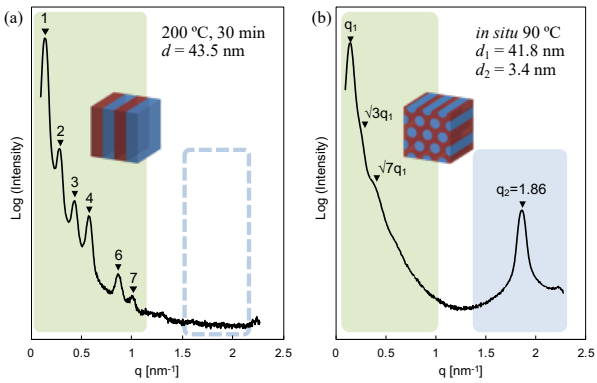


Fig. 2 SAXS profiles of (a) $P4VP_{252}$-*b*-$PTFEMA_{128}$, (b) $P4VP_{252}$(4DP)-*b*-$PTFEMA_{128}$.

4. Conclusions

P4VP-*b*-PTFEMAs with various M_n and f_{P4VP} have been synthesized. Bulk studies by SAXS and TEM have suggested the formation of microphase-separated structures depending on f_{P4VP}. The addition of 4DP resulted in a change in the higher-order structure. A detailed investigation of self-assembly will be performed to achieve various hierarchical porous materials.

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References

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