

Synthesis of random copolymers of 4-vinylpyridine with *n*-octadecyl acrylate/*n*-octadecyl methacrylate by metal-free ATRP

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Abstract:

Poly(4-vinylpyridine-*r*-*n*-octadecyl acrylate) and poly(4-vinylpyridine-*r*-*n*-octadecyl methacrylate) were successfully synthesised via atom transfer radical polymerization (ATRP) using 10-phenylphenothiazine as the photo-induced catalyst. The resulting copolymers were structurally characterised by proton nuclear magnetic resonance (¹H NMR) and the interactions were analysed by Fourier-transform infrared (FTIR) spectroscopy.

Keywords: ATRP, metal-free, *n*-octadecyl, pyridine.

Classification number: 2.2

Introduction

Controlled radical polymerization (CRPs) has emerged as one of the most far reaching developments in polymer synthesis and has contributed fundamental techniques to prepare polymers with well-defined structure and architecture [1, 2]. Concerning CRP techniques, atom transfer radical polymerization (ATRP) is arguably the most utilized method as it is applicable to the polymer synthesis of a variety of monomers. One limitation of using ATRP is metal contamination of the products. Although metal loadings in a catalyst can be limited to parts per million (ppm), the residual metal in the products may cause difficulties in many sensitive applications such as biomaterials, microelectronics, etc [3]. However, recently developed photocatalysts for ATRP have been introduced as a potential method to synthesise polymers with complete elimination of transition metal residue and thus be less affected by reaction media [4].

N-octadecyl is a hydrocarbon chain (18C) that possesses highly hydrophobic properties. These long alkyl chains may crystalline when present in a polymer as side functional groups, even in the amorphous polymer backbone. Due to these properties, polymers consisting of *n*-octadecyl groups may be used for applications in self-assembling amphiphilic polymers [5] or self-healing materials [6].

Pyridine is also an interesting chemical structure. It possesses one lone pair of electrons excluded from the aromaticity such that they can bind with protons. Therefore, pyridine is alkaline and could also coordinate with transition metal ions or hydrogen to form complexes or hydrogen bonding interactions [7, 8]. This work focuses on combining

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the special properties of the two functional groups stated above into one copolymer with the expectation of compatible polymerization as well as interaction formation between polymer chains.

In this study, 10-phenylphenothiazine was used as a commercial photo-induced catalyst. We report the synthesis and characterisation of two copolymers of 4-vinylpyridine and *n*-octadecyl acrylate (or *n*-octadecyl methacrylate) as a first step toward applying metal-free ATRP to the synthesis of those potential copolymers. We expect the hydrophilicity of 4-vinylpyridine, as well as hydrophobicity of the *n*-octadecyl long chains, to contribute interesting properties, such as self-assembly or micelle formation, to the resulting copolymers.

Experimental section

Materials

4-vinylpyridine (4VP, 95%), *n*-octadecyl acrylate (OA, 97%), *n*-octadecyl methacrylate (OMA, 97%) were purchased from SigmaAldrich and passed through an alumina column to remove the inhibitor. 10-phenylphenothiazine (P, Sigma Aldrich, >95%), ethyl 2-bromo-2-methylpropionate (I, Sigma Aldrich, 98%), tetrahydrofuran (THF, 99.8%, no stabilizer) were purchased from Acros Organics. Methanol and other solvents (Fisher, >98%) were also used.

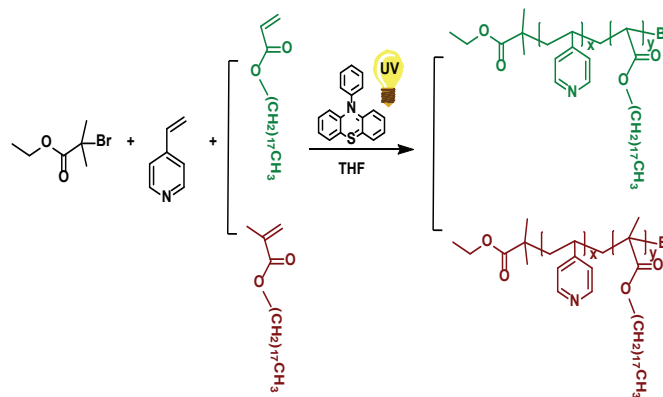
Instrumentation

The ¹H NMR spectra were recorded in deuterated chloroform (CDCl₃), with TMS as the internal reference, on a Bruker Avance 500 MHz spectrometer. Gel permeation chromatography (GPC) measurements were performed on a PL-GPC 50 gel permeation chromatograph system equipped with a refractive index (RI) detector. THF was used as the eluent at a flow rate of 1.0 ml/min and the molecular weights and molecular weight distributions were calculated with reference to polystyrene standards. The FTIR spectra collected from the average of 252 scans with a resolution of 4 cm⁻¹, were recorded from a KBr disk on an FTIR Bruker Tensor 27.

Synthesis of copolymers

Poly (4-vinylpyridine-*r*-*n*-octadecyl acrylate) - P(4VP-*r*-OA) and poly (4-vinylpyridine-*r*-*n*-octadecyl methacrylate) - P(4VP-*r*-OMA) were prepared in two-neck flasks (Scheme 1). The reaction systems were flamed three times and filled with nitrogen before any chemicals were added. 4-vinylpyridine, *n*-octadecyl acrylate (or *n*-octadecyl methacrylate), THF, 10-phenylphenothiazine,

and ethyl 2-bromo-2-methylpropionate ([4VP]/[OA]/[I]/[P] and [4VP]/[OMA]/[I]/[P]=100/50/1/1) were, respectively, added into the flask under nitrogen. The mixture was stirred at RT for 15 min and then degassed with three freeze-pump-thaw cycles. Then, polymerization was carried out in a UV box while the mixture was continuously stirred. After 48 h of reaction time, the UV light was turned off and the mixtures were stirred in the dark for 30 min for stabilisation. Finally, the copolymers were precipitated twice in cold methanol and dried under vacuum until the weight was unchanged.



Scheme 1. Synthesis of P(4VP-*r*-OA) and P(4VP-*r*-OMA).

Results and discussion

After a 48 h reaction time, P(4VP-*r*-OA) and P(4VP-*r*-OMA) were received, giving gravimetric yields of 75 and 80%, respectively. From the GPC analysis (Fig. 1), the average molecular weight (*M_w*) of P(4VP-*r*-OA) was 12032 (PDI=1.77) whereas that of (4VP-*r*-OMA) was 18556 (PDI=1.59). The large distribution of molecular weights may result from poor compatibility between the monomers present in reaction mixtures during the period of co-polymerization [9].

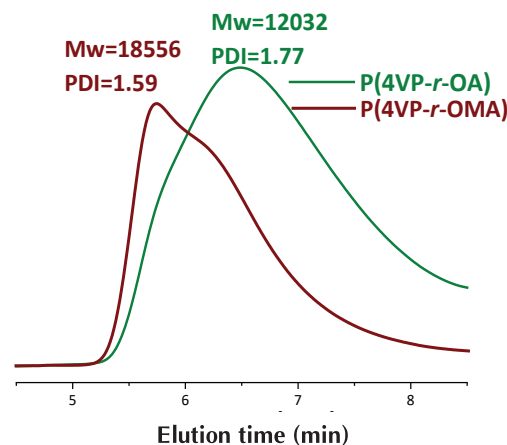


Fig. 1. GPC chromatograms of P(4VP-*r*-OA) and P(4VP-*r*-OMA).

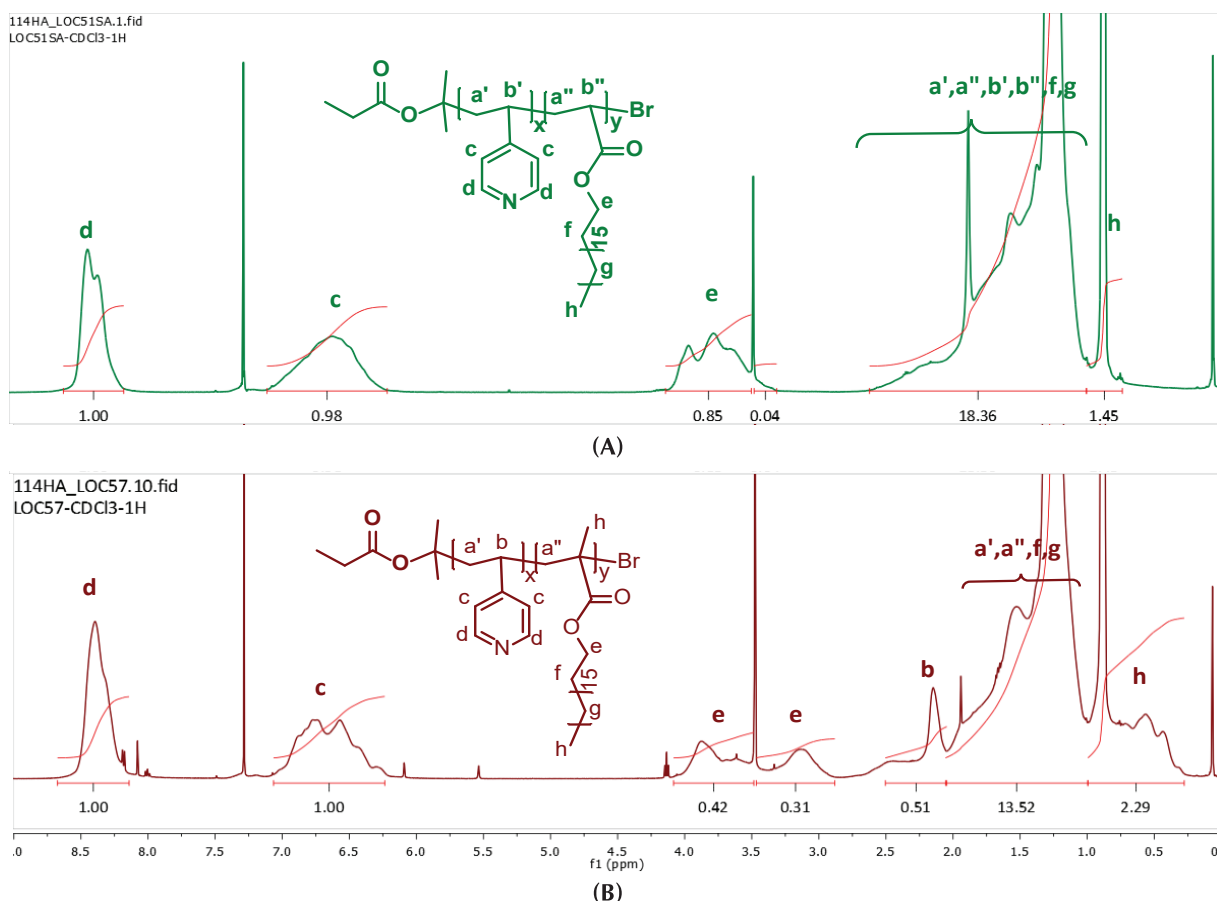


Fig. 2. ¹H-NMR spectra of P(4VP-r-OA) (A) and P(4VP-r-OMA) (B).

Study of copolymer structures

The structure of P(4VP-r-OA) and P(4VP-r-OMA) was characterised by proton nuclear magnetic resonance spectroscopy. The results are shown in Fig. 2. For P(4VP-r-OA), the chemical shifts (δ) were 8.20-8.56 ppm (d, 2H, meta-protons from pyridine ring), 6.27-7.07 ppm (c, 2H, ortho-protons from pyridine ring), 3.30-4.08 ppm (e, 2H, -O-CH₂- from *n*-octadecyl group), 0.99-2.61 ppm [a', a'', b', b'', f, g, 38H, protons from vinyl group (6H) and -CH₂-[CH₂]₁₅- from *n*-octadecyl group (32H)], and 0.71-0.99 ppm (h, 3H, methyl protons (CH₃) from *n*-octadecyl group). For P(4VP-r-OMA), the δ = 8.15-8.60 ppm (d, 2H, meta-protons from pyridine ring), 6.34-7.0 ppm (c, 2H, ortho-protons from pyridine ring), 2.87-4.00 ppm (e, 2H, -O-CH₂- from *n*-octadecyl group), 2.04-2.26 ppm (b, 1H, -CH- from vinyl group), 1.00-2.04 ppm (a'', a'', f, g, 36H, -CH₂- from vinyl and methacrylate groups (4H) and -CH₂-[CH₂]₁₅- from *n*-octadecyl group (32H)), and 0.28 -1.00 ppm (h, 6H, methyl protons (CH₃) from *n*-octadecyl and methacrylate groups). The different ratios, as well as interaction between the two units in the two copolymer chains, may be the cause of the atypical of chemical shifts at 2.125 and 3.125 ppm.

In addition, by measuring the relative intensities of the meta-protons from the pyridine ring (d, 2H) and the methylene protons (e, 2H) from the *n*-octadecyl group, the molar ratio of the two units in the copolymers can be calculated. Particularly, the fraction of 4VP/OA in P(4VP-r-OA) was 1.03 and the value of 4VP/OMA in P(4VP-r-OMA) was 1.31, whereas the feeding ratio of 4VP over OA (or OMA) was 2/1.

Study of interaction in copolymers

Both P(4VP-r-OMA) and P(4VP-r-OA) were analysed by FTIR, which illustrated the characteristic vibrations of the pyridine ring evidenced by the absorption bands at 1596.99 cm⁻¹ (Fig. 3). The absorption bands at 1068.52 and 993.30 cm⁻¹ are observed to confirm the in-plane and out-of-plane rings C-H bending, respectively [10].

The absorption band of C=O at 1730 cm⁻¹ in poly (*n*-octadecyl acrylate) and poly (*n*-octadecyl methacrylate) were slightly broadened at the lower wavenumber may be caused by the hydrogen bonding of C=O and pyridine in the copolymer. Moreover, the formation of hydrogen bonding also slightly shifts the deformation band of pyridine at 1068.52 cm⁻¹ to 1070.45 cm⁻¹.

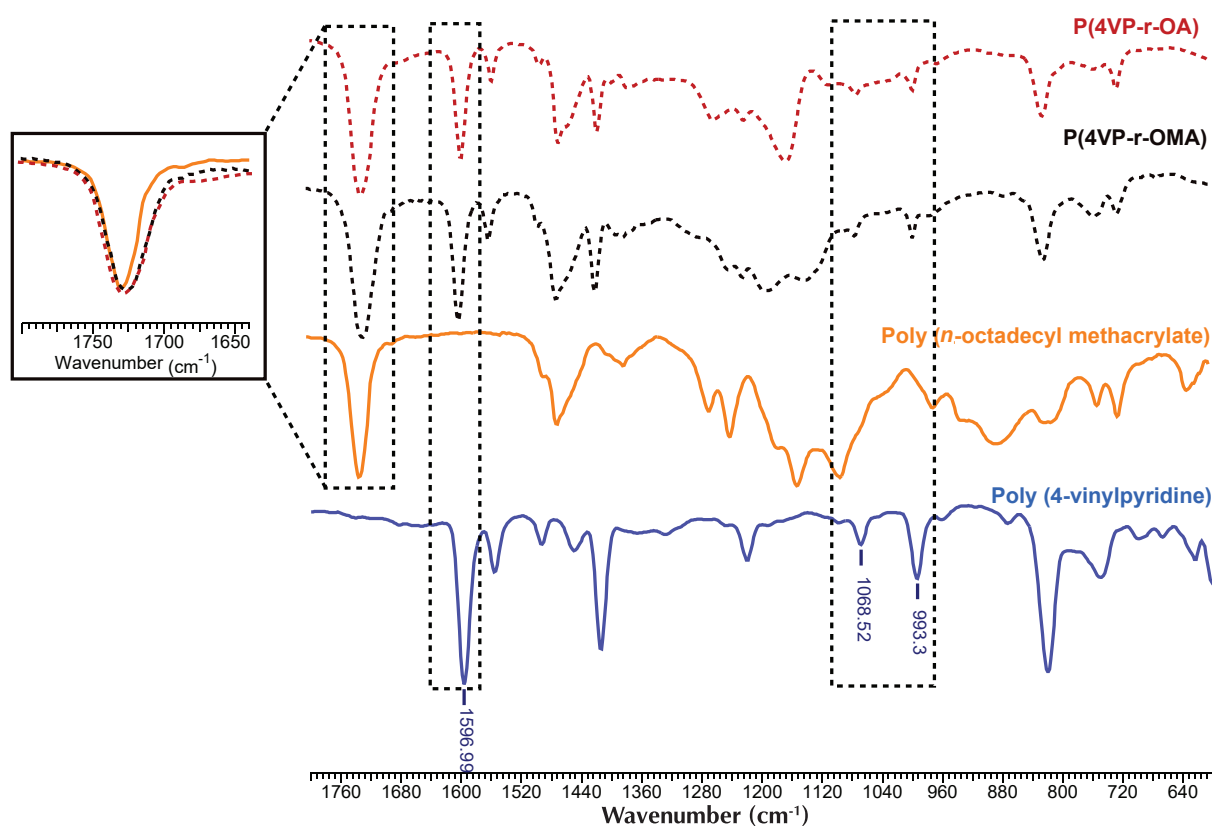


Fig. 3. FTIR spectrum of P4VP (blue line), POMA (orange line), P(4VP-*r*-OMA) (black line) and P(4VP-*r*-OA) (red line).

Conclusions

In conclusion, P(4VP-*r*-OMA) and P(4VP-*r*-OA) were successfully prepared via ATRP using 10-phenylphenothiazine as the photocatalyst with the feeding ratio of [4VP]/[OA or OMA]/[I]/[P] = 100/50/1/1, which gave high yields. More importantly, the use of an organic catalyst generated products with no metal contamination. When the feeding ratio of 4VP/OA (or OMA) was 2/1 (mol/mol), the unit fraction of 4VP/OA in P(4VP-*r*-OA) was 1.03 and that of 4VP/OA in P(4VP-*r*-OMA) was 1.31.

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The authors declare that there is no conflict of interest regarding the publication of this article.

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