

Synthesis of antimicrobial block copolymers bearing immobilized bacteriostatic groups

N. D. Koromilas,^a G. Ch. Lainioti,^{a,b} G. Vasilopoulos,^c A. Vantarakis^c and J. K. Kallitsis^{*,a,b}

^a Department of Chemistry, University of Patras, GR–26504, Patras, Greece.

^b FORTH/ICE-HT, Stadiou Str., P.O. Box 1414, GR–26504, Rio-Patras, Greece.

^c Environmental Microbiology, Department of Public Health, Medical School, University of Patras, Greece.

SI-1 Synthesis and characterization of PMMA-*b*-PVBCHAM_x copolymers

The chemical structure of PMMA-*b*-PVBCHAM_x copolymers was verified through ATR-FTIR spectroscopy. As shown in Figure S1, the characteristic bands of PMMA(1) macro-initiator and PVBCHAM appeared also in the spectra of PMMA(1)-*b*-PVBCHAM₆₅ copolymer, verifying the success of the polymerization. More specifically, the absorbance peaks of VBCHAM unit at 1610 cm⁻¹ and 1510 cm⁻¹, attributed to the aromatic C=C stretching, as well as the peaks at 1460 cm⁻¹ and 1482 cm⁻¹, assigned to the -CH₃ bending of the amines and the C-N bond respectively, appear in all copolymers' spectra. The aforementioned peaks, in combination with the band at 1730 cm⁻¹, assigned to the carbonyl stretching, verifying the existence of both VBCHAM and MMA units in the copolymer.

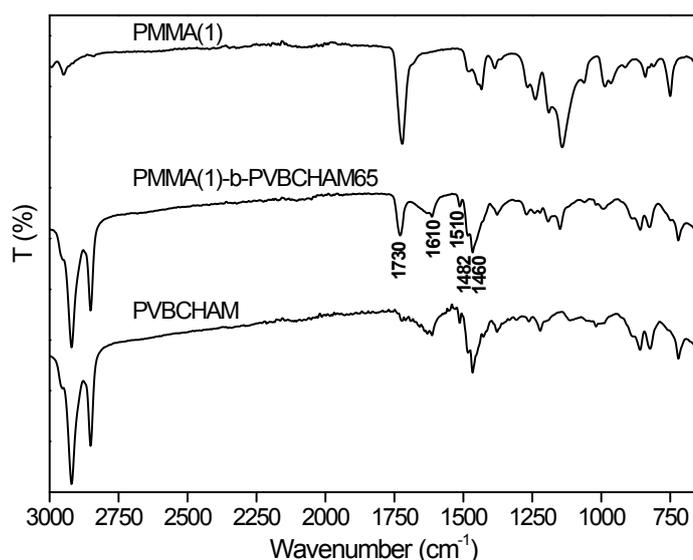


Fig. S1 ATR-FTIR spectra of the diblock copolymer PMMA(1)-*b*-PVBCHAM₆₅, the macro-initiator PMMA(1) and the homopolymer PVBCHAM.

SI-2 Size Exclusion Chromatography (SEC) measurements of PtBA macro-initiator

SEC measurements were conducted for the PtBA macro-initiator, where the estimated M_n , M_w and the polydispersity were 10379, 11638 and 1.12 respectively, indicating the controlled polymerization of the monomer. An example of the spectra obtained from SEC is shown in **Figure S2**.

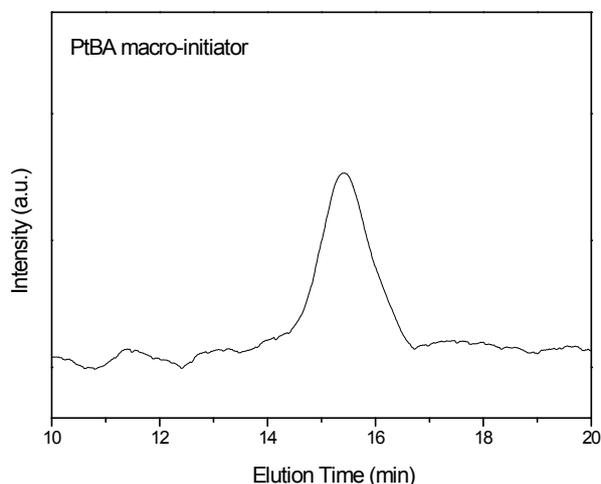


Fig. S2 Size exclusion chromatography for PtBA macro-initiator using CHCl_3 as eluent.

SI-3 Synthesis and characterization of VBCHAM and SSAmC₁₆ diblock copolymers

For the synthesis of SSAmC₁₆ and VBCHAM diblock copolymers, two different synthetic routes were followed as it is analytically described in the main manuscript. Briefly, in the first case, PVBCHAM macro-initiators were initially prepared via ATRP followed by the polymerization of SSAmC₁₆, whereas in the second synthetic route, due to difficulties in the direct polymerization of SSAmC₁₆ via ATRP, PSSAmC₁₆ macro-initiators were synthesized after ATRP of SSNa monomer followed by reaction with AmC₁₆. Subsequently, VBCHAM was polymerized, using PSSAmC₁₆ as macro-initiator.

The chemical structure of this new class of block copolymers was verified through ATR-FTIR spectroscopy. As shown in Figure S3 (first synthetic route) for the PVBCHAM(1)10-b-PSSAmC₁₆ copolymer, the ATR-FTIR spectra resembles mostly with the spectra of the homopolymer PSSAmC₁₆, due to the high molar percentage of the SSAmC₁₆ unit in the copolymer. More specifically, the peak at 1037 cm^{-1} attributed to the S=O stretching vibrations, while the peak at 1120 cm^{-1} assigned to the S-O stretching vibration.¹ Despite the low molar percentage of VBCHAM unit in the copolymer, the peaks at 1465 and 1484 cm^{-1} assigned to the CH_3 bending of the amines and the C-N formation bond respectively. Finally, the peak at 750 cm^{-1} , proved also the existence of the VBCHAM moiety.

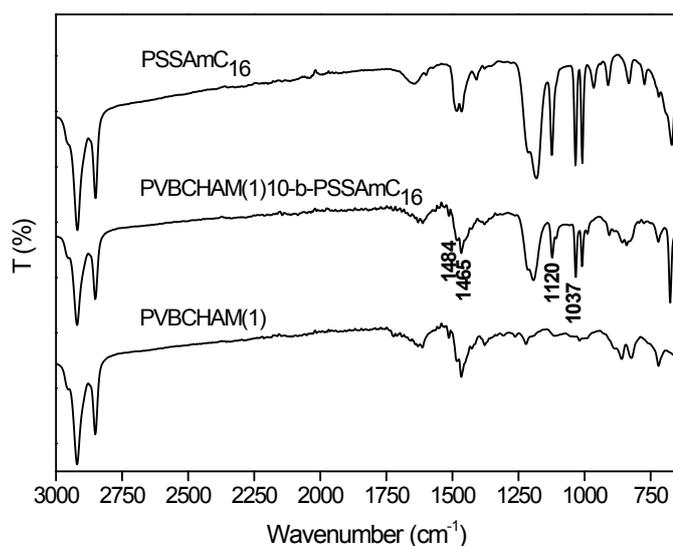


Fig. S3 ATR-FTIR spectra of the diblock copolymer PVBCHAM(1)10-b-PSSAmC₁₆, the macro-initiator PVBCHAM(1) and the homopolymer PSSAmC₁₆.

The chemical structure of the copolymers synthesized according to the second synthetic route was also verified with ATR-FTIR (Figure S4). The peaks correspondence was described above.

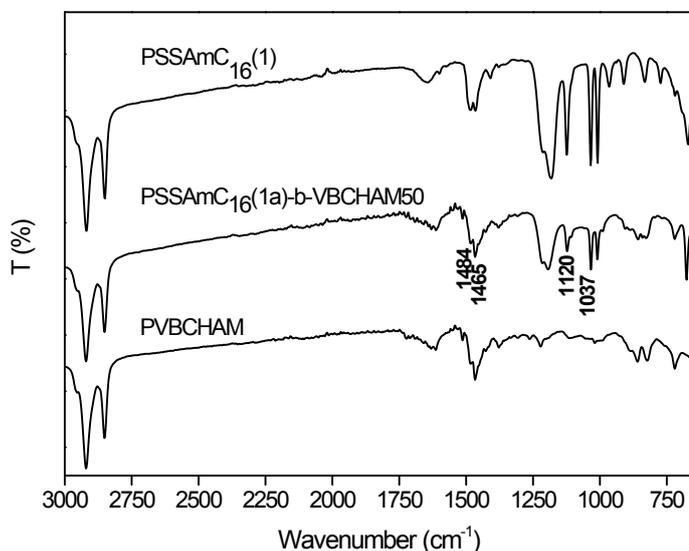


Fig. S4 ATR-FTIR spectra of the diblock copolymer PSSAmC₁₆(1a)-b-PVBCHAM50, the macro-initiator PSSAmC₁₆(1) and the homopolymer PVBCHAM.

Notes and references

- 1 J. Luo, Y. Chen, Q. Ma, R. Liu and X. Liu, *RSC Adv.*, 2013, **3**, 17866.

