Synthesis of Modified Guanidine-based Polymers and their Antimicrobial Activities Revealed by AFM and CLSM

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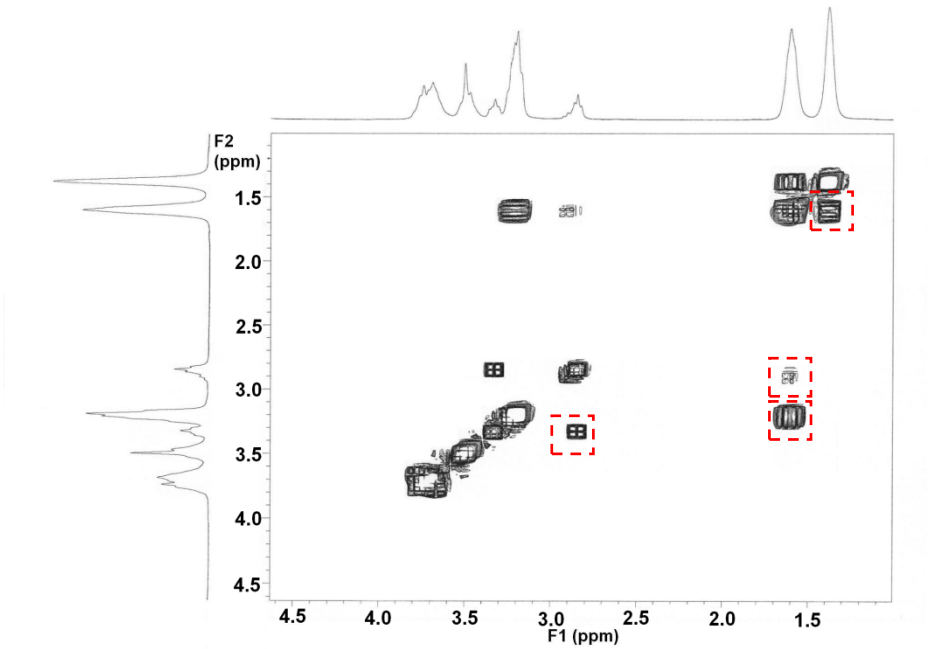
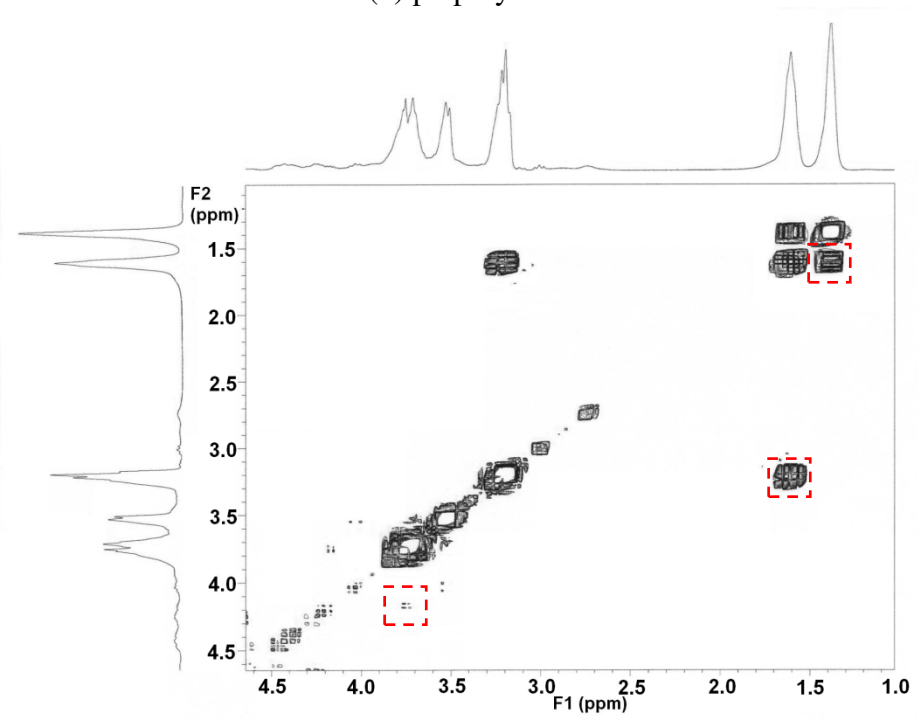
Supporting Information. Figures 1 and 2 show the 2D NMR spectra of prepolymer and modified guanidine-based polymer prepared with DETA and HMDA, which not only gave the chemical shift but also showed the correlation between various atoms (shown in dash squares). For the modified guanidine-based polymers with or without DETA, the chemical shifts of methylene protons a and b were assigned to 1.4ppm and 1.6ppm respectively for their similar chemical environment. A strong correlation between protons a and b in HH COSY spectra of prepolymer and modified guanidine-based polymer also indicated that the two protons were connected to the neighboring carbon atoms. The chemical shifts of carbons a and b were 25.8ppm and 28.2ppm, respectively, from the CH COSY 2D NMR spectra (see Supporting Information Figure 2). The chemical shift of proton c was assigned to 3.2ppm downfield by adjacent amine group, and the chemical shifts of carbon c were 41.3ppm and 43.1ppm for the interplay from different groups next to amine group. Both proton d and e showed two chemical shifts because the imino group in DETA competitively reacted with other two monomers in condensation in addition to amine group, which resulted in the complicated structures of prepolymer and various chemical shifts of the same proton. From Supporting Information Figure 1 (1), chemical shifts of proton d and e were assigned to 2.8-2.9ppm and 3.4ppm respectively for the prepolymer without imino group reaction, meanwhile a strong correlation existed between the two protons. For the prepolymer containing reactive imino groups, there were two possible reaction schemes, depending on the monomers reacted with. For the imino groups in DETA reacted with amine group in GH, the chemical shifts of both protons d and e were 3.5ppm due to the similar chemical circumstances and influence from positive charge in guanido groups; for the imino groups in DETA reacted with amine group in HMDA, the chemical shifts of proton d and e were 3.8ppm and 3.9ppm, respectively. There was almost no correlation between the protons;

meanwhile CH COSY 2D spectrum (Supporting Information Figure 2 (1)) showed that those protons with the same chemical shift were connected with different carbon atoms. With the reaction of prepolymer and EP, the imino groups in DETA were consumed gradually, resulting in proton peaks at 2.8-2.9ppm and 3.4ppm disappeared (see Supporting Information Figure 1 (2)). Protons g and h from EP in polymer were assigned the same chemical shift (3.9ppm) as proton e owing to their similar chemical environments; and those protons also showed the correlation with proton f (chemical shift=4.2ppm). Comparing the CH COSY 2D spectra of polymer and prepolymer (see Supporting Information Figure 2), one more carbon atom in polymer was correlated with the proton at 3.7-3.8ppm than that in prepolymer. For the modified guanidine-based polymer without DETA, the similar results of 2D NMR spectra were obtained, and protons g and h in EP were located at 3.6-3.8ppm with overlapped area. Both of them have correlation with proton f (4.0ppm and 4.2ppm).

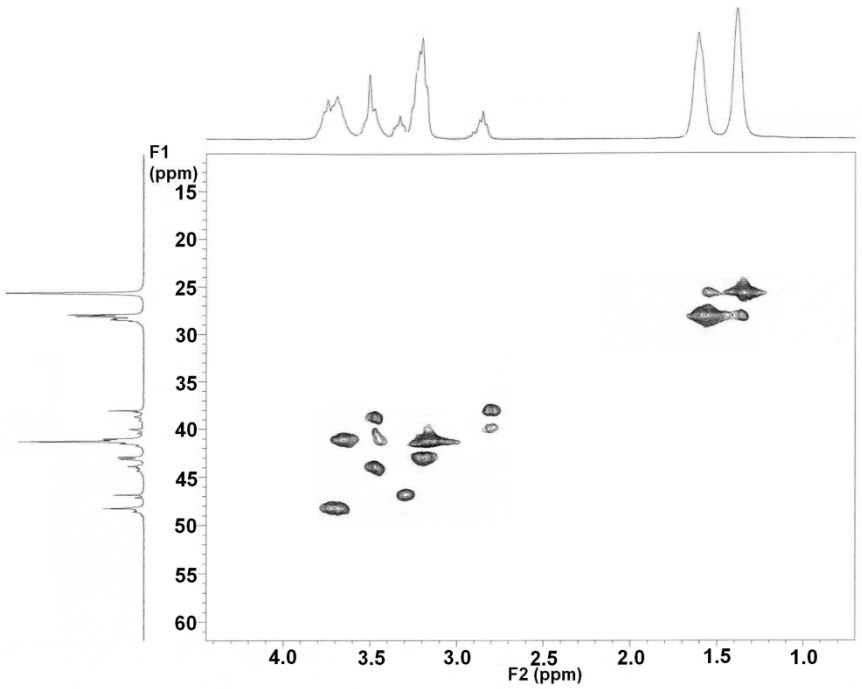


(1) prepolymer

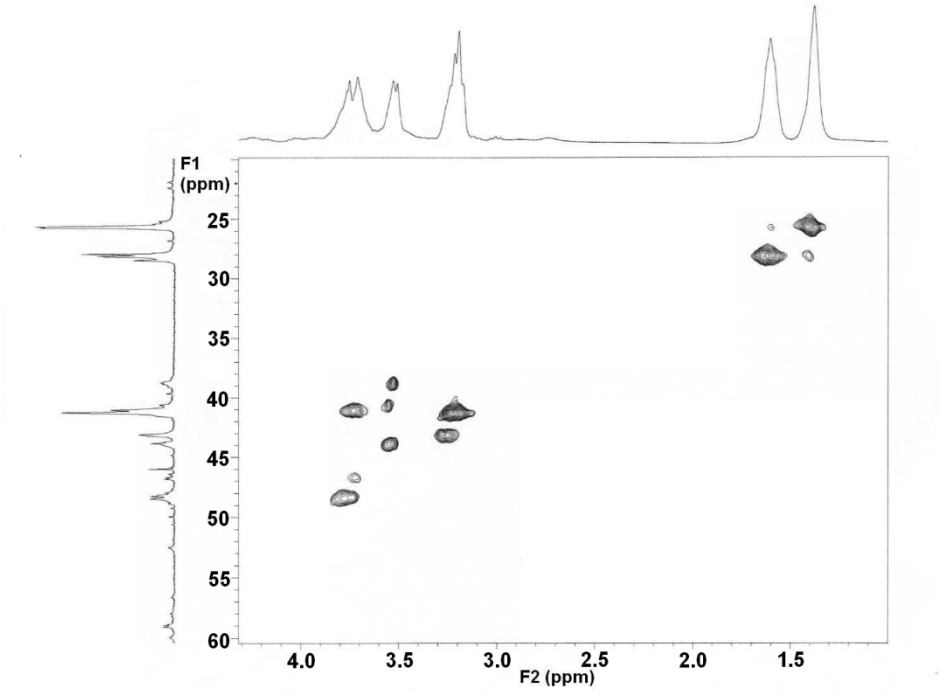


(2) polymer

Supporting Information Figure 1. HHCOSY 2D NMR spectrum of modified guanidine-based polymer (E-PHDGC)



(1) prepolymer



(2) polymer

Supporting Information Figure 2. CHCOSY 2D NMR spectrum of modified guanidine-based polymer (E-PHDGC)