Supporting Information for

Synthesis and characterization of block copolymer of polyphosphoester and poly(epsilon-caprolactone)

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Synthesis Procedures:

Block copolymerization was carried out in toluene using A_3 of $Al(O^iPr)_3$ as an initiator, which was obtained according to the method reported by A. Duda[1] et al., and contained 86.7% of trimer A_3. Poly(ε-caprolactone) macroinitiator was synthesized at 25□ for two hours and an aliquot of the "living" poly(ε-caprolactone) solution was taken out, deactivated, and precipitated in diethyl ether anhydrous for Gel Permeation Chromatography (GPC) and NMR analysis. A known amount of phosphoester (R= $^iC_3H_7$ or Et) was then added to the "living" poly(ε-caprolactone) solution. The final copolymer was deactivated by an excess of acetic acid solution and precipitated in cold methanol.

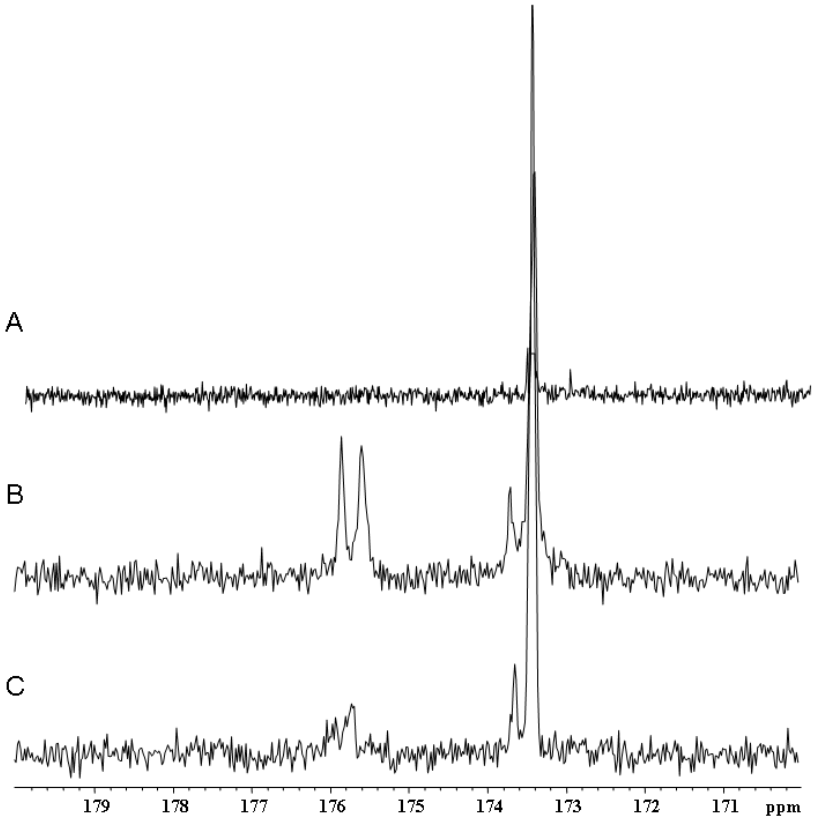

Figure S1. Carbon resonance of carbonyl of block copolymer without transesterification (A), random copolymer (B), and block copolymer with transesterification (C) of ε-caprolactone and phosphoester (R= $^{i}C_3H_7$).

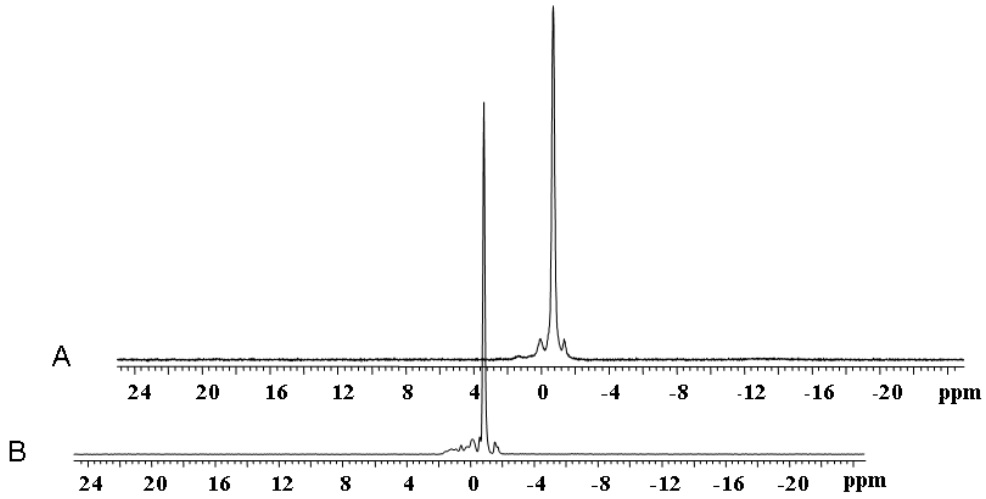

Figure S2. ^{31}P-NMR spectra of block copolymer of ε-caprolactone and phosphoester without transesterification (A), and with transesterification (B) (R= $^{i}C_3H_7$).

Gel permeation chromatography (GPC) measurement was carried out using a Waters 1515 ISOCRATIC HPLC PUMP equipped with Waters Styragel HT4×2 and HT5 HPLC columns. Tetrahydrofuran was used as the mobile phase at 1 mL/min flow rate. Sample was detected with a differential refractive index detector (Wyatt Technology, Santa Barbara, CA, USA) and analyzed using polystyrene as standard.

References:

1. A. Duda, S. Penczek, *Makrol Rapid Commun*. 1995, **16**, 67-76.