Supporting information

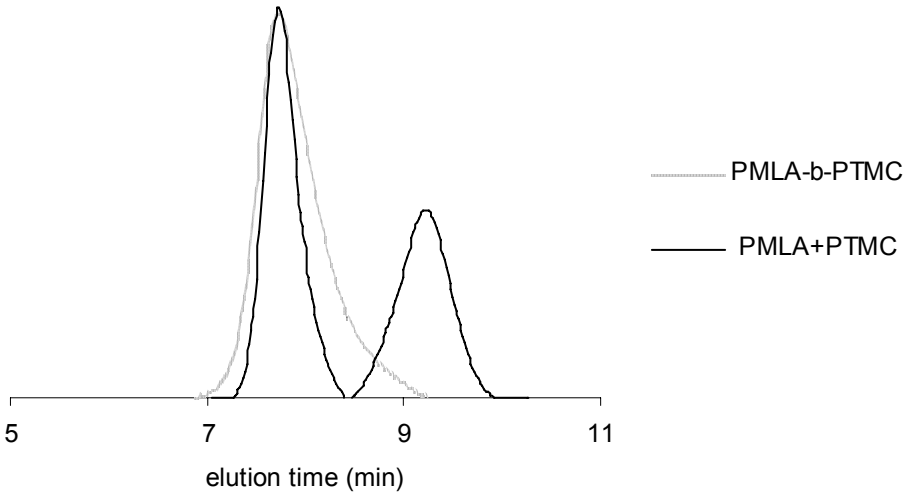
^{1}H and ^{13}C NMR data of (co)polymers.

H-PMLABe-OBn: ^{1}H NMR (400 MHz; $CDCl_3$; δ (ppm)): 7.25 (s, (5n+5)H, CHC(O)OCH$_2$*Ph*, OCH$_2$*Ph*), 5.45 (m, 1nH, C*H*C(O)OCH$_2$Ph), 5.04 (s, (2n+2)H, CHC(O)OC*H$_2$*Ph, OC*H$_2$*Ph), 2.87 (m, 2nH, CHC*H$_2$*C(O)). ^{13}C NMR (100 MHz; $CDCl_3$; δ (ppm)): 168.7 (*C*(O)), 128.3 (*C$_6$*H$_5$), 68.7 (*C*H), 68.0.7 (*C*H$_2$C$_6$H$_5$), 38.8 (*C*H$_2$). IR: υ = 1745 cm^{-1} (νC(O)).

H-PTMC-*b*-PMLABe-OBn: ^{1}H NMR (400 MHz; $CDCl_3$; δ (ppm)): 7.32 (m, (5n+5)H,, CO$_2$CH$_2$*Ph*-PMLABe, OCH$_2$*Ph*), 5.51 (m, 1nH, C*H*CO$_2$CH$_2$Ph-PMLABe), 5.04 (m, (2n+2)H, CO$_2$C*H$_2$*Ph-PMLABe, OC*H$_2$*Ph), 4.25 (m, 4mH, C*H$_2$*O-PTMC), 2.93 (m, 2nH, CHC*H$_2$*C(O)-PMLABe), 2.08 (m, 2mH, CH$_2$C*H$_2$*CH$_2$-PTMC). ^{13}C NMR (100 MHz; $CDCl_3$; δ (ppm)): 167.9 (*C*(O)-PMLABe), 154.7 (O*C*(O)O-PTMC), 128.0 (*C$_6$*H$_5$-PTMC and -PMLABe), 68.0 (*C*H-PMLABe), 67.3 (*C*H$_2$C$_6$H$_5$-PMLABe), 64.6 (*C*H$_2$*C*H$_2$-PTMC), 34.2 (*C*H$_2$-PMLABe), 27.7 (*C*H$_2$-PTMC).

C$_6$H$_5$CH$_2$C(O)O-PMLABe-*b*-PTMC-OBn: ^{1}H NMR (300 MHz; $CDCl_3$; δ (ppm)): 7.51 (m, 5H, OC(O)CH$_2$*Ph*-PTMC), 7.28 (m, 5nH, CHOC(O)CH$_2$*Ph*-PMLABe), 5.52 (m, 1nH, C*H*CO$_2$CH$_2$Ph-PMLABe), 5.10 (m, 2nH, CO$_2$C*H$_2$*Ph-PMLABe), 4.25 (m, 4mH, C*H$_2$*O-PTMC), 2.92 (m, 2nH, CHC*H$_2$*C(O)-PMLABe), 2.07 (m, 2mH, CH$_2$C*H$_2$*CH$_2$-PTMC). ^{13}C NMR (75 MHz; $CDCl_3$; δ (ppm)): 167.6 (*C*(O)-PMLABe), 154.7 (O*C*(O)O-PTMC), 128.4 (*C$_6$*H$_5$-PTMC and -PMLABe), 67.9 (*C*H-PMLABe), 67.5 (*C*H$_2$C$_6$H$_5$-PMLABe), 64.7 (*C*H$_2$*C*H$_2$-PTMC), 34.7 (*C*H$_2$-PMLABe), 28.2 (*C*H$_2$-PTMC).

Figure S1. SEC chromatograms of a mixture of a PMLABe ($\overline{Mn}_{SEC}$ = 9 300 g.mol^{-1}, $\overline{Mw}/\overline{Mn}$ = 1. 40 -plain trace) and a PTMC ($\overline{Mn}_{SEC}$ = 5 700 g.mol^{-1}, $\overline{Mw}/\overline{Mn}$ = 1.60 -plain trace) and of the PMLABe-*b*-PTMC ($\overline{Mn}_{SEC}$ = 9 230 g.mol^{-1}, $\overline{Mw}/\overline{Mn}$ = 1.46 - dashed trace) block copolymer obtained by their coupling.



Note that one would indeed expect a shorter elution time for the copolymer PMLA-*b*-PTMC as compared to each homopolymer. Such behaviour most likely arises from the different affinity of the copolymers and of the PMLA homopolymer towards the SEC support. This is similar to the behaviour of the homopolymers of PMLARs[**Error! Bookmark not defined.**a,d,**Error! Bookmark not defined.**a] and of other related four membered ring such as β-butyrolactone.[**Error! Bookmark not defined.**,**Error! Bookmark not defined.**d,**Error! Bookmark not defined.**and references therein