Synthesis of Poly(ε-caprolactone)-based Miktoarm Star Copolymers through ROP, SA ATRC, and ATRP

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Supplementary Materials

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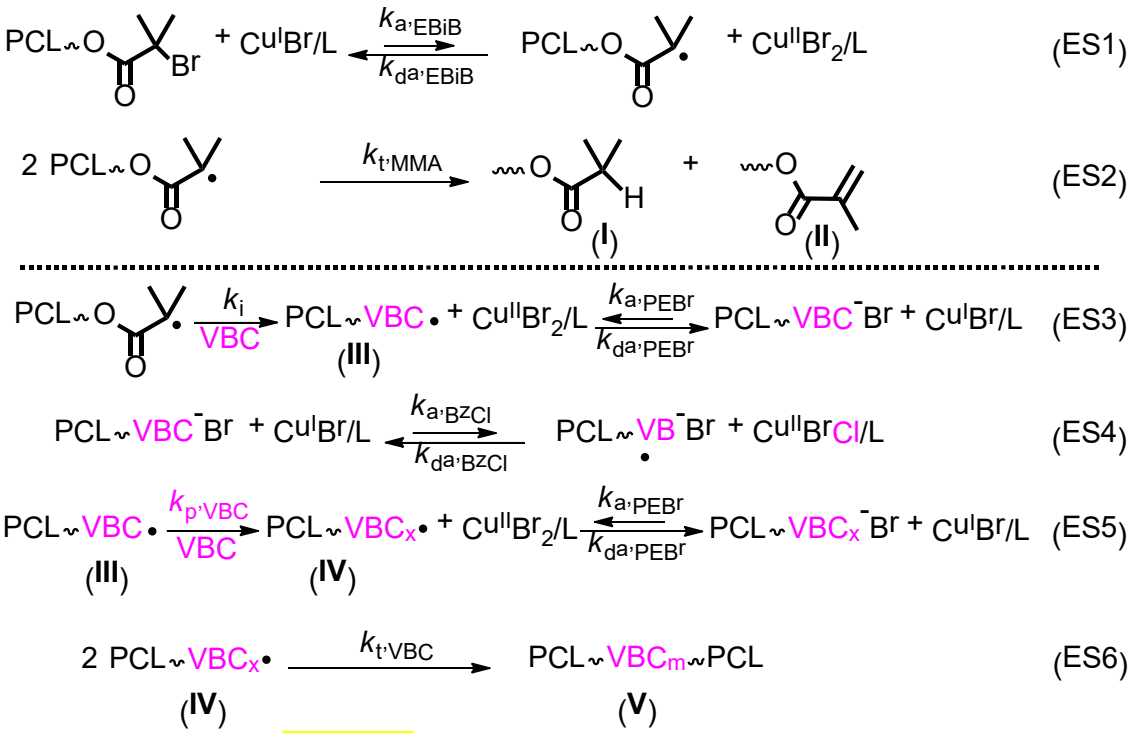
Table S1. Various inserted VBC units after SA ATRC of PCL–Br: estimated (Cal.) and measured (Exp.) m/z values in Fig. 3 ($M_{n,GPC}$ = 5700, PDI = 1.18, x_c = 0.94).

Formula of (PCL_n)-VBC_m-$(PCL_n)/Na^+$ (based on n = 14)	Inserted VBC units (m)	m/z values	
		Cal.	Exp.
$C_{92}H_{154}O_{32}(C_9H_9Cl)_2/Na^+$	2	2099.61	
$C_{92}H_{154}O_{32}(C_9H_9Cl)_3/Na^+$	3	2252.23	
$C_{92}H_{154}O_{32}(C_9H_9Cl)_4/Na^+$	4	2404.85	2405.54
$C_{92}H_{154}O_{32}(C_9H_9Cl)_5/Na^+$	5	2557.47	

Table S2. Summary of rate constants based on initiators of EBiB, BzCl, and PEBr and monomers of MMA and St.

Rate constant	Value [M^{-1} s^{-1}]	Reference
$k_{a,EBiB}$	1.4	[1-3]
$k_{da,EBiB}$	1.9×10^{7}	[1-3]
$k_{t,MMA}$	6.1×10^{8}	[4]
$k_{a,BzCl}$	2.9×10^{-3}	[1-3]
$k_{da,BzCl}$	8.1×10^{5}	[1-3]
k_{i}	5.41×10^{3}	[5]
$k_{p,VBC}$	172.1	[1-3,6]
$k_{a,PEBr}$	8.8×10^{-2}	[1-3]
$k_{da,PEBr}$	2.7×10^{6}	[1-3]
$k_{t,VBC}$	3.99×10^{8}	[7]

k_a: ATRP activation rate constant; k_{da}: ATRP deactivation rate constant. The conditions to estimate the constants were described in the references (i.e. values of ethyl α-bromoisobutyrate (EBiB), benzyl chloride (BzCl) and 1-phenyl ethylbromide (PEBr) with CuBr/PMDETA measured in acetonitrile (MeCN) at 22 °C [1-3]; MMA: methyl methacrylate and St: styrene). k_i: rate constant for addition from methacrylic radical to St (value calculated from the frequency factor and activation energy) [5]. $k_{p,VBC}$: propagation rate constant of VBC; $k_{t,VBC}$: termination rate constant referred to the value of St.



Scheme S1. Reaction mechanisms of SA ATRC.

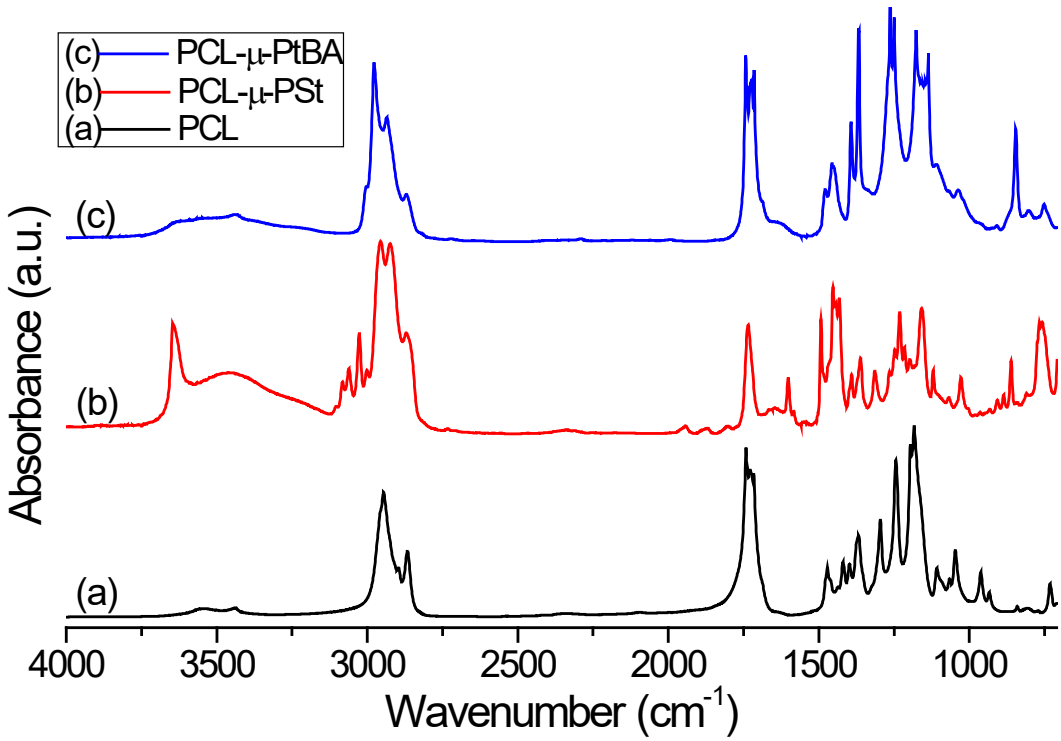


Figure S1. FT-IR spectra of (a) PCL, (b) PCL-μ-PSt, and (c) PCL-μ-PtBA (co)polymers.

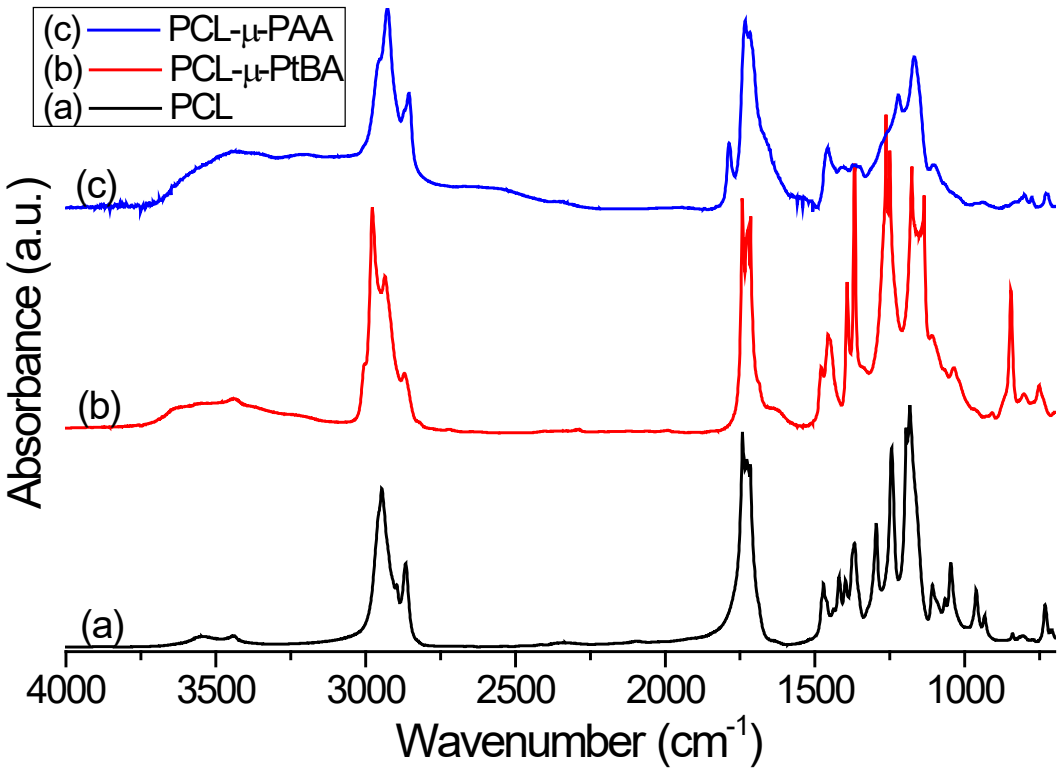


Figure S2. FT-IR spectra of (a) PCL, (b) PCL-μ-PtBA, and (c) PCL-μ-PAA (co)polymers.

3. References

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