

Supporting Information

Determination of composition of P(VCL-t-BOCAPMA) copolymers by FT-IR technique. To characterize copolymer composition with FT-IR technique, we have synthesized homopolymers of VCL and t-BOCAPMA – PVCL and P(t-BOCAPMA), respectively. Figure 1S shows that PVCL has a strong adsorption band at 1633 cm^{-1} associated with the stretching vibration of the carbonyl group in VCL ring, while in the spectrum of P(t-BOCAPMA), there are two overlapping peaks at $1689\text{ and }1638\text{ cm}^{-1}$ (peaks 1 and 2, respectively) associated with two types of carbonyl groups of t-BOC and of methacrylamide groups, respectively. To separate the overlapping peaks 1 and 2 of P(t-BOCAPMA), as well as to separate absorbances of P(t-BOCAPMA)/PVCL mixtures in region 1 and 2, we have applied curve-fitting using GRAMS Spectroscopy software. For the P(t-BOCAPMA) homopolymer, the ratio of integral intensities of the peaks centered at 1689 cm^{-1} and 1638 cm^{-1} (peaks 1 and 2, respectively) was found to be $A_2/A_1 = 0.8$. For mixtures of P(t-BOCAPMA) and PVCL with known compositions, the ratio of extinction coefficients in region 2, R_e , was calculated from the following equation:

$$R_e = \frac{f_{P(t-BOCAPMA)}(A_{\Sigma 2} - 0.8A_1)}{A_1(1 - f_{P(t-BOCAPMA)})} \quad (1)$$

where A_1 and $A_{\Sigma 2}$ are total integral absorbances of P(t-BOCAPMA)/PVCL mixtures in regions 1 and 2, respectively, and ($f_{P(t-BOCAPMA)}$) is a molar fraction in repeating units of P(t-BOCAPMA) in the mixture.

The R_e value was found to be 1.46. This value was then used to calculate the unknown fraction f of t-BOCAPMA monomer units in P(VCL-t-BOCAPMA) copolymers:

$$f = \frac{1.46A_1}{A_{\Sigma 2} + 0.66A_1} \quad (2)$$

Fig. S1. FT-IR spectra of P(t-BOCAPMA) (top) and PVCL (bottom) homopolymers.

Determination of composition of P(VCL-t-BOCAPMA) copolymers by H^1 NMR.

Figure S2 shows the NMR spectrum of one of P(VCL-t-BOCAPMA) copolymers (i.e. that containing 9% of t-BOCAPMA units as determined by FT-IR), before (a) and after (b) hydrolysis of a t-BOC protective group. From the change in the integral intensity (ΔI_a) in the region of 1-2 ppm, the fraction of t-BOC-containing units in the P(VCL-t-BOCAPMA) copolymers was calculated as follows:

$$f = \frac{\Delta I_a / 9}{\Delta I_a / 9 + \Delta I_d} \quad (3)$$

where ΔI_a is the integral intensity in the area of 1-2 ppm, and ΔI_d is the integral intensity in the area of 4-5 ppm associated with $-CH-N$ protons in the PVCL ring (Fig. 2S, d). Significantly, FT-IR and NMR techniques gave consistent results. The estimated amount of amino-containing groups in the hydrolyzed P(VCL-t-BOCAPMA) copolymer shown in Fig. S2 was 8.5%, while FT-IR analysis yielded 9%.

As seen in Fig. S3, the 1694 cm^{-1} peak associated with t-BOC carbonyl groups ($-\text{NH}-\text{C=O}$) present in the P(VCL-t-BOCAPMA-9) copolymer (A), disappeared after acidic hydrolysis of the copolymer (B), confirming complete removal of t-BOC groups.

Fig. S2. H^1 NMR spectra of P(VCL-t-BOCAPMA-9) (A) and PVCL-co-NH₂-9 (B), copolymers in CDCl_3 .

Figure S3. FT-IR spectra of P(VCL-t-BOCAPMA-9) (top) and PVCL-co-NH₂-9 (bottom) copolymers.

GPC analysis of PVCL-co-NH₂-X copolymers. GPC analysis of the PVCL-co-NH₂-X copolymers revealed bimodal molecular weight distribution, probably caused by locally high concentrations of t-BOCAPMA resulting from drop-wise addition of the monomer. Table 1 summarizes data on synthesis and characterization of the PVCL-co-NH₂-X copolymers.

Table 1. Percentage of amino-containing units and molecular weights of the synthesized PVCL-co-NH₂ copolymers.

Copolymer	% of NH ₂ units		Molecular mass, GPC	
	NMR	FT-IR	Peak 1	Peak 2
PVCL-co-NH ₂ -5	4.5	5	M_w 367 kDa M_n 360 kDa	M_w 202 kDa M_n 200 kDa
PVCL-co-NH ₂ -9	8.5	9	M_w 375 kDa M_n 370 kDa	M_w 206 kDa M_n 203 kDa
PVCL-co-NH ₂ -20	19	20	M_w 381 kDa M_n 376 kDa	M_w 210 kDa M_n 204 kDa

Fig. S1

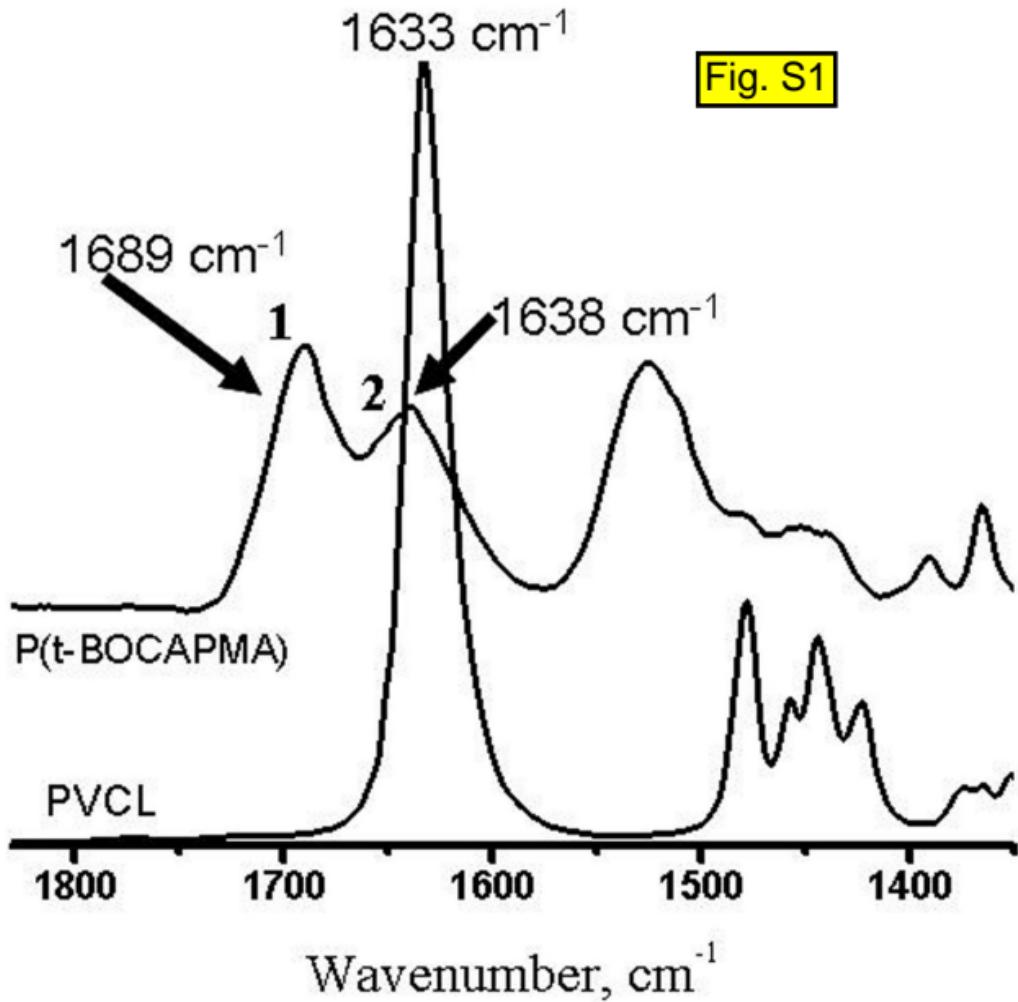


Fig. S2

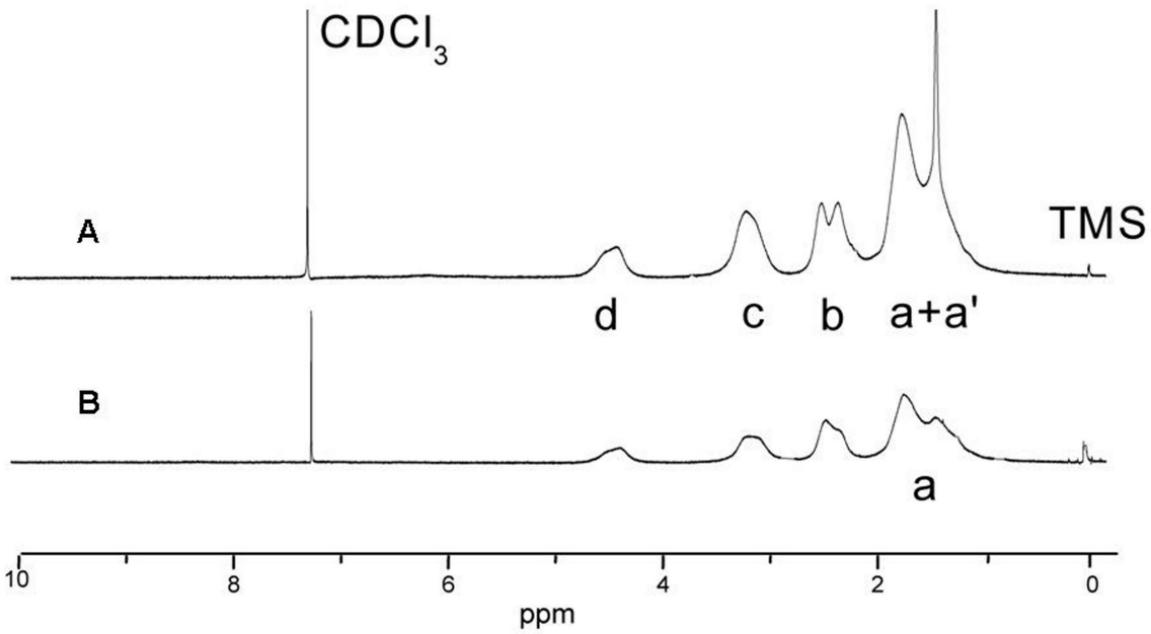
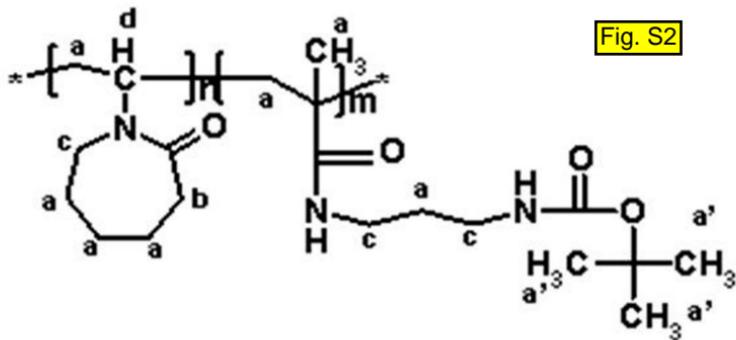


Fig. S3

