Facile synthesis of quantitatively tertiary-amine functionalized poly(styrene-co-1,3-pentadiene) copolymers with controlled narrow composition distributions by LAP

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Experiment parts.

1.1 Experimental Reagents

The main reagents used during the experiment are listed in Table S1.

Table S1. Main Chemical Reagents

reagents	purity	manufacturer
p-Methyl dimethylamino styrene (VBDMA)	≈ 99 %	Self-made
p-Methyl pyrrolidinyl styrene (VBTFP)	≈ 99 %	Self-made
p-Methyl piperidinyl styrene (VBMP)	≈ 99 %	Self-made
1,3-Pentadiene(PD)	Z+E≈ 98 %	Self-made
p-chloromethylstyrene(VBC)	99%	Shandong Xingshun New Materials Co., Ltd
Dimethylamine (DMA)	AR	China National Pharmaceutical Group Chemical Reagent Co., Ltd
Pyrrolidine (THP)	AR	China National Pharmaceutical Group Chemical Reagent Co., Ltd
Piperidine (MP)	AR	China National Pharmaceutical Group Chemical Reagent Co., Ltd
Styrene(ST)	99.5%	Yueyang Baoying Petrochemical Co., Ltd
Deuterated chloroform($CDCl_3$)	AR	Sinochem Saen Chemical Technology Co., Ltd.
Cyclohexane(CH)	AR	Aladdin Reagent Co., Ltd.
Anhydrous methanol(MeOH)	AR	China National Pharmaceutical Group Chemical Reagent Co., Ltd
n-Butyllithium(n-BuLi)	2.5 M(in hexane)	Yueyang Baoying Petrochemical Co., Ltd
High-purity argon(Ar)	99.999 %	Changsha Rizhen Gas Co., Ltd.
Calcium hydride(CaH_2)	AR	Aladdin Reagent Co., Ltd.
potassium hydroxide (KOH)	AR	Aladdin Reagent Co., Ltd.
Sodium hydroxide(NaOH)	AR	Aladdin Reagent Co., Ltd.

(1) ***Purification of 1,3-pentadiene.*** (a) Under Ar protection, add the crude product of PD to a distillation flask, add an appropriate amount of solid potassium hydroxide, stir for 24 hours, and distill at 50 °C; (b) Add an appropriate amount of silver ammonia solution to the fraction obtained in (a), stir for 5 to 6 hours, let it stand until the oil and water phases are significantly separated, collect the oil phase and then add CaH_2. Then stir for 4 hours, and continue to distill at 50 °C; (c) Transfer the fraction obtained in (b) to another distillation flask and add an appropriate amount of n-BuLi, continue to distill at 50 °C to obtain the fraction. All the distillations mentioned above are carried out under Ar protection, and the final fraction is sealed with Ar gas for storage.
(2) ***Purification of CH***. Add an appropriate amount of CaH_2 to CH, stir for 12 hours under a Ar atmosphere, and distill at 90 to 95 °C under normal pressure. The fraction is sealed with Ar gas for storage.
(3) ***Purification of ST***. Add an appropriate amount of CaH_2 to ST, stir for 12 hours under an Ar atmosphere, and distill at 40 to 45 °C under reduced pressure (-0.1MPa). The fraction is sealed with Ar gas for storage.
(4) ***Preparation of VBDMA***. Under nitrogen atmosphere and in ice-water bath or at room temperature, the dimethylamine (13.52g, 0.30 mol) of 40% mole fraction in water was added to a 100 mL three-necked flask. Then the 4-Vinylbenzyl chloride (21.66g, 0.15 mol) was added dropwise via a constant pressure dropping funnel. The reaction was intensely exothermic during the process. After the apparatus cooled down, it was heated to 70 °C and reacted for 2 h. After thorough stirring and cooling, 30 mL of deionized water was added. The mixture was allowed to stand for 12 h, and the upper clear layer was extracted to obtain 20mL of the crude product, vinylbenzyl-N,N-dimethylamine. Pure vinylbenzyl-N,N-dimethylamine (22.85g, 0.12mol) was obtained by vacuum distillation, collecting the distillate while maintaining the external flask wall temperature at 120 °C. The resulting sample was stored in a -10 °C refrigerator for subsequent use.
(5) Other polar monomers, like **VBTHP and VBMP**, are synthesized with a similar method (Figure S1).
(6) Other reagents can be used directly without purification.

1.2 Experimental Methods

All reactions in this experiment were carried out in a glove box filled with argon gas under strictly anhydrous and oxygen-free conditions. The specific experimental steps are as follows: (1) Place magnetic stirring bars in clean and dry Schlenk tubes and number them. Heat to the specified temperature and transfer to the transition chamber. After three consecutive vacuum evacuations and argon gas purges, reduce the water and oxygen content in the tubes to below 10 ppm and transfer them to the glove box in numerical order. (2) Use a pipette to add 0.5 mL of solvent and m=0.3 g of monomer to the reaction tubes. Start magnetic stirring to thoroughly mix the monomer and solvent, and add n-BuLi as the initiator to start the anionic polymerization reaction. Transfer the reaction tubes to an IKA reactor and initiate the polymerization reaction at the preset temperature (all reactions in this experiment were conducted at 50 °C). (3) When the reaction reaches the preset time point, add degassed methanol as the reaction terminator. Transfer the terminated reaction product from the Schlenk tube to the corresponding numbered centrifuge tube (previously placed on an electronic analytical balance and weighed, with its mass recorded as m_0), and add an adequate amount of methanol for product precipitation and washing. Repeat this operation three times. Finally, place the centrifuge tube containing the product in a vacuum drying oven and dry it at -0.04 MPa and 40 °C. Weigh the dried centrifuge tube containing the product and record its mass as m_1. Calculate the monomer conversion rate x using the following formula:

$$x = \frac{m_1 - m_0}{m} \times 100\%$$

m - total mass of monomer (g); m_0 - mass of empty centrifuge tube (g); m_1 - mass of centrifuge tube containing product (g); x - monomer conversion rate (%).

1.3 Analysis and Characterization

(1) Nuclear Magnetic Resonance (NMR) spectroscopy for determining the microstructure of polymers. The Bruker AVANCE-Ⅲ-HD-400 NMR spectrometer (400 MHz) was used for the determination. Deuterated solvents were used as the test solvents, and tetramethylsilane was used as the internal standard. The test temperature was controlled at 25 °C, and the sample mass for ^{1}H NMR was 10-15 mg.

(2) Fourier Transform Infrared Spectroscopy (FT-IR) for determining the functional group structure of polymers. The Nicolet AVATAR-370 FT-IR spectrometer was used for the determination. The samples were prepared by the coating method, and KBr pellets were used for measurement. The test solvent was THF, with a wavenumber range of 4000-400 cm^{-1}, and the transmission rate T% was set at 30-50%, with a resolution of 2 cm^{-1}.

(3) Differential Scanning Calorimetry (DSC) for determining the glass transition temperature of polymers. The TA DSC25 differential scanning calorimeter was used for the determination. The sample mass was 10 mg. After setting the required temperature range, the first heating rate was 15 °C/min, and the second heating rate was 10 °C/min.

(4) Gel Permeation Chromatography (GPC) was performed using a Breeze system (Waters Corporation, USA) to determine the number-average molecular weight (Mn), weight-average molecular weight (M_w), and molecular weight distribution (PDI) of the polymer. The test conditions were as follows: tetrahydrofuran (THF) was used as the mobile phase, the test temperature was 35 °C, and the flow rate was 1.0 mL/min. Polystyrene (PS) standards were used for molecular weight calibration. The sample was dissolved in the mobile phase and filtered through a 0.22 μm filter membrane before injection, with an injection volume of 20 μL. This method was mainly used to characterize the molecular weight of the polymer and the uniformity of its distribution.

Figures:

Figure S1. The synthesized routine for the polar monomers in this work

Figure S2. The kinetic analysis of ST, PD, and VBN polar monomer terpolymerization (m_{ST}/m_{PD} = 80/20 at 323K)

Figure S3.The kinetic analysis of ST, PD, and VBN polar monomer terpolymerization (m_{ST}/m_{PD} = 85/15 at 323K)

Figure S4. The typical ^{1}H NMR spectrum of the ST/PD/VBDMA copolymer ($CDCl_3$).

Figure S5. The typical ^{1}H NMR spectrum of the ST/PD/VBTHP copolymer ($CDCl_3$).

Figure S6. The typical ^{1}H NMR spectrum of the ST/PD/VBMP copolymer ($CDCl_3$).

Figure S7. ^{1}H NMR spectra (A) of the copolymers at different conversions and the copolymer composition distribution (B) in the case of m_{ST}/m_{PD} = 80/20 copolymerization.

Figure S8. ^{1}H NMR spectra of the copolymers at different conversions under different VBDMA content (A-5%, C-10%, E-15%) and the copolymer composition distribution (B-5%, D-10%, F-15%) in the fixed ratio of m_{ST}/m_{PD} = 80/20 copolymerization.

Figure S9. [1]H NMR spectra of the copolymers at different conversions under different VBTHP content (A-5%, C-10%, E-15%) and the copolymer composition distribution (B-5%, D-10%, F-15%) in the fixed ratio of m_{ST}/m_{PD} = 80/20 copolymerization.

Figure S10. [1]H NMR spectra of the copolymers at different conversions under different VBMP content (A-5%, C-10%, E-15%) and the copolymer composition distribution (B-5%, D-10%, F-15%) in the fixed ratio of m_{ST}/m_{PD} = 80/20 copolymerization.

Figure S11. [1]H NMR spectra (A) of the copolymers at different conversions and the copolymer composition distribution (B) in the case of m_{ST}/m_{PD} = 85/15 copolymerization.

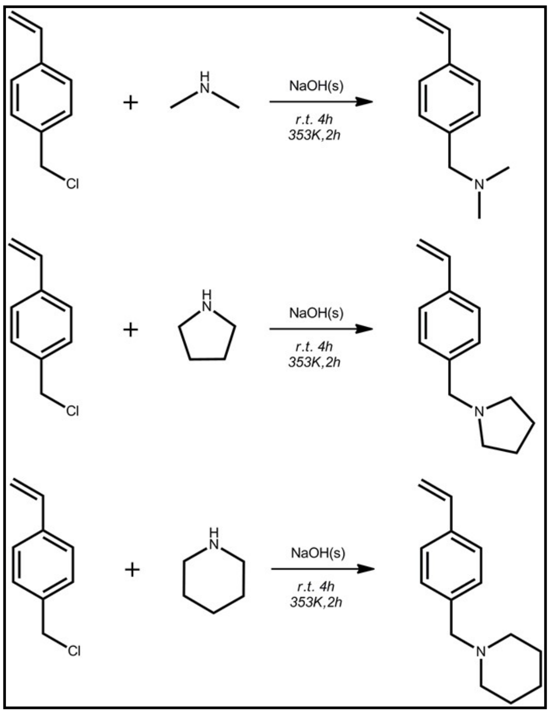
Figure S12. [1]H NMR spectra of the copolymers at different conversions under different VBDMA content (A-5%, C-10%, E-15%) and the copolymer composition distribution (B-5%, D-10%, F-15%) in the fixed ratio of m_{ST}/m_{PD} = 85/15 copolymerization.

Figure S13. [1]H NMR spectra of the copolymers at different conversions under different VBTHP content (A-5%, C-10%, E-15%) and the copolymer composition distribution (B-5%, D-10%, F-15%) in the fixed ratio of m_{ST}/m_{PD} = 85/15 copolymerization.

Figure S14. [1]H NMR spectra of the copolymers at different conversions under different VBMP content (A-5%, C-10%, E-15%) and the copolymer composition distribution (B-5%, D-10%, F-15%) in the fixed ratio of m_{ST}/m_{PD} = 85/15 copolymerization.

Figure S15. The GPC traces of the binary copolymer products

Figure S16. The effect of tertiary amine model compounds on the microstrucure of polyisoprene



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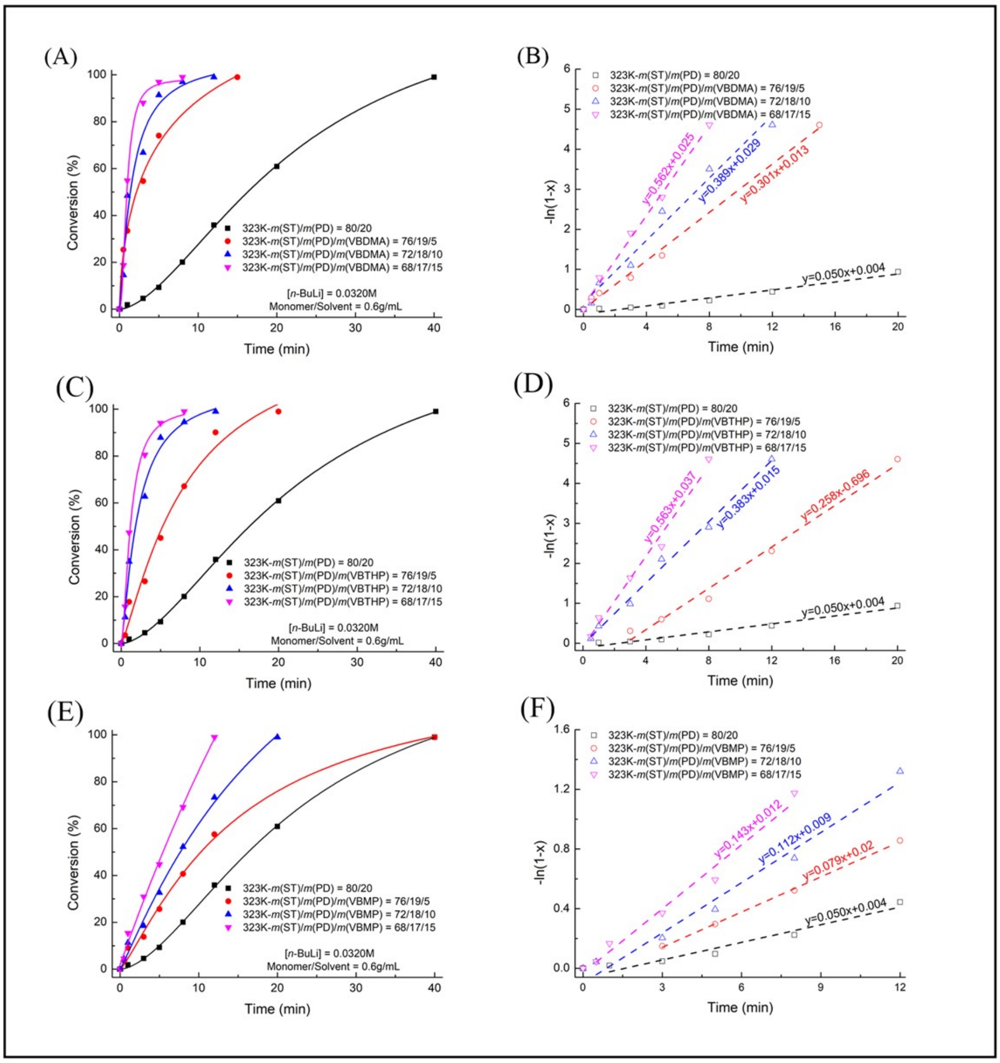

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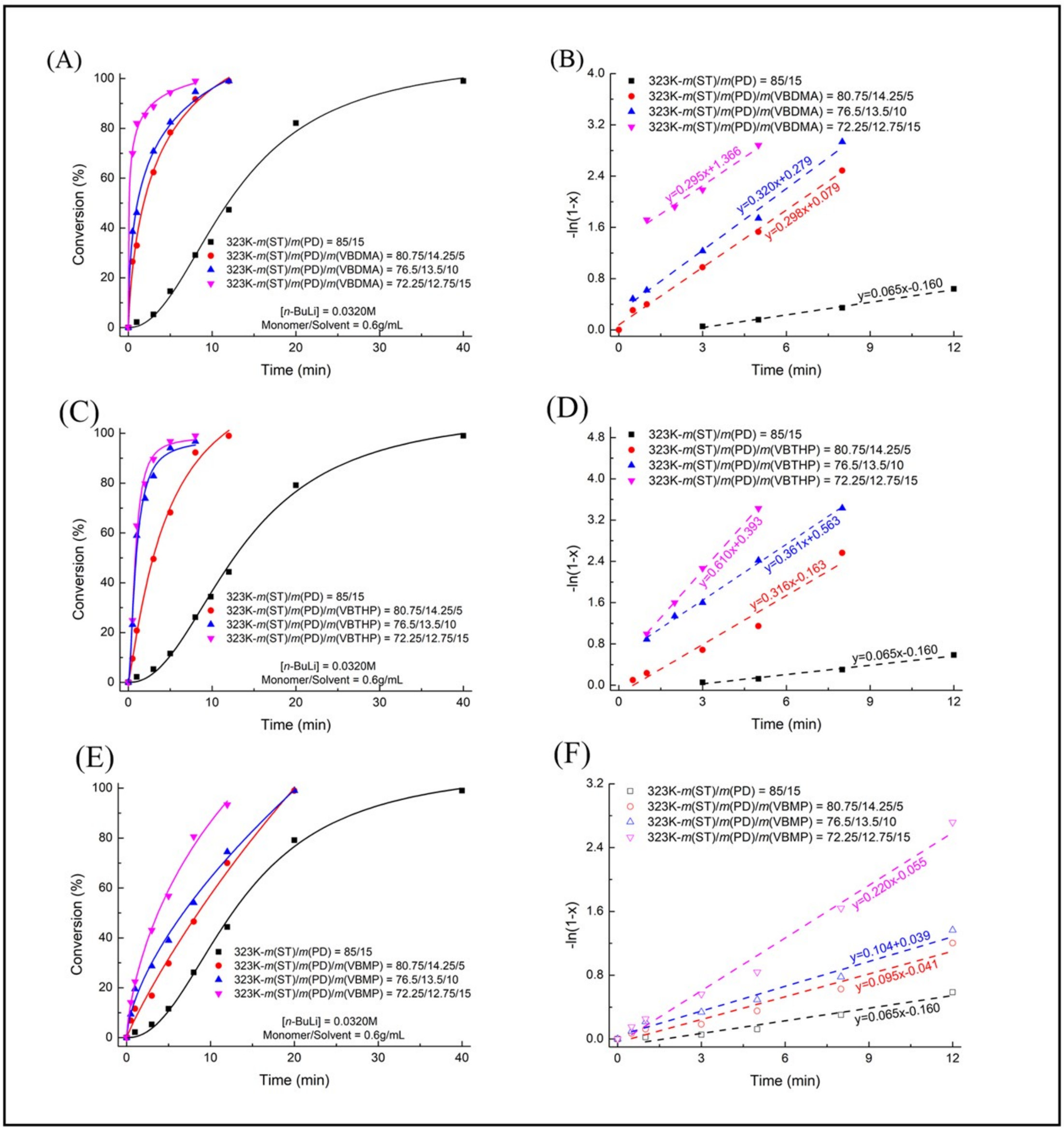

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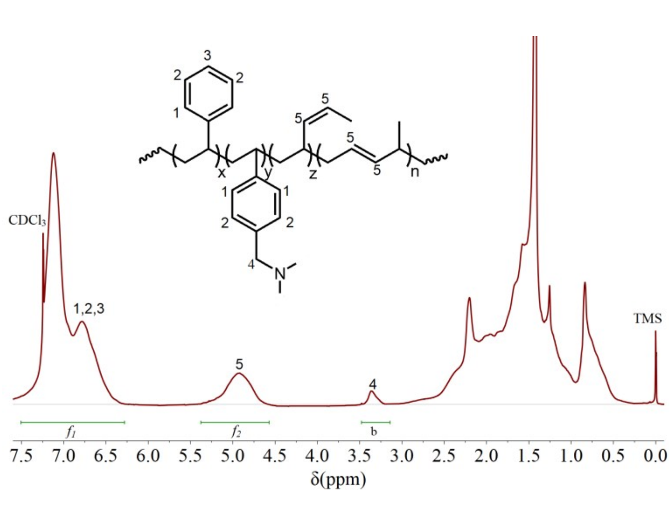


Figure S4. The typical ^{1}H NMR spectrum of the ST/PD/VBDMA copolymer ($CDCl_3$).

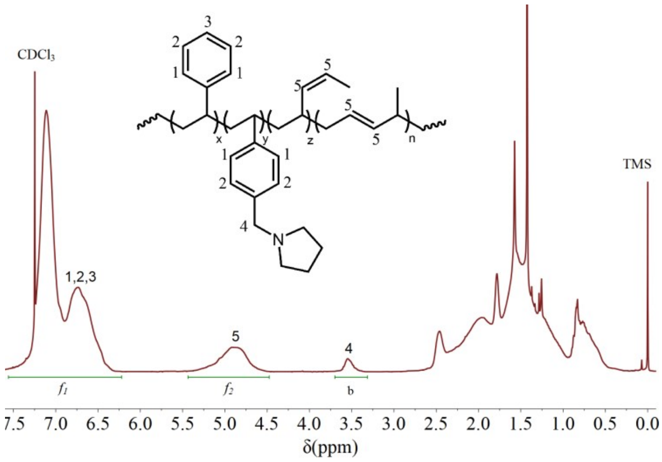


Figure S5. The typical [1]H NMR spectrum of the ST/PD/VBTHP copolymer ($CDCl_3$).

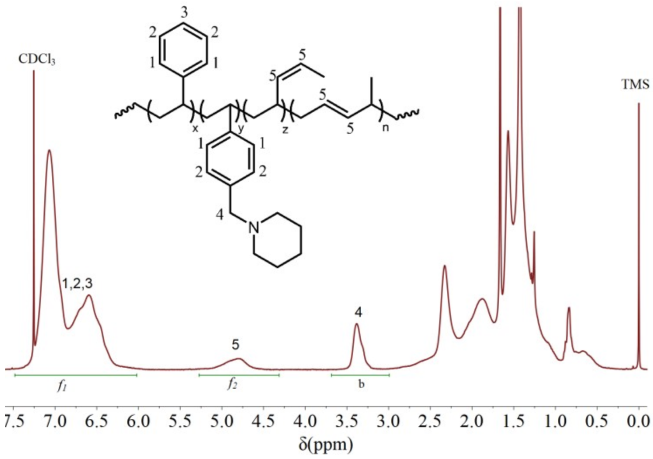


Figure S6. The typical [1]H NMR spectrum of the ST/PD/VBMP copolymer ($CDCl_3$).

Copolymer composition determined by equations (1)-(6) obtained from Figure S4-S6

$$x_{ST} = \frac{I_{f_1} - \frac{I_b}{2} * 4}{5} \tag{1}$$

$$x_{PD} = \frac{I_{f_2}}{2} \tag{2}$$

$$x_N = \frac{I_b}{2} \tag{3}$$

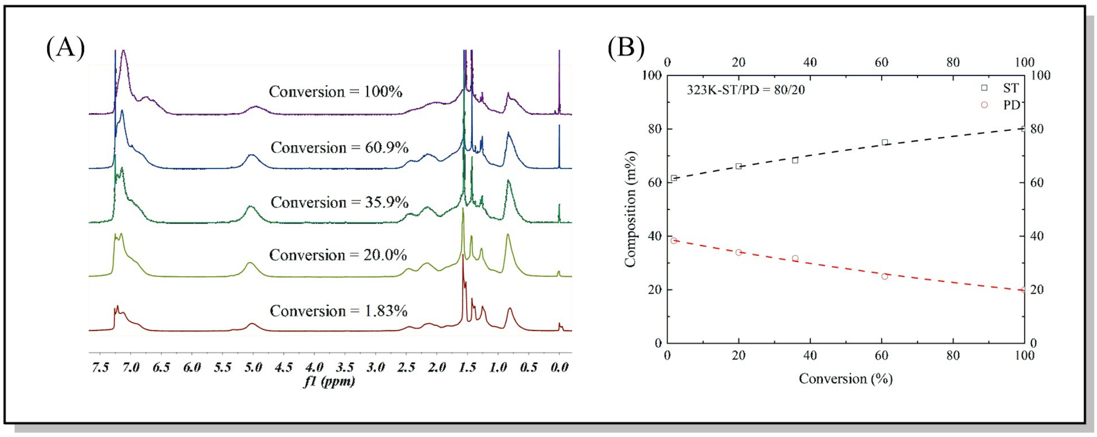
$$w_{ST} = \frac{x_{st} \times M_{ST}}{x_{st} \times M_{ST} + x_{PD} \times M_{PD} + x_N \times M_N} \tag{4}$$

$$w_{PD} = \frac{x_{PD} \times M_{PD}}{x_{st} \times M_{ST} + x_{PD} \times M_{PD} + x_N \times M_N} \tag{5}$$

$$w_N = \frac{x_N \times M_N}{x_{st} \times M_{ST} + x_{PD} \times M_{PD} + x_N \times M_N} \tag{6}$$

(1) Calculate the relative molar content of each component from the integrated area by equations (1) to

(3). Herein, x_{ST}, $x_{PD,}$ and x_N correspond to the molar fraction of ST, PD, and VBN comonomers, respectively; (2) Calculate the mass fraction of each component in the copolymer by using equations (4) to (6). Herein, w_{ST}、$w_{PD,}$ and w_N correspond to the mass fraction of ST, PD, and VBN comonomers, respectively. M_{ST}、$M_{PD,}$ and M_N are the relative molecular mass of ST, PD, and VBN monomers.



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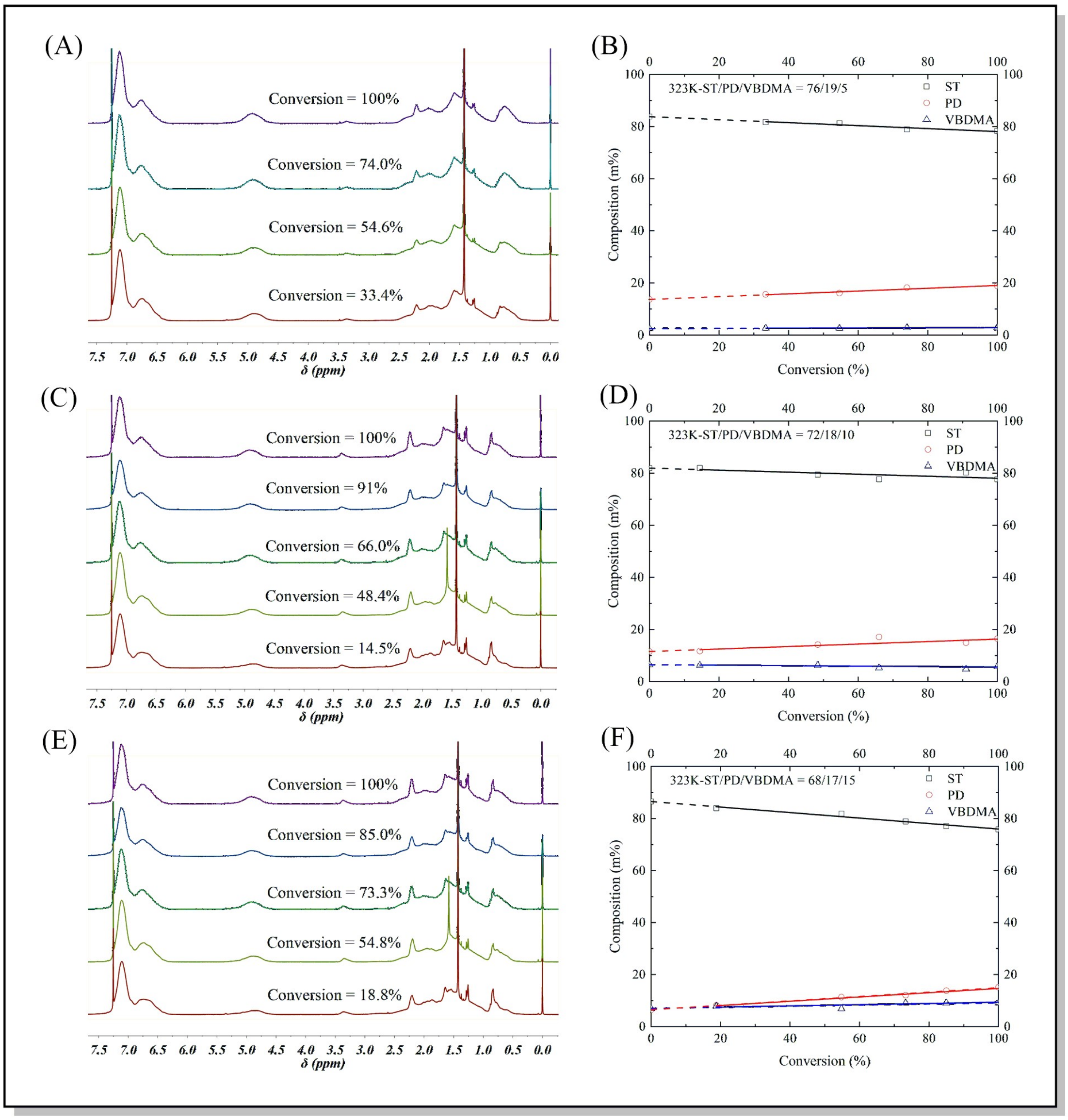
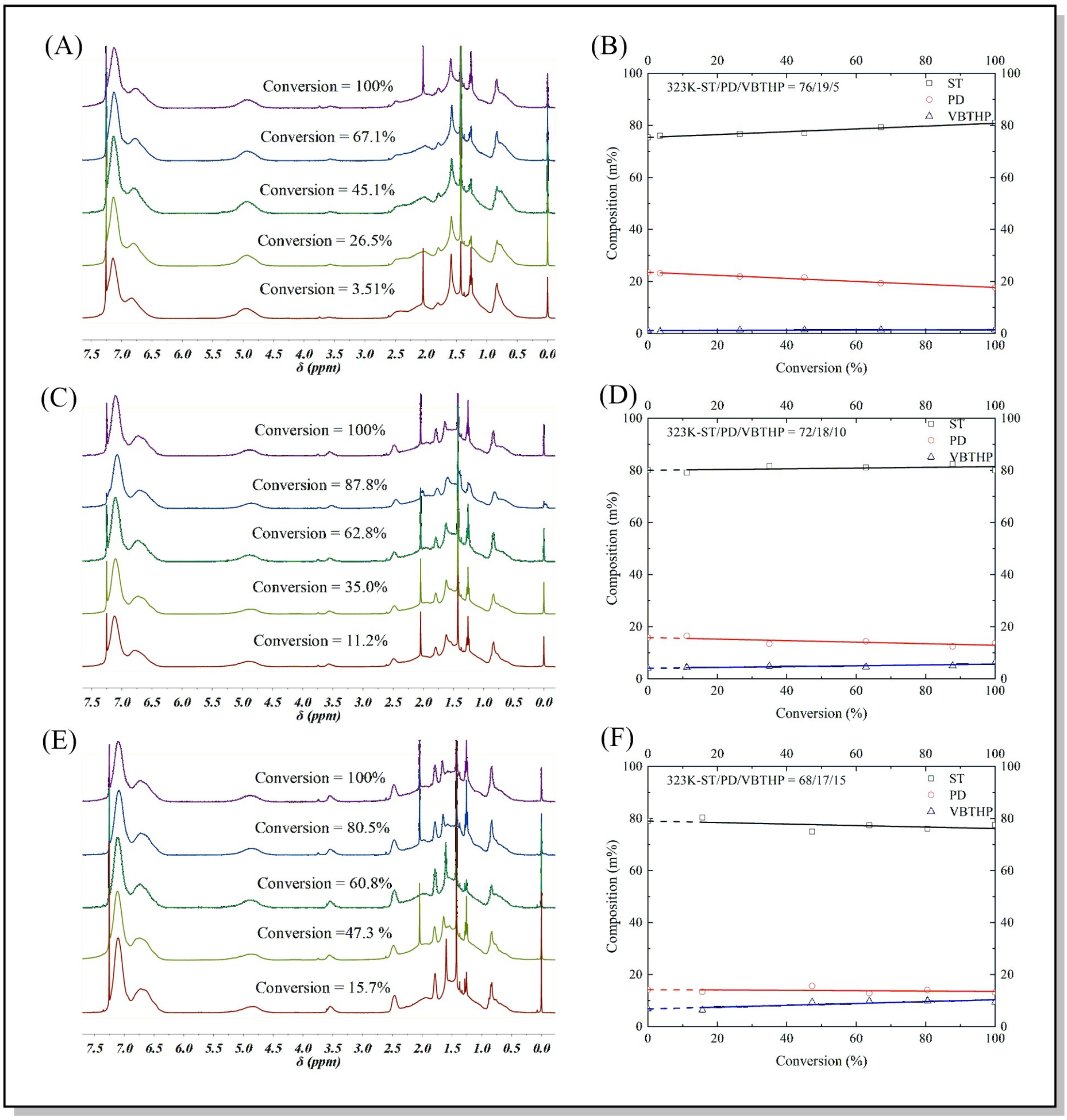


Figure S8. ^{1}H NMR spectra of the copolymers at different conversions under different VBDMA content (A-5%, C-10%, E-15%) and the copolymer composition distribution (B-5%, D-10%, F-15%) in the fixed ratio of m_{ST}/m_{PD} = 80/20 copolymerization.



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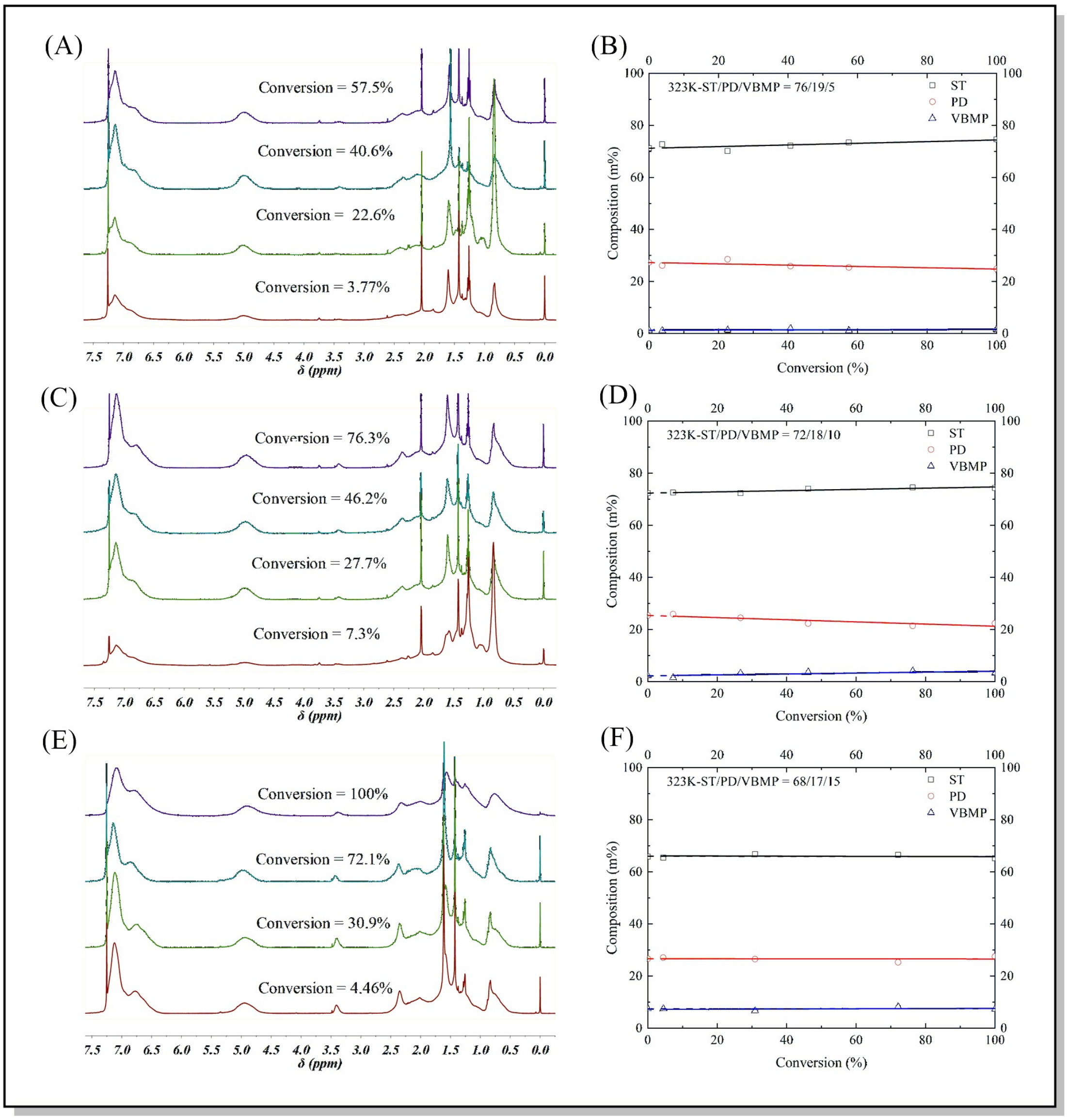

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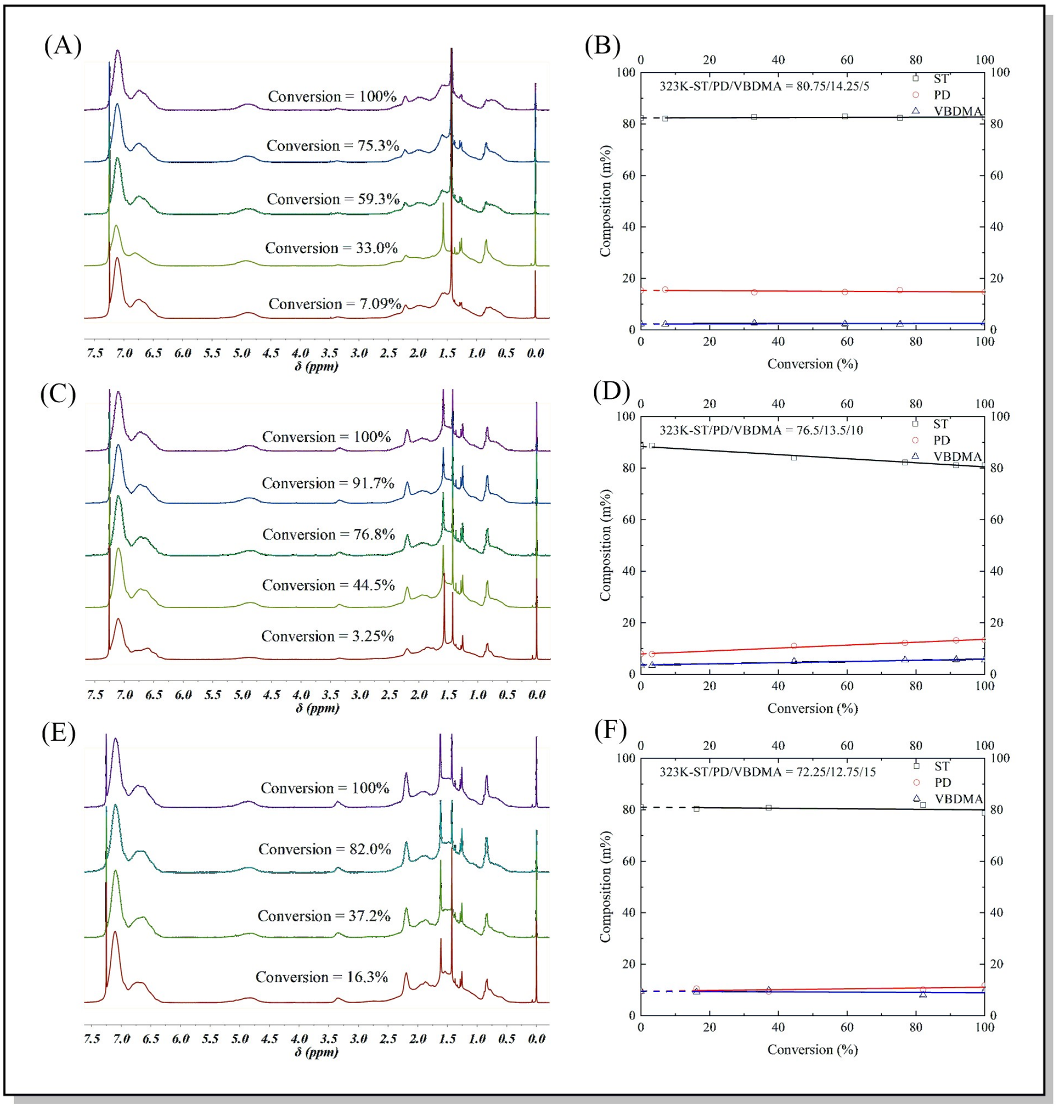

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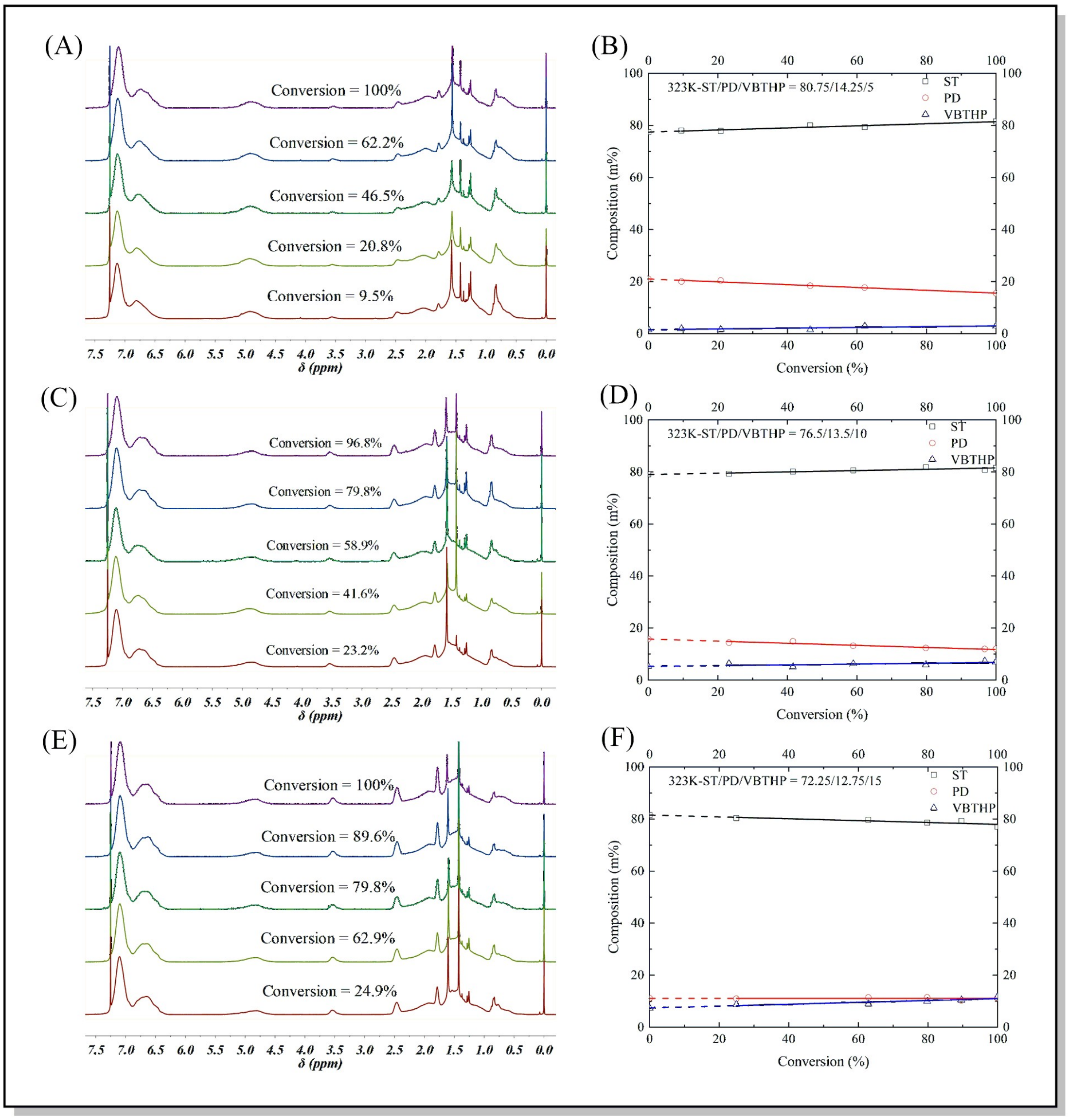

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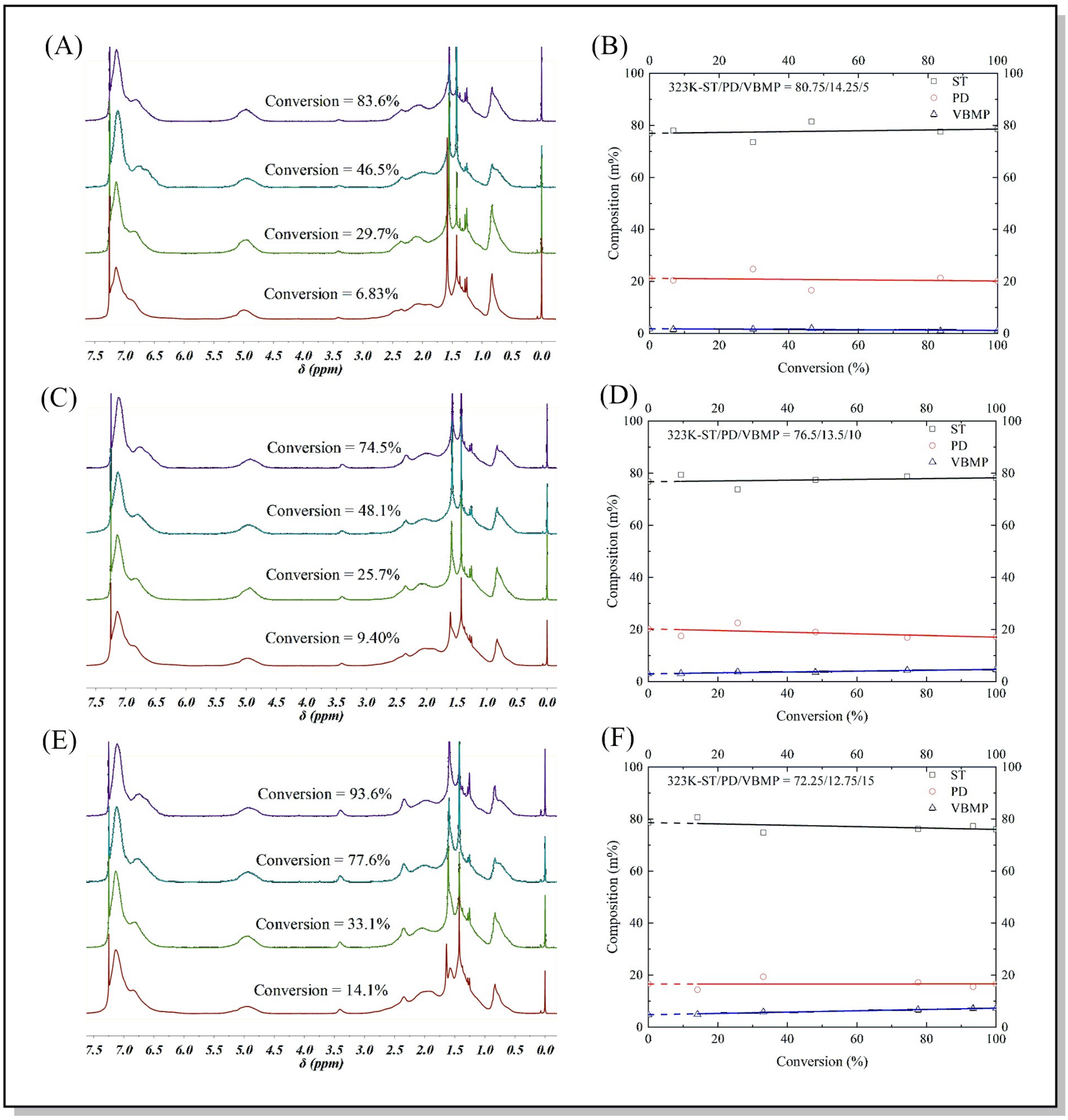

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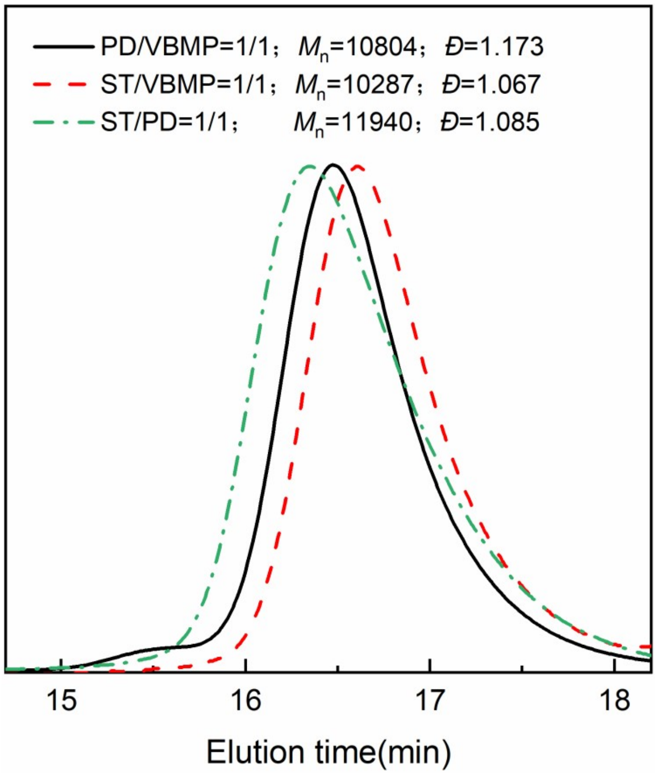

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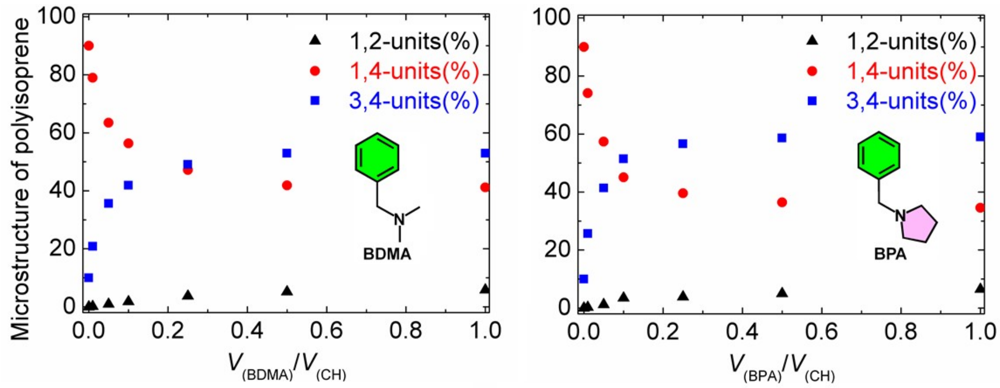

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