Induced Circular Dichroism of Stereoregular Vinyl Polymers

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Supplementary Information

Figure S1. ^{13}C NMR (125 MHz) spectrum of iP2VP (M_n = 81,600 g/mole, M_w/M_n = 1.46) (solvent CD_3OD; temperature 40 ^oC).

Figure S2. ^{13}C NMR (125 MHz) spectrum of aP2VP (M_n = 65,500 g/mole, M_w/M_n = 1.11) (solvent CD_3OD; temperature 40 ^oC).

Figure S3. ^{13}C NMR (125 MHz) spectrum of sP2VP (M_n = 94,000 g/mole, M_w/M_n = 1.28) (solvent CD_3OD; temperature 40 ^oC).

Figure S4. FT-IR spectra of iP2VP (black line) complexing with D-LA (blue line) and L-LA (red line) in chloroform solution. The polymer concentration is 3mg/0.3ml complexing with 2.57mg of lactic acid ([LA]/[2VP]=1).

Figure S5. (a) CD; (b) UV-Vis spectra of LA in chloroform solution. The concentration for LA in CD and UV-Vis measurement is 0.86mg/1.5ml.

Figure S6. CD spectra of iP2VP complexing with LA, HMA, and MA in chloroform dilute solution. The solution concentration is 1mg (9.52μmol of monomer units)/1.5ml complexing with 9.52μmol chiral acid.

Figure S7. (a) CD; (b) UV-Vis spectra of iP2VP-LA and Pyridine-LA complex in chloroform solution. The concentration in CD and UV-Vis measurement

is 1mg (9.52μmol of monomer units)/1.5ml for iP2VP, and is 0.75mg (9.52μmol)/1.5ml for pyridine. The concentration of LA is 0.86mg (9.52μmol)/1.5ml. ([LA]/[2VP]=1).

Figure S8. (a) CD; (b) UV-Vis spectra of Pyridine-MA complex in chloroform solution. The pyridine concentration in CD ans UV-Vis measurement is 0.75mg/1.5ml complexing with 1.45mg of MA ([MA]/[pyridine] = 1).

Figure S9. (a) CD spectra of P2VPs complexing with HMA in chloroform solution. The polymer concentration in CD measurement is 1mg (9.52 μmol of monomer units)/1.5ml complexing with 15mg (95.2 μmol) of HMA. (b) CD spectra of Pyridine complexing with HMA in chloroform solution. The pyridine concentration in CD measurement is 0.75mg (9.52 μmol of monomer units)/1.5ml complexing with 15mg (95.2 μmol) of HMA ([HMA]/[2VP or pyridine] = 10).

Experimental Section

Materials. All the chemicals and solvents were used as received unless otherwise stated. L- and D-lactic acid, (*R*)-mandelic acid, (*R*)-hexahydromandelica acid, and (*S*)-hexahydromandelic acid were purchased from Aldrich, and (*S*)-mandelic acid is purchased from Alfa Aesar. Anhydrous chloroform was purchased from J. T. Baker.

General Procedure. All reactions and manipulations were conducted under a nitrogen atmosphere using standard Schlenk line or dry box techniques. Solvents and common reagents were commercially obtained and used either as received or purified by distillation with sodium/benzophenone. Phenylmagnesium bromide (1M in THF), *n*-Butyllithium (*n*-BuLi, 1.6 M in hexane), *tert*-Butyllithium (*t*-BuLi, 1.6 M in pentane) and triethylaluminum (TEA, 25% in toluene) were purchased from Aldrich, and used as received. The 2-Vinylpyridine (purity > 97%) was obtained form Aldrich and purified by distillation from CaH_2 before use.

Synthesis of Isotactic Poly(2-vinyl pyridine) (iP2VP). The iP2VP was prepared *via* isospecific polymerization of 2-vinyl pyridine using phenylmagnesium bromide as the initiator and was isolated as a crude reaction product by the method described in the literature.[1] In order to enhance the stereoregularity of iP2VP, the crude polymer was washed with a THF/acetone solution mixture (THF : acetone = 1:10) to remove atactic P2VP. The resulting insoluble polymer was dried under vacuum to provide

iP2VP as a pale yellow powder. The isotacticity (mm = 80%; mmmm = 47%)[2,3] was determined by ^{13}C NMR analyses (in CD_3OD at 40 ^{o}C; as shown in Figure S1). M_n = 81,600 g/mole, M_w/M_n = 1.46 by GPC (in THF at 40 ^{o}C).

Synthesis of Atactic Poly(2-vinyl pyridine) (aP2VP). The aP2VP was prepared *via* anionic polymerization of 2-vinyl pyridine using n-butyl lithium as the initiator and was isolated as an off-white powder by the method described in the literature.[4] The stereoregularity (mm = 42%)[2] of the resulting aP2VP was determined by ^{13}C NMR analyses (in CD_3OD at 40 ^{o}C; as shown in Figure S2). M_n = 65,500 g/mole, M_w/M_n = 1.11 by GPC (in THF at 40 ^{o}C).

Synthesis of Syndiotactic Poly(2-vinyl pyridine) (sP2VP). The sP2VP was prepared by syndiospecific polymerization of 2-vinyl pyridine using *t*-BuLi /TEA (*t*-BuLi : TEA = 1 : 15) as the initiator and was isolated as a crude reaction product by the method described in the literature.[3] The resulting crude polymer was purified by extracting it with boiling THF/acetone (1:10) in a Soxhlet extractor to remove the aP2VP. The resulting insoluble polymer was collected and dried under vacuum overnight to provide sP2VP as an off-white powder. The stereoregularity (rrrr = 23%; mm = 18%)[2,3] of the sP2VP was determined by ^{13}C NMR analyses (in CD_3OD at 40 ^{o}C; as shown in Figure S3). M_n = 94,000 g/mole, M_w/M_n = 1.28 by GPC (in THF at 40 ^{o}C).

Polymer Characterization. The molecular weight and molecular weight distribution (MWD) were determined through GPC (Waters 2410-CALAC/GPC) with a refractive index (RI) detector and a set of U-Styragel HT columns with 10^6, 10^5, 10^4, and 10^3 pore sizes in series. The measurements were taken at 40 ^oC using THF as the solvent. Polystyrene (PS) samples with narrow MWDs were used as the standards for calibration. The standards were in the range of absolute molecular weight, which is from 980 to 2110000; the *R* square of the ideal calibrated line was limited to up to 0.999. All ^1H and ^{13}C NMR spectra were recorded on a Bruker AV-600 NMR spectrometer. The P2VP samples were dissolved in CD_3OD. The recorded temperature was 40 ^oC.

Circular Dichroism Spectroscopy (CD). CD spectra were measured on JASCO J-815 spectrometer. UV-Vis absorption and CD spectra could be obtained simultaneously during measurements. Solution samples were placed in a cylindrical quartz cell with light path of 1.0 mm. The concentration of the polymer solution was 1mg in 1.5ml chloroform or dichloromethane as dilute solution.

Fourier Transform Infrared Spectroscopy (FT-IR). FT-IR spectra were measured on JASCO FVS-6000 spectrometer. Solution samples were placed in a cylindrical BaF_2 cell with light path of 50 μm. The concentration of the polymer solution was 3mg in 0.3ml chloroform as solution.

iP2VP-LA Complex. To confirm the formation of hydrogen bonding between iP2VP and LA, Fourier transform infrared spectroscopy (FTIR) experiments were conducted. Figure S4 shows the FTIR spectra of iP2VP and iP2VP in the presence of LAs. The characteristic absorption bands of P2VP are 1593cm^{-1} and 1570cm^{-1} corresponding to the contribution of the ring stretching of pyridine. In the presence of LA, these bands become broadening and shift toward higher wavenumber attributed to the increase in stiffness of the pyridine ring as a result of hydrogen bonding association. Therefore, the formation of hydrogen bonding between iP2VP and LA can be verified.

Optical Activities of LAs and Pyridine-LA Complexes. Note that the ICD of the iP2VP might be attributed to the chiral entity on LA or complexation of pyridine with LA regardless of the formation of helical chain conformation. To further investigate the origins of the ICD, CD and UV-Vis spectra of LA and pyridine-LA complex were measured. As shown in Figure S5, both CD spectra of D-LA and L-LA are silent at wavelength larger than 240nm and no significant UV absorption at wavelength around 260nm can be identified. At wavelength lower than 240nm, positive and negative Cotton effect can be observed for L-LA and D-LA, respectively. Therefore, the ICD of iP2VP and LA complex at wavelength ranging from 240 nm to 290nm indeed results from the complexation regardless of intrinsic LA. In Figure S6, the CD spectra of pyridine-LA and iP2VP-LA complex were examined. The difference in CD

and UV-Vis spectra between the complex of iP2VP-LA and pyridine-LA can be clearly observed. In contrast to the results of iP2VP, the CD spectra of pyridine-LA complex is silent at pyridine absorption band around 255 nm, reflecting that the ICD of iP2VP mainly results from the formation of helical chain conformation.

Optical Activities of iP2VP complexing with LA, HMA, and MA in chloroform dilute solution. To explore the ICD behavior of iP2VP, a variety of optically active small molecules were used. As shown in Fig. S6, the helicity of the split-type ICD corresponds well with the configuration of the chiral acid used, suggesting that the formation of right-handed and left-handed helical conformations can be driven by introducing chiral acids with (*R*)-and (*S*)-configurations, respectively. The magnitude of ICD increases in the order of LA < HMA < MA at which the ICD for MA is especially significant. Considering the effect of the bulkiness of chiral acid,[5,6] it is reasonable to give intense ICD for MA in comparison with LA. However, this rule does not apply to HMA at which the ICD for HMA with similar bulkiness to MA is only slightly higher than LA. As a result, we speculate that, in addition to the bulkiness, the acidity of chiral acid should play important role for the ICD signals. To quantitatively examine the effect of the acidity of chiral acid on the ICD signals, the predicted pKa values of LA, HMA and MA are 3.92, 4.03 and 3.42 so as to give the acidity of chiral acid increases in the order of HMA < LA < MA.[7] As a result, the

iP2VP complexing with stronger acid like MA gives rise to higher population of acid-base complex resulting in the enhancement of the ICD whereas the ICD signals for the iP2VP complexing with HMA is only slightly higher than LA.

Optical Activities of Pyridine-MA Complexes. In Figure S8, the CD spectra of pyridine-MA complexes show Cotton effect at pyridine absorption band around 255 nm, suggesting the induced chirality of pyridine-MA complex whereas the CD in pyridine-LA complex is silent (Figure S7(a)). This discrepancy might result from the difference in acidity between LA and MA. Since stronger acid result in higher concentration of acid-base complex, this complex would give rise to ICD because of its primary structure. In comparison with the ICD of sP2VP and pyridine, similar magnitude of ICD and CD pattern suggest that the ICD of sP2VP may mainly result from primary structure regardless of its conformation.

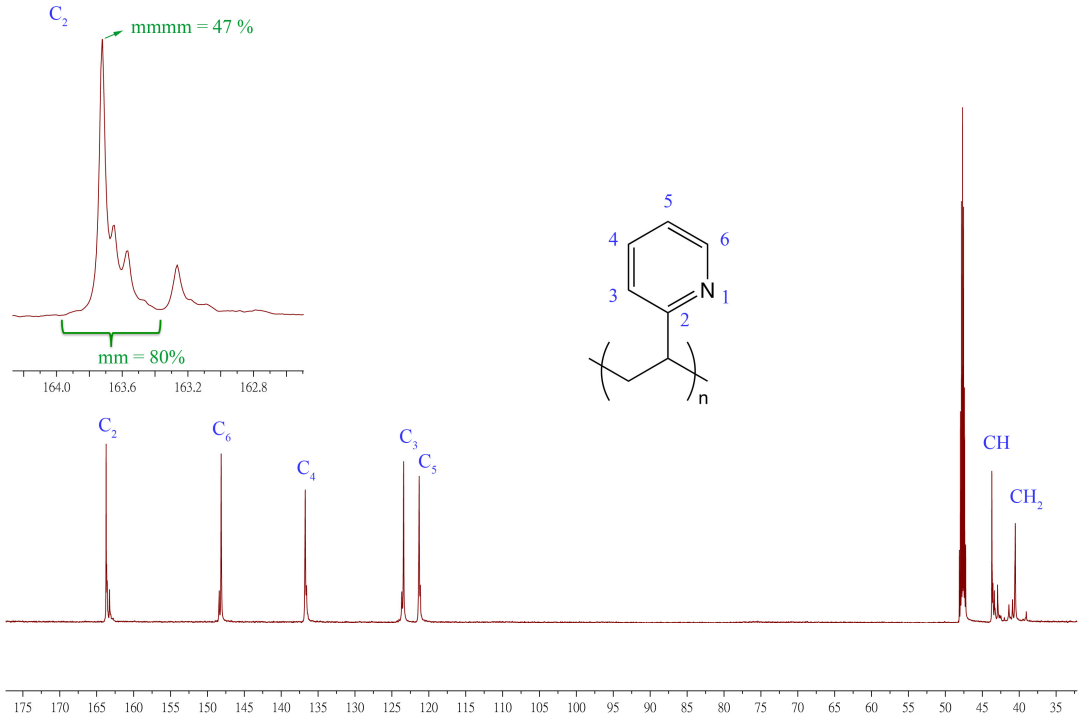


Figure S1. ^{13}C NMR (125 MHz) spectrum of iP2VP (M_n = 81,600 g/mole, M_w/M_n = 1.46) (solvent CD_3OD; temperature 40 ^oC).

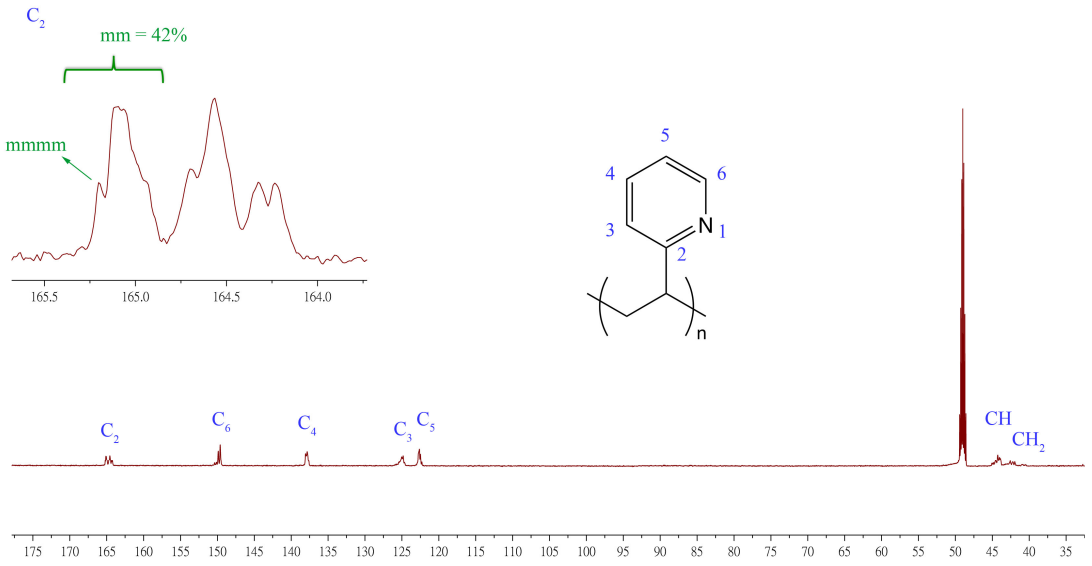
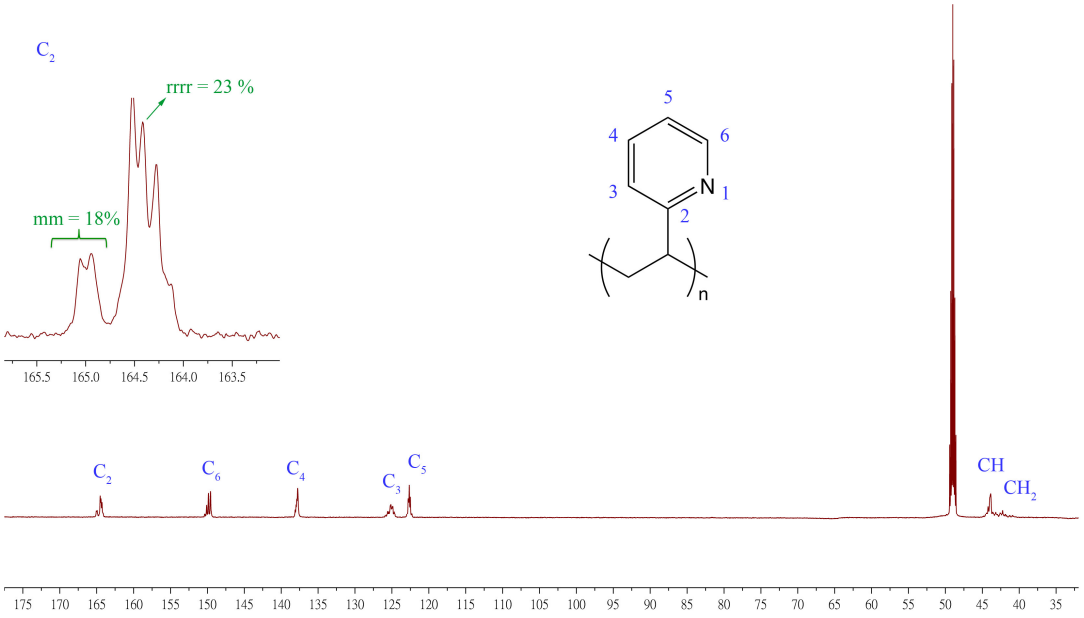


Figure S2. ^{13}C NMR (125 MHz) spectrum of aP2VP (M_n = 65,500 g/mole, M_w/M_n = 1.11) (solvent CD_3OD; temperature 40 ^oC).



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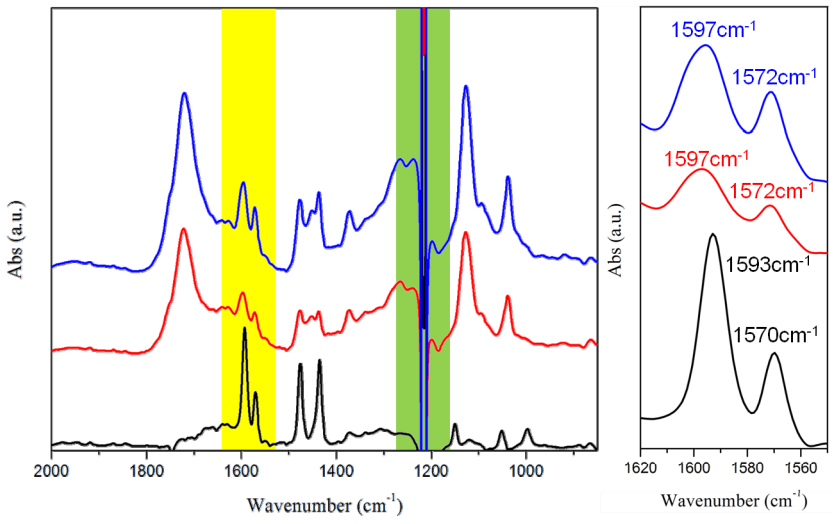

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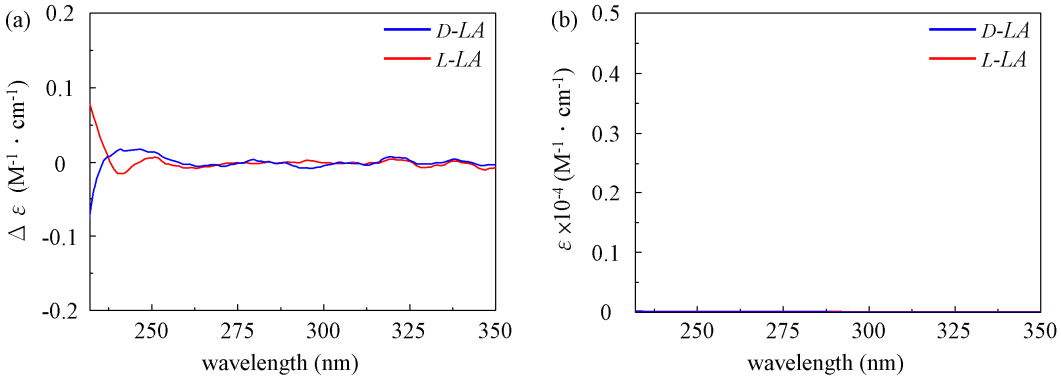

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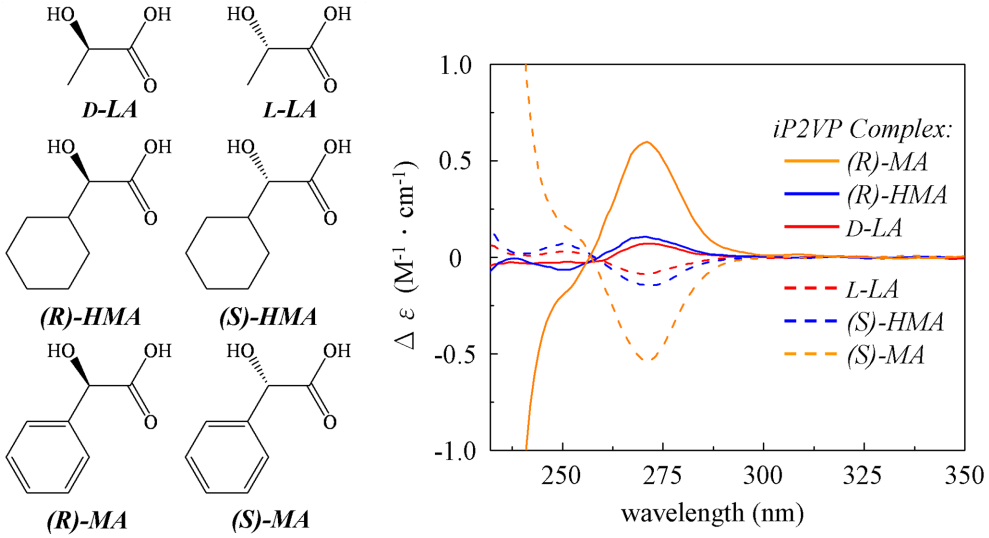
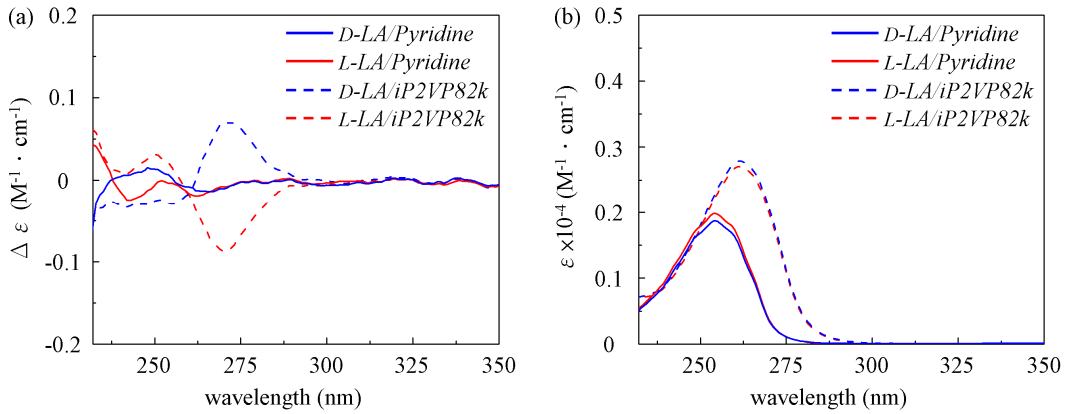


Figure S6. CD spectra of iP2VP complexing with LA, HMA, and MA in chloroform dilute solution. The solution concentration is 1mg (9.52μmol of monomer units)/1.5ml complexing with 9.52μmol chiral acid.



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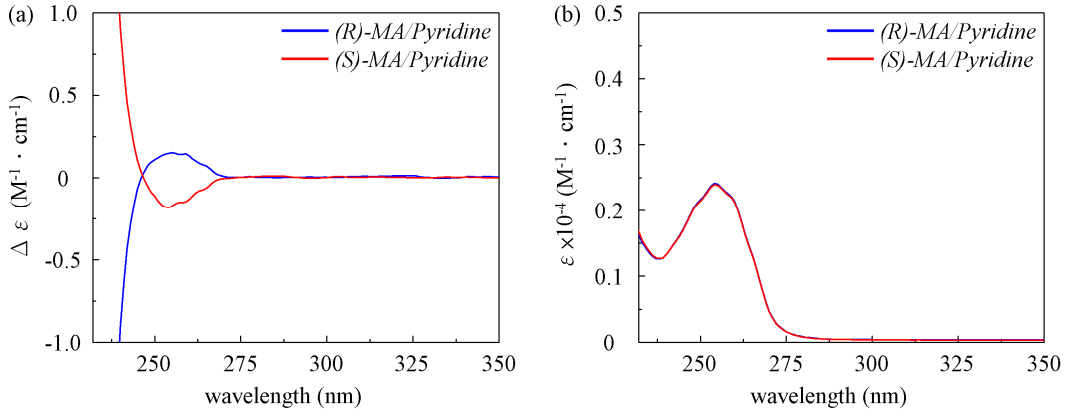

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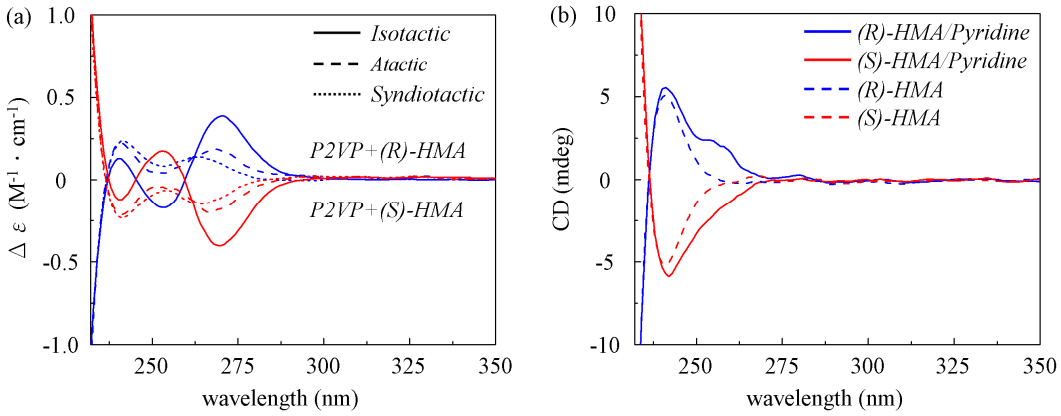

Figure S9. (a) CD spectra of P2VPs complexing with HMA in chloroform solution. The polymer concentration in CD measurement is 1mg (9.52 μmol of monomer units)/1.5ml complexing with 15mg (95.2 μmol) of HMA. (b) CD spectra of Pyridine complexing with HMA in chloroform solution. The pyridine concentration in CD measurement is 0.75mg (9.52 μmol of monomer units)/1.5ml complexing with 15mg (95.2 μmol) of HMA ([HMA]/[2VP or pyridine] = 10).

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