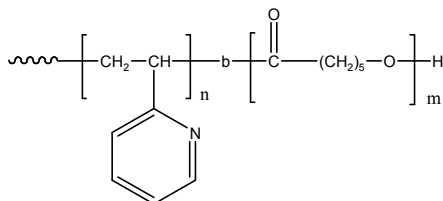


Sample Name:
Poly(2-vinyl pyridine -b- ε-caprolactone)

Sample #: P11325C- 2VPCL

Structure:



Composition:

| | |
|------------------------------------|------|
| Mn x 10 ³ P2VP-b-PCL | PDI |
| 20.5-b-35.0 | 1.10 |

Synthesis Procedure:

Poly(2-vinyl pyridine -b- ε-caprolactone) is prepared by living anionic polymerization of 2-vinyl pyridine and coordination polymerization of ε-caprolactone.

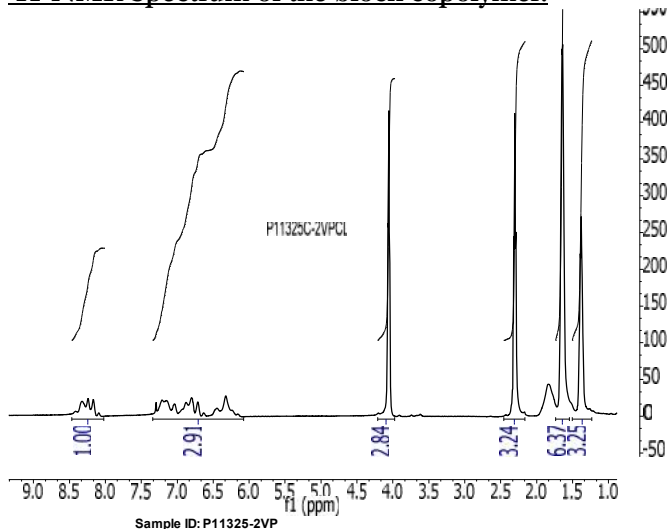
Characterization:

An aliquot of the poly(2-vinyl pyridine) block was terminated before addition of caprolactone and analyzed by size exclusion chromatography (SEC) to obtain the molecular weight and polydispersity index (PDI). The final block copolymer composition was calculated from ¹H-NMR spectroscopy by comparing the peak area of the pyridine protons at about 6.0-8.5ppm with the ε-caprolactone protons at about 1.0-4.1ppm deducted the 2-vinyl pyridine backbone contribution.

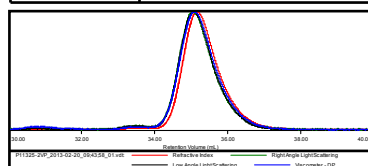
Solubility:

Poly(2-vinyl pyridine -b- ε-caprolactone) is soluble in CHCl₃, THF, DMF, toluene and precipitated out from hexane.

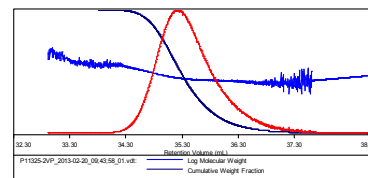
¹H-NMR Spectrum of the block copolymer:



| | |
|-----------------------|-------------------------|
| Concentration (mg/mL) | 17.4604 |
| Sample dn/dc (mL/g) | 0.1670 |
| Method File | PS80K-Feb-2013-0001.vcm |
| Column Set | 3x PL 1113-6300 |
| System | System 1 |

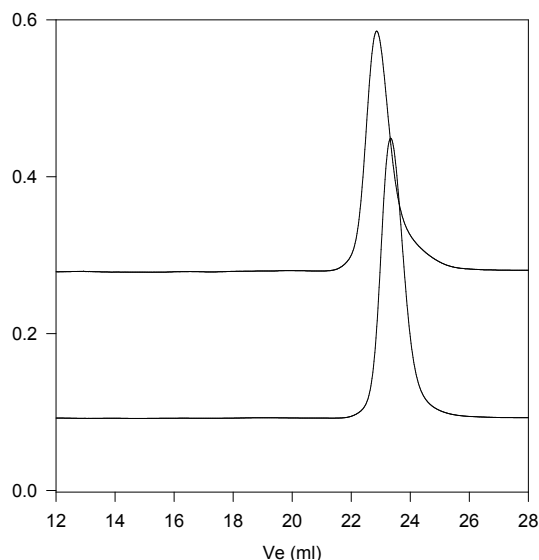


| Sample | Mn (Da) | Mw (Da) | Mp (Da) | Mw/Mn | IV (dL/g) |
|-------------------------------------|---------|---------|---------|-------|-----------|
| P11325-2VP_2013-02-20_09:43:58_01.v | 22,748 | 23,788 | 23,388 | 1.046 | 0.1542 |



SEC of the block copolymer:

P11325C- 2VPCL



Size exclusion chromatography:

— Poly(2-vinylpyridine), M_n=20,500, M_w=21,600, PI=1.05

— Block Copolymer P2VP(20,500)-b-PCL(35,000), PI=1.10

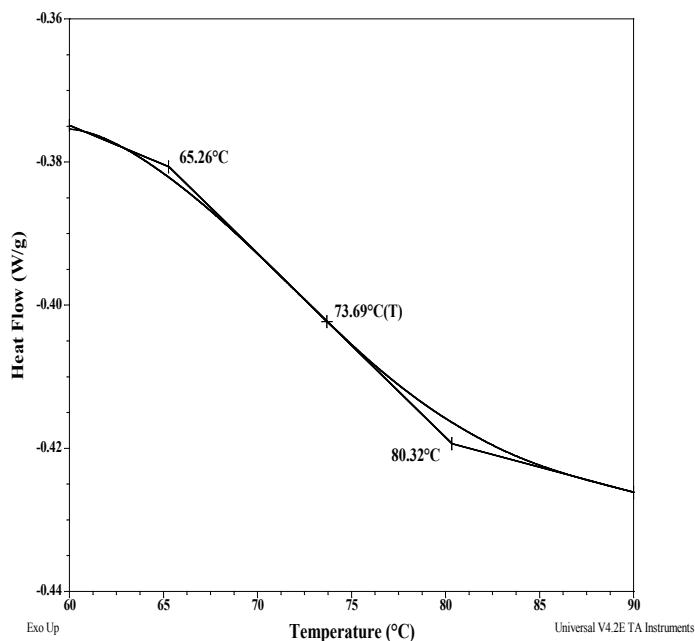
Thermal analysis of the sample# P11325C-2VPCL

Thermal analysis of the samples was carried out on a TA Q100 differential scanning calorimeter at a heating rate of 10°C/min. The midpoint of the slope change of the heat flow plot of the second heating scan was considered as the glass transition temperature (T_g).

Thermal analysis results at a glance

| Sample | T_m (°C) | T_c (°C) | T_g (°C) |
|-----------------------------|------------|------------|--------------|
| 2VP ($M_n=30k$) | - | - | 81 |
| ϵ -CL ($M_n=8k$) | 49 | 29 | -69 |
| 2VP block in sample | - | - | 74 |
| CL block in sample | 54 | 16 | Not distinct |

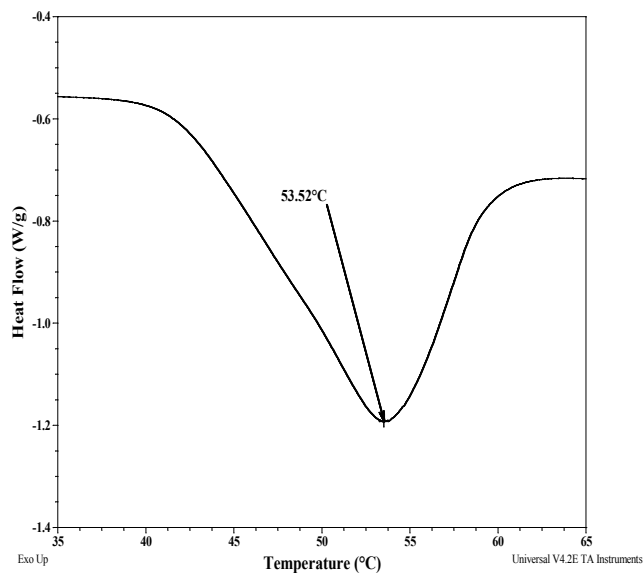
Thermogram for the 2VP block



Melting and crystallization curve for the sample

The melting temperature (T_m) was taken as the maximum of the endothermic peak where as the crystallization temperature (T_c) was considered as the minimum of the exothermic peak.

Melting curve for ϵ -caprolactone block



Crystallization curve for ϵ -caprolactone block

