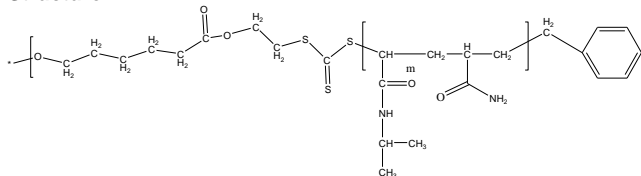


**Sample Name: Random blockcopolymer of Poly(N-isopropyl acrylamide and acrylamide )ran-b-Caprolactone**

**Sample #:**

**P10611A-NIPAMAMDranCL**

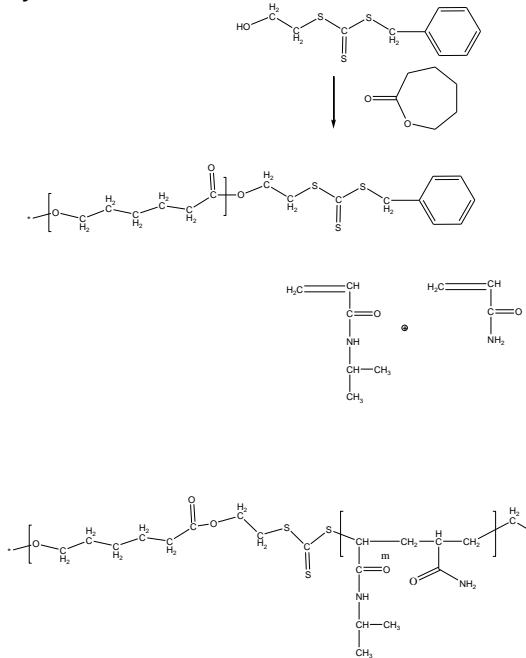
**Structure:**



**Composition:**

Mn x 10 <sup>3</sup> NIPAMAMDran-b-CL	PDI
15.0-b-2.6	1.28
AMD 10 wt%	
Lower Critical Solution Temperature (LCST)	43.46 oC

**Synthesis Procedure:**



**Purification of polymer:**

Unreacted monomer was removed by dissolving the product in cold water than warming up the solution. The polymer separated out. This procedure was applied 2 times to remove the unreacted monomer. The obtained polymer was dissolved in acetone and reprecipitated in cold ether.

**Characterization:**

Size exclusion chromatography (SEC) was carried out on a Varian liquid chromatograph equipped with a refractive index detector. A Shodex 806L GPC columns from Supelco was used with DMF(0.05M LiBr) as the eluent at 65 oC and also in THF following the procedure as out lined in **Macromolecules, 2000,33,6738**. The columns were calibrated with monodisperse polystyrene standards. The polydispersity index was calculated.

Here SEC illustrate only the purity of the diblock copolymer from Poly caprolactone-RAFT bearing macroinitiator used to initiate NIPAM containing 10 % by weight Acrylamide. The yield of the polymer was quantitative therefore it is estimated incorporation of AMD monomer in Poly NIPAM as random copolymer

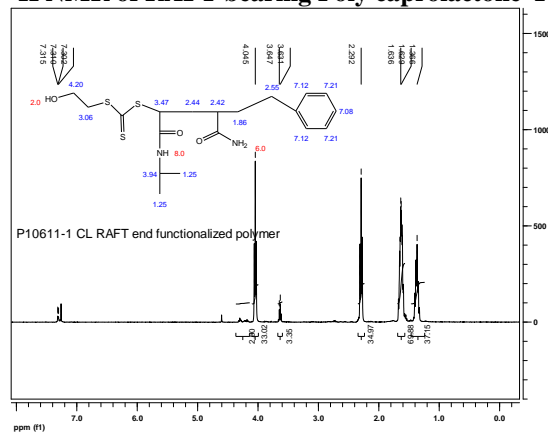
Viscosity measurement was carried out in a Ubbelohde viscometer at 25°C. Four solutions in methanol of different concentrations were measured. The intrinsic viscosity was obtained by extrapolation to c=0. From viscosity-molecular weight relationship  $[\eta] = 2.99 \times 10^{-2} M^{0.64}$  (Makromolecular Chem. V180, P969, 1979), the viscosity average molecular weight was calculated accordingly.

It is important that the values of molecular weights determined in DMF and in THF were found quite different. It might be possible that end functionalized polymer might be present in the form of aggregates and gives much higher or lower values than determined by viscosity data.

**Solubility:**

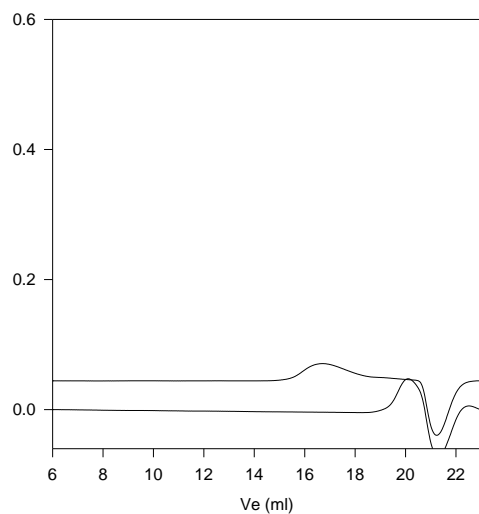
The polymer is soluble in water methanol, ethanol, DMF, and dioxane, not soluble in hexane.

**<sup>1</sup>H NMR of RAFT bearing Poly caprolactone First block:**



## SEC of the polymer carried out in DMF:

### P10611A-NIPAMAMDran-CL



Size exclusion chromatography of the polymer in DMF at 65 °C:  
Eluent containing 0.05 M LiBr

— First block of Caprolactone :  $M_n=2600$  ,  $PI=1.15$  (values determined by HNMR)

— Random blockcopolymer of  
-Caprolactone -b- N-isopropylacrylamide and acrylamide-b-Caprolactone  
 $M_n=2600$ -b-8,500 ,  $PI=1.25$  (values determined by HNMR)

## LCST of P10611A-NIPAMAMDran-CL:

