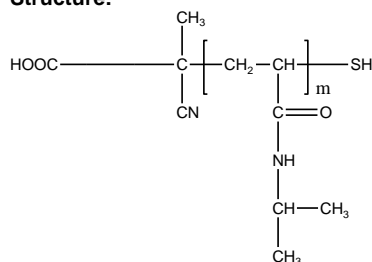


Sample Name: α -thiol ω -carboxylic acid terminated Poly(N-isopropyl acrylamide)

Sample #: P5739-NIPAMSHCOOH

Structure:

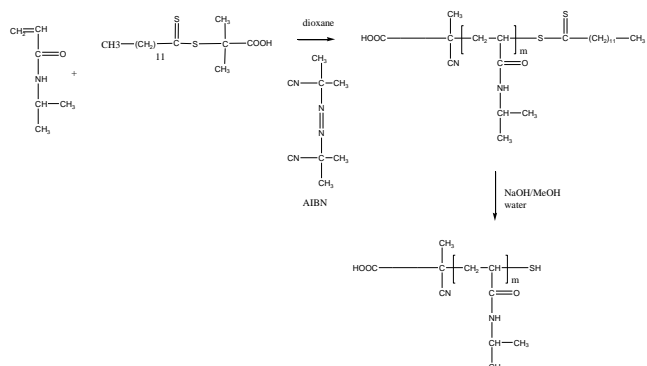


Composition:

Mn x 10 ³	PDI
1.3	1.35

Synthesis Procedure:

The polymer was prepared by reversible addition-fragmentation chain transfer polymerization (RAFT) of N-isopropyl acrylamide. The scheme of the reaction is illustrated below:



Purification of polymer:

Unreacted monomer was removed by dissolving the product in cold water then 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.

Hydrolysis of the Dithiocarbamate End Groups in Poly(NIPAM-SH). The dithio end groups of the obtained polymer samples were hydrolyzed to yield the corresponding thiol-terminated polymers under basic conditions. For this purpose, the polymer was dissolved in a mixture of MeOH/aq. 28% NaOH (2:1) and stirred under nitrogen overnight. The reaction mixture was acidified with 88% formic acid, MeOH was evaporated and the residue was dissolved filter and then precipitated in cold diethyl 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(0.01M LiBr) as the eluent and also in THF following the procedure as out lined in **Macromolecules, 2000,33,6738**. To avoid the effect of concentration and the amount of water present in the sample, on line triple detectors were used and the dn/dc was calculated and found : 0.104mL/g in THF at 35 oC The columns were calibrated with monodisperse polystyrene standards. The polydispersity index was calculated.

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. (data are reported in the following Table with respect to polystyrene as reference material).

In DMF Mn (Mw/Mn)	In THF Mn (Mw/Mn)	Mv by Viscosity	$[\eta]$ in CH ₃ OH at 25 oC
55,000(1.25)	1800(1.3)	1800	0.03 dl/g

From the above results we have consider the viscosity values were found comparable.

Solubility:

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

HNMR of the RAFT reagent used:

