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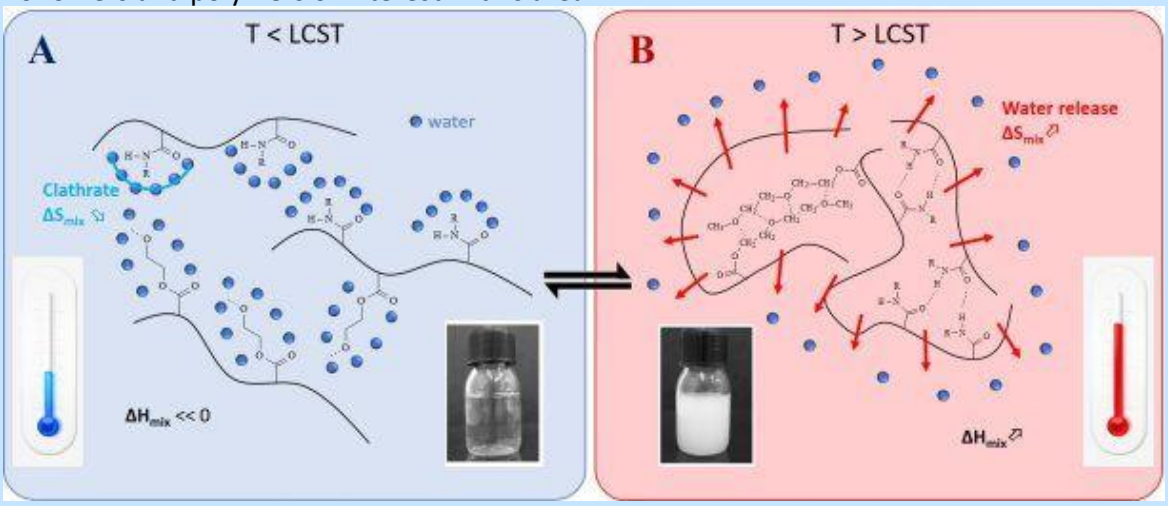
THERMOSENSITIVE POLYMERS AS SMART MATERIALS

Thermosensitive polymers are a class of "smart" materials that have the ability to respond to a change in temperature. Such polymers are uncommon as they are soluble in water at low temperature and become non-soluble when increasing the temperature. Because of their change of physical properties triggered by temperature stimulus, thermosensitive polymers are materials of interest in a wide range of applications such as drug delivery, surface coating, films and membranes, actuators or water treatment. SPECIFIC POLYMERS synthesize a broad array of monomers and polymers of interest in this area.



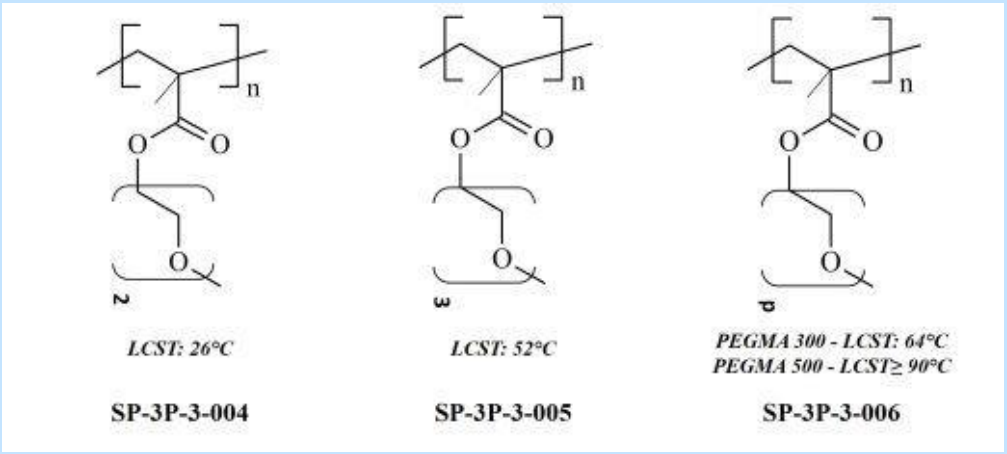
The change of thermosensitive polymer physical state occurs at the LCST and depends on the polymer chemical structure and its interaction with water.

A - Below the LCST, the presence of hydrogen bonds between polymer and water as well as the creation of salvation cages (clathrates) result in a low enthalpy of mixing. In this case, Polymer-Water interactions are stronger than Polymer- Polymer interactions and thus the **polymer is soluble in water**.

B - Increasing the temperature above the LCST makes the hydrogen bonds break and favor the release of water out of the polymer chains. Both enthalpy and entropy of mixing increase, Polymer–Polymer interactions become dominant compared to Polymer-Water interactions which lead to **the loss of solubility.**

OLIGO(ETHYLENE GLYCOL) METHACRYLATES

A first class of thermosensitive polymers are based on oligo(ethylene glycol) methacrylate. Depending on the number of ethylene oxide units, LCST values from 25°C to more than 90°C can be obtained.

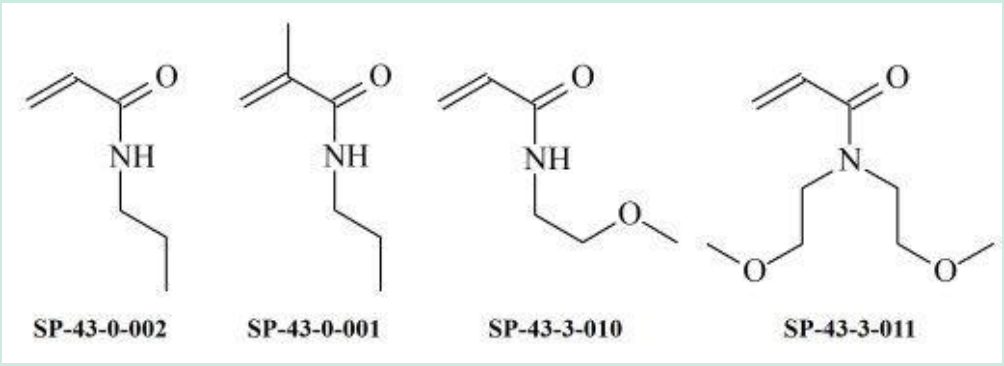


Related Paper : Lutz, J. -F., et al., J. Polym. Sci. Part A: Polym. Chem. vol. 46 (2008)

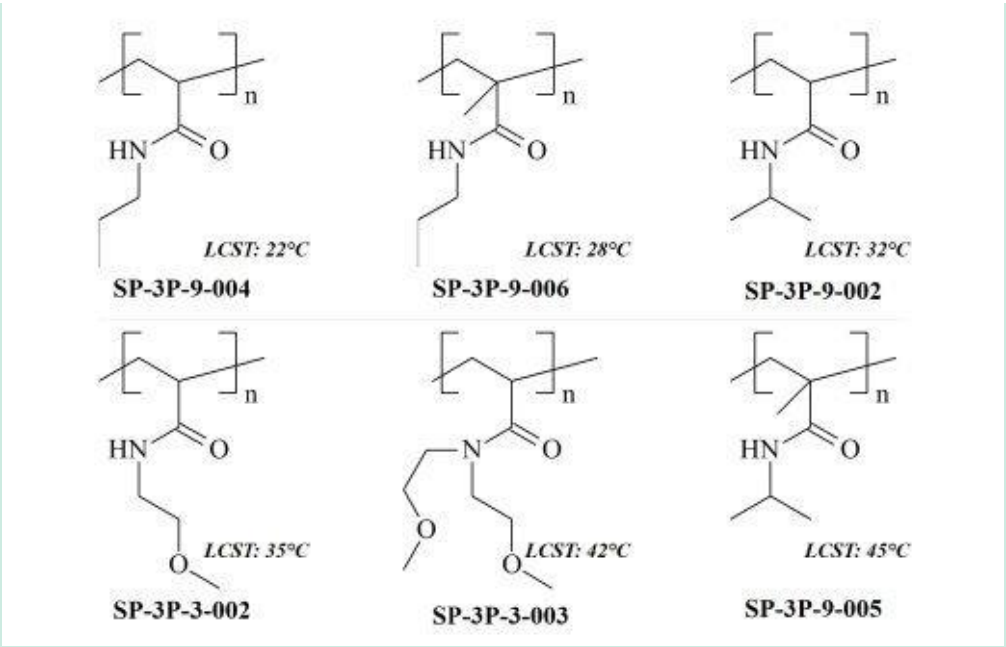
(METH)ACRYLAMIDES

The best-known class of thermosensitive polymers are based on (meth)acrylamide monomers. Among them, N-*iso*-propylacrylamide (NiPAm) has been the most studied to synthesize Poly(NiPAM) Thermosensitive Polymer (LCST: 32°C). SPECIFIC POLYMERS offers variation (meth)acrylamide monomers and corresponding homopolymers that exhibit LCST values in different temperature domains and thus interesting for various applications.

- **Methacrylamide Monomers @ SP**



- **Methacrylamide Homopolymers @ SP**



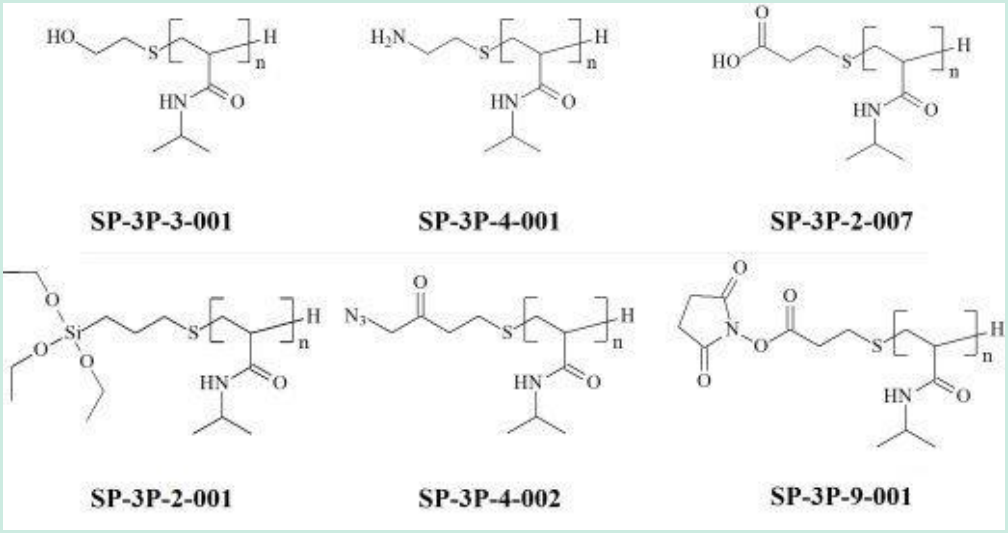
Of course, all LCST mentioned here **depends on polymer concentration and homopolymer molecular weight**. The concentration directly influence polymer-water interactions. Increasing homopolymers molecular weight is in favor of polymer-polymer interaction and thus lead to a decrease of the LCST.

Other factors can have a significant impact on the LCST :

- **Chain end functionalized thermosensitive polymers** : Hydrophilic functional groups will tend to increase the LCST value. This will be all the more pronounced for low molecular weight homopolymers. (See examples of chain-ends functional polyNiPAM below).
- **Thermosensitive copolymers** : Copolymerization of aforementioned monomers with hydrophilic or hydrophobic co-monomers can have significant impact on the LCST value. Hydrophlic co-monomers will increase the LCST and conversely. High ratio of co-monomers can even lead to the loss of thermosensitive properties. (See examples of thermosensitive copolymers below).
- **Thermosensitive copolymers architecture** : For block polymers, each block conserve its own LCST whereas, for statistical copolymers, resulting LCST value an average value of each corresponding homopolymers
- **Dispersity** have an influence on the width of the transition from soluble to insoluble. To reduce polydispersity, Controlled Radical Polymerizations (CRP) can be used.

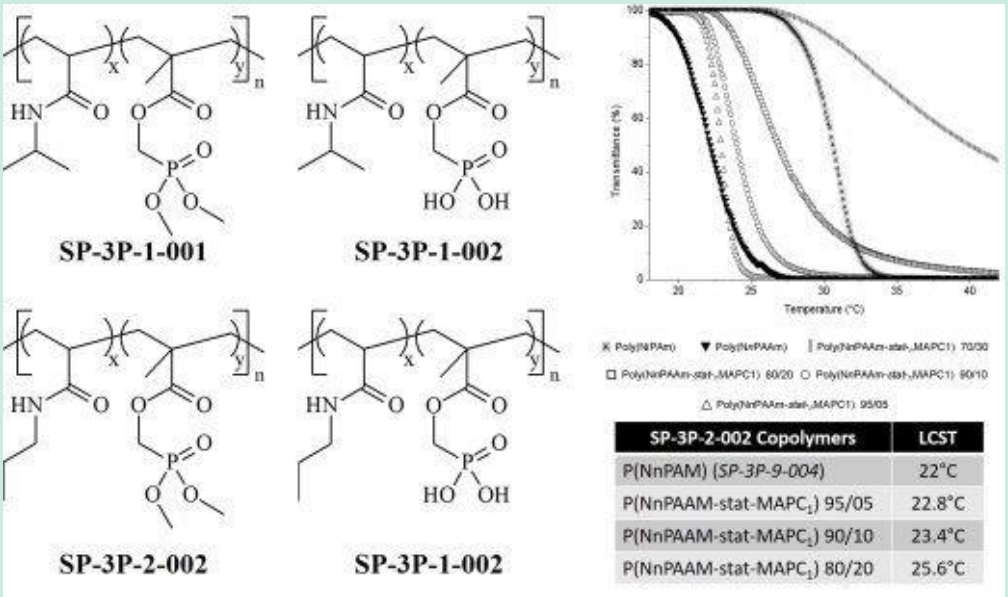
FUNCTIONAL POLY(NIPAM)

Telomerization or controlled radical polymerization allow preparing chain-ends functional thermosensitive polymers. Post modification can then give access to various functionalities (hydroxyles, amines, carboxylic acid, alkoxysilane, azide, NHS, etc.).



THERMOSENSITIVE COPOLYMERS

SPECIFIC POLYMERS can copolymerize aforementioned monomers in order to prepare functional thermosensitive copolymers. As for examples, NiPAM or NnPAM were copolymerized with $MAPC_1$ leading to thermosensitive copolymers bearing phosphonic acid moieties. Increasing the ratio of phosphonated functional groups came with an increase of the LCST. Such polymers were shown to be of great interest for the treatment of metallic pollution in wastewater.



SP-3P-2-002 Copolymers	LCST
P(NnPAM) (*SP-3P-9-004*)	22°C
P(NnPAAM-stat-$MAPC_1$) 95/05	22.8°C
P(NnPAAM-stat-$MAPC_1$) 90/10	23.4°C
P(NnPAAM-stat-$MAPC_1$) 80/20	25.6°C

Related Papers :

Graillot, A. et al., RSC Adv., 2014, 4, 19345–19355

Graillot, A. et al., J.Hazard. Mat. 244– 245 (2013) 507– 515

Looking for a specific thermosensitive polymer ?
SPECIFIC POLYMERS offer CUSTOM SYNTHESIS programs

- SPECIFIC POLYMERS can produce **from grams to hundred grams** depending on the targeted molecule.
- All products are delivered with a **synthesis report** including experimental details and analyses.
- Report on the project progress by **regular phone meeting**
- **Feasibility evaluation** can be proposed depending of customer wishes (targeted structures, quantities)

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