pH-tunable temperature sensitive materials from NIPAAm-methacrylic acid copolymers with hydrophobic spacers

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Goal

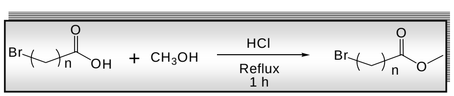
The aim of this work was to develop a series of NIPAAm-copolymers with tuning capacity for their LCST based on comonomers with hydrophobic spacers and hydrophilic ionizable groups. Furthermore, the study of the importance of intrachain hydrogen-bonding, regarding LCST of NIPAAm copolymers in pure water and in solutions with varying pH using partially hydrophobic comonomers is a further goal of this work. Finally, since linear copolymers can be easily characterized, their investigation is the basis for the better understanding of the behaviour of their corresponding polymer networks to be developed in the future.

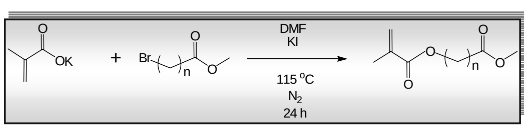
Introduction

During the last years there has been a growing interest in temperature-sensitive polymers because they are potential candidates for applications as intelligent sensors, separation systems and drug release devices. It has been shown that the temperature-sensitivity of these polymers is connected with their lower critical solution temperature (LCST). There are some polymers which exhibit a LCST in aqueous solutions, the most studied polymer being the poly (***N***-isopropylacrylamide) (PNIPAAm) whose LCST lies between 30 and 35 °C . The LCST of these polymers is a result of a fine balance of hydrophilic and hydrophobic groups in their molecular structure. If the balance is slightly altered there is a possibility to vary its LCST. This can be achieved by varying the chemical composition of the polymer.

Experimental

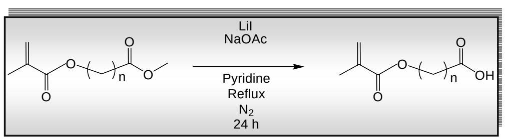
Synthesis of hydrophobic monomer derived from methacrylic acid:





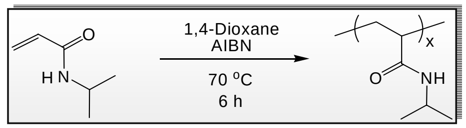
n = 4, 7 and 10

Synthesis of hydrophilic monomer derived from methacrylic acid:

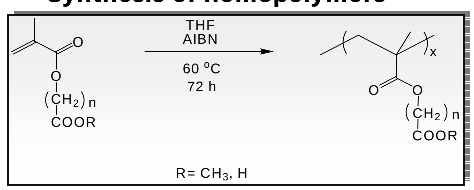


n = 4, 7 and 10

Synthesis of PNIPAAm via free radical polymerization

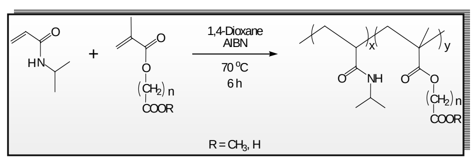


Synthesis of homopolymers



n = 4, 7 and 10

Synthesis of copolymers



n = 4, 7 and 10
y = 5, 10, 15, 20 and 25 mol%

Results

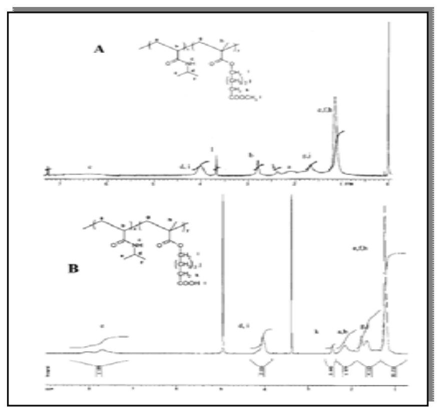


Figure 1. Selected NMR-spectra of NIPAAm-copolymers: (A) copolymers with protected acid groups, (B) copolymers with free acid groups.

Table 1. Results of protected copolymers characterization.

Polymer	Co-monomer content [mol%]	dn/dc [mL/g]	M_w [g/mol]	R_g in THF [nm]	T_g [°C]	Yield [%]
PNIPAAm	-----	0.09299	237 000	27	139	92
COPN4-05	6.2	0.09530	264 000	27	128	77
COPN4-10	9.9	0.08870	292 000	28	114	87
COPN4-15	16.8	0.08900	281 000	27	106	82
COPN4-20	20.4	0.08380	297 000	24	106	85
COPN4-25	19.6	0.09330	208 000	21	97	84
COPN7-05	7.8	0.08098	398 000	31	128	90
COPN7-10	11.6	0.07264	514 000	31	114	87
COPN7-15	15.5	0.08871	406 000	34	105	70
COPN7-20	24.6	0.04360	832 000	32	104	78
COPN7-25	29.0	0.08207	445 000	33	93	73
COPN10-05	4.8	0.09141	368 000	32	127	81
COPN10-10	8.4	0.09105	343 000	30	108	73
COPN10-15	11.3	0.08514	414 000	44	100	45
COPN10-20	23.0	0.08613	296 000	30	78	89
COPN10-25	25.6	0.07859	332 000	32	68	98

Table 2. Results of deprotected copolymers characterization.

Polymer	Co-monomer content [%mol]	dn/dc [mL/g]	M_w [$gmol^{-1}$]	R_g in THF [nm]	T_g [°C]	Yield [%]
CODN4-05	7.8	0.09310	291000	26	133.8	94.3
CODN4-10	12.4	0.09219	340000	23	126.7	82.0
CODN4-15	18.0	0.16656	241000	19*	121.8	87.0
CODN4-20	24	0.16912	310000	30*	117.1	95.0
CODN7-05	7.2	0.09438	354 000	29	127.9	90.9
CODN7-10	12.4	0.09497	318 000	24	118.6	86.0
CODN7-15	17.4	0.16564	275 000	19*	109.6	93.5
CODN10-05	6.6	0.09370	287 000	24	126.4	94.2
CODN10-10	12.8	0.09352	289 000	22	112.5	94.3
CODN10-15	17.3	0.17395	231 000	23*	99.7	90.3

Behaviour of linear polymer in aqueous solution

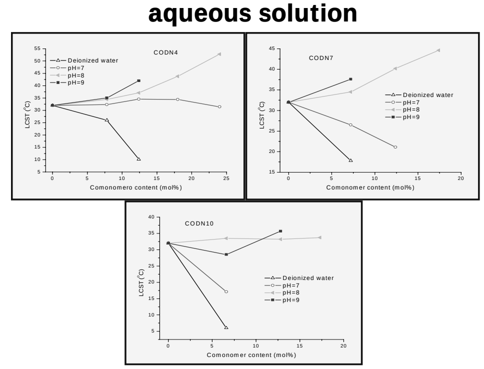


Figure 2. LCST behaviour of NIPAAm-copolymers with free acid groups in buffers of different pH as a function of comonomer content.

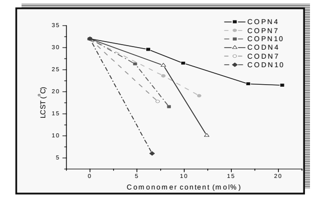


Figure 3. LCST behaviour of NIPAAm-copolymers in pure water in dependence on comonomer content.

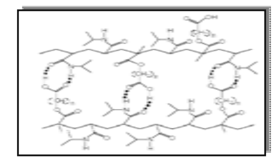


Figure 4. Proposed hydrogen-bonding interactions in the NIPAAm-copolymers.

Conclusions

- ☑ Two series of random NIPAAm-copolymers were successfully prepared using acid comonomers with aliphatic spacers (4, 7 and 10 methylene units) having the acid group either methoxy-protected or free.
- ☑ Solution free radical polymerization proved to be a good technique for their preparation since high yields (close to 90%) in 6 h were achieved. Furthermore, the copolymer composition was close to the monomer feed composition indicating a truly random distribution of the monomeric units in the copolymers.
- ☑ In the solid state, the aliphatic spacers bring side chain flexibility lowering the T_g of the copolymers while the free acid groups give the chance of interchain hydrogen-bonding increasing the T_g as a result.
- ☑ The water solubility and LCST behaviour of the prepared NIPAAm-copolymers depends on the hydrophilic/ hydrophobic balance in the copolymer chain and on the hydrogen-bonding capabilities from its chemical structure. The hydrophilic/hydrophobic balance depends mainly on three elements, (a) the amount of comonomer; (b) the kind of comonomer, regarding the spacer (n = 4, 7 and 10, methylene units) and the acid group (protected or free); (c) the pH of the solution of the copolymer, which affects the extent of ionization of the carboxylic acid groups.
- ☑ Finally, our results show that both: hydrophobic interactions and hydrogen- bonding are very important for the behaviour of NIPAAm-copolymers depending strongly on the fine chemical structure of the used copolymeric units.

Acknowledgements

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