Thermosensitive polymer structures based on segmented copolymer networks

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SUMMARY: Segmented polymer networks with LCST-behavior have been prepared by free radical initiated copolymerization of α,ω-bis-methacrylate terminated poly(methyl vinyl ether) (PMVE) with 2-hydroxy ethyl methacrylate (HEMA) or butyl acrylate (BA). The PMVE bis-macromonomers have been obtained via a semi-continuous process by end-capping the living cationic polymerization of methyl vinyl ether (MVE) with HEMA. The phase separation temperature can be varied by changing the PMVE/comonomer ratio. Incorporation of PMVE-grafts in the hydrogels increases the rate of deswelling and improves the mechanical properties. The application of the segmented networks for thermo-controllable solid phase extraction has been demonstrated by their thermosensitive adsorption behavior of toluene from a water solution.

Introduction

Some polymers are soluble in water at low temperatures, but separate from these solutions when the temperature is raised above a certain temperature, the so-called lower critical solution temperature (LCST). These polymers have attracted much attention, due to a wide range of potential applications as carriers for controlled drug release(1,2) and in drug targeting(3,4), biotechnology(4,5), ecology(6) and even in architecture(7).

Different methods have been described to regulate the phase separation temperature of a thermosensitive polymer system, such as the variation of the polymer concentration in aqueous solutions(8-10), the change of the molecular weights(11), the introduction of low molecular(12,13) or high molecular weight additives(14), copolymerization(15) and crosslinking(16,17).

A well-known example of a polymer with LCST behavior is poly(methyl vinylether) (PMVE)(18). PMVE has a LCST in water around 37°C. In this paper, we present a new type of thermosensitive bicomponent hydrogel structure, which is formed by copolymerization of low molecular weight PMVE's with polymerizable endgroups (bismacromonomers), with another vinyl monomer having the desired phylicity. In this way it is possible to control the LCST-behavior of the networks by changing the PMVE concentration, the nature of the comonomer

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and the length of the PMVE-segments. The hydrogels have been evaluated as activators and as systems for thermo-controllable solid phase extraction.

Results and discussion

Synthesis of PMVE-macromonomers and PMVE-bismacromonomers

A living cationic polymerization procedure was used to prepare PMVE-macromonomers and PMVE-bismacromonomers. For the synthesis of the PMVE-macromonomers, a monofunctional initiator system based on diethoxy ethane (DEE)/trimethyl silyl iodide (TMSI)/ZnI_2 was used as described earlier[19]. A bifunctional initiator based on 1,1,3,3-tetramethoxypropane (TMP)/TMSI/ZnI_2 was used to prepare PMVE-bismacromonomers[20]. End-group functionalization was obtained by end-capping the living chain-ends with 2-hydroxy ethyl methacrylate (HEMA) in the presence of triethylamine as a proton trap (Fig. 1).

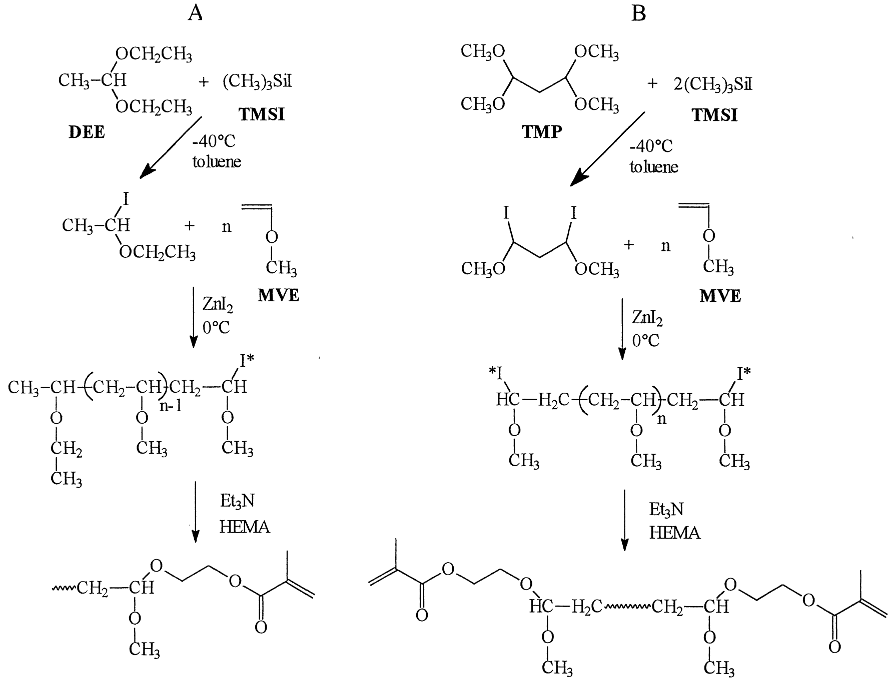

Fig. 1: Synthetic scheme for preparation of PMVE-macromonomers (A) and PMVE-bismacromonomers (B) with methacrylate end-groups.

The polymerizations have been performed by making use of a semi-continuous process, which makes it possible to obtain quantities of PMVE-(bis)-macromonomers up to 30g with relative narrow molecular weight distributions (MWD ≤ 1.2)[21].

The good agreement between M_n obtained from GPC-analysis and M_n calculated from end-group analysis by ^{1}H-NMR indicates a quantitative end-group functionalization (Table 1).

Table 1. Molecular weights and polydispersities of PMVE-macromonomers and PMVE-bismacromonomers, respectively obtained with DEE/TMSI/ZnI_2 and TMP/TMSI/ZnI_2 initiating system in toluene[a].

$\overline{M}_n$ (^{1}H NMR)[b]	$\overline{M}_n$(GPC)[c]	$\overline{M}_w/\overline{M}_n$
	PMVE-bismacromonomers	
4000	4100	1.2
6300	5900	1.2
	PMVE-macromonomer	
2900	3100	1.2

[a] at 0°C, [ZnI_2]: [bis-α-iodo ether] = 1:5 ; termination with HEMA

[b] Calculated from HEMA endgroups

[c] Measured by GPC equipped with a light-scattering (RALLS)/differential pressure detector

Segmented networks from PMVE-(bis)macromonomers

Segmented networks have been prepared by free radical copolymerization (thermal initiation) of the PMVE-bismacromonomers with HEMA as a hydrophilic comonomer or butyl acrylate (BA) as a hydrophobic comonomer. Soluble fractions lower than 5% have been measured for all networks after soxhlet extraction. The networks showed an increasing equilibrium swelling degree in water with increasing length of the PMVE-bismacromonomers (Fig. 2). Due to the LCST behavior of the PMVE-segments, the swelling degree in water is much smaller at 40°C than at 20°C.

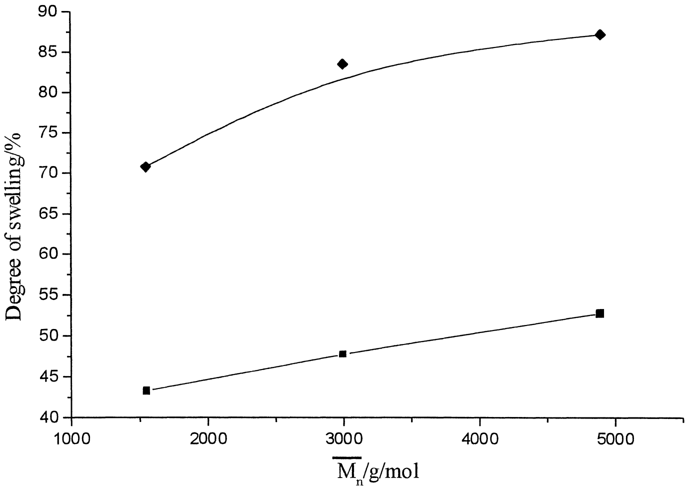

Fig. 2: Equilibrium swelling degree of net-poly(MVE-co-HEMA) networks (PMVE/HEMA 25/75 wt%) as a function of molecular weight of PMVE-bismacromonomers (◆ = at 20°C, ■ = at 40°C).

The LCST-behavior of the networks is controllable by variation of network composition. In the case of the net-poly(MVE-co-BA) segmented networks the temperature at which phase separation ($T_{ph.s.}$) occurs, decreases with increasing content of hydrophobic poly(butyl acrylate) chains. The opposite effect is obtained for the PHEMA-containing networks (Fig. 3).

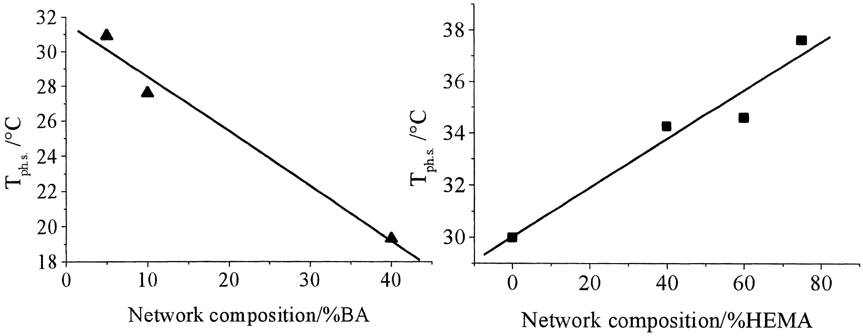

Fig. 3: Phase separation temperature ($T_{ph.s.}$) as a function of BA (▲) or HEMA (■) content in the PMVE-containing segmented networks (measured as onset of DSC endotherm).

Okano et al. have shown that comb-type grafted gels have larger deswelling rates than polymer gels that do not bear polymer chains with freely mobile ends[22)]. In the present work, PMVE-grafts have been incorporated in the net-poly(MVE-co-HEMA) networks by free radical copolymerization of PMVE-macromonomers, PMVE-bismacromonomers and HEMA. When the water temperature is raised from 20°C to 40°C, the deswelling rate of the networks that contain PMVE-grafts is significantly increased compared to the networks without PMVE-grafts (Fig. 4).

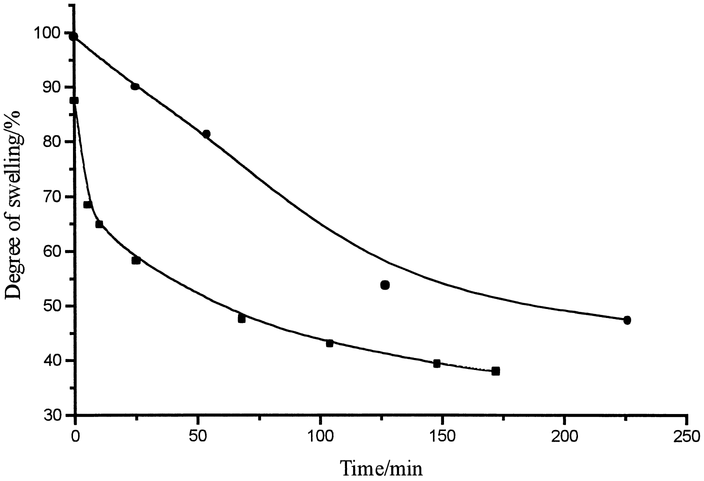

Fig. 4: Deswelling of a net-poly(MVE-co-HEMA) hydrogel (1mm thickness) as a function of time after temperature increase from 20 to 40°C (● = 40% PMVE-bismacromonomer and 60% HEMA, ■ = 20% PMVE-bismacromonomer, 20% PMVE-macromonomer and 60% HEMA; M_n(PMVE-bismacromonomer) = 4100 g/mol and M_n(PMVE-macromonomer) = 3100 g/mol).

The incorporation of PMVE-grafts also improved the mechanical properties of the swollen networks in water. The networks composed of only PMVE-bismacromonomers and HEMA as a comonomer showed some cracks after several swelling-deswelling cycles. This was not the case for the networks containing more than 20% PMVE-macromonomer. Such mechanical stability opens perspectives for the use of these networks as actuators that are triggered when the water temperature is raised above the LCST. To evaluate this application, the following test has been developed: the networks were fitted between two clamps in a water tank and kept at zero elongation as determined by their equilibrium swelling degrees. The water temperature was continuously raised and the stress, resulting from the shrinkage of the networks, was measured (Fig. 5). From Figure 5, it can be observed that a higher content of PMVE-bismacromonomer in the networks results in a higher stress development with increasing water temperature. The networks containing 40 or 20% PMVE-bismacromonomer eventually broke, while the network containing 2% PMVE-bismacromonomer and 38% PMVE-graft had an equilibrium stress at a water temperature about 50°C. This equilibrium stress decreases with lower overall PMVE-content and with higher contents of the PMVE-grafts. It is also clear that this equilibrium stress is reached in a faster way when more PMVE-grafts are introduced due to higher deswelling rates (see also Fig. 4).

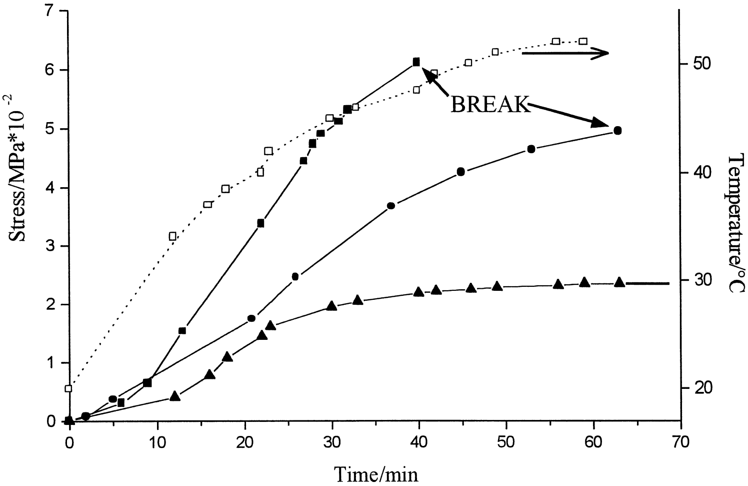

Fig. 5: Stress development of net-poly(MVE-co-HEMA) networks as a function of time and water temperature (■ = 20% PMVE-macromonomer, 40% PMVE-bismacromonomer, 40% HEMA; ● = 20% PMVE-macromonomer, 20% PMVE-bismacromonomer, 60% HEMA; ▲ = 38% PMVE-macromonomer, 2% PMVE-bismacromonomer, 60% HEMA, □ = water temperature).

Another application of interest is the use of thermoresponsive polymer networks for thermo-controllable chromatography. Ise et al. already used porous glass beads modified with thermoresponsive polymers for thermosensitive gel permeation chromatography$^{23)}$. We have been investigating whether the application field could be further extended by the use of thermoresponsive networks for thermo-controllable solid phase extraction (SPE). SPE is a technique used for the separation and pre-concentration of analytes from non-volatile solvents (e.g. water). Normally, the selectivity is determined by the nature of the packing material.

Thermoresponsive polymer materials exhibit a change in hydrophilicity when the water temperature is varied. Therefore, the selectivity for SPE could be controlled by changing the water temperature.

Contact angle measurements showed that the surface of the net-poly(MVE-co-HEMA) networks becomes more hydrophobic when the water temperature is raised from 20°C to 40°C. As a model for the thermo-controllable extraction behavior, toluene adsorption on the networks has been measured as a function of water temperature. The preliminary results in Fig. 6 demonstrated that, at a water temperature of 40°C, the net-poly(MVE-co-HEMA) networks are amphiphilic and are able to adsorb toluene from the water solution. When the water temperature is lowered to 20°C, the networks become more hydrophilic and much of the adsorbed toluene is released again (curve A). This behavior was not found for PHEMA homopolymer networks (curve B).

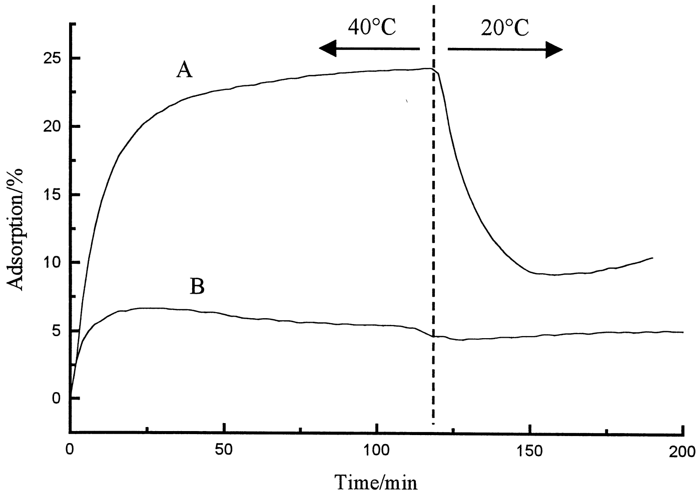

Fig. 6: Toluene adsorption on polymer networks as a function of water temperature: A: 60% PMVE-bismacromonomer, 40% HEMA; B: 100% HEMA (30 ml of a 200 ppm toluene solution in water; 1g of polymer material).

Acknowledgments

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