

Synthesis and Properties of New Thermosensitive Polymer Systems

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ABSTRACT: The controlled thermal release of aqueous solvent mixtures from polymeric gel particles was investigated. A new type of a polymeric gel consisting of a maleic anhydride/poly(ethylene glycol) condensation product as a crosslinking macromonomer and acrylamides was synthesized by solution or inverse emulsion polymerization for the investigation. Afterward a shell of crosslinked polystyrene was coated to stabilize this new kind of "microcontainer" for the application. This concept was shown as generally useful for various mixtures of organic solvents and water. The

cloud point temperature of the polymer gel strongly depended on the following parameters: the type and content of organic cosolvent, the degree of polymerization and constituents of the polyester moiety, and the type and content of the comonomers. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 2122–2129, 2007

Key words: stimulus-sensitive polymers; polycondensation; hydrogels; crosslinking; core-shell polymers

INTRODUCTION

In recent years "smart" polymers and polymeric materials have attracted increasing academic and technical interest because they have undergone a dramatic change in physical properties triggered by external stimuli. The response of polymeric materials toward external stimuli is most often discussed in the case of pH and/or temperature changes. The latter is represented by a couple of different structures, which display a lower critical solution temperature (LCST) in aqueous systems. The most frequently mentioned polymer systems with thermosensitive behavior are homopolymers and copolymers containing poly(*N*-isopropylacrylamide) (pNIPAM). Mostly crosslinked NIPAM copolymers with nonionic^{1–3} and far more ionic^{4–11} comonomers were synthesized and their swelling behavior dependency on external parameters was investigated. The temperature and pH sensitivity were studied in copolymer gels consisting of NIPAM and acrylic acid,^{12,13} ionizable acrylamides,¹⁴ certain sulfonamides,¹⁵ *N*-[3-dimethylamino)-propyl]methacrylamide,¹⁶ or vinyl acetic acid.¹⁷ Furthermore, corresponding graft^{18–20} and block copolymers^{21,22} containing pNIPAM units were synthesized and investigated.

Various NIPAM-free thermoresponsive polymers are known, for example, poly(*N*-vinylcaprolactam),^{23,24} poly(methyl-2-propionamidoacrylate),²⁵ derivatives of maleic anhydride (MA) copolymers,^{26,27} poly(organophosphazenes),²⁸ poly(*N,N*-diethylacrylamide-*co*-methacrylic acid),²⁹ methacrylamides with lactate side chains,³⁰ and poly(vinyl alcohol-*co*-vinyl acetates).³¹

Special morphologies for pNIPAM-based thermoresponsive materials such as hydrogel nanoparticles,³² poly(L-lactic acid) microcapsules as a pNIPAM gel container,^{33,34} shell-crosslinked vesicles,³⁵ and an interpenetrating network with gelatin³⁶ were studied.

These types of phase transition polymers are preferentially investigated for applications in biology and medicine for use in drug delivery systems,^{1,13,32,33,35} carriers for gene delivery,³ thermosensitive superabsorbents,² determination of enzyme concentrations,¹⁶ and control of enzymatic activity.³⁷

We sought to develop thermosensitive gel particles for the discharge of aqueous solvent mixtures by gel collapse. The (high boiling) cosolvent could then act as a pore builder in polymer film formation, for example.

Although thermosensitive polymers in the human environment require a phase transition around body temperature, for some technical processes (e.g., precipitation coagulation of polyurethanes) it is desirable to control the phase transition of a polymer gel in a temperature range of 40–100°C. Hence, an appropriate material that was not based on the thermoresponsive properties of pNIPAM had to be developed. In order to disperse this material in various environ-

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ments, crosslinked hydrogel particles are necessary. Finally, the possibility of the mechanical protection of these particles by encapsulation was examined.

High boiling alcohols such as ethylene glycol or glycerol were chosen as organic cosolvents because of their hydrophilic nature. This allows investigations in a wide range of solvent compositions and phase transition temperatures.

Up to now, only a few groups have conducted detailed studies of the effect of additives (salt, organic solvents) on the thermal behavior of LCST materials,^{38,39} especially pNIPAM derivatives.

In this article we report on the synthesis of new polymeric gel particles using a condensation product of MA/poly(ethylene glycol) (MA/PEG) as crosslinkable macromonomers and acrylamides as comonomers. The dependence of the phase transition temperature of the gel on parameters like the type and content of organic cosolvent, degree of polymerization (DP) of the polyester moiety, and type and content of crosslinking agent was thoroughly investigated using hydrogels obtained by solution polymerization. Then, the optimized conditions and mixture compositions were transferred into inverse emulsion polymerization (IEP) in order to receive hydrogel particles. These particles were covered with a shell of crosslinked polystyrene to stabilize them for various application environments.

EXPERIMENTAL

All solvents except Isopar (ICI) were supplied by Sigma-Aldrich and used as received. MA, PEG 300, PEG 600, PEG 700 diacrylate, NIPAM, *tert*-butylacrylamide (TBAA), Span 80, Tween 85, ethylenediamine tetraacetic acid (EDTA), styrene, and divinylbenzene were provided by Sigma-Aldrich and used as received. Hypermer 2296 (ICI), 2,2'-azobis-(2,4-dimethylvaleronitrile) (V-65, Wako), and 2,2'-azobis-(*N,N'*-dimethyleneisobutyramidine) dihydrochloride (VA-044, Wako) were commercial grade and used as received.

Synthesis

Polycondensates **P1–P3** (**3**, Fig. 1) were synthesized. Typically, equimolar amounts of MA and a corresponding PEG (PEG 600 for **P1**, PEG 300 for **P2**, **P3**) were heated with stirring under an argon atmosphere (1 h at 100°C, 5–7 h at 200°C) in a 3-necked 250-mL flask. The DP was checked as often as necessary by acid-base titration. At the desired P_n the reaction was stopped and the polycondensate was used directly. The DP for **P1** was 3.28 (cloud point at 61°C in 60:40 glycerol/water, v/v), for **P2** was 4.23 (cloud point at 95°C in 30:70 ethylene glycol/water, v/v), and for **P3** was 4.35 (cloud point at 85°C in 30:70 diethylene glycol/water, v/v).

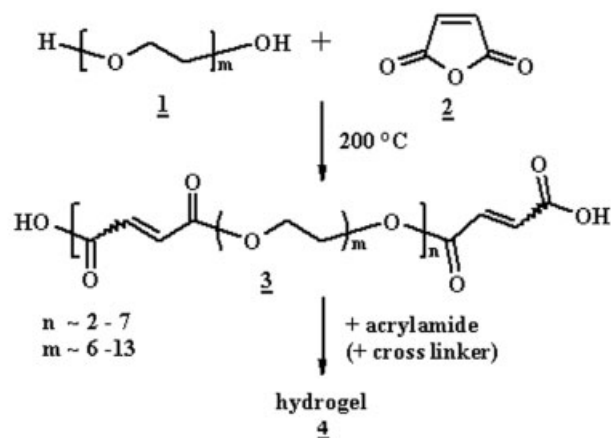


Figure 1 The synthesis of the hydrogel.

The polymerization experiments were carried out as follows. For solution polymerization the polyester and comonomers (see Table I) were dissolved in the required solvent composition, which was initiated with VA-044 (Wako), heated to 44–60°C (depending on the phase transition temperature expected, which should be 10°C below it), and stirred for 8–20 h under argon.

Hydrogel **H2** (**4** in Fig. 1) was synthesized as follows. Polyester **P2** (6.8 g) was dissolved under argon in a solution of 122.1 mL of deionized water and 67.7 mL of ethylene glycol in a stirred and thermostated flask. After the addition of 1.1 g of PEG-700 diacrylate, NIPAM (3 g) dissolved in 20 mL of water was added. The reaction was initiated at 40°C by adding 25 mg of VA-044 in 5 mL of water. After 3 h the temperature was increased to 43°C, and 3 h later another 25 mg of VA-044 was added. The temperature was increased to 45°C after 1 h, the polymerization was stopped after 10 h, and the cloud point temperature was determined. An aliquot of 20 g of the gel solution was heated to 100°C for control of the quantitative polymerization. The liquid was decanted from the coagulated solid, this was washed 3 times with acetone, and dried at 60°C under reduced pressure until the mass remained constant. The obtained mass was 0.74 g (0.768 g expected).

For IEP, the aqueous phase (Table I) was combined with the oil phase (Table I) while stirring at 3000 rpm. The mixture was flushed with argon; initiated with VA-044, which was added gradually in small portions over 5 h; heated to 44–60°C; and stirred for 10 h under argon.

Hydrogel **H2** (IEP) was synthesized as follows. The aqueous phase containing polyester **P2** (19.1 g), NIPAM (8.4 g), PEG-700 diacrylate (3.0 g), water (320.4 g), ethylene glycol (171.6 g), and EDTA (0.4 g) and the organic phase containing Isopar M (200.9 g), Span 80 (17.1 g), Tween 85 (34.2 g), and Hypermer 2296 (2.23 g) were mixed for 1 min at 3000 rpm. Transfer of the

TABLE I

Hydro-gel	Polyester	Aqueous phase composition (g)	Oil phase composition (g)	Coating composition (g)	Cloud point (Hydrogel) (°C)
H1	P1	polyester 10.1; TBAA 1.84; glycerol 120; water 80; VA 044 0.05;	—	—	59.0 ¹
H2	P2	polyester 6.8; NIPAM 3.0; EG 67.7; water 142.1; PEG-700 diacrylate 1.1; VA 044 0.05	—	—	67.5 ¹
H3	P3	polyester 6.8; NIPAM 3.0; diethylene glycol 60; water 140; PEG-700 diacrylate 1.1; VA 044 0.05	—	—	74.7 ¹
H1 (IEP)	P1	polyester 5.24; TBAA 0.96; glycerol 63; water 42; EDTA 0.11 (1% in water); VA 044 0.026	Isopar M 43.7; Span 80 3.73; Tween 85 7.44; Hypermer 2296 0.49	H1 (IEP) 40.1; styrene 3.7; divinylbenzene 3.7; Span 80 3.5; octane 50; AIBN 0.75 (9% in DMF);	~ 59 ²
H2 (IEP)	P2	polyester 19.1; NIPAM 8.4; ethylene glycol 171.6; water 320.4; PEG-700 diacrylate 3.0 EDTA 0.4 (1% in water); VA 044 0.14	Isopar M 200.9; Span 80 17.1; Tween 85 34.2; Hypermer 2296 2.23	H2 (IEP) 236.4; styrene 22.5; divinylbenzene 22.5; Span 80 21.2; octane 292.5; V65 4.5 (16% in toluene)	~ 64 ²
H3 (IEP)	P3	polyester 5.1; NIPAM 2.25; diethylene glycol 45; water 105; PEG-700 diacrylate 0.765; EDTA 0.16 (1% in water); VA 044 0.08	Isopar M 46.5; Span 80 3.9; Tween 85 7.95; Hypermer 2296 0.51	H3 (IEP) 29.55; styrene 2.85; divinylbenzene 2.85; Span 80 1.0; Tween 85 0.325; Isopar M 36.6; V65 1.863 (16% in toluene)	~ 69 ²

¹ Thermoturbidimetry² DSC

mixture into a nitrogen flushed lab reactor was followed by the stepwise addition of VA-044 (0.07 g) dissolved in 5 mL of water over 2 h. Then, the temperature was increased to 45°C. After another 3 h a second portion of VA-044 (0.07 g) in water was added over 30 min. After 10 h the polymerization was stopped.

This was followed by coating the primary gel particles with a 1:1 (w/w) mixture of styrene/divinylbenzene in a 1:1 (w/w) proportion to the gel particles in a one-pot procedure. An oil soluble initiator was used at temperatures below the phase transition as previously described.³⁴

In the procedure for encapsulation of **H2** (IEP), the gel particles of **H2** (IEP) (236.4 g) were mixed with octane (292.5 g), Span 80 (21.2 g), styrene (22.5 g), and divinylbenzene (22.5 g). The mixture was poured into a stirred (200 rpm) lab reactor, purged with nitrogen, and heated to 45°C. Then, 2.25 g of V-65 (16% in toluene) was added during 2 h. More V-65 (2.25 g) was added after 5 h, and the polymerization was stopped after 10 h.

The coated particles were allowed to settle and then washed 3 times with hexane in order to remove impurities.

Hydrogels **H1** and **H3** and the encapsulated particles thereof were synthesized in the same manner.

The turbidimetry was examined using a temperature controlled turbidimeter (model TP1, E. Tepper) with an optical pathlength of 12 mm at $\lambda = 670$ nm. Polyesters **P1–P3** and hydrogels **H1–H3** were dissolved in the corresponding solvent mixture (2.5%). The turbidity of the solution was recorded as photo-induced voltage, where a value of -220 mV corresponded to a transparent solution (relative turbidity = 0%) and a value of 0 mV corresponded to a turbid solution (relative turbidity = 100%). The cloud point temperature was defined as the average of the temperatures of the first derivatives in the relative turbidity versus the temperature curves in heating and cooling modes (1.0 K min^{-1}).

The ¹³C-NMR spectrum was recorded in D₂O on a Unity 400/500 (Varian, Darmstadt, Germany). The cloud point temperatures of the uncoated and coated hydrogel particles [**H1–H3** (IEP)] were determined via differential scanning calorimetry (DSC, PerkinElmer DSC-7) as the relative maximum in the normalized heat flow (heating cycle at a temperature scan rate of 10 K min^{-1}). For this a decanted sample (35 mg) was

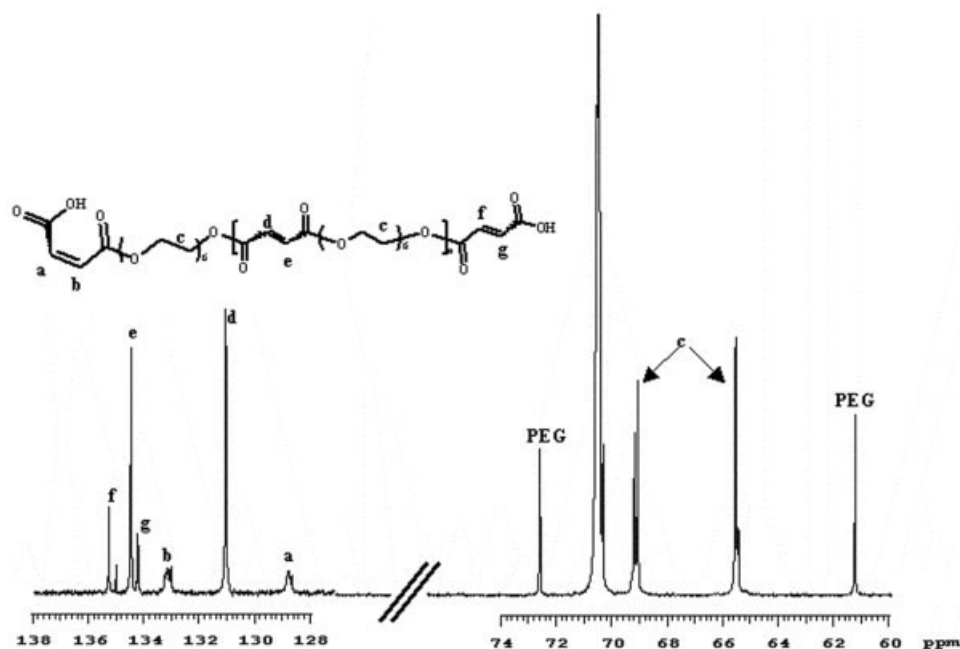


Figure 2 The ^{13}C -NMR spectrum of polyester MA/PEG 300.

placed in a high-pressure gold plated steel pan and heated.

End group analyses of polyesters were carried out by potentiometry (Metrohm Titroprocessor 670, Dosimat 665). Particles were imaged with transmission electron microscopy (Phillips CM 2000).

RESULTS AND DISCUSSION

In this work we looked for a polymeric system to tailor phase transition behavior at various temperatures for different aqueous mixtures. Generally, this correlation was investigated for linear pNIPAM in aqueous solutions with alcohols, acetone and dimethylformamide,³⁸ and *N*-vinylcaprolactam with dimethylsulfoxide²³ as cosolvents. The LCST decreased in most cases with increasing amounts of organic solvent, or a combined LCST and upper critical solution temperature (UCST) behavior was found. The dependence of the cosolvent effect on the structure of the LCST polymer has been demonstrated by Mori et al.³⁹ In contrast to pNIPAM, poly(*N*-vinylacetamide-*co*-methyl acrylate) shows increasing LCST values with increasing amounts of lower alcohols except *n*-butanol. The drawbacks of these materials are low phase transition temperatures (<50°C) and rather low contents of cosolvents at useful switching temperatures. For applications such as coagulation additives, gel materials with phase transition temperatures greater than 50°C with up to 50% nonaqueous solvent are required.

A new series of crosslinked polyesters of PEG malates was synthesized according to Figure 1.

By heating components 1 (PEG) and 2 (MA) without any solvent, unsaturated polyester 3 was obtained, which could be used without any purification procedure. A similar structure using fumaric esters as the unsaturated component was previously developed for a biodegradable system for tissue engineering applications.⁴⁰

The chain length of the polyester only depends on the PEG component that is used (PEG 300 and PEG 600) and the reaction time at a given temperature. The DP is easily monitored by titration of the carboxylic end groups, because the chain ends are always covered with acid units as revealed by ^{13}C -NMR. No signals of maleic acid or anhydride but peaks for unreacted PEG are to be found (see Fig. 2). The reaction is then stopped at the desired DP simply by cooling down. For the thermosensitive polyesters synthesized in this work a value of DP between 2 and 7 was adjusted corresponding to molecular weights between 1500 and 3000 g/mol. An example of a detailed investigation by ^{13}C -NMR spectroscopy is given in Figure 2.

It is obvious that maleic (Fig. 2, points a, b, d) and fumaric (Fig. 2, points e, f, g) units coexist in the reaction product. This is caused by the rather drastic reaction conditions at 200°C. Furthermore, the DP value can be calculated from the proportion of the signal intensities of end groups (Fig. 2, points a, b, f, g) and middle groups (Fig. 2, points d, e). The signals at around 61 and 73 ppm reveal a content of free PEG in the product that keeps it processable even at higher DP values.

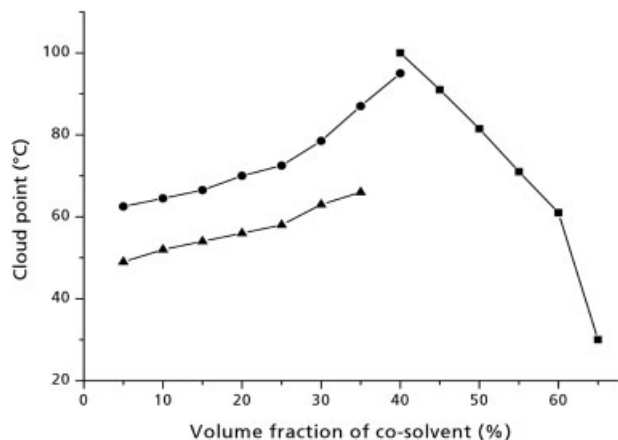


Figure 3 The cloud point temperature versus the volume fraction of solutions (2.5%) of (■) MA/PEG 600 polyester (DP = 3.28) in aqueous glycerol, (●) MA/PEG 300 polyester (DP = 4.35) in aqueous ethylene glycol, and (▲) MA/PEG 300 polyester (DP = 6.13) in aqueous diethylene glycol.

The phase transition behavior of **3** was investigated in aqueous solutions containing different amounts of glycerol, ethylene glycol, or diethylene glycol. For water/glycerol solutions a thermosensitivity was found for MA/PEG 600 polyesters, whereas the more hydrophobic MA/PEG 300 polyesters displayed a phase transition behavior in aqueous glycol solutions. The dependency of the cloud point of the MA/PEG polyesters on the type of cosolvent and the composition of the aqueous solution is shown in Figure 3.

There is a general shift of the curves toward lower cloud point temperatures with increasing DP values.

The reason for the reverse sensitivity of the cloud point temperature with the fraction of the different cosolvents is not yet clear. Ethylene glycols probably serve as better solvents than water for the more hydrophobic MA/PEG 300 polyesters, whereas aqueous glycerol solutions show the well-known behavior of decreasing cloud point temperature with growing content of organic solvent.

In order to obtain hydrogels, solution polymerizations were carried out with acrylamides and optionally with crosslinkers such as PEG-bis-acrylates. Note that the thermosensitive properties of the hydrogel are not caused by acrylamides such as NIPAM. The molar proportions of the reactive double bonds of the polyester and the acrylamides allow acrylamide chain lengths of not more than ~ 2 . The optimized monomer compositions as well as the reaction conditions were transferred to an IEP approach for hydrogel particle synthesis. Thermoturbidimetric measurement of hydrogels **H1–H3** prepared in solution and DSC investigation of the corresponding hydrogel particles obtained in inverse emulsion revealed the transferability of polymerization conditions from solution to IEP (see Experimental, Table I).

Preparation of hydrogels in solution

Polyesters **P1–P3** obtained by polycondensation of PEG and MA were polymerized with different acrylamides as comonomers in solution, yielding hydrogels **H1–H3**. All polymerizations were carried out at temperatures below the phase transition temperature. PEG type, DP of polycondensation product **3**, and amount of comonomers are the “tuning” parameters in this process. For the quantitative polymerization, we chose an excess of initiator added in two portions. Coagulation of the **H2** gel above the cloud point temperature and determination of the solid content after careful washing with acetone confirmed this assumption. The cloud point temperature of the gel material was adjusted between 45 and 90°C for different aqueous solutions and various solution compositions.

Figure 4 shows the dependence of the cloud point temperature of the resulting gel on the part of NIPAM or TBAA in the monomer mixture. As can be seen, the amount and choice of the comonomer distinctly alters the hydrophilic/hydrophobic balance of the resulting polymer network. Therefore, this is one way to control its phase transition temperature.

Figure 5 displays the sharpness of the phase transitions of hydrogels **H1–H3** in their corresponding solvent mixtures. The reason for the rather smooth phase transition of **H1** is probably the higher viscosity of glycerol-containing solutions. The decreasing reversibility of the volume phase transition of **H2** and **H3** could be due to a changing solvation mechanism of the cosolvents in water.

Preparation of hydrogels by IEP

The IEP was performed with the same monomer compositions and initiation conditions as the correspond-

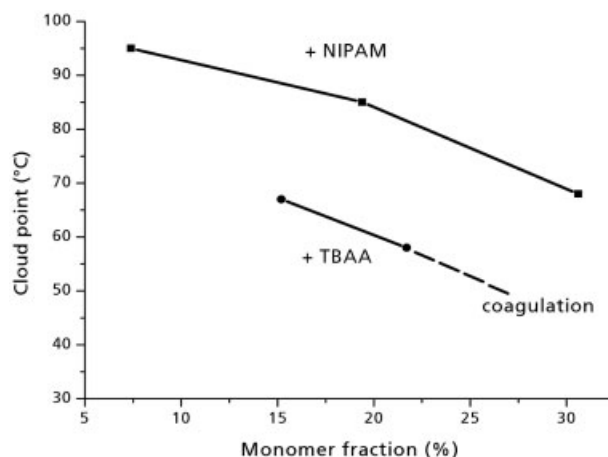


Figure 4 The cloud point temperature versus the kind and fraction of different comonomers in the copolymerization with MA/PEG 300 polyester (DP = 4.05) dissolved in ethylene glycol/water (30:70, v/v; 2.5%).

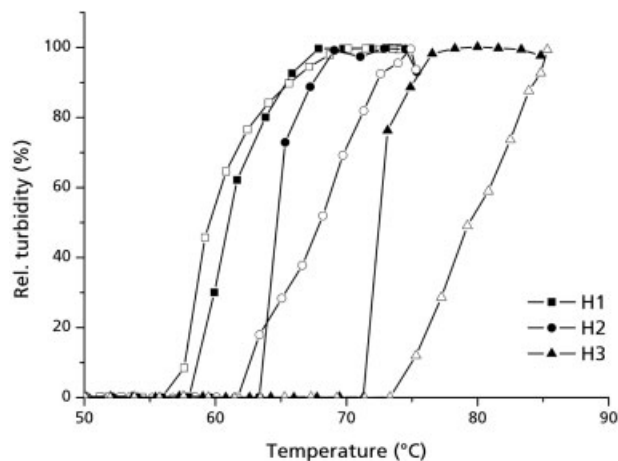


Figure 5 The phase transitions of **H1** (2.5% in 60:40 glycerol/water, v/v), **H2** (2.5% in 30:70 ethylene glycol/water, v/v), and **H3** (2.5% in 30:70 diethylene glycol/water, v/v); (■, ●, ▲) heating, (□, ○, △) cooling.

ing solution polymerization, yielding hydrogel particles **H1** (IEP) to **H3** (IEP). For the stabilization of the gel particles in the solvent Isopar M (high boiling mixture of isoparaffins, ICI), a mixture of surfactants of the sorbitan type [hydrophilic-lipophilic balance (HLB) = 8.6] was used. As can be seen in Figure 6, rather uniform gel particles with a size range between 0.5 and 1 μm were obtained. The hydrogel particles could be used without further purification.

For some applications of the “loaded” gel particles such as use as a coagulation additive in polyurethane processing, an impermeable but swellable shell is needed.³⁴ Hence, the polymeric gel particles were covered with a crosslinked polystyrene shell by precipitation polymerization of styrene and divinylbenzene. This provides mechanical protection and avoids dif-

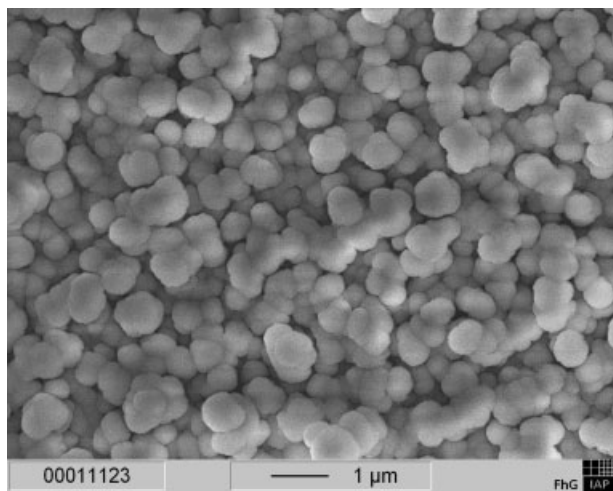


Figure 6 The particles of hydrogel **H1** obtained by inverse emulsion polymerization.

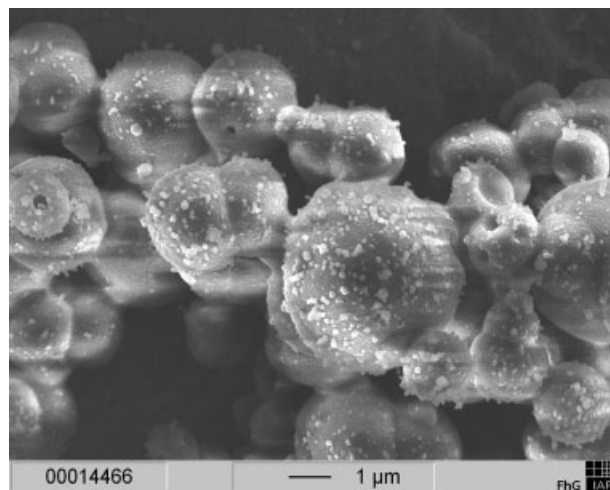


Figure 7 The particles of hydrogel **H2** coated with crosslinked polystyrene.

fusion exchange of solvents. A simple procedure to prepare hydrophilic core/hydrophobic shell particles via inverted emulsions was first proposed by Li and Ruckenstein.⁴¹ With some slight changes, this procedure was applied to encapsulate the particles of hydrogels **H1**–**H3**.

The hydrogel particles in the inverse emulsion were mixed with an octane phase containing the monomers, a mixture of stabilizers (see Table I, HLB \sim 4.5), and an oil soluble initiator. Because of the insolubility of crosslinked polystyrene in octane, the polymeric material precipitated on the surface of the hydrogel.

The swelling properties of the shell can be simply controlled by varying the amount and ratio of styrene and divinylbenzene. Increasing quantities of divinylbenzene lead to an increasingly impermeable and nonswellable shell. Nevertheless, different morphologies of the core-shell particles that were dependent on the nature of the hydrophilic core were obtained. Examples are the more separated small particles with a smooth surface of coated **H2** (Fig. 7) and the larger particle aggregates with a raspberry-like surface of coated **H3** (Fig. 8).

The particles are easy to purify by settling and decanting several times. The detection of the solvent release behavior of the encapsulated hydrogel turned out to be very challenging. DSC proved to be an appropriate method in this respect. It is known that pNIPAM containing gel networks display an endothermic phase transition from the swollen to the nonswollen state.⁴² The more complex inverse emulsions showed this behavior as well. As an example, the DSC results for particles of hydrogel **H2** and encapsulated particles of hydrogel **H2** are displayed in Figure 9. Because of the complicated sample preparation, only qualitative analysis of the results was reasonable.

Figure 9 shows that the phase transition occurs in a temperature range of \sim 30 K. This is caused by both

inhomogeneities of the gel network and the volume effect. The results for the maximum heat flow at 63.8°C fits well to the cloud point temperature of H2 obtained by thermoturbidimetry at 67.5°C (Fig. 5) and the corresponding peak of the coated particles at 62.4°C. The latter shows that the phase transition inside the coated particles can also be measured by DSC. These selected examples reveal the general transferability of the thermosensitive properties from polyesters via a soluble hydrogel to encapsulated hydrogel particles.

Intense attempts are currently being made to use these materials as responsive solvent depots in evaporation coagulation of polyurethanes. The results of these investigations will be published in the future.

CONCLUSIONS

The controlled thermal release of aqueous solutions of organic solvents from polymeric gel particles was investigated. Therefore, a MA/PEG condensation product was synthesized as a new basic thermosensitive material. Gel particles were obtained by copolymerizing this macromonomer with acrylamides and, if necessary, with crosslinking acrylates. The dependence of the phase transition temperature of the polymer gel on parameters like the type and content of organic cosolvent, DP of the polyester moiety, and type and content of the crosslinker was investigated. By varying these parameters, the temperature can be tuned between 45 and 90°C for aqueous mixtures with glycerol, ethylene glycol, and diethylene glycol at various solution compositions.

The gel properties were successfully transferred to hydrogel particles by polymerizing in an inverse emulsion. These particles were coated with a shell of crosslinked polystyrene in a precipitation polymerization to stabilize them. Analysis of the synthesized samples with DSC and thermoturbidimetry revealed

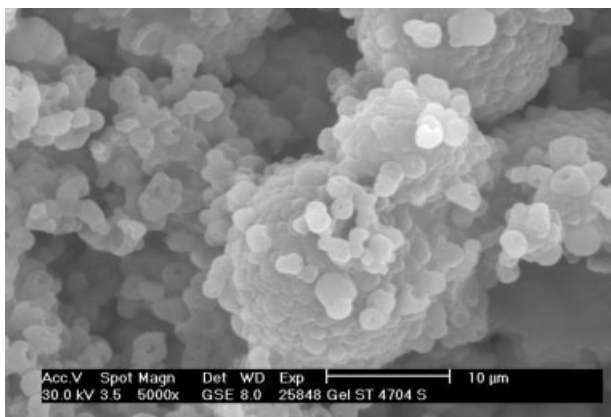


Figure 8 The particles of hydrogel H3 coated with crosslinked polystyrene.

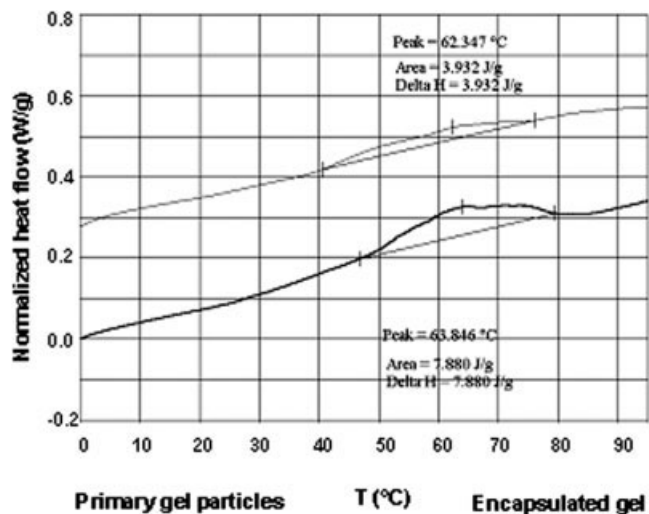


Figure 9 DSC plots for particles of hydrogel H2 and particles of hydrogel H2 coated with crosslinked polystyrene (shifted upward).

the general transferability of the phase transition properties from polyesters via a soluble hydrogel to encapsulated hydrogel particles.

The variety of solvent mixtures and the large range of phase transition temperatures are promising for potential applications in the controlled release of “add values” such as catalysts, curing agents, or solvents. The controlled release of additives during the manufacture of porous polymer layers in the coagulation process of polyurethanes is currently being investigated.

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References

- Escobar, J. L.; Garcia, D.; Valerino, A.; Zaldivar, D.; Hernaez, E.; Katime, I. *J Appl Polym Sci* 2004, 91, 3433.
- Neradovic, D.; van Steenberg, M. J.; Vansteelant, L.; Meijer, Y. J.; van Nostrum, C. F.; Hennink, W. E. *Macromolecules* 2003, 36, 7491.
- Kesim, H.; Rzaev, Z. M. O.; Dincer, S.; Piskin, E. *Polymer* 2003, 44, 2897.
- Ni, C.; Zhu, X. X. *Eur Polym J* 2004, 40, 1075.
- Ogawa, K.; Nakayama, A.; Kokufuta, E. *Langmuir* 2003, 19, 3178.
- Nonaka, T.; Hanada, Y.; Watanabe, T.; Ogata, T.; Kurihara, S. *J Appl Polym Sci* 2004, 92, 116.
- Nonaka, T.; Hua, L.; Ogata, T.; Kurihara, S. *J Appl Polym Sci* 2003, 87, 386.
- Isik, B. *Adv Polym Technol* 2003, 22, 246.
- Cai, W.; Gupta, R. B. *J Appl Polym Sci* 2003, 88, 2032.
- Arotçaréna, M.; Heise, B.; Ishaya, S.; Laschewsky, A. *J Am Chem Soc* 2002, 124, 3787.
- Hahn, M.; Goernitz, E.; Dautzenberg, H. *Macromolecules* 1998, 31, 5616.
- Tian, Q.; Zhao, X.; Tang, X.; Zhang, Y. *J Appl Polym Sci* 2003, 87, 2406.

13. Gutowska, A.; Kriminski, K. Pat. Appl. WO 02/00193 A2 (2000).
14. Harmon, M. E.; Kuckling, D.; Frank, C. W. *Macromolecules* 2003, 36, 162.
15. Kim, J.; Kim, K. Eur. Pat. Appl. EP 1 386 935 A1 (2002).
16. Tuncel, A.; Demirgöz, D.; Patir, S.; Piskin, E. *J Appl Polym Sci* 2002, 84, 2060.
17. Hoare, T.; Pelton, R. *Macromolecules* 2004, 37, 2544.
18. Kuckling, D.; Wohlrab, S. *Polymer* 2002, 43, 1533.
19. Virtanen, J.; Lemmetyinen, H.; Tenhu, H. *Polymer* 2001, 42, 9487.
20. Chourdakis, N.; Bokias, G.; Staikos, G. *J Appl Polym Sci* 2004, 92, 3466.
21. Hasan, E.; Zhang, M.; Müller, A. H. E.; Tsvetanov, Ch. B. *J Macromol Sci A Pure Appl Chem* 2004, A41, 467.
22. Zhu, P. W.; Napper, D. H. *Macromolecules* 1999, 32, 2068.
23. Lozinsky, V. I.; Simenel, I. A.; Kurskaya, E. A.; Kulakova, V. K.; Galaev, I. Y.; Mattiasson, B.; Grinberg, V. Y.; Grinberg, N. V.; Kokhlov, A. R. *Polymer* 2000, 41, 6507.
24. Loos, W.; Verbrugge, S.; Goethals, E. J.; Du Prez, F. E.; Bakeeva, I. V.; Zubov, V. P. *Macromol Chem Phys* 2003, 204, 98.
25. Okamura, H.; Mori, T.; Minagawa, K.; Masuda, S.; Tanaka, M. *Polymer* 2002, 43, 3825.
26. Yin, X.; Stöver, H. D. H. *Macromolecules* 2002, 35, 10178.
27. Behraves, E.; Shung, A. K.; Jo, S.; Mikos, A. G. *Biomacromolecules* 2002, 3, 153.
28. Song, S. C.; Lee, S. B.; Jin, J. I.; Sohn, J. S. *Macromolecules* 1999, 32, 2188.
29. Liu, S.; Liu, M. *J Appl Polym Sci* 2003, 90, 3563.
30. Soga, O.; van Nostrum, C. F.; Hennink, W. E. *Biomacromolecules* 2004, 5, 818.
31. Christova, D.; Ivanova, S.; Ivanova, G. *Polym Bull* 2003, 50, 367.
32. Hu, Z.; Xia, X. *Adv Mater* 2004, 16, 305.
33. Kidchob, T.; Kimura, S.; Imanishi, Y. *J Chem Soc Perkin Trans 2* 1997, 11, 2195.
34. Hahn, M.; Maedler, A. Ger. Pat. Appl. DE 10063197 A1 (2002).
35. Hales, M.; Barner-Kowollik, C.; Davis, T. P.; Stenzel, M. H. *Langmuir* 2004, 20, 10809.
36. Dhara, D.; Rathna, G. V. N.; Chatterji, P. R. *Langmuir* 2000, 16, 2424.
37. Park, T.; Hoffman, A. S. *Appl Biochem Biotechnol* 1988, 19, 1.
38. Costa, R. O. R.; Freitas, R. F. S. *Polymer* 2002, 43, 5879.
39. Mori, T.; Fukuda, Y.; Okamura, H.; Minagawa, K.; Masuda, S.; Tanaka, M. *J Polym Sci Part A: Polym Chem* 2004, 42, 2651.
40. Shin, H.; Temenoff, J. S.; Mikos, A. G. *Biomacromolecules* 2004, 4, 552.
41. Li, H.; Ruckenstein, E. *J Appl Polym Sci* 1996, 61, 2129.
42. Arndt, K. F.; Mueller, G. *Polymercharakterisierung*; Carl Hanser Verlag: Munich, 1996.