

Zsófia Osváth, Tamás Tóth, Béla Iván

Synthesis, characterization, LCST-type behavior and unprecedented heating-cooling hysteresis of poly(N-isopropylacrylamide-co-3-(trimethoxysilyl)propyl methacrylate) copolymers

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**Synthesis, characterization, LCST-type behavior
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of poly(N-isopropylacrylamide-co-3-(trimethoxysilyl)propyl methacrylate)
copolymers**

Zsófia Osváth*, Tamás Tóth, Béla Iván*

Polymer Chemistry Research Group, Institute of Materials and Environmental Chemistry,

Research Centre for Natural Sciences, Hungarian Academy of Sciences,

H-1117 Budapest, Magyar tudósok krt. 2, Hungary

E-mails of authors:

osvath.zsofia@ttk.mta.hu (Zsófia Osváth)

tohtomi7@gmail.com (Tamás Tóth)

ivan.bela@ttk.mta.hu (Béla Iván) (corresponding author)*

Abstract

Soluble poly(N-isopropylacrylamide-*co*-3-(trimethoxysilyl)propyl methacrylate), P(PNIPAAm-*co*-TMSPMA, copolymers with broad composition range, possessing condition and composition dependent LCST-type behavior, are successfully synthesized. Due to the hydrophobic character of the TMSPMA moieties, both the cloud point (T_{CP}) and clearing point (T_{CL}) decrease with increasing TMSPMA content, from 34.3 °C to 23.4 °C for the poly(N-isopropylacrylamide) homopolymer and copolymer with 11.1 mol% TMSPMA, respectively. Unexpected heating-cooling hysteresis with loss of transparency is found in the case of copolymers with higher TMSPMA contents due to *in situ* sol-gel cross-linking without any catalyst above the cloud point, which can be utilized for obtaining new smart hybrid materials. The copolymers possess closely the same, relatively high thermal and thermooxidative stabilities as that of PNIPAAm.

Keywords:

LCST-type poly(N-isopropylacrylamide-*co*-3-(trimethoxysilyl)propyl methacrylate)

copolymers

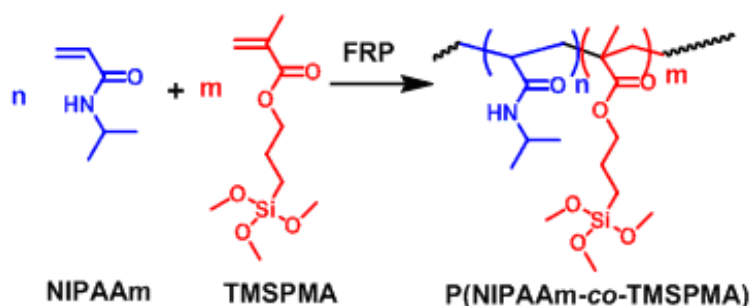
composition dependent heating-cooling hysteresis

in-situ sol-gel cross-linking

1. Introduction

Due to the great importance of responsive (smart, intelligent, adaptive, self-healing) polymers with well-defined functionalities from both scientific and industrial point of views, such macromolecular materials are intensively explored nowadays. Among these macromolecules, the thermally responsive poly(N-isopropylacrylamide) (PNIPAAm), its copolymers, gels, and hybrids have been undoubtedly the most investigated smart materials due mainly to its lower critical solution temperature (LCST) near to body temperature ~32-35°C, biocompatibility, ease of handling etc. (see e.g. Refs. 1-10 and references therein). NIPAAm copolymers possessing functional groups capable to result in PNIPAAm containing thermoresponsive organic-inorganic hybrid materials have gained especially significant interest in recent years [1,2,11-29]. One of the most versatile functional material platforms relies on alkoxy silane functionalities which can be utilized for either surface functionalization or as functional groups in polymers [11-30]. The later can be applied as building blocks for a variety of bi- or multicomponent polymeric or hybrid materials via suitable reactions, e.g. sol-gel processes. For obtaining PNIPAAm containing thermoresponsive organic-inorganic hybrids, both surface functionalization and functional PNIPAAm approaches have been investigated for a broad spectrum of purposes ranging from PNIPAAm coated surfaces and nanoparticles to controlled drug delivery matrices etc. (see e.g. Refs. 1,2,12-14,17,22-24 and references therein). For PNIPAAm-based hybrid material design, one of the most suitable options is NIPAAm copolymers with alkoxy silane functionalities, such as trialkoxy silanes. Several attempts have been reported on the synthesis of copolymers of NIPAAm with 3-(trimethoxysilyl)propyl methacrylate (TMSPMA) and on their subsequent utilization mainly by sol-gel chemistry to prepare PNIPAAm containing hybrid materials [15-29]. Because the thermoresponsive property of such copolymers is critical in the light of their chemistry and applications, the correlation between copolymer composition, the applied conditions and their

critical solution temperature (CST) are crucial aspects of the P(NIPAAm-*co*-TMSPMA) copolymers. However, such systematic investigations surprisingly have not been reported for these copolymers to the best of our knowledge yet. In few cases, when CSTs of NIPAAm-TMSPMA copolymers were determined under certain conditions, the same or slightly different values than that of the CST of PNIPAAm were reported [15,25-29]. It has to be noted, that the CST, or thermal phase transition temperature in general, obtained under a single-set of experimental condition, are broadly reported erroneously as the lower critical solution temperature (LCST) or upper critical solution temperature (UCST) for UCST-type polymers, which correctly are the minimum or maximum, respectively, of the full phase diagram, i.e. the CST as a function of the polymer/solvent ratio in the full polymer fraction region [9,31,32].



Scheme 1. The synthesis of P(NIPAAm-*co*-TMSPMA) copolymers by free radical copolymerization.

Herein, we report on the synthesis and characterization of P(NIPAAm-*co*-TMSPMA) copolymers in a broad composition range and on the dependence of the thermoresponsive behavior of these copolymers on composition and the applied conditions by cloud point (T_{CP}) and clearing point (T_{CL}) determinations, and on their thermal decomposition, the results of which can be widely utilized for a broad variety of future chemical, material science, biomaterial etc. explorations.

2. Experimental

2.1. Materials

N-isopropylacrylamide (NIPAAm, 97%, Sigma-Aldrich) was recrystallized from hexane twice. 3-(Trimethoxysilyl)propylmethacrylate (TMSPMA 98%, Sigma-Aldrich) was used without further purification. 2,2'-Azobisisobutyronitrile (AIBN, 98%, Sigma-Aldrich) was recrystallized twice from methanol. Tetrahydrofuran (THF, >99%, Molar Chemicals) and 1,4-dioxane (>99%, Molar Chemicals) were refluxed from LiAlH₄ and distilled under nitrogen prior to use. Diethyl ether (>99%) and abs. ethanol (>99,9%) were purchased from Molar Chemicals and used without further purification.

2.2. Preparation of a poly(N-isopropylacrylamide-*co*-3-(trimethoxysilyl)propyl methacrylate) P(NIPAAm-*co*-TMSPMA)

Poly(N-isopropylacrylamide-*co*-3-(trimethoxysilyl)propyl methacrylate) (P(NIPAAm-*co*-TMSPMA)) copolymers were synthesized by free radical polymerization. NIPAAm and AIBN were added in a round bottom flask and were degassed by bubbling with argon for 20 min. Then 40 mL of deoxygenated dioxane and TMSPMA were charged in the flask. The reaction mixture was warmed to 60 °C and the polymerization was terminated with air and cooled to room temperature after 20 hours. The resulting polymers were precipitated twice by addition of diethyl ether and filtered. The product was dried in vacuum at 30 °C until constant weight. The homopolymer PNIPAAm was also synthesized as a reference. Table S1 in the Supporting Information (SI) shows the exact weight of materials.

2.3. Measurements

¹H NMR spectra were recorded on a Varian 200 instrument. The polymer was dissolved in CDCl₃. The transmittance versus temperature curves, and thus the cloud point (T_{CP}) and clearing point (T_{CL}) were measured by a Jasco V-650 spectrophotometer equipped

with Jasco MCB-100 mini Circulation Bath and Peltier thermostat heating and cooling system. Standard 1x1 cm cuvettes were used for these measurements. Deionised water was used as reference and as solvent. The polymer solutions were heated and then cooled from 10 to 40 °C and 40 to 10 °C. The sample was dissolved in deionised water and was diluted to the appropriate concentration.

Gel permeation chromatography (GPC) was carried out with a chromatographic setup equipped with a Waters 515 HPLC pump, and Waters Styragel HR1, HR2, HR3 and HR4 columns and Agilent 1260 Infinity RI detector. THF was used as eluent with a flow rate of 1 ml/min at 35°C. Calibration with polystyrene (PSt) standards of narrow molecular weight distributions is available, however, due to the unknown difference between the hydrodynamic volumes of PSt and the NIPAAm copolymers, only a chromatographic curves are displayed (Fig. S1).

Thermogravimetric analyses (TGA) were carried out with a Perkin Elmer TGA6 equipment with 10 mg of samples under nitrogen and oxygen atmospheres from 30 to 750 °C with a heating rate of 10 °C/min.

3. Results and discussion

A series of P(NIPAAm-*co*-TMSPPMA) copolymers (Table 1 and Table S1 in the Supporting Information, SI) were obtained by free radical copolymerization as depicted in Scheme 1. The GPC curves indicate the formation of copolymers with similar molecular weight distributions (Fig. S1 in the SI). The copolymer compositions were obtained by evaluating the ¹H NMR spectra (see Fig. 1 for a typical spectrum). The integral ratios of the signals at 3.6 ppm (–Si–(OCH₃)₃ and at 4.0 ppm (overlapping –CH– and –CH₂– proton signals from the NIPAAm and TMSPPMA monomer units, respectively) [15,16] were used for the determination of the compositions of the copolymers. It should be noted that the ¹H NMR

signal of $-CH_2-$ next to the ester group in TMSPMA was not taken into account in several cases in the literature [17-21].

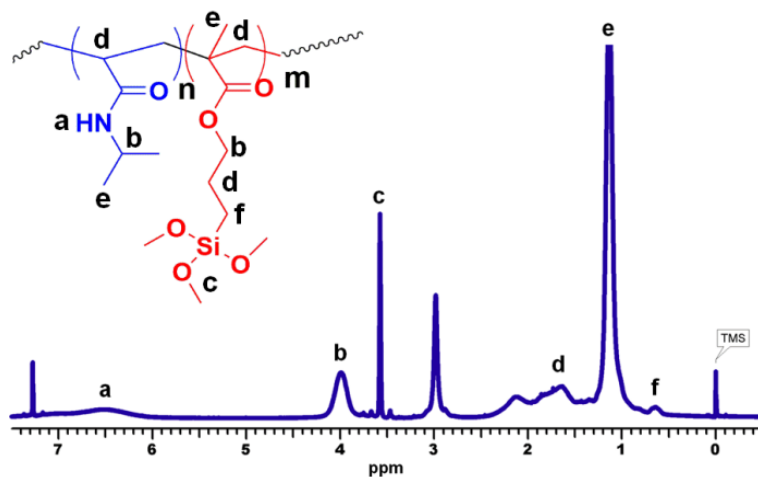


Fig. 1. The ¹H NMR spectrum of a P(NIPAAm-*co*-TMSPMA) copolymer (sample co_1).

As shown in Table 1 and in Fig. S2, the feed composition fits well with that of the copolymers up to 3.8 mol% TMSPMA in the feed. At higher than 6 mol% TMSPMA in the feed, the apparent TMSPMA content in the copolymers is somewhat less than that in the feed. Due to the fact that the copolymerization ratios of NIPAAm with methacrylates (glycidyl methacrylate) are 0.39 (r_{NIPAAm}) and 2.69 (r_{GMA}) [33], and their product is close to one, copolymer compositions near to the feed compositions are expected at high monomer conversions (P(NIPAAm-*co*-TMSPMA)s were obtained with 60-75% yields). It is plausible to assume that the lower than feed content in the copolymers is due to certain extent of alkoxy silane decomposition at higher TMSPMA ratios during work-up or storage, which may lead to low extent of intra- and/or inter-polymer coupling as well without gelation. This is in accordance with literature results reporting on even the formation of insoluble copolymers of NIPAAm with TMSPMA [15,22]. It has to be emphasized that this process is most likely unavoidable when the copolymerizations with TMSPMA are carried out in solvents with even

weak acidity, such as alcohols [22], due to the acidic catalysis of the hydrolysis of the alkoxy silanes. However, as our results indicate (see Table 1 and Fig. 1 and Fig. S2 in the SI), soluble P(NIPAAm-*co*-TMSPMA) copolymers with relatively high TMSPMA contents (higher than 10 mol%) can be prepared reproducibly by using anhydrous dioxane as polymerization medium, diethylether as precipitating agent and storing the resulting copolymers under moisture free conditions. Considering the hydrophobic nature and the steric effect of the bulky trimethoxysilyl group, one can also assume lower reactivity of the TMSPMA monomer than that expected on the basis of the polar glycidyl methacrylate. This may also lead to the lower than feed TMSPMA content in the copolymers at higher TMSPMA/NIPAAm feed ratios in accordance with the composition data in Table 1.

Table 1. The TMSPMA content in the feed, the yield of the radical polymerizations, the TMSPMA content in the resulting P(NIPAAm-*co*-TMSPMA) copolymers, and the cloud point (T_{CP}) and clearing point (T_{CL}) during heating and cooling, respectively (0.1 wt% aqueous solutions, 0.2 °C heating/cooling steps with 5 min equilibration, 488 nm).

Sample	TMSPMA in the feed (mol%)	Yield (%)	TMSPMA in copolymer ^a (mol%)	T_{CP} (°C)	T_{CL} (°C)
PNIPAAm	-	74.3	-	34.3	31.1
co_1	16.7	36.3	11.1	23.4	18.1
co_2	9.1	68.8	7.3	26.7	26.3
co_3	6.2	69.3	5.3	28.1	26.8
co_4	3.8	76.5	3.7	31.3	31.7
co_5	2.0	62.6	2.0	33.0	31.9
co_6	1.0	67.5	1.2	33.2	32.1

^aDetermined by ¹H NMR.

In order to investigate the LCST-type behavior of the P(NIPAAm-*co*-TMSPMA) copolymers, the critical solution temperatures (CST) were determined by measuring the transmittance (T_r) versus temperature (T) curves. First, the effect of the concentration and the wavelength of the incident light on the transmittance-temperature relationships were examined with sample *co_6*. In line with recent findings for PNIPAAm [32], the temperature was raised (or decreased) by 0.2 °C/min followed by 5 min awaiting time (equilibration) before every gradual increase (or decrease) of temperature by 0.2 °C to reach nearly equilibrium state in these experiments. This broadly adaptable, or even standardizable conditions were used in all the transmittance-temperature measurements in this study. As shown in Fig. 2, the thermal phase transition, and thus both the cloud point (T_{CP}) and clearing point (T_{CL}) strongly depend on concentration during heating and cooling, respectively. Both the T_{CP} and T_{CL} are defined as the inflection point of the transmittance-temperature curves (see Fig. S3 in the SI) [32]. The transmittance-temperature curves are shifted to lower temperature regimes and as a consequence both the T_{CP} and T_{CL} decrease with increasing polymer concentration. Due to the observation that 0.1 wt% copolymer concentration is sufficient to obtain full scale transmittance change, and polymer solutions with such a concentration are usually undemanding to prepare, this concentration is used to determine the T_{CP} and T_{CL} . It has to be noted that this polymer concentration can be even considered as a standard to obtain standardized CST values for LCST- or UCST-type thermoresponsive polymers by any kind of techniques. The data in Fig. 2 and Fig. S3 also reveal that the P(NIPAAm-*co*-TMSPMA) copolymers possess remarkable hysteresis, that is relatively large differences exist between the T_{CP} and T_{CL} values, which is important also from practical point of view as well. As to the effect of the wavelength on the dependence of transmittance on temperature (see Fig. S4 in the SI), two major observations can be made: (i) the transmittance does not reach zero at higher wavelengths which is due to the $1/\lambda^4$ dependence of the

intensity of the scattered light; (ii) both the T_{CP} and T_{CL} slightly increases with the wavelength of the incident light. For comparison purposes with light scattering (LS) measurements, we propose to use 488 nm to determine the transmittance-temperature relationship, and thus T_{CP} and T_{CL} , due to the fact that this is a quite typical wavelength for laser light scattering measurements on thermoresponsive polymers.

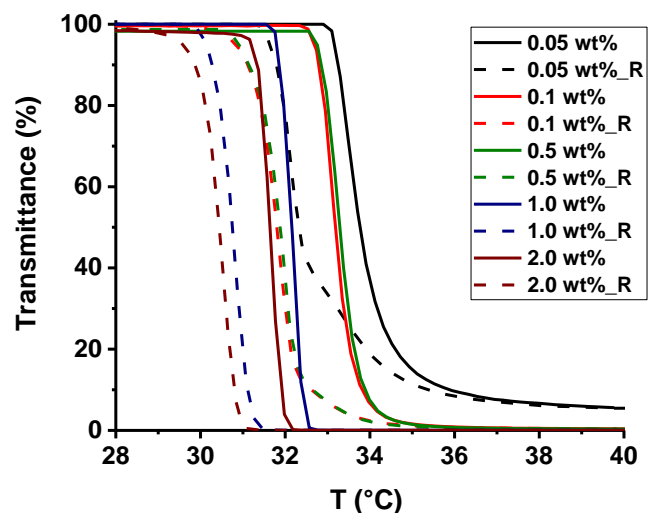


Fig. 2. Transmittance-temperature curves during heating (solid lines) and cooling (dashed lines) of the P(NIPAAm-*co*-TMSPMA) solutions with different concentrations (conditions: 0.2 °C/min heating rate with 5 min equilibration, 488 nm wavelength).

The transmittance-temperature curves of the P(NIPAAm-*co*-TMSPMA) copolymers with different compositions in the heating and cooling cycles are displayed in Fig. 3. As shown in this Figure, the transmittance-temperature curves are shifted towards lower temperature ranges during both heating and cooling with increasing the TMSPMA content in these copolymers. The T_{CP} decreases from 34.3 °C (T_{CP} of PNIPAAm homopolymer) to 23.4 °C for the copolymer with 11.1 mol% TMSPMA content (see also Table 1 and Fig. S5 in the SI). This can be attributed to the hydrophobic nature of the TMSPMA monomer units, which results in T_{CP} and T_{CL} decrease with increasing hydrophobic content.

It is interesting that the width of hysteresis (X_H), that is the difference between T_{CP} and T_{CL} ($X_H = T_{CP} - T_{CL}$), is smaller for the copolymers than that for the PNIPAAm homopolymer with the exception of sample co_1 with the highest TMSPMA content (Fig. 3B). However, surprisingly no full transmittance recovery occurs during cooling with copolymer samples having the three highest TMSPMA contents, i. e. 5.3, 7.3 and 11.1 mol%, on the one hand. On the other hand, the transmittance reached during cooling (Tr_{Cl}) at 10 °C decreases with increasing TMSPMA content in these samples.

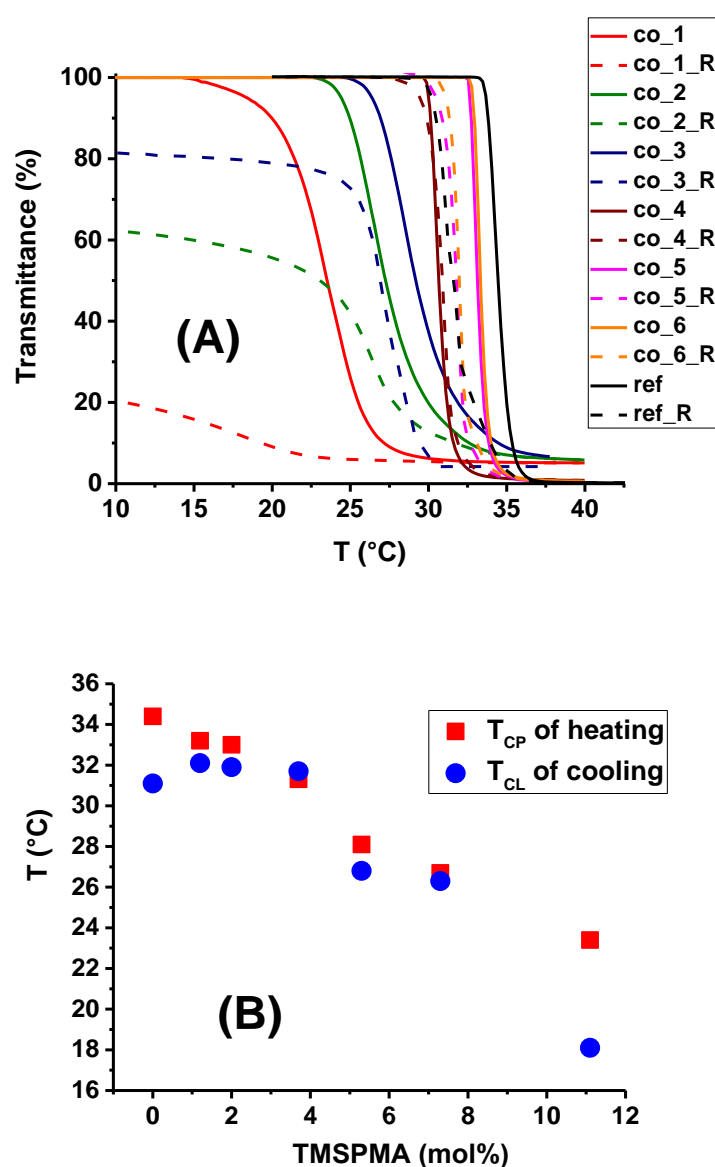


Fig. 3. Transmittance-temperature curves (A) and the cloud point and clearing point (B) during heating (solid lines) and cooling (dashed lines) of the P(NIPAAm-co-TMSPMA)

solutions in different composition (conditions: 0.1 wt%, 0.2 °C/min heating rate with 5 min equilibration, 488 nm).

The extent of transmittance recovery can be defined according to the following equation:

$$Y_H(T_1, T_2) = (Tr_{C1} - Tr_{H2}) / (Tr_{H1} - Tr_{H2})$$

where T_1 , T_2 , Tr_{C1} , Tr_{H1} and Tr_{H2} stand for the starting and ending temperatures of the temperature range of the measurement, the transmittance after cooling at T_1 , at the beginning of the heating cycle at T_1 and ending of heating (starting of cooling) at T_2 temperatures, respectively. Plotting Y_H as a function of copolymer composition in Fig. 4A clearly shows that 100% transmittance recovery can be observed up to about 4 mol% TMSPMA content while significant decrease occurs in Y_H with nearly linear decrease as a function of TMSPMA in the copolymers above this composition value. As shown in the photograph in Fig. 4B, the starting solution of sample co_1 is fully transparent. However, the copolymer solution after the first and even a second heating-cooling cycle remains milky with 21% and 11% transmittance, respectively, even after long dissolution times (even more than several months) at low temperature. Repeating the heating-cooling process third times led to further decrease of the transmittance to 9% after cooling to 10 °C (Fig. S6). It is interesting to note that the first cooling and second heating, and the second cooling and third heating transmittance-temperature curves coincide well as shown in Fig. S6. This indicates that there is no formation of insoluble fraction during storage of the P(NIPAAm-co-TMSPMA) copolymers in water at low temperatures, e.g. at 10 °C for even a long time. Thus, it can be concluded that gelation occurs in the higher temperature ranges, i.e. above the cloud point. Because the gelled copolymers did not settle in weeks, the gel fraction was determined by centrifugation followed by drying and gravimetry of the insoluble copolymers. In the case of samples co_1 and co_2 relatively high, 82% and 76% gel fractions were obtained, respectively. These

unexpected results allow to conclude that aqueous solutions of P(NIPAAm-*co*-TMSPMA) copolymers even with high TMSPMA contents can be stored without transparency change at low temperatures, i. e. below the T_{CP} , for a long time. However, copolymers with higher than 4 mol% of TMSPMA undergo gelation at temperatures higher than the cloud point, and stable dispersions of the resulting gels are formed. This indicates that hydrolysis of the trimethoxysilyl groups followed by condensation between the silyl moieties of the copolymers, that is cross-linking, occurs at higher temperatures even in the absence of acid or base which are usually applied to catalyze such sol-gel reactions. These unexpected findings affords designing copolymers for obtaining organic(polymer)-inorganic hybrid materials with desired structures by such *in situ* sol-gel reaction in water at suitable temperatures, i.e. without charging additional catalysts.

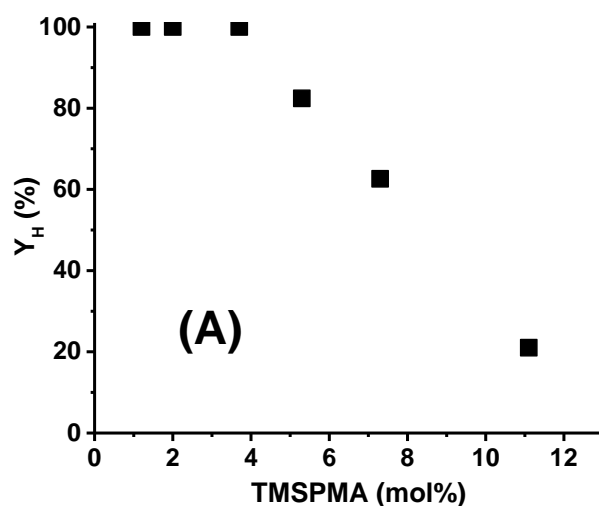


Fig. 4. The extent of transmittance recovery (Y_H) as a function of TMSPMA content in the P(NIPAAm-*co*-TMSPMA) copolymers (A) and photographs of the copolymer (sample co_1) solutions before the first heating, and after the first and second cooling cycles (left to right) (B) (conditions: 0.1 wt% P(NIPAAm-*co*-TMSPMA), 0.2 °C/min heating rate with 5 min equilibration, 488 nm).

For a variety of processes and materials, the thermal and thermooxidative stability of precursor polymers is of paramount importance. Thermogravimetric analysis (TGA) was used to investigate the thermal and thermooxidative stability and decomposition of the P(NIPAAm-*co*-TMSPMA) copolymers. As shown in Fig. S7 and Table S2, these copolymers possess relatively high stability upon heating in both inert (nitrogen) and oxidative (oxygen) atmosphere. The decomposition starts in nitrogen in the region of 340 °C, while in oxygen

atmosphere, these copolymers are stable up to about 300 °C, and the temperatures of the highest decomposition rates lie in the region of 340-380 °C . These findings indicate that the P(NIPAAm-*co*-TMSPMA) copolymers can be handled and processed without significant decomposition up to about 300-340 °C depending on the conditions, i.e. a variety of new materials with remarkable thermal stability can be made with these copolymers. It has to be also noted that residues with amounts higher than theoretical SiO₂ contents are formed indicating additional char formation during both inert and oxidative thermal decomposition (see Fig. S7 and Table S2 in the SI).

4. Conclusions

In sum, it can be concluded that in contrast to literature results on the unpredictable gelation during preparation, successful synthesis of a series of stable and water soluble P(NIPAAm-*co*-TMSPMA) copolymers in a broad composition range (up to 11 mol% TMSPMA) was achieved via free radical copolymerization of NIPAAm with TMSPMA under moisture, acid and base free conditions with using inert solvents. At higher TMSPMA contents, partial spontaneous decomposition of the trimethoxysilyl groups may occur resulting in less TMS groups than that expected on the basis of the feed ratios. Turbidity measurements revealed remarkable hysteresis, strong concentration effect of the cloud point (T_{CP}) and clearing point (T_{CL}), and slight increase of these parameters with the increase of the applied wavelength of the incident light. For comparison purposes, polymer solutions with 0.1 wt% concentration, 488 nm wavelength (widely used argon laser's wavelength for LS measurements) and 0.2 °C/min heating rate with 5 min equilibration are proposed for standardisable conditions to determine the critical solution temperatures (CST). In contrast to literature reports, significant decrease of T_{CP} with increasing TMSPMA content was observed, which is attributed to the hydrophobic character of the TMSPMA comonomer.

Unprecedentedly, the P(NIPAAm-*co*-TMSPMA) copolymers with higher than 4 mol% TMSPMA contents showed not only composition dependent heating-cooling hysteresis, but incomplete transmittance recovery in the heating-cooling cycles. Unsuccessful efforts to redissolve these copolymers by long dissolution times and the repeated heating-cooling cycles indicate that gelation occurs by an *in situ* sol-gel reaction between the TMSPMA units in these copolymers above the cloud points leading to stable gel dispersions. These findings offer sol-gel reactions with these and similar copolymers without any catalysts, on the one hand. On the other hand, utilization of the presented new results allows to explore new routes for obtaining a variety of novel smart thermoresponsive complex and hybrid materials.

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