

Temperature sensitive polymers based on 2-(dimethyl maleinimido)-*N*-ethyl-acrylamide: Copolymers with *N*-isopropylacrylamide

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Summary

Temperature sensitive polymers with pendant dimethyl maleinimide side groups were prepared by the copolymerization of *N*-isopropylacrylamide (NIPAAm) with varying amounts of a functional *N*-substituted acrylamide (2-(dimethyl maleinimido)-*N*-ethyl-acrylamide, DMIAAm). The polymers were characterized by ¹H-NMR, IR, DSC and TGA. Their relative reactivity ratios have been determined. Aqueous solutions of the copolymers showed lower critical solution temperature behaviour (LCST). The phase transition temperatures of the aqueous solutions of these copolymers decreased with increasing comonomer content and disappeared at DMIAAm contents at or above 15.9 mol-%.

Introduction

Water soluble polymers and swellable gels with thermosensitivity are of great scientific and technological importance. The characteristics of these polymeric materials have been studied extensively as starting materials for drug delivery systems, in separation systems, etc. [1, 2] The application of these materials in chemomechanical actuators has also been proposed [3]. One of the most intensively studied polymers in this field is poly(*N*-isopropylacrylamide) (PNIPAAm) which exhibits a sharp phase transition in water at 32 °C [4]. It undergoes a temperature induced collapse from an extended coil into a globule structure, a transition revealed on the macroscopic scale by a sudden decrease of the degree of swelling of PNIPAAm gels [5-9].

Because swelling/deswelling is a diffusion controlled process, the macroscopic size of the gel plays an important role. The swelling rate is inversely proportional to the square of the characteristic length of the gel [10]. To improve the response time to a usable level it is necessary to reduce the gel size dramatically. We aim to use these materials in microsystems (e. g. microactuators) in which the gel sizes are reduced to the μm-range [11, 12]. The photocrosslinking of a polymer film is a suitable method to obtain thin networks for microsystem technology and increasing interest is being shown in this method [13]. There exists only a few reports on the preparation of hydrogels via

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photocrosslinking of water-soluble polymers [14-19] as well as their photolithographic patterning [20-24]. By using PNIPAAm as the temperature sensitive component it has also been found that the pendant chromophore has a strong influence on the phase transition temperature (T_c). With a stilbazolium salt as chromophore and a chromophore content of 3 wt.-% a T_c below room temperature was obtained [24]. It has been known for several years that N-substituted dimethylmaleinimides undergo [2+2]-cycloadditions by exposure to light [25-28]. Polymers with pendant dimethylmaleinimide groups have been used in a variety of photopolymer applications [29]. Due to the size and the polar structure of the dimethyl maleinimide group temperature sensitive polymers with high chromophore contents and T_c values higher than room temperature might be accessible. In this article, we report the synthesis of NIPAAm polymers with pendant dimethylmaleinimide groups. The physical as well as the solution properties of the resulting polymers were studied.

Experimental

Materials

N-Isopropylacrylamide (NIPAAm, Aldrich) was purified by recrystallization from hexane and dried in vacuum. 2,2'-Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol. Dioxane, tetrahydrofuran (THF) and diethylether were distilled over potassium hydroxide. All other reagents were of analytical grade.

Synthesis of 2-(dimethyl maleinimido)-N-ethyl-acrylamide (DMIAAm)

The DMIAAm monomer was prepared according to the literature [30].

Synthesis of the polymer

The PNIPAAm homopolymer and copolymers were obtained by free radical polymerization of NIPAAm with DMIAAm initiated with AIBN at 70 °C in dioxane with a total monomer concentration of 0.55 mol/L under nitrogen. After specified times the polymer was precipitated in diethylether and purified by reprecipitation from THF into diethylether (1/3).

Characterization

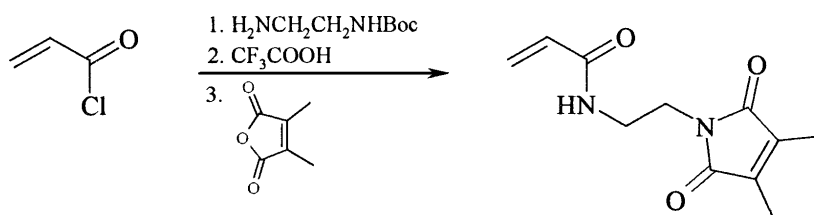
The ^1H NMR spectra were recorded on a BRUKER MSL 300 spectrometer (300 MHz). The solvent was used as an internal reference. IR spectra were measured on a UNICAM RS 1000 FTIR instrument. DSC measurements were carried out with a TA Instruments DSC 2920 to determine the glass transition temperature (T_g) of the polymers (T_g at $\Delta c_p/2$) and the T_c of the polymer solutions. The T_g were measured with a heating rate of 10 °C/min. The DSC thermograms of the polymer solutions were taken at a heating rate of 5 °C/min in a temperature range of 10-70 °C. The polymer concentration was 5 g/L in deionized water. Thermal stability studies were performed using a METTLER TG 50 thermogravimetric analyzer (TGA) at a heating rate of 10 °C/min.

The molecular weight (M_w) and the molecular weight distribution (polydispersity M_w/M_n) of the copolymers were determined by gel-permeation chromatography with a JASCO instrument equipped with UV and RI detector using Waters "Ultrastyrigel" columns. The

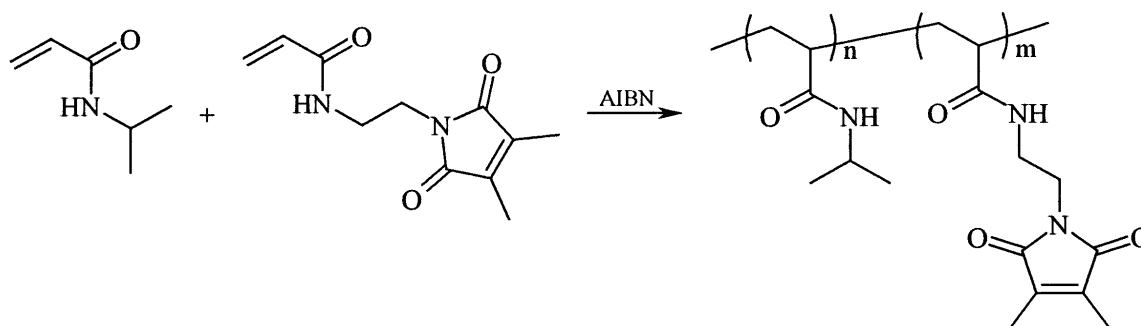
samples were measured at 30 °C in THF containing 0.3 vol.-% N-methyl acetamide as the mobile phase (flow rate 1 mL/min).

Results and Discussion

Photocrosslinking of hydrophilic polymers often proceeds with hydrophobic chromophors. When using a temperature sensitive polymer, the phase transition temperature (T_c) is strongly effected by the hydrophilicity of the substituents, resulting in a decrease of T_c [24]. Due to this fact a special monomer with a less hydrophobic chromophore and a polymerizable group was synthesized in order to prepare photocrosslinkable copolymers of NIPAAm. Scheme 1 illustrates the synthesis of the functional N-substituted acrylamide with the photo-dimerizable dimethyl maleinimide group.



Scheme 1: Synthesis of the DMIAAm monomer



Scheme 2: Synthesis of the polymers

Homo- and copolymers of NIPAAm with DMIAAm (Scheme 2) were made by free radical polymerization in dioxane. The products were characterized by IR and ^1H NMR spectra. In addition to the absorption bands of PNIPAAm at 1549 and 1657 cm^{-1} , typical for amides, absorption bands at 734 and 1704 cm^{-1} could be seen, which are typical for dimethyl maleinimide groups. The peak at 3.6 ppm in the ^1H NMR spectra in chloroform- d_3 was assigned to the protons of the N- CH_2 -groups, the peak at 4.0 ppm to the CH-proton of the N-isopropyl group. The polymer composition could not be determined from this data, due to the broad signals (Figure 1a). In order to separate the signals of the N-isopropyl proton and N-methylene protons the mobility of the side groups have to be increased, e. g. by elevated temperatures, and the coupling of these protons with the

amide proton have to be decreased, e. g. by an accelerated proton exchange with an acid. Hence, the ^1H NMR spectra were taken in DMSO-d_6 solutions at $80\text{ }^\circ\text{C}$ with containing a small amount of acetic acid- d_3 . The corresponding section of the NMR spectrum is shown in Figure 1b. It is clearly visible that the signals can be separated by this procedure. On this basis copolymer compositions could be obtained.

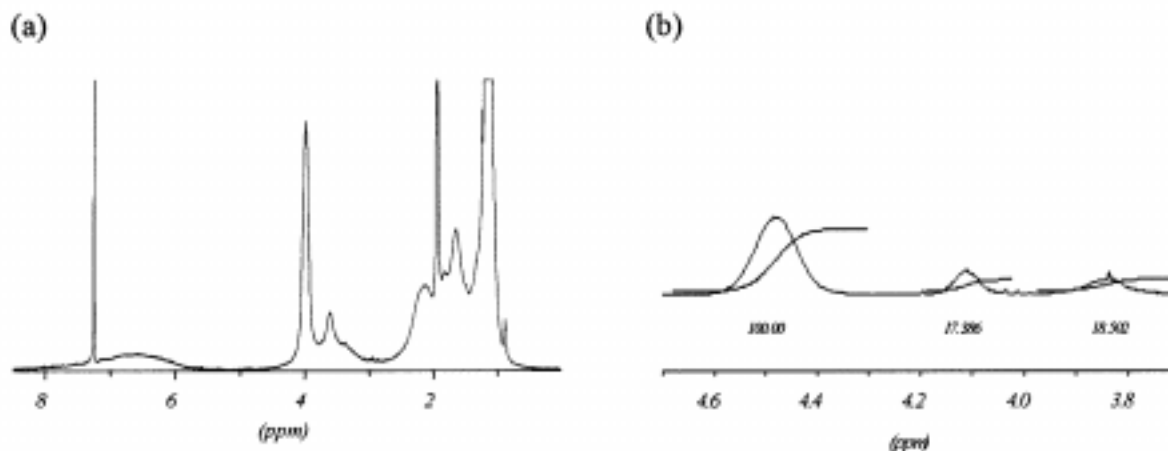


Figure 1: ^1H NMR spectra of poly(NIPAAm-co-DMIAAm) (PND 3) in (a) chloroform- d_3 at room temperature and (b) in DMSO-d_6 at $80\text{ }^\circ\text{C}$ containing a small amount of acetic acid- d_3 (enlargement of the area 3.7 - 4.7 ppm)

The simple and extended Kelen-Tüdös (KT) methods [31, 32] have been used to estimate the relative reactivity ratios of NIPAAm and DMIAAm. The later is especially useful for polymerizations with high conversions. The feed and the corresponding copolymer composition as well as the weight conversion of the NIPAAm/DMIAAm copolymerization are summarized in Table 1. Using these data the reactivity ratios can be easily estimated. The extended Kelen-Tüdös method provides values that are $r_{\text{NIPAAm}} = 1.45$ and $r_{\text{DMIAAm}} = 1.33$, implying that the propagating species have nearly the same reactivity. It is an ideal copolymerization, from the fact that the $r_{\text{NIPAAm}}r_{\text{DMIAAm}}$ value is near one. All values for the reactivity ratios are summarized in Table 2.

Table 1: Copolymerization of NIPAAm with DMIAAm

sample	DMIAAm content [mol-%]		polymerization time [min]	weight conversion [%]
	feed composition	polymer composition		
PND 1	2	1.3	30	27.9
PND 2	5	4.5	45	16.9
PND 3	10	8.0	60	15.5
PND 4	20	15.9	90	12.3
PND 5	30	27.5	120	7.0
PND 6	50	46.6	210	7.5

Table 2: Reactivity ratios for the copolymerization of NIPAAm with DMIAAm

method	Γ_{NIPAAm}	Γ_{DMIAAm}	$1/\Gamma_{\text{NIPAAm}}$	$1/\Gamma_{\text{DMIAAm}}$	$\Gamma_{\text{NIPAAm}} \cdot \Gamma_{\text{DMIAAm}}$
simple KT	1.39	1.26	0.72	0.79	1.75
extended KT	1.46	1.33	0.68	0.75	1.94

The physical properties of poly(NIPAAm-co-DMIAAm) are listed in Table 3. GPC was used to determine the molecular weight of the polymer, calibrated against polystyrene standards, and through the use in tandem of a UV detector and a RI detector, it was ascertained that poly(NIPAAm-co-DMIAAm) is not contaminated with low molecular weight UV-absorbing impurities and that all the chromophores are bound covalently to the polymer. By increasing the DMIAAm content the molecular weight of the polymer decreased. The dimethyl maleinimide groups acts as polymerization regulator being able to take over the radical function. Due to sterical hindrance this radical is not able to propagate the chain growth. Also no crosslinking was observed.

Table 3: Physical properties of the copolymers investigated

sample	M_w [g/mol]	M_w/M_n	T_g [°C]	T_c [°C]
PNIPAAm	69 700	1.81	145	32.0
PND 1	66 000	1.66	145	28.6
PND 2	63 200	1.80	142	26.9
PND 3	51 500	1.56	142	22.7
PND 4	32 500	1.77	142	-
PND 5	25 700	1.47	139	-
PND 6	13 500	1.45	139	-

The proposed application of these polymers is their use as actuator materials in microsystems. As these devices are employed in real world environments, the copolymers will encounter temperatures far in excess of their LCSTs (typically ca. 30 °C) in the course of their lifetimes. Thus, the thermal properties of the copolymers, especially the glass transition temperature (T_g) and the thermal decomposition, were investigated.

The T_g of the copolymers were determined by DSC and the data is presented in Table 3. The polymers show a single T_g , indicating the formation of random copolymers. The T_g of PNIPAAm is 145 °C. An increasing amount of the comonomer slightly decreases the T_g of the copolymer. However, in applications as photosensitive polymers, the T_g of the copolymers is much higher than the temperatures at which photocrosslinking take place (normally at room temperature).

During the manufacturing of devices containing PNIPAAm copolymers the stability of these polymers against thermal stress is of great importance. Hence, TGA studies under air and nitrogen, respectively, were carried out. The decomposition curves of some selected polymers are shown in Figure 2.

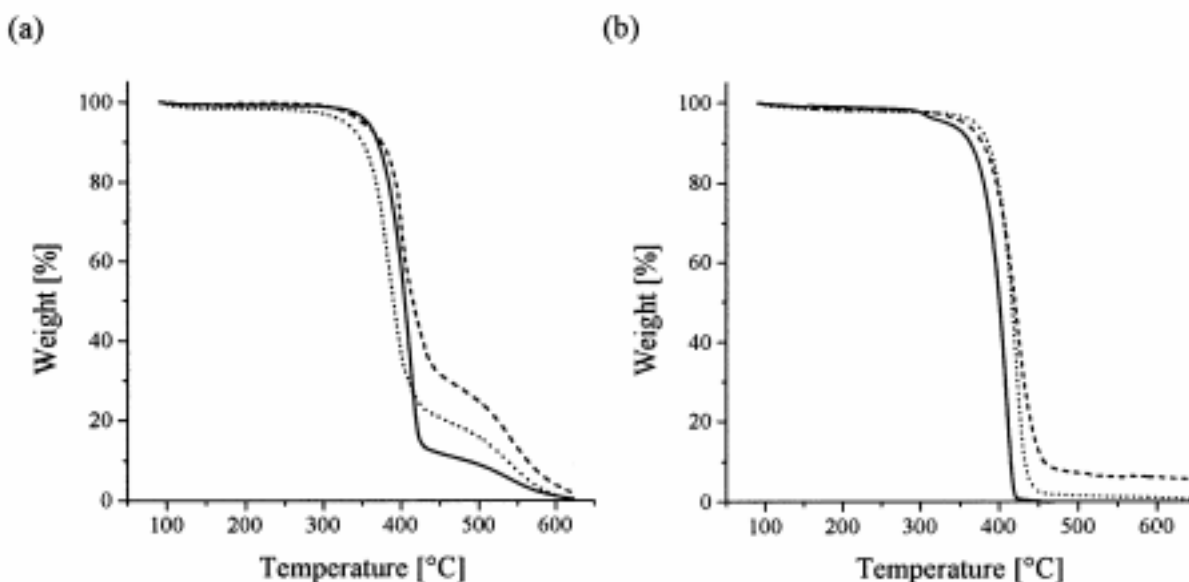


Figure 2: Thermogravimetric curves for (—) PNIPAAm, (.....) PND 2 and (----) PND 5 under (a) air and (b) nitrogen

The TGA study on PNIPAAm under nitrogen support an apparent, single-step decomposition [33]. Furthermore, when PNIPAAm degrades it leaves nearly no residue. FTIR analyses of the evolved gases during the main weight loss (ca. 420 °C) supports a mechanism of decomposition of the main chain and formation of oligomers, especially dimers and trimers, because they leave no residue and are thus rather volatile. There were no signs for the decomposition of the N-isopropylacrylamide group, as isopropylamine or acrylamide were not found. Also depolymerization did not occur [33]. Nearly the same behaviour was observed for the copolymers, but they left a larger residue. In air the polymers are also stable up to temperatures higher than 300 °C.

The effects of the DMIAAm content in these polymers on thermal-responding behaviour were determined by DSC. The DSC curves were obtained from a 5 wt.-% polymer solution. The onset of the thermogram corresponds to the temperature of collapse [34]. Figure 3 shows the DSC curves of the PNIPAAm homo- and copolymers in water. The phase transition temperatures are summarized in Table 3.

PNIPAAm has a lower phase transition temperature at around 32 °C. With an increase of DMIAAm in the polymer, the phase transition temperature decreased due to the decrease of the hydrophilic balance. For DMIAAm contents at or above 15.9 mol-%, DSC showed no significant phase transition. However, for applications of these polymers in hydrogels crosslinking densities of less than 10 % are required to obtain highly swellable networks. Polymers with these comonomer contents clearly show phase separation behaviour.

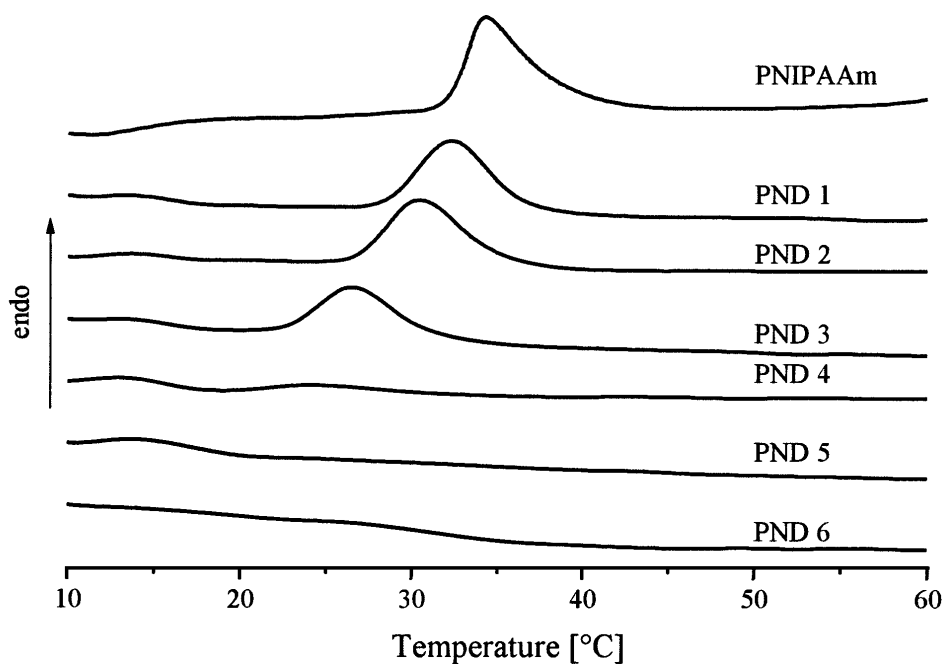


Figure 3: DSC thermograms for poly(NIPAAm-co-DMIAAm) polymers

Conclusion

Copolymers of NIPAAm and 2-(dimethyl maleinimido)-N-ethyl-acrylamide (DMIAAm) can easily be prepared by free radical polymerization in dioxane using AIBN as initiator at 70 °C. The composition of copolymers with various comonomer contents could be determined from ^1H NMR spectra recorded from polymer solutions in DMSO-d_6 at 80 °C containing a small amount of acetic acid- d_3 . With increasing DMIAAm content the molecular weight of the polymer decreased. The DMIAAm groups act as regulators, but no crosslinking was observed. The extended Kelen-Tüdös method provides relative reactivity ratio values of $r_{\text{NIPAAm}} = 1.45$ and $r_{\text{DMIAAm}} = 1.33$. Aqueous solutions of the copolymers showed lower critical solution temperature behaviour (LCST). The phase transition temperatures of the aqueous solutions of these copolymers decreased with increasing comonomer content and disappeared at DMIAAm contents at or above 15.9 mol-%. For DMIAAm contents smaller than 10 mol-% the T_c is higher than room temperature and thus, these polymers are suitable candidates as precursor polymers for the preparation of thin patterned hydrogels for microactuators. The photocrosslinking and gel properties of the polymers will be reported in a subsequent paper.

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