Tunable pH- and Temperature-Sensitive Copolymer Libraries by Reversible Addition−Fragmentation Chain Transfer Copolymerizations of Methacrylates

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ABSTRACT: Reversible addition−fragmentation chain transfer (RAFT) polymerizations have been performed on a Chemspeed Accelerator SLT100 automated synthesizer to polymerize *N*,*N*-(dimethylamino)ethyl methacrylate (DMAEMA) and poly(ethylene glycol) methyl ether methacrylate (PEGMA) at 70 °C. Azobis(isobutyronitrile) (AIBN) was used as source of radicals and 2-cyano-2-butyl dithiobenzoate (CBDB) as RAFT agent. A complete screening in composition of P(DMAEMA-*stat*-PEGMA) copolymers was elaborated from 0% of PEGMA to 100% of PEGMA. All polydispersity indices of the obtained copolymers are comprised between 1.11 and 1.30. The reactivity ratios have been determined by the extended Kelen−Tüdös method ($r_{\mathrm{DMAEMA}} = 0.93$ and $r_{\mathrm{PEGMA}} = 0.66$). The behavior of the pH- and temperature-sensitive copolymers was studied in aqueous solution by measuring the lower critical solution temperature (LCST) by UV/vis spectroscopy. The measurements were performed at three different pH values (4, 7, and 10). At pH 7 and pH 10 it has been observed that the LCST is increasing linearly with the wt % PEGMA in the copolymer feed. On the contrary, at pH 4, the hydrophilicity of the P(DMAEMA-*stat*-PEGMA) copolymers is too high due to the protonation of the DMAEMA units. Thus, no LCST has been detected for most of them. By varying the pH and the composition of the P(DMAEMA-*stat*-PEGMA) copolymers, the LCST can be easily tuned between 34.7 and 82.0 °C.

Introduction

Stimuli-responsive polymers, also called “smart polymers”, that undergo phase transitions in response to external stimuli have been widely investigated in various fields.[1−3] Such property means that the change must be reversible when the stimulus is stopped or another one is applied. Many stimuli exist such as, for example, temperature, pH, ionic strength, light, or photochemical processes.[4,5] In particularly, many studies are focused on pH- and temperature-responsive designed materials able to respond in a physiological environment.

To provide such materials, acrylamides and certain methacrylates have been widely studied because of their behavior in aqueous solution, i.e., the lower critical solution temperature (LCST). Indeed, below this LCST, the polymer chains are soluble in water solution and exist in random coil conformation because of the existing hydrogen-bonding interactions between the polymer and water molecules. However, when the temperature exceeds the LCST, these interactions are broken, and the polymer chains collapse and then precipitate in the media. *N*,*N*-(Dimethylamino)ethyl methacrylate or DMAEMA is part of the most studied monomers in various fields[6−8] (paints, membranes, gene delivery systems, etc.) since ionic interactions should be established with the cationic amino group of DMAEMA under acidic conditions.[9,10] Many polymerization techniques are described to synthesize PDMAEMA, which is a pH- and temperature-sensitive polymer, including anionic polymerization[11,12] or group transfer polymerization.[13,14] Concerning the controlled radical polymerizations, atom transfer radical polymerizations (ATRP) of DMAEMA were investigated to afford well-controlled polymers[15−18] even if the copper catalyst was complexed by amino groups in both monomer and polymer,[19] leading to a loss of control. Well-controlled PDMAEMA[20−23] were also synthesized via reversible addition−fragmentation chain transfer (RAFT) polymerizations.[24−26]

Furthermore, incorporating a comonomer in the polymer should provide a LCST change. Indeed, the LCST is strongly dependent on many parameters, such as the molecular weight and polydispersity index. It has been demonstrated that well-defined polymers (low polydispersity indices) synthesized by controlled radical polymerization techniques exhibit a much sharper LCST transition when compared to ill-defined polymers that were prepared by free radical polymerization.[27] The monomer composition of the polymers also influences the LCST because the hydrophilicity/hydrophobicity balance in the polymer is of crucial importance. If a hydrophobic comonomer is added, the LCST is decreasing, and on the contrary, if the comonomer is hydrophilic, the LCST is increasing. In this way, DMAEMA has been copolymerized with many comonomers to provide materials with different LCSTs. Methacrylates,[12,28] *N*-isopropylacrylamide (NIPAAM),[9,10,29−31] and styrene[12] have been successfully copolymerized with DMAEMA. Another monomer based on poly(ethylene glycol) methacrylate has attracted our attention. It has been randomly copolymerized mostly with alkyl methacrylates,[32,33] NIPAAM,[34,35] glycidyl methacrylate,[36] and styrene.[36] Indeed, poly(ethylene glycol) methacrylate is an interesting monomer since it is known for its hydrophilicity and its nonadhesive behavior toward proteins.[37,38] Very recently, Saunders et al.[39] have synthesized one random copolymer based on DMAEMA and poly(ethylene glycol) methacrylate via free radical polymerization and have used it as pH-responsive stabilizer for emulsions and dispersions. Actually, several derivatives of commercially available poly(ethylene glycol) methacrylate exist with different molecular weights and end chains such as methoxy or hydroxy groups. Poly(ethylene glycol) methyl ether methacrylate (PEGMA) with a relatively low molecular weight (∼300 Da) was chosen in

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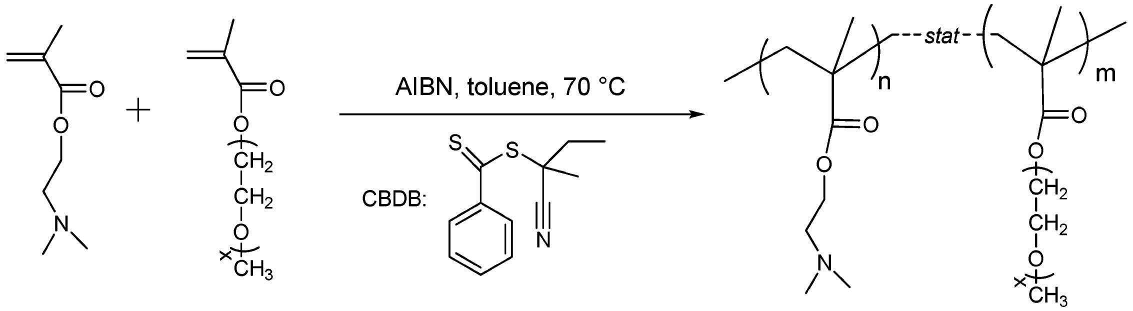
Scheme 1. Synthesis of Random P(DMAEMA-*stat*-PEGMA) Copolymers via the RAFT Process



this study because the methoxy end group can be easily detected by ^{1}H NMR, which simplifies the determination of the copolymer composition.

The copolymerization of DMAEMA and PEGMA should offer interesting properties since both monomers are thermosensitive and only DMAEMA is pH-sensitive. The lack of data relating to the RAFT copolymerization of DMAEMA and PEGMA motivated us to investigate this system.

In this paper, a complete library of random copolymers based on DMAEMA and poly(ethylene glycol) methyl ether methacrylate (PEGMA) was prepared using RAFT polymerization with 2-cyano-2-butyl dithiobenzoate as RAFT agent. Moreover, reactivity ratios for the copolymerization system have been determined using the extended Kelen−Tüdös method. LCSTs of all responsive materials have been measured at different pH values (4, 7, and 10) as well as the surface energy of spin-coated films.

Experimental Section

Materials. *N*,*N*-(Dimethylamino)ethyl methacrylate (DMAEMA, Aldrich) and poly(ethylene glycol) methyl ether methacrylate (PEGMA, $M_n \sim 300$ g mol^{-1}, Aldrich) were purified by passing over a basic aluminum oxide column. Azobis(isobutyronitrile) (AIBN, Aldrich) was recrystallized from methanol. 2-Cyano-2-butyl dithiobenzoate (CBDB) was prepared according a literature procedure for a related compound.[40] Analytical grade solvents were purchased from Biosolve Ltd.

Instrumentation. All polymerizations were performed on a Chemspeed Accelerator SLT100 automated synthesizer. The robot was equipped with a four-needle head and an array of 16 parallel 13 mL glass reactors. All reactors were connected to a Huber Unistat Tango (heating range: −40 to 145 °C) and were equipped with a coldfinger reflux condenser in which the temperature can be fixed from −5 to 40 °C. A double inert atmosphere was maintained by applying a 1.1 bar flow over the reactors and a 1.5 bar argon flow through the hood of the Accelerator.[41] GPC measurements were performed on a Shimadzu system equipped with a SCL-10A system controller, a LC-10A pump, a RID-10A refractive index detector, and a PL gel 5 μm Mixed-D column at 50 °C, using a mixture of chloroform, triethylamine, and 2-propanol (94:4:2) as eluent at a flow rate of 1 mL/min. GC measurements were performed on an Interscience Trace GC used with a Trace Column RTX-5 connected to a PAL autosampler. ^{1}H NMR spectra were recorded on a Varian Mercury 400 spectrometer using deuterated acetonitrile as solvent. Contact angle measurements were performed on polymer films that were prepared by spin-coating of chloroform solutions (20 mg/mL) of the polymers on precleaned microscopy slides at 1000 rpm for 90 s using a WS-400/500 series spin-coater from Laurell Technologies Corp. An OCA30 optical contact angle measuring instrument from Dataphysics was used to determine the contact angles of both diiodomethane and ethylene glycol as apolar and polar test liquids, respectively. UV/vis spectra were recorded on a Perkin-Elmer Lamda-45 UV−vis spectrophotometer equipped with a PTP-1 Peltier system to heat the UV cell.

Parallel Polymerizations of DMAEMA and PEGMA. The inert atmosphere in the hood of the Accelerator SLT100 was obtained by flushing with argon for at least 90 min. Before the beginning of the RAFT experiments, the reaction vessels were heated to 120 °C, evacuated for 15 min, and then filled with argon. This procedure was repeated three times to perform the reactions under an inert atmosphere. Different amounts from the four stock solutions of CBDB (in toluene), AIBN (in toluene), DMAEMA, and PEGMA were transferred into the reaction vessels. The monomer concentration was kept at 2.2 mol/L. The mixtures were heated at 70 °C and vortexed at 600 rpm. After 10 h, ∼15 mL of dichloromethane was added to the final mixtures, and the polymers were then manually precipitated into *n*-hexane. The liquid phase was then removed, and the precipitated polymers were washed twice with again *n*-hexane. After removal of solvents and residual monomers, the polymers were dried in a vacuum oven at 40 °C overnight prior to analysis.

Results and Discussion

Synthesis of a Library of Copolymers Based on DMAEMA and PEGMA. As it has been previously established,[27] the LCST of polymers is largely influenced by several parameters, such as the polydispersity of macromolecules and the molecular weight. To be able to better investigate the relationship between the properties and the utilized copolymers, reversible addition−fragmentation chain transfer polymerization (RAFT) was used to obtain well-controlled copolymers with low polydispersity indexes (PDI) and with molecular weights in the same range. To the best of our knowledge, the RAFT copolymerization of both monomers, DMAEMA and PEGMA, has never been completely studied regarding the induced properties in aqueous solution (such as the LCST). In consequence, in this study, statistical copolymerization of DMAEMA and PEGMA was investigated using the RAFT process with toluene as solvent, CBDB as RAFT agent, and AIBN as generator of radicals (Scheme 1).

The RAFT agent used in these experiments has previously shown a good behavior in RAFT polymerizations of different methacrylates at 70 °C.[22,42] Thus, 11 reactions were carried out using a Chemspeed Accelerator SLT100 automated synthesizer with the same previously determined optimal ratio[43] between CBDB and AIBN (1:0.25). The ratio monomers/CBDB was fixed at 100:1 with different proportions of both monomers DMAEMA and PEGMA. The resulting copolymer library was manually purified by precipitation in *n*-hexane, whereby all remaining monomers could be removed facilitated by the low molecular weight of the PEGMA that is liquid. The characterization results for these copolymerizations are summarized in Table 1.

The results obtained from GPC analysis indicated that the copolymers were relatively well-defined because the polydispersity indexes are in the range of 1.11−1.30 (Figure 1). Moreover, it could be observed that there is a correlation

Table 1. Results of the Random Copolymerization of DMAEMA and PEGMA[a]

$[DMAEMA]_0/[PEGMA]_0$ (mol %)[b]	conversion (%)[b] DMAEMA/PEGMA	$M_{n,GPC}$[c] (g/mol)	$M_{n,NMR}$[d] (g/mol)	PDI[b]	[DMAEMA]/[PEGMA] (mol %)[d]	[DMAEMA]/[PEGMA] (wt %)
100/0	58.6/−	9 500	13 850	1.11	100/0	100/0
90.8/10.2	44.5/49.2	8 950	12 560	1.11	89.3/10.7	81.4/18.6
81.9/18.1	48.3/48.0	9 000	13 740	1.13	77.7/22.3	64.6/35.4
68.6/31.4	67.6/59.5	10 900	14 720	1.14	70.2/29.8	55.2/44.8
57.8/42.2	72.3/66.1	11 200	16 320	1.15	59.0/41.0	43.0/57.0
48.4/51.6	74.9/67.0	13 200	19 920	1.21	51.0/49.0	33.5/66.5
39.8/60.2	79.9/69.3	13 300	13 800	1.19	41.2/58.8	26.9/73.1
27.2/72.8	75.8/67.9	14 200	17 700	1.22	29.3/70.7	17.8/82.2
18.0/82.0	84.0/74.8	15 500	19 200	1.22	19.9/80.1	11.5/88.5
8.9/91.1	85.7/77.8	17 400	15 600	1.26	10.2/89.8	5.6/94.4
0/100	-/65.7	17 600	20 180	1.30	0/100	0/100

[a] [Monomers]/[CBDB]/[AIBN] = 100/1/0.25, T = 70 °C, solvent: toluene, time = 10 h. [b] Calculated by GC. [c] Determined by GPC calibrated with PMMA standards. Solvent: CH_3Cl/Et_3N/2-propanol (94/4/2). [d] Determined by ^1H NMR. Solvent: CD_3CN.

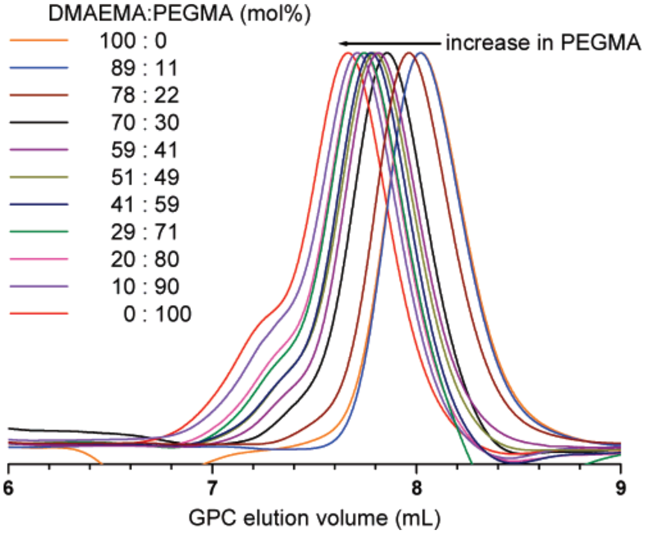


Figure 1. GPC traces of the library of P(DMAEMA-*stat*-PEGMA) copolymers.

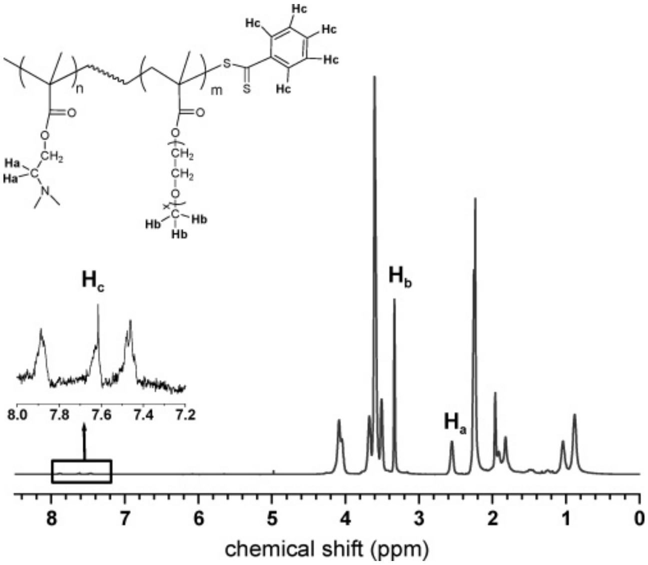


Figure 2. ^1H NMR spectrum (400 MHz, CD_3CN) of P(DMAEMA-*stat*-PEGMA) prepared by RAFT polymerization (mol % PEGMA = 58.8).

between the PEGMA content and both the peak molecular weight of the GPC traces and the PDI value of the copolymer, such that an increase in the PEGMA content results in a slight increase in the PDI value for the copolymer. This observed increase in PDI values is most likely due to a combination of the molecular weight distribution of the PEGMA monomer as well as the occurrence of some chain coupling reactions as is evident from the appearance of a higher molecular weight shoulder in the GPC traces.

The composition of P(DMAEMA-*stat*-PEGMA) copolymers was determined using ^1H NMR in deuterated acetonitrile. Figure 2 shows a typical ^1H NMR spectrum obtained from the precipitated copolymer without any trace of unreacted monomer. The typical resonance of the methoxy protons (3H, δCH_3O-) of the PEGMA unit appears approximately at 3.35 ppm, and the one from the methylene protons (2H, δCH_2N-) next to the nitrogen atom of the DMAEMA unit appears at 2.55 ppm. By taking into account the number of protons and the integration of those peaks, the molar percentage of each component could be determined. In addition, by considering the same peaks from the repetitive units and aromatic protons from the RAFT agent (5H, $\delta = 7.4-7.9$ ppm), the molecular weight of the copolymer was then calculated. In this way, the $M_{n,NMR}$ (molecular weight determined by ^1H NMR) of all copolymers are slightly higher than the $M_{n,GPC}$ (molecular weight determined by GPC) due to the PMMA calibration in the GPC system, resulting in a relative molecular weight.

To better know the macromolecular structure of the copolymers P(DMAEMA-*stat*-PEGMA), the reactivity ratios of DMAEMA and PEGMA were determined (r_{DMAEMA} and r_{PEGMA}). Up to now, several methods are currently used to determine such ratios among which the Fineman−Ross method,[44] the Mayo−Lewis terminal model,[45] and the Kelen−Tüdös method.[46,47] For living controlled copolymerizations, higher monomer conversions should be reached (i.e., superior to 20%) to determine the reactivity ratio[48] since it was established that during the initiation step different reactivities are usually detected.[49] However, the above-mentioned methods are mostly based on the analysis of the copolymer composition at relatively low conversion. Therefore, the extended Kelen−Tüdös method[50,51] was considered in this work to calculate both reactivity ratios (r_{DMAEMA} and r_{PEGMA}) because higher conversions could be used. According to this method, several parameters (z, F, G, η, and ξ) were determined.[51] The results are summarized in Table 2.

Figure 3 displays the plot of the obtained results and the linear fit, the latter allowing us to calculate both reactivity ratios. The plot reveals that the dependence of η on ξ is linear as indicated by the R^2 parameter ($R^2 = 0.9901$). The reactivity ratios were determined from the linear regression: $r_{DMAEMA} = 0.93$ and $r_{PEGMA} = 0.66$. Thus, the DMAEMA is preferentially incorporated at the beginning of the RAFT polymerization, resulting in a small gradient in monomer composition.

Table 2. Extended Kelen−Tüdös Parameters for the RAFT Copolymerization of DMAEMA and PEGMA[a]

f_{DMAEMA}	F_{DMAEMA}	conv (%)	z	F	G	η	ξ
0.908	0.893	0.445	1.150	0.091	−0.765	−0.567	0.067
0.819	0.777	0.483	0.991	0.292	−0.719	−0.464	0.188
0.686	0.702	0.676	0.802	0.660	−0.718	−0.374	0.344
0.578	0.590	0.723	0.843	0.979	−0.362	−0.162	0.437
0.484	0.490	0.749	0.802	1.618	0.051	0.018	0.562
0.398	0.412	0.799	0.736	2.635	0.580	0.148	0.677
0.272	0.293	0.758	0.801	3.762	1.764	0.351	0.749
0.180	0.199	0.840	0.752	7.115	4.022	0.480	0.850
0.089	0.102	0.857	0.709	17.497	11.002	0.587	0.933

[a] For the determination of parameters, see ref 51.

Table 3. LCSTs of P(DMAEMA-*stat*-PEGMA) at Different pH

		LCST[a]		
polymer	copolymer compositions DMAEMA/PEGMA (wt %)	pH 4	pH 7	pH 10
$DMAEMA_{100}$	100/0	no[b]	46.6	34.7
$DMAEMA_{81.4}$-*stat*-$PEGMA_{18.6}$	81.4/18.6	no[b]	52.4	42.1
$DMAEMA_{64.6}$-*stat*-$PEGMA_{35.4}$	64.6/35.4	no[b]	55.8	46.7
$DMAEMA_{55.2}$-*stat*-$PEGMA_{44.8}$	55.2/44.8	no[b]	60.1	51.2
$DMAEMA_{43.0}$-*stat*-$PEGMA_{57.0}$	43.0/57.0	no[b]	63.3	53.6
$DMAEMA_{33.5}$-*stat*-$PEGMA_{66.5}$	33.5/66.5	no[b]	64.5	55.5
$DMAEMA_{26.9}$-*stat*-$PEGMA_{73.1}$	26.9/73.1	no[b]	66.5	57.9
$DMAEMA_{17.8}$-*stat*-$PEGMA_{82.2}$	17.8/82.2	no[b]	68.5	59.1
$DMAEMA_{11.5}$-*stat*-$PEGMA_{88.5}$	11.5/88.5	no[b]	69.7	61.2
$DMAEMA_{5.6}$-*stat*-$PEGMA_{94.4}$	5.6/94.4	82.0	70.7	62.6
$PEGMA_{100}$	0/100	63.4	66.2	64.5

[a] LCST determined by UV/vis spectroscopy at 500 nm; concentration = 5 g/L in buffer solution, heating ramp = 1 °C/min. [b] No phase transition observed in the temperature range 15−95 °C.

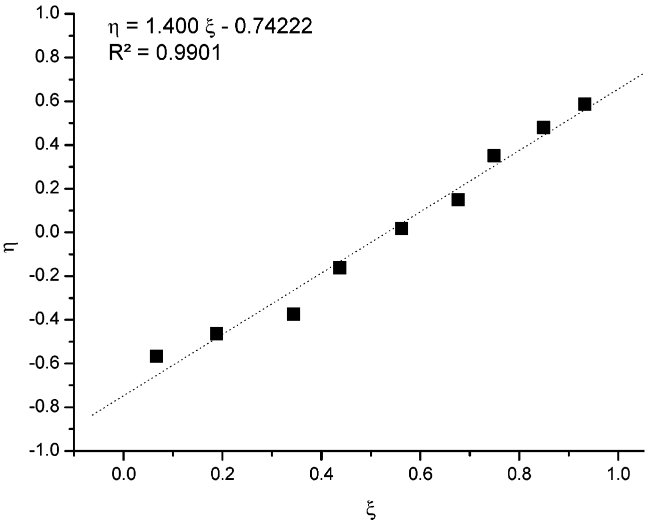


Figure 3. Determination of the reactivity ratios by the extended Kelen−Tüdös method.

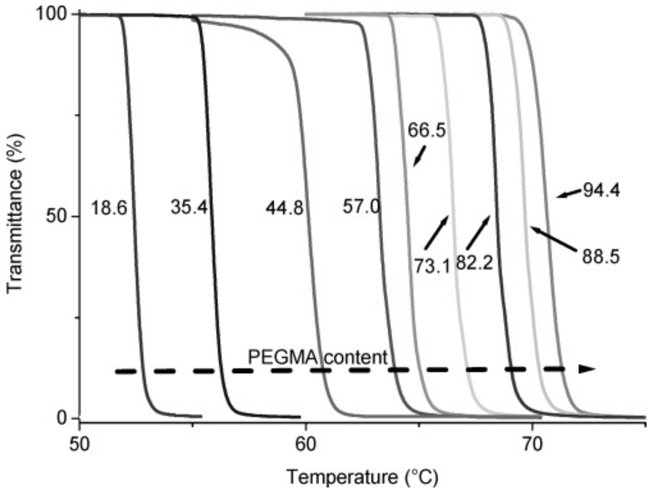


Figure 4. Phase transitions of P(DMAEMA-*stat*-PEGMA) at pH 7 as measured by UV/vis spectroscopy at 500 nm (indicated values next to the plots represent the weight content of PEGMA in the copolymer).

Study of Responsive Copolymers in Water Solution. As it was assumed that the P(DMAEMA) homopolymer is both thermo- and pH-sensitive, we decided to determine the LCSTs of all (co)polymers in different buffer solutions at pH 4, 7, and 10. Determinations of the LCSTs were carried out by UV/vis spectroscopy at 500 nm in which the heating ramp was fixed at 1 °C/min to reduce as much as possible the margin of error and to perform the measurements in a relatively short time. Table 3 shows the comparison of the LCSTs, determined at 50% transmittance, of all synthesized (co)polymers.

While all copolymers are soluble in buffer solution at pH 4, only the homopolymer $PEGMA_{100}$ and the copolymer with 5.6% in weight of DMAEMA exhibit a LCST (at 63.4 and 82.0 °C) in the studied temperature range from 15 to 95 °C. Indeed, the pK_a of DMAEMA is around 7.3−7.5 in water,[9,13,52] and at low pH it results in a protonation of the DMAEMA units. Consequently, its hydrophilicity is increasing. Thus, incorporated DMAEMA units allow the polymer to be more hydrophilic than the homopolymer PEGMA since the amine group of DMAEMA is protonated. On the contrary, at other studied pH values, all polymers have a LCST, and their LCST is comprised between 34.7 and 70.7 °C (Table 3).

Figure 4 represents typical transmittance against temperature curves for all synthesized polymers P(DMAEMA-*stat*-PEGMA) at pH 7. (The curves from the homopolymers are left out for more clearness.)

At pH 7, it can be observed that all curves exhibit a sharp decrease in transmittance around the LCST, proving the starting point of the precipitation of the copolymers. It can also be assumed that the distribution of both units in the copolymer is randomly since a block copolymer should not affect too much the LCST in comparison with the homopolymer. Moreover, the higher the PEGMA content in the copolymer is, the higher the LCST is (Figure 4). While the homopolymer PDMAEMA

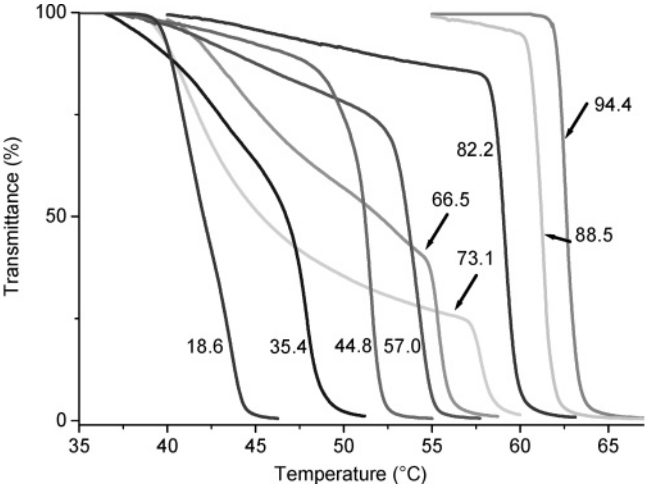


Figure 5. Phase transitions of P(DMAEMA-*stat*-PEGMA) at pH 10 as measured by UV/vis spectroscopy at 500 nm (indicated values next to the plots represent the weight content of PEGMA in the copolymer).

revealed a LCST at 46.6 °C, the LCST of P($\text{DMAEMA}_{5.6}$-*stat*-$\text{PEGMA}_{94.4}$) reached 70.7 °C. These results clearly indicate that incorporated PEGMA units in the copolymer make this latter more hydrophilic due to the poly(ethylene glycol) chains along the backbone. In other words, the balance between hydrophilicity/hydrophobicity of the copolymers is shifted toward hydrophilicity with increasing PEGMA content because of the increasing number of hydrogen-bonding interactions between the water molecules and the copolymers. The LCST difference observed for the copolymers, for instance, P($\text{DMAEMA}_{5.6}$-*stat*-$\text{PEGMA}_{94.4}$) at pH 4 (LCST = 82.0 °C) and at pH 7 (LCST = 70.7 °C), is caused by the fact that DMAEMA is less protonated. Therefore, hydrogen-bonding interactions are less strong as the pH is increasing to the pK_a value. Figure 5 shows the curves from UV measurements for all copolymers at pH 10.

As is shown in Figure 5, the PEGMA content influences the behavior of the copolymers. At pH 10, it is also observed that the LCST of the copolymers increases with the PEGMA percentage from 34.7 °C (for the homopolymer PDMAEMA) to 64.5 °C (for P($\text{DMAEMA}_{5.6}$-*stat*-$\text{PEGMA}_{94.4}$, the LCST values are reported in Table 3). Nevertheless, the observed phase transitions for the copolymers are not so pronounced as at pH 7, and the transmittance is decreasing much more slowly at pH 10, as has been already observed for other structures.[34,35,53] Thus, for the two copolymers which contain 66.5 and 73.1 wt % PEGMA, the LCSTs were considered in the range of temperatures when the transmittance is dramatically decreasing. The investigated pH 10 is higher than the pK_a of DMAEMA (pK_a = 7.3−7.5), and thus, the DMAEMA will be deprotonated, resulting in a more hydrophobic character resulting in copolymers consisting of a hydrophilic monomer (PEGMA) and a hydrophobic monomer above 35 °C, which is the LCST temperature of PDMAEMA at pH 10. This consideration together with the gradient monomer composition of the copolymers might result in the formation of aggregates above the LCST of the PDMAEMA in which the DMAEMA-rich part of the copolymer clusters together. Similar observations have been reported for, e.g., graft copolymers[54] and random copolymers.[55] This proposed aggregation of the copolymers is most pronounced for the copolymers consisting of a significant amount of both DMAEMA and PEGMA as is indicated by the sharp LCST transition of the copolymers with a low PEGMA content (PEGMA ≤18.6 wt %) or a high PEGMA content (PEGMA ≥82.2 wt %). This peculiar aggregation behavior of the copolymers will be the focus of future investigations. All LCST transitions from the UV/vis measurements are plotted against the weight percentage of PEGMA in the copolymer at the studied pH in Figure 6 to provide a better overview of the observed effects.

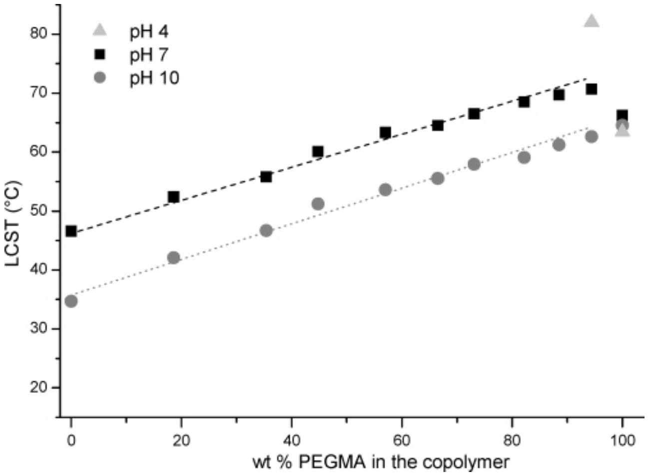


Figure 6. LCSTs of the studied polymers at three different pH values (4, 7, and 10).

The pH dependence is clearly shown, and at pH 7 and pH 10 it appears that the LCSTs are linearly increasing as the wt % PEGMA content is increasing. Furthermore, it should be considered that the LCSTs of copolymers can be easily tuned by the incorporation of PEGMA in the materials and by considering the used pH. Moreover, from Figure 6, it should be noted that the average difference with both linear fits of experimental data at pH 7 and pH 10 is 9.4 °C. As has been already mentioned above, only two LCSTs have been found at pH 4 because of the high hydrophilicity of the copolymers at low pH. Additionally, LCST measurements for the homopolymer P(PEGMA) done at pH 4, 7, and 10 are close to each other, confirming that this monomer is not pH-dependent.

Furthermore, a study was undertaken to determine the thin film properties of these copolymers. The surface properties of the resulting library of copolymers P(DMAEMA-*stat*-PEGMA) were investigated by measuring the contact angles of spin-coated films with two different test liquids: one apolar (diiodomethane) and one polar (ethylene glycol). The surface energies of the random copolymers were calculated from the difference of both obtained contact angles.[56]

Figure 7 depicts the resulting surface energies for the full range of copolymers P(DMAEMA-*stat*-PEGMA) against the wt % of PEGMA present in the copolymers. All measured surface energies are in the range 40−46 mN m^{-1}, indicating the hydrophilicity of these materials as expected. Thus, the surface energy is not linearly dependent on the copolymer composition as was established for the LCST study.

Conclusion

The reversible addition−fragmentation chain transfer polymerization of *N*,*N*-(dimethylamino)ethyl methacrylate and poly(ethylene glycol) methyl ether methacrylate was successfully performed using azobis(isobutyronitrile) and 2-cyano-2-butyl dithiobenzoate. A complete range of P(DMAEMA-*stat*-PEGMA) copolymers have been prepared from homopolymer PDMAEMA to homopolymer PEGMA by increasing the mol % PEGMA approximately every 10%. After 10 h reaction time at 70 °C, all polydispersity indices were found to be comprised between 1.11 and 1.30. The reactivity ratios were determined by the extended Kelen−Tüdös method (r_{DMAEMA} = 0.93 and

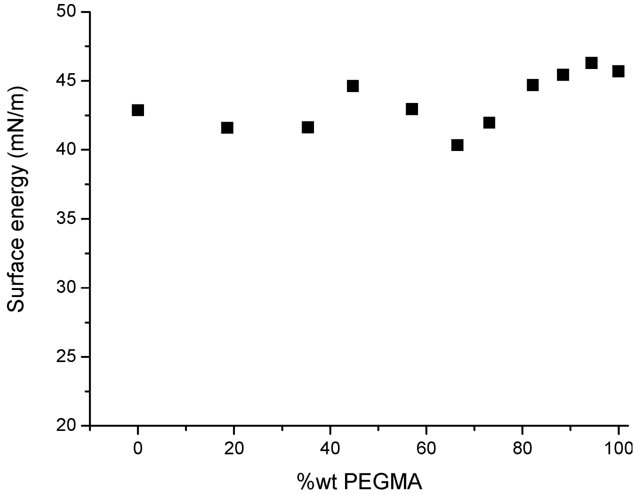


Figure 7. Surface energy values calculated from the contact angles of diiodomethane and ethylene glycol for the series of P(DMAEMA-*stat*-PEGMA) copolymers.

$r_{\mathrm{PEGMA}} = 0.66$). Selected properties of the well-defined random copolymers, such as their LCST behavior and their surface energies, have been studied. Results from UV/vis measurements demonstrated the pH and temperature dependence in water solution. At pH 4, no LCST was found for most of the copolymers because of the high hydrophilicity of incorporated DMAEMA units that are more protonated (pK_a = 7.3−7.5). On the contrary, all copolymers have shown a phase transition at pH 7 and pH 10. This phase transition is reversible when the sample is cooled down below the LCST. Moreover, it has been established that the LCSTs could be tuned as they are linearly dependent on the weight percentage of incorporated PEGMA in the copolymer, demonstrating a clear structure−property relationship. Finally, surface energy measurements confirmed the hydrophilicity of such copolymers.

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References and Notes

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