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(Quaternized/betainized) amino-based amphiphilic block copolymers: quantitative composition characterization via FTIR and thermogravimetry

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Abstract: The objective of the present study is the introduction of well known and readily accessible analytical methods as FTIR, thermogravimetric (TGA) and evolved gas analysis (EGA) for quantitative determination of the degree of polymerization (DP) and degree of quaternization (DQ)/betainization (DB) of amino-based amphiphilic block copolymers. For this purpose a series of amphiphilic poly(dimethylsiloxane)-*b*-poly[2-{dimethylamino)ethyl methacrylate] (PDMS-*b*-DMAEMA) diblock copolymers with DP of the PDMAEMA-block ranging from 22 to 162 was synthesized by atom transfer radical polymerization and analyzed by ^{1}H NMR, ATR-FTIR and TGA-co-EGA. The determined composition results have shown linear correlation between the FTIR or TGA and the ^{1}H NMR data and equations allowing the quantitative calculation of PDMAEMA-block DP were found. The errors estimated by ATR-FTIR were less than 1.5%. Further, the PDMAEMA-block was quaternized (or betainized) with DQ (or DB) from 25 % to 100 % and analyzed by TGA-co-EGA. Again, a linear correlation between the quaternized (betainized) PDMAEMA-block mass fraction and the DQ (DB) degrees was obtained by ^{1}H NMR.

Introduction

Amphiphilic block copolymers are present in a wide number of applications, such as surfactants, emulsifiers, compatibilizers, etc. Such versatility arises from the different types of supramolecular arrangements (micelles, vesicles, etc.) that can be formed in water or non-aqueous dispersive media for which each block presents different Flory-Huggins interaction parameter [1, 2, 3]. Among the polymer blocks used, the polyelectrolyte-based and especially poly[2-(dimethylamino)ethyl methacrylate] (PDMAEMA) revealed to be particularly attractive. Actually, PDMAEMA, due to its pK_a close to neutrality [4]) can be readily solubilized in aqueous medium through protonation of tertiary amine pending groups. Consequently, PDMAEMA-based homo- and copolymers and their quaternized derivatives like poly[2-(methacryloylethyl)trimethylammonium] iodide (PMAETMA-I) have been widely studied for a number of applications such as membranes for gas separations [5], polyelectrolyte complexes [6], DNA-binding agents for non-viral gene delivery systems [7] or non-leaching antifouling surfaces [8, 9]. Recently, PDMAEMA-based (co)polymers, containing both positive and negative charges on each monomer unit as poly[3-[2-(methacryloylethyl)dimethylammonium] propane sulfonate] (PMAEDMAPS)-based polybetaines attracted much attention [10, 11]. These (co)polymers could find potential applications in areas such as fungicide production, lubricating oil additives, emulsifying or antifouling agents [12]. Fine-tuning of composition and molecular weight of (PMAEDMAPS)-based copolymers thus appeared to be of key-importance.

The determination of PDMAEMA-based amphiphilic block copolymer composition is usually carried out by ^{1}H NMR spectrometry, taking into account the relative intensity ratio between the signal of the ester methylene protons of PDMAEMA sequences and other resonance signals arising from the second polymer block [13]. However, this method presents several difficulties, such as signal overlapping but also formation of insoluble or partially soluble micelles and other aggregates [14]. As an example, Haddleton et al. [14] studied diblock copolymers based on PDMAEMA and hydrophobic poly(dimethylsiloxane) (PDMS) and reported different ^{1}H NMR spectra and apparent compositions starting for the same PDMS-*b*-PDMAEMA diblock copolymer recorded in various solvents. To overcome this problem the use of specific mixtures of two (or more) deuterated solvents in appropriate ratios proved fully necessary.

The aim of this contribution is to investigate FTIR and thermogravimetric analysis (TGA) as readily accessible techniques for the straight and accurate determination of the composition of amphiphilic PDMAEMA-based copolymers. Both the polymerization degree of the polyaminomethacrylate block and the extent of amine quaternization or betainization reaction have been studied. Purposely a series of amphiphilic diblock copolymers PDMS-*b*-PDMAEMA have been synthesized in a controlled way, i.e. via atom transfer radical polymerization (ATRP) and characterized by FTIR and TGA and the results compared to those obtained by ^{1}H NMR in optimized deuterated solvent mixture.

Results and discussion

The structures of the amphiphilic diblock copolymers PDMS-*b*-PDMAEMA and their corresponding quaternized (PDMS-*b*-PMAETMA-I) and betainized (PDMS-*b*-PMAEDMAPS) derivatives are shown in Figure 1.

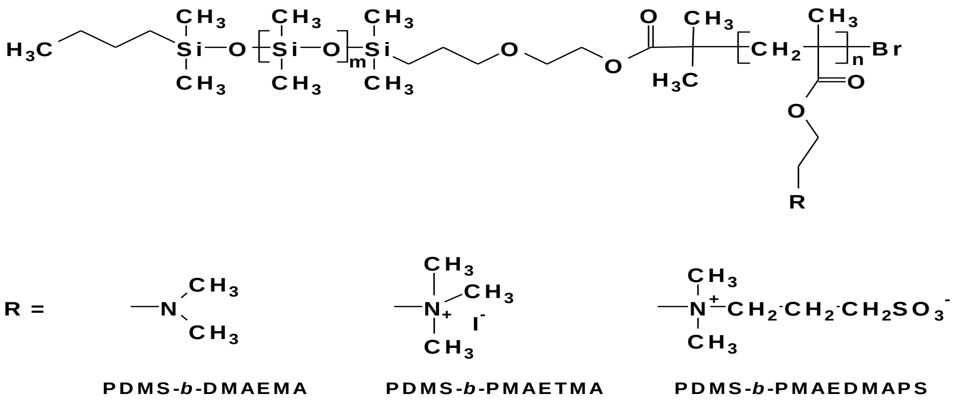

Fig. 1. Structure of the amphiphilic diblock copolymers PDMS-*b*-PDMAEMA and their corresponding quaternized and betainized derivatives.

A series of amphiphilic diblock copolymers PDMS-*b*-PDMAEMA have been synthesized by ATRP of DMAEMA initiated by ω-bromo PDMS macroinitiator and the CuBr·HMTETA adduct used as catalytic complex (see experimental) [14]. The performed ^{1}H NMR analyses have shown the absence of unreacted monomer in the purified PDMS-*b*-PDMAEMA copolymers (absence of multiplets at 5.6 and 6.1 ppm). Representative ^{1}H NMR spectra of the macroinitiator and a diblock copolymer recorded in $CDCl_3$ [14] are shown in Figure 2.

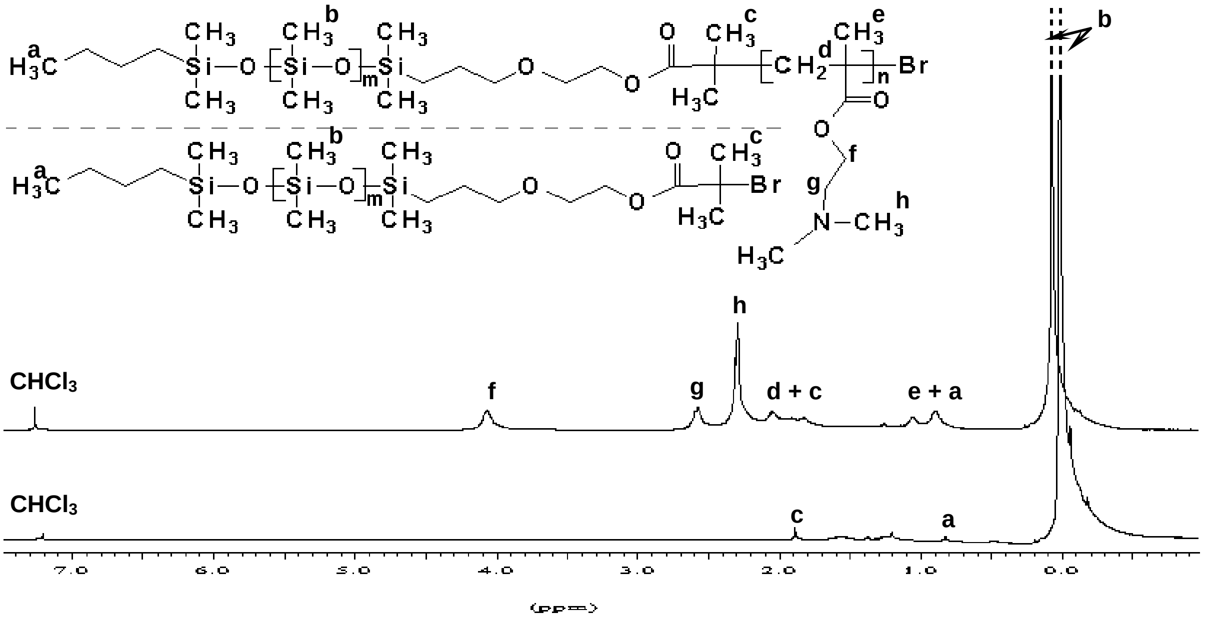

Fig. 2. ^{1}H NMR spectra of the ω-bromo PDMS macroinitiator and the recovered PDMS-*b*-PDMAEMA diblock copolymers as recorded in $CDCl_3$.

Tab. 1. Conversion and molecular parameters of the PDMS-*b*-PDMAEMA diblock copolymers.

Entry	IMMMR	Time	PolyDMAEMA block		Copolymers
		min	DP_{NMR} $^{(a)}$	$\overline{M}_n^{NMR}$ $^{(a)}$	$\overline{M}_W / \overline{M}_n$ $^{(b)}$
1	50	60	22	3500	1.32
2	50	90	41	6400	1.28
3	50	90	45	7100	1.35
4	100	90	82	12900	1.31
5	200	75	95	14900	1.32
6	200	120	118	18500	1.35
7	200	160	126	19800	1.33
8	200	210	145	22800	1.32

a) Experimental number-average molar mass as determined by ^{1}H NMR (see Figure 2): $\overline{M}_n^{NMR}$ = $DP_{NMR} \times MW_{DMAEMA}$, where DP_{NMR} is the degree of polymerization, as calculated from the relative intensities of the PDMS sequence methyl protons (b, δ ~ 0 ppm), and of the $O\text{-}C\underline{H}_2\text{-}CH_2\text{-}N(CH_3)_2$ methylene protons (f, δ = 4.12 ppm). b) Polydispersity index as determined by SEC in THF + 2 wt % Et_3N at 35 °C.

The degree of PDMAEMA-block polymerization ($DP_{PDMAEMA}$) varied from 25 to 150 (as controlled by the initial monomer-to-macroinitiator molar ratio (IMMMR) and polymerization time); while in all cases a ω-bromo PDMS macroinitiator with DP 133 was used (see Table 1). The synthesis of monomodal and narrowly dispersed PDMS-*b*-PDMAEMA amphiphilic diblock copolymers was evidenced by size exclusion chromatography (SEC).

The as synthesized PDMS-*b*-PDMAEMA copolymers were then quaternized with CH_3I or betainized with 1,3-propanesultone in THF to 25 %, 50 %, 75 % and 100 % degree of quaternization (DQ) or betainization (DB), respectively. Entries 2 and 3 (Table 1) were used in the synthesis of PDMS-*b*-PMAETMA-I and PDMS-*b*-PMAEDMAPS, respectively. It has to be mentioned that both PDMS-*b*-PMAETMA-I and PDMS-*b*-PMAEDMAPS precipitated during modification when the targeted DQ and DB exceeded 50 %. These observations are in agreement with the literature data [15] and might be explained by the increased copolymer hydrophilicity, leading to formation of aggregates consisting of hydrophilic PMAETMA-I or PMAEDMAPS core and PDMS shell, and their aggregation and precipitation in THF. Furthermore, resonance signal overlapping and complete loss of resolution occurred when ^{1}H NMR characterization was performed in deuterated THF. Thus an alternative solvent was needed. Considering the good solubility of the hydrophilic block in water, ^{1}H NMR spectra of PDMS-*b*-PMAETMA-I and PDMS-*b*-PMAEDMAPS in D_2O were attempted. Again signal overlapping and low resolution were observed, this time due to the insolubility of the PDMS block in polar medium and the corresponding formation of inversed aggregates consisting of a PDMS core and a hydrophilic block shell. Based on these observations, one could assume that a mixture of two miscible solvents, each displaying a good affinity towards one of the two blocks, might be suitable for PDMS-*b*-PMAETMA-I and PDMS-*b*-PMAEDMAPS characterization by ^{1}H NMR. A mixture of THF and water was then chosen taking into account the good solubility of the PDMS block in THF and the miscibility of this solvent with water.

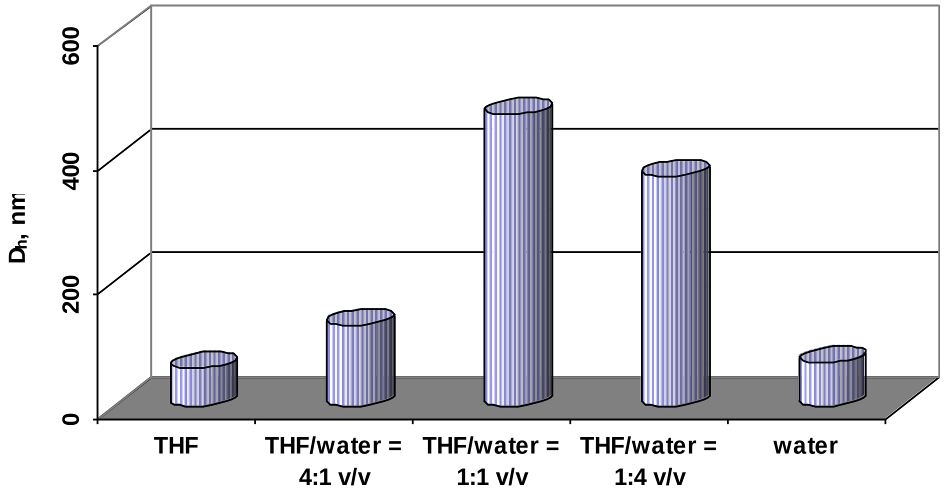

Fig. 3. Hydrodynamic diameter (D_h) of PDMS-*b*-PMAEDMAPS (DB 100 %) in THF-d_8, water and THF-d_8/water = 4:1, 1:1 and 1:4 v/v.

Several THF-to-water volume ratios (THF/water = 4:1, 1:1 and 1:4) have been evaluated by ^{1}H NMR and dynamic light scattering (DLS) as solvents for the fully betainized PDMS-*b*-PMAEDMAPS, which initially showed loss of resolution for the ^{1}H NMR spectra as recorded in THF-d_8 or D_2O. Interestingly, most resonance signals assigned to both PDMS and PMAEDMAPS blocks could be detected in the THF-d_8/D_2O (1:1 v/v) solvent mixture.

The reason for this observation became evident after performing DLS analyses of the PDMS-b-PMAEDMAPS solutions in THF-d_8, water and THF-d_8/water = 4:1, 1:1 and 1:4 v/v. As seen in Figure 3, independently of the solvent composition the presence of aggregates was detected. Their hydrodynamic diameter (D_h) increased on increasing water content and passed through a maximum at THF-d_8/water = 1:1 v/v. As far as the copolymer concentration in the studied solvent (mixture) remained constant (0.1 mg/ml), the observed increase in D_h on increasing water content might be explained by increased quality of the solvent towards the PMAEDMAPS blocks in the aggregates core. Thus, chain expansion and increased mobility leading to core swelling are most probably leading to higher D_h and corresponding improvement in the ^1H NMR spectra resolution. Moreover, rearrangement of the aggregates structure allowing the presence of part of PMAEDMAPS blocks on the particle surface may also take place. On another hand, one can also argue that the increase in D_h is due to an increase in the aggregation number or secondary aggregation of the formed self-assemblies. However, it is difficult to envisage the occurrence of secondary aggregation upon improving the solvent quality. Furthermore, the increase in aggregation number requires dynamic equilibrium between self-assemblies and unimers, the last ones not being observed in the DLS histograms. This is in agreement with the literature data [16, 17]. Nevertheless, the resolution remained too low for allowing quantitative determination of the degree of betainization (DB). Actually the characterization by ^1H NMR proved only possible in the case of PDMS-*b*-PMAETMA-I amphiphilic copolymers when recorded in THF-d_8/water = 1:1 (v/v) solvent mixture. For these copolymers no micelles or aggregates were observed by DLS. The corresponding DLS histograms were characterized with very low initial scattering intensity indicating that no micellization takes place.

Considering the potential applications of the aforementioned PDMS-*b*-PDMAEMA, PDMS-*b*-PMAETMA-I and PDMS-*b*-PMAEDMAPS block copolymers, other alternative methods have been approached for their quantitative characterization.

Fourier Transform Infrared Spectroscopy analysis of amino-based copolymers

FTIR spectroscopy has often been used as a method for surface analyses in PDMS-containing (nano)composites [18, 19]. The FTIR spectrum of the ω-bromo PDMS macroinitiator used in this study is characterized by strong absorptions in the 1260-795 cm^{-1} wavelength range (Figure 4). The band at 1260 cm^{-1} is ascribed to Si-CH_3 bending, the two bands at 1088 cm^{-1} and 1030 cm^{-1} - to asymmetric Si-O-Si stretching, and the band at 795 cm^{-1} - to Si-CH_3 rocking, all in agreement with literature data [16]. Surprisingly, despite the presence of a bromo-isobutyryl end group, no absorption due to the ester linkage could be detected in the macroinitiator. The lack of ester absorption in our case can be ascribed to the low ester concentration when PDMS DP is 133.

The ATR-FTIR spectra of the PDMS-*b*-PDMAEMA copolymers showed the PDMS characteristic absorptions, confirming the presence of the hydrophobic block in the diblock copolymers. No absorption was detected for C=C double bonds at 1640 cm^{-1}, which could be assigned to the presence of free DMAEMA, thus confirming the lack of unreacted monomer in the purified diblock copolymers. Weak absorptions at 1454 cm^{-1} (ascribed to PDMAEMA block CH_2 bending) and 1148 cm^{-1} (C-N or C-O stretching vibrations) ascribed to the PDMAEMA block were clearly present in the ATR-FTIR spectra [20]. An isosbestic point was observed between the absorption 1148 cm^{-1} and the broad PDMS peak at 1088 cm^{-1} (Figure 4). The C=O (1726 cm^{-1}) and C-H close to the nitrogen atom (2726 cm^{-1} and 2826 cm^{-1}) stretching for DMAEMA units in the PDMAEMA block were also clearly visible (on the inset of Figure 4). Moreover, the intensity of these absorptions increased while the intensity of the C-H stretching vibrations at 2941 cm^{-1} decreased on increasing PDMAEMA block length in agreement with literature data [21].

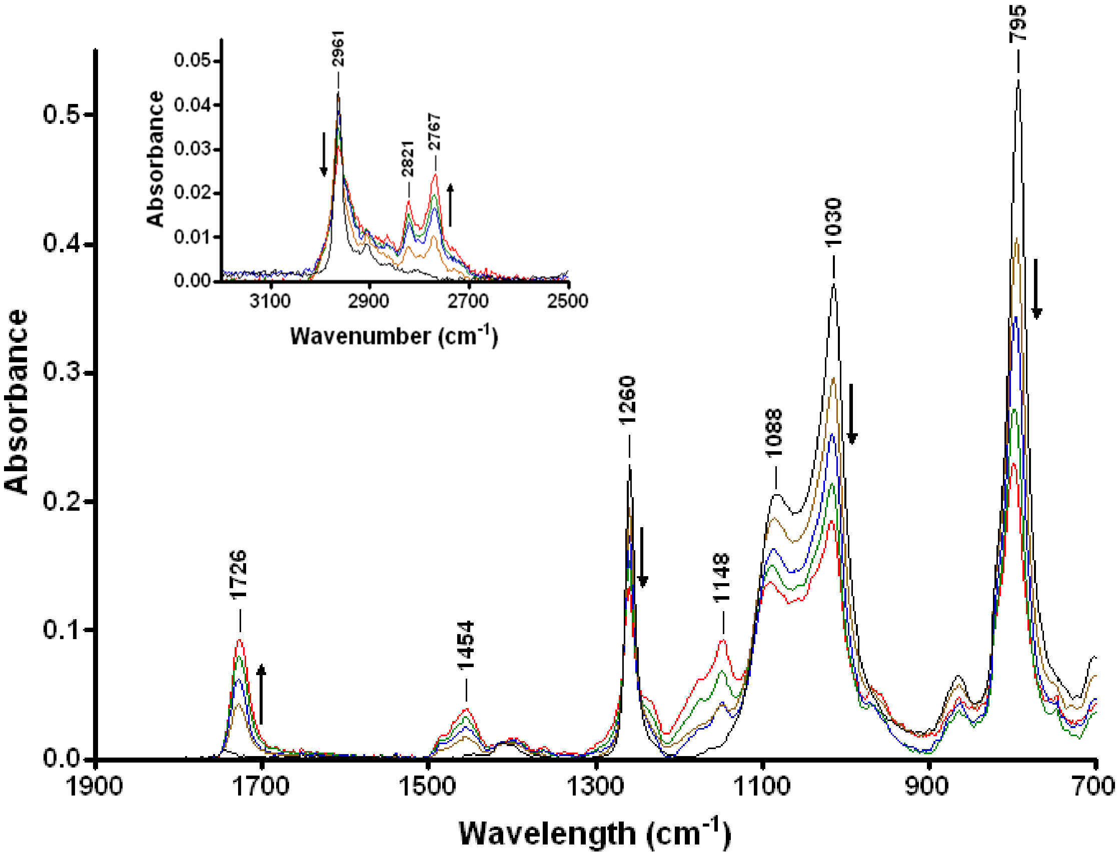

Fig. 4. ATR-FTIR spectra of ω-bromo PDMS (black line) and a series of PDMS-*b*-PDMAEMA block copolymers with DP$_{\text{PDMAEMA}}$ 22 (brown line), 41 (blue line), 82 (green line) and 126 (red line). In the inset the absorbance between 2500 cm^{-1} and 3100 cm^{-1} is shown.

It was noteworthy that upon increasing DMAEMA content, the absorption intensity ratio between the bands issued from ester functions in DMAEMA units and the absorptions characteristics for the PDMS block increased. This, together with the lack of absorption for the ω-bromo PDMS ester linkage gives the possibility to use ATR-FTIR as a quantitative method for determining the molar composition of the PDMS-*b*-PDMAEMA copolymers. To verify this hypothesis, the absorbance ratios between the C=O stretching mode at 1726 cm^{-1} and the 1260 and 795 cm^{-1} bands of the PDMS backbone were calculated for a series of PDMS-*b*-PDMAEMA copolymers with unmodified PDMAEMA-block. This set of data was used to plot ^{1}H NMR/ATR-FTIR correlation curves (Figure 5). The correlation equations were further used to calculate DMAEMA mol% (Table 2). Further, dependence between DMAEMA molar fraction (X) and the degree of PDMAEMA block polymerization (DP) was found (Equation 1) thus allowing direct DP calculation.

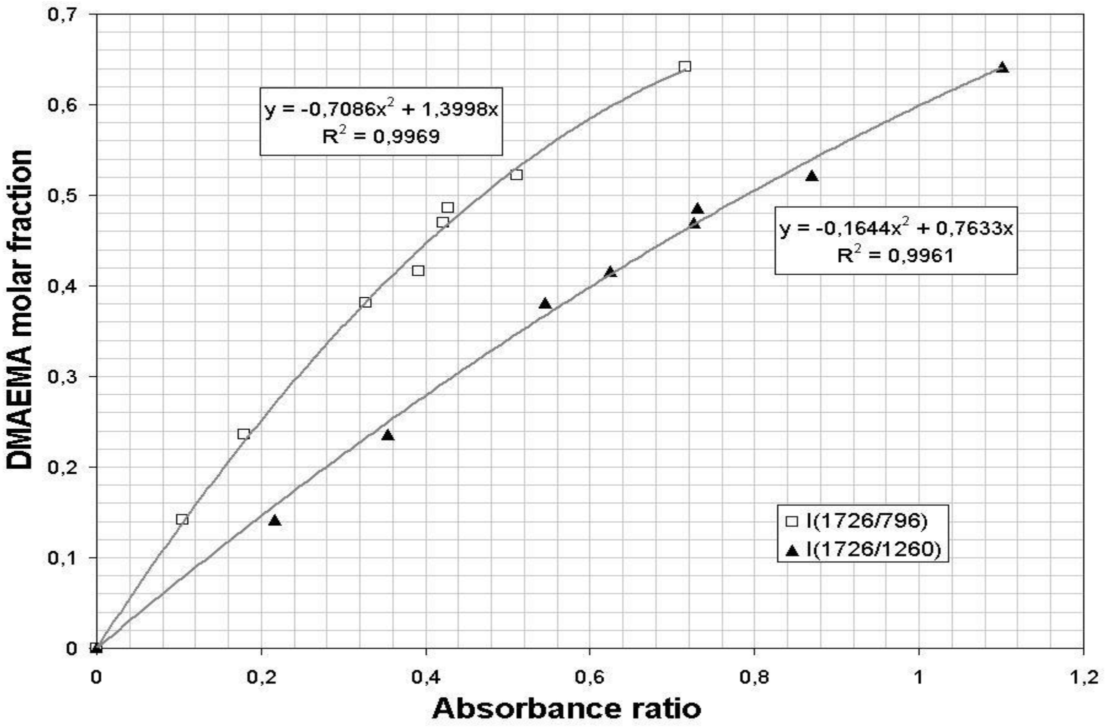

Fig. 5. ^{1}H NMR/ATR-FTIR correlation curves as obtained for PDMS-*b*-PDMAEMA diblock copolymers of different DMAEMA molar fractions.

The standard deviations of the mol% calculated using the I(1726/796) and the I(1726/796) ratio are ±1.5% and ±1.3%, respectively. The minimum mean-square error for both calibration curves is calculated to be 4% with respect to the ^{1}H NMR data with an absolute error (based on error propagation) of 9.2%. For the samples used in this work, this is roughly equivalent to ca. 2 repetitive units in the final DP calculation, and within the experimental error expected from peak integration in ^{1}H NMR spectra.

$$X_{PDMAEMA} = \frac{DP_{PDMAEMA}}{DP_{PDMAEMA} + DP_{PDMS}} \qquad (1)$$

The obtained results are reported in Table 2 and compared with the DMAEMA molar fractions as determined by ^{1}H NMR (in THF-d$_8$ as good solvent for the two blocks). As observed, the ^{1}H NMR and ATR-FTIR calculated molar fractions proved very close to each other.

Thus the ATR-FTIR method appears to be an accurate, readily accessible and useful technique for the fast characterization of the PDMS-*b*-PDMAEMA diblock copolymers.

Considering the significant differences in dipole moments taking place in the copolymers after quaternization or betainization reactions, ATR-FTIR has also been studied for determining the DQ and DB values. Unfortunately, the spectra resolution and the signal-to-noise ratio became much poorer for the PDMS-*b*-PMAETMA-I copolymers, resulting in a large scattering of results and poor correlation between the

DQ determined by 1H NMR and ATR-FTIR. Since phase segregation more likely occurs in quaternized copolymers (*vide supra*) and knowing that ATR-FTIR technique exchanges information only with the sample surface, it is likely that the observed absorption ratios will not be representative of the entire sample. For the PDMS-*b*-PMAEDMAPS copolymers, although the ATR-FTIR spectra showed the appearance of new peaks at 1028 and 1189 cm^{-1} (data not shown) characteristic for the symmetric and asymmetric S=O stretching vibrations of the SO_3^- groups in complexed and/or delocalized form [22], the low spectra resolution did not allow quantitative DB determination. Thus it came out that ATR-FTIR spectroscopy could be applied only as a method for qualitative characterization of quaternized/betainized amino-based copolymers.

Tab. 2. ^{1}H NMR and ATR-FTIR data for PDMS-*b*-PDMAEMA diblock copolymers.

Entry	^{1}H NMR		ATR-FTIR		
	DP_{DMAEMA}	$mol\%_{DMAEMA}$	I(1726/1260)	I(1726/796)	$mol\%_{DMAEMA}$ $^{(a)}$
1	22	14	0.104	0.217	15±0.6
2	41	24	0.179	0.355	24±1.0
3	45	25	0.221	0.402	27±1.0
4	82	38	0.327	0.546	37±1.5
5	95	42	0.392	0.624	43±1.7
6	118	47	0.421	0.726	47±1.9
7	126	49	0.428	0.731	47±1.9
8	145	52	0.511	0.870	53±2.1

(a) The values are the average obtained from I(1726/1260) and I(1726/796) with minimum mean-square error of 4%.

Thermogravimetric analyses of amino-based copolymers

Since quite different thermal behavior for the polymethacrylate blocks containing quaternized/betainized DMAEMA units might be expected, PDMS-*b*-PDMAEMA, PDMS-*b*-PMAETMA-I and PDMS-*b*-PMAEDMAPS have been further analyzed by thermogravimetry (TGA). As seen in Figure 6A, the ω-bromo PDMS (black line) showed one degradation step, starting at around 370 °C and finishing at around 600 °C with a maximum at 535 °C in agreement with the literature data [23]. In sharp contrast, the PDMS-*b*-PDMAEMA diblock copolymers (purple line) showed a three-step degradation profile. The first step started at around 110 °C and finished at about 350 °C with a maximum at 328 °C. The second one finished at around 470 °C with maximum at 430 °C and the third one finished at around 650 °C with a maximum at 545 °C. According to the literature [24], the first two steps are ascribed to PDMAEMA thermal degradation.

Interestingly enough, the partially quaternized copolymers showed a first degradation step, starting at around 100 °C and finishing at ca. 330 °C with a maximum at 255 °C. The next two decomposition peaks were similar to those of PDMS-*b*-PDMAEMA (at ~430 °C and ~545 °C). This suggests that the residues after the first decomposition steps are of the same nature and thus, that the first step involves the pending groups of DMAEMA and MAETMA-I units (Figure 1). The decreased thermal stability of the PDMS-*b*-PMAETMA-I copolymers might be explained by the fact that in the presence of a base, quaternary ammonium salts thermally decompose through Hoffman elimination, with free amine formation [25, 26]. Therefore, the decomposition step at 255 °C has been ascribed to a loss of TMAEMA-I pending group. One could also argue for the formation of CH_3I through a S_N2 nucleophilic attack of the iodide ions on the positively-charged ammonium-bound methyl groups at high temperature, resulting in a self-catalyzed step, thus explaining the absence of a second decomposition peak in the samples. This hypothesis has been confirmed by evolved gas analysis (EGA) performed on the PDMS-*b*-PDMAEMA and PDMS-*b*-PMAETMA-I copolymers using a termogravimetric analyzer simultaneously coupled to FTIR and mass spectrometer (MS) (TGA-co-FTIR/MS) (see last section of this paper).

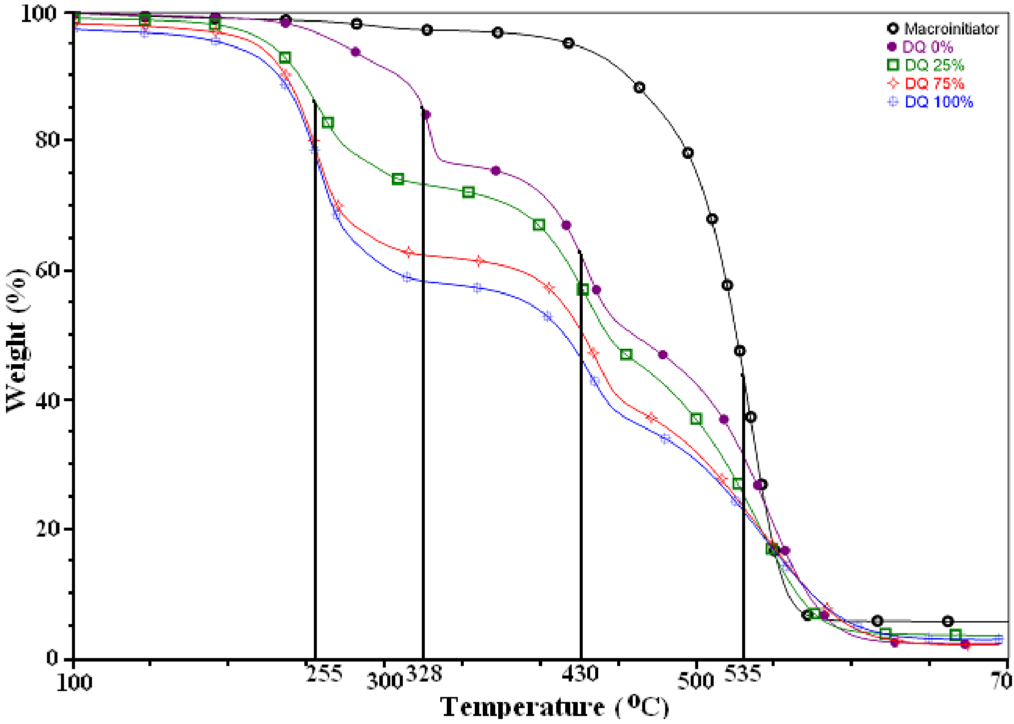

Fig. 6. TGA of a series of PDMS-*b*-PMAETMA-I with expected DQ 25 %, 75 % and 100 %. The ω-bromo PDMAS (macroinitiator) and PDMS-*b*-PDMAEMA (DQ 0 %) are given for the sake of comparison.

Comparing the weight loss values recorded at the first degradation step with the corresponding mass fractions PMAETMA-I calculated from the ^{1}H NMR results or the recovery yield in PDMS-*b*-PMAETMA-I (i.e., monomer conversion), a linear relationship could be drawn (Figure 7). Furthermore, since for a given degree of polymerization the PMAETMA-I mass fraction depends on DQ, a linear relationship could also be drawn between the first weight loss and the DQ value. Another possibility that might facilitate the researcher is the construction of multiple correlation curves for blends of two homopolymers in various ratios. However, as the present study aims on showing the utility of TGA in quantitative determination of DQ/DB, this method was not applied.

With respect to PDMS-*b*-PMAETMA-I copolymers, the betainized PDMS-*b*-PMAEDMAPS showed a more complicated thermal degradation profile. The initial degradation step started at around 100 °C and finished at ca. 360 °C and was characterized by two maxima at about 260 and 330 °C. The weight losses taking place at the first maximum did not exceed 10 wt.% and were found to slightly increase at higher DB values. The second and third steps appeared very comparable to the previously discussed results (at ~430 °C and ~545 °C). The occurrence of peaks at 330 °C and 420 °C was in agreement with literature data specifically dealing with the thermal decomposition of PMAEDMAPS homopolymers [25, 26]. The peak at ca. 260 °C was observed when thermal degradation proceeded in air. Since the thermal degradation of the here studied copolymers was performed under He, one can assume the release of SO_2 from the betaine-type structures within this temperature range as confirmed by TGA-EGA (see hereafter).

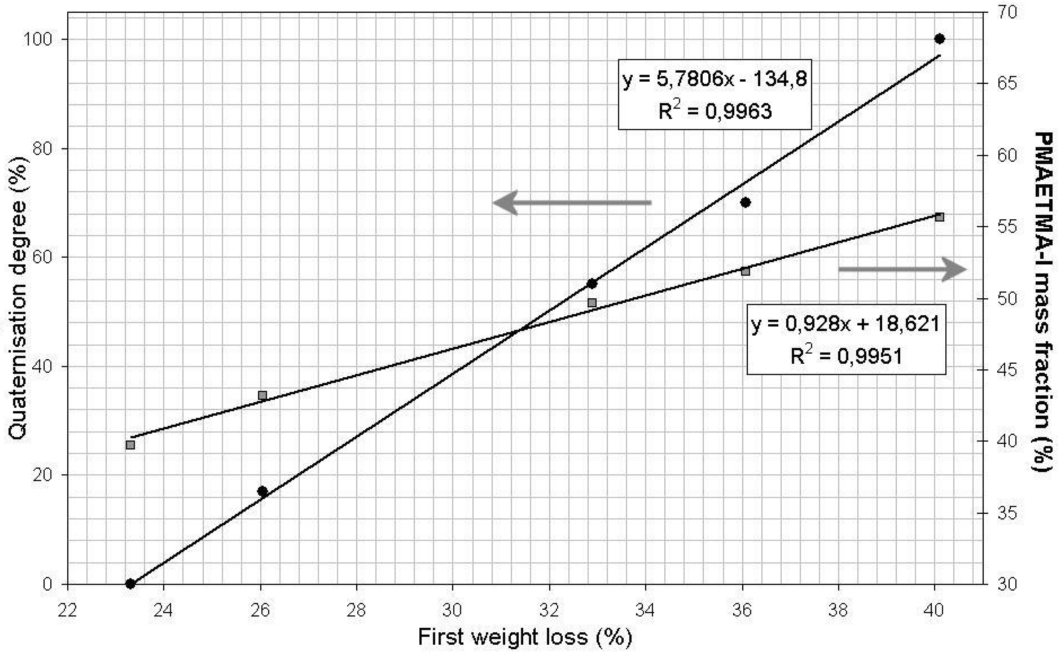

Fig. 7. Correlation between the degree of quaternization (DQ) and the mass fraction recorded at the first weight loss for PDMS-*b*-PMAETMA-I copolymers with different DQ values as determined by TGA.

Tab. 3. TGA results of copolymers with different DQ/DB values.

Entry	DQ$_{\text{NMR}}$/DB$_{\text{yield}}$(a) %	Hydrophilic block mass fraction(b), %	TGA	
			First weight loss, %	DQ/DB(c), %
2	0/0	39.19	23.31	0/0
9	17/0	43.21	26.05	16±0.7/0
10	55/0	49.68	32.90	55±2.4/0
11	70/0	51.85	36.08	74±3.2/0
12	100/0	55.67	40.12	97±4.2/0
13	0/25	46.44	23.65	0/15±0.6
14	0/49	50.16	44.82	0/48±2.1
15	0/73	53.69	60.41	0/73±3.1
16	0/98	57.38	79.00	0/100±4.3

(a) The degree of quaternization (DQ) was calculated based on the performed ^{1}H NMR analyses, and the theoretical degree of betainization (DB) was calculated from the recovery yield. (b) As calculated from the theoretical DQ/DB values. (c) As calculated from the first weight loss data with minimum mean-square error of 4.3%.

Very interestingly, comparing the first weight loss with the PMAEDMAPS mass fractions (calculated from the PDMS-*b*-PMAEDMAPS copolymers yield), a linear correlation could be observed again. Therefore, the experimental degree of quaternization/betainization can be calculated from the correlation equations found for the PDMS-*b*-PMAETMA-I and PDMS-*b*-PMAEDMAPS copolymers (Table 3). As seen the calculated DQ/DB are in agreement with the expected values. The minimum mean-square error for the DQ/DB calibration curves is calculated to be 4.3% with respect to the ^{1}H NMR data and the absolute error obtained from error propagation is 10%.

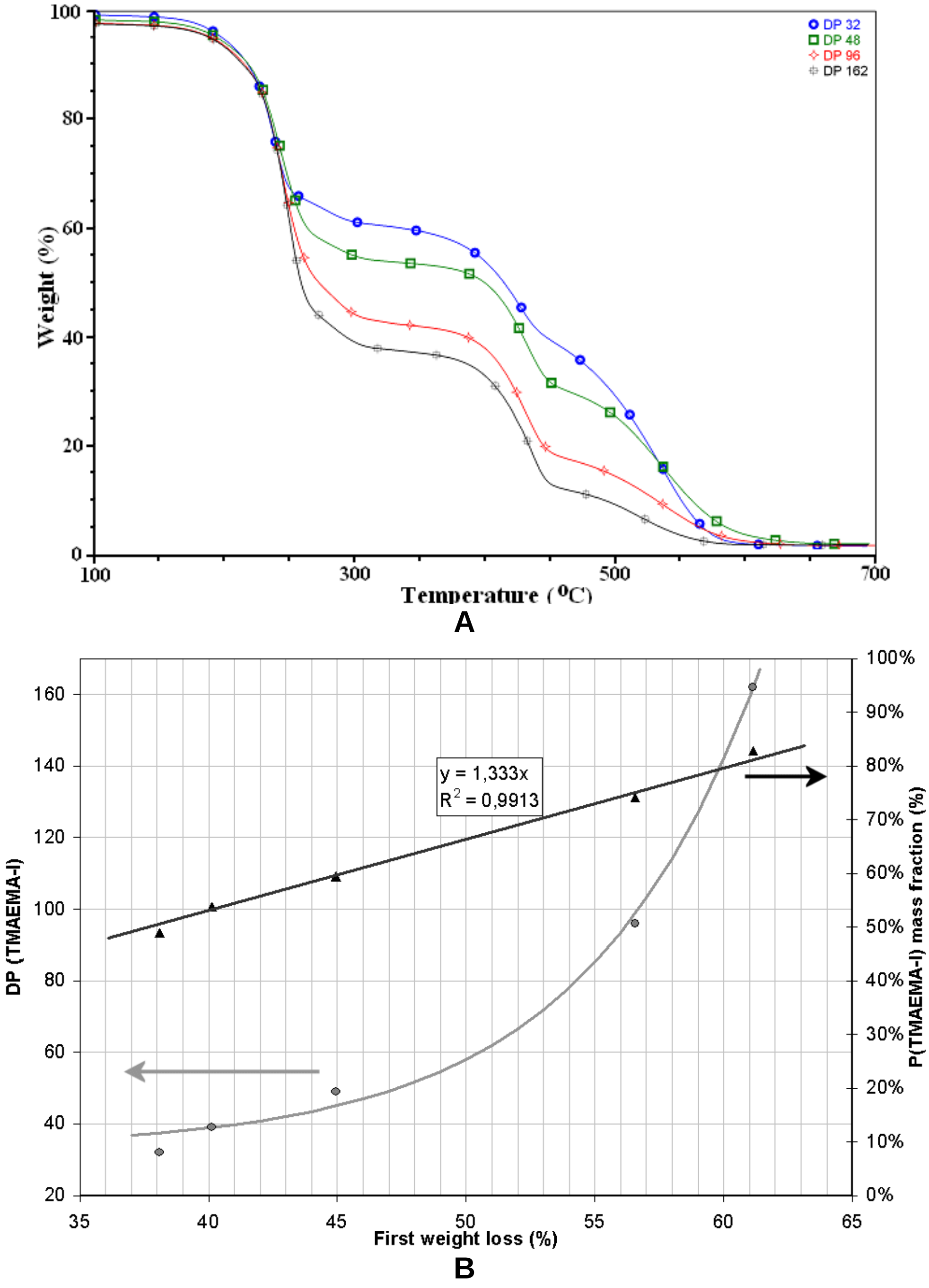

Fig. 8. TGA curves (A) and correlation between the degree of polymerization (DP) and the mass fraction on the first weight loss (B) for PDMS-*b*-PMAETMA-I copolymers with different PMAETMA-I block lengths.

For attesting the authenticity of the above results, thermal decomposition of fully quaternised copolymers characterized by different PMAETMA-I block lengths have been performed as well (Figure 8A). Again, a linear relationship was found out between the first weight loss (DTGA peak ranging from 245 °C to 255 °C) and the mass fraction of the hydrophilic block in the copolymer (Figure 8B). The obtained results are summarized in Table 4.

Tab. 4. ^{1}H NMR and TGA results for fully quaternized PDMS-*b*-PMAETMA-I copolymers with different $DP_{PMAETMA}$.

Entry	$DP_{PMAETMA-I}$	^{1}H NMR MAETMA-I mass fraction, %	TGA First weight loss, %	$DP_{PMAETMA-I}$
17	32	48.90	38.10	34
18	42	55.67	40.12	39
19	49	59.43	44.95	50
20	96	74.16	56.56	102
21	162	82.89	61.14	148

Using the Equation presented in Figure 8B, calculating the mass fraction for the PMAETMA-I block becomes possible. Also, by using the Equation 2 (where W is the weight fraction and M_n the number-average molar mass), it is possible to obtain the M_n values and consequently DP's. A discrepancy of less than 6% was observed when comparing the DP's calculated by TGA with those obtained by ^{1}H NMR.

$$W_{PMAETMA-I} = \frac{Mn_{PMAETMA-I}}{Mn_{PMAETMA-I} + Mn_{PDMS}} \qquad (2)$$

It is worth pointing out that the obtained equations depend on the PDMAEMA block length. Therefore, one has to pay attention on making specific calibration curves and finding the correct equations for each copolymer type and composition. An useful tool might be the preparation of multiple calibration curves based on blending homopolymers in different composition.

EGA / TGA-co-FTIR/MS analysis

As previously discussed the decreased thermal stability of the PDMS-*b*-PMAETMA-I copolymers (first degradation step with maximum at around 255 °C) in comparison with those of the nonquaternized PDMS-*b*-PDMAEMA copolymers (first degradation step at 330 °C) might be explained by Hoffmann elimination with the formation of a free amine [25, 26] and/or CH_3I. To confirm this hypothesis Evolved Gas Analyses (EGA) studies were performed, allowing the nature of the decomposition products to be evaluated (Figure 9).

As seen, a weak, yet clear signal appeared in the performed ATR-FTIR spectra around 2500 cm^{-1} during the first decomposition step. This signal might be assigned to the N^+-H stretching of trimethylammonium cations [27], probably formed by protonation of trimethylamine produced after Hoffman decomposition of the quaternary ammonium groups. The formation of trimethylamine is also detected in the mass spectra, by the expected M-1 peak at m/z 58 (spectrum not shown here). A less intense peak at m/z 59, assigned to the molecular ion, is also observed. Interestingly, the formation of CH_3I is fully confirmed by mass spectroscopy displaying signals at m/z 142 (methyl iodide) and 127 (iodine). Above 350 °C, CO and CO_2 are detected by FTIR in a decomposition step which is assigned to the breaking down of the PMAETMA-I backbone and pending carboxylic groups. The formation of volatile Si-containing species (cyclo-oligomers) is clearly observed in the last degradation step occurring above 450 °C as evidenced by strong FTIR absorptions at 1260, 1100 and 795 cm^{-1}, characteristic of Si-C and Si-O vibrational modes, and MS signals at m/z 191, 207 and 209.

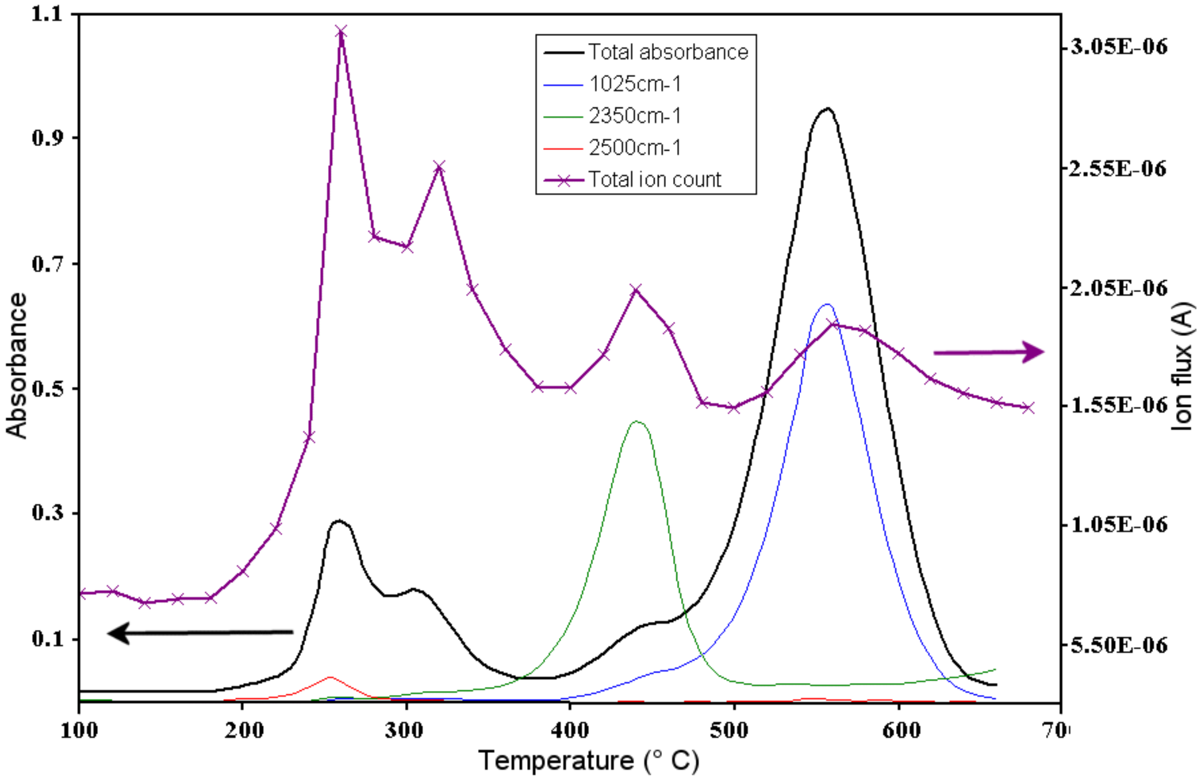

Fig. 9. Evolved gas analysis by ATR-co-FTIR/MS as obtained for Entry 10 (Table 3). Overlay of the total ion count by MS and total IR absorbance and those due to peaks at 2500 (Me_3N^+-H), 2350 (CO_2) and 1025 cm^{-1} (siloxane cyclo-oligomers).

EGA analyses were also performed in order to determine the nature of the first maximum (255 °C) in the first decomposition step of PDMS-*b*-PMAEDMAPS copolymers. A peak at m/z 44 showing the formation of CO_2 was again observed. The occurrence of SO_2 appeared in the second maximum (330 °C), together with signals ascribed to CH_2, CH_3 and $(NCH_3)_2$.

Conclusions

A series of amphiphilic copolymers PDMS-*b*-DMAEMA, as well as their quaternized/betainized derivatives PDMS-*b*-PMAETMA-I/PDMS-*b*-PMAEDMAPS, was synthesized and characterized by ^{1}H NMR, ATR-FTIR and TGA. Linear correlations were found between the DP (or DQ) values obtained by ^{1}H NMR and the PDMAEMA (PDMAETMA-I) molar and/or mass fractions obtained by ATR-FTIR and/or TGA, respectively. Based on the found correlations these techniques were applied to determine i) the polymerization degree of the PDMAEMA, PTMAEMA-I- or PMAEDMAPS-block; ii) the quaternization/betainization degrees of the PTMAEMA-I-/PMAEDMAPS-block. However, as far as TGA analyses are concerned, attention has to be paid on making a specific calibration curve for each copolymer type and composition. The use of multiple calibration curves obtained for blends of homopolymers of different composition may be envisaged. The performed evolved gas analysis (EGA, using a simultaneously coupled TGA-co-FTIR/MS system) confirmed the data obtained by TGA. Nevertheless, further analyses allowing a mechanism for the PDMS-*b*-DMAEMA, PDMS-*b*-PMAETMA-I and PDMS-*b*-PMAEDMAPS thermal degradation are needed.

Experimental part

Materials

2-Bromo-2-methylpropionylbromide (Br^{i}BBr, 98%, Aldrich-252271-100G), iodomethane (CH_3I, > 99 %, Merck-74-88-4), copper (I) bromide (CuBr, > 99%, Aldrich-254185-100G) and 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, 97 %, Aldrich-366404-5G) were used as received. 2-(Dimethylamino)ethyl methacrylate (DMAEMA, stabilized with 1000 ppm MEHQ, Aldrich-234907-1L) was purified by passing through a basic alumina column, dried over CaH_2 for 48 h and distilled under reduced pressure. The monomer was stored under N_2 at -20 °C prior to use. ω-OH functionalized polydimethylsiloxane (PDMS, $\overline{M}_n \sim 10000$, degree of polymerization, DP = 133) was supplied by ABCR Gelest (120359-07-1) and used after drying under vacuum. Triethylamine (Et_3N, 99%, Acros Organics-121-44-8, Belgium) was dried over BaO for 48 h and distilled prior to use. All other chemicals were of analytical grade of purity and used as received.

Copolymer synthesis and characterization

ω-Bromo PDMS (DP=133) macroinitiator was prepared as previously described by reaction of carbinol-terminated PDMS (PDMS-OH) and Br^{i}BBr [11, 12]. In a typical experiment 10 g of PDMS-OH (1 mmol, 1 eq) were dissolved in THF and 0.2 g of Et_3N (2 mmol, 2 eq) were added dropwise during 30 min, followed by the addition of a two-fold excess of Br^{i}BBr (0.45 g, 2 mmol). The mixture was maintained under stirring at 60 °C for 72 h, after which the resulting mixture was filtered to eliminate the insoluble salts and the solvent was evaporated under reduced pressure to constant weight. The oil thus obtained was dissolved in CH_2Cl_2 and washed with saturated $NaHCO_3$ solution and water. The organic layer was isolated and dried over $MgSO_4$, filtered, and then the solvent was removed out under vacuum to constant weight (yield: 80%). ^{1}H NMR spectra were obtained using a **Bruker** AMX-300 spectrometer operating at 300 MHz, in tetramethylsilane-free $CDCl_3$ or D_2O/THF-d_8 1:1 solution; all peaks were referenced to residual solvent peaks [28]. ^{1}H NMR (r.t., $CDCl_3$, δ ppm): 0.00 ($CH_3O–(Si(C\mathbf{H}_3)_2\text{-}O)_{135}$), 0.89 ($C\mathbf{H}_3O–(Si(CH_3)_2\text{-}O)_{135}$), 1.63 ($CH_3O–(Si(CH_3)_2\text{-}O)_{135}\text{-}Si(CH_3)_2\text{-}CH_2\text{-}C\mathbf{H}_2\text{-}CH_2\text{-}O$), 3.46 ($CH_3O–(Si(CH_3)_2\text{-}O)_{135}\text{-}Si(CH_3)_2\text{-}CH_2\text{-}CH_2\text{-}C\mathbf{H}_2\text{-}O$), 3.55 ($CH_3O–(Si(CH_3)_2\text{-}O)_{135}\text{-}Si(CH_3)_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}O\text{-}C\mathbf{H}_2\text{-}CH_2\text{-}O\text{-}CO$), 4.34 ($CH_3O–(Si(CH_3)_2\text{-}O)_{135}\text{-}Si(CH_3)_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}C\mathbf{H}_2\text{-}O\text{-}CO$), and 1.93 ($CH_3O–(Si(CH_3)_2\text{-}O)_{135}\text{-}Si(CH_3)_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CO\text{-}C(C\mathbf{H}_3)_2\text{-}Br$). Completion of the esterification reaction was indicated by the appearance of a sharp signal at 1.93 ppm assigned to the methyl protons of the ω-bromo PDMS and the shift of the signal at 3.7 ppm ($–C\mathbf{H}_2–OH$) in favor of a new resonance centered at 4.34 ppm.

A series of well-defined amphiphilic PDMS-*b*-PDMAEMA diblock copolymers (Table 1) were synthesized using previously elaborated conditions [13]. In a typical experiment PDMS-Br (6.5 g, 1 eq.) HMTETA (180 mg, 1.2 eq) and DMAEMA (5.2 ml, 50 eq.) were dissolved in toluene (10 ml) in a pear-shaped flask and degassed by 3 freeze-pump-thaw cycles. This pale-brown solution was transferred by cannula under N_2 to a round-bottom flask containing CuBr (100 mg, 1.1 eq.), and the resulting mixture was heated to 80° C in an oil bath. Within a few minutes a deep green colour developed in the reaction medium, which persisted for the rest of the reaction time. After 90 min, the round-bottom flask was removed from the heating bath and quenched in liquid N_2. The reaction mixture was then diluted in THF and quickly filtered through a basic alumina column, yielding a pale yellow solution. This solution was evaporated and the resulting material dried overnight in a vacuum oven at 80 °C, giving the PDMS-*b*-PDMAEMA copolymer as a sticky yellow solid (10.0 g). ^{1}H NMR (Bruker AMX-300 apparatus operating at 300 MHz, r.t., $CDCl_3$, δ ppm): 0.00 ($CH_3O{-}(Si(C\mathbf{H}_3)_2\text{-}O)_{135}$), 0.6-0.89 ($C(C\mathbf{H}_3)$ PDMAEMA block and $C\mathbf{H}_3O{-}(Si(CH_3)_2\text{-}O)_{135}$ from the macroinitiator), 1.63 ($CH_3O{-}(Si(CH_3)_2\text{-}O)_{135}\text{-}Si(CH_3)_2\text{-}CH_2\text{-}C\mathbf{H}_2\text{-}CH_2\text{-}O$), 1.89-1.93 ($C\mathbf{H}_2$ PDMAEMA block and $Br\text{-}C(C\mathbf{H}_3)_2{-}CO$ of PDMS-Br), 2.3 ($N(C\mathbf{H}_3)_2$ PDMAEMA block), 2.65 ($C\mathbf{H}_2N(CH_3)_2$ PDMAEMA block), 3.46 ($CH_3O{-}(Si(CH_3)_2\text{-}O)_{135}\text{-}Si(CH_3)_2\text{-}CH_2\text{-}CH_2\text{-}C\mathbf{H}_2\text{-}O$), 3.55 ($CH_3O{-}(Si(CH_3)_2\text{-}O)_{135}\text{-}Si(CH_3)_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}O\text{-}C\mathbf{H}_2\text{-}CH_2\text{-}O\text{-}CO$), 4.1 ($O\text{-}CH_2$ PDMAEMA block) and 4.34 ($CH_3O{-}(Si(CH_3)_2\text{-}O)_{135}\text{-}Si(CH_3)_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}C\mathbf{H}_2\text{-}O\text{-}CO$). Size exclusion chromatography (SEC) of PDMAEMA and POE_{114}-*b*-$PDMAEMA_n$ (n = 45, 70 and 140) was performed in THF + 2 wt% Et_3N at 35 °C, using a Polymer Laboratories liquid chromatograph equipped with a PL-DG802 degasser, an isocratic HPLC pump LC 1120 (flow rate = 1 mL/min), a Marathon autosampler (loop volume = 200 µL, solution conc. = 1 mg/mL), a PL-DRI refractive index detector, and three columns: a PL gel 10 µm guard column and two PL gel Mixed-B columns. Molecular weight and molecular weight distribution were calculated with reference to poly(methyl methacrylate) standards.

The so-obtained copolymers were further modified in terms of quaternization or betainization of the PDMAEMA block with iodomethane or 1,3-propanesultone, respectively. Different degrees of quaternization/betainization (DQ/DB = 25 %, 50 %, 75 % and 100 %) were targeted. The quaternization reaction were performed as follows: 6.0 g of P(DMS_{135}-*b*-$DMAEMA_{45}$) (7.9 mmol amino groups) were dissolved in 100 ml toluene and CH_3I (1,9 ml, 3,0 mmol) was added dropwise. The reaction was allowed to proceed at 60 °C for 18 h. The product was isolated by evaporation of the solvent under reduced pressure, washed with small portions of acetone and dried under vacuum to constant weight. White to off-yellow powder was obtained (yield: 90 %) [11]. The degree of quaternization of the $PDMS_{133}$-*b*-$PMAETMA_{45}$ was estimated by the ratio of intensity of the protons at 2.55 ppm and the CH_3 protons at 3.5 ppm for the non-quaternized and the quaternized DMAEMA units in the ^{1}H NMR spectra (Bruker AMX 300 NMR operating at 300 MHz, r.t., THF-d^8/D_2O = 1:1, v/v).

For the synthesis of betainized copolymers a round-bottom flask was charged with 5 g $PDMS_{135}$-*b*-$PDMAEMA_{45}$ (7.9 mmol amino groups) and 45 ml of dried THF were added to dissolve the copolymer and the mixture degassed for 15 min by flushing with N_2. A second flask was charged with the desired amount of 1,3-propanesultone, as needed for modification of 25 %, 50% or 75 % of the DMAEMA amino groups. Since 1,3-propanesultone is a highly hygroscopic and deliquescent solid, it was handled and weighed in a glove box, and then transferred to previously conditioned flask. Further, 5 ml of dried THF (degassed as described above) were added to dissolve the propanesultone before transfer to the PDMS-*b*-PDMAEMA solution under N_2-flow. The copolymer concentration in the reaction medium was 10 wt.%.

Betainization proceeded at 40 °C for 48 h under continuous stirring and the final product was recovered by solvent evaporation and drying to constant weight at 60 °C under reduced pressure (yield: 98 %).

Dynamic Light Scattering (DLS)

Dynamic light scattering (DLS) studies were performed at 25±0.1 ºC using a Malvern CGS-3 system at a scattering angle of 90 º. The experimental data were analyzed by the CONTIN method, which is based on an inverse-Laplace transformation of the data and which gives access to a size distribution histogram for the analyzed micellar solutions. A He-Ne laser operating at 633 nm wavelength and 17 mW power was used as light source.

Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) spectroscopy

FTIR analyses were performed using a BioRad Excalibur Spectrophotometer equipped with a Split-Pea® ATR (Si crystal) accessory (Harrick, USA). The spectra were recorded from 4000 cm^{-1} to 700 cm^{-1} with spectral resolution of 4 cm^{-1} using a Peltier-cooled DTGS detector. All samples were dried under reduced pressure prior to analysis.

Thermogravimetric (TGA) and evolved gas analysis (EGA)

Thermogravimetric analyses were carried out in a TA Instruments TGA Q50 device operating at 10 $°C\cdot min^{-1}$ under He and using ca. 10 mg sample in Pt pans.

The products of thermal degradation were investigated by EGA (evolved gas analysis) using a Hi-Res™ TGA 2950CE from TA Instruments (using He as purge gas and with a heating rate of 20 $°C\cdot min^{-1}$) simultaneously coupled to a BioRad Excalibur FTIR Spectrophotometer (equipped with a gas cell heated at 225 °C and an MCT detector cooled down by liquid N_2) and a Thermostar quadrupolar mass spectrometer from Balzers Instruments covering a mass range from 10 to 300 amu. Evolved gases were ionized by electron impact (70 eV) [29].

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