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European Polymer Journal 41 (2005) 1187–1195
EUROPEAN POLYMER JOURNAL
www.elsevier.com/locate/europolj

Amphiphilic poly(*N*,*N*-dimethylamino-2-ethyl methacrylate)-g-poly(ε-caprolactone) graft copolymers: synthesis and characterisation

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Received 10 November 2004; received in revised form 20 December 2004; accepted 20 December 2004
Available online 28 January 2005

Abstract

Amphiphilic poly(*N*,*N*-dimethylamino-2-ethyl methacrylate)-g-poly(ε-caprolactone) graft copolymers (PDMAEMA-g-PCL) with various compositions and molecular weights were synthesised via a fully controlled three-step strategy. First, poly(ε-caprolactone) macromonomers (PCLMA) were prepared by ring-opening polymerization (ROP) of ε-caprolactone (CL) initiated by aluminum triisopropoxide ($Al(O^iPr)_3$), followed in a second step by quantitative esterification of PCL hydroxy end-groups with a methacrylic acid derivative. Finally, the controlled copolymerization of PCLMA and *N,N*-dimethylamino-2-ethyl methacrylate (DMAEMA) was carried out by atom transfer radical polymerisation (ATRP) in THF at 60 °C using CuBr ligated with 1,1,4,7,10,10, hexamethyl triethylenetetramine and ethyl 2-bromoisobutyrate as catalyst and initiator, respectively. Furthermore, PDMAEMA-g-PCL graft copolymers were reacted with methyl iodide to convert the pendant tertiary amines into quaternary ammonium iodides increasing accordingly their water solubility. Some preliminary experiments was further carried out by tensiometry and dynamic light scattering in order to shed so light on the tensioactive behaviour of these amphiphilic graft copolymers (with protonated amines or quaternary ammonium cations).

Keywords: Amphiphilic graft copolymers; Atom transfer radical polymerization; Macromonomer; Copolymerization; Tensioactive properties

1. Introduction

The discovery of new mechanisms allowing the polymerization process to be under control has paved the way to new macromolecular architectures. Recently, considerable progress has been made in the design and synthesis of new graft copolymers by metal-catalyzed radical polymerization, most of them being obtained by copolymerization of an unsaturated macromonomer with a low molecular weight vinyl comonomer [1,2]. Compared to conventional free radical polymerization, the graft copolymers obtained by atom transfer radical polymerization (ATRP) are usually more homogeneous in terms of molecular weight distribution (lower polydispersity index) and number of grafts pending along the main backbone. As far as the grafts distribution is concerned, it is dictated by the reactivity ratios of both the

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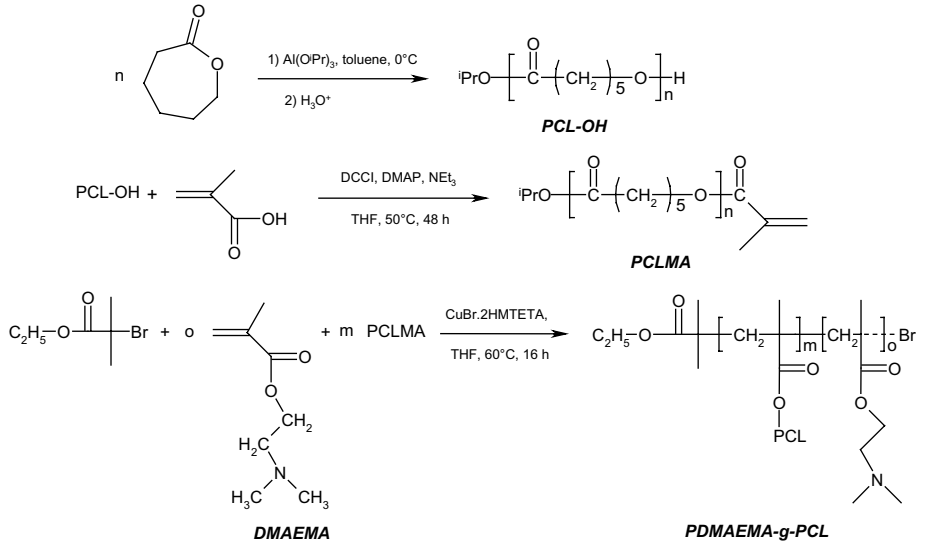
doi:10.1016/j.eurpolymj.2004.12.016

macromonomer and the low molecular weight comonomer. As a typical example Matyjaszewski et al. reported on the reactivity of (meth)acrylate-terminated polylactide macromonomers (PLAMA) in copolymerization with methyl methacrylate (MMA) in ATRP [3]. PLAMA reactivity proved to be similar to the inherent reactivity of the terminal 2-oxyethyl (meth)acrylate group, whatever the length of the attached PLA chain, attesting for the absence of diffusion control effect or simply incompatibility effect. Indeed, the two main factors that may reduce the reactivity of PLAMA compared to MMA are the kinetic excluded volume effect associated with the large size of the macromonomer relative to the free radical lifetime [4,5] and the potential incompatibility of the incoming macromonomer and grafted propagating chain due to thermodynamic repulsive interactions [6]. Furthermore in case of functionalized (macro)monomers containing for instance donor atoms such as N or O atom, their coordination to the transition-metal catalyst may also affect the reactivity ratios by either altering the electronic structure of the double bond, or simply through some mass effect [7]. In that respect, Haddleton et al. have copolymerized MMA with either various aminoethyl methacrylate monomers or poly(ethylene glycol) macromonomers (PEGMA) characterised by different molar masses, the reactivity ratio toward MMA comonomer was significantly reduced in ATRP compared to free radical copolymerisation [8]. Similarly, some of us have observed that functional monomers such as 2-hydroxyethyl methacrylate and PEGMA (with Mn of ca. 450), were preferably incorporated into growing copolymer chains with MMA by using $NiBr_2(PPh_3)_2$ and ethyl 2-bromoisobutyrate as catalyst and initiator, respectively, in toluene at 85 °C [9].

Here we aim reporting on the controlled synthesis and characterisation of new amphiphilic poly(*N*,*N*-dimethylamino-2-ethyl methacrylate)-g-poly(ε-caprolactone) graft copolymers (PDMAEMA-g-PCLMA) by ATRP between preformed poly(ε-caprolactone) macromonomer (PCLMA) and *N*,*N*-dimethylamino-2-ethyl methacrylate (DMAEMA) as functional comonomer. To the best of our knowledge, such amphiphilic graft copolymers with a pH and temperature sensitive water soluble poly(aminomethacrylate) backbone [10] and biodegradable aliphatic polyester grafts have never been synthesized, nor their tensioactive properties investigated by tensiometry and dynamic light scattering. It is worth mentioning that such polycations carrying a low content of hydrophobic side chains are of increasing interest for their properties in water solution and applications such as flocculants, thickening agents, latex particles, cosmetics, gene therapy, etc. [11,12]. Practically, the synthesis of PCLMA macromonomers has been first carried out according to a previously reported method [13] consisting of the controlled ring-opening polymerization (ROP) of ε-caprolactone (CL) initiated by aluminum triisopropoxide ($Al(O^iPr)_3$), followed by the quantitative esterification of ω-hydroxy groups by methacrylic acid derivatives. Then, the controlled copolymerization of PCLMA and DMAEMA was carried out by ATRP in THF at 60 °C using CuBr ligated with 1,1,4,7,10,10, hexamethyl triethylenetetramine and ethyl 2-bromoisobutyrate as catalyst and initiator, respectively (Scheme 1). PDMAEMA-g-PCL graft copolymers have also been reacted with CH_3I to convert tertiary



Scheme 1. Three-step synthesis pathway of poly(*N*,*N*-dimethylamino-2-ethyl methacrylate)-g-poly(ε-caprolactone) (PDMAEMA-g-PCL).

amines into quaternary ammonium iodides accordingly increasing their water solubility.

2. Experimental part

2.1. Materials

ε-Caprolactone (CL, from Acros, 99%) was dried over calcium hydride for 48 h at room temperature and distilled under reduced pressure just before use. Aluminum triisopropoxide ($Al(O^iPr)_3$, from Acros, 98%) was distilled under vacuum, quenched in liquid nitrogen, rapidly dissolved in dry toluene and stored under nitrogen. Accurate concentration was determined by back complexometric titration of Al^{3+} using ethylenediaminetetraacetic acid disodium salt and $ZnSO_4$ at pH 4.8. Methacrylic acid (from Acros, 99.5%) was dried over $MgSO_4$ at r.t. for 24 h and distilled under reduced pressure before use. *N,N′*-dicyclohexylcarbodiimide (DCCI, from Acros, 99%), *N,N*-dimethylamino-4-pyridine (DMAP, from Acros, 99%), ethyl 2-bromoisobutyrate (EB^iB, from Aldrich, 98%), 1,1,4,7,10,10 hexamethylenetetramine (HMTETA, from Aldrich, 97%) and copper bromide (CuBr, from Fluka, 98%) were used as received. Triethylamine (from Fluka, 99%) was dried over barium oxide for 48 h at r.t. and distilled under reduced pressure. *N,N*-dimethylamino-2-ethyl methacrylate (DMAEMA, from Aldrich, 98%) was passed through a column of basic alumina to remove the stabilizing agents and stored under nitrogen at −20 °C. Toluene (Labscan, 99%) and tetrahydrofuran (THF) (Labscan, 99%) were dried by refluxing over CaH_2 and Na/benzophenone complex, respectively, and distilled just before use.

2.2. Synthesis of α-isopropoxy, ω-hydroxy - poly(ε-caprolactone) (PCL-OH)

In a previously dried and nitrogen purged round bottom flask equipped with a three-way stopcock and a rubber septum, 30 ml (0.27 mol) of ε-caprolactone was added to 200 ml of freshly dried toluene. The solution was then maintained at 0 °C before adding 10 ml (18 mmol) of triisopropoxide in toluene solution (1.8 mol L^{-1}). After 10 min, the reaction was stopped by adding a few drops of an aqueous HCl solution (1 mol L^{-1}). The polymer was then selectively precipitated in a large volume of cold heptane, filtrated and dried under reduced pressure until constant weight. Al residues were extracted by liquid/liquid extraction by washing the polyester solution in chloroform once with an aqueous ethylenediaminetetraacetic acid solution buffered at pH = 4.8 (0.1 mol L^{-1}) and twice with water. The organic layer was finally poured into cold heptane to recover the α-isopropoxy, ω-hydroxy-poly(ε-caprolactone) by precipitation.

2.3. Synthesis of α-isopropoxy, ω-methacrylate - poly(ε-caprolactone) (PCLMA)

Freshly dried methacrylic acid (9 ml, 105 mmol) and *N,N′*-dicyclohexylcarbodiimide (10.86 g, 52 mmol) were dissolved in dried THF (100 ml) at r.t. The mixture was stirred at 0 °C for 6 h until dimethacrylic anhydride formation. In another previously dried and nitrogen purged round bottom flask equipped with a three-way stopcock and a rubber septum flask, 20 g of PCL-OH (11 mmol, M_n = 1850 g mol^{-1}) and 0.51 g of *N,N*-dimethylamino-4-pyridine (4.2 mmol) were previously dried by three consecutive toluene azeotropic distillations before adding dried THF (100 ml) and triethylamine (15 ml, 105 mmol). This latter mixture was slowly added to the solution of dimethacrylic anhydride and the temperature rose up to 50 °C. After 48 h, the precipitated dicyclohexylurea was filtered off and the α-isopropoxy ω-methacrylate-poly(ε-caprolactone) (PCLMA) was recovered by selective precipitation in a large volume of cold methanol, filtration and drying under reduced pressure at 40 °C until constant weight.

2.4. Synthesis of poly(N,N-dimethylamino-2-ethyl methacrylate)-g-poly(ε-caprolactone)) (PDMAEMA-g-PCL)

0.045 g of CuBr (0.31 mmol) and 0.139 g of 1,1,4,7,10,10 hexamethylenetetramine (0.62 mmol) and a magnetic stirrer were introduced in open air into a glass tube which was then closed by a three-way stopcock capped by a rubber septum and purged by three repeated vacuum/nitrogen cycles. Typically, 0.24 g of PCLMA (0.12 mmol, M_n = 2000 g mol^{-1}), 6.6 ml of THF and 4.6 ml of *N,N*-dimethylamino-2-ethyl methacrylate (29 mmol) were introduced in a dry round bottom flask and bubbled with nitrogen before transferring the mixture into the glass tube placed in an oil bath maintained at 60 °C. 1.2 ml (0.3 mmol) of degassed ethyl 2-bromoisobutyrate solution (0.25 mol L^{-1}) was added to the tube under nitrogen flow. After 16 h, the glass tube was cooled down to r.t. and its content was diluted with an extra volume of THF. The copolymer was recovered by precipitation from cold heptane. Comonomer conversion was determined by combining gravimetry and ^1H NMR spectroscopy. After extraction of the copper catalyst by passing the copolymer in THF solution through a column of basic alumina, the purified copolymer was recovered by precipitation in cold petroleum ether, filtration and drying under reduced pressure at 40 °C until constant weight.

2.5. Quaternization of tertiary amino groups in PDMAEMA-g-PCL copolymers (PTMAEMA-g-PCL)

Typically, 500 mg of PDMAEMA-g-PCL copolymer (3 mmol tertiary amine) were introduced in a round

bottom flask and dissolved in THF (20 ml) under stirring at room temperature. Then, a CH_3I (3.2 mmol) solution in THF (20 ml) was added drop wise. After 18 h, the precipitated quaternized copolymer was recovered by volatilizing the solvent and residual CH_3I.

2.6. Characterization

^{1}H-NMR spectra were recorded using a Bruker AMX-300 or AMX-500 apparatus at r.t. in $CDCl_3$ (30 mg/0.6 mL). Size exclusion chromatography (SEC) was performed in THF (poly(ε-caprolactone)) or THF + 2 wt% NEt_3 (DMAEMA containing copolymers) 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 10 μm columns (linear columns for separation of MW_{PS} ranging from 500 to 10^6 daltons). Poly(styrene) standards were used for calibration. FTIR spectra were recorded from 4000 to 700 cm^{-1} using a Bio-Rad Excalibur spectrometer equipped with an ATR Harrick Split Pea^{TM} from S.A.F.I.R. DSC measurements were carried out with a 2920 CE DSC from TA Instruments under nitrogen flow (heating rate 10 °C/min). The surface tensions were determined at 25 °C using a Drop Shape Analysis System DSA 10 Mk2 equipped with a thermostated chamber and a Circulator Thermo HAAKE DC 10. Dynamic light scattering measurements were carried out using a BI-160 apparatus (Brookhaven Instruments Corporation, USA) with a He–Ne laser source operating at 17 mW and delivering a vertically polarized light (λ = 633 nm) after previous filtration of the aqueous copolymer solutions on 1.2 μm Acrodisk® filter. The particle sizes and size distribution were calculated using CONTIN algorithms.

3. Results and discussion

3.1. Synthesis and characterization of PDMAEMA-g-PCL graft copolymers

The synthesis of amphiphilic poly(*N*,*N*-dimethylamino-2-ethyl methacrylate)-g-poly(ε-caprolactone) graft copolymers (PDMAEMA-g-PCL) with various compositions has been carried out following a three-step strategy consisting of the controlled ring-opening polymerization (ROP) of ε-caprolactone (CL) initiated by aluminum triisopropoxide ($Al(O^iPr)_3$) to selectively form α-isopropyloxy ω-hydroxy poly(ε-caprolactone) chains (PCL-OH), followed by the quantitative conversion of PCL-OH into α-isopropyloxy, ω-methacrylate poly(ε-caprolactone) macromonomer (PCLMA) and the simultaneous controlled copolymerization of *N*,*N*-dimethylamino-2-ethyl methacrylate (DMAEMA) and PCLMA by ATRP (Scheme 1). In order to facilitate the dissolution of PDMAEMA-g-PCL graft copolymers in water, the length of the hydrophobic PCL grafts has been kept short enough by initiating the ROP of CL by $Al(O^iPr)_3$ for an initial monomer-to-initiator molar ratio of 15 in toluene at 0 °C. In perfect agreement with a living coordination-insertion mechanism ($M_{n\,theor}$ = $[CL]_0/[Al(O^iPr)_3]_0 \times MW_{CL} \times$ conv. = 1800), the experimental number average molar mass (M_n) of the recovered PCL-OH chains reaches 1850 g mol^{-1} at complete monomer conversion while the molecular weight distribution is kept narrow (M_w/M_n = 1.26). M_n has been determined by ^{1}H NMR spectroscopy (300 MHz, $CDCl_3$) from the relative intensity of methylene protons of the repetitive units at 2.3 ppm (–CH_2–C(O)O–) and ω-hydroxy end-groups at 3.63 ppm (–CH_2–OH). In a next step, the PCL hydroxyl end-group has been reacted with preformed methacrylic anhydride in THF at 50 °C for 48 h in the presence of NEt_3 and *N*,*N*-dimethylamino-4-pyridine as catalyst. Methacrylic anhydride has been obtained by reacting methacrylic acid with *N*,*N*′-dicyclohexylcarbodiimide (DCCI) in THF at 0 °C for an initial $[\text{methacrylic acid}]_0/[\text{DCCI}]_0$ molar ratio of 2. In such conditions, the appearance of dicyclohexylurea precipitate is instantaneous and shifts the equilibrium reaction toward the formation of the anhydride. It is worth mentioning that these reactions have been sheltered from light to avoid photochemically induced polymerization of methacrylic derivatives. Fig. 1 shows the ^{1}H NMR spectrum of PCLMA as recovered after dicyclohexylurea filtration and selective precipitation in cold methanol (yield ~ 80%). The signal assigned to PCL ω-hydroxymethylene protons (–CH_2OH) at 3.63 ppm has completely disappeared to the benefit of ω-methylene methacrylate protons (–CH_2–C(O)O–CH(CH_3)=CH_2) at 4.14 ppm. It is also worth pointing out that the intensities of α-isopropyloxy methine proton at 5.1 ppm (Hb) and ω-methacrylate protons at 5.6 and 6.1 ppm (Hi and Hj) are comparable which gives credit to the quantitative formation of PCLMA macromonomer. Mn of PCLMA reaches 2000 g mol^{-1} as determined from the relative intensity of methylene protons of the repetitive units at 2.3 ppm (–CH_2–C(O)O–) and ω-methacrylate end-groups (–CH_2–C(O)O–CH(CH_3)=CH_2) at 5.6 and 6.1 ppm. The slight increase in PCL number average molar masses from 1850 (PCL-OH) to 2000 g mol^{-1} (PCLMA) can be attributed to a slight low molar masses fractionation during precipitation in cold methanol (recovery yield ~ 80%). As a result, the polydispersity is slightly decreased (M_w/M_n = 1.18 compared to 1.26 for PCL-OH). The actual formation of PCLMA macromonomer has also been confirmed by FTIR spectroscopy which

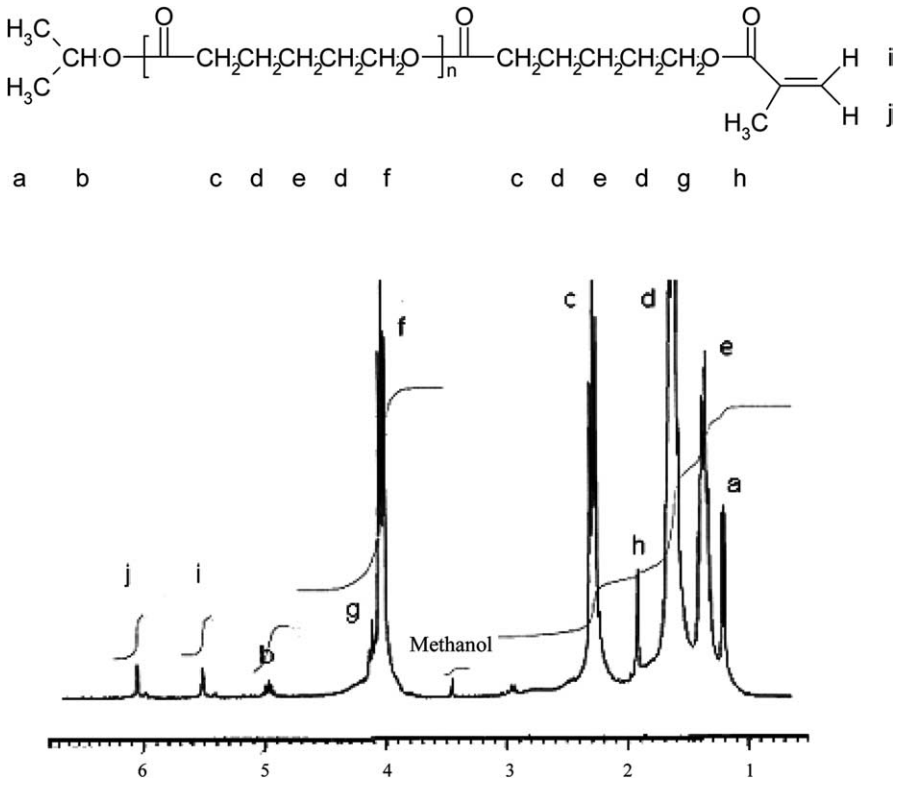


Fig. 1. ^{1}H NMR spectrum of α-isopropyloxy, ω-methacrylate poly(ε-caprolactone) macromonomer (PCLMA).

shows a typical band at 1625 cm^{-1} corresponding to the C=C stretching of methacrylate end-groups. The third step in the synthesis of PDMAEMA-g-PCL graft copolymers consists of the simultaneous copolymerization of PCLMA and DMAEMA by ATRP. Quite recently, Matyjaszewski et al have reported the controlled synthesis of poly(*N*,*N*-dimethylamino-2-ethylmethacrylate) and block copolymers thereof using copper bromide complexed by multidentate tertiary amino ligands as catalysts and ethyl 2-bromoisobutyrate (EB^{i}B) as initiator in a variety of solvents [14,15]. Accordingly, we have realized the copolymerization under similar conditions using 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) as ligand in THF at 60 °C for [PCLMA+DMAEMA]$_0$/[EB^{i}B]$_0$/[CuBr]$_0$/[HMTETA]$_0$ initial molar ratios of 100/1/1/2 and 200/1/1/2, respectively (Table 1). Initial weight fractions in PCLMA were maintained in between 5 and 15 wt%. Acronyms are used in Table 1 in which the superscript denotes the PCL initial weight fraction and the subscript recalls the molar mass of PCLMA in kg mol^{-1}. After 16 h, the copolymer solution was cooled down to r.t. and poured into a large excess of petroleum ether. The resulting precipitate is mainly composed by PDMAEMA-g-PCL graft copolymer but it may also contain some traces of unreacted PCLMA that is insoluble in such a low polarity solvent. In order to extract the catalyst, the reaction product has been dissolved in THF and passed through a basic alumina column. After complete volatilization of the solvent, ^{1}H NMR spectrum (500 MHz) of the recovered product was recorded in $CDCl_3$ (Fig. 2). Whatever the initial feed composition, it is worth pointing out that no trace of PCLMA could be detected as evidenced by the absence of ω-methacrylate end-groups (–CH_2-C(O)O-CH(CH_3)=CH_2) at 5.6 and 6.1 ppm. In other words, comonomer conversion could be calculated by gravimetry from the following relationship: $\text{Conv} = [(m_{\text{crude}} - m_{\text{cat}} - m_{\text{init}})/(m_{\text{à,PCLMA}} + m_{0,\text{DMAEMA}})] \times 100$ where m_{crude}, m_{cat}, m_{init}, $m_{0,\text{PCLMA}}$,

Table 1
Copolymerization of DMAEMA and PCLMA catalysed by CuBr.2HMTETA in THF at 60 °C for 16 h

PDMAEMA-g-PCL	[DMAEMA]$_0$ (mol L^{-1})	[PCLMA]$_0$ (mmol L^{-1})	[M]$_0$/[EB^{i}B]$_0$
C_2^5	2.32	9.7	100
C_2^{10}	2.32	20.0	100
C_2^{15}	2.32	32.0	100
C_2^{5*}	2.32	9.7	200

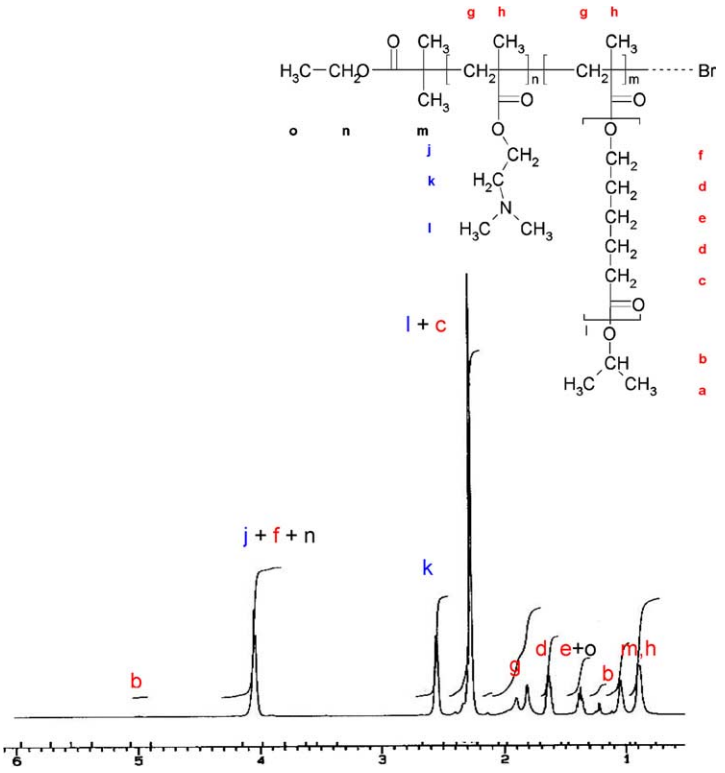


Fig. 2. ^{1}H NMR spectrum of poly(*N*,*N*-dimethylamino-2-ethyl methacrylate)-g-poly(ε-caprolactone) (PDMAEMA-g-PCL) (C_2^{15} in Table 2).

Table 2
Comonomer conversion and molecular characteristics of PDMAEMA-g-PCL graft copolymers

P(DMAEMA-g-PCL)	Conversion[a] (%)	fw_{PCLMA}[b]	Fw_{PCLMA}[c]	M_n[d] (g mol^{-1})	M_w/M_n[d]
C_2^5	0.66	0.05	0.06	23900	1.21
C_2^{10}	0.68	0.10	0.14	22000	1.25
C_2^{15}	0.68	0.15	0.19	21800	1.28
C_2^{5*}	0.60	0.05	0.08	25800	1.28

[a] Comonomer conversion as determined by gravimetry, $Conv = [(m_{crude} - m_{cat} - m_{init})/(m_{à,PCLMA} + m_{0,DMAEMA})] \times 100$.

[b] Initial weight fraction in PCLMA, $fw_{PCLMA} = m_{PCLMA}/(m_{PCLMA} + m_{DMAEMA})$ where m_{PCLMA} and m_{DMAEMA} are the macromonomer and DMAEMA weights in the feed.

[c] Effective weight fraction in PCLMA as determined by ^{1}H NMR spectroscopy, Fw_{PCLMA}:$[(I_{j+f+n} - I_k)/DP_{nPCLMA}] \times M_{nPCLMA}/[[[(I_{j+f+n} - I_k)/DP_{nPCLMA}] \times M_{nPCLMA}] + [I_k \times M_{nDMAEMA}]]$.

[d] Molecular weight parameters as determined by SEC in THF + 2 wt% NEt_3 with reference to a polystyrene calibration.

$m_{0,DMAEMA}$ are the weights of crude copolymerization product, complex catalyst, initiator, PCLMA and DMAEMA, respectively (Table 2). Table 2 also shows the effective weight fractions of PCL in the graft copolymers (Fw_{PCLMA}) as determined by ^{1}H NMR spectroscopy (500 MHz) from the intensities of methylene protons of DMAEMA repetitive units (Hj, Hk) compared to methylene protons of CL repetitive units (Hf), knowing the initial molar mass and polymerization degree of PCLMA (M_{nPCLMA} and DP_{PCLMA}, respectively) (see Fig. 2). Very interestingly, it comes out that Fw_{PCLMA} is close or even slightly higher than the initial weight fraction in PCLMA (f_{WPCLMA}) though monomers conversion is typically lower than 70%. This is consistent with a preferred incorporation of the macromonomer into the growing copolymer chains or a reduced reactivity toward DMAEMA. Such a behavior gives credit to the effect of functional monomer able to coordinate to the transition-metal catalyst on the reactivity ratios [8]. Furthermore, this is consistent with the formation of graft copolymers with a palm-tree like structure, i.e., with a higher proportion of the polyester

grafts close to the initiator residue extremity. As far as differential scanning calorimetry is concerned, it can be noted that whatever the PCL content, PDMAEMA-g-PCL graft copolymers do not exhibit the melting endotherm characterizing the starting PCLMA at 42 °C. This might result from the palm-tree architecture and the steric hindrance of dangling PCL grafts. Last but not least, size exclusion chromatography shows a shift toward higher elution volume for graft copolymers compared to PCLMA macromonomer while polydispersity remains narrow ($M_w/M_n < 1.3$) (Fig. 3).

Beyond the controlled synthesis of PDMAEMA-g-PCL graft copolymers, it was of interest to shed some light on their amphiphilic behaviour and tensioactive properties. Some preliminary experiments have been carried out by tensiometry and dynamic light scattering. Due to the fact that PDMAEMA-g-PCL graft copolymers containing more than 6 wt% PCLMA proved poorly soluble in both water (Millipore-grade) and up to 0.5 mol L^{-1} acetic acid/sodium acetate aqueous buffer, quaternization of tertiary amino groups by reaction with a slight excess of methyl iodide has been carried out in THF at r.t. for 18 h (Scheme 2) [16]. Quantitative

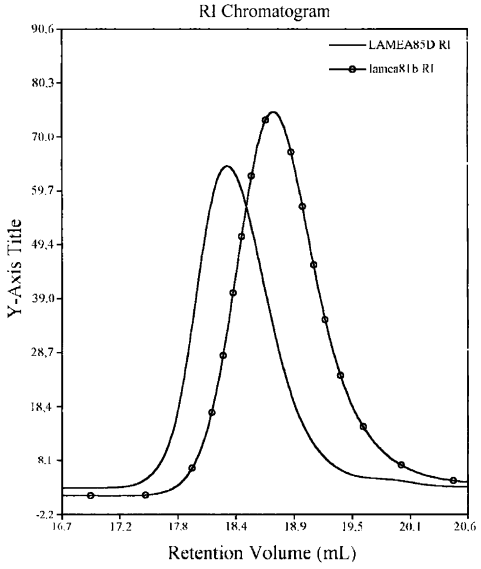


Fig. 3. SEC of PDMAEMA-g-PCL (full line, C_2^{5*} in Table 2) and PCLMA (full line with sphere).

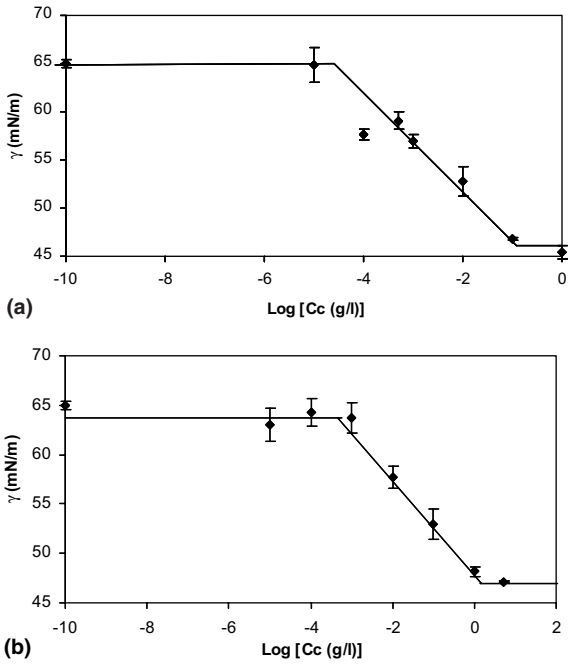
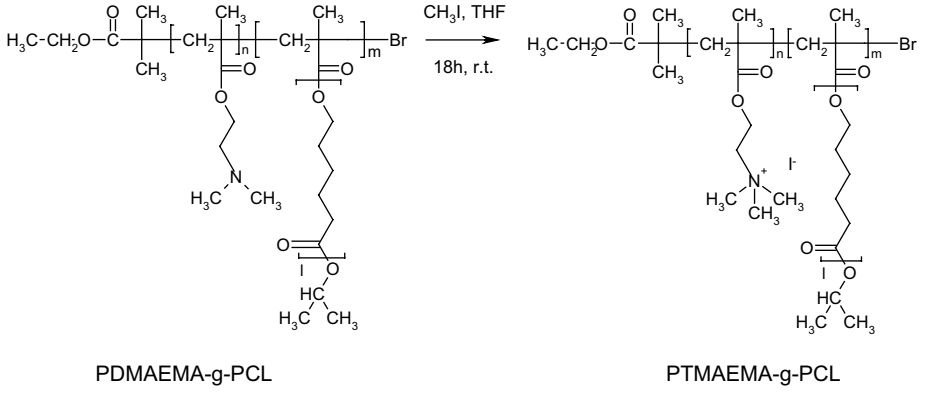


Fig. 4. Semilogarithmic plots of the surface tension (γ) *vs.* concentration (in g/l) of (a) C_2^5 PDMAEMA-g-PCL and (b) quaternized C_2^5 PTMAEMA-g-PCL in an acetic acid/sodium acetate aqueous buffer (pH = 4.8).



Scheme 2. Conversion of PDMAEMA-g-PCL into PTMAEMA-g-PCL graft copolymer.

quaternization and thus formation of poly(*N*,*N*,*N*-trimethylammonium-2-ethyl methacrylate iodide)-g-poly(ε-caprolactone) graft copolymers (PTMAEMA-g-PCL) has been demonstrated by ^{1}H NMR spectroscopy in D_2O from the up-field shift of α-methylene, β-methylene, and α-methyl amino protons (from 2.55, 4.06 and 2.65 ppm to 3.90, 4.55 and 3.40 ppm, respectively) (NMR spectrum not shown here).

3.2. Insight on the tensioactive properties of graft copolymers

Therefore, copolymer solutions have been prepared by dissolution in an acetic acid/sodium acetate aqueous buffer (0.5 mol L^{-1}) 24 h before measurements and then maintained at 25 °C for at least 30 min to reach equilibrium temperature. First, the concentration dependence of surface tension (γ, expressed in mN m^{-1}) has been examined according to the pendant drop method for PDMAEMA-g-PCL copolymer (C_2^5 in Table 2) and PTMAEMA-g-PCL (quaternized C_2^5) at 25 °C. In Millipore water, none of the PDMAEMA-g-PCL graft copolymers was soluble for an initial concentration of 1 g L^{-1} which prompts us to use an acetic acid/sodium acetate aqueous buffer with a concentration high enough to counterbalance the basicity of DMAEMA repeating units. Indeed, it is worth recalling that PDMAEMA is characterized by a p*K*a of 7.4 [17] so that in an acetic acid/sodium acetate aqueous buffer (pH = 4.8) most of the tertiary amino groups are in the ammonium acetate form. Fig. 4a and b show the semilogarithmic plots of the γ *vs.* [C_2^5] and [quaternized C_2^5], respectively. The critical aggregation concentration (cac) has been determined from the intersection between the straight lines from higher concentration portions of the linear plot [18,19]. The surface pressure (π_{cac}) is defined as the difference between the surface tension of the aqueous buffer (γ_0) and the surface tension at cac (γ_{cac}) ($\pi_{cac} = \gamma_0 - \gamma_{cac}$). It comes out that cac is somewhat lower for PDMAEMA-g-PCL copolymer (cac ≅ 0.1 g L^{-1}) compared to PTMAEMA-g-PCL (cac ≅ 1 g L^{-1}) while π_{cac} remains close 20 mN m^{-1}. Such behaviour might be related to the higher hydrophilicity of the quaternized copolymer. Anyway, these data attest for the effective-

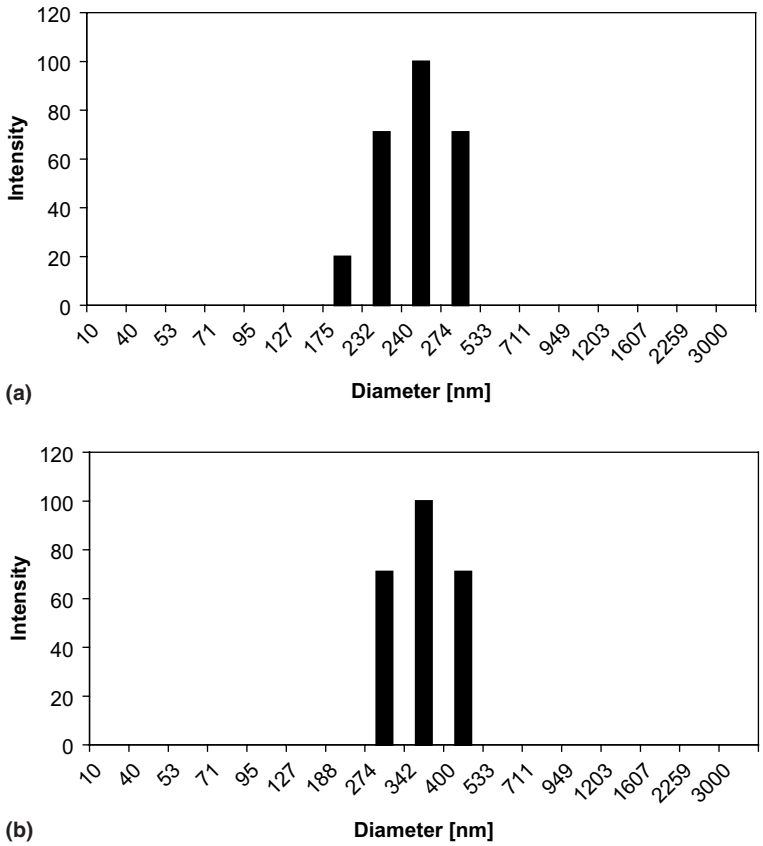


Fig. 5. Size distribution of PDMAEMA-g-PCL C_5^2 micellar aggregates in water at pH 4.8 for various concentrations: (a) 0.1 g L^{-1} and (b) 1.0 g L^{-1}.

ness of both PDMAEMA-g-PCL and PTMAEMA-g-PCL as tensioactive agents. Furthermore, first measurements by dynamic light scattering have been realized on C_5^2 graft copolymer at pH 4.8 ([acetic acid/sodium acetate] = 0.5 mol L^{-1}). Quite narrow and monomodal size distributions have been observed with apparent mean diameters of 240 and 340 nm for concentrations of 0.1 and 1 g L^{-1}, respectively (Fig. 5a and b). This may indicate that micellar structures are organized as aggregates whose size increases with the graft copolymer concentration.

4. Conclusions

New amphiphilic poly(*N*,*N*-dimethylamino-2-ethyl methacrylate)-g-poly(ε-caprolactone) graft copolymers (PDMAEMA-g-PCLMA) have been synthesised by atom transfer copolymerization between poly(ε-caprolactone) macromonomer (PCLMA) and *N*,*N*-dimethylamino-2-ethyl methacrylate (DMAEMA). The interest of such macromolecular structure relies upon the presence of a water soluble (protonable) poly(aminomethacrylate) backbone covalently linked to biodegradable aliphatic polyester grafts. Clearly, the control of the molecular parameters, i.e., molecular weight, composition and/or amine quaternisation, allows for tuning up the tensioactive behaviour of these amphiphilic copolymers as highlighted by some preliminary tensiometry and dynamic light scattering experiments.

Acknowledgments

Authors are very grateful to "Région Wallonne" and European Community (FEDER, FSE) for general support in the frame of "Objectif 1-Hainaut: Materia Nova". This work was partly supported by the Belgian Federal Government Office of Science Policy (SSTC-PAI 5/3). L. Mespouille is much indebted to the Belgian F.N.R.S (Fonds National de la Recherche Scientifique) for her PhD grant. Profs. R. Willem and M. Biesemans from Vrije Universiteit Brussel are thanked for access to their 500 MHz NMR spectrometer.

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