

Synthesis of pH- and thermo-responsive poly (ϵ -caprolactone-*b*-4-vinyl benzyl-*g*-dimethyl amino ethyl methacrylate) brush type graft copolymers via RAFT polymerization

Timur Şanal · Olgü Oruç · Temel Öztürk · Baki Hazer

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Abstract A novel pH- and thermo-responsive poly (ϵ -caprolactone-*b*-4-vinyl benzyl-*g*-2-(dimethyl amino ethyl) methacrylate), poly (CL-*b*-VB-*g*-DMAEMA), brush type copolymer has been described. In this study, a reversible addition–fragmentation chain transfer (RAFT) agent, 1,2-propanediol-3-ethyl xanthogenate, was obtained through the reaction of 3-chloro-1,2-propanediol with potassium salt of ethyl xanthogenate. Poly (CL-*b*-VB) block copolymer was synthesized in one-pot polymerization of ϵ -caprolactone (CL) and 4-vinyl benzyl chloride (VB) using a new dual macro-RAFT agent. In the second step of the work, chloride side groups of poly-VB in poly (CL-*b*-VB) block copolymer were reacted with potassium salt of ethyl xanthogenate to obtain another novel macro-RAFT agent, poly (CL-*b*-VB)-*g*-xanthate (PCL-PVB-Xa). Controlled free radical living polymerization of 2-(dimethylaminoethyl) methacrylate (DMAEMA) was initiated with this PCL-VB-Xa macro-RAFT agent to obtain new poly (CL-*b*-VB-*g*-DMAEMA) comb type pH- and thermo-responsive heterograft copolymer. The homopolymer was soluble in water at pH=10–11 and not soluble at pH=12.5. A pH-sensitive feature of the brush type graft copolymer was observed between pH9.4 and 11.5 in view of their swelling/solution properties depending on the acrylic polymer inclusion. The LCST values of the multiblock brush type copolymers were found to be as low as 42.8 °C, while that of PDMAEMA homopolymer was 46.6 °C. The characterization of the products was achieved using gel-

permeation chromatography (GPC), thermal, and spectrometric analysis techniques. pH- and thermo-responsiveness of the copolymers were verified by surface tension and zeta potential measurements.

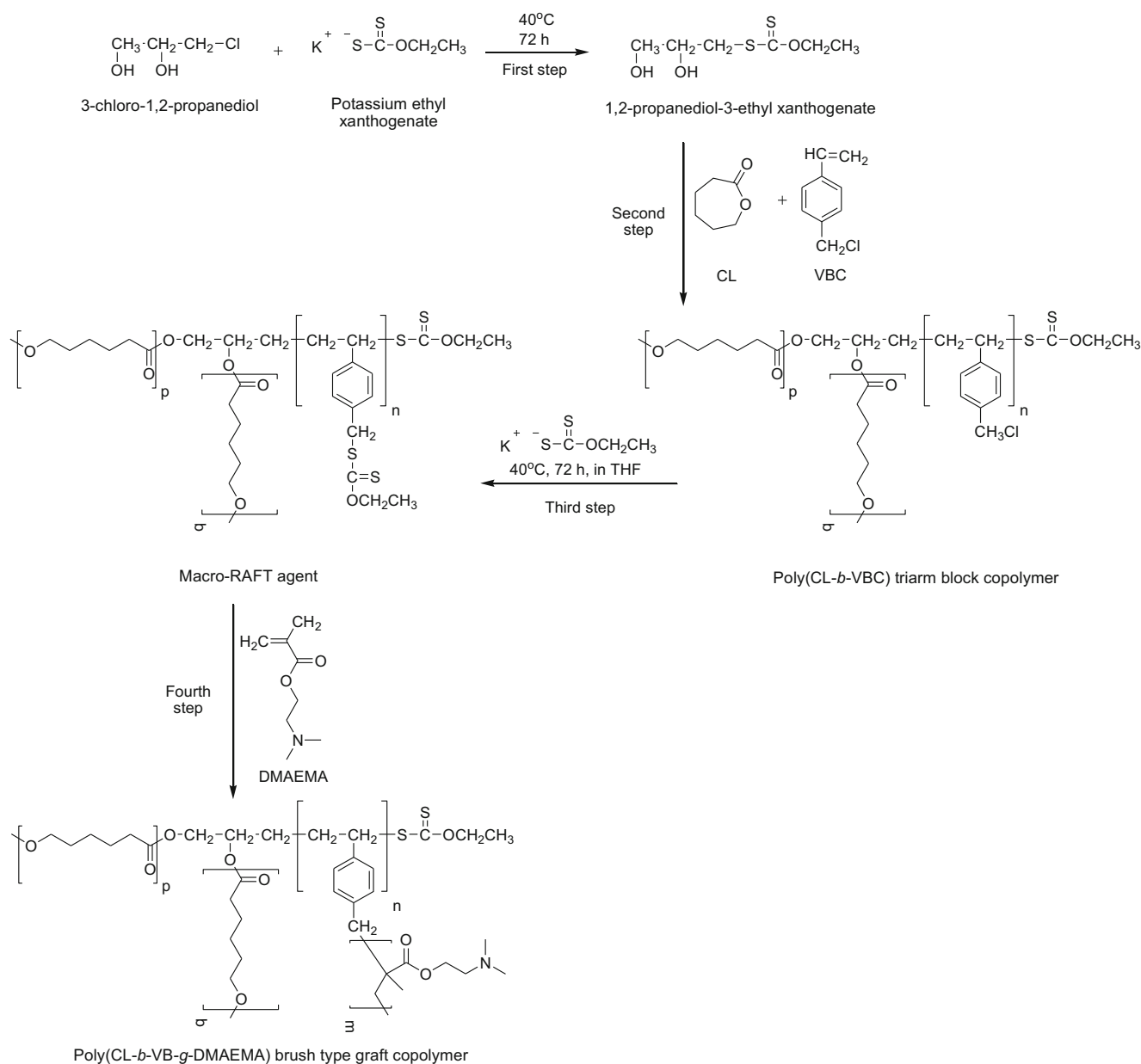
Keywords Graft/block copolymer · Reversible addition–fragmentation chain transfer (RAFT) polymerization · Ring-opening polymerization (ROP) · One-pot polymerization · Macro-RAFT agent · pH- and thermo-responsive polymer

Introduction

More than ever, there is pressure to offer polymers with tailored property profiles for industrial and medical applications in order to make daily life easy and simple. Block copolymers are two or more different polymer chains linked together and have long been used for this purpose [1–5]. Recent progress in synthetic polymer chemistry has unveiled unprecedented opportunities to prepare tailored block copolymers. Up to now, polymers with various kinds of architectures have been synthesized including linear, star shaped [6], tadpole shaped [7–9], comb type [10], brush type, hyperbranched [11–13], and dendrimer, since the properties of polymers are inherently dependent on their architectures [14, 15]. The increasing diversity in polymer architectures has offered versatility in developing novel polymer materials with unprecedented properties and functions [16]. The term “polymer brush” is broadly used as a synonym of the term “tethered polymer chain”. Polymers with comb-shaped architecture may also undergo microphase separation due to the repulsion between the backbone and the side chains. They may also exhibit the hierarchical structures with two distinct length scales [17–19]. When the distance between neighboring

T. Şanal · O. Oruç · B. Hazer (✉)
Department of Chemistry, Bülent Ecevit University,
Zonguldak 67100, Turkey
e-mail: bkhazer@beun.edu.tr

T. Öztürk
Department of Chemistry, Giresun University,
28100 Giresun, Turkey



Scheme 1 The reaction mechanism of the synthesis of poly (CL-*b*-VB-*g*-DMAEMA) brush type graft copolymer

grafting points is small, steric repulsion leads to chain stretching. At lower grafting densities, surface-tethered polymer chains can adopt various other conformations, which are referred to as mushroom or pancake, when the distance between neighboring grafting points is large enough [17]. Reversible addition-fragmentation chain transfer (RAFT) polymerization represents the most recently developed controlled radical-polymerization method and is a powerful technique for the macromolecular synthesis of a broad range of well-defined polymers [20–29]. The versatility of the method is proved by its compatibility with a very wide range of monomers and reaction conditions. Combination pathways of the

ring opening polymerization (ROP)/controlled radical polymerization (CRP) have been extensively used in the synthesis of graft copolymers in one step [30–41]. The dual initiators had two functional groups that could initiate ROP and reversible addition-fragmentation chain transfer (RAFT) polymerization independently and selectively.

In this study, a new pH- and thermo-responsive brush type of graft copolymer was synthesized in four steps via controlled living polymerization using a novel macro-RAFT agent based on poly (CL-*b*-VB). For this purpose, 1,2-propanediol-3-ethyl xanthogenate (RAFT agent) was prepared with the reaction of 3-chloro-1,2-propanediol (CPD) and

Table 1 Synthesis of poly (CL-*b*-VBC) triarm block copolymers

Code	CL (g)	VBC (g)	Time (h)	Yield (g)	M _n	M _w /M _n
PCL-VB-02*	2.06	2.16	10	2.0	7,042	1.31
PCL-VB-04*	10.03	10.08	12	13.2	-	-
PCL-VB-40**				7.2	16,672	1.56
PCL-VB-41***				6.0	6,765	1.20
PCL-VB-05*	10.03	2.16	12	9.1	-	-
PCL-VB-50**				7.4	12,786	1.79
PCL-VB-51***				1.7	6,409	1.22
PCL-VB-06*	10.03	10.08	14	10.0	-	-
PCL-VB-60**				4.4	13,439	3.12
PCL-VB-61***				5.6	6,807	1.22
PCL-VB-07*	10.03	2.16	14	6.5	-	-
PCL-VB-70**				4.1	7,219	2.10
PCL-VB-71***				2.4	4,974	1.64
PVBz-1*	-	2.16	12	1.18	4,132	1.20
PCL-VB-08*	10.03	16.20	14	13.1	7,578	2.08
PCL-VB-10*	5.15	10.08	14	8.0	6,667	1.79

RAFT agent=0.50 g; AIBN=0.10 g; polym. temp. = 90 °C; toluene=20 mL

* crude polymer

** first fraction

*** second fraction

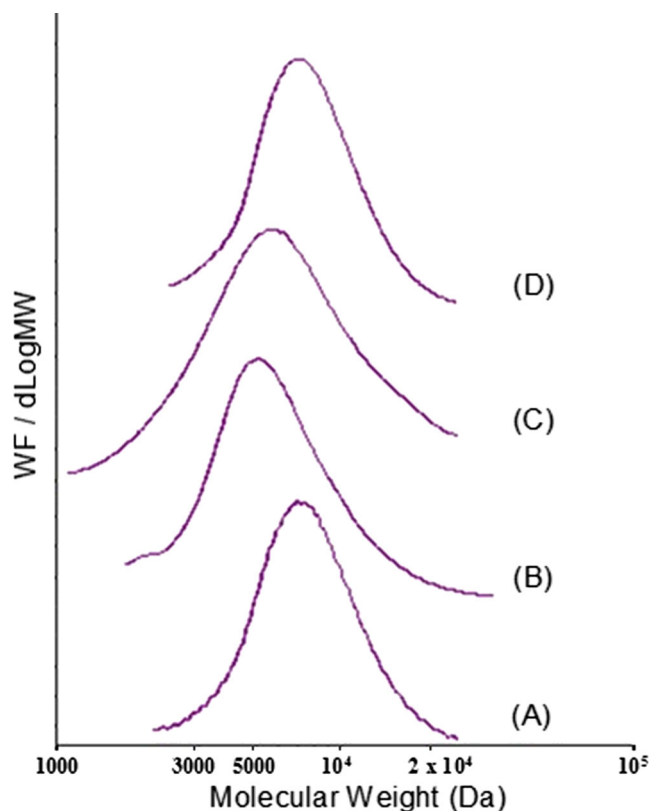


Fig. 1 GPC chromatograms of poly (CL-*b*-VBC) triarm block copolymers in Table 1 (A) PCL-VBC-41; (B) PCL-VBC-71; (C) PVBz-1; and (D) PCL-VBC-51

potassium salt of ethyl xanthogenate (EDTC). Poly (CL-*b*-VB) triarm block copolymers were synthesized using RAFT agent by the simultaneous RAFT and ROP of the reactants in one step. Macro-RAFT agent was prepared with the reaction of poly (CL-*b*-VB) triarm block copolymers and EDTC. The newly synthesized macro-RAFT agent initiated the RAFT polymerization of 2-(dimethylaminoethyl) methacrylate, (DMAEMA), in order to obtain poly (CL-*b*-VB-*g*-DMAEMA) brush type copolymer. The products obtained in each step were characterized by using spectrometric, thermal, and physicochemical methods.

Experimental

Materials

Potassium salt of ethyl xanthogenate, also referred to as potassium ethyl xanthate and potassium-O-ethyl dithiocarbonate (EDTC), was supplied from Alfa Aesar and used as received. 3-chloro-1,2-propanediol, CPD, was obtained from Sigma-Aldrich and used as received. 2,2'-azobisisobutyronitrile (AIBN) was supplied by Fluka A.G. and used as received. Diethyl ether was obtained from Sigma-Aldrich and used as received. 4-Vinyl benzyl chloride (VBC) was obtained from Sigma-Aldrich and passed through an Al₂O₃ column to remove the inhibitors before use. Tetrahydrofuran (THF) and

Table 2 Synthesis of macro-RAFT agent using PCL-*b*-PVBC and EDTC

Code	Poly (CL- <i>b</i> -VBC)		EDTC (g)	Yield (g)	M _n (g/mol)	M _w /M _n
	Code	(g)				
PCL- <i>b</i> -PVB40-Ksent	PCL- <i>b</i> -VBC40	2.30	9.26	6.23	6,420	1.33
PCL- <i>b</i> -PVB41-Ksent	PCL- <i>b</i> -VBC41	3.09	12.67	3.64	3,240	1.25
PCL- <i>b</i> -PVB50-Ksent	PCL- <i>b</i> -VBC50	0.80	3.26	0.89	7,124	1.26
PCL- <i>b</i> -PVB51-Ksent	PCL- <i>b</i> -VBC51	3.52	13.33	4.49	6,105	1.44

Polym. temp.=40 °C; polym. time=120 h; THF=10 mL

toluene were supplied by Sigma-Aldrich and distilled from sodium (Na). Tin (II) 2-ethylhexanoate was supplied by Sigma and used as received. Methanol was obtained from Riedel de Haen and used as received. Sodium (Na) was supplied by Sigma-Aldrich and used as received. 2-(Dimethylamino) ethyl methacrylate (DMAEMA) was obtained from Merck and passed through in Al₂O₃ column to remove the inhibitors before use. ϵ -caprolactone (CL) was supplied by Sigma-Aldrich and dried with anhydrous CaSO₄, then fractionally distilled. All other chemicals were reagent grade and used as received.

Instrumentation

The molecular weights and molecular weight distributions were measured with a Malvern Viscotek GPC and OmniSEC 4.7 Software Systems with THF as the solvent at a flow rate of 1 mL min⁻¹. A calibration curve was generated with eight polystyrene standards: 1.79 × 10⁶, 9.25 × 10⁵, 1.64 × 10⁵, 1.2 × 10⁵, 6.37 × 10⁴, 2.91 × 10⁴, 5.87 × 10³, and 955 g mol⁻¹, of low polydispersity. Fourier-transform infrared spectroscopy (FTIR) spectra were recorded using a Perkin Elmer Pyris model FTIR spectrometer. ¹H-nuclear magnetic resonance (¹H-NMR) spectra of the samples in CDCl₃ as the solvent, with tetramethylsilane as the internal standard, were recorded using a Bruker Ultra Shield Plus, ultra long hold time 400 MHz NMR spectrometer. Thermo gravimetric analyses (TGA) of the polymers were carried out using a SIIQ TG/DTA 7200 model instrument to determine thermal degradation. Dried sample was heated under nitrogen from 25 °C to 650 °C at a heating rate of 10 °C/min. Differential scanning calorimeter (DSC) traces of the polymer samples were obtained using a Perkin Elmer DSC 8000 series thermal analysis system. Dried sample was heated under nitrogen atmosphere from -50 to 250 °C at a rate of 10 °C/min. UV-VIS spectra of the polymer samples were recorded using an Agilent Cary 60 UV-vis Spectrophotometry. Surface tension values of the copolymers were measured via Du Nouy method using PHYWE P2140500 set. The zeta potential ζ of the samples

were at 25 °C with a Brookhaven Zeta Plus Zetasizer. pH values were measured with a “Hanna” pH-meter; HI 83141 was used to measure the pH values of the aqueous solution of the polymers.

Synthesis of RAFT agent (1, 2-propanediol-3-ethyl xanthogenate) (RA-1)

The same procedure described in the cited literature was applied to synthesize the RAFT agent [39]. For example, a mixture of 3.01 g of CPD and 6.01 g of EDTC in 45 mL of THF was stirred at 40 °C for 72 h under argon. The solution was filtered to remove the unreacted xanthate, and the solvent was removed by a rotary evaporator. For further purification, the solid product was redissolved in THF and poured into distilled water by continuous stirring with a glass rod. The solid precipitate was collected from the mixture after 24 h, then dried under vacuum at room temperature for 24 h.

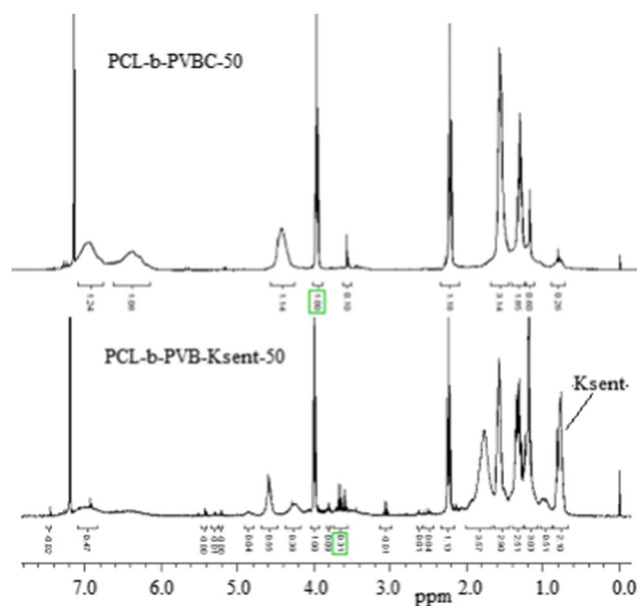


Fig. 2 /The ¹H NMR spectra of PCL-*b*-PVB-50 and PCL-*b*-PVB-Ksent-50

Table 3 Synthesis of PCL-*b*-PVB-*g*-PDMAEMA heterograft copolymers via RAFT polymerization at 90 °C for 14 h in toluene (5 mL) in the presence of AIBN (40 mg)

Code	PCL- <i>b</i> -VB-Ksent						
	Code	(g)	Mn (g/mol)	DMAEMA (g) wt%	Yield (g)	Mn (g/mol)	Mw
PCL- <i>b</i> -PVB- <i>g</i> -PDMAEMA-1 ₂₂	PCL- <i>b</i> -VB40	0.50	6,420	1.87 79	1.08	9,871	1.01
PCL- <i>b</i> -PVB- <i>g</i> -PDMAEMA-5 ₆₃	PCL- <i>b</i> -VB40	1.00	6,420	7.46 88	2.63	16,346	1.59
PCL- <i>b</i> -PVB- <i>g</i> -PDMAEMA-6 ₅	PCL- <i>b</i> -VB51	0.51	6,105	0.93 65	1.45	6,829	1.62
PCL- <i>b</i> -PVB- <i>g</i> -PDMAEMA-7 ₁₉	PCL- <i>b</i> -VB51	0.50	6,105	2.32 82	1.89	9,168	1.93
PCL- <i>b</i> -PVB- <i>g</i> -PDMAEMA-10 ₁₂₉	PCL- <i>b</i> -VB41	1.04	3,240	9.33 90	4.08	23,477	2.09
PDMAEMA	-	-	-	4.66	3.90	15,321	1.95

Melting point of the pale yellow solid RA-1 sample was 38 °C, while the precursor, CPD, was a liquid at room temperature.

One-step polymerization

In a typical example, 0.50 g of RAFT agent, 0.10 g of AIBN, 20 mL of toluene (as solvent), a drop of tin (II) 2-ethylhexanoate, 2.06 g of VBC, and 2.16 g of CL were charged separately into a Pyrex tube, and subsequently, argon was purged into the tube through a needle for 1 min. The tube was tightly capped with a rubber septum and was put into an oil bath at 90 °C for 14 h. Then, the reaction mixture was poured into an excess of methanol to precipitate poly (CL-*b*-VBC) triarm block copolymer. It was dried at 40 °C under vacuum for 3 days.

Synthesis of macro-RAFT agent, poly (CL-*b*-VB-Ksent)

In a typical example, 2.00 g of poly (CL-*b*-VBC) triarm block copolymer was reacted with 2.44 g of EDTC in 10 mL of THF at 40 °C for 72 h. The solution was filtered to remove the unreacted xanthate, and KCl formed. Solvent was removed using a rotary evaporator. The macro-RAFT agent, poly (CL-*b*-VB) containing xanthate pendant side groups, was precipitated in cold diethyl ether and dried under vacuum at room temperature for 24 h. The yield of macro-RAFT agent was determined gravimetrically.

Synthesis of poly (CL-*b*-VB-*g*-DMAEMA) brush type copolymer

In a typical example, 40 mg of AIBN, 5 mL of toluene (as solvent), 0.50 g of macro-RAFT agent, and 1.87 g of DMAEMA were charged separately into a Pyrex tube, and subsequently, argon was purged into the tube through a needle for 1 min. The tube was tightly capped with a rubber septum and was put into an oil bath at 90 °C for 14 h. After the

polymerization, the reaction mixture was poured into an excess of methanol to separate the poly (CL-*b*-VB-*g*-DMAEMA) heterograft copolymer. The polymers were dried at 40 °C under vacuum for 24 h. The yield of the copolymer was determined gravimetrically.

Fractional precipitations of the block copolymers

Block copolymers can be isolated from their homopolymer impurities using the fractional precipitation method. The formation of block or graft copolymers can also be confirmed via fractional precipitation. Fractional precipitations of the polymers were carried out according to the procedure described in the cited reference [4]. For example, a vacuum-dried polymer sample (approximately 0.5 g) was dissolved in 10 mL of chloroform (solvent). Methanol (nonsolvent) was added drop wise into the solution with stirring until turbidity occurs. When turbidity occurs, an excess of 2 mL of nonsolvent was added to complete the precipitation. The first polymer precipitate was isolated by filtration, and dried under vacuum. The nonsolvent addition into the filtrate solution was continued in order to precipitate the second

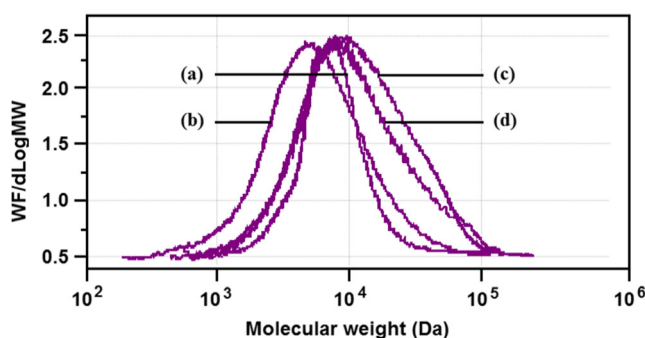


Fig. 3 GPC chromatograms of poly (CL-*b*-VB) triarm block and PCL-*b*-PVB-*g*-PDMAEMA heterograft copolymers: (a) PCL-VB-51; and (b) PCL-VB-41 in Table 1; (c) PCL-*b*-PVB-*g*-PDMAEMA-7; and (d) PCL-*b*-PVB-*g*-PDMAEMA-6 in Table 3

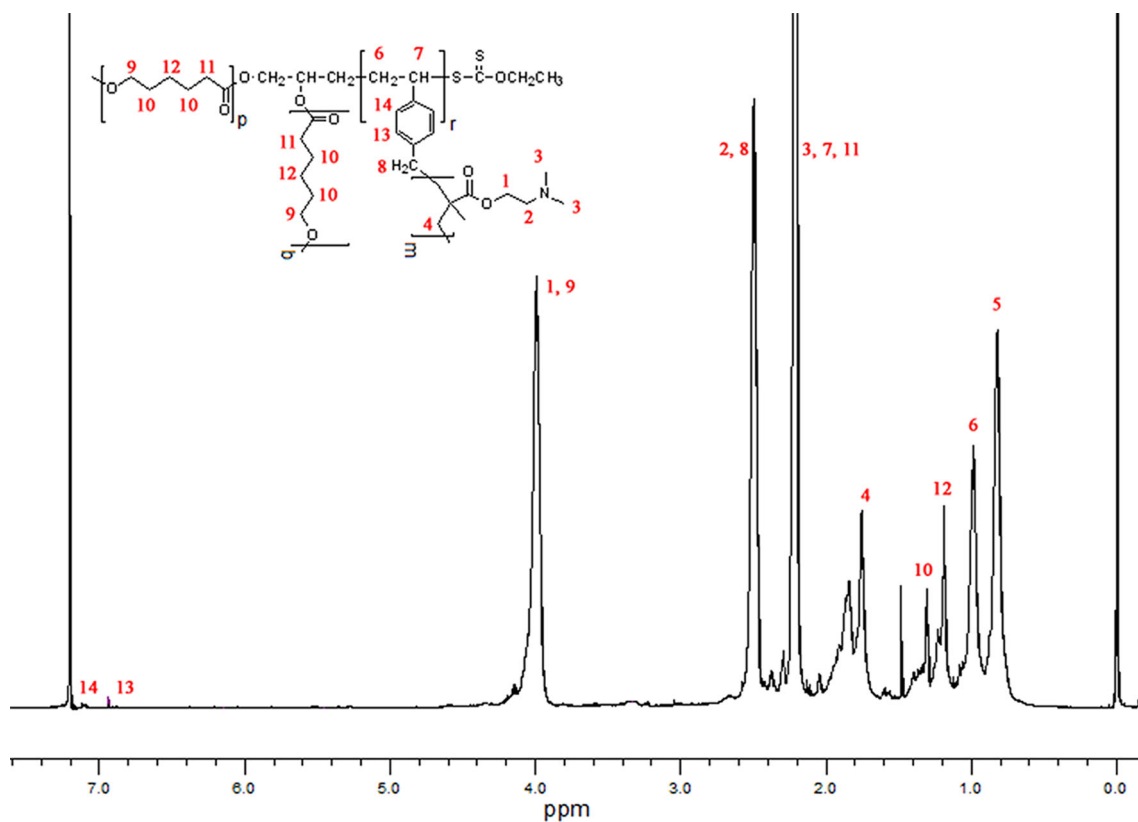


Fig. 4 ^1H NMR spectrum of the PCL-*b*-PVB-*g*-PDMAEMA-10 brush copolymer

fraction of the polymer dissolved. The precipitated polymers were dried under vacuum.

Thermo-responsive properties of graft copolymers

In a typical example, 1.5 g poly (CL-*b*-VB-*g*-DMAEMA) heterograft copolymer was dissolved in 200 ml water. Primarily, the transmittance values ($T\%$) of these solutions are obtained by their UV measurements at 600 nm from 22 °C to 45 °C. In addition, in order to determine their surface tensions, lower critical solution temperatures (LCST) of heterograft copolymers were measured from 28 °C to 44 °C with ranges of 2 °C. Each value was taken as the average of three readings.

pH sensitivity of graft copolymers

The zeta potential of poly (CL-*b*-VB-*g*-DMAEMA) heterograft copolymer was measured with zetasizer. To this aim, aqueous solutions at various pHs of the heterograft copolymers were prepared. The solutions were filtered through a 0.45- μm millipore filter before the measurement. Several solutions were prepared to study the influence of the pH of the solution. The pH was set by adding NaOH and HCl to the solution [42]. In order to obtain an average value for each data point, 30

iterations of the fitting routine were performed for each measurement to get an accurate reading of the phase signal.

Results and discussion

Synthesis of RAFT agent

Synthesis of polymers

In this study, we aimed to synthesize PCL-*b*-PVB-*g*-PDMAEMA amphiphilic brush copolymers in four steps for the first time and investigate the effects of structural alterations on their thermal and physicochemical behavior. In the first step, we prepared the dual initiator, (1, 2-propanediol-3-ethyl xanthogenate), RA-1, by the reaction between CPD with EDTC. In the second step, the one-pot RAFT and ROP polymerization of CL and VB was initiated by the dual RAFT-ROP agent in order to obtain the PCL-*b*-PVBCl block copolymers with pendent chloride groups. In the third step, PCL-*b*-PVBC was reacted with EDTC in order to obtain PCL-*b*-PVB-Xa block copolymers containing dithiocarbonate pendent chain transfer agent. In the fourth step, RAFT polymerization of DMAEMA was initiated by the PCL-



Fig. 5 The FT-IR spectra of 3-chloro 1,2-propane diol, 1, 2-propane diol-3-ethyl xanthogenate (01RA), PCL-*b*-PVB-40-Ksent, and PCL-*b*-PVB-*g*-PDMAEMA samples

b-PVB-*Xa* macro-RAFT agent in order to obtain PCL-*b*-PVB-*g*-PDMAEMA amphiphilic brush type graft copolymer. The basic outlines for the synthesis of PCL-*b*-PVB-*g*-PDMAEMA amphiphilic brush type graft copolymer starting from CPD the PCL-*b*-PVB block copolymers are shown in Scheme 1.

RAFT agent (1, 2-propanediol-3-ethyl xanthogenate), RA-1, was synthesized from the substitution reaction between CPD and EDTC with a weight ratio of 1:2, in THF solution at 40 °C for 72 h under argon. The first step of the overall reaction designed for the synthesis of RA-1 can be seen in Scheme 1. The five samples of RAFT agents were synthesized by using the same procedure during this work. The chemical structure of the RA-1 was confirmed using ¹H NMR spectrometry, in agreement with the cited literature [35].

The one-step polymerization of a vinyl monomer and a lactone initiated by RAFT agent creates three new active sites—two sites on an equal number of hydroxyl groups for ROP reaction and one on the thiocarbonate group for

RAFT polymerization. During this one-pot synthesis, RAFT polymerization of VBC is carried out simultaneously as the ROP of CL proceeds, in order to obtain poly (CL-*b*-VBC) triarm block copolymer in good yield. Table 1 summarizes results and conditions of the whole synthesis of the graft copolymers. The reactions can be seen in the second step of the Scheme 1.

GPC chromatograms of the fractionated triarm block copolymers were unimodal except the PCL-*b*-PVBC-10 triarm block copolymers. The molecular weights of the polymers (*M_n*) changed from 4,132 to 13,439 g/mol. Figure 1 shows the GPC chromatograms of the copolymers. The *M_w*/*M_n* values of second fraction samples were lower than those of first fraction samples.

As shown in the third step of the overall reaction in Scheme 1, macro-RAFT agent with polyvinyl benzyl with pendant ethyl xanthogenate groups and two poly-CL segments was prepared by the reaction of poly (CL-*b*-VBC) block copolymer and EDTC. The results of the reactions are gathered in Table 2. The *M_n* values of the macro RAFT agents were slightly lower than those of the precursors.

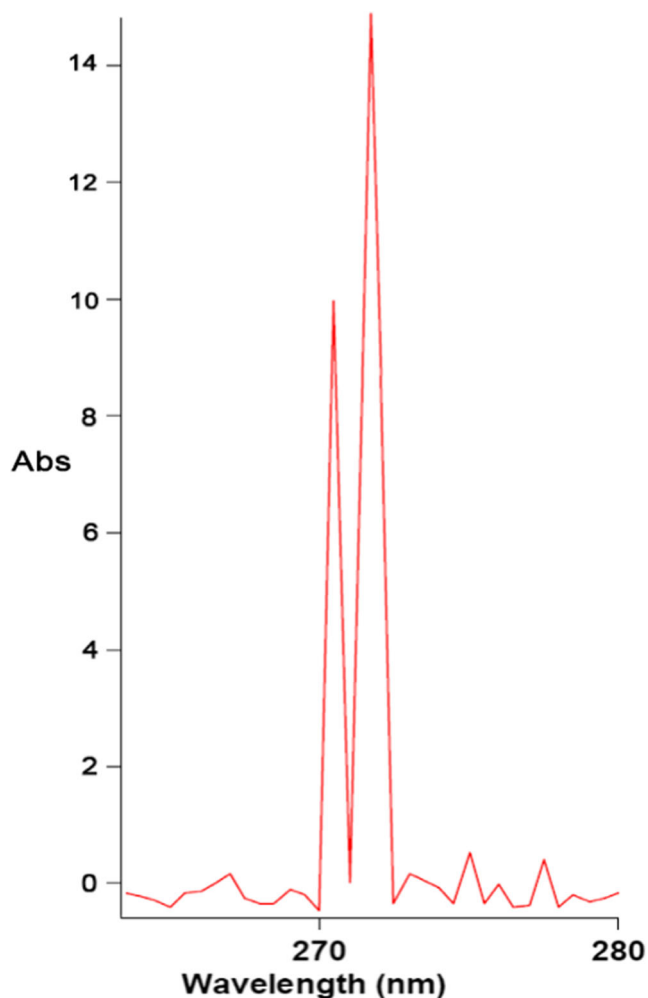


Fig. 6 UV spectra of the PCL-*b*-PVB-*g*-PDMAEMA-10 brush copolymer

Presumably, biodegradable PCL blocks are slightly degraded during the reaction with EDTC in order to get the macro RAFT agent.

Figure 2 shows the ^1H NMR spectra of PCL-*b*-PVBC-50 and PCL-*b*-PVB-Ksent-50. The characteristic chemical shifts of the xanthate units were observed at δ ppm: 3.05 for $-\text{CH}_2\text{-S- C (S)-}$ and 0.80 for $\text{CH}_3\text{-CH}_2\text{-O-}$. Aromatic protons of VB group were also observed at between 7.0 ppm and 7.5 ppm.

The RAFT polymerization of DMAEMA was initiated using macro-RAFT agent in order to obtain poly (CL-*b*-VB-*g*-DMAEMA) heterograft copolymers (fourth step in Scheme 1). The results of RAFT polymerization are shown in Table 3. There was an increase in the molecular weights of the heterograft copolymers compared to that of macro-RAFT agent. Increases in the molecular weights of the polymers when compared with the agent confirm the heterograft copolymer formation. Because of the branched structure, more than one propagating centers initiate the

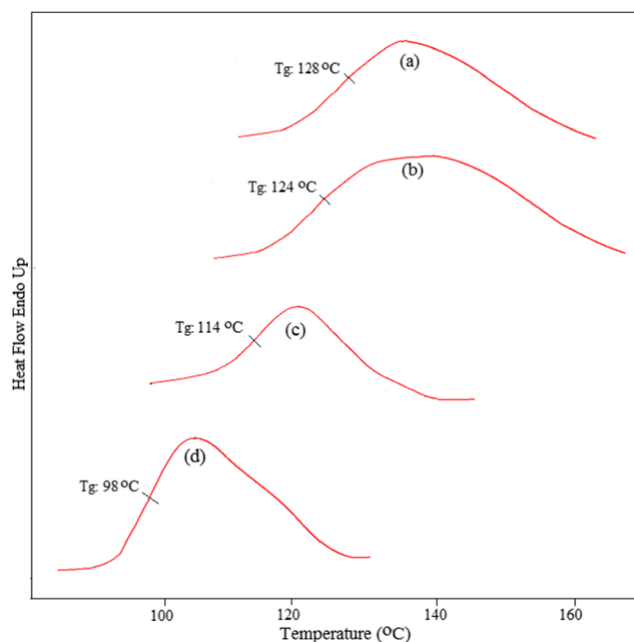


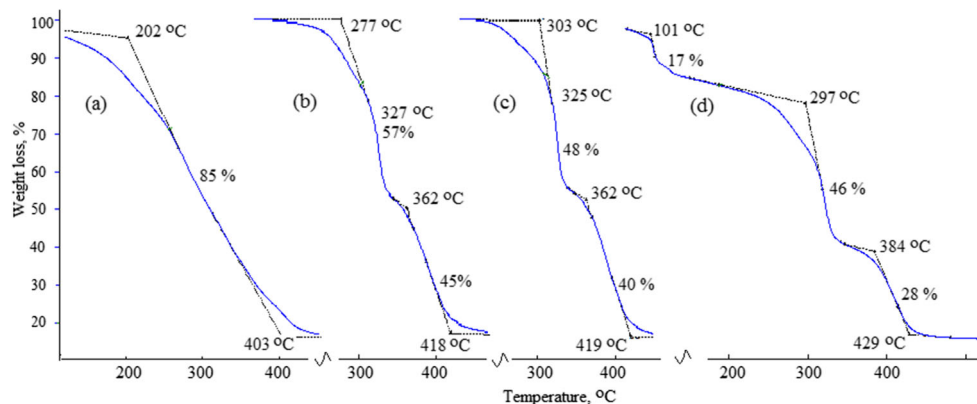
Fig. 7 DSC traces of the brush type graft copolymers: (a) PCL-*b*-PVB-*g*-PDMAEMA-6, (b) PCL-*b*-PVB-*g*-PDMAEMA-7, (c) PCL-*b*-PVB-*g*-PDMAEMA-10, and (d) PDMAEMA-homopolymer in Table 3

polymerizations, and the M_w/M_n values of the heterograft copolymers are relatively higher than expected. RAFT polymerization of DMAEMA were carried out using poly (CL-*b*-VB) macro-RAFT initiator in good yield. Increase in monomer concentration causes increase in both yield and molecular weight of the heterograft copolymer obtained (Run no.s PCL-*b*-PVB-*g*-PDMAEMA-6, -7, and -10 in Table 3).

GPC chromatograms of the PCL-*b*-PVB-*g*-PDMAEMA heterograft copolymers were unimodal and the heterograft copolymers indicated the higher molecular weight values than that of the triarm block copolymers, which was a typical confirmation of the heterografting reaction. Fig 3 shows the unimodal GPC curves of the precursor block copolymers and those of the heterograft copolymers.

Structural characteristics of the heterograft copolymers were evaluated using ^1H NMR spectrometry. Fig 4 shows ^1H NMR spectrum of the PCL-*b*-PVB-*g*-PDMAEMA-10 brush copolymer. The characteristic signals of each segment of the heterograft copolymer obtained were observed in this spectrum. The characteristic chemical shift of the xanthate unit was observed at 0.80 ppm for $\text{CH}_3\text{CH}_2\text{-O-}$. Aromatic protons of vinyl benzyl group were also observed at 7.0 and 7.1 ppm. Chemical shifts in PCL units can be assigned to the signal of independent methylene protons at 1.2-1.3 ppm, at 2.2 ppm to carboxyl groups adjacent to methylene protons, and at 4.0 ppm they can be assigned to oxygen atoms in acyloxy groups adjacent to methylene protons. Nitrogen atoms adjacent to methylene protons in DMAEMA units were

Fig. 8 TGA curves of poly (CL-*b*-VB-*g*-DMAEMA) heterograft copolymers: (a) poly (CL-*b*-VB-*g*-DMAEMA)-6, (b) poly (CL-*b*-VB-*g*-DMAEMA)-7, (c) poly (CL-*b*-VB-*g*-DMAEMA)-10, (d) poly (DMAEMA)-homopolymer



observed at 2.2 ppm like the carboxyl groups adjacent to methylene protons in PCL units.

The FTIR spectrum of the PCL-*b*-PVB-*g*-PDMAEMA was compared with those of 3-chloro 1,2-propane diol, 1,2-propane diol-3-ethyl xanthegonate (01RA), and PCL-*b*-PVB-40-Ksent in Fig. 5. The characteristic halogen signal at 831 cm^{-1} of the precursor was nearly diminished in that of RAFT agent. Typical xanthate signal at $1,638\text{ cm}^{-1}$ appeared in three polymer samples, which was confirmed the expected chemical structure. Additionally, -C=O signal at $1,723\text{ cm}^{-1}$ also confirms the presence of both PCL and PDMAEMA segments.

As an additional confirmation of the styrene units in the multiblock copolymers, UV spectra of the samples were taken, and the sharp peak which belongs to the benzene ring was observed at the wavelength 270 nm (Fig. 6).

Thermal analysis of poly (CL-*b*-VB-*g*-DMAEMA) heterograft copolymers

Thermal analysis of the poly (CL-*b*-VB-*g*-DMAEMA) heterograft copolymers was done by using DSC and TGA methods. DSC and TGA curves of the PCL-*b*-PVB-*g*-PDMAEMA-6, -7, and -10 in Table 3 were studied in view of the thermal analysis. DMAEMA concentration of the initial polymerization solution of PCL-*b*-PVB-*g*-PDMAEMA-6, -7, and -10 were 65, 82, and 90 wt.%, respectively. Tg values were obtained from the DSC curves of the heterograft copolymers and PDMAEMA-homopolymer (Fig. 7). Tgs of the heterograft copolymers were all higher than that of

PDMAEMA-homopolymer. Probably, polystyrene segments from the macro-RAFT agent increases the Tg of the copolymer.

The similar TGA curves were obtained in the heterograft copolymer samples except PCL-*b*-PVB-*g*-PDMAEMA-6 containing less PDMAEMA (Fig. 8). In this sample, decomposition starts from 202 °C to 403 °C, which can be attributed to the miscibility of the polymer segments in the heterograft copolymer. The others indicated two decomposition temperatures like the PDMAEMA homopolymer. The results of the thermal analysis were listed in Table 4.

In order to determine pH-responsive property of water soluble heterograft copolymer, poly (CL-*b*-VB-*g*-DMAEMA)-10, the transmittance values (T%) of its aqueous solution at different pH 10, 11, and 12.5 were measured using UV-VIS spectrometry.

T% values of the aqueous solutions of poly-DMAEMA homopolymer and poly (CL-*b*-VB-*g*-DMAEMA)-10 heterograft copolymer at different pHs versus wavelength are plotted in Fig. 9. The turbidity of the solution increased at $\text{pH} \geq 12$ and the T% values decreased. From here, it was observed that the precipitation of polymer took place. While the homopolymer and copolymer were soluble at $\text{pH}=10$ and $\text{pH}=11$, the polymers precipitate at $\text{pH}=12.5$.

The zeta potential was determined between pH 7–13 for heterograft copolymers. All measurements were performed after 5 min of equilibration time at 25 °C. The zeta potential values are shown in Fig. 10. When pH is

Table 4 Tg and Td values the poly (CL-*b*-VB-*g*-DMAEMA) heterograft copolymers

Code	Tg (oC)	Td1 (oC)	Weight loss (%)	Td2 (oC)	Weight loss (%)
PCL- <i>b</i> -PVB- <i>g</i> -PDMAEMA-6	128	202-403	85		
PCL- <i>b</i> -PVB- <i>g</i> - PDMAEMA-7	124	327	57	400	45
PCL- <i>b</i> -PVB- <i>g</i> - PDMAEMA-10	114	325	48	390	40
PDMAEMA homopolymer	98	298	46	405	28

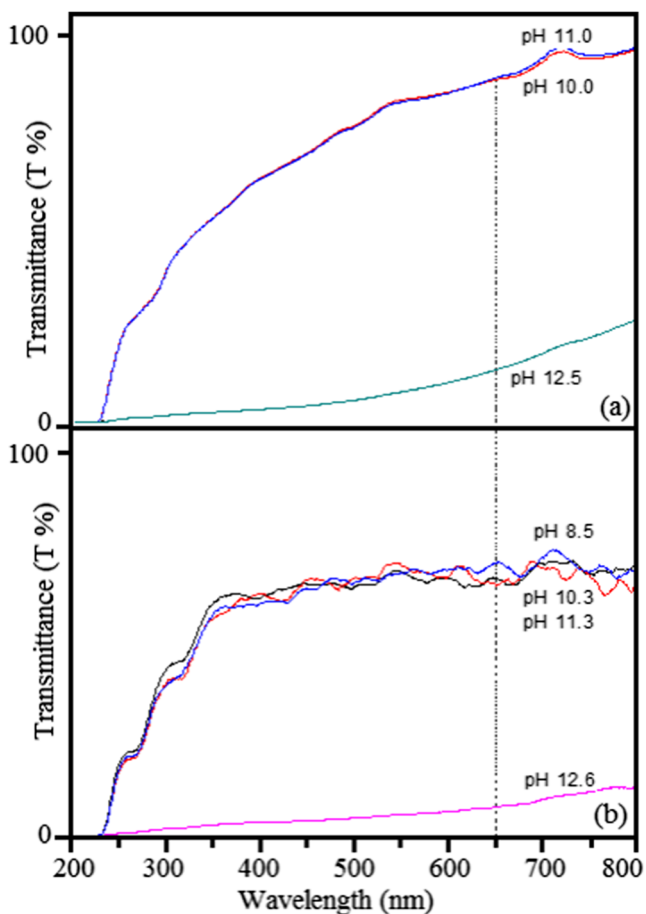
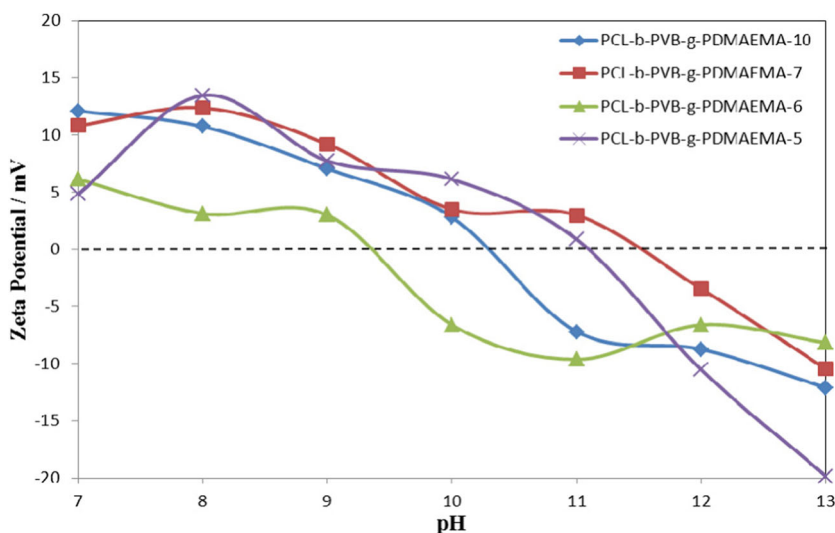


Fig. 9 T% values at 650 nm wavelength and different pH values of aqueous solutions of (a) PDMAEMA-homopolymer and (b) poly (CL-*b*-VB-*g*-DMAEMA)-10 heterograft copolymer

increased, the zeta potential decreases. The isoelectric points were at approximately pH 11.1 for PCL-*b*-PVB-*g*-PDMAEMA-5, pH 9.4 for PCL-*b*-PVB-*g*-

Fig. 10 A plot of zeta potential values of heterograft copolymers as a function of pH values in aqueous solution



PDMAEMA-6, pH 11.5 for PCL-*b*-PVB-*g*-PDMAEMA-7, and pH 10.3 for PCL-*b*-PVB-*g*-PDMAEMA-10. Under the isoelectric points, copolymers yield a net positive charge at low pH and a negative charge above this value. The surface charge of the heterograft copolymers decreases while the pH increases, which means that the hydrophobic interaction continues. Under acidic conditions, the amine groups on DMAEMA units are protonated, causing the polymer to be hydrophilic. The subsequent addition of the base deprotonates the amine groups [43].

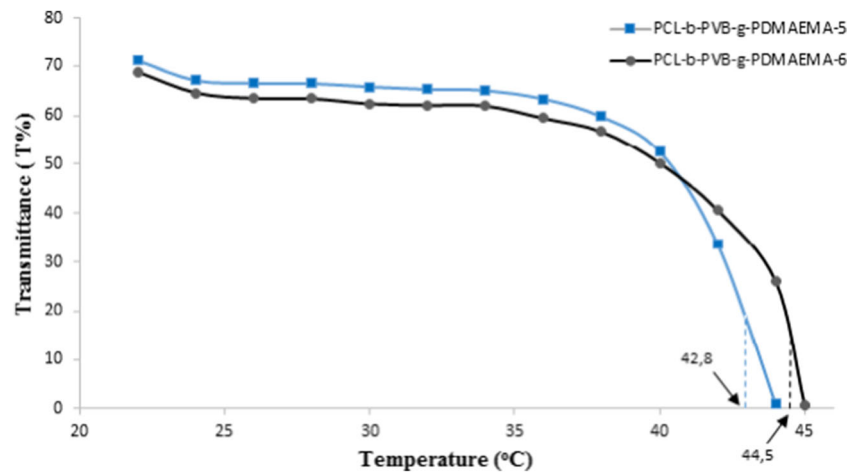
It is observed that the isoelectric points for the PCL-*b*-PVB-*g*-PDMAEMA vary with heterograft copolymers composition, with higher isoelectric points obtained for the more DMAEMA-rich copolymers. pH-sensitivity of heterograft copolymers was confirmed by UV and zetasizer measurements. It is seen that zetasizer measurements support the data obtained from UV.

With the UV measurements of the thermo-responsiveness of heterograft copolymers, the transmittance values (T%) at various temperatures were determined at 600 nm. Fig. 11 shows T% values of the copolymers. The LCST of PDMAEMA homopolymer which was 46.6 °C at pH 7 [44] has decreased to 42.8 °C and 44.5 °C due to the PDMAEMA amount in the obtained heterograft copolymer. It was reversible, thermosensitivity was observed during both heating and cooling process.

Normally, the hydrophilic balance is important for thermosensitivity, but in the case of block copolymers, the comonomer composition can be important. In this manner It could be possible to increase the hydrophilicity by increasing the amount of DMAEMA.

The LCST of PDMAEMA homopolymer was 46.6 °C, the LCST of the poly (CL-*b*-VB-*g*-DMAEMA) 5 heterograft

Fig. 11 T% values of aqueous solutions of PCL-*b*-PVB-*g*-PDMAEMA-5 and PCL-*b*-PVB-*g*-PDMAEMA-6 heterograft copolymers at 600 nm wavelength



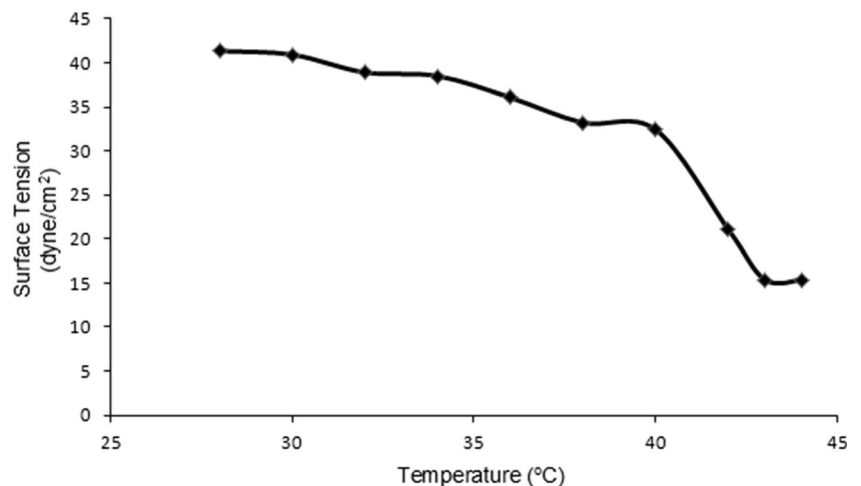
copolymer sample was obtained to be 42.8 °C from the surface tension measurements of the aqueous solution of the heterograft copolymer (Fig. 12). It is reversible and it is observed that there is no transmittance above 43 °C. It is seen that the LCST value is getting closer to 46.6 °C depending on the increase in the amount of DMAEMA.

Conclusions

Poly (CL-*b*-VB-*g*-DMAEMA) pH- and thermo-responsive amphiphilic heterograft copolymers were, for the first time, synthesized in four steps. The proposed procedure for the preparation of heterograft copolymers is simple and efficient. By changing the initial concentrations, the heterograft copolymer compositions can be adjusted. It is observed that the results obtained from both UV and surface tension measurements support each other. The LCST of PDMAEMA homopolymer was 46.6 °C, the LCST of poly (CL-*b*-VB-*g*-

DMAEMA) 5 heterograft copolymer was obtained to be 42.8 °C with the surface tension measurements which is shown in Fig. 11, with the aqueous solution of the heterograft copolymer. It is reversible and it is observed that there is no transmittance above 43 °C. The hydrophobic moieties of the multiblock copolymers cause the lower T_g than that of the homopolymer [45]. In addition to this, the LCST value is getting closer to 46.6 °C depending on the increase in the amount of DMAEMA. pH-sensitivity of the brush type graft copolymer was observed between pH9.4 and 11.5. The acrylic polymer inclusion affects their swelling/solution properties in water. At lower pH regions, electrostatic repulsion force and intermolecular hydrogen bonding are principally main factor. At higher pH values, interchain hydrophobic interactions come into prominence. This responsive branched, brush type of the novel pH- and thermo-responsive copolymer can be applied to various areas such as new types of adaptive surfaces, sensors, microfluidics, antibacterial materials, and gene delivery.

Fig. 12 Surface tension measurements to determine the lower critical solution temperature (LCST) value of poly (CL-*b*-VB-*g*-DMAEMA) 5 heterograft copolymer



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