End-Linked Amphiphilic Polymer Conetworks: Synthesis by Sequential Atom Transfer Radical Polymerization and Swelling Characterization

MARIA D. RIKKOU,¹ MARIA KOLOKASI,¹ KRZYSZTOF MATYJASZEWSKI,² COSTAS S. PATRICKIOS¹

¹Department of Chemistry, University of Cyprus, P.O. Box 20537, 1678 Nicosia, Cyprus

²Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213

Received 7 December 2009; accepted 20 January 2010 DOI: 10.1002/pola.23951 Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Conetworks based on end-linked homopolymers and amphiphilic gradient copolymers were synthesized by the atom transfer radical polymerization (ATRP) of 2-(dimethylamino)ethyl methacrylate (DMAEMA, hydrophilic monomer), methyl methacrylate (MMA, hydrophobic monomer), and ethylene glycol dimethacrylate (EGDMA, hydrophobic cross-linker). Sequential, rather than step-wise polymerizations, were performed to enhance the livingness of the polymerization, particularly for the end-linking step, and to ultimately obtain conetworks based on gradient rather than pure block copolymers. Amphiphilic conetworks based on end-linked MMA-DMAEMA-MMA gradient copolymers of different compositions were successfully synthesized as confirmed by the narrow molecular weight distributions of the linear precursors, the rigidity of the amphiphilic conetwork products and the low sol-fraction extracted from the conetworks. Similarly successful was the ATRP synthesis of an

INTRODUCTION Although the investigation of the properties and exploration of applications of polymer networks have very much progressed during the past 50 years,¹ little effort has been devoted to the controlled synthesis of these materials. Most polymer networks available today comprise chains between cross-linking nodes (so-called elastic chains) with broad molecular weight distributions, a result of the simultaneous free radical cross-linking copolymerization of monomer(s) and cross-linker. Availability of better-defined polymer networks may broaden their applications horizon, and would also enable the derivation of accurate structure-property relationships.²

For the past 10 years, our Research Team has been working on the development of well-defined functional polymer conetworks by the end-linking of ABA triblock copolymers, resulting in materials with elastic chains of narrowly distributed size and composition, but a broader distribution in the number of arms emanating from each cross-linked core.³ The network topologies were subsequently expanded to include end-linked star polymers,⁴ and, more recently, semiend-linked conetwork based on a DMAEMA-MMA statistical copolymer and of a randomly cross-linked conetwork that resulted from the simultaneous terpolymerization of DMAEMA, MMA and EGDMA. An amphiphilic conetwork based on an end-linked DMAEMA-MMA-DMAEMA gradient copolymer presented a less rigid, mucous-like, texture. The degrees of swelling (DS) in tetrahydrofuran of all the conetworks were higher than those measured in pure water, whereas the aqueous DS values increased by lowering the pH and increasing the DMAEMA content of the conetworks. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 1878–1886, 2010

KEYWORDS: atom transfer radical polymerization; amphiphiles; amphiphilic conetworks; 2-(dimethylamino)ethyl methacrylate; end-linked networks; ethylene glycol dimethacrylate; gels; gradient copolymers; methyl methacrylate; swelling

segmented structures.⁵ Most syntheses initially involved group transfer polymerization (GTP),⁶ a controlled anionic polymerization method best-suited for methacrylates, but were recently extended⁷ to include a controlled radical polymerization (CRP) method, and, in particular, reversible addition-fragmentation chain transfer (RAFT) polymerization.⁸

Atom transfer radical polymerization (ATRP) is another powerful CRP method,⁹ used for the preparation of block, graft, and star copolymers,¹⁰ and randomly cross-linked networks.¹¹ ATRP has also been used for the preparation of end-linked hydrophobic homopolymer networks based on nondegradable¹² and degradable¹³ initiators, but there are no reports for the employment of this technique for the synthesis of functional conetworks based on the end-linking of block copolymers, which is the aim of this investigation. In particular, herein we report on the one-pot, sequential ATRP of monomers and a cross-linker for the preparation of endlinked amphiphilic conetworks. The thorough characterization of the aqueous swelling and the mechanical properties of these conetworks are also reported.

Correspondence to: C. S. Patrickios (E-mail: costasp@ucy.ac.cy)

Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 48, 1878-1886 (2010) © 2010 Wiley Periodicals, Inc.

EXPERIMENTAL

Materials and Methods

2-(Dimethylamino)ethyl methacrylate (DMAEMA, 99%), methyl methacrylate (MMA, 99%), and ethylene glycol dimethacrylate (EGDMA, 98%) were purchased from Aldrich, Germany. Copper (I) bromide (99%), copper (II) bromide (99%), diethyl meso-2,5-dibromoadipate (mDBAP, 98%), 2,2'bipyridine (bpy, 99%) were also purchased from Aldrich and were used as received. N,N'-dimethylformamide (DMF, Merck 99%) was dried over calcium hydride and was freshly distilled under reduced pressure. The monomers and the crosslinker were passed through basic alumina columns to remove the polymerization inhibitor and any other acidic impurities and they were stirred overnight over calcium hydride to remove the last traces of moisture and protonic impurities. This was done in the presence of an added free radical inhibitor, 2,2-diphenyl-1-picrylhydrazyl hydrate (DPPH), to avoid undesired thermal polymerization. The monomers and the cross-linker were freshly distilled before the polymerization. 2-Bromoisobutyryl bromide (98%) and ethylene glycol (99%), used for the preparation of the bifunctional initiator ethylene glycol di(2-bromoisobutyrate) (EGDBiB), were purchased from Aldrich and used as received, while triethylamine (Et₃N, synthesis grade) was purchased from Scharlau, Spain.

Preparation and Characterization of the Bifunctional ATRP Initiator

The bifunctional initiator was prepared according to the procedure reported in the literature,¹⁴ and, in particular, by the esterification reaction of ethylene glycol (10 mL, 11.13 g, 0.18 mol) with a slight stoichiometric excess (5%) of 2-bromoisobutyryl bromide (46.7 mL, 86.8 g, 0.38 mol). The reaction was carried out under a dry nitrogen atmosphere at 0 $^{\circ}$ C, in 120 mL THF, in the presence of 150 mL Et₃N (109.3 g, 1.08 mol). The resulting insoluble salt of Et₃N HBr was removed from the reaction mixture by filtration. Subsequently, the filtrate was passed through a column of basic alumina to remove the formed (excess) isobutyric acid. The desired product was finally obtained after vacuum distillation at 120 °C as a yellowish solid at 40% yield. The structure of the initiator was confirmed by ¹H and ¹³C-NMR. ¹H NMR (300 MHz, CDCl₃, δ): 4.42 (s, 2 × 2H, $-0CH_2CH_2O-$), 1.92 (s, 4 × 3H, –C(CH₃)₂Br). ¹³C NMR (300 MHz, CDCl₃, δ): 171.4 (2C, -COOCH₂CH₂O-), 63.2 (2C, -OCH₂CH₂O-), 55.3 (2C, -C(CH₃)₂Br), 30.7 (4C, -C(CH₃)₂Br).

Conetwork Preparation

All amphiphilic polymer conetworks of this study were prepared by sequential ATRP. The polymerization procedure for the synthesis of the conetwork EGDMA_{0.5}-grad-MMA₂₅-grad-DMAEMA₅₀-grad-MMA₂₅-grad-EGDMA_{0.5} is described below. To a 25-mL Schlenk flask kept under a dry nitrogen atmosphere were added 55.8 mg CuBr (3.9×10^{-4} mol), 3.1 mg CuBr₂ (1.4×10^{-5} mol), 0.13 g bpy (8.1×10^{-4} mol), 2.34 mL DMAEMA (2.18 g, 0.014 mol), and 0.5 mL DMF. The mixture was degassed by two vacuum-nitrogen cycles. The reaction flask was heated to 50 °C and a deoxygenated solution of the EGDBiB bifunctional initiator (0.1 g, 2.78×10^{-4} mol) in 0.25 mL DMF was added. After 44 min of reaction, at a monomer conversion of 93%, samples were extracted for size exclusion chromatography (SEC) and ¹H NMR spectroscopy analyses (polymer number-average molecular weight (MW) = $M_{\rm n} = 13,700 \text{ g mol}^{-1}$ compared with the theoretically expected MW of 7670 g mol⁻¹; polydispersity index = PDI = $M_w/M_n = 1.31$; M_w is the weight-average MW). Then, the second monomer, MMA (1.49 mL, 1.39 g, 0.014 mol) was added and was allowed to react for another 179 min until its conversion reached 78%. After sampling for SEC and ¹H NMR spectroscopy ($M_n = 21,100 \text{ g mol}^{-1}$ compared with the theoretically expected MW of 11,580 g mol}^{-1}; PDI = 1.37; MMA content = 46% mol determined using ¹H NMR as compared with a theoretically expected content of 50%), EGDMA (0.05 mL, 0.06 g, 2.78 imes 10^{-4} mol, cross-linker: initiator molar ratio equal to 1:1) was added, leading to conetwork formation within 180 min. The polymerization reaction was kept at 50 °C for another 18 h after gel formation was observed. Conetworks of different compositions were prepared by varying the relative amounts of the two comonomers, whereas conetworks of different architectures were obtained by varying the addition sequences. In all cases, at each step of the sequential procedure the monomers were allowed to react until conversions between 80 and 90% were reached before proceeding to the next step.

Kinetics of Polymerization

The experimental procedure for the study of the polymerization kinetics of MMA is described below. To a 50-mL Schlenk flask kept under a dry nitrogen atmosphere were added 0.15 g CuBr (1.1 mmol), 8.3 mg CuBr₂ (3.7 \times 10⁻⁵ mol), 0.34 g bpy (2.17 mmol), 4.0 mL MMA (3.74 g, 0.04 mol) and 4.5 mL DMF. The mixture was degassed by two vacuum-nitrogen cycles. The reaction flask was heated to 50 °C and a deoxygenated solution of EGDBiB (0.30 g, 7.48 imes 10⁻⁴ mol) in 0.4 mL DMF was added. At regular time intervals, samples were extracted from the polymerization mixture to characterize the resulting linear polymer by SEC and ¹H NMR spectroscopy. The same procedure was followed for the investigation of the kinetics of DMAEMA polymerization. In the case of the EGDMA polymerization kinetics, a linear precursor of MMA was formed first. When MMA reached a conversion of about 80%, EGDMA was added to the polymerization mixture and samples were taken every 5 min until a network was formed.

Size Exclusion Chromatography

Samples of homopolymer and copolymer linear precursors obtained during the polymerizations, and samples of the sol-fraction from the conetworks were characterized by SEC to determine their MWs and their molecular weight distributions (MWD). SEC was performed on a Polymer Laboratories chromatograph equipped with an ERC-7515A refractive index detector and a PL Mixed "D" column. The mobile phase was THF, modified with 2% triethylamine, delivered at a flow rate of 1 mL min⁻¹ using a Waters 515 isocratic pump. The MW calibration curve was based on eight narrow MWD linear polyMMA standards with MWs of 850, 2810, 4900,

11,550, 30,530, 60,150, 138,500, and 342,900 g mol⁻¹ also from Polymer Laboratories.

Proton Nuclear Magnetic Resonance Spectroscopy

The compositions of the conetwork linear precursors and of the sol-fraction from the conetworks were determined by ¹H-NMR spectroscopy using a 300 MHz Avance Bruker NMR spectrometer equipped with an Ultrashield magnet. The solvent was CDCl₃ containing traces of tetramethylsilane (TMS), which was used as an internal reference. ¹H NMR spectroscopy was also used to confirm the structure and the purity of the EGDBiB bifunctional initiator, the monomers and the cross-linker, and also to determine monomer and crosslinker conversions.

Determination and Characterization of the Sol-Fraction from the Conetworks

Before extracting the sol-fraction from the entire conetwork, a small piece from each conetwork was extracted by being placed in CDCl₃ and allowed to equilibrate for one day. The thus obtained "early extractables" were characterized using ¹H-NMR spectroscopy to determine the final monomer and cross-linker conversions. Subsequently, the entire conetwork was extracted with 100 mL THF for 2 weeks to remove the sol-fraction. Next, the THF solution was recovered by filtration, and THF was subsequently evaporated off using a rotary evaporator. The recovered polymer was further dried for 2 days in a vacuum oven at room temperature. The solfraction was calculated as the ratio of the dried mass of the extracted polymer divided by the theoretical mass of the polymer in the conetwork, taken as the sum of the masses of the initiator and the polymerized monomers and cross-linker. The sol-fraction was finally characterized in terms of its MW and composition using SEC and ¹H NMR spectroscopy, respectively.

Measurement of the Degree of Swelling (DS)

The degrees of swelling (DSs) of the conetworks were measured in THF, pure water and aqueous solutions of various pHs covering the range between 2 and 12. In the case of THF, pieces from each THF-equilibrated conetwork were cut and weighed. Subsequently, each piece was dried in a vacuum oven at room temperature for 3 days and was reweighed. The DS was calculated as the ratio of the swollen divided by the dry conetwork mass. For the measurements of the DSs in water of different pHs, samples from each conetwork were dried in a vacuum oven at room temperature to determine their dry mass, and the samples were subsequently transferred to water where the appropriate volume of a 0.5M HCl standard solution was added to adjust the pH within the range between 2 and 8. For each different (co)network, about eight samples were used, each adjusted to a different pH corresponding to the range of degrees of ionization varying from 20 to 100%. The required number of moles of HCl in each case was calculated as the product of the desired degree of ionization times the number of equivalents of DMAEMA units present in the sample, estimated from the conetwork dry mass and composition. Small volumes of a 0.5M NaOH standard solution were added to two

samples from each network to cover the pH range from 8 to 12. All samples were allowed to equilibrate for 2 weeks. The DS was calculated again as the ratio of the swollen divided by the dry conetwork mass.

Dynamic Mechanical Analysis

A Tritec2000 Triton Technologies dynamic mechanical analyzer (DMA) was used for the investigation of the mechanical properties of the conetworks. All conetworks were measured in the compression mode at a frequency of 1 Hz, in their fully ionized state in low pH water. For the measurements, a dried sample of each conetwork was used which was allowed to equilibrate in acidified water to the appropriate pH. Subsequently, rectangular blocks were cut from the swollen conetwork using a blade. All samples were wiped gently with a tissue to remove excess surface water before the measurement to avoid possible slippage of the sample during the measurement.

RESULTS AND DISCUSSION

Polymerization Methodology

Figure 1 illustrates schematically the preparation of a conetwork based on an end-linked MMA-DMAEMA-MMA gradient copolymer. The hydrophilic DMAEMA and the hydrophobic MMA monomers were chosen because they are both widely used, commercially available inexpensive reagents. To find a proper system to achieve control over the copper-mediated polymerization of MMA and DMAEMA, different parameters were studied. First, two bifunctional initiators were tried: the commercially available mDBAP and the in-house synthesized EGDBiB. The latter was found to be a more efficient initiator by yielding polymers with better-controlled MWs, and PDIs lower than 1.3. This was attributed to its ability to produce initiating radicals faster than mDBAP since halogen abstraction from tertiary C-Br is faster than that from secondary C-Br, because of better stabilization of the generated radicals after the halogen abstraction step.9b,15 The ligand of the system was also studied: when bpy was used instead of N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA) in DMF, the control over the polymer MWs was better, because the bpy complex with copper has a lower K_{act} value than PMDETA,¹⁶ resulting in a higher concentration of dormant species. Improved results were also observed when 5% of Cu (II) deactivator relative to Cu (I) activator was charged into the system. The use of the halogen exchange technique was also explored to improve the MW control at high monomer conversions.¹⁷ In these experiments, CuCl was used instead of CuBr with EGDBiB as the initiator and bpy as the ligand. Longer polymerization times without any significant reduction in the PDIs were observed in these experiments. Thus, CuBr was preferred over CuCl.

For the sequential ATRP experiments, three different monomer concentrations, 3.0, 4.5 and 6.0*M*, were tested at a constant targeted degree of polymerization equal to 50. At a 3.0*M* concentration of MMA, it took 200 min of polymerization for the monomer conversion to reach 80%. The polymerization time was shortened as the monomer concentration was increased from 3.0 to 6.0*M*. Because of the long



FIGURE 1 Schematic representation of the sequential addition of monomers and cross-linker followed for the preparation of conetworks based on end-linked ABA gradient copolymers. The dark green and light blue circles represent the MMA and the DMAEMA monomer repeating units, respectively, whereas the black and red dumbbells depict the EGDMA cross-linker units and the initiator residues, respectively.

reaction time necessary at a 3.0M monomer concentration and because of the very viscous polymer solution resulting at 6.0M that prevented sampling at high monomer conversion, a monomer concentration of 4.5M was elected as a compromise for the network syntheses. At that monomer concentration, the polymerization kinetics was followed for MMA, DMAEMA, and EGDMA. Under these conditions, the polymerization of DMAEMA proved to be faster than that of MMA. In particular, the polymerization of DMAEMA to 80% conversion took half the time compared with that of MMA to the same conversion. From the kinetics of cross-linker polymerization, it appeared that networks formed only at a high (>90%) EGDMA conversion. The kinetics for the polymerization of the three methacrylates, MMA, DMAEMA, and EGDMA, initiated by EGDBiB and catalyzed by the CuBr/bpy system at monomer concentration 4.5M are shown in Figure 2. The first-order kinetic plots were linear, indicating a constant radical concentration throughout the polymerization.

Conetwork Synthesis

Considering the above, amphiphilic conetworks based on end-linked ABA gradient copolymers of various compositions were designed. The exploration of the conetwork architecture was also pursued, by the design of conetworks based on both ABA and BAB gradient copolymers, and also on a statistical copolymer. The corresponding randomly crosslinked conetwork of the statistical copolymer was also prepared, in which both comonomers and the cross-linker were simultaneously terpolymerized. Networks based on the endlinked homopolymers were prepared too. Table 1 lists the time and the conversion of monomers at each step of the sequential procedure, and displays the $M_{\rm n}$, the PDI and the composition of the linear homopolymer and the amphiphilic copolymer precursors to the conetworks, as determined using SEC and ¹H NMR spectroscopy. As shown in Table 1, when DMAEMA was used as the first monomer, the time required for the monomer to reach 74-92% conversion was shorter than the case when MMA was used first. This agreed with the results of homopolymerization kinetics which revealed that the polymerization of DMAEMA was faster. It was also observed that in the case of the amphiphilic conetwork based on the end-linked DMAEMA25-grad-MMA50-gradDMAEMA₂₅ copolymer, a mechanically inferior conetwork (free-flowing, mucous-like) was formed due to the longer total time needed for the preparation of this conetwork which probably allowed for more extensive deactivation and resulting in a low EGDMA conversion of 62%. Characterization using SEC indicated that the M_n values of the linear precursors of the conetworks were higher than the theoretical MWs due to partial deactivation of the active centers, but the PDIs of these precursors remained relatively low, at or lower than 1.4.

Characterization of the Conetworks. Sol-Fraction

The conetworks in this study were characterized in terms of their sol-fraction and the results are summarized in Table 2. In all conetworks, the sol-fraction was relatively low (5–26%), with the exception of conetwork EGDMA_{0.5}-grad-MMA_{12.5}-grad-DMAEMA₇₅-grad-MMA_{12.5}-grad-EGDMA_{0.5} which displayed a sol-fraction of 57%, because of the longer polymerization time needed for the formation of the linear precursor compared to the other amphiphilic conetworks. Thus, more chains were deactivated in the case of this conetwork. A high sol-fraction was also observed in the case of the homopolymer



FIGURE 2 Kinetics of the ATRP of MMA, DMAEMA and EGDMA in DMF (4.5*M* monomer concentration) initiated by EGDBiB at 50 °C using the CuBr/bpy catalyst/ligand system. [Monomer]/[EGDBiB]/[CuBr]/[bpy]/[CuBr₂] = 50:1:1.5:3:0.05.

TABLE 1 Conversion, Molecular Weight, and Composition Characteristics of the Linear Precursors to the End-Linked Conetworks Synthesized

		Conversion (mol %)		Gelation	 ∙ b	 : b	SEC Results		% mol MMA		
No.	Polymer Structure ^a	MMA	DMAEMA	EGDMA	(min)	(min)	MW _{theor} c	<i>M</i> _n	$M_{\rm w}/M_{\rm n}$	Theor.	¹ H NMR
1	M ₁₀₀	82	-	-		86	8,570	12,700	1.26	100	100
	E _{0.5} -grad-M ₁₀₀ -grad-E _{0.5}	94	-	68	74	194					
2	D ₁₀₀	-	92	_		72	14,270	18,600	1.0	30	0
	E _{0.5} - <i>grad</i> -D ₁₀₀ - <i>grad</i> -E _{0.5}	-	100	100	35	155					
3	D ₅₀	-	93	-		44	7,670	13,700	1.31	0	0
	$M_{25}\text{-}\textit{grad}\text{-}D_{50}\text{-}\textit{grad}\text{-}M_{25}$	78	95	_		179	11,580	21,100	1.37	50	46
	E _{0.5} -grad-M ₂₅ -grad-D ₅₀ - grad-M ₂₅ -grad-E _{0.5}	85	100	77	180	1,110					
4	D ₇₅	-	92	_		52	11,210	15,200	1.33	0	0
	M _{12.5} -grad-D ₇₅ -grad-M _{12.5}	89	97	-		120	13,440	20,400	1.39	25	23
	E _{0.5} - <i>grad</i> -M _{12.5} - <i>grad</i> -D ₇₅ - <i>grad</i> -M _{12.5} - <i>grad</i> -E _{0.5}	100	100	100	41	1,260					
5	D ₂₅	-	78	-		16	3,425	5,530	1.28	0	0
	M _{37.5} -grad-D ₂₅ -grad-M _{37.5}	83	87	_		90	9,660	18,000	1.39	75	77
	E _{0.5} - <i>grad</i> -M _{37.5} - <i>grad</i> -D ₂₅ - <i>grad</i> -M _{37.5} - <i>grad</i> -E _{0.5}	98	89	76	150	1,290					
6	M ₅₀	85	-	_		85	4,615	8,700	1.33	100	100
	D ₂₅ -grad-M ₅₀ -grad-D ₂₅	95	74	-		280	10,432	18,800	1.41	50	54
	E _{0.5} - <i>grad</i> -D ₂₅ - <i>grad</i> -M ₅₀ - <i>grad</i> -D ₂₅ - <i>grad</i> -E _{0.5}	100	89	62	225	1,080					
7	D ₅₀ - <i>co</i> -M ₅₀	78	81	-		74	10,550	13,600	1.30	50	46
	E _{0.5} -grad-(D ₅₀ -co-M ₅₀)-grad-E _{0.5}	93	89	77	35	1,320					
8	D ₅₀ - <i>co</i> -M ₅₀ - <i>co</i> -E ₁	95	77	91	30	1,370	-	-	-	50	53

 $^{\rm a}$ D, M and E are further abbreviations for DMAEMA, MMA and EGDMA, respectively.

^b Separate reaction time at each step of the sequential addition.

network of MMA. In the case of the amphiphilic conetwork having MMA as the middle block, the sol-fraction was only 22% but this conetwork was mechanically very weak. It is also possible that the sol-fraction from this conetwork was actually higher than 22%, but it was underestimated because of adher-

 $^{\rm c}$ MW_{theor.} = [monomer]/[initiator] \times (monomer conversion) \times (monomer MW)

ence of the viscous extractables on to the filter paper during their separation from the conetwork. The relatively low solfraction from most conetworks indicated that the amount of EGDMA cross-linker used with respect to the EGDBiB initiator (molar ratio 1:1) was sufficient to effect satisfactory

 TABLE 2 Mass Percentage, Molecular Weight, and Composition Characteristics of the Extractables from the End-Linked

 Conetworks Synthesized

	Extractables						
	%	% mo	ol MMA	SEC Results			
Polymer Structure		Theor.	¹ H-NMR	M _n	$M_{\rm w}/M_{\rm n}$		
E _{0.5} -grad-M ₁₀₀ -grad-E _{0.5}	75	100	100	16,300	2.39		
E _{0.5} -grad-D ₁₀₀ -grad-E _{0.5}	26	0	0.0	9,580	1.45		
$E_{0.5}\text{-}\textit{grad}\text{-}M_{25}\text{-}\textit{grad}\text{-}D_{50}\text{-}\textit{grad}\text{-}M_{25}\text{-}\textit{grad}\text{-}E_{0.5}$	26	50	42.4	15,000	1.49		
$E_{0.5}\text{-}grad\text{-}D_{25}\text{-}grad\text{-}M_{50}\text{-}grad\text{-}D_{25}\text{-}grad\text{-}E_{0.5}$	22	50	56.3	17,600	1.45		
E _{0.5} -grad-M _{12.5} -grad-D ₇₅ -grad-M _{12.5} -grad-E _{0.5}	57	25	23.1	19,700	1.72		
$E_{0.5}$ -grad- $M_{37.5}$ -grad- D_{25} -grad- $M_{37.5}$ -grad- $E_{0.5}$	21	75	71.1	16,000	1.96		
$E_{0.5}$ -grad-(D_{50} -co- M_{50})-grad- $E_{0.5}$ (statistical)	18	50	57.3	11,900	1.57		
D ₅₀ - <i>co</i> -M ₅₀ - <i>co</i> -E ₁ (random)	5	50	50.1	8,360	1.64		



FIGURE 3 Aqueous degrees of swelling and degrees of ionization of the copolymer conetworks as a function of the solution pH. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

interlinking of the polymer chain ends. These low final sol-fractions also indicated sufficient control over the conetwork structure. With the increase of the DMAEMA content in the conetworks, an increase in the sol-fraction was observed, because a longer polymerization time was required for the formation of the DMAEMA homopolymer precursors, and, consequently, more chains were deactivated. When the conetwork architecture was varied at constant composition, the sol-fraction was found to decrease in the more random architectures. In particular, the sol-fraction was lowest for the randomly cross-linked conetwork (5%), higher for the end-linked statistical conetwork (18%), and highest for the end-linked MMA-DMAEMA-MMA gradient copolymer-based conetwork (26%). The extractables were characterized in terms of their MWs and their

 TABLE 3 pKs of the DMAEMA Monomer Repeating Units in the

 End-Linked Conetworks Synthesized

Polymer Structure	Effective p <i>k</i>
$E_{0.5}\text{-}\mathit{grad}\text{-}M_{25}\text{-}\mathit{grad}\text{-}D_{50}\text{-}\mathit{grad}\text{-}M_{25}\text{-}\mathit{grad}\text{-}E_{0.5}$	5.8
$E_{0.5}\text{-}\textit{grad}\text{-}D_{25}\text{-}\textit{grad}\text{-}M_{50}\text{-}\textit{grad}\text{-}D_{25}\text{-}\textit{grad}\text{-}E_{0.5}$	6.3
$E_{0.5}$ -grad- $M_{12.5}$ -grad- D_{75} -grad- $M_{12.5}$ -grad- $E_{0.5}$	6.0
$E_{0.5}\text{-}\textit{grad}\text{-}M_{37.5}\text{-}\textit{grad}\text{-}D_{25}\text{-}\textit{grad}\text{-}M_{37.5}\text{-}\textit{grad}\text{-}E_{0.5}$	5.8
$E_{0.5}\text{-}grad\text{-}(D_{50}\text{-}co\text{-}M_{50})\text{-}grad\text{-}E_{0.5} \text{ (statistical)}$	5.5
D ₅₀ - <i>co</i> -M ₅₀ - <i>co</i> -E ₁ (random)	6.2

composition by SEC and ¹H-NMR spectroscopy, respectively. For all the conetworks, the extractables contained linear chains with lower MWs than the linear precursors because of early partial active site deactivation. The composition of those linear chains was found to be richer in the monomer of the middle



FIGURE 4 Degrees of swelling of the conetworks in THF and in water in the charged and uncharged states. (a) Effect of polymer composition. (b) Effect of polymer architecture. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

block of the linear precursor, indicating that most of the deactivation occurred at the beginning of the copolymerization.

Swelling Behavior of the Conetworks in Water as a Function of pH

Figure 3 shows the pH-dependence of the DSs in water and the degrees of ionization for all the conetworks. In water, the conetworks started to swell below pH 8 where the DMAEMA units begin to get ionized. Both neutral and ionized DMAEMA units are compatible with water. However, the ionization enhances swelling because of the repulsive electrostatic interactions between the charged chains, and the osmotic pressure built by the chloride counter-ions to the positively charged DMAEMA units. There was a decrease in the DS for some conetworks at very low pH, which can be attributed to the high ionic strength of the solution at this pH range. The DS curves followed closely the degree of ionization curves, indicating the importance of ionization on the swelling behavior of these conetworks.



FIGURE 5 Uniaxial compression elastic moduli and degrees of swelling in acidic water. (a) Effect of polymer composition. (b) Effect of polymer architecture. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

Effective pK Values of the DMAEMA Units in the Conetworks

The effective pK values of the DMAEMA units in the conetworks were taken from Figure 3 as the pHs at 50% ionization and are presented in Table 3. The effective pK values of the DMAEMA units in all conetworks were significantly lower than the intrinsic dissociation constant of the DMAEMA monomer (pK 8.6) because of a multitude of reasons, including the (linear) polyelectrolyte effect, Donnan equilibrium (ion-partitioning in the gel phase) and reduction in the conetwork dielectric constant from the presence of the hydrophobic units. All conetworks were found to have similar pK values of the DMAEMA units, which, however, span a range of values from 5.5 to 6.3.

Degree of Swelling at Low and Neutral pH and in THF

The experimentally measured DS values of the conetworks, in pure water and in low pH water, were extracted from Figure 3 and are summarized in Figure 4. Figure 4 also contains the experimentally measured DS values of the conetworks in THF that reflects the quality of cross-linking in the conetworks. Consequently, an increase in the DS values was observed with the sol-fraction of the conetworks. In all cases, the DS values in THF were higher than those measured in pure water because THF is a non-selective solvent for both MMA and DMAEMA, whereas water is a selective solvent for the DMAEMA units. The highest DS values were determined in low pH water due to the ionization of the DMAEMA units that became completely charged, causing electrostatic repulsive forces between the polymer chains and accumulating counter ions, leading to further swelling of the conetworks. Figure 4(a) shows the effect of polymer composition, while Figure 4(b) presents the effect of conetwork architecture. The DS values increased with an increase in the content of the network in hydrophilic DMAEMA units. When the compositions of the conetworks were constant and the architecture of the conetworks was altered, the highest DS values were observed in the case of EGDMA_{0.5}-grad-DMAEMA₂₅grad-MMA₅₀-grad-DMAEMA₂₅-grad-EGDMA_{0.5} due to the lowest cross-linking density. The DS of the statistical endlinked conetwork was about twice as high as that of its triblock isomeric conetwork EGDMA_{0.5}-grad-MMA₂₅-grad-DMAEMA₅₀-grad-MMA₂₅-grad-EGDMA_{0.5} due to the inability of the former conetwork to microphase separate. As a result, the ionized DMAEMA units drag along the MMA units, which also contribute to swelling in the statistical copolymer-based end-linked conetwork. The lowest DS values were measured for the randomly cross-linked conetwork, indicating a higher effective cross-linking density.

Mechanical Properties of the Conetworks

The mechanical properties of all conetworks swollen in acidic water were investigated using dynamic mechanical analysis (DMA) in the compression mode. For the conetworks with different compositions, the modulus increased with the MMA content for two reasons. First, polyMMA is a harder material than water-swollen polyDMAEMA segments. Second, as the MMA content increased the conetwork DS values decreased [Fig. 5(a)], leading to a further increase in the

modulus. In the case of the homopolymer network of DMAEMA, with no hydrophobic units, the network exhibited poor mechanical properties and broke into small pieces, thus preventing its analysis. Unlike the DMAEMA homopolymer network, the MMA homopolymer network exhibited high mechanical properties but still, it could not be analyzed, because of the high stiffness of the sample which prevented the preparation of a rectangular-shaped sample that was required for the measurement.

In the case of conetworks with the same composition but different architecture, the randomly cross-linked statistical copolymer conetwork exhibited a somewhat higher modulus as compared with its isomeric end-linked conetwork counterparts. This can be attributed to the higher effective crosslink density of the former conetwork because of the random distribution of the cross-linker units along the polymer chains, consistent with the lower DS values of this conetwork at low pH [Fig. 5(b)].

CONCLUSIONS

The first ATRP synthesis of end-linked amphiphilic polymer conetworks with different composition and architecture was accomplished by sequential terpolymerization. The relatively low sol-fraction of the amphiphilic conetworks and the narrow MWD of the linear precursors confirmed the controlled synthesis of the conetworks. All conetworks exhibited substantial increase in their DS values at low pH. The DS of the conetworks at low pH increased with their hydrophilic contents. The higher DS observed in the case of the amphiphilic statistical conetwork, as compared with that of the amphiphilic conetwork based on the MMA-DMAEMA-MMA gradient copolymer was attributed to the absence of microphase separation in the former conetwork. The mechanical properties of the conetworks varied with their composition and architecture, mainly through their effects on the DS values.

The authors thank the Cyprus Research Promotion Foundation and the European Union Structural and Cohesion Funds for Cyprus for jointly supporting this work in the form of a PENEK2008 research grant (Project ENISX/03/08/045) to M.D.R. They are also grateful to the A. G. Leventis Foundation for a generous donation that enabled the purchase of the NMR spectrometer of the University of Cyprus. Finally, they thank Prof. Y.-L. Loo of Princeton University for her advice related to the kinetic experiments.

REFERENCES AND NOTES

1 (a) Tanaka, T. Sci Am 1981, 244(1), 124–138; (b) Osada, Y.; Ross-Murphy, S. B. Sci Am 1993, 268(5), 82–87.

2 (a) Hild, G. Prog Polym Sci 1998, 23, 1019–1149; (b) Malkoch, M.; Vestberg, R.; Gupta, N.; Mespouille, L.; Dubois, P.; Mason, A. F.; Hedrick, J. L.; Liao, Q.; Frank, C. W.; Kingsbury, K.; Hawker, C. J Chem Commun 2006, 2774–2776; (c) Nilsson, C.; Malmström, E.; Johansson, M.; Trey, S. M. J Polym Sci Part A: Polym Chem 2009, 47, 5815–5826; (d) Themistou, E.; Patrickios, C. S. J Polym Sci Part A: Polym Chem 2009, 47, 5853–5870; (e) Ozturk, G.; Long, T. E. J Polym Sci Part A: Polym Chem 2009, 47, 5437–5447; (f) Subramanyam, U.; Kennedy, J. P. J Polym Sci Part A: Polym Chem 2009, 47, 5272–5277.

3 (a) Triftaridou, A. I.; Kafouris, D.; Vamvakaki, M.; Georgiou, T. K.; Krasia, T. C.; Themistou, E.; Hadjiantoniou, N.; Patrickios, C. S. Polym Bull 2007, 58, 185-190; (b) Simmons, M. R.; Yamasaki, E. N.; Patrickios, C. S. Macromolecules 2000, 33, 3176-3179; (c) Triftaridou, A. I.; Hadjiyannakou, S. C.; Vamvakaki, M.; Patrickios, C. S. Macromolecules 2002, 35, 2506-2513; (d) Georgiou, T. K.; Patrickios, C. S.; Groh, P. W.; Iván, B. Macromolecules 2007, 40, 2335-2343; (e) Hadjiantoniou, N. A.; Patrickios, C. S. Polymer 2007, 48, 7041-7048; (f) Kali, G.; Georgiou, T. K.; Iván, B.; Patrickios, C. S.; Loizou, E.; Thomann, Y.; Tiller, J. C. Macromolecules 2007, 40, 2192-2200; (g) Triftaridou, A. I.; Vamvakaki, M.; Patrickios, C. S. Biomacromolecules 2007, 8, 1615-1623; (h) Kali, G.; Georgiou, T. K.; Iván, B.; Patrickios, C. S.; Loizou, E.; Thomann, Y.; Tiller, J. C. Langmuir 2007, 23, 10746-10755; (i) Vamvakaki, M.; Patrickios, C. S. Soft Mater 2008, 4, 268-276; (j) Triftaridou, A. I.; Loizou, E.; Patrickios, C. S. J Polym Sci Part A: Polym Chem 2008, 46, 4420-4432; (k) Hadjiantoniou, N. A.; Patrickios, C. S.; Thomann, Y.; Tiller, J. C. Macromol Chem Phys 2009, 210, 942-950.

4 (a) Vamvakaki, M.; Patrickios, C. S.; Lindner, P.; Gradzielski, M. Langmuir 2007, 23, 10433–10437; (b) Achilleos D. S.; Georgiou, T. K.; Patrickios, C. S. Biomacromolecules 2006, 7, 3396–3405; (c) Vamvakaki, M.; Patrickios, C. S. Chem Mater 2002, 14, 1630–1638.

5 Kafouris, D.; Gradzielski, M.; Patrickios, C. S. Macromolecules 2009, 42, 2972–2980.

6 Webster, O. W.; Hertler, W. R.; Sogah, D. Y.; Farnham, W. B.; Rajanbabu, T. V. J Am Chem Soc 1983, 105, 5706–5708.

7 (a) Krasia, T. C.; Patrickios, C. S. Macromolecules 2006, 39, 2467–2473; (b) Achilleos, M.; Krasia-Christoforou, T.; Patrickios, C. S. Macromolecules 2007, 40, 5575–5581; (c) Achilleos, M.; Legge, T. M.; Perrier, S.; Patrickios, C. S. J Polym Sci Part A: Polym Chem 2008, 46, 7556–7565.

8 Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadynne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. Macromolecules 1998, 31, 5559–5562.

9 (a) Wang, J. S.; Matyjaszewski, K. J Am Chem Soc 1995, 117, 5614–5615; (b) Matyjaszewski, K.; Xia, J. Chem Rev 2001, 101, 2921–2990; (c) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. Macromolecules 1995, 28, 1721–1723; (d) Kami-

gaito, M.; Ando, T.; Sawamoto, M. Chem Rev 2001, 101, 3689–3746; (e) Tsarevsky, N. V.; Matyjaszewski, K. Chem Rev 2007, 107, 2270–2299; (f) Matyjaszewski, K.; Tsarevsky, N. V. Nat Chem 2009, 1, 276–288.

10 (a) Patten, T. E.; Matyjaszewski, K. Adv Mater 1998, 10, 901–915; (b) Coessens, V.; Pintauer, T.; Matyjaszewski, K. Prog Polym Sci 2001, 26, 337–377; (c) Matyjaszewski, K. Polym Int 2003, 52, 1559–1565; (d) Sheiko, S. S.; Sumerlin, B. S.; Matyjaszewski, K. Prog Polym Sci 2008, 33, 759–785.

11 (a) Tsarevsky, N. V.; Matyjaszewski, K. Macromolecules 2005, 38, 3087–3092; (b) Gao, H.; Min, K.; Matyjaszewski, K. Macromolecules 2007, 40, 7763–7770; (c) Mespouille, L.; Coulembier, O.; Paneva, D.; Degée, P.; Rashkov, I.; Dubois, P. Chem Eur J 2008, 14, 6369–6378; (d) Mespoulle, L.; Coulembier, O.; Paneva, D.; Degée, P.; Rashkov, I.; Dubois P. J Polym Sci Part A: Polym Chem 2008, 14, 6369–6378; (e) Gao, H.; Li, W.; Matyjaszewski, K. Macromolecules 2008, 41, 2335–2340; (f) Oh, J. K.; Drumright, R.; Siegwart, D. J.; Matyjaszewski, K. Prog Polym Sci 2008, 33, 448–477; (g) Gao, H.; Li, W.; Matyjaszewski, K. Macromolecules 2008, 41, 2335–2340; (i) Li, W.; Gao, H.; Matyjaszewski, K. Macromolecules 2008, 41, 235–2340; (j) Gao, H.; Matyjaszewski, K. Macromolecules 2008, 41, 235–2340; (i) Li, W.; Gao, H.; Matyjaszewski, K. Macromolecules 2009, 42, 927–932; (j) Gao, H.; Polanowski, P.; Matyjaszewski, K. Macromolecules 2009, 42, 5925–5932.

12 Asgarzadeh, F.; Ourdouillie, P.; Beyou, E.; Chaumont, P. Macromolecules 1999, 32, 6996–7002.

13 (a) Johnson, J. A.; Lewis, D. R.; Díaz, D. D.; Finn, M. G.; Koberstein, J. T.; Turro, N. J. J Am Chem Soc 2006, 128, 6564–6565; (b) Johnson, J. A.; Finn, M. G.; Koberstein, J. T.; Turro N. J.; Macromolecules 2007, 40, 3589–3598; (c) Johnson, J. A.; Baskin, J. M.; Bertozzi, C. R.; Koberstein, J. T.; Turro, N. J. Chem Commun 2008, 3064–3066.

14 Matyjaszewski, K.; Miller, P. J.; Pyun, J.; Kickelbick, G.; Diamanti, S. Macromolecules 1999, 32, 6526–6535.

15 Zhang, X.; Matyjaszewski, K. Macromolecules 1999, 32, 1763–1766.

16 (a) Nanda, A. K.; Matyjaszewski, K. Macromolecules 2003, 36, 1487–1493; (b) Tang, W.; Matyjaszewski, K. Macromolecules 2006, 39, 4953–4959; (c) Tang, W.; Kwak, Y.; Braunecker, W.; Tsarevsky, N. V.; Coote, M. L.; Matyjaszewski, K. J Am Chem Soc 2008, 130, 10702–10713.

17 Matyjaszewski, K.; Shipp, D. A.; Wang, J. L.; Grimaud, T.; Patten, T. E. Macromolecules 1998, 31, 6836–6840.