ARTICLE

Synthesis and Characterization of PEG Polymer Brushes via Cyclopolymerization of 1,2,3-Triazole Tethered Diacrylates

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Poly(ethylene glycol) (PEG) macromolecular brushes were synthesized directly via reversible addition-fragmentation chain transfer polymerization cyclopolymerization of diacrylate monomers bearing PEG functional groups through the formation of 11-member rings. The diacrylate monomers bearing PEG functional groups are the 1,2,3-triazole-tethered diacrylate macromolecular monomers with different PEG lengths synthesized via the so-called "click" chemistry. The bulky hindrance of PEG chains affected the polymerization behavior of the diacrylate macromolecular monomers, and the diacrylate monomers showed strong tendency to cyclopolymerization rather than crosslinking. NMR analysis and gel permeation chromatography profiles proved the high efficiency of cyclopolymerization without side reactions. The aqueous solutions of the obtained PEG macromolecular brushes were fluorescent under UV excitation. The fluorescence depended dramatically on the concentration of brush-like polymers due to the aggregation of cyclopolymer in water, and could be quenched by the addition of DNA.

Key words: Cyclopolymerization, Macromolecular brush, Fluorescence quenching, DNA

I. INTRODUCTION

Poly(ethylene glycol) (PEG) and PEG-based polymeric materials have been used for many biological applications because of PEG's capacity to repress protein adsorption and cell adhesion [1−4], as well as its nontoxicity and its nonimmunogenicity as deployed in the pharmaceutical industry to elongate the circulation time of protein drugs, stealth liposomes, and so forth [5]. Furthermore, PEG is a non-toxic, water soluble polymer, and hydrophobic molecules become soluble when coupled to PEG [1]. Stefania Galdiero and Marcus Weck reported a biodegradable delivery scaffold based on poly(lactide)-graft-PEG (PLA-g-PEG), and PEG decreased the hydrophobicity of the functionalized PLA [6]. The PEG brushes were often formed via the graft-to methodology, and usually could not be polymerized directly via the vinyl polymerization of PEG functionalized vinyl monomers because of the bulky hindrance.

In this work, we synthesized the aqueous soluble PEG brushes directly by means of the cyclopolymerizations of divinyl monomers. In cyclopolymerization, bifunctional monomers polymerize to yield linear polymers with cyclic repeating units. Cyclopolymerization of bifunctional monomers requires predominant intramolecular ring-closing reaction over intermolecular propagation that typically causes cross-linking reaction [7, 8]. However, only specifically designed divinyl monomers with fixed conformation that prefer intramolecular ring-closing reaction can be used for the cyclopolymerization, thus cyclopolymerization is currently limited by few choices of monomers. Endo *et al.* designed a bis-methacrylate monomer with conformations favorable for ring-closing owing to the directing effects of the chiral cyclohexane ring and the hydrogen bonds between the two vinyl groups [9]. Sawamoto *et al.* realized a high efficient cyclopolymerization of PEG tethered dimethacrylates via cation template-assisted formation of pseudo-crown ether, to give linear controlled polymers without cross-linking [10]. Furthermore, very dilute monomer concentration was often adopted to decrease the rate of intermolecular propagation, and to prevent crosslinking.

We design and synthesize new diacrylate monomers with PEG functionalized 1,2,3-triazole groups via the so-called "click" chemistry [11], cyclopolymerization was carried out readily to form 11-member ring repeating structures in the backbones and PEG brushes as the side chains. What's more, the functional 1,2,3-triazole groups render the products fluorescence properties.

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II. EXPERIMENTS

A. Materials

1,4-Butynediol, acryloyl chloride, sodium azide and DNA (fish sperm, Na salt) were purchased from Aladdin. Chloridized methoxypolyethylene glycols of two molecular weights were synthesized from methoxypolyethylene glycols (mPEG) (M_n=350 and 500) [12−14]. Triethylamine was dried by CaH_2, and then distilled. 2,2'-Azobis-(isobutyronitrile) (AIBN) was purified by recrystallization from ethanol. The chain transfer agent (CTA) 1-dodecyl-(dimethyl-acetic acid) trithiocarbonate was synthesized according to method in Ref.[15]. *N*,*N*-dimethyl formamide (DMF) was used as received.

B. Methods

^{1}H NMR and ^{13}C NMR spectra were recorded on an AVANCE III 400 MHz Super-conducting Fourier nuclear magnetic resonance spectrometer. The weight-average molecular weight (M_w) and polydispersity index (PDI) (M_w/M_n) of the polymers were determined by gel permeation chromatography (GPC) with a PLgel Mixed-C column (Agilent Technologies). Agilent Technologies 1100 Series GPC Analysis System with Isocratic G1310A pump and RI-G1362A refractive index (RI) detector (set at 35 °C) were used. The eluent was DMF at a flow rate of 1.0 mL/min. Fluorescence spectra were measured on a Shimadzu RF-5301PC fluorescence spectrophotometer.

C. Synthesis of the 1-methoxypolyethylene glycols-4,5-di(hydroxymethyl)-1H-[1,2,3]triazole

Two MDHMT (1-methoxypolyethylene glycols-4,5-di(hydroxymethyl)-1H-[1,2,3]triazole) with two different mPEGs (M_n=350 and 500) were synthesized through cyclo-addition between methoxypolyethylene glycols azide and 1,4-butynediol. As a typical process, MDHMT from mPEG with M_n of 350 was synthesized as follows: chloridized methoxypolyethylene glycols (8.0 g, 0.023 mol) was added dropwisely to the mixture of 1,4-butynediol (1.98 g, 0.02 mol) and sodium azide (1.93 g, 0.03 mol) in 20 mL DMF at room temperature, then the mixture was stirred at 130 °C for 9 h. Cooled to room temperature, the mixture was diluted with $CHCl_3$, filtered to remove the precipitate. The solution was purified by a neutral alumina column and DMF was removed under reduced pressure. MDHMT was obtained as light yellow liquid (8.5 g), yield of 78.7%. MDHMT from mPEG with M_n of 500 was synthesized with the same procedure, and was obtained as light yellow liquid (7.0 g) with yield of 70%.

D. Synthesis of the macromonomer MTDA

MDHMT (mPEG M_n=350, 6.0 g, 0.013 mol), triethylamine (5.7 mL, 0.04 mol), and copper powder were dissolved in CH_2Cl_2 (10 mL) in ice water bath, then acryloyl chloride (3.3 mL, 0.04 mol) was dissolved in CH_2Cl_2 (30 mL) and added dropwisely, warmed to room temperature and stirred for 48 h. The resulting mixture was treated with Na_2CO_3, stirred for 30 min, filtered and passed through a neutral alumina column using CH_2Cl_2 as the solvent. The crude product was dissolved in methanol, then dropped into Et_2O to remove the precipitate, and concentrated to obtain 5.2 g (72.2%) of MTDA (macromonomer 1-methoxypolyethylene glycols-4,5-di(acryloyloxymethy)-1H-[1,2,3]triazole) (mPEG M_n=350) which was named as monomer A. MTDA (mPEG M_n=500) was synthesized by the same procedure as that for MTDA (mPEG M_n=350) to obtain 4.7 g (68.2%), the product was named as the monomer B.

E. RAFT polymerization of the macromonomer MTDA

In a typical procedure, macromonomer A (1.8 mmol, 1 g), 1-dodecyl-(dimethyl-acetic acid) trithiocarbonate (0.054 mmol, 19.66 mg), and AIBN (0.018 mmol, 2.95 mg) were dissolved in DMF (2.25 mL) in 5 mL tube with a magnetic stirring bar. The mixture was degassed by three freeze-pump-thaw cycles, sealed under vacuum, and placed in an oil bath at 80 °C for 48 h while stirring. The polymer was purified by repeatedly precipitation in Et_2O, concentrated and dried under vacuum at 20 °C for 48 h. And the prouducts were named as polymer A. Polymerization of the macromonomer B was the same as the monomer A, and the series of polymers were named as polymer B.

F. Fluorescence of cyclopolymer and the interaction with DNA

The fluorescence of the polymers with different concentrations (ranging from 0 mol/L to 0.34 mol/L) in ultrapure water was tested. Effects of DNA in the fluorescence of the cyclopolymers were investigated, and both single and double strand DNAs were tested. The aqueous solution of single strand DNA was obtained by being placed in an oil bath at 92 °C for 30 min and then quickly cooled to room temperature.

III. RESULTS AND DISCUSSION

A. Synthesis of the macromonomer MTDA

We synthesized two kinds of macromonomer MTDA with two different mPEG groups (M_n=350 and 500)

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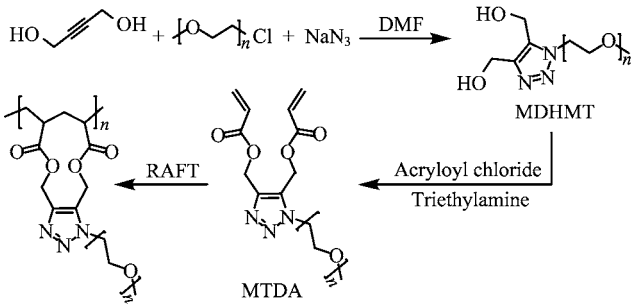

Scheme 1 Synthesis of the macromonomer MTDA and cyclopolymerization of the macromonomer MTDA.

through the "click chemistry" according to our previous work and followed with esterification reaction (Scheme 1) [11]. MDHMT was synthesized based on "Click chemistry" at first. In the one pot mixture, chloridized mPEG formed mPEG azide, and then reacted with 1,4-butynediol at high temperature to form 1,2,3-triazole with mPEG functional groups. The structure of MDHMT was verified by $^1H/^{13}C$ NMR spectrum as depicted in Fig.1. In ^1H NMR spectra (Fig.1(a)), the -CH_2- groups adjacent to the -OH of MDHMT were doublet peaks at 4.64 ppm due to coupling with -OH, and the -CH_2- groups adjacent to 1,2,3-triazole were two sets of three peeks at 4.4 and 3.7 ppm respectively because of spin splitting. In the ^{13}C NMR spectrum (Fig.1(b)), the chemical shifts of -CH_2- groups at 1- and 5-substitution positions in 1,2,3-triazole were at 144 and 134 ppm. The macromonomer MTDA was synthesized by esterification reaction of acryloyl chloride and MDHMT [16−19]. As shown in Fig.2, there were three sets of peaks between 5.5−6.5 ppm (a, a′, b, b′, c, c′) belonging to the vinyl groups of MTDA and the double peaks at 5.2 and 5.3 ppm were the methylene next to the 1,2,3-triazole, so the chemical shifts and proportion of peaks verified the structure of macromonomer MTDA. The NMR results of monomer were conducive to the structural analysis of cyclopolymers. The NMR analysis results revealed that both MDHMT and MTDA were obtained with high purity as well.

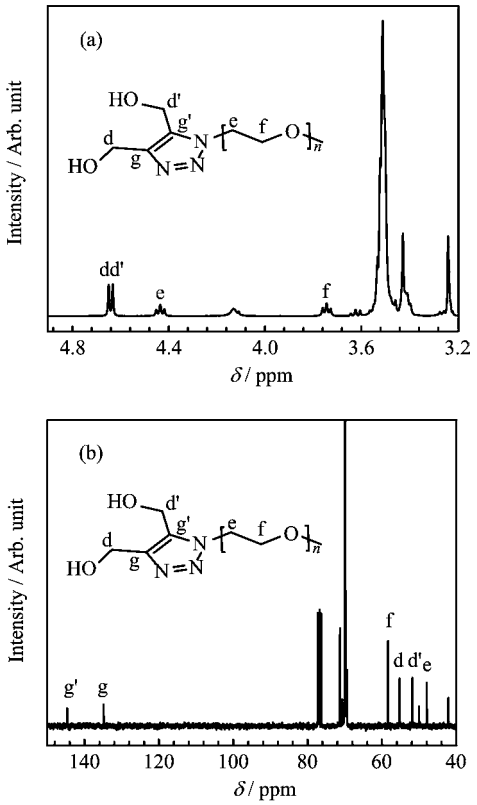

FIG. 1 (a) ^1H NMR and (b) ^{13}C NMR of MDHMT in $CDCl_3$.

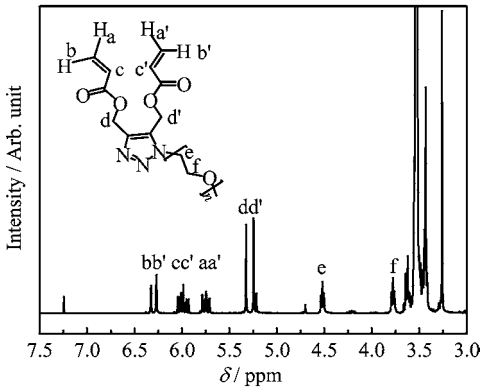

FIG. 2 ^1H NMR of the macromonomer MTDA in $CDCl_3$.

B. Cyclopolymerization of the macromonomer MTDA

For cyclopolymerization of divinyl monomers, it is essential to choose an appropriate monomer concentration to control sequential and intramolecular dimeric propagation of the macromonomer MTDA over intermolecular growth (cross-linking). For small divinyl monomers, the monomer concentration suitable for cyclopolymerization is usually very dilute, for example, 0.08 mol/L. We studied the reversible addition fragmentation chain transfer cyclopolymerization behaviors of macromonomer MTDA at different monomer concentrations. For each polymerization systems with different monomer concentrations, M_n and M_w/M_n obtained at different polymerization time versus monomer conversion are listed in Table I. The polymerization of macromonomer MTDA was carried out using AIBN as initiator at different time and different monomer concentration, and molar ratio [MTDA]/[CTA]/[AIBN] was 100/3/1. As the Table I exhibits, the molecular weight and conversion were both increased with the monomer concentration increasing. Even at very high monomer concentration, no gels were formed in all these systems, and all the PDIs were small. This indicated that the divinyl monomers showed strong tendency to

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TABLE I Characteristics of polymerization of MTDA in the presence of RAFT with molar ratio [MTDA]/[CTA]/[AIBN] of 100/3/1.

Run[a]	t/h	$[MTDA]_0$	Conv.[b]/%	M_n[c]/kD	PDI[c]	M_n[d]/kD
A1	9	0.8	25	9.3	1.42	8.5
A2	23	0.8	37.5	9.8	1.49	10.3
A3	33	0.8	55	10.1	1.46	12.6
A4	48	0.8	75	10.8	1.47	11.3
A5	68	0.8	76.5	11.2	1.45	12.8
A6	48	0.08	1.1	3.4	1.37	4.3
A7	48	0.16	1.3	4.8	1.55	5.6
A8	48	0.2	27.4	5.7	1.53	7.3
A9	48	0.4	29.3	8.9	1.54	9.6
A10	48	0.6	63.1	11.3	1.61	12.7
A11	48	1.0	78.1	13.3	1.77	15.8
B1	8	0.6	60	15.4	1.13	16.3
B2	21	0.6	66.5	16.3	1.12	17.2
B3	33	0.6	72.5	16.6	1.12	17.8
B4	48	0.6	75.5	16.6	1.13	17.7
B5	70	0.6	76.5	16.8	1.12	17.8
B6	48	0.04	45.2	14.3	1.11	14.6
B7	48	0.08	49.6	15.2	1.11	16.8
B8	48	0.2	50.0	15.2	1.14	16.2
B9	48	0.4	61.7	15.4	1.15	17.3
B10	48	0.8	66.2	18.3	1.17	20.1

[a] Polymer A (mPEG M_n=350), polymer B (mPEG M_n=500).
[b] Monomer conversion based on ^{1}H NMR analysis.
[c] M_n and PDI obtained with GPC.
[d] M_n calculated based on ^{1}H NMR.

cyclopolymerization rather than crosslinking. This was attributed to the bulky hindrance of PEG chains that affected the polymerization behavior of the diacrylate macromolecular monomers. This could also be proved by the fact that the series of polymers B with longer PEG chain lengths had higher M_n and smaller polydispersity index than that for polymers A. According to the results listed in Table I, we chose monomer concentration of 0.8 mol/L for further investigation of the cyclopolymerization of monomer A. However, phase-separation took place in monomer B at 0.8 mol/L, thus 0.6 mol/L was used instead. So we chose 0.8 mol/L as the concentration of monomer A and 0.6 mol/L as the concentration of monomer B to explore the kinetic of polymerization, respectively.

Cyclopolymerization kinetics of macromonomer A and B were studied as depicted in Fig.3. Though the obtained polymers showing very narrow molecular weight distribution, the rates of the cyclopolymerization of both monomer A and B were significantly suppressed due to the hindrance of PEG groups. Thus the curves of M_n *vs.* monomer conversion or poly-

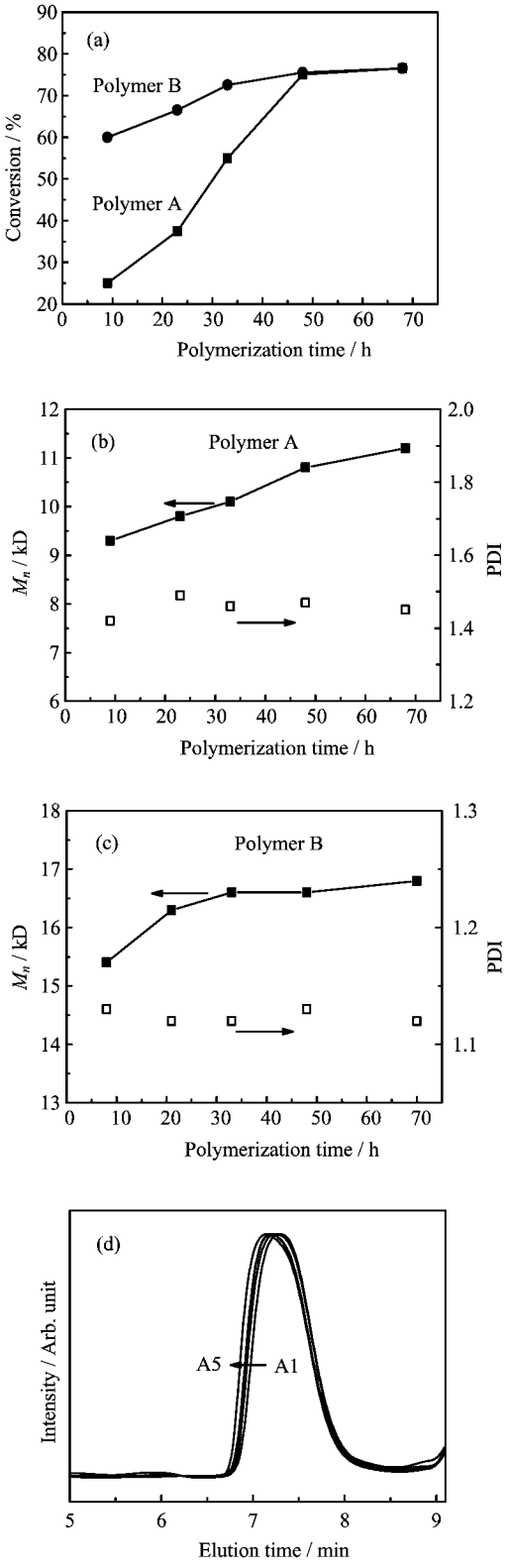

FIG. 3 Dependence of conversion (a), molecular weight and PDI of polymers A (b) and B (c) on polymerization time with [MTDA]/[CTA]/[AIBN]=100/3/1. (d) GPC traces of polymers of A1−A5.

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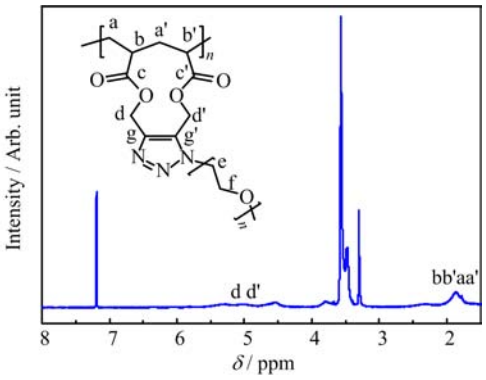

FIG. 4 ^{1}H NMR spectrum of cyclopolymer in $CDCl_3$.

merization time for either monomer A or B were not linear, but down-turning curves instead. As shown in Fig.3(a), the conversion of the macromonomer A and B was increased with the polymerization time, while the conversion of the macromonomer B was higher and changed slower than the macromonomer A because of the longer side chains and higher intramolecular addition efficiency. The curves of M_n *vs.* polymerization time demonstrated the same characteristics. Both the two polymerization systems yielded polymers with small PDIs, *i.e.*, the average PDI of polymer A was about 1.45 (Fig.3(b)) and about 1.12 of polymer B (Fig.3(c)). Contrast to the polymers A, the cyclopolymerization of polymers B with the lower PDI was easier to control the increasing of polymers chain. GPC profiles (Fig.3(d)) showed symmetry peaks which indicated the cyclopolymerization yielded linear polymers.

The structure of one of the obtained cyclopolymers was analyzed by ^{1}H NMR spectroscopy (Fig.4). Compared with the ^{1}H NMR spectrum of monomer, no signal assignable to pendant unsaturation was observed in the ^{1}H NMR characterization of cyclopolymer, clearly evidenced by the disappearance of vinyl signals in the range from 5.5 ppm to 6.5 ppm. The signals of some sets of width peaks at 1−2 and 4.5−5.4 ppm attributed to the -CH_2- groups (carbon a, a′, b, b′, d, d′) in the main and side chains of cyclopolymer respectively. So the disappearance of divinyl groups indicated the polymerization of the macromonomer was cyclopolymerization which was also in agreement with the GPC curves.

C. Fluorescence of the cyclopolymers and the interaction with DNA

The obtained cyclopolymers were well soluble in water. The aqueous solutions of the cyclopolymers showed green fluorescence upon excitation with the maximum excitation wavelength of 400 nm. The fluorescence arose from the 1,2,3-triazole groups. The dependence of the fluorescence on the concentration of the cyclopolymers was investigated. As shown in Fig.5(a), the fluorescence

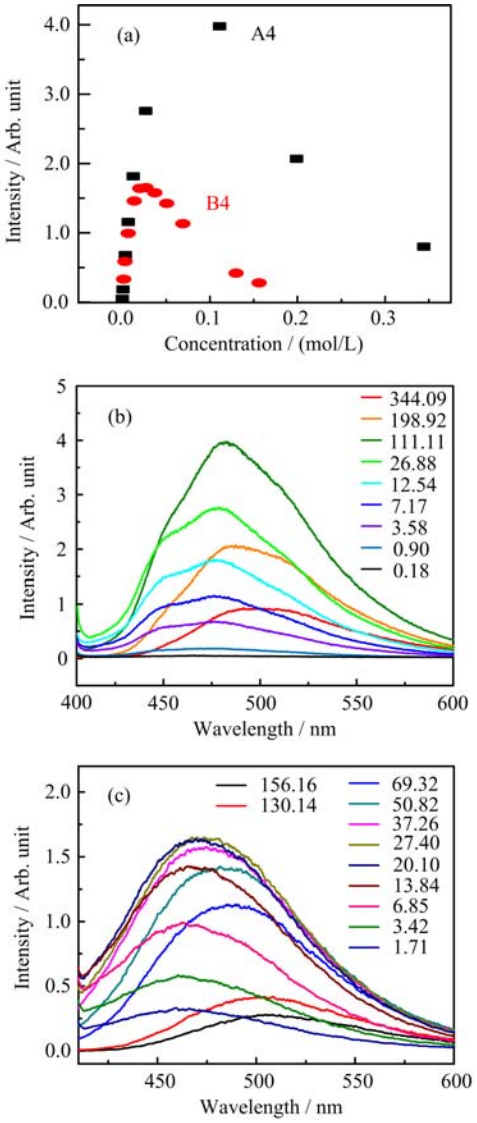

FIG. 5 (a) Fluorescence intensity of polymer A4 and B4 with the different concentration of polymers. (b) Fluorescence spectra of polymer A4 with different concentration. (c) Fluorescence spectra of polymer B4 with different concentration (mg/mL).

intensities of polymer A4 and B4 (see Table I) were increasing very quickly with increased polymer concentration at first and then decreasing at higher concentration. Thus there were fluorescence maxima when changing the polymer concentration. The very quick increase of fluorescence at increasing polymer concentration could be simply rationalized by the increase of the fluorophors, but most probably could be related to the phase transition occurring at increased polymer concentrations, which needs further investigation in the future. The decrease of the fluorescence at higher concentration might be due to the concentration quenching effect. As for A4, the fluorescence intensity increased with the polymer concentration until it reached 0.11 mol/L,

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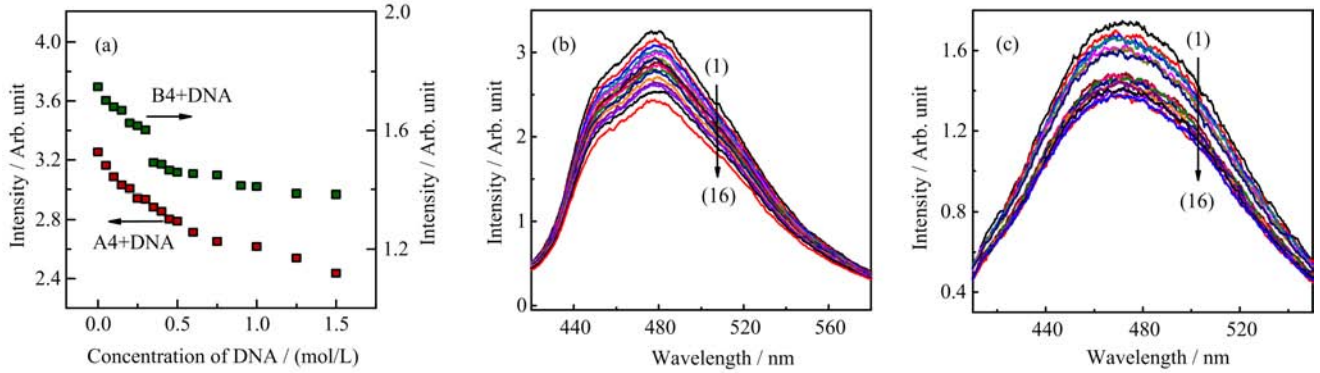

FIG. 6 (a) Fluorescence intensity of polymer A4 and B4 with the different concentration of DNA. Fluorescence intensity spectra of A4 (b) and B4 (c) the different concentration of DNA with 0 (1), 0.05 (2), 0.1(3), 0.15 (4), 0.2 (5), 0.25 (6), 0.3 (7), 0.35 (8), 0.4 (9), 0.45 (10), 0.5 (11), 0.6 (12), 0.75 (13), 1.0 (14), 1.25 (15), 1.5 mol/L (16).

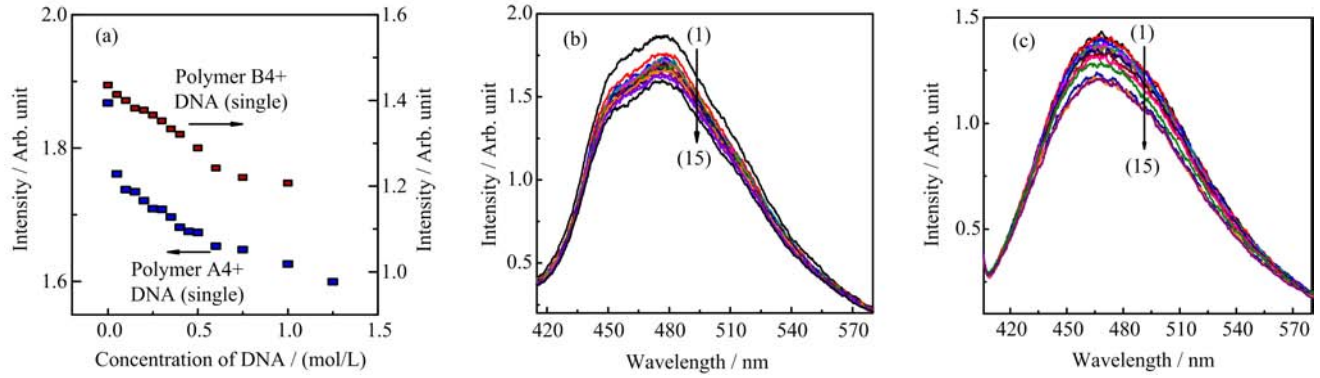

FIG. 7 (a) Fluorescence intensity of polymer A4 and B4 with the different concentration of single DNA. Fluorescence intensity spectra of A4 (b) and B4 (c) with the concentration single DNA with 0 (1), 0.05 (2), 0.1(3), 0.15 (4), 0.2 (5) 0.25 (6), 0.3 (7), 0.35 (8), 0.4 (9), 0.45 (10), 0.5 (11), 0.6 (12), 0.75 (13), 1.0 (14), 1.25 mol/L (15).

and the emission wavelength red-shifted from 406 nm to 504 nm with the increasing of the concentration of A4 (Fig.5(b)). The fluorescence of polymer B4 showed the similar characteristics to A4, and the maximum fluorescence intensity was at the concentration of 0.026 mol/L which was lower than A4 because of the longer side chain and higher molecular weight with the emission wavelength shifting from 460 nm to 507 nm (Fig.5(c)).

For the possible bio-applications of the obtained polymer brushes, we investigated the interaction of DNA on the polymer brushes according to the fluorescence analysis [20, 21]. Effects of DNA in the fluorescence of the cyclopolymers were investigated, and both the single and double strand DNAs were tested. The single strand DNA was freshly synthesized according to a standard procedure widely used in bio-chemistry by heating an aqueous solution of double strand DNAs. While the DNA was heated to 92 °C, the double helix of DNA was unwinding. We measured the variety of fluorescence intensity with the addition of either single or double strand DNAs. The original double strand DNA was a fluorescence quencher of cyclopolymers A4 and B4. With the concentration of DNA increasing, the fluorescence intensity of the polymer was decreasing (Fig.6(a)). The fluorescence intensity of A4 was decreased from 3.3 to 2.4 with increasing concentration of DNA (Fig.6(b)), and fluorescence intensity of B4 was decreased from 1.7 to 1.4 (Fig.6(c)). The fluorescence quench indicated that DNA could interact with the cyclopolymers obtained in this work. DNA quenched polymer A more significantly than polymer B with longer PEG chains. Longer PEG chains might shelter the interaction with DNA.

With the concentration of single DNA increasing, the fluorescence intensity of the polymer was decreasing (Fig.7(a)), the phenomenon was similar to the original double DNA. When the single strand DNA was used to quench the fluorescence of the cyclopolymers, the fluorescence intensity of A4 decreased from intensity of 1.9 to 1.2 and the range of decrease was smaller than that caused by the original DNA (Fig.7(b)). B4 was quenched from intensity of 1.4 to 1.2 (Fig.7(c)). This indicated that the single strand DNA had weaker interaction with the cyclopolymers compared with the double strand DNA.

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IV. CONCLUSION

PEG macromolecular brushes were synthesized directly via the RAFT cyclopolymerization of diacrylate macromolecular monomers carrying PEG functional groups through the formation of 11-member rings. The success of cyclopolymerization was confirmed by NMR, GPC, and kinetic analysis. The obtained polymer brushes were well soluble in water. The 1,2,3-triazole groups were fluorescent and thus were good marks for investigating the interaction of DNA with the cyclopolymers, because the fluorescence of the obtained cyclopolymers could be quenched by DNA. According to the fluorescence quenching analysis, the double strand DNA seemed to more strongly interact with the polymer brush than the single strand DNA.

V. ACKNOWLEDGMENTS

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