e-Polymers **2007**, no. 072

http://www.e-polymers.org

ISSN 1618-7229

The study of synthesis of poly(ethylene oxide)-*b*-poly(N,N-dimethylacrylamide) by atom transfer radical polymerization and self-assembly in selective solvents

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(Received: 27 April, 2007; published: 27 July, 2007)

Abstract : Poly(ethylene oxide)-*b*-poly(*N*, *N*-dimethylacrylamide) (PEO-*b*-PDMA) was synthesized by successive atom transfer radical polymerization (ATRP) of *N*,*N*-dimethylacrylamide (DMA) monomer using PEO-Br macro initiators as initiator, CuBr and 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazamacrocyclotetra decane ($Me_6[14]aneN_4$) as catalyst and ligand.PEO–Br macroinitiator was synthesized by esterification of PEO with 2-bromoisobutyryl bromide. GPC and ^{1}H NMR studies show that the plot of $\ln([DMA]_0/[DMA])$ against the reaction time is linear, and the molecular weight of the resulting PDMA increased linearly with the conversion. Within 3 h, the polymerization can reach almost 60% of conversion. PEO-*b*-PDMA copolymer with low polydispersity index ($M_w/M_n \approx 1.1$) is obtained. Self-assembly of PEO-b-PDMA in selective solvents is also studied. It could self-assemble into micelles in methanol/acetone (1/10, v/v) solution. TEM analyses of the PEO–b-PDMA micelles with narrow size distribution revealed that their size and shape depend much on the copolymer composition.

Introduction

Water-soluble macromolecules have attracted much attention due to their applications in medicine and biotechnology. PEO and PDMA are two of the most frequently investigated classes of hydrophilic polymer. Well-defined block copolymers with a PDMA block are of commercial interest and have many potential applications for their solubility in water depending on temperature or pH [1, 2]. The recent development of controlled/‘living’ radical polymerizations, especially ATRP, has opened a new route to synthesize functional and architectural polymers with well-defined structures [3]. Thus PEO-*b*-PDMA double hydrophilic block copolymer can be synthesized using this method. But ATRP of DMA remains challenging since both DMA and PDMA are strong coordinating ligands that can compete for the binding of the metal catalysts in polymerization system. The polymerization of DMA with $RuCl_2(PPh_3)_3$ in conjunction with an alkyl halide (R-X; X = Br, Cl) as an initiator in the presence of Al(O*i*-Pr)$_3$ in toluene produced PDMA with polydispersities higher than 1.6 [4]. When stronger binding ligand tris [2-(dimethylamino) ethyl] amine (Me_6TREN) was used in the solution ATRP of DMA, the linear increase of molecular weight with conversion was observed, and the PDMA with narrow polydispersities ($M_w/M_n \approx 1.1$-

1.2) was obtained [5-6]. Ding et al. [7] report when the ATRP of DMA using methyl 2-chloropropionate as the initiator and CuCl/ N,N'-bis (pyridin-2-ylmethyl 3-hexaoxo-3-oxopropyl) ethane-1, 2-diamine (BPED) as the catalyst and ligand, the polymerization reached very high conversions (>90%), producing PDMA with molecular weights very close to the theoretical values and low polydispersity. But the synthesis of ligand (Me_6TREN or BPED) is difficult. When 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (Me_4Cyclam) was used as the ligand in the ATRP of DMA, high yields of PDMA with very high molecular weight were obtained, but the polydispersity of PDMA was very broad (PDI $\approx$ 2.2) [8]. All these facts indicate that the ligand is very important for controlled radical polymerization of DMA.

In this paper, we select a macrocyclotertraamine ($Me_6[14]aneN_4$), which is synthesized easily but different from Me_4Cyclam, as ligand in the ATRP of DMA, and investigate the "living" nature of polymerization. First, a macroinitiator (PEO-Br) for atom transfer radical polymerization has been synthesized by reacted PEO with 2-bromoisobutyryl bromide. Then PEO-*b*-PDMA with well-controlled molecular weight and narrow molecular weight distribution was obtained by using ATRP of DMA with PEO-Br as macroinitiator, CuBr, $Me_6[14]aneN_4$ as catalyst and ligand. The "living" nature of polymerization and self-assembly of this block copolymer in methanol/acetone (1/10, v/v) by varying the length of PDMA block is also studied.

Results and Discussion

Synthesis of macroinitiator and PEO-b-PDMA copolymer

Fig. 1 reveals the representative FT-IR spectra of PEO, PEO–Br and the PEO-b-PDMA block copolymers. The absorption occurs at 1109 cm^{-1} which are attributed to the ether group of the copolymers and PEO precursor. After acetylation reaction, a carbonyl absorption occurs at 1734 cm^{-1} correspondingly in the spectrum of PEO–Br macroinitiator (Fig. 1b). A band at 1635 cm^{-1} is due to the carbonyl group of amide moiety of the PDMA chain. These data illustrate the presence of both PEO and PDMA blocks in the polymer chain (Fig. 1c).

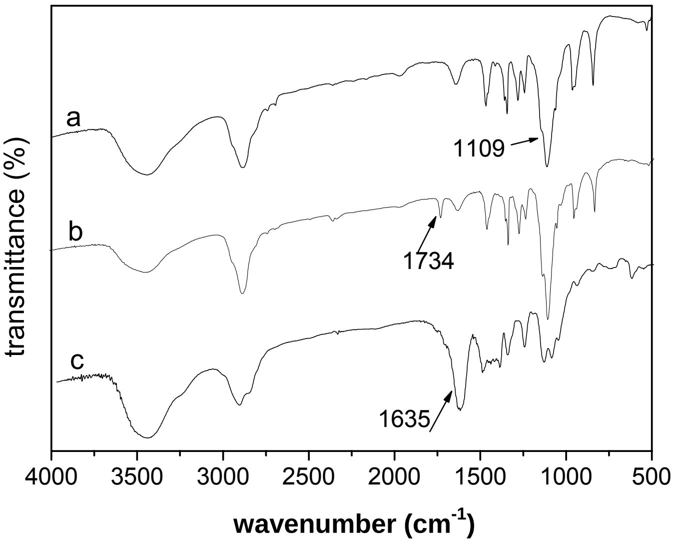

Fig. 1. FT-IR spectra of (a) PEO, (b) PEO–Br and (c) PEO-b-PDMA.

Figure 2 shows the ^{1}H NMR spectra of the esterified PEO in $CDCl_3$. The peak area ratio of b (δ=3.44 ppm), c (δ=4.32 ppm) and d (δ=1.94 ppm) is 3:2:6, which confirmed the complete esterification of hydroxyl end group of the PEO.

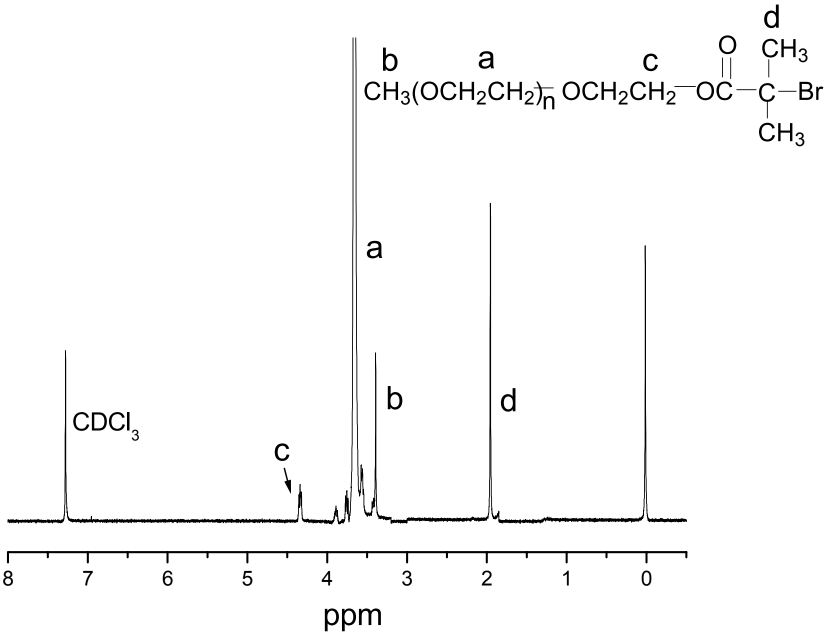

Fig. 2. ^{1}H NMR spectra (in $CDCl_3$) of PEO-Br macroinitiator.

DMA was polymerized in toluene using PEO-Br as the macroinitiator, CuBr/ Me_6[14]aneN_4 as the catalyst and ligand. The conditions and results are listed in Table 1. M_n calculated from theory ($M_{n,\ \mathrm{th.}}$) is lower than M_n ($M_{n,\ \mathrm{GPC}}$) obtained from GPC. The reason for *the* $M_{n,\ \mathrm{th}}$ and $M_{n,\ \mathrm{GPC}}$ difference is the linear polystyrene standards used as calibration in GPC measurement.

Tab. 1. ATRP of DMA initiated with PEO-Br/CuBr/ Me_6[14]aneN_4[a].

No.	time (h)	conversion(%)[b]	$M_{n,\ \mathrm{th}}$[c]	$M_{n,\ \mathrm{GPC}}$[d]	M_w/M_n[d]
PEO	0	0	2000	2200	1.06
PEO-*b*-PDMA-1	0.5	18	5600	6100	1.07
PEO-*b*-PDMA-2	1.0	29	7800	8200	1.16
PEO-*b*-PDMA-3	2.0	40	10100	12000	1.10
PEO-*b*-PDMA-4	3.0	54	12900	15200	1.21
PEO-*b*-PDMA-5	6.0	69	15900	19600	1.25

[a] Polymerization conditions: DMA/PEO-Br/CuBr/ Me_6[14]aneN_4=200/1/1/3 (molar ratio); Temperature: 20 ^{0}C; Solvent: toluene.

[b] Conv (%)=[$I_{1.3\text{-}1.9}$/ ($I_{1.3\text{-}1.9}$ +$I_{6.3}$)]×100%. Where $I_{1.3\text{-}1.9}$ and $I_{6.3}$ are the integral values of the peaks at δ=1.3-1.9 ppm (polymer CH_2) and δ= 6.3 ppm (monomer CH_2), respectively.

[c] $M_{n,\ \mathrm{th}}$ = (M_m×conversion×[M]/[I])+M_i, where M_m and M_i are the molar masses of monomers and macroinitiator, respectively, [M] and [I] are the concentration of monomer and macroinitiator, respectively.

[d] Obtained from GPC.

^{1}H NMR spectrum of PEO-*b*-PDMA is shown in Fig. 3. The peaks at δ=2.8-3.1 ppm is ascribed to molar contributions of the methyl protons ($N(CH_3)_2$) in DMA. The integration ratio of peaks b and c to the peaks of methene and methine protons in the main chain is 2:1, indicating the formation of PDMA. Careful analysis of Fig. 3, will show that the residual species of PEO-Br stand at both end of PDMA chain. The peaks at δ=1.2 ppm, 3.4 ppm corresponds to methyl protons respectively.

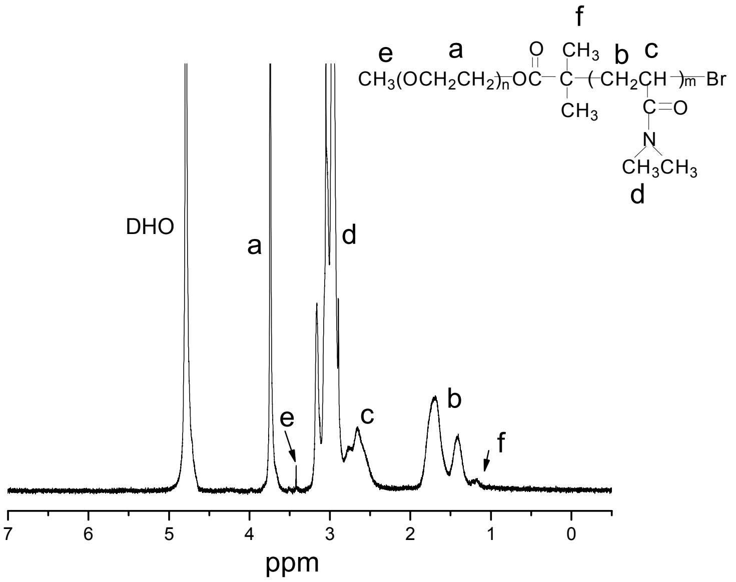

Fig. 3. ^{1}H NMR spectra (in D_2O) of PEO-b-PDMA prepared by ATRP with molar ratio PEO-Br/CuBr/ Me_6[14]aneN_4=1:1:3.

Fig. 4 illustrates the relationship of conversion and ln($[DMA]_0/[DMA]$) with the polymerization time. Conversion can be calculated from ^{1}H NMR of the crude product. After the reaction was carried out for a prescribed time, a small amount of sample was taken out, the conversion was measured based on ^{1}H NMR data.

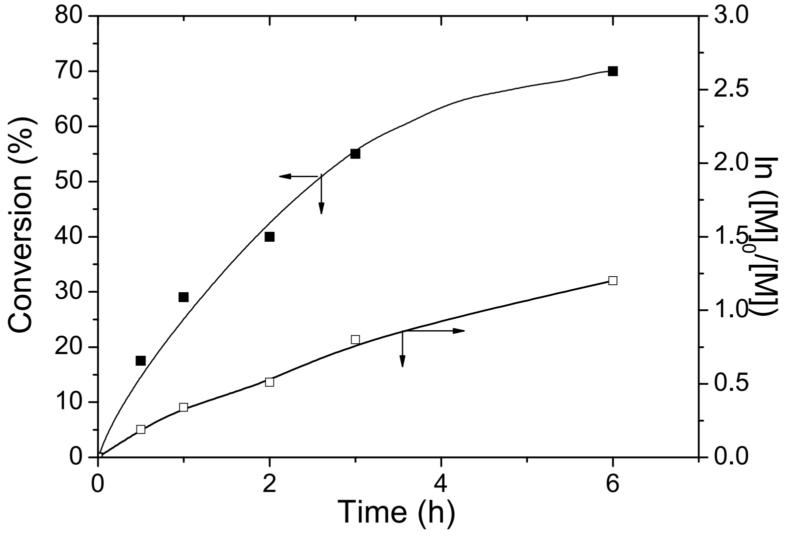

Fig. 4. Plots of conversion and ln ($[DMA]_0/[DMA]$) against polymerization time for the ATRP of DMA in toluene at 20 ^{0}C. $[DMA]_0/[PEO\text{-}Br]_0/[CuBr]_0/Me_6[14]aneN_4$ =200/1/ 1/3 (molar ratio).

The fast polymerization can be evidenced by almost 60% of conversion in 3 h (see Fig. 4), suggesting that a strong coordination between copper and the $Me_6[14]aneN_4$ ligand. A linear plot of $\ln([M]_0/[M])$ vs. time demonstrates that the number of propagating species remained constant (see Fig. 4). Hence, the molecular weight of resulting PDMA can be controlled by the initial feed ratio of DMA to PEO-Br and the conversion of DMA since the molecular weights of the resulting PDMA increased linearly with the conversion of the DMA as shown in Fig. 5.

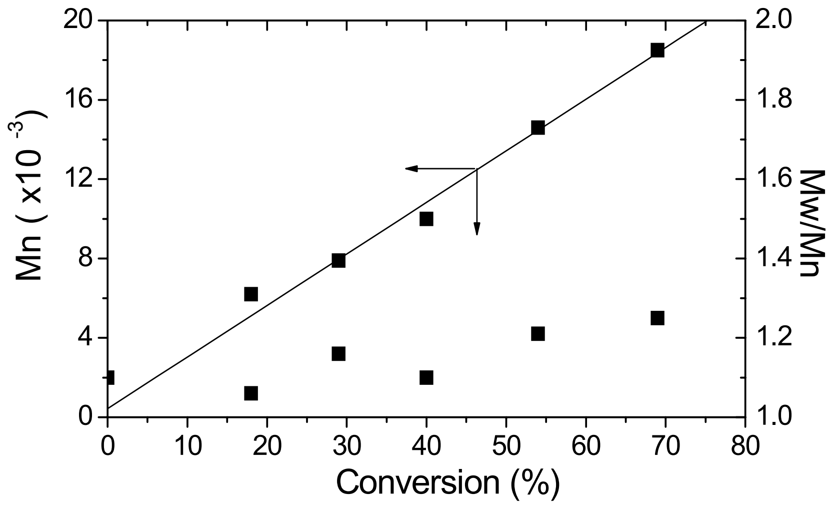

Fig. 5. Plots of M_n and M_w/M_n against conversion for DMA polymerizations in toluene at 20 ^{0}C.

But after the fast polymerization which was observed in initial 3 h, the polymerization slowed down. Probable reasons may be due to too much irresistible termination reactions between primary and chain radicals. Another reason may be the decrease of the concentration of DMA. These phenomena have also been found in other experiments [5-7].

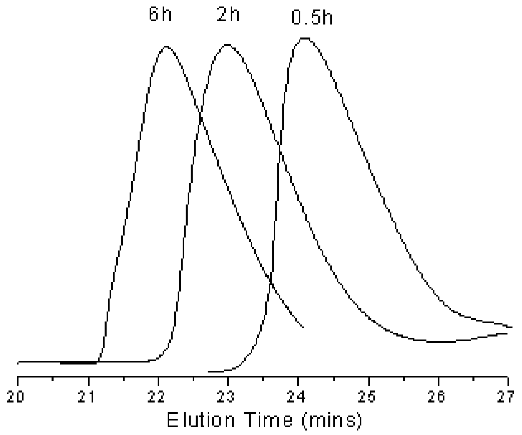

Fig. 6. GPC of PEO-*b*-PDMA copolymer prepared by ATRP of DMA at 20 °C from the PEO–Br macroinitiator with $[DMA]_0/[PEO–Br]/[CuBr]/[ligand]=200/1/1/3$.

The representative GPC curves of the PEO-*b*-PDMA shown in Fig. 6 are symmetrical and do not exist as double peaks, which implied that there are no homopolymers in the final block copolymer. The polydispersity of the PEO-*b*-PDMA remained quite low throughout the polymerization (M_w/M_n = 1.1-1.2, see Fig. 6). All these facts indicate that the polymerization of DMA with PEO-Br/CuBr/ $Me_6[14]aneN_4$ as initiation system is of “living” nature. There are fast equilibrium reactions between the active sites and the dormant species.

Thermal analysis

The DSC thermograms for PEO, PEO-*b*-PDMA are shown in Fig. 7. The glass transition temperature (T_g) was taken as the inflection point of the jump in heat capacity. The T_g of PEO was very low (about -60°C) and only T_m can be observed in Fig. 7a. The DSC results indicate that the PEO has a broad melting process on heating at temperature of about 52 °C. But when scanning calorimetry was done on the PEO-*b*-PDMA copolymers, the melting process on heating of PEO was eliminated, and the PEO-*b*-PDMA copolymer exhibited only one glass transitions (Fig. 7b, c, d), demonstrating that the PEO blocks are completely amorphous. The observations of these glass transition processes provide further evidences for the successful synthesis of PEO-*b*-PDMA using the ATRP. Compare the T_g of PEO-*b*-PDMA with different molecular weights of the second PDMA block (Fig. 7b to Fig. 7d), the low T_g obtained with PEO-b-PDMA-1 is about 98 °C. PEO-*b*-PDMA-1 has the same PEO block as PEO-*b*-PDMA-3 and PEO-*b*-PDMA-5 but the lowest molecular mass of PDMA block. The T_g of PEO-*b*-PDMA-5 increase to 113 °C when the molecular weight of PDMA block is 16400 g/mol. Previous work found that T_g of PDMA (M_v =50000 g/mol) is about 122 °C [9]. It appears that increasing the length of PDMA block segments seems to increase the T_g of the block copolymer.

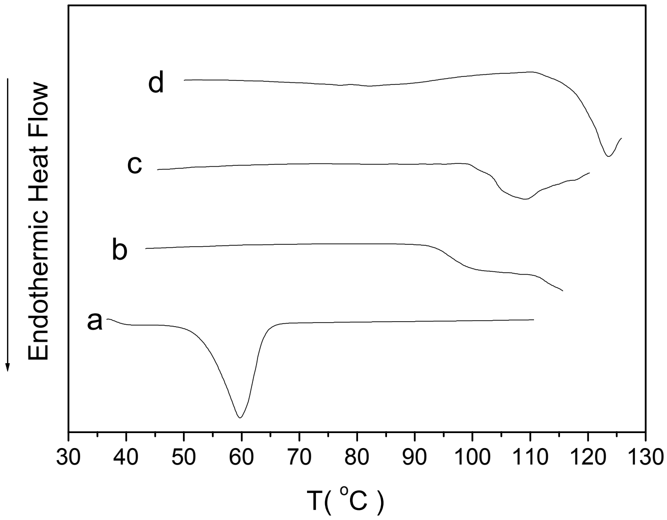

Fig. 7. DSC thermograms for the series of PEO-*b*-PDMA block copolymers. (a) PEO; (b) PEO-*b*-PDMA-1; (c) PEO-*b*-PDMA-3; (d) PEO-*b*-PDMA-5.

Self-assembly of PEO-b-PDMA copolymer in selective solvent

Amphiphilic block copolymers spontaneously form well-defined micelles aggregates in a selective solvent [10-13]. According to previous work, many factors may affect the final morphologies of the aggregates. Among these factors, the most important are the nature of the core-forming block and the shell-forming block, the composition of the copolymer, the nature of the common solvent and the precipitant, and the presence and nature of any additives [14]. Double hydrophilic block copolymer self-assembly in selective solvent has attracted much interest recently [15]. As for PEO-*b*-PDMA copolymer, acetone is a good solvent for PEO block, but it is not a good solvent for PDMA block, leading to the formation of aggregates with compact cores of insoluble blocks surrounded by a soluble shell composed of soluble blocks. PEO-*b*-PDMA with different molecular weights of the second PDMA block was chosen to study the effect. The micelles formed from PEO-*b*–PDMA block copolymer can be observed in methanol/acetone (1:10, v/v) solvent. The PDMA block formed the core and PEO block formed the shell of micelle, which has been proved by the TEM results. For the sample PEO-*b*-PDMA-2, these micelles are spheres with small cores and expanded shell, which have an average diameter of 150-180 nm (Fig 8a). When the block PDMA increased (PEO-*b*-PDMA-3), the aggregates of cores were still spherical. But the micelles have an average diameter of 120-160 nm due to the hydrophilic PEO chains adjusting their conformation stretch outside to stabilize the micelles (Fig 8b). The double layer core-shell structure can be observed clearly from Fig 8c which is the enlarged view of Fig 8b.

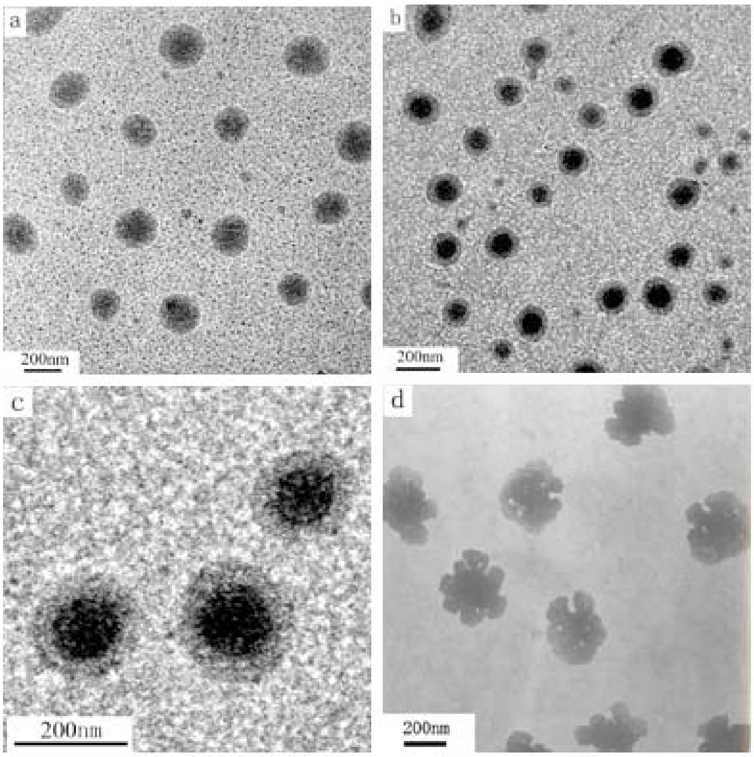

Fig. 8. TEM micrograph of PEO-*b*-PDMA specimen cast from methanol/acetone: 1/10(v/v) solution. (a) PEO-*b*-PDMA-2; (b) PEO-*b*-PDMA-3; (c) PEO-*b*-PDMA-3; (d) PEO-*b*-PDMA-5.

This block copolymer has a narrow molecular weight distribution of 1.10, as determined by GPC measurements. When the number of repeat units of PDMA continued to increase, vesicular aggregates started to form; most of aggregates were still spherical, but the average size increased. PEO-*b*-PDMA-5 self-assembly behavior is shown in Fig. 8d. The diameter of the micelle is about 200-220 nm. This increasing length of PDMA induces the interfacial tension at the core-shell interface to change continuously, which induces the aggregate morphology to alter progressively.

Conclusions

The ATRP of DMA with PEO-Br has been successfully carried out using the ligand, $Me_6[14]aneN_4$, and the linear increase of molecular weights with conversion has been observed. The living nature of the polymerization is evidenced by the following facts: linear evolution of molecular weight with conversion; the constant concentration of chain radical during the polymerization and low polydispersity indexes. The self-assembly behaviors of PEO-b-PDMA in methanol/acetone were studied. PEO-*b*-PDMA can self-assemble to form micelles with different sizes and shapes by varying the length of PDMA block.

Experimental section

Materials

N,N-Dimethylacrylamide (DMA, 99%, Aldrich) was distilled under vacuum and stored at -15 °C. 2-Bromoisobutyryl bromide (98%, Aldrich) was freshly distilled at room temperature under vacuum. Triethylamine (TEA) was refluxed with p-toluenesulfonyl chloride and then distilled. CuBr was purchased from the First Shanghai Chemical Reagent Company and purified before use. $Me_6[14]aneN_4$ was prepared according to previous work [16, 17]. PEO (M_n=2000, Fluka, monomethyl ether) was dried by azeotropic distillation with toluene before use.

Preparation of PEO macroinitiator

PEO-Br macroinitiator was prepared according to previous work [18]. The crude polymer was dried under vacuum, dissolved in water at pH 8-9, and then extracted with dichloromethane. The organic layers were collected and dried over $MgSO_4$, and removal of the solvent under vacuum afforded the purified macroinitiator.

General procedure for polymerization from macroinitiator

Into a dried glass tube with a magnetic bar, CuBr and ligand were added, and then monomer (DMA), macroinitiator (PEO-Br) and toluene were added. The mixture was degassed by three freeze-pump-thaw cycles. The tube was sealed under vacuum, and then immersed in a water bath thermostated at 20 °C. After the reaction was carried out for a prescribed time, the tube was broken. Polymer samples, dissolved in DMF, were passed through an alumina column to remove copper. By adding polymer solution into an excess of ether, the polymer was precipitated, filtered and dried at 40 °C in a vacuum oven for 24 h.

Characterization

^{1}H NMR spectra were performed in an AV-300 NMR spectrometer, using $CDCl_3$ or D_2O as a solvent and tetramethylsilane (TMS) as internal reference. FT-IR spectra were recorded using MAGNA-IR 750 (Nicolet Instrument Co. U.S.A). Molecular weight and molecular weight distribution were obtained using GPC (Waters Microstyragel columns (guard, 10^5, 10^3, and 10^2 Å), THF as eluent at 35 °C, flow rate of 1.00 mL/min). Linear polystyrene standards were used for calibration. Thermal characterization was carried out with the aid of VP-DSC (Microcal, USA) operated at a heating rate 10 °C/min and nitrogen was used as atmosphere.

Transmission electron microscopy

The morphologies of the copolymer were studied by transmission electron microscopy (TEM) performed on a JEOL – 2010 (JEOL, Japan). The PEO-*b*-PDMA copolymers were first dissolved in methanol, a common solvent for both PEO and PDMA blocks, to give a stock solution. The solutions of the aggregates were prepared by adding methanol / acetone solution drop-by-drop to the PEO-*b*-PDMA methanol solution in an ultrasonic bath. The concentration of PEO-*b*-PDMA in the final solutions (methanol / acetone=1/10, v/v) was 2.0 mg/mL. To prepare TEM samples for the study of the size and the morphology of the self-assembly, a drop of PEO-*b*-PDMA dilute methanol/acetone solution was deposited onto a copper EM grid, which had been precoated with a thin film of Formvar and then coated with carbon. Two minutes after the deposition, the solution was allowed to dry in air for a few hours. When taking photos, the polymer films were stained with phosphotungstic acid solution (0.5%).

Acknowledgments

We greatly acknowledge the support of this work by the National Natural Science Foundation of China (Grant No. 50373040) and the Foundation for Development of Talent of Anhui Province (Grant No. 2005Z026).

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