

SYNTHESIS AND CHARACTERIZATION OF WELL-DEFINED BLOCK COPOLYMERS CONTAINING PENDANT, SELF-COMPLEMENTARY QUADRUPLE HYDROGEN BONDING SITES*

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Abstract The title block copolymer (defined as PSUEA) containing pendant, self-complementary quadruple hydrogen bonding sites has been prepared successfully by three steps. First, poly(styrene-*b*-2-hydroxyethyl acrylate) (defined as PSHEA) was prepared by living radical polymerizing 2-hydroxyethyl acrylate (HEA) initiated by polystyrene (PSt) macro-initiator, which was prepared *via* nitroxide-mediated polymerization (NMP) technique. After treated by excessive 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate (IPDI), PSHEA was transferred into an intermediate polymer (defined as PSIEA) with isocyanate groups in the second block. Finally, PSIEA was reacted with excessive 2-amino-4-hydroxy-6-methyl-pyrimidone (MIS) to obtain PSUEA bearing pendant quadruple hydrogen bonding 2-ureido-4[1H]-pyrimidone (Upy) units. Based on ¹H-NMR, FT-IR and GPC analysis, all the polymers with well controlled structures were obtained. Preliminary thermal analysis of the block polymers indicated that the introduction of Upy units significantly increased the glass transition temperature. The possibility to form quadruple hydrogen bonding should make PSUEA suitable as new building component for supramolecular assembling.

Keywords: Block polymer; Controlled radical polymerization; Nitroxide-mediated polymerization (NMP); Quadruple hydrogen bonding.

INTRODUCTION

In recent years, great effort has been focused on the development of ‘living’/controlled radical polymerization (CRP) methods due to their possibility to prepare homopolymers and block copolymers with controlled molecular weight and narrow molecular weight distribution. The most well-known CRP methods include nitroxide-mediated polymerization (NMP)^[1], metal-catalyzed atom transfer radical polymerization (ATRP)^[2] and reversible addition-fragmentation chain transfer (RAFT)^[3]. To prepare a polymer with well-defined structures, the CRP methods should be properly selected according to the category of the monomers. For example, the NMP method is quite suitable for styrene and its derivatives^[4] but not for methyl acrylate monomers^[5].

During the past decade, the well-defined polymers prepared *via* CRP have been used frequently as building components for supramolecular assembly, which creates many kinds of colloidal aggregates under intermolecular attractions, such as hydrophobicity, electrostatic interaction and hydrogen bonding. It is well known that hydrogen bonding recognition plays an important role in both biological and artificial supramolecular systems. Especially, multiple hydrogen bonding (MHB) not only has a considerable strength but also recognizes each other precisely, therefore quite suitable for molecular self-assembly. The combination of MHB and well-defined block polymers should create new assembling structures due to the precise recognizing of the hydrogen bonding units. For this purpose, some researchers tried to prepared block polymers bearing MHB groups. For example, Frankamp *et al.* synthesized diblock copolymer with one block modified with triple

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hydrogen bonding sites^[6]. Li *et al.* prepared block polymers with pendant triple hydrogen bonding sites^[7]. However in these studies, the molecular weight distributions of the polymers were still wide and the contents of hydrogen bonding sites were rather low. To our knowledge, there is no report concerning the synthesis of well-defined block polymers with one block bearing MHB groups in all the structure units.

In 1998, Meijer *et al.* first described the self-complementary 2-ureido-4[1H]-pyrimidone (Upy) units, which dimerize at an association constant exceeding 10^6 in CDCl_3 ^[8]. Due to the strong association, Upy tailored oligomers displayed some polymer-like properties such as shear thinning, viscoelastic behavior and glass transition temperatures^[9]. The rheologic behaviors of Upy contained star polymers^[10], poly(alkyl acrylates)^[11] and random branching polymers^[12] have also been investigated by Long's group.

The purpose of this study is to provide a common approach to prepare well-defined block polymers with quadruple hydrogen bonding Upy sites on the same block. In this paper, we first prepared a well-characterized diblock copolymer with one block containing hydroxyl groups *via* NMP technique. After replacing hydroxyl groups by isocyanate groups, the resulting intermediate polymer was finally reacted with 2-amino-4-hydroxy-6-methyl-pyrimidone (MIS) to give the title polymer (PSUEA). Even after several reactions, PSUEA still possesses well-controlled molecular structure with narrow molecular weight distribution. Due to the well-defined structure and the precise hydrogen bonding recognizing, PSUEA should be a new building component for supramolecular assembly.

EXPERIMENTAL

Materials

4-Hydroxy-2,2,6,6-tetramethylpiperidine 1-oxyl (HTEMPO) (Hua Shan Additive Factory, Beijing) and 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate (IPDI) (Alfa Co.) were used as received. Styrene (St) (Beijing Chemical Reagents) and 2-hydroxyethyl acrylate (HEA) (Alfa Co.) were distilled at reduced pressure before use. Benzoyl peroxide (BPO) (Beijing Chemical Reagents) was recrystallized from CHCl_3 before use. 2-Amino-4-hydroxy-6-methyl-pyrimidone (MIS) was synthesized according to the literature method^[13]. Guanidine carbonate (Beijing Baili Chemical Development Center) and ethyl acetoacetate (Xi Long Chemical Industry, Shantou, China) were used as received.

Nitroxide Mediate Polymerization of Styrene (PSt Macro-initiator)

The polymerization of styrene in presence of HTEMPO was carried out according to the literature methods^[14]. $^1\text{H-NMR}$ (500 MHz, CDCl_3 , δ): 1.0–2.5 (polystyrene backbone), 6.5–7.3 (aromatic protons).

Synthesis of Poly(styrene-*b*-2-hydroxyethyl acrylate) (PSHEA)

After dissolving PSt macro-initiator (5.0 g, 0.6 mmol) in xylene (10.0 g), HEA (1.25 g, 10.8 mmol for PSHEA-1 and 2.5 g, 21.6 mmol for PSHEA-2) was added into the solution. Under stirring, nitrogen was allowed to bubble into the reaction flask for 15 min. Then the flask was heated at 125°C for 2 h. The product was precipitated with petroleum ether and dried under vacuum at 45°C for 24 h. $^1\text{H-NMR}$ (500 MHz, CDCl_3 , δ): 0.8–2.0 (PSHEA backbone), 3.9 ($-(\text{C}=\text{O})-\text{O}-\text{CH}_2-\text{CH}_2-\text{OH}$), 4.3 ($-(\text{C}=\text{O})-\text{O}-\text{CH}_2-\text{CH}_2-\text{OH}$), 6.5–7.3 (aromatic protons). FT-IR (ν): 3150–3700 cm^{-1} ($-\text{OH}$), 1724 cm^{-1} ($-(\text{C}=\text{O})-\text{O}-$), 1194 cm^{-1} ($-\text{CH}_2-\text{OH}$).

Modification of PSHEA with IPDI (PSIEA)

After dissolving PSHEA-1 (5.0 g) in toluene (10.0 g), IPDI (2.5 g, 11.3 mmol, more than 2.5 times molar ratio of $-\text{OH}$), was added into the solution. The reaction was stirred at 50°C for 24 h. The product was precipitated with petroleum ether and dried under vacuum at 45°C for 24 h. By the same procedure, PSIEA-2 was prepared from PSHEA-2. $^1\text{H-NMR}$ (500 MHz, CDCl_3 , δ): 0.8–2.0 (PSIEA backbone), 4.3 and 4.35 ($-(\text{C}=\text{O})-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-(\text{C}=\text{O})-\text{NH}-$), 6.5–7.3 (aromatic protons). FT-IR (ν): 3200–3500 cm^{-1} ($-\text{N}-\text{H}$), 2264 cm^{-1} ($-\text{N}=\text{C}=\text{O}$), 1523 cm^{-1} ($-(\text{C}=\text{O})-\text{NH}-$).

Modification of PSIEA (PSUEA)

PSIEA-1 (5.0 g) was dissolved in pyridine (10.0 g). MIS (1.0 g, 8 mmol, more than 2.5 times molar ratio of

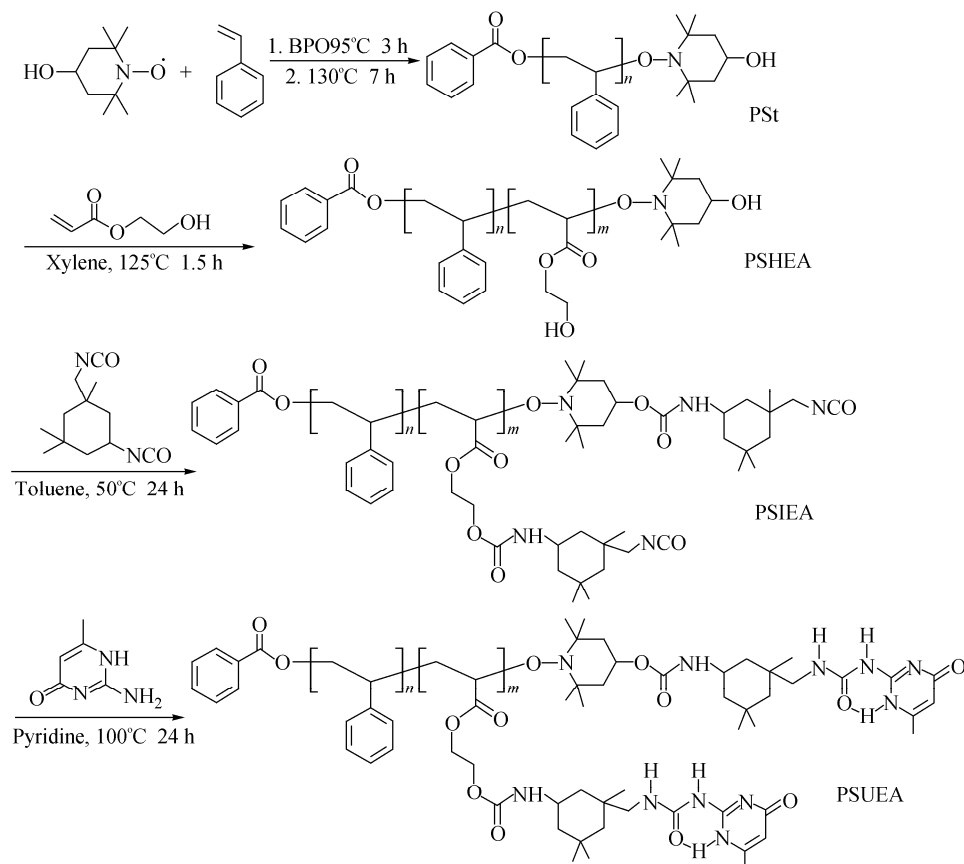
—NCO), was added into the solution. The reaction was stirred under reflux for 24 h under nitrogen atmosphere. The crude product was precipitated with methanol then dissolved in toluene, filtrated and precipitated with petroleum ether, and finally dried at 45°C under vacuum for 24 h to give PSIEA-1. By the same procedure, PSUEA-2 was prepared from PSIEA-2. $^1\text{H-NMR}$ (500 MHz, CDCl_3 , δ): 0.8–2.0 (PSUEA backbone), 4.3 and 4.35 ($-(\text{C}=\text{O})-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-(\text{C}=\text{O})-\text{NH}-$), 6.5–7.3 (aromatic protons), 10.1, 11.9 and 13.1 ($-\text{NH}-$ of Upy units). FT-IR (ν): 1660, 1581 cm^{-1} ($-(\text{C}=\text{O})-\text{N}=$ of Upy units).

Characterization

The molecular weight and molecular weight distributions were determined at 40°C in tetrahydrofuran (HPLC grade) at 1 mL/min using polystyrene standards on a Viscotec TDA300-Triple mode GPC system, with three independent detectors: refractive index detector, viscosity detector and small-angle laser light scattering device, equipped with two columns (GMHHR-H, M Mixed Bed). FT-IR experiments were performed using a Nicolet 560 instrument. $^1\text{H-NMR}$ spectra were recorded in CDCl_3 using a Bruker-500 (500 MHz) FTNMR spectrometer. Glass transition temperature (T_g) was determined with a Dupont-2400 DSC at a heating rate of 10 K/min.

RESULTS AND DISCUSSION

It is obvious that the well-defined block copolymers with MHB groups in one block can be prepared mainly by two approaches: (1) direct polymerization of MBH-contained monomers *via* ordinary CRP and (2) post-functionalization of a preformed well-defined block copolymer using MBH-contained reagent. For method (1), the selection of a suitable CRP method for MBH-contained monomers should be critical. For method (2), it is desired that the functional groups react to sufficient high degree, therefore maintaining the original structure. To achieve this, particular attention should be paid on choosing an effective modifying reaction.



Scheme 1 General synthetic procedure

In this paper, we prepared the title polymer (PSUEA) based on method (2) with the total synthetic procedure shown in Scheme 1. First, PSt macro-initiator was prepared in presence of HTEMPO according to the standard method^[4]. Then PSt macro-initiator was used to initiate the polymerization of HEA, therefore giving the block copolymer PSHEA with hydroxyl groups in the second block. After reacting PSHEA with excessive IPDI, a reactive intermediate polymer PSIEA with isocyanate groups at the second block was obtained. Finally, PSIEA was modified with excessive MIS to give PSUEA bearing pendant Upy units. Through adjusting the content of HEA block in PSHEA, two series of block copolymers were readily prepared (see Table 1). The synthesis and characterization of the polymers were described in detail in the following sections.

Table 1. Characterization and glass transition temperature of the polymers

Sample	GPC DRI ^a			GPC SALLS			¹ H-NMR calculation		<i>T_g</i> (°C)
	<i>M_n</i>	<i>M_w</i>	<i>M_w/M_n</i>	<i>M_n</i>	<i>M_w</i>	<i>M_w/M_n</i>	[St]:[HEA]	<i>M_{n,cal}</i> ^b	
PSt	8200	9600	1.17	5400	7200	1.33			54.2
Series 1	PSHEA-1	9000	9900	1.10	9600	11900	1.24	12: 1	49.7
	PSIEA-1	9700	10700	1.10	11400	13000	1.14		–
	PSUEA-1	9700	10900	1.12	11300	13200	1.17		78.5
	PSHEA-2	8800	10000	1.13	13400	15300	1.14	4.5: 1	47.9
Series 2	PSIEA-2	10300	11400	1.11	14100	16100	1.14		–
	PSUEA-2	10200	11700	1.15	18900	22000	1.16		90.3

^aEstablished using polystyrene standard;

^bCalculated using *M_n* of PSt determined by GPC and [St]:[HEA] according to ¹H-NMR analysis

NMP Synthesis and Characterization of PSHEA

The synthesis of PSHEA was performed *via* nitroxide mediate polymerization (NMP) in presence of HTEMPO. NMP is an efficient method to control the polymerization of styrene and its derivatives^[14]. But for acrylate monomers, this technique often results in polymers with wider molecular weight distribution and lower conversion^[5]. In this paper, we found that the molecular weight distributions of PSHEA-1 and PSHEA-2 both were rather narrow even 2-hydroxyethyl acrylate was used (see Table 1). The FT-IR spectrum of PSHEA-1 in Fig. 1(a) clearly indicates the presence of the characteristic peaks of poly(2-hydroxyethyl acrylate) (PHEA) segment, including the wide absorption between 3250–3600 cm^{−1} for –OH, 1724 cm^{−1} for ester –C=O and 1194 cm^{−1} for –CH₂–OH. In the ¹H-NMR spectrum of PSHEA-1 in Fig. 2(A), the peaks at δ = 6.5–7.3 (a) are assigned to aromatic protons in PSt segment, the peaks at δ = 0.8–2.0 (e) are ascribed to the protons of –CH₂–CH₂–, the backbone structure of the block copolymer. Due to the strong hydrogen bonding between monomer HEA and the block polymer PSHEA, HEA can not be removed completely from PSHEA^[15]. So the characteristic peaks of –CH=CH₂ in HEA at δ = 5.9, 6.2 and 6.5 (b) are still noticed. The signals at δ = 3.9 and 4.3 (c) are assigned to the four protons of –(C=O)–O–CH₂–CH₂– in both HEA and PSHEA. The integration ratio between δ = 0.8–2.0 (e) and 6.5–7.3 (a) is 0.65 for PSHEA-1 and 0.73 for PSHEA-2, both are higher than the integration ratio of 0.6 calculated from those of PSt chain. This result further proves that HEA segments have been incorporated into the block copolymer. The molar ratio of St units and HEA units can be calculated *via* the following equation:

$$\frac{[\text{St}]}{[\text{HEA}]} = \frac{I_{6.5-7.3}/5}{I_{0.8-2.0}/3 - I_{6.5-7.3}/5} \quad (1)$$

where *I*_{6.5–7.3} and *I*_{0.8–2.0} are the integral values of the peaks at δ = 6.5–7.3 and 0.8–2.0, respectively. Based on this calculation, the actual molar ratio of [St]:[HEA] is 12:1 for PSHEA-1 and 4.5:1 for PSHEA-2, therefore PSHEA-1 possesses much shorter PHEA block than PSHEA-2.

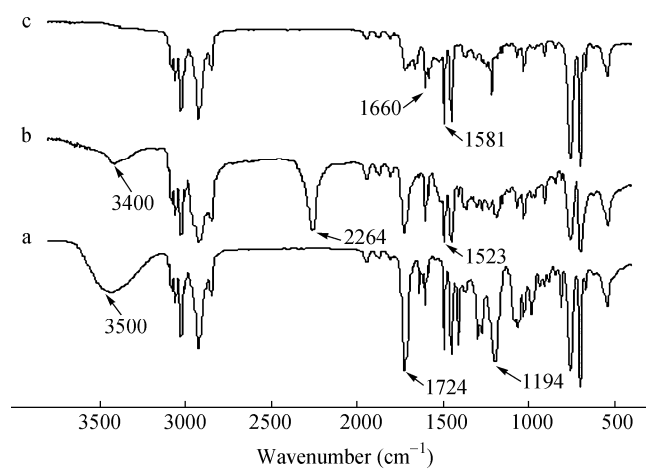


Fig. 1 FT-IR spectra of (a) PSHEA-1, (b) PSIEA-1 and (c) PSUEA-1

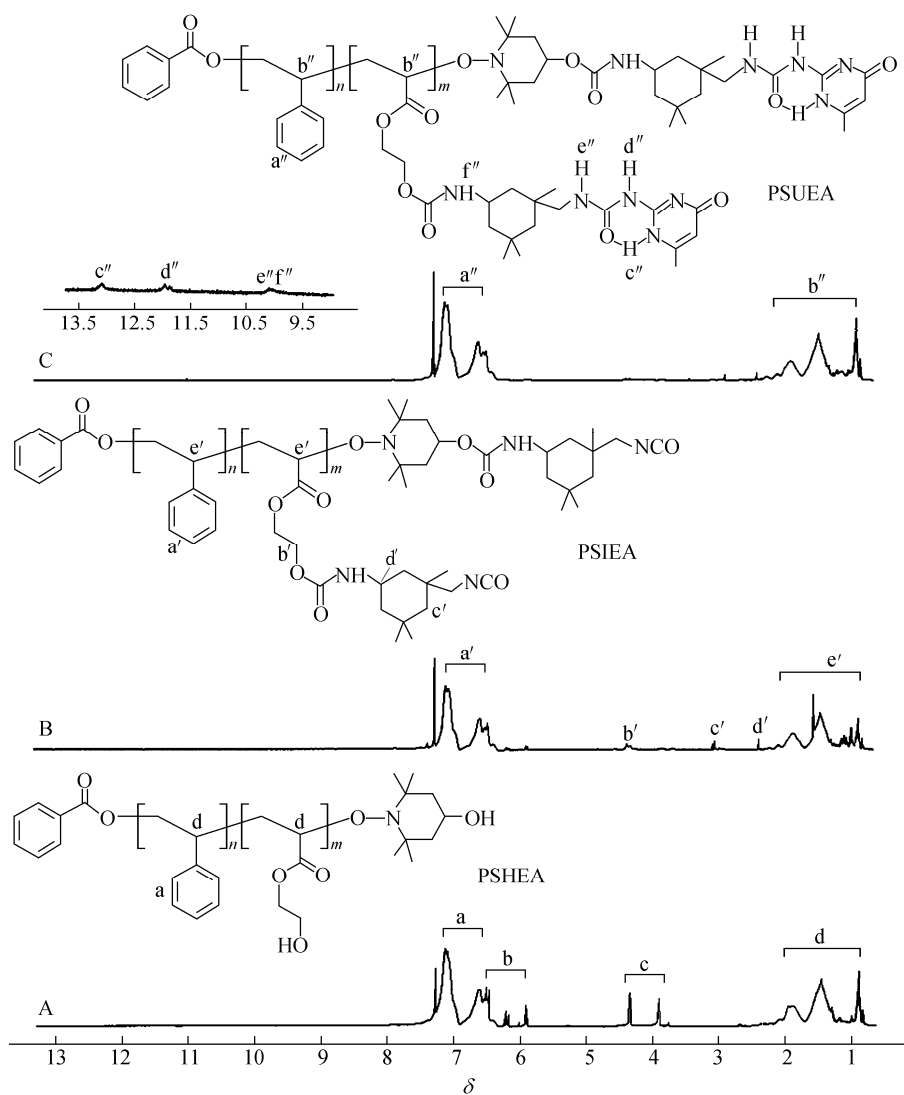


Fig. 2 ^1H -NMR spectra of (A) PSHEA-1, (B) PSIEA-1 and (C) PSUEA-1

Synthesis and Characterization of PSIEA

Based on the reaction between $-\text{OH}$ and $-\text{NCO}$, PSHEA was then treated by excessive IPDI in toluene to give PSIEA with $-\text{NCO}$ groups in the second block. Due to the different reactivity of the two $-\text{NCO}$ groups in IPDI, it is possible that the more active $-\text{NCO}$ group reacts with $-\text{OH}$ groups, while the less active $-\text{NCO}$ keeps stable and attaches on the polymer^[16, 17]. After reaction, the reaction mixture was precipitated into large amount of petrol ether to remove any residual IPDI. After dissolving in toluene and precipitating into petrol ether for additional two times, PSIEA was obtained as white powder.

Figure 1(b) is the FT-IR spectrum of PSIEA, in which spectrum the strong peak at 2264 cm^{-1} is assigned to $-\text{NCO}$ groups. The disappearance of the wide absorption for $-\text{OH}$ groups between $3250\text{--}3600\text{ cm}^{-1}$ indicates that $-\text{NCO}$ groups have been introduced into the polymer. The comparison of the $^1\text{H-NMR}$ spectra of PSIEA and PSHEA in Fig. 2 reveals that the signal at $\delta = 3.9$ for $-\text{CH}_2-\text{OH}$ in PSHEA is completely disappeared in PSIEA. A new peak presented at $\delta = 4.35$ (b') can be assigned to $\text{CH}_2-\text{O}-(\text{C}=\text{O})-\text{NH}-$ in PSIEA. All the peaks at $\delta = 2.38$ (d') and 3.0 (c') are originated from IPDI protons. Due to the consumption of hydroxyl groups, the strong interaction between HEA and PSHEA does not exist in PSIEA, so HEA can be removed effectively from PSIEA during the purifying process, and no peak of vinyl group is observed again in Fig. 2(B).

Synthesis and Characterization of PSUEA

Due to the existence of pendant reactive $-\text{NCO}$ groups, PSIEA was further reacted with excessive MIS in pyridine, therefore resulting in PSUEA with Upy units being introduced into the second block. To understand the reaction end point, the reaction solution was analyzed by using FT-IR spectrometer at different time interval until the peak at 2264 cm^{-1} was completely disappeared. To remove the remaining MIS from the products, a multiple purifying procedure was carried out. The reaction solution was first precipitated into methanol. The precipitate was then dissolved in toluene. After filtration, the solution was precipitated into petroleum ether. After drying the precipitate to a constant weight at 45°C under vacuum, PSUEA was obtained as brown powder.

The comparison of the $^1\text{H-NMR}$ spectra of PSUEA and PSIEA in Fig. 2 reveals that there are three characteristic NH peaks in Upy group^[18], including $\delta = 10.1$ (f' and e'') for $-\text{CH}_2\text{NH}-(\text{C}=\text{O})-$ and $-\text{CH}-\text{NH}-(\text{C}=\text{O})-\text{NH}-$, 11.9 (d'') for $-\text{NH}-\text{C}=\text{N}-$, and 13.1 (c'') for $-\text{NH}-\text{C}(\text{CH}_3)=$. Compared with PSIEA, the signals at $\delta = 4.3$ and 4.35 for $-(\text{C}=\text{O})-\text{O}-\text{CH}_2-\text{CH}_2$ reduce dramatically in PSUEA, which indicates that the aggregation of Upy contained blocks in CDCl_3 makes the block imbedded in the aggregate^[19]. In the FT-IR spectra of PSUEA in Fig. 1(c), the strong peak at 1660 and 1581 cm^{-1} are assigned to $-(\text{C}=\text{O})-\text{N}=-$ of Upy units.

Molecular Weight Characterization of Block Polymers

Table 1 shows the molecular weight and molecular weight distribution of the block polymers. $M_n(\text{GPC DRI})$ is obtained from PS standard, and $M_n(\text{GPC SALLS})$ is obtained using small-angle laser light scattering detector. The GPC traces of the samples of series 1 and series 2 according to GPC DRI are shown in Fig. 3 and Fig. 4, respectively. Because the $M_n(\text{GPC DRI})$ is calculated from PS standard, the $M_n(\text{GPC DRI})$ of PSUEA is lower than that of PSIEA due to the high polarity of PSUEA. As for PSt, because the $M_n(\text{GPC DRI})$ is calculated from PS standard, the $M_n(\text{GPC DRI})$ of PSt is reliable. When the molecular weight is below 10000, the $M_n(\text{GPC SALLS})$ data have considerable errors due to device limitation. As for the other polymers, the $M_n(\text{GPC DRI})$ is not reliable due to the polarity of these polymers and their different hydrodynamic volumes compared to PSt standard. However, GPC SALLS data could be used to compare these polymers because the data are the absolute molecular weight of the polymers. From the M_w data of SALLS, it is clear that the molecular weight increases as the modification reaction proceeds. The M_n calculated from $^1\text{H-NMR}$ are all higher than those measured by GPC DRI, which can be attributed to both the interaction between the polymer and the columns of GPC device, and the different hydrodynamic volumes of PSt and the copolymers. Furthermore, all the molecular weight distributions of the polymers obtained either by GPC DRI or by GPC SALLS are quite narrow. These results indicate that even PSHEA transferred into PSUEA by multiple steps, the molecular weight of the copolymers increases gradually while the molecular weight distribution keeps nearly unchanged.

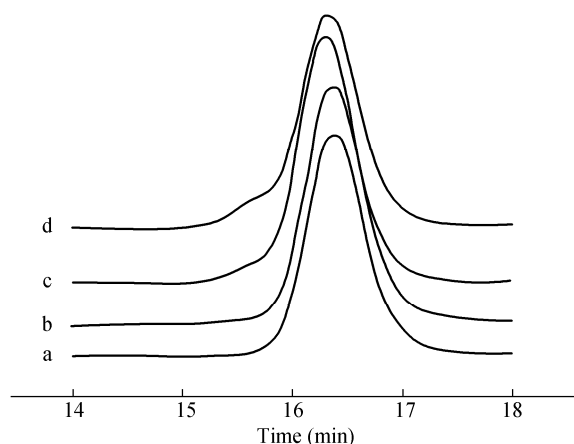


Fig. 3 GPC traces of (a) PSt, (b) PSHEA-1, (c) PSIEA-1 and (d) PSUEA-1

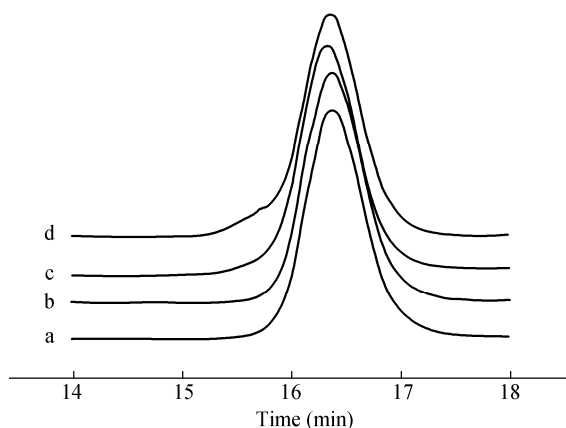


Fig. 4 GPC traces of (a) PSt, (b) PSHEA-2, (c) PSIEA-2 and (d) PSUEA-2

Based on a multiple synthetic approach, well-controlled block copolymers with self-complementary quadruple hydrogen bonding sites in the same block were successfully prepared. This polymer is unique compared with the literature polymers that bearing self-complementary quadruple hydrogen bonding sites^[6, 7, 12]. The specialties of the present block copolymer include: (1) the molecular weight is well controlled and the molecular weight distribution is rather narrow; (2) the hydrogen bonding sites locate densely in the same block; (3) the amount of hydrogen bonding sites can be adjusted simply by the composition of PSHEA; (4) according to the final application, different building blocks can be incorporated into the copolymer *via* CRP. The post-functionalization technique is not only suitable for block copolymer but also for some other polymers bearing hydroxyl groups.

Thermal Analysis of Block Polymers

The DSC curves for the samples of series 1 and series 2 are shown in Fig. 5 and Fig. 6, respectively. Because PSIEA is sensitive to moisture, the DSC measurement is not very suitable for it. The glass transition temperatures (T_g) of the block polymers are summarized in Table 1. It is clear that the same results are obtained for the samples of the two series. The T_g of PSHEA is lower than that of PSt due to the introduction of flexible PHEA segment. Due to the existence of considerable amount of Upy units, PSUEA possesses much improved T_g compared with those of PSt and PSHEA. Because of a higher Upy content, PSUEA-2 possesses higher T_g than PSUEA-1. So the improving in T_g should be attributed to the Upy units in the block copolymer.

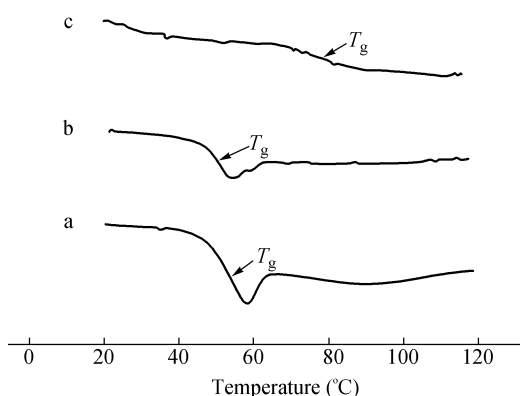


Fig. 5 DSC curves of (a) PSt, (b) PSHEA-1 and (c) PSUEA-1

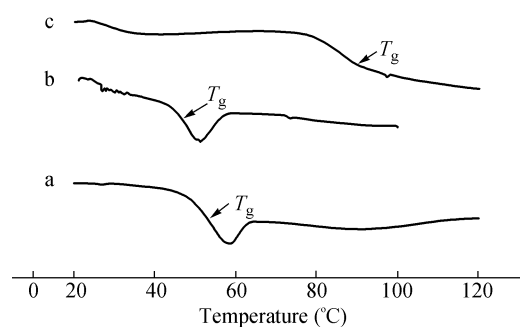


Fig. 6 DSC curves of (a) PSt, (b) PSHEA-2 and (c) PSUEA-2

Due to the existence of considerable amount of Upy units in the same block, PSUEA should be a new kind of building unit for self-assembly. The pH and temperature sensitivity of the hydrogen bonding should make the assembling structures sensitive to external stimuli. The self-assembly of PSUEA in solution is now in research.

CONCLUSIONS

The NMP polymerization of HEA using PSt macro-initiator displayed the living polymerization characters. Based on the post-functionalization technique, well-controlled block copolymers with self-complementary quadruple hydrogen bonding Upy sites in the same block were successfully prepared. These polymers were well characterized by $^1\text{H-NMR}$, FT-IR and GPC. The thermal analysis indicated that the Upy groups greatly affected the thermal properties of polymers. The possibility to form quadruple hydrogen bonding should make PSUEA suitable as a new building component for supramolecular assembly.

REFERENCES

- 1 Hawker, C.J., Bosman, A.W. and Harth, E., *Chem. Rev.*, 2001, 101: 3661
- 2 Matyjaszewski, K. and Xia, J.H., *Chem. Rev.*, 2001, 101: 2921
- 3 Moad, G., Rizzardo, E. and Thang, S.H., *Aust. J. Chem.*, 2005, 58: 379
- 4 Hsueh, M.L., Huang, B.H. and Lin, C.C., *Macromolecules*, 2002, 35: 5763
- 5 Moad, G. and Solomon, D., "The Chemistry of Radical Polymerization", Elsevier, Amsterdam, 2006, p.217
- 6 Frankamp, B.L., Uzun, O., Ilhan, F., Boal, A.K. and Rotello, V.M., *J. Am. Chem. Soc.*, 2002, 124: 892
- 7 Li, Z., Ding, J.F., Day, M. and Tao, Y., *Macromolecules*, 2006, 39: 2629
- 8 Beijer, F.H., Sijbesma, R.P., Kooijman, H., Spek, A.L. and Meijer, E.W., *J. Am. Chem. Soc.*, 1998, 120: 6761
- 9 Folmer, B.J.B., Sijbesma, R.P., Versteegen, R.M., van der Rijt, J.A.J. and Meijer, E.W., *Adv. Mater.*, 2000, 12: 874
- 10 Elkins, C.L., Viswanathan, K. and Long, T.E., *Macromolecules*, 2006, 39: 3132
- 11 Elkins, C.L., Park, T., McKee, M.G. and Long, T.E., *J. Polym. Sci., Part A: Polym. Chem.*, 2005, 43: 4618
- 12 McKee, M.G., Elkins, C.L., Park, T. and Long, T.E., *Macromolecules*, 2005, 38: 6015
- 13 Hirschberg, J.H.K.K., Beijer, F.H., van Aert, H.A., Magusin, P.C.M.M., Sijbesma, R.P. and Meijer, E.W., *Macromolecules*, 1999, 32: 2696
- 14 Benoit, D., Chaplinski, V., Braslau, R. and Hawker, C.J., *J. Am. Chem. Soc.*, 1999, 121: 3904
- 15 Vargun, E. and Usanmaz, A., *J. Polym. Sci., Part A: Polym. Chem.*, 2005, 43: 3957
- 16 Yamauchi, K., Lizotte, J.R., Hercules, D.M., Vergne, M.J. and Long, T.E., *J. Am. Chem. Soc.*, 2002, 124: 8599
- 17 Keizer, H.M., van Kessel, R., Sijbesma, R.P. and Meijer, E.W., *Polymer*, 2003, 44: 5505
- 18 Yamauchi, K., Lizotte, J.R. and Long, T.E., *Macromolecules*, 2003, 36: 1083
- 19 Garnier, S. and Laschewsky, A., *Colloid Polym. Sci.*, 2006, 284: 1243