Polymer Bulletin 61, 63–69 (2008)
DOI 10.1007/s00289-008-0930-x

Polymer Bulletin

# Preparation of amphiphilic hyperbranched polyesteramides by grafting mono methoxy polyethylene glycol onto hyperbranched polyesteramides via 2,4-tolylene diisocyanate

**Kuanjun Fang** (✉), **Zhengan Xu, Xue Jiang, Shaohai Fu**

Key Laboratory for Eco-textiles of Ministry of Education, Jiangnan University,
1800 Lihu Road, Wuxi, Jiangsu Province, China 214122
E-mail: fangkuanjun@vip.sina.com; Fax: +86 510 85912105

Received: 10 October 2007 / Revised version: 29 February 2008 / Accepted: 6 March 2008

## Summary

A novel amphiphilic copolymer of hyperbranched polyesteramides-graft-mono methoxy polyethylene glycol (HP-g-MPEG) was synthesized by solution polymerization in ethyl acetate using 2,4-tolylene diisocyanate (TDI) as a coupling agent. The copolymers were prepared by two-step reactions. First, the isocyanate-terminated intermediate (MPEG-NCO) was prepared by introducing one NCO group of TDI onto the hydroxyl end-group of mono methoxy polyethylene glycol (MPEG). Second, MPEG-NCO was grafted onto the chains of hyperbranched polyesteramides (HP) by the reaction between the unreacted NCO group and the hydroxyls of HP, and then, HP-g-MPEG was obtained. The chemical structure of HP-g-MPEG was confirmed by FT-IR and $^1$H NMR.

## Introduction

Hyperbranched polymers are macromolecular compounds built from multifunctional monomers $AB_n$, where the function A can couple with the function B as proposed by Flory [1] and demonstrated by Kim and Webster [2]. Hyperbranched polymers have drawn much attention of various research groups for 20 years [3-6]. The interest in such macromolecules stems from the possibility that, owing to their novel, highly branched, globular, and unentangled structure, they may be expected to show new and interesting properties both in solution and in bulk [7-8]. Compared to linear analogues, hyperbranched polymers have high solubility, low viscosity, so a variety of applications have been considered for hyperbranched materials, such as multifunctional initiators [9] and for rheology control compounds for surface modification [10], medical applications [11], nanofillers for polymer nanocomposites [12], nonlinear optics [13], and nanopore generators for low dielectric constant insulators [14].

Amphiphilic polymers have considerable practical value, for example, for potential uses such as protective colloids, emulsifiers, surfactants, wetting agents, or viscosity modifiers. It is only recently that people are interested in the study and use of amphiphilic hyperbranched polymers for various applications [15]. Daoji Gan et al.

reported that hyperbranched fluoropolymers were crosslinked by a reaction with diamino-terminated poly(ethylene glycol) (PEG) to form hyperbranched–linear copolymer networks which were amphiphilic, and the structure had been used to impart surface hydrophilicity to hydrophobic membranes and to resist protein adsorption [16]. Liming Tang et al. reported that amphiphilic hyperbranched polyester consisting of a hydrophobic core, surrounded by aromatic carboxylic acids, was self-assembled into aggregates in aqueous solution [17].

Amphiphilic hyperbranched polymers do not consist of individual surfactant fragments, but are made of a more or less large hydrophobic core coated with a hydrophilic shell. The amphiphilic character is thus based on the overall macromolecular architecture [18]. Amphiphilic hyperbranched polymers are of considerable interest for various applications in which the combination of hydrophilic and hydrophobic properties of these materials may be utilized, e.g. as emulsifiers, dispersion stabilizers, and compatibilizers [19]. MPEG is mostly studied as a hydrophilic block for amphiphilic block copolymers because of its biocompatibility and good water solubility, etc [20]. General types of MPEG based amphiphilic copolymers are block or graft type copolymers composed of their linear blocks. Other polymeric architectures, except linear or graft type copolymers, are rarely studied. Generally, these linear type polymers are synthesized by living anionic polymerization. Recently, controlled radical processes such as ATRP etc. are applied to amphiphilic copolymer synthesis. The micell behavior of PS-PEO-PS linear block copolymer synthesized by ATRP is studied by Yuan et al [21]. Dworak et al. reported hyperbranched poly[p-(chloromethyl)-styrene] (HPCMS) system containing linear PEO via Williamson synthesis [22]. However, these methods have some drawbacks such as difficulty in control of polymer architecture, broad molecular weight distribution, and the existence of unreactive compound, etc.

In this work, we focus on a new way to synthesis amphiphilic hyperbranched polyesteramides by using TDI as coupling agent. By using the active group of TDI, NCO groups, to react with the hydroxyl groups at the terminal of the MPEG and in the HP molecule, respectively, the MPEG with certain chain lengths are introduced onto the backbone of hyperbranched polyesteramides. HP-graft-MPEG was characterized by FT-IR and $^1$H NMR.

## Experimental

### *Materials*

Hyperbranched polyesteramides (HP) were prepared based on cis-hexahydrophthalic anhydride and bis(2-hydroxypropyl)amine, and the whole controlled synthesis of HP was performed as described previously [23]. Mono methoxy polyethylene glycol (MPEG, $M_n$=450) was dried by azeotropic distillation with benzene. 2,4-Tolylene diisocyancate (TDI) was purchased from The First Chemical Reagent Factory (Shanghai, China). Ethyl acetate was purified by vacuum distillation before use.

### *Measurements*

Infrared absorption spectra were measured by a Nicolet-5DX Fourier transform infrared spectrometer (FT-IR) in Nujol. $^1$H NMR spectra were recorded with a Varian UNITY INOVA (400 MHz) NMR spectrometer. Trichloromethane-d$_l$ ($CDCl_3$-d$_l$) was used as solvent, and tetramethylsilane (TMS) served as an internal standard. The intrinsic viscosity was measured with Ubbelohde viscosimeter in water bath at 25°C, using Polytetrahydrofuran as solvent.

### *Preparation of MPEG–NCO*

MPEG (10g) was dissolved in dry ethyl acetate (25g), and placed in three-necked flask. Then, the reactor was purged with nitrogen gas three times. After the reactor was placed in an oil bath at 60°C, TDI (1.74g) was slowly added into the reactor by an injector with agitation. The reaction was carried out at 60°C for 1 h under nitrogen atmosphere. When the reaction mixture was cooled to room temperature, the light yellow intermediate MPEG–NCO was obtained.

### *Synthesis of HP-g-MPEG*

HP (12.5g) was dissolved in dry ethyl acetate (25g). Then, the HP solution was slowly added into the reactor containing MPEG–NCO with stirring at 70 °C. The feed ratio of HP:MPEG:TDI ratio was 12.5:10:1.74 (w/w/w). When the reaction went on for 4 h, the reaction product was precipitated in alcohol and filtered. The unreacted MPEG and MPEG–NCO were removed by Soxhlet extraction with 1,2-dichloroethane until constant weight was reached. The dried pure graft copolymer powder was obtained after further drying under vacuum for 24 h. The yield (*Y*) and grafting efficiency (*GE*) were calculated by the flowing equation (1) and (2).

$$Y = \frac{W_1 - W_0}{W_0} \times 100\% \tag{1}$$

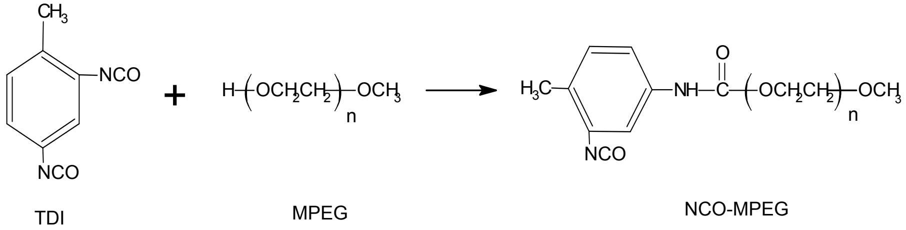
$$GE = \frac{W_1 - W_2 - W_0}{W_1} \times 100\% \tag{2}$$

Where $W_0$ is the starting weight of HP, and $W_1$ and $W_2$ are the weights of the refined products and TDI, respectively.

## Results and discussion

### *Synthesis of HP-g-MPEG copolymers*

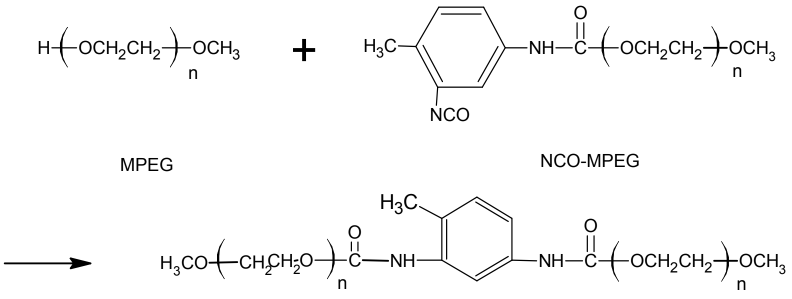
In general, isocyanates can easily react with compounds containing active protons, such as alcohols, amines, and acids. The intermediate MPEG–NCO produced as



Scheme 1. Preparation of MPEG–NCO

shown in Scheme 1, contains a carbamate group and an –N=C=O, indicating that only one of two NCO groups in TDI took part in the addition reaction.

Changing the ratios of MPEG to TDI makes it possible to control the side reaction that leads to chain extending as shown in Scheme 2.



Scheme 2. The side reaction of preparation of MPEG–NCO

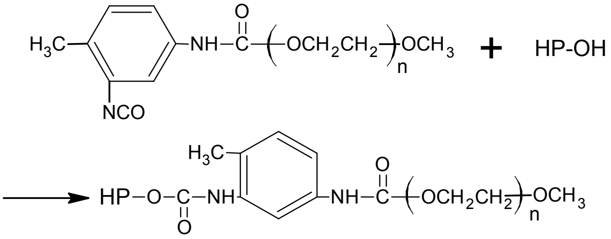
Since chain extending can lead to the increase of the intrinsic viscosity of MPEG, the relationship between the amount of TDI and the variation of the intrinsic viscosity of MPEG should be discussed so as to choose the right ratio of MPEG to TDI, which was shown in Table 1.

Table 1. The intrinsic viscosity ($\eta$) of MPEG-NCO at varying TDI/ MPEG ratios

| TDI(mol)/MPEG(mol) | $\eta$(mL/g) |
|---|---|
| 0 | 6.05 |
| 0.8 | 9.92 |
| 1.0 | 11.09 |
| 1.05 | 11.87 |
| 1.1 | 11.21 |
| 1.5 | 7.27 |
| 2 | 7.01 |

From Table 1 we can see that at the beginning, the intrinsic viscosity of the product increases with the amount of TDI, indicating that the chain extending as the side reaction had probably occurred. When the molar ratio of TDI to MPEG reached 1.05, the intrinsic viscosity of MPEG reached the maximum (11.87 mL/g). This indicated that the chain extending of the side reaction had probably reacted to its highest extent. Then, with the further increase of TDI amount, the intrinsic viscosity of MPEG-NCO decreased until reaching a constant value. From this we can infer that, when the molar ratio of TDI to MPEG reaches 1.5, the end groups of MPEG are likely to be terminated by TDI before the chain extending of the side reaction, hereby the MPEG–NCO is generated.

Then, the unreacted NCO group in the intermediate can be used in further isocyanation with HP as shown in Scheme 3, and the yield (*Y*) and grafting efficiency (*GE*) of HP-g-MPEG are shown in Table 2.



Scheme 3. Preparation of HP-g-MPEG

Table 2. *Y* and *GE* of HP-g-MPEG at various weight ratios of HP:MPEG:TDI

| HP:MPEG:TDI (g:g:g) | *Y* (%) | *GE* (%) |
|---|---|---|
| 7.5 :10:1.74 | 46.47 | 15.91 |
| 10 :10:1.74 | 63.13 | 28.02 |
| 12.5 :10:1.74 | 70.09 | 33.02 |
| 15 :10:1.74 | 65.71 | 32.66 |
| 17.5 :10:1.74 | 53.24 | 28.24 |

It can be seen that the yield (*Y*) and grafting efficiency (*GE*) of HP-g-MPEG change continuously with the ratio of HP:MPEG:TDI. At the beginning, both *Y* and *GE* increased with the increasing content of HP, because there are more initiating hydroxyls of increased HP for MPEG–NCO to graft onto. Then *Y* and *GE* reached their climaxes at the optimal HP:MPEG:TDI ratio of 12.5:10:1.74. With the further increase of HP feeding ratio, the hydroxyl of HP was excessive and the graft copolymerizaion reached saturation, so the increased HP content could not further promote the graft reaction, and the value of Y and GE decreased.

## *Characterization*

The expected synthesis route and structure of MPEG–NCO and HP-g-MPEG are shown in Schemes 1 and 3. The FT-IR spectra of MPEG, MPEG–NCO and HP-g-MPEG are given in Figure 1. The FT-IR spectrum of MPEG (Figure 1(a)) shows a strong hydroxyl peak at 3430 $cm^{-1}$, a strong absorption peak at 1130 $cm^{-1}$ for ether bonds and a sharp peak at 841 $cm^{-1}$ for methylene groups. By introducing NCO groups onto the MPEG terminal, the FT-IR spectrum of MPEG–NCO (Figure 1(b)) shows a new sharp peak around 2270 $cm^{-1}$ (marked by arrows) assigned to the NCO groups, at 1540 $cm^{-1}$ (NH) and 1750 $cm^{-1}$ (C=O) for the newly formed carbonate groups, as well as a new peak at 1600 $cm^{-1}$ which is due to the presence of the aromatic group originated from TDI. By grafting MPEG–NCO onto HP, the NCO peak at 2270 $cm^{-1}$ disappears in the FT-IR spectrum of HP-g-MPEG (Figure 1(c)), which means that the NCO group has been changed into the carbonate group and the absorption of amide NH groups at 1540 $cm^{-1}$ and aromatic groups at 1600 $cm^{-1}$ are retained. These results suggest that graft copolymer, HP-graft-MPEG, are formed via the reactions of the two NCO groups of TDI with hydroxyls of MPEG and HP, respectively.

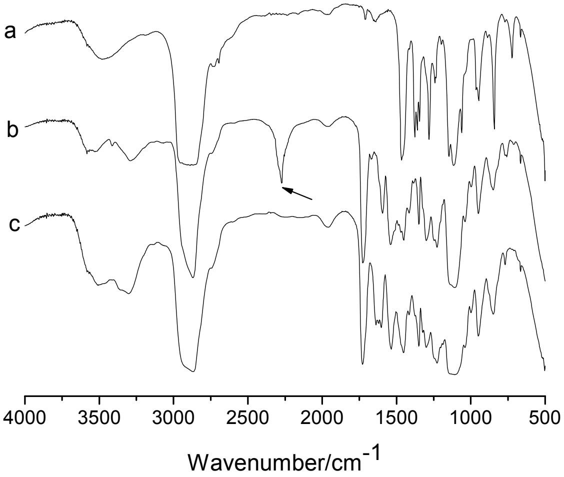


Figure 1. FT-IR spectra of MPEG (a), MPEG–NCO (b), and HP-g-MPEG (c).

In order to further confirm the chemistry structure of HP-g-MPEG, we performed the $^1$H NMR measurement. As shown in Figure 2, the $^1$H NMR spectrum showed signals assignable to the protons of HP. After reaction, a new strong signal appeared at 3.60-3.90 ppm, due to the substitution of $–CH_2CH_2O–$ groups of MPEG in Figure 3, The NMR spectrum of HP-g-MPEG shows the peaks of both HP and MPEG, indicating the formation of the graft copolymers HP-g-MPEG. The characteristic MPEG protons from side chain are seen in the region from 3.60 to 3.90 ppm. The peaks at 1.0-3.0 ppm connect to the protons from HP, while the majority of peaks from the main chain of HP are highly overlapped, therefore, they can not be assigned. The $^1$H NMR spectrum of HP-g-MPEG also shows resonance at 7.05 ppm for the benzene ring of TDI, and resonance at 4.42 ppm for the newly formed amide NH groups.

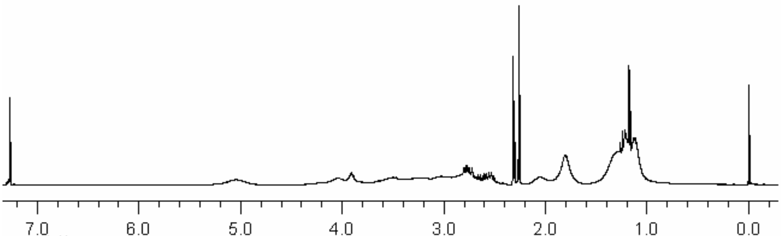


Figure 2. $^1$H NMR spectrum of HP.

## Conclusion

By using 2,4-tolylene diisocyanate (TDI) as a coupling agent, MPEG can be easily grafted onto hyperbranched polyesteramides to obtain HP-graft-MPEG amphiphilic copolymers. The yield (*Y*) and grafting efficiency (*GE*) of HP-g-MPEG change continuously with the ratio of HP:MPEG:TDI, and *Y* and *GE* reached their climaxes at the optimal HP:MPEG:TDI ratio of 12.5:10:1.74. The structure of the graft amphiphilic copolymers is confirmed by FT-IR and $^1$H NMR.

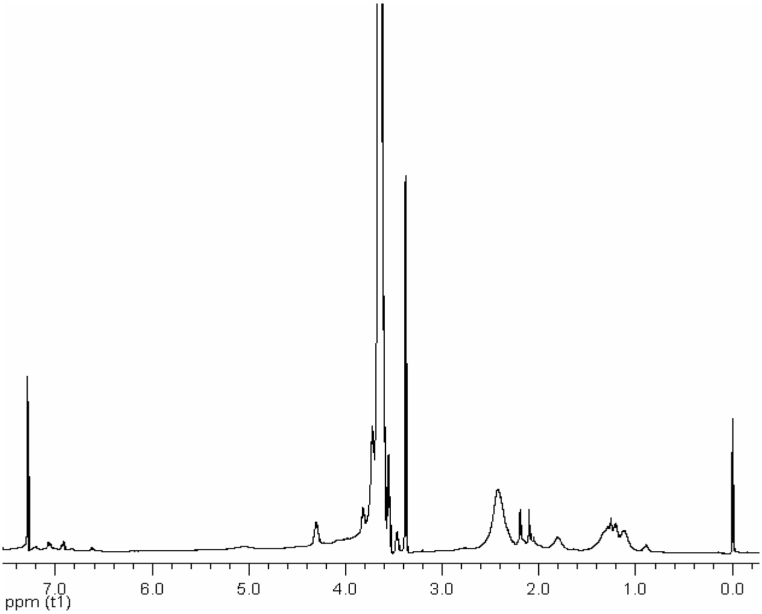


Figure 3. $^{1}$H NMR spectrum of HP-g-MPEG.

*Acknowledgements.* This work was sponsored by the National Science Foundation of China (Project: 20474025).

## References

1. Flory PJ (1952) J Am Chem Soc 74: 2718
2. Kim YH, Webster OW (1990) J Am Chem Soc 112: 4592
3. Mansfield ML (1993) Macromolecules 26: 3811
4. Inoue K (2000) Prog Polym Sci 25: 453
5. Ren Q, Gong FH, Jiang BB (2006) Polymer 47: 3382
6. Sun MH, Bo ZS (2007) J Polym Sci Part A: Polym Chem 45: 111
7. Emrick T, Chang HT, Frechet JMJ (1999) Macromolecule*s* 32: 6380
8. Gelade ETF, Goderis B, Koster CG (2001) Macromolecules 34: 3552
9. Kim YH, Webster OW (1992) Macromolecules 25: 5561
10. Tsukruk VV (1997) Prog Polym Sci 22: 247
11. Zou JH, Shi WF, Wang J, Bo J (2005) Macromol Biosci 5: 662
12. Xu J, Wu H, Mills, OP, Heiden PA (1999) J Appl Polym Sci 72: 1065
13. Zhang Y, Wang L, Wada T, Sasabe H (1996) J Polym Sci Polym Chem 34: 1359
14. Kim JS, Kim HC, Lee B, Ree M (2005) Polymer 46: 7394
15. Bosman AW, Jannsen HM, Meijer EW (1999) Chem Rev 99: 1665
16. Gan D, Mueller A, Wooley KL (2003) J Polym Sci Polym Chem 41: 3531
17. Tang LM, Qiu T, Tuo XL, Hu Y, Liu DS, Tang XL (2006) Colloid Polym Sci 284: 957
18. Krska SW, Seyferth D (1998) J Am Chem Soc 120: 3604
19. Lindman B, Alexandribis P (2000) Amphiphilic block copolymers Elsevier
20. An SG, Cho CG (2004) Polymer Bulletin 51: 255
21. Yuan J, Xu Z, Cheng S, Feng L (2002) European Polym. J 38: 1537
22. Dworak A, Kowalczuk-Bleja A, Trzebicka B, Walach W (2002) Polymer Bulletin 49: 9
23. Gelade ETF, Goderis B, Koster CG, Meijeerink N, Benthem RATM (2001) Macromolecule*s* 34: 3552