Well-Defined Polyethylene-*b*-Poly(ethylene glycol) Diblock Copolymers: New Synthetic Strategy and Applications*

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Introduction

Previously, well-defined polyethylene-*b*-poly(ethylene glycol) diblock copolymers (PE-*b*-PEG) was prepared by ATRP, RAFT or click chemistry. These methods were complicated and difficult to be industrialized.[1-6] In this paper, PE-*b*-PEG was successfully synthesized by a coupling reaction of hydroxyl-terminated polyethylene (PE-OH) and isocyanate-terminated poly(ethylene glycol) (PEG-NCO). By this method other polyethylene diblock copolymer also can be prepared with PE-OH and other hydroxyl-terminated polymers. So this simple and high-efficient method has potential for industrial application.

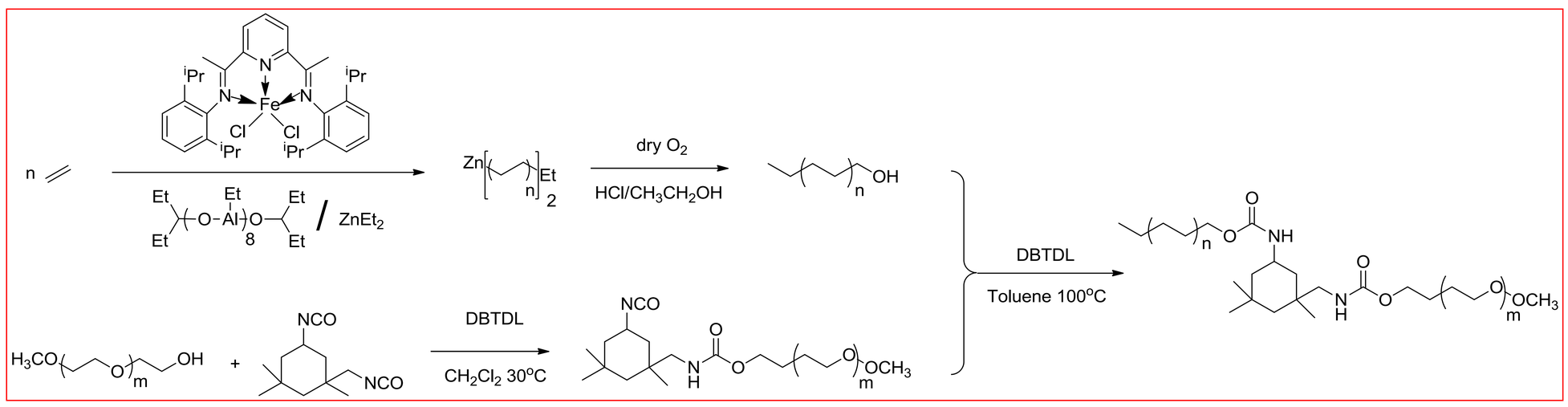
Experimental

PE-OH was prepared by means of coordination chain transfer polymerization (CCTP) using ethylene as monomer with 2,6-bis[1-(2,6-diisopropylphenyl)imino ethyl] pyridine iron (II) dichloride (complex **1**)/ethylaluminoxane (EAO)/diethyl zinc ($ZnEt_2$) in a procedure similar to that previously reported in literatures .[1-5]

PEG-NCO were prepared by monomethyl poly(ethylene glycol) (mPEG-OH) with diisocyanate. Isophorone diisocyanate (IPDI)(-NCO:-OH=20) and Dibutyltin dilaurate (DBTDL) (1 wt % relative to mPEG-OH) were added to the reactor under an nitrogen atmosphere. mPEG-OH was dissolved in CH_2Cl_2 and added dropwise to the stirred solution at room temperature followed by stirring for additional 3 h. After reaction the product was isolated by dissolution-precipitation technique with CH_2Cl_2 as solvent and diethylether as precipitant.The white powder was filtered and dried under vacuum at 30 ℃ to give PEG-NCO.

The block copolymer was formed by mixing PEG-NCO and PE-OH with the rate of 1.2 equiv of NCO to 1 equiv of OH followed by injection of DBTDL(1 wt % relative to PE-OH) and toluene. The product was extracted by acetone to remove the PEG and dried under vacuum at 60 ℃ to give PE-*b*-PEG.

Results and discussion



Scheme 1 Synthetic scheme for preparing PE-*b*-PEG copolymer.

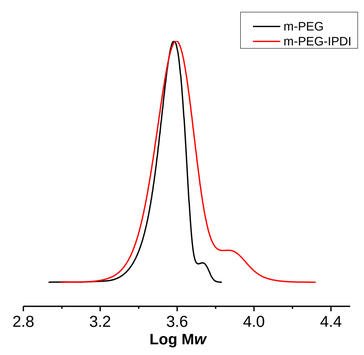


Fig. 1 Molecular weight curves of m-PEG and m-PEG-IPDI.

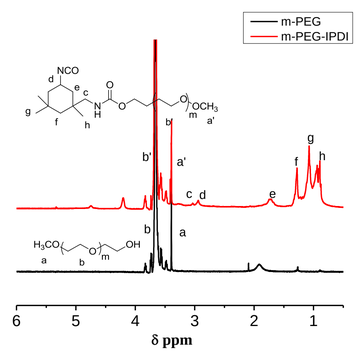


Fig. 2 ^{1}H-NMR spectra of m-PEG and m-PEG-IPDI in $CDCl_3$.

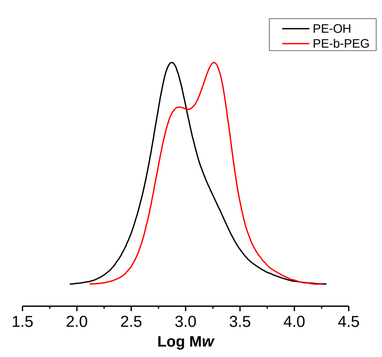


Fig. 3 Molecular weight curves of PE-OH and PE-*b*-PEG.

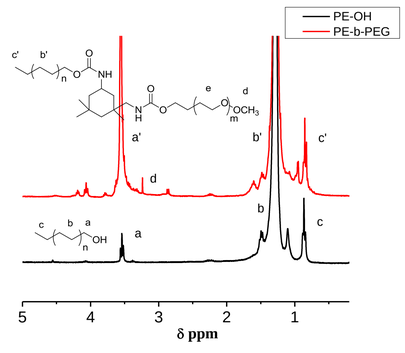


Fig. 4 ^{1}H-NMR spectra of PE-OH and PE-*b*-PEG in 1,2-Dichlorobenzene-d4.

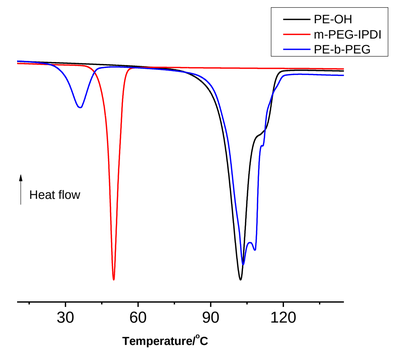


Fig. 5 DSC curves of m-PEG-IPDI,PE-OH and PE-*b*-PEG.

Table 1 Molecular weight Results of different samples

Entry	$M_{n,GPC}$[a]	Mw/Mn[a]	$M_{n,NMR}$[b]	Fn
m-PEG	3540	1.04	2100	
m-PEG-IPDI	3860	1.11	2300	92%[c]
PE-OH	760	1.54	1500	62%[d]
PE-b-PEG	1140	1.49		58%[c]

[a] Measured by GPC. [b] Measured by ^{1}H-NMR . [c] Calculated by GPC.
[d] Calculated by ^{1}H-NMR.

Table 2 DSC Results of different samples

Entry	Tm(℃)	ΔH(J/g)
PE-OH	102.3	221.6
m-PEG-IPDI	49.9	115.2
PE-b-PEG	36.1	23.3
	103.3	155.0

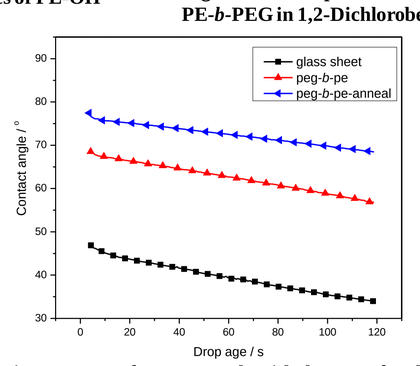


Fig. 6 Curves of contact angle with drop age for the unmodified and the modified glass sheet.

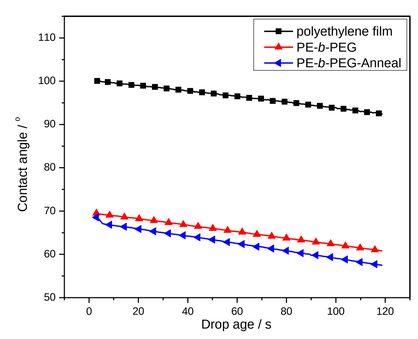


Fig. 7 Curves of contact angle with drop age for the unmodified and the modified polyethylene film.

Fig. 1 and Fig. 2 show that m-PEG-IPDI was successfully synthesized by m-PEG and IPDI and the yield of product was as high as 92% (calculated by Fig.1). Fig. 3, Fig. 4 and Fig. 5 reveal that the block copolymer PE-*b*-PEG was successfully synthesized by m-PEG-IPDI and PE-OH .The yield of this reaction was as high as 94% (calculated by Fig.3) .

Subsequently, The diblock copolymers were used as surface modification agent for different materials, such as polyethylene film and glass sheet. The contact angle of polyethylene film was significant reduced but that of glass sheet was increased. After annealing at 90℃ for 2h, the contact angle of glass sheet was obviously increased but for polyethylene film the contact angle was reduced because of interaction between the block copolymer and the matrix.

Conclusions

Characterization of the copolymer by GPC, ^{1}H-NMR, and DSC confirmed that the block copolymer PE-*b*-PEG was successfully synthesized and the yield of product was as high as 94%. This simple and high-efficient method has potential for industrial application. Subsequently, The diblock copolymers were used as surface modification agent for different materials, such as polyethylene film and glass sheet. The results of contact angle changed significantly because of the interaction between the blocky copolymer and the matrix.

References

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