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Study of Anionic Ring-Opening Polymerization and Macromolecular Structure Characterization for Poly(ethylene oxide)-poly(tetrahydrofuran)-poly(ethylene oxide) Triblock Copolymer

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A triblock copolymer with narrow molecular weight distribution (Mw/Mn < 1.2), poly(ethylene oxide)-poly(tetrahydrofuran)-poly(ethylene oxide), was synthesized by anionic ring-opening polymerization of ethylene oxide using alkoxide as a macroinitiator which was prepared by reacting hydroxyl-terminated poly(tetrahydrofuran) with NaH. The copolymer's structure was characterized by FTIR, ^{1}H NMR and ^{13}C NMR and well confirmed with its original structure design. The block copolymer's molecular weight and polydispersity as well as the crystalline behaviour were measured and analyzed by size exclusion chromatography/multi-angle laser light scattering (SEC/MALLS) and differential scanning calorimeter. The detailed synthesis conditions and possible polymerization mechanism including temperature, pressure and time on ring-opening polymerization were systematically explored. The results demonstrated that in order to obtain a well defined block structure with narrow molecular weight distribution, the optimum synthesis process was determined as the use of solution polymerization under the pressure of 200 psi at 70 °C for 8 h. It was also found that block copolymer's crystalline behaviour changes with the molecular weight.

Keywords: Anionic ring-opening polymerization, Macroinitiator, Triblock copolymer.

INTRODUCTION

Poly(ethylene oxide)-poly(tetrahydrofuran) block copolymer is an important polymer species in polyether related polyurethane (PU) industry[1], particularly, it plays a special role as a crucial adhesive for insensitive solid propellant, which is currently used in the HTPE rocket[2]. Because if this block copolymer with narrow molecular weight distribution was applied to HTPE type solid propellant, an uniform crosslinking network structure can be easily formed, leading to a significant improvement of mechanical strength and breaking elongation for the propellant.

Up to now, there are three major techniques for preparing this kind of block copolymer. The first is to utilize chemical reaction to couple the hydroxyl-terminated poly(ethylene oxide) and PTHF segments[3,4]. However, this strategy has a limited application due to polymer's molecular weight distribution and weak reactivity of terminal groups frequently failing to control the block copolymer's structure. The second is to use the macromolecular termination technique[5,6]. As Witte and Goethals[7] reported, the block copolymer can be prepared *via* termination of tetrahydrofuran cationic ring opening polymerization using poly(ethylene oxide) as a termination agent. But this method was often prohibited to have a wide application because of strict monomer feeding ratio in the synthesis process and often end-capped with methyl group in the target block copolymer. The third was introduced by Wang *et al.*[8]. They reported a new hydroxyl-terminated copolymer, PTHF-PEO-PTHF, which was synthesized by cationic ring opening polymerization of tetrahydrofuran with poly(ethylene oxide) in which poly(ethylene oxide) serves as a macroinitiator. A small amount of epoxy propane (PO) was also used as the ring-opening assistant agent and boron-trifuoride ethyl ether complex ($BF_3{\cdot}OEt_2$) as the catalyst. However, the macroinitiator based on poly(ethylene oxide) can not be completely reacted, as a result, complicated separation and purification processes for the product must be preceded due to large amount of poly(ethylene oxide) homopolymer and diblock copolymer existing in the final product.

To improve the shortcomings listed above, in this paper, a new strategy was developed. Firstly, a macromolecular alkoxide initiator was prepared by reacting hydroxyl-terminated PTHF with NaH. By using this special macroinitiator, a triblock copolymer, PEO-PTHF-PEO, can be synthesized by anionic ring-opening polymerization of ethylene oxide (EO). This technique not only provided a new synthesis method *via* a convenient process, but also the product obtained can be identified as possessing controllable molecular weight and narrow molecular weight distribution. Furthermore, the triblock copolymer's structure and crystalline behaviour were characterized and studied and the optimum synthesis parameters including temperature, reaction pressure and time were also verified and determined.

EXPERIMENTAL

Tetrahydrofuran was purchased from Shanghai Chemical Reagent Company and distilled with sodium, then dried over 3Å molecular sieve before use. Ethylene oxide was obtained from Chengdu Kelong Chemicals of China and dried by 3Å molecular sieve. The concentration of NaH (Ardrich) was determined by potentiometric titration. Ethyl alcohol (Shanghai Chemical Reagent Company) was dried by 3 Å molecular sieve also. PTHF (Mw 1660, 2590, 3690) was ordered from Ardrich and purified with PHF, then dried *via* freezing drying. Other reagents were throughly purified by common purification procedures.

Synthesis of macroinitiator: 34.3 g (13.2 mmol) of hydroxyl-terminated PTHF (Mw 2590) was first dissolved in 20 mL THF solvent and then added into a autoclave. Under the nitrogen atmosphere, 0.15 g (6.3 mmol) NaH was added. The system was degassed and then sealed plus maintaining a stirring condition at 60 °C. After the system was allowed to react for 3 h, the macromolecular initiator, alkoxide, was obtained.

Synthesis of triblock copolymer: 48 g (1.1 mol) ethylene oxide was added in the autoclave under nitrogen gas at 5 °C. The system was degassed and sealed to initiate the polymerization. The polymerization was conducted under stirring with a pressure of 200 psi at 75 °C for 8 h. Then, the reaction was terminated by addition of 1.5 g (15 mmol) phosphoric acid. For removing unreacted ethylene oxide monomer, the coarse product was washed with ethyl alcohol several times. The resulting block copolymer was obtained by filtration and then distillation treatment.

^{1}H NMR (300 MHz, δ ppm, CDCl$_3$): 3.64 (-OCH$_2$CH$_2$O), 3.41 (-OCH$_2$CH$_2$CH$_2$CH$_2$O-), 1.62 (-OCH$_2$CH$_2$CH$_2$CH$_2$O-).

Characterization: Fourier transform infrared (FT-IR) spectra were recorded on a NICOLET iS10 IR spectrometer. The ^{1}H NMR and ^{13}C NMR spectra were obtained from Bruker Avance 300 spectrometer (Bruker BioSpin, Switzerland) operating with 300 MHz (1 H) in CDCl$_3$. The molecular weight parameters of the copolymers were determined on a DAWN EOS size exclusion chromatography/multiangle laser light scattering (SEC/MALLS). HPLC grade THF (at 40 °C) was used as an eluent at a flow rate of 0.5 mL/min. Waters 515 pump and differential refractometer (OptilabrEX) were used. The solution concentrations of copolymers were determined by a 809 automatic potentiometric titrator (Wanton, Switzerland). Differential scanning calorimetry (DSC) measurement was conducted on a TA 2910 calibrated with indium. The sample (3-5 mg) treated by freeze drying was encapsulated in aluminum pan and scanned with a heating rate of 5 °C/min.

RESULTS AND DISCUSSION

Fig. 1 illustrates FTIR spectrum for Block (Mw 4910). Obviously, form the spectrum, there are a O-H stretching vibration band at 3404 cm^{-1} and C-H stretching vibration bands at 2858 cm^{-1} and 2936 cm^{-1} and also a C-O stretching vibration at 1110 cm^{-1}. All the FTIR absorption bands indicated that two different polymer chains are coexisting in the block copolymer.

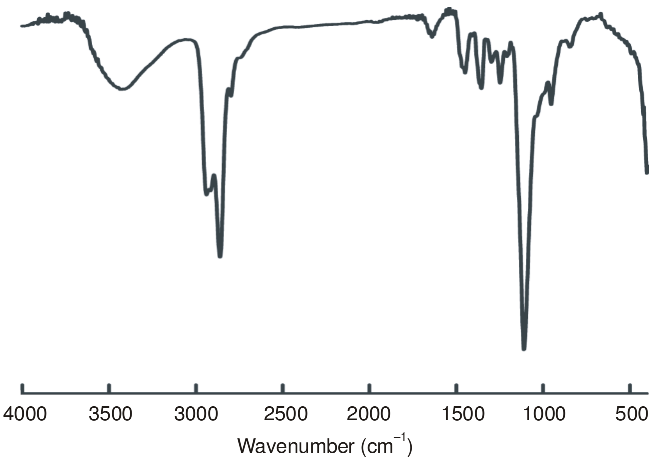
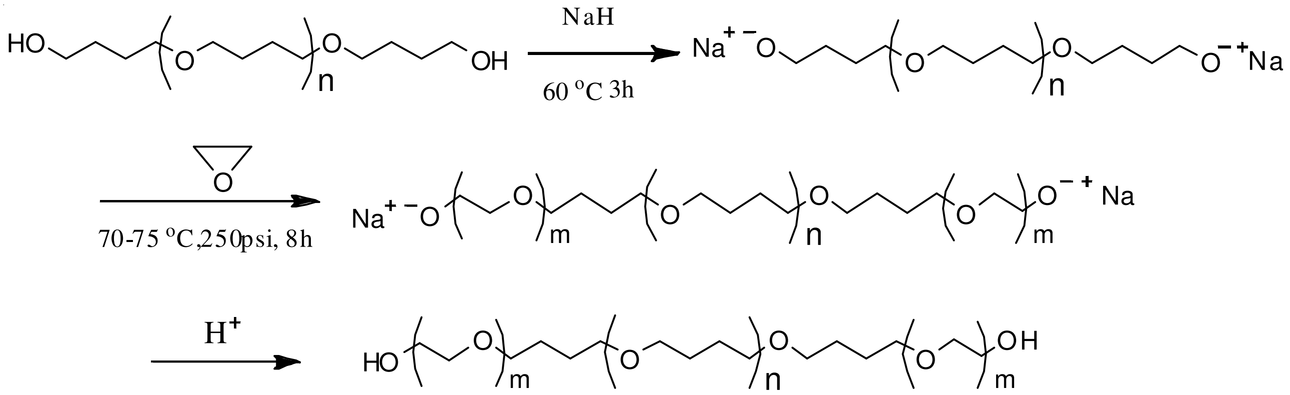


Fig. 1. FTIR spectrum of Block (Mw 4910)

Fig. 2 shows the ^{1}H NMR spectrum of Block (Mw 4910). Clearly, the chemical shifts at 1.62 and 3.41 can be assigned to the protons in -CH$_2$ and -OCH$_2$- segments which are belonging to PTHF polymer. Whereas a sharp signal at 3.65 can be assigned as the protons from -CH$_2$ segments in poly(ethylene oxide) polymer. This again demonstrated that PTHF-PEO block copolymer was synthesized successfully. The ratio of



Scheme-I

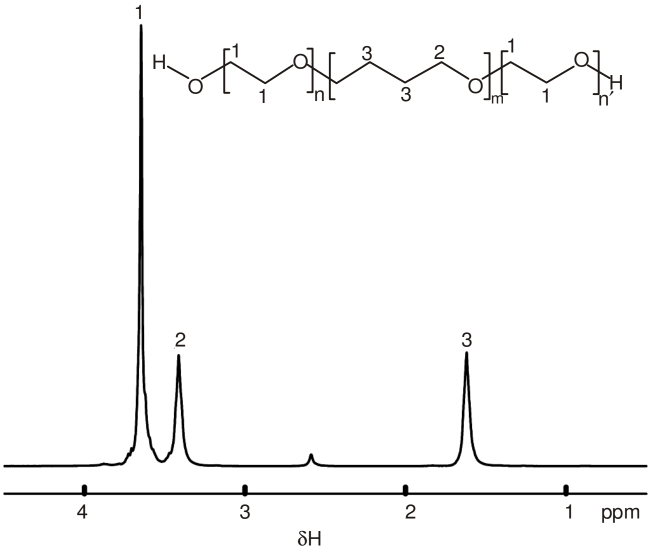


Fig. 2. ^{1}H NMR of Block (Mw 4910)

ethylene oxide *versus* THF structural units can be further calculated as 1.12 according to the NMR data. For identifying block copolymer's characteristic structure, ^{13}C NMR measurement was conducted (Fig. 3).

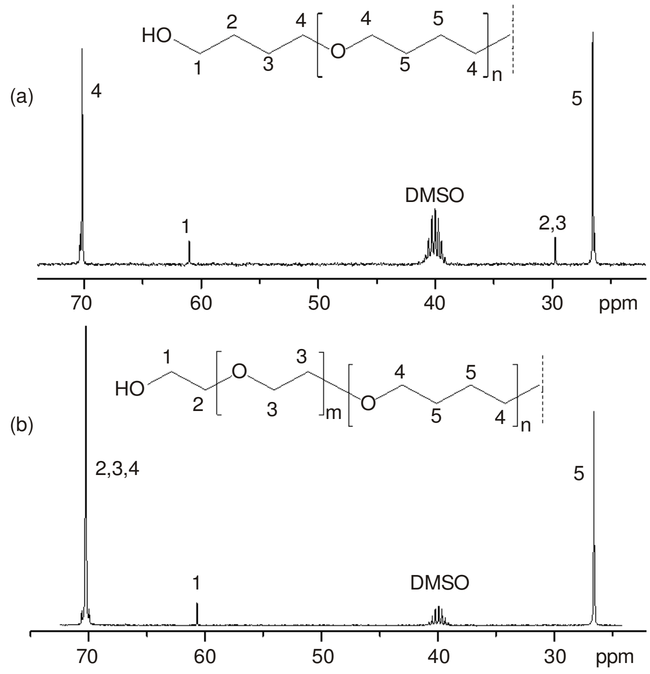


Fig. 3. ^{13}C NMR curve of PTHF (Mw2590) (a) and Block (Mw 4910) (b)

Compared the ^{13}C NMR curve of (A): PTHF (Mw 2590) with (B): Block (Mw 4910) in Fig. 3, it was observed that the sharp signal at δ 30 in (a) which can be assigned as the terminal groups of 2,3 in PTHF disappeared completely in (b). This reflected that the block copolymer synthesized is a PEO-PTHF-PEO type triblock copolymer.

Fig.4 shows the GPC traces of PTHF (Mw 2590) and its block copolymer Block (Mw 4910). As can be seen in Fig. 4, the resulting block copolymer possesses a narrow molecular weight distribution with higher purity. In addition, Block (Mw 4910) has a relatively higher molecular weight compared with its precursor PTHF (2590) which is strongly suggesting that both ends of PTHF chains indeed were linked with polyethylene oxide chains. The block copolymer's structural parameters were listed in Table-1.

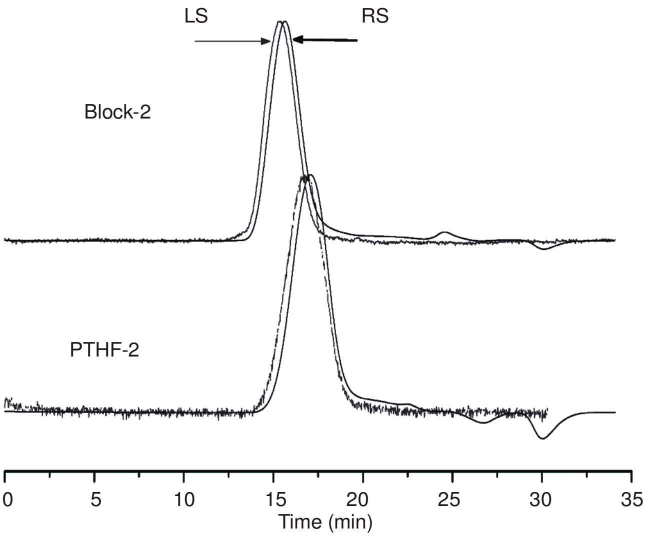


Fig. 4. GPC traces of PTHF (Mw 2590) and triblock copolymer Block (Mw 4910)

TABLE-1
MOLECULAR PARAMETERS OF POLYMER PTHF AND ITS RESULTING BLOCK COPOLYMER

Samples	M_w^a	M_n^a	M_w/M_n	PTHF in Block^b (wt %)
PTHF-2^c	2590	2140	1.21	100
Block-2	4910	4500	1.09	47.1

^{a}determined by GPC; ^{b}determined by ^{1}H NMR

Determination of polymerization parameters for triblock copolymer: In order to obtain the optimum polymerization condition such as solvents, monomer's feed ratio, polymerization temperature, time and reaction pressure, a series of experiments were conducted to coordinate these parameters for controlling synthesis of the block copolymer.

Effect of solvent on polymerization: The anionic ring-opening polymerization of ethylene oxide is a heat generating reaction. In this case, if bulk polymerization was applied, it could result in an inferior product and even induced an explosive polymerization due to the high activity of ethylene oxide monomer (Fig. 5). As can be seen, by using bulk polymerization, during the start for 4 min, the temperature and pressure of the system rapidly reached to 200 °C and 350 psi and this indicated an explosive reaction taking place. The final product obtained appears with dark color and also confirms this point.

In order to avoid this defect and conduct the polymerization under a smooth condition, we choose THF as the solvent to prepare the triblock copolymer, because the solution polymerization can decrease the reaction rate by reducing the concentration of ethylene oxide monomer as well as transfer reaction heat timely.

Fig. 6 presents the ethylene oxide polymerization which was carried out in THF. As can be seen, the highest temperature for the polymerization took place merely at 83 °C due to the reaction heat being easily transferred.

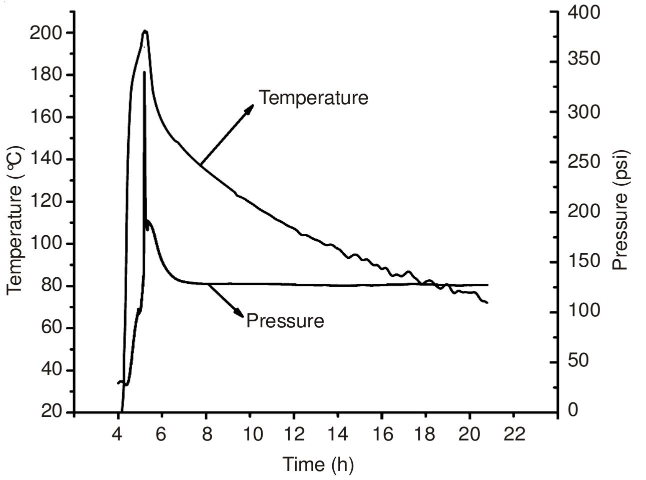


Fig. 5. Relationship between the pressure, temperature and the reaction time for bulk polymerization of ethylene oxide

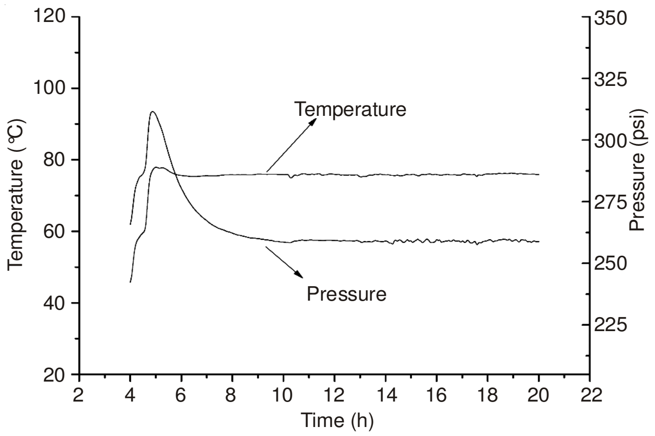


Fig. 6. Relationship between the pressure, temperature and the reaction time for solution polymerization of ethylene oxide

Selection of modification reagents on polymerization: For preparing a triblock copolymer, we used the hydroxyl-terminated PTHF (Mw < 4000) as the precursor which is carrying relatively less end groups with a lower reaction activity. For enhance the reactivity, we purposefully selected a reagent with high reaction activity to modify PTHF. It is well known that naphthalene potassium and naphthalene sodium (NaH) are often used as the high active modification reagents[9]. However, due to the difficulty of preparation of naphthalene potassium insoluble in THF for naphthalene potassium based macromolecular alkoxide[10,11], we chose NaH as the modification reagent.

As can be seen in **Scheme-I**, the ionization of the terminal hydroxyl groups in PTHF can be accomplished *via* addition of sodium hydride. However, the ionized hydroxyls in PTHF should be held to lower than 50 % for preventing initiator precipitation from THF. It was also found that as the exchange reaction between alcoholate active center and hydroxyl group is much faster than the initiation rate, which leads to simultaneous growth of polymer chains[12,13], explains the reason for using only 0.15 g (6.3 mmol) NaH to modify 34.3 g (13.2 mmol) of hydroxyl-terminated PTHF (Mw 2590); therefore, the ratio (PTHF:NaH) should larger than 2 and accurate feeding of NaH is not necessary, leading the synthesis process to be much easier to operate.

Effect of temperature on polymerization: The anionic ring-opening polymerization of ethylene oxide was usually carried out at the high temperature 90-120 °C[14], the product obtained often showed the dark colored because of vigorous reaction. However, if using macromolecular alkoxide as initiator, the polymerization can take a long time, it even can be last for more than 3 days, despite the polymerization can be carried out as a smooth and steady way at room temperature. For solving this problem, we raised the temperature up to 70 °C gradually and made the product conversion reach to 75 % within 8 h.

Effect of pressure on polymerization: In order to study the influence of pressure on the polymerization, a series of processes were conducted (Table-2) by changing the online pressure, at the same time, keeping other parameters unchanged; that is, polymerization temperature is settled at 70 °C and reaction time is fixed for 8 h. The polymer PTHF (Mw = 1660) was always used, the mole ratio for PTHF:NaH = 2.2 and monomer feeding ratio was fixed to EO:PTHF = 1:1.4. As shown in Table-2, under the pressure of 200 psi, the product conversion can reach to 76 %, at this point, the copolymer can gain a relatively narrow molecular weight distribution (1.06). Along with the increase of pressure (from 200 to 400 psi), molecular weight, molecular weight distribution and conversion essentially remain unchanged. Considering the higher the pressure, the higher production cost and more drastic situation may be subjected, therefore, we finally selected the optimal pressure as under 200 psi.

TABLE-2
EFFECT OF PRESSURE ON MOLECULAR WEIGHT AND MOLECULAR WEIGHT DISTRIBUTION OF COPOLYMERS

Sample	Pressure (psi)	M_w[a]	M_w/M_n	Conversion (%)
1	200	3950	1.06	76
2	300	4110	1.10	77
3	400	4280	1.12	80

[a]determined by GPC

In order to obtain a well defined block structure with narrow molecular weight distribution, our systematic experimental results leaded us to believe that the optimum synthesis process for the triblock copolymer should be determined as the use of solution polymerization under the pressure of 200 psi at 70 °C for 8 h. By using this defined technique, we synthesized three block copolymers, their structure parameters are listed in Table-3. Clearly, all copolymers have a controlled molecular weight with narrow molecular weight distribution.

TABLE-3
DATA OF PREPOLYMERS PTHF AND THEIR RESULTING BLOCK COPOLYMERS

Samples	M_w[a]	M_n[a]	M_w/M_n	PTHF in Block[b] (wt %)
PTHF-1[c]	1660	1330	1.25	100
PTHF-2	2590	2140	1.21	100
PTHF-3	3960	3300	1.20	100
Block-1	2950	2760	1.07	48.6
Block-2	4910	4500	1.09	47.1
Block-3	7810	7370	1.06	49.2

[a]determined by GPC; [b]determined by ^{1}H NMR; [c]PTHF-1 was used for Block-1

Relationship between crystallization and molecular weight: It was well known that triblock copolymer synthesis is consisting of both crystalline and amorphous segments, its crystallization processes and the resulting crystal morphology can be significantly influenced by microphase separation in melt[15]. However, our triblock copolymer, consisting of different crystalline segments, usually exhibits much more complicated crystallization behaviour[16]. In this case, it may include confined crystallization, competitive or interactive crystallization.

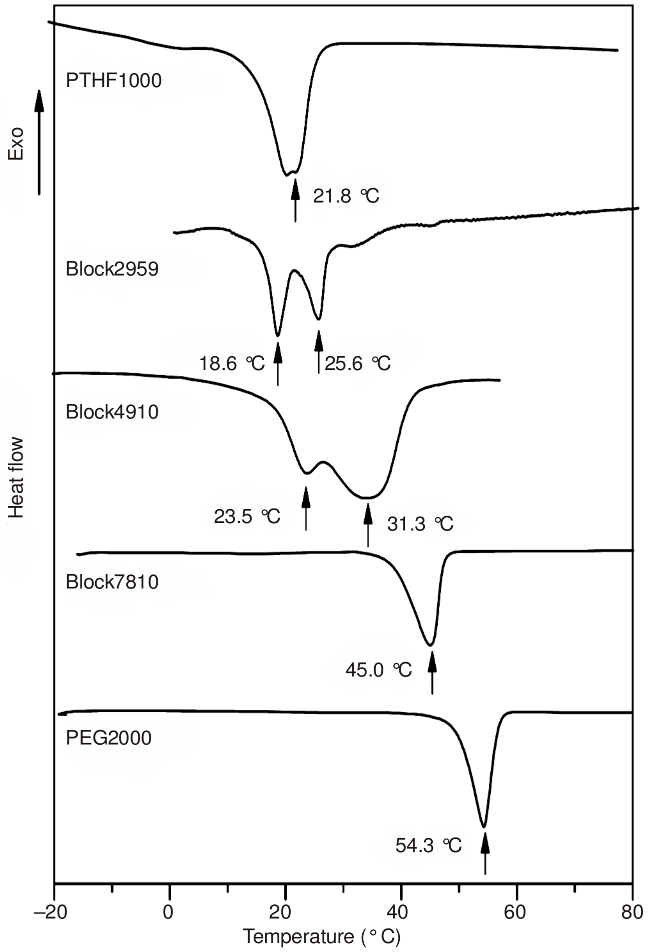


Fig.7. DSC thermograms of a series of block copolymers and the pure PTHF and poly(ethylene oxide)

For better understanding the triblock copolymer's crystalline behaviour, the melting and crystallization for different PEG-PTHF-PEG triblock copolymers were investigated by DSC. Homopolymers of PEG2000 and PTHF1600 were also tested for comparison. Fig.7 presents DSC thermograms of a series of block copolymers and their pure PTHF and poly(ethylene oxide) homopolymers. On the heating curves, there are two obvious melting points of Block-1(Mw = 2950): one around 18.6 °C due to PTHF blocks and one around 25.6 °C due to poly(ethylene oxide) blocks. Block-2 (Mw = 4910) also exhibits two melting points around 18.6 and 31.3 °C. These observations demonstrated that these block copolymers possess phase separation[6] during crystallization process. Whereas only one melting point for Block-3(Mw = 7810) around 45 °C was observed, it means that only poly(ethylene oxide) blocks crystallized. The different crystallization behaviours among a series of block copolymers can be ascribed to the stronger crystallizability of poly(ethylene oxide) blocks than PTHF blocks. This suggests that the crystallizability of PTHF blocks was inhibited by poly(ethylene oxide) blocks. Furthermore, with the increasing length of poly(ethylene oxide) blocks, their interaction became more intensive. This explains that Block-3 only shows one crystal melting point at 45 °C.

Conclusion

A macromolecular alkoxide initiator was prepared using hydroxyl-terminated PTHF to react with NaH, by using it, a new PEO-PTHF-PEO triblock copolymer was synthesized *via* anionic ring-opening polymerization of ethylene oxide. This synthetic presents a new way to have triblock copolymer with controllable molecular weight, narrow molecular weight distribution *via* a convenient process.

The study on triblock showed that the structure of triblock copolymers were totally consistent with what we expect from our design. DSC analysis of triblock copolymers found that copolymerization and molecular weight distribution have great effects on crystallization behaviour of poly(ethylene oxide) segment and PTHF segment. With the increasing length of poly(ethylene oxide) segment, the crystallization of PTHF was effectively restrained.

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