

Review

**SYNTHESIS AND CHARACTERIZATION OF HYDROPHOBIC-
HYDROPHILIC MULTIBLOCK COPOLYMERS FOR BIOMEDICAL
APPLICATIONS***

Yong Kiel Sung

*Department of Chemistry, College of Natural Science, Dongguk University, 3Ga 26, Phildong, Junggu,
Seoul 100-715, Korea*

Yong Joo Kim

*Reliability Technology Division, NITQ, 2 Chungangdong, Kwachoncity
Kyunggido 427-010, Korea*

Sung Wan Kim

Center for Controlled Chemical Delivery, University of Utah, Salt Lake City, Utah 84112, U.S.A.

Abstract The synthesis and characterization of amphiphilic copolymers of poly(dimethyl siloxane)(PDMS), poly(ethylene oxide)(PEO), and heparin(Hep) were investigated. These multiblock copolymers were identified using $^1\text{H-NMR}$, FTIR, end group analysis, and sulfur elemental analysis. The multiblock copolymers were characterized by using DSC and X-ray diffractometry. The glass transition temperature, crystalline melting characteristics, annealing effect, and cold crystallization of the block copolymers were determined by DSC. The crystallinity of the block copolymers was also determined by X-ray diffraction method.

Keywords Heparinized block copolymer, Biomedical polymer, Synthesis, Characterization

INTRODUCTION

Multiblock copolymers exhibiting heterogeneous microphase separated structures of hydrophilic and hydrophobic microdomains have been shown to suppress platelet adhesion and morphological changes of adhering platelets^[1, 2]. One interesting new application of block copolymers is in the field of blood-contacting biomaterials. The microdomains present on the surface of block copolymers have been implicated in the unique behaviors of these materials in contact with blood^[3]. From a thermodynamic standpoint, an enrichment of low-energy segments at the surface might be anticipated and, indeed, has been confirmed experimentally in di- and triblock amphiphilic copolymers^[4, 5] and polyurethanes^[6]. These surface enrichment phenomena have been generally observed for films cast and analyzed in hydrophobic environments, which favor low-energy surfaces.

Gallot et al.^[7, 8] first carried out a study on the synthesis and microheterophase structure determination of AB type diblock copolymers. Nakajima et al.^[9] synthesized ABA type triblock copolymers and characterized the microheterophase structure. Okano et al.^[2] proposed that the

* Corresponding author: Yong Kiel Sung, E-mail: yksung@cakra.dongguk.ac.kr

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polymeric hydrophilic/hydrophobic micro-phase separated structure is a key parameter for controlling the antithrombogenic activity of polymers due to its apparent inhibition of platelet aggregation. Feijen et al.^[3] reported the synthesized ABC type block copolymers containing heparin block, hydrophilic poly(ethylene oxide) block, and hydrophobic polystyrene block, and also characterized their blood compatibility. Kim et al.^[10] reported the synthesis and characterization of amphiphilic ABC type block copolymers containing poly(dimethyl siloxane), poly(ethylene oxide), and heparin. Sung et al.^[11] reported the bulk and surface characteristics of biocompatible poly(dimethyl siloxane)-poly(ethylene oxide)-heparin multiblock copolymers. Other works^[12] described the synthesis, characterization, and surface properties of amphiphilic ABC and ABCBA type block copolymers containing PDMS, PEO, and heparin. Silicone polymers have shown significant and widespread success as biomaterials in implant and pharmaceutical applications. PEO has also received much attention as a potential biomaterial with unique, biocompatible properties. By attaching these polymers linearly as block copolymers, the aim of these efforts was to provide a blood compatible, heparinized coating to improve the bulk and surface properties of existing polymer substrates.

In this work, we reviewed the characteristics of ABA and ABCBA type amphiphilic block copolymers containing PDMS, PEO, and bioactive heparin segments. The swelling degrees of the multiblock copolymers were determined. The glass transition temperature, crystalline melting characteristics, annealing effect and cold crystallization of the block copolymers were determined by differential scanning calorimetry. The crystallinity of the block copolymers was also determined by X-ray diffraction method.

EXPERIMENTAL SECTION

Synthesis of Multiblock Copolymers

PDMS-PEO-NH₂ block copolymers were synthesized by a procedure analogous to that used to prepare polystyrene-HEMA^[2, 13] and polystyrene-poly(ethylene oxide) block copolymers^[3]. PDMS-PEO-NH₂ block copolymers were synthesized by adding PDMS-N=C=O solutions (15% w/v) in toluene dropwise over a period of 48 h to a solution of H₂N-PEO-NH₂ (15% w/v) in toluene until the final ratio of [NH₂]/[NCO] was 2.4. This reaction was performed under nitrogen at room temperature. Reactions were terminated by utilizing a dual precipitation technique after evaporating toluene to 50% of its original volume. Unreacted PDMS-N=C=O was removed by precipitation of the reaction contents into a 10-fold excess of diethyl ether, leaving a white powder consisting of a mixture of H₂N-PEO-NH₂ and PDMS-PEO-NH₂ block copolymers. Unreacted PEO was then removed by chopping the powder into small granules and stirring gently in 50-fold excess water for 3 h. Filtration, rinsing, and freeze-drying yielded a spongy, white block copolymer solid. The polymer was used immediately or stored at -20°C.

PDMS-PEO-Heparin block copolymers were synthesized via coupling reactions of PDMS-PEO-NH₂ block copolymers with derivatized heparin. Commercial heparin was subjected to cation exchange with benzyltrimethyl ammonium bromide to yield the Triton-B form. The cation exchange procedure involves the replacement of Na⁺ cations in heparin with more hydrophobic quarternary ammonium cation. The process entails addition of 3.5 g of Triton-B to an aqueous solution of heparin (2.3 g in 150 mL water) at pH = 7.5. Refrigeration for 16 h was followed by dialysis against distilled water for 24 h to remove low-molecular-weight salt and heparin fragments with *M_w* less than 5000 daltons. Repeating this entire operation three times followed by lyophilization produces a heparin salt with enhanced solubility in organic solvents but showing lower bioactivity.

This heparin form was coupled to PDMS-PEO-NH₂ block copolymers by reductive amination. Freshly prepared copolymer (2.0 g) was first dissolved in THF (45 mL) and water (1 l

mL) was then added slowly with brief sonication until a clear solution was obtained. Heparin was dissolved separately in water (1.5 g in 12 mL) and THF (50 mL) dropped slowly to the solution with stirring at 37°C until a clear solution was obtained. The two solutions were mixed and adjusted to pH = 6.5 with 1 N HCl or 1 N NaOH. Sodium cyanoborohydride (NaCNBH_3) was dissolved in water (150 mg in 1 mL) and THF (5 mL) was added. This solution was then added to the copolymer-heparin solution. The reaction was stirred at room temperature for 7 days with 100 mg NaCNBH_3 added on the third day and fifth day and the pH was maintained at 6.5. Reaction products were recovered by removing the THF by evaporation, lyophilization, and thorough rinsing of the white solid with water to remove unreacted heparin and reducing agent.

Heparin-PEO-PDMS-PEO-Heparin block copolymers were synthesized via a coupling reaction of $\text{PDMS}(\text{PEONH}_2)_2$ with derivatized heparin. In order to increase its solubility, heparin was treated with a cation exchanger, benzyltrimethyl ammonium bromide to yield the triton-B form with one aldehyde group per molecule. Commercial heparin (3 g) was dissolved in water (150 mL) followed with the addition of NaNO_2 (0.034 g). Subsequently, the pH was adjusted to 2.7 with 1 N HCl and this solution was gently stirred at room temperature for 20 h, then the reaction mixture was adjusted to pH=7 with 1 N NaOH. Triton-B (4.46 g) was added to the solution. Refrigeration for 24 h was followed by dialysis against distilled water for 72 h at 5 °C to remove low molecular weight salt and followed by lyophilization to yield derivatized heparin (2.5 g). PEO-PDMS-PEO block copolymer (1 g) was first dissolved in THF (50 mL) and water (1.5 mL) was then added slowly with stirring until a clear solution was obtained. Heparin (1.25 g) was dissolved separately in water (65 mL) and THF (50 mL) was dropped slowly with stirring. The two solutions were mixed and brought to pH=6.5 with 1 N HCl or 1 N NaOH. Sodium cyanoborohydride (0.1 g) was dissolved in water (1 mL) and THF (5 mL) was added. This solution was then added to the copolymer-heparin solution. The reaction mixture was stirred at room temperature for 5 days with NaCNBH_3 (0.07 g) added on 3 days. Reaction products were recovered by removing THF by N_2 flow to 5 mL and then solid was separated. The solid was dissolved in toluene and filtered. Unreacted heparin and NaCNBH_3 were removed by soaking in water for 24 h, filtration, rinsing and freeze-drying yielded a white block copolymer solid (0.5 g).

Characterization of Multiblock Copolymers

Infrared spectra of the prepolymers and block copolymers were obtained from film cast on sodium chloride crystals by using a Nicolet 5-MX spectrometer. ^1H -NMR spectra were obtained from samples in CDCl_3 solvent by using a Varian EM 360A instrument.

Amino group functionalization for the PDMS and PEO prepolymers as well as the PDMS-PEO copolymers were analyzed with potentiometric titration. Sulfur elemental analysis was obtained on a Lecox Corp. model SC132IR analyzer.

For swelling measurements, solutions of block copolymers in chloroform (5% w/v) were cast in silanized petri dishes and air dried for 24 h followed by vacuum drying for 24 h. The thickness of the films was measured with a micrometer, and then cut into pieces of identical geometry and size using a grid pattern. Film pieces were then weighed, immersed completely in water and monitored for swelling after 2 h. Films were removed carefully from water, gently wiped dry with a dust-free towel and weighed.

For DSC measurement, Perkin-Elmer DSC-4 equipped with TADS computer was used to measure T_g and T_m . Calibration is most conveniently carried out by melting a carefully weighed sample of very pure material such as semiconductor-grade indium. The samples were measured from -150°C to 150°C under helium at a scanning rate of 20°C per min. Prior to the annealing-transient study experiments, samples of each material were compression molded for 10 min at a temperature approximately 20°C above the temperature of the highest DSC endotherm exhibited by the received samples, then slowly cooled under pressure.

X-ray diffraction profiles were recorded using a Cu K_α beam in an X-ray diffractometer (Rigaku D-MAX IIIB) by the powder diffraction method.

RESULTS AND DISCUSSION

Identification of Multiblock Copolymers

The IR spectra of PDMS(NH₂)₂, PDMS(TDI)₂ and PEO(NH₂)₂ are shown in Fig. 1. Telechelic isocyanated PDMS was prepared by using the TDI in solution coupling reactions. IR spectra demonstrate evidence of urea bond in this reaction by the presence of N-H stretch at 3320 cm⁻¹, amide I at 1645 cm⁻¹ and amide II at 1540 cm⁻¹ as shown in Fig. 1(B). These peaks were observed for the TDI functionalizations and were not present in simple mixtures of the PDMS and diisocyanates. A strong absorption at 2270 cm⁻¹ is characteristic of the free isocyanate group. The IR spectra of the block copolymer and heparinized block copolymers are also shown in Figs. 2(A) and 2(B), respectively. When these isocyanated prepolymers were coupled to amino telechelic PEO, IR scans demonstrate new N-H stretching vibration shifts at 3520 and 3380 cm⁻¹ as well as amide I and II peaks at 1670 and 1540 cm⁻¹, respectively, and the prominent isocyanate peak disappears, indicating the formation of urea linkages between PDMS and PEO into two different chemical environments. The proton NMR spectra of PEO, PDMS and PEO-PDMS-PEO block copolymer are shown in Figs. 3 and 4, respectively. It shows CH₃- proton resonance of siloxane backbone at δ = 0.1 and —CH₂— resonance at δ = 3.4–3.8. Integration of the signals confirms the proper ratio of protons in the block copolymer constituents as listed in Table 1. NMR integral ratios indicate that coupling reactions in the desired stoichiometry have been accomplished. In addition, end-group analysis, as shown in Table 1, demonstrates the presence of functional amino groups in all steps of the synthetic process. This further proves that the desired stoichiometric products are obtained. Pure heparin contains 6.1% sulfur by weight, while the sulfur content of PDMS(PEO-Hep)₂ was 1.3% by weight. This indicated that the heparinized block copolymers contain about 21.3% (W/W) of heparin. This result shows that 2 moles of heparin were coupled to

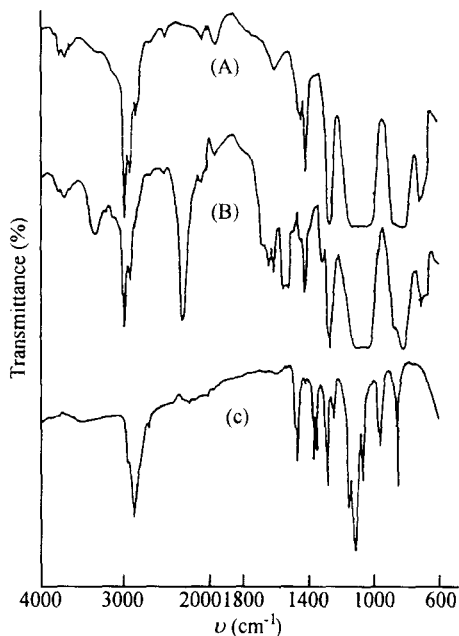


Fig. 1 FTIR spectra for PDMS(NH₂)₂ (A); PKDMS(TDI)₂ (B) and PEO(NH₂)₂ (C)

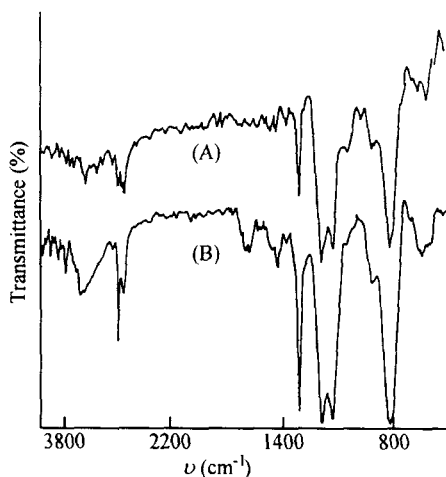


Fig. 2 FTIR spectra for block copolymers: (A) PDMS(PEO-NH₂)₂; (B) PDMS(PEO-Hep)₂

the polymer chain, indicating that ABCBA type block copolymer has been formed.

Table 1. The composition and end-group concentration of blocok copolymers

Polymer ^a	PEO (mol%) ^a	Mole ratio ^b		Amino group (mole/g × 10 ⁻⁵)
		PEO	PDMS	
PDMS(PEO2) ₂	10.2	1	4.5	4.38
PDMS(PEO4) ₂	20.5	1	1.9	4.14
PDMS(PEO6) ₂	30.7	1	1.3	1.26

a: in feed, b: by ¹H-NMR peak integration, * 2,4,6 represent mol. wt. 2000, 4000 and 6000

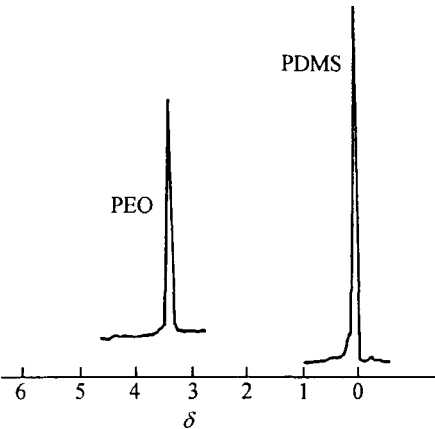


Fig. 3 NMR spectra for PDMS and PEO

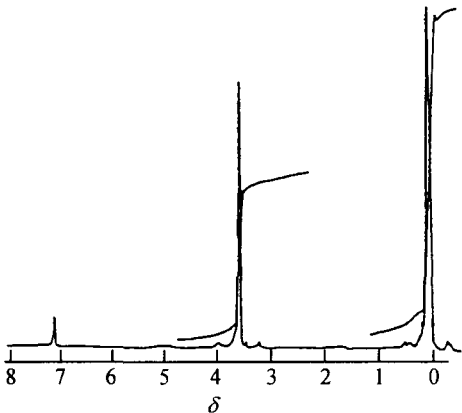


Fig. 4 NMR spectra for PDMS(PEO-NH₂)₂ block copolymer

Swelling Property

The swelling quantities of water in the block copolymers are shown in Fig. 5. The heparinized block copolymers containing PEO 6000 yielded pasty, white films lacking mechanical strength. The heparinized block copolymer containing PEO 4000 yielded a rubbery, flexible and translucent film lacking tear resistance but the unheparinized block copolymers were tough. The swelling degrees of the block copolymers in water were increased with increasing the molecular weight of PEO. The strength of the films prepared from heparinized block copolymers containing PEO 4000 and PEO 6000 appeared to improve with increased exposure time to air, indicating that evaporation of water may have occurred in the block copolymers. Pieces measuring 2 × 2 cm turned gray in color and lost their rigidity immediately on contact with water. After 2 h of hydration, the films of heparinized block copolymers containing PEO 2000 demonstrated nearly 250% (±40%)

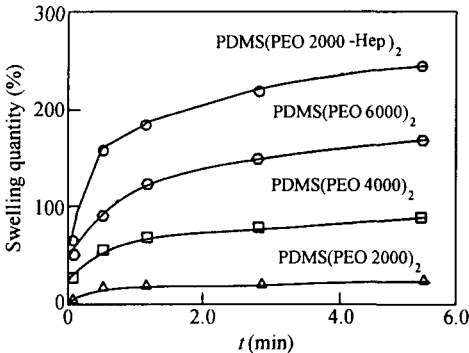


Fig. 5 The swelling quantity of block copolymers in water

absorption of water by weight. Measurements after 5 h were not possible due to loss of mechanical integrity. It appears as though the PEO phase maintains a dominant influence on the physical properties of the block copolymers.

DSC Thermograms of Block Copolymers

In the DSC data, PEO shows a T_g at -41°C and T_m at 59°C . The melting temperature location is consistent with that found by others^[14]. PDMS shows a T_g at -123°C , a crystalline transition at -90°C and a melting peak of crystalline PDMS at -50°C ^[15]. Heparin displays a large exothermic peak at 250°C due either to thermal degradation or recrystallization. A representative DSC thermogram of block copolymer shows well-defined thermal transitions which are easily identified as follows: nearly -123°C , glass transition of the PDMS chains; -103°C , crystalline transition of the PDMS chains; -53°C , melting transition of crystalline of PDMS; $50\text{--}57^\circ\text{C}$, endothermic peak related to the melting of the crystalline PEO fraction. The DSC results of PEO and PDMS in the block copolymers and the heparinized block copolymers are summarized in Tables 2 and 3, respectively. The T_m of PEO in the block copolymer is shifted to near 45°C , indicating a small degree of phase mixing with PDMS. The T_m of PEO in the heparinized block copolymer shifted down slightly to 40°C , indicating a small degree of miscibility of the PEO and heparin phase. These data also suggest that the copolymers are semicrystalline materials which are characterized by the coexistence of different segregated chemically homogeneous domains.

Table 2. DSC analysis of PEO in the block copolymers

Polymer	$T_m(^{\circ}\text{C})$	$\Delta H_m(\text{cal/g})$	$\Delta S_m(\text{cal/g-deg})$
PDMS(PEO2) ₂	33.5	7.5	0.22
PDMS(PEO4) ₂	45.0	11.2	0.24
PDMS(PEO6) ₂	46.6	10.0	0.21
PDMS(PEO2-Hep) ₂	35.7	1.6	0.04
PDMS(PEO4-Hep) ₂	38.6	5.2	0.13
PDMS(PEO6-Hep) ₂	42.8	6.7	0.15

Table 3. DSC analysis of PDMS in the block copolymers

Polymer	$T_g(^{\circ}\text{C})$	$T_c(^{\circ}\text{C})$	$T_m(^{\circ}\text{C})$	$\Delta H_c(\text{cal/g})$	$\Delta H_m(\text{cal/g})$
PDMS(PEO2) ₂	-124.1	-85.0	-53.4	-1.5	4.2
PDMS(PEO4) ₂	-124.1	-101.3	-57.9	-2.0	2.1
PDMS(PEO6) ₂	-123.1	-103.7	-55.6	-1.7	2.7
PDMS(PEO2-Hep) ₂	-122.2	-105.3	-53.4	-1.5	4.2
PDMS(PEO4-Hep) ₂	-121.8	-102.8	-53.8	-1.9	3.0
PDMS(PEO6-Hep) ₂	-122.1	-103.7	-56.4	-1.3	2.4

Depression of Melting Point

Melting in crystalline polymers typically occurs over a range of temperature. This phenomenon is a result of the fact that most crystalline polymers are not entirely crystalline and contain regions of crystallites surrounded by amorphous areas of various sizes. Depending on the ratio of amorphous to crystalline amounts, different melting temperatures will be recorded. DSC thermograms showing enthalpic peaks of melting of PEO and PDMA in the block copolymers and the heparinized block copolymers versus temperature are displayed in Table 2 and 3. In agreement with others^[16], their endothermic melting points shift to higher temperature ranges and become higher with increasing PEO molecular weight. A plot of PEO molecular weight versus T_m for the PEO, block copolymers and heparinized block copolymers is shown in Fig. 6. Melting point depression exhibited in these systems is an interesting phenomenon. From a theoretical standpoint, melting points should not fluctuate and should be independent of composition if the crystalline block is large enough and if the system is at thermal equilibrium^[17]. Given the various levels of crystalline and amorphous fractions and subsequent varying levels of miscibility present in the block copolymers, the

progressive shifts in melting point peaks with PEO content could be explained by Flory's polymer diluent theory^[18]. The lowering of PEO's crystalline melting point may be caused in part by differing degrees of phase mixing^[19] of PEO with amorphous PDMS phases or by different forms of PEO crystals in the block copolymers and heparinized block copolymers^[20]. Other systems^[21] comparing polymer-diluent mixtures demonstrate melt peak shifts which can be modeled by Flory's theory correlating T_m to thermodynamic interaction parameters and volume fractions of each phase. Phase mixing of PEO and PDMS probably accounts for the peak shifts in T_m as well as differing degrees of crystalline fraction in each case. The increasing amorphous PDMS content induces increasing levels of phase mixing, leading to crystalline imperfections which cause melting point depressions.

Degrees of Crystallinity

Calorimetric summation of different temperatures and relative populations of crystallites bearing these T_m will result in broad calorimetric peaks. Crystallite size and amorphous fraction, in turn, are a function of branching, chain length, and molecular weight distribution as well as thermal history^[22]. The enthalpy change associated with this first order transition is calculated as a ratio of peak areas in comparison to a known standard whose enthalpy change and peak area are well characterized and reproducible. A plot of PEO molecular weight versus ΔH_m for the PEO, block copolymers and heparinized block copolymers is shown in Fig.7. The linear relationship in block copolymers and heparinized block copolymers suggests some correlation between PEO molecular weight and the peak shift. By assuming the Gibbs free energy change during a phase transition is nearly zero, the entropy of the transition can be calculated from the known data of ΔH and melting temperature:

$$\Delta G_m = \Delta H_m - T_m \Delta S_m,$$

$$\Delta G \cong 0 (\text{melting equilibrium})$$

$$\Delta S_m = \Delta H_m / T_m$$

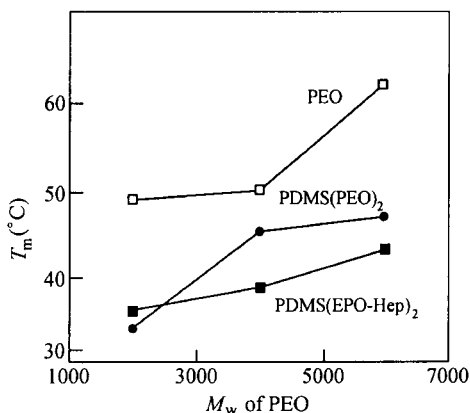


Fig. 6 PEO melting point versus PEO molecular weight in block copolymers

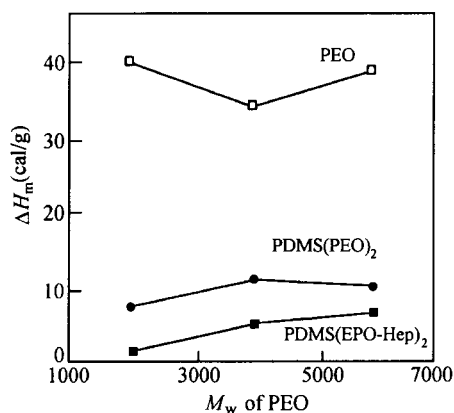


Fig. 7 PEO melting enthalpy versus PEO molecular weight in block copolymers

Table 2 shows T_m derived from DSC thermogram peaks, ΔH_m obtained from peak areas and ΔS_m calculated from ΔH_m and T_m . ΔS_m values of the heparinized block copolymers were increased by increasing the molecular weight of PEO. The enthalpy of melting, ΔH_m , can be used to calculate the degree of crystallinity (χ_c) of unknown samples if a sample of 100% crystalline phase can be used as a reference. The degree of crystallinity, χ_c , was calculated by the following equation:

$$\chi_c = \Delta H_m / \Delta H_m^0$$

where ΔH_m is found from thermograms as described previously and ΔH_m^0 is the enthalpy change of melting for a 100% crystalline sample standard. Calculations of χ_c according to molecular weight

of PEO in the block copolymers are shown in Table 4. The degree of crystallinity of the PEO phase was calculated from both the experimentally determined enthalpy change of fusion and also from a value of 194 J/g for ΔH_m^0 as derived for 100% crystalline PEO^[18,19]. The weight fractions of crystalline PEO increases with increasing PEO molecular weight in the block copolymers as in agreement with earlier works^[18,19]. It may be assumed that the ΔH_m measured is a contribution of the heat of rotation and the heat of melting for PEO.

Table 4. Crystallinity of PEO in the block copolymers

Polymer	ΔH_m (cal/g)	PEO Crystal(%)
PDMS(PEO2) ₂	7.5	16
PDMS(PEO4) ₂	11.2	24
PDMS(PEO6) ₂	10.0	21
PDMS(PEO2-Hep) ₂	1.6	3
PDMS(PEO4-Hep) ₂	5.2	11
PDMS(PEO6-Hep) ₂	6.7	14

The X-ray method allows the calculation of relative amounts of crystalline and amorphous material in a sample, if it is possible to resolve the contributions of the two types of structure to the X-ray diffraction pattern. The X-ray diffraction patterns for PEO, heparin and block copolymers were measured as shown in Fig. 8. The first main reflection of PEO is very sharp and corresponds to an intermolecular spacing of the linear chain, which is 0.46 nm. Regarding the diffraction patterns of the block copolymers and heparinized block copolymers, the first reflections are at the same position as that of PEO, and become broader as the amount of PDMS increases.

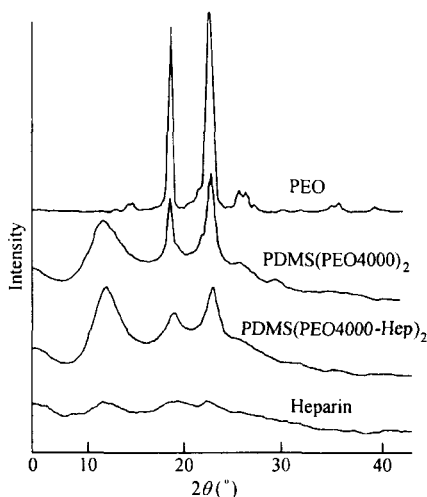


Fig. 8 The X-ray diffraction profiles of PEO, heparin and block copolymers

Annealing Effect

Annealing was impossible in these block copolymers with a T_m above 70°C because of their poor thermal stability. However, a sample of these block copolymers was heated for a few minutes to 50 °C and then studied in the usual calorimetric way. The annealing results of PEO and PDMS in the block copolymers and the heparinized block copolymers are also summarized in Tables 5 and 6, respectively. The PEO T_m peak shows shifts from near 45°C in the initial thermogram towards its pure T_m of 50°C with annealing effect. The initial, low T_m for PEO in this system suggests that PEO is quite phase mixed to begin. It is difficult to know whether PEO is mixed predominantly with heparin or PDMS. However, based on the shifts seen for block copolymers and heparinized

block copolymers, there probably exist phase mixed regions of both PEO-heparin and PEO-PDMS, with a larger portion of PDMS-PEO. The appearance of thermal transitions associated with pure PDMS, PEO and heparin phases as well as phase mixed regions of all constituents suggests that the heparinized block copolymer is phase separated to a certain extent with associated areas of phase mixing.

Table 5. Annealing effects of PEO in the block copolymers

Polymer	$T_m(^{\circ}\text{C})$	$\Delta H_m(\text{cal/g})$	$\Delta S_m(\text{cal/g-deg})$
PDMS(PEO2) ₂	30.9	4.5	0.14
PDMS(PEO4) ₂	49.8	10.9	0.22
PDMS(PEO6) ₂	52.1	9.7	0.19
PDMS(PEO2-Hep) ₂	28.2	1.1	0.03
PDMS(PEO4-Hep) ₂	43.9	5.2	0.11
PDMS(PEO6-Hep) ₂	48.1	7.2	0.15

Table 6. Annealing effects of PDMS in the block copolymers

Polymer	$T_m(^{\circ}\text{C})$	$\Delta H_m(\text{cal/g})$	$\Delta S_m(\text{cal/g-deg})$
PDMS(PEO2) ₂	-44.0	4.0	0.09
PDMS(PEO4) ₂	-44.7	2.4	0.05
PDMS(PEO6) ₂	-43.9	2.5	0.05
PDMS(PEO2-Hep) ₂	-42.6	4.0	0.09
PDMS(PEO4-Hep) ₂	-43.3	2.8	0.06
PDMS(PEO6-Hep) ₂	-43.7	2.5	0.05

Cooling Thermograms

The block copolymers and the heparinized block copolymers show different thermal behavior even after a melting recrystallization cycle. The cooling results of PEO and PDMS in the block copolymers and the heparinized block copolymers are also summarized in Tables 7 and 8, respectively. Since these block copolymers involve not only the melting of the polymer, but also inevitably its crystallization, it becomes imperative to consider the behavior of the sample under precisely controlled cooling conditions. Tables 7 and 8 illustrate the crystallization behavior of the

Table 7. Cooling effects of PEO in the block copolymers

Polymer	$T_c(^{\circ}\text{C})$	$\Delta H_c(\text{cal/g})$
PDMS(PEO2) ₂	-34.6	2.3
PDMS(PEO4) ₂	23.2	7.1
PDMS(PEO6) ₂	24.7	2.5
PDMS(PEO2-Hep) ₂	-42.0	0.5
PDMS(PEO4-Hep) ₂	-31.9	3.0
PDMS(PEO6-Hep) ₂	21.7	1.6

Table 8. Cooling effects of PDMS in the block copolymers

Polymer	$T_c(^{\circ}\text{C})$	$\Delta H_c(\text{cal/g})$	$\Delta S_c(\text{cal/g-deg})$
PDMS(PEO2) ₂	-81.5	3.7	0.04
PDMS(PEO4) ₂	-78.0	2.8	0.03
PDMS(PEO6) ₂	-77.1	3.2	0.04
PDMS(PEO2-Hep) ₂	-72.2	4.2	0.05
PDMS(PEO4-Hep) ₂	-75.1	3.1	0.04
PDMS(PEO6-Hep) ₂	-71.8	2.7	0.04

two different types of crystals in the block copolymer and the heparinized block copolymer. The block copolymers and the heparinized block copolyemrs exhibit two crystallization exotherms, one near 30°C, and the other near -80°C. The occurrence of two exotherms 100°C apart suggests a difference in nucleation phenomenon at the two temperatures.

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