

Synthesis, characterization and surface properties of amphiphilic polystyrene-*b*-polypropylene glycol block copolymers

Abdulkadir Allı^a, Baki Hazer^{a,*}, Yusuf Menceloğlu^b, Şefik Süzer^c

^a Zonguldak Karaelmas University, Department of Chemistry, Akademi street, 67100 Zonguldak, Turkey

^b Sabancı University, Faculty of Engineering and Natural Science, 81474 Istanbul, Turkey

^c Bilkent University, Department of Chemistry, 06800 Ankara, Turkey

Received 17 August 2005; received in revised form 18 September 2005; accepted 21 September 2005

Available online 28 November 2005

Abstract

The new macroazoinitiators containing poly (propylene glycol), (PPG), with molecular weight 400 and 2000, having hydrophilic character, were synthesized and polymerized with styrene to prepare PS-*b*-PPG block copolymers. Cast films and e-spun films were prepared and contact angles of these films with water drop were measured to examine hydrophilic/hydrophobic behavior of the copolymers. Each e-spun film with average fiber diameters from 0.25 to 2.20 μm was prepared in *N,N*-dimethylformamide (DMF) under controlled electrospinning process parameters such as polymer concentration, applied voltage and tip-to-collector distance. Scanning electron microscope (SEM) images of the electrospun films were taken to determine the fiber diameters. Surface compositions of the block copolymers were also determined by using an electron spectrometer with Mg K α X-rays. NMR, and FT-IR spectroscopic, and GPC measurements were employed to characterize and determine the PPG contents (6–43%). From the results, electrospinning process increased the hydrophilic properties of the block copolymers obtained, compared their cast film forms. Our results suggest that these polymers are favorable in biological applications in cases where high ratio of the surface to volume and hydrophilicity are required simultaneously. Both chemical structure and topology of the films are important in wetting and hydrophobicity.

© 2005 Elsevier Ltd. All rights reserved.

Keywords: Macroazoinitiator; Amphiphilic copolymers; Electrospinning; E-spun fiber

1. Introduction

Block copolymers have been used for a wide range of biomedical applications. Functionalized block copolymers can be used to immobilize bioac-

tive molecules [1], drug delivery, and using micellar structures for targeted drug delivery [2,3]. The ability to utilize the unique physical and biologic properties of block copolymers and the ability to control structure on the same magnitude as proteins and cell receptors offers exciting opportunity for new biomaterials with unique biologic functionality. Electrospun fibers have the potential to be used for biological applications such as wound dressings in medical industry and scaffolds for tissue engineering

* Corresponding author. Tel.: +90 372 322 1703; fax: +90 372 323 8693.

E-mail addresses: bkhazer@karaelmas.edu.tr, bhazer2@yahoo.com (B. Hazer).

[4], especially for the high ratio of the surface to volume they introduce. However, films formed by electrospun fibers have rather hydrophobic features due to their rough nature, which is not favorable in biological applications. Electrospun polymer fibers, which were first introduced by Formhals in 1934 [5], are produced by applying a high voltage DC to the tip of a capillary, in which the polymer solution exists. The applied voltage causes the polymer solution to be drawn towards a grounded collector in the form of fine jets that dry to form polymeric fibers. The morphology of the fibers produced via electrospinning depends on various parameters such as solution concentration, applied electric field strength and tip-to-collector distance [6]. Electrospun fibers have several extraordinary features such as high surface to volume ratio, flexibility in surface functionality and improved mechanical properties [7], which led to systematic studies with a variety of polymers [8,9]. Remarkable properties of electrospun fibers have made them recently emerging candidates for filtration, membrane and composite applications, tissue templating, biomedical applications such as wound dressing, protective clothing and medical prosthesis, optical and electrical applications, nanoscale tube fabrication [7] and superhydrophobic surfaces [10].

Block copolymers can be prepared from various types of macroinitiators through radical and ionic polymerization. Macroinitiators generating radicals can be classified as macroazoinitiators, azoperoxidic initiators, redox macroinitiators [11,12] and macrophotoinitiators [13]. Macroazoinitiators which can be prepared by the condensation reactions of a prepolymer with azobis-isobutyronitrile [14], 4,4'-azobis(4-cyanopentanoyl chloride) [15,16], 4,4'-azobiscyanopentanol [17,18] provide a useful means of preparing amphiphilic block copolymers via radical process.

Amphiphilic block copolymers such as polystyrene-*b*-polyethylene glycol [19,20], PS-*b*-PEG, and polystyrene-*b*-polypropylene glycol, PS-*b*-PPG have been greatly attracted by scientists for several decades. According to our knowledge there are not much studies on PS-*b*-PPG block copolymers in the literature. In this work, macroazoinitiators were prepared by using PPG with primary amines ends in contrast to the ones with hydroxyl ends. Highly reactive amine end groups of PPG can easily react with 4,4'-azobis(4-cyanopentanoyl chloride) to give PPG-macroazoinitiator leading to PS-*b*-PPG block copolymers. At the point of examining hydrophilic/

hydrophobic behavior of cast film and e-spun film of copolymers, contact angles with water drop were measured and their surface composition were determined by using XPS.

2. Experimental

2.1. Materials

4,4'-Azobis-4-cyanopentanoic acid (ACPA) was supplied from Fluka AG and poly(propylene) bis(2-aminopropyl ether) (PPG-NH₂) (amine groups at both ends of each chain) of average MW 400 and MW 2000 were supplied from Aldrich. Styrene was obtained from Merck AG. It was dried with Na₂SO₄ and freshly distilled under reduced pressure before use. Solvents and other reagents were extra pure commercial product 4,4'-azobis-4-cyanopentanoyl chloride (ACPC) was prepared by the reaction of ACPA with phosphorus pentachloride. The reaction was carried out in benzene at room temperature. The filtration and purification procedure were applied as described in the literature [21].

2.2. Characterization

IR-spectra of the macroazoinitiators and the copolymers were taken using a Jasco 300 E IR spectrometer. ¹H NMR spectra of the products were recorded by a Varian Inova 500 MHz NMR spectrometer. Gel permeation chromatography (GPC) was used to determine molecular weights of the samples and their distributions with Knauer eurogel columns B71, B72 and B73 were used. Polystyrene standards of low polydispersity were used to generate a calibration curve. The water contact angles were measured by a sessile drop method at room temperature using an optical bench-type contact angle goniometer (Model DSA 10 Mk 2 Krüss), by image processing of sessile drop with a DSA 1.8 software. Scanning electron microscope (SEM) analysis was carried out with a LEO Supra VP35 FE-SEM. XPS spectra are recorded using Kratos ES300 Electron Spectrometer with Mg K α X-rays.

2.3. Synthesis of macroazoinitiator

A solution of 2.0 g (6.3 mmol) of ACPC in 50 mL CHCl₃ was added to the mixture of 25.24 g (12.6 mmol) of poly(propylene) bis(2-aminopropyl ether) (PPG-NH₂-2000) and 10 mL of aqueous NaOH (20 wt%) and stirred for 24 h at room

temperature. The molar ratio of ACPC to PPG-2000 was 1:2. After the reaction, the mixture was washed with water three times to secure the removal of salts and ACPA from the product. The organic phase was dried with Na_2SO_4 overnight at 0°C . Solvent was evaporated. Viscous liquid was dried under vacuum and stored at 0°C until use.

2.4. Synthesis of PPG-*b*-PS block copolymer

A given amount of styrene and the macroinitiator (MI-PPG) were charged into a Pyrex tube. Nitrogen was introduced through a needle into the tube to expel the air. The tightly capped tube containing a small magnet was put in an oil bath at 80°C for 5 h. Subsequently the contents of the tube were dissolved in chloroform and then precipitated in methanol. The copolymeric sample obtained was dried in vacuum at room temperature for 24 h.

2.5. Electrospinning

Electrospinning uses an electric field to draw a polymer solution, which causes a jet of the solution to be drawn towards a grounded collector. The fine jets dry to form polymeric fibers, which can be collected on a web. The electrospinning process has been documented using a variety of fiber forming polymers [8,9]. By choosing a suitable polymer and solvent system, nanofibers with diameters in the range of 40–2000 nm can be made.

The electrospinning setup employed in this study consisted of a vertically located syringe controlled by a Univentor 801 Syringe pump and a high voltage (HV) power supply (GPS HV power supply Model 2594) additionally (Fig. 1). For each electrospinning, 20 wt% solutions of polymers were prepared in DMF and the flow rate and applied voltage were ranged between 7–12 $\mu\text{l}/\text{min}$ and 7.5–15 kV, respectively, according to the optimum deposition to the collector while the tip to collector screen distance was kept constant at 13 cm.

2.6. Contact angle measurements

The contact angles of water were measured on the solution cast films and electro spun films. The preparation of the electro spun films was performed like this: Electro spun nanofiber which can be collected on a web had formed a flat film on the aluminum foil. A piece of aluminum foil which has nanofiber scaffold was properly cut and the contact

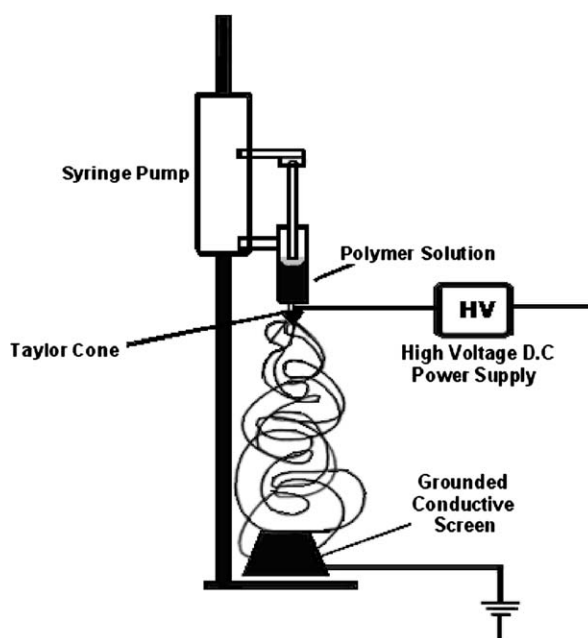


Fig. 1. Electrospinning setup.

angle of water drop on the electro spun nanofiber was measured by a goniometer.

The contact angles were measured on a Krüss GmbH DSA 10 Mk 2 goniometer, by image processing of sessile drop with a DSA 1.8 software. At least 6 droplets of freshly distilled ultra pure water were averaged. Drops of purified water, 3 μl , were deposited onto the film surface to form sessile drops using a micro-syringe attached on the goniometer. Contact angles on different parts of the film were measured and averaged.

2.7. Surface analysis

XPS spectra are recorded using Kratos ES300 Electron Spectrometer with $\text{Mg K}\alpha$ X-rays. The O1s region reveals only a single peak at 532.7 eV whereas in the C1s region peaks belonging to C–H and C–O groups, which can be deconvoluted at 285.0 and 286.5 eV, respectively. Accordingly, the surface composition can be determined using either the O/C atomic ratio or the C–O/C–H ratio or both.

2.8. SEM analysis

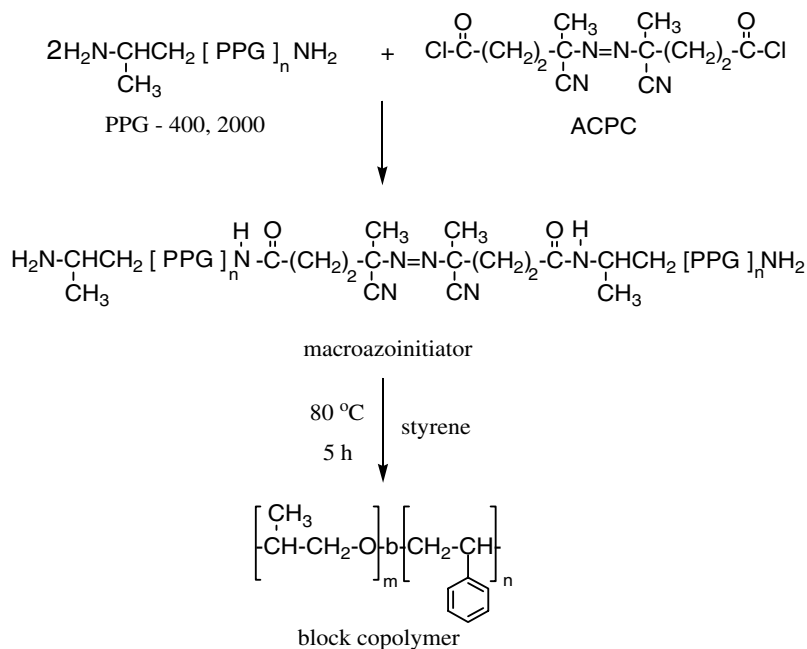
SEM imaging of the electrospun films was performed on a LEO Supra VP35 FE-SEM, after sputter deposition of a thin conductive gold coating onto the films.

3. Results and discussion

3.1. Synthesis of macroazoinitiators

Acid chlorides react with primary amines faster than alcohols. Therefore we have chosen polypropylene glycols with amine terminal groups in order to react with ACPC in mol ratio 2:1 (Scheme 1). Preparation conditions of the macroazoinitiator synthesis

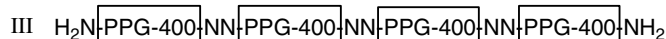
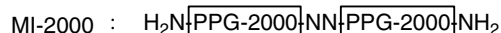
have been giving in Table 1. Macroazoinitiators have two PPG terminals and an azo group in the middle such as PPG-2000-NN-PPG-2000. MI-2000, more or less, has the structure shown in Scheme 2. When we compare with the molecular weights found by GPC and theoretical one. Molecular weight measured by GPC of MI-400 was two times greater than the theoretical value. Therefore we can say that (a) partial chain extension has occurred during the amidiation



Scheme 1. Synthesis of macroazoinitiators and block copolymers.

Table 1
Preparation conditions of macroazoinitiators

Initiators	PPG-2000 (g)	PPG-400 (g)	ACPC (g)	Yield (wt%)	GPC		M_n theoretical	Appearance
					M_n	M_w/M_n		
MI-2000	25.24	–	2.00	90.6	3700	1.65	4244	Pale yellow waxy solid
MI-400	–	15.14	6.00	71.2	2300	1.55	1044	Pale yellow viscous liquid



Scheme 2. The types of the macroazoinitiators.

reaction between ACPC and PPG-400 as in case of macroperoxyester [16] synthesis. We can formulate MI-400 as shown in Scheme 2. IR and ^1H NMR spectra of the macroinitiator confirmed the expected structure of the products. Fig. 2 shows the IR transmittance spectrum of MI-PPG obtained. The characteristic peaks of MI-PPG were observed at 3350 cm^{-1} and 3550 cm^{-1} for $-\text{NH}$ stretching vibration band, at 1110 cm^{-1} for $\text{C}-\text{O}-\text{C}$ stretching vibration band, at 1660 cm^{-1} and 1550 cm^{-1} for carbonyl absorption. The ^1H NMR spectrum of macroazoinitiator MI-PPG confirms the structural formula. In Fig. 3, we observed the signals of the $-\text{CH}_3$ groups (at δ 1.2) and $-\text{CH}_2$ groups (at δ 3.4–3.6) of PPG. $-\text{CH}_2$ groups (at δ 2.25–2.4) of ACPC [22]. The signals that appeared at 4.10–4.20 ppm due to $-\text{NH}$ groups in the macroazoinitiator.

3.2. Block copolymerization of styrene with MI-PPG

Styrene was polymerized with MI-PPG at 80°C . Since free radical polymerization of styrene leads to combination termination, PPG-PS-PPG (ABA) type of block copolymers occur when used MI-PPG-2000. Similarly MI-PPG-400 also gives ABA type of block copolymers with a small amount of mixture of

multiblock copolymers such as ABABA type. The polymerization reaction conditions and the yields are given in Table 2. Molecular weight of the block copolymers measured by GPC technique varied from 15,000 to 35,000 for the MI-400s and from 38,000 to 130,000 for the MI-2000. As expected, molecular weights of block copolymers obtained from MI-400s were higher than that of MI-2000s because MI-2000 has lower radical source (azo group) per molecule than MI-400. Molecular weights of the copolymers determined by GPC technique are shown in Table 2. M_n and M_w values of block copolymers decrease with increasing PPG content in the copolymers. Polydispersity of copolymer samples show a variation in the range of 1.6–2.4. However yields of block copolymers show peculiarities: in respect of the polymerization kinetics, the lower initiator concentration cause lower polymer yield. In this case, high polymer yields were obtained in the lower initiator concentration. Probably, polypropylene initiator in higher concentration acts as a chain transfer agent. So, in Table 2, the yield of number 10 is lower than that of number 6 or 7.

Block copolymer yields obtained with MI-400 were higher than those obtained with MI-2000. In order to explain this situation we can presume that

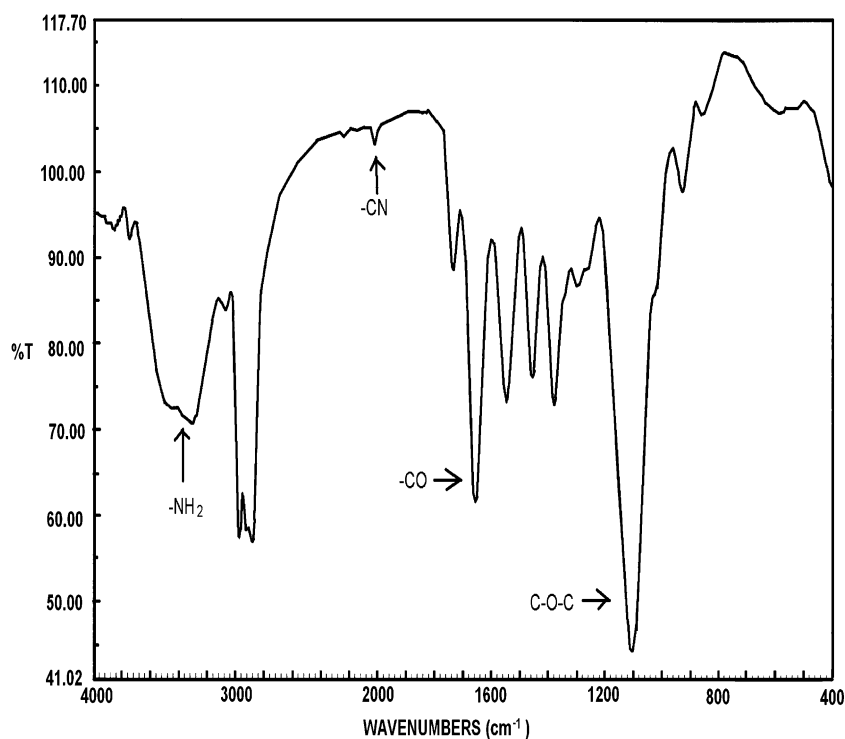


Fig. 2. IR spectrum of macroazoinitiator MI-PPG-400 in Table 1.

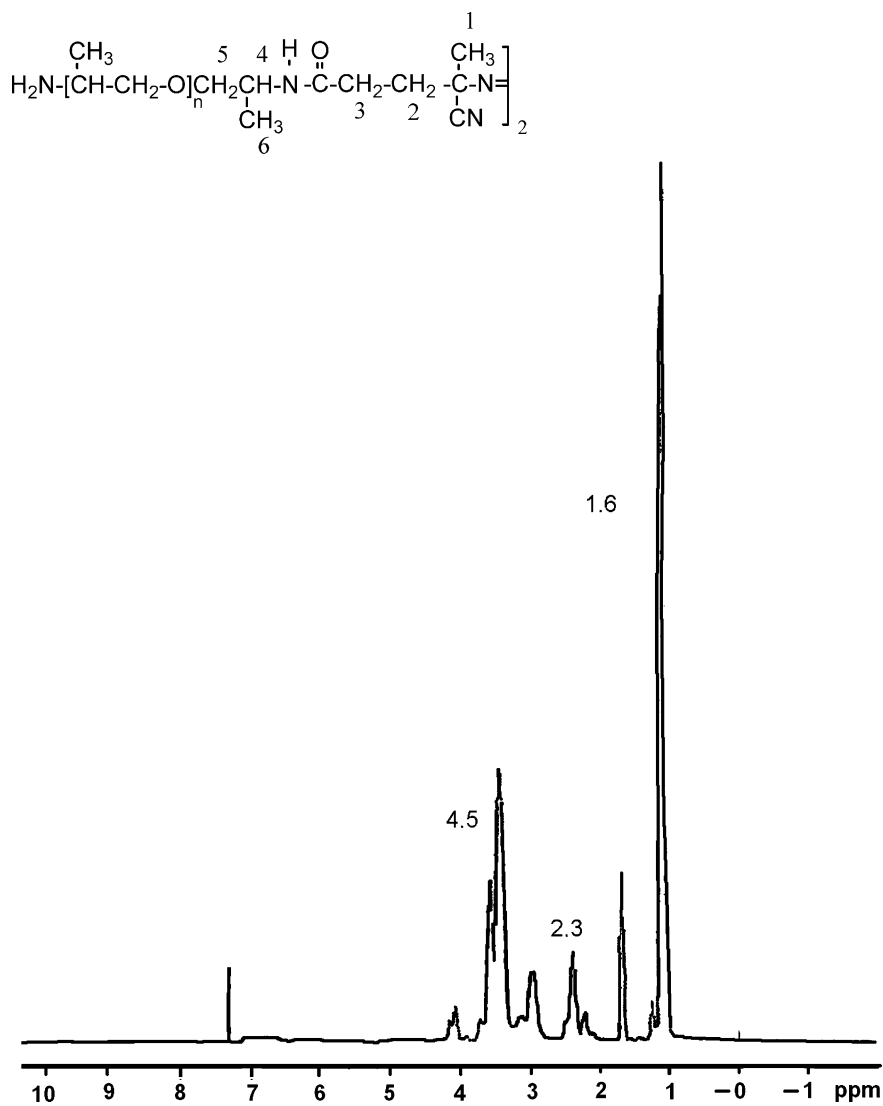
Fig. 3. ¹H NMR spectrum of macroazoinitiator MI-PPG-400 in Table 1.

Table 2

Free radical polymerization of styrene initiated by using PPG- macroazoinitiator at 80 °C for 5 h

Sample no.	Macroazoinitiators		Styrene (g)	Yield (%)	Fractionation γ _{0.4-0.6} (wt%)	GPC	
	MI-400g	MI-2000 (g)				$M_n \times 10^{-3}$	M_w/M_n
6	0.25	–	3.02	91.9	95	35	2.4
7	0.50	–	3.01	85.7	85	30	2.5
8	1.01	–	3.01	67.8	40	29	2.0
9	2.00	–	3.01	84.0	50	21	1.8
10	2.70	–	3.01	78.2	55	15	2.2
16	–	0.25	3.02	55.7	50	130	1.6
17	–	0.50	3.00	50.0	49	42	1.6
18	–	1.02	3.01	58.3	70	76	2.0
19	–	2.04	3.02	63.0	72	38	2.4
20	–	2.717	3.04	71.3	45	59	1.6

relatively higher $-\text{NH}_2$ end groups and lower azo groups present at MI-2000 might cause lower yields with the higher molecular weights. The pure block copolymers were isolated from related homopolymers by fractional precipitation with chloroform as a solvent and methanol as a nonsolvent. The γ values of the polymers were also determined as the ratio of the volume of methanol used for precipitation to the volume of the chloroform solution. Of the PPG-b-PS pure block copolymer (ABA-type), 40–95 wt% was precipitated between $\gamma=0.4$ and $\gamma=0.6$, whereas γ was 0.4–0.9 for homo-PS. This could be explained by the higher PS concentration in the copolymer.

3.3. Spectrometric analysis of the block copolymers

Block copolymers obtained were characterized by using IR and ^1H NMR spectroscopy. In Fig. 4 a typical IR spectrum of PPG-b-PS block copolymer (sample 18 in Table 2 with 36 mol% PS) can be seen. This spectrum has phenyl bands of polystyrene at 1600 cm^{-1} and characteristic bands of PPG at 3000 cm^{-1} , 2900 cm^{-1} and 1100 cm^{-1} . $-\text{NH}$ peak in this spectrum (around 3400 cm^{-1}) indicates the incorporation of macroazoinitiator into the copoly-

mers. Fig. 5 exhibits typical ^1H NMR spectrum of PS-b-PPG block copolymer (sample 18 in Table 2). ^1H NMR was also used to determine the propyleneoxide contents in mol% by calculating the peak areas of the phenyl protons in polystyrene (6.5–7.1 ppm) and the propylene protons in propyleneoxide segments (3.4–3.6 ppm) given in Table 2. In this manner, pure block copolymers isolated by fractional precipitation indicated the characteristic unimodal GPC traces which can be attributed pure block copolymer confirmation (Fig. 6).

3.4. Contact angle measurements of cast and e-spun films of block copolymers

At the point of examining hydrophilic/hydrophobic behavior of copolymers, air and petry surface of cast films contact angles and e-spun films contact angles with water drop were measured and shown in Table 3. Contact angles cast films of PS-b-PPG block copolymers range between 81° and 21° . As the amount of PPG in the structure increases, the contact angle decreases. The decrease in the cast film contact angles from samples 6 to 10 and 16 to 20 is an obvious consequence of the increase in the PPG ratio. The marked difference between the contact

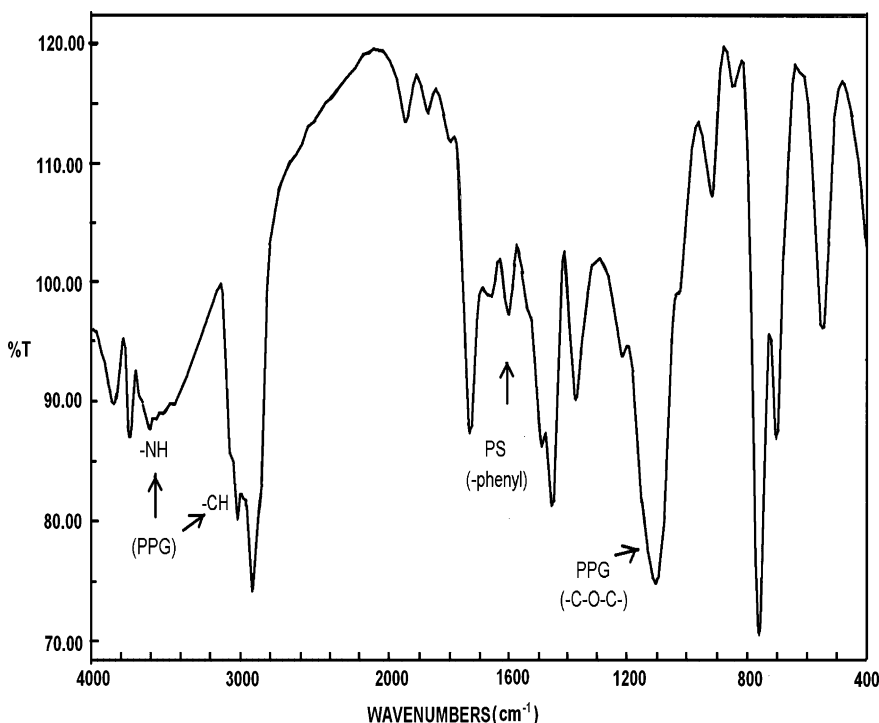


Fig. 4. IR spectrum of PS-b-PPG block copolymer (sample 18 in Table 2).

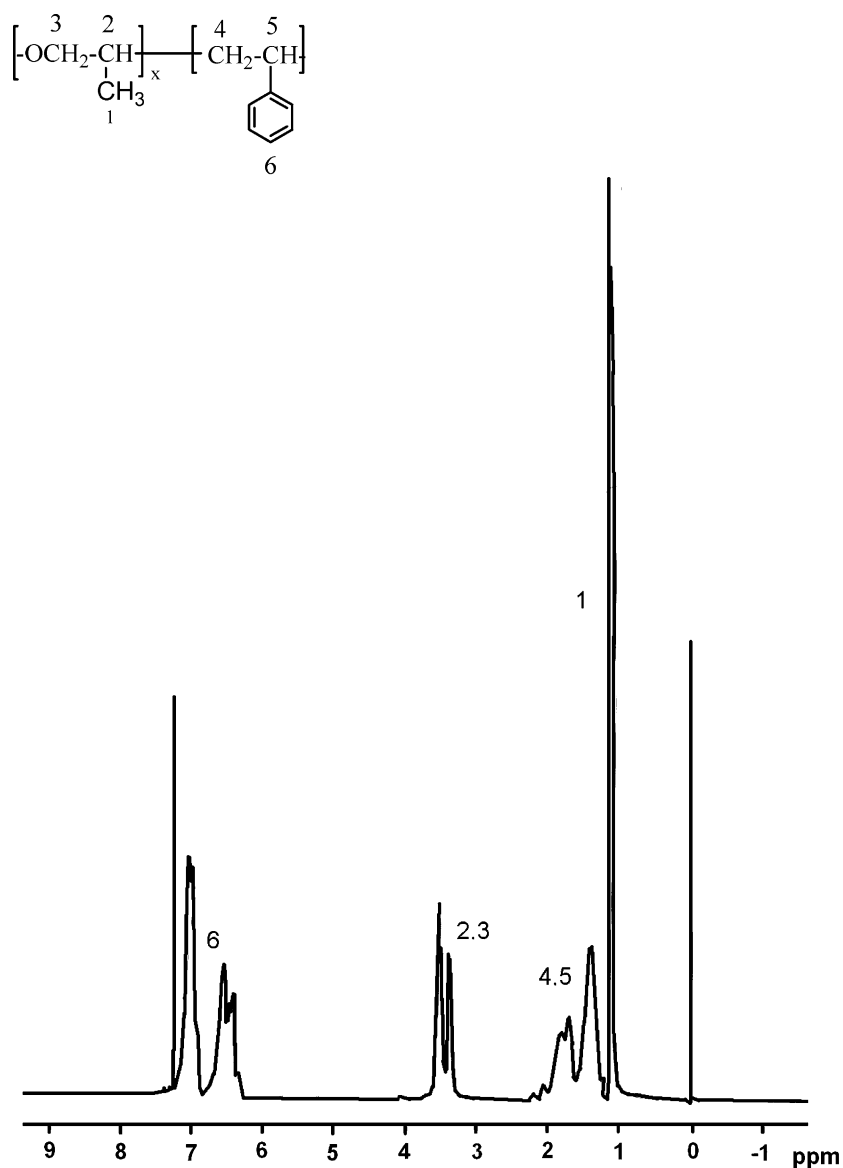


Fig. 5. ¹H NMR spectrum of PS-b-PPG block copolymer (sample 18 in Table 2).

angles of samples 10 and 20 is a cause of the difference in the amount of hydrophilic NH₂ groups in the polymer, which is more in PPG-400. Also small amounts of PPG content in the samples 6 and 16 contributes nearly same to the hydrophilicity and result nearly same contact angles.

As these polymers have the potential use in biomedical applications and coatings, we also studied the electrospinning and the resulting wetting behavior. Electrospun fibers shown in Fig. 7 have the potential to be used for biological applications such as tissue engineering, especially for the high surface

to volume ratio they introduce. However, films formed by electrospun fibers have rather hydrophobic features due to their rough nature, which is not favorable in biomedical applications. For sample 6, the contact angle of the cast film was doubled and increased to 140.8 due to the micron sized roughness introduced by fiber formation [8]. For samples 8, 10, 18, 20, the electrospun films showed contact angles over 140° when water droplets were first deposited on the surface during analysis again due to the micron or sub-micron level roughness; however, after a short interval, they were completely wetted

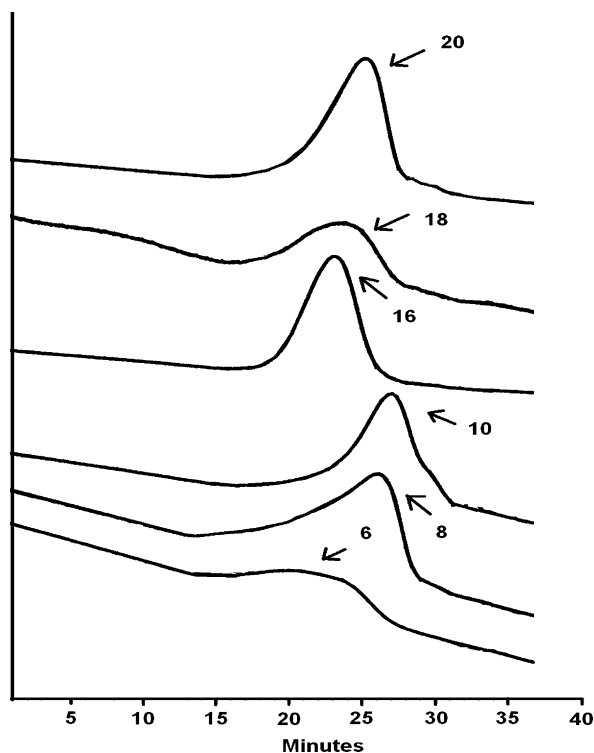


Fig. 6. GPC spectra of PS-b-PPG block copolymers (Sample nos. 6, 8, 10, 16, 18, 20 in Table 2).

because relatively more hydrophilic nature of the polymers causes strong intermolecular interactions with water molecules, which overcomes the surface tension of the water in the course of a time and causes complete wetting by the penetration of water through the fibers. In the case of sample 16, although the polymer has the highest hydrophobic nature, the 250 nm fibers are too small to form roughness induced hydrophobicity and penetration of water through the fibers is inevitable. These results also confirm that both the chemical structure

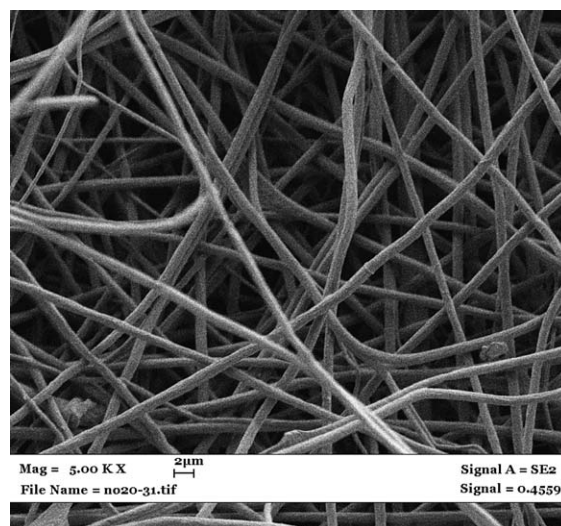


Fig. 7. A typical SEM micrograph of the PS-b-PPG sample (no. 20).

and the topology of the films are important in wetting and hydrophobicity.

In our case, electrospinning of the polymers increased the hydrophilic property, compared to their cast film forms, due to the penetration of water through the fibers. For instance, e-spun film of sample 16 is completely wetted although its cast film contact angle is 75°. Consequently, these polymers can be used in cases where high surface to volume ratio and hydrophilicity is required simultaneously.

3.5. Surface analysis of the block copolymers

Binding energies and C1 s and O1 s intensities of C–H and C–O groups were used for surface analysis. Fig. 8 shows the C1s region of the XPS spectra of the 5 block copolymers used in this work. The surface composition of the samples are given in Table 4 deter-

Table 3
Contact angle measurements of the (i) cast film and (ii) electrospun film samples

	Sample no.	PPG molar ratio by NMR (%)	Average fiber ^a diameter (μm)	Contact angle		
				Cast film		Electrospun film
				Air	Petry	
PPG 400	6	6	2.20	81	67	140.8 ± 2.16
	8	16	1.00	71	62	Wetted
	10	43	0.75	21	27	Wetted
PPG 2000	16	6	0.25	75	72	Wetted
	18	36	0.70	32	39	Wetted
	20	39	1.20	34	37	Wetted

^a Average fiber diameter of the nanofiber were calculated from the SEM films.

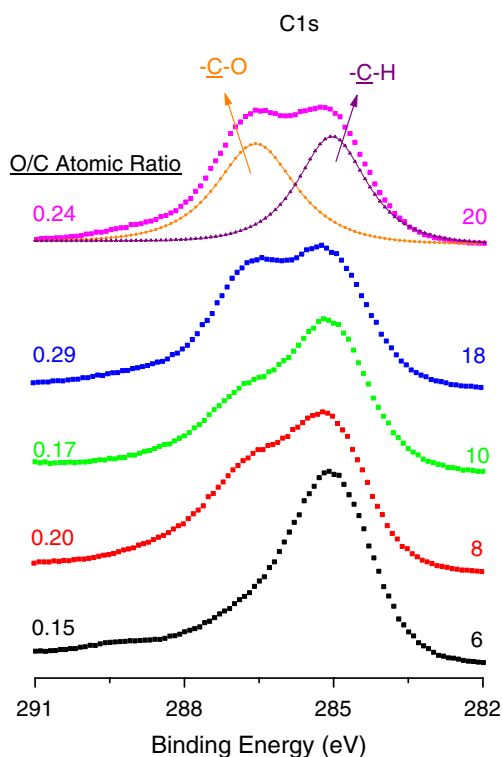


Fig. 8. C1s region of the XPS spectra of the copolymer samples (sample nos. 6, 8, 10, 18, 20 in Table 2). The spectra are deconvoluted into one hydrocarbon peak (C–H) and one etheric peak (C–O). Atomic ratios are determined using the procedure given in Table 4.

Table 4
Surface composition of PPG and PS block copolymers determined by XPS

Sample no.	PPG molar ratio		Using NMR
	Using O1s/C1s peaks ^a	Using C–O/C–H peaks ^b	
6	60	50	6
8	67	71	16
10	63	67	43
18	74	80	36
20	71	80	39

^a One PPG monomer has 3 C and 1 O atoms, and one PS monomer has 8 C atoms. Hence 1:1 (PPG:PS) should give 1 O atom/11 C atom or 0.1 O/C atomic ratio.

^b Similarly there are 1 C–O groups in PPG and 1 C–H, whereas 8 C–H groups in PS. Hence 1:1 (PPG:PS) should give 1 C–O/8 C–H = 0.125 peak ratio.

mined using; (i) the O/C atomic ratio, derived from area of the O1s peak to that of the total C1s peaks and corrected with their corresponding sensitivity factors, (ii) the C–O/C–H peak ratio [23,24]. For both determinations, interestingly, the XPS derived surface composition reveals a higher PPG content

than expected from NMR results. Probably, the PPG terminal blocks of the copolymers are oriented towards the film surface. Increasing surface oxygen content as derived from XPS data also shows some degree of correlation (except for the sample number 10) with the observed decrease in the contact angle of the corresponding samples.

4. Conclusions

The macroazoinitiators were prepared by using PPG with primary amine ends which can be easily react with 4,4'-azobis-4-cyanopentanoic acid chloride. A given amount of PPG content in PS-b-PPG block copolymers can be optimized by changing MI mol ratios in the initial feed of styrene polymerization. Electrospinning of the polymers increased the hydrophilic property, compared to their cast film forms, due to the penetration of water through the fibers. In addition the results, both the chemical structure and the topology of the films are important in wetting and hydrophobicity. Consequently, these polymers are favorable in biological applications in cases where high surface to volume ratio and hydrophilicity is required simultaneously.

Acknowledgement

This work was financially supported by Zonguldak Karaelmas University Research Fund.

References

- [1] Goosen MFJ, Sefton MV. *J Biomed Mater Res* 1979; 13(3):347.
- [2] Forster S, Plantenberg T. *Angew Chem Int* 2002;41:688.
- [3] Kumar N, Majeti NV, Ravikumar A, Domb AJ. *Adv Drug Del Rev* 2001;53:23.
- [4] Bowlin GL, Pawlowski KJ, Boland E, Simpson DG, Fenn JB, Wnek GE, et al. In: Lewandrowsky K, Trantolo DJ, Gresser JD, Yaszemski MJ, Altobelli DE, Wise DL, editors. *Tissue engineering and biodegradable equivalents: scientific and clinical applications*, vol. 178. Marcel Dekker; 2002, p. 165.
- [5] Formhals A. US Patent 1934;975(1):504.
- [6] Fong H, Chun I, Reneker DH. *Polymer* 1999;40:4585.
- [7] Koski A, Yim K, Shivkumar S. *Mater Lett* 2004;58:493.
- [8] Chung I, Reneker DH, Fong H, Fang X, Deitzel J, Beck Tan N. *J Adv Mater* 1999;31:36.
- [9] Reneker DH, Chun I. *Nanotechnology* 1996;7:216.
- [10] Acatay K, Simsek E, Ow-Yang C, Menciloglu YZ. *Angew Chem Int* 2004;43:5210.
- [11] Arslan H, Hazer B, Kowalczyk M. *J Appl Polym Sci* 2002;85:965.
- [12] Macit H, Hazer B. *J Appl Polym Sci* 2004;93:219.
- [13] Değirmenci M, Cianga I, Yagci Y. *Macromol Chem Phys* 2002;203:1279.

- [14] (a) Hazer B. Synthesis and characterization of block copolymers. In: Cheremisinoff NP, editor. Handbook of polymer science and technology, vol. 1. New York: Marcel Dekker; 1989. p. 133;
- (b) Walz R, Bomer B, Heitz W. Makromol Chem 1977;178:2527;
- (c) Hazer B. Macrointermediates for block and graft copolymers. In: Cheremisinoff NP, editor. Handbook of engineering polymeric materials. New York: Marcel Dekker; 1997. p. 725–34;
- (d) Dicke HR, Heitz W. Macromol Chem Rapid Commun 1981;2:83;
- (e) Anand PS, Stahl HG, Heitz W, Weber G, Bottenbruch L. Makromol Chem 1982;183:1685;
- (f) Laverty JJ, Gardlund ZG. J Polym Sci A: Polym Chem 1977;15:2001.
- [15] Haneda Y, Terada H, Yashida M, Ueda A, Nagai S. J Polym Sci A: Polym Chem 1994;32:2641.
- [16] Hazer B, Erdem B, Lenz RW. J Polym Sci A: Polym Chem 1994;32:1739.
- [17] Yürük H, Özdemir AB, Baysal BM. J Appl Polym Sci 1986;31:2171.
- [18] Fukawa J, Takamori S, Yamashita S. Angew Makromol Chem 1967;1:92.
- [19] Cheng S, Wang C, Chen C. Mater Chem Phys 2003;78:581.
- [20] Uyanık N, Baysal BM. J Appl Polym Sci 1990;41:1981.
- [21] Smith AD. Macromol Chem 1967;103:301.
- [22] Hamurcu EE, Hazer B, Baysal BM. Polymer 1997;12:2981.
- [23] Briggs D, Seah MP. Practical surface analysis, 2nd ed.(vol. 1). Chichester: Wiley; 1996.
- [24] Beamson G, Briggs D. High resolution XPS of organic polymers. Chichester: Wiley; 1992.