Polymer 49 (2008) 5191–5194

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Polymer Communication

Synthesis and physicochemical characterization of a well-defined poly(butadiene 1,3)-*block*-poly(dimethylsiloxane) copolymer

Andrés E. Ciolino [a,*], Leopoldo R. Gómez [b], Daniel A. Vega [b], Marcelo A. Villar [a], Enrique M. Vallés [a]

[a] *Planta Piloto de Ingeniería Química, PLAPIQUI (UNS-CONICET), Camino La Carrindanga Km. 7, 8000 Bahía Blanca, Argentina*
[b] *Departamento de Física, Universidad Nacional del Sur (UNS), Av. Alem 1253, 8000 Bahía Blanca, Argentina*

ARTICLE INFO

Article history:
Received 27 June 2008
Received in revised form 5 September 2008
Accepted 12 September 2008
Available online 8 October 2008

Keywords:
Anionic polymerization
Poly(butadiene)
Poly(dimethylsiloxane)

ABSTRACT

For the first time, order–order and order–disorder transitions were detected and characterized in a model diblock copolymer of poly(butadiene-1,3) and poly(dimethylsiloxane) (PB-*b*-PDMS). This model PB-*b*-PDMS copolymer was synthesized by the sequential anionic polymerization (high vacuum techniques) of butadiene 1,3 (B) and hexamethylciclotrisiloxane (D_3), and subsequently characterized by nuclear magnetic resonance (^{1}H and ^{13}C NMR), size exclusion chromatography (SEC), Fourier Transform infrared spectroscopy (FTIR), Small-Angle X-ray scattering (SAXS) and rheology. SAXS combined with rheological experiments shows that the order–order and order–disorder transitions are thermoreversible. This fact indicates that the copolymer has sufficient mobility at the timescale and at the temperatures of interest to reach their equilibrium morphologies.

1. Introduction

Poly(dimethylsiloxane) (PDMS) is a silicon-based homopolymer which exhibits a low glass transition temperature, high gas permeability, usability over a wide range of temperatures, low chemical reactivity, and essentially a non-toxic nature [1]. Consequently, the synthesis of complex macromolecular architectures based on PDMS seems to be an interesting research field not only for academic studies but also for many biomedical and industrial applications, like the development of a new group of thermoplastic elastomers [2].

In this communication we report the synthesis and physicochemical characterization of a *model block* copolymer of butadiene 1,3 and dimethylsiloxane (PB-*b*-PDMS). This copolymer was synthesized using sequential addition of monomers employing high-vacuum anionic polymerization techniques [3]. Although the synthesis of similar materials has been reported [4], up to our knowledge, an exhaustive analysis of their rheological properties regarding its order–order and order–disorder transitions has never been discussed. Consequently, the molar mass of this PB-*b*-PDMS copolymer was chosen in order to fall into the intermediate regime where the transitions from a spatially homogeneous (disordered) state to a microphase-separated (ordered) state occur. Both, molecular and morphological properties of the *block* copolymer so obtained were characterized by different experimental techniques.

2. Experimental

2.1. Materials

All materials were purified by standard anionic polymerization procedures. The initiator employed *sec*-Butyl lithium (*sec*-Bu^-Li^+) was prepared *in vacuo* from *sec*-butyl chloride and lithium metal. The monomers 1,3-Butadiene (B) and hexamethylcyclotrisiloxane (D_3) were purified according to the conventional routines described elsewhere [3]. Tetrahydrofuran (THF) was used as promoter of D_3 polymerization whereas cyclohexane and degassed methanol were used as the solvent and terminating agent, respectively.

2.2. Synthesis of model PB-b-PDMS copolymer

All manipulations were performed under high vacuum in glass reactors equipped with break-seals for the addition of the reagents and constrictions for the removal of products [5,6]. The synthesis of PB-*b*-PDMS was achieved by sequential anionic polymerization as already reported [4]. A scheme of the polymerization apparatus used for the synthesis is shown in Fig. 1. A description of the synthetic pathway employed is briefly described as follows.

The apparatus was connected to the vacuum line, checked for pinholes, flamedried and pumped for 20–30 min in order to remove the volatile species. Then, 5 mL of concentrated *n*-Bu^-Li^+ 2 M solution in hexane (Aldrich) was injected through the purge constriction (PC) into the purge section flask. The whole apparatus was pumped for an additional 30 min in order to remove the

---

[*] Corresponding author.
E-mail address: aciolino@plapiqui.edu.ar (A.E. Ciolino).

0032-3861/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2008.09.058

hexane and air inserted during the injection, and an appropriate amount of pure cyclohexane (40–50 mL) was then distilled and degassed over 45 min. The apparatus was removed from the vacuum line by heat-sealing the constriction (VLC), and was washed with the diluted *n*-Bu$^-$Li$^+$ solution inside by gentle manual agitation. After washing, the purge section was removed by heat-sealing the middle constriction (MC) leaving the clean reactor with an appropriate amount of solvent.

The break-seal of the B monomer solution was first broken and the content was poured into the reactor flask, followed by addition of the *sec*-Bu$^-$Li$^+$ ampoule. Both ampoules were rinsed with the solution in order to remove any traces of initiator or monomer and the polymerization was left to proceed until all the B monomer was consumed (usually, 24 h). An ampoule of living PB was then collected for characterization. Subsequently, the ampoule containing the D_3 monomer was broken and rinsed with the living polymer solution, and the reaction was left to proceed for ≅20 h at room temperature, then, the THF ampoule was broken to promote D_3 polymerization. This polymerization was carried out in two steps. The first involves the initiation of D_3 with PB$^-$Li$^+$ in cyclohexane at room temperature, and propagation in a mixture of cyclohexane/THF (1/1 v/v) up to 50% conversion; whereas in the second step the polymerization continued at −20 °C until completion. The addition of 1–3 mL of well-degassed methanol terminated the reaction. The *block* copolymer thus obtained was precipitated in stabilized methanol, dried under vacuum and chemically characterized.

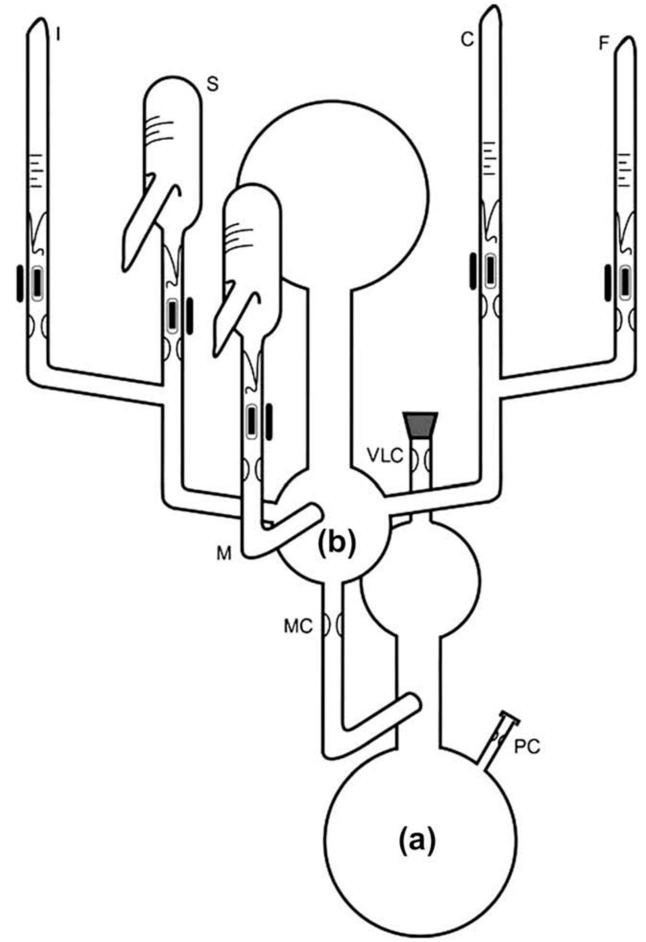

Fig. 1. Polymerization apparatus for the synthesis of PB-*b*-PDMS. References: I: *sec*-Bu$^-$Li$^+$ ampoule. S: THF ampoule. M: B monomer ampoule. C: D3 monomer ampoule. F: Methanol ampoule. (a) Purge section. (b) Reactor. VLC: vacuum line constriction. PC: purge constriction. MC: middle constriction.

3. Characterization

3.1. Size exclusion chromatography (SEC)

The SEC experiments were performed on a Waters model 410 differential refractometer (equipped with 4 columns with a porosity range of 10^2–10^6 Å). The solvent employed was toluene at 25 °C flowing at a rate of 1 mL/min. The injection volume was 200 μL, and polystyrene standards were used for calibration (because d*n*/d*c* values for PDMS in THF are extremely low, in order to obtain a good SEC chromatogram toluene was chosen as solvent instead of THF).

3.2. Nuclear magnetic resonance (^{1}H NMR)

The ^{1}H NMR spectra of PB-*b*-PDMS copolymers were recorded on a Bruker 300 MHz instrument using deuterated chloroform as solvent. The chemical composition of the PB-*b*-PDMS copolymer was obtained by the ratio of the integrated areas of the vinyl to methylic ^{1}H signals.

3.3. Fourier transform infrared (FTIR) spectroscopy

The FTIR spectra of the resulting polymer were obtained on a *Nicolet FTIR 520* spectrometer using cast films from diluted copolymer's solutions (1 wt% in hexane).

3.4. Small-angle X-ray scattering (SAXS)

The microphase structure was assessed through small-angle X-ray scattering (SAXS); the apparatus and procedures are described elsewhere [7,8]. Data are presented as the desmeared absolute intensity I vs. the scattering vector magnitude $q = 4\pi/\lambda \sin\theta$. Here λ is the Cu-Kα radiation wavelength and 2θ is the scattering angle.

3.5. Rheology

The viscoelastic properties of the PB-*b*-PDMS copolymers were studied on a rotational rheometer *Rheometrics RDA-II* in the parallel plate geometry, using discs of 50 mm diameter and samples about 1 mm thick. The rheological characterization was performed by small-amplitude oscillatory shear flow tests in a nitrogen atmosphere. The viscoelastic response was determined in the linear viscoelastic regime, at temperatures between 20 and 100 °C.

4. Results and discussion

The synthesis of PB-*b*-PDMS copolymer involves a sequential monomer addition procedure. First, the polymerization of B monomer with *sec*-Bu$^-$Li$^+$ as initiator was carried out for 24 h to ensure the complete conversion of B to PB. Then, the polymerization of D_3 monomer was carried out by a two-step methodology, where the controlled and complete polymerization of D_3 was achieved [9]. Fig. 2 shows representative SEC chromatograms of the PB precursor and the corresponding PB-*b*-PDMS copolymer. It can be seen that both polymers show a narrow molecular weight distribution (*e.g.* polymers with high structural homogeneity). The displacement of the PB-*b*-PDMS chromatograph with respect to that of the PB precursor towards lower elution volumes is a clear evidence of a higher molar mass in the copolymer. From the analysis of both SEC chromatographs the molar masses and the molar masses' distribution were calculated. Analyzing the ^{1}H NMR spectra, the molar and weight fractions were calculated. All these data are condensed in Table 1. As additional information, FTIR spectra (from cast films samples) showed characteristic absorption bands at 1261 cm^{-1}, 1094 cm^{-1}, 1022 cm^{-1}, and 802 cm^{-1} that

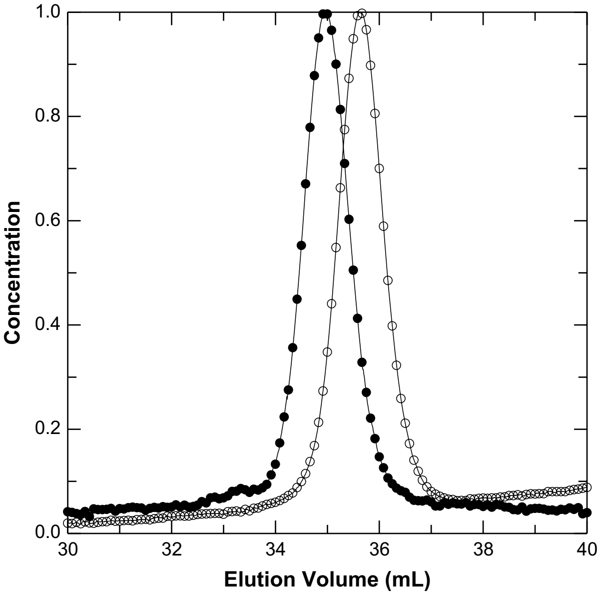

Fig. 2. Size exclusion chromatograms (SEC) of PB precursor (○) and PB-*b*-PDMS copolymer (●).

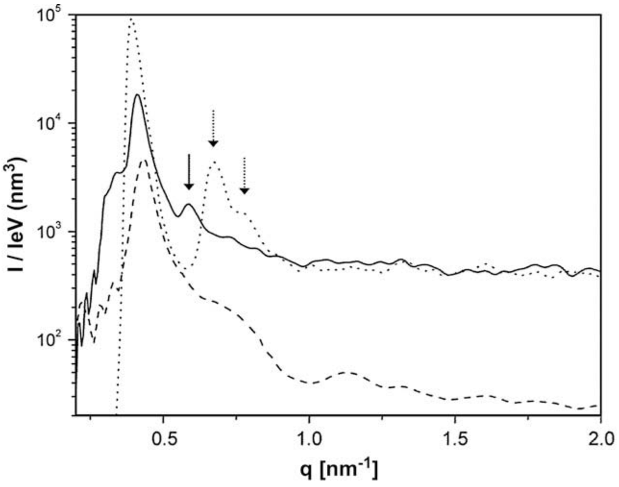

Fig. 3. SAXS patterns for the PB-*b*-PDMS copolymer at three different temperatures. The solid curve represents SAXS data at $T = 30$ °C (hexagonally packed cylinders) and dotted and dashed lines correspond to $T = 70$ °C (bcc structure) and $T = 90$ °C (disordered) structures, respectively. Scattered intensities are on an absolute scale. Arrows indicate the positions of higher order reflections characteristic of the mesophase structures.

reveal the presence of the PDMS block in the corresponding copolymers [10]. Based on the densities of the blocks [11] and their mass fraction, the volume fraction f of PDMS was estimated to be $f = 0.171$.

The SAXS analysis reveals the existence of order–order and order–disorder transitions. The morphology can be easily identified through the ratios of the q values of primary and high order peaks. At room temperature, in Fig. 3 we can observe that the PB-*b*-PDMS shows SAXS peaks in a q/q^* ratio of 1, $1/\sqrt{3}$, $1/\sqrt{4}$, characteristic of hexagonally packed cylinders (here q^* represents the primary peak position). As the temperature is increased above 50 °C we observe a transition from hexagonally packed cylinders to body centered cubic packing (bcc). Fig. 3 also shows SAXS of the PB-*b*-PDMS copolymer at $T = 70$ °C. In this case, the SAXS peaks appear in a q/q^* ratio of 1, $1/\sqrt{2}$, characteristic of a bcc ordering [7]. SAXS data also indicate that beyond 86 °C the system presents an order–disorder transition with the typical spectrum associated to a liquid-like order. The order–order and order–disorder transitions were confirmed to be thermoreversible. Cooling the block copolymer to 10 °C or more below the order–order or the order–disorder transition temperatures causes the transformation to completely reverse within 10 min. The thermoreversible transitions observed for this block copolymer indicates within the range of temperatures covered in this work and at the timescale considered, the copolymer has sufficient mobility to reach their equilibrium morphologies.

Rheological measurements are very useful in locating order–disorder temperature ($T_{\rm odt}$), since the viscoelastic response differs markedly between the homogeneous phase and microphase-separated states [12,13]. Well above $T_{\rm odt}$, the dynamic storage (G') and loss moduli (G'') of block copolymers in the homogeneous phase resemble those of homopolymers. The moduli are higher in the phase-separated state ($T < T_{\rm odt}$) at low frequencies. As a consequence, plots of G vs. T at low frequencies often show an abrupt drop or change in slope at the $T_{\rm odt}$. To explore the rheological behavior of the PB-*b*-PDMS copolymer, small-amplitude oscillatory shear flow tests were performed. Since the long-range order can be perturbed through deformation, the viscoelastic response of block copolymers is extremely influenced by its thermo-rheological history [12,14]. To prevent thermo-rheological effects a sufficiently large specimen to fill the test gap was placed on the lower plate of the rheometer, and then the rheometer oven was set to a temperature above the order–disorder temperature to relax the normal force as the upper plate was lowered.

The viscoelastic response of block copolymers is strongly influenced by its microstructure. As a consequence of their three-dimensional cubic structure, both bicontinuous gyroid and BCC spheres behave like viscoelastic solids ($G^* \sim \omega^0$) [15]. In the hexagonally packed cylinders it has been observed that the complex modulus follows a power law at low frequencies: $G^* \sim \omega^{1/3}$ [16]. In the case of diblock lamellar structures, it has been clearly observed that $G^* \sim \omega^{1/2}$ [17].

Fig. 4 shows the storage G' and the loss G'' modulus as a function of temperature at low frequency. In agreement with the SAXS data, three different zones can be clearly distinguished. At ∼45 °C the transition from hexagonally packed PDMS cylinders to bbc ordered spheres is evidenced as an abrupt increase of the storage modulus G'. The strong increase of G' is due to the appearance of an elastic three-dimensional structure. A similar behavior for the dynamical response has been also observed in other block copolymer systems with order–order transitions between mesophases. For example, in

Table 1
SEC and ^{1}H NMR characterization

Polymer	$M_{\rm n}$ theor[a] (g/mol)	$M_{\rm n}$[b] (g/mol)	$M_{\rm n}/M_{\rm w}$[b]	$M_{\rm n}$ PDMS[b] (g/mol)	$x_{\rm PDMS}$[c]	$w_{\rm PDMS}$[c]
PB	9,750	9,500	1.03	–	–	–
PB-*b*-PDMS	12,400	11,700	1.05	2,200	0.147	0.191

[a] Expected molecular weight according to stoichiometry.

[b] Molar mass and molar masses' distribution relative to poly(styrene) standards (SEC at 25 °C using toluene as solvent).

[c] Calculated from ^{1}H NMR spectra (25 °C, $CDCl_3$ as solvent).

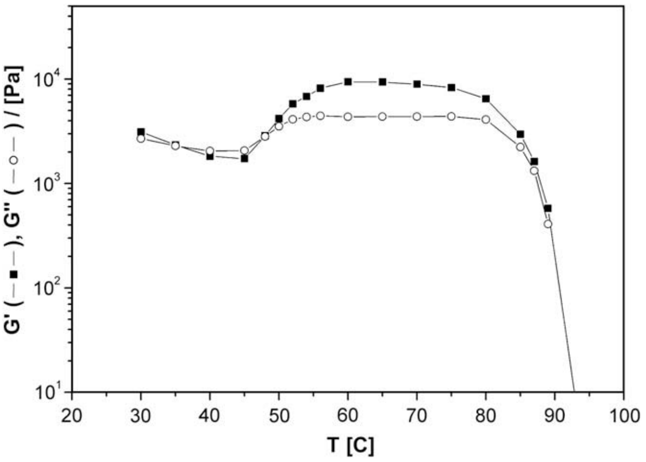

Fig. 4. Storage modulus (G') and loss modulus (G'') as a function of temperature (T) at $\omega = 0.04$ rad/s.

PEP-*b*-PDMS diblock copolymers it was observed a similar increment in the moduli due to presence of an order–order transition between lamellar and gyroid phases [18]. By increasing the temperature beyond ~80 °C there is a sharp decrease in G'. This feature indicates that the presence of the order–disorder transition is in agreement with the SAXS data.

5. Conclusions

In summary, a model copolymer was synthesized by sequential anionic polymerization of B and D_3, using high-vacuum techniques. Sequential addition of monomers and a two-step methodology were applied, by which PB-*b*-PDMS copolymer with structural homogeneity and narrow molecular weight distributions was obtained. Similarly to other model block copolymer systems, the PB-*b*-PDMS diblock copolymer exhibits thermo-rheological complexity and a very rich temperature and compositional phase behavior. In view of the complex phase behavior observed in this system, future studies will be focused in the analysis of molecular weight and compositional effects.

Acknowledgments

We express our gratitude to Richard A. Register and Sasha Myers for their assistance with the SAXS experiments and useful discussions. Financial support for this study came from the Consejo Nacional de Investigaciones Científicas y Técnicas de la República Argentina (CONICET), the Agencia Nacional de Promoción Científica y Tecnológica (ANPCyT), and the Universidad Nacional del Sur (UNS, Argentina).

References

[1] Lötters J, Olthuis W, Veltink P, Bergveld P. J Micromech Microeng 1997;7:145–7.
[2] Deníz S, Baran N, Akgün M, Akgün N, Dincer S. Turk J Chem 2004;28:645–57.
[3] Hadjichristidis N, Iatrou H, Pispas S, Pitsikalis M. J Polym Sci Part A Polym Chem 2000;38:3211–34.
[4] Ciolino A, Sakellariou G, Pantazis D, Villar M, Vallés E, Hadjichristidis N. J Polym Sci Part A Polym Chem 2006;44:1579–90.
[5] Morton M, Fetters L. Rubber Chem Technol 1975;48:359–409.
[6] Uhrig D, Mays J. J Polym Sci Part A Polym Chem 2005;43:6179–222.
[7] Adams JLM, Quiram DJ, Graessley WW, Register RA, Marchand GR. Macromolecules 1996;29:2929–38.
[8] Register RA, Bell TR. J Polym Sci Part B Polym Phys 1992;30:569–75.
[9] Bellas V, Iatrou H, Hadjichristidis N. Macromolecules 2000;33:6993–7.
[10] Anderson D. In: Smith Lee, editor. Analysis of silicones. New York: John Wiley & Sons; 1974. p. 247 [chapter 10].
[11] Fetters LJ, Lohse DJ, Richter D, Witten TA, Zirkelt A. Macromolecules 1994;27:4639–47.
[12] Colby RH. Curr Opin Colloid Interface Sci 1996;1:454–65.
[13] Adams JLM, Graessley WW, Register RA. Macromolecules 1994;27:6026–32.
[14] Fredrickson GH, Bates FS. Annu Rev Mater Sci 1996;26:501–50.
[15] Kossuth M, Morse DC, Bates FS. J Rheol 1999;43:167–96.
[16] Ryu CY, Lee MS, Hajduk DA, Lodge TP. J Polym Sci Part B Polym Phys 1997;35:2811–23.
[17] Rosedale JH, Bates FS. Macromolecules 1990;23:2329–38.
[18] Vigild ME, Almdal K, Mortensen K, Hamley IW, Fairclough JPA, Ryan AJ. Macromolecules 1998;31:5702–16.