CRYSTALLINITY BEHAVIOUR OF POLYDIMETHYLSILOXANE AND POLYCAPROLACTONE BASED BLOCK COPOLYMERS

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Abstract: *The paper presents the synthesis and characterization of star block copolymers based on polydimethylsiloxane and polycaprolactone. These copolymers were prepared by the ring opening polymerization of ε-caprolactone, using a single end type di-hydroxyalkyl terminated siloxane oligomer as macromonomer and stannous octoate as catalyst. Their chemical structures and molecular weights were characterized by ^{1}H-NMR, FTIR and SEC, and thermal properties were determined by DSC. DSC analyses were also conducted to estimate the crystallinity degree of the PCL and PDMS blocks.*

Keywords: *crystallinity, star block copolymer, polydimethylsiloxane, polycaprolactone*

1. Introduction

The interest towards block copolymers is extensively discussed in the literature due to the unique properties they have compared to homopolymers, properties determined by their structure, molecular weight, and block ratio.

The advantages of block copolymer is that rigid blocks can be combined with flexible blocks, hydrophobic blocks with hydrophilic blocks and amorphous with crystalline ones. In this way it can be tailored their structure and subsequently their properties, particularly their ability to order into nanometer sized domains, leading to various applications [1-3].

Crystallization of polymers is also important due to the mechanical properties which can vary from the change in molecular conformation. Modification of mechanical and structural properties of a crystalline homopolymer can be achieved by synthesizing a block copolymer with a crystalline block and another rubbery or glassy block. The overall crystallinity depends on the copolymer composition, volume fractions of each block, the interaction parameters and morphology and crystallinity of each block. [4].

Introducing a biodegradable block in block copolymers structure widen their applications especially in the biomaterials field. In this case

biodegradable polyesters show great potential, many of which can be bioderived. [5]

Polycaprolactone (PCL) is a hydrophobic polyester, biodegradable, and biocompatible. Is a semi-crystalline polymer and its crystallinity varies depending on its molecular weight. PCL can be dissolved in a variety of solvents, has low to moderate melting temperatures (59–64°C) and a glass transition temperature (approximately −60 °C) which allow easy processing. Moreover, is compatible with many types of polymers and biopolymers when blended, thereby being considered for various biomedical applications. PCL can be decomposed in various natural environments or by extracellular depolymerase, enhancing their potential use as a biodegradable packaging material. Such features of PCL and its derivatives (copolymers, blends and composites) led to their wide use in many fields, especially in biomaterials area.[6] Despite its many advantages, PCL on its own has a limited applicability because of its thermal properties. The low melting point of PCL allows easy processing but also limits its application. Therefore, their blends and their copolymers have been extensively studied, to improve the thermal and mechanical properties of PCL and to increase their scope of applications [7,8].

Polydimethylsiloxane (PDMS) is an elastomeric polymer with a wide variety of uses in medicine and cosmetics, sensors, electronics, biomedical devices, industrial lubrication. [9]

It possess interesting properties for biomedical applications compared to other polymeric materials; is chemically inert, has excellent resistance to biodegradation and biocompatibility, has good gas permeability and impermeability to liquids, is optically transparent, has good mechanical properties, very high chain flexibility, excellent optical transparency and simple fabrication by replica moulding. [10]

Despite these advantages, PDMS has some properties that limit their applications in certain areas. PDMS chains present a hydrophobic surface because of its methyl groups, limiting their application especially when solutions composed of biological samples are involved. Methods of modifying PDMS polymers can include bulk, surface and other modification techniques. Bulk modification techniques include copolymerization, blending, functionalization or obtaining of interpenetrating polymer networks. [11] Modification of biocompatible PDMS through blending with other polymers is sought in various biomedical applications to improve their properties. To enhance the compatibility of PDMS with other polymers, PDMS based block copolymers can be used, the other block acting as an anchoring between the PDMS and matrix. [12-14]

From the large variety of block copolymers, those based on PCL and PDMS combine biodegradability and compatibilization effect of PCL with surface-modifying and toughening characteristics of PDMS to provide the desired surface, mechanical and thermal characteristics to a variety of blends with other polymer matrices. These features makes them excellent candidates for surface-modifying additives, emulsion stabilization and other biomaterials applications.

In this paper are presented the results regarding synthesis and characterization of star block copolymers PDMS-b-(PCL)$_2$, which could be used as micellization agents for emulsion stabilization and as plasticizers for poly (vinyl chloride). These copolymers could act as hemocompatibilizers and surface modifying agents for blends of poly (vinyl chloride) - poly (ε-caprolactone) with potential use in biomaterials field.

2. Materials and methods

2.1. Materials

ε-caprolactone (CL, 99%, Aldrich), toluene (99%, Alfa Aesar) and single end di -hydroxyl terminated poly(dimethylsiloxane) (PDMS-(OH)$_2$, M_n = 3200, ShinEtsu-Japan) were kept under nitrogen on molecular sieves (3 Å).

Tin(II) 2-ethylhexanoate (stannous octoate Sn(Oct)$_2$, 96%, Alfa Aesar), benzyl alcohol (99%, Sigma-Aldrich), methanol (Chromasolv, Sigma-Aldrich) n-heptane (99%, Riedel de Haën) and poly(e-caprolactone) (PCL, Fluka, Mw = 10,000 g/mol) were used as received.

2.2 Characterization

The synthesized block copolymers were characterized from the point of view of chemical structure, molecular weight, molecular weight distribution and thermal properties using Proton Nuclear Magnetic Resonance (^{1}H-NMR) (AC-400F Brucker spectrometer, 400MHz, using deuterated chloroform as solvent and tetramethylsilane as the internal standard), Size Exclusion Chromatography (SEC) (Waters instrument equipped with microstyragel columns and a refractive detector, THF was used as the solvent with a flow rate of 1 ml/min), Furrier Transmission Infrared Spectroscopy (FTIR) (IFS48 Bruker spectrometer with the number of scans was fixed to 100 with a resolution of 4 cm^{-1}), Differential Scanning Calorimetry (DSC) (Mettler TA 4000 differential scanning calorimeter, thermograms recorded between –150°C and +150°C with a heating rate of 10°C/min).

2.3. Polymer synthesis (example A)

All the polymerizations were carried out in a previously dried Schlenk tube equipped with a magnetic stirring bar under nitrogen. The tube was degassed three times by repeated vacuum nitrogen cycles. To a Schlenk tube

equipped with a magnetic stirring bar was added under nitrogen 2.5 g (7.8 mmol) of PDMS-$(OH)_2$ (3200 g mol^{-1}) in 50 mL of toluene. An amount of 0.05 mL of stannous octoate (0.156 mmol) was then introduced and the mixture was stirred at 110°C, under nitrogen for one hour. After that time, 3.64 mL (0.034 mol) of CL was introduced and the polymerization was allowed to proceed for 8 h at 110 °C and 2 mL of methyl alcohol was added at the end of the reaction time, to stop the reaction. The reaction mixture was then concentrated, and the polymer was precipitated into heptane, filtered and dried to provide a white powder. SEC results: Mn (SEC) = 13600 g mol^{-1} and dispersity PD = Mm/Mn = 1.21.

3. Results and discussions

This work was based on the results obtained during Ph.D. thesis "Synthesis and characterization of block copolymers from heteromultifunctional initiators", 2009, Iași, Gheorghe Asachi Technical University in cotutelle with Haute Alsace University, France.

Three PDMS-$(PCL)_2$ star block copolymers with the structure presented in Figure 1 have been obtained, varying the length of the PCL blocks.
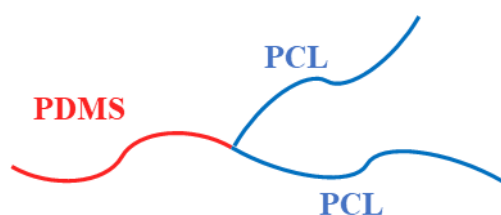

Figure 1. *Structure of star block copolymers*

The chemical structure of the copolymers and the molecular weight of PCL blocks were determined by ^{1}H-NMR spectroscopy. The number average molecular weight (M_n) of the block copolymers was determined by comparing the proton signals from hydrocarbon -CH_2-OH of the PCL to the signals from methyl groups bonded to silicon atoms in the backbone. The results showed

that the M_n of the PCL blocks determined by ^{1}H-NMR are close as those predicted.

The molecular weight of synthesized block copolymers was also determined by SEC, using polystyrene as etalon. The results confirm the synthesis of block copolymers, fact sustained by the monomodale chromatograms obtained and by the small values of polydispersity (~1). The block copolymers characteristics are summarized in Table 1.

Table 1. *Characteristics of synthesized block copolymers*

Block copolyme	Mn PCL^a (g/mol)	Mn Block copolymer^a (g/mol)	Mw Block copolymer^b (g/mol)	PDI^b
A	5500	8700	13600	1.21
B	9000	12200	17200	1.23
C	20800	24000	20900	1.31

^{a} determined by ^{1}H NMR
^{b} determined by SEC

DSC analyses were conducted in order to estimate the thermal properties (melting temperature – Tm and melting enthalpy – ΔHm) and the crystallinity degree ($χ_c$) of the PCL and PDMS blocks (Table 2 and 3). In all three star block copolymers melting temperatures for each block, PDMS and PCL respectively were recorded, indicating that, both sequences (PCL and PDMS) may crystallize.

Table 2. *DSC results corresponding to PDMS block*

Sample	%wt	Tm, °C	ΔHm, Jg^{-1}	$χ_c$, %
PDMS-$(OH)_2$	100	-41.2	15.22	24.84
A	36.79	-49.54	4.21	6.88
B	26.23	-44.25	5.34	8.72
C	13.34	-41.17	9.12	14.90

The results presented in table 2 show that the melting temperatures of the PDMS blocks are relatively close to those of the homopolymer and that they are only slightly influenced by the molecular weight of the PCL chain. It was observed that the melting temperatures of the PDMS blocks slightly

increase as the weight percentage (%wt) of PCL in block copolymer increases.

Table 3. *DSC results corresponding to PCL block*

Sample	%wt	Tm, °C	ΔHm, Jg^{-1}	χ_c, %
PCL	100	50.3	109.8	81.33
A	63.21	47.26	72.73	53.87
B	73.77	61.75	76.97	56.61
C	86.66	63.99	82.42	61.05

The results presented in table 3 show that the values recorded for the melting temperature corresponding to the PCL blocks are not significantly influenced by the molecular weight of the PCL blocks.

The crystallinity degrees (χ_c) of PCL and PDMS were calculated by dividing the melting enthalpy corresponding to each polymer by the reference enthalpy of a totally crystalline polymer (135 J/g for PCL [15] and 61.19 J/g for PDMS [16]). Crystallinity degree corresponding to PDMS blocks increases as the PDMS percentage decreases. Therefore, by increasing the PCL block length the crystallinity degree (χ_c) of PDMS blocks increases (Figure 2).

Figure 3. *Crystallinity degree of the PCL block*

This could be explained by the fact that PDMS is a very flexible polymer with high chain mobility which will hider PCL chain ability to crystalize. By increasing the PCL block length, organization of PCL chains is favored and the crystallinity degree (χ_c) of these blocks increases.

4. Conclusions

Syntheses of PDMS-(PCL)$_2$ star block copolymers were realized via ring-opening polymerization of CL using hydroxyl-terminated PDMS oligomers as initiators. Formation of desired structures was confirmed using ^{1}H NMR spectroscopy, FTIR spectroscopy and SEC. Thermal transitions and degrees of crystallinity of the various copolymers where investigated using DSC. Considering PDMS-(PCL)$_2$ star block copolymers, the results demonstrate the complex effect of polymer architecture on the ability of the PDMS or PCL blocks to crystallize or not.
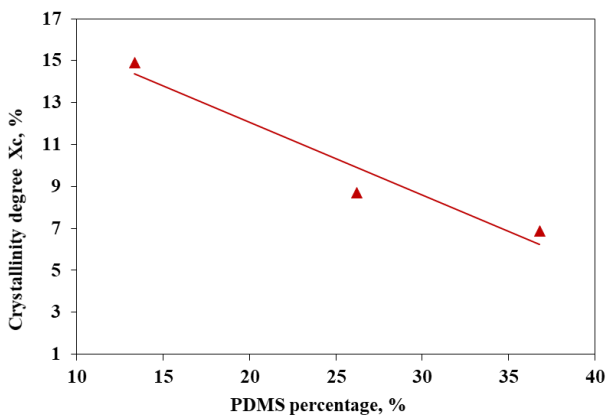

Figure 2. *Crystallinity degree of the PDMS block*

As it can be observed in Figure 3, crystallinity degree corresponding to PCL blocks increases with increasing the PCL percentage which is equivalent with decreasing the PDMS percentage.
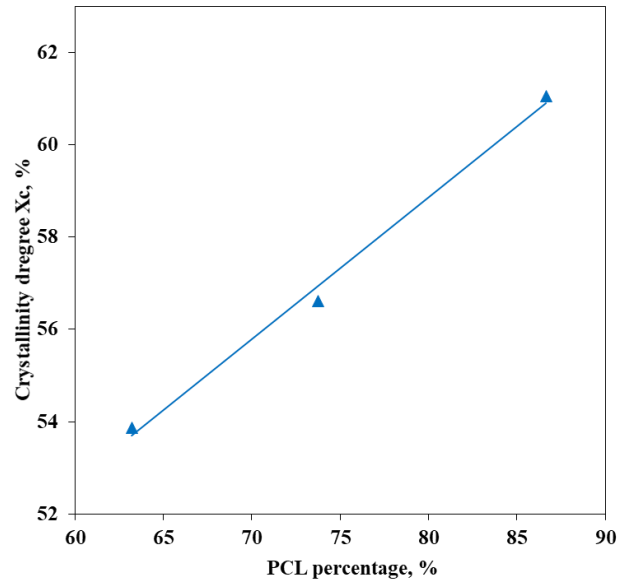
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