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Synthesis and Morphology of Model 3-Miktoarm Star Terpolymers of Styrene, Isoprene and 2-Vinyl Pyridine

Agapi Zioga, Stella Sioula and Nikos Hadjichristidis*

Department of Chemistry, University of Athens, Panepistimiopolis,
Zografou, 157 71 Athens, Greece

SUMMARY: The combination of anionic polymerization and controlled chlorosilane chemistry made possible for the first time the synthesis of model 3-miktoarm star terpolymers of styrene (PS), isoprene (PI) and 2-vinylpyridine (P2VP) (3μ-SIV). The morphology of a nearly symmetric 3μ-SIV star terpolymer, was also studied. From the preliminary results, it seems that the PI and P2VP phases form hexagonally packed adjoined cylinders, whereas the PS phase occupies the remaining space forming non-regular curved hexagons, hexagonally packed as well. The star junction points reside on periodically spaced, parallel lines defined by the intersection of the three microdomain interfaces. Non of the phases form the matrix. The star molecular architecture gives the molecule the ability to "choose" which arms directly interact in the microphase segregate state, in order to minimize the most highly unfavorable contact between the PI and P2VP arms.

Introduction

Designing molecules with specific properties for certain applications has been of recent interest both scientifically and technologically. The key point in synthesizing polymeric materials with predetermined properties, and thus applications, is to know the relationship between structure and properties. In order to study this relationship, it is essential to synthesize model megamolecules with well defined macromolecular architecture and high degrees of molecular and compositional homogeneity.

Anionic polymerization, high vacuum techniques and controlled chlorosilane chemistry are very powerful tools for manipulating macromolecular architecture. Controlled substitution of chlorine atoms of chlorosilanes by macroanions produces a

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wide variety of model non-linear block copolymers with high degrees of molecular and compositional homogeneity and complex architectures $^{1)}$.

Although non-linear block copolymers have been extensively studied, leading to very interesting results $^{2)}$, rather little attention has been given to the non-linear architecture of terpolymers (3-miktoarm star terpolymers), due to synthetic difficulties. A number of synthetic approaches have been used for the synthesis of 3-miktoarm star terpolymers. The controlled chlorosilane chemistry was used in the case of the 3-miktoarm star terpolymers of PS, 1,4-PI and 1,4-polybutadiene (1,4-PBd) (3μ-SIB) $^{3)}$. The macromonomer approach was used for the synthesis of the 3-miktoarm star terpolymers of PS, poly(dimethylsiloxane) (PDMS) and poly(tert-butyl methacrylate) (PtBMA) $^{4)}$, and of PS, PBd-1,2 and PMMA $^{5)}$. In the case of the 3-miktoarm star terpolymers of PS, 1,4-PI and poly(methyl methacrylate) (PMMA) (3μ-SIM), incorporation of the polymethacrylate branch by the chlorosilane method has not been possible, simply because the reaction of SiCl with the living polymethacrylate fails to give the linked product. In order to overcome this difficulty, the SiCl group was transformed to $SiC(Ph_2)(CH_2)_2C^-(Ph_2)Li^+$, which is an efficient initiator for the polymerization of the methyl methacrylate (MMA) $^{6)}$. Finally, the synthesis of 3-miktoarm star terpolymers of PS, poly(ethylene oxide) and poly(ε-caprolactone) was performed by preparing first a diblock copolymer having a protected anionic initiator at the junction point, followed by deprotection and polymerization of the third compound $^{7)}$.

The challenging synthesis of suitable model star polymers makes quite difficult the morphological study of such materials and the construction of a phase diagram. Morphological studies of the 3μ-SIB showed that the two dienes are mixed because of their low interaction parameter and the structure consists of only two kind of microdomains $^{8)}$. The nearly symmetric 3-miktoarm star terpolymers of PS, PDMS and PtBMA $^{9)}$ seems to microphase separate into three microdomain structures, but no specific model was proposed. Finally in the case of the 3μ-SIM star terpolymers the microdomain structure was governed by the pronounced incompatibility of the PMMA and PI arms and the low interaction parameter between PS and PMMA. Thus, in the case of the nearly symmetric 3μ-SIM star terpolymers, the PI and PS phases form prism-shape columns (triangular and rectangular) surrounding a cylindrical core region of PMMA [10)]. In these samples the junction points reside on periodically spaced, parallel lines defined by the intersection of the three microdomain interfaces. The non-symmetric (in respect of their composition) 3μ-SIM star terpolymers exhibited an inner PI column with a surrounding PS annulus in a matrix of PMMA. Depending on the composition and molecular weight PI/PS and PS/PMMA interfaces were either cylindrical (%vol. PS/PI/PMMA: 20.5/25/54.5, 22.3/27.2/50.5) or had a non-constant mean curvature (non-CMC) diamond prism shape (%vol. PS/PI/PMMA: 25.3/30.7/44, 29/49.3/21.7). The star junction points are distributed over the PI/PS intermaterial dividing surface due to partial mixing of PS and PMMA arms [11)].

In all the above cases, all the three arms of the star terpolymers are amorphous. However, in the case of the 3-miktoarm star terpolymer of PS, poly(ethylene oxide) (PEO) and poly(ε-caprolactone) (PεCL) the situation is totally different. The megamolecule consists of two crystallizable arms (PEO and PεCL) and one amorphous (PS). Thus, crystallization is the main force that drives the microphase separation and the final structure formation [12)].

In this paper we report the synthesis and preliminary results of the morphological characterization of 3-miktoarm star terpolymers of styrene, isoprene and 2-vinyl pyridine, in order to study the influence of the macromolecular architecture and the chemical nature of the arms on the properties of these polymeric materials.

Experimental

The synthesis of 3μ-SIV was performed using anionic polymerization, high vacuum techniques and controlled chlorosilane chemistry. The first step is the synthesis of the macromolecular monofunctional chlorosilane linking agent $(PS)(PI)(CH_3)SiCl$ according to the standard procedure [3)], followed by condensation of the benzene solution and dilution with tetrahydrofuran (THF). In order to avoid side reactions, the polymerization of 2-vinyl pyridine was performed in THF at –78°C using 1,1-diphenylhexyllithium as initiator. The solution of $(PS)(PI)(CH_3)SiCl$ was added to an excess of $P2VP^{(-)}Li^{(+)}$ in THF at –78°C, in order to incorporate the third arm. The excess of P2VP was extracted with treatment of the final product with methanol.

All steps were monitored by size exclusion chromatography (SEC). The number average weight, M_n, was determined in toluene by membrane osmometry (MO) at 35^0C with a Wescan 230 membrane osmometer. The weight average molecular weight, M_w, was measured with a Chromatix KMX-6 , operating at λ=633nm in THF at 25°C. The refractive index increment (dn/dc) was determined with a Chromatix KMX-16 operating at λ=633nm.

The composition of the terpolymers was analyzed by ^{1}H-NMR in $CDCl_3$ using a Vanity Unity Plus 200 instrument. The PI arm analyzed by ^{1}H and ^{13}C-NMR was found to have the following microstructure : 70% wt cis 1,4; 20% wt trans 1,4 and 10%wt 3,4.

For Small Angle X-Ray Scaterring (SAXS) and Transmission Electron Microscopy (TEM) characterization the nearly symmetric 3μ-SIV sample was slowly cast into a ~1 mm thick film from THF solution (~4 wt %) and annealed at 135°C under vacuum for 10 days in order to obtain near-equilibrium morphology. For TEM investigation 40-50nm thick sections were cryomicrotomed at –120°C using a Reichert-Jung FC 4E cryoultramicrotome equipped with a diamond knife. Sections were picked on copper-grids and selectively stained with OsO_4 or CH_3I. The morphology was observed with a Jeol 200CX transmission electron microscope operating at an accelerating voltage of 200kV in the bright field mode.

Results and Discussion

Synthesis

The synthesis of the 3-miktoarm star terpolymers of polystyrene (PS), polyisoprene (PI) and poly(2-vinyl pyridine) (P2VP), 3μ-SIV, was performed according to the following basic reactions:

$$\text{Isoprene} + \text{s-BuLi} \xrightarrow{C_6H_6} \text{PI}^-\text{Li}^+$$

$$\text{PI}^-\text{Li}^+ + \text{excess } (CH_3)SiCl_3 \longrightarrow \text{PI}(CH_3)SiCl_2 + LiCl + (CH_3)SiCl_3 \uparrow$$

$$\text{Styrene} + \text{s-BuLi} \xrightarrow{C_6H_6} \text{PS}^-\text{Li}^+$$

$$\text{PI}(CH_3)SiCl_2 + \text{PS}^-\text{Li}^+ \xrightarrow{\text{titration}} (\text{PI})(\text{PS})(CH_3)SiCl + LiCl$$

$$\text{s-BuLi} + CH_2{=}C(Ph)_2 \xrightarrow[-78^0C]{THF} \text{s-Bu - }CH_2\text{ - }C^-(Ph)_2Li^+$$

$$\text{s-Bu - }CH_2\text{ - }C^-(Ph)_2Li^+ + \text{2-Vinylpyridine} \xrightarrow[-78^0C]{THF} \text{P2VP}^-\text{Li}^+$$

$$\text{P2VP}^-\text{Li}^+ \text{ (excess)} + (\text{PI})(\text{PS})(CH_3)SiCl \xrightarrow[-78^0C]{THF} (\text{PS})(\text{PI})(\text{P2VP}) \qquad [3\mu\text{-SIV}]$$

The monofunctional linking agent, (PS)(PI)(CH_3)SiCl, was synthesized by controlled substitution of two chlorine atoms of trichloromethylsilane by PS and PI arms, using methods developed by our group $^{3)}$. Polyisoprenyllithium, prepared in benzene with sec-butyllithium (s-BuLi) as initiator, was reacted with a large excess of trichloromethylsilane (TCMS), in order to substitute only one of the three chlorine atoms with the PI arm (Fig. 1). After careful removal of the TCMS, the (PI)Si(CH_3)Cl_2 was dissolved in benzene and titrated with polystyryllithium, prepared in benzene with s-BuLi. The titration was monitor by SEC (Fig. 1). Subsequently the solution of (PS)(PI)(CH_3)SiCl was condensed and diluted with THF. The incorporation of the P2VP arm was achieved by reacting the (PS)(PI)(CH_3)SiCl with an excess of the living anion P2VP$^-$Li$^+$, prepared in THF at –78°C using 1,1-diphenylhexyllithium as initiator. This last reaction was performed in polar solvent (THF) and at low temperatures (-78^{0}C), in order to avoid termination reactions of the P2VP$^-$Li$^+$ anion. In order to eliminate the excess of the P2VP arm, the reaction product was treated with methanol (Fig. 1), which is a good solvent for P2VP and a non-solvent for the 3μ-SIV.

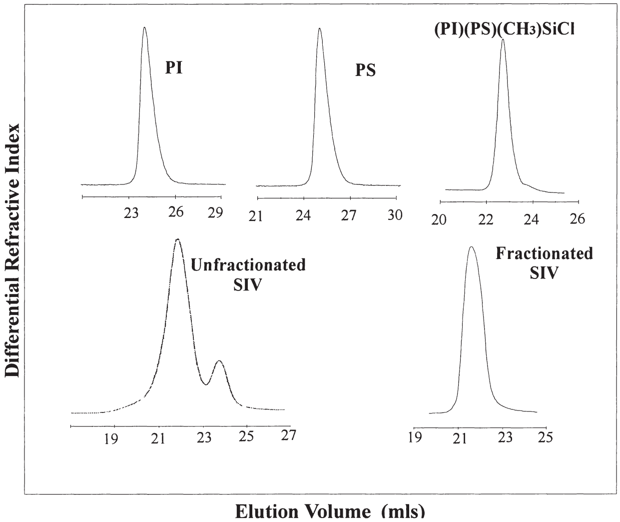

Fig.1: Size exclusion chromatograms for monitoring the synthesis of 3-miktoarm star terpolymer SIV-15/14/13.

The molecular characteristics of the fractionated star terpolymers are given in Table 1. The nomenclature used is SIV-*x/y/z*, where *x, y, z* are the respective arm molecular masses in kg/mol.

Table 1. Molecular characteristics of the 3-miktoarm star terpolymers

Polymer	$M_w \cdot 10^{-3}$ [a)]	$M_n \cdot 10^{-3}$ [b)]	M_w/M_n [c)]	PS/PI/P2VP (%w.f.)[d)]
PS	15	14.5	1.02	-
PI	14.5	14	1.02	-
SIV-15/14/13	45		1.1	34.2/34/31.8
PS	35	35	1.02	-
PI	15.5	15	1.02	-
SIV-35/15/20	70		1.09	57.7/22.3/20

[a)] LALLS in THF at 25^0C
[b)] MO in toluene at 35^0C
[c)] SEC in THF at 30^0C
[d)] ^{1}H-NMR in $CDCl_3$ at 35^0C

The above results indicate a high degree of molecular and compositional homogeneity.

Morphological Characterization

The preliminary results of the nearly symmetric 3-miktoarm star terpolymer, SIV-15/14/13, indicate a novel, very interesting morphological behavior for this kind of materials. The degree of segregation $\chi_{ij}(N_i+N_j)$ and the lowest order *d* spacing of SIV-15/14/13 are given in Table 2. The Flory-Huggins interaction parameters of PS-PI and PS-P2VP at 135^0C are determined as ~0.05 and 0.12 respectively [13-14]. Based on the solubility parameters [THF: $\delta = 9.1$ $(cal/cm^3)^{1/2}$, PI: $\delta = 8.2$ $(cal/cm^3)^{1/2}$, PS: $\delta = 9.1$ $(cal/cm^3)^{1/2}$, P2VP: $\delta = 10$ $(cal/cm^3)^{1/2}$] the χ parameter between PI and P2VP is expected to be the highest, $[\chi_{ij} \sim (\delta_i - \delta_j)^2]$.

Table 2. The lowest order d spacing and the degree of segregation of SIV-15/14/13

Polymer	PS/PI/P2VP (%v.f.)$^{a)}$	ϕ_1: ϕ_2: ϕ_3	$\chi_{SI}N_{SI}$$^{b)}$	$\chi_{SV}N_{SV}$$^{b)}$	d_1^{SAXS} (Å)
SIV-15/14/13	33.7/38.1/28.2	1.2/.1.3/1	18	32	249

$^{a)}$ From %w.f. from ^{1}H-NMR and $\rho(PS)=1.06$ g/ml, $\rho(PI)=0.913$ g/ml and $\rho(P2VP)=1.1$ g/ml

$^{b)}$ $\chi_{ij}(N_i+N_j)$ at 135^0C.

The results from SAXS and TEM for the THF cast SIV-15/14/13 sample are given in Fig.2 and 3, respectively. The SAXS pattern suggests that the sample exhibits a hexagonal arrangement of microdomains, because the $q_n : q_1$ values are 1.0: 1.7: 1.96: 2.61, very close to 1: $\sqrt{3}$: $\sqrt{4}$: $\sqrt{7}$, which are characteristic for hexagonally packed units.

The bright field TEM micrograph of section stained with OsO_4 is given in Fig. 3a. OsO_4 preferentially stains the PI phase, which appears dark, whereas the PS and P2VP phases are not distinguished and appear as the light matrix. From this micrograph it is obvious that the PI phase forms hexagonally packed cylinders in a matrix of PS and P2VP. The TEM micrograph of section stained with CH_3I, which stains preferentially the P2VP phase, shows that the P2VP microdomains, which appear dark, also form hexagonal cylinders in a matrix of PS and PI (Fig. 3b.).

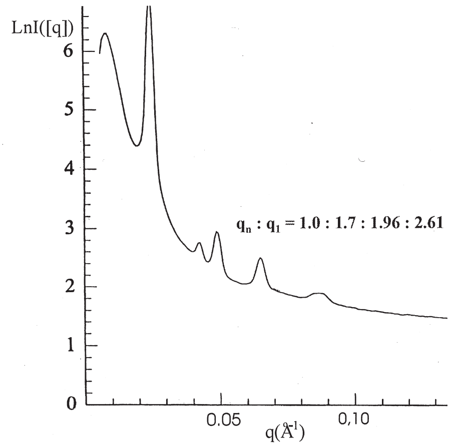

Fig. 2: SAXS pattern of SIV-15/14/13. The ratios of the q vectors for the various peaks are also given.

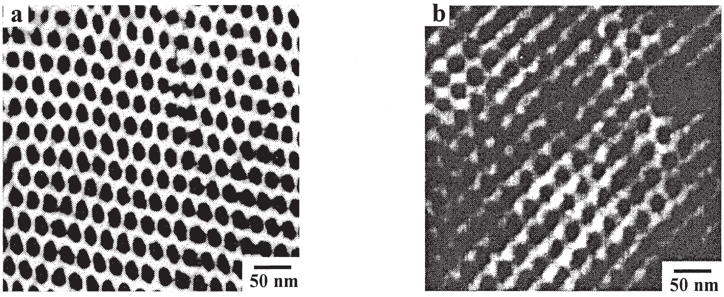

Fig. 3: Bright field TEM images of SIV-15/14/13 stained with (a) OsO_4 and (b) CH_3I. In the OsO_4 stained micrograph, the dark regions correspond to the PI phase, which forms hexagonally packed cylinders, whereas in the CH_3I stained micrograph the dark regions correspond to the P2VP phase, which also seems to form hexagonally packed cylinders.

Combining the two sets of TEM data with the hexagonal packing indicated by SAXS and the star macromolecular architecture leads to the schematic given in Fig. 4 for the proposed morphology. The PI and P2VP phases form hexagonally packed cylinders, whereas the PS phase forms non-regular curved hexagons, hexagonally packed as well. The two kinds of cylinders adjoin at the star junction points, which thus reside on periodically spaced, parallel lines defined by the intersection of the three microdomain interfaces. The structure is two-dimensionally periodic with plane group symmetry p3m1. All components form one-dimensionally continuous domains and there is no matrix component.

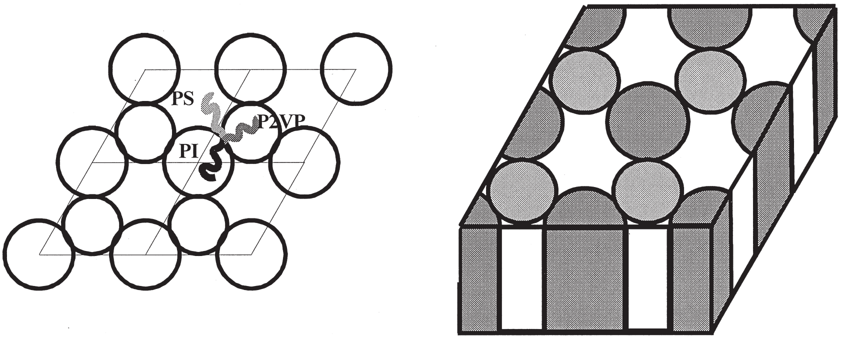

Fig. 4: Schematic representation of the proposed microdomain morphology of SIV-15/14/13 sample. The chain conformation of the three blocks and the location of the junction point are also presented.

Comparing the preliminary morphological results for the SIV-15/14/13 sample with the microdomain structure of the nearly symmetric SIM 3-miktoarm star terpolymers[10] (ϕ_1/ ϕ_2/ ϕ_3: SIV-15/14/13 = 1.2/1.3/1, SIM-72/77/109 = 1/1.2/1.3 and SIM-92/60/94 = 1.3/1/1.2) a lot of similarities are observed. First of all, there is no interface between the most incompatible phases, that is the PI/P2VP and the PI/PMMA phases. The star molecular architecture gives the molecule the ability to “choose” which arms directly interact in the microphase segregate state. Since χ_{IV} and χ_{IM} have the highest value, the arms microphase separate to obtain microdomain structures which minimize the unfavorable contact between the PI/P2VP and PI/PMMA arms. In addition the star junction points reside on periodically spaced, parallel lines defined by the intersection of the three microdomain interfaces, while non of the phases form the matrix.

A possible scenario for the formation pathway of the proposed structure is as follows: THF was the solvent used for casting. According to the solubility parameters of the solvent and the three components, it is most probable that PI and P2VP segregate first forming, according to their volume fraction (38% and 28% respectively), cylinders hexagonally packed in a swollen matrix of PS. Since these two blocks are covalently bonded to each other, these two kind of cylinders are obliged to adjoin at the junction point of the star. That way the interface between the two most incompatible arms (PI and P2VP) is minimum. Upon further evaporation of the solvent the PS phase occupies the remaining space forming this strange shape column, while there is no need for any deformation of the two kind of cylinders, since there interface is already minimum.

In order to confirm the proposed morphology and the similarities observed with the nearly symmetric SIM 3-miktoamr star terpolymers, more detailed examination of the sample is needed. The next step is to perform a TEM experiment using two kind of stainers (e.g. both OsO_4 and CH_3I) in order to achieve two levels of contrast and be able to "see" the two kind of cylinders in the same micrograph 15).

Conclusions

Controlled chlorosilane chemistry can be successfully used for the synthesis of 3-miktoarm star terpolymers of styrene, isoprene and 2-vinyl pyridine. It is a general and very powerful method for the synthesis of model megamolecules with complex architecture, that was up to now mainly used with non-polar monomers (such as styrenic and dienic) and now expanded to the polar 2-vinyl pyridine monomer, opening new horizons for the synthesis of model polymeric materials with more potential applications. The preliminary study of the morphology of the nearly symmetric 3μ-SIV sample revealed a very interesting microstructure, consisting of two kind of hexagonally packed cylinders of PI and P2VP adjoining at the star junction points, which reside on periodically spaced parallel lines defined by the intersection of the three microdomains. Very interesting results can also be obtained by comparing the nearly symmetric 3μ-SIV with the corresponding 3μ-SIM star terpolymers. Although the chemical nature of the third arm of the two kinds of 3-

miktoarm star terpolymers is different (P2VP versus PMMA), some common rules are followed for the formation of the microdomain structure: minimization of the most unfavorable contact and localization of the star junction points on periodically spaced parallel lines. A more detailed future study of the 3μ-SIV star terpolymers with various compositions is necessary in order to propose a phase diagram for this system and to further use it for predicting the morphological behavior and thus the properties of this kind of polymeric materials15).

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