

24 in several solutions. The functional nanostructured polymers offer a great usage potential in
25 the fields of micro system technology and efficient power generation.

26 Controlling of the properties of the nano formations could lead to better understanding of
27 correlations between molecular structure, morphology, interface functionality, and the
28 macroscopic materials. The reproducibility and long-term stability of these nano
29 aggregations are also important to design of novel functions (6,7).

30 On the other hand, nanosolutions are also important to thermodynamically and kinetically
31 controlling of the nanoparticles. The solvents can have an effect on solubility, stability and
32 reaction rates of polymer. The knowledge of nano structural content, inner morphologies of
33 the nano aggregations, the electron densities and assembly kinetics of the core-shell part of
34 the nano formations in polymer solutions are very important in their potential usage in
35 technological applications (8).

36 In this study tetrahydrofuran (THF) and chloroform (CLF) were selected as solvents because
37 of their polar aprotic and nonpolar properties. THF and CLF have functional molecular
38 groups which may cause chemical transformations and they are suitable for molecular
39 oxidation. Therefore, these solvents are widely used to research optoelectronic properties of
40 the polymers (9–11).

41 The studied polymer has electro negative charge distributions around its mid-chain (CH) part
42 due to the presence of double bond of cyclohexene ring. With the help of the physico-
43 chemical interactions between polymer and the solvents, the different sized nano formations
44 may be aggregated. The molecular weights of the PSt in tetrahydrofuran and chloroform
45 solvents are not expected to be the same because of different cross-linking of PSt part of the
46 polymer. These solvents are also effective and kinetically include valuable information on the
47 size, shape, morphology and the distributions of the nanoaggregations (12).

48 In the present work, it was firstly examined whether the PSt-CH-PSt polymer has nano
49 aggregations or not. If it was determined, the answers were looked for about the questions
50 related with their nano structural and molecular stabilizations. The molecular structures,
51 nano scale shapes and inner morphologies were examined and the first step was taken to
52 research the potential usage of PSt-CH-PSt in nano technological applications.

53 It may be briefly said that, the non-spherical, polymer-based, core-shell nanoparticle
54 fabrications with different 3D morphologies and their nanocrystalline arrangements are the
55 main center of the focused study because of these type of nanoparticles' potential usage in
56 energy storage, photonics, and biomedical applications (13).

57 **2. EXPERIMENTAL DETAILS**

58 **2.1 XRD**

59 XRD pattern of the powdered polymer was obtained by a Bruker AXS, D8 Advance system
60 by using CuK_α (with $I=40\text{mA}$ and $V=40\text{kV}$) to investigate crystalline or amorphous structural
61 properties of the polymer.

62 **2.2 XRD**

63 The thermal behaviors of the polymer were determined using differential scanning
64 calorimetry (DSC) (Shimadzu DSC60 Model at a scanning rate of $10^{\circ}\text{C min}^{-1}$ and
65 temperature range from 23 to 250°C).

66 **2.3. FTIR Spectra**

67 FTIR spectra of solid phase polymer and polymer in chloroform (CHCl_3) and tetrahydrofuran
68 ($(\text{CH}_2)_4\text{O}$) were recorded by Perkin Elmer Spectrum One FTIR Spectrometer equipment
69 with total reflectance diamond ATR unit at room temperature in the $4000\text{--}450\text{ cm}^{-1}$ range
70 with a resolution of 4 cm^{-1} at 32 scans.

71 For variable-temperature measurement solid polymer were cast from 5 wt% solution in
72 chloroform. The spectra were carried out in the temperature range between 20 and 120°C
73 within 5°C interval by Graseby Specac Automatic Temperature controller unit. The samples
74 were equilibrated in the cell for at least 10 min at each temperature. The region $4000\text{--}1000$
75 cm^{-1} was used for thermal studies using CaF_2 . After 120°C , the samples were naturally
76 cooled down to room temperature.

77 **2.4. SAXS**

78 Small-angle X-ray scattering method was utilized to further evaluate the liquid crystal
79 systems observed by polarized microscopy. SAXS experiments were performed with Kratky
80 compact Hecus system (Hecus X-ray systems, Graz, Austria) equipped with a linear
81 collimation system and X-ray tube with a Cu target ($\lambda = 1.54\text{ \AA}$). The generator was operated
82 at a power of 2 kW (50 kV and 40 mA). Simultaneous measurements of SAXS and WAXS
83 range were possible in the system with a linear-position sensitive detector used with 1024
84 channel resolution. Distances between channels and the sample-detector were $54\text{ }\mu\text{m}$ and
85 31.05 cm , respectively. SAXS measurements in solutions were also carried out in the
86 temperature range of $23\text{--}50^{\circ}\text{C}$ within 5°C interval by using an external temperature control
87 unit.

88 The relative position of the SAXS peaks on the scattering vector (q) axis was used to
89 determine the structure of the liquid crystal phases. Data for each test were acquired for
90 900s.

91 **3. RESULTS AND DISCUSSION**

92 The aim of this study is to investigate whether this polymer may be useful to prepare micelle
93 globules in different solvents. The PSt-CH-PSt was synthesized by atom transfer radical
94 polymerization (ATRP) of styrene (St) using 3-cyclohexene-1,1-diyldi(methylene) bis(2-
95 bromopropanoate) as the initiator and Cu(I)/bpy as the catalyst system. As known, ATRP is
96 a controlled/living free radical polymerization (CRP) technique which provides the synthesis
97 of polymers with controlled molecular weights, lower molecular weight distributions and well-
98 defined architectures. The theoretical, gel permeation chromatography (GPC), and $^1\text{H NMR}$
99 molecular weights of PSt-CH-PSt ($M_n\text{ theo} = 4173$, $M_n\text{ GPC} = 4200$ and $M_n\text{ H NMR} = 4550$)
100 are in good agreement with each other and its polydispersity is low ($M_w/M_n = 1.21$),
101 indicating the formation of the PSt-CH-PSt with well-defined structure through a controlled
102 process. A polymer synthesized via controlled polymerization methods has superior
103 properties than a polymer synthesized by normal conventional polymerization techniques.
104 The detailed synthesis, polymerization conditions and characterization processes were given
105 in previous article (2)

106

107 3.1. XRD

108 Both of crystalline and amorphous phases can be observed in the polymers containing PSt
109 (14). The phenyl rings cause to parallel ordering and crystalline phase while the molecular
110 chains are responsible of the random amorphous phase. Because of these dual structural
111 properties, the usage of PSt is preferable in design and synthesis of new polymers. XRD
112 profile (Figure 1) of PSt-CH-PSt has Bragg peaks especially in 2θ range of $20^\circ - 43^\circ$. These
113 peaks are evidence of polystyrene crystalline phase (14). The broad peak in Bragg
114 diffraction angle of 20° indicates crystallographic planes with interplanar distance of $d=4.43$
115 \AA ($\lambda= 1.54 \text{\AA}$). This value was determined as 4.67\AA for the crystalline form of PSt by
116 Wecker's research group (14).

117 Even though, polystyrene (PSt) has polymeric nature, the structure of PSt-CH-PSt has
118 crystalline and well regulated form. The reason of these stable crystallographic planes is the
119 presence of planar phenyl groups which are parallel ordered respect to each other.

120

Figure 1.

121 3.2. DSC AND FTIR ANALYSIS

122 The DSC curve of PSt-CH-PSt is given in Figure 2. DSC curve reveals that the glass
123 transition of the PSt-CH-PSt at 73.1°C .

124

Figure 2.

125 It is known that vibrational spectra of polymers may provide independent information on
126 crystallinity, chain conformational regularity and chain stereoregularity (15,16).

127 FTIR spectra of powder form PSt-CH-PSt and its FTIR spectra in CHL and THF are given in
128 Figure 3. The FTIR spectrum of PSt-CH-PSt showed absorption bands at 3026 and 2849
129 cm^{-1} corresponding to aromatic and aliphatic C-H stretchings respectively. The bands at
130 1601 and 1493 cm^{-1} are assigned to aromatic C=C stretchings. The out of plane C-H
131 bending vibration band of benzene ring is seen at 758 cm^{-1} and ring bending vibration was
132 observed at 698 cm^{-1} (17).

133 The band at 1735 cm^{-1} is assigned to C=O ester band in the mid point of polymer chain. The
134 C-Br stretching vibration of the polymer is observed at 620 cm^{-1} in the FTIR spectrum.

135 The FTIR results of polymer in solution indicate that there are no significant shifts of the
136 almost all band wavenumbers. Only the carbonyl band at 1735 cm^{-1} of PSt-CH-PSt shifts to
137 1732 cm^{-1} in solution.

138

Figure 3.

139 We also determine the phase transition temperature of PSt-CH-PSt by temperature-
140 dependent FTIR spectroscopy. To investigate of the effect of thermal cycling on the FTIR
141 Spectra, similar thermal cycle as used above in recording the DSC response of PSt-CH-PSt.
142 After complete evaporation of chloroform, the FTIR spectra of cast film of PSt-CH-PSt were
143 collected in situ during the heating process.

144 The C=O band at 1735 cm^{-1} is sensitive to the temperature elevation. Figure 4 shows
145 temperature-dependent FTIR spectra of the C=O band of PSt-CH-PSt in the region from
146 1770 to 1700 cm^{-1} . As can be seen from Figure 4, the changes are at frequency and
147 intensity of this band. The absorbance band position remains constant for the temperature
148 from 20°C to 45°C . The band wavenumber shifts to slightly higher wavenumbers in the
149 temperature range of 50°C and 65°C and significantly shifts to higher wavenumber after
150 70°C . The higher band intensity was also observed at 75°C which indicated that the polymer
151 phase is changing.

152

Figure 4.

153 The thermal behavior of aromatic C=C bands are quite opposite to C=O band intensity
154 variation. After 75°C , the band intensity of the C-C-O mode at 1254 cm^{-1} lower than
155 compare to the temperature range $20 - 45^\circ\text{C}$.

156 Kim and co-workers (18) reported that the orientation of C-C-O moiety in polystyrene-block-
157 poly(n-pentyl methacrylate) at lower temperatures is different from that at higher
158 temperatures. They concluded that the orientation of this moiety was affected by the
159 presence of PSt chains.

160 Therefore, we can also conclude that the conformation of this group in the PSt-CH-PSt is
161 different in the two temperature regions.

162 The heating and cooling FTIR experiments of the sample showed that the sample is
163 reversible.

164 3.3. SAXS

165 The recorded SAXS data were illustrated in Figure 5 $\{I(q)$ scattering intensities, q magnitude
166 of scattering vector ($q = 4\pi \sin\theta/\lambda$, with 2θ being the scattering angle) $\}$.

167

Figure 5

168 When the SAXS profiles of the sample was investigated, first observations are indicating the
169 presence of three peaks in $q = 0.17; 0.46$ and 0.57 \AA^{-1} . These considered peaks are big
170 probably occurred by the effect of high order Bragg diffractions from crystalline structure of
171 PSt groups.

172 The other SAXS data (except the peaks) were used to determine the shape, size and inner
173 morphologies of the nanoaggregations in the polymer structure. The scattering intensity $[I$
174 $(q)]$ equations of oblate core-shell model (19) were used for fitting process of the measured
175 data to the calculated intensities. The structural model was illustrated in Figure 6 and the
176 obtained structural parameters about the model were given in Table 1.

177

Figure 6.

178

Table 1.

179 SAXS analyses showed that the obtained oblate core shell shapes of the nano aggregations
180 are stable at different temperatures in the range of $23-50^\circ\text{C}$. The related model including
181 molecular representations and solution effects may be also understandable by using Figure
182 7.

183

Figure 7.

184 In the oblate core-shell model, the bigger electron densities are indicating the presence of Br
185 atoms which have bigger electronegativity than the other atoms According to this
186 information, it may obtain that, the tails (including Br atoms) are located in the core part of
187 the nanoglobules in THF and in the shell part of the aggregations in CLF solutions.

188 When the temperature dependence of core and shell volume was investigated in the
189 solutions, it was seen that the core volume is slightly changing (initially increasing up to of
190 30-35°C and then decreasing). On the other hand, the shell volume of the nanoaggregations
191 is exponentially changing especially in THF solution (Figure 8) and these thermo responsive
192 change was defined by an empirical equation of $V=A \exp (-BT)$, (A and B are coefficients
193 and their values were determined as 22026 Å³ and 0.023 °C⁻¹, respectively).

194

Figure 8.

195 The studied polymer (in powder and solution forms) may be defined by nano structured and
196 self-assembled systems. The significant results may be briefly given as follows.

- 197 i. The molecular structure of PSt-CH-PSt has stable and reversible in both of powder and
198 two studied (THF and CLF) solution forms in the temperature range of 20-75°C.
- 199 ii. The glass transition temperature of the polymer was measured as 73.1°C.
- 200 iii. Polymer structure forms ellipsoidal core-shell aggregations in both of powder and
201 solutions forms in nanoscale.
- 202 iv. According to the successfully determined structural model, the electron densities of
203 the core and shell parts may be obtained and it may be also, consequently defined
204 which molecular groups are located in these parts. As a result of this analysis, the
205 head part (CH) is located in shell part for THF solution while CH is a corona for both
206 of powder and CLF. So it may be briefly said that the tail part and CH part of the
207 polymer are cross-linkable in THF and CLF solutions, respectively.
- 208 v. When the thermo response behaviors were examined for two solvents, it was
209 obtained that the shell volume is decreasing with increasing temperature and an
210 empirical (exponential) formula may define this changing for THF.
- 211 vi. The size of the polymer micelles is not in the expected range of 1-100 nm as nano
212 micelles in the studied solvents. The size range of the big radius of elliptical micelles
213 are 71.71-83.55 nm for THF and 79.39-81.80 nm for CLF. But it is also predicted
214 that if the water percentage is increased in the solutions, the size of the
215 aggregations will be decreased and the more compact new morphologies such as
216 core-shell cylinders will be appeared because of polar properties of water molecules
217 (20).

218 This secondary phase of the present work was also planned to take under the control of the
219 micellar size.

220 **4. CONCLUSION**

221 Consequently, it may be briefly said that, the first step was taken to investigate whether this
222 polymer may be useful to prepare micelle globules in different solvents or not. The results

223 were positive but the nano globular formations, their morphologies and inner structures of
224 the polymer indicate that the researches on the polymer should be developed by using the
225 other concentrations and different additional solvents to cause more compact (smaller sized)
226 globules, the opening and closing of the defined ellipsoidal micelles, etc. The nano carrier
227 micelles of the PSt-CH-PSt may be developed and used in near planned technological
228 applications especially because of their reverse micelle-forming properties and stable
229 structures under the studied temperatures.

230 As a general scientific vision and plan, it may be said that PSt-Ch-PSt nano aggregations
231 obtained in chloroform are also the most valuable sample because of their polymer brushes
232 in the PSt shell part of the nanoglobules. It is also known that these types of polymeric PSt
233 brushes are convenient to build 3D colloidal crystal blocks and to design new periodic
234 dielectric materials (21).

235 In near future works, these samples will be interacted with silica nanoparticles in different
236 solutions to reach 3D colloidal crystal structures.

237 **CONFLICT OF INTEREST**

238 The authors confirm that there are no known conflicts of interest associated with this
239 publication and there has been no significant financial support for this work that could have
240 influenced its outcome.

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