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Aggregation Behavior of Polyisoprene–Pluronic Graft Copolymers in Selective Solvents

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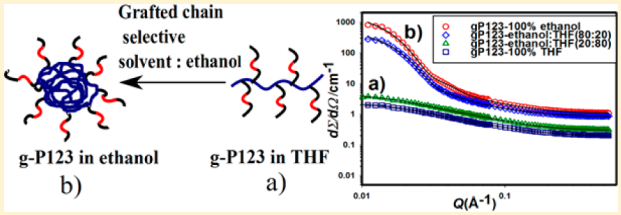
Supporting Information

ABSTRACT: Novel amphiphilic graft copolymers composed of a polyisoprene (PIP) backbone with Pluronic side chains, polyisoprene-*g*-Pluronic, have been synthesized using a "graft onto" technique. Small-angle neutron scattering (SANS) has been used to characterize the conformation of the P123 and P103 Pluronic graft copolymers in selective solvents such as ethanol and hexane and in a nonselective solvent, tetrahydrofuran (THF). The results indicated that, in a selective solvent for the side chain Pluronics (e.g., ethanol), "crew-cut" micelles were formed with a large core of radius ∼ 120 Å; data were fitted with a core–shell model. In a good solvent for the backbone (e.g., hexane), "flowerlike" micelles were formed with a small inner radius of ∼64 Å. In the nonselective solvent, a swollen polymer coil was found, which was described using the Guinier–Debye model. As THF/ethanol and THF/hexane can be prepared in any ratio, it was possible to vary the solvent composition gradually in order to study the transition from swollen coil to micelle. When going from 100% THF to 100% ethanol, the transition to micellar behavior was observed at a ratio of 20:80 (v/v %) THF/ethanol for both grafted copolymers and 40:60 (v/v %) THF/hexane for grafted P123 copolymers.



INTRODUCTION

Pluronics are commercially available block copolymers of ethylene oxide and propylene oxide that exhibit a range of useful properties, many of which are related to their surface activity. The formation of Pluronic copolymer micelles is very temperature and concentration sensitive. At low temperatures and concentrations, the copolymers exist as unimers, and above the critical micellization concentration (CMC) and temperature (CMT) they form multimolecular micelles. As a result, micelles only exist under specific conditions, somewhat limiting some practical applications.[1−5]

Amphiphilic graft copolymers (AGCs), in comparison to other surface active amphiphilic materials, have varied intramolecular association structures which make them much less influenced by concentration. In addition, intermolecular structures can be formed at very low concentrations due to the large size of these molecules. This enables graft copolymers to be used for a wide range of applications and even to stabilize colloidal systems at very low equilibrium concentrations.[6−10]

One strategy to increase the versatility of Plutonic polymers is the synthesis of graft copolymers, which often leads to greater amphiphilicity but requires multistep synthesis. Much research has been carried out in modifying Pluronics by grafting them to biological or nontoxic polymers in order to improve their limitations. These grafted copolymers have been characterized by many different methods including nuclear magnetic resonance (NMR), Fourier transform infrared spectroscopy (FTIR), surface tension (ST), dynamic light scattering (DLS), and small-angle neutron scattering (SANS).[6,11−15] AGCs have been synthesized by a number of routes including grafting from, grafting onto the macromonomer, or grafting through, methodologies.[16] A family of novel AGCs which combine a polyisoprene (PIP) backbone with poly(ethylene oxide) (PEO) side chains of varying molecular weight have been developed by our research group using the grafting onto method.[17]

A common element of the resulting structures, however, is that the backbone and graft may be clearly defined as being hydrophobic and hydrophilic in nature, or vice versa. In recent years, several research groups have examined the ability of AGCs to form stable aggregates of a principally core–shell structure in solution,[18−22] to interact with surfaces,[23] and to form antifouling coatings.[24] However, the behavior of AGCs remains comparatively neglected in comparison to the

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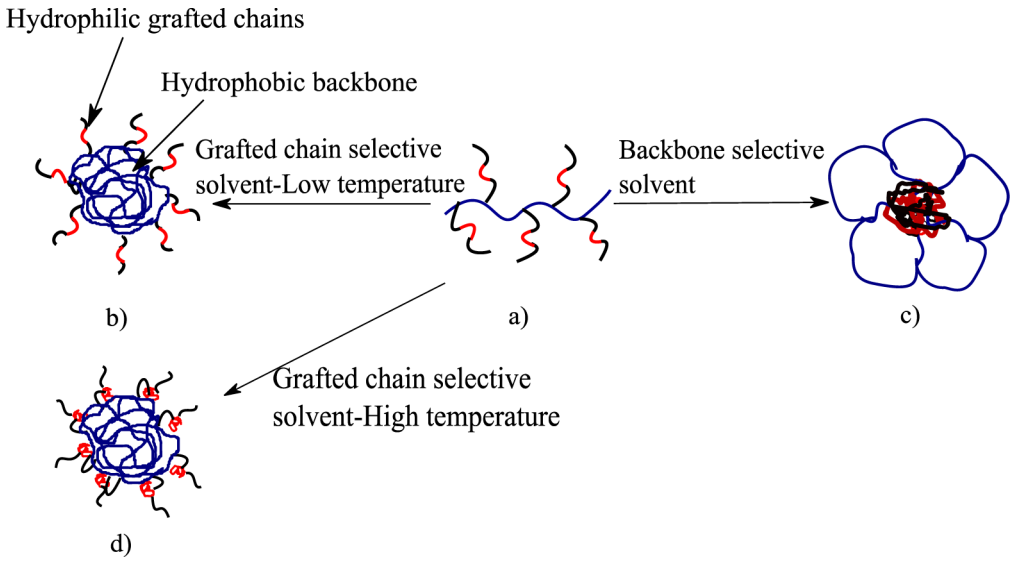

Figure 1. Possible conformations which might be taken on by grafted Pluronics in solution: (a) swollen graft copolymer in a nonselective good solvent, (b) crew-cut micelle, (c) flower micelle, and (d) crew-cut micelle with insoluble PPO blocks.

significant body of work studying the behavior of amphiphilic block copolymers.

As with other micellization and aggregation processes, the behavior of AGCs is determined by the interactions between solvent molecules and between solvent and each part of the amphiphilic species. In the specific case of AGCs, however, the strength of these interactions can be varied by changing the composition of the solvent involved and a number of different morphologies become possible. Consequently, the aggregation properties (size, shape and aggregation number) of an AGC are determined by the ratio of hydrophobic to hydrophilic portions (grafting degree),[25] length of the backbone and the grafted chains, kinetics of the self-assembly process,[26] and by solubility parameters of each polymer block in the solvent of interest. In a selective solvent for the side chains, a "star" structure can be obtained where the side chains surround a core of hydrophobic backbone either as a single molecule or micellar aggregate if the side chains are longer than the backbone.[18] However, when the grafted chains are much shorter than the insoluble backbone, "crew-cut" micelles are typically formed, where the core is large compared to the corona thickness.[26] In a solvent selective for the backbone, a "flower" type structure is expected, with the corona polymer forming loops.[27] These possible conformations of Pluronic graft copolymers in solutions are schematically shown in Figure 1.

The conformation that the AGC adopts in solution will determine the potential scope of applications for which it might be suitable. Clearly, it would be of great advantage to understand and be able to accurately predict the conformation of the polymer in a given environment from its structural components. It is hoped this will consequently allow the control of their full potential in a wide range of applications such as the stabilization of commercial product formulations that are highly demanding in terms of component compatibility and environmental conditions.

In this work, we describe the synthesis and characterization of polyispoprene-*graft*-Pluronic copolymers. The hydrophobic backbone that was used in the synthesis is a polyisoprene grafted with approximately 10 units of the monomethyl ester of maleic anhydride sold under the name LIR-410. The high reactivity of the PIP is due to the relatively large number of carboxylic groups in the backbone, and this makes the LIR-410 a good candidate for the *graft onto* method.[28,29] In our previous studies, we described a structural study using SANS from Pluronics P103 and P123, under a variety of conditions, such as addition of the hydrophobic drug flurbiprofen, changes in temperature, concentration and cosolvent.[1,3,5] As a consequence and for comparison, the grafted chains chosen for this study are two different modified triblock Pluronic copolymers (Pluronic P123 and Pluronic P103) with differing molecular weights. The synthesis was carried out by a "grafting onto" technique which connects the polyol chains onto the polyisoprene backbone via a functional group. In this instance, this method has disadvantages such as long reaction times and the requirement that the backbones have functional groups available for grafting. However, for this work, the clear advantage is that the molecular mass and dispersity of both grafted chain and the backbone are known before the grafting reaction, resulting in a better characterized polymer.

The effect of selective solvents for both the backbone and the chains has been measured using small-angle neutron scattering. The solvent composition in the experimental medium was altered with tetrahydrofuran (THF; good solvent for both polymers), ethanol (good solvent for Pluronics), and hexane (good solvent for polyisoprene) in order to utilize the different solubility profiles of the backbone and graft to manipulate the polymer conformation.

EXPERIMENTAL SECTION

The Pluronic samples were provided by BASF and were modified before grafting as described below. Polyisoprene-*graft*-monoacid monomethyl ester (PIP-*g*-MaMme, LIR-410) was provided by Kuraray Co. Ltd. D_2O (99.94 at% D), d_8-THF, and d_6-ethanol (99 at% D) were purchased from Goss Scientific Instruments Ltd. and were used as received.

Synthesis of Functionalized Pluronics. Pluronic P123 (15 g, 2.58 mmol) was dissolved in THF (70 mL) and KOH (0.2 g, 1.3 mol equiv) and added to a round-bottom flask (250 mL). The reaction mixture was stirred for 2 h at 65 °C under a nitrogen atmosphere before CH_3I (0.5 g, 1.3 mol equiv) was added dropwise over 15 min. The reaction was refluxed overnight, allowed to cool to ambient temperature, and subsequently precipitated in hexane (500 mL). The

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product was separated from the solvent and dissolved in $CHCl_3$ (20 mL) and filtered through Celite 521 to remove unreacted KOH and KI, after which the solvent was removed by rotary evaporation. The sample was then twice dissolved in chloroform (20 mL) and reprecipitated in hexane (200 mL) for further purification. The product was then purified by dialysis in distilled water for 3 days with twice-daily water changes before being dried by lyophilization. The reaction scheme is shown in Figure 2. The final product (66.6% yield) was fully characterized using ^{1}H NMR, HSQC, and MALDI-TOF. The details of the characterization can be found in the Supporting Information.

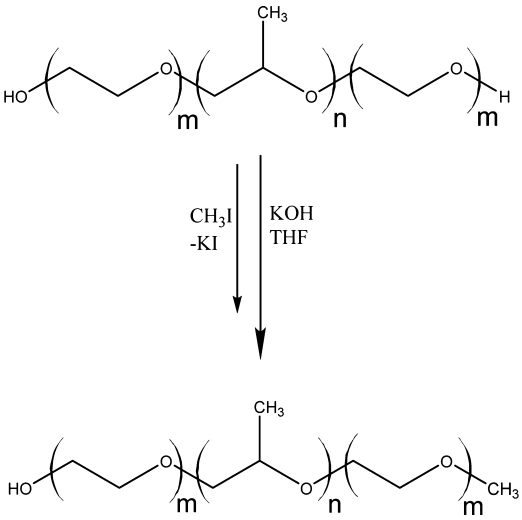

Figure 2. Synthesis of monofunctionalized Pluronic (f = 1).

As the reaction proceeds, there will be a mixture of monofunctional, bifunctional, and nonfunctionalized Pluronic formed. The probability of each of these components being formed depends on the molar ratio of end groups to the concentration of CH_3I. The bifunctional product will not react in the grafting onto step and can be ignored. Any functionalized polymer will graft, but the probability that it will cross-link between chains is very small and, as described later, can be ignored.

A functionalized derivative of Pluronic P103 was prepared in a similar manner using Pluronic P103 (15 g, 3.03 mmol) and CH_3I (0.6 g, 1.3 mol equiv).

Synthesis of Graft Copolymers Using Functionalized Pluronics. PIP-*g*-MaMme (5 g, 0.2 mmol) and Me-Pluronic P123 (12.8 g, 2.2 mmol) were dissolved in toluene (200 mL) by sonicating the mixture for a few minutes. The reaction was carried out using 1.1 equiv modified with respect to the number of functional groups (maleic anhydride) in each chain (~10). The polymer in toluene solution was sonicated and transferred to a three-neck round-bottom flask equipped with a Dean–Stark head, and the solution was refluxed at 145 °C for 3 days. During this time, extra toluene was added to the flask to replace that lost by evaporation, so that the volume of the solution stayed constant.

After 3 days, the polymer was precipitated in a large excess of distilled water and further purified by using a dialysis membrane (12 000–14 000 Mw) in distilled water for 3–4 days with twice-daily water changes. The final product was isolated by freeze-drying. The polymer was analyzed by ^{1}H NMR, PFGSE-NMR, and GPC. Characterization details for the AGC can be found in the Supporting Information. No evidence of cross-linking was found, justifying the functionalization procedure adopted above.

A graft copolymer of monomethylated Pluronic P103 was prepared in a similar manner using PIP-*g*-MaMme (5 g, 0.2 mmol) and Me-Pluronic P103 (11 g, 2.2 mmol).

Sample Preparation for SANS. Solutions of 10 wt % of the grafted polymers in d_8-THF were prepared before diluting with d_6-ethanol in order to obtain PIP-*g*-P123 and PIP-*g*-P103 (1 and 5 wt/v %) in six solvent mixtures (100% THF, 80:20 (THF/ethanol), 60:40, 40:60, 20:80, and 100% ethanol). The dilution was carried out by gradually pouring the THF solutions into measured quantities of d_6-ethanol, while stirring with a magnetic stirrer. In the same way, PIP-*g*-P123 samples were prepared at five concentrations of hexane (20%, 40%, 60%, 80%, and 100%) in d_8-THF/d_{14}-hexane.

Small-angle Neutron Scattering. SANS measurements were carried out on the PAXY instrument at Laboratoire Léon Brillouin (LLB), Gif sur Yvette, France. Neutrons with a wavelength between 4 and 10 Å and two sample–detector positions (1 and 2.3 m) were used, to provide a Q-range of 0.01–0.56 Å. All samples were measured in 1 mm path-length rectangular quartz cells, and an empty cell was run as a background sample. Performing the experiments below the critical micellar temperature of the Pluronics prevented any free ungrafted chains from becoming a source of micellar scattering. Therefore, the experiments on the AGCs solutions were carried out at around at 283 K unless otherwise stated. The sample holder was surrounded by a clear box in order to keep the temperature constant.

The Guinier–Debye model was applied to study the unimers. Debye derived a model for polymer chains in the theta state where there is a Gaussian distribution of polymer segment.[30] This model can also be applied for describing the scattering from polymers in a good solvent. The scattering form factor and the parameters have been given in detail elsewhere.[1] Additional corrections can be applied to polymers in good solvents;[31] however, these corrections are not exact for the copolymers we report here and so are not included.

The parameters for the Guinier–Debye model are scattering length density difference between the polymer and solvent, $(\Delta\rho)^2$, concentration, c, of polymer present in the sample, average molecular weight of the polymer, M_n, used, radius of gyration, R_g, and density of the bulk polymer, δ. In this model, the concentration, molecular weight, and scattering length density are covariant and are completely known; therefore, two of these parameters were fixed throughout the fitting.

A core–shell model was also used for fitting the data from the AGCs aggregates; the overall sphere (copolymer micelles) has an inner core (poorly solvated) and an outer shell (well solvated corona). Three regions can be defined corresponding to the inner core, the outer shell, and the solvent (medium). Assuming the aggregates do not interact and therefore there is no structure factor ($S(Q)$ = 1), the differential cross section of the model is given by

$$\frac{\delta\Sigma}{\delta\Omega}(Q) = \frac{N}{V}\Bigg[3V_{\text{core}}(\rho_{\text{core}} - \rho_{\text{shell}}) \times \frac{[\sin(QR_{\text{in}}) - QR_{\text{in}}\cos(QR_{\text{in}})]}{(QR_{\text{in}})^3} + 3V_{\text{core+shell}}(\rho_{\text{shell}} - \rho_{\text{medium}})\frac{[\sin(QR_{\text{out}}) - QR_{\text{out}}\cos(QR_{\text{out}})]}{(QR_{\text{out}})^3}\Bigg]^3 + B \quad (1)$$

where V_{core} is the volume of the core. $V_{\text{core}} = (4\pi/3)R_{\text{in}}^3$, N is the number of core–shell particles in the solution, and $V_{\text{core+shell}}$ is the volume of the core and shell. $V_{\text{core+shell}} = (4\pi/3)R_{\text{out}}^3$, ρ_{core} is the scattering length density for the core, ρ_{shell} is the scattering length density for the shell, ρ_{mdium} is the scattering length density of the solvent, and V is the total volume of the solution. R_{in} is the inner radius, and R_{out} is the outer radius. Note that thickness of the shell, L/Å, is $R_{\text{out}} - R_{\text{in}}$.

RESULTS AND DISCUSSION

Synthesis of Graft Copolymers. Commercially available Pluronic polymers possess two primary hydroxyl groups at either end of their chains (f = 2).[32] As a result, any attempt to react them with a functionalized backbone will result in cross-linking and the formation of a network unless a large excess of Pluronic is used. In order to minimize this side reaction, the

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polymers were functionalized and the stoichiometry of the reaction was optimized. For example, the monofunctional polymer (f = 1) is synthesized by deactivating one of the hydroxyl groups (Figure 2).

Statistically, some product in which both ends were methylated (f = 0) and some unmodified Pluronic chains (f = 2) could exist. The unmodified Pluronic could react with two PIP chains resulting in chain extension and an insoluble network. GPC analysis of the final graft copolymers however suggests that although some unmodified Pluronic was present, it was not in large enough quantities to create an insoluble polymer. The bifunctional product can be ignored as it will not react in the subsequent grafting reaction. The functionalized Pluronics were then reacted onto commercially available polyisoprene-*graft*-monoacid monomethyl ester (PIP-*g*-MaMme) to synthesize graft copolymers (Figure 3).

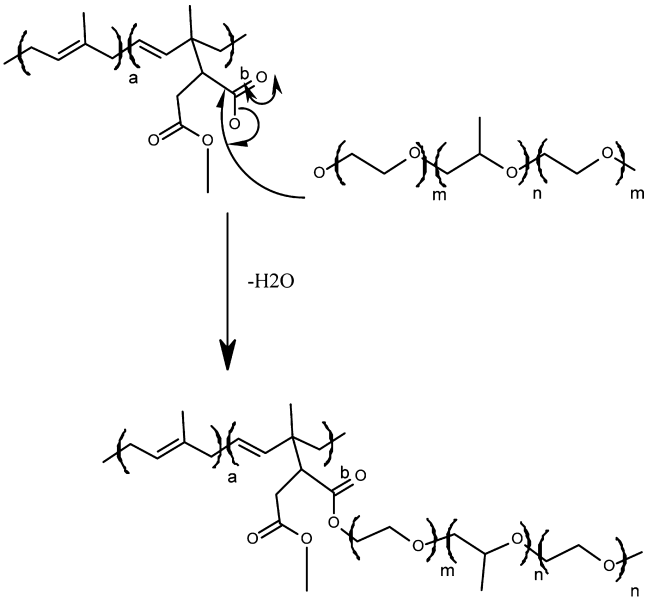

Figure 3. Reaction scheme for synthesis of polyisoprene−Pluronic graft copolymers.

Two graft copolymers were synthesized with different Pluronic grafts and are shown in Table 1.

Table 1. Comparison of the Two Grafted Different Molecular Weight Pluronics

sample	molecular mass of graft chains/ g mol^{-1}[a]	% cross-linked Pluronic	no. of grafted Pluronic chains/PIP	no. of free Pluronic chains/PIP
PIP-*g*-P103	5600	8	5.8	2.4
PIP-*g*-P123	6500	10	4.5	4

[a]By MALDI-TOF. The given molecular weight from the manufacture is 4950 and 5750 g mol^{-1} for P103 and P123, respectively.

Despite a thorough attempt to remove ungrafted Pluronic from the AGC samples through a purification procedure that included dialysis, some remained in the isolated polymers. Consequently, the presence of free Pluronic was accounted for in the analysis and study of the AGC samples.

Effect of Solvent Quality on the Aggregation Behavior of the Grafted Pluronics. The scattering data from the two different grafted copolymers in a range of solvent compositions is shown in Figure 4. It is evident that the

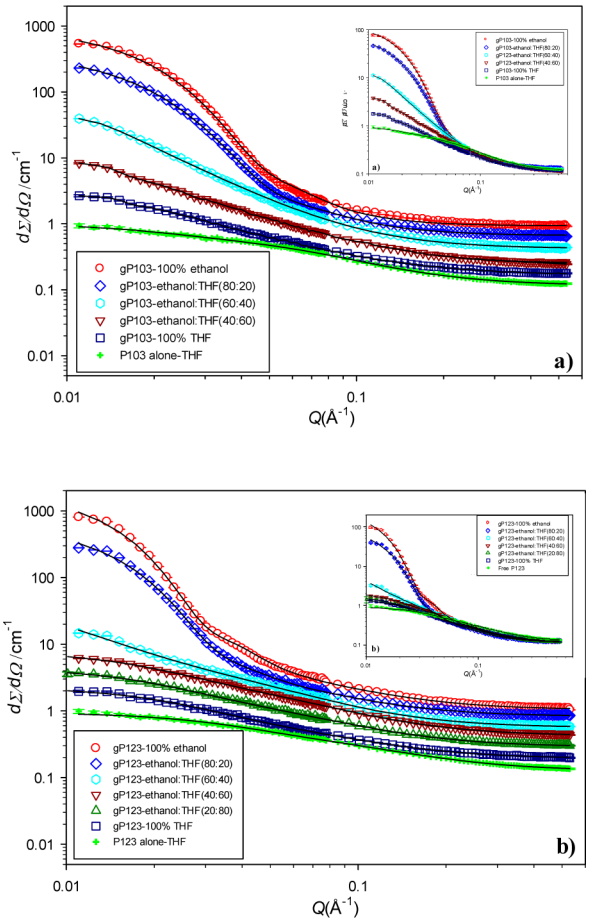

Figure 4. Small-angle neutron scattering from grafted copolymers in a range of solvent composition from 100% THF to 100% ethanol at 283 K. (a) 1 wt/v % PIP-*g*-P103 and (b) 1 wt/v % PIP-*g*-P123. Solid lines are fits to various models which are discussed in the text. Data have been shifted vertically to see the clarity of fits; the inset shows the data without shifting.

polymer aggregation behavior is very different in the presence of a good compared to a selective solvent. The clear increase of scattering intensity with increasing ethanol concentration immediately suggests that addition of ethanol leads to aggregation. Data from the grafted P103 copolymers in 100% d_8-THF (a good solvent for both backbone and graft) were fitted with a double Guinier−Debye function, supporting the prediction that the copolymers adopted a swollen polymer coil. The data could not be fitted with a single Guinier−Debye function due to the presence of the free Pluronics. Therefore, the model was modified to include two different size estimates of nonaggregated graft and free copolymers. The results of the fitting are shown in Table 2 in which component 1 (C1), corresponds to the grafted P103 copolymers and component 2 (C2) to the free Pluronic P103 copolymers. Gradually increasing the amount of ethanol decreases the solvent quality for the backbone while still being a good solvent for the PEO and PPO segments.[33] Therefore, the grafted copolymers form aggregates in order to minimize the unfavorable interaction of the polyisoprene block with ethanol. Increasing amounts of ethanol result in the observed increase of the R_g, R_{out}, and the

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Table 2. Fitting Parameters Obtained Using the Double Guinier−Debye Model and a Core−Shell Model with Free Polymer for the Grafted P103 Copolymers

samples	PIP-*g*-P103: 100% THF	PIP-*g*-P103: (60:40) THF/ethanol
$R_{g(C1)}$/Å	89 ± 2.2	129 ± 5.1
$Ø_{C1}$	0.01 ± 0.01	0.01 ± 0.0004
$R_{g(C2)}$/Å	18.2 ± 0.7	21.9 ± 2.1
$Ø_{C2}$	0.004 ± 0.003	0.006 ± 0.0006
samples	PIP-*g*-P103: (20:80) THF/ethanol	PIP-*g*-P103: 100% ethanol
$Ø_{core}$ [a]	0.003 ± 0.00002	0.006 ± 0.00005
$Ø_{corona}$ [b]	0.002 ± 0.0005	0.003 ± 0.0005
R_{in} /Å	110 ± 1.3	111 ± 0.95
R_{out}/Å	150 ± 15	164 ± 59
L/Å	40	53
[c]σ	0.28	0.23
$R_{g(free\ polymer)}$/Å	16 ± 0.58	11 ± 0.89
$Ø_{free\ polymer}$	0.005 ± 0.006	0.001 ± 0.00003
N_{agg}	123 ± 2.1	127 ± 0.9

[a]Total volume fraction of core segments in the dispersion. [b]Volume fraction of polymer in the corona. [c]Polydispersity.

aggregation number values, and indeed in the large increase in scattering intensity observed in Figure 4. Estimates of the aggregation number (N_{agg}) calculated using the volume of the core (V_{core}) and the PIP backbone. Note the model used to calculate the aggregation number excludes solvent from the core and therefore gives an upper bound to the number of segments in the core.[3]

Data from grafted P103 copolymers in 100% d_6-ethanol (Table 2) (a good solvent for the grafted chains, but poor solvent for the backbone) were fitted by a core−shell model with free polymer. A conformation arises in which the backbone comprises the core of the structure and the Pluronic chains form a comparatively small corona (crew cut micelles). Then attention was focused on the different solvent ratios to determine exactly where the association takes place.

Grafted P103 copolymers in THF/ethanol (60:40) were also fitted with a double Guinier−Debye model where the grafted copolymer R_g increases indicating the onset of aggregation as the backbone solvency becomes poorer. In THF/ethanol (20:80) they could only be fitted with a core−shell model with free polymer. The scattering data in THF/ethanol (40:60) could not be fitted clearly by either the core−shell or the Guinier−Debye model. However, the data can be fitted by the Guinier−Porod model[34,35] with R_g = 135 Å and fractional dimension, s = 1, which suggest the formation of rod-shaped aggregates. Formation of rod-shaped aggregates from a certain chain length of the grafted PEG with polystyrene backbone in DMF/water, was observed by Eisenberg et al., where spherical aggregates were also observed for the longer chain length of the grafted PEG.[10]

As can be seen in Figure 4b, the grafted P123 copolymers in various solvent compositions showed slightly different behavior compared to the grafted P103. For the grafted P103, the intensity changes gradually as the solvent composition is changed; however, for grafted P123 there is a more sudden transition that takes place between 60% and 80% ethanol. The samples with between 100% THF and 60% THF were fitted by the double Guinier−Debye model (Table 3) and indeed no intermediate structure was observed. The copolymers in 100% and 80% ethanol were fitted with a core−shell model with free polymer, the results of which are presented in Table 3. The grafted P123 copolymers form larger aggregates with a very small volume fraction in the corona and a R_{out} with large standard deviation. This could be due to the effect of the number of grafts per backbone; grafted P123 polymers have a lower number of grafts and a higher percentage of free copolymer. This prevents a sharp phase separation between the core and the grafted chains, which in turn prevents a well-defined core−shell structure.

As is shown in Table 3, in 80% and 100% ethanol, the micelles formed by PIP-*g*-P123 have a larger core radius and thicker corona compared to those formed by PIP-*g*-P103. The thicker corona is naturally connected to the Pluronic P123 having a longer contour length than the Pluronic P103. However, there are also fewer grafted Pluronic chains (see Table 1) for the grafted P123 copolymer than for the grafted P103 copolymer. The subsequent lower ratio of side-chain to backbone allows the formation of a larger core.

In Figure 5, the effect of hexane on the aggregation behavior of the PIP-*g*-P123 copolymer (5 wt/v %) was examined. Hexane is a good solvent for the PIP backbone but bad for the grafted chains. Again, a clear increase in intensity is observed with increasing hexane concentration, indicating that aggregation takes place. The data for the samples containing between

Table 3. Fitting Parameters Obtained Using the Double Guinier−Debye Model (for 1 wt/v % grafted Pluronic P123 in 100% to 40% d_8-THF) and a Core−Shell Model with Free Polymer (for (100%) and (80:20) d_6-ethanol/d_8-THF) at 283 K

samples	PIP-*g*-P123: 100% THF	PIP-*g*-P123: (60:40) THF/ethanol	PIP-*g*-P123: (40:60) THF/ethanol
$R_{g(C1)}$/Å	69 ± 2.1	86.5 ± 4.1	119 ± 5.1
$Ø_{C1}$	0.008 ± 0.0002	0.012 ± 0.0005	0.01 ± 0.005
$R_{g(C2)}$/Å	15.9 ± 0.7	21.6 ± 0.8	24.4 ± 1.1
$Ø_{C2}$	0.004 ± 0.003	0.008 ± 0.0007	0.007 ± 0.0006
samples		PIP-*g*-P123: (20:80) THF/ethanol	PIP-*g*-P123: 100% ethanol
$Ø_{core}$		0.002 ± 0.00002	0.004 ± 0.00005
$Ø_{corona}$		0.001 ± 0.0001	0.0016 ± 0.0001
R_{in}/Å		153 ± 1.9	164 ± 1.5
R_{out}/Å		214 ± 156	234 ± 150
L/Å		61	70
σ		0.24	0.21
$R_{g(free\ polymer)}$/Å		22 ± 0.86	18 ± 0.77
$Ø_{free\ polymer}$		0.0055 ± 0.0005	0.0044 ± 0.0004
N_{agg}		332 ± 6.8	409 ± 3.3

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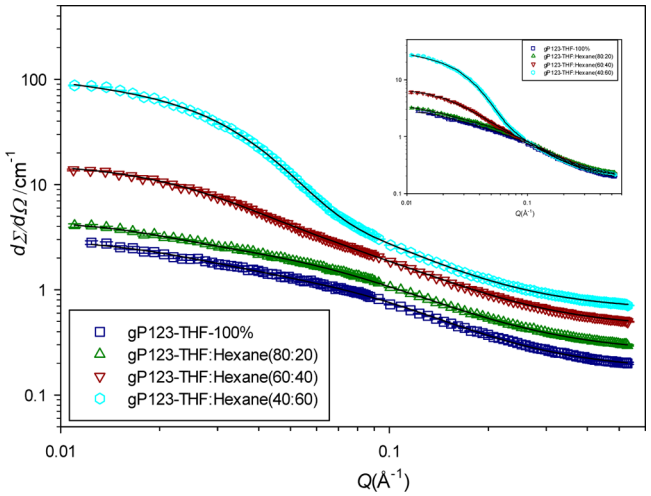

Figure 5. Small-angle neutron scattering from 5 wt/v % PIP-*g*-P123 copolymers in a range of solvent composition from 100% THF to 60% hexane, at 283 K. Solid lines are fits to the double Guinier–Debye model (for the copolymers in 100% to 60% THF) and core–shell model with free polymer (for samples in 40% THF). Data have been shifted vertically to see the clarity of fits; the inset shows the data without shifting.

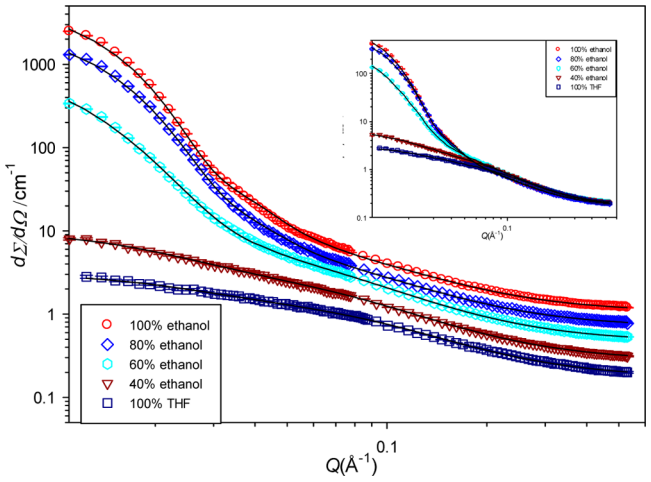

Figure 6. Small-angle neutron scattering from 5 wt/v % PIP-*g*-P123 copolymers in a range of solvent composition from 100% THF to 100% ethanol, at 283 K. Solid lines are fits to the double Guinier–Debye model (for the copolymers in 100% to 60% THF) and the core–shell model with free polymer (for samples in 60%, 80%, and 100% ethanol). Data have been shifted vertically to see the clarity of fits; the inset shows the data without shifting.

100% and 60% THF were fitted with the double Guinier–Debye model with the $R_{g(C1)}$ of approximately 70 ± 4 Å corresponding to the grafted copolymers and $R_{g(C2)}$≈ 16.4 ± 0.24 Å corresponding to the free P123 copolymers. However, the data in 40:60 THF/hexane could only be fitted by a core–shell model with some free polymer; comprising small core of the Pluronic side-chains, with the backbone PIP forming a large corona in a flower-like micelle morphology (R_{inner} = 64 ± 0.3 Å, *L* of 155 Å, and $R_{g(free\ polymer)}$ = 18 ± 0.4 Å). The grafted samples in 80% and 100% hexane were not stable in solution and phase separation was observed. This is again due to the low ratio of hydrophilic to hydrophobic segments. The increase in stability of these aggregates in hexane would be expected for the samples with the higher number of grafts.

Micellization Behavior of the Grafted Pluronics at Higher Polymer Concentrations. In this section, PIP-*g*-P123 was chosen as a representative sample and the dependence of the structures on the concentration of this copolymer was investigated. The solutions all contained 5 wt/v % of the grafted copolymers in a THF/ethanol mixture, significantly more than that of the 1.0 wt/v % described earlier (Figure 4b). It was found that the copolymer in THF and THF/ethanol (60:40) adopted a swollen morphology and the data were fitted with the double Guinier–Debye model with R_g ≈ 80 Å ± 4, which is comparable with the data from the1 wt/v % grafted polymers experiments.

The noticeable difference between these two concentrations is the data in 40:60 THF/ethanol solutions. A unimeric structure was observed for 1 wt % grafted copolymers at this solvent composition, however, by increasing the concentration to 5 wt %; the AGCs adopted a core–shell structure, as is shown in Figure 6. This is primarily due to the change in solubility of the grafted polymers in the solvent mixture.

The fitting results of the 5 wt % grafted P123 copolymers in higher quantities of ethanol are shown in Table 4. As can be seen from the results, the radius of the micelles, the shell thickness, and the radius of the free polymer are hardly affected by the concentration of the copolymers and are comparable with the results of 1 wt % copolymers (Table 3). The aggregation number increases slightly for 5 wt % PIP-*g*-P123 in (100%) and (20:80) THF/ethanol, in line with a small change in the core radius. This indicates that the size, shape, and aggregation behavior of these graft polymers are not influenced greatly by concentration and this facilitates the use of graft copolymers in wide range of applications, in particular where dilution becomes an issue.

■ CONCLUSIONS

Here, we have shown that it is possible to functionalize Pluronic polymers and graft them to highly hydrophobic backbones by the "grafting onto" method without any cross-linking. Small-angle neutron scattering was used to investigate the interesting solution and micellization behavior observed for polyisoprene-*g*-P103 and polyisoprene-*g*-P123 copolymers. The graft copolymers were studied in different ratios of d_8-THF/d_6-ethanol mixtures, used as selective solvents for the grafted chains, in order to determine the ratio at which the micellization transition takes place. It was observed that these copolymers adopted a swollen coil morphology in low ethanol/THF ratios; however, micellization was observed at the compositions with more than 60% ethanol in the system. The size of the aggregates did not vary significantly with polymer concentration, but the transition at which the micellization took place as solvent composition was varied was influenced strongly, showing that the polymers can self-assemble more readily at 5 wt % compared to 1 wt %. The solvent composition was also altered in order to go from a good solvent mixture to one that is selective for the backbone: d_8-THF/d_{14}-hexane. In this solvent mixture with high ratios of hexane, phase separation was observed; however, the copolymers in 40:60 THF/hexane were stable and scattering data indicated the formation of core–shell aggregates with the small inner radius of ∼64 Å. These results will assist us to design and investigate the formulation of these amphiphilic graft copolymers for use in applications such as stabilizers in colloidal systems as well as delivery vehicles.[36]

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Table 4. Fitting Parameters Obtained Using the Core−Shell Model with Polydispersity and Free Polymer (for 5 wt/v % PIP-*g*-P123 in (100%), (20:80), and (40:60) d_8-THF/d_6-ethanol) at 283 K

samples	PIP-*g*-P123: (40:60) THF/ethanol	PIP-*g*-P123: (20:80) THF/ethanol	PIP-*g*-P123: 100% ethanol
$Ø_{core}$	0.005 ± 0.0001	0.012 ± 0.0001	0.015 ± 0.0002
$Ø_{corona}$	0.001 ± 0.009	0.006 ± 0.0001	0.007 ± 0.0001
R_{in}/Å	204 ± 6.8	165 ± 1.7	168 ± 1.7
R_{out}/Å	226 ± 136	230 ± 113	235 ± 27
L/Å	22	65	67
σ	0.28	0.26	0.23
$R_{g(free\ polymer)}$/Å	22 ± 1.1	17 ± 0.32	17 ± 0.39
$Ø_{free\ polymer}$	0.002 ± 0.003	0.003 ± 0.001	0.002 ± 0.0002
N_{agg}	788 ± 314	417 ± 4.9	440 ± 4.9

■ ASSOCIATED CONTENT

Supporting Information

Additional details of the characterization of the AGCs including bulk structure by ^{1}H NMR, number of grafts by PFGSE-NMR, and molecular weight distribution by GPC. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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