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# Rheology of Thermoreversible Hydrogels from Multiblock Associating Copolymers

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**ABSTRACT:** Multiblock copolymers of poly(ethylene oxide)<sub>99</sub>-poly(propylene oxide)<sub>67</sub>-poly(ethylene oxide)<sub>99</sub> (F127) were synthesized by chain extending with hexamethylene diisocyanate (HDI). The resulting multiblock copolymer poly-F127 maintained the thermoreversible properties of the original F127 triblock copolymer. The rheological and structural properties of the gels were characterized as a function of temperature, composition and degree of polymerization. Neutron scattering reveals that a large degree of alignment can be induced in the F127 gel, but no long-range order could be found in the multiblocks or the mixtures of F127 with multiblocks. The shear strain at yield in polymers having an average of 3.2 or more F127 repeats was nearly an order of magnitude higher than in the F127 gel. For F127 solutions just below their gel point, substitution of F127 with as little as 1% multiblock succeeded in forming a physical gel. Percolation theory was used to understand the modulus growth when multiblock was added to F127 solutions just below their gel point, assuming the multiblocks form bridges between adjacent micelles.

## Introduction

Nonionic amphiphilic triblock copolymers of poly(ethylene oxide)<sub>99</sub>-poly(propylene oxide)<sub>67</sub>-poly(ethylene oxide)<sub>99</sub> (Pluronic F127, PEO<sub>99</sub>-PPO<sub>67</sub>-PEO<sub>99</sub>) have attracted a great deal of attention due to their thermoreversible gel-like behavior.<sup>1–7</sup> Numerous studies have been performed using a battery of complementary techniques,<sup>8–17</sup> to try to understand the structure–property relations responsible for the formation of these “smart” gels. In general, both PPO and PEO are water soluble at low temperatures and hence the F127 copolymer chains are fully miscible in aqueous solution. As the temperature increases, the PPO block is no longer hydrated and becomes hydrophobic. As a result, when the concentration is larger than the critical micellization concentration (cmc) = 6.1 mg/mL,<sup>8,9</sup> individual micelles begin to form with a PPO core and PEO corona. Combining small-angle X-ray scattering (SAXS) and small angle neutron scattering (SANS), Wu et al. showed that the micelles had a mean radius close to 11 nm and an aggregation number of 60. When the block copolymer concentration was increased even further (> 15% w/w,  $T \approx 30$  °C) the micelles spontaneously self-assembled into a face centered cubic structure.<sup>10</sup> Prud’homme et al. proposed that the ordered micelle structures were due to repulsive interactions among the close-packed spherical micelles.<sup>11</sup> The material therefore exhibits a gel-like rheological response, even though none of the components are physically or chemically cross-linked to each other. On the other hand, the lack of actual cross-links results in the F127 micelle gel having a very low yield strength as the micelle layers can easily slide past each other under shear.<sup>12</sup> Hence,

the rheological and structural properties of F127 gels limit their applications in some fields, such as tissue engineering and implantation, which requires high elastic modulus and yield strain.

In order to improve the mechanical properties of the gel, while still maintaining the thermo-reversibility, we synthesized multiblock copolymers, where the F127 triblocks would be repeated several times.<sup>4–7</sup> In this manner, physical interconnections between the micelles could occur as the multiblock copolymers formed interlocking loops and tails, thereby greatly increasing the mechanical strength of the gels. Furthermore, by adding even a small amount of the multiblock to the F127 gels, we propose a model where a large enhancement of the mechanical properties could occur, as the longer chains could span more than one micelle. This allows a new class of thermoreversible gels to be made, where the rheological properties can be tailored to specific applications.

## Experimental Section

Pluronic F127 (12 600 Da, 70% w/w PEO) was obtained from BASF (Mount Olive, NJ). Gel permeation chromatography (GPC) measurements indicated that the Pluronic F127 had a polydispersity index of  $M_w/M_n \sim 1.4$ . The deionized water came from a Millipore-Q water purification system. Hexamethylene diisocyanate (HDI) and the stannous 2-ethylhexanoate ( $\text{SnOct}_2$ ) catalyst were purchased from Aldrich and Sigma, respectively, and were used as received. The multiblocks were synthesized according to the procedures developed by Cohn et al.,<sup>18</sup> where identical units of F127 are linked together. A list of the copolymers used is presented in Table 1. The multiblock copolymers generated have the following general structure:  $[-\text{F127-HDI-}]_p$ , where  $p$  denotes the degree of polymerization, as shown in Figure 1. The molecular weight, polydispersity and degree of polymerization ( $p$ ) of the different polymers, were determined by gel permeation chromatography (Differential Separations Module Waters 2690 with Refractometer Detector Waters 410 and Millennium Chromatography Manager), using polystyrene standards between 472 and 360 000 Da. The elution solvent was chloroform and the flow was 1 mL/min. The

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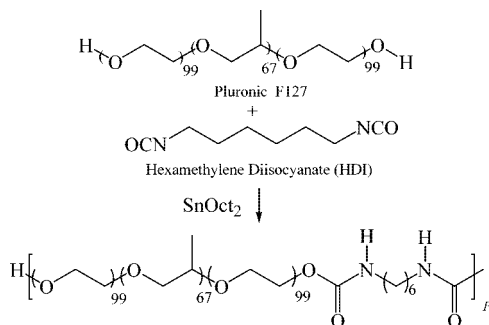
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**Table 1. Molecular Characteristics of Triblock F127 and the Multiblock Copolymers**

name	degree of polymerization <sup>a</sup> (p)	molecular weight (g/mol)	polydispersity ( $M_w/M_n$ )
F127 $\equiv$ PF1.0	1.0	12600	1.40
PF1.9	1.9	23900	1.63
PF2.5	2.5	31500	1.67
PF3.2	3.2	40300	1.46
PF4.6	4.6	58000	1.85
PF5.6	5.6	70600	2.08
PF6.0	6.0	75600	1.44

<sup>a</sup> Degree of polymerization was calculated as the ratio of GPC molecular weight and that of the "monomeric" F127 (which we run with all samples as an internal standard).

**Figure 1.** Chain extension of Pluronic F127 with hexamethylene diisocyanate.

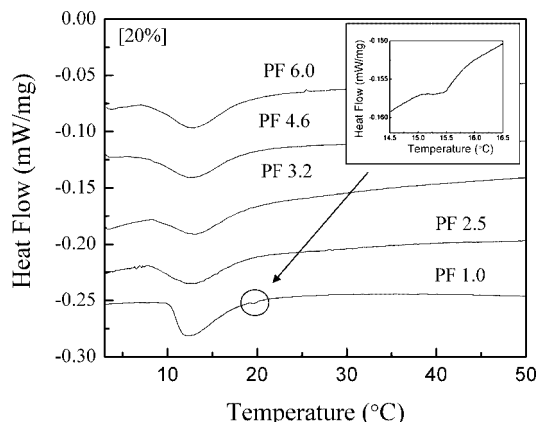
degree of polymerization of  $P[F127]_p$  was calculated from the ratio of  $M_{nPF127p}/M_{nF127}$ , as determined by GPC. These data indicated that the molecular weight increased from 12,600 for the native F127, up to 58,000, for a material with  $p = 4.6$ . This polymer is denoted by PF 4.6. A variety of similar multiblocks were synthesized and their GPC molecular weights and polydispersity indices are listed in Table 1.

The gels were prepared by dissolving various amounts of the different polymers in deionized water which was stirred in an ice–water mixture at  $\sim 2^\circ\text{C}$  for 2 h. These solutions were then refrigerated at  $4^\circ\text{C}$  for 1–2 days to ensure that all the polymers were fully dissolved.

A Mettler Toledo DSC821 scanning calorimeter was used to study the heat capacity of solutions as a function of temperature. Typically 6–12 mg solutions were placed in aluminum pans, which were then carefully sealed. The scans were carried out in a dry nitrogen environment at a constant heating rate of  $1^\circ\text{C}/\text{min}$  between 2 and  $50^\circ\text{C}$ , with an empty aluminum pan as reference.

To study the structure of the Pluronic F127 and the multiblock copolymer gels, SANS experiments were performed at the National Institute of Standards and Technology reactor division. Data were collected on an area sensitive detector at the NG3 (NIST/Exxon/U.Minn) SANS beamline, with sample to detector distance of 3.45 m. The nominal wavelength of the neutrons was  $6.00\text{ \AA}$  with a dispersity  $\Delta\lambda/\lambda$  of 0.10 and an average incident intensity of approximately 464 500 neutrons/s. The accessible range in  $q \equiv (4\pi/\lambda) \sin(\theta/2) = 0.0055$  to  $0.1858\text{ \AA}^{-1}$ , where  $\theta$  is the angle between incident and scattered beam. The samples were placed inside a sample holder with a width of 5 mm. Samples were loaded carefully at  $2^\circ\text{C}$  to minimize the shear effects, and then temperature was increased to  $37^\circ\text{C}$  and stabilized for 20 min.

Rheological measurements of polymer gels were performed on a strain-controlled rheometer, Rheometrics Fluids Spectrometer II (RFS II), using concentric cylinders, with an inner diameter of 16.5 mm, an outer diameter of 17.1 mm, and 13.7 mm height. Temperature control was achieved by using a water bath surrounding the outer cylinder. The concentric cylinder geometry was loaded with the polymer solutions at  $2^\circ\text{C}$  (liquid state). Temperature sweep measurements were performed at a constant heating rate of  $1^\circ\text{C}/$

**Figure 2.** DSC measurements on the 20% solutions of different multiblock copolymers at  $1^\circ\text{C}/\text{min}$  heating rate.

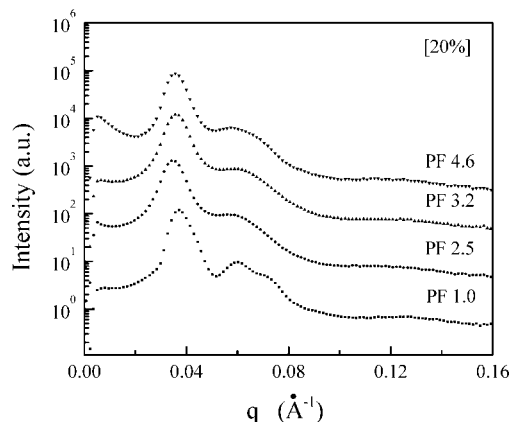
min. Low viscosity silicone oil was added to the surface of the sample to minimize evaporation of water.

The instrument was used in the oscillatory mode, in which the outer cylinder is rotated sinusoidally at a given frequency. The frequency dependence of the complex modulus was determined between 0.01 and 100 rad/s. The sol–gel transition temperature of polymer gels was determined from an oscillatory shear temperature sweep at 1 rad/s. The sol–gel transition temperature was measured for all the gels, operationally defined here as the temperature at which the storage modulus  $G'$  was half of the largest value for the high-temperature gel.<sup>19</sup> A parallel plate set up for the strain sweep test was used to obtain enough torque. In this case, we were just looking for the yield of the system, rather than absolute evaluation of the magnitudes.

## Results

**Differential Scanning Calorimetry.** DSC measurements were carried out on F127 and multiblock copolymer solutions. The results are shown in Figure 2, where we see that a large endothermic peak occurs, at the same position,  $T \approx 12^\circ\text{C}$ , for all the Pluronic gels, which has been shown to arise from the desolvation of the PPO groups.<sup>15</sup> The peak is broader for the multiblock copolymers than for the basic F127 triblock, indicating that the desolvation process may be partially hindered by the block structure. A second small peak (enlarged in the inset) is also apparent for F127 at  $T \approx 20^\circ\text{C}$ . This peak was previously reported by Wanka et al.<sup>20,21</sup> who attributed it to the transition from an isotropic micelles solution to cubic packing of micelles. The endothermic nature of the transition was postulated to be caused by slight desolvation of the PPO block which was required in order to modify the micelle structure during packing into the cubic phase. This small peak is not observed for the multiblock copolymers, implying that, as we will show later, they do not form well-ordered cubic structures.

**SANS.** In order to determine the micelle structure of the copolymers, we performed small angle neutron scattering. The scattering at small angles is usually attributed to the Bragg diffraction caused by interparticle interference, while the scattering at larger angles is recognized as intraparticle scattering. A detailed discussion of the structure of the micelle gel formed in the F127 system is given in ref 12. In Figure 3 we compare the structures of the PF copolymers with that of F127 for increasing degrees of polymerization,  $p$ . The curves shown reveal that as  $p$  increases the resolution to observe the higher order peaks decreases. On the other hand the position of the primary peak is unchanged. Using the relationship,  $d_{hkl} = a/(h^2 + k^2 + l^2)^{1/2}$ , where  $h, k, l$ , are the Miller indices and  $a$  is the dimension of a unit cell, the nearest neighbor distance between micelles in an FCC packing ( $d \approx 17.2\text{ nm}$ ) was obtained. The



**Figure 3.** SANS scattering profiles on the 20% solutions of different PF copolymers gels at 37 °C at rest.

second set of peaks, which are clearly resolved in the F127 copolymer, but overlapping for the multiblock structure, indicate that the micelles adopt an FCC structure when gelation occurs.<sup>9</sup> The second peak is actually a doublet corresponding to the (220) and (311) plane reflections, which are barely resolved for the F127 polymer, but nonexistent for the multiblocks, indicating significantly less long-range order in the latter.

Figure 4 shows SANS scattering patterns from 20% solutions of F127 (Figure 4a), PF4.6 (Figure 4b) and a mixture containing 2% multiblock, and 18% F127 (Figure 4c) at rest (leftmost) and at shear rates of 1, 10, and 100 s<sup>-1</sup>, moving from left to right. As clearly shown by the figures, F127 becomes increasingly oriented with shear. The onset of the orientation was previously shown by Jiang et al.,<sup>12</sup> to occur almost immediately at shear rates of 0.01 s<sup>-1</sup>. On the other hand, the pure multiblock systems become disordered with increasing shear. The structure of F127 under a transition from a face center cubic (FCC) lattice to a two-dimensional hexagonal close packing (HCP) layered structure under steady shear.<sup>12</sup> However, parts b and c of Figure 4 demonstrate that no layered structures were formed by any of the multiblock gels. In fact, the ring nearly disappears altogether for the multiblocks. In ref 12, the alignment was described as planes of micelles that slide across each other under steady shear. Gliding planes are not possible unless bridges stay within a plane. It is interesting to note that in the mixture of the two gels, the behavior under shear is much closer to that of the multiblock than to the response of the single triblock structure, again indicating that even a small amount of interconnected micelles is sufficient to destroy the long-range order previously observed for F127 FCC gels.<sup>10,12</sup>

**Rheology.** The rheological behavior of the multiblock copolymers was studied as a function of concentration and degree of polymerization, and the results were compared to that of the F127 triblock at the same total copolymer concentration. Figure 5 compares linear viscoelastic data in the form of frequency sweeps at 37 °C for 20% PF 3.2 and 20% F127 (inset). The two samples exhibit similar storage modulus but the PF 3.2 gel shows more relaxation (higher loss modulus and stronger frequency dependence of storage modulus) in the rubbery plateau, owing to its less perfect structure. In contrast, the FCC structure of the F127 gel has  $\tan \delta \equiv G''/G' < 0.1$  in the midst of the rubbery plateau, suggesting minimal relaxations in F127 for  $1 < \omega < 5$  rad/s.

Figure 6 reports strain sweep data for 20% F127, PF 3.2 and PF 4.6 gels at 1 rad/s and 37 °C. The F127 gel begins to yield starting at very low strain (0.01), consistent with the sliding plane model proposed from analysis of the SANS data.<sup>12</sup> As long as the planes are not physically connected they can easily slide past each other. An abrupt change can be seen in the

response of all copolymers with degree of polymerization exceeding three. These materials have slightly higher modulus than the F127 gel but twenty times larger yield strain (0.2). The considerably larger yield strain is consistent with the expected structure, with multiblock chains spanning (and connecting) several micelles in different layers. To focus on the linear response, we utilize a strain amplitude of 0.001 in what follows.

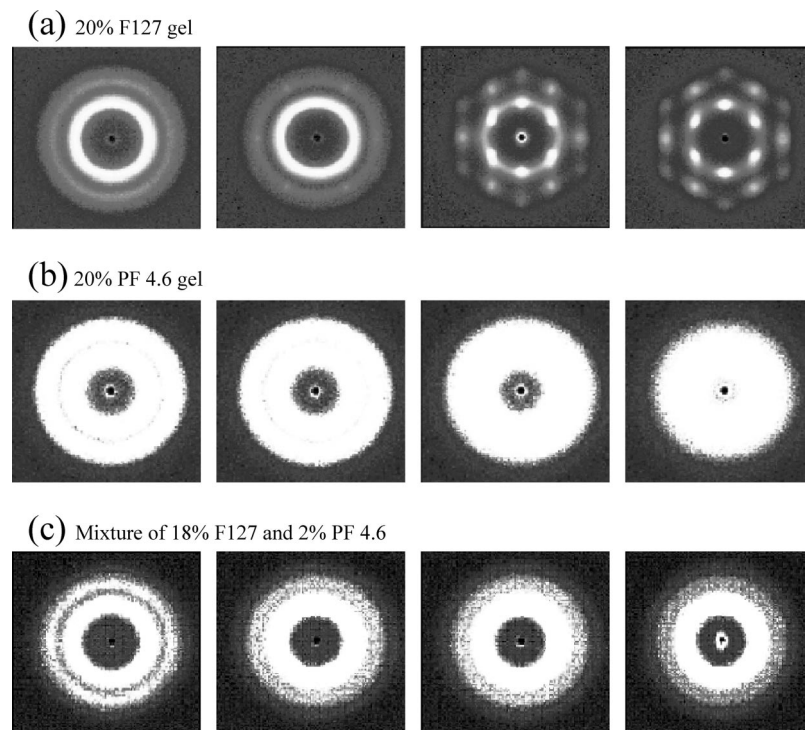
**PF Multiblock Gel.** Figure 7 presents temperature sweeps at 1 rad/s for different concentrations of PF 3.2, showing that the storage modulus ( $G'$ ) sharply increases with temperature, near the gel point, for all concentrations greater than 5%. This abrupt increase in  $G'$  becomes more pronounced and takes place within a narrower temperature interval, as the concentration of PF 3.2 increases. Polymer solutions of 5% or lower do not gel even at high temperature. In Figure 8, we plot the highest value of  $G'$  attained by PF3.2 gels, as a function of its concentration. In the inset in Figure 8, a gelation temperature ( $T_{\text{gel}}$ ) versus concentration curve is presented. As apparent from the data shown, the storage modulus of the gel increases by more than 3 orders of magnitude when the concentration of polymer increases from 5 to 10%. The modulus continues to increase with concentration above 10%, but at a much slower rate. Hence, an additional important difference between the F127 triblock and the PF 3.2 multiblock is the concentration needed for the onset of gelation. While the minimal concentration required for a detectable reverse thermo-responsive behavior was determined by Sosnik and Cohn<sup>22</sup> to be 14.6, PF 3.2 gels already at concentrations below 9%. The inset of Figure 8 shows that the gelation temperature of PF 3.2 has a similar concentration dependence to that observed for F127.<sup>15,21,23</sup>

The temperature dependence of the storage modulus at  $\omega = 1$  rad s<sup>-1</sup> for multiblock copolymers with different degree of polymerization at a fixed concentration of 20% is shown in Figure 9. The gelation temperature seems to be fairly independent of the degree of polymerization (for  $\text{PF} > 3$ ), consistent with the assumption that the gelation temperature is mainly due to desolvation of the PPO block. Hence, the interconnected micelles that are created can form a gel, even if they do not form an ordered lattice, as is the case for F127. The maximum of the temperature dependence of  $G'$  (1 rad s<sup>-1</sup>) for each sample in Figure 9, increases with degree of polymerization but rapidly levels off, as shown in Figure 10. The largest difference occurs between a degree of polymerization of 1 (F127 triblock) and a degree of polymerization of 2.5. No significant increase occurs for larger multiblock copolymers. These results indicate that the rheological behavior of the multiblock is due to formation of a reversible physical gel, or a network of interconnected micelles at high concentration.

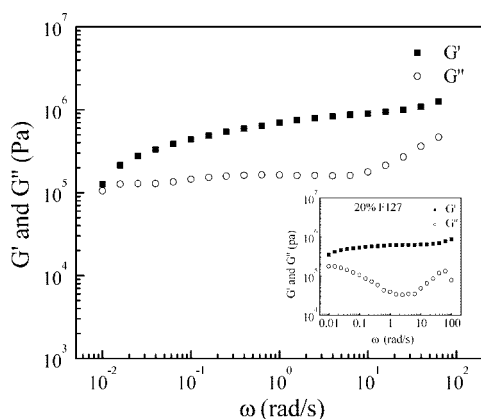
**Mixtures of F127 and PF Multiblock Copolymer.** In order to determine whether the addition of PF multiblock copolymer could enhance the viscoelastic response of the F127 gel, we measured the storage modulus of F127 gels mixed with PF 4.6. In Figure 11, we plot the elastic modulus,  $G'$ , of a gel composed of a total of 25% by weight polymer, consisting of a mixture of F127 and PF 4.6, with the concentration of the latter increasing up to 5%.  $G'$  increases sharply as the multiblock is added, eventually leveling off at a value 1 order of magnitude higher than that of the pure F127 triblock, at the same concentration. It is worth stressing that at an overall concentration of 25%, the F127 solution is far above the micelle gel concentration. Yet, despite the relatively low concentration of multiblock, it is effective in raising the modulus by nearly an order of magnitude.

A much more dramatic effect can be seen when the multiblock copolymer is added to an F127 solution just below its gelation concentration of 15%. In Figure 12, we show the





**Figure 4.** SANS scattering patterns for (a) 20% F127 gel, (b) 20% PF 4.6 gel, and (c) a mixture of 18% F127 and 2% PF 4.6, with increasing shear rate of 0, 1, 10, and 100 1/s. Shear direction is perpendicular to the beam direction.

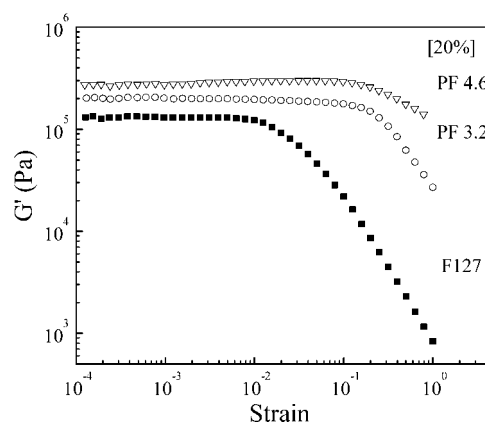


**Figure 5.** Frequency dependence of storage and loss modulus of 20% PF 3.2 and 20% F127 (inset) at a strain of 0.001 and 37 °C.

temperature dependence of the storage modulus of F127, when mixed with varying amounts of PF 4.6, where the total polymer concentration is fixed at 14.5%. The 14.5% solution of F127 is liquid-like at all temperatures. Addition of 4.83% PF 4.6 multiblock increases the modulus by nearly 3 orders of magnitude, at 40 °C, indicating that the gel has already formed. The percolation theory,<sup>24</sup> states that the modulus of a system close to its gel point follows a power law. We apply these percolation ideas to the concentration of multiblock  $c$  and the concentration of multiblock corresponding to the gel point  $c_{\text{gel}}$ .

$$G \sim \left( \frac{c - c_{\text{gel}}}{c_{\text{gel}}} \right)^{(\beta+1)/\sigma} \quad (1)$$

For a three-dimensional percolation, the exponents are  $\beta = 0.41$  and  $\sigma = 0.45$ , making  $(\beta + 1)/\sigma = 2.6$ . Figure 13 shows the plot of  $(G'_{\text{max}})^{0.38}$  as a function of concentration for the different multiblocks, where a good fit is obtained without any other free parameters, indicating that the classical gelation theory is applicable to this system. This is in contrast to the pure F127



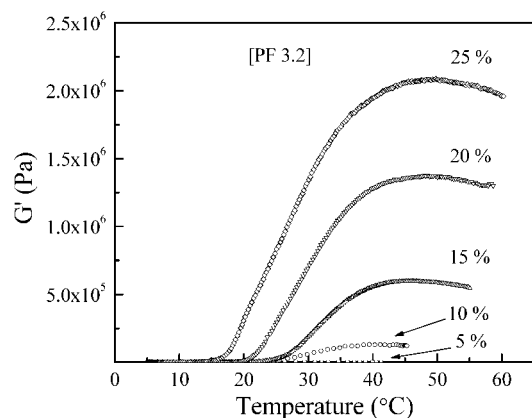
**Figure 6.** Storage modulus as a function of strain amplitude for 20% gels of F127 and different PF multiblock copolymers at a frequency 1 rad/s and 37 °C.

solutions, known to be composed of unconnected micelles, forming a FCC crystal of micelles.<sup>10,12</sup> Addition of the multiblocks, physically connects the isolated micelles, hence the ordering into the FCC lattice which occurs at higher concentration is no longer needed to form a physical gel.

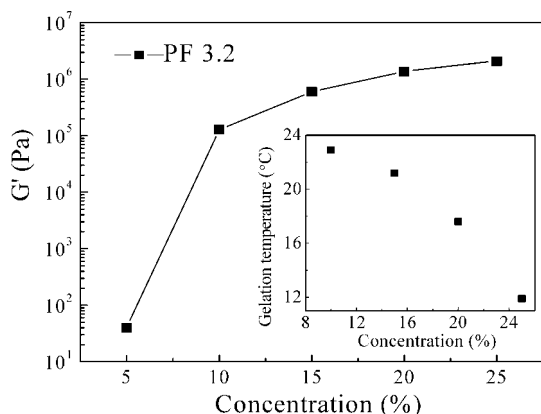
In order to estimate the percolation concentration,  $c_{\text{gel}}$ , for each multiblock, we note the concentration at which the data in the linear regions shown in Figure 13, extrapolate to a zero modulus. These gel concentrations are all close to  $c_{\text{gel}} = 1\%$  multiblock, apparently independent of the degree of polymerization of the multiblocks.

## Discussion

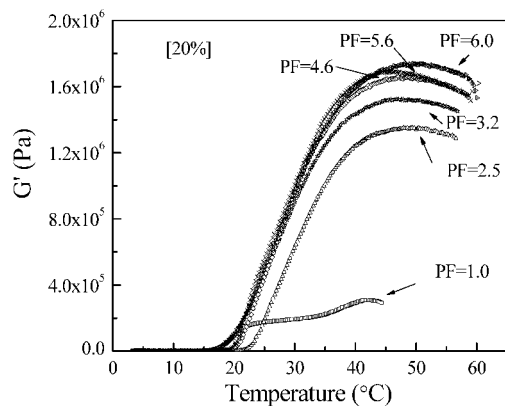
In the absence of multiblock copolymer, SAXS data<sup>10</sup> indicate that the polymer solution of 14.5% is far above its critical micellization concentration (CMC), and that the F127 triblock exists in the form of micelles ( $\sim 20$  nm in diameter). When the F127 concentrations are above the critical gelation concentration



**Figure 7.** Storage modulus of different concentrations of PF 3.2 polymer gels during heating at 1 °C/min at a frequency of 1 rad/s and strain amplitude of 0.001.



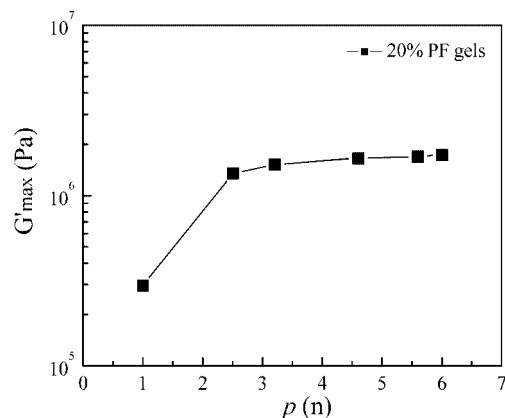
**Figure 8.** Storage modulus and gelation temperature (inset) of PF 3.2 gels as functions of concentration.



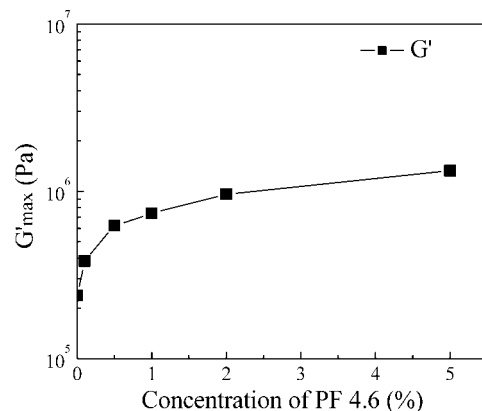
**Figure 9.** Storage modulus of 20% polymer gels during heating at 1 °C/min at a frequency of 1 rad/s and strain amplitude of 0.001.

(~15%), the gels spontaneously order into an FCC structure of close packed micelles, which obstructs flow and increases the viscosity. Since the F127 micelles are not physically connected, this structure yields easily in shear and at a shear rate of 0.01 s<sup>-1</sup>, planes of micelles slide past each other.<sup>12</sup>

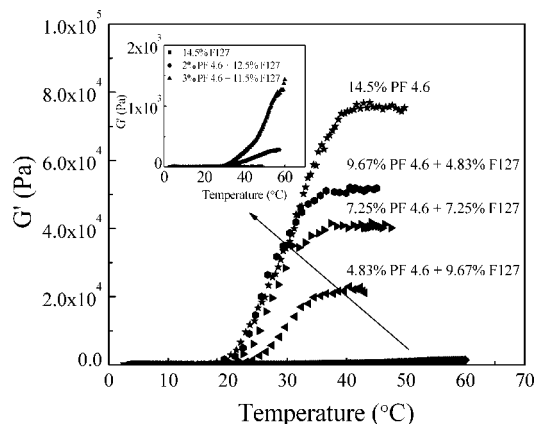
At the concentration of 14.5%, SANS data indicate no long-range order in the F127 solution.<sup>12</sup> From the rheological data on the pure multiblock solutions, we know that a physical gel forms, at a critical concentration of slightly below 9%. Therefore, when we only add a small amount of the multiblock to F127 solutions, it can be assumed that there is insufficient copolymer to form the FCC structure of close packed micelles. Instead, the copolymer chains may become incorporated into



**Figure 10.** Maximum storage modulus of 20% polymer gels as a function of degree of polymerization.



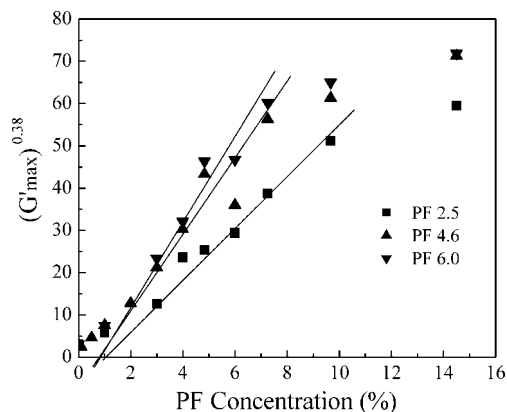
**Figure 11.** Storage modulus of 25% polymer gels of F127/PF 4.6 mixtures as a function of the concentration of PF multiblock copolymer.



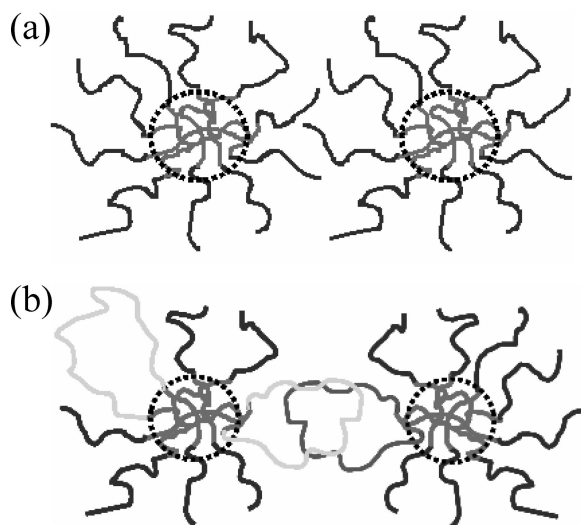
**Figure 12.** Storage modulus of F127 and F127/PF 4.6 mixtures, all with an overall concentration of 14.5%, during heating at 1 °C/min at a frequency of 1 rad/s and strain amplitude of 0.001. (The inset represents the storage modulus of low PF 4.6 concentrations which is not distinguishable in the scale of the original figure.)

the F127 micelles, as shown in Figure 14. The multiblocks can form connections between micelles (Figure 14b) resulting in physical cross-links between the micelles. The nature of these connections may occur either through one chain spanning over two micelles or entangled chains of different micelles, generating interconnecting loops.

In order to estimate the relative probability of this conformation we ran a self-consistent field calculation (SCF) of polymer chains that can connect between adjacent micelles.<sup>25</sup> In the



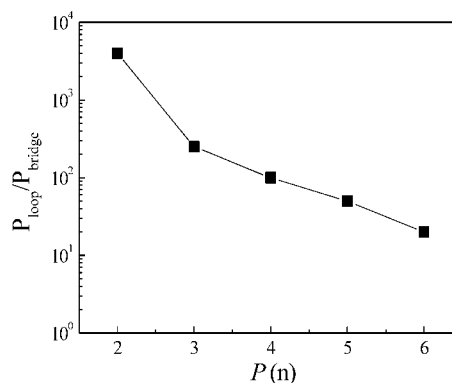
**Figure 13.** Maximum value of the (high temperature) storage modulus of gels made by mixing F127 with three different multiblocks, all with an overall concentration of 14.5%, as a function of the concentration of PF multiblock copolymers. Equation 1 suggests that this plot should yield a straight line that extrapolates to  $c_{gel}$  at  $G = 0$ .



**Figure 14.** Schematic diagram for intermicellar interaction with corresponding observations in scattering and rheology measurements: (a) F127 triblock copolymer; (b) a mixture of F127 and PF multiblock copolymers.

calculation, which is a lattice method, we consider multiblock chains (that have the same degree of polymerization as the experimental system) as tracer chains. The tracer chains are constrained such that one end of the chain is fixed at the core of one of the micelles. We then examine the concentration profiles of the tracer chains as a function of the number of blocks in the tracer chain ( $n$ ) for a fixed intermicellar spacing of  $\sim 20.5$  nm.<sup>12</sup> To check that we were probing the statistics of a single chain, we also calculated the probability distribution of the end to end distance of the chain, when it was located far away from the micelle surface and confirmed that it obeyed Gaussian statistics for a single chain. In Figure 15, we plot the ratio of the probabilities that a tracer chain forms a loop or a bridge between the micelles. We can see from the figure that the short blocks ( $p = 2$ ) are the most likely to form loops. As  $p$  increases the probability drops sharply, but loops are still at least ten times more likely even for  $p = 6$ .

Figure 13 suggests that the percolation concentration,  $c_{gel}$ , is 1% multiblock. Knowing the concentration of F127 and the aggregation number of F127 micelles,<sup>10</sup>  $N = 60$ , and the coordination number of the micelles, we estimate that  $c_{gel} = 1\%$  multiblock corresponds to 0.966 multiblock chains per micelle for 1% PF 4.6 in 13.5% F127 solutions with an overall



**Figure 15.** Probabilities of loops versus bridges as a function of degree of polymerization.

concentration of 14.5%. The number of 0.966 suggests that each PF 4.6 chain contributes, on average, one intermicellar cross-link, as the gel point corresponds to one cross-link per structural unit.<sup>17</sup> This number is consistent with an interconnected chain connection between micelles, since a simple bridge would have required one chain bridging two micelles, while a loop type connection involves at least one chain per micelle, in agreement with the experimental results.

## Conclusion

Multiblock copolymers of poly(ethylene oxide)<sub>99</sub>-poly(propylene oxide)<sub>67</sub>-poly(ethylene oxide)<sub>99</sub> were synthesized by chain extending with hexamethylene diisocyanate (HDI). The resulting multiblock copolymer P[F127]<sub>p</sub> maintained the thermoreversible properties of the original F127 triblock. The rheological and structural properties of the gel were characterized as a function of temperature, composition and degree of polymerization. Mixtures of multiblocks and F127 triblocks, were also studied. Using neutron scattering we found that a large degree of alignment could be induced in the F127 gel,<sup>12</sup> but no long-range order could be found in the gels formed in multiblock solutions or in the F127/multiblock mixed solutions. The yield strain of gels formed by multiblocks consisting of 3.2 or more triblocks was nearly an order of magnitude higher than that of the F127 gel, making these multiblocks and their mixtures with F127, potentially useful for biomedical applications. For F127 solutions slightly below the concentration needed to form a gel, substitution of F127 with multiblocks at constant overall concentration forms a gel, with a modulus described by the percolation theory.

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## References and Notes

- (1) Xiong, X. Y.; Tam, K. C.; Gan, L. H. *J. Nanosci. Nanotechnol.* **2006**, *6*, 2638–2650.
- (2) Chun, K. W.; Lee, J. B.; Kim, S. H.; Park, T. G. *Biomaterials* **2005**, *26*, 3319–3326.
- (3) Higuchi, A.; Yamamoto, T.; Sugiyama, K.; Hayashi, S.; Tak, T. M.; Nakagawa, T. *Biomacromolecules* **2005**, *6*, 691–696.
- (4) Cohn, D.; Sosnik, A.; Garty, S. *Biomacromolecules* **2005**, *6*, 1168–1175.
- (5) Sosnik, A.; Cohn, D. *Biomaterials* **2005**, *26*, 349–357.
- (6) Cohn, D.; Sosnik, A. *J. Mater. Sci.: Mater. Med.* **2003**, *14*, 181–186.
- (7) Cohn, D.; Sosnik, A.; Malal, R.; Zarka, R.; Garty, S.; Lando, G. *Polym. Adv. Technol.* **2007**, *18*, 731–736.
- (8) Mortensen, K.; Talmon, Y. *Macromolecules* **1995**, *28*, 8829–8834.
- (9) Alexandridis, P.; Holzwarth, J. F.; Hatton, T. A. *Macromolecules* **1994**, *27*, 2414–2425.
- (10) Wu, C.; Liu, T.; Chu, B.; Schneider, K. D.; Graziano, V. *Macromolecules* **1997**, *30*, 4574–4583.

- (11) Prud'homme, R. K.; Wu, G.; Schneider, D. K. *Langmuir* **1996**, *12*, 4651–4659.
- (12) Jiang, J.; Burger, C.; Li, C.; Lin, M. Y.; Rafailovich, M. H.; Sokolov, J. C. *Macromolecules* **2007**, *40*, 4016–4022.
- (13) Ivanova, R.; Lindman, B.; Alexandridis, P. *Adv. Colloid Interface Sci.* **2001**, *89*, 351–382.
- (14) Perreur, C.; Habas, J. P.; Francose, J.; Peyrelasse, J. *Phys. Rev. E* **2002**, *65*, 41802–41808.
- (15) Pozzo, D. C.; Hollabaugh, K. R.; Walker, L. M. *J. Rheol.* **2005**, *49*, 759–782.
- (16) Hamley, I. W.; Pople, J. A.; Fairclough, J. P. A.; Booth, A. J. C.; Yang, Y.-W. *Macromolecules* **1998**, *31*, 3906–3911.
- (17) Eiser, E.; Molino, F.; Porte, G.; Pithon, X. *Rheol. Acta* **2000**, *39*, 201–208.
- (18) Cohn, D.; Sosnik, A.; Levy, A. *Biomaterials* **2003**, *24*, 3707–3714.
- (19) Edsman, K.; Carlfors, J.; Peterson, R. *Eur. J. Pharm. Sci.* **1998**, *6*, 105–112.
- (20) Wanka, G.; Hoffmann, H.; Ulbricht, W. *Macromolecules* **1994**, *27*, 4145–4159.
- (21) Wanka, G.; Hoffmann, H.; Ulbricht, W. *Colloid Polym. Sci.* **1990**, *268*, 101–117.
- (22) Sosnik, A.; Cohn, D. *Biomaterials* **2004**, *25*, 2851–2858.
- (23) Ricci, E. J.; Bentley, M.; Farah, M.; Bretas, R.; Marchetti, J. M. *Eur. J. Pharm. Sci.* **2002**, *17*, 161–167.
- (24) Rubinstein, M.; Colby, R. H. *Polymer Physics*; Oxford University Press: New York, 2003.
- (25) Pu, Y.; Rafailovich, M. H.; Sokolov, J. C.; Gersappe, D.; Peterson, T.; Wu, W.-L.; Schwarz, S. A. *Phys. Rev. Lett.* **2001**, *87*, 206101.

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