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Electrospinning Physical Gels: The Case of Stereocomplex PMMA

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PMMA is used in many applications in everyday life, for example, as plexiglass, bone cement, or tooth fillings, etc. We are used to thinking about PMMA as an amorphous, brittle, glassy polymer whose main advantage is the ease of polymerization. However, their monomeric units are prochiral, and hence, the resulting polymer chain contains a series of chiral centers, which can be arranged in three different ways: (i) randomly arranged in the atactic PMMA (a-PMMA), (ii) all having the same configuration (R or S) in an isotactic PMMA (iso-PMMA), and (iii) regularly alternating chiral centers in a syndiotactic PMMA (syn-PMMA). Both stereoregular forms of PMMA adopt helical structures[1−3] and are crystalline,[4] while the most common, a-PMMA, is amorphous. An even more exciting structure, known as the *stereocomplex*,[5] forms via a stereospecific interaction when the two stereoregular forms of PMMAs are mixed together. This self-assembled stereocomplex, also crystalline with a well-defined melting point, was first observed in 1958 by Fox,[4] and its structure and properties have been extensively studied.[6−10] Previous reports showed that the two polymer chains form a double helix,[6,7] where the syndiotactic chain wraps around the isotactic chain in a 1:2 iso:syn ratio.[8,9] However, Yashima's group[10] later suggested that the stereocomplex forms a triple helix where an outer syn-PMMA helix wraps an inner iso-PMMA double helix. The very formation of the multiple-stranded helix gives rise to the increased melting temperature of the stereocomplex over the individual iso-PMMA or syn-PMMA.

The stereocomplex introduces a whole new array of interesting properties to PMMA.[8] Atactic PMMA does not crystallize, but stereocomplex PMMA helices can pack together and form crystals with a well-defined melting point.[4] The stereocomplex forms in the bulk after lengthy annealing, while it forms very quickly in solution. The complexation in solution is strongly solvent dependent.[11] Concentrated stereocomplex solutions in strongly complexing solvents form thermoreversible physical gels. The cross-linking points in these physical gels have been shown to be bundles of helices.[12] These properties have been recently utilized in various attempts to produce new supramolecular structures. For example, the stereocomplex formation has been used to form nonionic layer-by-layer assembly to produce hollow microparticles[13] and protein scaffolds,[14] while the physical gelation has been used to produce a highly porous interconnected network.[15]

When a composite consists of the same polymer as a matrix and reinforcing fiber, it is called self-reinforced composite or single-polymer composite. One of the main problems in self-reinforced PMMA composites using only a-PMMA is the temperature stability of oriented a-PMMA fibers.[16] At the temperatures required for the composite processing, which is far above the glass transition temperature of PMMA, most of the chain orientation in a-PMMA fibers is lost. In order to form self-reinforced PMMA composites, one needs to maintain the rigid fiber characteristics even at the processing temperature.

We have spun fibers from stereocomplex solutions using wet spinning and gel spinning and observed that the birefringence is not lost even after treating the fibers at 160 °C. Herein we present a method for electrospinning PMMA stereocomplex solutions and discuss how these solutions behave differently from regular PMMA polymer solutions. We ascribe these differences to the properties arising from the multiple helix stereocomplex formation, namely the possibility of physical gelation.

Electrospinning is a fiber spinning technique capable of producing submicrometer size fibers. A polymer solution is extruded from a syringe, and high voltage is applied at the syringe tip. The solution is expunged toward a grounded target, forming a Taylor cone. Bending instabilities result in a whipping instability,[17−19] which is responsible for making very thin, submicrometer size fibers (see Figure 1). During the electrospinning process, the solution undergoes rapid cooling due to the heat loss from solvent evaporation. The speed of the fluid jet is around 5 m/s, making the time-of-flight in our setup around 0.04 s.

Physical gelation is a phenomenon where a liquid undergoes a reversible liquid−gel transition. The physical cross-links in such a gel are reversible, in contrast to chemical gels where the cross-links are irreversible strong covalent bonds. This reversibility and the associated viscoelastic behavior during the transition from a liquid to a solid are of great interest anywhere where a sharp, reversible transition from liquid to solid is needed, such as fracturing fluids in oil drilling, manufacturing of solid objects through molding, etc. The three-dimensional network in a physical gel can undergo changes, as the bonds keep breaking and forming. In this paper, we show how the process of gelation affects the electrospinning of stereocomplex PMMA solutions.

Experimental Results

We have dissolved iso-PMMA and syn-PMMA (both from Polymer Source) in a 1:2 weight ratio in dimethylformamide (DMF, supplied by Aldrich, 99%) and heated the solution above the gelation temperature. DMF is classified as a "strongly complexing" solvent.[11] The stereocomplex formation and physical gelation occur rapidly and readily. We have determined the gelation temperatures for different overall polymer concentrations, as shown in Figure 2. Solutions were sealed in glass vials and kept at a set temperature for 30 min. After that, the vials were tipped over, and if the solution flowed liquidlike, it was determined to be liquid or sol. If the solution did not flow, it was determined to be a gel. Upon heating, the gel−sol transition is about 22 °C higher than the sol−gel transition upon cooling. This hysteresis is similar in all the concentration ranges previously studied.[20]

It is not possible to electrospin any material in solid or gel form; therefore, we first heated the stereocomplex PMMA/DMF mixtures above their upper gel points. The solutions were transferred into a custom-built electrospinning setup shown above and kept there until their temperatures reached the equilibrium at selected temperatures.

We first examined the relationship between the concentration and the morphology of the spun fibers at 91 °C. We found that

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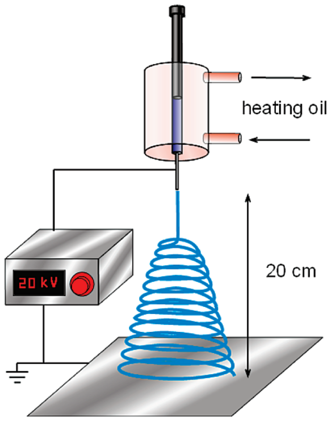

Figure 1. Schematic diagram of the electrospinning apparatus. The polymer solution is loaded in a syringe equipped with a nonconductive heating jacket. The temperature is controlled by an external thermostat with flow-through heating oil. The charged fluid jet undergoes bending and whipping and is collected on a grounded target.

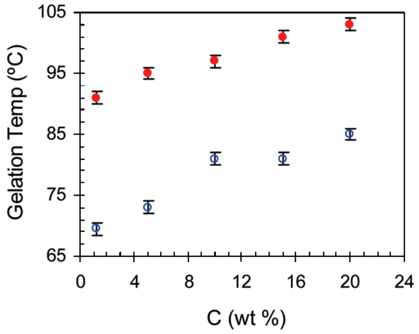

Figure 2. Gelation temperature at different concentration of 1:2 iso: syn-PMMA solutions in DMF. Filled circles represent the gel-to-sol transition temperatures upon heating, and open circles represent the sol-to-gel transition temperatures upon cooling.

stereocomplex PMMA solutions in DMF above the gelation temperature can be electrospun into continuous fibers at a very low concentration, which is lower than what is necessary for a-PMMA solutions of the same molecular weight.[21] We then examined the influence of temperature of the solution on fiber morphology in the 96−105 °C range. In Figure 3, we display the different morphologies produced from the stereocomplex solutions in the 1.25−5 wt % concentration range at several temperatures. At 1.25 wt %, beads connected with very thin fibers are produced, at 2.5 wt %, the beads are connected with fibers, whose diameter is on the same order of magnitude as the bead diameter, and at 5 wt % smooth stereocomplex fibers are produced. The presence of stereocomplex was confirmed by differential scanning calorimetry (DSC) analysis of the fiber mats, which showed a melting peak at 172 °C.

The morphology of the electrospun fibers did not change with temperature, and the diameter of the spun products was also unaffected. This behavior is in line with regular polymer solution behavior because the surface tension and viscosity of the solution do not change drastically with temperature in the range studied.

Discussion

The viscoelasticity and spinnability of a polymer solution are closely related to the solvent type, temperature, and polymer concentration. For a good solvent, where polymer−solvent interaction is favored over polymer−polymer interaction, the chains behave like a single molecule below C^*, the overlap concentration, related to molecular weight as $C^* \sim M^{-a} \sim M^{-0.5}$ from the Berry number and Mark−Houwink−Sakurada equation.[22] As the

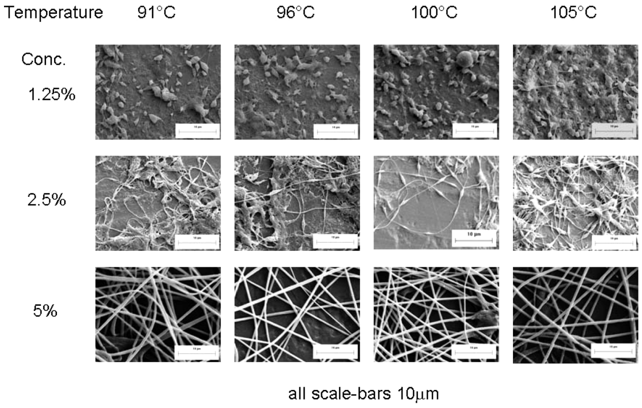

Figure 3. Effect of temperature and concentration of the spinning solution on the morphology of the electrospun stereocomplex PMMA. All the scale bars represent 10 μm.

name suggests, polymer chains start to overlap beyond the overlap concentration, and hence the viscosity of the system increases steeply with concentration above it. It has been shown that the formation of stereocomplex helices increases the persistence length and makes the polymer chain more rodlike.[23] In that case, the Mark−Houwink coefficient a becomes larger,[24] and the overlap occurs at a much lower concentration C^*. Thus, gelation can occur at a lower concentration than the C^* calculated for a Gaussian or a flexible chain. While the increase in viscosity is linear with concentration for dilute regime, it increases by $C^{4.5}$ in the semidilute regime. This is due to presence of entanglements that act as temporary cross-links and hence also impart gel-like elasticity to the polymer solution. Gupta et al. have determined that a-PMMA solutions in DMF need a concentration ratio C/C^* of at least 4 to produce smooth electrospun fibers.[21]

The C/C^* ratio of the 5 wt % stereocomplexing mixture that produced smooth fibers was 2 in our case, which is much lower than reported for linear a-PMMA polymers. We can attribute this to the helix formation and physical gelation during the electrospinning process. It has been shown previously that physical gels require a lower concentration to electrospin smooth, continuous fibers.[25] In our case, the comparison with a-PMMA is all the more relevant, as the only difference between the a-PMMA solution and the stereocomplex PMMA solution is the occurrence of physical gelation. Although stereocomplex-like interactions in atactic PMMA solutions in strongly complexing solvents (DMF is a strongly complexing solvent) have been detected by spectroscopic methods (NMR, FTIR)[26−28] and DSC,[28,29] the observation of physical gelation was not reported. Most likely the length of the isoatactic and syndiotactic sequences in atactic PMMA polymers was not sufficient to facilitate the formation of long helices and subsequent packing into bundles and gelation. For illustration, the average length of isotactic sequences reported in atactic PMMA was 1.33−1.53 monomer units,[28] while it takes 9 isotactic monomer units for one pitch of the helix.[30] During gelation, the polymer chains interact with each other and aggregate into a 3D percolated structure, essentially increasing the effective molecular weight of the system. The polymer chains can do this even below the critical overlap concentration C^*. Therefore, C^* is not the most important parameter that describes the interactions of a physical gel. The elastic modulus also increases during the gelation process. Recently, Yu et al. have determined that the elasticity of the fluid is more important for electrospun jet stability than the number of entanglements.[31] With solutions that will form physical gels, either argument can explain their peculiar behavior. The polymer chains associate in the solution, forming a cross-linked network. This structure increases the elasticity of the fluid and therefore stabilizes the fluid jet, resulting in smooth, continuous fibers at lower concentrations than those reported for noncomplexing linear polymers.

Conclusions

By examining the behavior of stereocomplex PMMA solutions during electrospinning, we have found that the heated solutions of stereocomplex PMMA undergo a sol−gel transition during electrospinning. The rapid evaporation of the solvent facilitates a temperature drop, which appears sufficient to bring the temperature of the fluid jet below its gelation temperature very quickly. The stereocomplex chains in the helical form pack to generate a percolating network, all of this within a short time frame of around 0.04 s. The evidence for this is the appearance of smooth fibers at a concentration lower than that of noncomplexing polymer ($C/C^* = 4$ for a-PMMA) and the presence of an endothermic melting peak at 172 °C in the DSC trace. These results offer the possibility of forming PMMA stereocomplex fibers that are more temperature resistant than regular a-PMMA fibers. Therefore, electrospun stereocomplex PMMA fibers can be used to reinforce the PMMA matrix in a variety of biomedical applications because the resultant self-reinforced composites will have much better interfacial strength while retaining the excellent biocompatibility of PMMA. The occurrence of physical gelation during the electrospinning process also opens the possibility of other transitions or reactions occurring during electrospinning.

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Supporting Information Available: Micrographs and DSC data. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Kusanagi, H.; Tadokoro, H.; Chatani, Y. *Macromolecules* **1976**, *9* (3), 531–532.
(2) Kusanagi, H.; Chatani, Y.; Tadokoro, H. *Polymer* **1994**, *35* (10), 2028–2039.
(3) Saiani, A.; Guenet, J. M. *Macromolecules* **1997**, *30* (4), 966–972.
(4) Fox, T. G.; Garrett, B. S.; Goode, W. E.; Gratch, S.; Kincaid, J. F.; Spell, A.; Stroupe, J. D. *J. Am. Chem. Soc.* **1958**, *80* (7), 1768–1769.
(5) Liquori, A. M.; Anzunino, G.; Coiro, V. M.; Dalagni, M.; Desantis, P.; Savino, M. *Nature (London)* **1965**, *206* (4982), 358–362.
(6) Schomaker, E.; Challa, G. *Macromolecules* **1989**, *22* (8), 3337–3341.
(7) Bosscher, F.; Tenbrinke, G.; Challa, G. *Macromolecules* **1982**, *15* (5), 1442–1444.
(8) Spevacek, J.; Schneider, B. *Adv. Colloid Interface Sci.* **1987**, *27* (1−2), 81–150.
(9) Hatada, K.; Kitayama, T. *Polym. Int.* **2000**, *49* (1), 11–47.
(10) Kumaki, J.; Kawauchi, T.; Okoshi, K.; Kusanagi, H.; Yashima, E. *Angew. Chem., Int. Ed.* **2007**, *46* (28), 5348–5351.
(11) Buter, R.; Tan, Y. Y.; Challa, G. *J. Polym. Sci., Part A: Polym. Chem.* **1973**, *11* (11), 2975–2989.
(12) Guenet, J. M. *J. Rheol.* **2000**, *44* (4), 947–960.
(13) Kida, T.; Mouri, M.; Akashi, M. *Angew. Chem., Int. Ed.* **2006**, *45* (45), 7534–7536.
(14) Matsuno, H.; Nagasaka, Y.; Kurita, K.; Serizawa, T. *Chem. Mater.* **2007**, *19* (9), 2174–2179.
(15) Kawauchi, T.; Kumaki, J.; Yashima, E. *J. Am. Chem. Soc.* **2006**, *128* (32), 10560–10567.
(16) Gilbert, J. L.; Ney, D. S.; Lautenschlager, E. P. *Biomaterials* **1995**, *16* (14), 1043–1055.
(17) Shin, Y. M.; Hohman, M. M.; Brenner, M. P.; Rutledge, G. C. *Appl. Phys. Lett.* **2001**, *78* (8), 1149–1151.
(18) Shin, Y. M.; Hohman, M. M.; Brenner, M. P.; Rutledge, G. C. *Polymer* **2001**, *42* (25), 9955–9967.
(19) Hohman, M. M.; Shin, M.; Rutledge, G.; Brenner, M. P. *Phys. Fluids* **2001**, *13* (8), 2201–2220.
(20) Chiang, R.; Burke, J. J.; Threlkel, Jo; Orofino, T. A. *J. Phys. Chem.* **1966**, *70* (11), 3591–3595.
(21) Gupta, P.; Elkins, C.; Long, T. E.; Wilkes, G. L. *Polymer* **2005**, *46* (13), 4799–4810.
(22) Larson, R. G. *The Structure and Rheology of Complex Fluids*; Oxford University Press: New York, 1999; p xxi, 663 p.
(23) Fazel, N.; Brulet, A.; Guenet, J. M. *Macromolecules* **1994**, *27* (14), 3836–3842.
(24) Millich, F.; Hellmuth, E. W.; Huang, S. Y. *J. Polym. Sci.: Polym. Chem. Ed.* **1975**, *13* (9), 2143–2150.
(25) Shenoy, S. L.; Bates, W. D.; Wnek, G. *Polymer* **2005**, *46* (21), 8990–9004.
(26) Spevacek, J.; Fernandezpierola, I. *Makromol. Chem., Macromol. Chem. Phys.* **1987**, *188* (4), 861–870.
(27) Spevacek, J. *Makromol. Chem., Macromol. Symp.* **1990**, *39*, 71–83.
(28) Gu, Q.; Song, R.; Shen, D. Y. *Polym. Bull.* **2000**, *44* (5−6), 533–538.
(29) Wang, J. J.; Zhao, J.; Gu, Q.; Shen, D. Y. *Macromol. Rapid Commun.* **2001**, *22* (12), 948–951.
(30) Kumaki, J.; Kawauchi, T.; Okoshi, K.; Kusanagi, H.; Yashima, E. *Angew. Chem.* **2007**, *119* (28), 5444–5447.
(31) Yu, J. H.; Fridrikh, S. V.; Rutledge, G. C. *Polymer* **2006**, *47* (13), 4789–4797.