

The Assembly of PPTA Nanofibers and the Applications

Subjects: Polymer Science

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Poly (*p*-phenylene terephthalamide) (PPTA) is one kind of lyotropic liquid crystal polymer. Kevlar fibers made from PPTA is widely used in many fields due to the superior mechanical properties resulted from highly oriented macromolecular structure. However, the “infusible and insoluble” characteristic of PPTA gives rise to its poor processability, which limits its scope of application. The strong interactions and orientation characteristic of aromatic amide segments make PPTA attractive in the field of self-assembly. The chemical derivations have proved an effective way to modify the molecular structure of PPTA to improve its solubility and amphiphilicity, which resulted in different liquid crystal behaviors or supramolecular aggregates, but the modification of PPTA is usually complex and difficult. Alternatively, higher order all-PPTA structures have also been realized through the controllable hierarchical self-assembly of PPTA from the polymerization process to the formation of macroscopic products. It briefly introduces the self-assembly methods of PPTA based materials in recent years, and focuses on the polymerization-induced PPTA nanofibers which can be further fabricated into different macroscopic architectures when other self-assembly methods are combined. This monomer-started hierarchical self-assembly strategy evokes the feasible processing of PPTA, and enriches the diversity of product, which is expected to be expanded to other liquid crystal polymers.

Keywords: poly (*p*-phenylene terephthalamide) ; liquid crystal polymer ; self-assembly ; nanofiber ; all-aramid material

1. Introduction

Poly(*para*-phenylene terephthalamide) (PPTA) is a kind of liquid crystal polymer prepared generally by polycondensation of *p*-phenylene diamine and terephthaloyl chloride at a low temperature. The products made from PPTA are also named *para*-aromatic amides, or in the abbreviation form *para*-aramids. In the 1970s, DuPont first dissolved PPTA in concentrated sulfuric acid when preparing a liquid crystal solution, and then the liquid crystal solution was fabricated into *para*-aramid fibers by a specially designed dry-jet wet-spinning process. *Para*-aramid fibers are widely used in aerospace, defense and military industries, and many important civil fields owing to its characteristics of high strength, high modulus, high temperature resistance, corrosion resistance and high dimensional stability ^{[1][2][3]}. Nevertheless, the “infusible and insoluble” characteristic of PPTA, which is attributed to its molecular rigidity, strong intermolecular hydrogen bonding and conjugation, makes it difficult to be processed via traditional methods. As a result, the fiber is the only product form that has been successfully industrialized on a large scale at present. Furthermore, the performance of *para*-aramid-fiber-enhanced composites is also challenged by the weak interfaces between *para*-aramid fibers and the matrix ^{[4][5]}. The development of novel PPTA adaptive processing strategies is practical and urgent.

Self-assembly refers to the behavior of basic structural units, including molecules and nanomaterials, that spontaneously organize or aggregate into higher-order structures under non-covalent bonding interactions ^{[6][7][8][9][10]}. The rigid planar conjugated structure and strong intermolecular interactions endow PPTA with strong tendencies in terms of orientation and self-assembly; however, the study is much retarded by the poor solubility of PPTA. Recently, interest in the self-assembly of PPTA has been relit by aramid nanofibers. No matter whether the aramid nanofibers are made with the “top down” or “bottom up” method, the essential structure consists of ordered aggregation of PPTA at the nano-scale. Therefore, retroactive research on PPTA self-assembly strategies over the years should be important and suggestive for the further design of PPTA or more high-performance polymers.

2. Self-Assembly of PPTA

The rigid rod-like structure lacking the flexibility of soft segments is facilitated by the planar conjugation and ordered hydrogen bonding of PPTA molecules, but also results in poor solubility, and PPTA can only be dissolved in concentrated sulfuric acid. The famous Kevlar[®] fibers are fabricated through dry-jet wet-spinning of a PPTA/concentrated sulfuric acid solution, followed by a washing, hot stretching and winding process. Various techniques are applied to analyze the structure of aramid fibers, such as diffraction, electron microscopy, atomic force microscopy and scanning tunneling

microscopy. It has been more and well more recognized that the extraordinary mechanical properties of aramid fibers (which have high crystallinity) are derived from the highly ordered microstructure formed through the self-assembly of PPTA during the fabricated process. The angle between the amide and carbonyl end groups is 160° , as calculated from XRD data, and the characteristic distance of adjacent PPTA chains is 3 \AA , suggesting it is the strong hydrogen bonding which links the adjacent chains to the lattice planes [11]. In addition, based on the observed result, a skin-core conceptual model of aramid fiber is well accepted. A high degree of 3D ordered crystallinity exists at the core region, and the strong 1D macromolecular orientation dominates in the skin region, which is generally non-crystalline. Hence, the outstanding mechanical properties of aramid fibers originate from the radially anisotropic, hierarchically ordered microstructures [12].

In 2016, Tuo's group developed a novel self-assembly method to prepare the polymerization-induced aramid nanofiber (PANF) [13]. The researcher introduced methoxy polyethylene glycol (mPEG) into the copolymerization system as the dispersing agent for controlling the aggregation degree of PPTA molecular chains and stabilizing the formed aggregations. With the assistance of mPEG, PANF with the diameter range of 20–50 nm could be directly fabricated during the polymerization and dispersed uniformly in an aqueous system. Similarly to the chemically modified PPTA described above, the copolymerization of the flexible segments would result in a decrease in thermal resistance.

For the purpose of eliminating the influence of chemically bonded mPEG, the nonreactive polyethylene glycol dimethyl ether (DME) was used to replace the reactive mPEG as the dispersing agent so that the added DME could be removed by the repeated washing and filtration [14]. The thermal stability of the obtained PANF was then significantly improved. In the recent report by the same group, an improved polymerization-induced self-assembly strategy was proposed which prepares PANF without using any dispersing agent or auxiliary outside the formulation list of PPTA polymerization [15]. As a heterogeneous means of polymerization, the growth of the molecular weight and the aggregation of PPTA molecular chain were carried out simultaneously until the gel finally formed. The presence of solvent and CaCl_2 in the reaction system was utilized to adjust the hydrogen bonding association, and the hydrophilicity of these intrinsic solubilizers assisted the dispersing of the assembled nanofiber aggregation into aqueous mediums. Hence, the stable PANF could be obtained in an environmentally friendly aqueous dispersion form. The scheme of the PANF self-assembly process is described. The direct and time saving technology greatly simplifies the preparation process of aramid nanofibers and provides the possibility of industrialization. In China, Shandong Jufang New Material Co. Ltd. has built up a production line of PANF with an output of 300 tons/year.

3. The Assembly of PPTA Nanofibers and the Applications

Owing to their intrinsic mechanical and thermal properties, and large surface area and aqueous dispersibility characteristics, PPTA nanofibers have drawn much attention as nano-building blocks for higher-order architectures, including films, hydrogels, aerogels, fibers and different kinds of composites. The enthusiasm started with the breakthrough work of Kotov's group in 2011 [16]. Until now, different preparation approaches have been developed focusing on the "top-down" processing of commercial PPTA fibers (deprotonation [16], electrospinning techniques [17], mechanical disintegration [18], immersion rotary jet-spinning methods [19], etc.). The relevant achievements of the "top-down" PPTA nanofibers, especially those from the chemical cleavage methods, can be seen in recent reviews [20][21][22]. In this part, the discussion is mainly on the assembly of PANF toward the application of all-aramid materials.

The recent progress in the self-assembly and applications of PPTA-based polymers was briefly summarized. Being a well-known liquid crystal polymer, the potential of PPTA to be applied as an effective molecular unit for self-assembly has been increasingly addressed and attempted from the aspects of chemical structure modification and polymerization process optimization. The emerging concept of aramid nanofibers and their fast development suggest new possibilities for the fabrication of all PPTA macroscopic structures and the composites when the idea of hierarchical self-assembly has been added in. The results should be promising considering the performance advantages of *para*-aramids. However, the work is just beginning. There are still a lot of problems in the intrinsic mechanisms, process control and final applications. Challenges have been proposed for both the polymer scientists and the industrial engineers, but a bright future is worth expecting.

References

1. Tanner, D.; Fitzgerald, J.A.; Phillips, B.R. The Kevlar story-an advanced materials case study. *Angew. Chem. Int. Ed. Engl.* 1989, 28, 649–654.
2. Chae, H.G.; Kumar, S. Rigid-rod polymeric fibers. *J. Appl. Polym. Sci.* 2006, 100, 791–802.

3. Garcia, J.M.; Garcia, F.C.; Serna, F.; de la Pena, J.L. High-performance aromatic polyamides. *Prog. Polym. Sci.* 2010, 35, 623–686.
4. Khodadadi, A.; Liaghat, G.; Vahid, S.; Sabet, A.R.; Hadavinia, H. Ballistic performance of Kevlar fabric impregnated with nanosilica/PEG shear thickening fluid. *Compos. Part B* 2019, 162, 643–652.
5. Cheng, Z.; Li, X.; Lv, J.W.; Liu, Y.; Liu, X.Y. Constructing a new tear-resistant skin for aramid fiber to enhance composites interfacial performance based on the interfacial shear stability. *Appl. Surf. Sci.* 2021, 544, 148935.
6. Whitesides, G.M.; Grzybowski, B. Self-assembly at all scales. *Science* 2002, 295, 2418–2421.
7. Qiu, H.; Hudson, Z.M.; Winnik, M.A.; Manners, I. Multidimensional hierarchical self-assembly of amphiphilic cylindrical block comicelles. *Science* 2015, 347, 1329–1332.
8. Philp, D.; Stoddart, J.F. Self-assembly in natural and unnatural systems. *Angew. Chem. Int. Ed.* 1996, 35, 1154–1196.
9. O'Leary, L.E.R.; Fallas, J.A.; Bakota, E.L.; Kang, M.K.; Hartgerink, J.D. Multi-hierarchical self-assembly of a collagen mimetic peptide from triple helix to nanofibre and hydrogel. *Nat. Chem.* 2011, 3, 821–828.
10. Lopes, W.A.; Jaeger, H.M. Hierarchical self-assembly of metal nanostructures on diblock copolymer scaffolds. *Nature* 2001, 414, 735–738.
11. Graham, J.F.; McCague, C.; Warren, O.L.; Norton, P.R. Spatially resolved nanomechanical properties of kevlar® fibers. *Polymer* 2000, 41, 4761–4764.
12. Rebouillat, S.; Peng, J.C.M.; Donnet, J.B. Surface structure of kevlar® fiber studied by atomic force microscopy and inverse gas chromatography. *Polymer* 1999, 40, 7341–7350.
13. Yan, H.; Li, J.; Tian, W.; He, L.; Tuo, X.; Qiu, T. A new approach to the preparation of poly(p-phenylene terephthalamide) nanofibers. *RSC Adv.* 2016, 6, 26599–26605.
14. Xie, C.; He, L.; Shi, Y.; Guo, Z.-X.; Qiu, T.; Tuo, X. From monomers to a lasagna-like aerogel monolith: An assembling strategy for aramid nanofibers. *ACS Nano* 2019, 13, 7811–7824.
15. Xie, C.; Guo, Z.-X.; Qiu, T.; Tuo, X. Construction of aramid engineering materials via polymerization-induced para-aramid nanofiber hydrogel. *Adv. Mater.* 2021, 33, 2101280.
16. Yang, M.; Cao, K.Q.; Sui, L.; Qi, Y.; Zhu, J.; Waas, A.; Arruda, E.M.; Kieffer, J.; Thouless, M.D.; Kotov, N.A. Dispersions of aramid nanofibers: A new nanoscale building block. *ACS Nano* 2011, 5, 6945–6954.
17. Yeager, M.P.; Hoffman, C.M., Jr.; Xia, Z.Y.; Trexler, M.M. Method for the synthesis of para-aramid nanofibers. *J. Appl. Polym. Sci.* 2016, 133, 44082.
18. Ifuku, S.; Maeta, H.; Izawa, H.; Morimoto, M.; Saimoto, H. Facile preparation of aramid nanofibers from Twaron fibers by a downsizing process. *RSC Adv.* 2014, 4, 40377–40380.
19. Gonzalez, G.M.; Ward, J.; Song, J.; Swana, K.; Fossey, S.A.; Palmer, J.L.; Zhang, F.W.; Lucian, V.M.; Cera, L.; Zimmerman, J.F.; et al. para-Aramid fiber sheets for simultaneous mechanical and thermal protection in extreme environments. *Matter* 2020, 3, 742–758.
20. Yang, B.; Wang, L.; Zhang, M.Y.; Luo, J.J.; Lu, Z.Q.; Ding, X.Y. Fabrication, applications, and prospects of aramid nanofiber. *Adv. Funct. Mater.* 2020, 30, 2000186.
21. Zhang, B.; Wang, W.C.; Tian, M.; Ning, N.Y.; Zhang, L.Q. Preparation of aramid nanofiber and its application in polymer reinforcement: A review. *Eur. Polym. J.* 2020, 139, 109996.
22. Fan, Y.Y.; Li, Z.H.; Wei, J.C. Application of aramid nanofibers in nanocomposites: A brief review. *Polymers* 2021, 13, 3071.