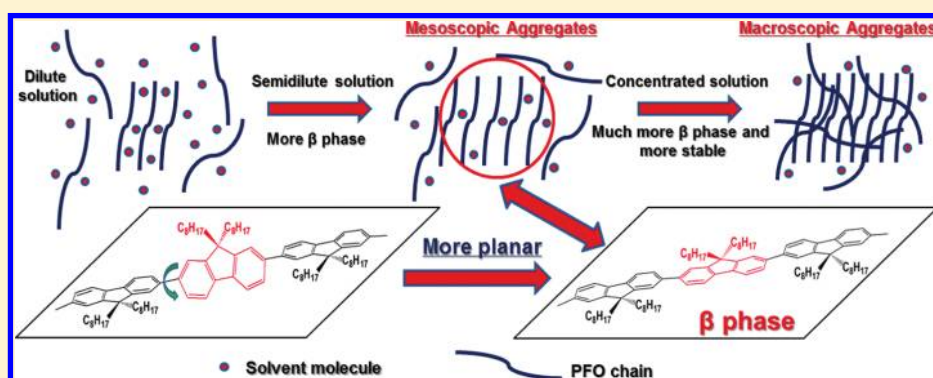


Study of β phase and Chains Aggregation Degrees in Poly(9,9-dioctylfluorene) (PFO) Solution

Long Huang, Xinan Huang, Guannan Sun, Cheng Gu, Dan Lu,* and Yuguang Ma

College of Chemistry/State Key Laboratory of Supramolecular Structure and Materials, Jilin University, 2699 Qianjin Avenue, Changchun, 130012, China

S Supporting Information



ABSTRACT: In this work, the effects of solvation and desolvation on the β phase of poly(9,9-dioctylfluorene) (PFO) are studied. The content of β phase is approximately calculated for comparison. The content of β phase can be enhanced up to 40% by the solvation effect and become a metastable state; the desolvation effect is a dynamic process and can enhance the content of β phase remarkably by 18%age units. It is found that the contents of β phase are always changing with the aggregation degrees of PFO chains. To fully understand it, the concepts of mesoscopic aggregates and macroscopic aggregates are proposed and well proved by the filtration experiment. In the solution (the ethanol content less than 30%), the mesoscopic aggregates are beneficial to enhance the content of β phase; in the solution (the ethanol content more than 40%), which is close to the condensed state of fabricated optoelectronic film, the macroscopic aggregates can make the content of β phase not only much higher but also stable. The content of β phase can be controlled by changing the aggregation characteristics of PFO chains in solution. This work will be significant in fabricating the optoelectronic devices from solutions to films with high carrier mobility and good stability.

1. INTRODUCTION

As a particularly important family of conjugated polymers, polyfluorenes (PFs) have attracted much attention over the past few years because of their excellent photophysical and optoelectronic characteristics.^{1–4} The research on the relationship between the PFs chain conformations and the carrier mobility is a key to enhance the performance of optoelectronic devices to apply to solar cells, field effect transistors (FETs), and organic lasers. The PFs chain conformations mainly include an α phase and a β phase.^{5–7} The α phase does not refer to the crystalline structure but rather individual locally separated chains. The β phase is likely located in the weakly ordered domains as shown by X-ray scattering.^{8,9} The β phase has a larger intrachain torsion angle than the α phase and shows a coplanar conformation, which results in an extended PF chain conjugation length and increased conformational order (parts a and b of Figure 1, schematic presentation). This structural characteristics of the β phase are beneficial in enhancing the carrier mobility of optoelectronic devices,^{10,11} therefore it is very important to control the contents of the β phase of PFs during the formation of films from solutions. It has been proven that only the

PFs with linear side chains could form β phase, and the β phase is easier to form in poly(9,9-dioctylfluorene) (PFO).¹²

Because the β phase was first found by Bradley et al,¹³ many researches were focused on the β phase of PFO in films,^{14–20} but β phase in solution has not been well studied. In fact, the properties of polymer thin films are closely related to the chain conformations in solutions. Hence, the understanding to the chain conformations in the solution state is very critical. In this work, both of the effects of solvation and desolvation on PFO chain conformations are studied; the aim is to control the contents of the β phase from solutions to films. It is found that the contents of β phase are always changing with the aggregation degrees of molecular chains. According to the different aggregation degrees, chains aggregations are defined as mesoscopic aggregates, and macroscopic aggregates, respectively.

Received: February 2, 2012

Revised: March 20, 2012

Published: March 26, 2012

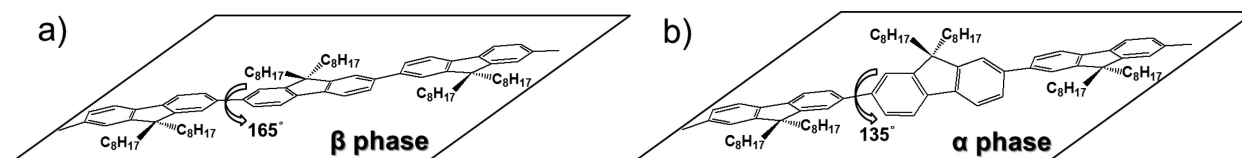


Figure 1. (a) β phase of PFO, (b) α phase of PFO.

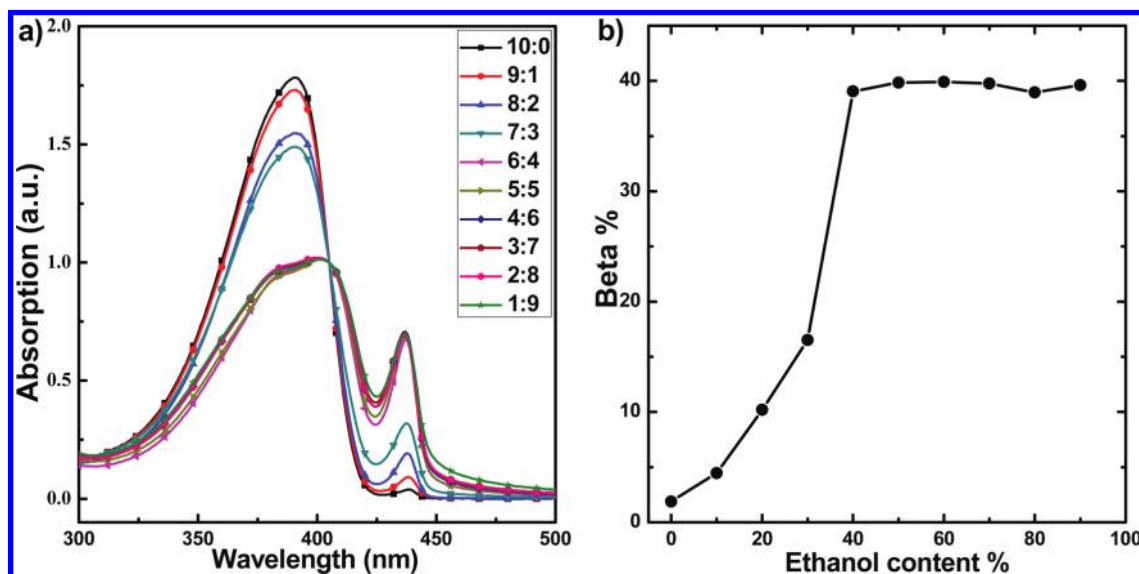


Figure 2. (a) Normalized UV-vis absorption spectra of 10 PFO samples with different ratios of chloroform/ethanol: 10:0, 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, 1:9. All of the curves were normalized at the isosbestic point (405 nm). (b) The contents of β phase of ten PFO samples with different ratios of chloroform/ethanol.

2. EXPERIMENTAL SECTION

2.1. Materials and Samples Preparation. PFO (poly-(9,9-dioctylfluorene)) was produced by American Dye Source, ADS329BE. The weight-average molecular weight (M_w) was 46 000 g/mol and the polydispersity index (PDI) was 1.84, which were measured by Gel permeation chromatography (GPC) using THF as the eluent and polystyrene as standard. Chloroform was chosen as the good solvent and ethanol was chosen as the poor solvent, both produced by Beijing Chemical Company. All of the processes of dissolution were done by the magnetic stirring at room temperature (293 K) in the dark for 24 h. The process of solvent removal was operated by an EYELA N-1001 rotary evaporator at 308 K under reduced pressure, this temperature does not have any effect on the stability of β phase containing PFO aggregates.^{8,21} To remove the effect of concentration on β phase, each sample was kept at the same volume 20 mL after the process of solvent removal, and the initial concentrations were all 0.05 mg mL⁻¹.

2.2. Measurements. UV-vis absorption spectra were measured using a Shimadzu spectrophotometer. The distribution curves of hydrodynamic diameters were measured using a Brookhaven 90Plus particle size analyzer, which applied the principle of dynamic light scattering and could reflect the change of the aggregation degree of molecular chains in solution. The filtration experiment was done using a 0.45 μ m membrane, the aim was to demonstrate the difference of chains aggregation degree. All of the measurements were done at room temperature.

2.3. Theoretical Calculation of the Content of β Phase. The content of β phase in PFO solutions can be calculated according to Lambert-Beer's law (eq 1), where c_α and c_β are

the concentrations of α phase and β phase, respectively, A (obtained from experiments) is the absorbency and ϵ is the absorption coefficient. In UV-vis absorption spectra of PFO solutions, it is difficult to obtain the ϵ for α phase and β phase. Thus we used the method of molecular simulation to the absorption spectra to calculate the proportion of $\epsilon_\beta/\epsilon_\alpha$.²²

$$\beta\% = \frac{c_\beta}{c_\beta + c_\alpha} = \frac{A_\beta \times \epsilon_\alpha}{A_\beta \times \epsilon_\alpha + A_\alpha \times \epsilon_\beta} \quad (1)$$

By defining six monomer units as the conjugation length,²³ we optimized the symmetry geometries of PFO chains for the approximate calculation of ϵ using DFT.²⁴ To calculate the oscillator strengths (f), Time-dependent DFT (TD-DFT) was used,²⁵ as this method has been found to give reliable results.²⁶ DFT and TD-DFT are both with a B3LYP hybrid functional basis set level of 6-31G*.²⁷ All calculations were performed using the Gaussian 03 package.²⁶ The oscillator strengths (f) of the two conformations are 4.46 for α phase at 386 nm and 4.83 for β phase at 437 nm (Figure S1 of the Supporting Information). Thus, the proportion of $\epsilon_\beta/\epsilon_\alpha$ can be obtained from eq 2 and eq 3, where k is a constant and ν is the vibration frequency of two conformations. We can approximately calculate the contents of β phase in each UV-vis absorption spectra of PFO solutions using eq 1 and eq 3.

$$f = k \int \epsilon d\nu, f \propto \epsilon \quad (2)$$

$$\frac{\epsilon_\beta}{\epsilon_\alpha} = \frac{f_\beta}{f_\alpha} = \frac{4.83}{4.46} = 1.08 \quad (3)$$

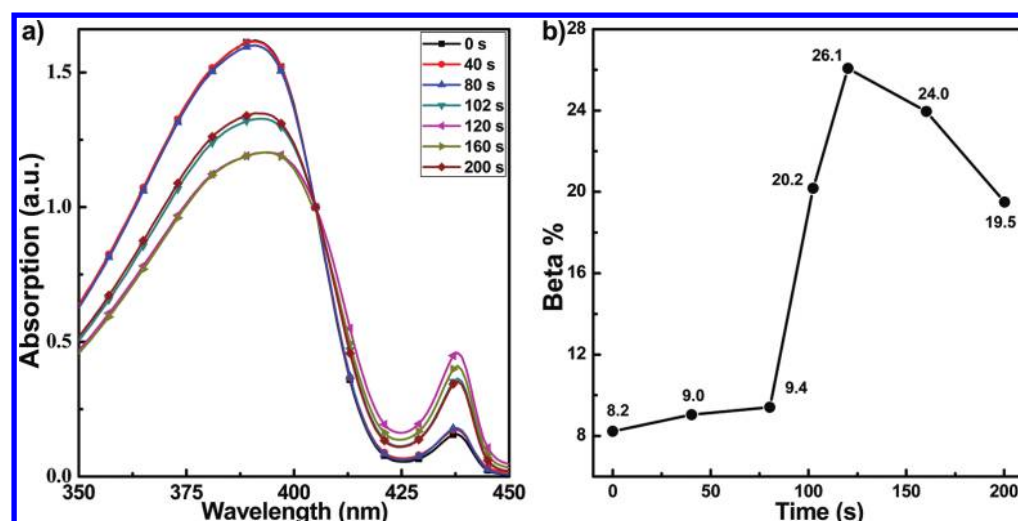


Figure 3. (a) Normalized UV–vis absorption spectra of the solutions with the ratio of chloroform/ethanol 5:1 over time during solvent removal: 0 s, 40 s, 80 s, 102 s, 120 s, 160 s, 200 s. (b) The contents of β phase with the ratio of chloroform/ethanol 5:1 over time during solvent removal.

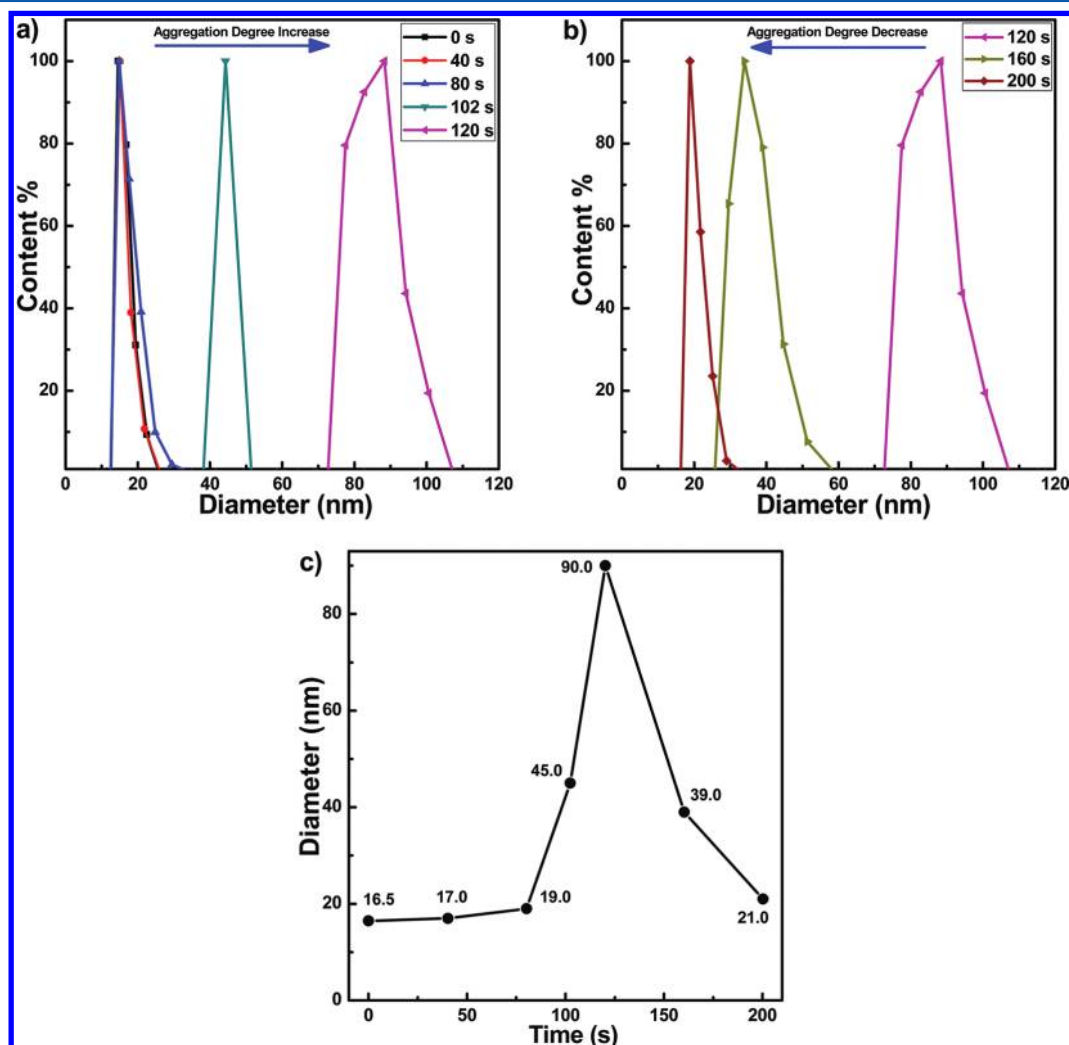


Figure 4. (a) Distribution curves of hydrodynamic diameters of the solutions with the ratio of chloroform/ethanol 5:1 from 0 to 120 s during solvent removal. (b) From 120 to 200 s during solvent removal. (c) The mean hydrodynamic diameters of the solutions with the ratio of chloroform/ethanol 5:1 over time during solvent removal.

3. RESULTS AND DISCUSSION

3.1. β Phase and Macroscopic Aggregates in the Solution (the Ethanol Content More than 40%). Research

about the effect of solvation on β phase is necessary to tune the content of β phase.^{3,28} The normalized UV–vis absorption spectra of ten PFO samples with different ratios of chloroform/ethanol

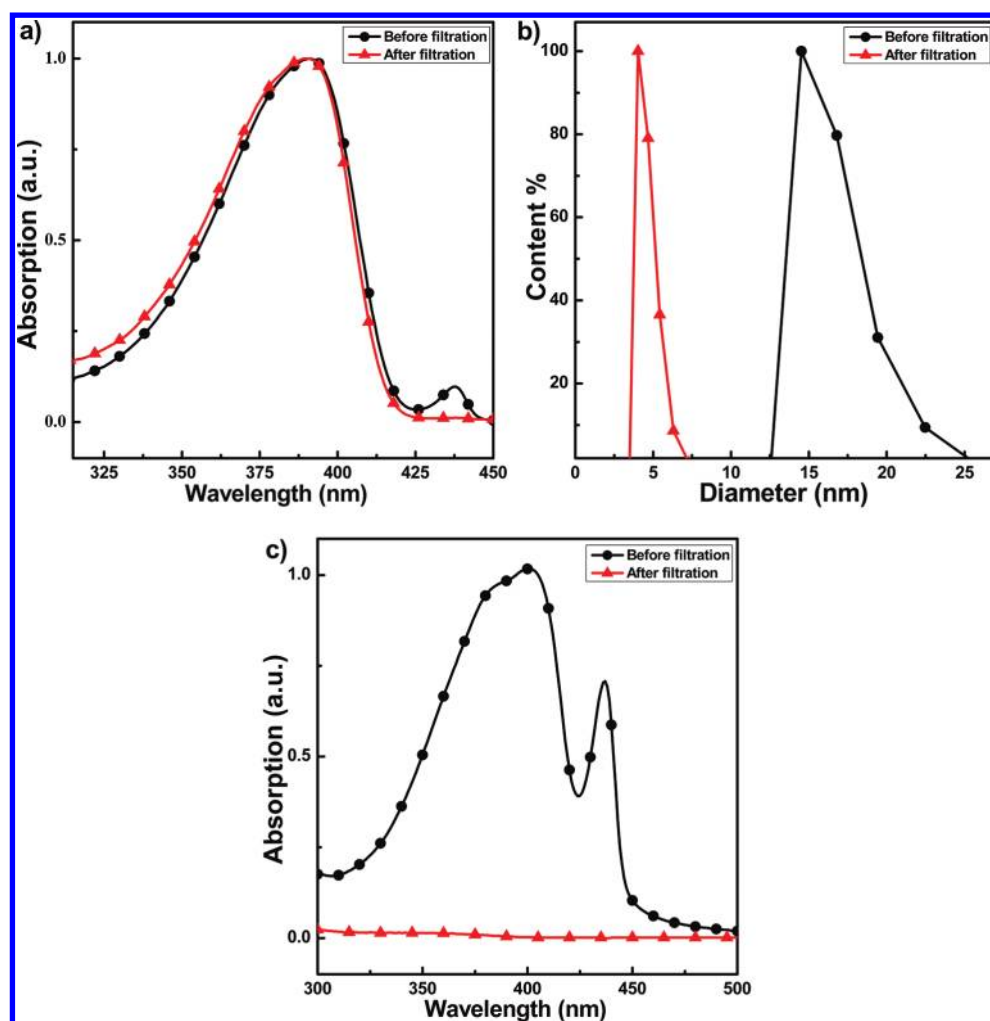


Figure 5. (a) Normalized UV-vis absorption spectra of the solution with the ratio of chloroform/ethanol 5:1 before filtration (circle) and after filtration (triangle). (b) The distribution curves of hydrodynamic diameters with the ratio of chloroform/ethanol 5:1 before filtration (circle) and after filtration (triangle). (c) Normalized UV-vis absorption spectra of the solution with the ratio of chloroform/ethanol 4:6 before filtration (circle) and after filtration (triangle).

are presented in part a of Figure 2. All of the curves were normalized at the isosbestic point (405 nm) identified previously in relevant report to correct for precipitation effects.^{29,30} The main band at 391 nm is α phase, whereas the peak at 437 nm is β phase.²⁹ The contents of β phase of the ten PFO samples are presented in part b of Figure 2. From chloroform/ethanol solutions with the ratios of 10:0 to 7:3, the content of β phase increases gradually with the increasing ratio of ethanol, which demonstrates that the solvation effect can induce the formation of β phase when the ethanol content of PFO solution is not high. From the ratios of chloroform/ethanol 7:3 to 6:4, the peak of β phase shows a sharp rise in part a of Figure 2; meanwhile, the solution with the ratio of 6:4 becomes cloudy. However, from the ratios of chloroform/ethanol 6:4 to 1:9 in part b of Figure 2, the content of β phase changed only a little and shows the maximum value of 40% in the range. It is notable that the main band is red-shifted with a new peak appearing at 401 nm in part a of Figure 2, which is thought to be the result of aggregates absorption and proved by Monkman et al.¹² According to the different aggregation degrees of PFO chains, we define the aggregation in the solution (the ethanol content more than 40%) as macroscopic aggregates, its evident sign is that the main band is red-shifted

in corresponding UV-vis absorption spectra. From results above, it is found that once the macroscopic aggregates appear, the contents of β phase are high and almost cannot be changed by the solvation effect, which has not been reported before, and indicates that the macroscopic aggregates can make β phase a metastable state. This experiment was repeated and the results were similar.

3.2. β Phase and Mesoscopic Aggregates in the Solution (the Ethanol Content Less than 30%). Compared to the macroscopic aggregates, we define the aggregation in the solution (the ethanol content less than 30%) as mesoscopic aggregates, its evident sign is that the main band is not red-shifted in the UV-vis absorption spectra. The solution with the ratio of chloroform/ethanol 5:1 shows light yellow and is transparent, which can be considered as the semidilute solution here.

We chose the solution with the ratio of chloroform/ethanol 5:1 for the solvent-removal experiment. The solvent removal is a dynamic process over time, which can explore the change rules of β phase and chains aggregation. Here, the normalized UV-vis absorption spectra are shown in part a of Figure 3. The contents of β phase over time are presented in part b of Figure 3. In the range of 0 to 120 s, the contents of β phase increase

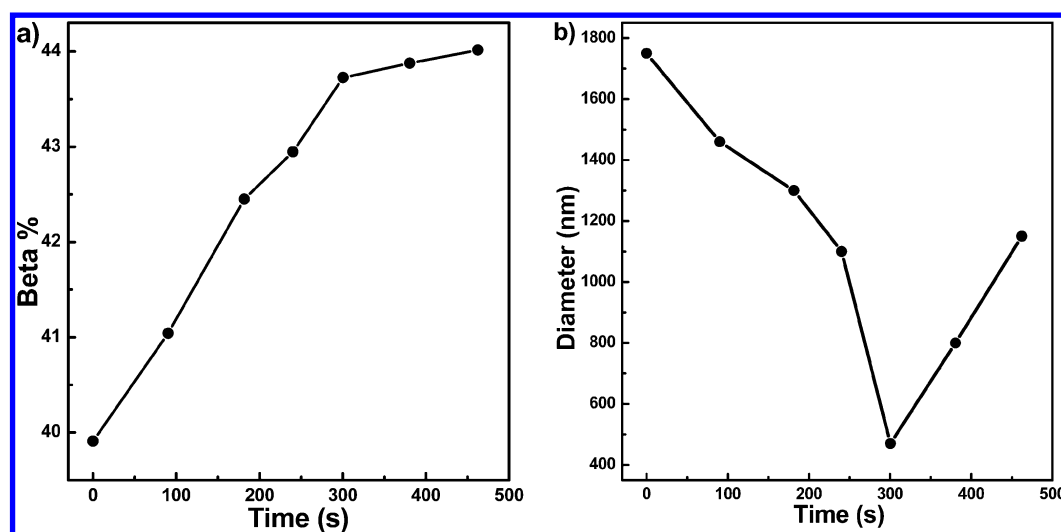


Figure 6. (a) Contents of β phase of the solutions with the ratio of chloroform/ethanol 4:6 over time during solvent removal: 0 s, 90 s, 182 s, 240 s, 300 s, 381 s, 462 s. (b) The mean hydrodynamic diameters of the solutions with the ratio of chloroform/ethanol 4:6 over time during solvent removal.

gradually from 8% to 26%, it indicates the desolvation effect can enhance the content of β phase remarkably. In the range of 120 to 200 s, the contents of β phase decrease gradually. It can be seen from that the contents of β phase are strongly associated with the dynamic process of the solvent removal. To well understand this process, the distribution curves of hydrodynamic diameters were introduced.

As mentioned in the Experimental Section, the distribution curves of hydrodynamic diameters can reflect the change of the aggregation degree of molecular chains. Here, the hydrodynamic diameters with the ratio of chloroform/ethanol 5:1 during solvent removal are shown in parts a and b of Figure 4. And the mean hydrodynamic diameters are shown in part c of Figure 4. In the range of 0 to 120 s, the aggregation degree of molecular chains is enhanced gradually; in the range of 120 to 200 s; however, the aggregation degree of molecular chains is lowered gradually. Taking part c of Figure 4 and part b of Figure 3 for comparison, it can be found that the variation trend of the aggregation degrees of PFO chains is similar to that of the content change of β phase. This result demonstrates that the desolvation effect can control the content of β phase by changing the aggregation characteristics of PFO chains. To fully understand this result, the interdigitated model which was proposed by Monkman et al. is cited here.¹² The essence of interdigitated model is the side-chain interaction, which can supply enough energy to the PFO backbone to overcome the steric hindrance and make it more planar, leading to more formation of β phase. The side-chain interactions play an important role for the formation of β phase, which was also proved by Justino et al.³¹

In fact, Lupton and co-workers have suggested that aggregation is not a requirement for β phase formation and that it can be formed in single chains of PFO with the 1D crystalline state, which is reasonable.³² However, in the solution state, solvent acting as an external field, just like force, temperature and electricity, has an effect of weak stimulation with strong response on PFO chains. In the initial stage of solvent removal, the distances between chains become shorter with the solvent being removed gradually, and the aggregation degrees of mesoscopic aggregates become higher. Meanwhile, the interactions between chains become stronger, especially the

side-chain interactions leading to forming β phase more easily. In the later stage of solvent removal, both the aggregation degrees and the content of β phase are lowered possibly due to the solvation effect. From the above analysis, it can be concluded that the mesoscopic aggregates are beneficial to enhance the content of β phase in solution. The experiment of solvent removal was well repeated.

3.3. Proof of Experiment on Mesoscopic Aggregates and Macroscopic Aggregates. To explore the difference of chains aggregation degree, the filtration experiment was carried out. Previous reports only pointed out the filtration experiment could reduce the absorption peak of β phase.^{29,30} But the differences of the aggregation degrees of PFO chains have not been explored. To prove the existence of mesoscopic aggregates, in our experiment, the solution with the ratio of chloroform/ethanol 5:1 shows light yellow and transparent initially, when the solution is filtered through a 0.45 μm membrane, it shows transparent with blue color (dilute solution of PFO in good solvent). In the UV-vis absorption spectrum, the absorption peak of β phase at 437 nm can be greatly reduced upon filtration, as shown in part a of Figure 5. In the distribution curve of hydrodynamic diameter, the aggregation degree of molecular chains was also lowered obviously upon filtration, as shown in part b of Figure 5. The above two experiments prove the existence of mesoscopic aggregates and indicate that most of the β phase are contained in the mesoscopic aggregates.

To prove the existence of macroscopic aggregates, the solution with the ratio of chloroform/ethanol 4:6 was chosen for the filtration experiment. The solution is cloudy initially, which can be considered as the concentrated solution here. But it becomes transparent and colorless after the filtration experiment. In the UV-vis absorption spectrum, there is no absorption peak at the site of α phase or β phase upon filtration, as shown in part c of Figure 5. In the measurement of hydrodynamic diameter, there is no scattering signal appearance upon filtration. This result indicates the existence of macroscopic aggregates, and α phase and β phase of PFO are all contained in the macroscopic aggregates. Therefore, the obvious distinction between mesoscopic aggregates and macroscopic aggregates can be seen from the two experiments above. The previously reported structural data of PFO aggregates are

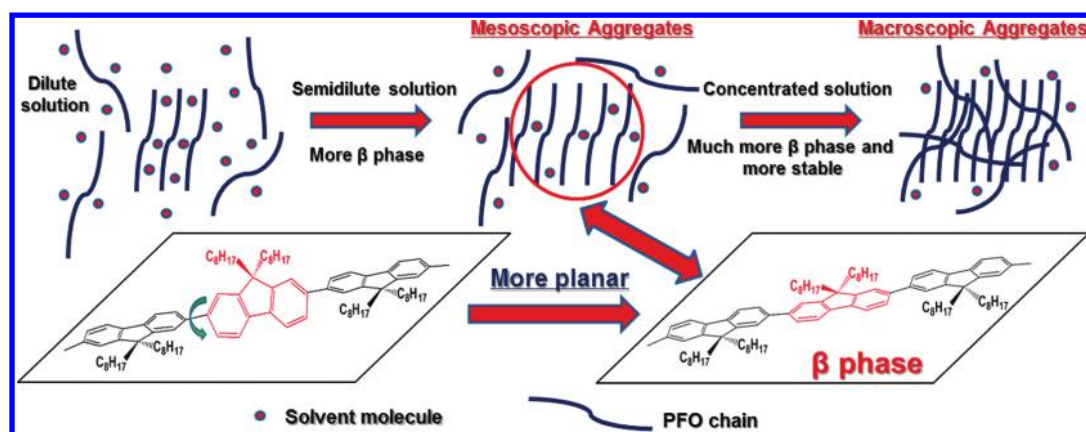


Figure 7. Variation trend of the aggregation characteristics of PFO chains from PFO dilute solution to concentrated solution (the ethanol content becomes higher gradually in the same PFO concentrations 0.05 mg mL^{-1}).

fully consistent with the present results and can well prove that our definitions about mesoscopic aggregates and macroscopic aggregates are reasonable.^{8,9,33}

3.4. Further Proof of the Effect of Macroscopic Aggregates on the Stability of β Phase. As mentioned in part b of Figure 2, once the macroscopic aggregates appear, the contents of β phase can be hardly changed in the range of 40% by the solvation effect. However, we would like to know whether the macroscopic aggregates can further stabilize the β phase in concentrated solution upon the desolvation effect, which can enhance the contents of β phase remarkably in semidilute solution. The contents of β phase of the solutions with the ratio of chloroform/ethanol 4:6 over time during solvent removal are shown in part a of Figure 6. In order to explore the mechanism, the changes of the aggregation degree of PFO chains with time are investigated, the mean hydrodynamic diameters are shown in part b of Figure 6. (The specific UV–vis absorption spectra and distribution curves of hydrodynamic diameters are shown in Figures S2 and S3 of the Supporting Information.) From parts a and b of Figure 6, it is clear that the reduction of the aggregation degree of PFO chains is corresponding to the increase of the content of β phase, which is enhanced by 4% at most.

This result is attributed to the distinction between macroscopic aggregates and mesoscopic aggregates. In PFO concentrated solution, there are many kinds of complex interactions, but free volume is thought to be the critical factor in changing the chain conformations. The high aggregation degrees of macroscopic aggregates make PFO difficult to change chain conformations as to enhance the contents of β phase. When the solvent is removed from the solution, the presence of closed packed chains can further increase the aggregation degree of molecular chains, which hinders the planarization of PFO backbones, leading to the content of β phase hardly to change and relative stable.

As mentioned above, it can be concluded that neither solvation effect nor desolvation effect can change the contents of β phase significantly when the macroscopic aggregates appear. It can be further demonstrated that the macroscopic aggregates are closely related to the high content of β phase and can make it a metastable state. From PFO dilute solution to concentrated solution (the ethanol content becomes higher gradually in the same PFO concentrations 0.05 mg mL^{-1}), the probable variation trend of the aggregation characteristics of PFO chains is shown in Figure 7. From dilute solution to semidilute solution, the β phase of PFO is formed more by the side-chain interac-

tions in mesoscopic aggregates; from semidilute solution to concentrated solution, the content of β phase is so high that it is stabilized by the macroscopic aggregates.

4. CONCLUSIONS

The effects of solvation and desolvation can control the content of β phase by changing the aggregation characteristics of PFO chains in solution. The content of β phase can be enhanced up to 40% by the solvation effect and tend to be a metastable state; the desolvation effect can enhance the content of β phase remarkably by 18%age units. The contents of β phase are always changing with the aggregation degrees of PFO chains. In the solution (the ethanol content less than 30%), the mesoscopic aggregates are beneficial in enhancing the content of β phase; but in the solution (the ethanol content more than 40%), which is close to the condensed state of fabricated optoelectronic film, the macroscopic aggregates can make the content of β phase not only much higher but also stable. This work will be significant in fabricating the optoelectronic devices from solutions to films with high carrier mobility and good stability. Also, this research enlightens us that the desolvation effect can be considered as a new way to study the dynamic process of chain conformations change.

■ ASSOCIATED CONTENT

📄 Supporting Information

Optimization of the symmetry geometries of PFO chains, the UV–vis absorption spectra and distribution curves of hydrodynamic diameters of the solution with the ratio of chloroform/ethanol 4:6 over time during solvent removal, and the UV–vis absorption spectra of the solutions with the ratio of chloroform/ethanol 5:1 and 4:6 in different concentrations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*Tel: +86 431 85167057, Fax: +86 431 85193421, E-mail: lud@jlu.edu.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work is supported by grants from the Natural Science Foundation of China (21174049) and the Ministry of Science and Technology of China (2009CB623605).

■ REFERENCES

- (1) Inganas, O.; Zhang, F. L.; Andersson, M. R. *Acc. Chem. Res.* **2009**, *42*, 1731–1739.
- (2) Wu, H. B.; Ying, L.; Yang, W.; Cao, Y. *Chem. Soc. Rev.* **2009**, *38*, 3391–3400.
- (3) Scherf, U.; List, E. J. W. *Adv. Mater.* **2002**, *14*, 477–487.
- (4) Monkman, A. P.; Rothe, C.; King, S. M.; Dias, F. B. In *Polyfluorenes*; Scherf, U., Neher, D., Eds.; Springer: Berlin, 2008; pp 187–226.
- (5) Chunwaschirasiri, W.; Tanto, B.; Huber, D. L.; Winokur, M. J. *Phys. Rev. Lett.* **2005**, *94*, 107402–107406.
- (6) Chen, S. H.; Su, A. C.; Su, C. H.; Chen, S. A. *Macromolecules* **2005**, *38*, 379–385.
- (7) Chen, S. H.; Chou, H. L.; Su, A. C.; Chen, S. A. *Macromolecules* **2004**, *37*, 6833–6838.
- (8) Chen, C. Y.; Chang, C. S.; Huang, S. W.; Chen, J. H.; Chen, H. L.; Su, C. I.; Chen, S. A. *Macromolecules* **2010**, *43*, 4346–4354.
- (9) Knaapila, M.; Bright, D. W.; Stepanyan, R.; Torkkeli, M.; Almasy, L.; Schweins, R.; Vainio, U.; Preis, E.; Galbrecht, F.; Scherf, U.; Monkman, A. P. *Phys. Rev. E* **2011**, *83*, 051803–051814.
- (10) Peet, J.; Brocker, E.; Xu, Y. H.; Bazan, G. C. *Adv. Mater.* **2008**, *20*, 1882–1885.
- (11) Lu, H. H.; Liu, C. Y.; Chang, C. H.; Chen, S. A. *Adv. Mater.* **2007**, *19*, 2574–2579.
- (12) Bright, D. W.; Dias, F. B.; Galbrecht, F.; Scherf, U.; Monkman, A. P. *Adv. Funct. Mater.* **2009**, *19*, 67–73.
- (13) Bradley, D. D. C.; Grell, M.; Long, X.; Mellor, H.; Grice, A. W.; Inbasekaran, M.; Woo, E. P. *Proc. SPIE* **1997**, *3145*, 254.
- (14) Bansal, A. K.; Ruseckas, A.; Shaw, P. E.; Samuel, I. D. W. *J. Phys. Chem. C* **2010**, *114*, 17864–17867.
- (15) Bright, D. W.; Galbrecht, F.; Scherf, U.; Monkman, A. P. *Macromolecules* **2010**, *43*, 7860–7863.
- (16) Chen, M. C.; Hung, W. C.; Su, A. C.; Chen, S. H.; Chen, S. A. *J. Phys. Chem. B* **2009**, *113*, 11124–11133.
- (17) Morgado, J.; Alcaccer, L.; Charas, A. *Appl. Phys. Lett.* **2007**, *90*, 201110–201113.
- (18) Zhu, R.; Lin, G. M.; Wang, W. Z.; Zheng, C.; Wei, W.; Huang, W.; Xu, Y. H.; Peng, J. B.; Cao, Y. *J. Phys. Chem. B* **2008**, *112*, 1611–1618.
- (19) Chen, S. H.; Su, A. C.; Chen, S. A. *J. Phys. Chem. B* **2005**, *109*, 10067–10072.
- (20) Grell, M.; Bradley, D. D. C.; Ungar, G.; Hill, J.; Whitehead, K. S. *Macromolecules* **1999**, *32*, 5810–5817.
- (21) Knaapila, M.; Stepanyan, R.; Torkkeli, M.; Garamus, V. M.; Galbrecht, F.; Nehls, B. S.; Preis, E.; Scherf, U.; Monkman, A. P. *Phys. Rev. E* **2008**, *77*, 051803–051817.
- (22) Gu, C.; Tang, S.; Yang, B.; Liu, S. J.; Lv, Y.; Wang, H.; Yang, S. M.; Hanif, M.; Lu, D.; Shen, F. Z.; Ma, Y. G. *Electrochim. Acta* **2009**, *54*, 7006–7011.
- (23) Ng, M. F.; Sun, S. L.; Zhang, R. Q. *J. Appl. Phys.* **2005**, *97*, 103513–103519.
- (24) Hohenberg, P.; Kohn, W. *Phys. Rev. B* **1964**, *136*, 864–871.
- (25) Runge, E.; Gross, E. K. U. *Phys. Rev. Lett.* **1984**, *52*, 997–1000.
- (26) Hirata, S.; Lee, T. J.; Gordon, M. H. *J. Chem. Phys.* **1999**, *111*, 8904–8912.
- (27) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789.
- (28) Khan, A. L. T.; Sreearunothai, P.; Herz, L. M.; Banach, M. J.; Köhler, A. *Phys. Rev. B* **2004**, *69*, 085201–085209.
- (29) Dias, F. B.; Morgado, J.; Macanita, A. L.; da Costa, F. P.; Burrows, H. D.; Monkman, A. P. *Macromolecules* **2006**, *39*, 5854–5864.
- (30) Kitts, C. C.; Vanden Bout, D. A. *Polymer* **2007**, *48*, 2322–2330.
- (31) Justino, L. L. G.; Ramos, M. L.; Knaapila, M.; Marques, A. T.; Kudla, C. J.; Scherf, U.; Almasy, L.; Schweins, R.; Burrows, H. D.; Monkman, A. P. *Macromolecules* **2011**, *44*, 334–343.
- (32) Como, E. D.; Becker, K.; Feldmann, J.; Lupton, J. M. *Nano Lett.* **2007**, *7*, 2993–2998.
- (33) Knaapila, M.; Garamus, V. M.; Dias, F. B.; Almasy, L.; Galbrecht, F.; Charas, A.; Morgado, J.; Burrows, H. D.; Scherf, U.; Monkman, A. P. *Macromolecules* **2006**, *39*, 6505–6512.