Macromolecules

ARTICLE

pubs.acs.org/Macromolecules

Optically Active Helical Substituted Polyacetylenes as Chiral Seeding for Inducing Enantioselective Crystallization of Racemic *N*-(*tert*-Butoxycarbonyl)alanine

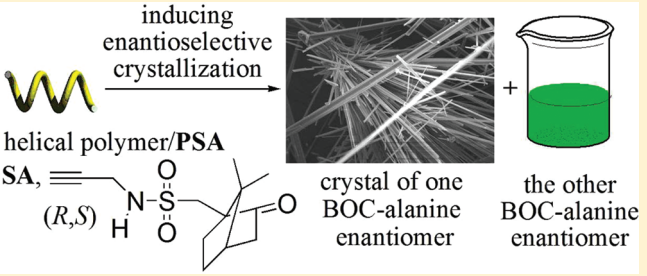
Bo Chen, Jianping Deng,* Xin Cui, and Wantai Yang

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China

College of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China

Supporting Information

ABSTRACT: Helical substituted polyacetylenes were investigated for inducing enantioselective crystallization of racemic *N*-(*tert*-butoxycarbonyl)alanine (BOC-alanine) enantiomers. For this purpose, helical substituted polyacetylenes [(*R*)-PSA and (*S*)-PSA)] were dissolved in supersaturated racemic BOC-alanine solutions. Upon cooling the solutions, (*R*)-PSA preferentially induced BOC-L-alanine to crystallize, while (*S*)-PSA facilitated the enantioselective crystallization of BOC-D-alanine, according to the characterizations by circular dichroism, XRD, SEM, and optical rotation analyses. As expected, no enantioselective crystallization was observed in such cases: racemic BOC-alanine enantiomers in the absence of optically active helical PSA and racemic BOC-alanine enantiomers in the presence of equal amount of (*R*)-PSA and (*S*)-PSA. The present study provides the first direct evidence for the role of artificially synthetic helical polymers in inducing efficiently enantioselective crystallization.



INTRODUCTION

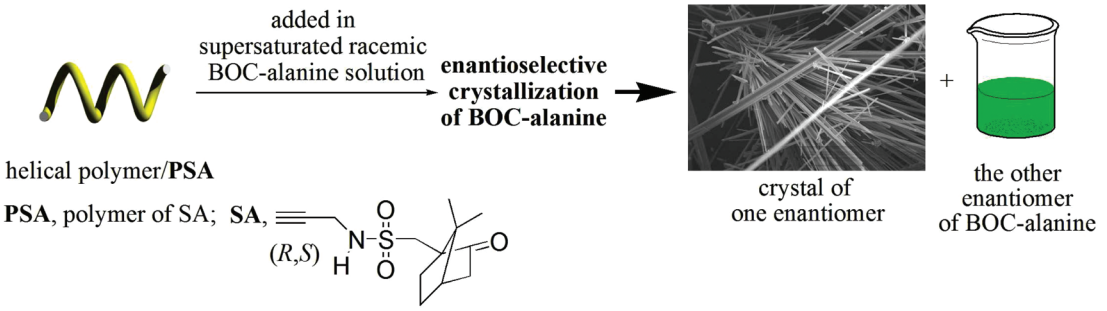
Synthetic helical polymers have been actively studied over the past two decades due to their unique structures and interesting properties.[1] More recently, helical polymers with much complex structures have been elegantly created, including polymers with double-helix,[2] fun-structured pendent groups,[3] etc. Helical polymers are always considered being of some significantly potential applications in particular for chiral catalysis,[4] separation materials,[5] optical materials,[6] and advanced functional materials.[7] For chiral resolutions in the literature, a majority of the investigations are conducted in the state of (hydro)gels made up of helical polymers.[8] We also prepared (hydro)gels consisting of helical substituted polyacetylenes showing intriguing chiral recognition performances.[9] The present study attempted another unprecedented approach of general interest and high promise, i.e., selective chiral crystallization of racemic isomers induced by helical polymers from initial homogeneous solution. Herein, the helical polymers function as chiral seeding, as to be reported in detail below.

We live in a chiral world containing chiral compounds at both molecular and macromolecular levels. These compounds are responsible for the maintenance of life. Even though the origin for the nature to favor one of the enantiopure chiral structures over the opposite one is still open to discussion, chiral resolution of a chiral isomer from its mirror image form is thus an undoubtedly significant research theme. Despite the various techniques developed for chiral resolution, considerable disadvantages of them make more facile and effective approaches still required. Among the relatively new chiral resolution techniques, chiral HPLC (high-performance liquid chromatography) may be the most powerful and the most widely studied one.[10] However, tedious process, high cost, and in particular the difficulty in selecting a suitable chiral resolving medium largely limit further extended practical applications of HPLC. Another technique, crystallization[11] of a long history, is an industrial process for enantioseparation and thus attracts our special attention recently.[12] In practice, enantioselective seeding of racemic solution is frequently adopted to substantially shorten the separation process and meanwhile to enhance the separation efficiency.[13] So far, chiral polymers,[14] chiral polymer-based miniemulsions[15] and microspheres,[16] self-assembled films,[17] chiral solvents,[18] chiral host–guest system,[19] etc., have been investigated as chiral additives to induce enantioselective crystallization. Nevertheless, no other reports with the exception of our earlier one[12] focus on enantioselective crystallization induced by synthetic helical polymers.

In preceding studies, we have prepared a unique type of polymeric particles consisting of helical substituted polyacetylenes.[20,21] Hollow microspheres bearing helical polymer segments demonstrated remarkable capacity for chiral recognition.[21] Chiral hybrid nanoparticles consisting of optically active helical polymer/silica were capable of facilitating considerable chiral discrimination in aqueous systems.[12,20f] Although such chiral hybrid

Received: June 15, 2011
Revised: August 22, 2011
Published: September 01, 2011

Scheme 1. Schematic Illustration of the Strategy for Inducing Enantioselective Crystallization of Racemic BOC-alanine by Using (*R*)-PSA or (*S*)-PSA



nanoparticles exhibited considerable chiral discrimination performance, they are considered as being of some disadvantages including the complex preparing processes and particularly the utility limited in aqueous medium. More importantly, no direct evidence has been achieved to identify the role of helical structures in chiral resolution. With the aim to directly verify the function of helical polymers in inducing enantioselective crystallization, we in the present study directly used helical polymers to induce enantioselective crystallization in solution, following a novel, effective, and facile methodology schematically outlined in Scheme 1.

In Scheme 1, helical polymer (PSA) was utilized to induce enantioselective crystallization of racemic BOC-alanine (*N*-(*tert*-butoxycarbonyl)alanine) in $CHCl_3$. We found (*R*)-PSA enabled BOC-L-alanine to crystallize preferentially, whereas (*S*)-PSA favored enantioselective crystallization of BOC-D-alanine. The chiral resolution results are satisfying, and the role of helical polymers is clearly identified. Also noteworthy is that in the methodology under discussion helical polymers are applicable in organic solvents, while in the earlier paper[12,20f] the hollow particles are applicable in aqueous systems. Accordingly, the present study together with the earlier ones[12,20f] is expected to provide a novel efficient approach for chiral resolution from either organic or aqueous solutions.

EXPERIMENTAL SECTION

Materials. Solvents were purified by distillation under reduced pressure under a N_2 atmosphere in advance. Deionized water was used for polymerizations. 1*R*-(−)- and 1*S*-(+)-10-camphorsulfonyl chloride and propargylamine were purchased from Aldrich and used as received without further purification. BOC-D- and L-alanine (D- and L-*N*-(*tert*-butoxycarbonyl)alanine, respectively) were purchased from Aladdin Reagent Co. (Shanghai, China) and were used directly. All the other reagents were directly used. *N*-Propargyl-(1*R* and 1*S*)-camphor-10-sulfamide, denoted as (*R*)-SA and (*S*)-SA, respectively, were synthesized and polymerized (providing (*R*)-PSA and (*S*)-PSA, respectively) according to the method described by us earlier.[22] (nbd)$Rh^+B^-(C_6H_5)_4$ was prepared through the synthetic procedure.[23] The parameters of the (*R*)-PSA and (*S*)-PSA used in this study are M_n (number-average molecular weight) = 4000 and 3600 and M_w/M_n (polydispersity of the molecular weight) = 1.86 and 1.98, respectively.

Enantioselective Crystallization Experiments. All enantioselective crystallizations were accomplished in supersaturated BOC-alanine solutions in $CHCl_3$ under room conditions. A typical crystallization experiment was performed as follows. BOC-D- and L-alanine (270 mg, each) were simultaneously added in 3 mL of $CHCl_3$. The solution was stirred for ca. 5 min until BOC-alanine was completely dissolved and then heated to 35 °C. A predetermined amount of substituted polyacetylene (chiral PSA) was added in the above racemic BOC-alanine/$CHCl_3$ supersaturated solution and stirred for ca. 10 min, and then the solution was left to cool spontaneously to room temperature (~25 °C) under ambient conditions. In the course of cooling, crystals first visually formed and then grew larger. The crystals were filtrated, collected, and subject to circular dichroism (CD), X-ray diffraction (XRD), and scanning electron microscopy (SEM) analyses, and the residual filtrate was subject to optical rotation measurements. The other processes are similar to those reported in our previous investigations.[12,20f]

Characterizations. CD and UV−vis absorption experiments were conducted on a Jasco-810 spectropolarimeter. Specific rotations were measured on a JASCO P-1020 digital polarimeter with a sodium lamp as the light source at room temperature by using the BOC-alanine $CHCl_3$ solutions. The molecular weights and molecular weight polydispersities were determined by GPC (Shodex KF-850 column) calibrated by using polystyrenes, with THF as eluent. SEM was performed by a Hitachi S-4700 electron microscope at an accelerating voltage of 20.0 kV. XRD analyses of the crystals were conducted with a Shimadzu XRD-6000.

RESULTS AND DISCUSSION

We have previously examined the chiral recognition and chiral resolution ability of helical substituted polyacetylenes. Such polymers in the state of gels[9] and spheres[21] both showed the expected ability. In particular, the hybrid hollow chiral particles demonstrated remarkable ability for inducing enantioselective crystallization.[12] Nevertheless, the crucial role of the helical polymers cannot be directly observed in both gels and spheres. Therefore, taking helical substituted polyacetylene (PSA) and BOC-alanine system as a typical model system in the present study, we directly used the synthetic helical polymers for inducing enantioselective crystallization from BOC-alanine enantiomers solution. The major sequence and advantages of this practice are illustratively presented in Figure 1.

Figure 1 depicts the major procedure for enantioselective separation of BOC-alanine by optically active PSA as chiral seeding in $CHCl_3$ solution, taking (*R*)-PSA inducing BOC-L-alanine as a representative. A typical enantioselective crystallization experiment was performed as briefly stated below. A predetermined amount of chiral PSA (*R*- or *S*-PSA) was dissolved in a racemic D,L-alanine supersaturated solution in $CHCl_3$. The related concept is schematically presented in Scheme 1 and Figure 1. At beginning the racemic BOC-alanine solution is clear and pale yellow (Figure 1A) (the yellowish color is derived from the helical structures of PSA[22]). After staying for ca. 120 h at room temperature (~25 °C), precipitation began to occur in the solution (Figure 1B). The precipitate grew larger gradually, and

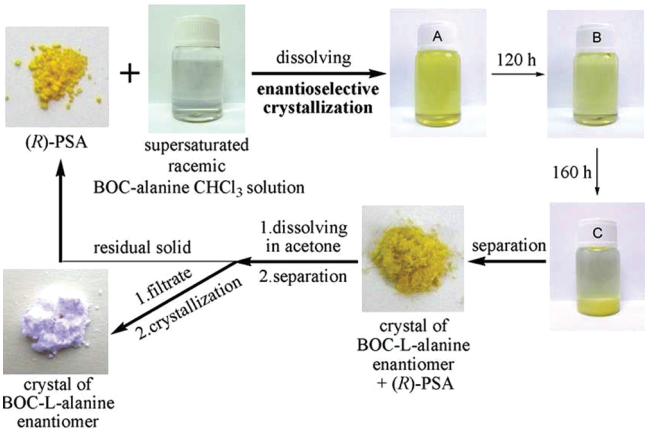


Figure 1. Schematic representation of the major procedure for enantioselective crystallization of BOC-D- or L-alanine enantiomers induced by chiral PSA, taking (*R*)-PSA inducing BOC-L-alanine as example: (A) supersaturated racemic BOC-alanine/$CHCl_3$ solution; (B) the alanine−PSA system after crystallization for 120 h and (C) after 160 h.

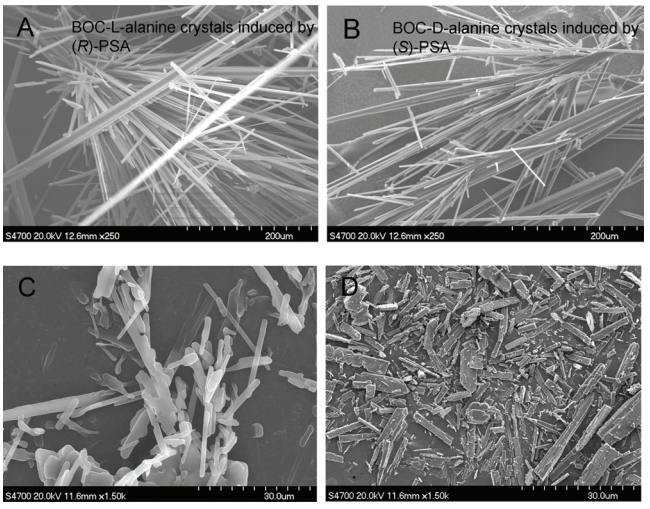


Figure 2. SEM images of crystals formed via enantioselective crystallization in racemic BOC-alanine supersaturated solutions induced by (A) (*R*)-PSA and (B) (*S*)-PSA under otherwise identical experimental conditions (time = 180 h, c = 2.25 M; the solutions were left to cool spontaneously from 35 °C to ∼25 °C). (C) Racemic BOC-alanine crystals obtained by using the equal amount of (*R*)- and (*S*)-PSA (time = 200 h). (D) Typical morphology of racemic BOC-alanine crystals obtained in the absence of PSA under otherwise identical conditions (time = 240 h).

then crystals can be observed visually (Figure 1C). About 160 h later, the crystallization was ended and the precipitate was filtrated, providing pale yellow solid crystals. (Both BOC-alanine and PSA are simutaneously present. See below.) According to their different solubility, the crystallized BOC-alanine and PSA can be readily separated. For the recovered PSA, it can be reused for another cycle of enantioselective crystallization. We find that (*R*)-PSA prompted the enantioselective crystallization of BOC-L-alanine while (*S*)-PSA enabled BOC-D-alanine to preferentially crystallize. This consideration was evidently confirmed by CD, XRD, and optical rotation measurements, as to be introduced in detail below. Herein it should be noted that, after optimization of the structure of the helical polymers and the experimental conditions for enantioselective crystallization, the crystallization time shall be shortened largely.

After crystallization and separation, the as-obtained enantiopure BOC-alanine was subject to measurements. The morphology of the formed crystals is observed by SEM, as presented in Figure 2. Both BOC-L- and BOC-D-alanine formed needlelike crystals (Figure 2A,B). The two crystals demonstrate little difference in visual appearance and in SEM images. We further observed the orginal pure BOC-D- and L-alanine enantiomers, and the SEM images are presented in Figure S1 of the Supporting Inormation. Both the two enantiopure isomers also form needlelike crystals. This is rather different from our earlier investigations.[12,20f] Therein racemic alanines were used as the chiral compound for chiral separation via enantioselective crystallization by using PSA/silica core/shell particles. The obtained two enantiopure alanines formed different crystal morphologies.[12,20f] In more detail, L-alanine formed octahedral crystals while D-alanine formed needlelike crystals. Therein we also revealed that (*S*)-PSA preferentially induced L-alanine to crystallize, while (*R*)-PSA is favorable for D-alanine. On the basis of these two cases (the present study and the preceding ones[12,20f]), it is thus clearly indicated that the enantioselective crystallization is dependent on the racemics, the chiral additives, the chiral environment, etc. It further indicates that the crystal morphologies are closely related with the chiral additives, which largely influence the nucleation and orientation of the crystals.[24] Nonetheless, the enantioselective crystallization is an elegant process, and more investigations are required for us to obtain deep understanding of it. The SEM images in Figure 2 cannot offer much information for us to analyze the enantioselective crystallization. Fortunately, additional experiments provide remarkable evidence, as to be reported next.

In order to verify and understand enantioselective crystallization of soluble chiral PSA toward BOC-alanine enantiomers, PSA consisting of equal amounts of (*R*)-PSA and (*S*)-PSA were used for crystallization of racemic BOC-alanine. In this case no pure and regular BOC-D- or L-alanine enantiomer crystals generated under the otherwise identical experimental conditions. The relevant SEM images are exhibited in Figure 2C. Figure 2D presents the SEM images of the obtained crystals for racemic BOC-alanine via self-crystallization in the absence of PSA. In both Figures 2C and 2D, no regular crystals are observed. The e.e. of the residual racemic BOC-alanine solutions in these two cases was determined to be ∼8%. The two experiments in Figures 2C and 2D plus Figures 2A and 2B clearly demonstrate the significant role of helical PSA as chiral selector for enantioselective crystallization. Namely, the chirality of PSA was the decisive origin for the regular crystals formed in enantioselective crystallization process. Additionally, we also used DMF as solvent instead of $CHCl_3$ for performing crystallization. Just as expected, DMF provided not-so-satisfactory effects as in Figures 2A,B (see Figure S2), since DMF is not favorable for PSA to maintain helical structures.[22] Figure S2 shows that the crystals, even though they can be formed, are not so regular in morphology when compared with the corresponding crystals in Figures 2A,B. Furthermore, when DMF is used as the solvent, crystallization took a much longer time (∼360 h) than in $CHCl_3$. Accordingly, it is further identified the dominant role of helical structures of PSA in inducing enantioselective crystallization. More specifically, the chirality of the induced chirally pure BOC-alanine is dominated by the added chiral PSA. It should be highlighted that this is the first report on using synthetic helical

dx.doi.org/10.1021/ma2013628 |*Macromolecules* 2011, 44, 7109–7114

macromolecules to induce enantioselective crystallization from a homogeneous solution system.

To acquire more insights into the induced crystals via preferential crystallization, we characterized the crystals by XRD. Also, taking BOC-L-alanine crystals as the representative, the obtained XRD profile are illustrated in Figure 3. The two profiles for original pure BOC-L-alanine and BOC-L-alanine obtained via enantioselective crystallization are almost completely identical, since PSA cannot form crystal structures under the investigated conditions. BOC-D-alanine crystals and the corresponding originally enantiopure BOC-D-alanine showed the same phenomenon, as shown in Figure S3. Similar observations were also attained in preferential crystallization induced by hollow two-layered chiral PSA-silica NPs and PSA-silica core/shell NPs in our earlier study.[12,20f]

The obtained crystals were further investigated by CD and UV—vis spectra measurements, referring to our previous investigations.[12,20f]

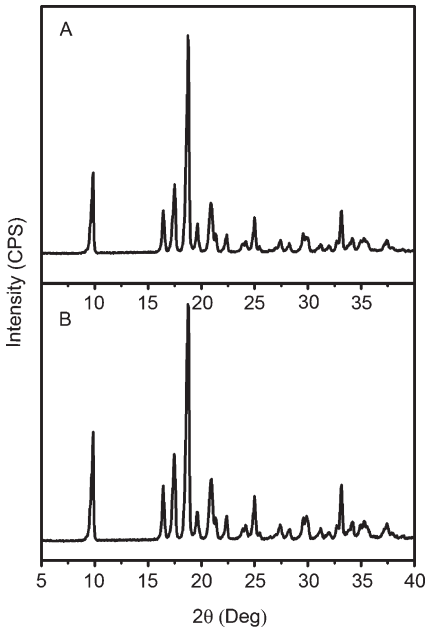


Figure 3. Typical X-ray diffraction profiles of BOC-alanine crystals: (A) original enantiopure BOC-L-alanine and (B) BOC-L-alanine crystals induced by chiral (*R*)-PSA. For the crystallization conditions, refer to Figure 2.

The relevant results are illustrated in Figure 4. For [(*R*)-PSA + BOC-L-alanine] enantioselective crystallization system, the induced BOC-L-alanine crystals containing chiral (*R*)-PSA simultaneously exhibited the CD signals of both (*R*)-PSA (λ_{max} = 415 nm) and BOC-L-alanine (λ_{max} = 215 nm) (see Figure 4A). UV—vis spectra in Figure 4B demonstrate similar results.

In addition to the CD and UV—vis spectra, optical rotation of the residual racemic alanine/$CHCl_3$ solution after crystallization was also measured. Figure 5 indicates the change of e.e. as a function of crystallization time. After ca. 180 h, the maximum chiral resolution was achieved. The preferential crystallization process seem to be somewhat slow; however, e.e. could be as high as 78%. The results obtained in the case of [(*S*)-PSA + BOC-D-alanine] system gave similar data, for which BOC-D-alanine was preferentially crystallized and a maximum e.e. up to 77% was also achieved in the residual BOC-L-alanine. The related CD and UV—vis spectra and the e.e. plot against crystallization time in the [(*S*)-PSA + BOC-D-alanine] system are presented in Figures S4 and S5.

After dissolving the induced BOC-D- or L-alanine crystals containing the chiral PSA in acetone and then centrifuging the solution mixture, the chiral additive PSA can be easily isolated, as

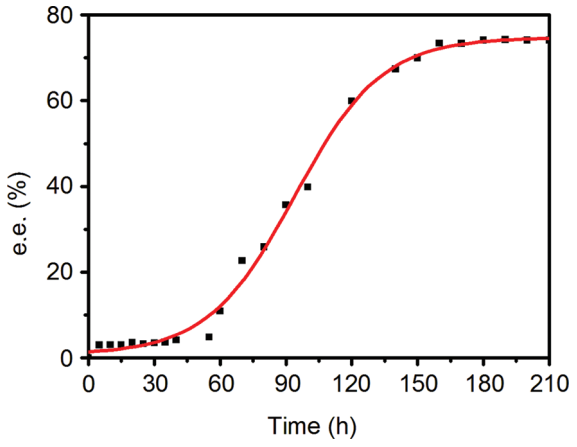


Figure 5. Plot of e.e. (%) as a function of crystallization time (the remaining BOC-D-alanine in excess in solution). 15 mL racemic alanine supersaturated solutions (BOC-D-alanine/BOC-L-alanine = 1735/1735, in mg), 2.5 mg of chiral (*R*)-PSA. For crystallization conditions, refer to Figure 2.

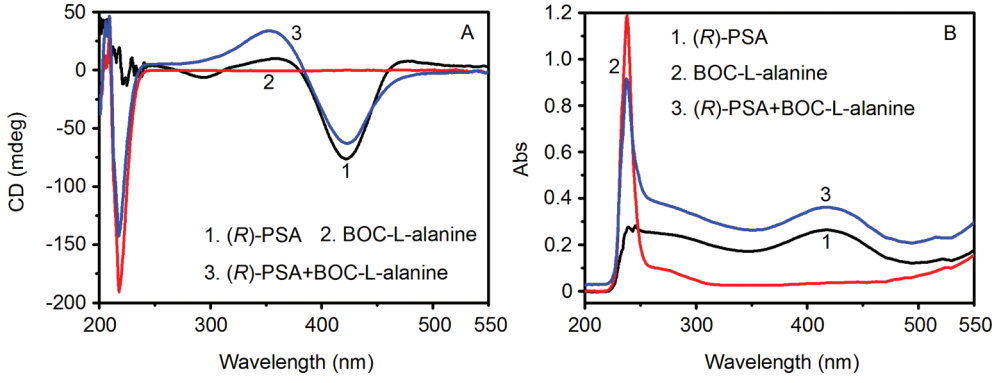
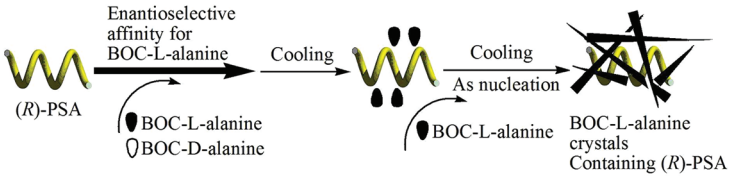


Figure 4. (A) CD and (B) UV—vis spectra of the crystals [BOC-L-alanine + (*R*)-PSA] obtained via enantioselective crystallization, pure (*R*)-PSA, and pure BOC-L-alanine (for crystallization conditions, refer to Figure 2; crystallization for 180 h). All the spectra were measured in $CHCl_3$ solution; concentration of the samples = 0.1 mM; at room temperature.

dx.doi.org/10.1021/ma2013628 |*Macromolecules* 2011, 44, 7109–7114

Scheme 2. Schematic Showing the Possible Mechanism for Chiral Helical Polymers To Induce Enantioselective Crystallization



conceptually illustrated in Figure 1. The white crystals of BOC-alanine enantiomer were obtained via recrystallization from the clear acetone solution, and the residual yellow-green solid was identified to be chiral PSA and thus can be reused. The present study undoubtedly provided new insights and better understanding of optically active polymers with helical structures regarding practical applications and remarkably broadened new applications of helical substituted polyacetylenes.

The investigations presented above convincingly demonstrate the vital role of helical chiral PSAs as chiral nucleating agent for inducing enantioselective crystallization on BOC-alanine isomers. With the crystalys in hand, now we consider another question, i.e., what induced the enantioselective crystallization? We proposed our opinion below for this question. For the enantioselective crystallization of racemic BOC-alanine induced by chiral helical PSA, again taking (*R*)-PSA toward BOC-L-alanine as an example, the possible underlying mechanism is presented in Scheme 2. In the solution of racemic BOC-alanine in $CHCl_3$ in the presence of (*R*)-PSA, BOC-L-alanine molecules are preferentially adsorbed on (*R*)-PSA macromolecules at the beginning of cooling. This process results from the enantioselective affinity of (*R*)-PSA toward BOC-L-alanine molecules due to the different stereospecific configurations of racemic BOC-alanines. As temperature continues to decrease, more BOC-L-alanine molecules are adsorbed and agglomerated surrounding (*R*)-PSA macromolecules, which then act as chiral nucleation sites for the formation of crystals. Along with this reasoning, further cooling leads to tiny crystals appeared; they gradually grow larger forming a suspension from the initial clear solution. In this process, an increase in the crystals size and concentration gives rise to a slight decrease in the transparency of the sample (Figure 1A, B). Finally, the induced crystals griw so large that precipitation (finally formed crystals) occurs from the $CHCl_3$ solution, as observed in Figure 1C.

The present methodology is expected to find remarkable applications in practice. Moreover, the flexibility of designing helical polymers with favorable functional groups in side chains and the easy recovery of the chiral additives make the present concept considerably advantageous over common chiral polymers in inducing enantioselective crystallization. This study opens up new possibility toward effective and facile enantioseparations. However, more studies are still required for us to understand well the enantioselective crystallization induced by chiral helical polymers. Some fundamental questions need to be solved including the correlation between the specific conformation of helical polymers with the efficiency and chiral configuration of the enantiomer preferentially crystallized, the detailed enantioselective crystallization mechanism, etc. For answering these questions, the novel concept is currently tried on other chiral helical polymers and chiral isomers.

CONCLUSIONS

Helical substituted polymers (PSAs) were added in a supersaturation solution of BOC-alanine racemate in $CHCl_3$, forming a homogeneous system. Cooling the solution resulted in enantioselective crystallization of BOC-alanine, in which PSA served as chiral seeds. SEM, CD, XRD, and optical rotation measurements demonstrated that (*R*)-PSA induced preferential crystallization toward BOC-L-alanine, while (*S*)-PSA toward BOC-D-alanine. The enantioselective crystallization is decided by the screw sense of the helical structures of PSA. This is the first direct evidence to demonstrate the role of helical structures in inducing enantioselective crystallization. We believe that after optimizing the structures of PSA and crystallization conditions a higher chiral separation efficiency will be realized. Such investigations are currently in progress in our lab.

ASSOCIATED CONTENT

Supporting Information. Crystal morphology of pure BOC-D- and L-alanine; typical X-ray diffraction profile of BOC-D-alanine crystals; CD and UV−vis spectra of the crystals obtained via enantioselective crystallization toward [(*S*)-PSA + BOC-D-alanine]; and e.e. (%) as a function of crystallization time (BOC-L-alanine in excess). This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*Tel +86-10-6443-5128; Fax +86-10-6443-5128; e-mail dengjp@mail.buct.edu.cn.

ACKNOWLEDGMENT

This work is supported by the "National Natural Science Foundation of China" (20974007, 20574004), the "Fundamental Research Funds for the Central Universities" (ZZ1117), the "Program for New Century Excellent Talents in University" (NCET-06-0096), and the "Project of Polymer Chemistry and Physics, Beijing Municipal Commission of Education".

REFERENCES

(1) Some representative articles: (a) Kennemur, J. G.; Clark, J. B.; Tian, G.; Novak, B. M. *Macromolecules* **2010**, *43*, 1867. (b) Yashima, E.; Maeda, K.; Iika, H.; Furusho, Y.; Nagai, K. *Chem. Rev.* **2009**, *109*, 6102. (c) Liu, J.; Lam, J. E. Y.; Tang, B. Z. *Chem. Rev.* **2009**, *109*, 5799. (d) Sakamoto, T.; Fukuda, Y.; Sato, S.; Nakano, T. *Angew. Chem., Int. Ed.* **2009**, *48*, 9308. (e) Fujiki, M. *Top. Curr. Chem.* **2008**, *284*, 119. (f) J. G. Rudick, J. G.; Percec, V. *Acc. Chem. Res.* **2008**, *41*, 1641. (g) Akagi, K.; Mori, T. *Chem. Rec.* **2008**, *8*, 395. (h) Palmans, A. R. A.; Meijer, E. W. *Angew. Chem., Int. Ed.* **2007**, *46*, 8948. (i) Masuda, T. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 165. (j) Aoki, T.; Kaneko, T.; Maruyama, N.;

Sumi, A.; Takahashi, M.; Sato, T.; Teraguchi, M. *J. Am. Chem. Soc.* **2003**, *125*, 6346. (k) Nakano, T.; Okamoto, Y. *Chem. Rev.* **2001**, *101*, 4013. (l) Green, M. M.; Park, J.-W.; Sato, T.; Teramoto, K.; Lifson, S.; Selinger, R. L. B.; Selinger, J. V. *Angew. Chem., Int. Ed.* **1999**, *38*, 3138.

(2) (a) Furusho, Y.; Yashima, E. *Macromol. Rapid Commun.* **2011**, *32*, 136. (b) Tanaka, Y.; Katagiri, H.; Furusho, Y.; Yashima, E. *Angew. Chem., Int. Ed.* **2005**, *44*, 3867.

(3) Percec, V.; Won, B. C.; Peterca, M.; Heiney, P. A. *J. Am. Chem. Soc.* **2007**, *129*, 11265.

(4) (a) Yamamoto, T.; Suginome, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 539. (b) Terada, K.; Masuda, T.; Sanda, F. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 4971.

(5) (a) Kawauchi, T.; Kitaura, A.; Kwauchi, M.; Takeichi, T.; Kumaki, J.; Iida, H.; Yahima, E. *J. Am. Chem. Soc.* **2010**, *132*, 12191. (b) Okamoto, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 1731.

(6) Khan, A.; Hecht, S. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 1619.

(7) Park, B.; Kim, M.; Lim, S. W.; Jang, W.; Takezoe, H.; Kim, Y.; Choi, E. H.; Seo, Y. H.; Cho, G. S.; Kang., S. O. *Adv. Mater.* **2009**, *21*, 771.

(8) (a) Liu, R. Y.; Sanda, F.; Masuda, T. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 4175. (b) Goto, H.; Zhang, H. Q.; Yashima, E. *J. Am. Chem. Soc.* **2003**, *125*, 2516. (c) Nomura, R.; Yamada, K.; Tabei, J.; Takakura, Y.; Takigawa, T.; Masuda, T. *Macromolecules* **2003**, *36*, 6939.

(9) (a) Du, X. Y.; Liu, J. B.; Deng, J. P.; Yang, W. T. *Polym. Chem.* **2010**, *1*, 1030.(b) Liu, D.; Du, X. Y.; Zhang, Y. Y.; Deng, J. P.; Yang, W. T. *Macromol. Res.* (DOI: 10.1007/s13233-011-macro0259).

(10) (a) Ward, T. J.; Ward, K. D. *Anal. Chem.* **2010**, *82*, 4712. (b) Welch, C. J. *Chirality* **2009**, *21*, 114. (c) Okamoto, Y.; Ikai, T. *Chem. Soc. Rev.* **2008**, *37*, 2593. (d) Ilisz, I.; Berkecz, R.; Péter, A. *J. Sep. Sci.* **2006**, *29*, 1305.

(11) (a) Vogl, O. *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49*, 1299. (b) Myerson, A. S. *Handbook for Industrial Crystallization*; Butterworth-Heineman Series in Chemical Engineering: Butterworth-Heineman: Boston, 1993.

(12) Chen, B.; Deng, J. P.; Yang, W. T. *Adv. Funct. Mater.* **2011**, *21*, 2345.

(13) Mastai, Y. *Chem. Soc. Rev.* **2009**, *38*, 772.

(14) (a) Menahem, T.; Pravda, M.; Mastai, Y. *Chirality* **2009**, *21*, 862. (b) Mastai, Y.; Sedlák, M.; Cölfen, H.; Antonietti, M. *Chem.—Eur. J.* **2002**, *8*, 2430.

(15) Menahem, T.; Mastai, Y. *New J. Chem.* **2008**, *32*, 925.

(16) Medina, D. D.; Goldshtein, J.; Margel, S.; Mastai, Y. *Adv. Funct. Mater.* **2007**, *17*, 944.

(17) Dressler, D. H.; Mastai, Y. *Chirality* **2007**, *19*, 358.

(18) (a) Tulashie, S. K.; Lorenz, H.; Morgenstern, A. S. *Cryst. Growth Des.* **2009**, *9*, 2387. (b) Tulashie, S. K.; Lorenz, H.; Hilfert, L.; Edelmann, F. T.; Morgenstern, A. S. *Cryst. Growth Des.* **2008**, *8*, 3408.

(19) Bathori, N. B.; Nassimbeni, L. R. *Cryst. Growth Des.* **2010**, *10*, 1782.

(20) (a) Luo, X. F.; Deng, J. P.; Yang, W. T. *Angew. Chem., Int. Ed.* **2011**, *50*, 4909. (b) Ding, L.; Huang, Y. Y.; Zhang, Y. Y.; Deng, J. P.; Yang, W. T. *Macromolecules* **2011**, *44*, 736. (c) Chen, B.; Deng, J. P.; Yang, W. T. *Colloid Polym. Sci.* **2011**, *289*, 133. (d) Zhang, Y. Y.; Luo, X. F.; Deng, J. P.; Yang, W. T. *Macromol. Chem. Phys.* **2011**, *212*, 353. (e) Luo, X. F.; Li, L.; Deng, J. P.; Guo, T. T.; Yang, W. T. *Chem. Commun.* **2010**, *46*, 2745. (f) Chen, B.; Deng, J. P.; Yang, W. T. *Macromolecules* **2010**, *43*, 9613. (g) Chen, B.; Deng, J. P.; Liu, X. Q.; Yang, W. T. *Macromolecules* **2010**, *43*, 3177. (h) Deng, J. P.; Chen, B.; Luo, X. F.; Yang, W. T. *Macromolecules* **2009**, *42*, 933.

(21) Zhou, K.; Tong, L. Y.; Deng, J. P.; Yang, W. T. *J. Mater. Chem.* **2010**, *20*, 781.

(22) (a) Zhang, Z. G.; Deng, J. P.; Li, J. W.; Yang, W. T. *Polym. J.* **2008**, *40*, 436. (b) Zhang, Z. G.; Deng, J. P.; Zhao, W. G.; Wang, J. M.; Yang, W. T. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 500.

(23) Schrock, R. R.; Osborn, J. A. *Inorg. Chem.* **1970**, *9*, 2339.

(24) (a) Ma, Y.; Cölfen, H.; Antonietti, M. *J. Phys. Chem. B* **2006**, *110*, 10822. (b) Lee, A. Y.; Ulman, A.; Myerson, A. S. *Langmuir* **2002**, *18*, 5886.