

RSC Advances



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



RSC Advances

COMMUNICATION

An Unusual Spherulite Morphology Induced by Nano-fillers from Concentrated Cellulose/Ionic Liquid Solution

Received 00th January 20xx,
Accepted 00th January 20xx

Meichun Ding,^{a,b} Jian Yu,^{*a} Jiasong He^a and Jun Zhang^{*a}

DOI: 10.1039/x0xx00000x

www.rsc.org/

An unusual spherulite morphology consisting of an eye-like region surrounded by a normal region was found in concentrated cellulose solutions in an ionic liquid AmimCl, especially in the presence of 0.5 wt% MWCNTs. In comparison with the normal region, the eye-like region had different growth rate and different morphology, such as birefringence and band spacing, although both regions had similar crystalline modification and microstructure. On heating, the regions with initial positive birefringence transformed to more thermodynamically stable negative ones without influencing the band spacing, and the change was irreversible upon cooling.

Spherulites are a kind of important morphological forms in the crystal structure of semicrystalline polymers. The microstructure and size of the spherulites have great influence on performance of polymers.¹⁻³ For most of the linear semicrystalline polymer, spherulites can be formed through melt or solution crystallization. The formation and morphology of spherulites depend on many factors, such as crystallization temperature, sample thickness, polymer molar mass and additives. The influence of additives, especially the nano-fillers, on polymer crystallization has attracted increasing attention during the past decades. It can change the spherulitic size, morphology, and growth rate, consequently modulate the physical and mechanical properties of polymer materials.⁴⁻⁹

Cellulose is the most abundant natural polymer on the earth, well-known for its renewable, biodegradable, and biocompatible properties. Nowadays, various cellulose-based materials, including regenerated cellulose materials (fibers and films) and cellulose derivatives (esters and ethers), are widely applied. However, cellulose cannot be melted due to its strong intramolecular and intermolecular hydrogen bonding interaction. So far, spherulites of cellulose were observed only in a very few cellulose solutions, the first report was cellulose-N-methylmorpholine-N-oxide (NMMO)

system. However, whether the spherulites were formed from cellulose or NMMO is still under dispute.¹⁰⁻¹³ Recently, room temperature ionic liquids have received considerable attentions for cellulose dissolution due to their excellent dissolution ability,¹⁴⁻¹⁷ which provides a new and robust platform for both cellulose science in chemistry and physics and cellulose technology in processing and functionalization.^{18,19} In our previous study, ring-banded spherulites of cellulose were obtained from concentrated microcrystalline cellulose/1-allyl-3-methylimidazolium chloride (MCC/AmimCl) solutions,²⁰ of which the size and morphology are associated with the crystallization temperature and the solution concentration. It would provide not only the new insight into cellulose crystallization, but also new opportunities to manipulate the properties of regenerated cellulose materials by controlling the crystallization conditions.

In this letter, an unusual ring-banded spherulite of cellulose, which contained two different regions, i.e., an eye-like region and a normal region, was observed clearly by adding 0.5 wt% multi-walled carbon nanotubes (MWCNTs) in MCC/AmimCl solution. The polarized optical microscopy (POM) images of these spherulites are shown in Figure 1. To the best of our knowledge, this unusual morphology has never been observed in solution crystallization, while it has been reported only in melt-crystallized poly[(R)-3-hydroxyvalerate] (PHV) at appropriate temperatures.²¹

The spherulites were obtained by keeping MCC/AmimCl solutions with high concentrations (16 and 20 wt%) and nano-fillers at certain temperatures (40 and 60 °C) and a relative humidity of 25% for 6 days. It can be seen from Figure 1 that the eye-like region grew from the center of spherulites, which was surrounded by the normal region. Some of them were symmetrical (Figures 1e and 1f), while the others were asymmetric (Figures 1g and 1h). Moreover, the direction of the eye-like region changed when the cellulose spherulite was rotated in the plane (Figure S1), indicating the eye-like region was a physical entity in the spherulite with a fixed position. And it displayed the birefringence opposite to that of the surrounding normal region independent of its direction, i.e., the eye-like region with positive birefringence was surrounded by the normal region with negative birefringence, and vice versa. And the

^a Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Engineering Plastics, Institute of Chemistry, Chinese Academy of Sciences (CAS), Beijing, 100190, China.

^b University of Chinese Academy of Sciences, Beijing, 100039, China.

Electronic supplementary information (ESI) available: Fig. S1–S4 and Animations S1–S2. See DOI: 10.1039/x0xx00000x

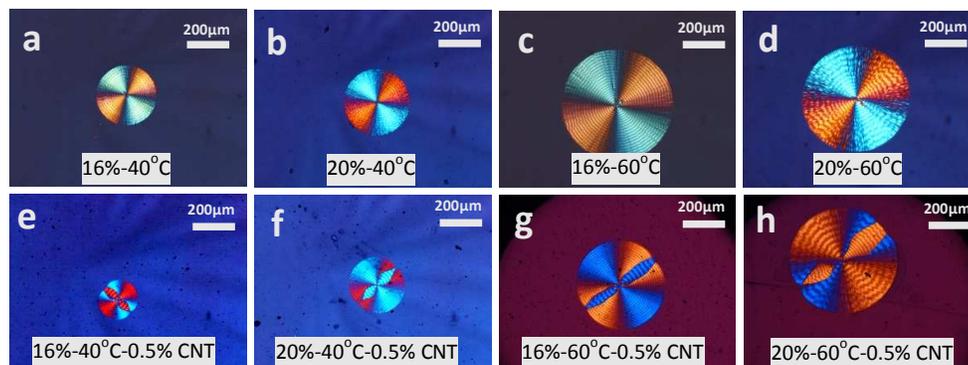


Figure 1. POM images of cellulose spherulites crystallized from 16 wt% and 20 wt% MCC/AmimCl solution at 40 °C and 60 °C (16 wt%-40 °C (a), 20 wt%-40 °C (b), 16 wt%-60 °C (c), and 20 wt%-60 °C (d)); and with 0.5 wt% MWCNTs (16 wt%-40 °C-0.5% CNT (e), 20 wt%-40 °C-0.5% CNT (f), 16 wt%-60 °C-0.5% CNT (g), and 20 wt%-60 °C-0.5% CNT (h)).

band spacing was also different in these two regions. As shown in both Figures 1g and 1h, the regions with negative birefringence had a bit smaller band spacing than those with positive birefringence. The results of the micro-Raman spectra (Figure S2) and atomic force microscopy (Figure S3) confirmed that these two regions have no significant difference in microstructure and crystalline modification. By comparison, the eye-like region was hardly observed in spherulites obtained from pure cellulose solutions (Figures 1a-d), and few spherulites can be found to have the eye-like region in the samples containing less contents of MWCNTs (Figure S4). The similar spherulite morphology was also observed for concentrated MCC/AmimCl solution containing 0.5 wt% nanoclay and graphene oxide (GO) (Figure 2). Therefore, it is clear that the eye-like morphology was formed in the crystallization of cellulose from AmimCl solutions, especially in the presence of proper amount of nano-fillers.

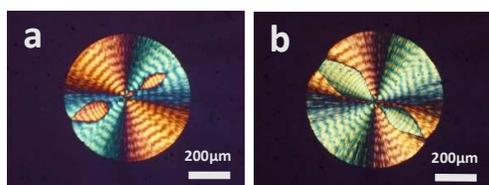


Figure 2. POM images of cellulose spherulites crystallized from 20 wt% MCC/AmimCl solution at 60 °C with different fillers of 0.5 wt% nanoclay (a), and 0.5 wt% GO (b).

As indicated in the literature,²¹ the lamellae in the eye-like region have different growth axis from those in the normal region, and the spherulites can grow in both axes simultaneously. In the present study, due to the relatively large aspect ratio of the nano-fillers having fiber-like (MWCNTs) and sheet-like (nanoclay and GO) shapes, the nano-fillers and the baby lamellae would preferentially adopt an orientation parallel to the substrate in a thin film. Subsequently, the baby lamellae can grow along both axes

without confinement to the film thickness. As revealed in Figure S3, two regions developed from the center of the spherulite simultaneously. However, one region grew along the radial direction with a lower rate than the other one, and surrounded by the latter to form eye-like shape eventually. Figure 3 shows that the eye-like region stopped growing after 5 days, and the size of normal region increased slowly and continuously. It also shows that the growth rate of spherulites reduced in the presence of 0.5 wt% MWCNTs, compared to spherulites obtained from pure MCC/AmimCl solution, due to the nano-fillers blocking the movement of cellulose chains.

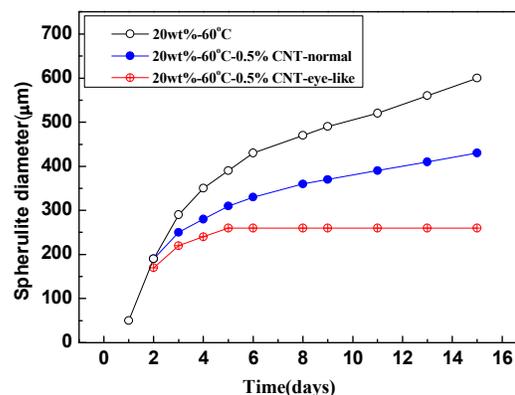


Figure 3. Growth profiles of cellulose spherulites crystallized from 20 wt% MCC/AmimCl solution at 60 °C.

It is worth to note that the birefringence of these spherulites changed after heating. The heating process of two kinds of typical cellulose spherulites was followed by POM observation from 30 to 100 °C at a heating rate of 10 °C/min (Animations S1 and S2), and the images at different temperatures were shown in Figure 4. The

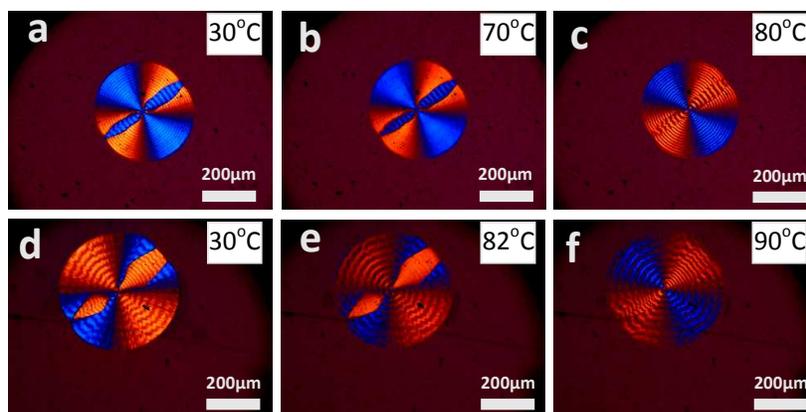


Figure 4. POM images of cellulose spherulites during heating. Sample 16 %-60 °C-0.5% CNT at 30 °C (a), 70 °C (b), and 80 °C (c); sample 20 %-60 °C-0.5% CNT at 30 °C (d), 82 °C (e), and 90 °C (f).

initial spherulites in sample 16%-60 °C-0.5 % CNT (Figure 4a) have the eye-like region with positive birefringence and the normal region with negative birefringence, while in the sample 20%-60 °C-0.5 % CNT (Figure 4d) have the negative eye-like region and the positive normal region. On heating, all the regions with positive birefringence transformed to negative regions, hence spherulites with complete negative birefringence were obtained in both cases. It was shown in Figure 4 that the transition temperature of the sample 16%-60 °C-0.5 % CNT (Figures 4a-c) was lower than that of the sample 20%-60 °C-0.5 % CNT (Figures 4d-f). At the same time, the band spacing remained unaltered as the birefringence varied. Therefore, an eye-like region can also be discerned, which had same birefringence with the surrounding region. More importantly, the changes were irreversible when the sample cooled down at 10 °C/min. The transformation of birefringence was also observed for cellulose spherulites obtained in the presence of nanoclay and GO. Therefore, the negative region in cellulose spherulite was thermodynamically stable compared with the positive one, while the positive normal region was kinetically favorable under high temperature (60 °C), high concentration (20 wt%), and a relatively high additive content (0.5 wt%), as shown in Figure 4d.

In conclusion, we have obtained an unusual spherulite morphology consisting of the eye-like region and the normal region from concentrated cellulose solutions in AmimCl. The morphology was observed more clearly by adding 0.5 wt% nano-fillers (MWCNTs, nanoclay and GO), which could induce the baby lamellae to preferentially adopt a flat-on orientation in the thin film. Then these lamellae grow in two different axes with different rates to form the two regions and the unusual spherulites eventually. Micro-Raman spectra and AFM images showed that the both regions had similar crystalline modification and microstructure. However, from the POM images, the normal region and the eye-like region had different birefringence and band spacing. Moreover, the regions with initial positive birefringence transformed to negative regions on heating, while the band spacing remained unaltered. Therefore, spherulites with complete negative birefringence were obtained irreversible,

indicating that the negative cellulose spherulites were thermodynamically stable compared with positive ones.

ACKNOWLEDGMENT

This work was supported by the National Natural Science Foundation of China (No. 51425307).

References

- J. H. Magill, *Journal of Materials Science*, 2001, **36**, 3143-3164.
- S. Safari and T. G. M. van de Ven, *Journal of Materials Science*, 2015, **50**, 3686-3696.
- A. Sepe, Z. Rong, M. Sommer, Y. Vaynzof, X. Sheng, P. Müller-Buschbaum, D.M. Smilgies, Z.K. Tan, L. Yang, R. H. Friend, U. Steiner and S. Hüttner, *Energy and Environmental Science*, 2014, **7**, 1725-1736.
- Z. Jia, F. Zeng, Q. Yuan and R. D. K. Misra, *Mater. Sci. Eng., B*, 2012, **177**, 666-672.
- K. B. Lu, N. Grossiord, C. E. Koning, H. E. Miltner, B. van Mele and J. Loos, *Macromolecules*, 2008, **41**, 8081-8085.
- P. Maiti, P. H. Nam, M. Okamoto, N. Hasegawa and A. Usuki, *Macromolecules*, 2002, **35**, 2042-2049.
- G. Z. Papageorgiou, M. Nerantzaki, I. Grigoriadou, D. G. Papageorgiou, K. Chrissafis and D. Bikiaris, *Macromol. Chem. Phys.*, 2013, **214**, 2415-2431.
- L. Priya and J. P. Jog, *J. Polym. Sci., Part B: Polym. Phys.*, 2002, **40**, 1682-1689.
- D. F. Wu, L. Wu, L. F. Wu, B. Xu, Y. S. Zhang and M. Zhang, *J Nanosci Nanotechno*, 2008, **8**, 1658-1668.
- H. Chanzy, M. Dube and R. H. Marchessault, *J. Polym. Sci., Polym. Lett. Ed.*, 1979, **17**, 219-226.
- M. Dube, Y. Deslandes and R. H. Marchessault, *J. Polym. Sci., Polym. Lett.*, 1984, **22**, 163-171.
- S. H. Park, Y. H. Jeong, W. S. Lee and H. J. Kang, *Polymer-Korea*, 1998, **22**, 779-785.
- O. Biganska, P. Navard and O. Bedue, *Polymer*, 2002, **43**, 6139-6145.
- R. P. Swatloski, S. K. Spear, J. D. Holbrey and R. D. Rogers, *J Am Chem Soc.*, 2002, **124**, 4974-4975.

COMMUNICATION

Journal Name

- 15 J. Wu, J. Zhang, H. Zhang, J. S. He, Q. Ren and M. Guo, *Biomacromolecules*, 2004, **5**, 266-268.
- 16 H. Zhang, J. Wu, J. Zhang and J. S. He, *Macromolecules*, 2005, **38**, 8272-8277.
- 17 Z. Z. Wan, L. Li and S. X. Cui, *Biopolymers*, 2008, **89**, 1170-1173.
- 18 H. Wang, G. Gurau and R. D. Rogers, *Chem Soc Rev.*, 2012, **41**, 1519-1537.
- 19 Y. Cao, J. Wu, J. Zhang, H. Li, Y. Zhang and J. He, *Chem. Eng. J.*, 2009, **147**, 13-21.
- 20 H. Z. Song, Y. H. Niu, J. Yu, J. Zhang, Z. G. Wang and J. S. He, *Soft Matter*, 2013, **9**, 3013-3020.
- 21 H. M. Ye, J. Xu, B. H. Guo and T. Iwata, *Macromolecules*, 2009, **42**, 694-701.
- 22 D. Li, M. B. Muller, S. Gilje, R. B. Kaner and G. G. Wallace, *Nat. Nanotechnol.*, 2008, **3**, 101-105.