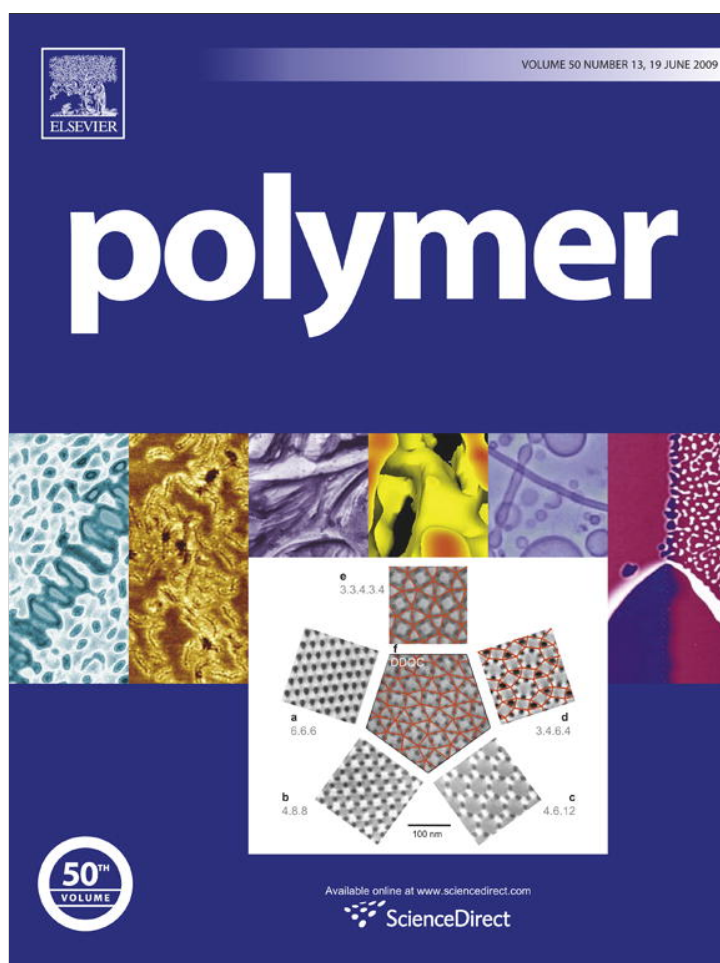


Provided for non-commercial research and education use.
Not for reproduction, distribution or commercial use.

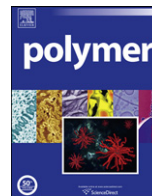


This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/copyright>



Polymer Vol. 50, No. 13, 19 June 2009

Contents

POLYMER PAPERS

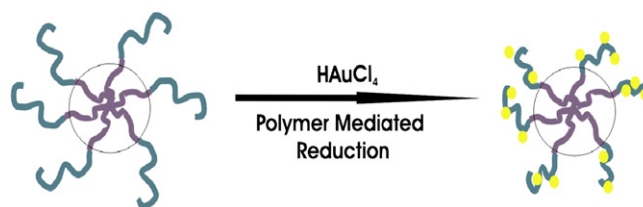
Polymer mediated formation of corona-embedded gold nanoparticles in block polyelectrolyte micelles

pp 2743–2751

Anastasia Meristoudi^{a,b}, Stergios Pispas^{a,*}

^a *Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48 Vassileos Constantinou Avenue, Athens 116 35, Greece*

^b *University of Patras, Department of Materials Science, Patras 26 504, Greece*

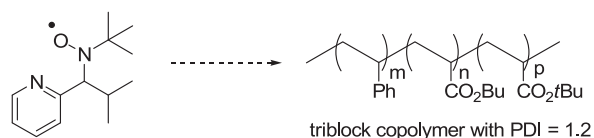


Synthesis and evaluation of a new polar, TIPNO type nitroxide for “living” free radical polymerization

pp 2752–2761

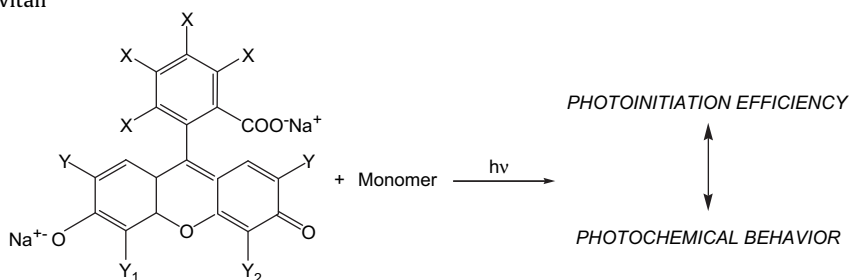
Lucien Marx^{*}, Patrick Hemery

Laboratoire de Chimie des Polymères, UMR 7610, Université Pierre et Marie Curie – Paris 6, 4 Place Jussieu, 75252 Paris Cedex 05, France



Xanthene dyes/amine as photoinitiators of radical polymerization: A comparative and photochemical study in aqueous medium

pp 2762–2767

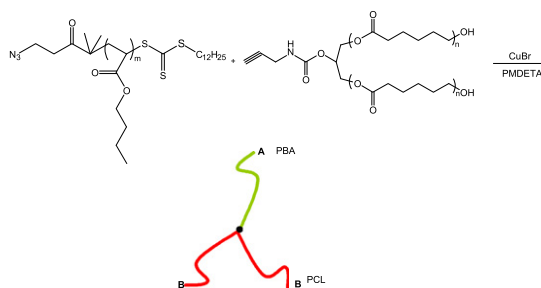
M.V. Encinas^{a,*}, A.M. Rufs^a, S.G. Bertolotti^b, C.M. Previtali^b^a Facultad de Química y Biología, Universidad de Santiago de Chile, Casilla 307-2, Santiago, Chile^b Departamento de Química, Univ. Nacional de Río Cuarto, Argentina

A new approach to 3-miktoarm star polymers using a combination of reversible addition-fragmentation chain transfer (RAFT) and ring opening polymerization (ROP) via "Click" chemistry

pp 2768–2774

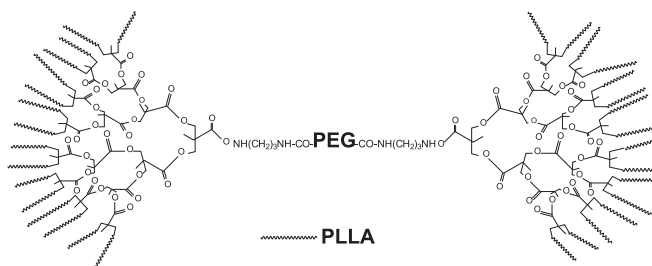
Ankit Vora, Kunal Singh, Dean C. Webster^{*}

Department of Coatings and Polymeric Materials, North Dakota State University, PO Box 6050, Dept 2760, Fargo, ND 58108, United States



Biodegradable comb-dendritic tri-block copolymers consisting of poly(ethylene glycol) and poly(L-lactide): Synthesis, characterizations, and regulation of surface morphology and cell responses

pp 2775–2785

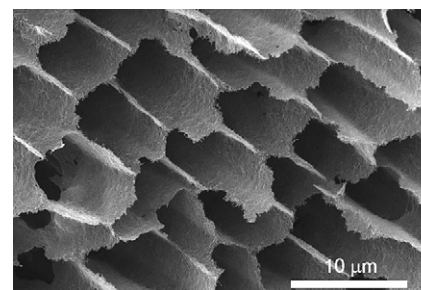
Feirong Gong^a, Xiaoyan Cheng^a, Shanfeng Wang^{b,*}, Yang Wang^c, Yun Gao^a, Shujun Cheng^{a,**}^a Key Laboratory for Ultrafine Materials of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, China^b Department of Materials Science and Engineering, The University of Tennessee, Knoxville, TN 37996, USA^c Shanghai Medical College, Fudan University, 138 Yi-xue-yuan Road, Shanghai 200032, China

Multiwalled carbon nanotube cryogels with aligned and non-aligned porous structures

pp 2786–2792

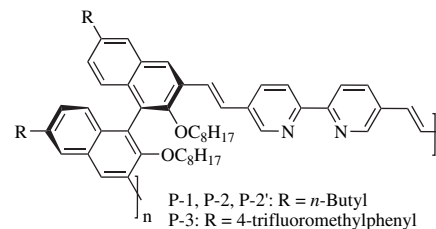
Soon-Min Kwon, Hun-Sik Kim, Hyoung-Joon Jin^{*}

Department of Polymer Science and Engineering, Inha University, Incheon 402-751, Republic of Korea

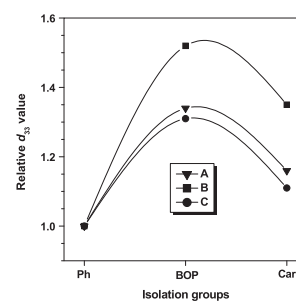


Synthesis and properties of chiral helical polymers based on optically active polybinaphthyls

pp 2793–2805

Xiaobo Huang^{a,b}, Ying Xu^a, Qian Miao^b, Lili Zong^a, Hongwen Hu^a, Yixiang Cheng^{a,*}^a Key Lab of Mesoscopic Chemistry of MOE, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China^b College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou 325027, China**The role of introduced isolation groups in PVK-based nonlinear optical polymers: Enlarged nonlinearity, improved processibility, and enhanced thermal stability**

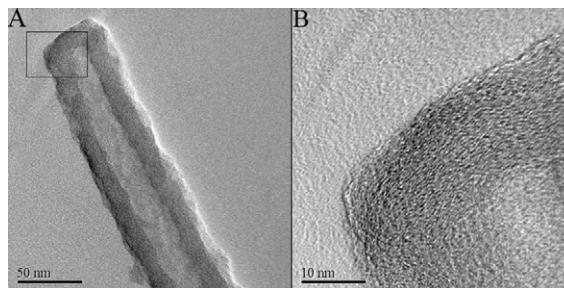
pp 2806–2814

Zhong'an Li^a, Gui Yu^b, Shoucheng Dong^a, Wenbo Wu^a, Yunqi Liu^b, Cheng Ye^b, Jingui Qin^a, Zhen Li^{a,*}^a Department of Chemistry, Wuhan University, Wuhan 430072, China^b Organic Solids Laboratories, Institute of Chemistry, The Chinese Academy of Sciences, Beijing 100080, China**Easy synthesis of carbon nanotubes with polypyrrole nanotubes as the carbon precursor**

pp 2815–2818

Songmin Shang^{*}, Xiaoming Yang, Xiao-ming Tao

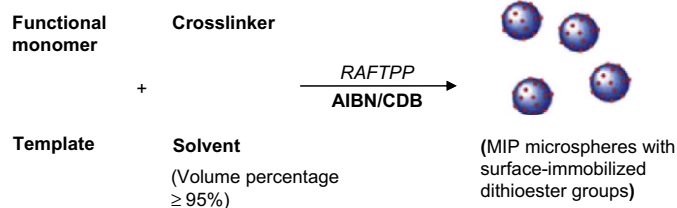
Institute of Textiles and Clothing, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, PR China

**Preparation of molecularly imprinted polymer microspheres via reversible addition–fragmentation chain transfer precipitation polymerization**

pp 2819–2825

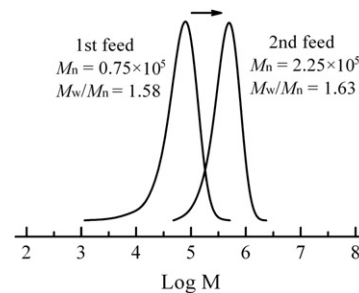
Guoqing Pan, Baiyi Zu, Xianzhi Guo, Ying Zhang, Chenxi Li, Huiqi Zhang^{*}

Key Laboratory of Functional Polymer Materials (Nankai University), Ministry of Education, Department of Chemistry, Nankai University, Tianjin 300071, PR China



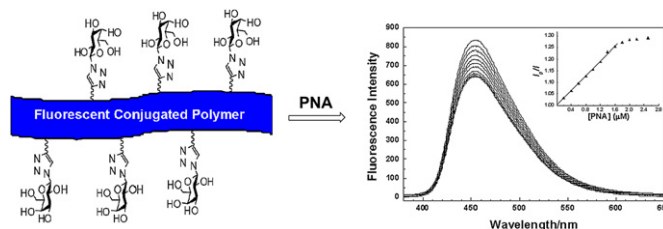
Living polymerization of 1,3-butadiene by a Ziegler–Natta type catalyst composed of iron(III) 2-ethylhexanoate, triisobutylaluminum and diethyl phosphite

pp 2826–2829

Dirong Gong^{a,b}, Weimin Dong^a, Jinchang Hu^a, Xuequan Zhang^{a,*}, Liansheng Jiang^a^a Laboratory of Polymer Engineering, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 5625 Renmin Street, Changchun 130022, PR China^b Graduate School of the Chinese Academy of Sciences, Beijing 100049, PR China

Triphenylamine-based fluorescent conjugated glycopolymers: Synthesis, characterization and interactions with lectins

pp 2830–2835

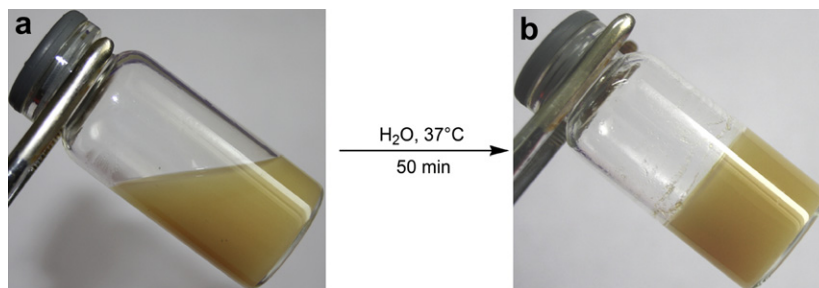
Qi Chen^a, Yonghua Xu^b, Yuguo Du^b, Bao-Hang Han^{a,*}^a National Center for Nanoscience and Technology, No. 11, Beiyitiao Zhongguancun, Beijing 100190, China^b State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

Thermosensitive hydrogels synthesized by fast Diels–Alder reaction in water

pp 2836–2840

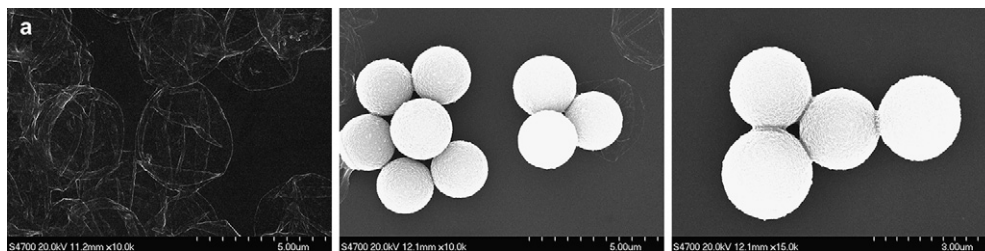
Hong-Liang Wei^{*}, Zhe Yang, Li-Mei Zheng, Yan-Min Shen

School of Chemistry and Chemical Engineering, Henan University of Technology, Zhengzhou 450001, PR China



Assembled alginate/chitosan micro-shells for removal of organic pollutants

pp 2841–2846

Yang Ding^{a,b}, Yi Zhao^a, Xia Tao^{a,*}, Yan-Zhen Zheng^{a,b}, Jian-Feng Chen^{b,*}^a Key Laboratory for Nanomaterials of the Ministry of Education, Beijing University of Chemical Technology, Bei San Huan East Road 15, Beijing 100029, China^b Research Center of the Ministry of Education for High Gravity Engineering & Technology, Beijing University of Chemical Technology, Beijing 100029, China

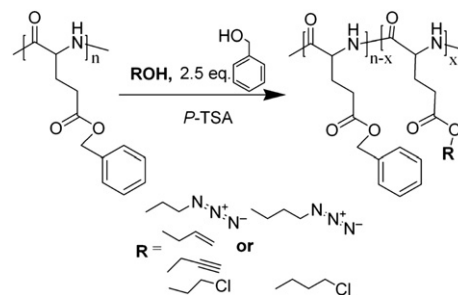
Synthesis and characterization of functional poly(γ -benzyl-L-glutamate) (PBLG) as a hydrophobic precursor

pp 2847–2855

Jinshan Guo^{a,b}, Yubin Huang^{a,*}, Xiabin Jing^a, Xuesi Chen^a

^a State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, PR China

^b Graduate School of Chinese Academy of Sciences, Beijing 100039, PR China



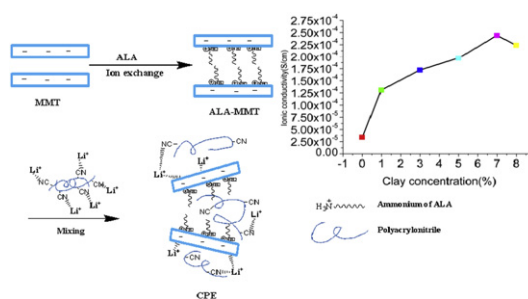
Effect of the addition of hydrophobic clay on the electrochemical property of polyacrylonitrile/LiClO₄ polymer electrolytes for lithium battery

pp 2856–2862

Y.W. Chen-Yang^{a,*}, Y.T. Chen^a, H.C. Chen^b, W.T. Lin^b, C.H. Tsai^a

^a Department of Chemistry and Center for Nanotechnology, Chung Yuan Christian University, 200 Chung-Pei Road, Chung-Li, Taoyuan County 32023, Taiwan, ROC

^b Taiwan Textile Research Institute, Taipei County 23674, Taiwan, ROC

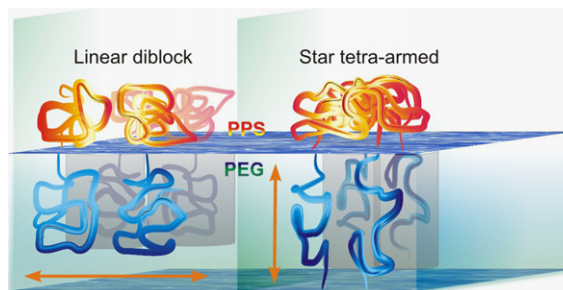


Amphiphilic star block copolymers: Influence of branching on lyotropic/interfacial properties

pp 2863–2873

Lei Wang, Ping Hu, Nicola Tirelli*

School of Pharmacy and Pharmaceutical Sciences, University of Manchester, Oxford Road, Manchester, M13 9PT, United Kingdom



Biomimetic apatite coating on P(EMA-co-HEA)/SiO₂ hybrid nanocomposites

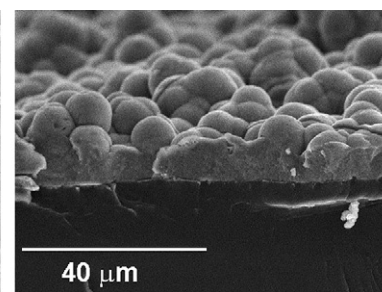
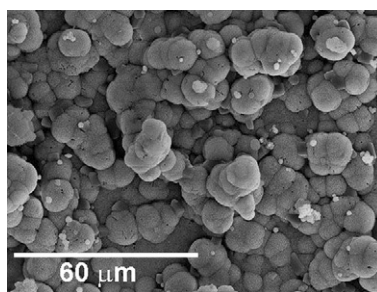
pp 2874–2884

A. Vallés Lluch^{a,*}, G. Gallego Ferrer^{a,b,c}, M. Monleón Pradas^{a,b,c}

^a Center for Biomaterials and Tissue Engineering, Universidad Politécnica de Valencia, Cno. de Vera s/n, 46022 Valencia, Spain

^b Regenerative Medicine Unit, Centro de Investigación Príncipe Felipe, Av. Autopista del Saler 16, 46013 Valencia, Spain

^c Networking Research Center on Bioengineering, Biomaterials and Nanomedicine, Valencia, Spain

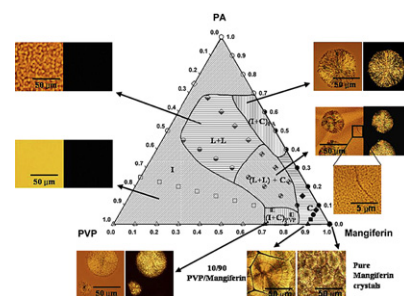


Hydrogen bonding interactions and miscibility studies of poly(amide)/poly(vinyl pyrrolidone) blends containing mangiferin

pp 2885–2892

Chandrasekaran Neelakandan, Thein Kyu*

Department of Polymer Engineering, University of Akron, Akron, OH 44325, USA

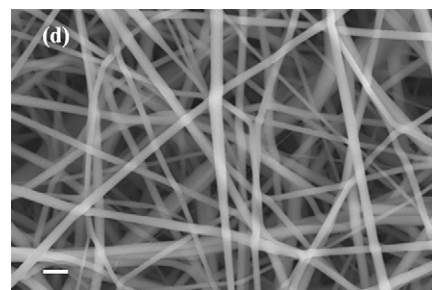


Formation of functional polyethersulfone electrospun membrane for water purification by mixed solvent and oxidation processes

pp 2893–2899

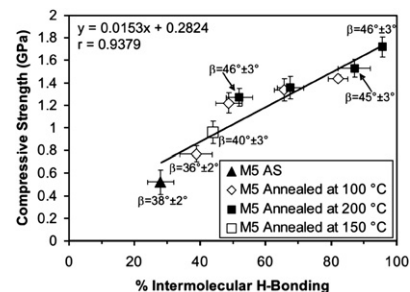
Kyunghwan Yoon, Benjamin S. Hsiao*, Benjamin Chu**

Department of Chemistry, Stony Brook University, Stony Brook, NY 11794-3400, USA



Effect of hydrogen bonding and moisture cycling on the compressive performance of poly-pyridobisimidazole (M5) fiber

pp 2900–2905

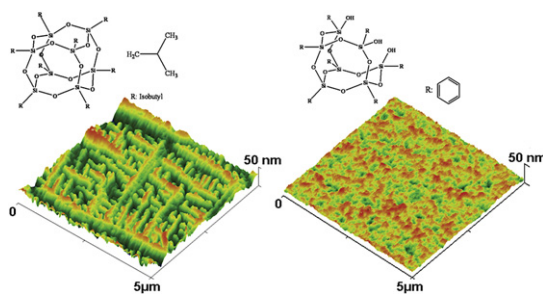
A. Andres Leal^{a,b}, Joseph M. Deitzel^a, Steven H. McKnight^d, John W. Gillespie, Jr.^{a,b,c,*}^a Center for Composite Materials (UD-CCM), University of Delaware, Newark, DE 19716, United States^b Department of Materials Science and Engineering, University of Delaware, Newark, DE 19716, United States^c Department of Civil and Environmental Engineering, University of Delaware, Newark, DE 19716, United States^d Army Research Laboratory, Materials Division, Aberdeen, MD 21005, United States

Molecular miscibility and chain dynamics in POSS/polystyrene blends: Control of POSS preferential dispersion states

pp 2906–2918

Rahul Misra, Alp H. Alidedeoglu, William L. Jarrett, Sarah E. Morgan*

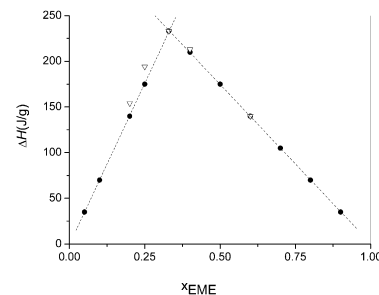
School of Polymers and High Performance Materials, University of Southern Mississippi, 118 College Dr., Box 10076, Hattiesburg, MS 39406-0076, USA



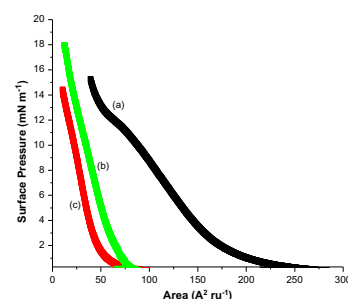
On the curing of linseed oil epoxidized methyl esters with different cyclic dicarboxylic anhydrides

pp 2919–2925

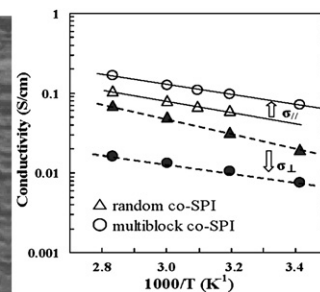
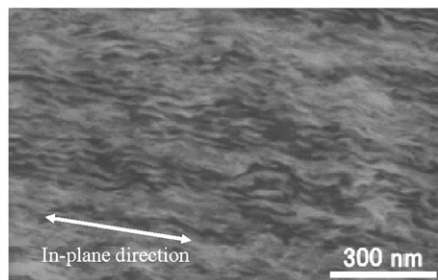
Denise dos Santos Martini, Bibiana Aguiar Braga, Dimitrios Samios*

Laboratório de Instrumentação e Dinâmica Molecular, Instituto de Química Universidade Federal do Rio Grande do Sul, Av. Bento Gonçalves 9500, Caixa Postal 15003, CEP 91501-970 Porto Alegre, RS, Brazil**Inclusion complexes containing poly(ϵ -caprolactone)diol and cyclodextrins. Experimental and theoretical studies**

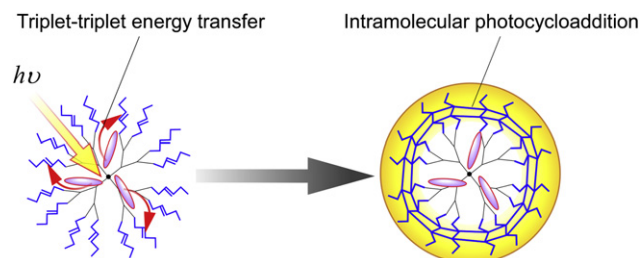
pp 2926–2932

César Saldías^a, Ligia Gargallo^{a,*}, Claudia Sandoval^a, Angel Leiva^a, Deodato Radic^a, Julio Caballero^b, Mario Saavedra^b, Fernando D. González-Nilo^b^a *Departamento de Química Física, Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 302, Correo 22, Santiago, Chile*^b *Centro de Bioinformática y Simulación Molecular, Universidad de Talca, 2 Norte 685, Casilla 721, Talca, Chile***Synthesis and properties of sulfonated multiblock copolynaphthalimides**

pp 2933–2943

Zhaoxia Hu^a, Yan Yin^b, Kazuaki Yaguchi^a, Nobutaka Endo^a, Mitsuru Higa^a, Ken-ichi Okamoto^{a,*}^a *Graduate School of Science & Engineering, Yamaguchi University, Tokiwadai 2-16-1, Ube, Yamaguchi 755-8611, Japan*^b *Tianjin University, Weijin Road 92, Nankai Dis, Tianjin 30072, PR China***Photochemical and photophysical reactions of poly(propylene imine) dendrimers tethering cinnamamide groups**

pp 2944–2952

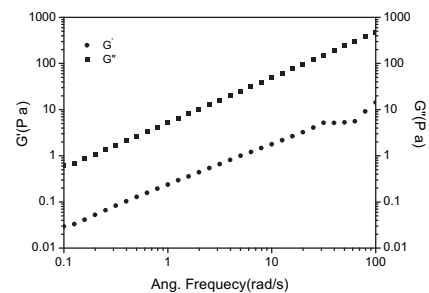
Seiichi Furumi^{a,b,*}, Akira Otomo^b, Shiyoshi Yokoyama^{b,c}, Shinro Mashiko^b^a *National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan*^b *National Institute of Information and Communications Technology (NICT), 588-2 Iwaoka, Nishi-ku, Kobe 651-2492, Japan*^c *Institute for Materials Chemistry and Engineering (IMCE), Kyushu University, 6-1 Kasuga-koen, Kasuga, Fukuoka 816-8580, Japan*

The synthesis of functionalized carbon nanotubes by hyperbranched poly(amine-ester) with liquid-like behavior at room temperature

pp 2953–2957

Jiaoxia Zhang, Yaping Zheng*, Peiyong Yu, Su Mo, Rumin Wang

Department of Applied Chemistry, School of Natural and Applied Science, Northwestern Polytechnical University, Xi'an 710129, China



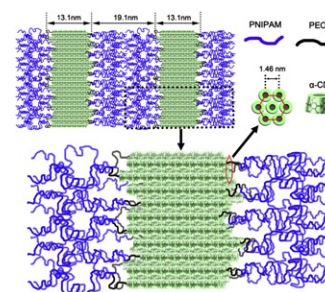
Supramolecular self-assembly through inclusion complex formation between poly(ethylene oxide-*b*-*N*-isopropylacrylamide) block copolymer and α -cyclodextrin

pp 2958–2966

Cheng-Wei Tu^a, Shiao-Wei Kuo^{b,**}, Feng-Chih Chang^{a,*}

^a Institute of Applied Chemistry, National Chiao-Tung University, 30050 Hsinchu, Taiwan

^b Department of Materials and Optoelectronic Science, Center for Nanoscience and Nanotechnology, National Sun Yat-Sen University, Kaohsiung, Taiwan



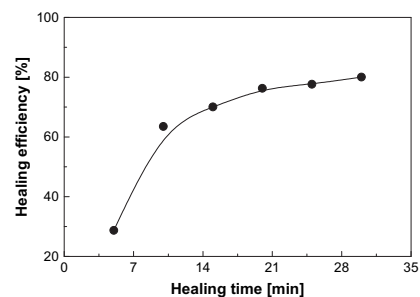
Self-healing epoxy based on cationic chain polymerization

pp 2967–2975

Ding Shu Xiao^a, Yan Chao Yuan^a, Min Zhi Rong^{b,*}, Ming Qiu Zhang^b

^a Key Laboratory for Polymeric Composite and Functional Materials of Ministry of Education, OFCM Institute, School of Chemistry and Chemical Engineering, Zhongshan University, Guangzhou 510275, PR China

^b Materials Science Institute, Zhongshan University, Guangzhou 510275, PR China



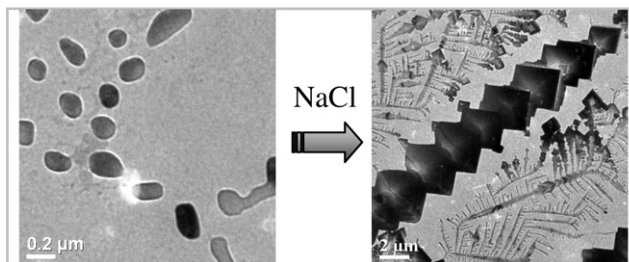
Self-assembly microstructures of amphiphilic polyborate in aqueous solutions

pp 2976–2980

Haiying Wang^a, Liyuan Chai^a, Anjun Hu^b, Chunxu Lü^{b,*}, Bingdong Li^b

^a School of Metallurgical Science and Technology, Central South University, Changsha 410083, PR China

^b School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, PR China

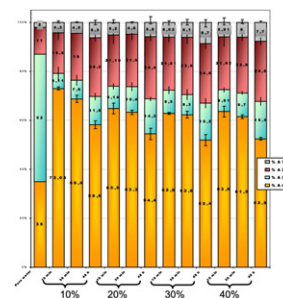


Application of FTIR spectroscopy to determine transport properties and water-polymer interactions in polypropylene (PP)/poly(ethylene-co-vinyl alcohol) (EVOH) blend films: Effect of poly(ethylene-co-vinyl alcohol) content and water activity pp 2981–2989

Aurora Lasagabáster^a, María José Abad^b, Luis Barral^{b,*}, Ana Ares^b, Rebeca Bouza^b

^a Departamento de Química Orgánica I, Escuela de Optica, Universidad Complutense de Madrid (UCM), Arcos de Jalón s/n, 28037 Madrid, Spain

^b Grupo de Polimeros, Departamento de Física, E.U.P. Ferrol, Universidad de A Coruña, Avda. 19 febrero s/n, 15405 Ferrol, Spain



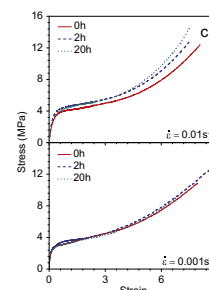
Effects of spinodal decomposition on mechanical properties of a polyolefin blend from high to low strain rates pp 2990–2998

Liang Yang^{a,b}, Yanhua Niu^{a,*}, Howard Wang^c, Zhigang Wang^{a,*}

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

^b Graduate School, Chinese Academy of Sciences, Beijing 100049, PR China

^c Department of Mechanical Engineering, State University of New York at Binghamton, Binghamton, NY 13902, USA



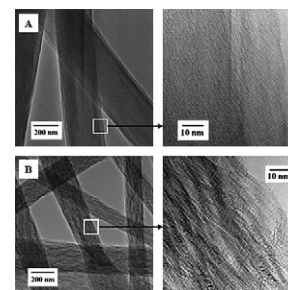
Development of carbon nanofibers from aligned electrospun polyacrylonitrile nanofiber bundles and characterization of their microstructural, electrical, and mechanical properties pp 2999–3006

Zhengping Zhou^a, Chuilin Lai^{a,b}, Lifeng Zhang^b, Yong Qian^a, Haoqing Hou^{a,*}, Darrell H. Reneker^c, Hao Fong^{b,**}

^a College of Chemistry and Chemical Engineering, Jiangxi Normal University, Nanchang 330027, China

^b Department of Chemistry, South Dakota School of Mines and Technology, 501 East St. Joseph Street, Rapid City, SD 57701-3995, USA

^c Department of Polymer Science, University of Akron, Akron, OH 44325, USA

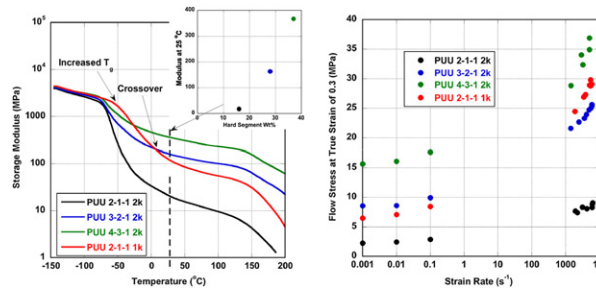


The effect of microstructure on the rate-dependent stress-strain behavior of poly(urethane urea) elastomers pp 3007–3015

Sai S. Sarva^a, Alex J. Hsieh^{a,b,*}

^a Institute for Soldier Nanotechnologies, Massachusetts Institute of Technology, 500 Technology Square, Cambridge, MA 02139, USA

^b U.S. Army Research Laboratory, AMSRD-ARL-WM-MD, Aberdeen Proving Ground, MD 21005-5069, USA



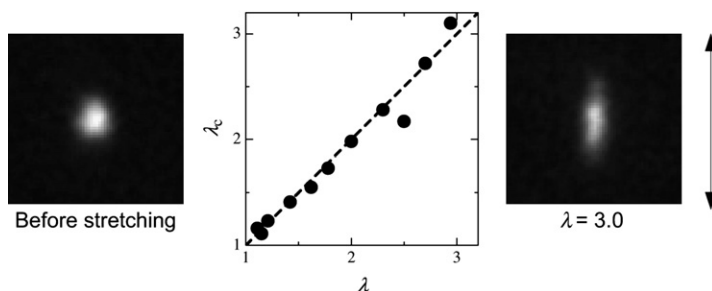
Affine deformation of single polymer chain in poly(methyl methacrylate) films under uniaxial extension observed by scanning near-field optical microscopy

pp 3016–3021

Toru Ube^a, Hiroyuki Aoki^{a,*}, Shinzaburo Ito^a, Jun-ichi Horinaka^b,
Toshikazu Takigawa^b, Toshiro Masuda^b

^a Department of Polymer Chemistry, Kyoto University,
Nishikyo, Kyoto 610-8510, Japan

^b Department of Material Chemistry, Kyoto University,
Nishikyo, Kyoto 610-8510, Japan

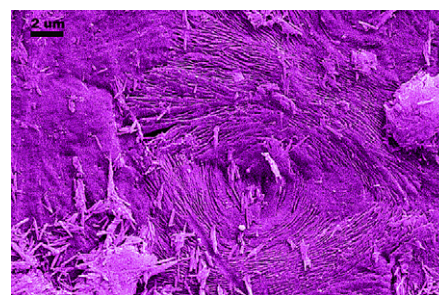


Halloysite nanotubes as a novel β -nucleating agent for isotactic polypropylene

pp 3022–3030

Mingxian Liu, Baochun Guo^{*}, Mingliang Du, Feng Chen, Demin Jia

Department of Polymer Materials and Engineering, South China University of Technology,
Guangzhou 510640, China

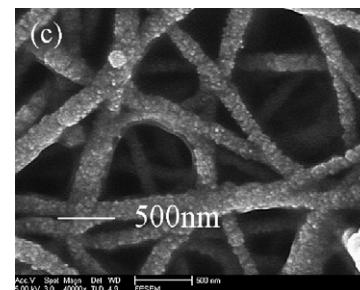


Preparation and photocatalysis of TiO₂-fluoropolymer electrospun fiber nanocomposites

pp 3031–3036

Tieshi He, Zhengfa Zhou, Weibing Xu^{*}, Fengmei Ren, Haihong Ma, Jin Wang

Department of Polymer Science and Engineering, Hefei University of Technology,
Hefei, 230009, China



Transesterification-controlled compatibility and microfibrillation in PC-ABS composites reinforced by phosphorus-containing thermotropic liquid crystalline polyester

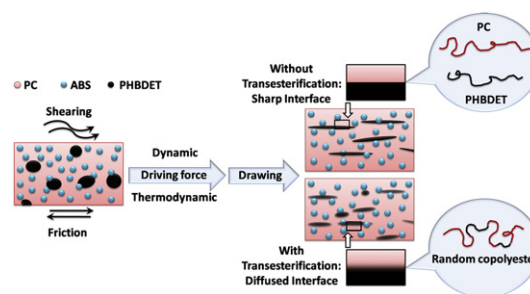
pp 3037–3046

Li Chen^a, Heng-Zhen Huang^a, Yu-Zhong Wang^{a,*}, Jinder Jow^b, Kenny Su^{b,c}

^a Center for Degradable and Flame-Retardant Polymeric Materials (ERCEPM-MoE),
College of Chemistry, State Key Laboratory of Polymer Materials Engineering,
Sichuan University, Chengdu 610064, China

^b The DOW Chemical Company, 2301 N. Brazosport Blvd., Freeport, TX 77541, USA

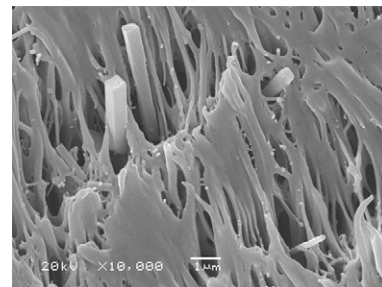
^c The DOW Chemical Taiwan Ltd., 17 Ren Jen Road, Hukou, Hsinchu 303,
Taiwan, China



Effect of entropy penalty on selective distribution of aluminum borate whiskers in isotactic polypropylene (iPP)/syndiotactic polypropylene (sPP) blends

pp 3047–3054

Tan Zhang, Xiao-Xuan Zou, Shu-Juan Zhang, Wei Yang, Ming-Bo Yang*

College of Polymer Science and Engineering, Sichuan University, State Key Laboratory of Polymer Materials Engineering, Chengdu, 610065 Sichuan, People's Republic of China**OTHER CONTENT****Corrigendum to “Preparation of core cross-linked micelles using a photo-cross-linking agent” [Polymer 50 (2009), 2204–2208]**

p 3055

*Corresponding author

Full text of this journal is available, on-line from **ScienceDirect**. Visit www.sciencedirect.com for more information.

Abstracted/indexed in: AGRICOLA, Beilstein, BIOSIS Previews, CAB Abstracts, Chemical Abstracts, Current Contents: Life Sciences, Current Contents: Physical, Chemical and Earth Sciences, Current Contents Search, Derwent Drug File, Ei compendex, EMBASE/ Excerpta Medica, Medline, PASCAL, Research Alert, Science Citation Index, SciSearch. Also covered in the abstract and citation database SCOPUS®. Full text available on ScienceDirect®



ELSEVIER

ISSN 0032-3861

Author Index

- Abad, M. J. 2981
 Alidedeoglu, A. H. 2906
 Aoki, H. 3016
 Ares, A. 2981

 Barral, L. 2981
 Bertolotti, S. G. 2762
 Bouza, R. 2981
 Braga, B. A. 2919

 Caballero, J. 2926
 Chai, L. 2976
 Chang, F.-C. 2958
 Chen, F. 3022
 Chen, H. C. 2856
 Chen, J.-F. 2841
 Chen, L. 3037
 Chen, Q. 2830
 Chen, X. 2847
 Chen, Y. T. 2856
 Chen-Yang, Y. W. 2856
 Cheng, S. 2775
 Cheng, X. 2775
 Cheng, Y. 2793
 Chu, B. 2893

 Deitzel, J. M. 2900
 Ding, Y. 2841
 Dong, S. 2806
 Dong, W. 2826
 Du, M. 3022
 Du, Y. 2830

 Encinas, M. V. 2762
 Endo, N. 2933

 Fong, H. 2999
 Furumi, S. 2944

 Gallego Ferrer, G. 2874
 Gao, Y. 2775
 Gargallo, L. 2926
 Gillespie, Jr., J. W. 2900
 Gong, D. 2826
 Gong, F. 2775
 González-Nilo, F. D. 2926
 Guo, B. 3022
 Guo, J. 2847
 Guo, X. 2819

 Han, B.-H. 2830
 He, T. 3031
 Hemery, P. 2752
 Higa, M. 2933
 Horinaka, J.-i. 3016
 Hou, H. 2999
 Hsiao, B. S. 2893
 Hsieh, A. J. 3007
 Hu, A. 2976
 Hu, H. 2793
 Hu, J. 2826
 Hu, P. 2863
 Hu, Z. 2933
 Huang, H.-Z. 3037

 Huang, X. 2793
 Huang, Y. 2847

 Ito, S. 3016

 Jarrett, W. L. 2906
 Jia, D. 3022
 Jiang, L. 2826
 Jin, H.-J. 2786
 Jing, X. 2847
 Jow, J. 3037

 Kim, H.-S. 2786
 Kim, J. S. 3055
 Kuo, S.-W. 2958
 Kwon, S.-M. 2786
 Kyu, T. 2885

 Lai, C. 2999
 Lasagabáster, A. 2981
 Leal, A. A. 2900
 Leiva, A. 2926
 Li, B. 2976
 Li, C. 2819
 Li, Zhen 2806
 Li, Zhong'an 2806
 Lin, W. T. 2856
 Liu, M. 3022
 Liu, Y. 2806
 Lü, C. 2976

 Ma, H. 3031
 Martini, D. d. S. 2919
 Marx, L. 2752
 Mashiko, S. 2944
 Masuda, T. 3016
 McKnight, S. H. 2900
 Meristoudi, A. 2743
 Miao, Q. 2793
 Misra, R. 2906
 Mo, S. 2953
 Monleón Pradas, M. 2874
 Morgan, S. E. 2906

 Neelakandan, C. 2885
 Niu, Y. 2990

 Okamoto, K.-i. 2933
 Otomo, A. 2944

 Pan, G. 2819
 Pispas, S. 2743
 Previtali, C. M. 2762

 Qian, Y. 2999
 Qin, J. 2806

 Radic, D. 2926
 Ren, F. 3031
 Reneker, D. H. 2999
 Rong, M. Z. 2967
 Rufs, A. M. 2762

 Saavedra, M. 2926
 Saldías, C. 2926
 Samios, D. 2919

 Sandoval, C. 2926
 Sarva, S. S. 3007
 Shang, S. 2815
 Shen, Y.-M. 2836
 Singh, K. 2768
 Su, K. 3037

 Takigawa, T. 3016
 Tao, X. 2841
 Tao, X.-m. 2815
 Tirelli, N. 2863
 Tsai, C. H. 2856
 Tu, C.-W. 2958

 Ube, T. 3016

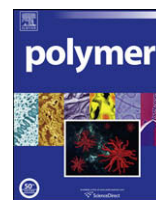
 Vallés Lluch, A. 2874
 Vora, A. 2768

 Wang, H. 2976, 2990
 Wang, J. 3031
 Wang, L. 2863
 Wang, R. 2953
 Wang, S. 2775
 Wang, Y. 2775
 Wang, Y.-Z. 3037
 Wang, Z. 2990
 Webster, D. C. 2768
 Wei, H.-L. 2836
 Wu, W. 2806

 Xiao, D. S. 2967
 Xu, W. 3031
 Xu, Ying 2793
 Xu, Yonghua 2830

 Yaguchi, K. 2933
 Yang, L. 2990
 Yang, M.-B. 3047
 Yang, W. 3047
 Yang, X. 2815
 Yang, Z. 2836
 Ye, C. 2806
 Yin, Y. 2933
 Yokoyama, S. 2944
 Yoon, K. 2893
 Youk, J. H. 3055
 Yu, G. 2806
 Yu, P. 2953
 Yuan, Y. C. 2967

 Zhang, H. 2819
 Zhang, J. 2953
 Zhang, L. 2999
 Zhang, M. Q. 2967
 Zhang, S.-J. 3047
 Zhang, T. 3047
 Zhang, X. 2826
 Zhang, Y. 2819
 Zhao, Y. 2841
 Zheng, L.-M. 2836
 Zheng, Y. 2953
 Zheng, Y.-Z. 2841
 Zhou, Z. 2999, 3031
 Zong, L. 2793
 Zou, X.-X. 3047
 Zu, B. 2819



Halloysite nanotubes as a novel β -nucleating agent for isotactic polypropylene

Mingxian Liu, Baochun Guo*, Mingliang Du, Feng Chen, Demin Jia

Department of Polymer Materials and Engineering, South China University of Technology, Guangzhou 510640, China

ARTICLE INFO

Article history:

Received 22 August 2008

Received in revised form

13 April 2009

Accepted 22 April 2009

Available online 3 May 2009

Keywords:

Polypropylene

β -Crystal

Halloysite

ABSTRACT

The nucleating ability of halloysite nanotubes (HNTs) towards isotactic polypropylene (iPP) was investigated by differential scanning calorimetry (DSC), X-ray diffraction (XRD), polarized optical microscopy (POM) and scanning electron microscopy (SEM). HNTs are identified to have dual nucleating ability for α -iPP and β -iPP under appropriate kinetics conditions. The formation of β -iPP is dependent on the HNTs loading in the iPP/HNTs composites. The composite with 20 phr of HNTs is found to have the highest content of β -iPP. Under non-isothermal crystallization the content of β -iPP increases with decreasing of the cooling rate. The maximum β -crystal content is obtained at cooling rate of 2.5 °C/min. The supermolecular structure of the β -iPP is identified as β -hedrites with flower-cup-like and axialite-like arrangements of the lamellae. Under isothermal crystallization the β -crystal can be formed in the temperature range of 115–140 °C. Outside the temperature range, no β -iPP can be observed. The content of β -crystal reaches the maximum value at crystallization temperature of 135 °C. The formation of the β -iPP in the composites is correlated to the unique surface characteristics of the HNTs.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

As a semi-crystalline polymer, isotactic polypropylene (iPP) is probably one of the most interesting commodity thermoplastic widely used in many areas such as home appliances, automotive, construction, and other industrial applications, not only for its balance of physical and mechanical properties, but also due to its environmental friendliness (non-toxicity and recyclability) and low cost [1]. Recently iPP nanocomposites consisting nanosized inclusions have attracted great attentions due to their scientific and technology importance. Compared with the conventional composites of iPP, the iPP nanocomposites usually exhibited very different processibility and performance, which are tremendously affected by the crystallization of iPP matrix [2–10].

iPP is a polymorphic material with several crystal modifications including monoclinic (α), trigonal (β), and orthorhombic (γ) forms [11]. The experimental observations suggested that the α modification is thermodynamically stable. Commercial iPP crystallizes mostly in α modification under normal processing conditions and adding some α -crystal nucleating agents can enhance the clarity and reduce haze of iPP [12,13]. The β form is thermodynamically metastable and can only be obtained under some special conditions such as using temperature gradient [14,15], flow-induced crystallization [16–22] and adding special nucleating agent [23]. γ Modification is the least frequently observed, although it has been obtained after crystallizing

samples at high pressures [24–26]. As the β -crystals have many performance characteristics such as improved ductility and impact strength, many research groups have focused their interest on the β -iPP. Among the techniques for preparing high content of β -iPP, adding the β -nucleating agent is the most effective and accessible method. Incorporating nanoparticles to iPP can bring the changed crystallization behavior. Generally, the nanoparticles influence the crystallization process of iPP by acting as heterogeneous nuclei. The heterogeneous nucleation leads to the increases in nucleating and crystallization rate. As a result, the increased crystallization temperature and finer spherulites are observed. On the other hand, addition of nanoparticles to iPP alters the polymorphism of iPP. Nanosized fillers such as montmorillonite (MMT) [27,28], carbon nanotubes (CNTs) [29], silica [30], magnesium hydroxide [31], calcium carbonate [32], zinc oxide [33], aluminum oxide [34], rare earth [35] etc. have been reported to have β -nucleating ability. However, the β -crystal content (ϕ_β , calculated according the XRD result) in these composites is relatively low (not higher than 30%). In addition, the dependence of β -crystals on thermodynamic conditions for these composites has not been disclosed. Although the β -nucleating mechanism of iPP by small organic molecules has been suggested by Lotz and co-workers [36–40], the formation mechanism of β -iPP in the PP/inorganics systems has not been elucidated.

Halloysite nanotubes (HNTs) modified polymer composites have raised researcher's interest in the recent years due to their unique structures and properties [41–46]. HNTs, with molecular formula of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$ are naturally occurred multi-walled inorganic nanotubes which have a similar geometry of CNTs. HNTs from

* Corresponding author. Fax: +86 20 2223 6688.
E-mail address: psbcguo@scut.edu.cn (B. Guo).

different regions vary in dimension and the typical size of halloysite is 300–1500 nm in length, 40–120 nm for the outer diameter and 15–100 nm for the inner diameter. The HNTs were reported to have high mechanical strength and modulus. They are considered as the ideal materials for preparing polymer composites due to the following facts: (i) HNTs are rigid materials and with a higher aspect ratio; (ii) comparing with other nanoparticles such as fumed silica, montmorillonite, and carbon nanotubes, HNTs are more easily dispersed in polymer matrix by shearing due to the following two facts. Geometrically, the rod-like geometry of HNTs is easily dispersed due to the limited intertubular contact area. Chemically, HNTs are recognized as with relative low hydroxyl density on the HNTs outer surfaces compared with fumed silica and other layered silicates such as montmorillonite [44]. Therefore, the aggregation induced by the intertubular hydrogen bonding is susceptible to the shearing force. In fact, morphology study for many polymer/HNTs composites has shown single-tube dispersed HNTs in the matrix [42,47,48]; (iii) HNTs are cheap, abundantly available and biocompatible [49]. HNTs incorporated polymer composites show promising properties especially for the largely increased mechanical performance. For example, the storage modulus of the epoxy/HNTs hybrid with 12 wt% HNTs is 58.6% higher at 50 °C and 121.7% higher at 210 °C than that of the neat epoxy [42]. Polypropylene/HNTs and rubber/HNTs composites also show about 50% increased modulus by 30 phr HNTs than those for the neat polymers and the increase is consistent with the Halpin–Tsai model [44,48,50]. In the present paper, we compound the HNTs with iPP for preparing the iPP/HNTs nanocomposites. The influence of the HNTs on the crystallization of iPP was investigated in detail. The β -crystal of iPP induced by HNTs was firstly reported and the nucleating mechanism was suggested. The present work presents a controllable approach to obtain high level β -iPP in the iPP/inorganics composites.

2. Experimental

2.1. Materials

The isotactic iPP, with a melt flow index of 2.84 g/10 min (after ISO-1133: 1997(E)), was purchased from Lanzhou Petro-chemical Co., China. The HNTs were mined from Yichang, Hubei, China and were purified according to the reference [51]. The elemental composition of HNTs by X-ray fluorescence (XRF) was determined as follows (wt.%): SiO₂, 58.91; Al₂O₃, 40.41; Fe₂O₃, 0.275; TiO₂, 0.071. The Brunauer–Emmett–Teller (BET) surface area of the used HNTs was 50.4 m²/g [42].

2.2. Preparation of iPP/HNTs nanocomposites

A two-screw extruder was used to prepare the iPP/HNTs nanocomposites. The temperature setting of extruder from the hopper to the die was 180/190/195/200/200/190 °C, and the screw speed was 100 rpm. The pelletized granules were dried for 5 h under 80 °C and then injection molded under the temperature of 200 °C. The contents of HNTs in the recipes are weight parts per 100 part iPP.

2.3. Characterization of the iPP/HNTs nanocomposites

2.3.1. Differential scanning calorimetry (DSC)

DSC data of all samples were measured by a TA Q20 using nitrogen as purging gas. The samples were heated to 210 °C at the ramping rate of 40 °C/min. The sample was kept at 210 °C for 5 min to eliminate the thermal history before it was cooled down to 40 °C at the rate of 10 °C/min. The second endothermic and exothermic flows were recorded as a function of temperature.

To study the formation of β -iPP during non-isothermal crystallization, the neat iPP and iPP/HNTs composite (100/20, weight ratio) were selected to conduct the following DSC measurements. The samples were heated from ambient temperature to 210 °C at the heating rate of 40 °C/min and the temperature was hold at 210 °C for 5 min to eliminate the thermal history. Then the samples were cooled to ambient temperature at the constant cooling rates of 2.5 °C/min, 5 °C/min, 10 °C/min, 20 °C/min, and 40 °C/min. Finally, they were heated to 210 °C at the heating rate of 10 °C/min. The crystallization and melting curves were recorded.

The percentage of β -crystal, Φ_{β} , can be obtained from the crystallinities of the α -crystal and β -crystal according to Ref. [52]

$$\Phi_{\beta}(\%) = \frac{X_{\beta}}{X_{\alpha} + X_{\beta}} \times 100 \quad (1)$$

$$X_i(\%) = \frac{\Delta H_i}{\Delta H_{i0}} \times 100 \quad (2)$$

where X_{α} and X_{β} are the crystallinities of the α - and β -crystal, respectively, which can be calculated separately according to Eq. (2), where ΔH_i is the calibrated specific fusion heat of either the α - and the β -form, ΔH_i^{β} is the standard fusion heat of the α - and β -crystals of iPP, being 178 J/g and 170 J/g, respectively [53]. Because the DSC curves of some samples exhibit both α - and β -crystal, the fusions were determined according to the following calibration method [54]. A vertical line was drawn through the minimum between the α - and β -fusion peaks and the total fusion heat was divided into β -component, ΔH_{β}^* , and α -component, ΔH_{α}^* . Since the less-perfect α -crystals melt before the maximum point during heating and contributed to the ΔH_{β}^* , the true value of β -fusion heat, ΔH_{β}^* , has approximated by a production of multiplying ΔH_{β}^* with a calibration factor A.

$$\Delta H_{\beta} = A \times \Delta H_{\beta}^* \quad (3)$$

$$A = \left[1 - \frac{h_2}{h_1} \right]^{0.6} \quad (4)$$

$$\Delta H_{\alpha} = \Delta H - \Delta H_{\beta} \quad (5)$$

h_1 and h_2 are the heights from the base line to the β -fusion peak and minimum point respectively (Fig. 1). Although the calibration method was applied, this method for determining the β -iPP content

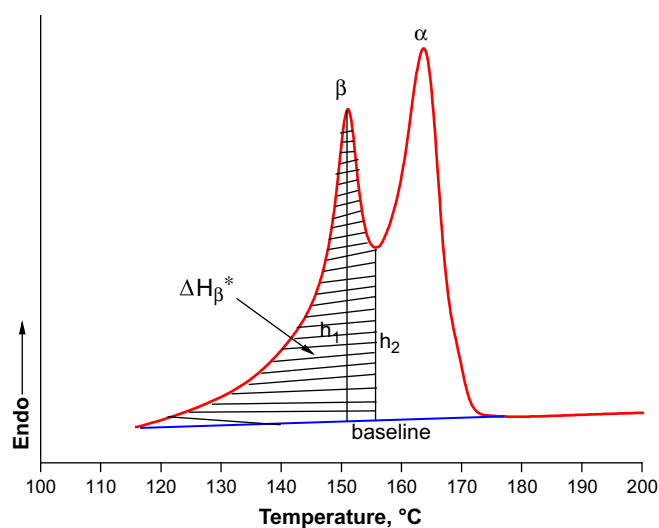


Fig. 1. DSC melting curves of iPP containing β -crystal.

was an approximate method and the obtained Φ_{β} value was not equal to the real value.

To study the formation of β -iPP during isothermal crystallization, the iPP/HNTs composite (100/20, weight ratio) was heated from ambient temperature to 210 °C at the heating rate of 40 °C/min and then quickly cooled to the crystallization temperature of 115 °C, 120 °C, 130 °C, 135 °C, 140 °C and 145 °C at a rate of 60 °C/min. The samples were crystallized at the crystallization temperature for 120 min and then quickly cooled to 40 °C at cooling rate of 60 °C/min. Finally, the samples were heated to 210 °C at the heating rate of 10 °C/min. The second melting curves were recorded.

2.3.2. X-ray diffraction (XRD)

The XRD patterns were recorded using the PANalytical X'pert PRO X-RAY Diffractometer. The CuK α radiation source was operated at 40 kV power and 40 mA current. Patterns were recorded by monitoring those diffractions that appeared from 5° to 40°. The scanning speed was 1°/min. The XRD samples were prepared by DSC TAQ 20 under the same conditions described above. The relative content of β -crystal, K_{β} , was calculated according to Equation (6) suggested by Turner-Jones [55]:

$$K_{\beta} = I_{\beta 1} / (I_{\beta 1} + I_{\alpha 1} + I_{\alpha 2} + I_{\alpha 3}) \quad (6)$$

where $I_{\beta 1}$ is the diffraction intensity of β (300) planes at diffraction angle $2\theta = 16^{\circ}$, $I_{\alpha 1}$, $I_{\alpha 2}$ and $I_{\alpha 3}$ are the diffraction intensities of the α (110), α (040), and α (130) planes at diffraction angles $2\theta = 14.1^{\circ}$, 16.9° and 18.8° respectively. For all the XRD profiles, the amorphous background was extracted and then the peaks were deconvoluted with the X'Pert HighScore Plus software. After that the diffraction intensity for the reflection peaks are obtained. It should be noted that the K_{β} value obtained by this method was recognized as a relative measure of the proportion of β -crystal, since it included in the calculation only selected peaks instead of the entire collection of diffractions.

2.3.3. Polarized optical microscopy (POM)

The morphologies of the crystallites of the composites were recorded with an Olympus BX41 polarized optical microscopy with a Linkam hot stage. The extruded samples were placed between two microscopy slides, melted and pressed at 210 °C for 5 min to remove any trace of crystal. The morphology of the neat iPP and the composites were recorded to give the information for dispersion of HNTs in the melt. Then the composite samples (with 20 phr HNTs) were cooled to ambient temperature at the constant cooling rates of 2.5 °C/min, 5 °C/min, 10 °C/min, 20 °C/min, 40 °C/min and the final morphology of the crystallites were recorded.

2.3.4. Scanning electron microscopy (SEM)

The SEM micrographs were taken using LEO1530 VP SEM machine. The iPP/HNTs composites (100/20, weight ratio) samples were firstly heated to 210 °C and kept for 10 min and then cooled to room temperature at the cooling rate of 2.5 °C/min. Then the sample was immersed in a permanganate solution to etch the amorphous iPP [56]. The specimen was coated with a very thin layer of gold before SEM observation.

3. Results and discussion

3.1. DSC analysis for the iPP/HNTs nanocomposites

Fig. 2(a) shows the crystallization curves of the iPP/HNTs nanocomposites with different HNTs content. It is clear that the crystallization peaks of iPP shift to higher temperature with HNTs content. The observed effects can be attributed to the nucleating effect of

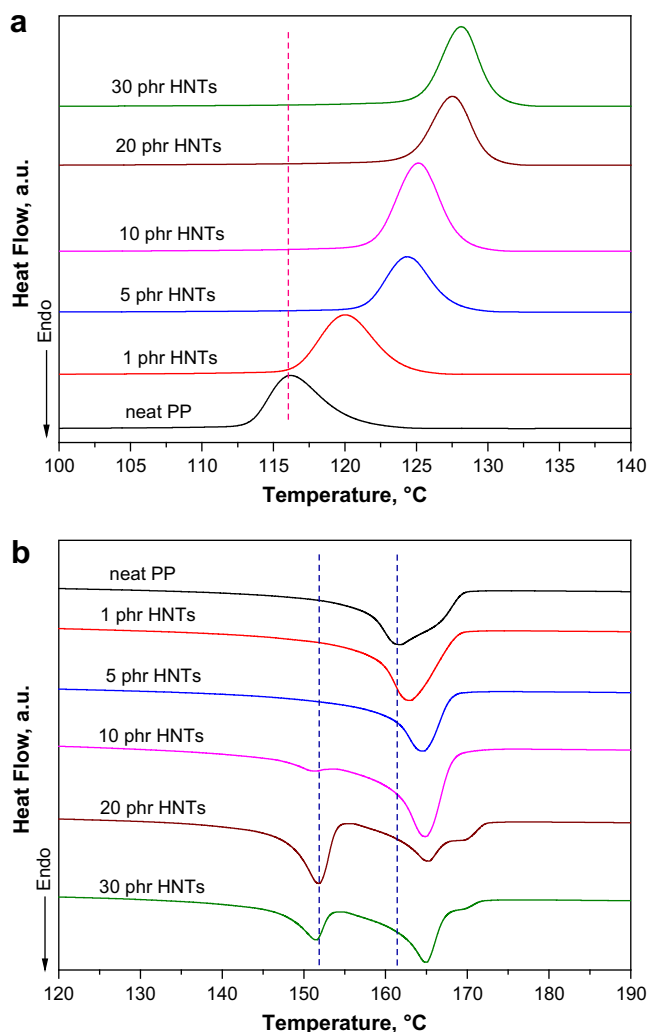


Fig. 2. DSC exothermic (a) and endothermic (b) curves of neat iPP and iPP/HNTs nanocomposites.

HNTs in iPP crystallization process. Overloading of HNTs (30 phr) in composite, however, does not provide further increase in the crystallization peak temperature. The crystallization temperature of the composites with 30 phr HNTs is nearly not changed comparing with that of with 20 phr HNTs. The over loaded HNTs may aggregate in iPP matrix and the aggregated HNTs have lower nucleating ability due to the reduced specific surface area. Similar results of the effect of HNTs in the polyvinyl alcohol (PVA) matrix have also been suggested [57]. Fig. 2(b) shows the melting curves for the iPP/HNTs nanocomposites. The peaks around 165 °C and 155 °C can be attributed to the melting of the α -crystal and β -crystal of iPP respectively [58]. The endothermic shoulder peak around 170 °C for the composite with relative high HNTs contents (above 20 phr) could be attributed to the melting of interphase between HNTs and iPP. Similar phenomena has also been reported in other composite systems such as PP/CNTs and PA/CNTs composites [59–61]. Incorporating HNTs to iPP leads to the increased melting temperature of the α -iPP although the increasing trend is not obvious at overloading (30 phr). When the HNTs loading is higher than 10 phr, the fusion of the β -iPP is observed. This phenomenon indicates the HNTs have the dual nucleating ability both for α -iPP and β -iPP. According to Equations (1)–(5), the percentage of β -crystal (Φ_{β}) can be calculated and the results are summarized in Table 1. Generally, the higher the content of nucleating agent is, the higher the proportion of β -crystal is. However,

Table 1

DSC data of the iPP/HNTs composites with variable HNTs content.

HNTs content (phr)	ΔH_{β}^* (J/g)	ΔH_{β} (J/g)	ΔH (J/g)	ΔH_{α} (J/g)	X_{β} (%)	X_{α} (%)	X_{all} (%)	Φ_{β} (%)
0	–	–	–	66.42	–	37.3	37.3	0
1	–	–	–	67.35	–	38.2	38.2	0
5	–	–	–	71.23	–	42.0	42.0	0
10	13.93	3.51	65.89	62.38	2.3	38.6	40.8	5.6
20	34.01	33.06	61.96	28.90	23.3	19.5	42.8	54.5
30	23.07	18.67	62.20	43.53	13.2	29.4	42.5	31.0

from Table 1, the β -crystal form content does not increase constantly. The maximum value is obtained at 20 phr of HNTs, while overloading of HNTs leads to lowered β -crystal content. This may also be attributed to the more aggregated HNTs in the composites as evidenced by the below POM result. Similar results were also reported in other β -iPP nucleating agent systems [31,62,63]. Noticeably, the total crystallinity (X_{all}) of iPP in the composites, calculated from the fusion heat in DSC result, is higher than that of neat iPP which is attributed to the heterogeneous nuclei effect of HNTs.

To investigate the dispersion of HNTs in the iPP matrix, the POM photos of iPP/HNTs nanocomposites were taken under cross-polarized light in the iPP melt and shown in Fig. 3. The morphology of HNTs in the melted iPP can be clearly observed in these photos. The dispersion of HNTs in iPP is uniform when the HNTs content is low. With increasing the content of HNTs, the aggregation of HNTs in iPP can be observed and the size of the aggregates increases gradually. When HNTs content is higher than 20 phr, the size of the HNTs aggregates is as large as 20 μm . Such big aggregates may lose

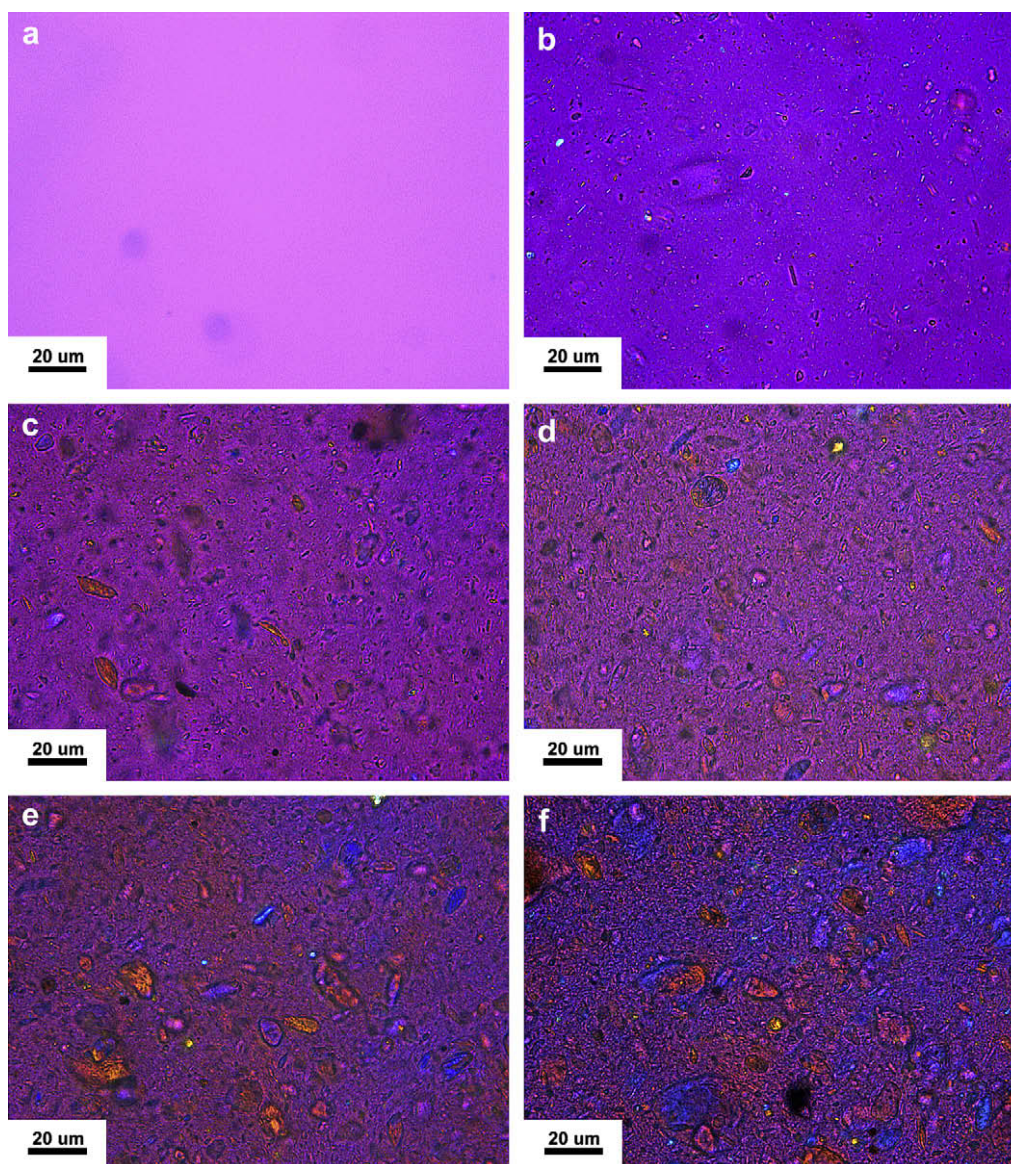


Fig. 3. POM photos of the melts of iPP and the composites with variable HNTs content (a) 0, (b) 1 phr, (c) 5 phr, (d) 10 phr, (e) 20 phr and (f) 30 phr.

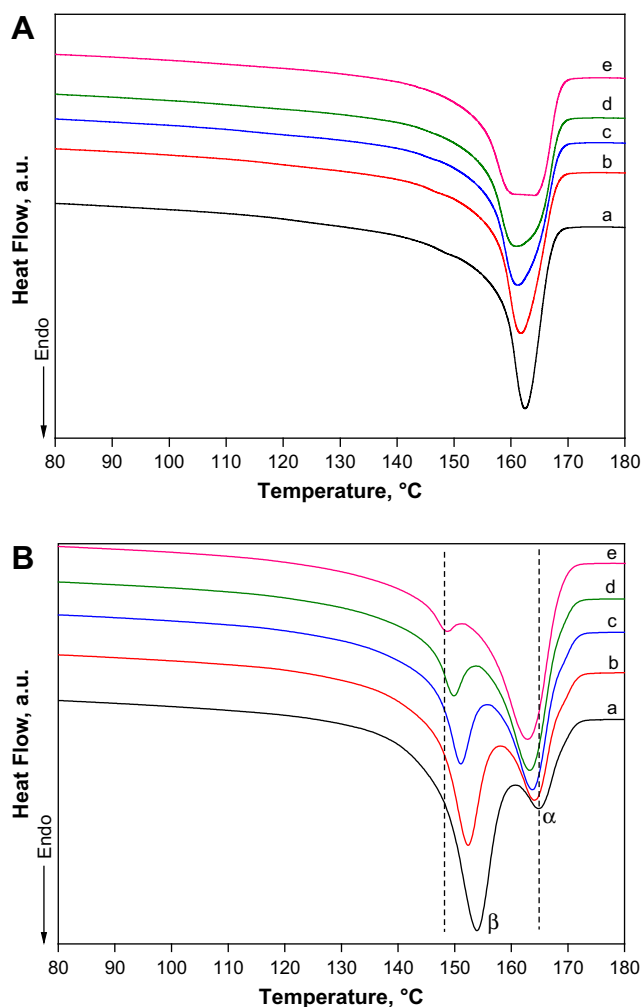


Fig. 4. DSC melting curves of neat iPP (A) and the composites (B, 20 phr of HNTs) samples non-isothermally crystallized at different cooling rate: (a) 2.5 °C/min; (b) 5 °C/min; (c) 10 °C/min; (d) 20 °C/min; (e) 40 °C/min.

their β -nucleating efficiency [63]. Therefore, the changing in Φ_{β} can be correlated to the dispersion change of HNTs in the matrix.

3.2. Formation of β -crystals in non-isothermal crystallization process

DSC analysis was performed to investigate the formation of β -crystals during non-isothermal crystallization with variable cooling rate. As described above the composite with 20 phr of HNTs may yield the highest content of β -crystals during non-isothermal crystallization, it is therefore selected for further study. Fig. 4(A) shows the melting curves of the neat iPP which is non-isothermally crystallized under variable cooling rate. It is clear that the crystal form of iPP is independent on the cooling rate of the non-isothermal crystallization. In absence of HNTs, all the iPP samples crystallize in the form of α -crystal. This indicates the neat iPP does not have the β -crystal nucleating ability. In the presence of HNTs, as shown in Fig. 4(B), two melting peaks, characterizing α -crystal and β -crystal, are observed in all the melting curves, suggesting dual nucleation ability of HNTs for the iPP. It is evident that the melting peak for β -crystals is consistently enlarged with decreasing cooling rate of non-isothermal crystallization, while the content of α -crystal is consistently decreased. The maximum β -crystal percentage detected by DSC reaches 64.3% at the cooling rate of 2.5 °C/min, which is

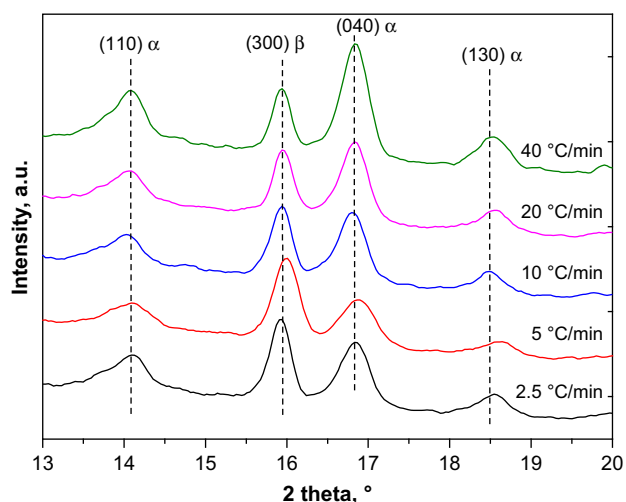


Fig. 5. XRD profiles of iPP/HNTs composite samples (20 phr of HNTs) non-isothermally crystallized at variable cooling rate.

considerably higher than that of previously reported iPP/inorganics systems [6,30,31,33,64]. When the cooling is slower, the sample will stay in the high temperature regime longer. The high crystallization temperature leads to increase in β -crystal content since the growth rate of β -crystal is considerably faster than that of α -crystal in the range of 105–140 °C [38,65–67]. The present result is consistent with that of iPP nucleated by dicyclohexylterephthalamide [68]. However, our result is contradictory with the work done by Grady et al., in which higher cooling rate led to the increased content of β -crystal in the quinacridone-pigment Remafin Rot E3B (Hoechst) nucleated iPP. Their explanations on their results were based on the relationship between thermal stability for the different crystals form of iPP and the crystallization temperature [69]. Noticeably, the melting peak temperatures of both α -crystal and β -crystal in the composites are consistently shifted to higher temperatures when the cooling rate is decreased. This may attributed to the increased perfection of the crystals when the crystallization is conducted at lower cooling rate [70–72].

The formation of β -iPP under above non-isothermal crystallization is also substantiated by XRD experiments. Fig. 5 shows the XRD patterns of the iPP/HNTs nanocomposites non-isothermally

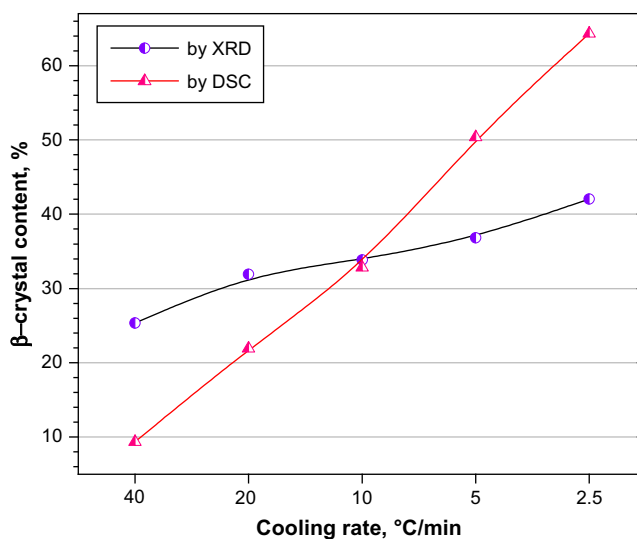


Fig. 6. Dependence of relative β -crystal content on the cooling rate.

crystallized with different cooling rates. The peaks at diffraction angles 2θ of 14.1° , 16° , 16.9° , and 18.8° are attributed to α (110), β (300), α (040), and α (130) planes respectively. Consistent with the results from DSC, β -iPP diffraction peaks are observed for all the samples. According to Equation (6), the relative content of β -crystal (K_β) is calculated. The K_β and combined with the Φ_β calculated by DSC data are plotted in Fig. 6 as a function of cooling rate. It can be seen the increasing trend of K_β with decreasing cooling rate is consistent with that for Φ_β from DSC method, although the absolute value is incomparable which is raised from different calculating theory. It should be emphasized that compared with XRD method the DSC analysis is less reliable due to the possible overlap of the melting peaks for α - and β -crystal in DSC curves.

POM was a visual method for observing the morphology of different crystals and it was employed in the present study. α - and β -crystal forms of iPP are easily distinguished under polarized light microscopy, in view of their different optical properties [37,73,74]. β -iPP spherulites are highly birefringent as a result of conventional spherulite architecture, with radiating lamellae and tangential orientation of the molecular stems in the lamellae. However, α -iPP

spherulites usually are weaker birefringent as a result of a specific mechanism of lamellar branching. Therefore, in the optical micrographs, β -iPP spherulites are brighter than α -iPP spherulites [58,75,76]. Fig. 7 shows the POM morphology of iPP/HNTs composite samples (with 20 phr of HNTs) which are non-isothermally crystallized at different cooling rates. In the iPP/HNTs composite a large number of nuclei are introduced by HNTs. The nucleation rate is fast and the spherulites growth on them is a heterogeneous nucleation. Owing to large number of nuclei, the growth of spherulite is suppressed as a result of collision of the spherulites. Consequently, as shown in Fig. 7, very fine crystals with blurry boundary are observed. The cyan color parts in these photos are the bright region which indicates the presence of β -crystal of iPP. With the decrease of the cooling rate, the number of the cyan color parts in the composites increase and the area enlarges. This can be explained by the fact that the content of β -iPP in the sample crystallized at lower cooling rate is higher than that crystallized at higher cooling rate, which is consistent with the above XRD and DSC results.

The existence of β -crystals in the composite was also observed by SEM. Different types and features of supermolecular structure of

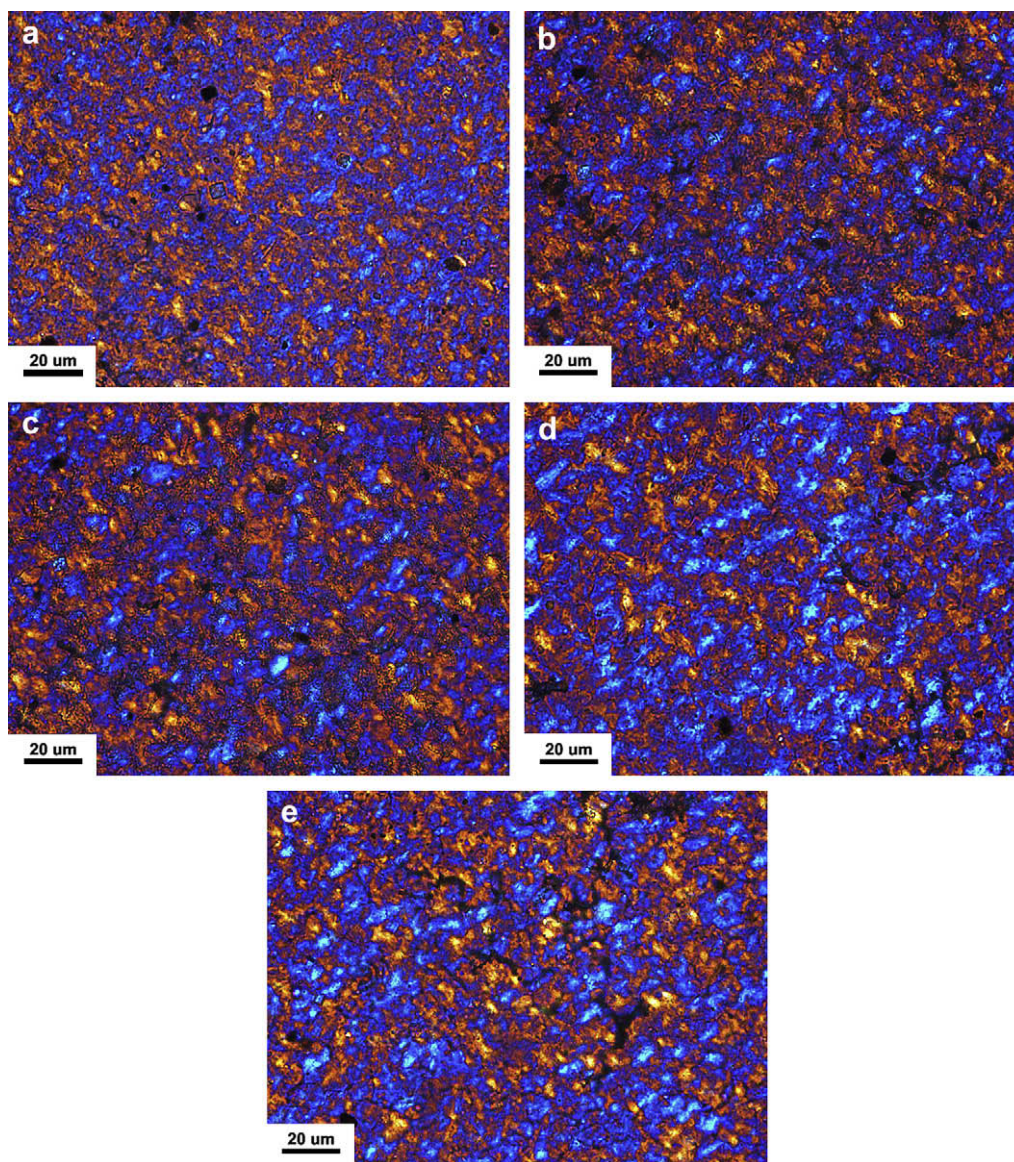


Fig. 7. POM photos of the iPP/HNTs composite samples non-isothermally crystallized at variable cooling rate: (a) $40^\circ\text{C}/\text{min}$; (b) $20^\circ\text{C}/\text{min}$; (c) $10^\circ\text{C}/\text{min}$; (d) $5^\circ\text{C}/\text{min}$; (e) $2.5^\circ\text{C}/\text{min}$.

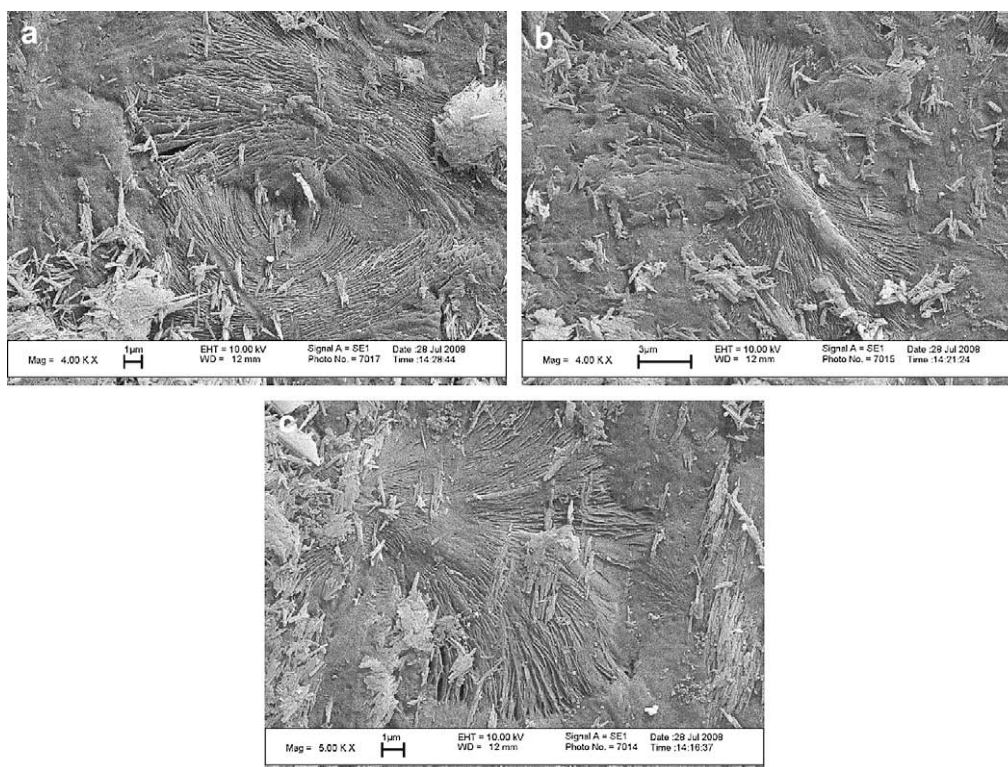


Fig. 8. SEM photos of supermolecular structure of β -crystals in the iPP/HNTs composite: (a) flower-cup-like arrangement of lamellae (b) and (c) axialite-like arrangement of lamellae.

β -iPP can be formed which are influenced by the thermal conditions of crystallization, by the melt history, by mechanical stress to the crystallizing system, and by the presence of extraneous materials. Varga has reviewed morphology features of the various supermolecular formations of β -iPP [23]. Depending on the crystallization conditions and nucleating agent, different types of the supermolecular structure of β -iPP, such as β -spherulite, β -hedrites, β -cylindrites, transcrystalline, epitaxial crystallization and single crystal-like crystalline, can be obtained. Fig. 8 shows the morphology of the etched composite sample in which the amorphous PP is essentially removed. The sheaf-like β -iPP lamellae which are curved

and twisted can easily be identified under SEM [56,77]. Both flower-cup-like (Fig. 8a) and axialite-like arrangements of lamellae (Fig. 8b and c) which are subtypes of the β -hedrites are observed in the samples. Noticeably, HNTs and their aggregates are also observed in the samples which are relatively white parts in the SEM photos, as they are inert to the permanganate solution.

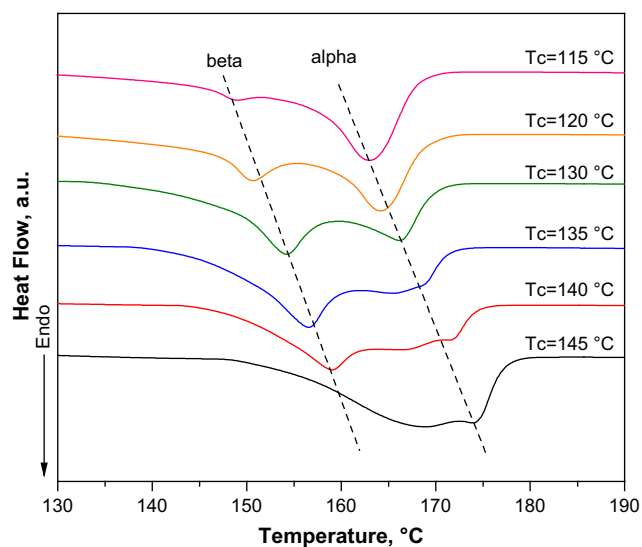


Fig. 9. DSC melting curves of iPP/HNTs composite samples (20 phr HNTs) crystallized at the variable temperature.

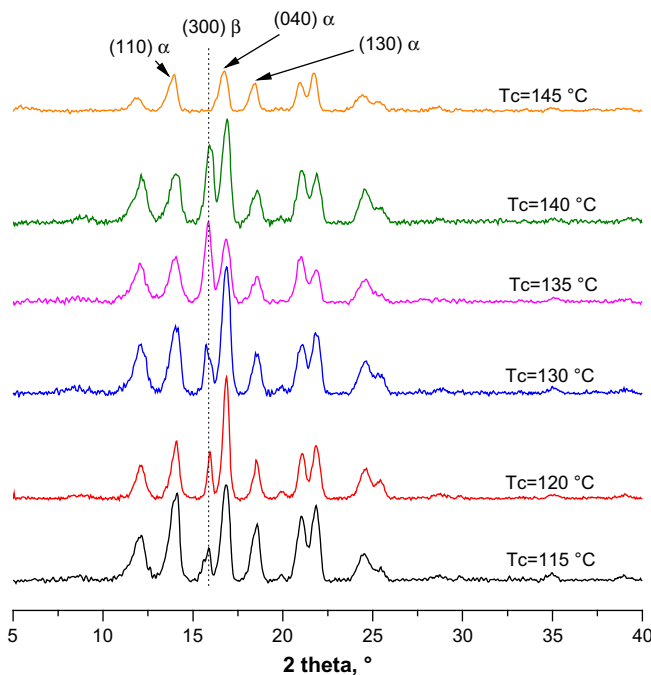


Fig. 10. XRD profiles of iPP/HNTs composite samples (20 phr HNTs) crystallized at the variable temperature.

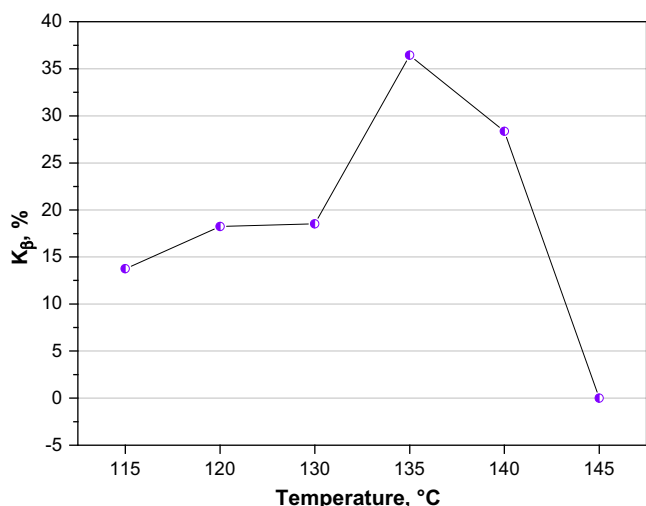


Fig. 11. Dependence of relative content of β -crystal (K_{β}) in the iPP/HNTs composite samples (20 phr HNTs) on the isothermal crystallization temperature.

3.3. Formation of β -crystals in isothermal crystallization process

Crystallization temperature has great influences on the β -crystal nucleating ability of the nucleating agent, which in turn will influence the phase structure of the iPP. Many works have been done on investigating the influence of the crystallization temperature on the final crystal structure in the β -nucleated iPP [62,68,78]. Fig. 9 shows the DSC melting curves of the composite samples isothermally crystallized from melt at different temperatures. It is clear that the β -crystal can be obtained in a certain temperature range (from 115 °C to 140 °C) although its accurate content is hardly calculated owing to highly overlap of β -crystal melting and α -crystal melting. When the crystallization temperature is higher than 140 °C, no β -crystal melting peak can be observed. This result is consistent with some reported systems [62,63,68]. Su et al. have attributed to this phenomenon to the result of two competing kinetic and thermodynamic effects [62]. In the range of 100–140 °C the linear growth rate of the β -crystal is greater than that of α -crystal. Outside

the temperature range, the growth rate of α -iPP is higher than that of β -iPP [79]. As a result, no β -crystal melting is observed for the composite sample crystallized at 145 °C. In addition, the melting temperatures of both α -iPP and β -iPP increase with increasing crystallization temperature. This may be explained according to the kinetic theory of crystallization [65].

To further verify the influence of the crystallization temperature on the crystal forms of iPP, XRD experiment was performed on the composite samples. Fig. 10 shows the XRD profiles of the composite samples crystallized at different temperatures. It can be seen a diffraction peak at 15.9° assigning to β (300) is observed in all the samples, except the sample crystallized at 145 °C. This is consistent with the DSC result. The calculated K_{β} value from the XRD profiles was plotted in Fig. 11. It is clear that the increasing crystallization temperature of the composites leads to the increase in the content of β -crystal in the temperature range of 115–135 °C. The content of β -crystal in the composites reaches the maximum value of 36.4% at the crystallization temperature of 135 °C. Although the content of β -crystal for the sample crystallized at 140 °C is higher than that for 115 °C, 120 °C, and 130 °C, it starts to decrease and eventually disappears when the crystallization temperature is 145 °C. This result again confirms the upper limit temperature for β -iPP nucleation.

3.4. β -Crystal nucleation mechanism of HNTs for iPP

Understanding the nucleation mechanism of β -nucleating agent is both scientifically and technologically significant. However, the nucleation mechanism of the β -iPP for nucleating agent is still not well understood. The “dimensional lattice matching theory” proposed by Lotz et al. have been widely accepted for some β -nucleating agents of iPP [22,36–39,80], although it is not applicable to all β -nucleating agents [62]. In the theory, Lotz et al. explained the β -iPP nucleating ability through analyzing the structure relationship between nucleating agent and the β -iPP. A lattice matching between c -axis periodicity of iPP (6.5 Å) and a corresponding distance in the substrate crystal face of nucleating agent is the main reason for inducing the β -iPP polymorph. The nucleating agents provide the nucleation surfaces for iPP crystal. HNTs have unique morphology among other common nanoparticles such as nanosilica and other clay such as MMT. They are multi-walled inorganic nanotubes and rolled

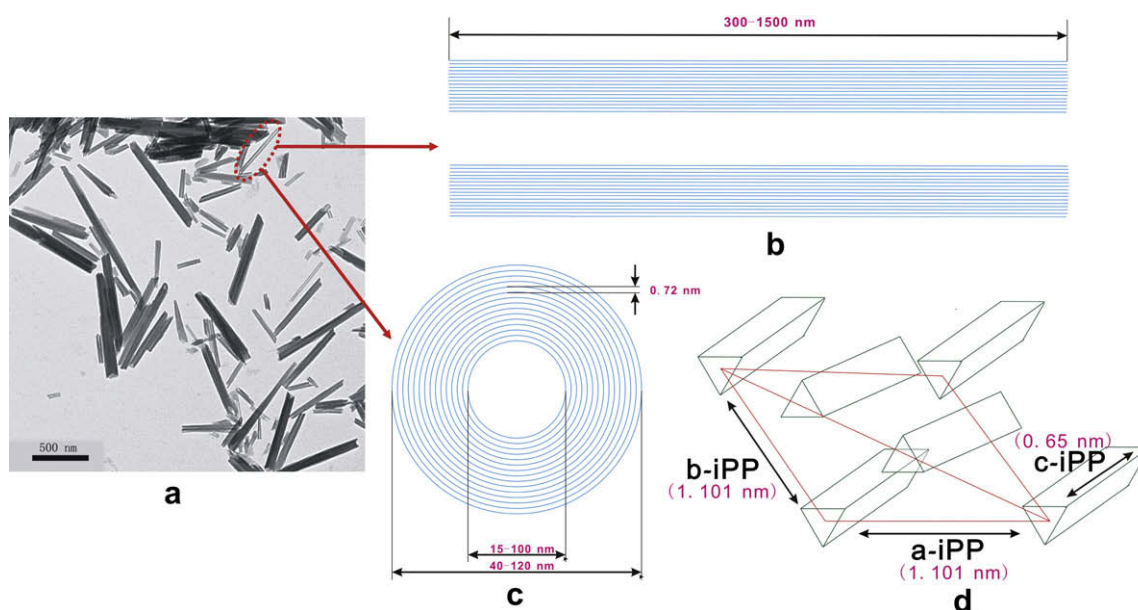


Fig. 12. TEM photos of the HNTs (a) and schematic of the crystalline structure of HNTs (b) and (c) and β -iPP (d).

by 15–20 aluminosilicate layers. The XRD diffraction spectra of HNTs (not shown) indicate a layer spacing of 0.73 nm [41]. The morphology of HNTs, the structure parameters of the HNTs, and the cell parameters of β -iPP [37,81] are depicted in Fig. 12. It can be seen the length of c -axis corresponding to the period of the 3_1 helix of iPP is 0.65 nm, while the layer spacing of HNTs is 0.73 nm. These two values are fairly close. Kawai et al. proposed the equation of misfit factor (f_m) between the two crystal structures of iPP and the nucleating agent which can be calculated as

$$f_m = \frac{PB - PA}{PA} \times 100 \quad (7)$$

where PA and PB are the appropriate period length of substrate and polymer respectively [82]. If $f_m < 15\%$, the epitaxy is regarded good. The f_m between the layer spacing of HNTs and the c -axis of iPP is 10.96%, indicating good epitaxy. For the present systems, both the outer surface and the ends of HNTs may provide the nucleation surfaces for iPP crystal. Particularly, the defects on the surfaces with appropriate size and the ends of HNTs may provide numerous nucleation surfaces when they are close to the dimension of the c -axis of PP. Therefore, it should be believed that the ability of HNTs inducing the nucleation of β -iPP is related to its unique microstructure and surface properties. The composites with high HNTs content (above 10 phr) provided enough sites for the nucleation and development of the β -iPP crystal and this leads to the formation of high β -iPP content under appropriate kinetics conditions.

4. Conclusions

HNTs are identified to have dual nucleating ability for α -iPP and β -iPP under non-isothermal and isothermal crystallization. The formation of β -iPP is dependent on the HNTs loading in the iPP/HNTs composites. The composite with 20 phr of HNTs is found to have the highest content of β -iPP. Under non-isothermal crystallization the content of β -iPP increases with the decrease in the cooling rate. The maximum β -crystal content is obtained at cooling rate of 2.5 °C/min. The supermolecular structure of the β -iPP is identified as β -hedrites with flower-cup-like and axialite-like arrangements of the lamellae. Under isothermal crystallization the β -crystal can be formed in the temperature range of 115–140 °C. Outside the temperature range, no β -iPP can be observed. The content of β -crystal reaches the maximum value at crystallization temperature of 135 °C. The formation of the β -iPP in the composites is correlated to the unique surface characteristics of the HNTs.

Acknowledgments

We are grateful for the financial support by the National Natural Science Foundation of China with grant number of 50603005 and the Doctorate Foundation of South China University of Technology.

References

- [1] Pasquini N, Addeo Antonio. Polypropylene handbook. 2nd ed. Hanser Gardner Publications; 2005.
- [2] Maiti P, Nam PH, Okamoto M, Hasegawa N, Usuki A. *Macromolecules* 2002; 35:2042.
- [3] Lozano K, Barrera EV. *J Appl Polym Sci* 2001;79:125.
- [4] Asuka K, Liu BP, Terano M, Nitta KH. *Macromol Rapid Commun* 2006;27:910.
- [5] Chen JH, Chiou YD. *J Polym Sci Part B Polym Phys* 2006;44:2122.
- [6] Labour T, Gauthier C, Seguela R, Vigier G, Bomal Y, Orange G. *Polymer* 2001; 42:7127.
- [7] Song SJ, Wu PY, Feng JC, Ye MX, Yang YL. *Polymer* 2009;50:286.
- [8] Vanegas ME, Quijada R, Serafini D. *Polymer* 2009. doi:10.1016/j.polymer.2009.03.006.
- [9] Baïilly M, Kontopoulou M. *Polymer* 2009. doi:10.1016/j.polymer.2009.03.034.
- [10] Lonkar SP, Morlat-Therias S, Caperaa N, Leroux F, Gardette JL, Singh RP. *Polymer* 2009;50:1505.
- [11] Lotz B, Wittmann JC, Lovinger AJ. *Polymer* 1996;37:4979.
- [12] Bernlander K, Tervoort T, Smith P. *Polymer* 2009. doi:10.1016/j.polymer.2009.03.010.
- [13] Housmans J-W, Gahleitner M, Peters GWM, Meijer HEH. *Polymer* 2009. doi:10.1016/j.polymer.2009.02.050.
- [14] Fujiwara Y. *Colloid Polym Sci* 1975;253:273.
- [15] Lovinger AJ, Chua JO, Gryte CC. *J Polym Sci Polym Phys Ed* 1977;15:641.
- [16] Jay F, Haudin JM, Monasse B. *J Mater Sci* 1999;34:2089.
- [17] Varga J. *Angew Makromol Chem* 1983;112:191.
- [18] Varga J, Karger-Kocsis J. *Polym Bull* 1993;30:105.
- [19] Varga J, Karger-Kocsis J. *J Polym Sci Part B Polym Phys* 1996;34:657.
- [20] Varga J, Karger-Kocsis J. *J Mater Sci Lett* 1994;13:1069.
- [21] Kalay G, Bevis MJ. *J Polym Sci Part B Polym Phys* 1997;35:265.
- [22] Huo H, Jiang SC, An LJ. *Macromolecules* 2004;37:2478.
- [23] Varga J. *J Macromol Sci Phys* 2002;41:1121.
- [24] Campbell RA, Phillips PJ, Lin JS. *Polymer* 1993;34:4809.
- [25] Meille SV, Phillips PJ, Mezghani K, Bruckner S. *Macromolecules* 1996;29:795.
- [26] Bruckner S, Phillips PJ, Mezghani K, Meille SV. *Macromol Rapid Commun* 1997;18:1.
- [27] Medellín-Rodríguez FJ, Mata-Padilla JM, Hsiao BS, Waldo-Mendoza MA, Ramirez-Vargas E, Sanchez-Valdes S. *Polym Eng Sci* 2007;47:1889.
- [28] Ding C, He H, Guo BC, Jia DM. *Polym Compos* 2008;29:698.
- [29] Grady BP, Pompeo F, Shambaugh RL, Resasco DE. *J Phys Chem B* 2002; 106:5852.
- [30] Jain S, Goossens H, van Duin M, Lemstra P. *Polymer* 2005;46:8805.
- [31] Shen H, Wang YH, Mai KC. *Thermochim Acta* 2007;457:27.
- [32] Zhang QX, Yu ZZ, Xie XL, Mai YW. *Polymer* 2004;45:5985.
- [33] Zhao H, Li RKY. *Polymer* 2006;47:3207.
- [34] Zhao H, Li RKY. *J Polym Sci Part B* 2005;43:3652.
- [35] Feng JC, Chen MC, Huang ZT, Guo YQ, Hu HQ. *J Appl Polym Sci* 2002;85:1742.
- [36] Wittmann JC, Lotz B. *Prog Polym Sci* 1990;15:909.
- [37] Lotz B. *Polymer* 1998;39:4561.
- [38] Stocker W, Schumacher M, Graff S, Thierry A, Wittmann JC, Lotz B. *Macromolecules* 1998;31:807.
- [39] Mathieu C, Thierry A, Wittmann JC, Lotz B. *Polymer* 2000;41:7241.
- [40] Mathieu C, Thierry A, Wittmann JC, Lotz B. *J Polym Sci Part B Polym Phys* 2002;40:2504.
- [41] Du ML, Guo BC, Jia DM. *Eur Polym J* 2006;42:1362.
- [42] Liu MX, Guo BC, Du ML, Cai XJ, Jia DM. *Nanotechnology* 2007;18:455703.
- [43] Ning NY, Yin QJ, Luo F, Zhang Q, Du RN, Fu Q. *Polymer* 2007;48:7374.
- [44] Liu MX, Guo BC, Zou QL, Du ML, Jia DM. *Nanotechnology* 2008;19:205709.
- [45] Ye YP, Chen HB, Wu JS, Ye L. *Polymer* 2007;48:6426.
- [46] Mu B, Zhao MF, Liu P. *J Nanopart Res* 2008;10:831.
- [47] Liu MX, Guo BC, Lei YD, Du ML, Jia DM. *Appl Surf Sci* 2009;255:4961.
- [48] Du ML, Guo BC, Lei YD, Liu MX, Jia DM. *Polymer* 2008;49:4871.
- [49] Lvov YM, Shchukin DG, Mohwald H, Price RR. *ACS Nano* 2008;2:814.
- [50] Du ML. PhD dissertation. South China University of Technology, 2007.
- [51] Shchukin DG, Sukhorukov GB, Price RR, Lvov YM. *Small* 2005;1:510.
- [52] Shangguan YG, Song YH, Peng M, Li BP, Zheng Q. *Eur Polym J* 2005;41:1766.
- [53] Li JX, Cheung WL, Jia DM. *Polymer* 1999;40:1219.
- [54] Li JX, Cheung WL. *Polymer* 1998;39:6935.
- [55] Turner-Jones A, Alizlewood JM, Beckett DR. *Macromol Chem* 1964;75:134.
- [56] Xu W, Martin DC, Arruda EM. *Polymer* 2005;46:455.
- [57] Liu M, Guo B, Du M, Jia D. *Appl Phys A* 2007;88:391.
- [58] Padden FJ, Keith HD. *J Appl Phys* 1959;30:1479.
- [59] Brosse AC, Tence-Girault S, Piccione PM, Leibler L. *Polymer* 2008;49:4680.
- [60] Phang IY, Ma JH, Shen L, Liu TX, Zhang WD. *Polym Int* 2006;55:71.
- [61] Saeed K, Park SY. *J Appl Polym Sci* 2007;106:3729.
- [62] Su ZQ, Dong M, Guo ZX, Yu J. *Macromolecules* 2007;40:4217.
- [63] Zhao SC, Cai Z, Xin Z. *Polymer* 2008;49:2745.
- [64] Supaphol P, Thanomkiat P, Junkasem J, Dangtungee R. *Polym Test* 2007;26:20.
- [65] Varga J. In: Karger-Kocsis J, editor. *Poly(propylene): structure, blends and composites*, Vol. 1. London: Chapman & Hall; 1995. p. 56–115 [chapter 3].
- [66] Lotz B, Fillon A, Thierry A, Wittmann JC. *Polym Bull* 1991;25:101.
- [67] Sun X, Li H, Wang J, Yan S. *Macromolecules* 2006;39:8720.
- [68] Zhang YF. *J Polym Sci Part B Polym Phys* 2008;46:911.
- [69] Grady A, Sajkiewicz P, Minakov AA, Adamovsky S, Schick C, Hashimoto T, et al. *Mater Sci Eng A* 2005;413:442.
- [70] Di Lorenzom ML, Silvestre C. *Prog Polym Sci* 1999;24:917.
- [71] Xu WB, Ge ML, He PS. *J Polym Sci Part B Polym Phys* 2002;40:408.
- [72] Supaphol P. *J Appl Polym Sci* 2000;78:338.
- [73] Bruckner S, Meille SV. *Nature (London)* 1989;340:455.
- [74] Boucher E, Flolers JP, Creton C, Hervet H, Leger L. *Macromolecules* 1997; 30:2102.
- [75] Norton DR, Keller A. *Polymer* 1985;26:704.
- [76] Varga J. *J Mater Sci* 1992;27:2557.
- [77] Li JX, Cheung WL, Chan CM. *Polymer* 1999;40:2089.
- [78] Varga J, Menyhard A. *Macromolecules* 2007;40:2422.
- [79] Li H, Sun X, Yan S, Schultz JM. *Macromolecules* 2008;41:5062.
- [80] Yamaguchi M, Fukui T, Okamoto K, Sasaki S, Uchiyama Y, Ueoka C. *Polymer* 2009;50:1497.
- [81] Lu QL, Dou Q. *e-Polymers* 2008. Article number: 076.
- [82] Kawai T, Iijima R, Yamamoto Y, Kimura T. *Polymer* 2002;43:7301.