

张全兴

报告人简介：

张全兴（1938.12~），江苏常州人。环境工程和高分子材料专家，中国离子交换与吸附技术的主要开拓者之一，树脂吸附法治理有毒有机工业废水及其资源化领域的开创者。1962年毕业于南开大学化学系，2007年当选中国工程院院士，2009年荣获全国模范教师称号。现任南京大学环境学院教授，博士生导师，院学术委员会主任，南京大学国家有机毒物污染控制与资源化工程技术研究中心名誉主任，江苏省太湖污染控制与蓝藻治理专家委员会副主任和《离子交换与吸附》期刊主编以及国家环境咨询委员会委员等职。曾任南京大学环境工程教研室主任、环科所副所长、省部和国家工程技术研究中心主任以及教育部第三、六届科技委地学与资源环境学部委员等职。自大学毕业至1985年，师从南开大学何炳林院士，在国内率先开展了大孔离子交换与吸附树脂的合成与应用研究，研制成功系列大孔离子交换树脂和超高交联吸附树脂，广泛应用于工业水处理、有机催化、铀和贵金属提取、药物提取分离、人体血液灌流以及环境保护等领域。1985年之后到常州大学和南京大学任教，主要在水污染防治方向从事复合功能等特种树脂的合成与性能研究以及树脂吸附理论、吸附新技术、新工艺的研究及其工程应用，引领和推动了我国高浓度难降解有机工业废水治理与资源化，为工业水污染治理与节能减排和重点流域水环境安全做出了重要贡献。2010年以来，针对我国“白色污染”控制的难题，组织团队开展绿色聚乳酸系列环境友好材料的研发与产业化，取得了重要进展。先后荣获1964年国家新产品发明三等奖、1987年国家自然科学二等奖、2001年国家科技进步二等奖、2006年何梁何利基金科学与技术创新奖和2007、2015年国家技术发明二等奖等；主持（或参与）国家、省部级科技项目40余项，通过科技鉴定（或验收）30多项，发表研究论文300多篇（其中SCI收录152篇），获授权中国发明专利80多项和美、日、英等国专利14项，为我国高等教育和环境保护事业的发展做出了突出贡献。



QuanXing Zhang

Profile of the Author:

Zhang Quanxing (1938.12~), Changzhou, Jiangsu. Environmental Engineering and Polymer Materials Zhang Quanxing (1938.12~), Changzhou, Jiangsu. Environmental engineering and polymer materials experts, one of the main pioneers of ion exchange and adsorption technology in China, the pioneer of resin adsorption treatment of toxic organic industrial wastewater and its resource. Materials experts, one of the main pioneers of ion exchange and adsorption technology in China, the pioneer of resin adsorption treatment of toxic organic industrial wastewater and its resource. He graduated from the Chemistry Department of Nankai University in 1962. In 2007, he was elected as an academician of the Chinese Academy of Engineering. In 2009, he was awarded the title of National Model Teacher. He is currently a professor at the School of Environmental Studies of Nanjing University, a doctoral tutor, director of the academic committee of the institute, honorary director of the National Center for Organic Toxic Pollution Control and Resource Engineering Technology Research at Nanjing University, and deputy director of the Expert Committee on Pollution Control and Cyanobacteria Management in Taihu, Jiangsu Province. Editor of Journal of Adsorption and member of the National Environmental Advisory Committee. He used to be the director of the Environmental Engineering Teaching and Research Section of Nanjing University, the deputy director of the Institute of Environmental Sciences, the director of the provincial and national engineering technology research centers, and the third and sixth members of the Ministry of Education's Department of Geosciences and Resources and Environment. From university to 1985, he studied under the academician He Binglin of Nankai University. He has taken the lead in the synthesis and application of macroporous ion exchange and adsorption resin in China, and successfully developed a series of large pore ion exchange resins and ultrahigh crosslinked adsorption resins. In industrial water treatment, organic catalysis, uranium and precious metal extraction, drug extraction and separation, human blood perfusion and environmental protection. After 1985, he taught at Changzhou University and Nanjing

University. He mainly engaged in the research on the synthesis and performance of special resins such as composite functions in the direction of water pollution prevention, as well as resin adsorption theory, adsorption new technology, new technology research and engineering application, leading and promoting. China's high-concentration refractory organic industrial wastewater treatment and resource utilization has made important contributions to industrial water pollution control, energy conservation and emission reduction, and water environment safety in key river basins. Since 2010, in response to the problem of China's "white pollution" control, the organization team has carried out research and development and industrialization of green polylactic acid series of environmentally friendly materials, and has made important progress. He has won the third prize of National New Product Invention in 1964, the second prize of National Natural Science in 1987, the second prize of National Science and Technology Progress Award in 2001, the Heliang Heli Fund Science and Technology Innovation Award in 2006 and the second national technological invention in 2007 and 2015. Awards, etc.; hosted (or participated in) more than 40 national, provincial and ministerial-level scientific and technological projects, passed more than 30 scientific and technological appraisals (or acceptance), published more than 300 research papers (including 152 in SCI), and authorized Chinese invention patents 80 A number of patents in the United States, Japan, and the United Kingdom have made outstanding contributions to the development of higher education and environmental protection in China.

李弘

报告人简介：

李弘，男，1940 年出生，南开大学高分子化学研究所暨教育部功能高分子材料重点实验室教授、博士生导师。2010 年 10 月起受聘担任南京大学环境学院“国家有机毒物污染控制与资源化工程技术研究中心”特聘教授。曾赴加拿大麦吉尔大学、法国国家科研中心、法国波尔多大学、日本早稻田大学等国外高等学府研修，荣获天津市级优秀教师及南京大学双创之星（2018）称号。出版专 2 本，译著 2 本，在国内外重要学术刊物发表论文 200 余篇。获授权中国发明专利 50 余项、美国专利 9 项、日本专利 3 项、英国专利 1 项。被英国剑桥国际传记中心(IBC, Cambridge, England)评为“20 世纪世界 2000 名杰出学者”。目前主要从事仿生催化剂的分子设计、环境友好材料的合成研究及成果产业化研发工作。



Hong Li

Profile of the Author:

Mr. Hong Li was born in 1940, He is a full professor and PhD supervisor in the Institute of Polymer Chemistry of Nankai University and Key Laboratory of Functional Polymer Materials of the Education Ministry of China. He was invited and appointed as a “distinguished professor” in The “National Engineering Research Center for Organic Pollution Control and Resource Reuse” by Nanjing University since 2010. As a Visiting Research Professor he visited and worked at Chemistry Department of McGill University of Canada, French National Scientific Research Center (CNRS), Polymer Institute of CNRS in the University of Bordeaux, Polymer Department of Waseda University of Japan. He has published 2 monographs (one in English, one in Chinese), 2 translated monographs, more than 200 scientific papers, 50 China Invention patents, 9 US Patents, 1 British patent, 3 Japanese patents. He won the honorary titles of “The Outstanding Professor of Tianjin”, “The star of Innovation and Entrepreneurship of Nanjing University”, and “2000 Outstanding Intellectuals of the

Twentieth Century” (International Biographical Centre, Cambridge, England). His current research focuses on molecular design of biogenic catalysts, study, development and industrialization of environment-friendly materials, and so forth.

有机胍催化法可控合成聚乳酸系环境友好材料

摘要：可控聚合反应是进行大分子结构设计及获得优异性能聚合物的重要手段。作者近年来设计合成/筛选了若干种无毒有机胍化合物作为催化剂/引发剂，实现了可控缩聚、开环聚合、解聚反应。以生物质有机胍肌酐(CR)为催化剂实现了 L-/D-乳酸(LLa/DLa)的等规熔融缩聚(Iso-MP)，高产率(85%)合成得到了高等规度聚 L-/D-乳酸(PLLA、PDLA, Iso. > 98%)；以 CR 催化 Iso-MP 反应得的中分子量聚 L-/D-乳酸($M_w = 2.2 \times 10^4$, Iso. = 98.2%)为原料经熔融-固相缩聚(MP-SSP)联用法合成得到高分子量、高等规度 PLLA、PDLA ($M_w = 1.0 \times 10^5$, Iso. > 98%)，聚合物热分解温度($T_{d,i} = 324.3$ °C)较 $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ 催化法合成聚合物高 120 °C；由 CR 催化 LLa/DLa 的 Iso-MP 及其后解聚反应合成得到了光学纯 L-/D-丙交酯(LLA、DLA, e.e. 100%)，副产的聚合物残渣 r-PLLA/r-PDLA 经水解后循环用作 LLa/DLa 合成原料，光学纯 LLa/DLa 总产率达到 98%。设计合成了数种位阻型有机胍羧酸盐(HBG·OAc、CRA、CRG、CRL、TBDA)，表征了其分子结构，用以实现 LLa 的活性开环聚合。合成了单一光学构型的 L-乳酸-L-丝氨酸吗啉二酮(3S,6S-BMMD)，测定了其单晶分子结构并以 CRA 为引发剂进行了 3S,6S-BMMD 的活性开环聚合，聚合物经脱保护后合成得到双亲功能基化生物降解聚合物聚(L-乳酸-L-丝氨酸)。采用 $^1\text{H-NMR}$ 、 $^{13}\text{C-NMR}$ 跟踪监测法表征了大分子物种的精细结构，推断了上述可控反应的机理。

关键词：有机胍，立构专一性缩聚，活性开环聚合，环境友好聚合物

Controlled Synthesis of PLA-series Environment-friendly Polymers with Guanidine Catalysts

Abstract: Controlled polymerization is of great significance for the tailoring of macromolecular structure and synthesis of polymers with excellent properties. Several non-toxic organic guanidines were prepared/selected in our laboratory in recent years and used as the catalysts/initiators to realize controlled melt polycondensation (MP), ring-opening polymerization (ROP), and depolymerization (DEP). Isotactic melt polycondensation (Iso-MP) of L-lactic acid/D-lactic acid (LLa/DLa) was carried out for the first time with biogenic creatinine (CR) catalyst and poly(L-lactic acid)/poly(D-lactic acid) (PLLA/PDLA) with high isotacticity (Iso. >98%) was obtained; Combined MP with solid state polycondensation (MP-SSP) of the medium molecular weight PLLA/PDLA ($M_w = 2.2 \times 10^4$ Iso. = 98.2%), prepared by the Iso-MP with CR, was carried out, and high molecular weight PLLA/PDLA ($M_w > 1.0 \times 10^5$) with high isotacticity (Iso. >98%) was obtained. The initial decomposition temperature (Td.i) of the synthesized PLLA reached up to 324.5°C, which was 120°C higher than that of PLLA synthesized by SnCl₂•2H₂O catalyst; Optical pure (e.e. 100%) L-lactide/D-lactide (OP-LLA/OP-DLA) were synthesized via Iso-MP and the subsequent depolymerization (DEP) of LMW-PLLA/LMW-PDLA ($M_w = 8.0 \times 10^2 - 9.0 \times 10^2$) with CR catalyst. The polymer residues (r-PLLA/r-PDLA), produced accompanying with the lactides formation, were reused as the raw material for LLa/DLa synthesis after being hydrolyzed. The total yield of OP-PLLA/OP-DLA reached up to 98%; Several sterically hindered guanidine carboxylates (HBG•OAc, CRA, CRG, CRL, TBDA) were synthesized and used to realize living ROP of LLa. An optical pure morpholine-2,5-dione (3S,6S-BMMD), derived from LLa and L-serine, was synthesized P(3S,6S-BMMD), an amphiphillic copolymer P(LLa-co-Ser) was obtained, which is a useful support material in biomedical areas. The fine molecular structures and isotacticities of growing polymeric species were characterized by in situ monitoring with ¹H-NMR, ¹³C-NMR. And the mechanisms of the above mentioned controlled polymerization

were proposed.

Keywords: Organic guanidine, Isotactic polycondensation, Living ring-opening polymerization, Environment-friendly polymers