

COVER PAPER

Advanced Polymer-Based Bioink Technology for Printing Soft Biomaterials

Kangseok Lee and Chaenyung Cha*

Vol. 28, No. 8, pp 689–702 (2020) | JUL 25, 2020 | DOI 10.1007/s13233-020-8134-9



3D bioprinting technology is widely utilized to develop a diverse array of biomaterials with tunable physical, chemical and bioactive properties for biomedical applications, such as tissue engineering, drug delivery, and biosensing. With the maturation of 3D printing apparatus, the focus is now shifting to “bioinks” that can accommodate the versatility of biological systems, while still maintaining their printability. In this article, state-of-the-art bioinks based on various polymers that can impart multifunctionality to printed structures are introduced.

REVIEW

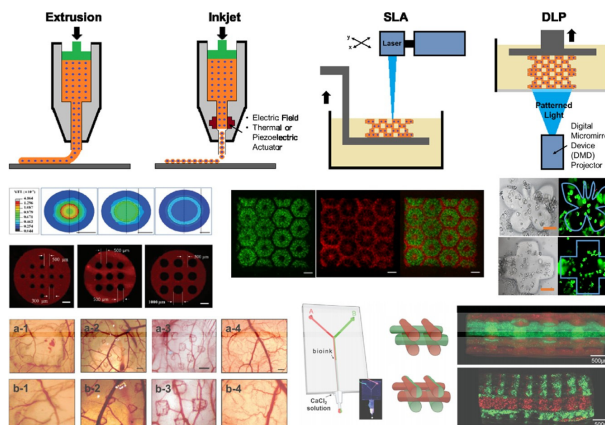
Advanced Polymer-Based Bioink Technology for Printing Soft Biomaterials

Kangseok Lee and Chaenyung Cha*

Macromol. Res., **28**, 689 (2020)

Cover Paper

3D bioprinting technology is widely adopted to create various biomaterials with high specificity for biomedical applications. There is a growing need to develop “bioinks” that can that can accommodate the versatility of biological systems, while still maintaining their printability. In this comprehensive review, bioink technologies based on various polymers to produce soft biomaterials, such as hydrogels and elastomers, having a diverse array of physicochemical and bioactive properties are introduced and highlighted.



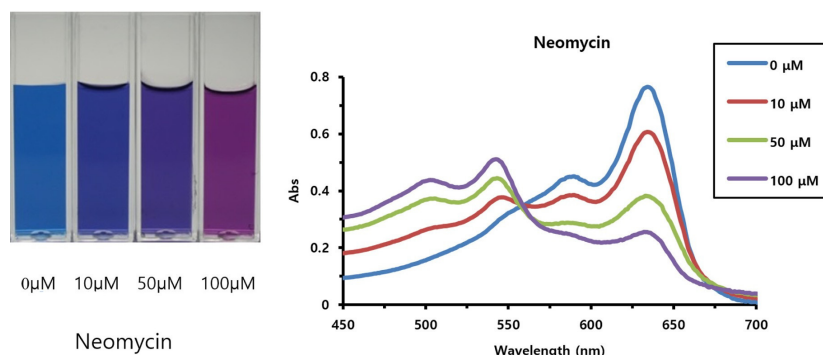
ARTICLES

Detection of Neomycin Using Amino-Functionalized Polydiacetylene

Min Jae Shin*

Macromol. Res., **28**, 703 (2020)

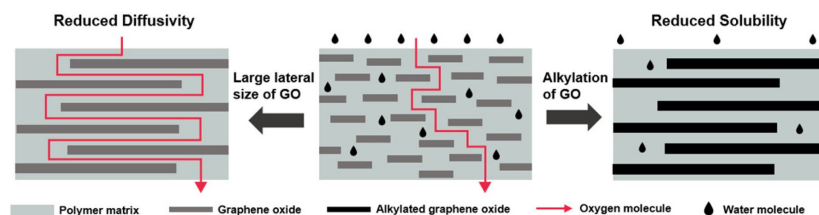
The chromatic detecting system for neomycin was fabricated using the diacetylene compound. The compound which has an amino group showed the chromatic activity for the aminoglycoside antibiotics. Both more than 3 glucose units and amino functional group were needed to show the chromatic activity. The order of the detecting ability to the aminoglycoside antibiotics was neomycin > gentamycin >> streptomycin.



Improvement in Barrier Properties Using a Large Lateral Size of Exfoliated Graphene Oxide

Jinhwa You, Beomjin Oh,
Young Soo Yun*,
and Hyoung-Joon Jin**Macromol. Res.*, **28**, 709 (2020)

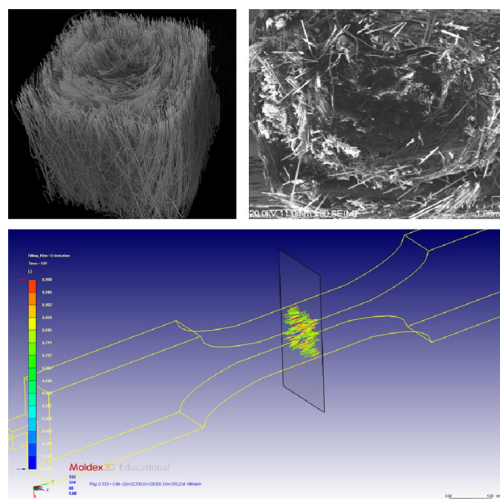
Lateral size and hydrophobicity of graphene oxide (GO) were controlled to reduce the gas permeability of the polymer composite films. Large lateral sized GO (~45 μm) effectively reduced gas diffusivity in composite film, while hydrophobic alkylated GO reduced the solubility of the composite film.



Fabrication and Analysis of Long Fiber Reinforced Polypropylene Prepared via Injection Molding

Seon Yeong Park
and Young Seok Song**Macromol. Res.*, **28**, 714 (2020)

Fiber orientation is one of key factors in fiber reinforced composites prepared using injection-molding. We fabricated long fiber incorporated composites and investigated the fiber orientation in the composite part experimentally and numerically.

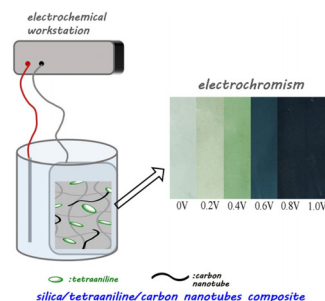


Fabrication and Electrochromic Performance of Silica/Tetraaniline/Carbon Nanotubes Composite Film

Xincai Liu, Yan Zhou,
and Danming Chao*

Macromol. Res., **28**, 721 (2020)

A novel electrochromic composite is prepared from tetraaniline and carbon nanotubes through an electrochemistry-assisted hydrolytic crosslinking reaction. The resultant composite film displays enhanced electrochromic performance, attributed to its interpenetrating network architecture, porous structure and good conductivity of the carbon nanotubes.

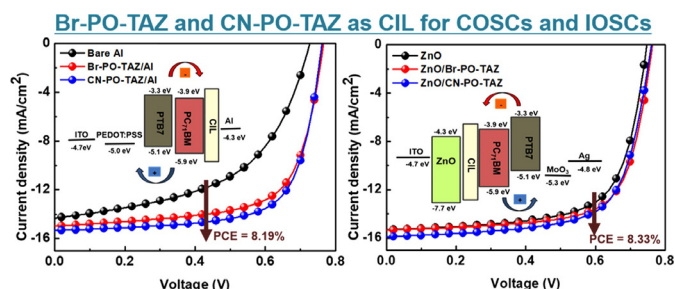


Efficient Cathode Interfacial Materials Based on Triazine/Phosphine Oxide for Conventional and Inverted Organic Solar Cells

Um Kanta Aryal,
Saripally Sudhaker Reddy,
Jungmin Choi, Chae Young Woo,
Seokhoon Jang, Youngu Lee*,
Bong Soo Kim*, Hyung Woo Lee*,
and Sung-Ho Jin*

Macromol. Res., **28**, 727 (2020)

The incorporation of new cathode interfacial layer (CIL) layers significantly enhanced the photovoltaic performance compared to conventional and inverted based organic cells without the CILs. The CN-PO-TAZ exhibited a power conversion efficiency (PCE) of 8.19% for COSCs and 8.33% for IOSCs, whereas Br-PO-TAZ yielded a PCE of 8.15% for COSCs and 8.23% for IOSCs, respectively.

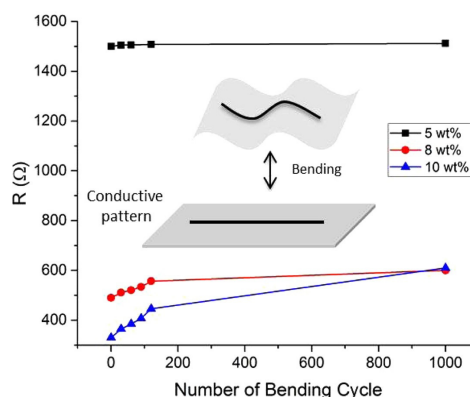


Preparation of MWCNT/PDMS Conductive Micro-Patterned Nanocomposites

Saeid Aslnejad, Morteza Nasiri*,
Farhang Abbasi,
and Hamed Abdipour

Macromol. Res., **28**, 733 (2020)

While the composite containing 5 wt% multi-walled carbon nanotube (MWCNT) has the highest (1,500 Ω) initial resistance, its resistance was almost unchanged after 1,000 bending cycles, indicating that, the morphology of the composite did not alter under the bending process. So the mechanical properties were dictated by polydimethylsiloxane (PDMS) while the MWCNT bridges maintained their connectivity. In the composites containing 8 and 10 wt%, initial electrical resistances were 490 and 330 Ω , respectively and after 1,000 cycles of bending it reached 600 and 640 Ω , respectively. These results indicate that by increasing MWCNT concentration, while initial resistance decreases, it is not stable under bending due to the micro-crack formation and MWCNT debonding from the PDMS matrix.

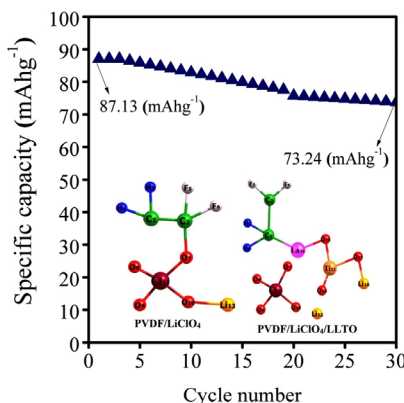


Performance Enhancement of PVDF/LiClO₄ Based Nanocomposite Solid Polymer Electrolytes *via* Incorporation of La TiO Nano Filler for All-Solid-State Batteries

Pazhaniswamy Sivaraj, Karuthedath Parameswaran Abhilash, Balakrishnan Nalini, Pandurangam Perumal, Kalimuthu Somasundaram, and Paneerselvam Christopher Selvin*

Macromol. Res., **28**, 739 (2020)

The all-solid-state cell exhibits an excellent initial specific capacity of 87.13 and 73.24 mAh g⁻¹ after 30 cycles, demonstrating higher capacity retention. The unprecedented specific capacity of the cell is attributed to the excellent compatibility, excellent ionic conductivity, and better transference number of the PVDF/LiClO₄/LLTO solid polymer electrolyte.

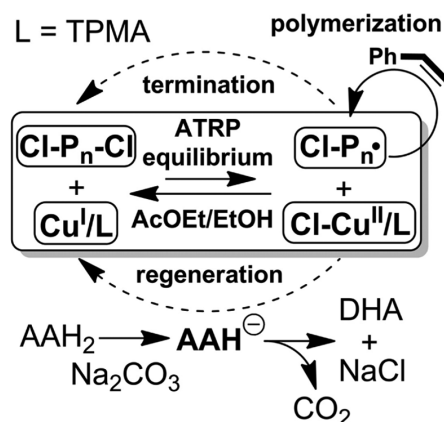


Copper-Catalysed “Activators Regenerated by Electron Transfer” “Atom Transfer Radical Polymerisation” of Styrene from a Bifunctional Initiator in Ethyl Acetate/Ethanol, Using Ascorbic Acid/Sodium Carbonate as Reducing System

Niccolò Braidi, Mirko Buffagni*, Franco Ghelfi*, Manuel Imperato, Alberto Menabue, Francesca Parenti, Armando Gennaro, Abdirisak A. Isse*, Elena Bedogni, Luisa Bonifaci, Gianfranco Cavalca, Angelo Ferrando, Aldo Longo*, and Ida Morandini

Macromol. Res., **28**, 751 (2020)

The salient features of the method are: i) simultaneous use of ascorbic acid and Na₂CO₃, ii) employment of a bifunctional initiator (ethyl 2,2-dichloropropionate) and iii) utilisation of a green solvent mixture. Na₂CO₃ plays a dual role since it preserves the ligand from protonation and activates the reducing agent. Working at 100 °C and with a metal load of only 0.025 mol%, an almost perfectly controlled telechelic polystyrene is produced, provided that conversion is kept below 50%.

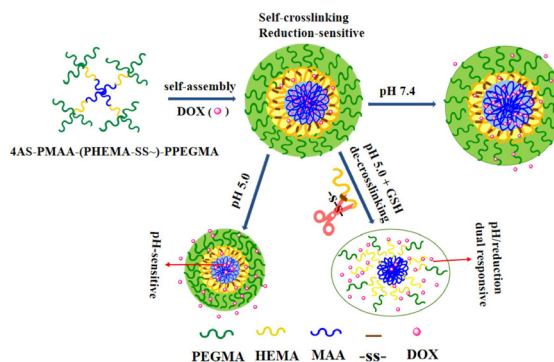


Dual-Responsive Cross-Linked Micelles from Amphiphilic Four-Arm Star Copolymers with Different Block Ratios for Triggering DOX Release

Yunwei Huang, Yanzhe Li, Zilun Tang, Qiuping Su, Tingting Liao, Yuxin Gu, Xiaofeng Lin, Xihong Zu, Wenjing Lin*, and Guobin Yi*

Macromol. Res., **28**, 762 (2020)

The pH/reduction dual-responsive 4AS-PMMA-(PHEMA-SS~)-PPEGMA cross-linked micelles owned good stability and low release of DOX in bloodstream and normal tissues, while fast release in tumor cells higher GSH concentration and lower pH value conditions.

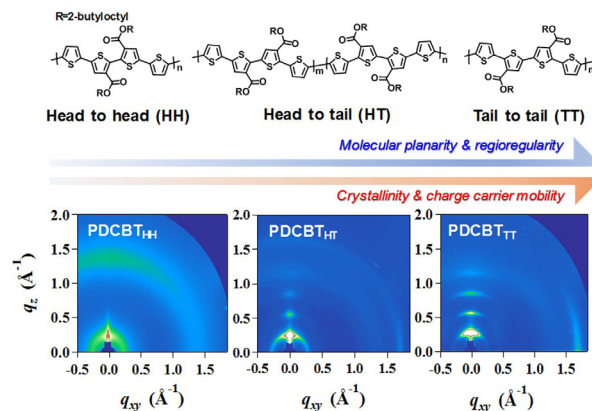


Regioisomeric Polythiophene Derivatives: Synthesis and Structure–Property Relationships for Organic Electronic Devices

Young Woong Lee, Kawon Pak,
Song Yi Park, Na Gyeong An,
Junghoon Lee, Jin Young Kim*,
and Han Young Woo*

Macromol. Res., **28**, 772 (2020)

Three types of regioisomeric polythiophene copolymers, tail-to-tail (PDCBT_{TT}), head-to-tail (PDCBT_{HT}), and head-to-head (PDCBT_{HH}) were synthesized. Their regiochemistry influenced significantly the chain conformation, and optical, electrochemical, morphological, and charge-transport characteristics of the polymers. A highly regioregular and planar PDCBT_{TT} exhibited the highest field-effect hole mobility of $\mu = 0.065 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and photovoltaic performance for the blend film with a fullerene acceptor (PC₇₁BM).

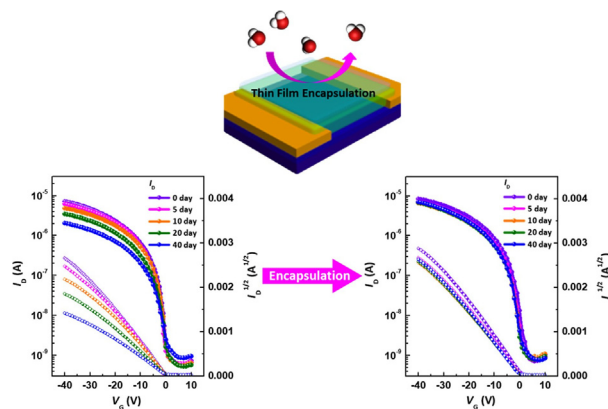


Solution-Processed Flexible Gas Barrier Films for Organic Field-Effect Transistors

Jisu Hong, Hyeok-jin Kwon,
Nahae Kim, Heqing Ye,
Yonghwa Baek, Chan Eon Park,
Geon Oh Choe, Tae Kyu An*,
Juyoung Kim*, and Se Hyun Kim*

Macromol. Res., **28**, 782 (2020)

Organic-inorganic hybrid sol-gel materials and cyclic transparent optical polymer (CYTOP) were used as the bottom and top layers of the barrier films, respectively, to effectively protect against gas permeation through the barrier films. The encapsulated organic field-effect transistors (OFETs) based on 6,13-bis(triisopropylsilyl)ethynyl (TIPS)-pentacene maintained their initial hole mobility over 40 days.

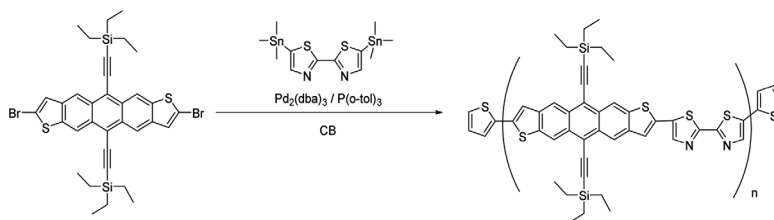


Synthesis and Characterization of Poly(triethylsilyl ethynylantrathiophene-bithiazole) for Organic Thin Film Transistor

Ji-Hyun Park, Soon-Ki Kwon,
and Yun-Hi Kim*

Macromol. Res., **28**, 789 (2020)

The new donor-acceptor copolymer with triethylsilyl ethynylantrathiophene as donor and bithiazole as acceptor, poly(triethylsilyl ethynylantrathiophene-bithiazole), was synthesized through stille coupling. The organic field effect transistor (OFET) employing poly(triethylsilyl ethynylantrathiophene-bithiazole) spin-cast from chloroform solutions at 100°C annealing showed the mobility of $4.93 \times 10^{-6} \text{ cm}^2/\text{V}\cdot\text{s}$.



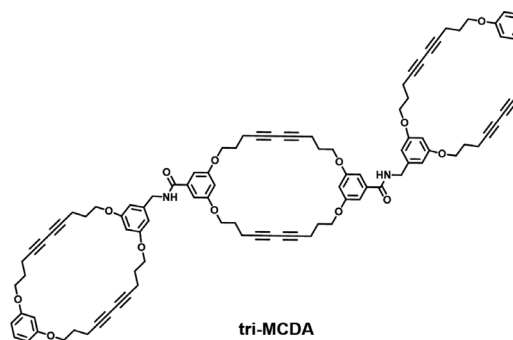
NOTE

Synthesis of a Trimeric Macrocylic Diacetylene

Hansol Kim and Jong-Man Kim*

Macromol. Res., **28**, 793 (2020)

The first reported synthesis of linearly connected, trimeric macrocyclic diacetylene (MCDA) (tri-MCDA) is described. The ultimate step in the sequence involves a coupling of an amine-functionalized MCDA with a dicarboxylic acid-containing MCDA. UV irradiation of the self-assembled fibrous tri-MCDA results in generation of a polydiacetylene (PDA).

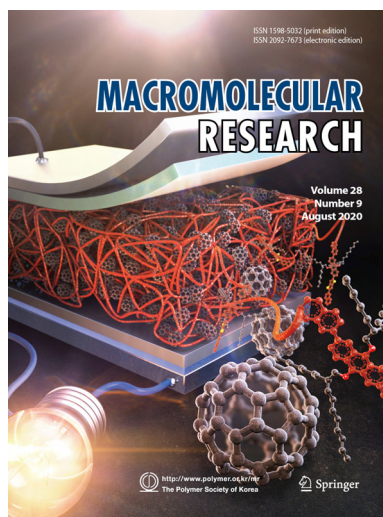


COVER PAPER

Effects of Bulk Heterojunction Morphology Control *via* Thermal Annealing on the Fill Factor of Anthracene-based Polymer Solar Cells

Hyojung Cha, Jiaqiang Li, Yifan Li, Seul-Ong Kim, Yun-Hi Kim*, and Soon-Ki Kwon*

Vol. 28, No. 9, pp 820–825 (2020) | AUG 25, 2020 | DOI 10.1007/s13233-020-8107-z



A polymeric semiconductor (ODATT) containing alkoxy anthracene (ODA) and thienothiophene (TT) was developed. Morphological analysis of the polymer:PC71BM blend films demonstrate the influence of ODATT polymer segregation on device performance by atomic force microscopy (AFM) and transmission electron microscopy (TEM). ODATT has enhanced fill factor (FF) after thermal annealing treatment due to the reduced series and shunt resistance from morphological enhancement.

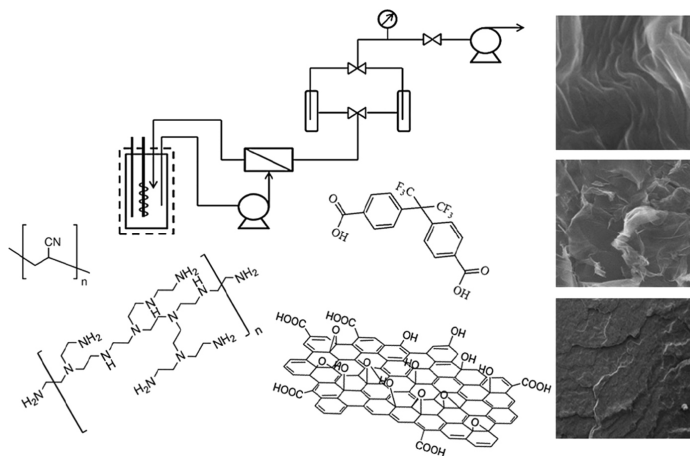
ARTICLES

Novel Branched Polyamide/Poly(acrylonitrile)/Graphene Oxide Membranes for Separation of Chlorinated Volatile Organic Compounds from Water *via* Pervaporation

Shafagh Mokhtarzadeh, Samira Agbolaghi*, and Yaghoob Mansourpanah

Macromol. Res., **28**, 797 (2020)

Branched polyamides (BPAs) were blended with poly(acrylonitrile) (PAN) to construct the membranes having various concentrations of graphene oxide (GO). The BPA/PAN and BPA/PAN/GO membranes were applied for selective removal of chlorinated volatile organic compounds (Cl-VOCs) from water by pervaporation. Impacts of feed composition, GO content and distinct feed types were investigated on pervaporation performance.

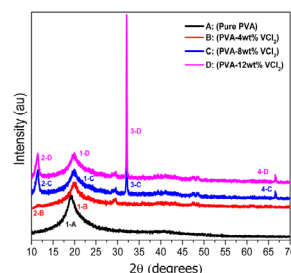


Highly Precise Determination of Structural and Optical Parameters of an Innovative (PVA-VOCl) for Flexible Polymer-Semiconductor Devices

Fayez M. Ali* and Fethi Maiz

Macromol. Res., **28**, 805 (2020)

Polymer-semiconductor nanocomposite films based on polyvinyl alcohol-oxovanadium chloride (PVA-VOCl) were prepared by the solution casting technique. The particle size of VOCl in the PVA polymer increases dramatically by increasing VOCl in the polymer matrix. The Fourier transform infrared and UV-Vis and Near-infrared measurements implies that, incorporation of VOCl nanoparticles in the polymer significantly affect structural and optical properties of the PVA films where the optical band gap reduced from 5.2 to 2.85 eV and the high frequency refractive index increased from 1.7 to 2.07. These films can be considered as promising candidates in manufacturing of organic semiconductors for various optoelectronics applications.

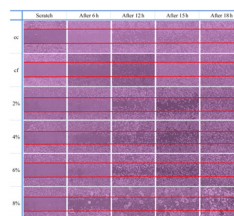


Effect of CMC Concentration on Cell Growth Behavior of PVA/CMC Hydrogel

Ji-Yeon Shin, Deuk Yong Lee*,
Jung In Yoon, and Yo-Seung Song

Macromol. Res., **28**, 813 (2020)

In this study, the compressive strength, the drug release rate, the cytotoxicity, the cell proliferation, the cell growth, and the pore distribution of the irradiated PVA/CMC hydrogels are investigated to evaluate the effects of molecular porosity and mechanical property on L-929 cell growth behavior. The L-929 cell migration into the cell-free area is examined by observing the gap closure rate from the scratch assay. In addition, an ELISA assay reveals that the amounts of HGF and VEGF increase dramatically from 724.5 ± 36.5 to 2019.3 ± 30.1 pg/mL and from 2173.4 ± 651.5 to 6273.9 ± 290.2 pg/mL with increasing time from 6 to 15 h, respectively. Among the samples, the highest strength of 99.2 ± 9.6 kPa, the highest amounts of HGF and VEGF, and the fastest L-929 cell growth are observed for the PVA/6 wt% CMC hydrogels, suggesting that they are highly suitable for wound healing biomaterials requiring fast healing regeneration.



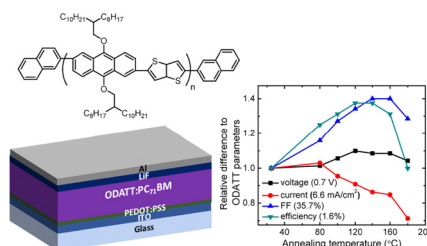
Effects of Bulk Heterojunction Morphology Control via Thermal Annealing on the Fill Factor of Anthracene-based Polymer Solar Cells

Hyojung Cha, Jiaqiang Li, Yifan Li,
Seul-Ong Kim, Yun-Hi Kim*,
and Soon-Ki Kwon*

Macromol. Res., **28**, 820 (2020)

Cover Paper

Here we report a polymeric semiconductor (ODATT) comprising alkoxy anthracene (ODA) and thienothiophene (TT) polymerized by stille coupling reaction with the Pd catalyst. The optical properties of the polymer:PC₇₁BM blend films are used by the UV-visible absorption spectroscopy. The ODATT blends with PC₇₁BM exhibit a maximal power conversion efficiency of 2.2% via thermal annealing treatment. Morphological analysis of the polymer:PC₇₁BM blend films demonstrate the influence of ODATT polymer segregation on device performance by atomic force microscopy and transmission electron microscopy. We confirmed that ODATT has enhanced fill factor after thermal annealing treatment from the reduced series and shunt resistance from morphological enhancement.

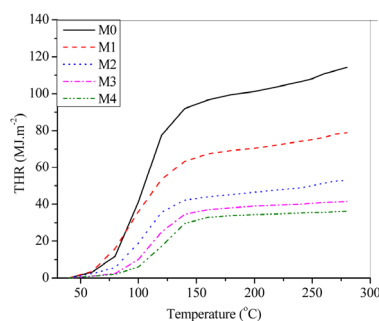


Effects of DOPO-Grafted Epoxidized Soybean Oil on Fracture Toughness and Flame Retardant of Epoxy Resin/Rice Husk Silica Hybrid

Cuong Manh Vu
and Quang-Vu Bach*

Macromol. Res., **28**, 826 (2020)

9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) was grafted with epoxidized soybean oil (ESO) to form the ESO-G-DOPO *via* ring opening reaction. The ESO-G-DOPO was utilized as additive for simultaneous improvement of fracture toughness and flame retardant of Epoxy Resin/Rice Husk Silica Hybrid. The fracture energy was improved up to 111.36%, while the limited oxygen index (LOI) was improved 50.2%. The total heat release (THR) value of epoxy resin was increased up to 68.41%.

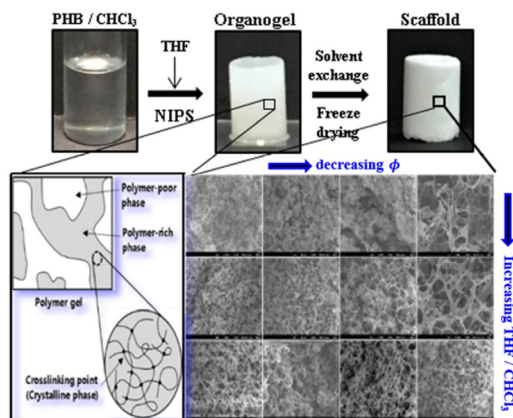


Porous Poly(3-hydroxybutyrate) Scaffolds Prepared by Non-Solvent-Induced Phase Separation for Tissue Engineering

Jiseon Kang, Ji-Young Hwang,
Mongyoung Huh, and Seok Il Yun*

Macromol. Res., **28**, 835 (2020)

Highly porous poly(3-hydroxybutyrate) (PHB) scaffolds were fabricated using non-solvent-induced phase separation with chloroform as the solvent and tetrahydrofuran as the non-solvent. The microporosity, nanofiber morphology, and mechanical strength of the scaffolds were adjusted by varying the fabrication parameters, such as the polymer concentration and solvent composition.

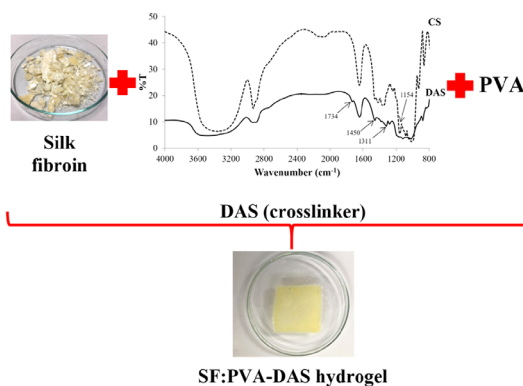


Silk Fibroin/Poly (vinyl alcohol) Hydrogel Cross-Linked with Dialdehyde Starch for Wound Dressing Applications

Pusita Kuchaiyaphum*,
Chatrachatchaya Chotichayapong,
Nuttthaya Butwong,
and Worapong Bua-ngern

Macromol. Res., **28**, 844 (2020)

Normally, silk fibroin (SF) and poly(vinyl alcohol) (PVA) polymers are phase-separated. In this study, hydrogel containing SF and PVA was successfully fabricated using DAS as a non-toxic crosslinker, without the need for a conventional chemical crosslinker. The 50:50 SF:PVA hydrogel with 5 wt% DAS has the potential to be useful in wound dressing applications.

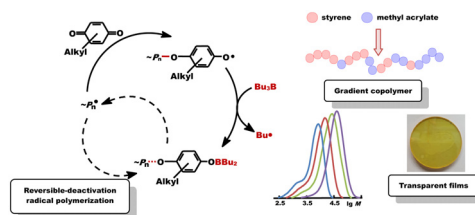


Polymerization with Borane Chemistry. Tributylborane/*p*-Quinone System as a New Method of Reversible-Deactivation Radical Copolymerization for Styrene and Methyl Acrylate

Dmitrii Ludin*, Yulia Voitovich, Evgenia Salomatina, Yulia Kuznetsova, Ivan Grishin, Igor Fedushkin, and Sergey Zaitsev

Macromol. Res., 28, 851 (2020)

p-Quinones, such as 1,4-naphthoquinone, 2,3-dimethyl-1,4-benzoquinone, 2,5-di-*tert*-1,4-butylbenzo-quinone, and duroquinone, with addition of a catalytic amount of tributylborane, allow for the control over styrene/methyl acrylate copolymerization. The process proceeds in a controlled manner *via* a reversible homolytic dissociation of the active macromolecules with terminal aryloxyboron-groups. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) results that the macromolecules contained internal fragments of *p*-quinone. Also, the terminal aryloxyboron-groups were detected in the mass-spectra. On realization of the "living" mechanism of copolymerization, the structure of copolymers obtained at high conversions can be considered as similar to the gradient structure.

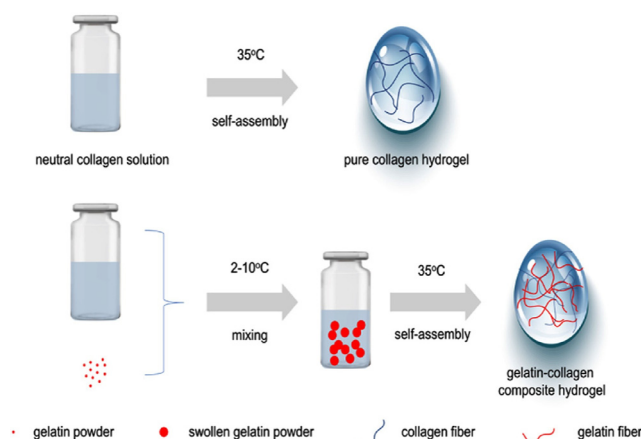


A New Method of Gelatin Modified Collagen and Viscoelastic Study of Gelatin-Collagen Composite Hydrogel

Lang He, Sheng Li, Chengzhi Xu, Benmei Wei, Juntao Zhang, Yuling Xu, Beirong Zhu, Yang Cao, Xilin Wu, Zhijin Xiong, Rongrui Huang, Jian Yang, and Haibo Wang*

Macromol. Res., 28, 861 (2020)

At low temperature (2–10 °C), gelatin powder was swelled in 2 mg/mL neutral bovine tendon collagen solution to form a gelatin-collagen mixed solution, which was later incubated at 35 °C to obtain a novel gelatin-collagen composite hydrogel.

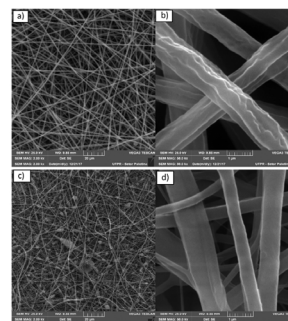


Antimicrobial Activity of Polymeric Microfibers Containing *Coix Lacryma-Jobi* Extract

Gabriela Lauer Breitenbach, Marina Giombelli Rosenberger, Andressa Giombelli Rosenberger, Josiane Caetano, Michelly Cristina Galdioli Pellá, Desirée Tamara Scheidt, Cleide Viviane Buzanello Martins, Edvani Curti Munizc, and Douglas Cardoso Dragunski*

Macromol. Res., 28, 869 (2020)

Obtaining Ecovio microfibers containing *Coix lacryma-jobi* extract, with antimicrobial action. A polymeric membrane was obtained that can be used in the future as a dressing to aid in wound healing. This material was characterized using thermal and morphological analysis, in which it was possible to verify the interaction between the extract and the polymeric membrane. There is a decrease in the diameter, roughness, and homogeneity of the fiber after the incorporation of the extract, finally, in the microbiological analysis, the membrane with the extract proved to be effective when tested in the *Staphylococcus aureus* bacterium.



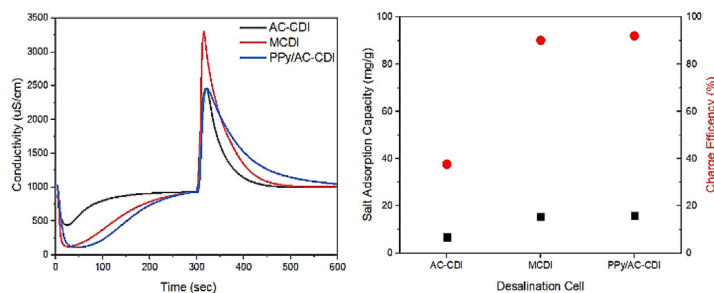
NOTES

Synthesis of Ion-Exchange Polypyrrole/Activated Carbon Composites and Their Characterization as Electrodes for Capacitive Deionization

Oneeb ul Haq, Jae-Hwan Choi*,
and Youn-Sik Lee*

Macromol. Res., **28**, 877 (2020)

The electrodes fabricated by the synthesized polypyrrole (PPy)/activated carbon (AC) composites contains immobilized amino and sulfonic functional groups along with the conducting polymer network that makes the electrode highly ion-exchangeable, less resistant, hydrophilic and efficient in the deionization performance as compared to the pristine AC electrodes.



Enhancement of Yarn Pull-Out Force of *Para*-Aramid Fabric at High Speed by Dispersion and Phenolic Anchoring of MWCNT on the Fiber Surfaces in the Presence of Surfactant and Ultrasonic Process

Jinsil Cheon and Donghwan Cho*

Macromol. Res., **28**, 881 (2020)

The effect of a small amount of multi-walled carbon nanotubes (MWCNT) physically anchored on the fiber surfaces on the pull-out forces occurring between the inter-yarns of *para*-aramid fabrics at high speed was investigated. The yarn pull-out force strongly depended on phenolic resin and MWCNT concentrations as well as on ultrasonic processing time, showing the combined effect by phenolic anchoring and MWCNT incorporation.

