Polymer Reference List

Transition Metal Coupling Polymerizations

1. Park, Y.S.; Wu, Q.; Nam, C.-Y.; Grubbs, R.B. Polymerization of Tellurophene Derivatives by Microwave-Assisted Palladium-Catalyzed Ipso-Arylative Polymerization. Angew. Chem. Int. Ed. **2014**, *53*, 10691–10695. DOI: 10.1002/anie.201406068.
   - Professor R.B. Grubbs, Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, NY
   - Polymer could be synthesized in a microwave through ipso arylative, Stille coupling or Suzuki coupling polymerization
   - Polymers absorb light of longer wavelengths in comparison to the thiophene analog

2. Lei, T.; Dou, J-H.; Cao, X-Y.; Wang, J-Y.; Pei, J.; Electron-Deficient Poly(p-Phenylene Vinylene) Provides Electron Mobility Over 1 $cm^2V^{-1}S^{-1}$ Under Ambient Conditions. J. Am. Chem. Soc. **2013**, *135*, 12168-12171. DOI:10.1021/ja403624a.
   - Professor Jian Pei at Beijing National Laboratory for Molecular Sciences, College of Chemistry and Molecular Engineering, Peking University
   - Rapid electron transport in a polymer under ambient conditions
   - By incorporating electron withdrawing groups into poly(p-phenylene vinylene) they were able to increase electron mobility
   - Palladium catalyzed Stille coupling polymerization

3. Liu, X.; Hsu, B.B.Y.; Sun, Y.; Mai, C.-K.; Heeger, A.J.; Bazan, G.C. High Thermal Stability Solution-Processable Narrow-Band Gap Molecular Semiconductors. J. Am. Chem. Soc. **2014**, *136*, 16144–16147. DOI: 10.1021/ja510088x.
   - Professor Guillermo Bazan, Center for Polymers and Organic Solids and Department of Chemistry and Biochemistry, UCSB, Santa Barbara
   - Microwave-assisted Stille coupling polymerization for the synthesis of highly thermally stable semiconductors
   - Polymer was synthesized in under an hour using a step-wise heating process
   - Substitution of fluorine into the backbone produced controllable thermal stability and phase transition temperatures

4. Fei, Z.; Pattanasattayavong, P.; Han, Y.; Schroeder, B.C.; Yan, F.; Kline, R.J.; Antopoulos, T.D.; Heeney, M. Influence of Side-Chain Regiochemistry on the Transistor Performance of High-Mobility, All-Donor Polymers. J. Am. Chem. Soc. **2014**, *136*, 15154–15157. DOI: 10.1021/ja508798s.
   - Professor Martin Heeney, Department of Chemistry and Centre for Plastic Electronics, Imperial College London
   - Microwave-assisted Stille coupling polymerization
   - Three polymers differing only in side chain synthesized reveal significant changes in optoelectronic and aggregation properties

5. Stuart, A. C.; Tumbleston, J. R.; Zhou, H.; Li, W.; Liu, S.; Ade, H.; You, W. Fluorine Substituents Reduce Charge Recombination and Drive Structure and Morphology Development in Polymer Solar Cells. J. Am. Chem. Soc. **2013**, *135*, 1806–1815. DOI: 10.1021/ja309289u.
   - Professor Wei You, Department of Chemistry, University of North Carolina at Chapel Hill
   - Using a CEM Discover® , researchers performed the synthesis of a number of fluorinated BnDT-DTBT polymers via microwave-assisted Stille coupling polymerization
   - The electrical properties of varied fluorine substituted polymers were investigated

6. Matthews, J. R.; Niu, W.; Tandia, A.; Wallace, A. L.; Hu, J.; Lee, W.-Y.; Giri, G.; Mannsfeld, S. C. B.; Xie, Y.; Cai, S.; Fong, H. H.; Bao, Z. He, M. Scalable Synthesis of Fused Thiophene-Diketopyrrolopyrrole Semiconducting Polymers Processed from Nonchlorinated Solvents into High Performance Thin Film Transistors. Chem. Mater. **2013**, *25*, 782–789. DOI: 10.1021/cm303953e.
   - Professors Hon Hang Fong, Zhenan Bao, and Mingqian He - Polymerization reactions were completed using a CEM Discover® or CEM MARS
   - Up to 100 g quantities of the title polymer were synthesized by a Pd catalyzed Stille coupling polymerization
   - This polymer was incorporated into a thin film transistor with hole mobilities in excess of 2 $cm^2/V{\cdot}s$

7. Lu, S.; Drees, M.; Yao, Y.; Boudinet, D.; Yan, H.; Pan, H.; Wang, J.; Li, Y.; Usta, H.; Facchetti, A. 3,6-Dithiophen-2-yl-diketopyrrolo[3,2-b]pyrrole (isoDPPT) as an Acceptor Building Block for Organic Opto-Electronics. Macromolecules **2013**, *46*, 3895–3906. DOI: 10.1021/ma400568b.
   - Doctors Shaofeng Lu and Antonio Facchetti, Polyera Corporation
   - A number of 3,6-dithiophen-2-yl-diketopyrrolo[3,2-b]-pyrrole (isoDPPT) copolymers were synthesized by microwave irradiation
   - These new polymers hole mobility of up to 0.03 $cm^2/(Vs)$ and solar cell power conversion efficiency (PCE) of 5.1%

8. Mei, J.; Kim, D. H.; Ayzner, A. L.; Toney, M. F.; Bao, Z. Siloxane-Terminated Solubilizing Side Chains: Bringing Conjugated Polymer Backbones Closer and Boosting Hole Mobilities in Thin-Film Transistors. J. Am. Chem. Soc. **2011**, *133*, 20130–20133. DOI: 10.1021/ja209328m.
   - Professor Zhenan Bao, Department of Chemical Engineering, Stanford University
   - Synthesized isoindigo based polymers with siloxane-terminated side chain utilizing the CEM Discover® “power cycling” method
   - As compared to a reference polymer, the synthesized polymer exhibited almost a ten-fold increase in average hole mobility when incorporated into a thin film transistor
   - The more efficient average conductivity is attributed to a shorter π- π stacking distance

9. Kudla, C. J.; Koenen, N.; Pisula, W.; Scherf, U. First Synthesis of Isotactic Poly(9-alkyl$_1$-9-alkyl$_2$fluorene) via Directed Aryl-Aryl Coupling of Chiral AB-Type Monomers. Macromolecules **2009**, *42*, 3483–3488. DOI: 10.1021/ma8028503.
   - Professor Ullrich Scherf, Max-Planck-Institute for Polymer Research
   - Substituted chiral 9-alkyl$_1$-9-alkyl$_2$fluorene monomers were heated for 12 min at 120 °C in a CEM Discover® to furnish either atactic or isotactic polymers
   - Physical and chemical properties of each sample were investigated, displaying characteristics consistent with each type of polymer

10. Yang, L.; Zhou, H.; Price, S. C.; You, W. Parallel-like Bulk Heterojunction Polymer Solar Cells. J. Am. Chem. Soc. **2012**, *134*, 5432–5435. DOI: 10.1021/ja211597w.
   - Professor Wei You, Department of Chemistry, University of North Carolina at Chapel Hill
   - Using previously established methodologies (see 10.1021/ja1112595), a parallel-like bulk heterojunction (PBHJ) cell was synthesized which mimicked the efficacy of polymer tandem cells but offers the low cost of single junction cells
   - PBHJ devices demonstrate improvements of up to 40% in J_{sc} and 30% in overall efficiency

11. Merino, E.; Verde-Sesto, E.; Maya, E. M.; Iglesias, M.; Sánchez, F.; Corma, A. Synthesis of Structured Porous Polymers with Acid and Basic Sites and Their Catalytic Application in Cascade-Type Reactions. Chem. Mater. **2013**, *25*, 981–988. DOI: 10.1021/cm400123d.
   - Professor Avelino Corma, Instituto de Tecnología Química, UPV-CSIC
   - Researchers synthesized a porous polymeric aromatic framework (PPAF) through a Pd catalyzed Suzuki coupling
   - The (PPAF) was functionalized with acid and base active sites and used as a bifunctional catalyst

12. Ouhib, F.; Desbief, S.; Lazzaroni, R.; De Winter, J.; Gerbaux, P.; Jérôme, C.; Detrembleur, C. Thermally Induced Coupling of Poly(thiophene)-Based Block Copolymers Prepared by Grignard Metathesis Polymerization: A Straightforward Route toward Highly Regioregular Multiblock Conjugated Copolymers. Macromolecules **2012**, *45*, 6796–6806. DOI: 10.1021/ma3009405.
   - Professor Christophe Detrembleur, Department of Chemistry, University of Liège
   - Poly(thiophene)-based multiblock copolymers were synthesized using a Ni catalyst and Grignard metathesis polymerization (GRIM)
   - Reaction was complete in a few hours at 80 °C conventionally, or in only 10 minutes at 120 °C in a CEM Discover®

13. Dössel, L.; Gherghel, L.; Feng, X.; Müllen, K. Graphene Nanoribbons by Chemists: Nanometer-Sized, Soluble, and Defect-Free. Angew. Chem. Int. Ed. **2011**, *50*, 2540–2543. DOI: 10.1002/anie.201006593.
   - Professor Klaus Müllen, Max-Planck-Institute for Polymer Research
   - Researchers detail a bottom-up organic synthesis of defect-free graphene nanoribbons
   - Microwave-assisted Suzuki reaction was used to construct polymers which were efficiently converted to graphene nanoribbons by an intramolecular Scholl reaction

14. Price, S. C.; Stuart, A. C.; Yang, L.; Zhou, H.; You, W. Fluorine Substituted Conjugated Polymer of Medium Band Gap Yields 7% Efficiency in Polymer-Fullerene Solar Cells. J. Am. Chem. Soc. **2011**, *133*, 4625–4631. DOI: 10.1021/ja1112595.
   - Professor Wei You, Department of Chemistry, University of North Carolina at Chapel Hill
   - The CEM Discover® was used to polymerize benzotriazole(HTAZ/FTAZ)/benzodithiophene(BnDT) monomers and form two medium band gap copolymers
   - Resulting fluorinated polymer PBnDT-FTAZ exhibited efficiencies above 7% when combined with fullerenes in a heterojunction
   - Synthesized polymers in a layer of 1 µm outperformed current polymers used for solar cells through high photovoltaic efficiency and a low band gap

15. Pina, J.; Seixas de Melo, J.; Burrows, H. D.; Maçanita, A. L.; Galbrecht, F.; Bünnagel, T.; Scherf, U. Alternating Binaphthyl-Thiophene Copolymers: Synthesis, Spectroscopy, and Photophysics and Their Relevance to the Question of Energy Migration versus Conformational Relaxation. Macromolecules **2009**, *42*, 1710–1719. DOI: 10.1021/ma802395c.
   - Professor J. Seixas de Melo, Department of Chemistry, University of Coimbra
   - Alternating binaphthyl-oligothiophene copolymers were synthesized by microwave-assisted Stille-type polymerizations
   - Spectral and photophysical properties investigations were carried out on four novel copolymers

16. Moulé, A. J.; Tsami, A.; Bünnagel, T. W.; Forster, M.; Kronenberg, N. M.; Scharber, M.; Koppe, M.; Morana, M.; Brabec, C. J.; Meerholz, K.; Scherf, U. Two Novel Cyclopentadithiophene-Based Alternating Copolymers as Potential Donor Components for High-Efficiency Bulk-Heterojunction-Type Solar Cells. Chem. Mater. **2008**, *20*, 4045–4050. DOI: 10.1021/cm8006638.
   - Researchers detail the synthesis of two low-band-gap polythiophenes, PCPDTTBTT and PCPDTQ
   - After preparation of the monomers, polymerization reaction are carried out in a CEM Discover® at 150 °C for only 15 min
   - While the PCPDTQ polymer did not produce efficient solar cells, a high power efficiency of 2.1% was found for a mixture of PCPDTTBTT and fullerene
   - The power efficiency was achieved through addition of a solvent additive which altered the phase mixing ratios

17. Saleh, M.; Baumgarten, M.; Mavrinskiy, A.; Schäfer, T.; Müllen, K. Triphenylene-Based Polymers for Blue Polymeric Light Emitting Diodes. Macromolecules **2010**, *43*, 137–143. DOI: 10.1021/ma901912t.
    - Professor Klaus Müllen, Max-Planck-Institute for Polymer Research
    - Triphenylene derived monomers and polymers all synthesized using microwave irradiation
    - Novel co- and homopolymers formed through Suzuki-Miyaura and Yamamoto polycondensation reactions in a CEM Discover®
    - Emission spectrum of synthesized compounds show promising use in blue polymeric light emitting diodes

18. Weber, J.; Thomas, A. Toward Stable Interfaces in Conjugated Polymers: Microporous Poly(p-phenylene) and Poly(phenyleneethynylene) Based on a Spirobifluorene Building Block. J. Am. Chem. Soc. **2008**, *130*, 6334–6335. DOI: 10.1021/ja801691x.
    - Drs. Jens Weber and Arne Thomas, Max Planck Institute of Colloids and Interfaces
    - Polymers based on spirobifluorene were synthesized in about 5 min at 145 °C using microwave irradiation
    - Conventional heating methods were plagued by long reaction times, lower yields, and specific surface area
    - The microporous, conjugated polymer networks have great potential for applications in organic electronics

19. Kleinhenz, N.; Yang, L.; Zhou, H.; Price, S. C.; You, W. Low-Band-Gap Polymers That Utilize Quinoid Resonance Structure Stabilization by Thienothiophene: Fine-Tuning of HOMO Level. Macromolecules **2011**, *44*, 872–877. DOI: 10.1021/ma1024126.
    - Professor Wei You, Department of Chemistry, University of North Carolina at Chapel Hill
    - Utilizing a quinoid strategy, a series of polymers using thienothiophene (TT) monomers with various comonomers were synthesized using microwave irradiation and Stille coupling polymerizations
    - Polymerizations complete in only 20 min at 150 °C using a CEM Discover®
    - Incorporation of TT with any comonomer results in a small-band-gap polymer with applications in solar cells

20. Dallos, T.; Beckmann, D.; Brunklaus, G.; Baumgarten, M. Thiadiazoloquinoxaline - Acetylene Containing Polymers as Semiconductors in Ambipolar Field Effect Transistors. J. Am. Chem. Soc. **2011**, *133*, 13898–13901. DOI: 10.1021/ja2057709.
    - Dr. Martin Baumgarten, Max Planck Institute for Polymer Research
    - Conjugated copolymers PPTQT and PTTQT were synthesized from thiadiazoloquinoxalines and thiophenes connected by ethynylene spacers; a Sonogashira cross-coupling strategy was used to combine monomers
    - Microwave heating PTQ and TTQ monomers at a low temperature resulted in polymer formation after only 100 min
    - Copolymers displayed electron and hole mobilities of 0.042 and 0.028 cm^2/V s respectively, making them the first example of a triple bond containing polymer with ambipolar characteristics

Cationic Polymerizations

21. Rudolph, T.; Kempe, K.; Crotty, S.; Paulus, R.M.; Schubert, U.S.; Krossing, I.; Schacher, F.H. A Strong Cationic Brønsted Acid, $[H(OEt_2)_2][Al\{OC(CF_3)_3\}_4]$, as an Efficient Initiator for the Cationic Ring-Opening Polymerization of 2-Alkyl-2-Oxazolines. Polym. Chem. **2013**, *4*, 495–505. DOI: 10.1039/C2PY20598J.
    - Professor Schacher, Organic and Macromolecular Chemistry, Friedrich Schiller University, Humbodtstr, Germany
    - Cationic ring opening polymerization and copolymerization of several oxazolines
    - Successful formation of block copolymers despite being insoluble in organic solvents

22. Hong, M.; Chen, E.Y.-X. Proton-transfer Polymerization (HTP): Converting Methacrylates to Polyesters by an N-Heterocyclic Carbene. Angew. Chem. Int. Ed. **2014**, *53*, 11900-11906. DOI: 10.1002/anie.201406630.
    - Professor Chen Department of Chemistry, Colorado State University, Fort Collins, CO
    - Polymerization of dimethacrylates to unsaturated polyesters
    - Termed proton(H) transfer polymerization (HTP)

23. Gizdavic-Nikolaidis, M. R.; Stanisavljev, D. R.; Easteal, A. J.; Zujovic, Z. D. Microwave-Assisted Synthesis of Functionalized Polyaniline Nanostructures with Advanced Antioxidant Properties. J. Phys. Chem. C. **2010**, *114*, 18790–18796. DOI: 10.1021/jp106213m.
    - Professors Marija R. Gizdavic-Nikolaidis and Zoran D. Zujovic, Department of Chemistry, University of Auckland
    - Copolymers of aniline and 2-aminobenzoic acid and 2-aminosulfonic acid were synthesized comparing conventional and microwave methods
    - Nanostructured functionalized copolymers synthesized by microwave were produced in a 2.5-3 times higher yield and exhibited a 2.1-2.4 times better radical scavenger ability than conventionally synthesized counterparts
    - Polymerization reactions were performed at room temperature in as little as 5 min

24. Ren, S.; Bojdys, M. J.; Dawson, R.; Laybourn, A.; Khimyak, Y. Z.; Adams, D. J.; Cooper, A. I. Porous, Fluorescent, Covalent Triazine-Based Frameworks Via Room-Temperature and Microwave-Assisted Synthesis. Adv. Mater. **2012**, *24*, 2357–2361. DOI: 10.1002/adma.201200751.

- Professor Andrew Cooper, University of Liverpool, Department of Chemistry and Centre for Materials
- Using the CEM Discover® with camera accessory, researchers synthesized porous organic polymers (POPs) in 30 min
- Conventional reaction procedure requires an overnight reaction
- Materials exhibit BET surfaces exceeding 1100 m^2g^{-1} and exceptional CO_2 capacities up to 4.17 mmol g^{-1}

25. Wood, C. D.; Tan, B.; Trewin, A.; Niu, H.; Bradshaw, D.; Rosseinsky, M. J.; Khimyak, Y. Z.; Campbell, N. L.; Kirk, R.; Stöckel, E.; Cooper, A. I. Hydrogen Storage in Microporous Hypercrosslinked Organic Polymer Networks. Chem. Mater. **2007**, *19*, 2034–2048. DOI: 10.1021/cm070356a.

- Professor Andrew Cooper, Department of Chemistry, The University of Liverpool
- Polymers of hypercrosslinked poly(vinyl-benzyl chloride) (HCPVBC) and dichloroxylene (DCX) were synthesized using microwave irradiation in 1 h or less; conventional reactions required 18 h
- The products are predominantly microporous with surface areas of up to 1904 m^2/g and gravimetric storage capacity of up to 3.68 wt % at 15 bar and 77.3 K

26. Fogel, Y.; Zhi, L.; Rouhanipour, A.; Andrienko, D.; Räder, H. J.; Müllen, K. Graphitic Nanoribbons with Dibenzo[*e,l*]pyrene Repeat Units: Synthesis and Self-Assembly. Macromolecules **2009**, *42*, 6878–6884. DOI: 10.1021/ma901142g.

- Dr. Klaus Müllen, Max-Planck-Institute for Polymer Research
- A homologous series of five monodispersed polyphenylene ribbons with sizes ranging from 132 to 372 carbon atoms in the aromatic backbone was synthesized using a microwave-assisted Diels-Alder reaction
- Polyphenylene ribbons were converted to large polyaromatic hydrocarbon (PAH) graphene-like sheets through a single cyclodehydrogenation
- The electronic properties of these sheets make them candidates for future applications in electronic devices

Radical Polymerizations

27. Olvera-Mancilla, J.; Lopez-Morales, S.; Palacios-Alquisira, J.; Morales-Morales, D.; Le Lagadec, R.; Alexandrova, L. Thermal and Microwave-Assisted Polymerization of Vinyl Acetate Catalyzed by Cyclometalated Ruthenium (II) Complexes, Polymer **2014**, *55*, 1656. DOI: 10.1016/j.polymer.2014.02.007.

- Polymerization carried out using a series of Ru catalysts with CCl_4 as radical initiator
- Polymerization proceeds much faster under microwave irradiation
- Successful chain extension under microwave irradiation revealed an ATRP mechanism

28. Roy, D.; Ullah, A.; Sumerlin, B. S. Rapid Block Copolymer Synthesis by Microwave-Assisted RAFT Polymerization. Macromolecules **2009**, *42*, 7701–7708. DOI: 10.1021/ma901471k.

- Professor Brent S. Sumerlin, Department of Chemistry, Southern Methodist University
- Acrylamido and acrylate monomers were used for microwave-assisted reversible addition-fragmentation chain transfer (RAFT) polymerizations
- Microwave heated reactions proceeded much faster (as little as 2 min) than conventional reactions (50 min) with up to an apparent six-fold increase in reaction rate
- Low polydispersity and high molecular weights seen for all samples

29. Nguyen, C. T.; Nghiem, Q. D.; Kim, D. P.; Chang, J. S.; Hwang, Y. K. Microwave-Assisted Synthesis of High Molecular Weight Polyvinylsilazane via Raft Process. Polymer **2009**, *50*, 5037–5041. DOI: 10.1016/j.polymer.2009.08.035.

- Professor Dong-Pyo Kim, Department of Fine Chem. Eng. & Chemistry and Graduate School of Analytical Science and Technology, Chungnam National University
- Using a CEM MARS, scientists synthesized high molecular weight, low polydispersity polyvinylsilazane (PVSZ) by reversible addition-fragmentation chain transfer (RAFT) polymerization
- Microwave reactions resulted in higher molecular weight and higher yield than comparable conventional reactions
- Polymerizations formed block polymers after 3-4 h of heating at 120 °C in toluene

30. Adlington, K.; Jones, G. J.; El Harfi, J.; Dimitrakis, G.; Smith, A.; Kingman, S. W.; Robinson, J. P.; Irvine, D. J. Mechanistic Investigation into the Accelerated Synthesis of Methacrylate Oligomers via the Application of Catalytic Chain Transfer Polymerization and Selective Microwave Heating. Macromolecules **2013**, *46*, 3922–3930. DOI: 10.1021/ma400022y.

- Professor Derek J. Irvine, School of Chemistry, University of Nottingham
- Methyl methacrylate (MMA) oligomers were synthesized under microwave-assisted catalytic chain transfer polymerization conditions
- Researchers demonstrated a significant (100 fold) microwave time reduction as compared to conventional heating
- Optimization of reaction conditions allowed for the same product control for both types of heating, regardless of reaction time

31. Delfosse, S.; Borguet, Y.; Delaude, L.; Demonceau, A. Single-Mode Microwave-Assisted Atom Transfer Radical Polymerization Catalyzed by [RuCl2(p-cymene)(PCy3)]. Macromol. Rapid Commun. **2007**, *28*, 492–503. DOI: 10.1002/marc.200600790.

- Professor Albert Demonceau, Laboratory of Macromolecular Chemistry and Organic Catalysis, University of Liège
- Methyl methacrylate was polymerized by an atom transfer radical polymerization (ATRP) using microwave irradiation
- At 120 °C, a three-fold rate increase was seen as compared to the conventionally heated protocols
- Higher temperatures resulted in an uncontrolled reaction, while under ideal conditions polymers of up to 30 kDa with a low polydispersity were synthesized in 3 h or less

32. Gizdavic-Nikolaidis, M. R.; Jevremovic, M.; Stanisavljev, D. R.; Zujovic, Z. D. Enhanced Microwave Synthesis: Fine-Tuning of Polyaniline Polymerization. J. Phys. Chem. C **2012**, *116*, 3235–3241. DOI: 10.1021/jp2086939.

- Professor Zoran D. Zujovic at the School of Chemical Sciences, the University of Auckland
- Synthesis of polyaniline by oxidative polymerization revealed relationships between conditions and molecular weight
- Higher power levels resulted in higher molecular weight polymers in the same amount of time
- Microwave-synthesized samples displayed higher conductivity and areas as compared to those made conventionally
- Demonstrated use of microwaves to fine tune thermal and mechanical characteristics of polymers

33. Guo, W. Hensarling, R. M.; LeBlanc, A. L.; Hoff, E. A.; Baranek, A. D.; Patton, D. L. Rapid Synthesis of Polymer Brush Surfaces via Microwave-Assisted Surface-Initiated Radical Polymerization. Macromol. Rapid Commun. **2012**, *33*, 863–868. DOI: 10.1002/marc.201100829.

- Professor Derek Patton, University of Southern Mississippi, School of Polymers and High Performance Materials
- Researchers synthesized N,N-dimethylacrylamide (DMA) and 2-hydroxyethyl acrylate (HEA) polymer brush surfaces on a functionalized silicon/glass wafer
- Microwave reaction were complete in as short as 2 minutes with as much as a 39-fold increase in brush thickness over a direct temperature comparison to conventional methods

34. Zhu, J.-F.; Zhu, Y-J.; Ma, M-G.; Yan, L-X.; G, L. Simultaneous and Rapid Microwave Synthesis of Polyacrylamide – Metal Sulfide (Ag_2S, Cu_2S, HgS) Nanocomposites. J. Phys. Chem. C **2007**, *111*, 3920–3926. DOI: 10.1021/jp0677851.

- Professor Ying-Ji Zhu at the State Key Laboratory of high Performance Ceramics and superfine Microstructures and Shanghai Institute of Ceramics, Chinese Academy of Sciences
- Fast, microwave-assisted synthesis of polyacrylamide metal sulfides using metal salt, sulfur powder, and acrylamide monomer
- Heated in ethylene glycol, which acted as solvent and reducing agent. Created low-cost preparation of polymeric metal sulfide nanoparticles without additional need for initiator or surfactant
- Reaction run in open vessel format, samples heated to 125 °C or 190 °C for 15 – 60 min
- Took over 2 h to complete in oil bath
- Overall, variable heating times, temperatures resulted in monodispersed, size control synthesis of metal sulfide nanoparticles

Step-Growth/Condensation Polymerizations

35. Choi, S.J.; Kuwabara, J.; Kanbara, T.; Microwave-Assisted Polycondensation via Direct Arylation of 3,4-Ethylenedioxythiophene with 9,9-Dioctyl-2,7-dibromofluorene. ACS Sustain. Chem. Eng. 2013, 1, 878 – 882. DOI: 10.1021/sc4000576

- Professor Kanbara at Tsukuba Research Center for Interdisciplinary Materials Science (TIMS), University of Tsukuba, Japan
- Polymer formation through direct arylation of C-H bonds providing high molecular weights of up to 147 000
- High purity polymer obtained only through microwave methods
- Synthesized using CEM Discover® SP and Explorer

36. Takase, N.; Kuwabara, J.; Choi, S.J.; Yasuda, T.; Han, L.; Kanbara. T. Microwave-Assisted Polycondensation of 4-Octylaniline with Dibromoarylene J. Polym. Sci. A Polym. Chem. **2015**, *52*, 536–542. DOI: 10.1002/pola.27469.

- Professor Takaki Kanbara, Tsukuba Research Center for Interdisciplinary Materials Science (TIMS), Graduate School of Pure and Applied Sciences, University of Tsukuba, Japan
- Faster reaction times and increased molecular weights with microwave heating vs. conventional
- 1 mol % loading of Pd catalyst under microwave irradiation provided comparable results to 5 mol % loading under conventional reaction conditions

37. Chen, J.; Shu, J.; Schobloch, S.; Kroeger, A.; Graf, R.; Muñoz-Espí, R.; Landfester, K.; Ziener, U. A New Design Strategy for the Synthesis of Unsubstituted Polythiophene with Defined High Molecular Weight. Macromolecules **2012**, *45*, 5108–5113. DOI: 10.1021/ma301074p.

- Professor Ulrich Ziener, University of Ulm
- A combination of synthetic methods (Stille-type polycondensation, ultrasound-assisted dispersion,and microwave-assisted thionation and condensation) were used to create unsubstituted polythiophenes with defined high molecular weights
- Microwave reaction complete in 2 h at 190 °C
- This method allows precise control of high molecular weight polymers and has potential applications in the production of semiconducting materials

38. Nagahata, R.; Sano, D.; Suzuki, H.; Takeuchi, K. Microwave-Assisted Single-Step Synthesis of Poly(lactic acid) by Direct Polycondensation of Lactic Acid. Macromol. Rapid Commun. **2007**, *28*, 437–442. DOI: 10.1002/marc.20060071.

- Dr. Kazuhiko Takeuchi, National Institute of Advanced Industrial Science and Technology, Japan
- Researchers note a drastic rate enhancement of microwave heating versus conventional methods of PLA formation
- Polymers with high molecular weights were obtained by irradiating at 200 °C for 30 min under vacuum

39. Bray, C. L.; Tan, B.; Higgins, S.; Cooper, A. I. Polymer CO_2 Solubility. Structure/Property Relationships in Polyester Libraries. Macromolecules **2010**, *43*, 9426–9433. DOI: 10.1021/ma1016055.

- Professors Christopher Bray and Bien Tan, Department of Chemistry and Centre for Materials Discovery, University of Liverpool
- CEM Discover® used for high-throughput synthesis (300+ compounds) of alkyl polyester library
- All synthetically difficult reactions required use of the microwave over conventional methods

40. 40. Cook, J. P; Goodall, G. W.; Khutoryanskaya, O. V.; Khutoryanskiy, V. V. Microwave-Assisted Hydrogel Synthesis: A New Method for Crosslinking Polymers in Aqueous Solutions. Macromol. Rapid Commun. **2012**, *33*, 332–336. DOI: 10.1002/marc.201100742.

- Professors Vitaliy V. Khutoryanskiy, Reading School of Pharmacy, School of Chemistry, University of Reading
- Microwave irradiation used to crosslink PVA and PAA polymers, forming hydrogels in as little as 15 min at 150 °C
- This method of hydrogel synthesis eliminates the need for removal of unreacted monomers and yielded gels with equilibrium swelling degrees of 500-1000 g/g
- One-pot synthetic strategy proved to be efficient, simple, and reproducible

Reviews

41. Komorowska-Durka, M.; Dimitrakis, G.; Bogdal, D.; Stankiewicz, A.I.; Stefanidis, G.D. A Concise Review on Microwave-Assisted Polycondensation Reactions and Curing of Polycondensation Polymers with Focus on the Effect of Process Conditions. Chem. Eng. J. **2015**, *264*, 633–644. DOI: 10.1016/j.cej.2014.11.087.

42. Kempe, K.; Becer, C. R.; Schubert, U. S. Microwave-Assisted Polymerizations: Recent Status and Future Perspectives. Macromolecules **2011**, *44*, 5825–5842. DOI: 10.1021/ma2004794.

43. Ebner, C.; Bodner, T.; Stelzer, F.; Wiesbrock, F. One Decade of Microwave-Assisted Polymerizations: Quo vadis?. Macromol. Rapid Commun. **2011**, *32*, 254–288. DOI: 10.1002/marc.201000539.

44. Sosnik, A.; Gotelli, G.; Abraham, G. A. Microwave-Assisted Polymer Synthesis (Maps) as a Tool in Biomaterials Science: How New And How Powerful. Prog. Polym. Sci. **2011**, *36*, 1050–1078. DOI: 10.1016/j.progpolymsci.2010.12.001.