

Novel Green-Chemistry Micro-Fluidic Synthesis of Anthracene-Based Microporous for H₂ Storage by Capillary-Furnace LED Based Reactor

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Abstract

Microfluidic controlled multistep thermal-polymerization by Capillary-Furnace under LED irradiation (TPCFL) synthesis procedures used as a novel way for synthesis of series of anthracene-based microporous polymers (AMPs) in terms of improved product control, reproducibility and automation. The majority of microfluidic research to date has involved single-phase flow reactors, in which miscible reagent streams are continuously injected into channels where they react to form the final product. Droplet-based flow reactors have proven to be of particular value for the controlled synthesis of functional materials whose properties are strongly influenced by the reaction conditions. Microparticles materials were prepared through thermal-polymerization by capillary-furnace LED polymerization (TPCFL) method. Two-phase flow reactors that generation of the fluid segments and PTFE mixers (200 cm length, 1 mm I.D.) was used in continuous-microflow systems to control adding micro amounts of reagent to a flowing stream of droplets. By using a gas phase to maintain an even droplet spacing, simple T-junctions was used to repeatedly inject new reagent into the droplets at up to double the volume of the existing droplets. The outlined procedure therefore provides a simple means of implementing multistep chemical reactions in droplets, on which the size range of few microns to hundreds of micrometers with an extremely narrow size distribution.

Keywords: Green chemistry; Capillary; Anthracene; Microporous; Anthracene-Based Microporous Polymers (AMP); Microfluidic synthesis

Introduction

Microfluidic controlled multistep thermal-polymerization by Capillary-Furnace under LED irradiation (TPCFL) synthesis procedures used as a novel way for synthesis of series of anthracene-based microporous polymers (AMPs) in terms of improved product control, reproducibility and automation [1]. The majority of microfluidic research to date has involved

single-phase flow reactors, in which miscible reagent streams are continuously injected into channels where they react to form the final product [2]. Two-phase flow reactors that generation of the fluid segments and PTFE mixers (200 cm length, 1 mm I.D.) placed inside a temperature-controlled block (100°C) with application of an electric field to make fusion by lower the interfacial tension between droplets. The new quantitative amounts of reagents were introduced into the flow reactor as a separate droplet stream has been attracting interest for greater polymerization operational stability [3,4]. Key advantages of (TPCFL) two-phase micro-channel flow based synthesis over continuous flow and flow injection system (FIS) include: Enhanced mixing, superior synthetic control due to lower sample volumes, improved control over their size, lowering nanoparticles aggregation and saving time-solvent, lowering synthesis cost of AMPs and 6-reduced susceptibility to fouling [5].

Droplet-based flow reactors have proven to be of particular value for the controlled synthesis of functional materials whose properties are strongly influenced by the reaction conditions. For instance, significant improvements in product control (with respect to both batch and continuous flow synthesis) have been demonstrated for a broad range of optoelectronic materials including metal nanocrystals [6-8] quantum dots [9-12] and conjugated polymers [13,14]. To date, however, droplet synthesis has been largely limited to simple one-step procedures, in which all reagents are loaded into the droplets at the outset, greatly restricting the range of chemistries that can be employed. To properly exploit the benefits of droplet flow, and widen the palette of accessible chemistries/materials, there is an obvious need to develop multistep droplet reactors (TPCFL) in which reagents can be sequentially added into the flowing droplets as the reaction proceeds.

Materials and Methods

Direct injection of reagents via a T-junction

The process of reagent addition is shown in the time-lapse images in **Figure 1**.

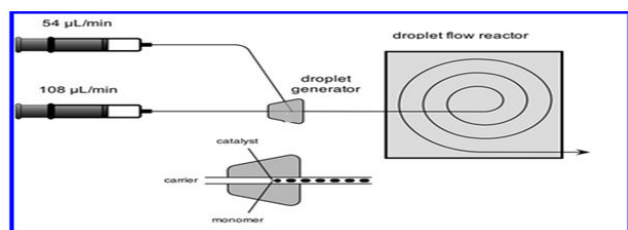


Figure 1 T-junction droplet stream system of two-phase AMP monomer/Ar flow, in which monomers droplets travel along a 1-mm diameter channel at a linear velocity of 11.4 mms^{-1} .

Additional reagent (dissolved in the droplet-phase solvent) is continuously introduced into the flowing droplet stream at a T-junction, where it inserts into the existing droplets, causing them to grow in volume. The images and movie show a pregenerated two-phase AMP monomer/Ar flow, in which monomers droplets travel along a 1-mm diameter channel at a linear velocity of 11.4 mms^{-1} and pass through a T-junction where a laminar stream of DMF is injected. When a gas bubble is transiting the T-junction (for example, $t=0, 120 \text{ ms}$), the monomers accumulates at the outlet and continues to do so until a droplet arrives ($t=240 \text{ ms}$), at which point it fuses with the droplet.

The liquids were delivered to the junction via fluorinated ethylene propylene (FEP) tubing (Upchurch Scientific, ID $356 \mu\text{m}$, OD 1.57 mm) using Braun 'Injekt' disposable syringes loaded onto syringe pumps (Harvard Apparatus PHD 2000 and Pump 11+ models). The syringes were connected to the tubing using polyether ether ketone Luer-Lock interconnects (Upchurch Scientific). Argon gas was delivered to the junction from a gas cylinder via fused silica capillary (CM Scientific, ID $150 \mu\text{m}$, OD $375 \mu\text{m}$), with the flow rate regulated by a mass flow controller (Sierra Instruments MicroTrak 101).

Capillary-Furnace (TPCFL) based devices

The capillary-based (TPCFL) device is composed of a single co-axial capillaries inserted along the main axis of a T-junction. The capillaries' tips exit from the T-junction in the centerline of a 500 Rm ID PTFE tubing. To synthesize simple composite microparticles, a single fused silica capillary (Polymicro) is used (ID $250 \times$ OD 360 Rm). The monomer and continuous phases are injected through the capillary and the second T-junction inlet respectively (**Figure 2**). Both fluids are delivered thanks to digital pumps (Harvard Apparatus) [15] which provide accurate constant flow rates in the range of 0.1 to $10 \text{ mL}\cdot\text{min}^{-1}$. Once generated, the monomer droplets were polymerized by LED-irradiation which wavelength was set $400 < \lambda < 450 \text{ nm}$ directly in the outlet PTFE tubing. Violet LED consist from gallium nitride (GaN) LEDs on silicon demonstrated high-power InGaN LEDs grown on silicon substrates commercially [16].

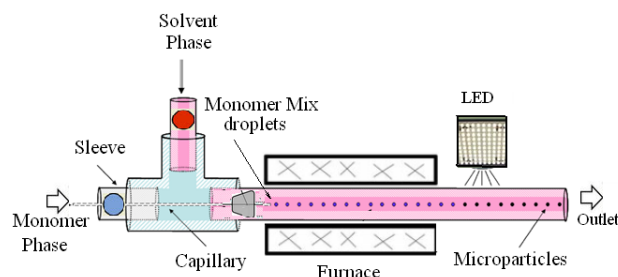


Figure 2 Schematic drawing of the capillary-based system for the production of simple AMPs microparticles using LED-Furnace system. Two-phase flow reactors that generation of the fluid segments and PTFE mixers (200 cm length, 0.5 mm I.D.) placed inside a temperature-controlled block (90°C) with application of an electric field to make fusion by lower the interfacial tension between droplets.

Adding additional solvent/reagent to a flowing droplet stream

The presence of the gas phase is critical to achieving controlled direct reagent addition for two principal reasons. First, the gas maintains uniform droplet spacing, thereby ensuring each droplet receives the same dose of new reagent. Second, since it is the gas and not the carrier liquid that keeps the droplets apart, there is an insufficient volume of carrier liquid to allow the formation of new droplets. Therefore, the new DMF solvent must add into the droplets or else it must form new droplets within the gas as shown in **Figure 3**, with the latter process splitting the gas bubble in two.

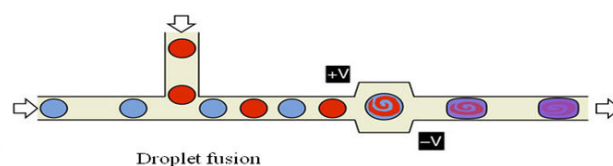


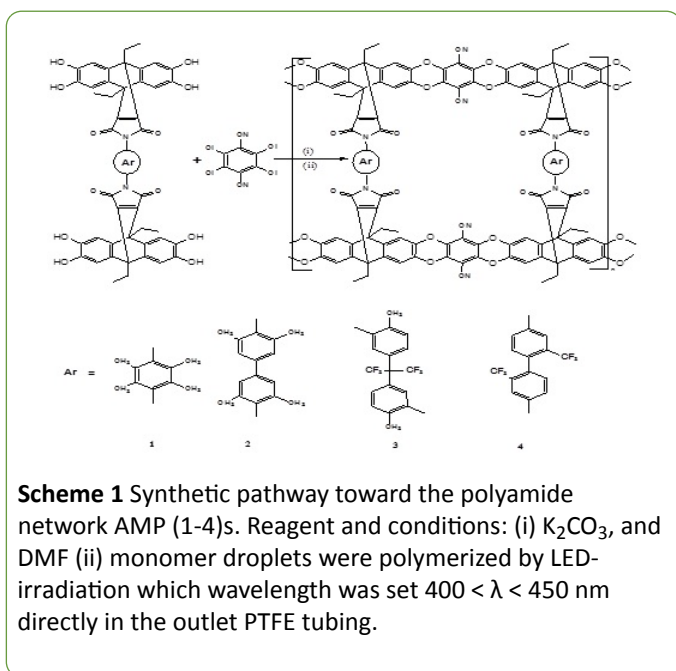
Figure 3 Dosing droplets controlled multistep synthesis by droplet flow.

Splitting the gas bubbles results in much larger interfacial areas compared with injection into the droplets and is consequently disfavored energetically. There are very few reports of controlled multistep synthesis in droplet flow due to the difficulty of introducing quantitative amounts of reagent into a flowing droplet stream [17]. The new reagents are introduced into the flow reactor as a separate droplet stream, which is then merged on a pairwise basis with the original droplet stream. This can be achieved using special channel architectures to bring the droplets together [18-20], sometimes assisted by the application of an electric field to lower the interfacial tension between droplets [21-23]. **Figure 3** showing the principal method for adding additional solvent/reagent to a flowing droplet stream (droplet fusion), in which a second droplet stream containing the new solvent/reagent is

merged on a pairwise basis with the original droplet stream, using an applied voltage or specially engineered channel structure [20].

(TPCFL) Synthesis of AMPs

Microporous rigid polymers (AMPs) based on 9,10-dihydro-9,10-ethanoanthracenes monomers bridged by imide links was synthesized efficiently by the double aromatic nucleophilic substitution reaction as shown in **Scheme 1**.



Scheme 1 Synthetic pathway toward the polyamide network AMP (1-4)s. Reagent and conditions: (i) K_2CO_3 , and DMF (ii) monomer droplets were polymerized by LED-irradiation which wavelength was set $400 < \lambda < 450$ nm directly in the outlet PTFE tubing.

This nucleophilic substitution reaction apply dioxane, [24] forming reaction between the corresponding octahydroxy monomers and tetrachloro-terphthalonitrile (instead of tetrafluoro-terphthalonitrile) in dry DMF and $100^\circ C$.

The network polymer was washed with a variety of organic solvents and dried under vacuum. The anthracene based monomers (AMP [1-4]) were prepared in good yield by the straight forward one step imidisation reaction between corresponding anhydride and different amines in refluxing acetic acid. The proposed structure and purity of the obtained monomers were confirmed by routinely spectroscopic techniques as well as elemental analysis (See Supporting Information). The polymers AMP-[1-4] were synthesized by the dibenzodioxane formation reaction between the tetrol, and tetra-chloroterephthalonitrile in dry DMF as illustrated in **Scheme 1**. The structures of all prepared AMPs were characterized by FT-IR, solid state ^{13}C NMR spectroscopy and elemental analysis. All materials retained its characteristic stretching bands related to the imide groups ($C=O$ symmetric and asymmetric stretching in the range of 1722-1792). Moreover it is clear from the spectrum that the base catalyzed polymerization condition does not make any destruction in the imide units (See Supporting Information). The ^{13}C NMR spectra of the AMPs were fully consistent with their proposed structures (See Supporting Information). The signals originating from the hydroxyl groups of tetrol were disappeared, suggesting that the reaction was carried out

completely through dibenzodioxane formation. The broad aromatic and aliphatic signals of AMPs were enough to confirm the formation of high molecular weight polymers. The thermal properties were evaluated by TGA and DSC. The decomposition temperatures were also very high; where a 5% to 10% initial loss around $400^\circ C$, were observed, corresponding to the vaporation of the residual solvents which has been identified as the entrapped solvents in the micropores used for processing the sample. The good thermal stability can be attributed to its double stranded structures. In DSC analysis, no melting (T_m) and glass transition (T_g) was observed. Wide Angle X-ray Diffraction (WAXD) analysis of the AMPs was conducted to display no crystalline peaks and revealed that all the prepared materials were amorphous.

Results and Discussion

Structure-property relationship

Different spacers have been employed in order to evaluate the structure feature on surface area. The anthracene groups as thermally and oxidatively stable, rigid moiety can improve physical properties such as enhanced thermal stability, increased chain stiffness, and decreased crystallinity [24]. However, for AMP-1 there is very highly restricted rotation about the imide bond linkages, giving rigidity to the polymer. In AMP-2, there is potentially more flexibility in the backbone, but the hexafluoroisopropylidene unit provides a kink in the chain and may be regarded as an additional site of contortion. The unique shape of the anthracene unit lead to a rigid network structure composed of nonporous frameworks. The molecular structures of these PIM-polyimides have features of the spiro-center providing a site of contortion as well as having conventional imide linkages, this results a very highly restricted rotation about these bonds, giving rigidity to the polymer. The shape of this monomer constrains the growth of the polymer within the same plane to provide a rigid macromolecular structure with large concavities. The faces of the ribbon-like "struts" between the anthracenes are oriented nearly perpendicular to the plane of the macromolecular growth. This arrangement blocks face-to-face association between these planar struts, leading to greater IM. For the attainment of microporosity in network polymers, it appears that the requirement for the prevention of rotation about single bonds is unperturbed, presumably due to the network itself preventing structural rearrangement that could result in a collapse of the porous structure. Hence, the formation of rigid amorphous network polymers using anthracene monomer is compatible with obtaining highly micro porous materials. Perhaps the clearest demonstration of IM is found for well-defined rigid oligomers containing triptycenes as the concave unit. An interesting structure-property relationship is evident for these materials in that the longer the linear struts between the branch points, the lower is the porosity.

Synthesis of AMP-3

In the (TPCFL) device, a solution of octahydroxy-anthracene (0.2 g, 0.21 mmol) and 2,3,5,6-tetrachlorophalonitrile (0.08 g,

0.43 mmol) in dry DMF (40 mL), K_2CO_3 (0.35 g, 2.52 mmol) was added to dosing droplets controlled multistep. Two-phase flow reactors that generation of the fluid segments and PTFE mixers (200 cm length, 1 mm I.D.) placed inside a temperature-controlled block (100°C) with application of an electric field to make fusion by lower the interfacial tension between droplets. Then, the reaction mixture was allowed to cool and precipitated in acidified water. The precipitate was filtered off and washed with de-ionised water and then with methanol. The purification was done by washed repeatedly with THF and methanol. The resulting AMP-3 is brown solid and dried in vacuum at 80°C for 12 hrs (yield 84%).

Yield 85%; m.p. > 300°C; MS (EI): m/z (%) 1851(M+). IR/cm⁻¹ (KBr): 1788 (asym C=O, str), 1722 (sym C=O, str), 1366 (C-N, str), 744 (imide ring deformation). ¹³C NMR (100 MHz): 169.7, 148.7, 145.3, 142.8, 141.5, 139.5, 138.2, 128.8, 121.6, 123.8, 115.8, 115.2, 104.6, 109.2, 55.8, 55.5, 42.9, 39.6, 15.5, 10.3, 8.6. CHN Calculated for C₁₀₅H₈₀F₆N₁₀O₁₆ (1851): C 68.02; H, 4.32; N, 7.56. Found: C, 67.70; H, 4.21, N, 7.22. BET surface area = 988 m²/g; total pore volume = 0.41 cm³/g.

Nitrogen adsorption analysis

Nitrogen adsorption measurements of AMPs were measured, for example, the BET surface area of AMPs is relatively high, which is higher than the Trip-PIM [25] but less than the HCPs as shown in **Figure 4**.

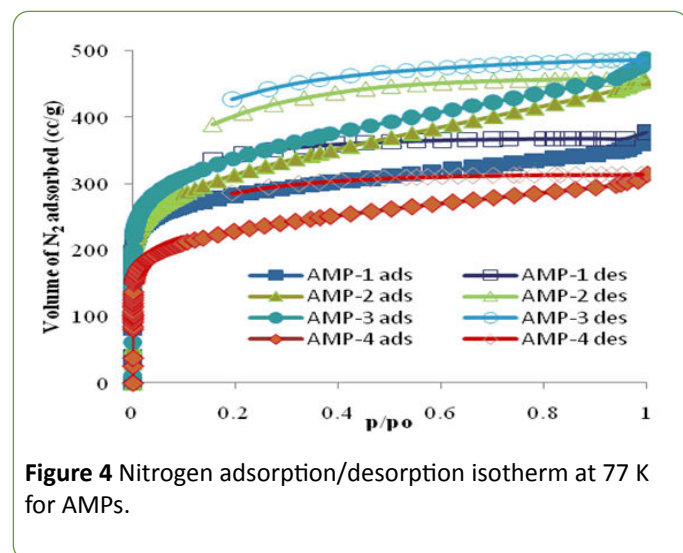


Figure 4 Nitrogen adsorption/desorption isotherm at 77 K for AMPs.

Conclusion

In conclusion, micro-particles materials were prepared through thermal-polymerization by capillary-furnace LED polymerization (TPCFL) method. Two-phase flow reactors that generation of the fluid segments and PTFE mixers (200 cm length, 1 mm I.D.) was used in continuous-microflow systems to control adding micro amounts of reagent to a flowing stream of droplets. By using a gas phase to maintain an even droplet spacing, simple T-junctions was used to repeatedly inject new reagent into the droplets at up to double the volume of the existing droplets. The outlined procedure therefore provides a simple means of implementing multistep

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References

1. Tabeling P (2005) Introduction to microfluidics. Oxford University Press, UK.
2. Wiles C, Watts P (2008) Continuous flow reactors, a tool for the modern synthetic chemist. *Eur J Org Chem* 10: 1655-1671.
3. Nightingale AM, DeMello JC (2013) Segmented flow reactors for nanocrystal synthesis. *Adv Mater* 25: 1813-1821.
4. Song H, Chen DL, Ismagilov RF (2006) Reactions in droplets in microfluidic channels. *Angew Chem Int Ed* 45: 7336-7356.
5. Ibrahim F (2015) Synthesis of smectic and discotic liquid crystals derivatives by flow injection system. *Int J Nanotech Appl* 5: 9-16.
6. Duraiswamy S, Khan SA (2009) Droplet-based microfluidic synthesis of anisotropic metal nanocrystals. *Small* 5: 2828-2834.
7. Duraiswamy S, Khan SA (2010) Plasmonic nanoshell synthesis in microfluidic composite foams. *Nano Lett* 10: 3757-3763.
8. Lazarus LL (2012) Two-phase microfluidic droplet flows of ionic liquids for the synthesis of gold and silver nanoparticles. *ACS Appl Mater Interface* 4: 3077-3083.
9. Nightingale AM (2011) A stable droplet reactor for high temperature nanocrystal synthesis. *Lab Chip* 11: 1221-1227.
10. Yao S (2013) Picoliter droplets developed as microreactors for ultrafast synthesis of multi-color water-soluble CdTe quantum dots. *Chem Commun* 49: 7114-7116.
11. Shestopalov, I, Tice JD, Ismagilov RF (2004) Multi-step synthesis of nanoparticles performed on millisecond time scale in a microfluidic droplet-based system. *Lab Chip* 4: 316-321.
12. Nightingale AM (2013) Large-scale synthesis of nanocrystals in a multichannel droplet reactor. *J Mater Chem A* 1: 4067-4076.
13. Bannock JH (2013) Continuous synthesis of device-grade semiconducting polymers in droplet-based microreactors. *Adv Funct Mater* 23: 2123-2129.
14. Bannock JH (2014) Controlled synthesis of conjugated random copolymers in a droplet-based microreactor. *Mater Horiz* 1: 214-218.
15. Khler JM, Held M, Hübner U, Wagner J (2007) Formation of Au/Ag nanoparticles in a two step micro flow-through process. *Chem Eng Tech* 30: 347-354.
16. OSRAM (2012) Success in research: First gallium-nitride LED chips on silicon in pilot stage at the Wayback Machine, Accessed on: September 15, 2012.
17. Chabert M, Dorfman KD, Viovy JL (2005) Droplet fusion by alternating current (AC) field electrocoalescence in microchannels. *Electrophoresis* 26: 3706-3715.
18. Hung LH (2006) Alternating droplet generation and controlled dynamic droplet fusion in microfluidic device for CdS nanoparticle synthesis. *Lab Chip* 6: 174-178.
19. Niu X, Gulati S, Edel JB, De Mello AJ (2007) Pillar-induced droplet merging in microfluidic circuits. *Lab Chip* 8: 1837-1841.
20. Bremond N, Thiam AR, Bibette J (2008) Decompressing emulsion droplets favors coalescence. *Phys Rev Lett* 100: 024501.

21. Ghanem BS, Msayib KJ, McKeown NB, Harris KDM, Pan Z, et al. (2007) A triptycene-based polymer of intrinsic microporosity that displays enhanced surface area and hydrogen adsorption. *Chem Commun* 7: 67-69.
22. Frenz L (2008) Droplet-based microreactors for the synthesis of magnetic iron oxide nanoparticles. *Angew Chem Int Ed* 47: 6817-6820.
23. Jiang JX, Cooper A (2010) Microporous organic polymers: Design, synthesis and function topics. *Curr Chem* 293: 1-33.
24. Hofman D, Ulbrich J, Fritsch D, Paul D (1996) Molecular modelling simulation of gas transport in amorphous polyimide and poly (amide imide) membrane materials. *Polymer* 37: 4773-4785.
25. Kohler JM, Held M, Hübner U, Wagner J (2007) Formation of Au/Ag nanoparticles in a two-step micro flow-through process. *Chem Eng Tech* 30: 347-354.