MICROWAVE-ASSISTED POLYFLUORENE SYNTHESIS

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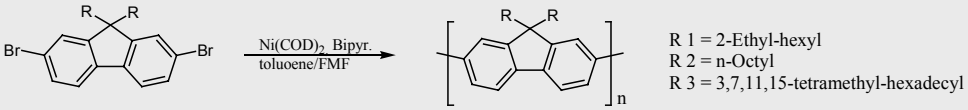
Introduction:

One of the most popular classes of conducting polymers is polyfluorenes, which are candidates for applications in light emitting diodes (LEDs) and field effect transistors (FETs). We were interested in preparing the previously unknown 3,7,11,15-tetramethyl-hexadecyl-poly-fluorene and expand the microwave protocol to other metal mediated cross-coupling reactions. A recent report concerns the Ni(0) mediated polymerisation of 2,7-dibromo-9,9-dihexyl-fluorene using microwaves as an energy source which afforded high molecular weight polmers in ca. ten minutes.[1]

Method development:

The reactions were carried out in sealed 10 mL vials which were filled under glove box conditions using a single-mode reactor.[2] The reaction parameters such as time, applied power, catalyst etc. were varied to define an optimal procedure on polyfluorens R1-R3 .



R 1 = 2-Ethyl-hexyl
R 2 = n-Octyl
R 3 = 3,7,11,15-tetramethyl-hexadecyl

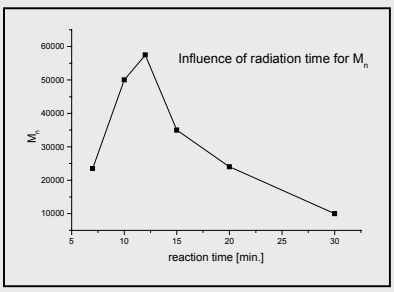
• Energy

Only appreciable degrees of polymerisation are obtained when the power level is about 300 W. Lower energies lead to oligomers.

• Time

Molecular weight versus time study at 300 W showed that M_n values increased to a maximum between 9-12 min.

Longer times resulted in lower molecular weights, however no observable differences in NMR, UV-Vis or PL-spectra



Redissolved polymers are not affected by microwave irradiation. Solutions of polymers with catalyst are „broken“, but again spectroscopic data remain unchanged.

Time min. (without cat.)	M_n	Time min. (with cat.)	M_n
0	45200	0	46100
30	44300	30	40000
60	44550	60	28200
90	43000	90	25000

Furthermore the influence of catalyst, catalyst-concentration, monomer concentration and energy have been investigated and are analogous to conventional thermal heating experiments. Several experiments have shown that this method is reproducible.

Comparsion and Results:

Microwave versus conventional heating reveals

1.) reaction times are dramatically reduced

2.) molecular weights and yields are comparable

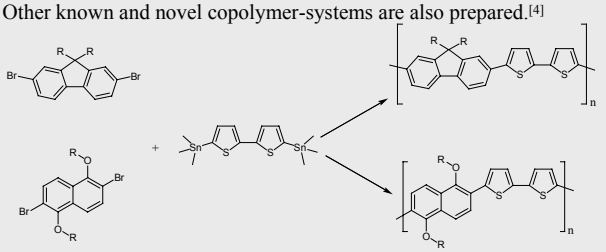
3.) spectroscopic analysis shows no structural and electronic differences

Polymer	MW		Conv.	
	Mn	Y	Mn	Y
R1	115000	67%	83500	60%
R2	135000	76%	150000	81%
R3*	56000	65%	45000	68%

* before extraction

Outlook:

Further studies demonstrates that microwave heating is equally successful in the preperation of other semiconducting polymers via transition metal catalysed Suzuki and Stille coupling reactions.[3] Other known and novel copolymer-systems are also prepared.[4]



References:

[1] K.R.Carter, *Macromolecules*, **2002**, *35*, 6757

[2] CEM-Discovery single mode reactor

[3] B.S.Nehls, U.Asawapirom, S.Füldner, E.Preis, T.Farrell, U.Scherf, *submitted to Angew.Chem.*

[4] U.Asawapirom, R.Güntner, T.Farrell, M.Forster, U.Scherf, *Synthesis*, **2002**, *9*, 1136

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