Controlled Synthesis of Branched Polymers by Anionic Polymerization and Synthesis of Polymers for Fuel Cell and Solar Cell Applications

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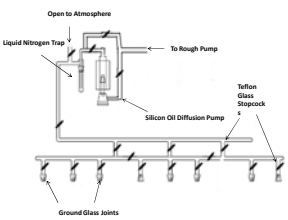
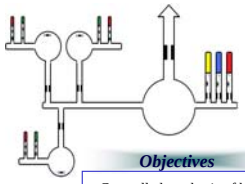
Introduction

High vacuum line and anionic apparatus

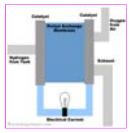




Objectives

- Controlled synthesis of branched polymers
- Characterizations
- Dilute solution properties and
- Rheology

Fuel cells and their applications

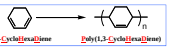


Simply to say, fuel cells are devices that can generate electricity by using oxygen in the air and fuel such as hydrogen.

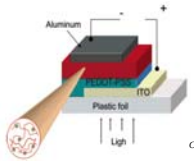
Advantages:
- Zero pollution
- Only emit water
- Ultimate way to solve Global Warming

Applications:
Mainly used to power automobiles

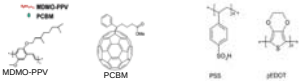
What is PCHD?
PCHD is a polymer made of 1,3-cyclohexadiene



Schematic device structure of photovoltaic solar cells

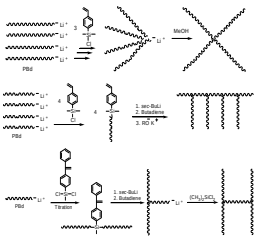


Chem. Rev. **2007**, *107*, 1324

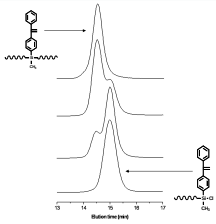


Controlled Anionic polymerization of Branched Polymers

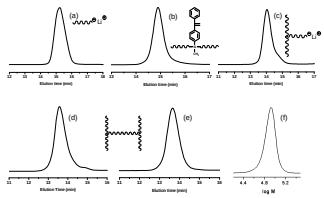
Synthesis of star, comb and H-shaped polymers



Titration of DCMSDPE



SEC-LS profile of precursor and H-PBd



The samples were analyzed by SEC-TALLS in THF at 40 ˚C

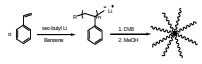
Molecular characteristics of H-PBd

Sample	*Mn*(arm) Kg/mol	*Mn*(star) Kg/mol	*Mn*(cross-bars) Kg/mol	*Mn*(H) Kg/mol	*Mw*/*Mn* (H)
1	10.6	41.0	39.9	82	1.03
2	11.3	49.5	53.3	98	1.03
3	15.3	82.4	97.0	158	1.04
4	29.6	80.2	42.6	161	1.06
5	41.6	105.0	45.6	212	1.05

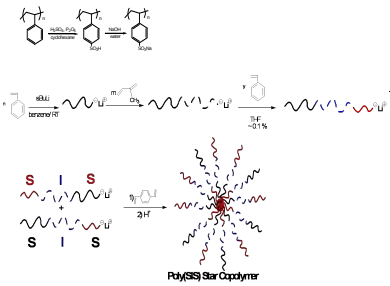
Mn and *Mw*/*Mn* were measured by SEC-LS in THF at 40 ˚C

Rahman and Mays *et. al. Macromolecules* **2008**, *41*, 8225.

Synthesis of symmetric and asymmetric stars

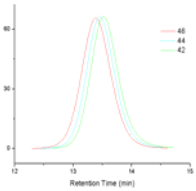


Sulfonation of precursor to produce NaPSS star



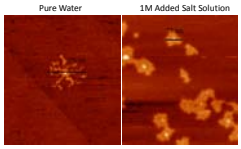
GPC characterization of star branched polymers

Sample	M_w (x10^{-5}g mol^{-1})	R_{gz} (nm)	R_{gz} (nm)	$[\eta]^b$	R_h (nm)	M_w/M_n
42p	1.382	10.2	<10	0.191	9.0	1.10
44p	1.681	9.9	<10	0.192	9.5	1.10
46p	2.041	9.6	<10	0.198	10.0	1.11
52p	5.167	19.0	19.2	0.701	19.7	1.14
54p	7.927	20.2	20.5	0.549	21.5	1.13
56p	8.245	19.7	21.3	0.644	22.4	1.14
62p	10.30	25.9	26.0	0.966	27.9	1.15
64p	12.65	26.8	26.5	0.942	28.7	1.13
66p	14.40	27.0	33.2	0.961	30.4	1.12



0.01 M NaCl scattering, AFM data for NaPSS stars

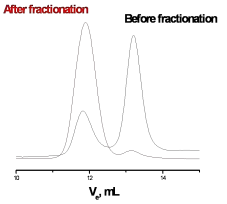
Sample	R_g	R_h	R_{gfm}	R_g/R_h
42	20.7	17.7	17	1.17
44	44.7	21.7	21	2.05
46	72.7	27.2	17	2.67
52	51.1	53.0	32	0.964
54	59.0	52.5	48	1.12
56	63.2	57.6	54	1.10
62*	80.8	64.0	66	1.26
64*	96.7	71.9	82	1.34
66*	124.8	84.6	97	1.48
LS2.69M*	151.8	46.0		3.3



Effect of added salt on NaPSS star conformation

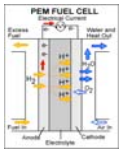
Results of asymmetric star copolymers

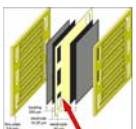
Sample	*DVB/RLi* [a]	*Triblock P(SIS) Star* [b] *SEC-LS* [c] $M_w \times 10^{-6}$ (g/mol)	*PDI* [d]	*Weight % of block segments in star copolymer* [e] *PS*	*PI*	*Number of arms* [f] *N*
1	2	1.432	1.08	69.4	30.6	7.8
2	4	1.607	1.07	67.2	32.8	8.8
3	6	1.656	1.07	67.4	32.6	9.1



Synthesis of Materials for Proton Exchange Fuel Cell Membranes and Solar Cells

Proton Exchange Fuel Cell Membranes



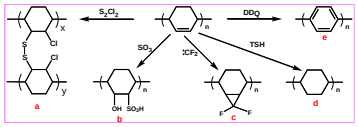


Key part of a fuel cell

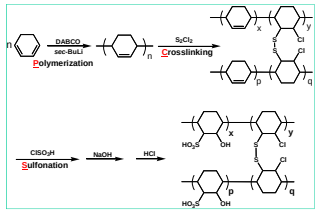
- Low cost
- Good mechanical strength
- Chemical & thermal stability
- Low gas permeability
- High proton conductivity

PCHD: Polymer with Great Potentials

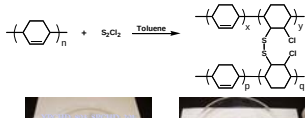
* Six-membered rings in the chain backbone
* 1,2- *vs.* 1,4-Microstructure
* Higher T_g (>100°C) than other polydienes
* Potentially low cost
* Easy post polymerization modification

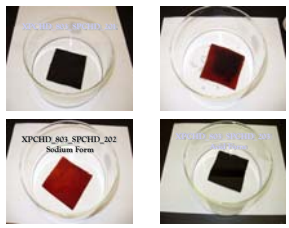


PCS Approach to Fuel cell Membranes

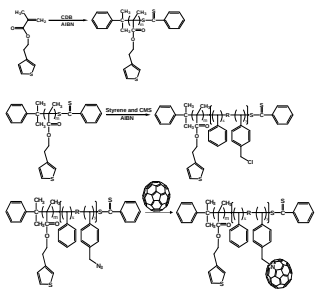


Cross-linking and photos of PEMs in various forms



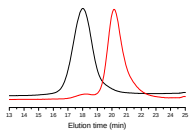


Synthesis of conjugated polymers for photovoltaic solar cell

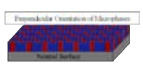


Results of PMET-b-PS/PCMS

Sample	Time (h)	Conv. (%)	M_n (obs.)[a]	M_w/M_n [a]	PMET:PS/PCMS
PMET-CTA-1	5	50	23,000	1.17	-
PMET-CTA-2	5	40	32,000	1.16	-
PMET-CTA-3	5	50	26,000	1.19	-
PMET-*b*-PS/PCMS	5	60	42,000	1.42	37:63
PMET-b-PS/PCMS	5	25	130,000	1.38	18:82
PMET-b-PS/PCMS	5	35	97,000	1.35	32:68



Objectives



Parallel Orientation of Cylinders

Figure. Orientation of cylindrical microphases in diblock copolymer films.

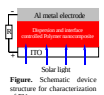


Figure. Schematic device structure for characterization of PV processes.

Conclusions

- Synthesis of symmetric and asymmetric branched polymers with narrow PDI (PDI = 1.03 ~ 1.14.)
- Flexible thermally stable fuel cell membrane having proton conductivity (0. 135 S/cm) higher than that of Nafion® (0.08 S/cm) and good mechanic streng th have been successfully synthesized.
- Conductivity of Membranes has met the DOE (Department of Energy) Year 2 Milestone (0.07 S/cm at 80% RH at 120ºC).