PENNSTATE

Design and Synthesis of New Polyolefin Materials; (a) Proton Conductive Membranes for Fuel cells (b) Oil Super-Absorbent for Oil Spill Recovery

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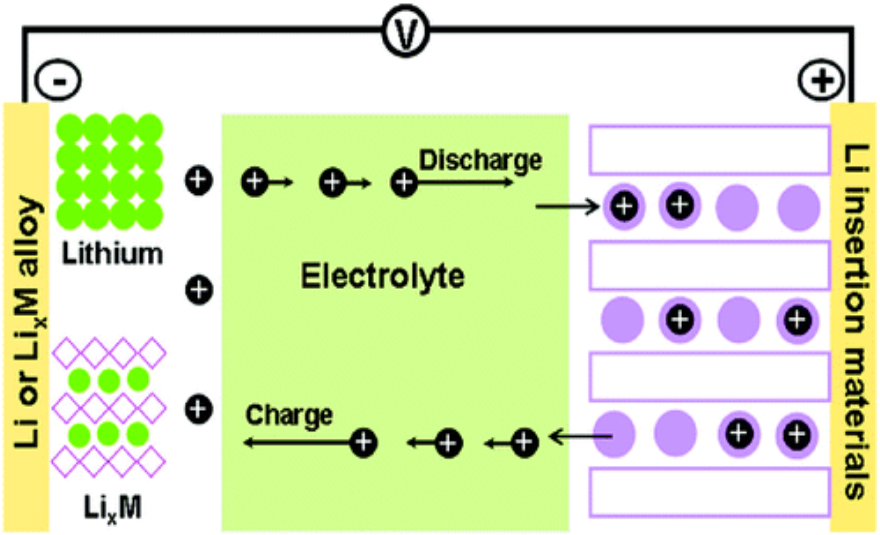
DOE Hydrogen Program

Ben Franklin Foundation

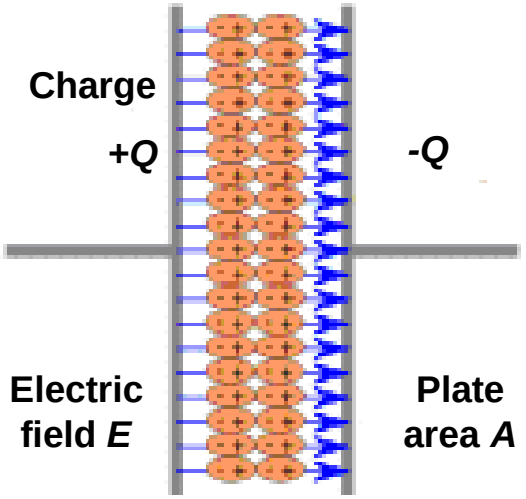
Polyolefin in Electrochemical Devices

Li^+ *Battery*



PP separator

Capacitor



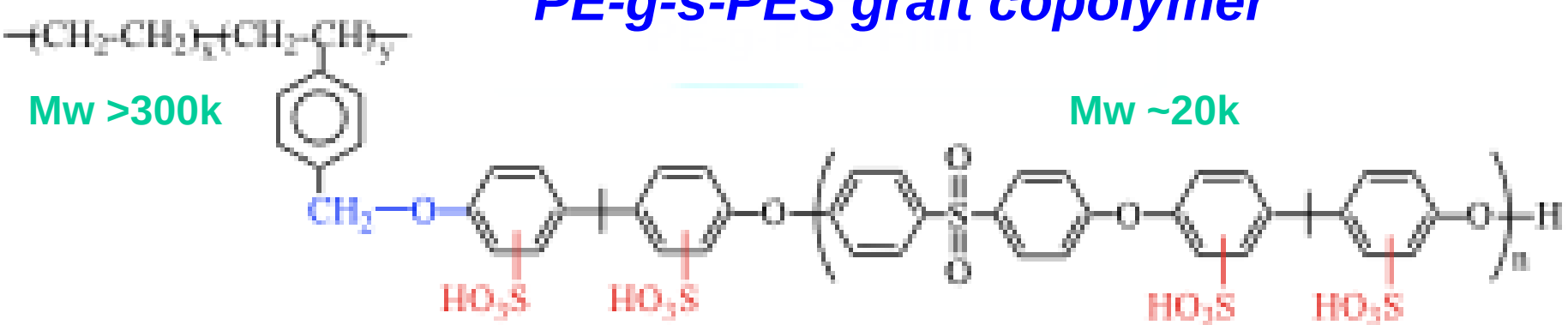
PP dielectric

- Excellent electric insulation
- Excellent electrical and electrochemical stability
- Good mechanical strength and thermal stability
- Cost effective

Can PE or PP become a polyelectrolyte with both functions of separator and conductor?

New PE-based PEM

PE-g-s-PES graft copolymer



PE matrix/separator function

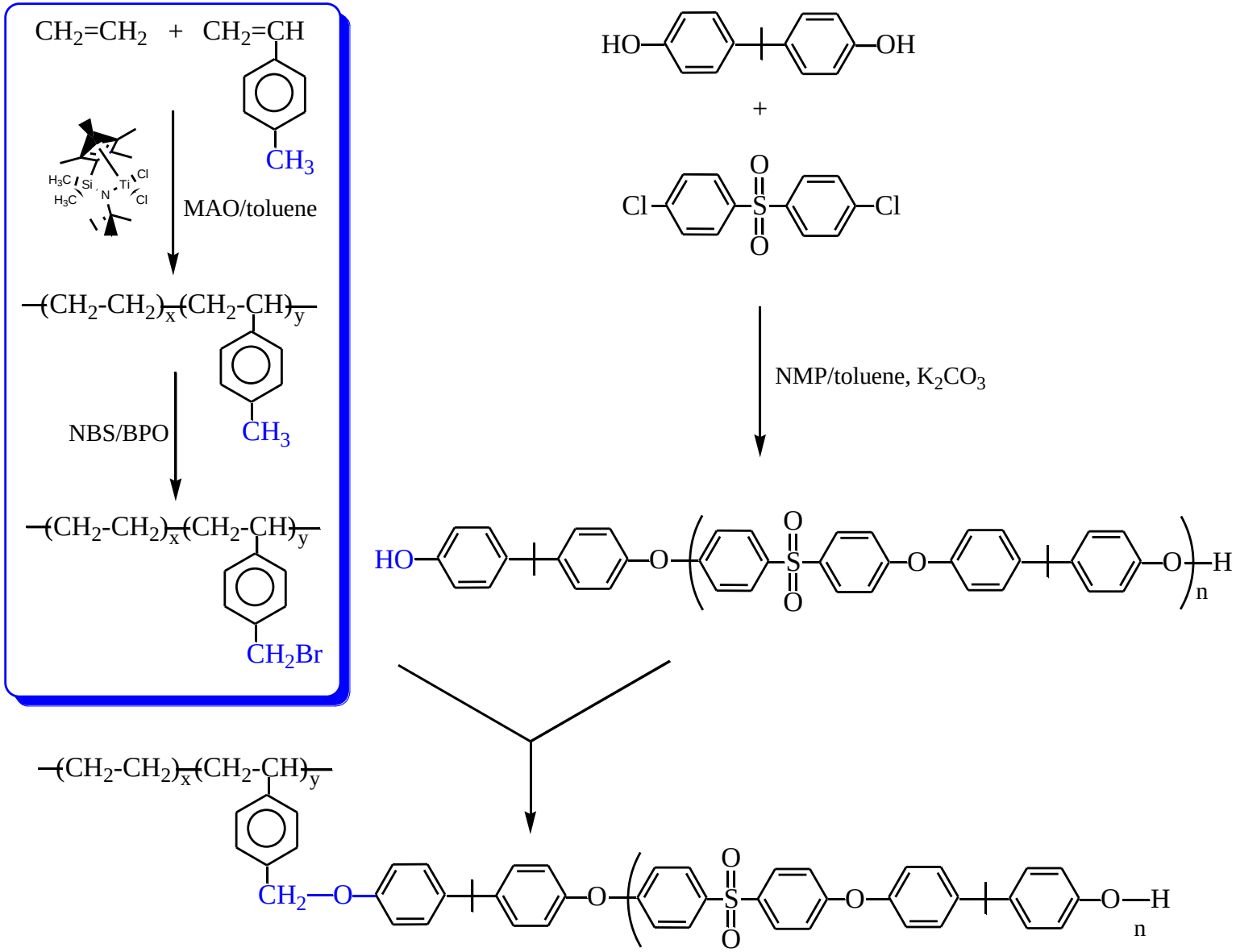
- *Stability: chemical and electrochemical stability*
- *Mechanical Strength: high molecular weight and high crystallinity*
- *Hydrophobicity: prevent excess water swelling*

s-PES/ion-conductive channels

- *High IEC (ion exchange capacity) without excess water-swelling*
- *Through-plane conductive channels with high conductivity*

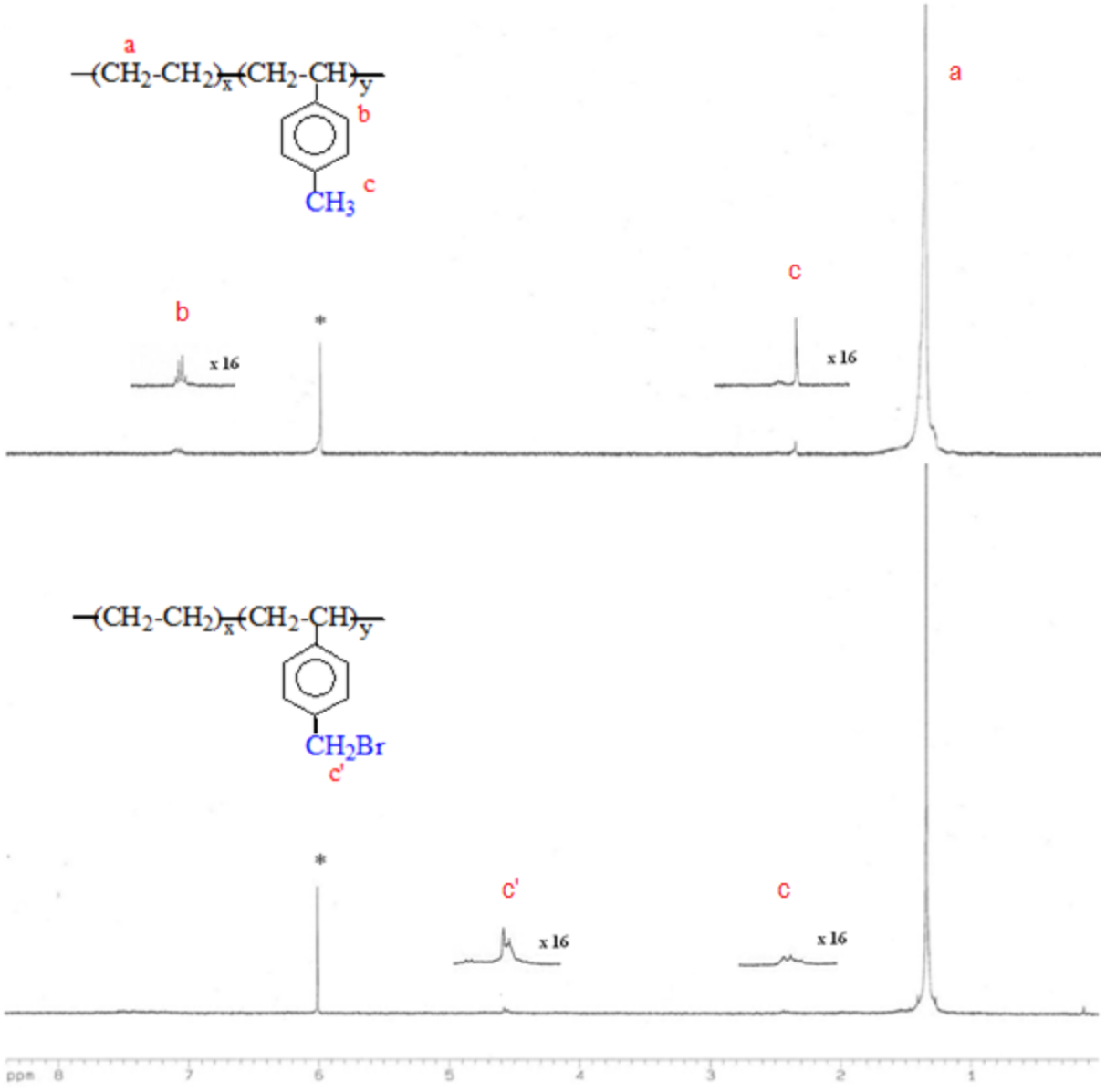
Cost effective

Synthesis of PE-g-PES



"*Functionalization of Polyolefins*", T. C. Chung, Academic Press, London , 2002

^{1}H NMR Spectra

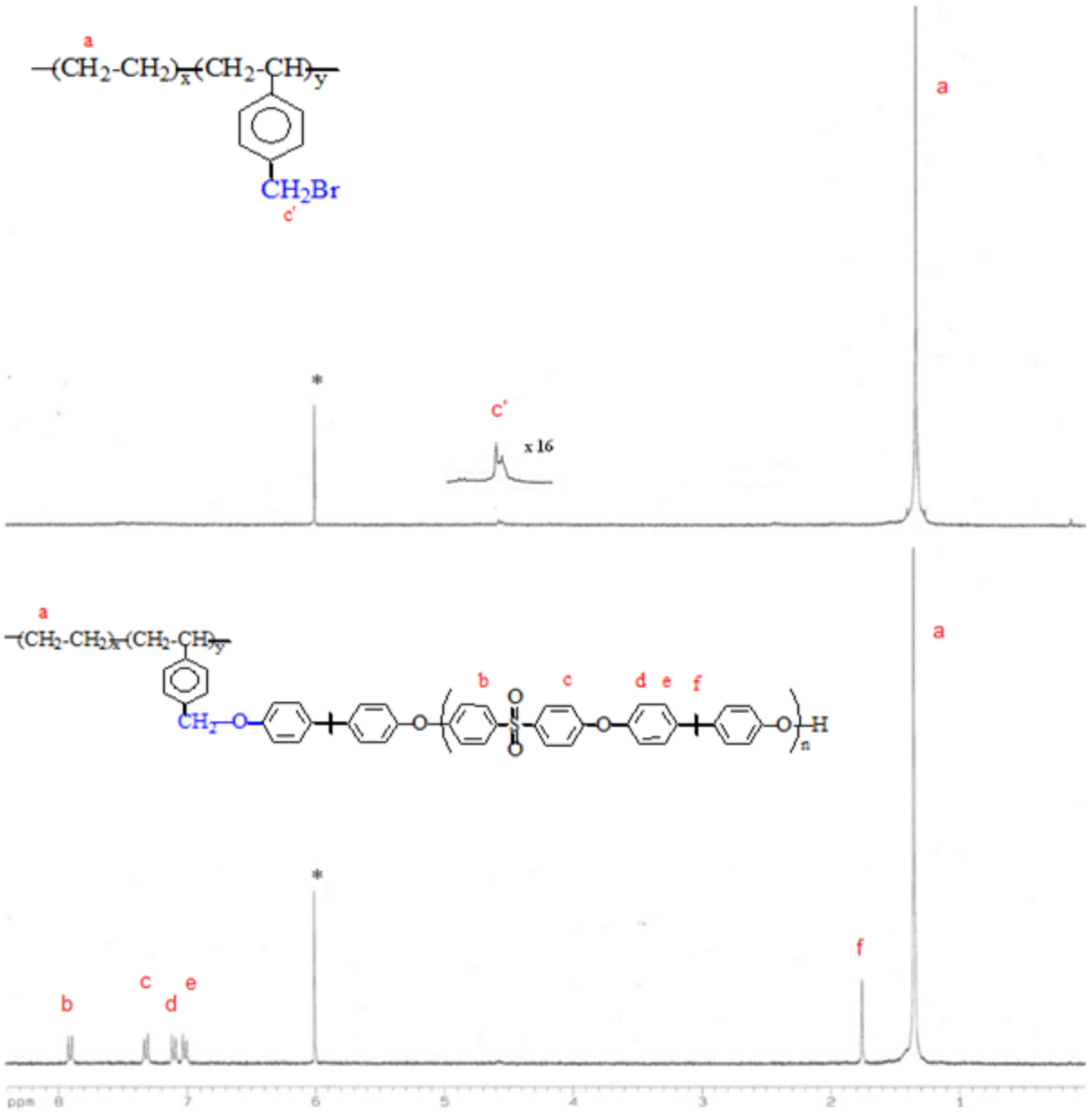


PE-co-p-MS and PE-co-p-MS-Br

Run	PE-co-p-MS		PE-co-p-MS-Br		
	Mw	P-MS (mol%)	Br-time (h)	Br-content (mol%)	Br-efficiency (%)
1	200k	1.8	1	0.6	33
2	200k	1.8	2	1.0	56
3	200k	1.8	3	1.2	67
4	320k	1.4	1	0.5	35
5	320k	1.4	2	0.7	50
6	390k	1.5	2	0.5	33
7	**390k**	**1.5**	**3**	**0.8**	**53**

BPO initiator; [NBS]/[p-MS]= 10; Temp.= 75^{o} C;

^{1}H NMR Spectra

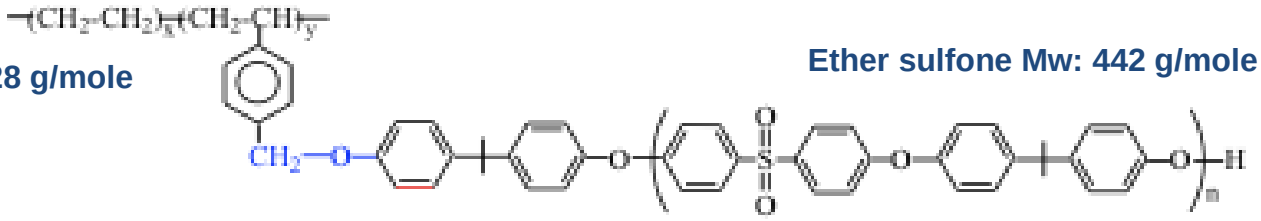


PE-g-PES Graft Copolymers

PE-co-p-MS-Br (Mw: 390k; Br: 0.8 mol%) PES: Mw: 20k

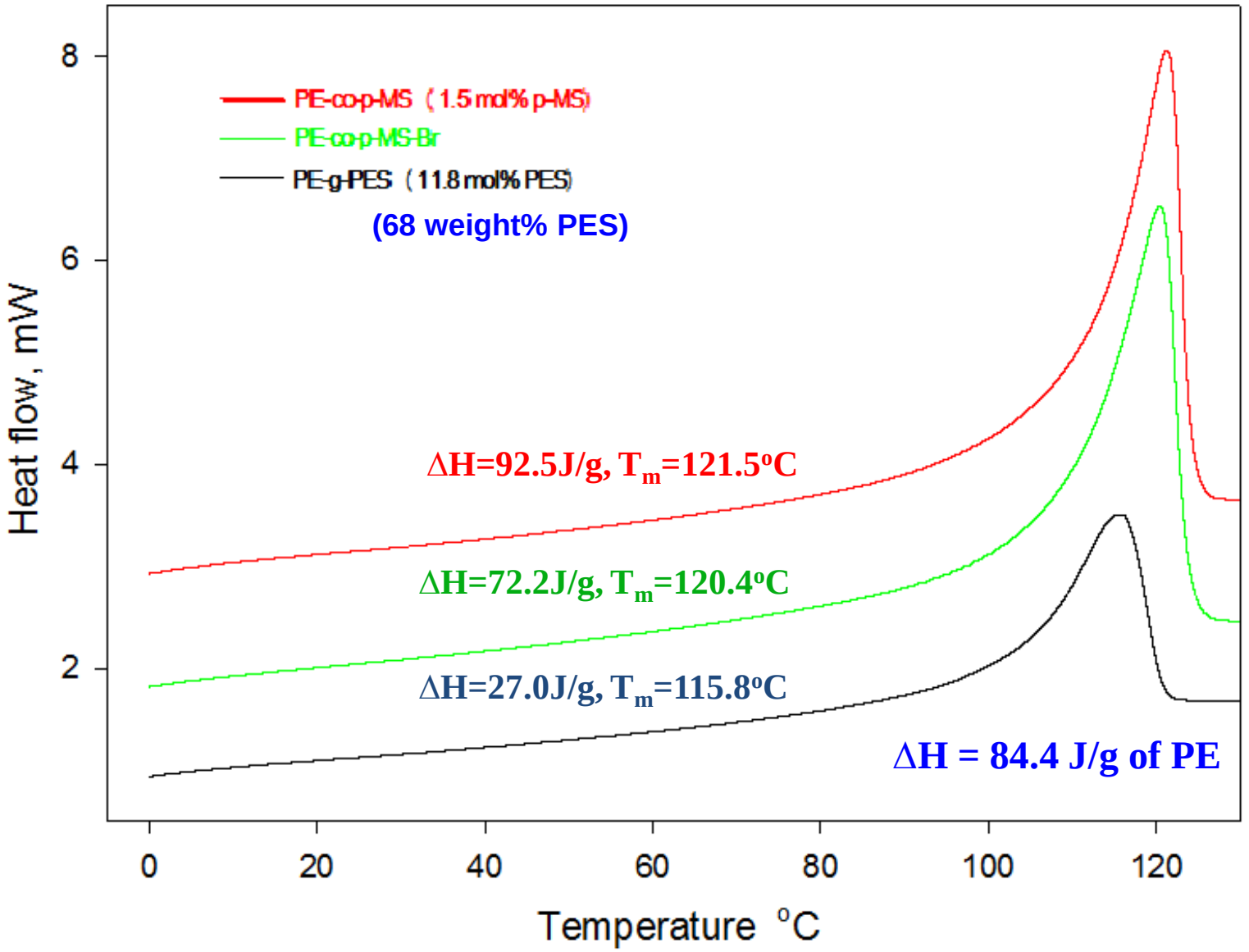
Entry	Reaction Temp. (°C)	Reaction Time (h)	# PES chains per PE backbone	PES Mole%	PES Weight%	PES Volume%
A-1	**150**	**6**	**9.2**	**5.4**	**47**	**38**
A-2	**150**	**9**	**13.1**	**7.7**	**56**	**46**
A-3	**150**	**12**	**16.2**	**9.5**	**62**	**52**
A-4	**150**	**24**	**17.9**	**10.5**	**65**	**54**
B-1	110	6	4.6	2.7	31	23
B-2	110	9	7.7	4.5	42	33
B-3	110	12	9.4	5.5	46	38
B-4	110	24	14.5	8.5	60	49

Ethylene Mw: 28 g/mole



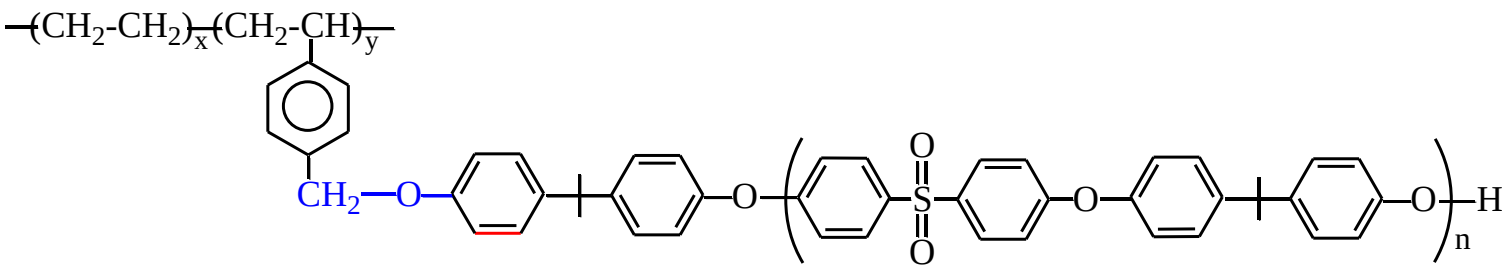
Ether sulfone Mw: 442 g/mole

DSC Curves



PE-g-PES morphology: Clear phase separation with highly crystalline PE domains

Sulfonation of PE-g-PES Film

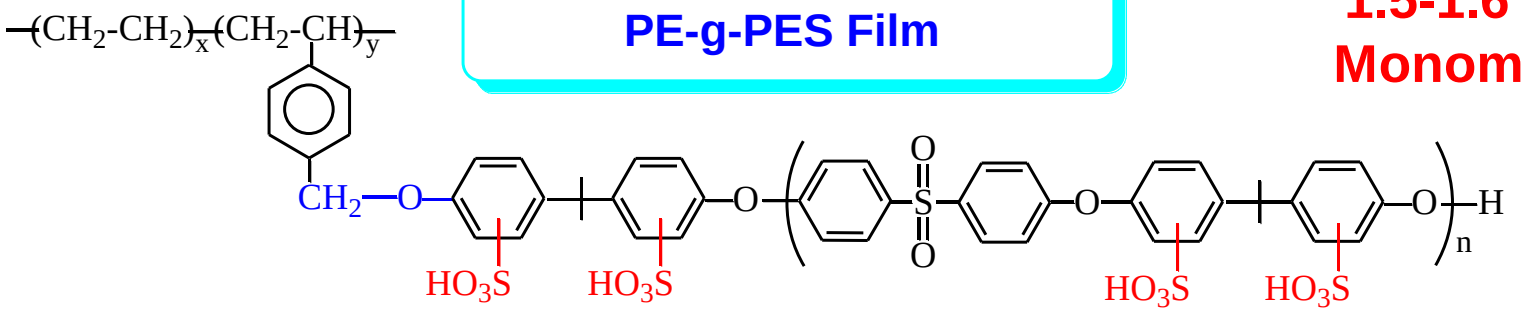


Hot Press in Melt

PE-g-PES Film
(thickness ~ 40 μm)

Sulfonation reaction

Sulfonated PE-g-PES Film



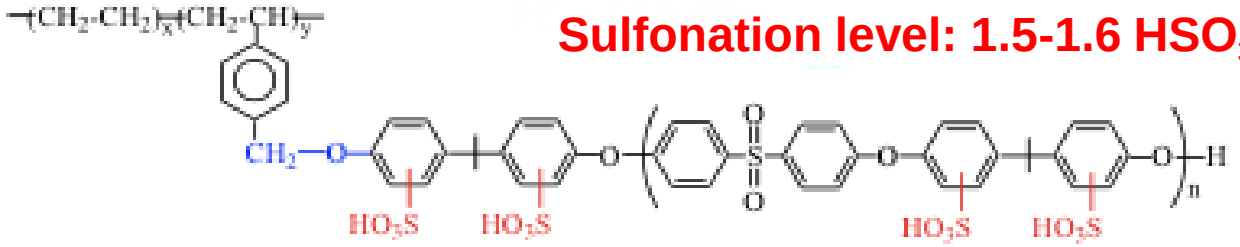
Sulfonation level: 1.5-1.6 HSO_3/ Monomer unit

Before (left) and After (right) Sulfonation

Sample	Tensile Strength [Mpa]	Young's Modulus [Mpa]	Elongation [%]
PE-co-p-MS	12.8	60.0	238
PE-g-PES	48	1744.5	4.3
Sulfonated PE-g-PES	20.2	1114.6	1.9
Nafion 117	13.7	117	208

Properties of Sulfonated PE-g-PES PEMs

Entry	IEC (mmol/g)	IEC (mmol/g of s-PES)	Water uptake (%)	Hydration number (λ)	In-plane conductivity (ms/cm)	Trough-plane conductivity (ms/cm)
A-1-S	1.67	3.55	34	11	64	99
A-2-S	1.88	3.36	42	12	80	129
A-3-S	2.05	3.31	48	13	86	155
A-4-S	2.16	3.46	55	14	94	167
Nafion 117	0.91	0.91	24	15	77	81



Sulfonation level: 1.5-1.6 HSO_3/Monomer unit

Contact Angle Comparison

	PE-co-p-MS	Unsulfonated PE-g-PES	Sulfonated PE-g-PES	Nafion117
Contact Angle (deg) 0 min	103.95	100.34	98.41	80.27
Contact Angle (deg) 3mins	--	99.97	86.61	38.03

Summary

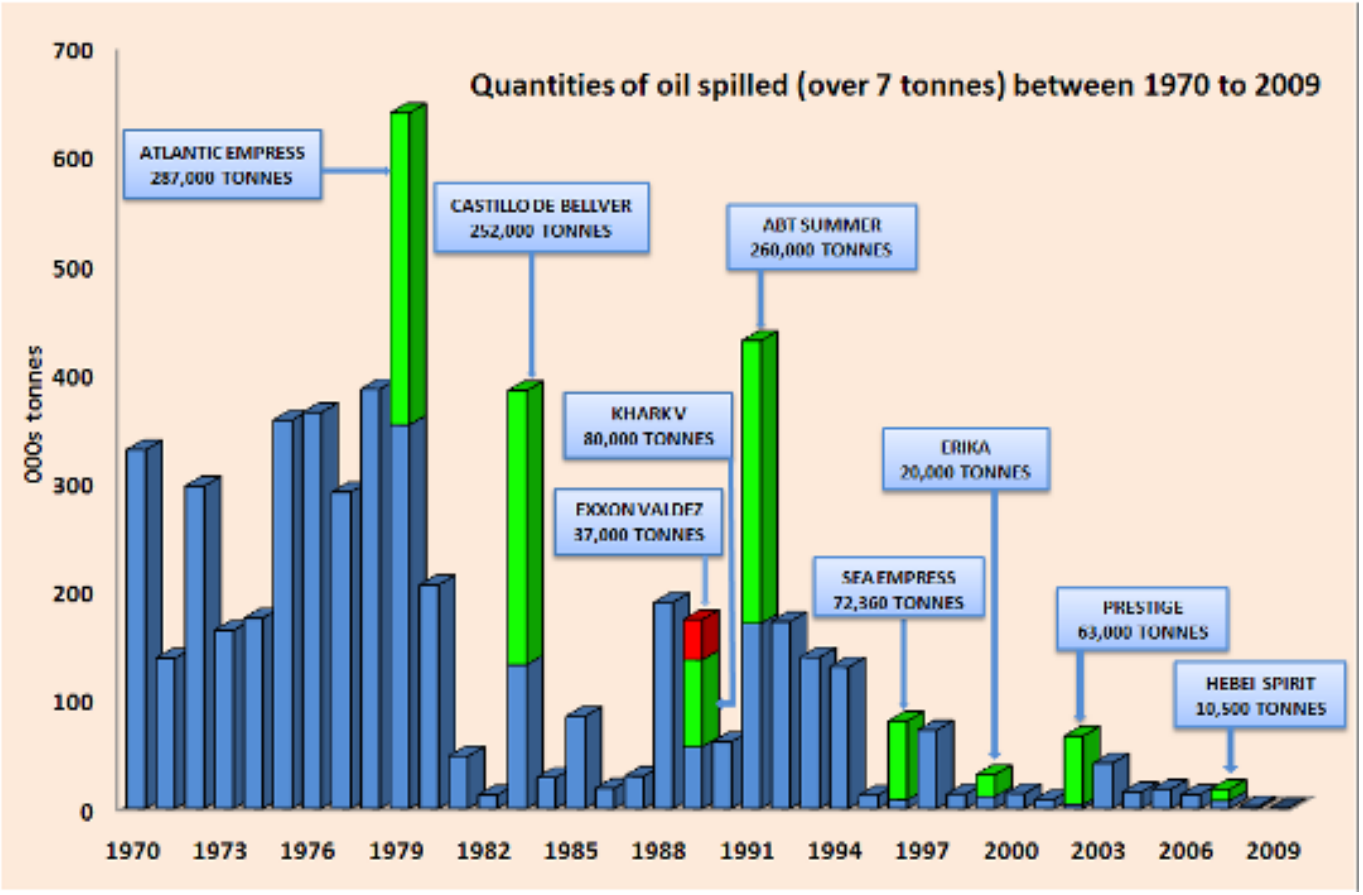
An effective chemical route: ***to prepare well-defined sulfonated PE-g-PES copolymers with high PE backbone and controllable PES side chains (graft density and graft length).***

Sulfonated PE-g-PES morphology: ***shows clear microphase separation with a hydrophobic and highly crystalline PE matrix and imbedded ionic channels, and also a thin hydrophobic layer (low surface energy PE-rich surface layer).***

Sulfonated PE-g-PES PEMs performance: ***PEMs with high IEC value and thickness= 20-40 μm exhibit excellent mechanical strength, moderate hydration (λ= 14), high through-plane conductivity (σ= 167 mS/cm), and good selectivity (~7).***

BP Oil Spill in the Gulf of Mexico, 2010

Major Oil Spills



International Tanker Owners Pollution Federation

The *Exxon Valdez* spilled 11 million gallons oil, but even that did not make the top ten list of the largest oil spills (the smallest spill on the list was four times larger than that of *Exxon Valdez*). Indeed, 33 oil spills were measured as larger and more devastating in the past 40 years.

Current Methods for Combating Oil Spills

Boom and Skimmer:

Labor and equipment intensive operation with low yield. Only10 percent of the BP's oil was removed by mechanical recovery.

Dispersants:

Breaking up the oil into droplets, suspending in the water with a longer-term environmental problems down below the surface.

Control Burning:

Oil is corralled using booms to thickness where enough volatiles are present to sustain a controlled burn.

Traditional Oil Absorbents

Granules: based on minerals (i.e. clay, silica, zeolites, etc.) and vegetable products (corn corb, wood fiber, cotton fiber, etc.)

- **Natural or renewable (biodegradable) products.**

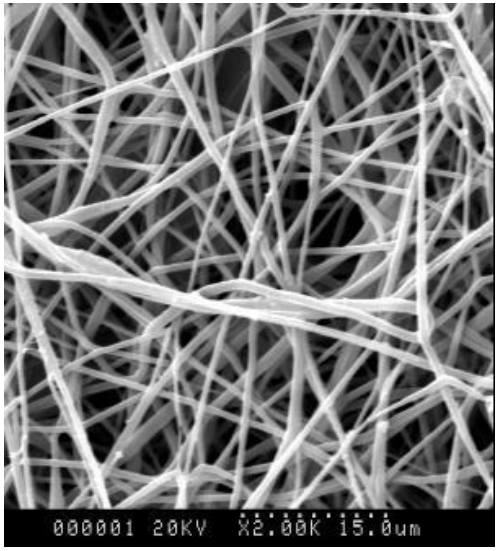
- ***Low oil absorption capacity (1-3 times).***
- ***Also absorb water.***
- ***Recovered solids: Landfills.***

State-of-the-art Oil Absorbents



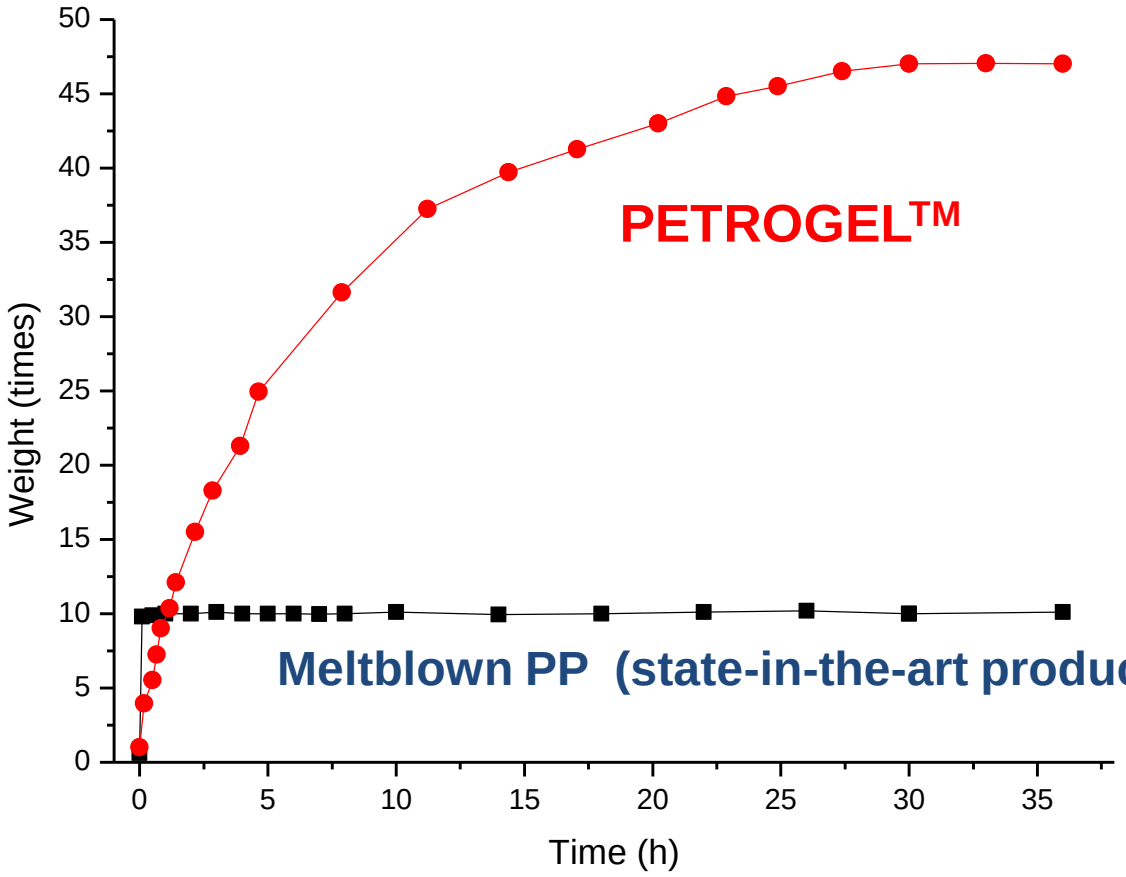


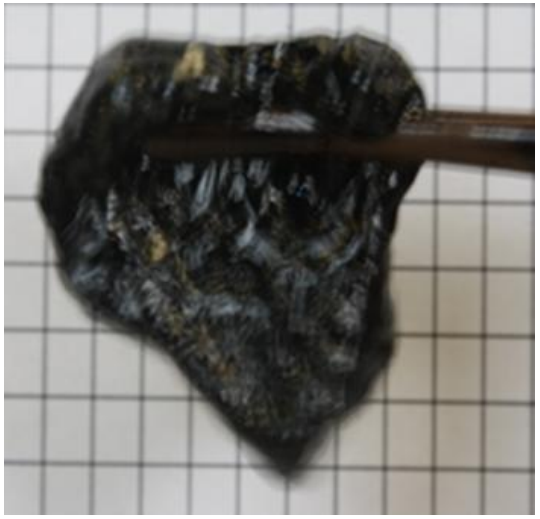
Meltblown PP fibers: pads, mats, pillows, socks, and booms.



- ***<u>Adsorption</u> in their interstices by capillary action.***
- ***Fast kinetics (high surface area and low bulk density).***
- ***Limited Capacity: <10 times (favor to aromatics; poor on aliphatics)***
- ***Easy re-bleeding of the adsorbed oil under a slight external force.***
- ***Recovered solids: <u>Landfills/Calcinations or Laundering/Recycling</u>***

Comparison of Oil Absorption

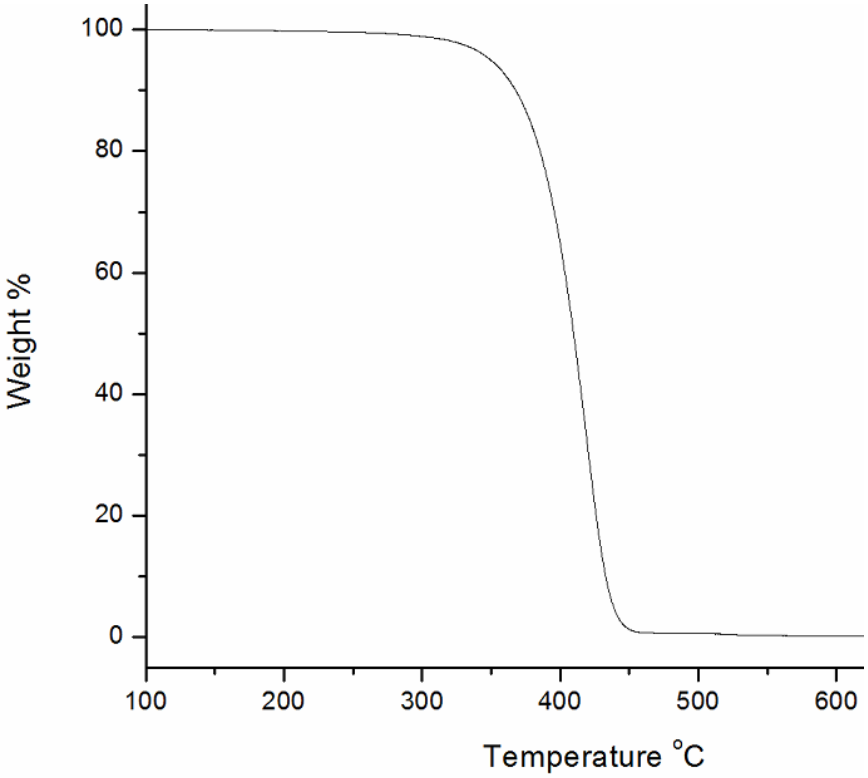


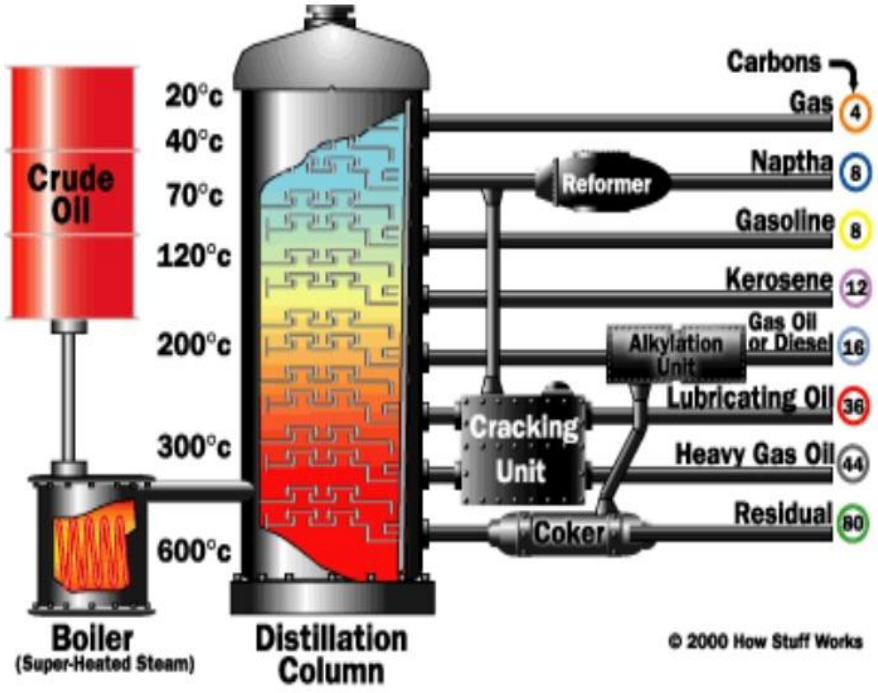


Sample	toluene	Benzene	Hexane	Cyclohexane	Crude oil
Granules	9.60	8.34	5.55	7.43	7.72
Fibres	10.0	10.4	8.10	11.3	9.21
PETROGEL™	**36.2**	**32.9**	**31.3**	**33.5**	**31.8**

Absorption time: 12 hours

Treatment of Oil/Petrogel Mixtures





The resulting oil/PETROGEL™ mixture can be treated as regular crude oil. No air or water pollution.

Cost Analysis

- **With conservative estimate, the production cost of polyolefin based Petrogel may be below $2 per pound in the large-scale industrial production.**
- **One pound of Petrogel can recover 6-7 gallons of the spilled oil (currently treated as pollutants and wastes) to regular crude oil that is worth more than $10 (based on $75/barrel).**
- **For the 1.5-2.5 million gallons of BP oil leaking every day in the Gulf of Mexico, it may only cost between $500,000 and $700,000 per day to use polyolefin-based Petrogel to recover all the spilled oils; the recovered oil would be worth between $2.5 and $3.5 million (without considering the huge environmental and economic impacts from the oil spill).**

Advantages of Petrogel™ Technology

- *High oil absorption capacity: >40 times by weight.*
- *No water absorption.*
- *Fast kinetics in capturing the spilled oil before evaporating and dispersing into a large area.*
- *Good mechanical strength and floatation on water surface for easy recovery.*
- *The recovered Petrogel can be treated as crude oil for regular refining process.*
- *Cost effective and economic feasible.*
- *No pollution and no waste.*