

Solution Behaviour of Branched Polyelectrolytes

IPR Symposium 2006

Abdul Munam

Institute for Polymer Research

Department of Chemistry

University of Waterloo

May 16th, 2006



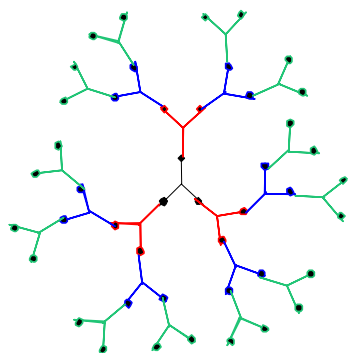
Outline

- Background
- Introduction
 - Dendritic Polymers
 - Arborescent Polymer Synthesis: General Concepts
 - Polyelectrolyte Precursors
- Viscometry measurements
 - In methanol, DMF, H₂O
 - Comparison with linear poly(2-vinylpyridine)
 - Effect of added salt
- Conclusions
- Acknowledgements

Background

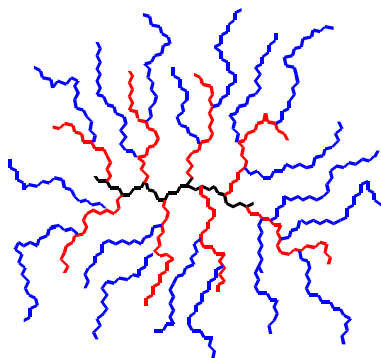
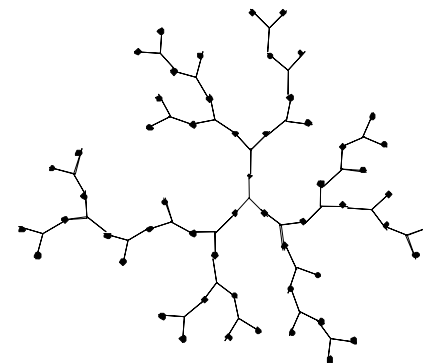
- Polyelectrolytes
 - Polymers with a high density of ionic groups covalently bonded along the chain
 - Properties in solution depend on
 - Degree of dissociation of the ionic groups
 - Solvent quality for the polymer backbone
 - Dielectric constant (ϵ) of the solvent
 - Presence of salts
 - Factors controlling solution properties
 - Intramolecular interactions (at low concentrations)
 - Intermolecular interactions (at high concentrations)
- Linear polymers investigated in detail, but the behaviour of branched polyelectrolytes still not very clear

Dendritic Polymers



Dendrimers: Step by step synthesis, using AB_n -type monomers with protecting groups; Well-defined structure, very low polydispersity ($M_w/M_n < 1.01-1.05$)

Hyperbranched polymers: Synthesis in one step, using AB_n -type monomers; Imperfect structure, high polydispersity ($M_w/M_n > 2$)

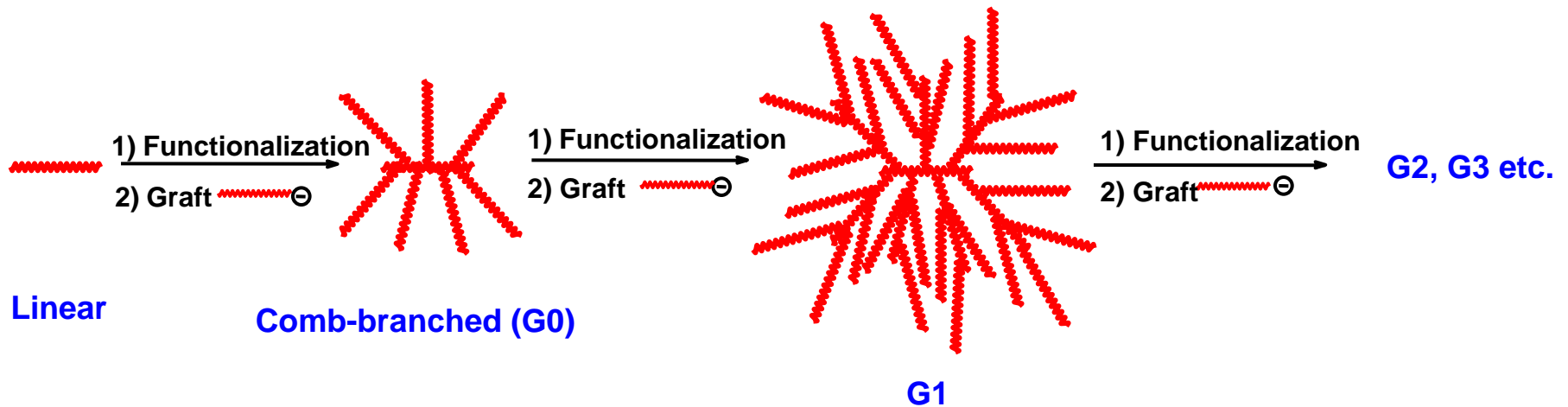


Arborescent polymers: Step by step synthesis using macromolecular building blocks; Rapid increase in molecular weight; Controllable architecture, low polydispersity ($M_w/M_n < 1.1$)
Arborescent = tree-like

Arborescent Polystyrene

"Graft-upon-Graft" Approach

- Linear polystyrene functionalized with grafting sites
- Living polystyryl anions coupled with grafting sites on the backbone polymer to yield comb-branched (G0) polystyrene
- Successive functionalization and anionic grafting reactions yield highly branched (arborescent) polystyrenes (G1, G2, ...)

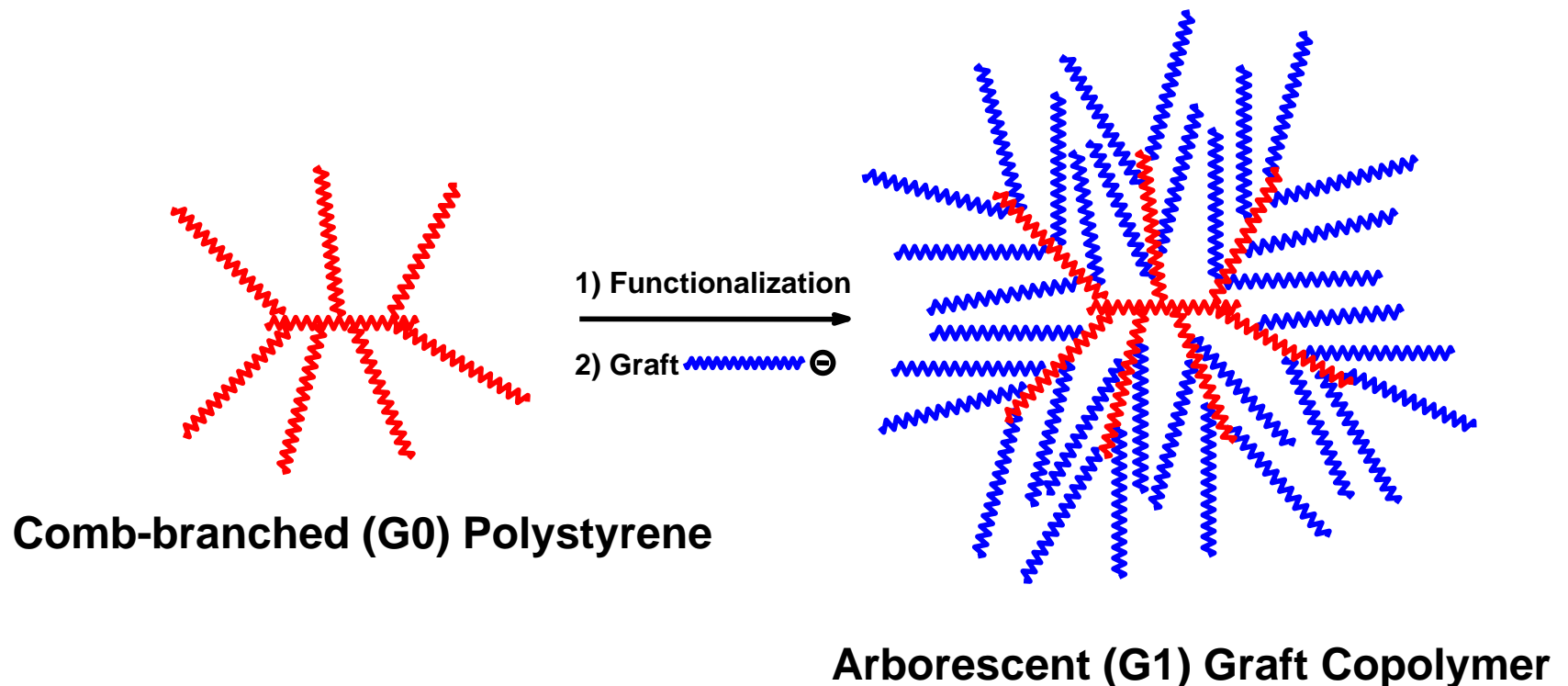


→ High molecular weights achieved in a few synthetic steps while maintaining a controlled molecular architecture

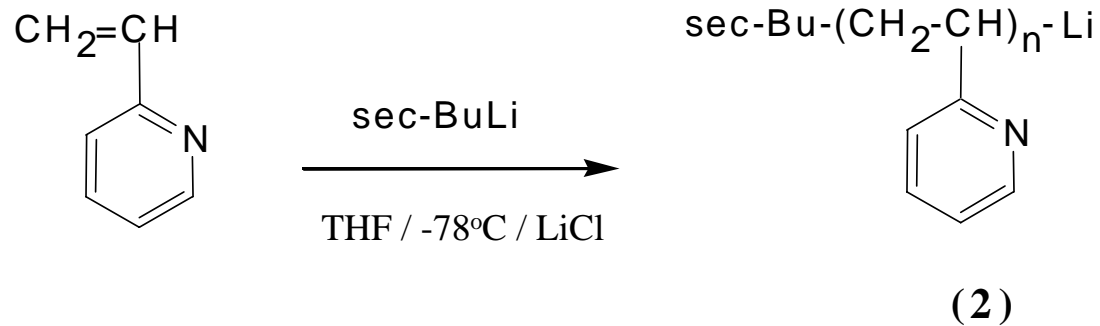
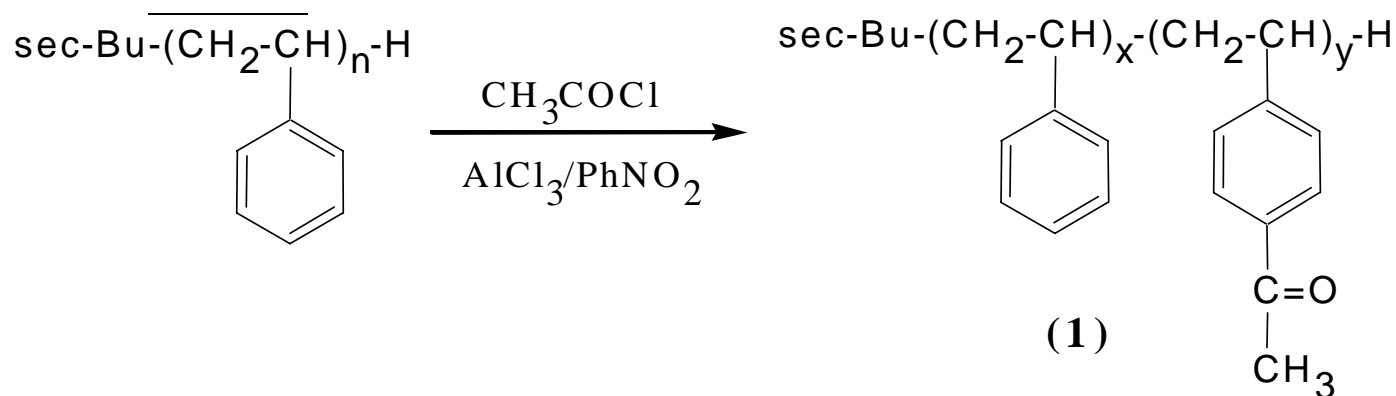
Arborescent Graft Copolymers

Objective:

- To prepare arborescent copolymers incorporating an ionizable comonomer as a **major component** by extending the “graft-upon-graft” technique used for the synthesis of arborescent polystyrenes

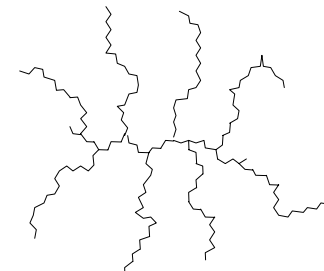
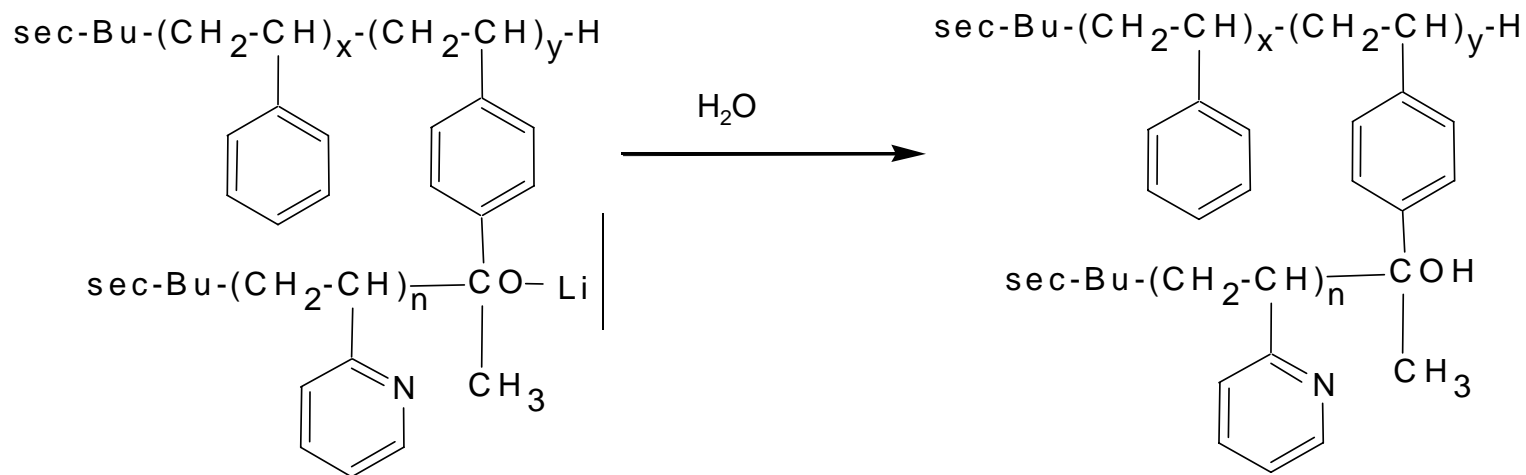
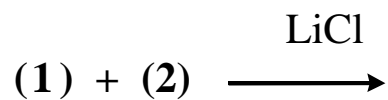


Synthesis: Precursors



- LiCl used 5:1 with respect to initiator
- 10-fold dilution of 2VP monomer used

Synthesis: Coupling



G0

Characterization Results - PS Substrates

Sample	Side Chains		Graft Polymers		
	M_w g/mole	PDI	M_w g/mole	PDI	Grafting Yield (%)
PS5	5300	1.06	—	—	—
PS-PS5	5800	1.06	5.3×10^4	1.07	95
G0-PS5	5400	1.06	1.8×10^5	1.07	90
G1-PS5	4500	1.09	6.0×10^6	1.08	70

- Side chain M_w constant at ca. 5K, narrow apparent MWD
- M_w increases geometrically for successive generations
- Fraction grafted decreases for higher generations
 - Impurities, grafting sites accessibility

Characterization Results - Copolymers I

Sample	Side Chains		Graft Polymers			
	M_w g/mole	PDI	M_w g/mole	PDI	Grafting Yield (%)	Composition Weight % P2VP
PS-P2VP5	5400	1.10	4.4×10^4	1.08	96	82
G0-P2VP5	4900	1.09	1.2×10^5	1.08	90	83
G1-P2VP5	4500	1.11	1.7×10^5	1.09	70	82

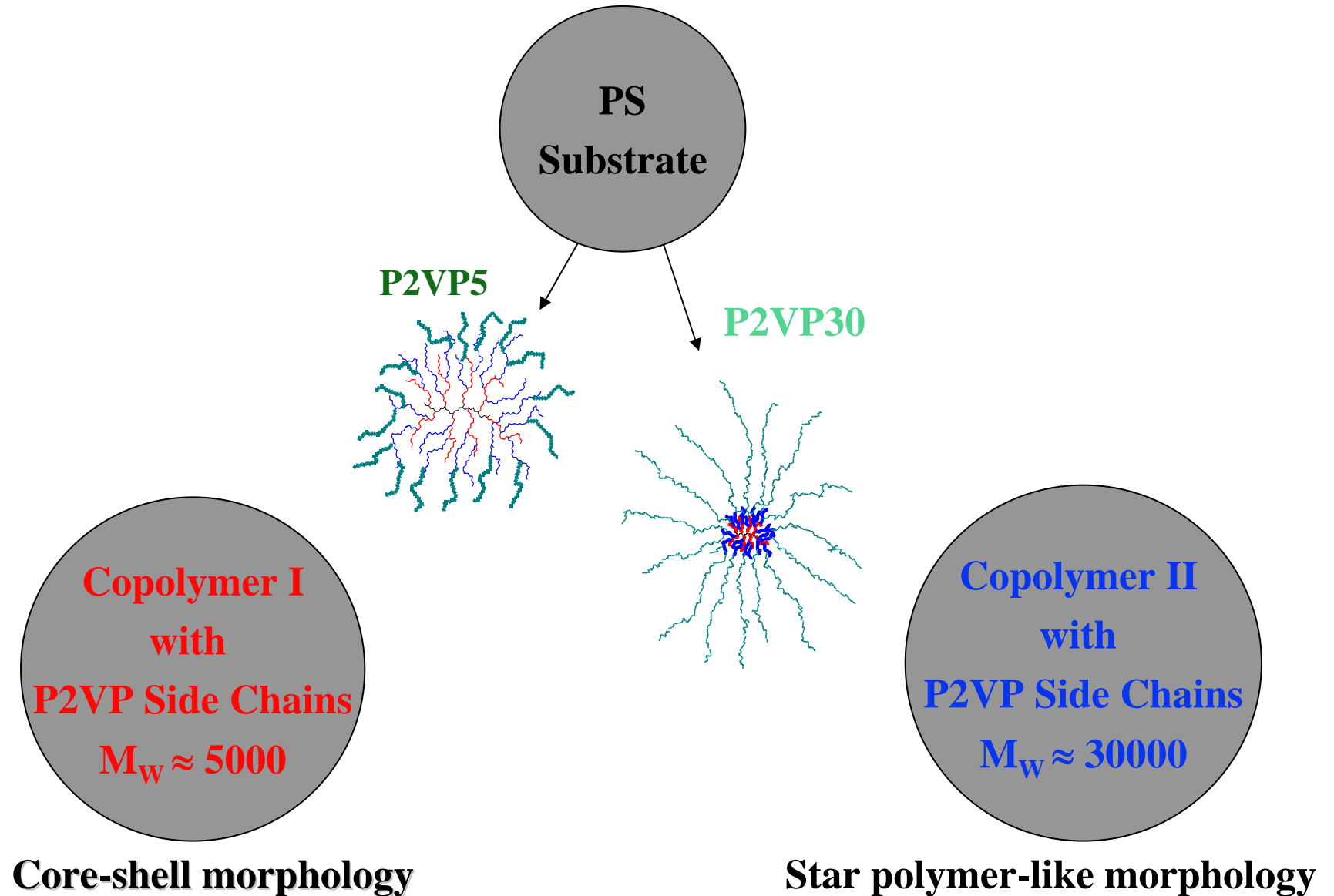
- PS content significant when 5K P2VP side chains used
 - **Core-shell morphology, micellar properties expected**
- Fraction grafted decreases for higher generations
- M_w increases geometrically for successive generations

Characterization Results - Copolymers II

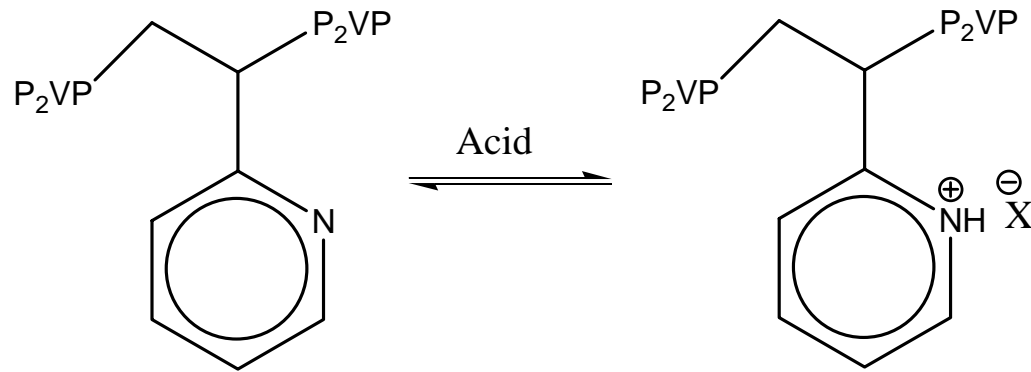
Sample	Side Chain		Graft Polymer			
	M_w	PDI	M_w	PDI	Grafting Yield (%)	Composition Weight % P2VP
PS-P2VP30	27700	1.08	1.2×10^5	1.08	80	90
G0-P2VP30	27800	1.09	2.5×10^5	1.10	71	90
G1-P2VP30	28700	1.09	—	—	25	89

- PS content very low when 30K P2VP side chains used
 - **Star polymer-like morphology expected**
- Same trends observed for fraction grafted, M_w
 - Living ends concentration lower, side chains larger

Polyelectrolyte Precursors

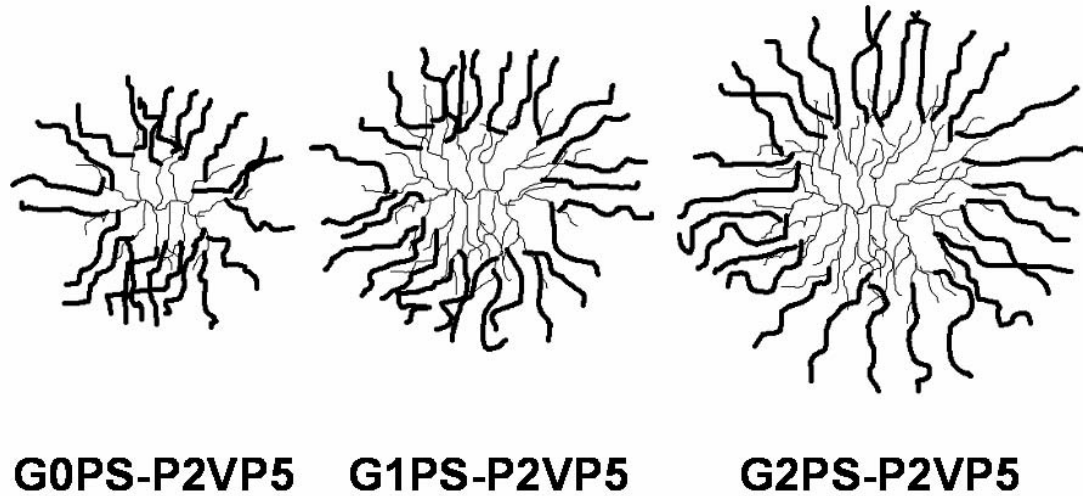


Polyelectrolyte Precursors (Cont'd)



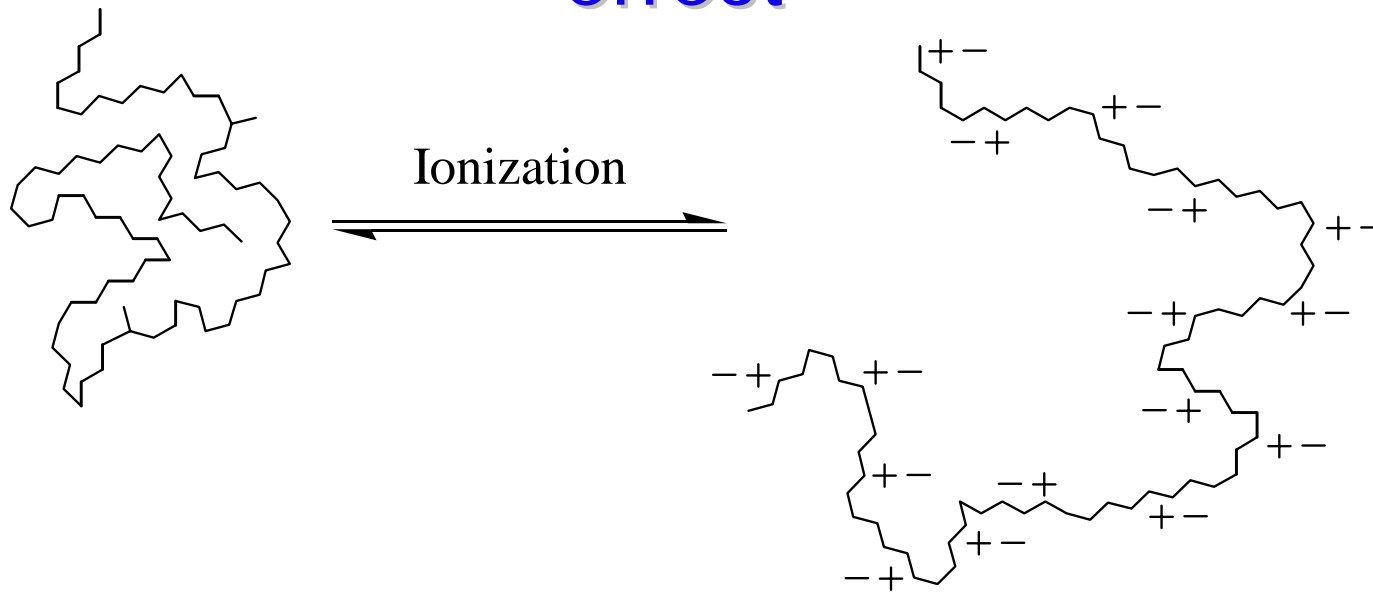
- P2VP segments can be protonated by strong acids to yield **cationic polyelectrolytes**
- Freely soluble in water, polar organic solvents (e.g. methanol, N,N-dimethylformamide – DMF)

Polyelectrolyte Precursors (Cont'd)



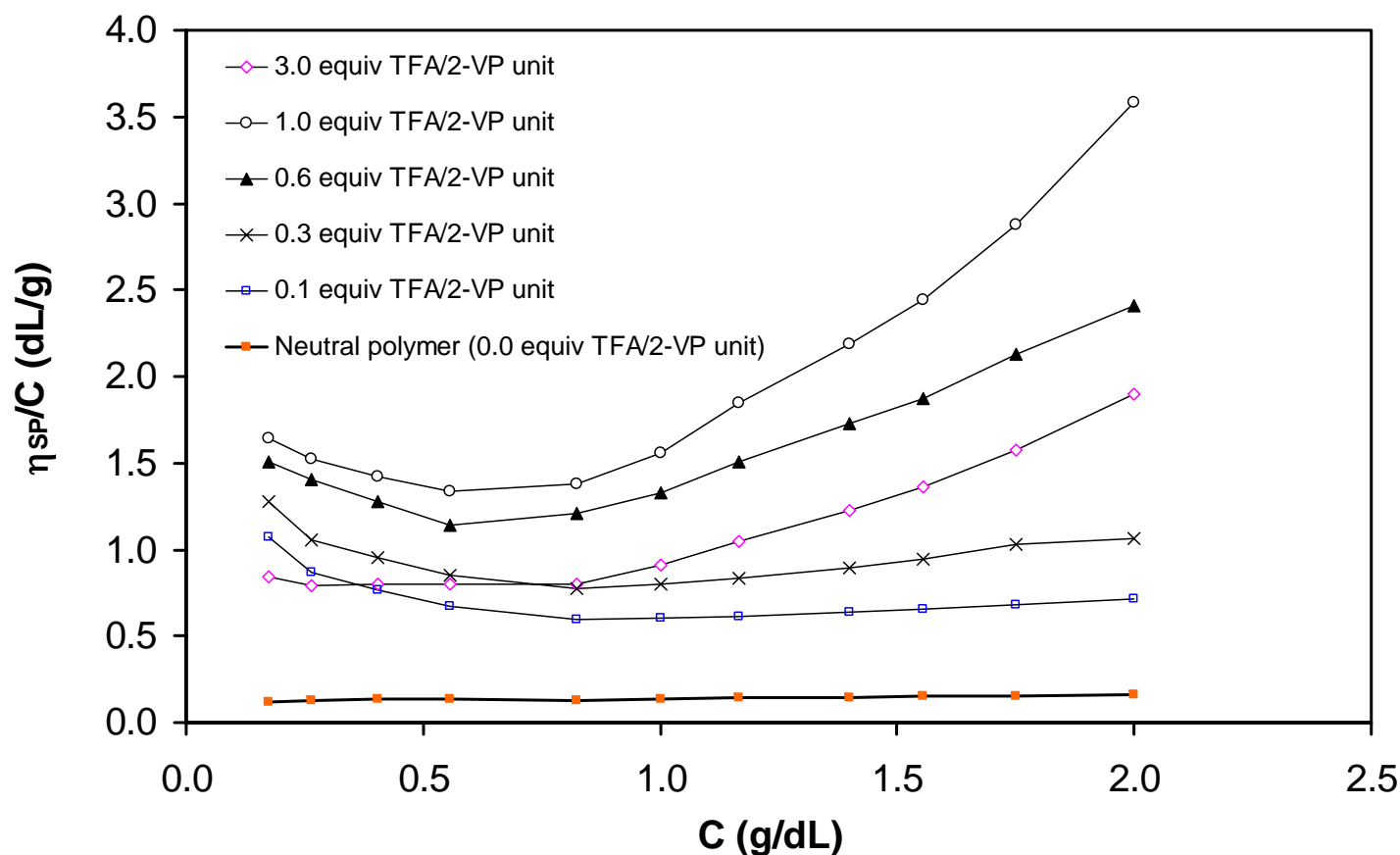
- Reduced viscosity (η_{sp}/c) of arborescent polyelectrolyte solutions investigated as a function of concentration (c) and polymer structure for the two families of P2VP copolymers synthesized

Solution properties - Polyelectrolyte effect



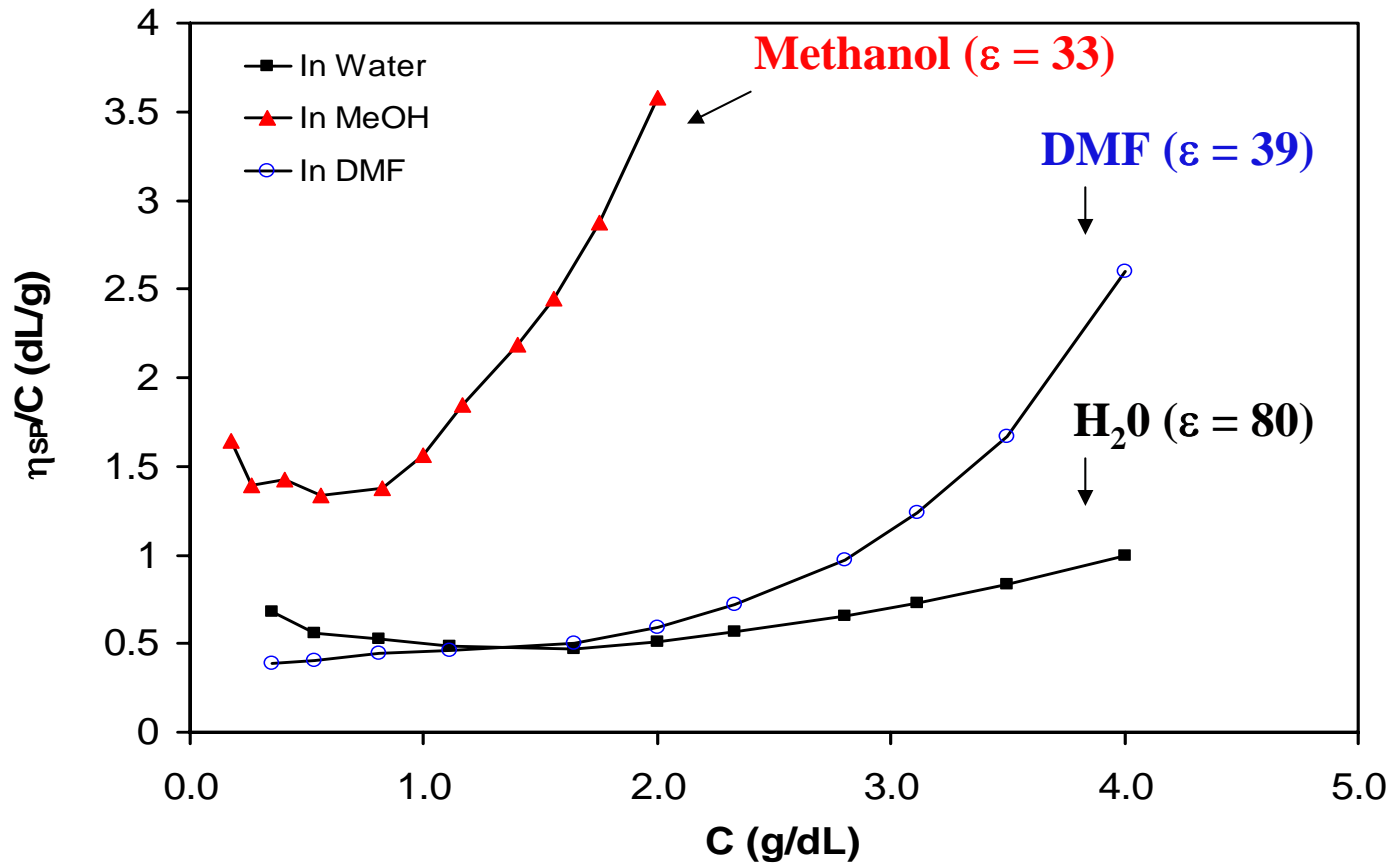
- Coil expansion due to electrical repulsions along backbone
 - Can lead to pH-dependent viscosity variations, sol-gel transitions
- Arborescent polymers have hydrodynamic volumes V_h 10-50 times smaller than linear polymers
 - Is chain expansion favored?
 - Increased electrostatic repulsions vs. increased rigidity

Behaviour of G0PS5-*g*-P2VP5 Protonated by TFA in Methanol



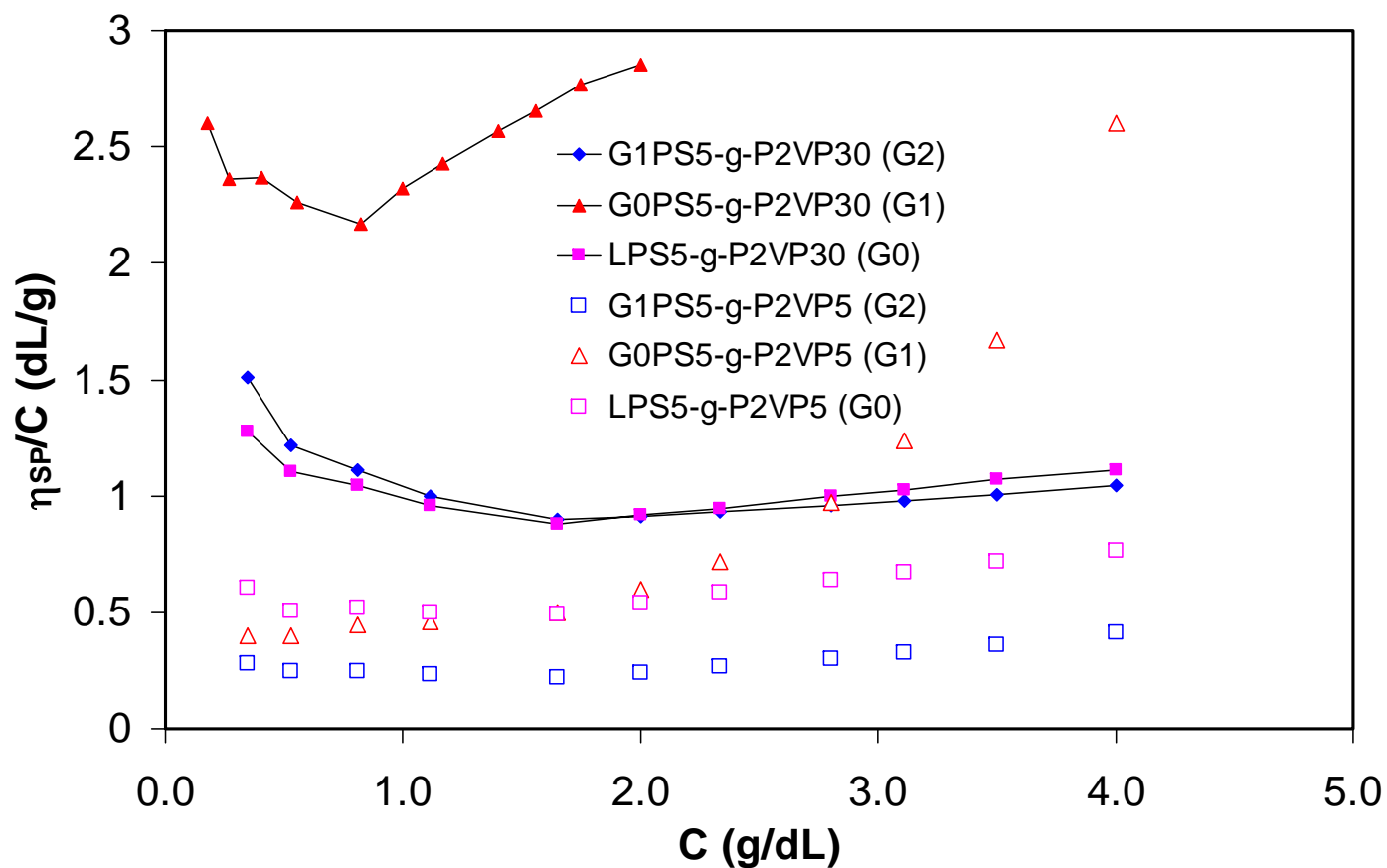
- Classical polyelectrolyte behaviour, event at low protonation levels (0.1 equiv TFA/2-VP)
- Upswing at low concentrations accentuated up to 1.0 equiv TFA/2-VP unit
- Upswing suppressed when excess TFA (3.0 equiv TFA/2-VP unit) added
- Upwards curvature at higher concentrations reflects increasing intermolecular association
- Gels formed at concentrations above those used in the measurements

Viscosity of G0PS5-*g*-P2VP5 in Different Solvents with 1.0 Equivalent TFA/2-VP Unit



- Viscosity enhancement in high concentration range correlates with solvent polarity (methanol < DMF < water)
- Intermolecular association favoured in less polar solvents
- Upturn at low concentrations linked to coil expansion, only visible in protic solvents due to their higher ionizing power

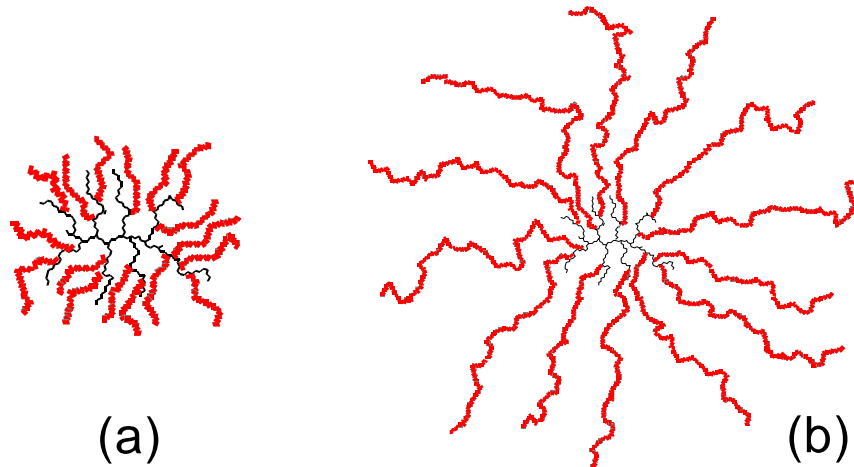
Reduced Viscosity of Arborescent P2VP: 5K *V/S.* 30K with 1.0 Equiv TFA/2-VP Unit in DMF



- Reduced viscosity for P2VP30 > P2VP5 for all generations
- **Reflects the smaller size of the P2VP5 molecules**

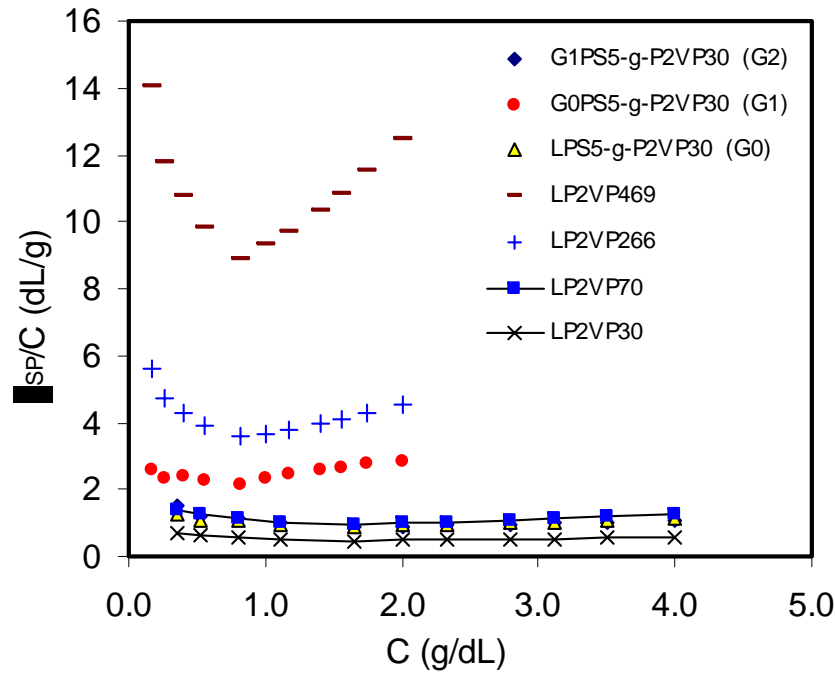
Polyelectrolyte Effect: Molecular Expansion

- Differences in molecular expansion and increase in reduced viscosity consistent with structure of polymers:

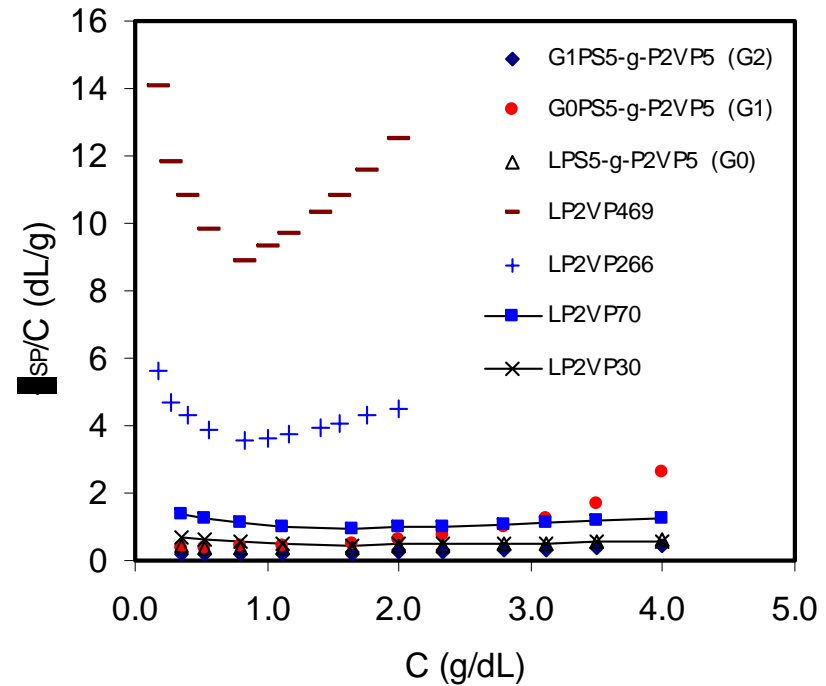


- Increased structural rigidity for type (a) because of higher branching density and shorter P2VP side chains - P2VP5 series
- Flexible structure for type (b) because of lower branching density and longer P2VP side chains - P2VP30 series
- Reduced viscosity of P2VP30 > P2VP5 for all generations

Reduced Viscosity of Arborescent P2VP Copolymers and Linear P2VP with 1.0 Equiv TFA/2-VP Unit in DMF



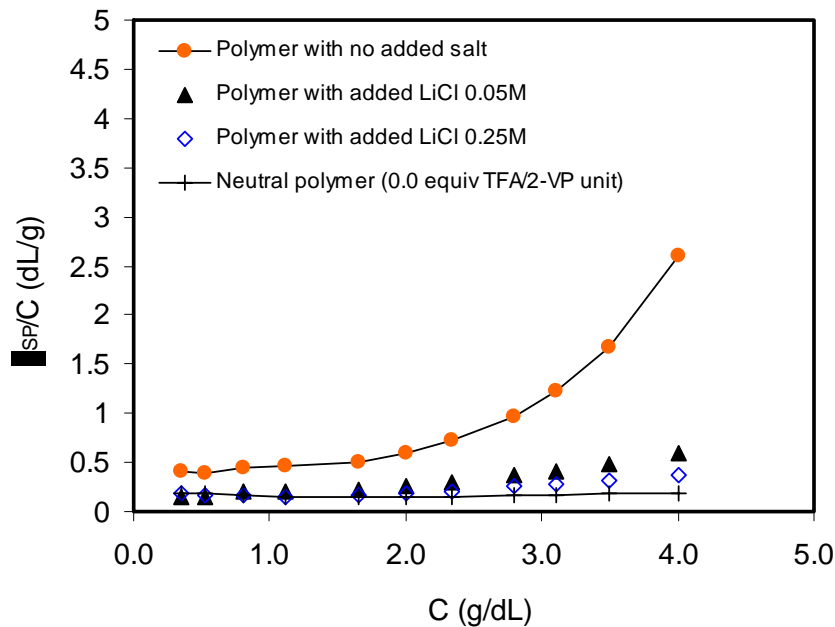
P2VP Copolymers 30K



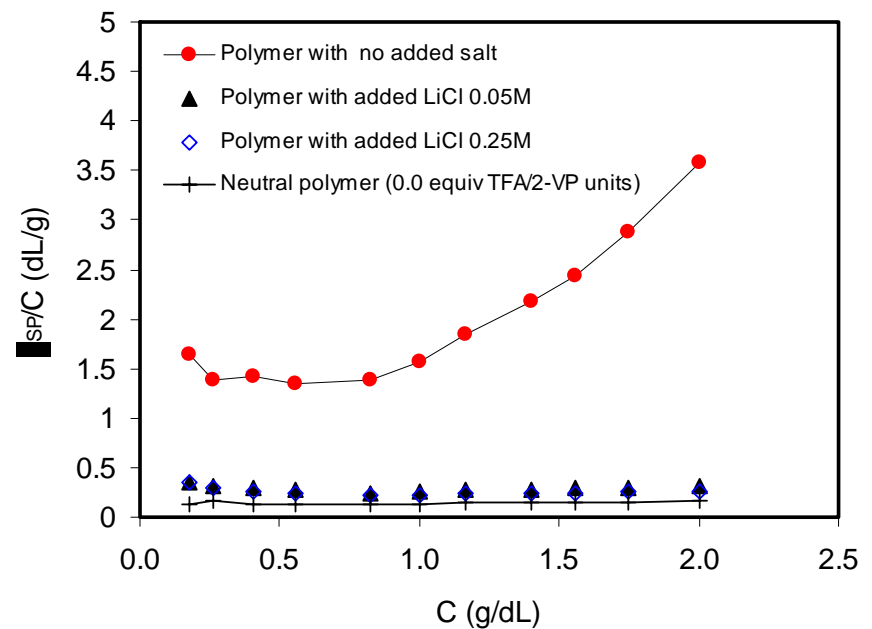
P2VP Copolymers 5K

In spite of their very high M_w , the reduced viscosity of arborescent copolymers is much lower than for linear P2VP samples of comparable molecular weights, due to the small dimensions of the molecules

Effect of Added Salt on Reduced Viscosity of GOPS5-*g*-P2VP5 with 1.0 Equiv TFA/2-VP Unit



In DMF

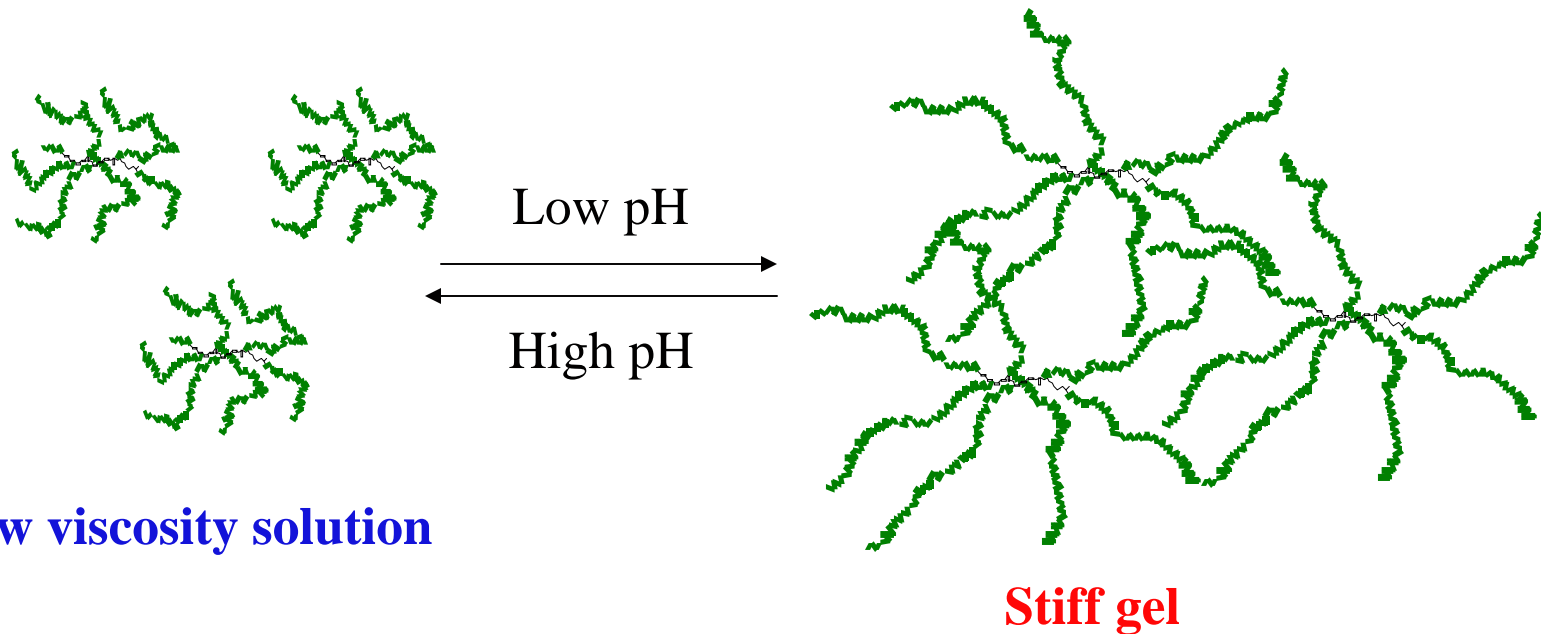


In Methanol

- Concave shape reverts to a straight line in the presence of salts and becomes similar to neutral polymer solutions
- Counterion binding enhanced in the presence of salts, leading to decreased repulsive interactions between the ionic moieties along the polymer chains, a smaller coil size and a lower reduced viscosity

Uses

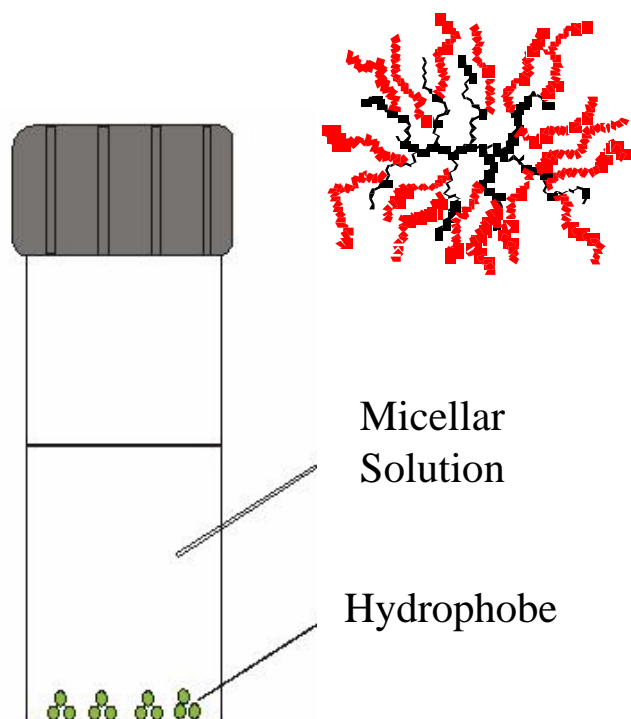
Smart Gels Based on Arborescent Polyelectrolytes



- Reversible gelation/viscosity modification of organic and aqueous solutions
 - pH- or neutralization level-dependent
- Solution viscosity depends of different parameters
 - Neutralization level, ionization method, solvent type, salts...

Uses

Solubilization of Hydrophobic Compounds by Amphiphilic Copolymers



- Soluble when ionized (low pH)
 - Unimolecular micelles
- Heterogeneous morphology
 - Solubilization of hydrophobic compounds
 - Kinetics monitored by UV/Visible spectroscopy
- Applications in microencapsulation

Conclusions

- Polyelectrolyte behaviour of arborescent polystyrene-*graft*-poly(2-vinylpyridine) copolymers investigated
- The solutions display properties typical of polyelectrolytes, including strong curvature in plots of reduced viscosity (η_{sp}/c) versus concentration (c) at both low and high concentrations
- Viscosity enhancement in the high concentration range correlates with solvent polarity (methanol < DMF < water), intermolecular association being favoured in less polar solvents
- Upturn at low concentrations, linked to coil expansion, is only visible in protic solvents due to their stronger ionizing power
- Reduced viscosity of arborescent polyelectrolytes much lower than for linear P2VP samples of comparable molecular weight, due to the small dimensions of the molecules
- The addition of salt to the branched polyelectrolyte solutions decreases their viscosity and suppresses the curvature of the reduced viscosity plots, presumably due to charge screening



Acknowledgements

- Professor Mario Gauthier
- All group members