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Steve Teertstra

Abstract

Presentation

Viscoelastic Properties of Arborescent Polystyrene-*graft*-Polyisoprenes

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Arborescent graft polymers are highly branched, high molecular weight polymers that are constructed by coupling of linear polymer chains in a “graft-on-graft” synthetic strategy. The first examples of arborescent polymers reported in the literature were comprised entirely of polystyrene chains.¹ The initial step of the synthesis involves grafting of polystyrene chains onto a linear polystyrene backbone containing randomly-spaced reactive coupling sites, to produce a comb-branched structure termed a generation G0 arborescent polymer. The introduction of new reactive sites on the comb-branched polystyrene, followed by further grafting with polymeric chains, yields a twice-grafted G1 arborescent polystyrene. Repeated functionalization and grafting reactions yields arborescent polystyrenes up to generation G4. The arborescent polystyrenes have been investigated extensively, both in solution² and in the bulk³, to determine the influence of structural variation on the physical properties. The conclusions drawn from these studies show that arborescent polystyrenes act increasingly as rigid spheres as either the branching density is increased or the size of the grafted arms is reduced.⁴

More recently, the preparation of several different arborescent copolymers was achieved by grafting of polymer chains of a different type onto polystyrene substrates. One such copolymer was prepared by the grafting of polyisoprene chains onto polystyrene substrates of different generations to obtain arborescent polystyrene-*graft*-polyisoprenes.⁵ These arborescent isoprene copolymers possess a hard-core-soft-shell topology, of polystyrene and polyisoprene phases, respectively. This concept is illustrated in Figure 1 for a series of copolymers ranging from overall generation G0 (once grafted) to G3 (four times grafted). The synthesis of the isoprene copolymers is well established, however, there has been very little work performed to date involving physical property studies of these highly branched elastomeric materials. In the present work, the dynamic mechanical behavior of a series of well-defined arborescent polystyrene-*graft*-polyisoprenes was studied as a function of polyisoprene arm length and grafting generation.

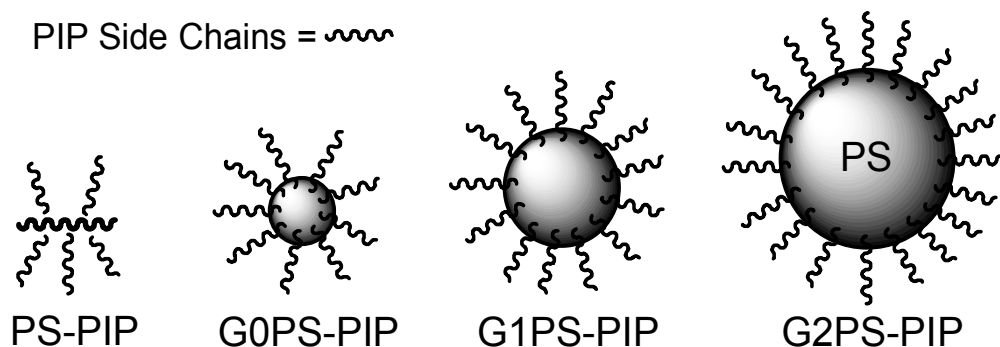


Figure 1 Hard core-soft shell topology of arborescent polystyrene-graft-polyisoprenes.

The moduli-frequency curves measured for the G0 and G1 copolymers display similar features to those found in other highly branched polymer systems, such as star and comb polymers. The G2 and G3 copolymer moduli-frequency curves displayed very different features, similar to networks or filled polymer systems. The significant change in behavior observed within the dynamic moduli-frequency curves is caused by a topological change from flexible branched structures at generation G1 or lower, to spherically shaped rigid molecules at generation G2 and higher. This change in behavior at generation G2 has been observed in previous studies involving arborescent polystyrenes.^{2(a), 3(c)} Partial failure of time-temperature superposition was observed during construction of the master moduli-frequency curves for some of the highest generation copolymers. Superposition of the low frequency data onto one single master curve could not be performed for the G2 and G3 copolymers containing short polyisoprene arms. The proportion of polystyrene within these molecules was significantly large (8 – 28 % w/w) to contribute to the overall modulus of the material, causing thermorheological complexity. The modulus shift factors required to fit the moduli-frequency data for the G2 and G3 copolymers differed significantly from those required to fit the linear polyisoprenes, G0, and G1 copolymers. This is further evidence of a change in molecular topology at generation 2, as increased structural rigidity within the G2 and G3 molecules hinders thermal expansion.

The terminal region of the moduli-frequency curves were used to determine the zero-shear viscosity η_0 , steady-state compliance J_s^0 , and terminal relaxation times. The arborescent isoprene copolymers are characterized by low zero-shear viscosities

compared to linear polyisoprenes of comparable molecular weight, as observed in Figure 2. The zero-shear viscosities measured for the G0 and G1 copolymers increased with polyisoprene arm molecular weight. The upturn observed in the zero shear viscosity η_0 versus molecular weight curves for the G0 and G1 copolymers with increasing polyisoprene arm molecular weight was evidence of viscosity enhancement by entanglement coupling of the longer polyisoprene arms of adjacent molecules. The zero-shear viscosities for the G2 copolymers, estimated by a steady-stress creep experiment, show a decrease with increasing polyisoprene arm molecular weight. This behavior reflects the change in molecular topology of the G2 copolymers to a more rigid, spherical structure. The terminal properties for G2 copolymers were more strongly influenced by the branching density rather than the molecular weight of the polyisoprene arms.

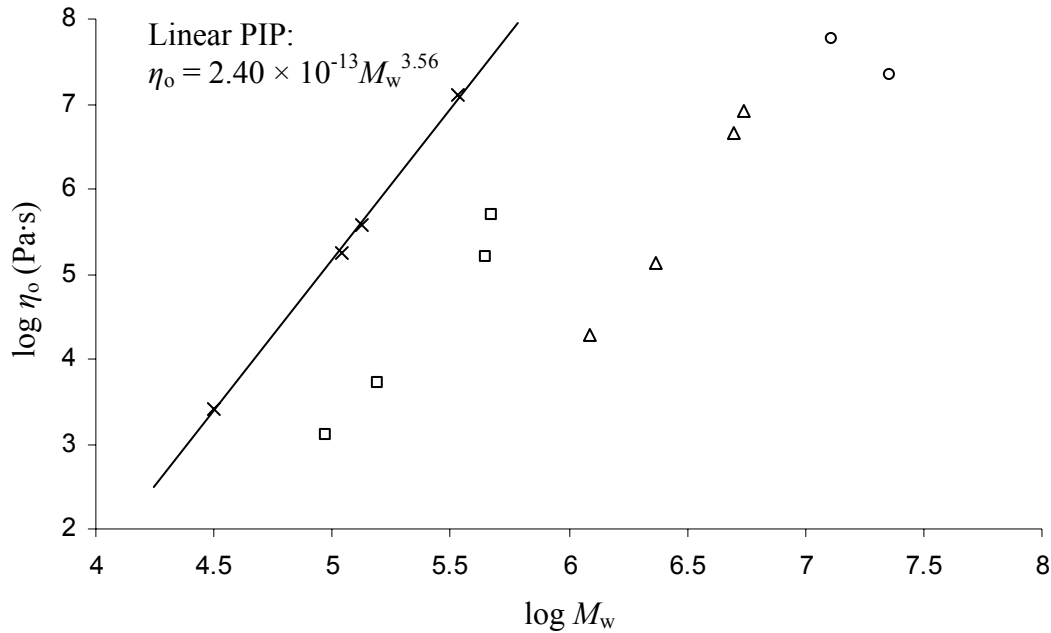


Figure 2 Zero-shear viscosity (η_0) at 20°C versus molecular weight (M_w): (×) linear polyisoprene; (□) G0 copolymers; (Δ) G1 copolymers; (○) G2 copolymers.

The higher generation copolymers (G2 and G3) were characterized by increasingly long relaxation times that could not be measured within the time scale of the rheological measurements, as configurational renewal of molecules was severely hindered by structural stiffness within the highly branched copolymers. The steady-shear compliance J_s^0 was observed to increase roughly monotonically with molecular weight

for the G0 and G1 copolymers, as observed in Figure 3. This behavior is quite different from linear polyisoprenes for which J_s^0 is usually independent of molecular weight. The highly branched arborescent isoprene copolymers are characterized by low viscosity and high elasticity, an interesting combination of properties which show the potential of these materials as rheological modifiers.

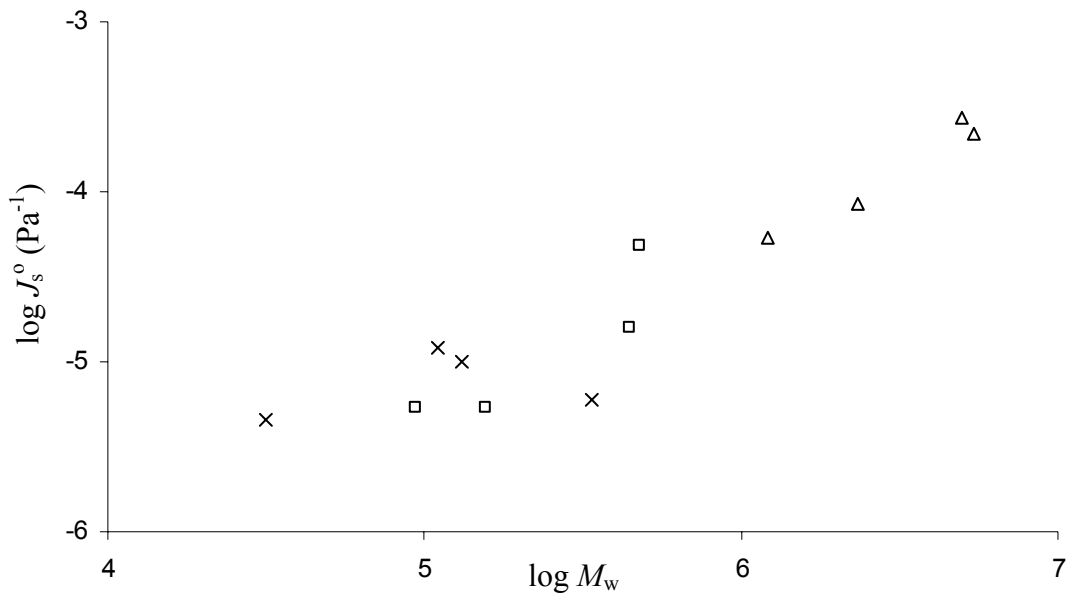


Figure 3 Steady-shear compliance J_s^0 at 20°C against M_w : (x) linear polystyrene; (□) G0 copolymers; (Δ) G1 copolymers.

1. Gauthier, M.; Möller, M. *Macromolecules* **1991**, *24*, 4548.
2. (a) Gauthier, M.; Tichagwa, L. *Polymer* **1997**, *38*, 6363; (b) Choi, S.; Briber, R.M.; Bauer, B.J.; Topp, A.; Gauthier, M.; Tichagwa, L. *Macromolecules* **1999**, *32*, 7879; (c) Striolo, A.; Prausnitz, J.M.; Bertuccio, A.; Kee, R.A.; Gauthier, M. *Polymer* **2001**, *42*, 2579.
3. (a) Sheiko, S.S.; Gauthier, M.; Möller, M. *Macromolecules* **1997**, *30*, 2343; (b) Choi, S.; Briber, R.M.; Bauer, B.J.; Liu, D-W.; Gauthier, M. *Macromolecules* **2000**, *33*, 6495. (c) Hempenius, M.A.; Zoetelief, W.F.; Gauthier, M.; Möller, M. *Macromolecules* **1998**, *31*, 2299.
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Viscoelastic Properties of Arborescent Polystyrene-*graft*-Polyisoprenes

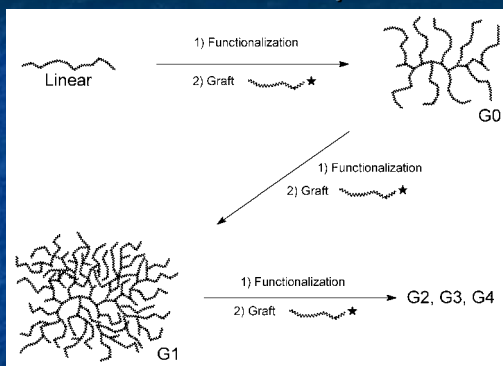
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Outline

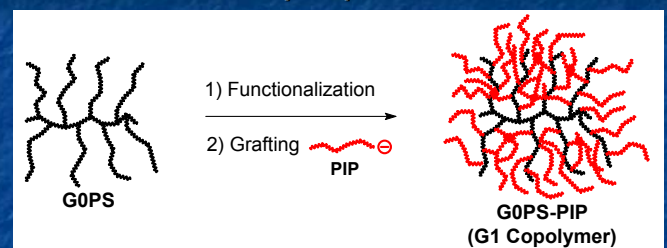
- Introduction: Arborescent Polymers
- Arborescent Polystyrene-*graft*-Polyisoprenes
- Synthesis / Characterization
- Rheological Measurements
 - Methods
 - Moduli-frequency master curves for linear PIP, arborescent isoprene copolymers
 - Zero-shear viscosity
 - Steady-state compliance
 - Relaxation modeling
 - Time-temperature superposition failure
- Conclusions

Arborescent Polymers



- Anionic polymerization and grafting techniques yield highly branched polymers with controlled structures

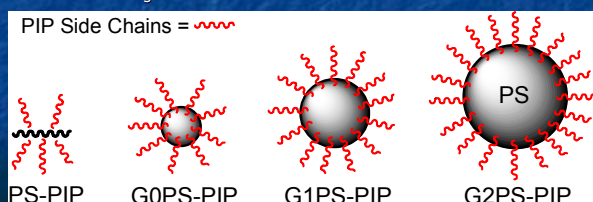
Arborescent Polystyrene-*graft*-Polyisoprenes



- Living anionic polyisoprene chains grafted onto functionalized polystyrene cores of different sizes
- Hard-core-soft-shell topology
- Composition and physical properties dominated by the shell polymer – Highly Branched Elastomer

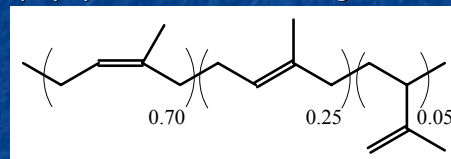
Viscoelastic Properties of Arborescent Isoprene Copolymers

- Synthesis of arborescent polystyrene-*graft*-polyisoprenes well established
- Viscoelastic properties have not been investigated
- Interesting properties due to heterogeneous morphology?
- Copolymer molecules are envisioned to resemble multi-arm stars with a rigid polystyrene core at temperatures below the T_g for PS ($\sim 100^\circ\text{C}$)



Synthesis of Arborescent *cis*-1,4-Isoprene Copolymers

- A series of arborescent copolymers prepared by coupling of *cis*-1,4- polyisoprene chains of different lengths with polystyrene cores of different generations



$T_g \approx -60^\circ\text{C}$ to -70°C

- Isoprene polymerized in hexanes results in a high *cis*-1,4- isoprene units content
- Elastomeric material (low softening temperature) analogous to natural rubber
- G0, G1, G2 and G3 copolymers prepared

Molecular Weight Characterization Data

	cPIP Side Chains		Graft Copolymer		
	M_w^{LS}	M_w/M_n^{SEC}	M_w^{SEC}	M_w/M_n^{SEC}	M_w^{LS}
PS-cPIP5	4860	1.08	73 000	1.08	94 200
PS-cPIP10	9370	1.06	98 000	1.06	157 000
PS-cPIP30	33 900	1.06	350 000	1.06	446 000
PS-cPIP40	40 400	1.05	410 000	1.05	477 000
G0PS-cPIP5	4950	1.09	290 000	1.07	1 120 000
G0PS-cPIP10	9830	1.07	370 000	1.05	2 040 000
G0PS-cPIP30	26 100	1.06	1 050 000	1.27*	4 990 000
G0PS-cPIP40	40 100	1.05	1 060 000	1.37*	5 450 000
G1PS-cPIP5	4800	1.07	1 330 000	1.40*	13 000 000
G1PS-cPIP30	29 800	1.06	-	-	22 600 000
G2PS-cPIP5	4810	1.07	-	-	42 700 000
G2PS-cPIP30	27 500	1.06	-	-	53 100 000

* - Band broadening effects of ultra-high molecular weight SEC columns

PIP Content and Microstructure

	PIP Content / % w/w		PIP Microstructure / mol %		
	1H NMR	M_w	cis-1,4-	trans-1,4-	3,4-
PS-cPIP5	94	93	69	24	7
PS-cPIP10	95	96	69	21	10
PS-cPIP30	>98	>98	71	23	7
PS-cPIP40	>98	>98	73	20	7
G0PS-cPIP5	93	92	69	24	7
G0PS-cPIP10	95	96	70	20	10
G0PS-cPIP30	>98	>98	71	22	7
G0PS-cPIP40	>98	>98	73	20	7
G1PS-cPIP5	94	92	68	23	9
G1PS-cPIP30	>98	95	72	22	6
G2PS-cPIP5	90	72	68	23	9
G2PS-cPIP30	90	78	71	23	6

Molecular Dimensions and Glass Transition Temperature Data

	# PIP Arms	Core Radius (nm)	Shell Thickness (nm)	Side Chain T_g (°C)	Copolymer T_g (°C)
PS-cPIP5	18	1.4	2.1	-65.7	-64.2
PS-cPIP10	16	1.4	2.7	-63.7	-61.6
PS-cPIP30	14	1.4	4.4	-64.1	-62.4
PS-cPIP40	12	1.4	4.5	-63.5	-62.5
G0PS-cPIP5	210	3.2	6.7	-65.5	-63.6
G0PS-cPIP10	200	3.2	8.1	-64.3	-62.3
G0PS-cPIP30	170	3.2	12	-64.9	-64.0
G0PS-cPIP40	130	3.2	12	-64.3	-63.1
G1PS-cPIP5	2400	7.4	16	-66.3	-63.2
G1PS-cPIP30	720	7.4	20	-65.2	-63.5
G2PS-cPIP5	6400	17	25	-66.2	-63.1
G2PS-cPIP30	1500	17	25	-64.6	-63.3

Linear Polyisoprenes

- Several linear polyisoprenes synthesized to serve as baseline materials for rheological studies
- Identical conditions used as the polymerization of PIP side chains for the copolymers

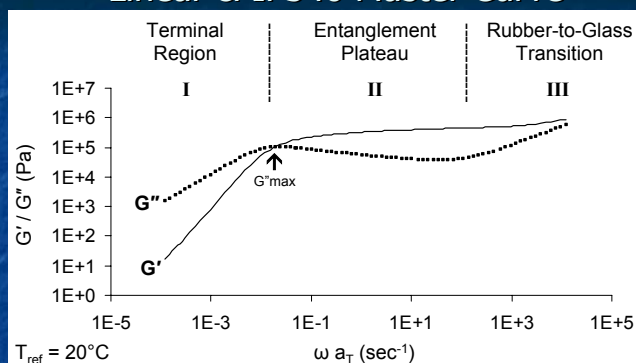
Polymer	M_w	M_w/M_n	PIP Microstructure / mol%			T_g / °C
			cis-1,4-	trans-1,4-	3,4-	
cPIP30	32 000	1.05	72	22	6	-64.2
cPIP110	110 000	1.06	75	20	5	-64.9
cPIP130	132 000	1.06	76	19	5	-65.0
cPIP340*	340 000	1.07	78	17	5	-64.7
cPIP1M*	1 150 000	1.19	78	16	6	-64.6

* - polymers prepared using a semi-bulk polymerization method

Rheology

- 0.25 % w/w *N,N'*-diphenyl-1,4-phenylene-diamine added to stabilize polyisoprene samples
- Rheometrics RDSII used for dynamic (oscillatory) measurements
 - Parallel plate geometry (25 mm diameter)
 - Plate gaps ranging from 1.5 to 3 mm
 - Strain sweeps performed to determine the linear viscoelasticity range (1 – 20%)
 - Frequency sweeps performed at set temperatures ranging from -40°C to 80°C
 - Time-temperature superposition used to build master moduli-frequency curves ($T_{REF} = 20^\circ\text{C}$)
- Paar Physica UDS200 used for steady-stress creep experiments

Linear cPIP340 Master Curve



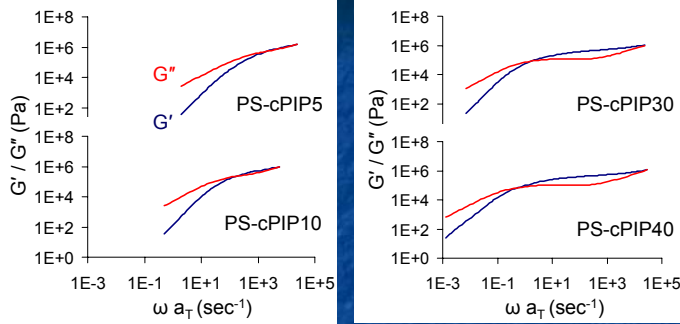
Zero-shear viscosity:

$$\eta_0 = \lim_{\omega \rightarrow 0} \frac{G''(\omega)}{\omega}$$

Zero-shear compliance:

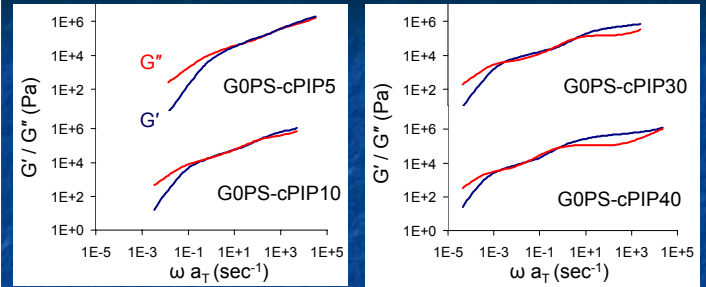
$$J_e^0 = \frac{1}{\eta_0^2} \lim_{\omega \rightarrow 0} \frac{G'(\omega)}{\omega^2}$$

G0 Copolymer Mastercurves



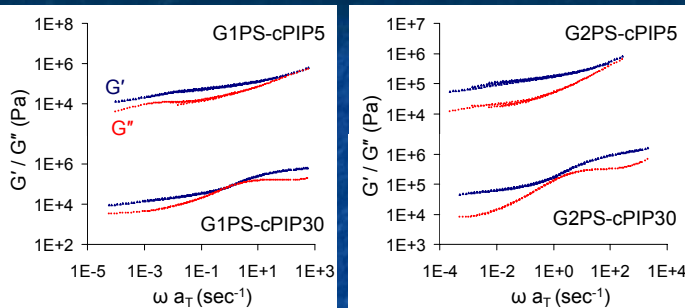
- No entanglement plateau for short PIP arms
- Moduli-frequency curves similar to star and comb-branched polymers (flexible branched polymers)
- Terminal relaxation shifted to lower frequency with increasing arm molecular weight

G1 Copolymer Mastercurves



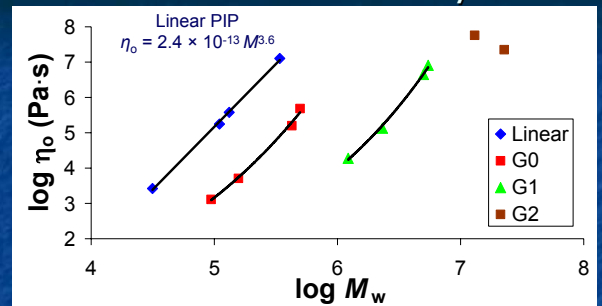
- 2 distinct maxima observed in G'' curves corresponding to arm (short time) and molecular motions (long time)
- Modulus curves similar to highly branched star polymers and G1 arborescent polystyrenes
- Terminal relaxation shifted to lower frequency with increasing arm molecular weight

G2 and G3 Copolymer Mastercurves



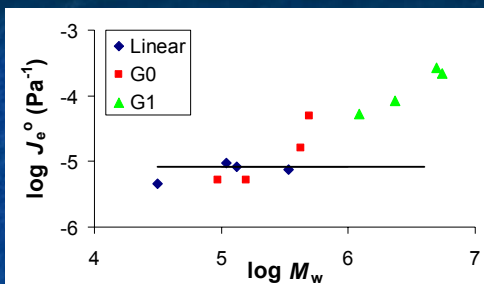
- No terminal region observed (hindered flow)
- $G' > G''$ over entire frequency range
- Modulus curves similar to networks or filled polymers
- G2 and G3 copolymers behave as more rigid spherical molecules

Zero-Shear Viscosity



- η_0 much lower for copolymers compared to linear polyisoprenes of comparable M_w due to branching
- Viscosity enhancement for copolymers with long arms due to entanglement coupling
- Branching density is the dominant factor effecting η_0 in G2 copolymers (hard sphere behavior)

Steady-state Compliance



- J_e^0 independent of M_w for linear PIP above $M_w \approx 50,000$
- Compliance increases with M_w for G0 and G1 copolymers more than 10 fold compared to linear PIP
- Interesting combination of properties: high degree of elasticity with low viscosity

Relaxation Times

Maxwell Model:

$$\eta'(\omega) = \eta_{\infty}' + G_m \sum_{i=1}^N \frac{\tau_{m,i}}{1 + \omega^2 \tau_{m,i}^2} + G_n \sum_{j=1}^N \frac{\tau_{n,j}}{1 + \omega^2 \tau_{n,j}^2}$$

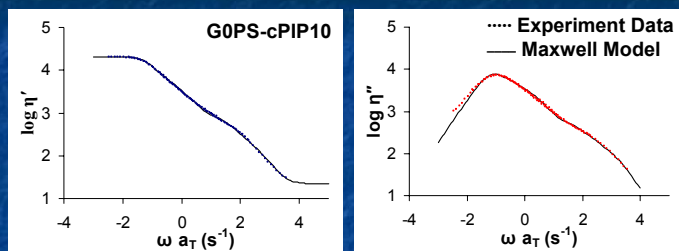
$$\eta''(\omega) = \eta_{\infty}'' + G_m \sum_{i=1}^N \frac{\omega \tau_{m,i}^2}{1 + \omega^2 \tau_{m,i}^2} + G_n \sum_{j=1}^N \frac{\omega \tau_{n,j}^2}{1 + \omega^2 \tau_{n,j}^2}$$

where:

$$\tau_{m,i} = \tau_{m,1} / i^2 \quad \tau_{n,j} = \tau_{n,1} / j^2$$

- Experimental dynamic viscosity curves fit with a generalized Maxwell model
- Two groups of long ($\tau_{m,i}$) and short ($\tau_{n,i}$) relaxation times with appropriate relaxation strengths (G_m and G_n) entered into the model
- Each group of times expressed relative to the longest time for each relaxation mode

Relaxation Times



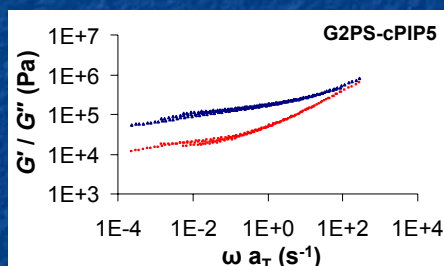
- G0 copolymers with long arms ($M_w = 30\,000, 40\,000$) and all G1 copolymers were fit with 2 groups of relaxation times
- G0 copolymers with short arms ($M_w = 5000, 10\,000$) and linear PIP fit with a single group of relaxation times

Relaxation Times

Polymer	$\tau_{G''_{max}}$ (s)	$\tau_{n,1}$ (s)	$\tau_{m,1}$ (s)
cPIP30	0.0063		0.013
cPIP110	0.25		2.1
cPIP130	0.55		4.0
cPIP340*	50		100
PS-cPIP5	0.001		0.0063
PS-cPIP10	0.0063		0.032
PS-cPIP30	0.13	0.79	0.26
PS-cPIP40	0.83	2.9	16
G0PS-cPIP5	0.001	0.0032	1.1
G0PS-cPIP10	0.0079	0.025	13
G0PS-cPIP30	0.13	1.1	1100
G0PS-cPIP40	0.78	3.4	2000

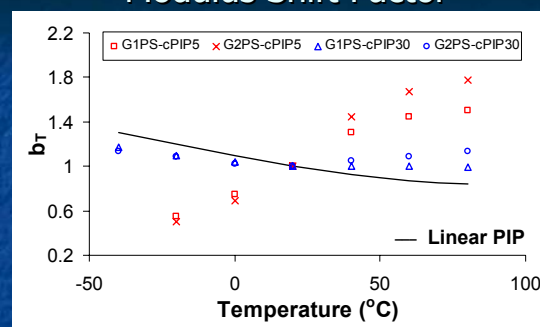
- Relaxation times estimated from G''_{max} are comparable for similar PIP arm M_w
- Short time relaxations ($\tau_{n,i}$) determined from the Maxwell model fit are comparable to G''_{max} times
- Long time relaxations ($\tau_{m,i}$) increase with PIP arm M_w

Partial Failure of Time-temperature Superposition (TTS)



- Partial failure of TTS at low frequencies ($T > 0^\circ$) for G2 and G3 copolymers with short PIP arms due to participation of polystyrene core to overall modulus of material (thermorheological complexity)
- Similar effects observed with linear polyisoprenes filled with silica or polystyrene particles

Modulus Shift Factor



Modulus shift factor:

$$b_T = \frac{\rho T}{(\rho T)_0}$$

- Modulus fitting parameters for G2 and G3 copolymers with short PIP arms display an opposite temperature dependence
- Further evidence of polystyrene core participation to the overall modulus in G2 and G3 copolymers

Conclusions: Rheology of Polystyrene-graft-Polyisoprene Copolymers

- G0 and G1 copolymers behave as flexible branched polymers
- G2 and G3 copolymers exhibit hard sphere behavior
- η_0 enhancement observed for long PIP arms
- J_e^0 increases with molecular weight (high elasticity)
- Arm relaxation times comparable for copolymers with similar molecular weight PIP arms
- Molecular (terminal) relaxation times increase with PIP arm molecular weight
- Polystyrene core acting as a filler in G2 and G3 copolymers causing thermorheological complexity
- Interesting properties: potential rheological modifiers

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