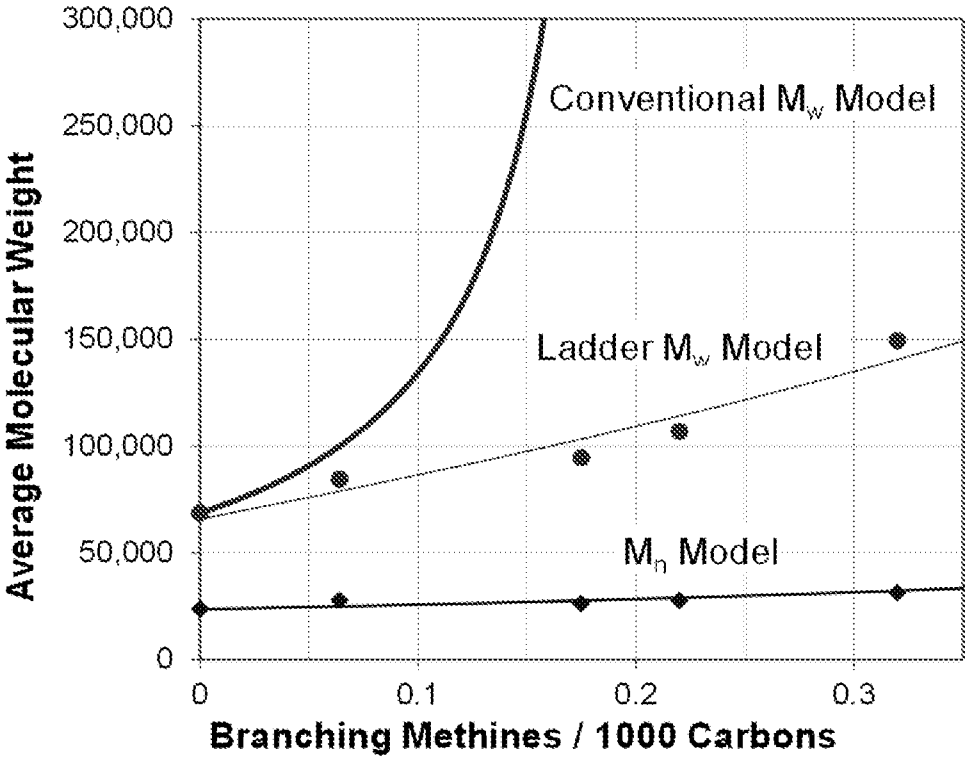

300,000
250,000
200,000
150,000
100,000
50,000
0
Average Molecular Weight
Conventional M_w Model
Ladder M_w Model
M_n Model
0
0.1
0.2
0.3
Branching Methines / 1000 Carbons

FIG. 1

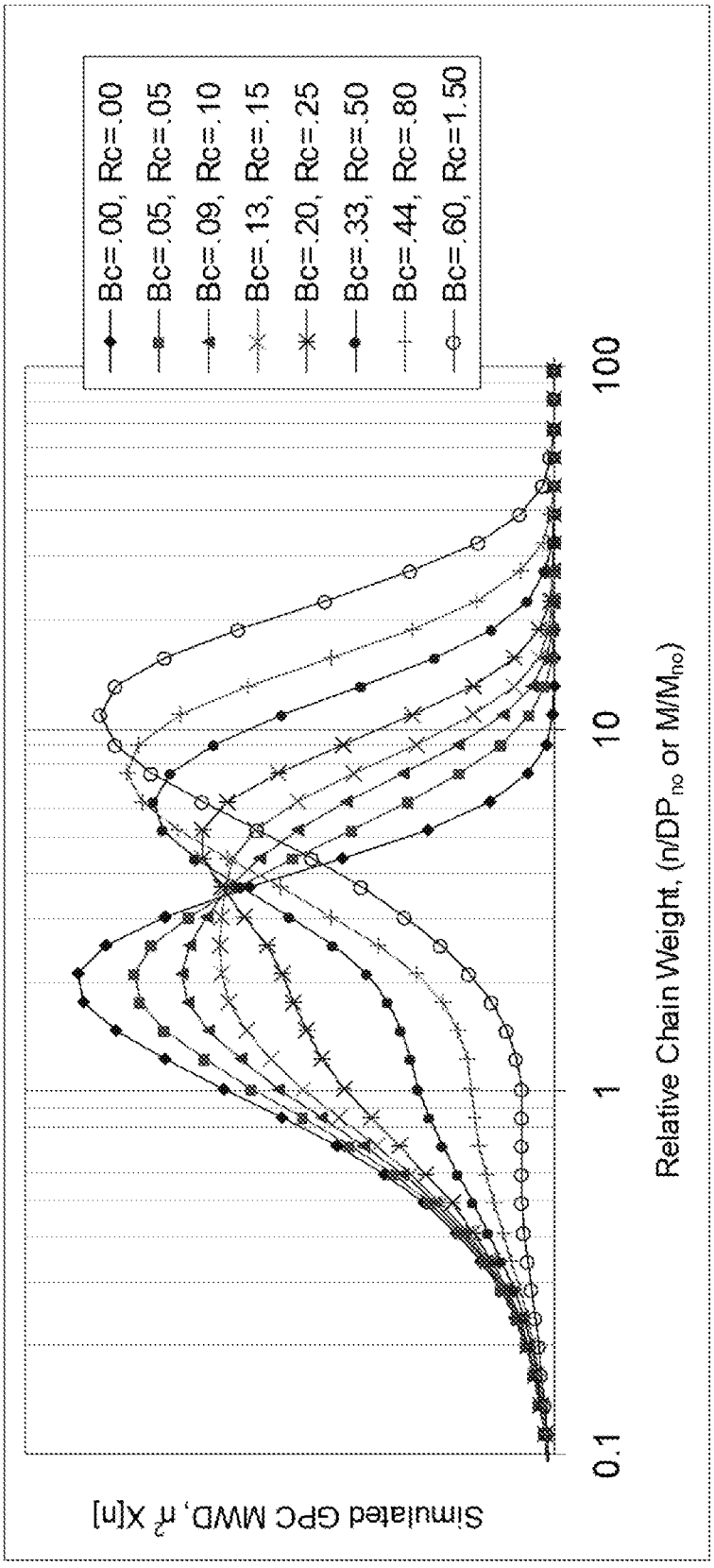

Bc=.00, Rc=.00
Bc=.05, Rc=.05
Bc=.09, Rc=.10
Bc=.13, Rc=.15
Bc=.20, Rc=.25
Bc=.33, Rc=.50
Bc=.44, Rc=.80
Bc=.60, Rc=1.50
0.1
1
10
100
Relative Chain Weight, (n/DP$_{no}$ or M/M$_{no}$)
Simulated GPC MWD, n^2 X[n]

FIG. 2

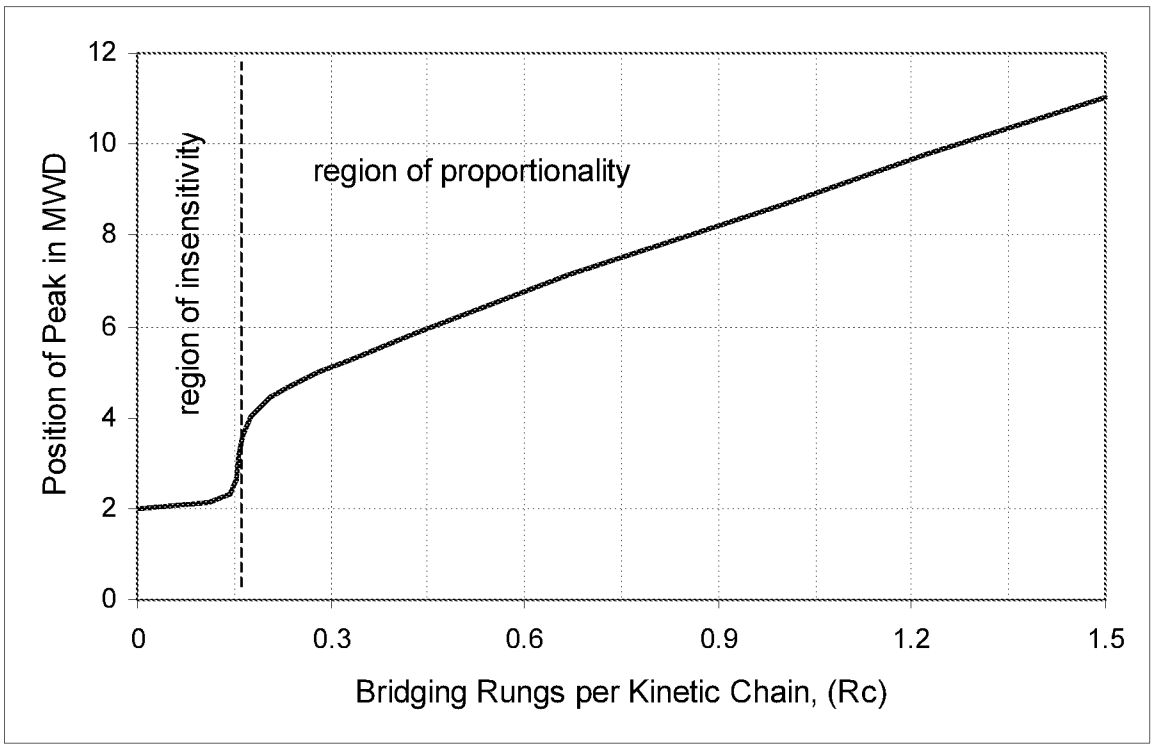

Position of Peak in MWD
region of insensitivity
region of proportionality
Bridging Rungs per Kinetic Chain, (Rc)
0
2
4
6
8
10
12
0
0.3
0.6
0.9
1.2
1.5

FIG. 3

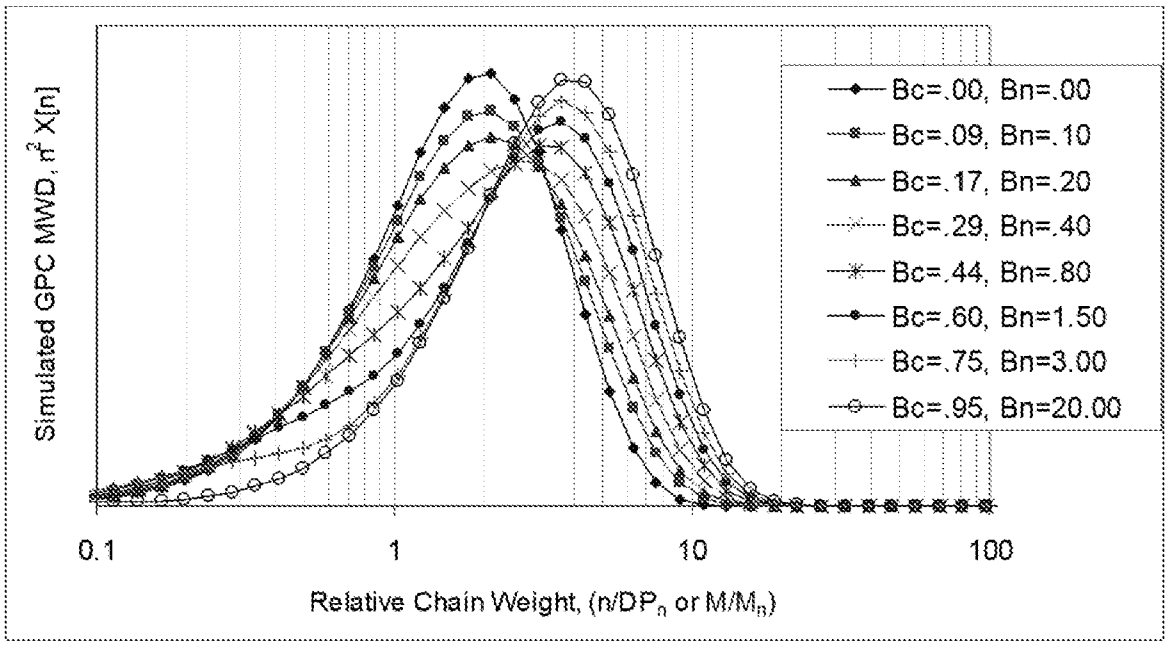

Simulated GPC MWD, n^2 X[n]
Relative Chain Weight, (n/DP$_n$ or M/M$_n$)
Bc=.00, Bn=.00
Bc=.09, Bn=.10
Bc=.17, Bn=.20
Bc=.29, Bn=.40
Bc=.44, Bn=.80
Bc=.60, Bn=1.50
Bc=.75, Bn=3.00
Bc=.95, Bn=20.00
0.1
1
10
100

FIG. 4

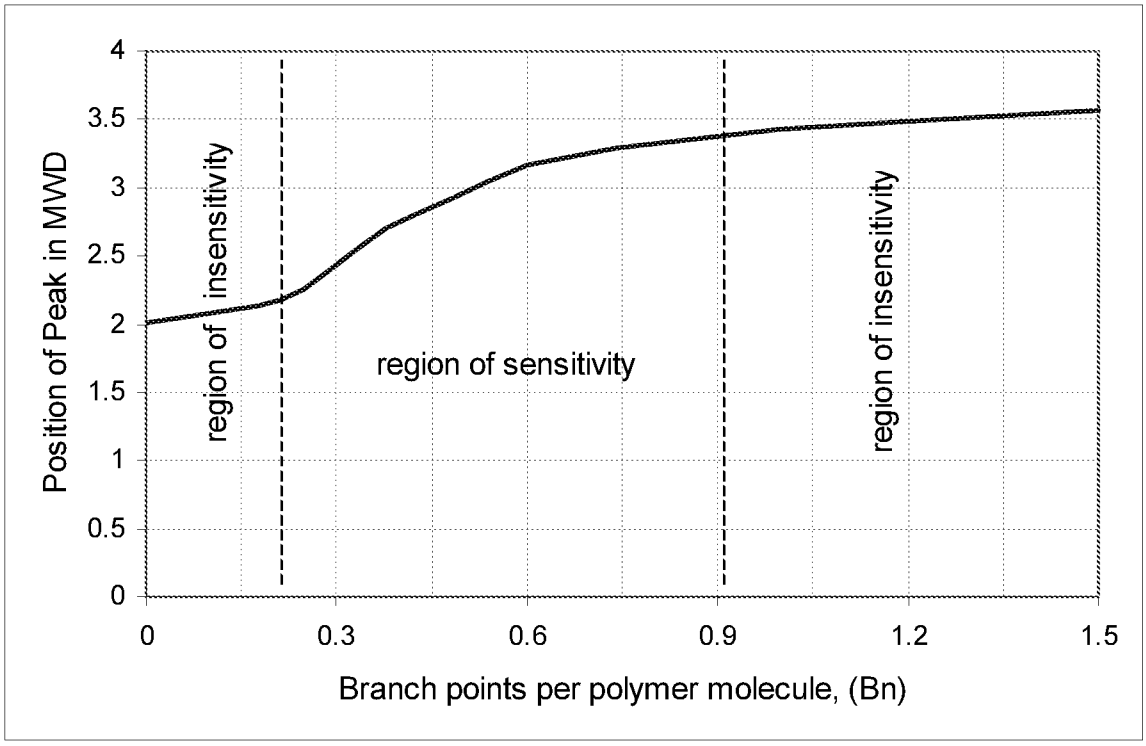

Position of Peak in MWD
4
3.5
3
2.5
2
1.5
1
0.5
0
region of insensitivity
region of sensitivity
region of insensitivity
0
0.3
0.6
0.9
1.2
1.5
Branch points per polymer molecule, (Bn)

FIG. 5

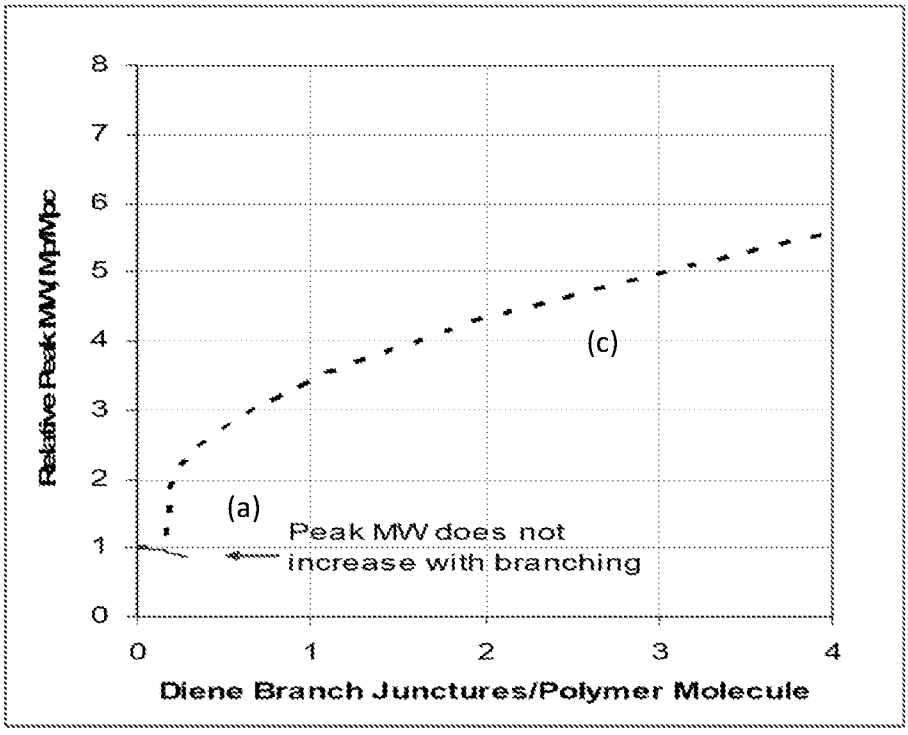

Relative Peak MW, Mp/Mpc
Diene Branch Junctures/Polymer Molecule
(a)
Peak MW does not increase with branching
(c)

FIG. 6

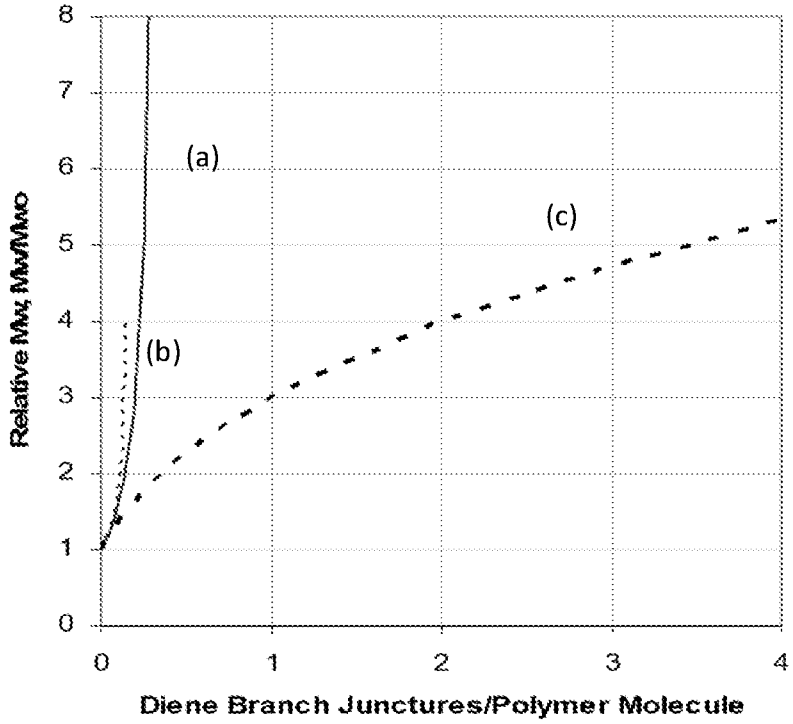

Relative Mw, Mw/Mwo
Diene Branch Junctures/Polymer Molecule
(a)
(b)
(c)

FIG. 7

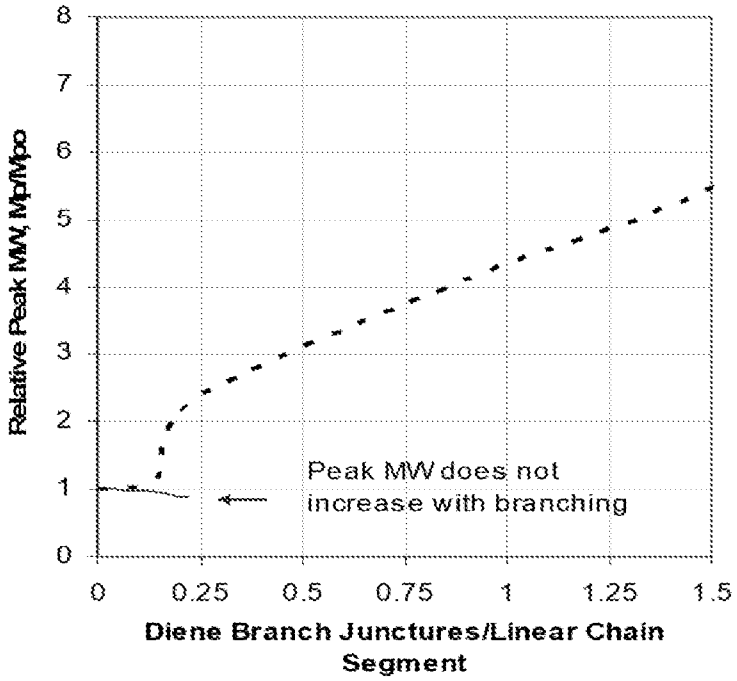

Relative Peak MW, Mp/Mpo
Peak MW does not increase with branching
Diene Branch Junctures/Linear Chain Segment

FIG. 8

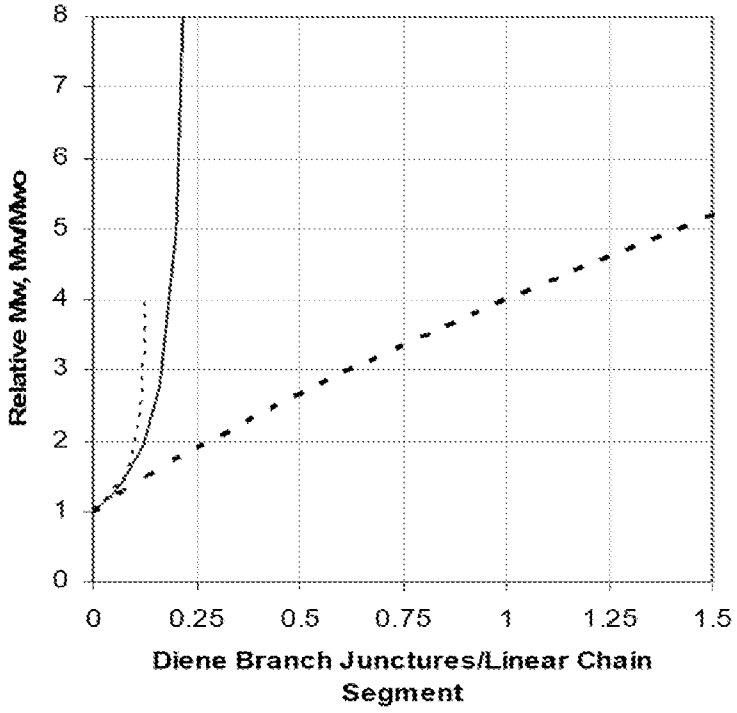

Relative Mw, Mw/Mwo
Diene Branch Junctures/Linear Chain Segment

FIG. 9

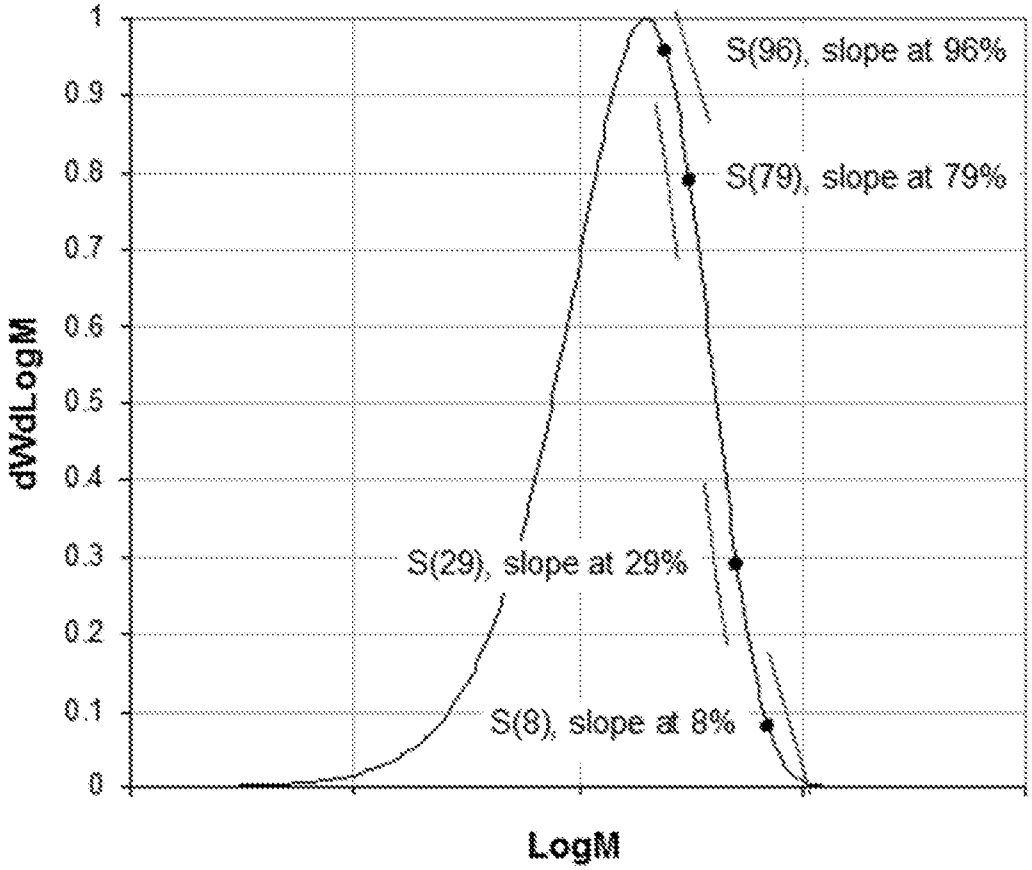

dWdLogM
LogM
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
S(96), slope at 96%
S(79), slope at 79%
S(29), slope at 29%
S(8), slope at 8%

FIG. 10

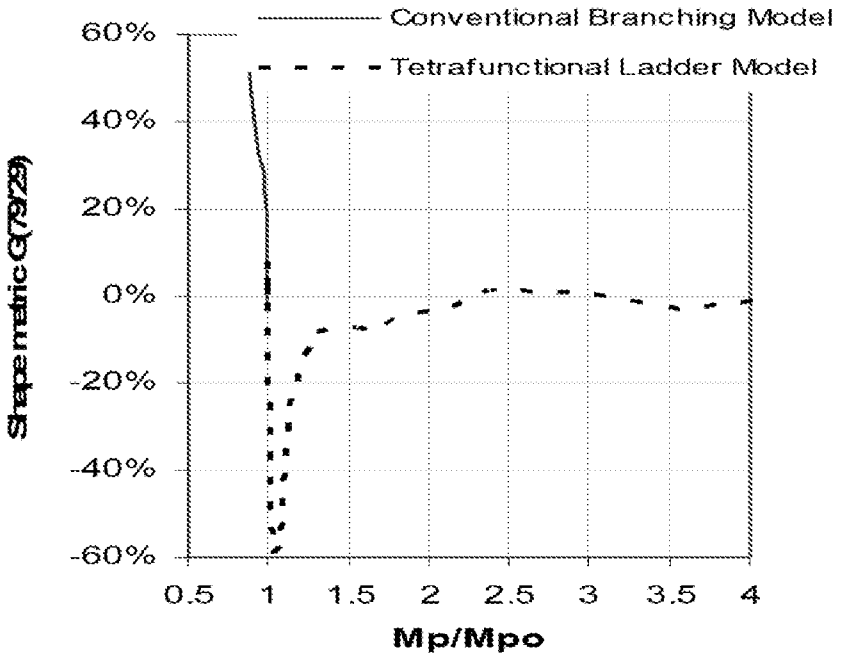

Conventional Branching Model
Tetrafunctional Ladder Model
60%
40%
20%
0%
-20%
-40%
-60%
Shape metric G(79/29)
0.5
1
1.5
2
2.5
3
3.5
4
Mp/Mpo

FIG. 11

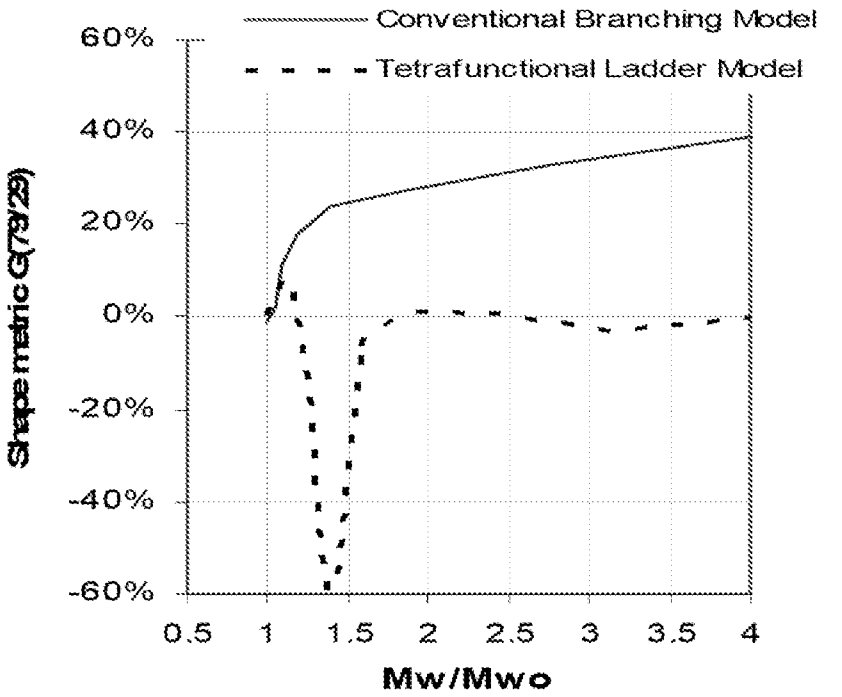

Conventional Branching Model
Tetrafunctional Ladder Model
60%
40%
20%
0%
-20%
-40%
-60%
Shape metric G(79/29)
0.5
1
1.5
2
2.5
3
3.5
4
Mw/Mwo

FIG. 12

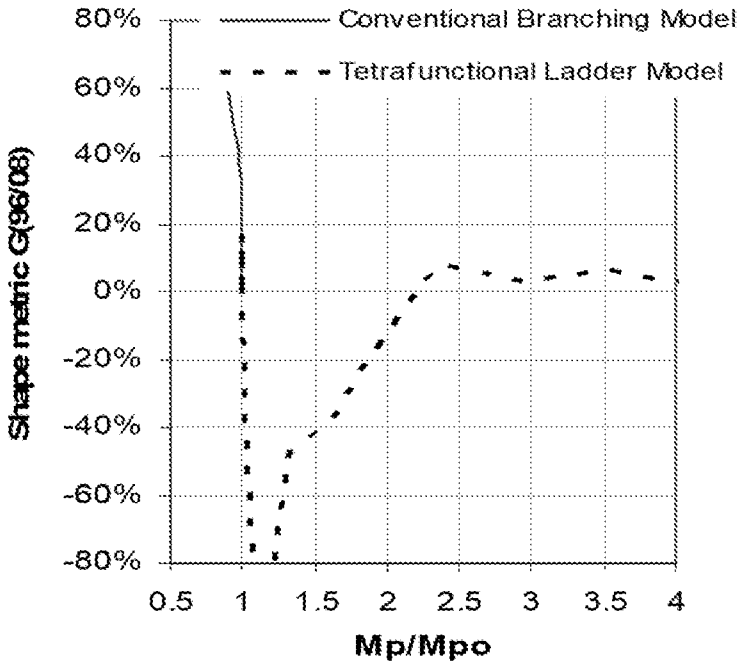

Conventional Branching Model
Tetrafunctional Ladder Model
Shape metric G(96/08)
80%
60%
40%
20%
0%
-20%
-40%
-60%
-80%
0.5
1
1.5
2
2.5
3
3.5
4
Mp/Mpo

FIG. 13

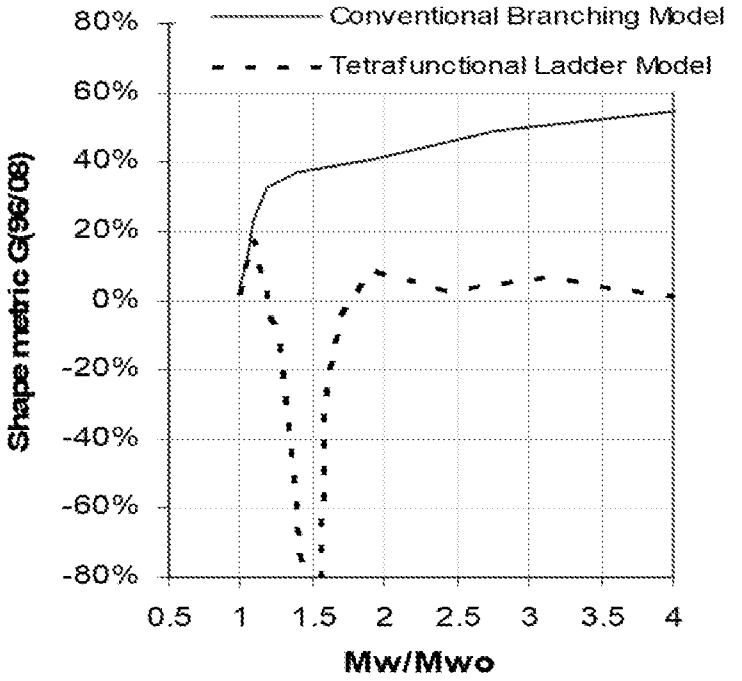

Conventional Branching Model
Tetrafunctional Ladder Model
Shape metric G(96/08)
80%
60%
40%
20%
0%
-20%
-40%
-60%
-80%
0.5
1
1.5
2
2.5
3
3.5
4
Mw/Mwo

FIG. 14

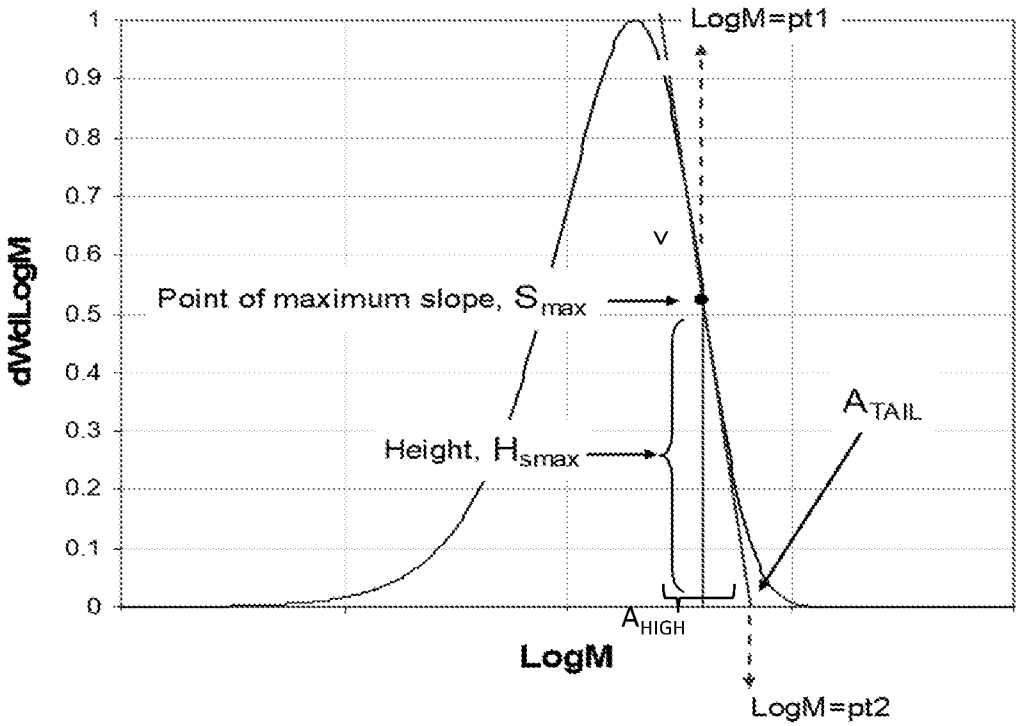

LogM=pt1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
dWdLogM
V
Point of maximum slope, S_{max}
Height, H_{smax}
A_{TAIL}
A_{HIGH}
LogM
LogM=pt2

FIG. 15

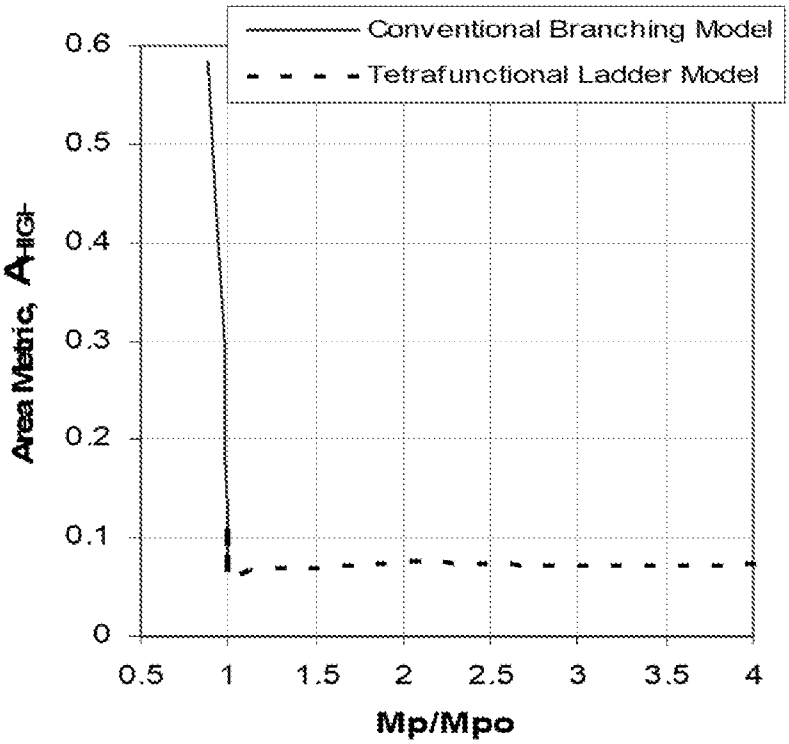

Conventional Branching Model
Tetrafunctional Ladder Model
Area Metric, A_{HGI}
0.6
0.5
0.4
0.3
0.2
0.1
0
0.5
1
1.5
2
2.5
3
3.5
4
Mp/Mpo

FIG. 16

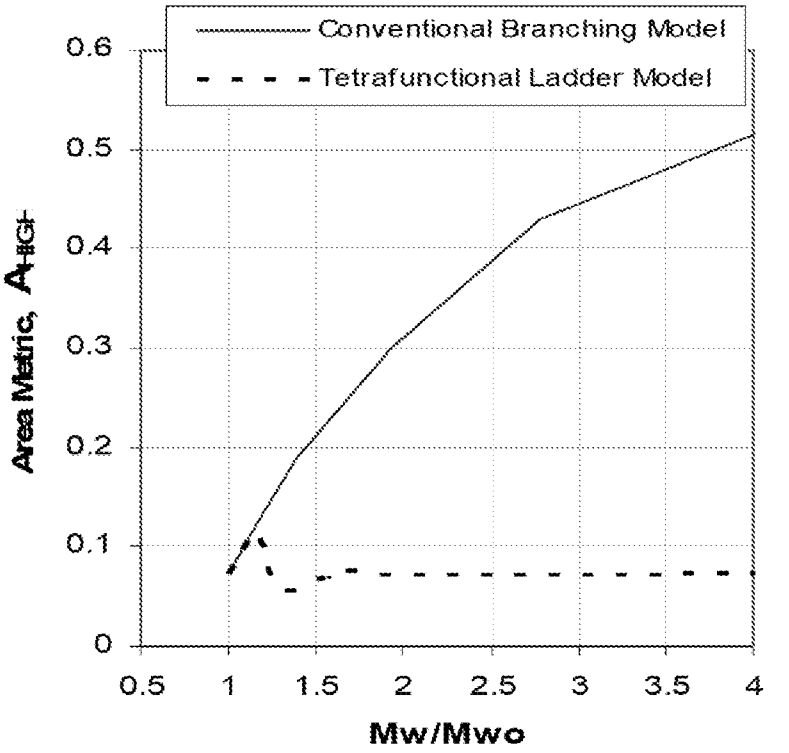

Conventional Branching Model
Tetrafunctional Ladder Model
Area Metric, A_{HGI}
0.6
0.5
0.4
0.3
0.2
0.1
0
0.5
1
1.5
2
2.5
3
3.5
4
Mw/Mwo

FIG. 17

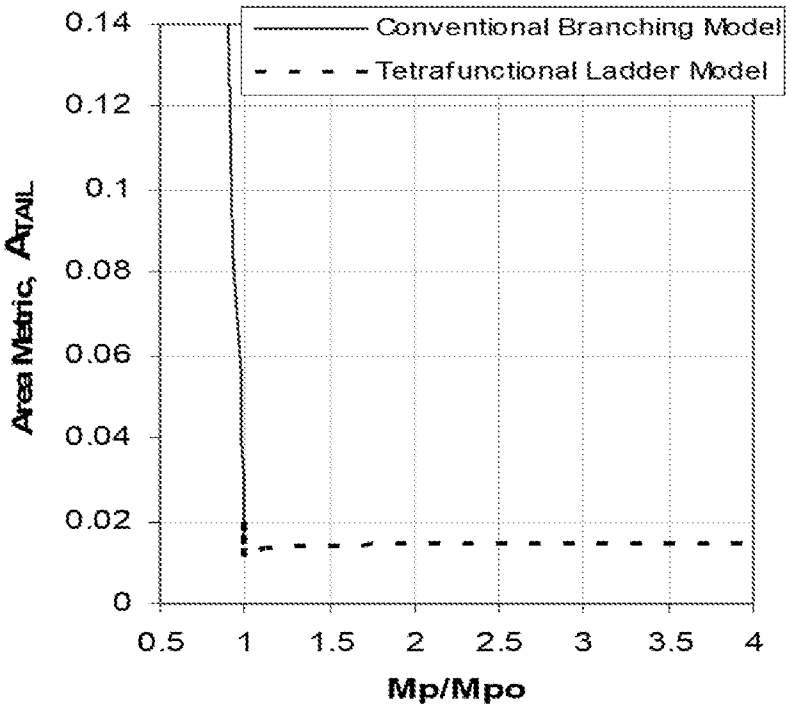

Conventional Branching Model
Tetrafunctional Ladder Model
Area Metric, A_{TAIL}
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
0.5
1
1.5
2
2.5
3
3.5
4
Mp/Mpo

FIG. 18

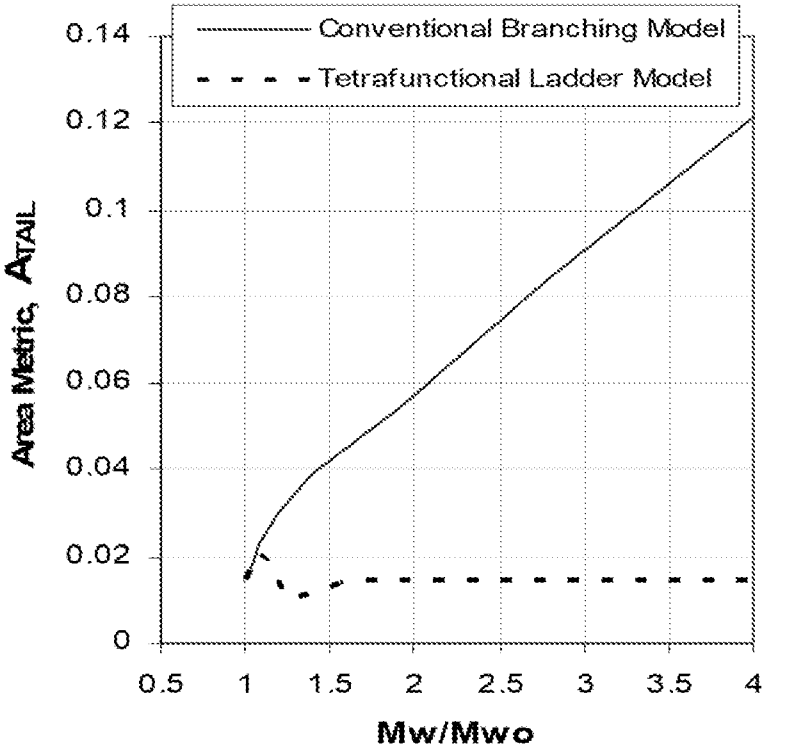

Conventional Branching Model
Tetrafunctional Ladder Model
Area Metric, A_{TAIL}
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
0.5
1
1.5
2
2.5
3
3.5
4
Mw/Mwo

FIG. 19

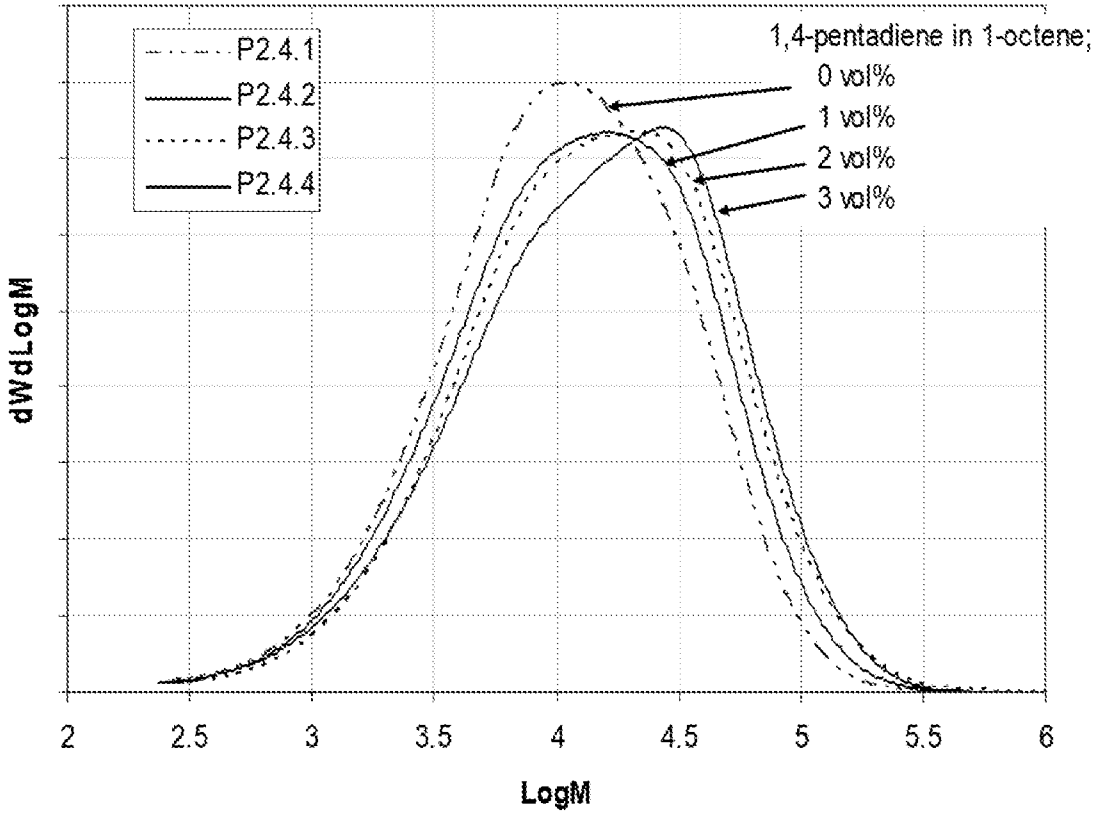

P2.4.1
P2.4.2
P2.4.3
P2.4.4
1,4-pentadiene in 1-octene;
0 vol%
1 vol%
2 vol%
3 vol%
dWdLogM
2
2.5
3
3.5
4
4.5
5
5.5
6
LogM

FIG. 20

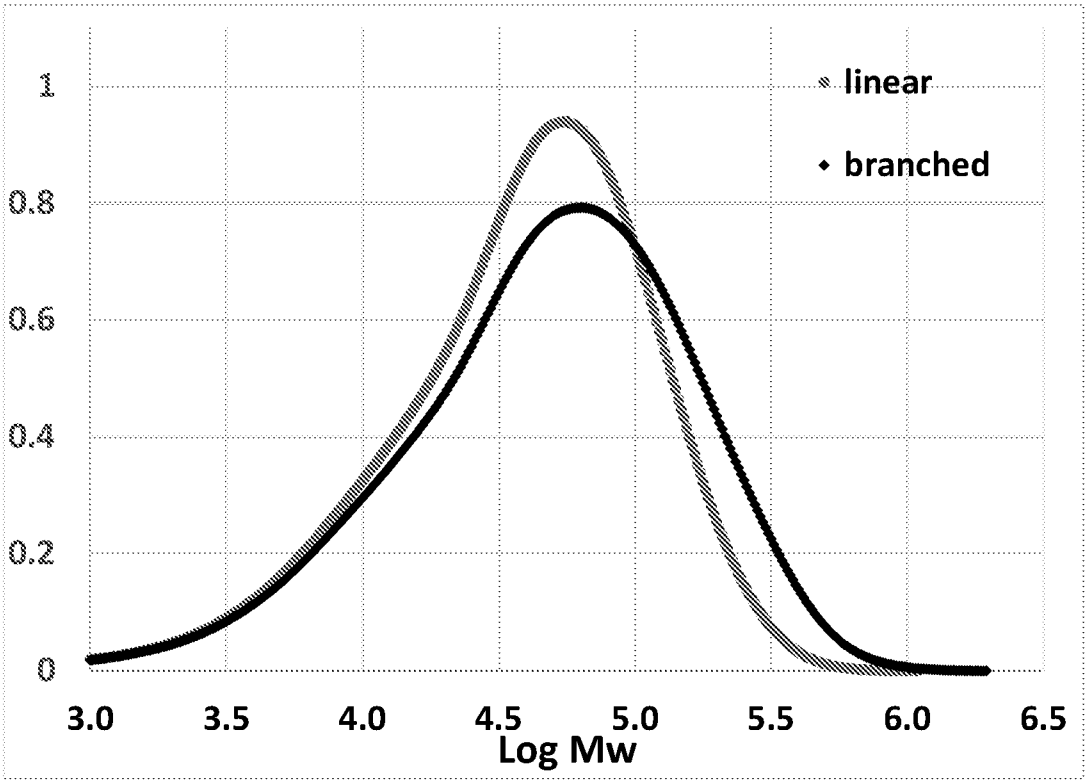

linear
branched
1
0.8
0.6
0.4
0.2
0
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
Log Mw

FIG. 21

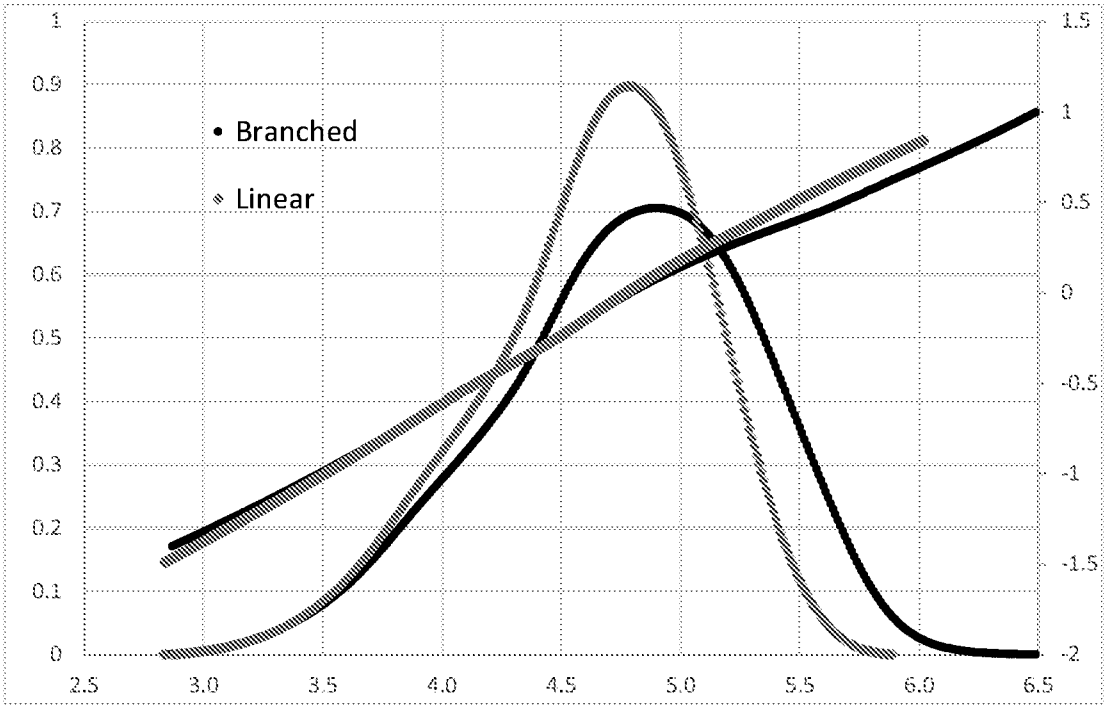

Branched
Linear
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
1.5
1
0.5
0
-0.5
-1
-1.5
-2
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5

FIG. 22

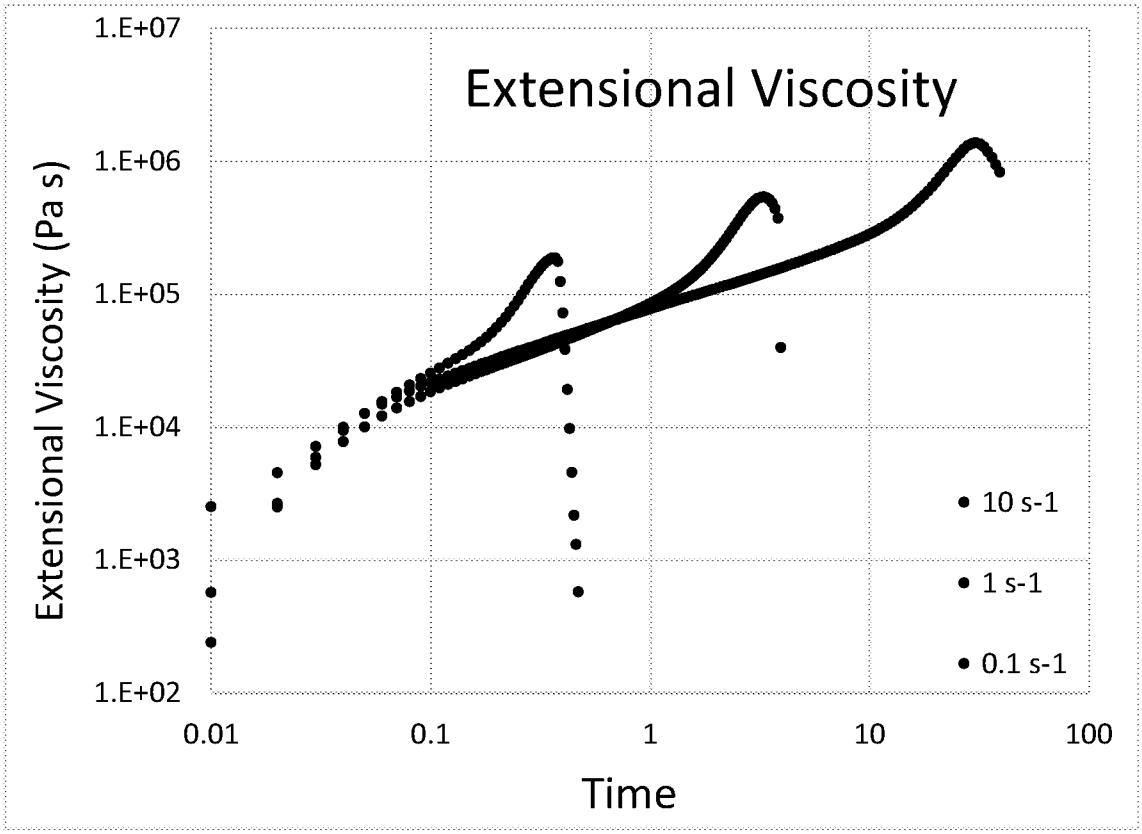

Extensional Viscosity
Extensional Viscosity (Pa s)
1.E+07
1.E+06
1.E+05
1.E+04
1.E+03
1.E+02
0.01
0.1
1
10
100
Time
10 s-1
1 s-1
0.1 s-1

FIG. 23

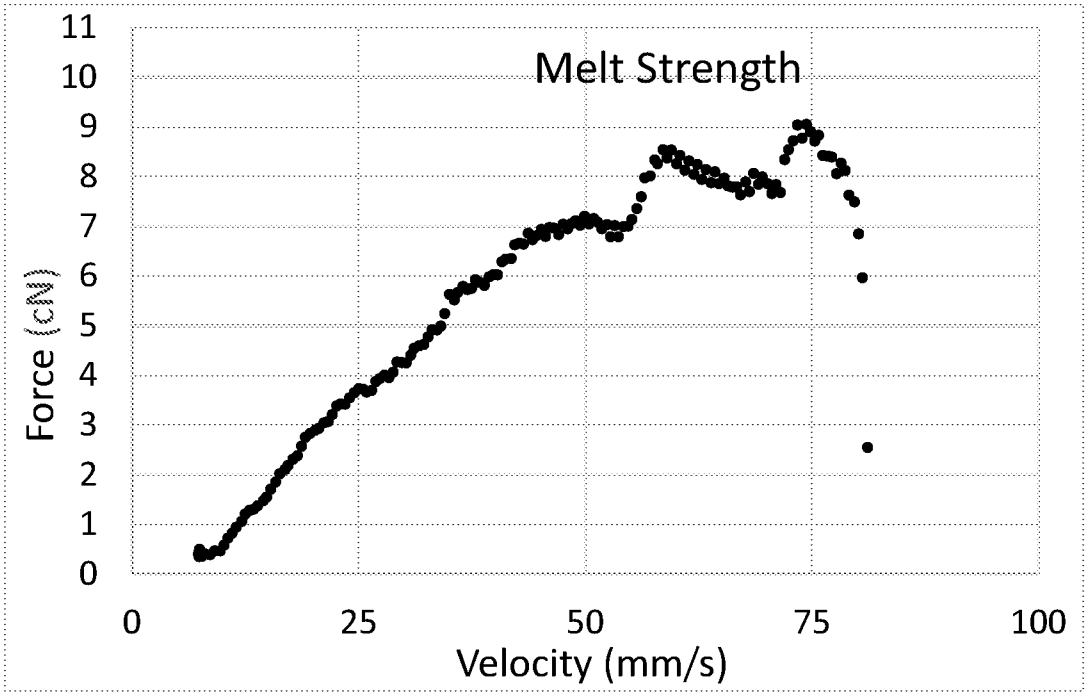

Melt Strength
Force (cN)
11
10
9
8
7
6
5
4
3
2
1
0
0
25
50
75
100
Velocity (mm/s)

FIG. 24

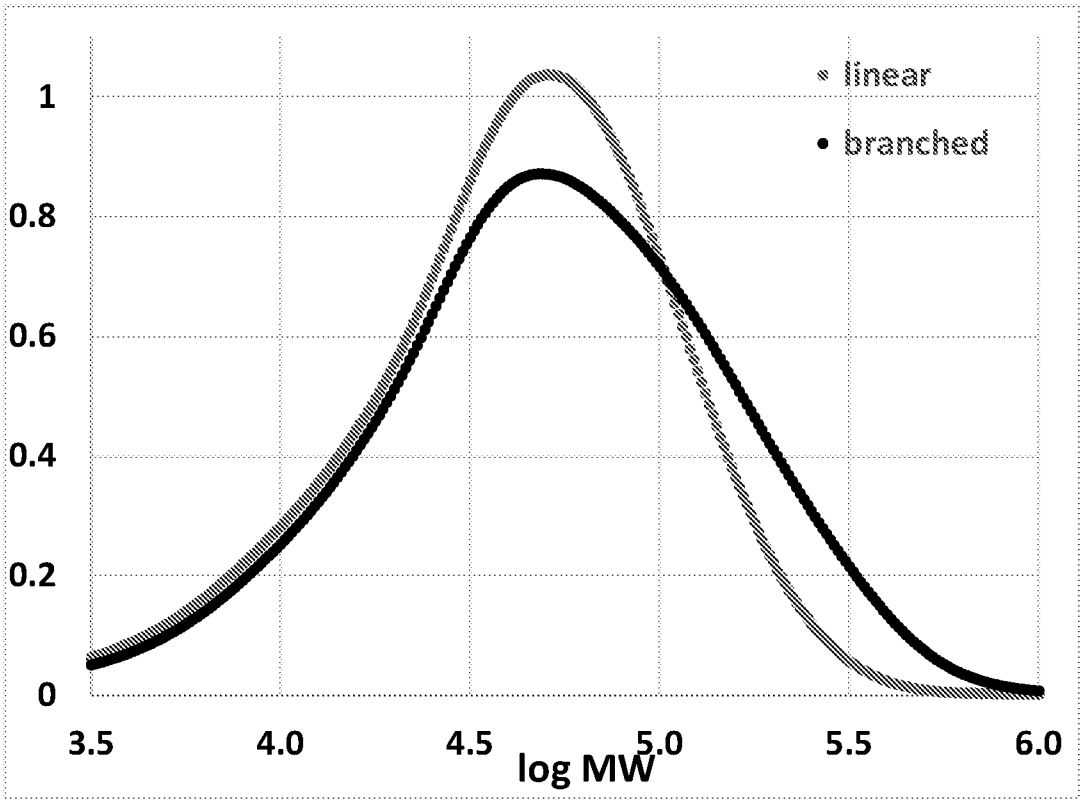

linear
branched
1
0.8
0.6
0.4
0.2
0
3.5
4.0
4.5
5.0
5.5
6.0
log MW

FIG. 25

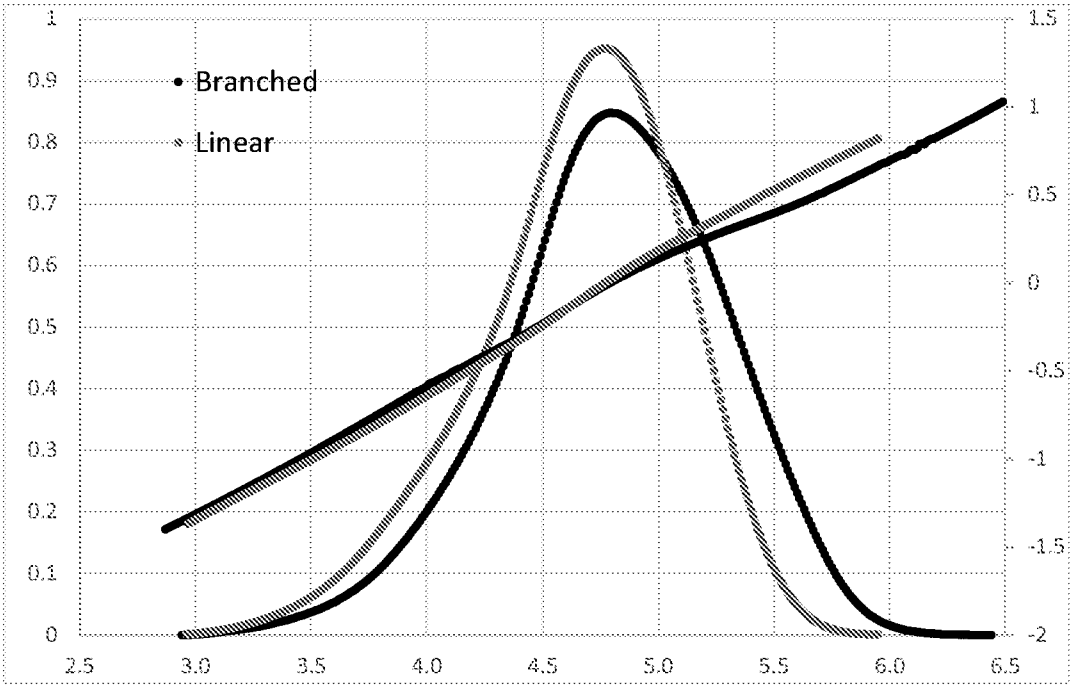

Branched
Linear
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
1.5
1
0.5
0
-0.5
-1
-1.5
-2
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5

FIG. 26

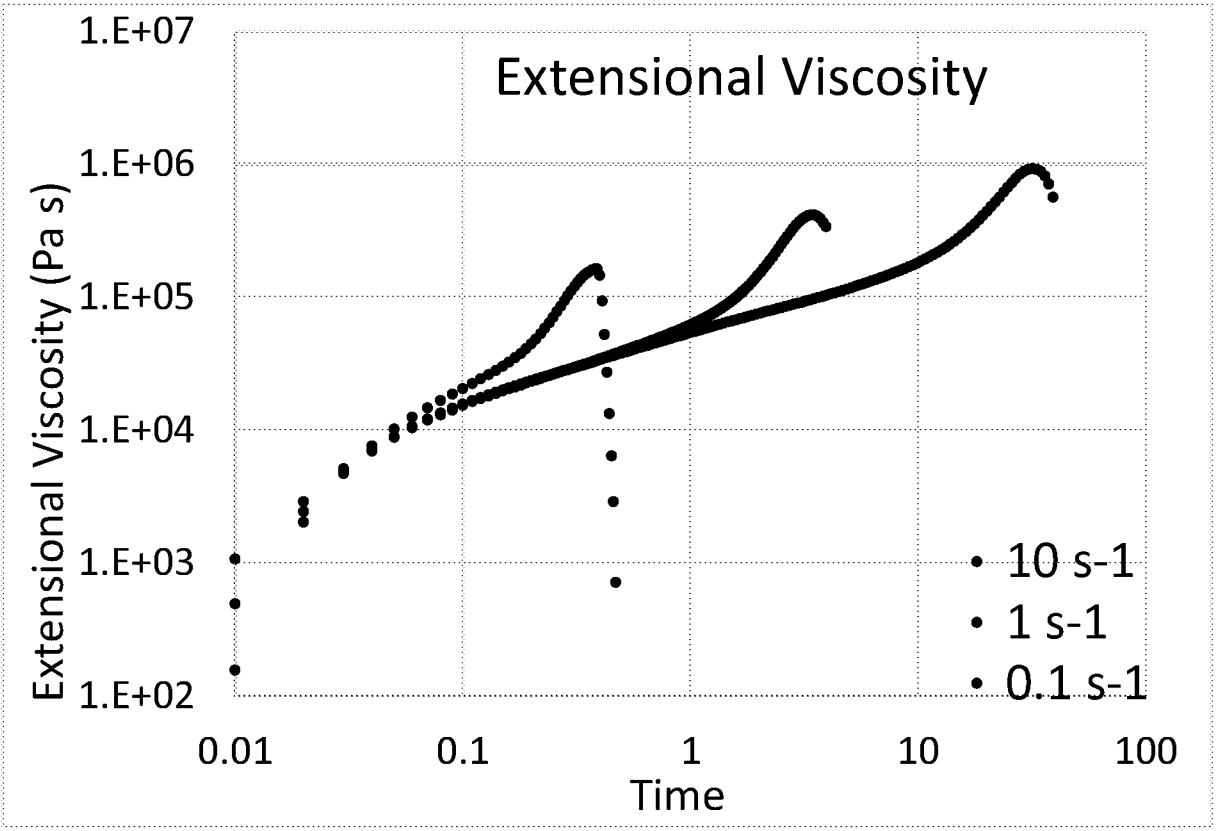

Extensional Viscosity
Extensional Viscosity (Pa s)
1.E+07
1.E+06
1.E+05
1.E+04
1.E+03
1.E+02
0.01
0.1
1
10
100
Time
10 s-1
1 s-1
0.1 s-1

FIG. 27

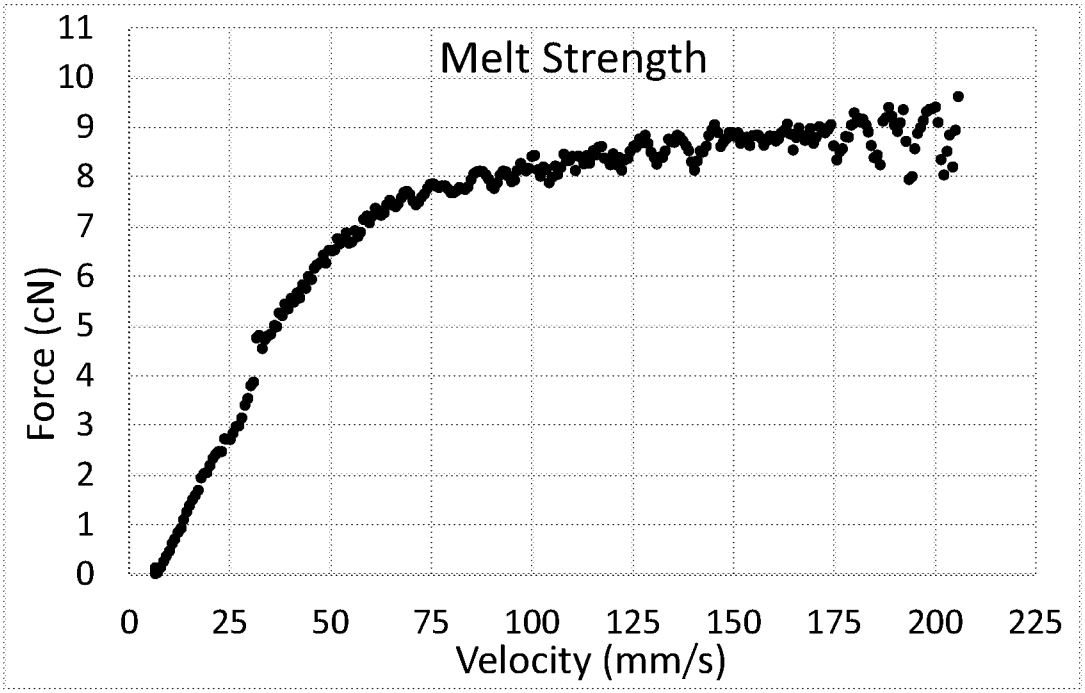

Melt Strength
Force (cN)
11
10
9
8
7
6
5
4
3
2
1
0
0
25
50
75
100
125
150
175
200
225
Velocity (mm/s)

FIG. 28

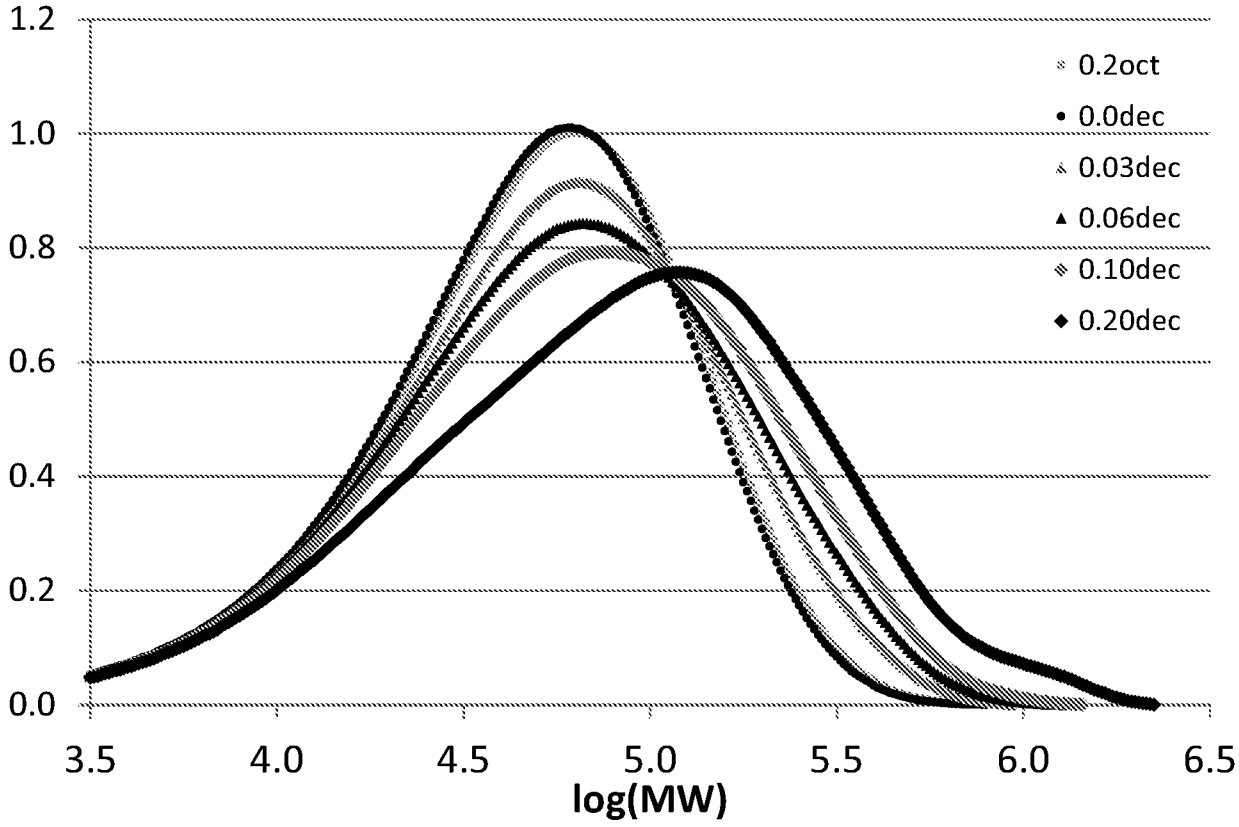

1.2
1.0
0.8
0.6
0.4
0.2
0.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
log(MW)
0.2oct
0.0dec
0.03dec
0.06dec
0.10dec
0.20dec

FIG. 29

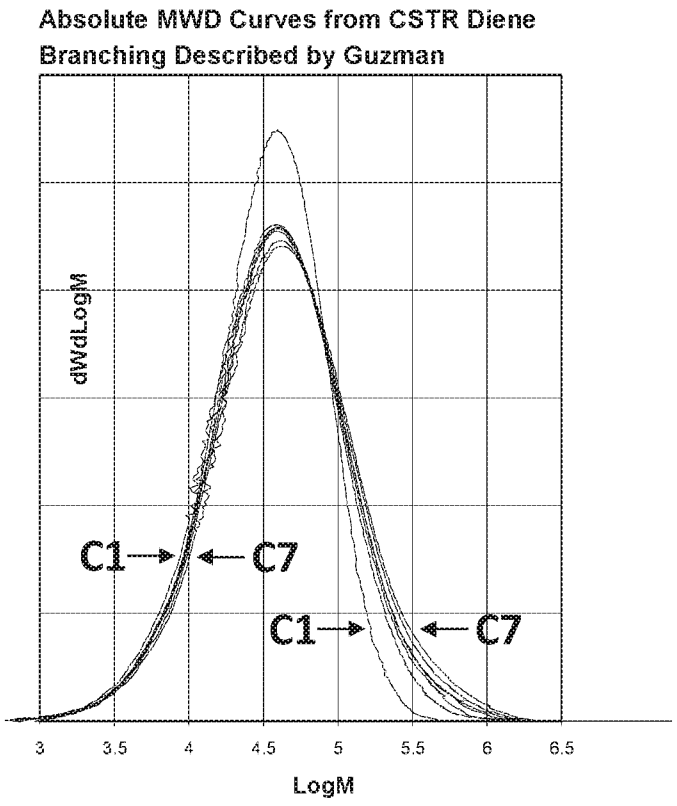


FIG. 30A

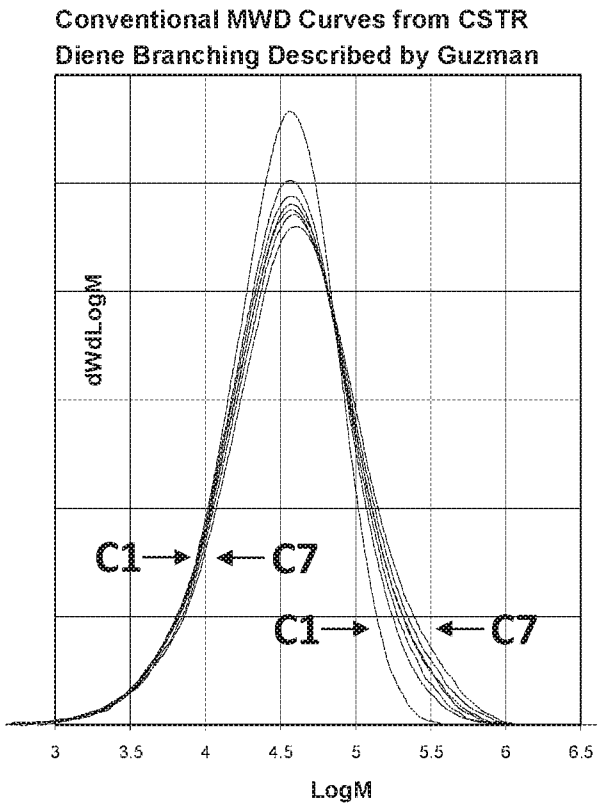


FIG. 30B

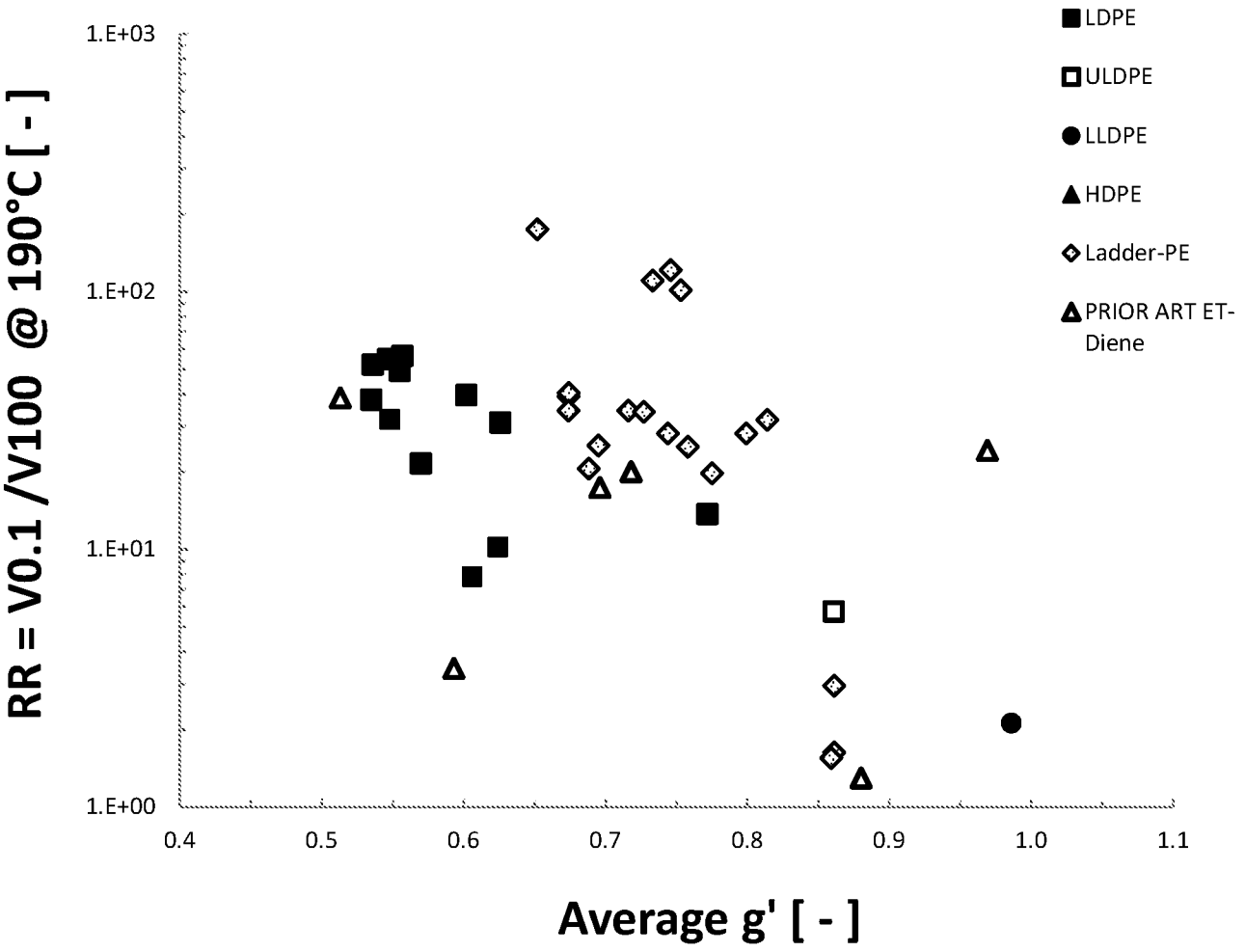

RR = V0.1 /V100 @ 190°C [-]
1.E+03
1.E+02
1.E+01
1.E+00
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
Average g' [-]
LDPE
ULDPE
LLDPE
HDPE
Ladder-PE
PRIOR ART ET-Diene

FIG. 31

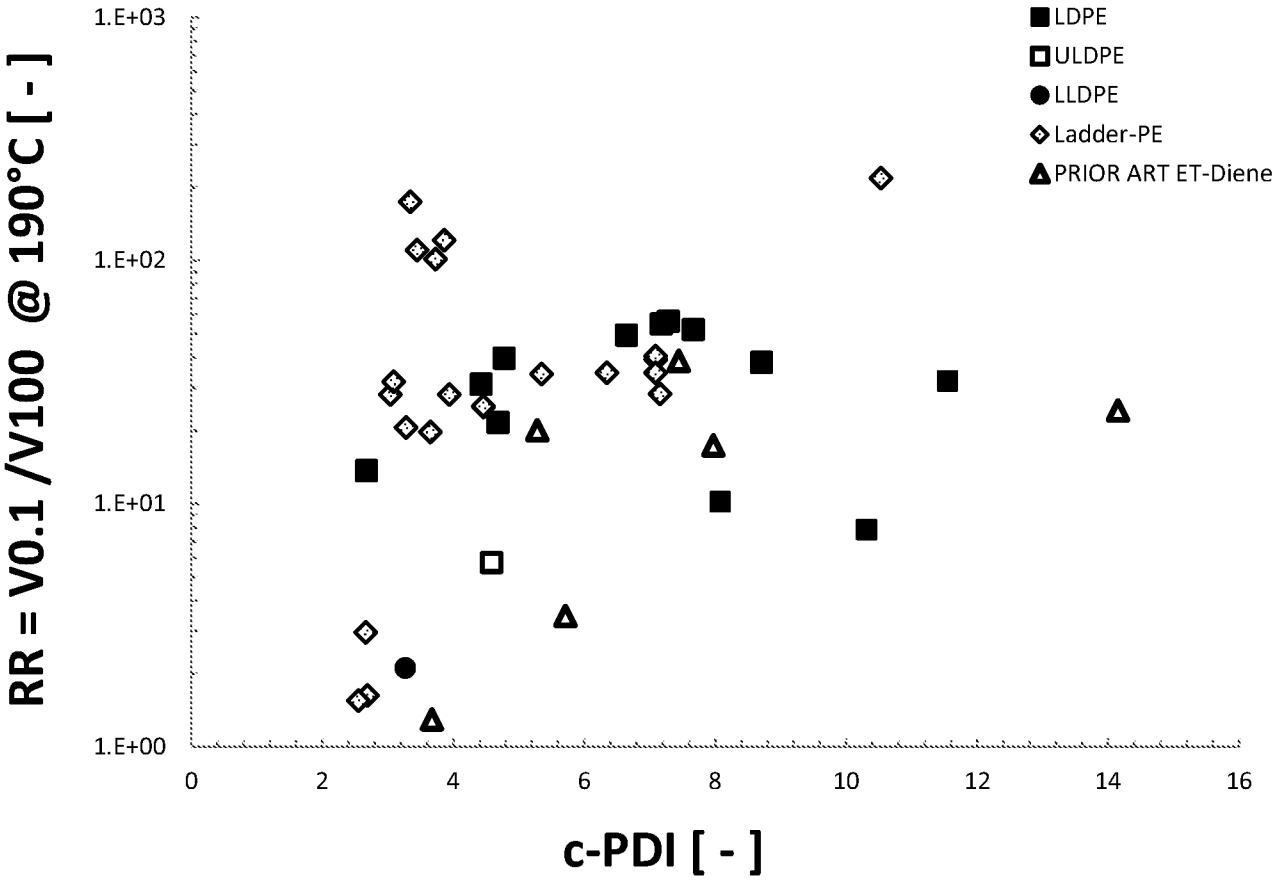

RR = V0.1 /V100 @ 190°C [-]
1.E+03
1.E+02
1.E+01
1.E+00
0
2
4
6
8
10
12
14
16
c-PDI [-]
LDPE
ULDPE
LLDPE
Ladder-PE
PRIOR ART ET-Diene

FIG. 32

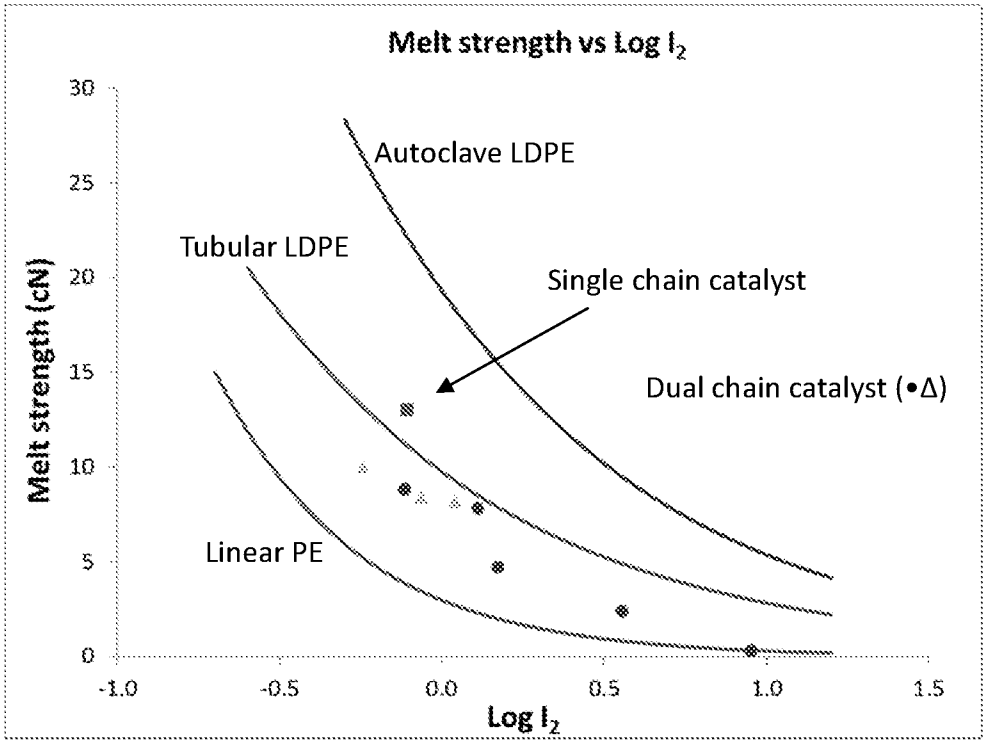

Melt strength vs Log I_2
Melt strength (cN)
30
25
20
15
10
5
0
-1.0
-0.5
0.0
0.5
1.0
1.5
Log I_2
Autoclave LDPE
Tubular LDPE
Single chain catalyst
Dual chain catalyst (•Δ)
Linear PE

FIG. 33