

Supporting Information:

The Use of Methyl 2-(Bromomethyl) Acrylate as a Chain-transfer Agent to Yield Functionalized Macromonomers via Conventional and Living Radical Polymerizations

Stefan A. F. Bon, Stuart R. Morsley, Carl Waterson, and David M. Haddleton**

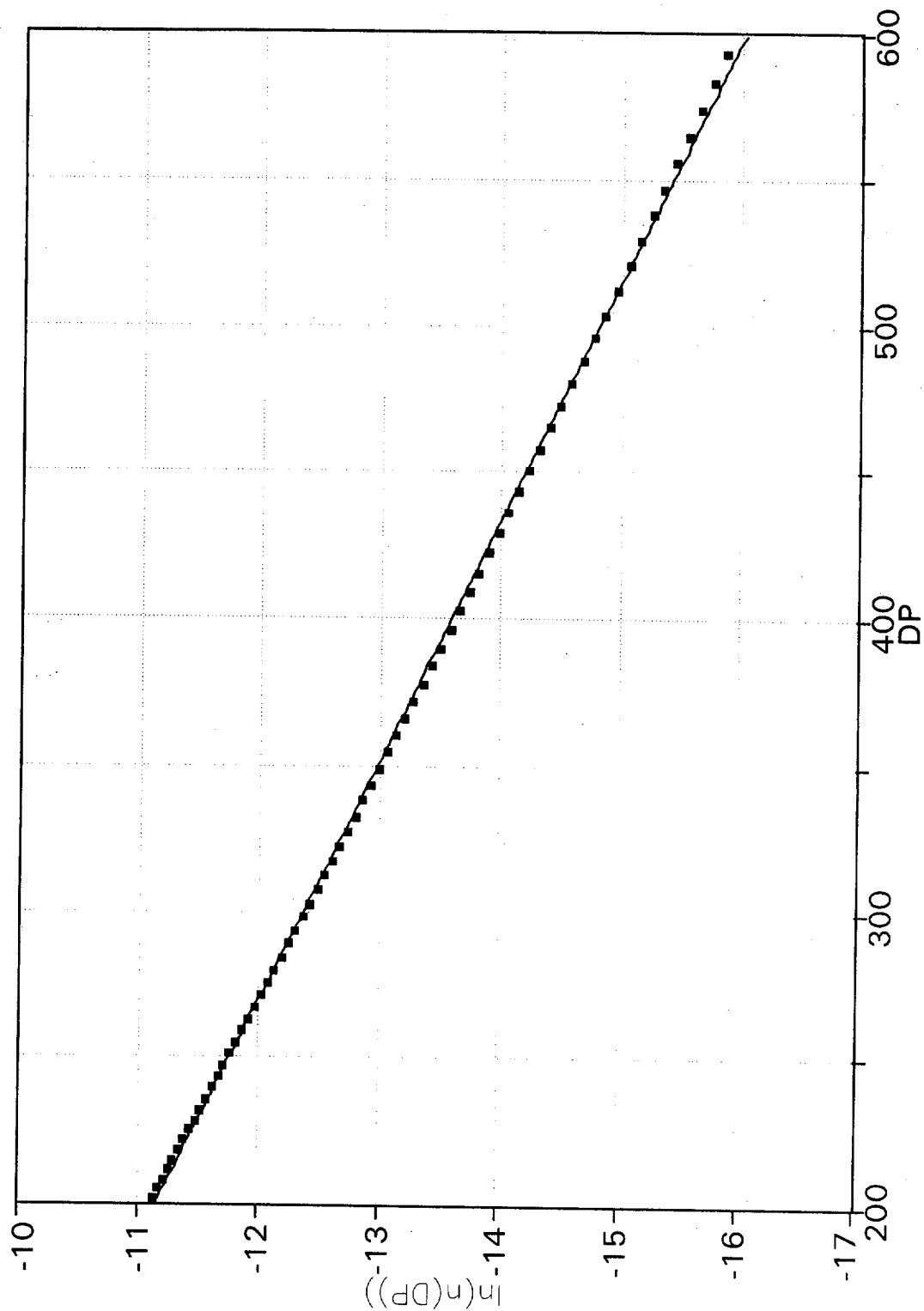
Department of Chemistry, University of Warwick, Coventry, CV4 7AL, UK.

*E-mail: S.Bon@warwick.ac.uk or D.M.Haddleton@warwick.ac.uk; Tel 44-(0)24 7652 8438 or 3256; Fax 44-(0)24 7652 4112.

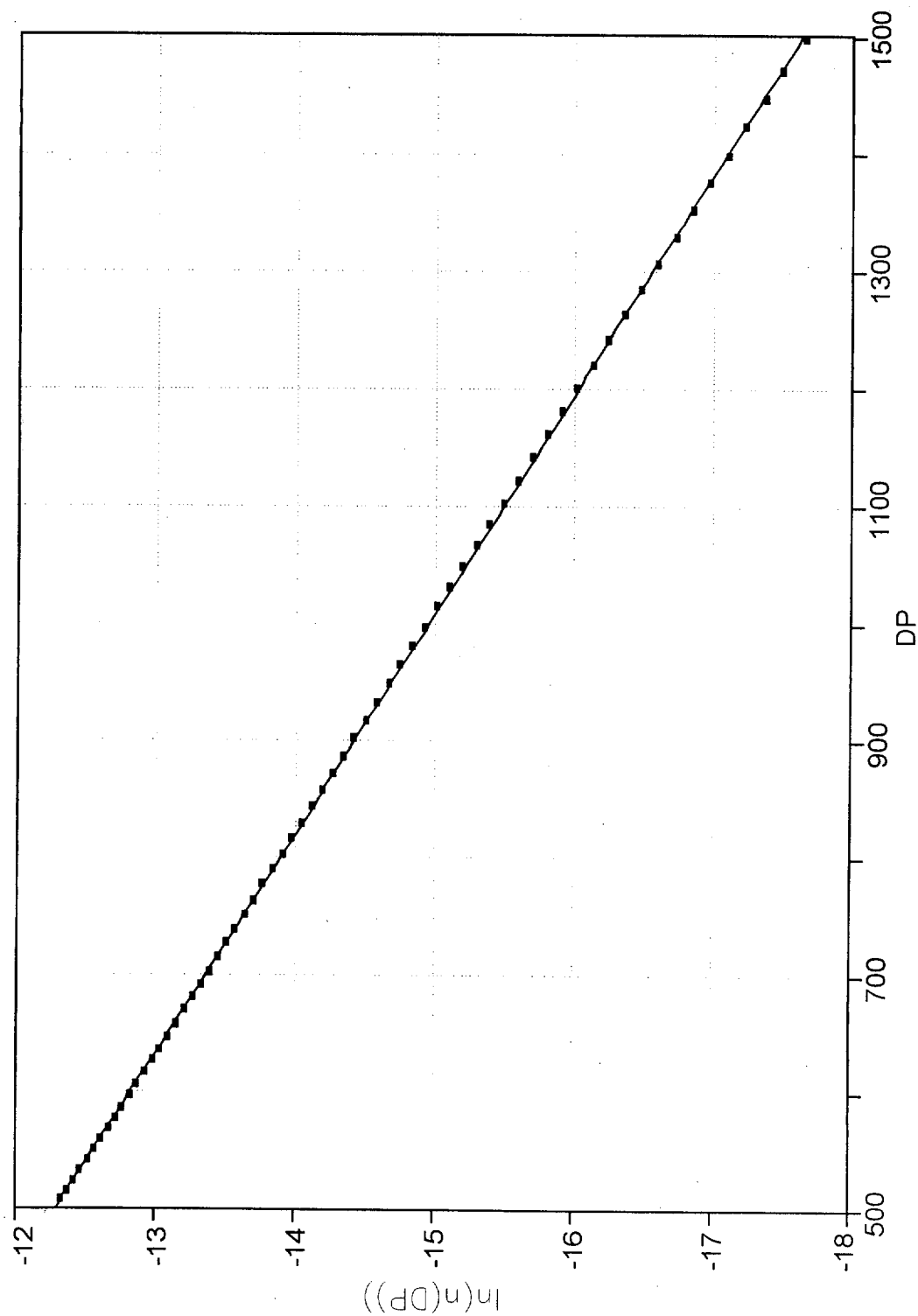
Contents:

- 1) linear fit on the high molar mass part of $\ln[n(DP)]$ (natural logarithm of the number molar mass distribution as a function of the degree of polymerization) with significant signal intensity for different samples MMA/MBrMA-A to E and Sty/MBrMA-A to E.
- 2) $[S]/[M]$, $\langle M_n \rangle$, $\langle M_w \rangle$, Mayo fits and CLD fits for the determination of the chain transfer constant for both MMA and Styrene.
- 3) Details of the atom transfer polymerization reactions.

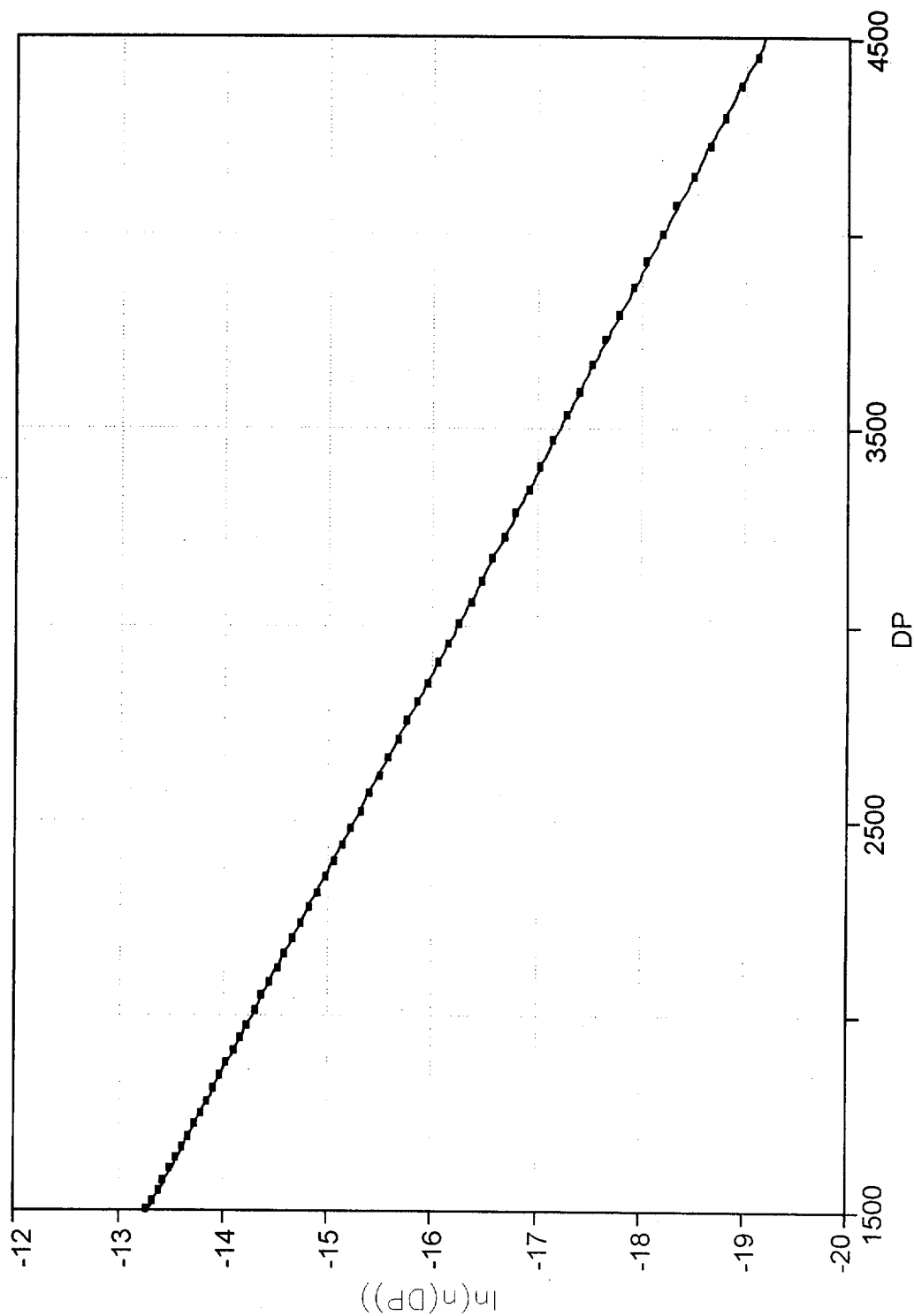
MMA/MBrMMA-A

Rank 4 Eqn 1 $y = a + bx$ $r^2 = 0.999571603$ DF Adj = 0.999558621 FitStdErr = 0.0290744413 Fstat = 156329.825 $a = -8.7206468$ $b = -0.012205184$ 

MMA/MBrMMA-B

Rank 2 Eqn 1 $y=a+bx$ $r^2=0.999929046$ DF Adj $r^2=0.999926793$ FitStdErr=0.0131061595 Fstat=901927.889 $a=-9.6335935$ $b=-0.0053304796$ 

MMA/MBrMMA-C

Rank 1 Eqn 1 $y=a+bx$ $r^2=0.999975056$ DF Adj $r^2=0.999974225$ FitStdErr=0.00856407918 Fstat=2445421.12 $a=-10.356909$ $b=-0.0019658456$ 

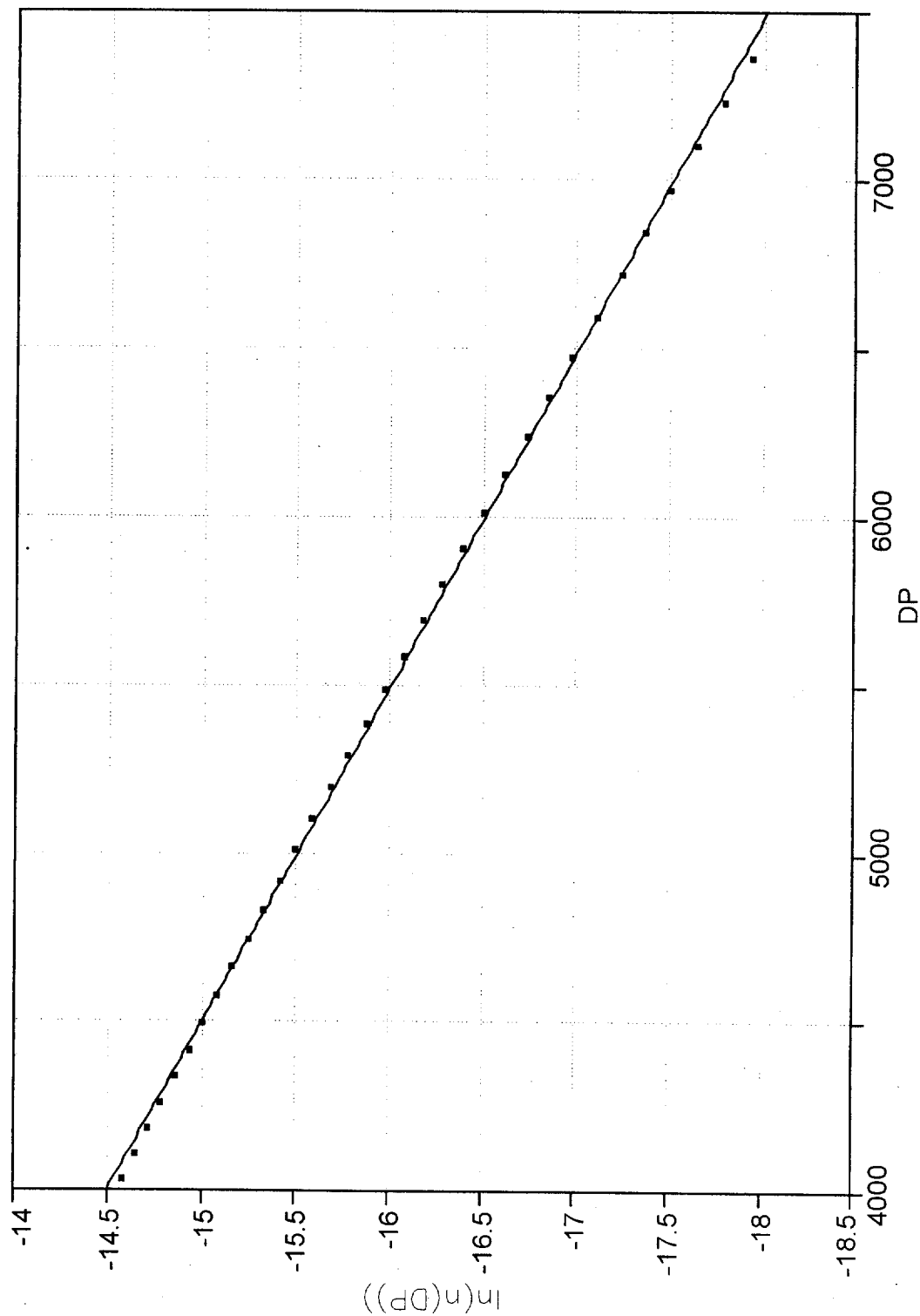
MMA/MBrMMA-D

Rank 8 Eqn 1 $y=a+bx$

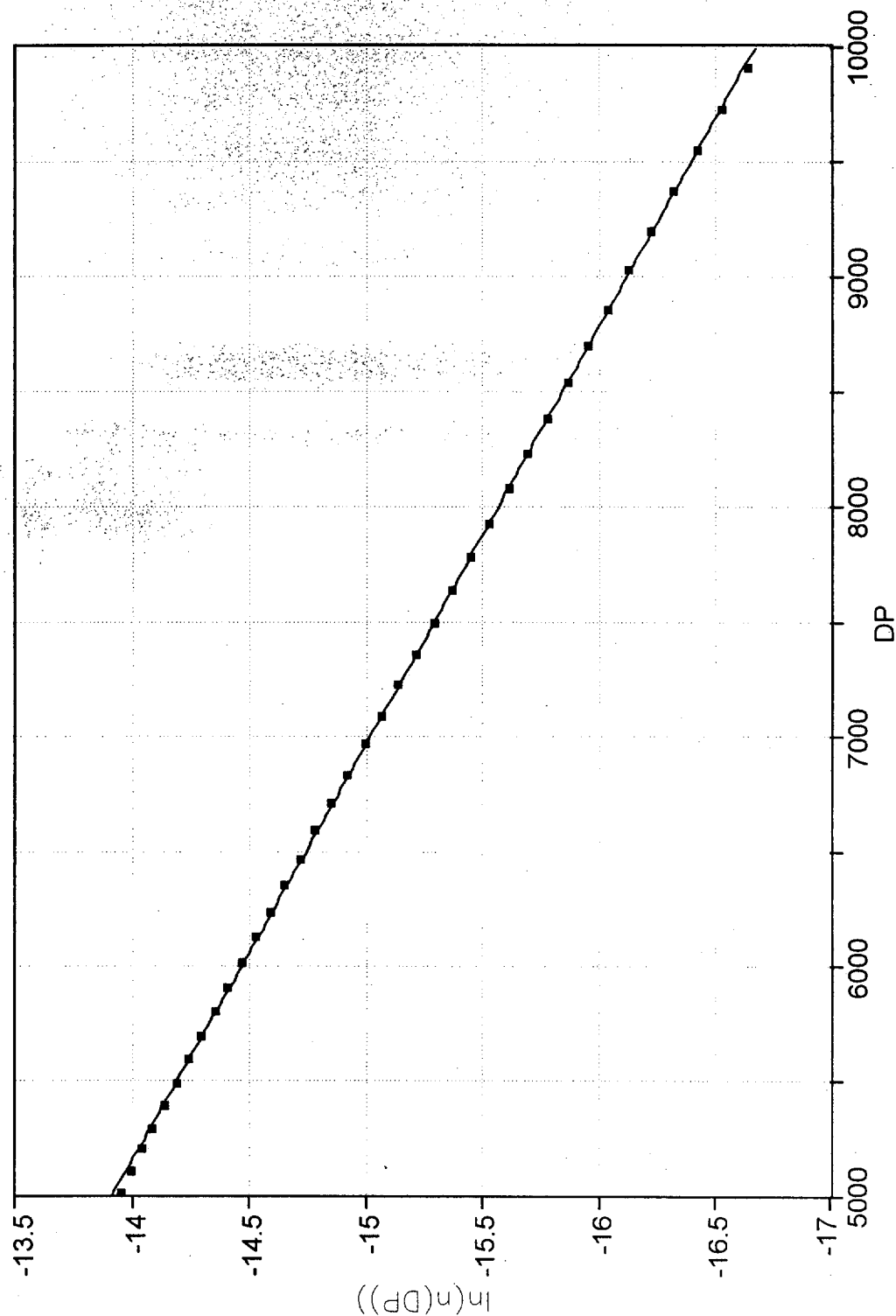
$r^2=0.999400136$ DF Adj $r^2=0.999361435$ FitStdErr=0.0250875805 Fstat=53313.4562

$a=-10.483229$

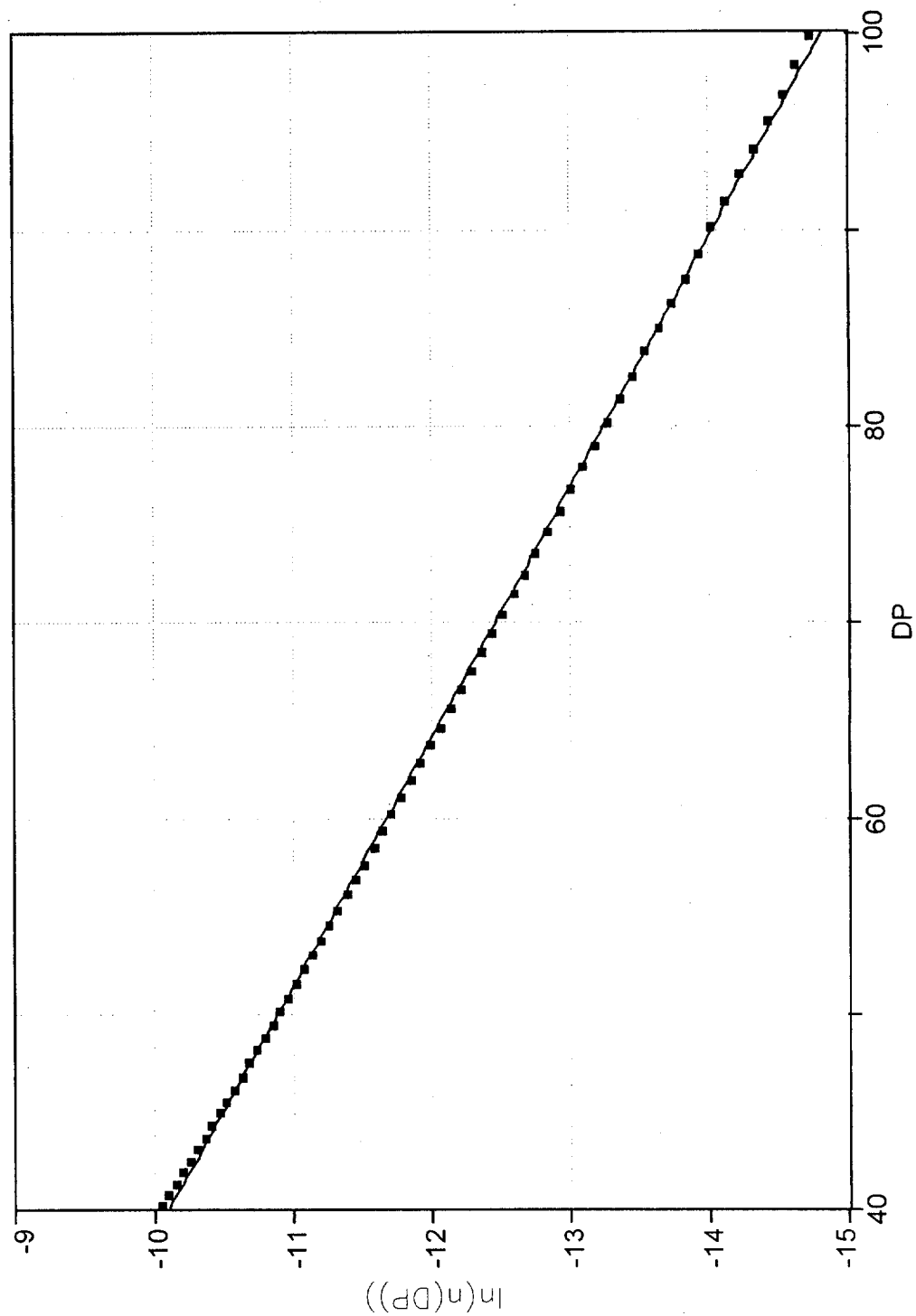
$b=-0.0010058016$



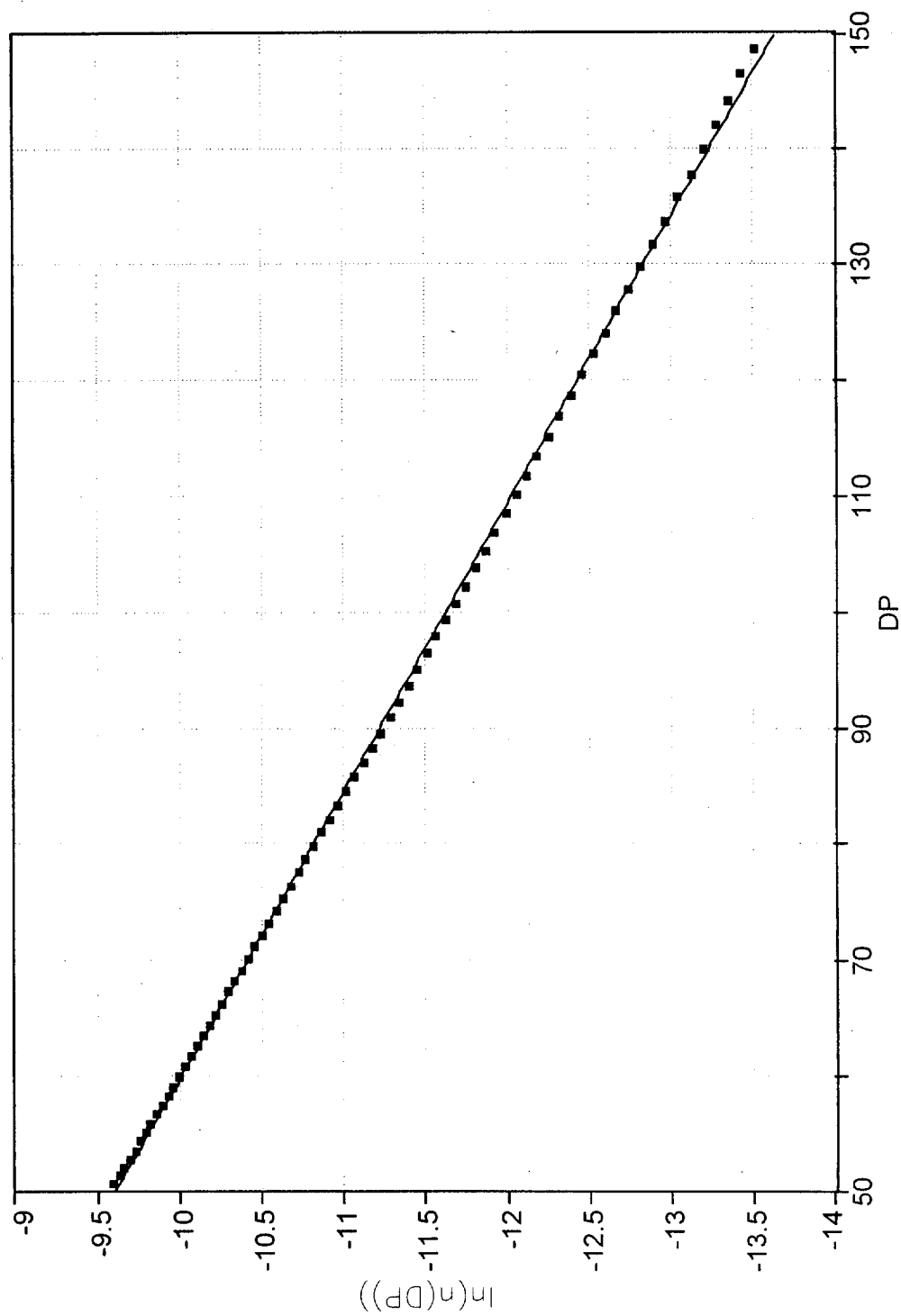
MMA/MBrMMA-E

Rank 4 Eqn 1 $y=a+bx$ $r^2=0.999869885$ DF Adj $r^2=0.99986245$ FitStdErr=0.00934980113 Fstat=276641.861 $a=-11.16161$ $b=-0.00055166008$ 

Sty/MBrMA-A

Rank 4 Eqn 1 $y=a+bx$ $r^2=0.999633339$ DF Adj $r^2=0.999621511$ FitStdErr=0.0265523394 Fstat=171757.774 $a=-6.9571249$ $b=-0.078696628$ 

Sty/MBrMA-B

Rank 4 Eqn 1 $y=a+bx$ $r^2=0.999616847$ DF Adj $r^2=0.999606204$ FitStdErr=0.0226892852 Fstat=190451.435 $a=-7.5991953$ $b=-0.040312124$ 

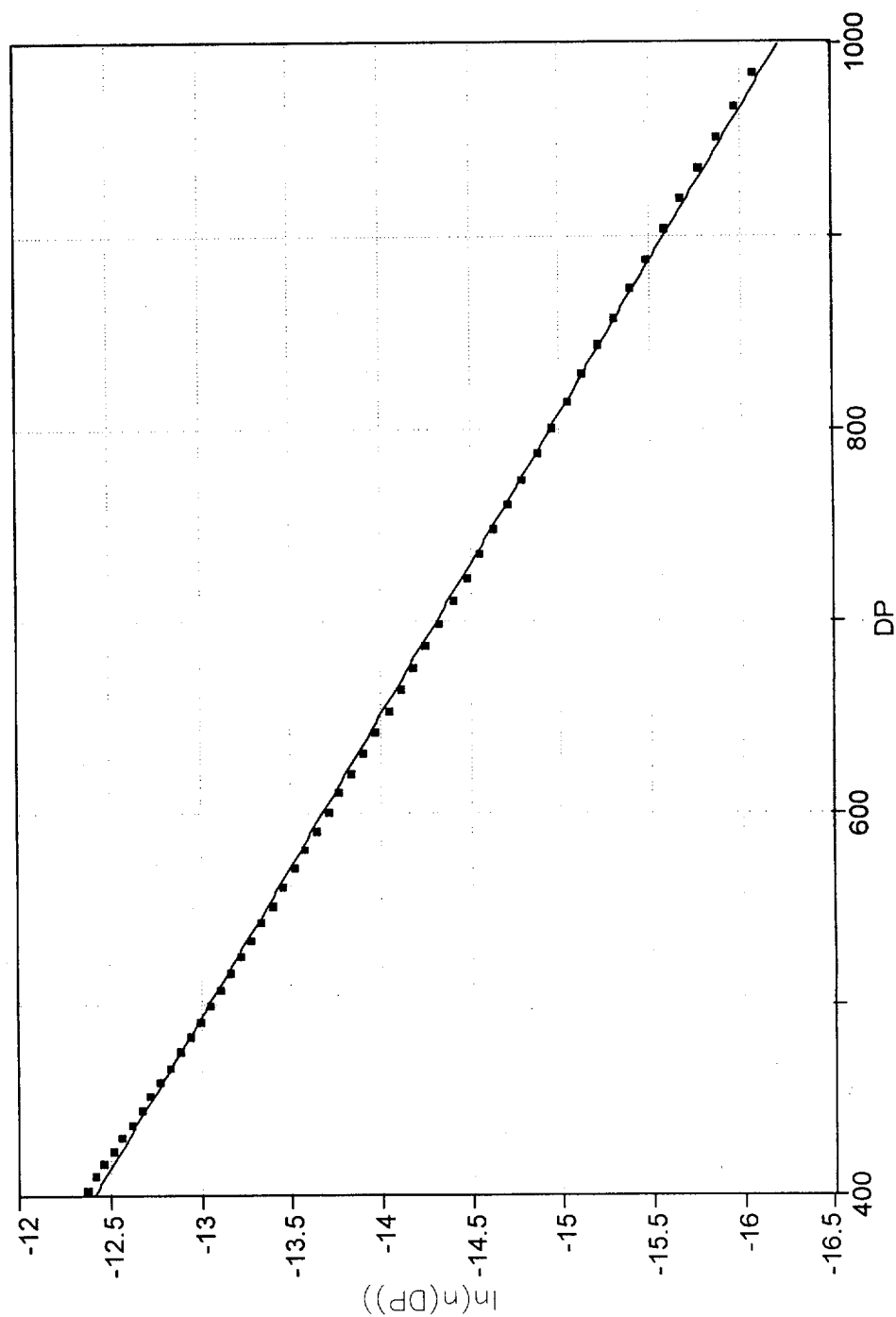
Sty/MBrMA-C

Rank 6 Eqn 1 $y=a+bx$

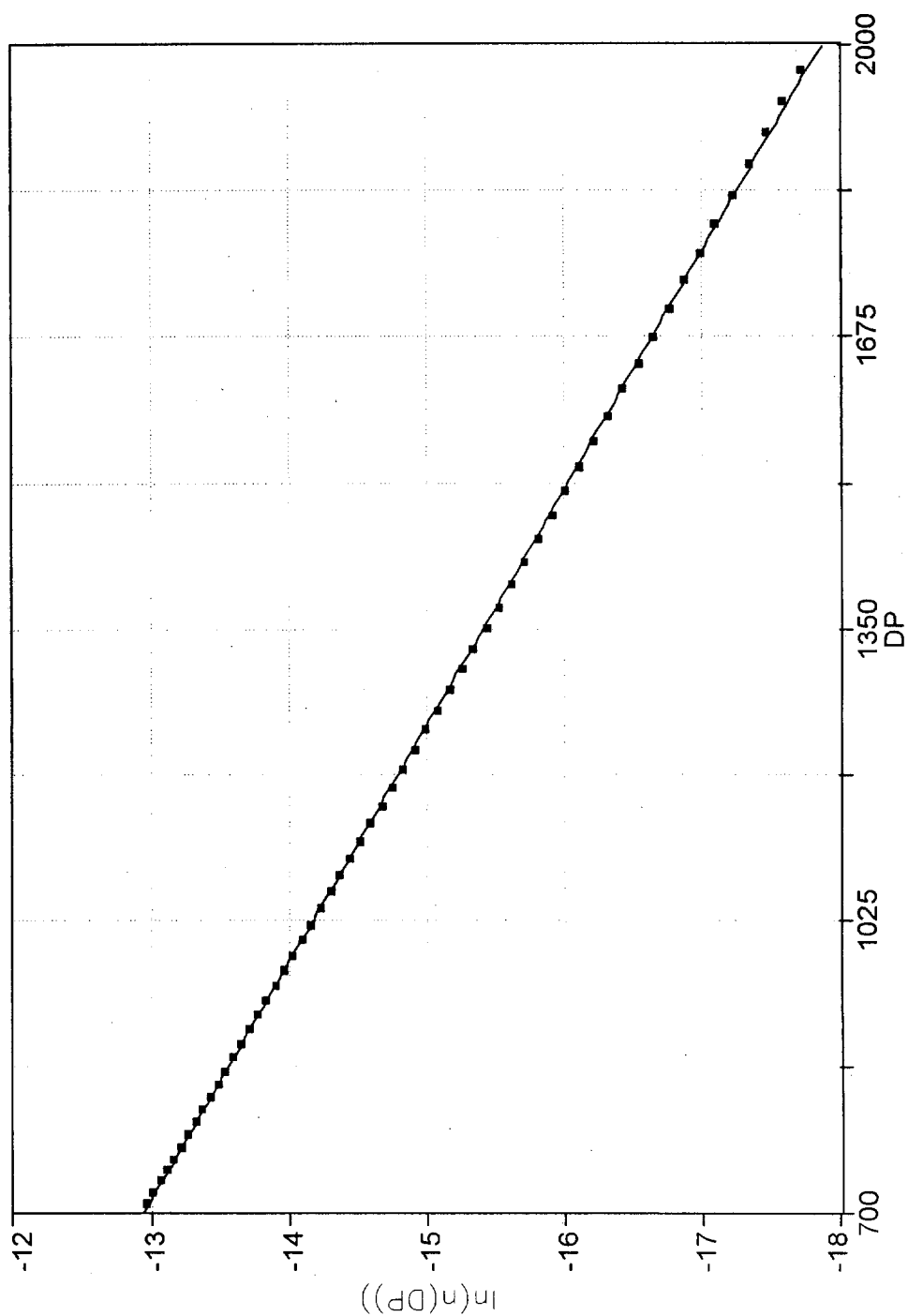
$r^2=0.99937121$ DF Adj $r^2=0.999346552$ FitStdErr=0.0275452778 Fstat=82646.5201

$a=-9.8774159$

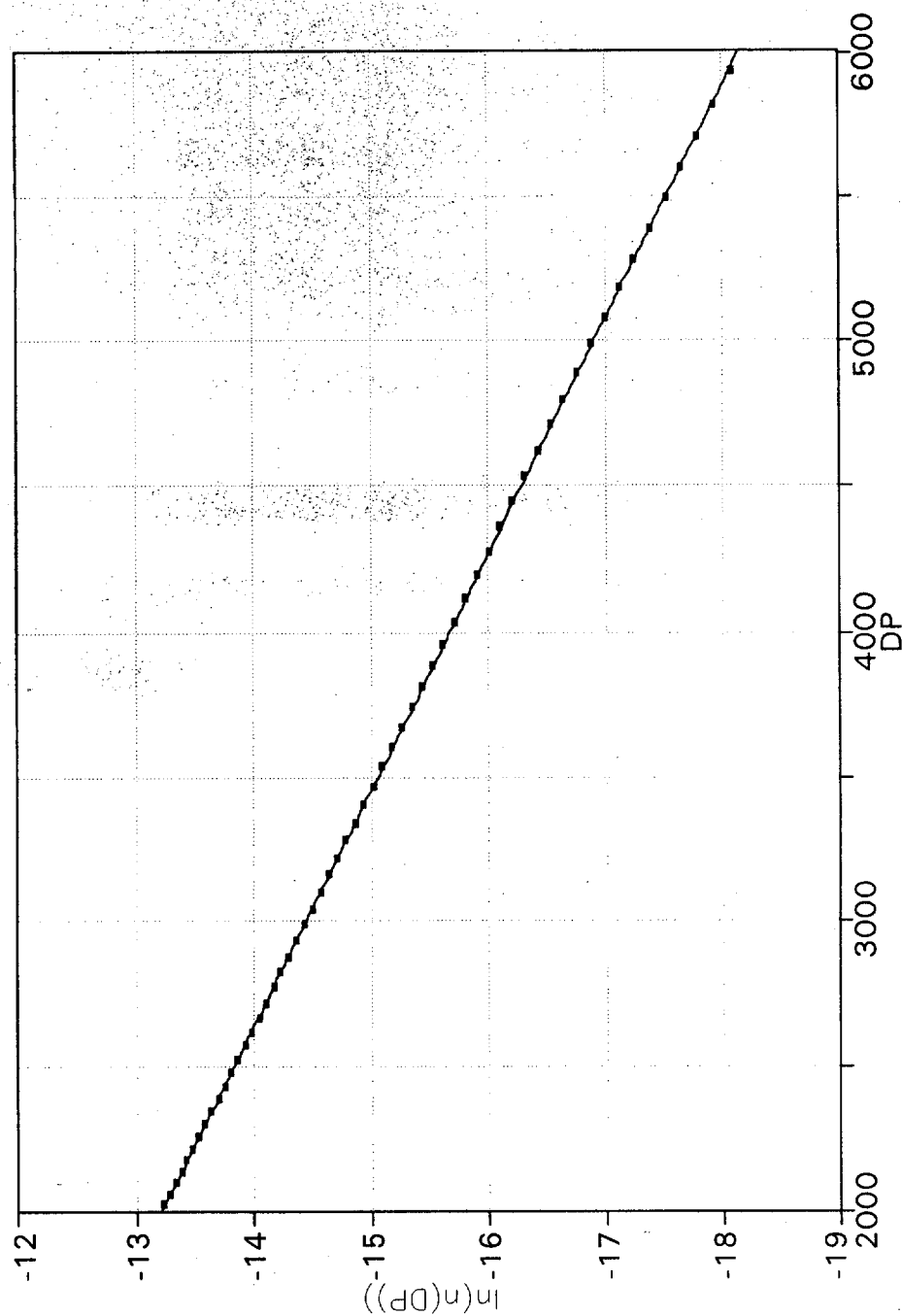
$b=-0.0063476798$



Sty/MBrMA-D

Rank 2 Eqn 1 $y=a+bx$ $r^2=0.999886719$ DF Adj $r^2=0.999882673$ FildErr=0.0150739445 Fstat=503116.39 $a=-10.287205$ $b=-0.0037972021$ 

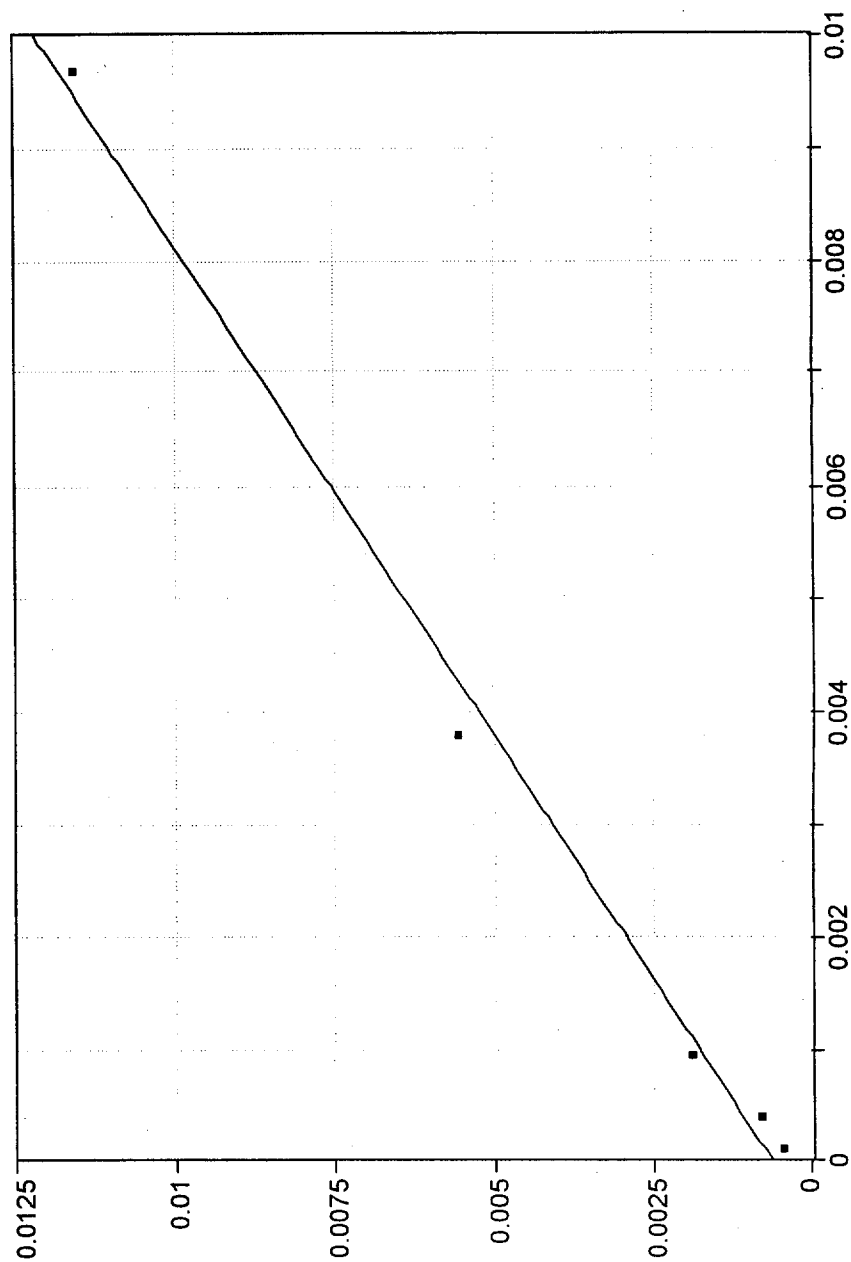
Sty/MBrMA-E

Rank 1 Eqn 1 $y = a + bx$ $r^2 = 0.999978748$ DF Adj $R^2 = 0.999977975$ FitStdErr = 0.00658063264 Fstat = 2634934.38 $a = -10.756998$ $b = -0.0012332251$ 

DETERMINATION OF CHAIN-TRANSFER CONSTANTS

METHYL METHACRYLATE IN PRESENCE OF METHYL (2-BROMOMETHYL) ACRYLATE AT 70 °C

i.d.	[S]/[M]	$\langle M_n \rangle$	$\langle M_w \rangle$
A	9.69×10^{-3}	8672	15613
B	3.78×10^{-3}	18062	34842
C	9.36×10^{-4}	53203	100613
D	3.87×10^{-4}	125843	219412
E	9.29×10^{-5}	219203	391583

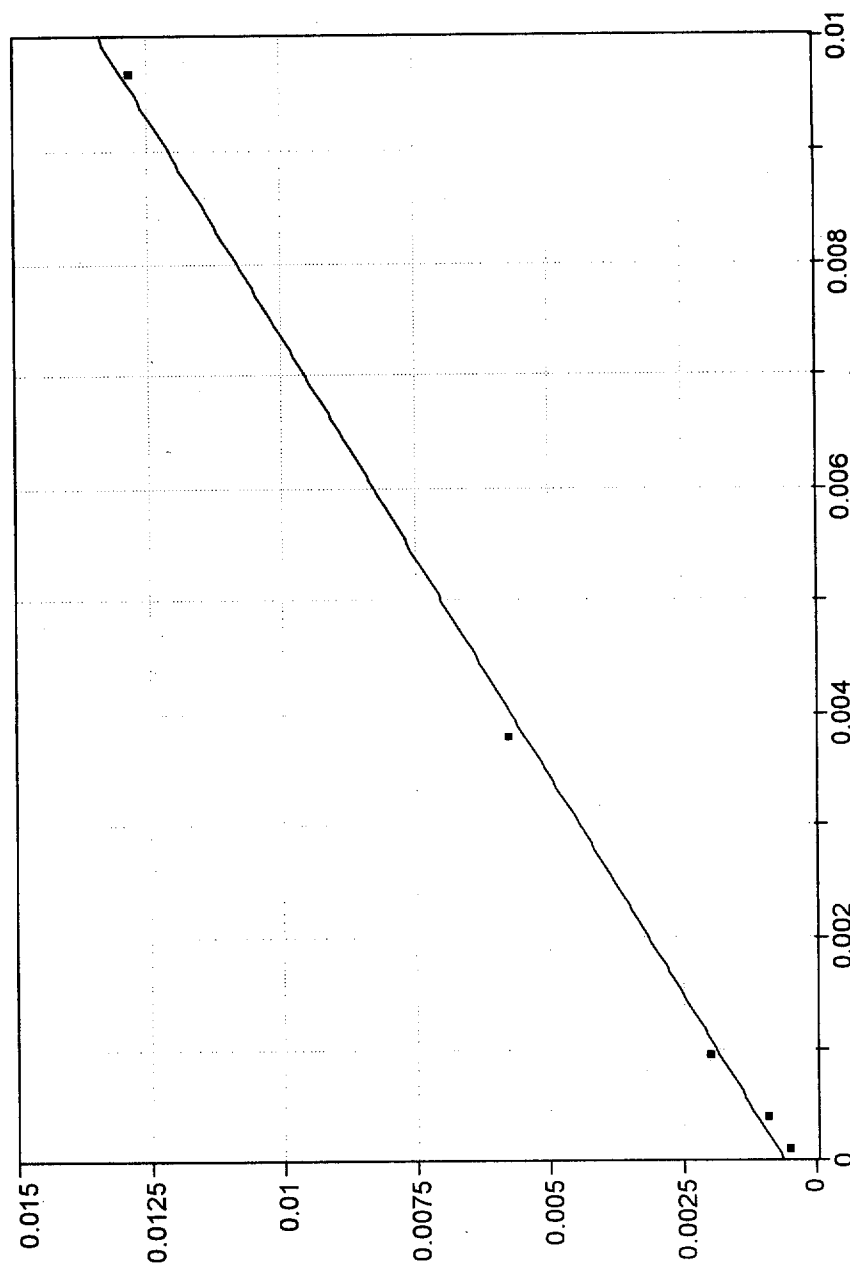
MAYO EQUATION:**Mayo FIT for Methyl Methacrylate using 1/DP_n**Rank 13 Eqn 1 $y=a+bx$ $r^2=0.993493824$ DF Adj r $2=0.986987648$ FitSdErr= 0.000433399551 Fstat= 458.100352 $a=0.00061679014$ $b=1.1513111$ 

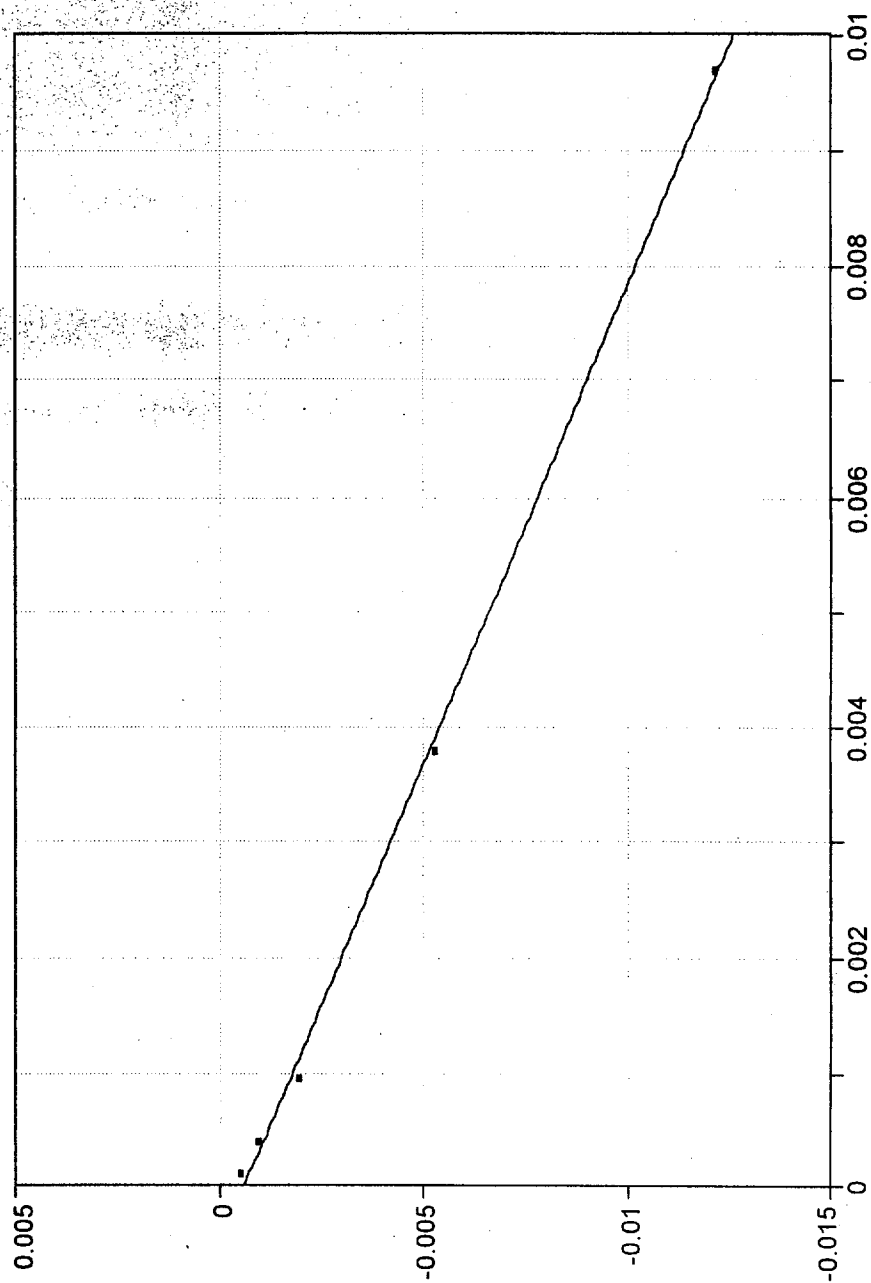
Mayo FIT for Methyl Methacrylate using 2/DPw

Rank 7 Eqn 1 $y=a+bx$ $r^2=0.997724735$ DF Adj r²=0.99544947 FitStdErr=0.00028338787 Fstat=1315.52778

a=0.00059918955

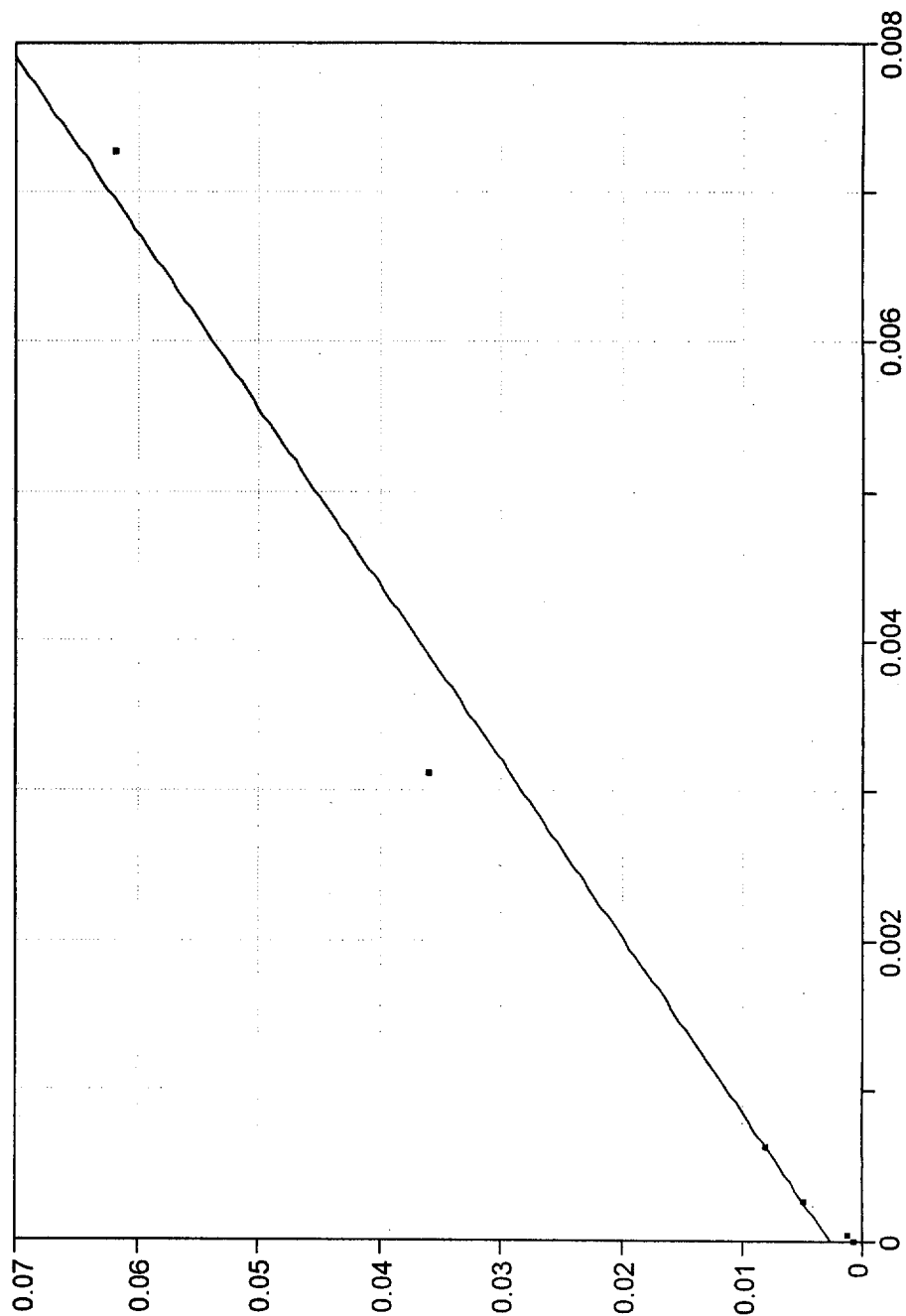
b=1.2757194



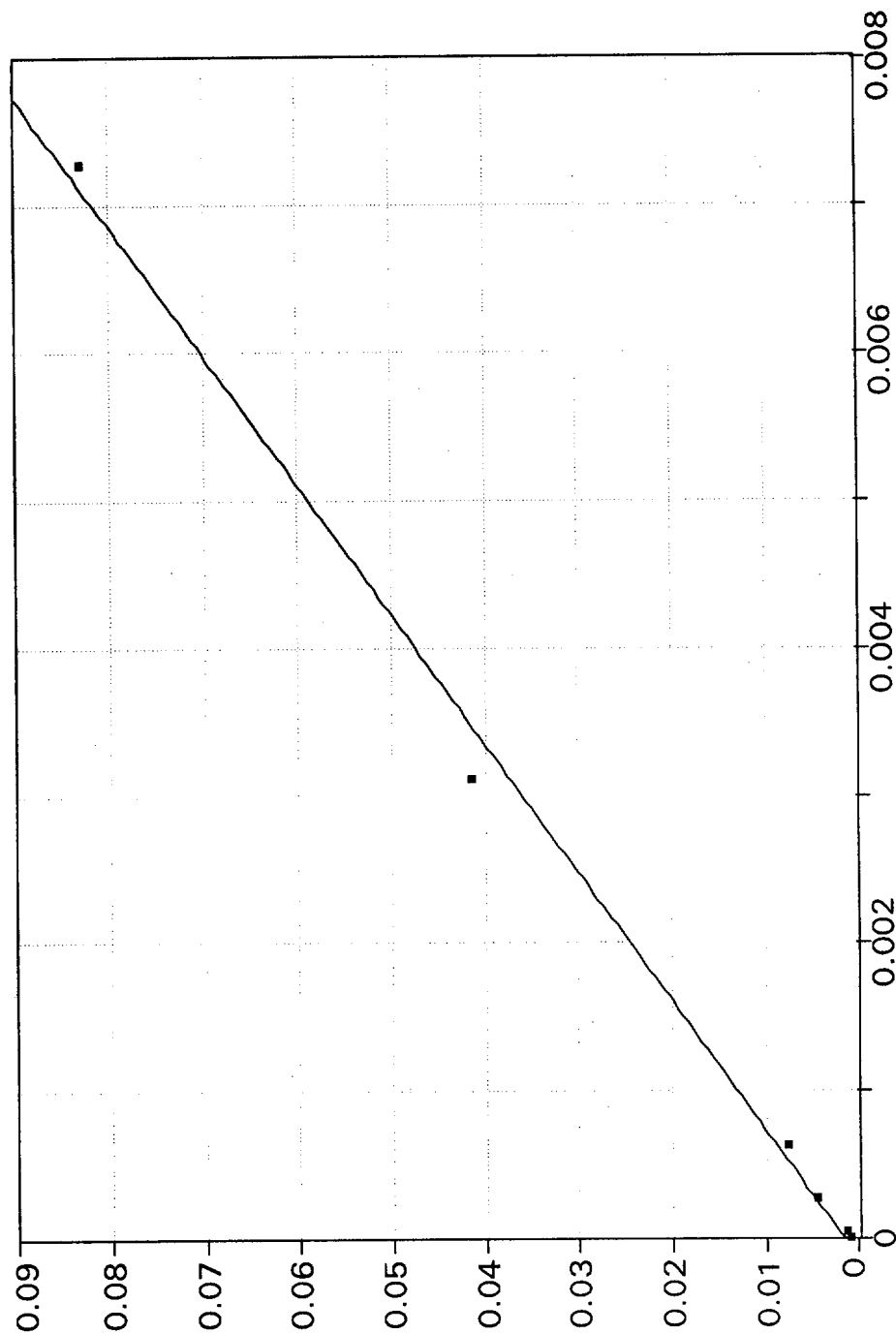
CLD METHOD:**CLD FIT for Methyl Methacrylate**Rank 4 Eqn 1 $y=a+bx$ $r^2=0.998710643$ DF Adj $r^2=0.997421287$ F_{Stat}=2323.74171 $a=-0.00063718638$ $b=-1.2008537$ 

STYRENE IN PRESENCE OF METHYL (2-BROMOMETHYL) ACRYLATE AT 70 °C

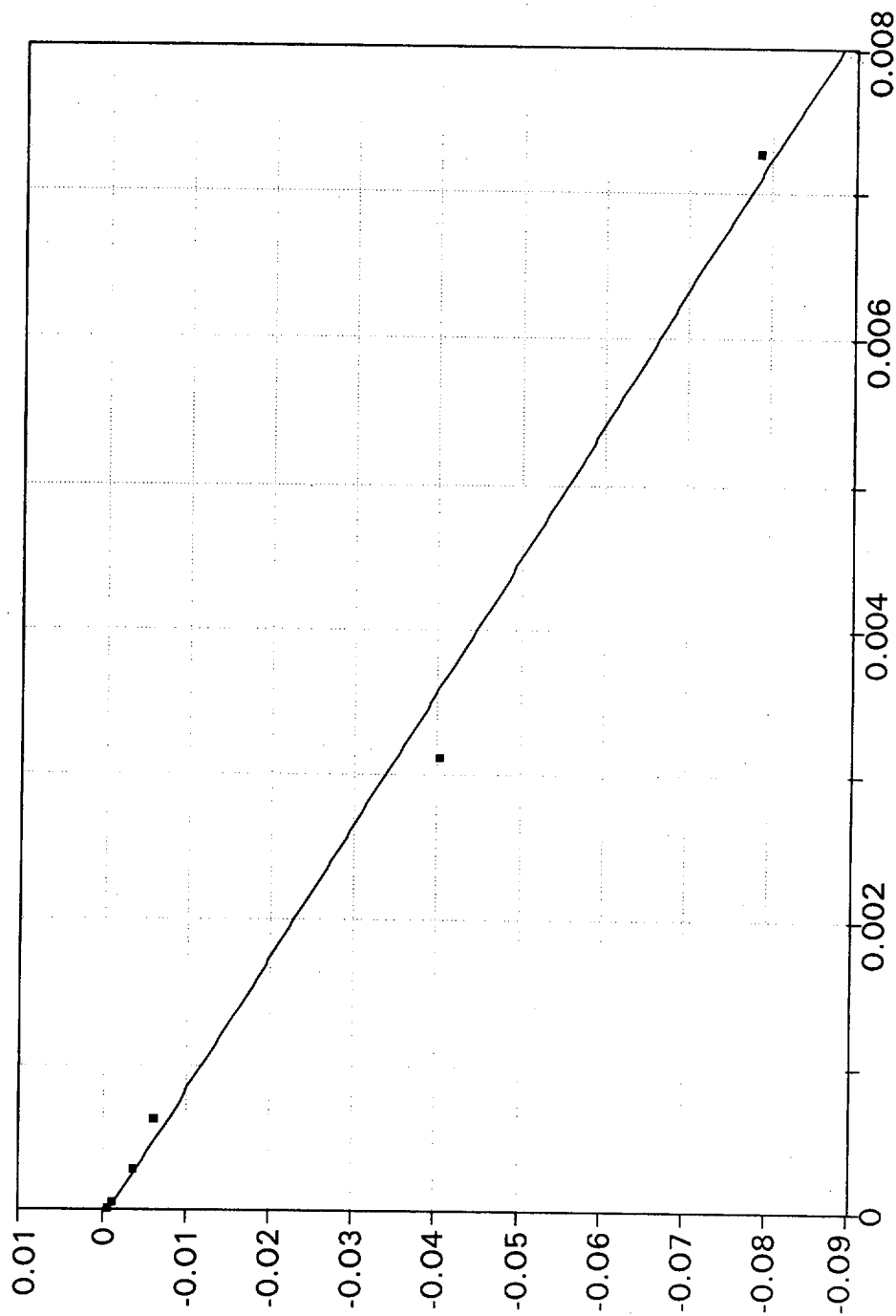
i.d.	[S]/[M]	$\langle M_n \rangle$	$\langle M_w \rangle$
0	0	183842	294582
A	7.28×10^{-3}	1688	2512
B	3.13×10^{-3}	2904	5036
C	6.32×10^{-4}	13247	27800
D	2.76×10^{-4}	21920	47759
E	5.65×10^{-5}	91587	169031

MAYO FIT for Styrene using 1/DP_nRank 5 Eqn 1 $y=a+bx$ $r^2=0.980458602$ DF Adj $r^2=0.967431003$ FitStdErr=0.00388715573 Fstat=200.693646 $a=0.0024866641$ $b=8.524893$ 

MAYO FIT for Styrene using 2/DPw

Rank 5 Eqn 1 $y = a + bx$ $r^2 = 0.99577338$ DF Adj 0.992955633 FitStdErr = 0.00240776286 Fstat = 942.382617 $a = 0.0013220591$ $b = 11.442411$ 

CLD FIT for Styrene

Rank 3 Eqn 1 $y = a + bx$ $r^2 = 0.993537221$ DF Adj 0.989228702 FitStdErr = 0.00284407314 Fstat = 614.928821 $a = -0.0011677082$ $b = -10.918007$ 

ATOM TRANSFER POLYMERIZATION REACTIONS

Table 1 Conditions utilised for ATP of MMA with α -Bromo-isobutyric acid phenyl ester as initiator

MMA (cm ³)	MMA (moles)	Ligand (moles)	CuBr (moles)	Xylene (cm ³)	Initiator (moles)
10	9.34×10^{-2}	1.86×10^{-3}	9.34×10^{-4}	20	9.34×10^{-4}

The reactions were sampled gravimetrically. At 45 minutes one of the polymerisations had 0.22 mL (1.86×10^{-3} moles) of methyl (2-bromomethyl)acrylate (MBrMA) introduced.

Table 2 Polymerisation of MMA in xylene at 90°C, $[MMA]/[Cu(I)Br]/[lig]/[I]$

= 100 : 1 : 2 : 1

t/secs	M_n	PDi	Conv %	$\ln([M]_0/[M])$
1800	2520	1.15	25.0	0.288
3600	3280	1.13	34.7	0.426
5400	3830	1.13	41.3	0.532
7200	4390	1.13	49.8	0.689
9000	4840	1.13	56.1	0.823
10800	5250	1.13	62.3	0.974
14400	5850	1.13	70.5	1.222
14400(Ppt)	6970	1.09	-	-

Table 3 Polymerisation of MMA in Xylene at 90°C, [MMA]/[Cu(I)Br]/[lig]/[I]
= 100 : 1 : 2 : 1 with addition of 2 Equivalents of MBrMA at 45 minutes

t/secs	M_n	PDi	Conv %	$\ln([M]_0/[M])$
1800	2410	1.13	23.9	0.274
2700	Addition of Brominated Monomer			
3600	2840	1.14	32.6	0.395
5400	2840	1.14	32.7	0.397
7200	2820	1.15	33.3	0.405
9000	2890	1.12	33.4	0.407
10800	2830	1.14	33.6	0.409
14400	2840	1.14	33.6	0.409
14400(Ppt)	3130	1.11	-	-

Table 4 Polymerisation of MMA in xylene at 90°C, [MMA]/[Cu(I)Br]/[lig]/[I]

= 100 : 1 : 2 : 1 with addition of 2 equivalents of MBrMA and Cu(0) at 45 minutes

t/secs	M_n	PDi	Conv %	$\ln([M]_0/[M])$
1800	2200	1.12	20.38	0.228
2700				
Addition of Brominated Monomer & Cu(0)				
3600	3500	1.14	40.32	0.516
5400	4160	1.21	53.05	0.756
7200	4310	1.26	59.44	0.902
9000	4590	1.30	63.97	1.021
10800	4620	1.36	69.58	1.190
14400	5080	1.39	74.74	1.376
14400(Ppt)	6340	1.28	-	-

Table 5 Polymerisation of MMA in xylene at 90°C, $[MMA]/[Cu(I)Br]/[lig]/[I]$

= 100 : 1 : 2 : 1 with addition of 3 equivalents of MBMA and Cu(0) at 45 minutes

t/secs	M_n	PDI	Conv %	$\ln([M]_0/[M])$
1800	2880	1.12	22.9	0.260
2700				
Addition of Brominated Monomer & Cu(0)				
3600	3620	1.13	36.0	0.447
5400	4090	1.18	49.9	0.693
7200	4050	1.26	55.9	0.818
9000	4350	1.28	61.0	0.942
10800	4430	1.31	64.4	1.035
14400	4520	1.35	68.8	1.166
14400(Ppt)	4820	1.31	-	-

Table 6 Polymerisation of MMA in xylene at 90°C, [MMA]/[Cu(0)Br]/[lig]/[I]
= 100 : 1 : 2 : 1 with addition of 4 equivalents of MBMA and Cu(0) at 45 mins

t/secs	M_n	PDi	Conv %	$\ln([M]_0/[M])$
1800	2850	1.14	24.4	0.279
2700	Addition of Brominated Monomer & Cu(0)			
3600	3680	1.18	38.3	0.483
5400	3860	1.21	46.0	0.617
7200	3820	1.25	51.9	0.731
9000	3840	1.29	57.7	0.862
10800	3930	1.30	61.9	0.965
14400	3980	1.32	64.6	1.038
14400(Ppt)	4030	1.31	-	-

Table 7 Polymerisation of MMA in xylene at 90°C, $[MMA]/[Cu(I)Br]/[lig]/[I]$
= 100 : 1 : 2 : 1 with addition of 5 equivalents of MBrMA and Cu(0) at 45 mins

t/secs	M_n	PDI	Conv %	$\ln([M]_0/[M])$
1800	2620	1.15	20.4	0.227
2700	Addition of Brominated Monomer & Cu(0)			
3600	3560	1.16	37.8	0.475
5400	3600	1.21	44.9	0.597
7200	3520	1.25	51.3	0.720
9000	3260	1.31	56.4	0.830
10800	3220	1.31	58.1	0.871
14400	3300	1.32	59.5	0.905
14400(Ppt)	3540	1.25	-	-

