Supporting Information:

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

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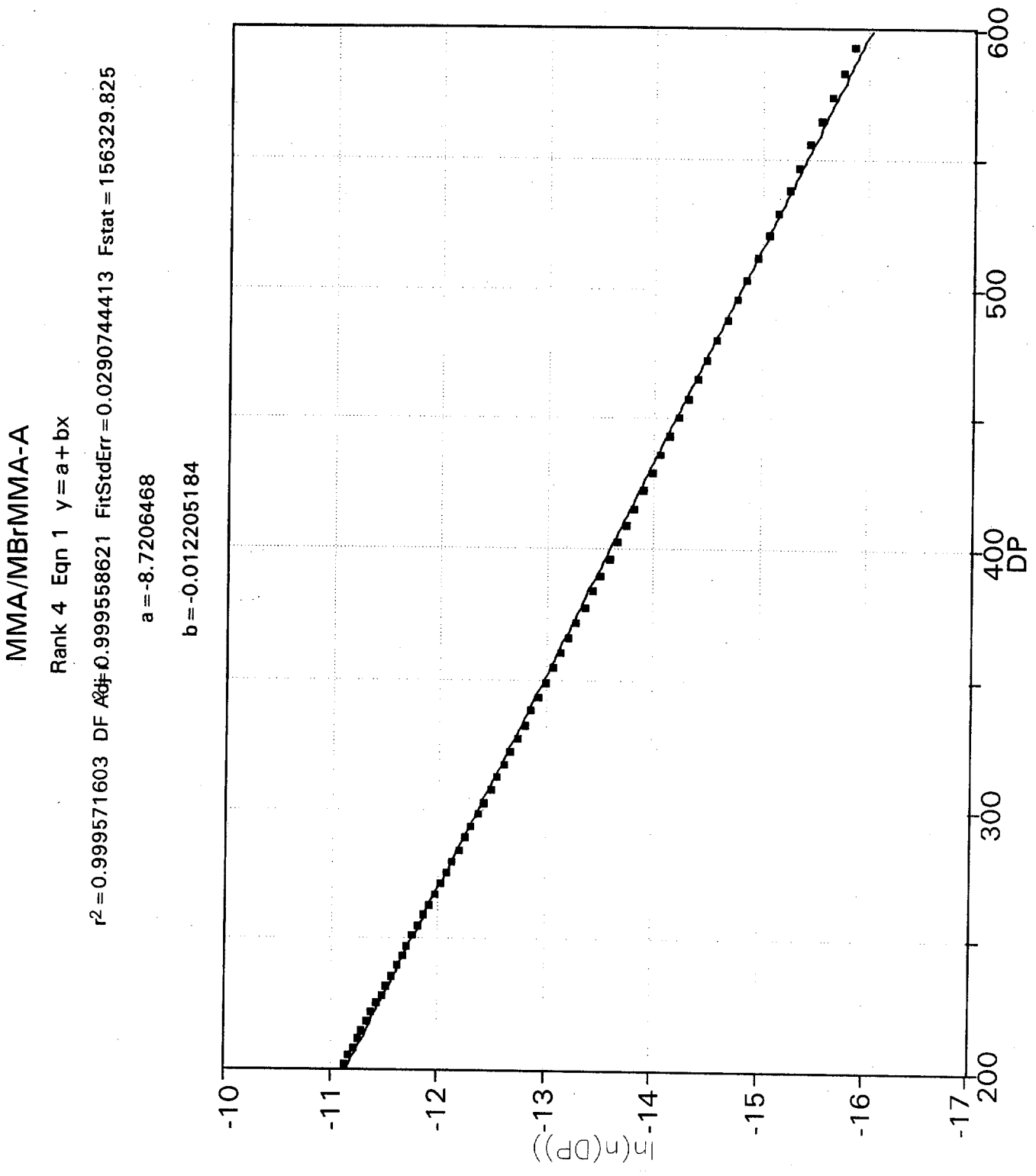

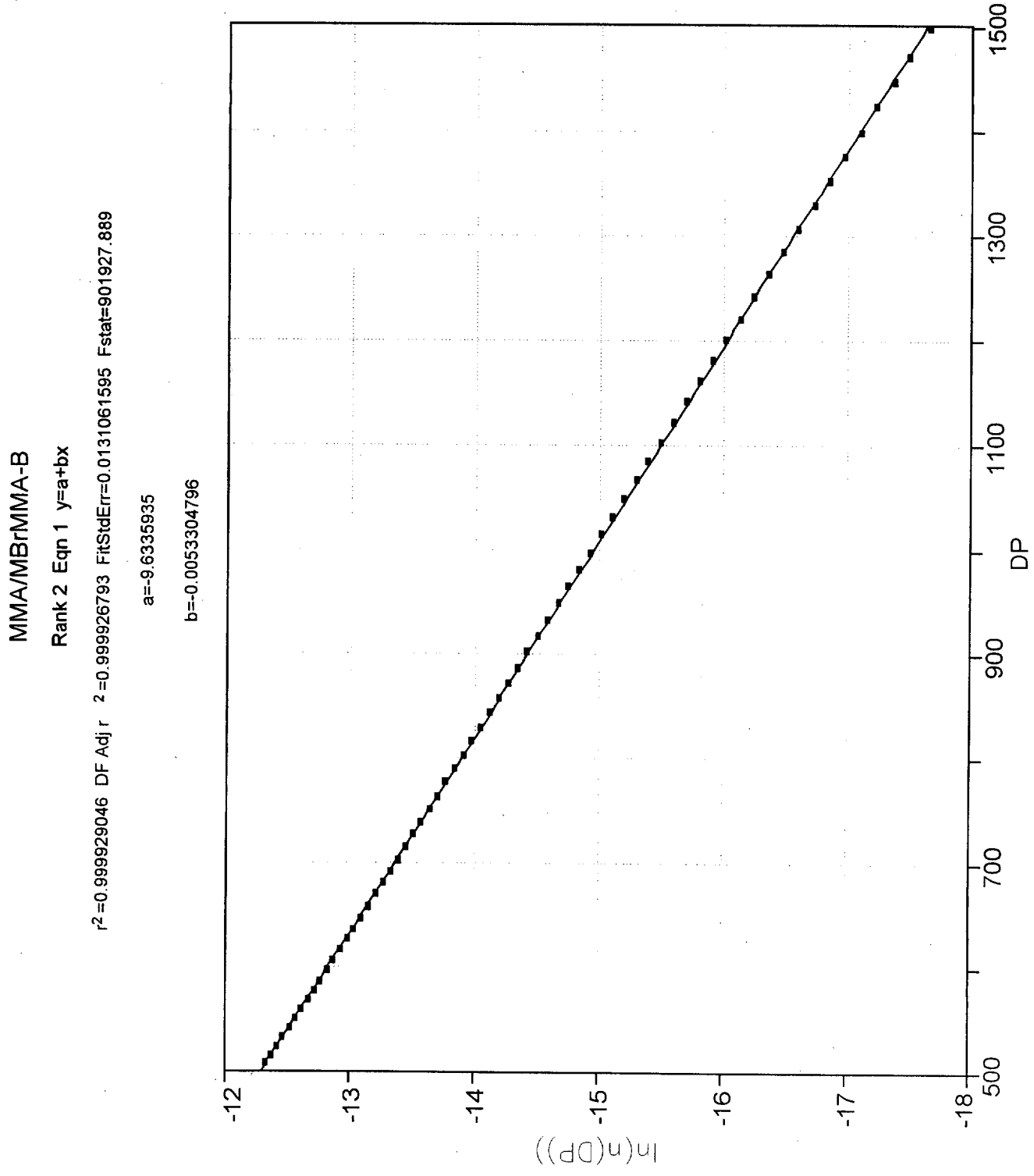

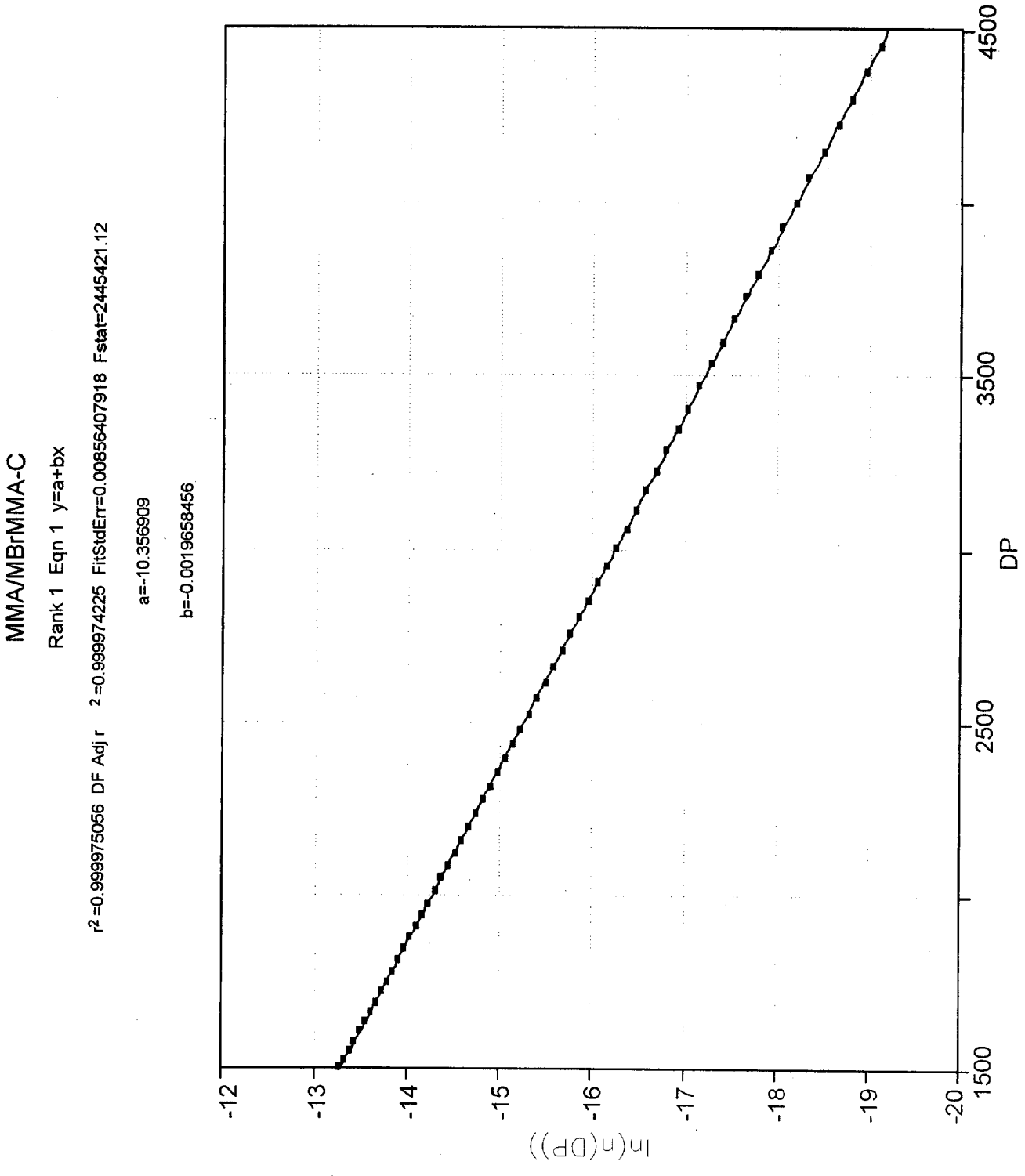

MMA/MBrMMA-D

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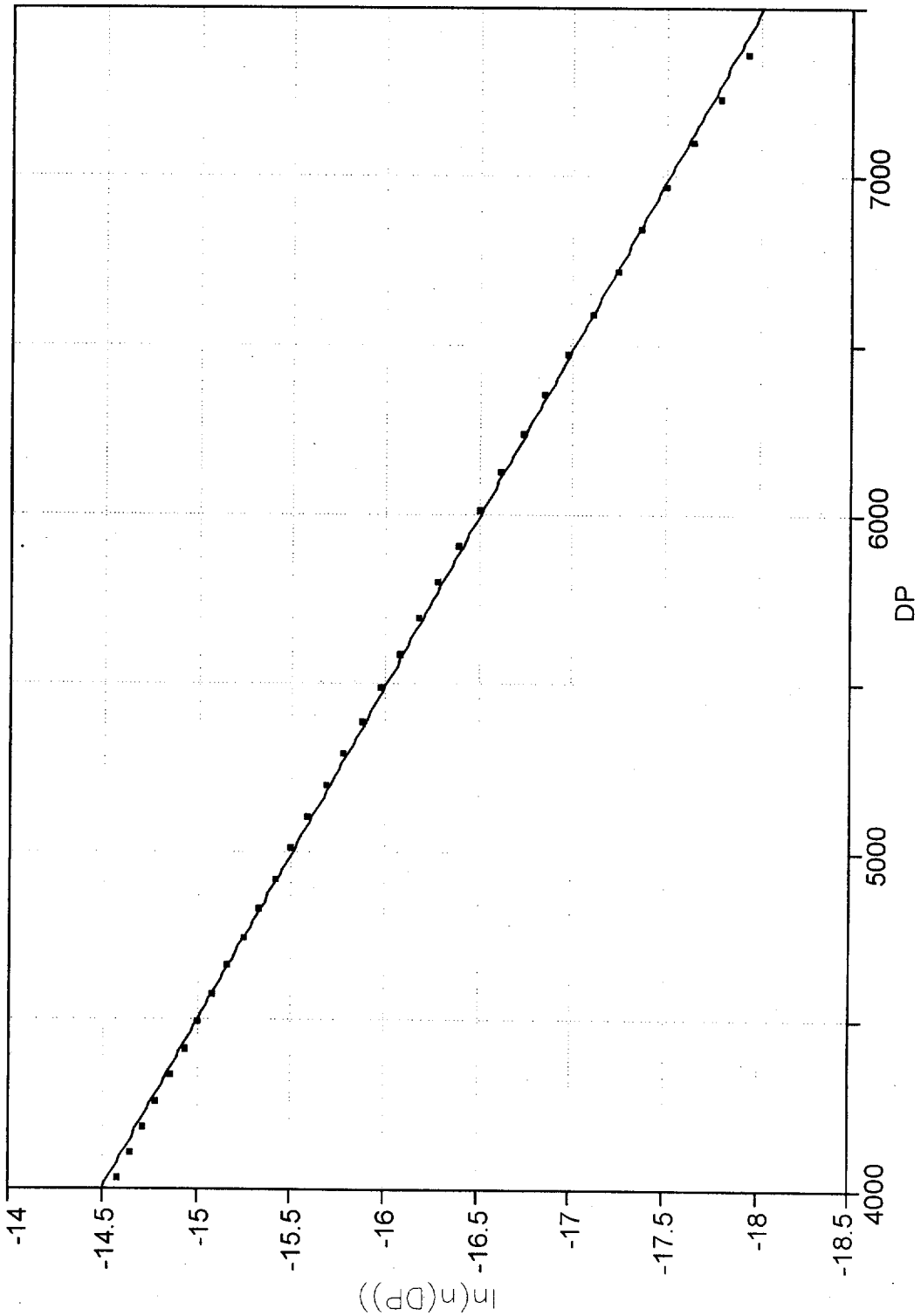
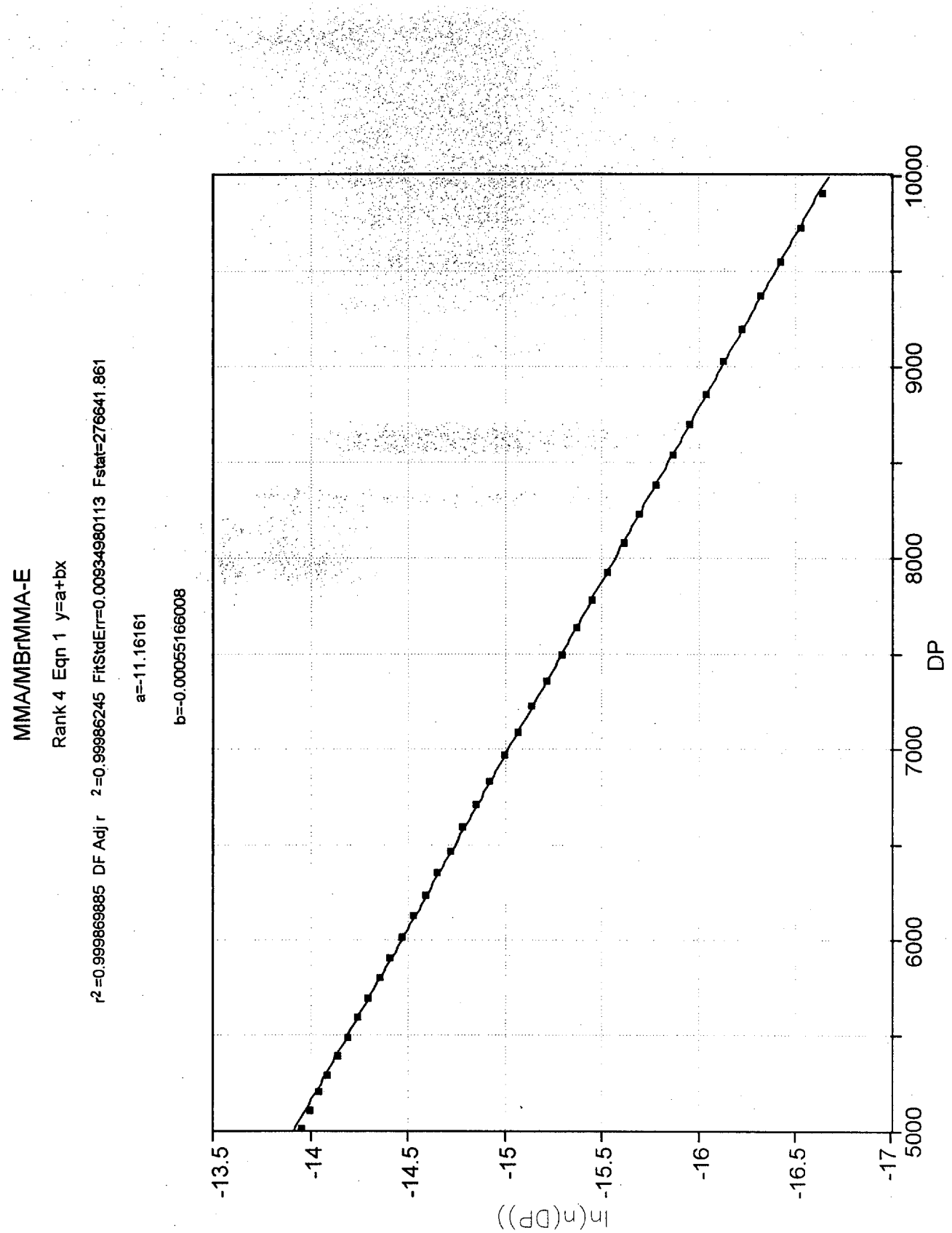
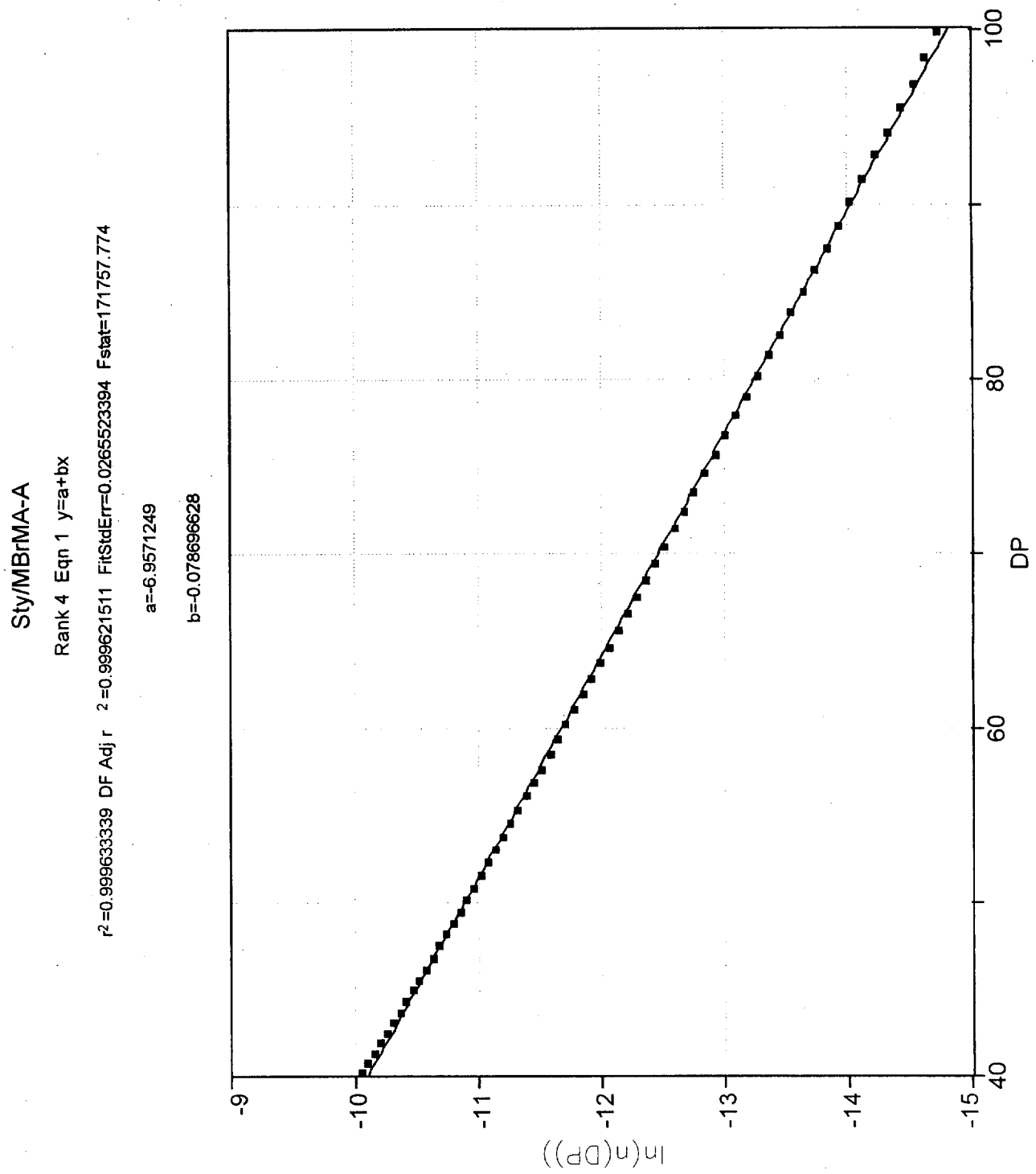
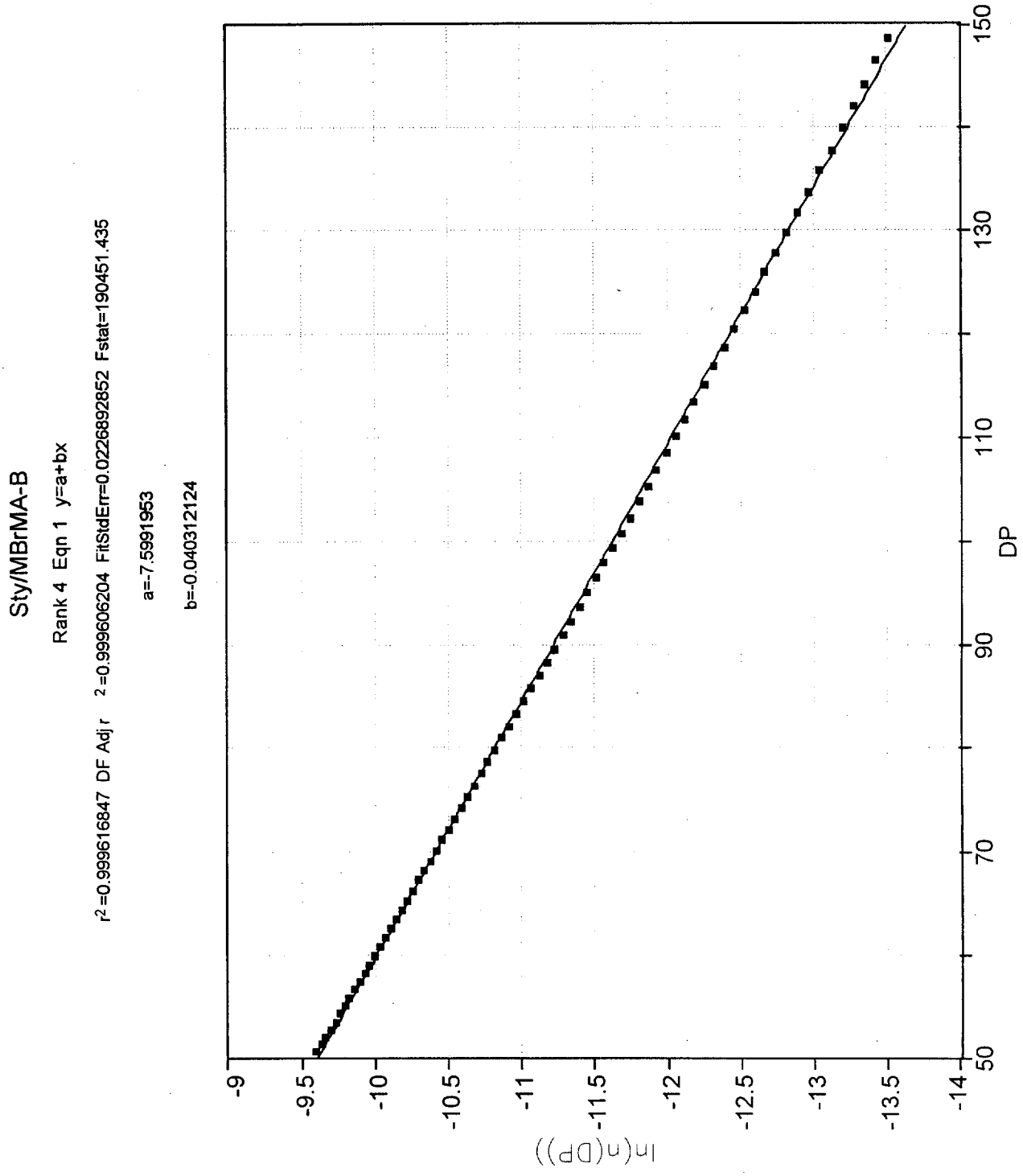
a=-10.483229

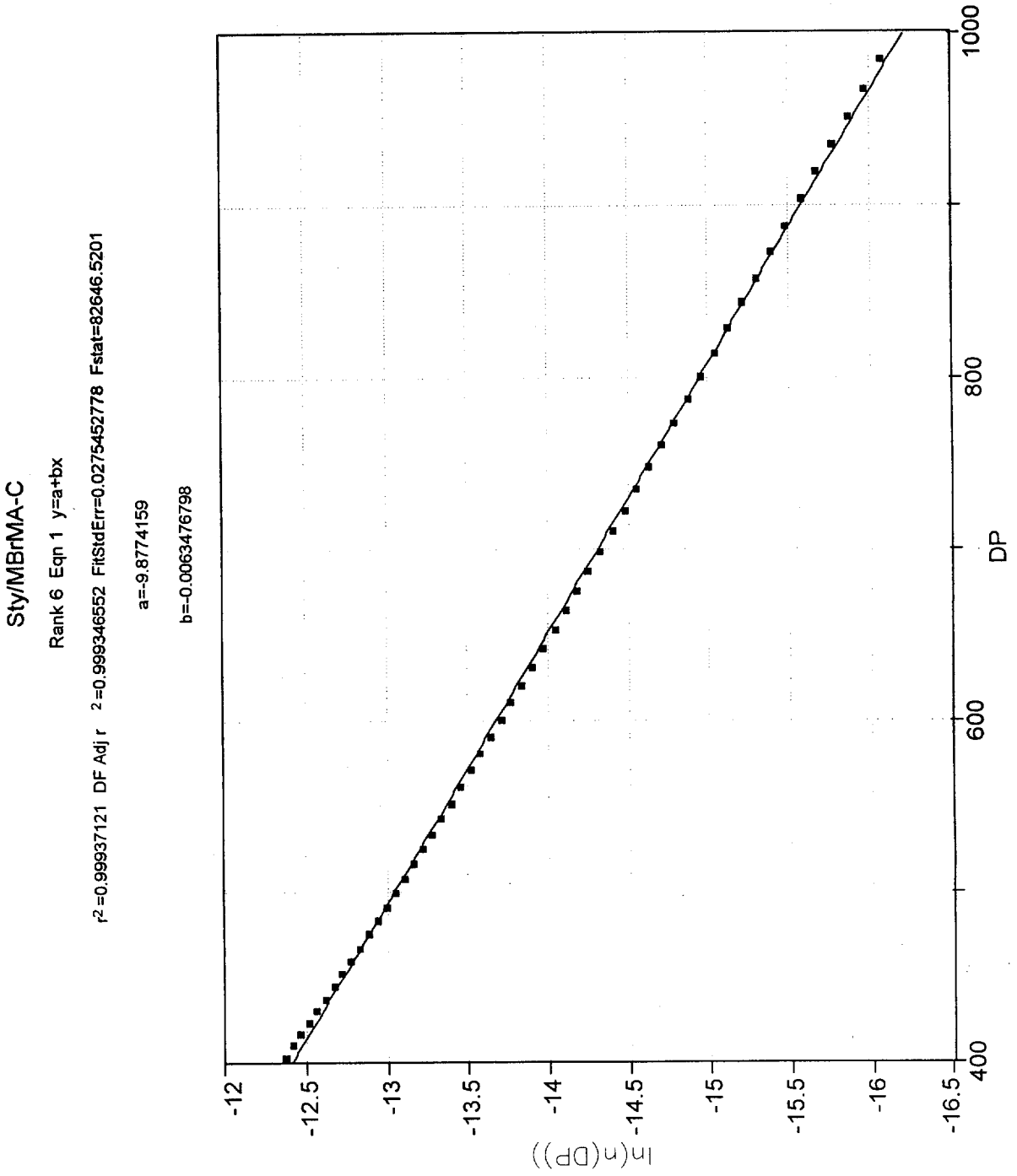
b=-0.0010058016

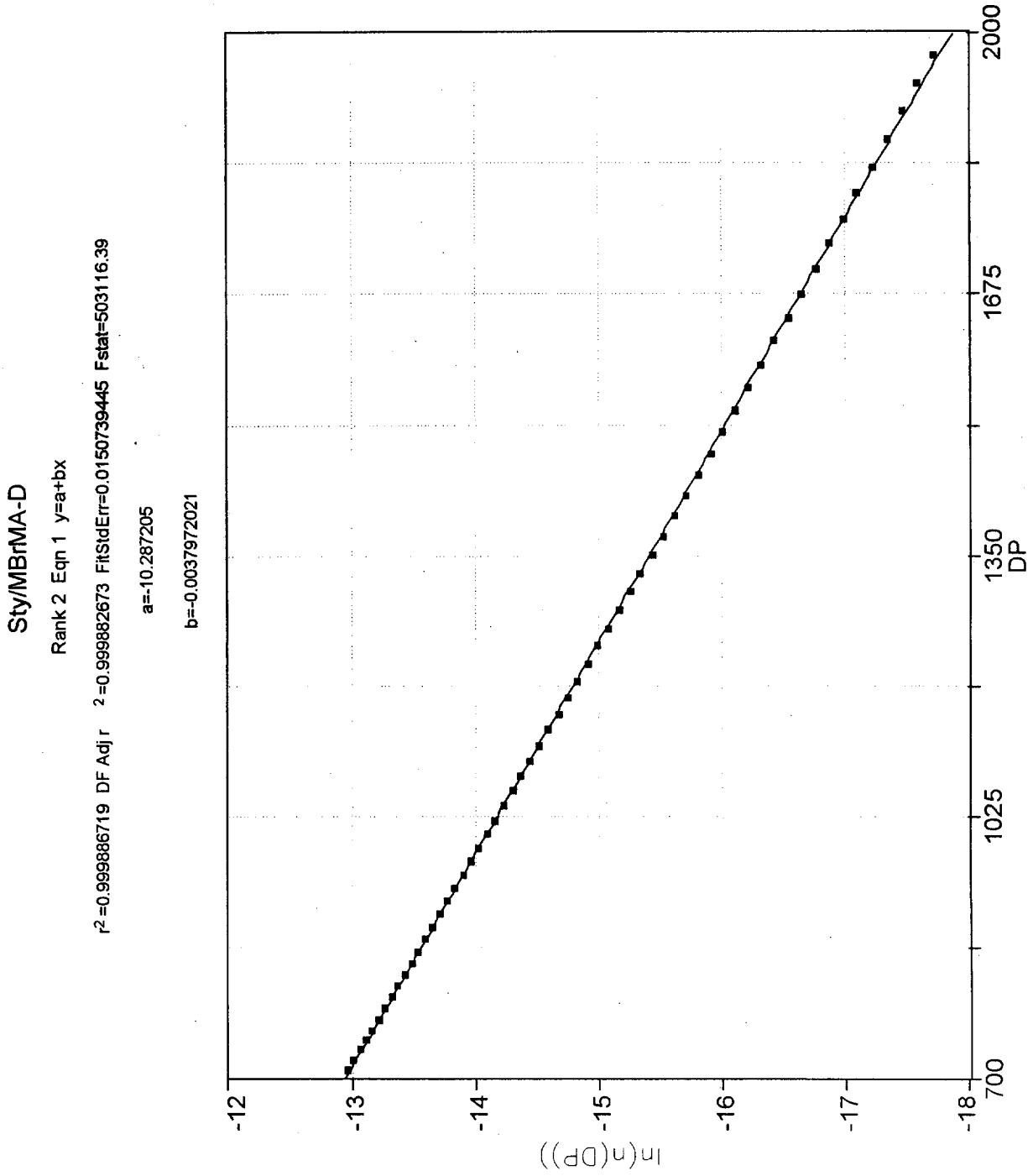


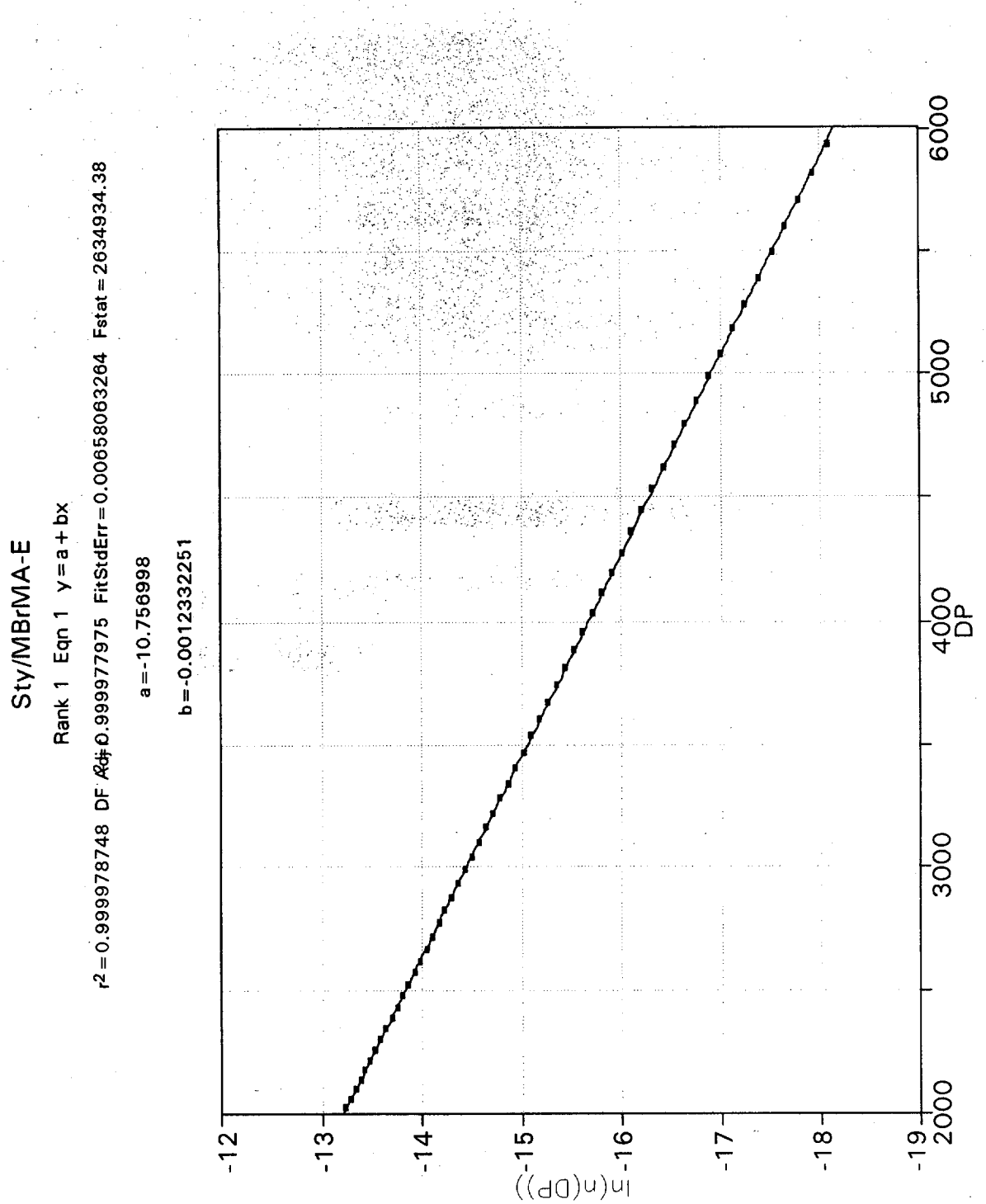










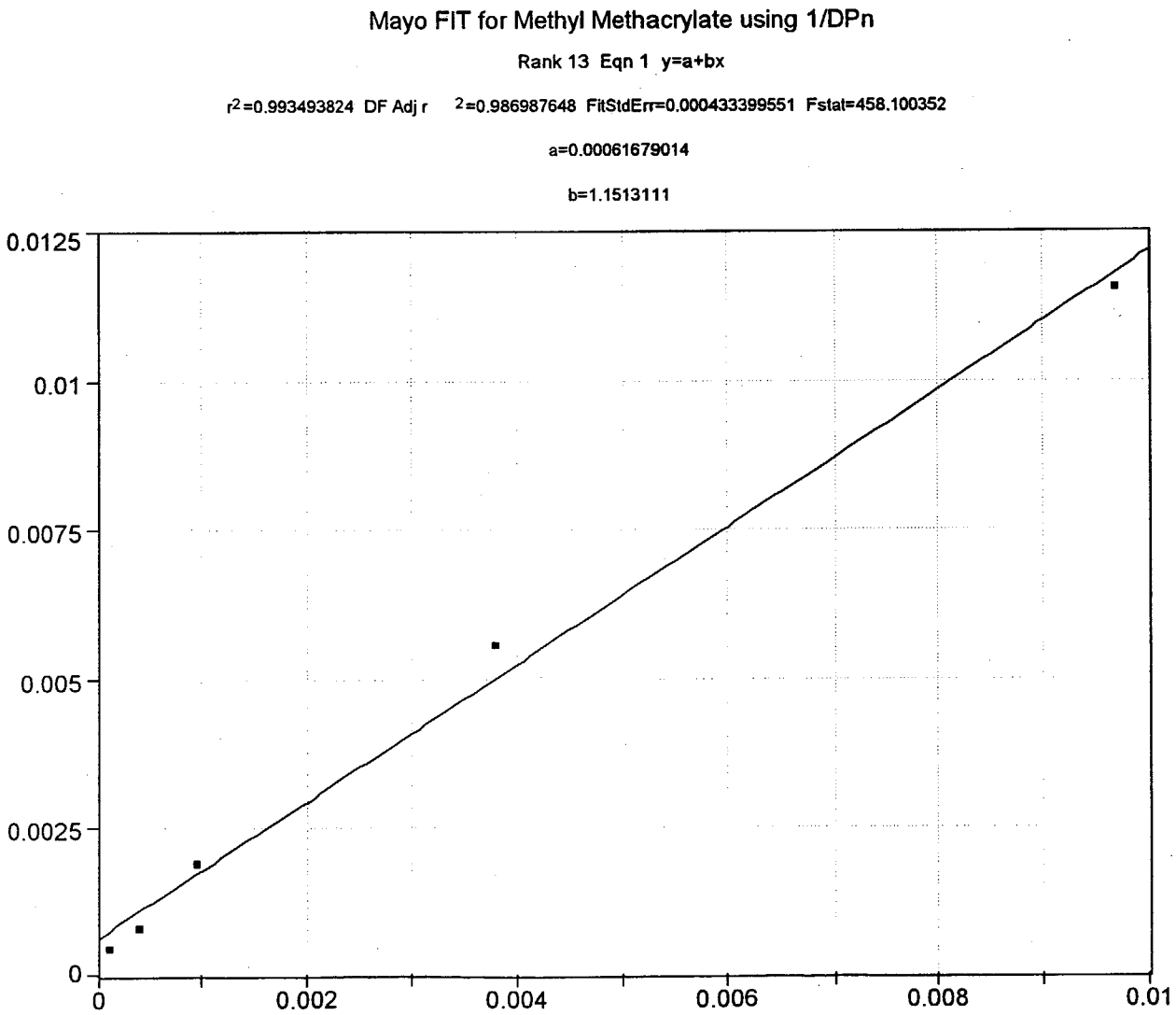


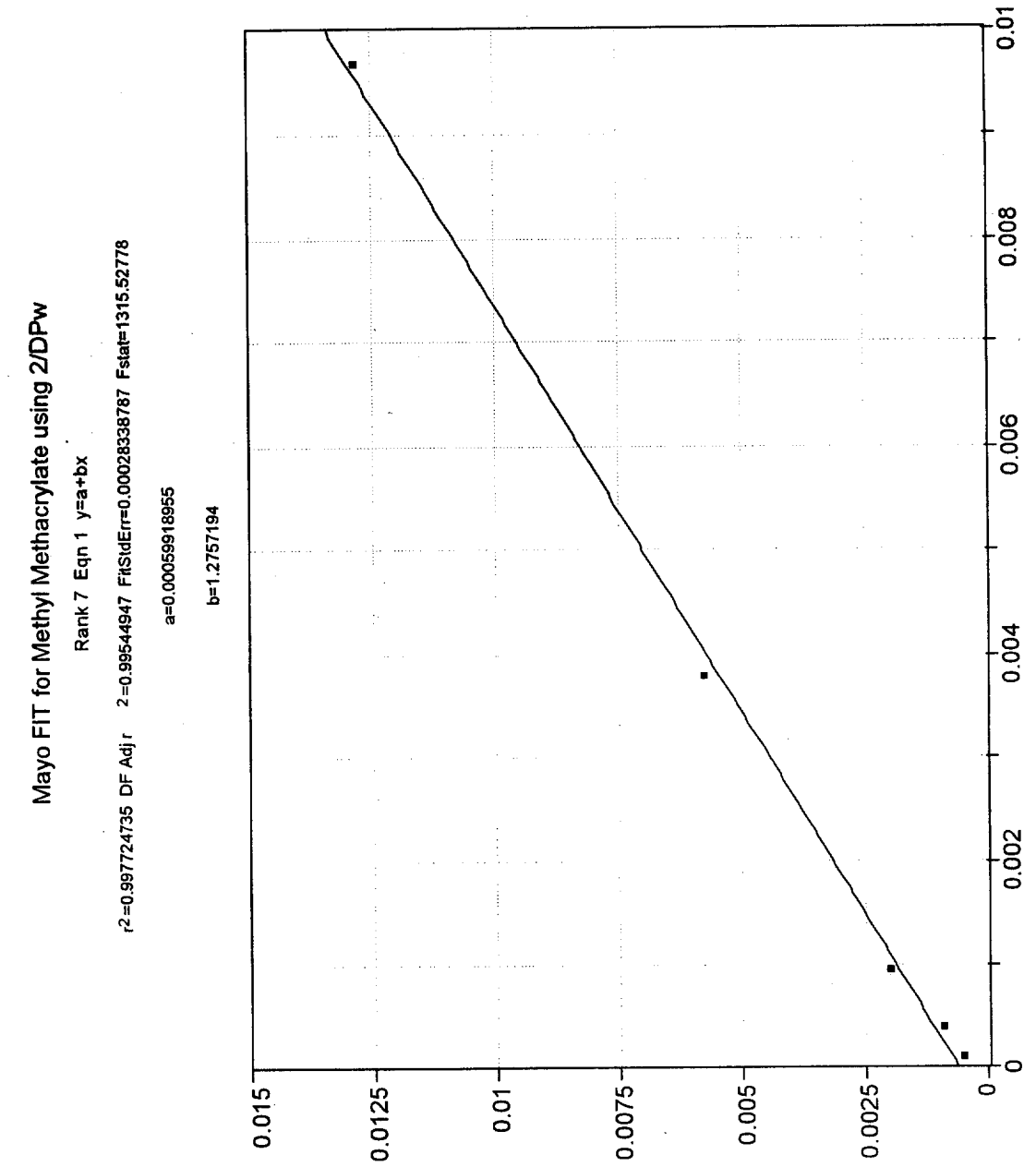
DETERMINATION OF CHAIN-TRANSFER CONSTANTS

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

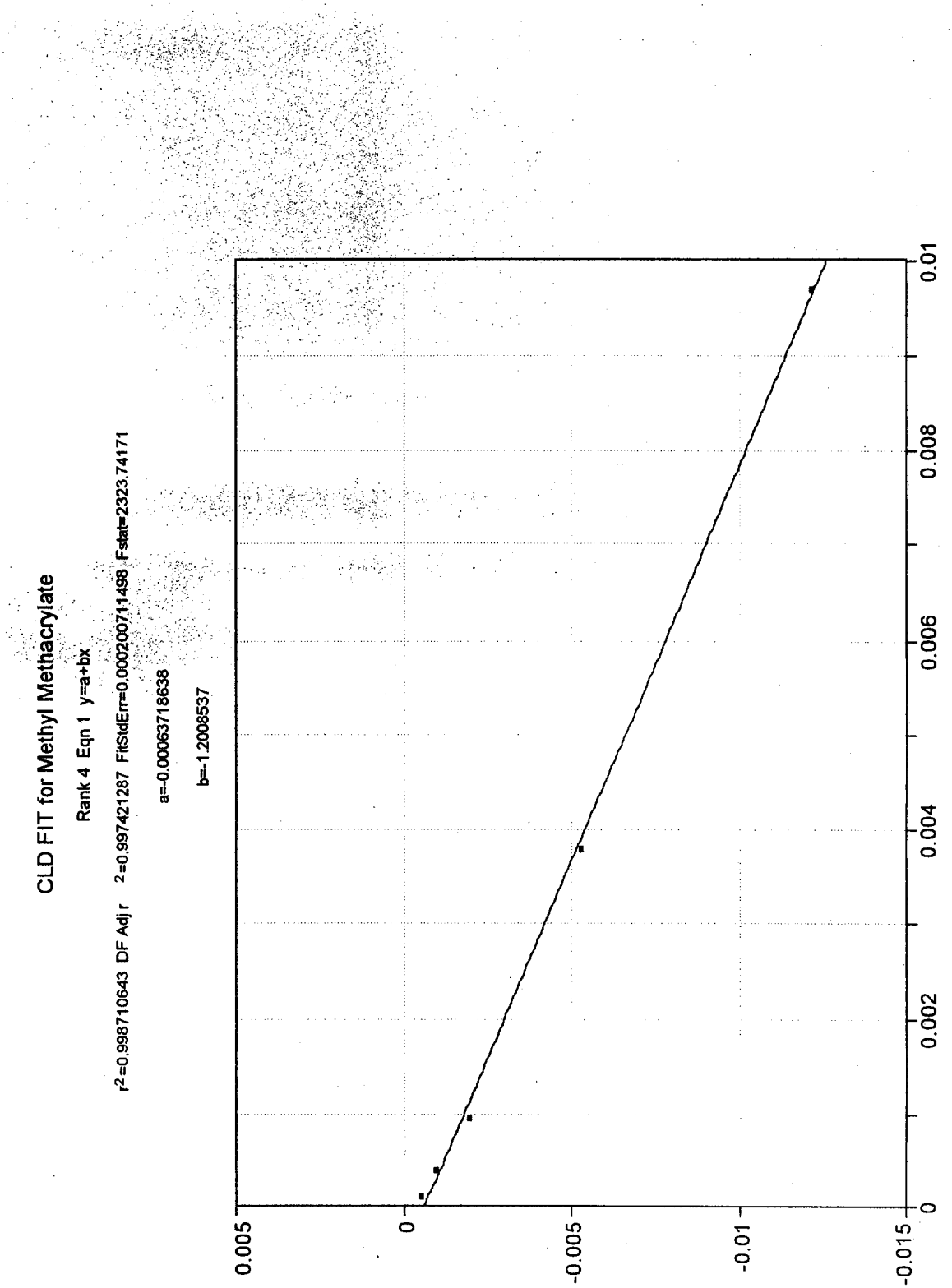
i.d.	[S]/[M]	$\langle M_n \rangle$	$\langle M_w \rangle$
A	9.69×10^{-3}	**8672**	**15613**
B	3.78×10^{-3}	**18062**	**34842**
C	9.36×10^{-4}	**53203**	**100613**
D	3.87×10^{-4}	**125843**	**219412**
E	9.29×10^{-5}	**219203**	**391583**

MAYO EQUATION:



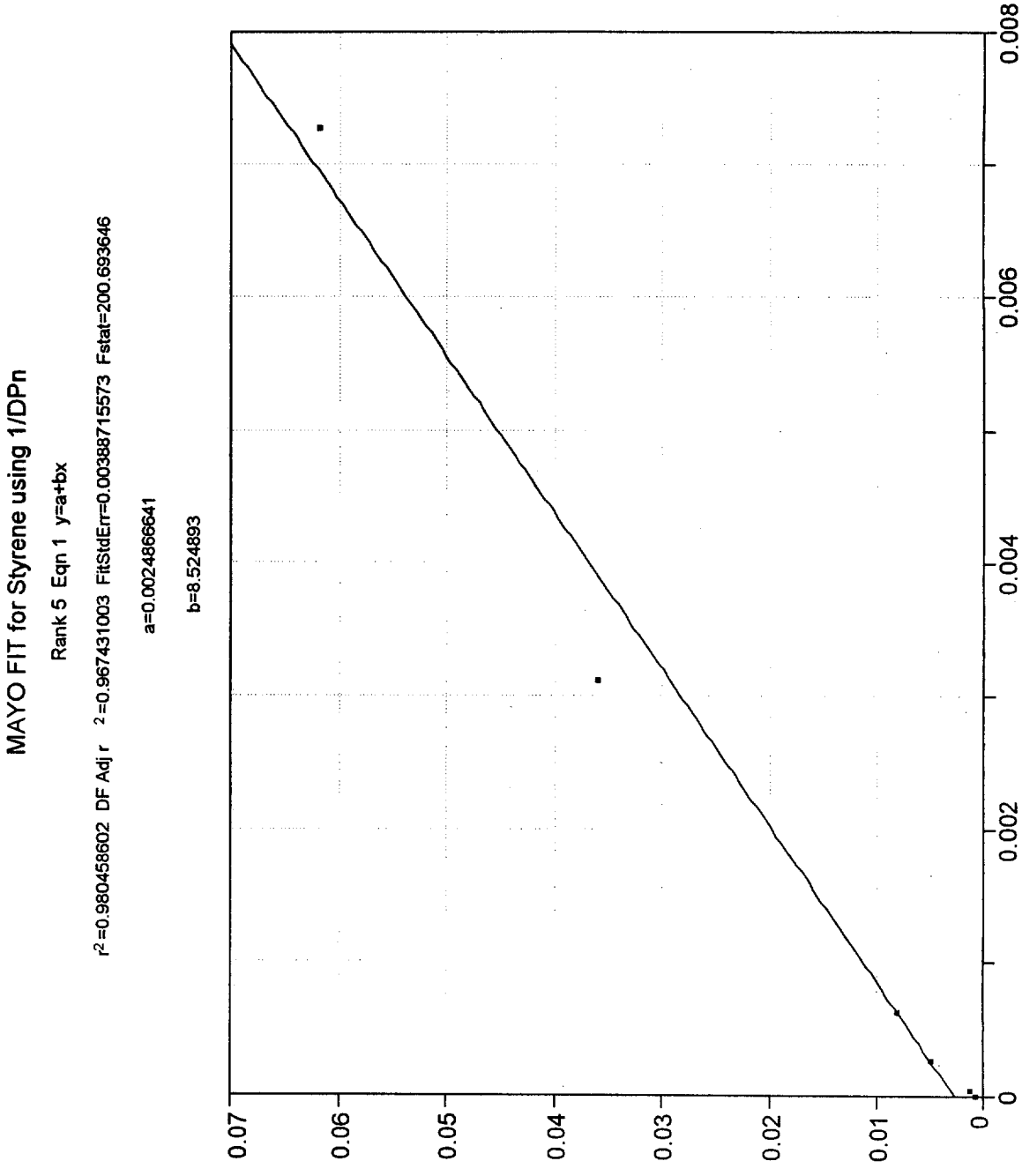


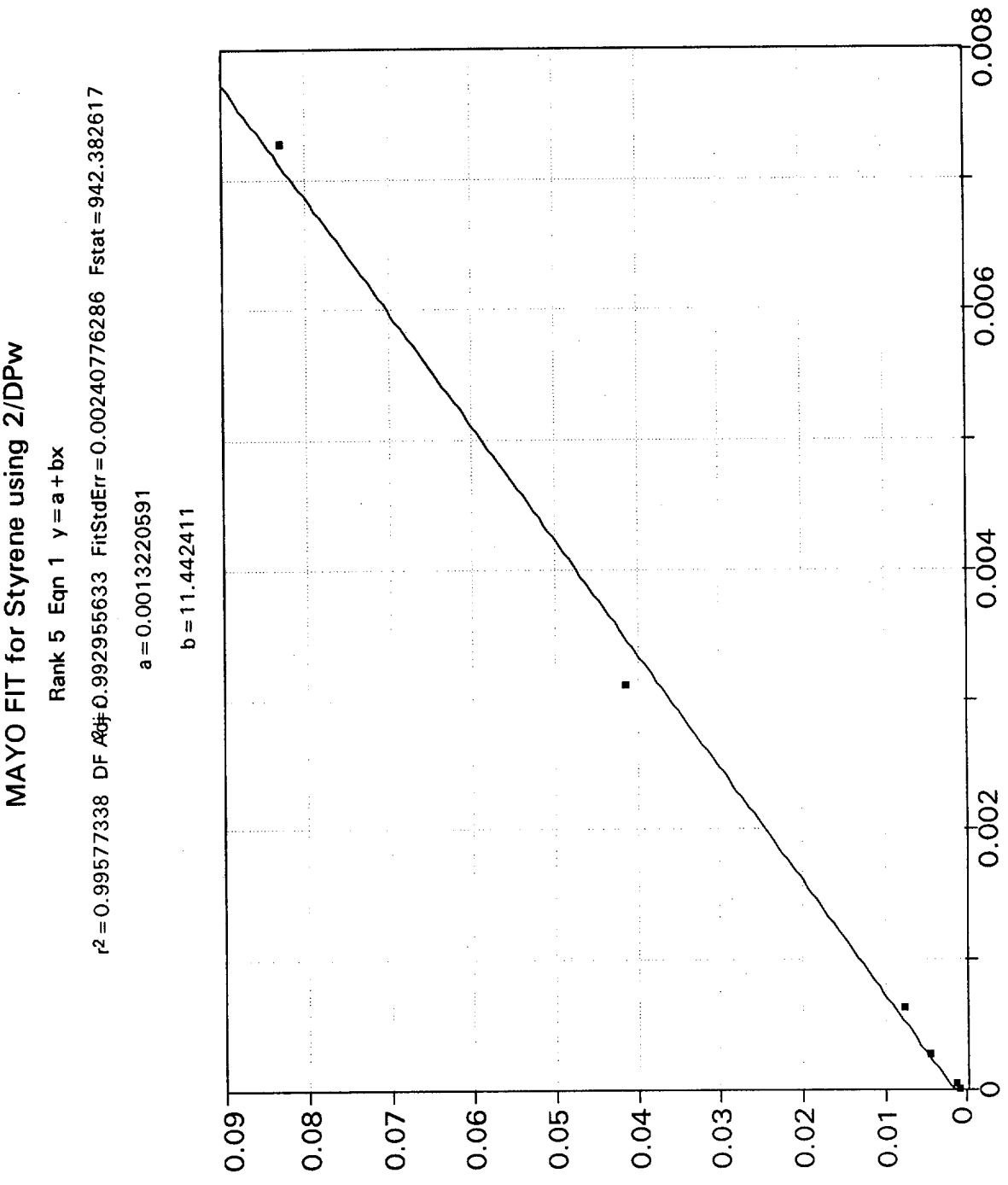
CLD METHOD:

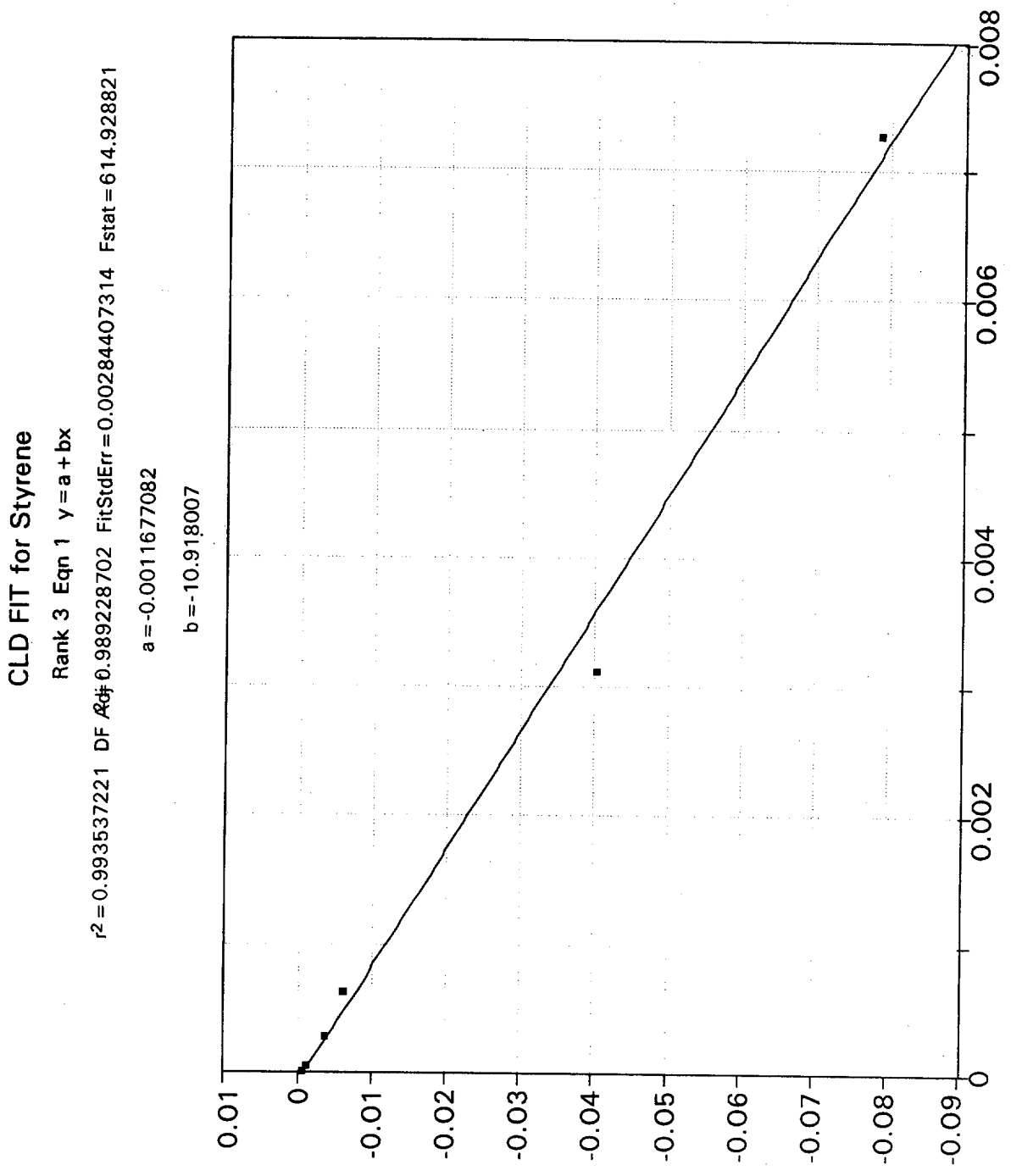


STYRENE IN PRESENCE OF METHYL (2-BROMOMETHYL) ACRYLATE AT 70 °C

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**







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(I)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	-	-