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Supporting Information for

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Synthesis, Characterization, and Properties of $[n]$ -Polyurethanes

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Experimental Procedures

Materials. Di-*tert*-butyltricarboxylate, 7-amino-heptanol, 8-amino-octanol, 9-amino-nonanol, 10-amino-decanol, 11-amino-undecanol, and 12-amino-dodecanol were prepared using standard procedures. 2-amino-ethanol, 3-amino-propanol, 4-amino-butanol, 6-amino-hexanol, and dibutyltin dilaurate were purchased from Aldrich Chemical Co, 5-amino-pentanol and *m*-cresol from Acros, and zirconium(IV)acetylacetonate from Fluka. The amino alcohols were dried over P_2O_5 , chloroform was dried over molecular sieves. All polymerizations were carried out under a dry argon atmosphere.

Instrumentation. NMR spectra of the polymers in $[D_6]$ DMSO were recorded on a Bruker 400 spectrometer. Size exclusion chromatography (SEC) was performed on a Shimadzu LC10-AT, using a Polymer Laboratories Plgel 5 μ m MIXED-D column, a Shimadzu RID-6A detector, and N-methylpyrrolidone as eluent. Molecular weights were calculated relative to polystyrene standards. Differential scanning calorimetry (DSC) was performed on a Perkin DSC 7, at a heating rate of 10°C min⁻¹. Thermogravimetric analysis (TGA) were performed with a Perkin-Elmer TGA 7, samples were heated from 50°C to 300°C at 10°C min⁻¹. Solution viscosities were measured with a SCHOTT-GERÄTE Ubbelohde micro-viscometer with a suspended level bulb of type 538/20: K=0.1 and 538/10: K=0.01. The sample was thermostated with a bath of type CT1450, and retention times were measured with a SCHOTT AVS 350. *m*-Cresol was distilled prior to use.

[5]-Polyurethane; $(C_4H_8NHCOO)_n$:

¹H-NMR ($[D_6]$ DMSO, 20°C, TMS): δ = 7.10 (br.tr, 0.9H; NH trans conformer), 6.70 (br.m, 0.1H; NH cis conformer), 3.90 (tr, 2H; CH₂O), 2.96 (q, 2H; CH₂N), 1.48 (m, 2H; CH₂CH₂O), 1.40 (m, 2H; CH₂CH₂N) ppm; IR (KBr): ν = 3317 (br.s), 2954 (m), 1689 (s), 1541 (s), 1271 (s) cm⁻¹; Elemental analysis;

(C₅H₉NO₂)_n: C 51.79% (calc. 52.16%), H 8.03% (7.88%), N 11.92% (12.17%); T_m =194°C; T_{decomp} =180°C.

[6]-Polyurethane; (C₅H₁₀NHCOO)_n:

¹H-NMR (400 MHz, [D₆]DMSO, 20°C, TMS): δ = 7.04 (br.tr, 0.9H; NH trans conformer), 6.72 (br.m, 0.1H; NH cis conformer), 3.89 (tr, ³J=6.2 Hz, 2H; CH₂O), 2.95 (q, ³J=6.0 Hz, 2H; CH₂N), 1.50 (m, ³J=7.2 Hz, 2H; CH₂CH₂O), 1.40 (m, ³J=7.7 Hz, 2H; CH₂CH₂N), 1.28 (m, ³J=6.6 Hz, 2H; CH₂CH₂CH₂CH₂CH₂) ppm; ¹³C-NMR (100 MHz, [D₆]DMSO, 100°C, TMS): δ = 156.4 (C=O), 63.5 (CH₂O), 40.1 (CH₂N), 29.4 (CH₂CH₂O), 28.7 (CH₂CH₂N), 26.0 (CH₂CH₂CH₂CH₂CH₂) ppm; IR (KBr): ν = 3318 (br.s), 2944 (m), 2870 (w), 1684 (s), 1535 (s), 1263 (s) cm⁻¹; Elemental analysis; (C₆H₁₁NO₂)_n: C 55.46% (calc. 55.80%), H 8.67% (8.58%), N 10.55% (10.85%); T_m =127°C; T_{decomp} =200°C.

[7]-Polyurethane; (C₆H₁₂NHCOO)_n:

¹H-NMR (400 MHz, [D₆]DMSO, 20°C, TMS): δ = 7.03 (br.tr, 0.9H; NH trans conformer), 6.75 (br.m, 0.1H; NH cis conformer), 3.90 (tr, 2H; CH₂O), 2.94 (q, 2H; CH₂N), 1.50 (m, 2H; CH₂CH₂O), 1.37 (m, 2H; CH₂CH₂N), 1.17 (m, 4H; CH₂CH₂CH₂CH₂CH₂) ppm; IR (KBr): ν = 3319 (br.s), 2938 (m), 2860 (w), 1687 (s), 1542 (s), 1257 (s) cm⁻¹; Elemental analysis; (C₇H₁₃NO₂)_n: C 58.67% (calc. 58.72%), H 9.21% (9.15%), N 9.57% (9.78%); T_m =157°C; T_{decomp} =210°C.

[8]-Polyurethane; (C₇H₁₄NHCOO)_n:

¹H-NMR (400 MHz, [D₆]DMSO, 20°C, TMS): δ = 7.03 (br.tr, 0.9H; NH trans conformer), 6.73 (br.m, 0.1H; NH cis conformer), 3.89 (tr, 2H; CH₂O), 2.93 (q, 2H; CH₂N), 1.48 (m, 2H; CH₂CH₂O), 1.38 (m, 2H; CH₂CH₂N), 1.24 (m, 6H; CH₂CH₂CH₂CH₂CH₂) ppm; IR (KBr): ν = 3327 (br.s), 2934 (m), 2856 (w), 1687 (s), 1534 (s), 1252 (s) cm⁻¹; Elemental analysis; (C₈H₁₅NO₂)_n: C 60.66% (calc. 61.12%), H 10.09% (9.62%), N 8.65% (8.91%); T_m =114°C.

[9]-Polyurethane; (C₈H₁₆NHCOO)_n:

¹H-NMR (400 MHz, [D₆]DMSO, 100°C, TMS): δ = 6.47 (br.tr, 1H; NH), 3.93 (tr, 2H; CH₂O), 2.97 (q, 2H; CH₂N), 1.51 (m, 2H; CH₂CH₂O), 1.40 (m, 2H; CH₂CH₂N), 1.27 (m, 8H; CH₂CH₂CH₂CH₂CH₂) ppm; IR (KBr): ν = 3321 (br.s), 2928 (m), 2852 (w), 1686 (s), 1545 (s), 1261 (s) cm⁻¹; Elemental analysis; (C₉H₁₇NO₂)_n: C 62.84% (calc. 63.13%), H 10.64% (10.01%), N 7.88% (8.18%); T_m =146°C.

[10]-Polyurethane; (C₉H₁₈NHCOO)_n:

¹H-NMR (400 MHz, [D₆]DMSO, 120°C, TMS): δ = 6.43 (br.tr, 1H; NH), 3.95 (tr, 2H; CH₂O), 3.00 (q, 2H; CH₂N), 1.56 (m, 2H; CH₂CH₂O), 1.43 (m, 2H; CH₂CH₂N), 1.28 (m, 10H; CH₂CH₂CH₂CH₂CH₂)

ppm; IR (KBr): $n = 3325$ (br.s), 2925 (m), 2852 (w), 1686 (s), 1535 (s), 1254 (s) cm^{-1} ; Elemental analysis; $(\text{C}_{10}\text{H}_{19}\text{NO}_2)_n$: C 64.74% (calc. 64.83%), H 10.79% (10.34%), N 7.33% (7.56%); $T_m = 116^\circ\text{C}$.

[11]-Polyurethane; $(\text{C}_{10}\text{H}_{20}\text{NHCOO})_n$:

^1H -NMR (400 MHz, $[\text{D}_6]$ DMSO, 120°C , TMS): $d = 6.43$ (br.tr, 1H; NH), 3.95 (tr, 2H; CH_2O), 3.00 (q, 2H; CH_2N), 1.55 (m, 2H; $\text{CH}_2\text{CH}_2\text{O}$), 1.43 (m, 2H; $\text{CH}_2\text{CH}_2\text{N}$), 1.28 (m, 12H; $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$) ppm; IR (KBr): $n = 3324$ (br.s), 2922 (m), 2851 (w), 1687 (s), 1543 (s), 1250 (s) cm^{-1} ; Elemental analysis; $(\text{C}_{11}\text{H}_{21}\text{NO}_2)_n$: C 65.86% (calc. 66.30%), H 11.01% (10.62%), N 6.82% (7.03%); $T_m = 148^\circ\text{C}$.

[12]-Polyurethane; $(\text{C}_{11}\text{H}_{22}\text{NHCOO})_n$:

^1H -NMR (400 MHz, $[\text{D}_6]$ DMSO, 100°C , TMS): $d = 6.40$ (br.tr, 1H; NH), 3.92 (tr, 2H; CH_2O), 2.97 (q, 2H; CH_2N), 1.51 (m, 2H; $\text{CH}_2\text{CH}_2\text{O}$), 1.40 (m, 2H; $\text{CH}_2\text{CH}_2\text{N}$), 1.28 (m, 14H; $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$) ppm; IR (KBr): $n = 3327$ (br.s), 2922 (m), 2851 (w), 1684 (s), 1534 (s), 1246 (s) cm^{-1} ; Elemental analysis; $(\text{C}_{12}\text{H}_{23}\text{NO}_2)_n$: C 66.98% (calc. 67.57%), H 11.16% (10.87%), N 6.22% (6.57%); $T_m = 119^\circ\text{C}$.

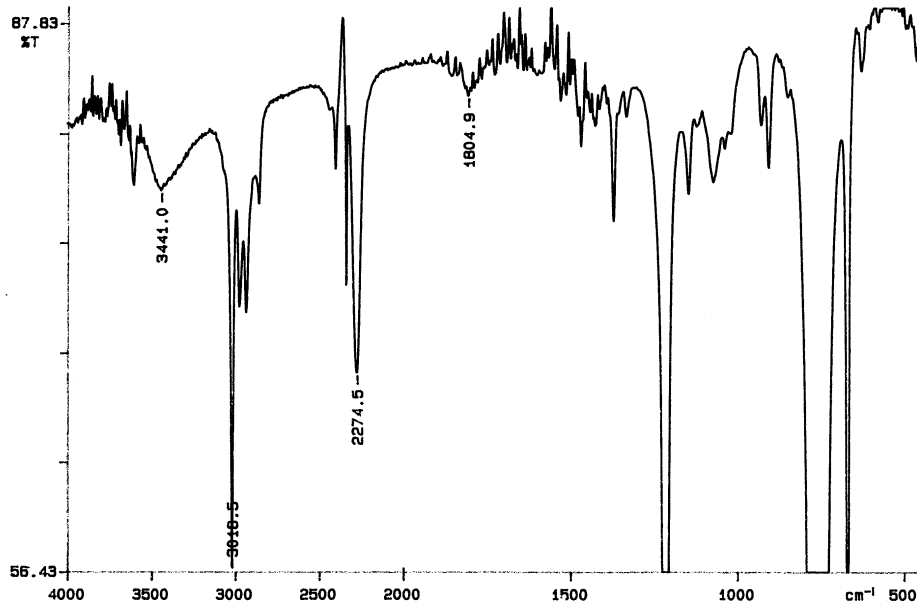
[13]-Polyurethane; $(\text{C}_{12}\text{H}_{24}\text{NHCOO})_n$:

^1H -NMR (400 MHz, $[\text{D}_6]$ DMSO, 100°C , TMS): $d = 6.38$ (br.tr, 1H; NH), 3.92 (tr, 2H; CH_2O), 2.95 (q, 2H; CH_2N), 1.51 (m, 2H; $\text{CH}_2\text{CH}_2\text{O}$), 1.40 (m, 2H; $\text{CH}_2\text{CH}_2\text{N}$), 1.25 (m, 16H; $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$) ppm; IR (KBr): $n = 3326$ (br.s), 2921 (m), 2850 (w), 1686 (s), 1542 (s), 1242 (s) cm^{-1} ; Elemental analysis; $(\text{C}_{13}\text{H}_{25}\text{NO}_2)_n$: C 68.25% (calc. 68.68%), H 11.40% (11.08%), N 5.93% (6.16%); $T_m = 141^\circ\text{C}$.

[6-co-7]-Polyurethane; $(\text{C}_5\text{H}_{10}\text{NHCOO-co-C}_6\text{H}_{12}\text{NHCOO})_n$:

^1H -NMR (400 MHz, $[\text{D}_6]$ DMSO, 20°C , TMS): $d = 7.05$ (br.tr, 0.9H; NH trans conformer), 6.73 (br.m, 0.1H; NH cis conformer), 3.90 (tr, 2H; CH_2O), 2.94 (q, 2H; CH_2N), 1.50 (m, 2H; $\text{CH}_2\text{CH}_2\text{O}$), 1.38 (m, 2H; $\text{CH}_2\text{CH}_2\text{N}$), 1.27 (m, 3H; $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$) ppm; IR (KBr): $n = 3324$ (br.s), 2941 (m), 2850 (w), 1687 (s), 1540 (s), 1259 (s) cm^{-1} ; Elemental analysis; $(\text{C}_{5.5}\text{H}_{11}\text{NO}_2)_n$: C 56.84% (calc. 57.26%), H 8.94% (8.87%), N 9.98% (10.32%); $T_g = 8^\circ\text{C}$.

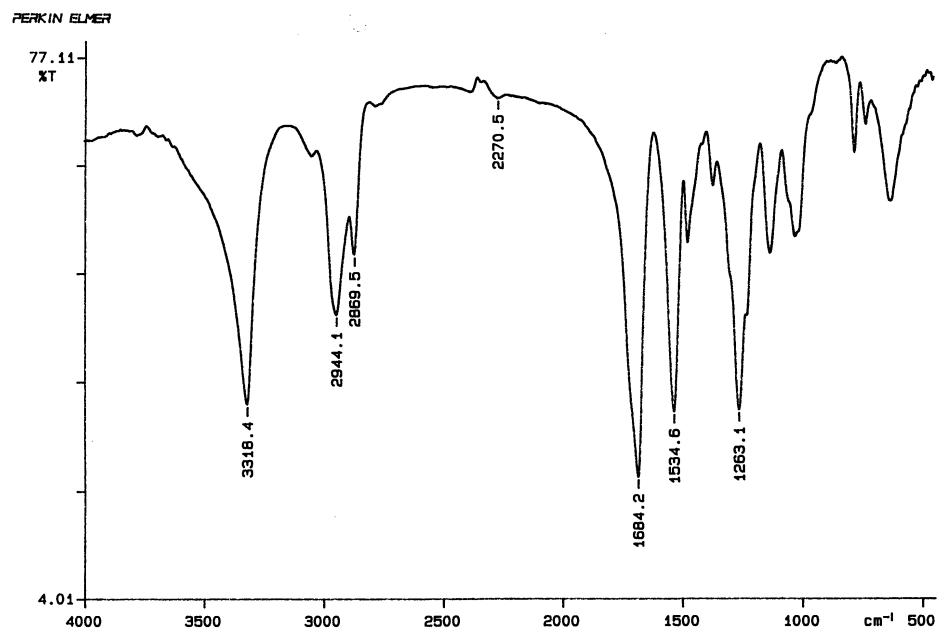
PERKIN ELMER



98/12/09 16:59 rs
Z: 4 scans, 4.0cm⁻¹

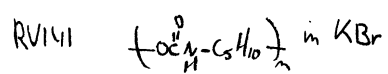
HO-C₅H₁₀-NCO in CH₂Cl₂

FT-IR of 5-isocyanato-pentanol in
 CHCl_3 .

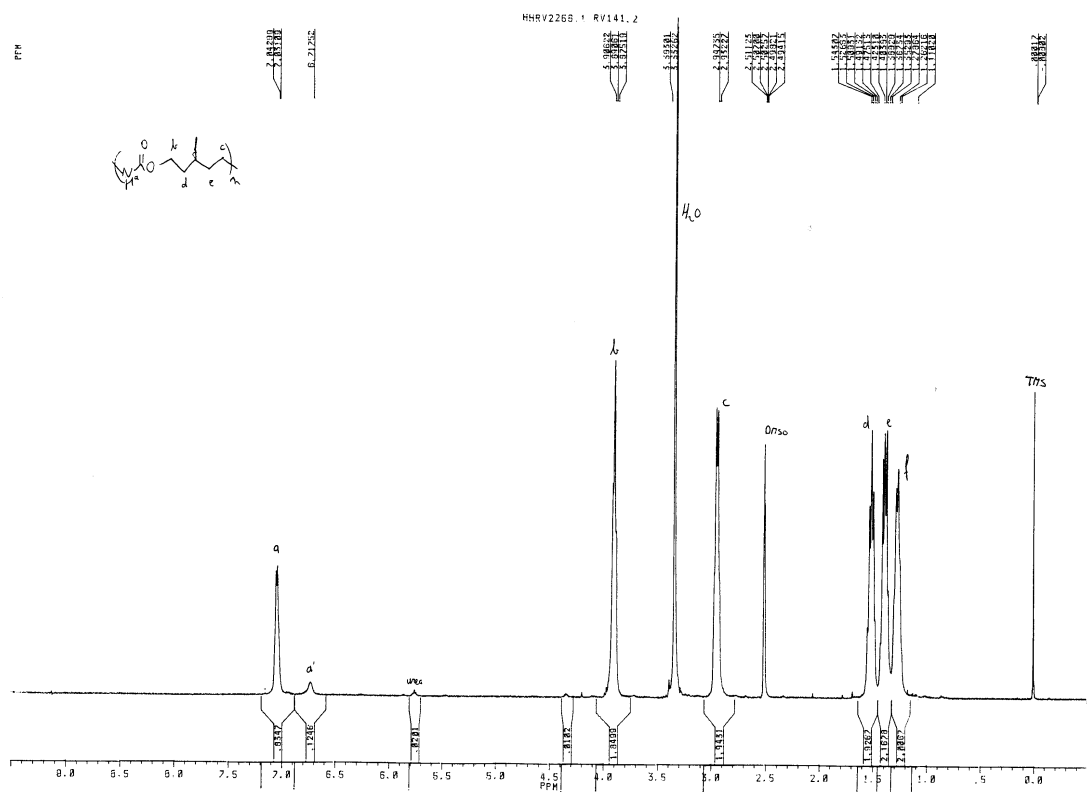


98/06/27 13:39 rs
X: 4 scans, 16.0 cm^{-1}

RV141

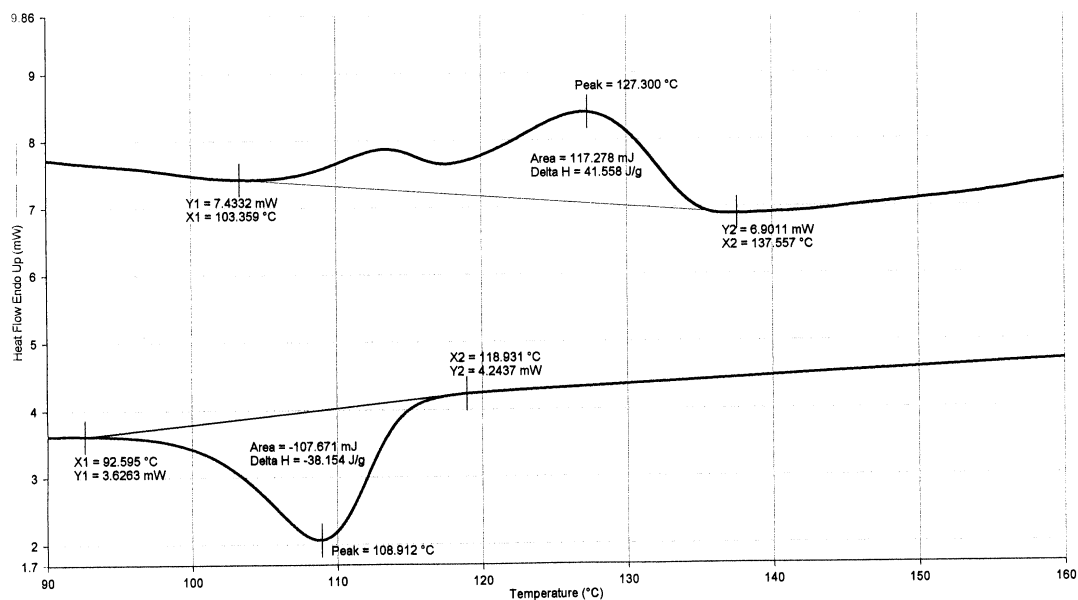


FT-IR of [6]-polyurethane in KBr.



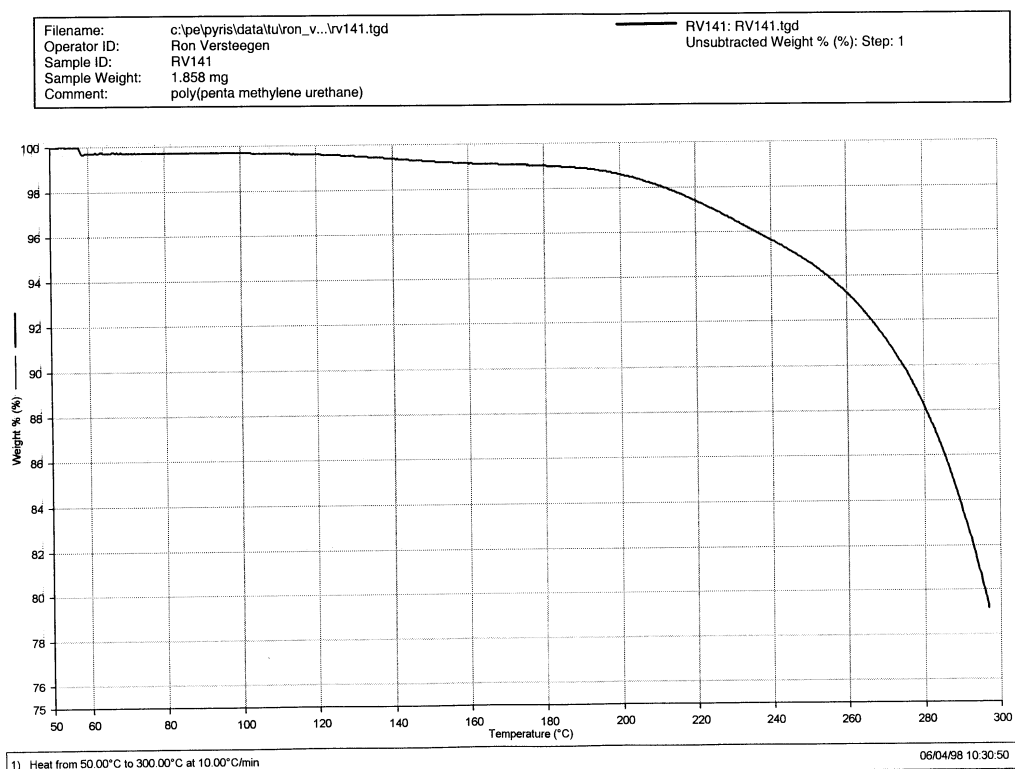
¹H-NMR of [6]-polyurethane in DMSO,
20°C.

Filename: D:\USERS\TG TORV\pu6_2.dcd
Operator ID: Ron
Sample ID: pu6
Sample Weight: 2.822 mg
Comment: rv141 pu6 na calibrate



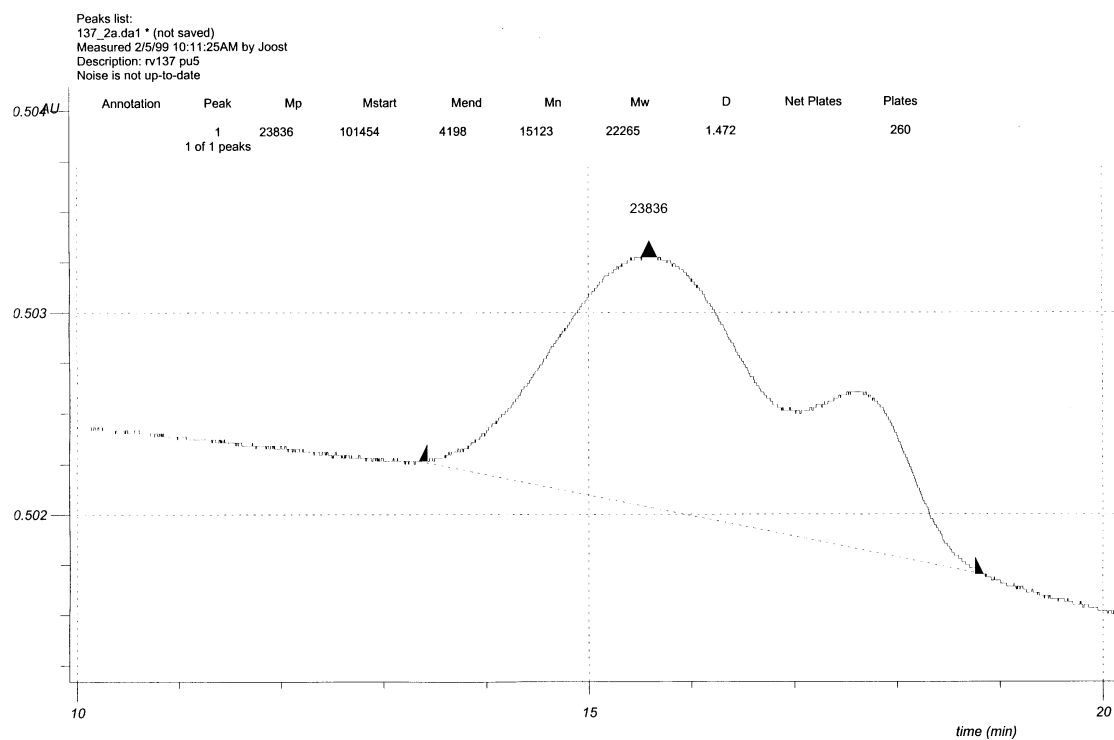
1) Hold for 1.0 min at 160.00°C
2) Cool from 160.00°C to 80.00°C at 10.00°C/min
3) Hold for 1.0 min at 80.00°C
4) Heat from 80.00°C to 200.00°C at 10.00°C/min
5/6/99 3:47:50 PM

DSC of [6]-polyurethane,
10°C/min.



TGA of [6]-polyurethane,
10°C/min.

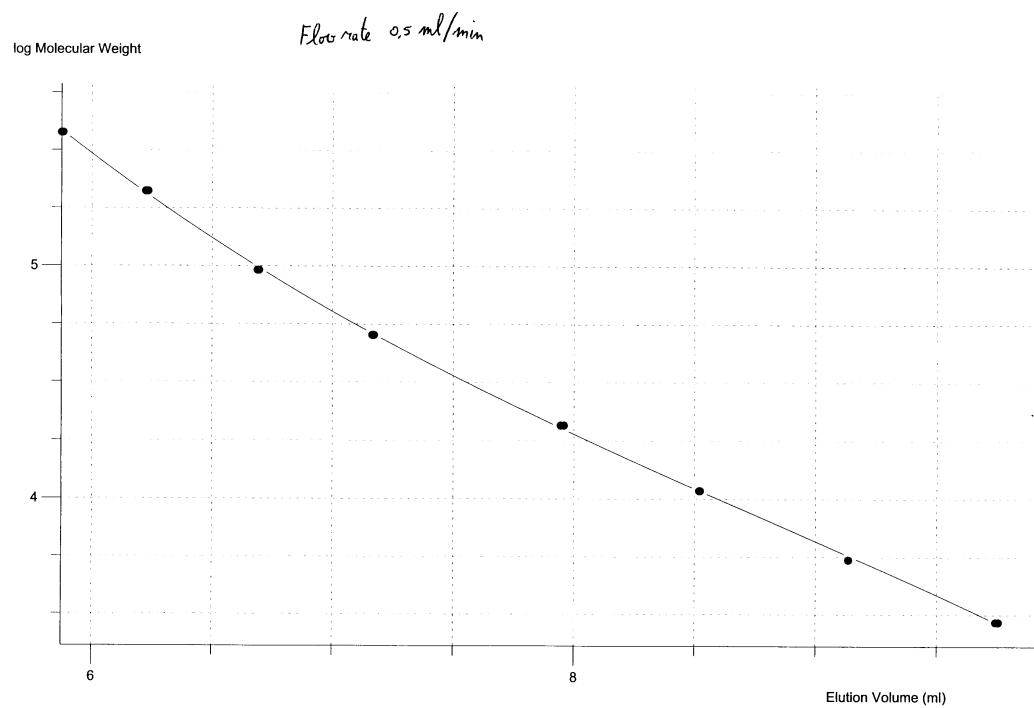
p. 1



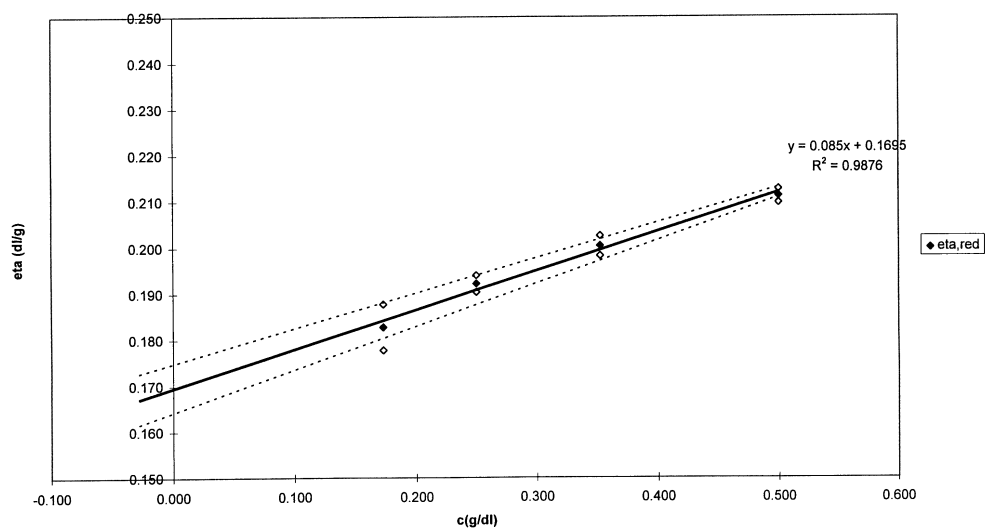
SEC of [6]-polyurethane in
NMP.

DAX 7.0: GPC Calibration Parameters, file C:\SEC\CALIBRATION\PL51NMP.GPC
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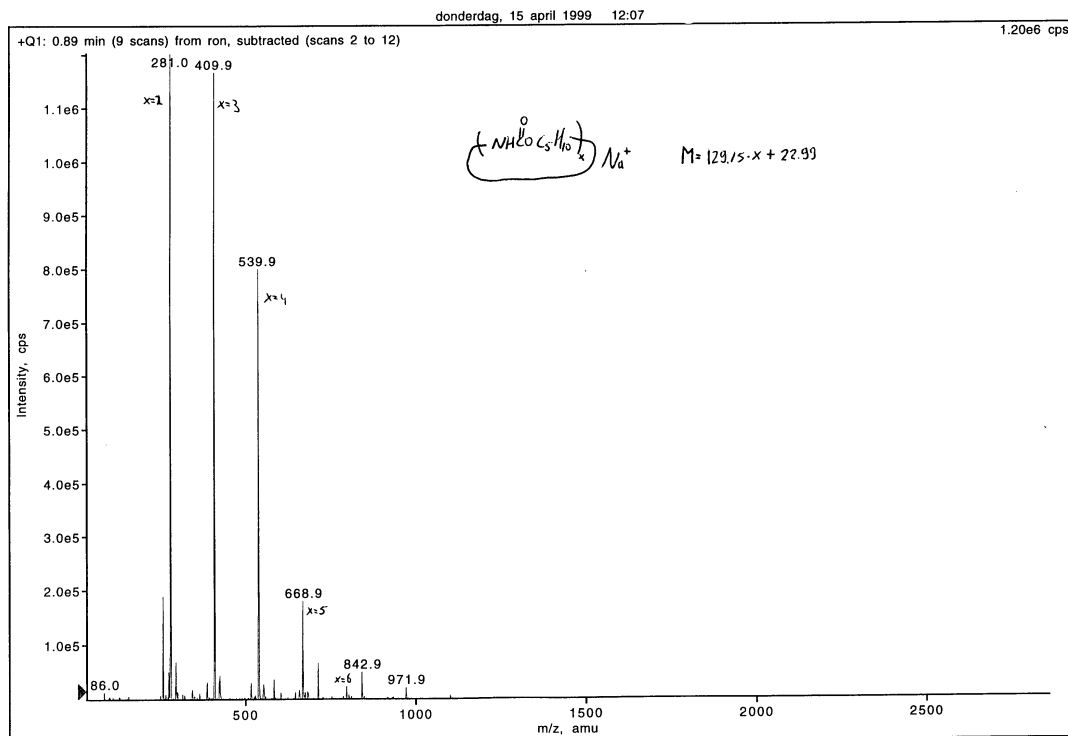
p. 1



Calibrationcurve SEC, flow rate=0.5
ml/min.



Intrinsic viscosity of [6]-polyurethane in *m*-cresol at 20°C.



ES-MS of cyclic oligomers of [6]-polyurethane.