

# GIN

# 3167-3169

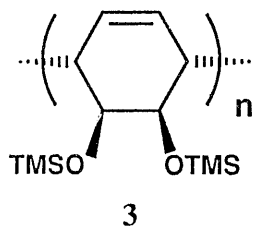
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J-3169-m1

## Characterization of



400 MHz  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):

$\delta$  5.1-6.2 (2H);  $\delta$  3.3-4.1 (2H);  $\delta$  2.7-3.2 (1H);  $\delta$  2.1-2.6 (1H);  $\delta$  -0.4-0.5 (18H)

Elemental Analysis  $\text{C}_{12}\text{H}_{24}\text{O}_2\text{Si}_2$ :

calculated (%):	C: 56.19	H: 9.43	Si: 21.90
found (%):	C: 55.91	H: 9.34	Si: 22.21

IR Analysis (thin film on NaCl):

• characteristic absorptions ( $\text{cm}^{-1}$ ):	2957	$\nu$ (C-H), $-\text{CH}_2-$
	2898	
	1251	$\delta$ [Si-( $\text{CH}_3$ ) $_3$ ]
	1111	
	1087	$\nu$ (Si-OR)
	1046	
	837	$\nu$ [Si-( $\text{CH}_3$ ) $_3$ ]
	748	

Powder X-Ray Diffraction:

- peak at 9.725 Å, and an amorphous halo centered at 5.5 Å (peaks at 4.110, 3.723 Å are diffractometer artifacts).

Scanning Tunneling Microscope Imaging:

- stacked and ordered rod-like chains approximately 400-700 Å in length.

J-3169-m2

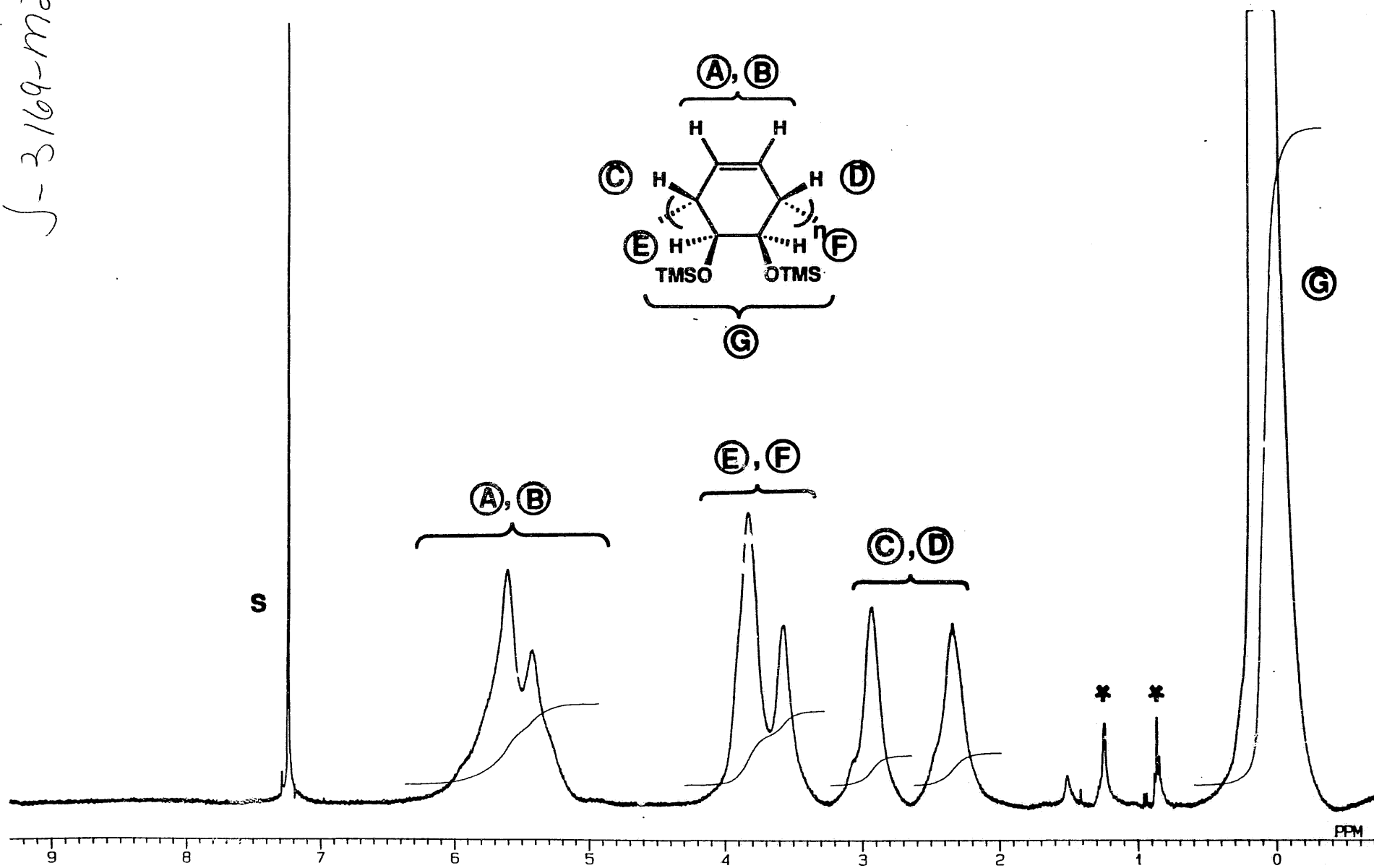


Figure 1. 400 MHz <sup>1</sup>H NMR Spectrum of Polymer 3 in CDCl<sub>3</sub>.

J-3169-m3

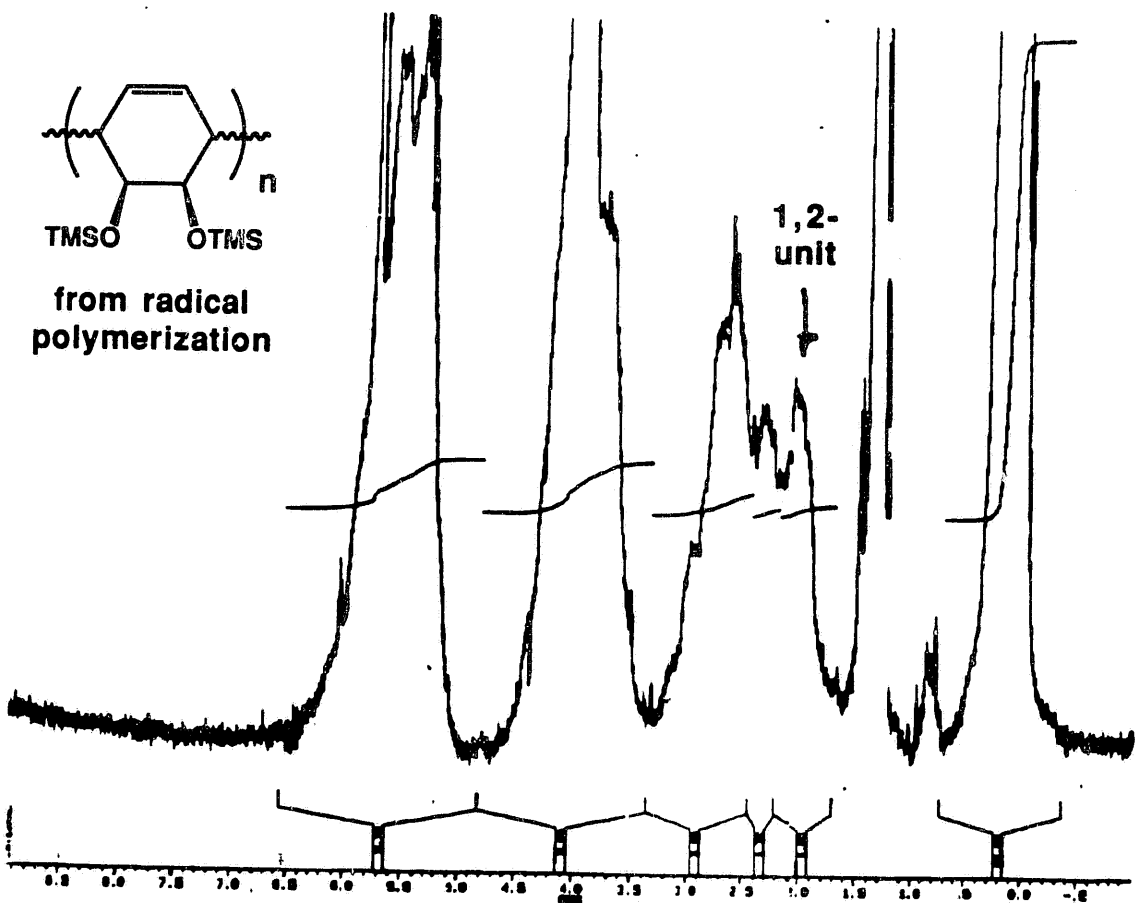
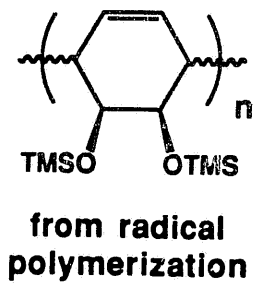
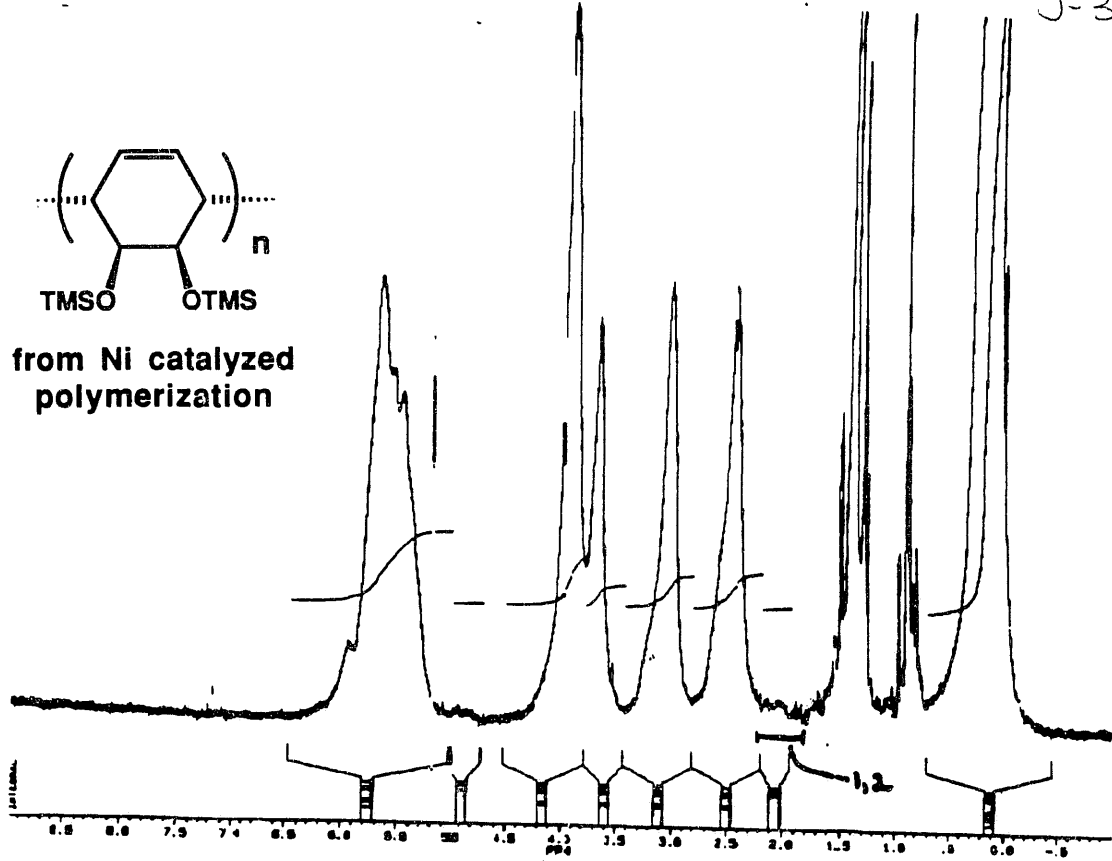
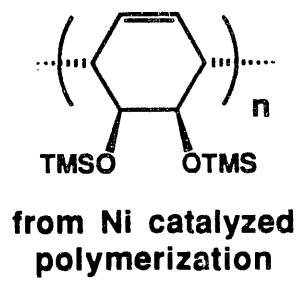
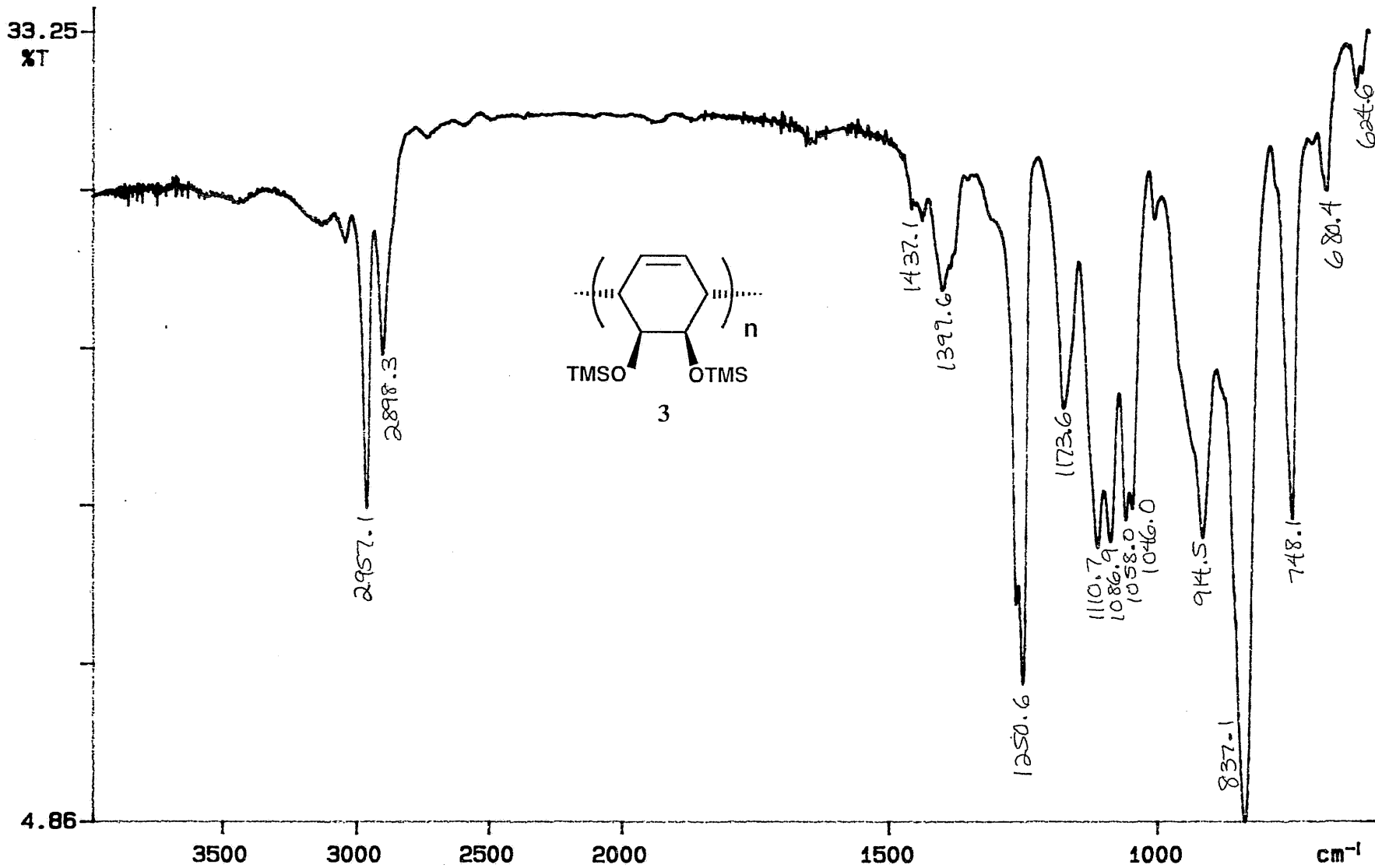


Figure 2. Comparative 500 MHz <sup>1</sup>H NMR Spectra of Polymer 3 and Radically Polymerized Oligomers.

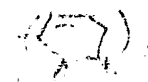
P-12



89/09/18 14:05  
Y: 16 scans, 2.0cm⁻¹, flat

Figure 3. IR Spectrum of Polymer 3 on NaCl.

89046



5-3169-m4

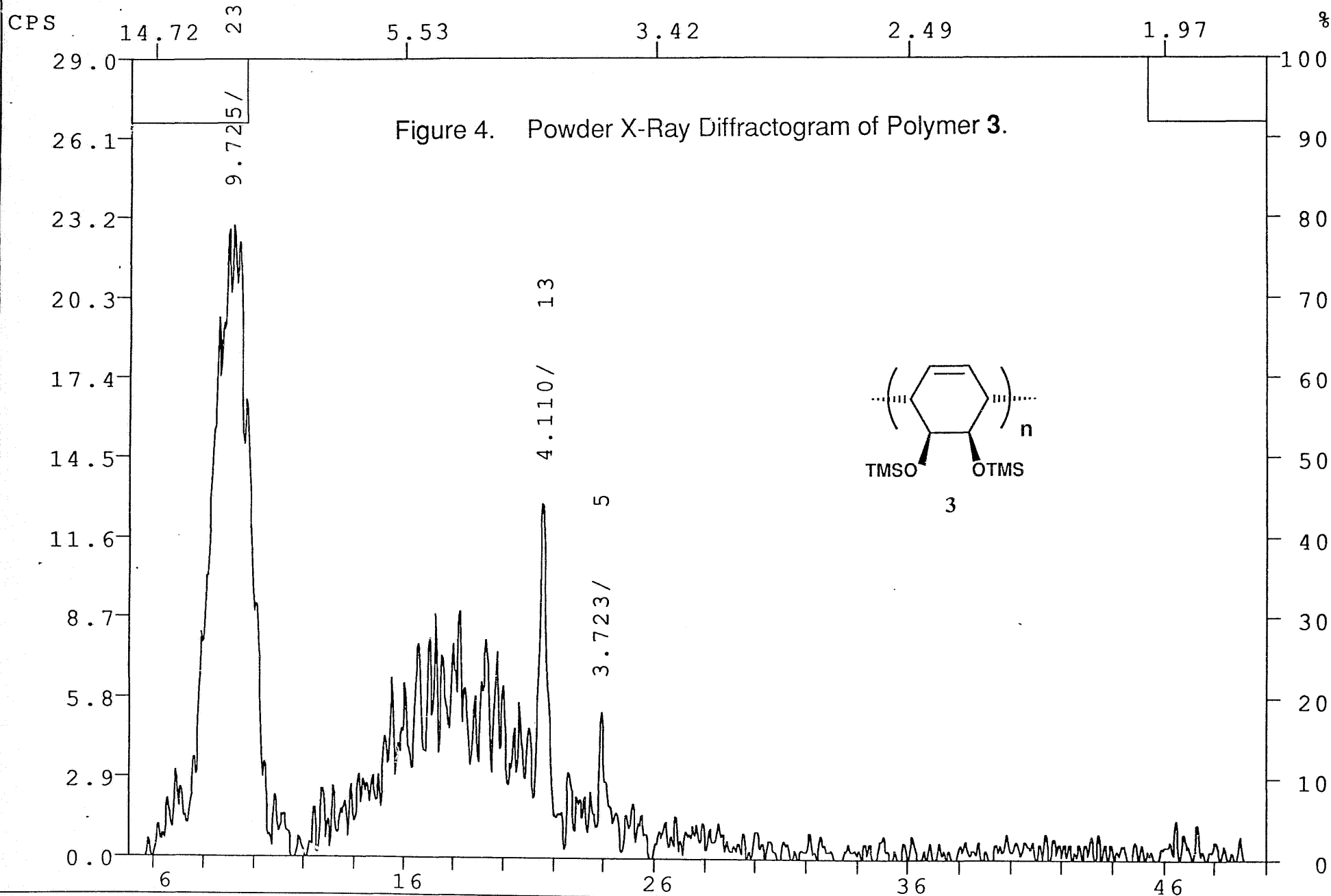
FN:dlg0912.NI  
DATE: 9/12/91

ID:1,4-POLY(TMS-DHCD) 91DLG035/3  
TIME:23: 1

SCINTAG/USA  
WL:1.54059

PT:30.000 STEP:0.040

FULL-COPY PCOPY PAGE TITLE CYCLE D ANGLE END OVERLAP REPOS CURSOR LABEL



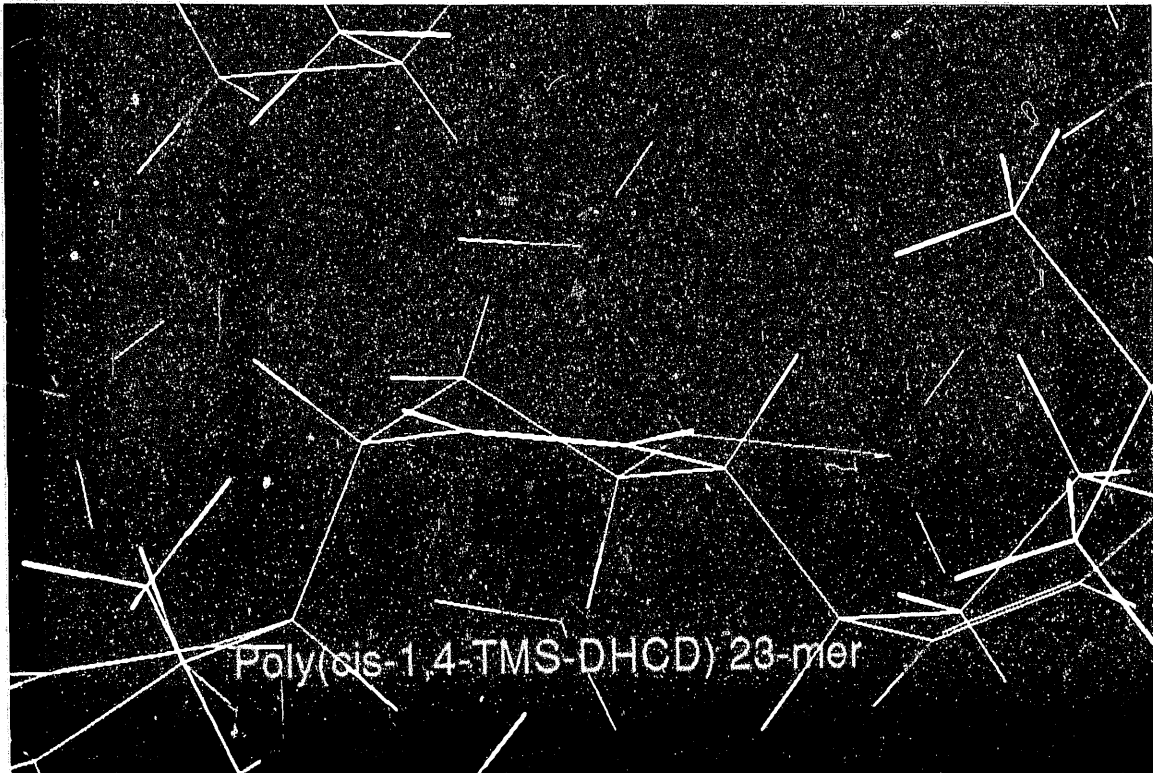


Figure 5a. Biograf Computer Model of a Repeat Unit of Polymer 3.

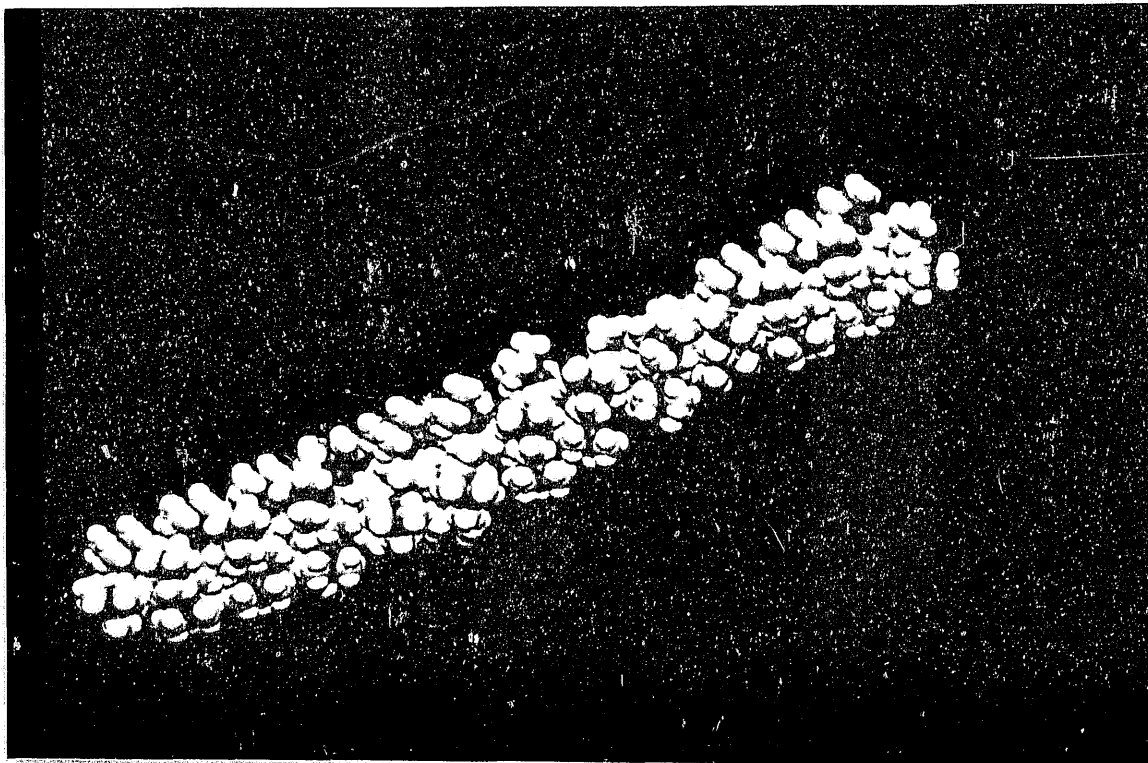


Figure 5b. Biograf Computer Model of a 23-Unit Chain of Polymer 3.

J-3169-m7



Figure 6. STM Image of Chains of Polymer 3 on Graphite (Top View).



J-3169-m8

nanoclusters.015 03/04/91 11:19:30  
Aggregate of 1,4-Poly(TMS DHCD) Chains on Graphite

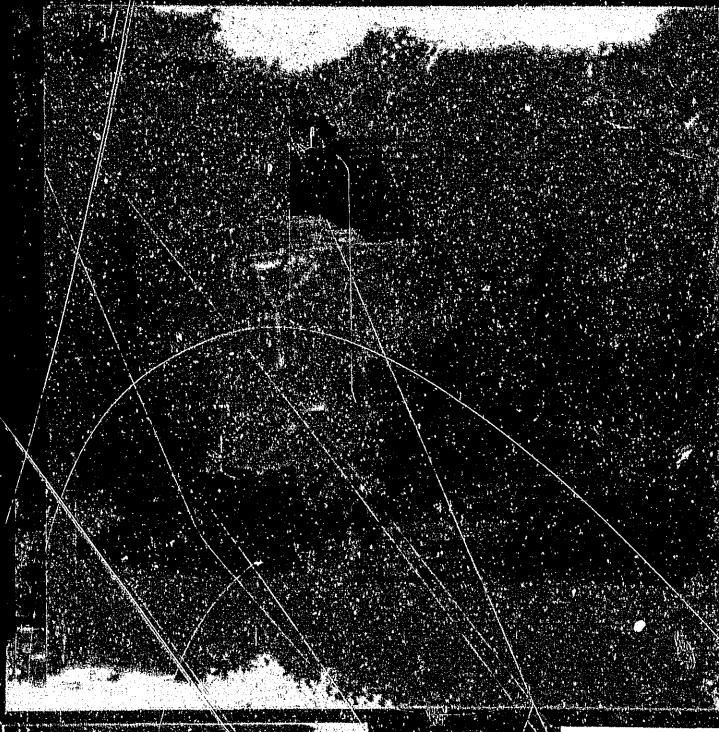


Figure 7a.

Figure 7b.

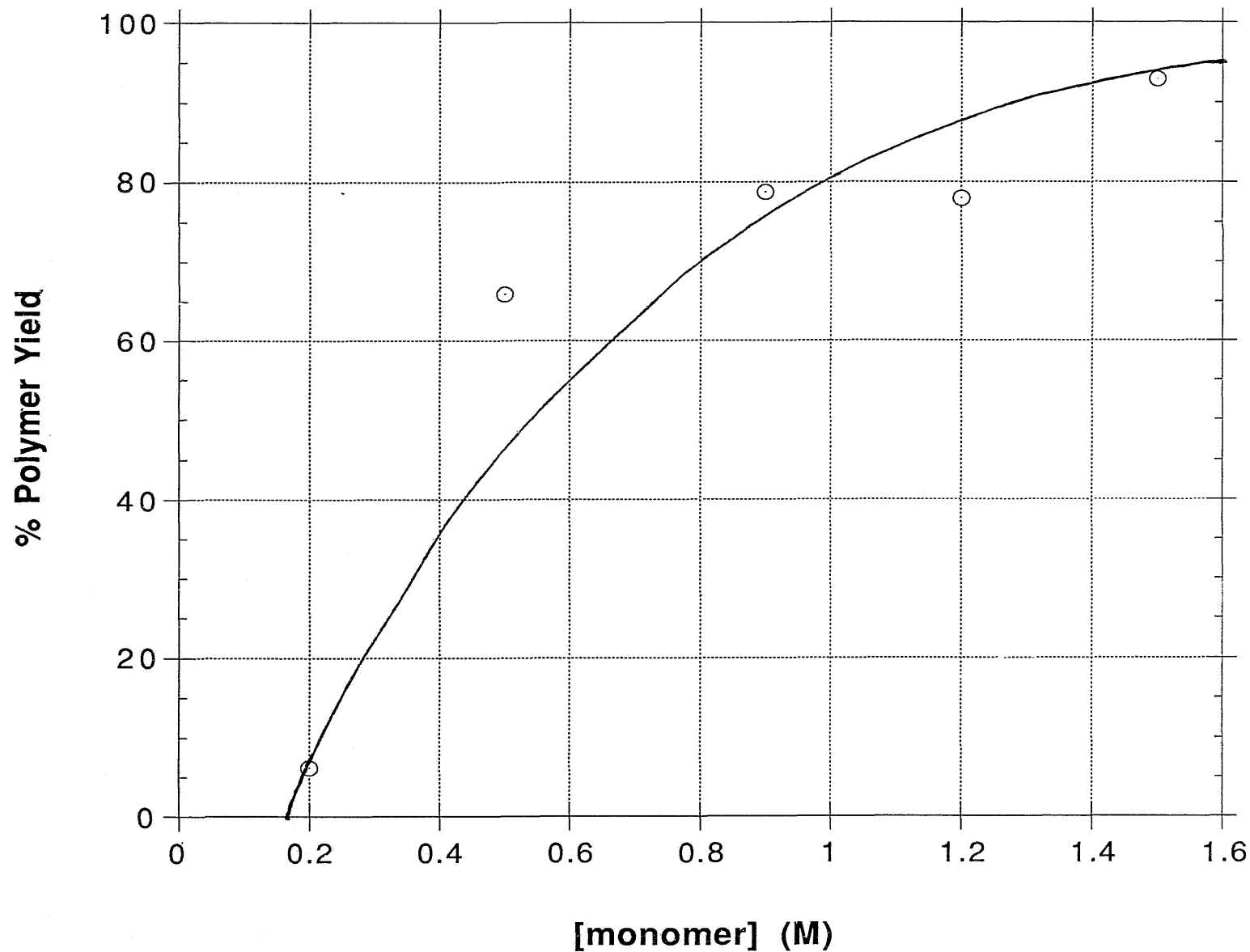
Color range / 200 Angstroms 2000 Angstroms



STM Image of an Aggregate of Polymer 3 Chains on Graphite.

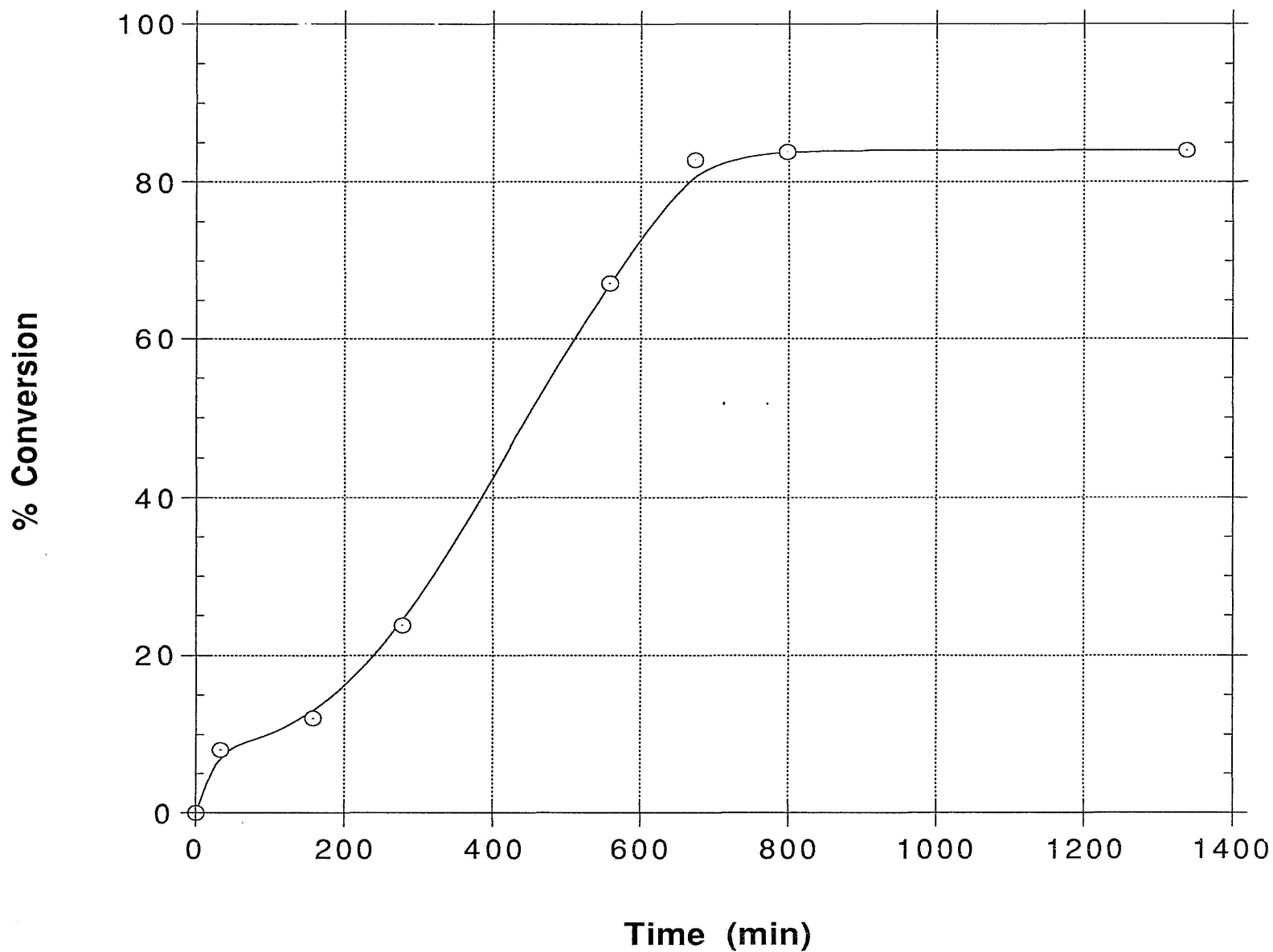
Figure 7a. Top View; Figure 7b. 3-D Representation

**Figure 8a.**  
**Polymer Yield vs. Monomer Conc. Plot for**  
**(ANiFA)<sub>2</sub>/TMS-CHD System at 50 °C in PhCl;**  
**(monomer:cat.=80:1)**



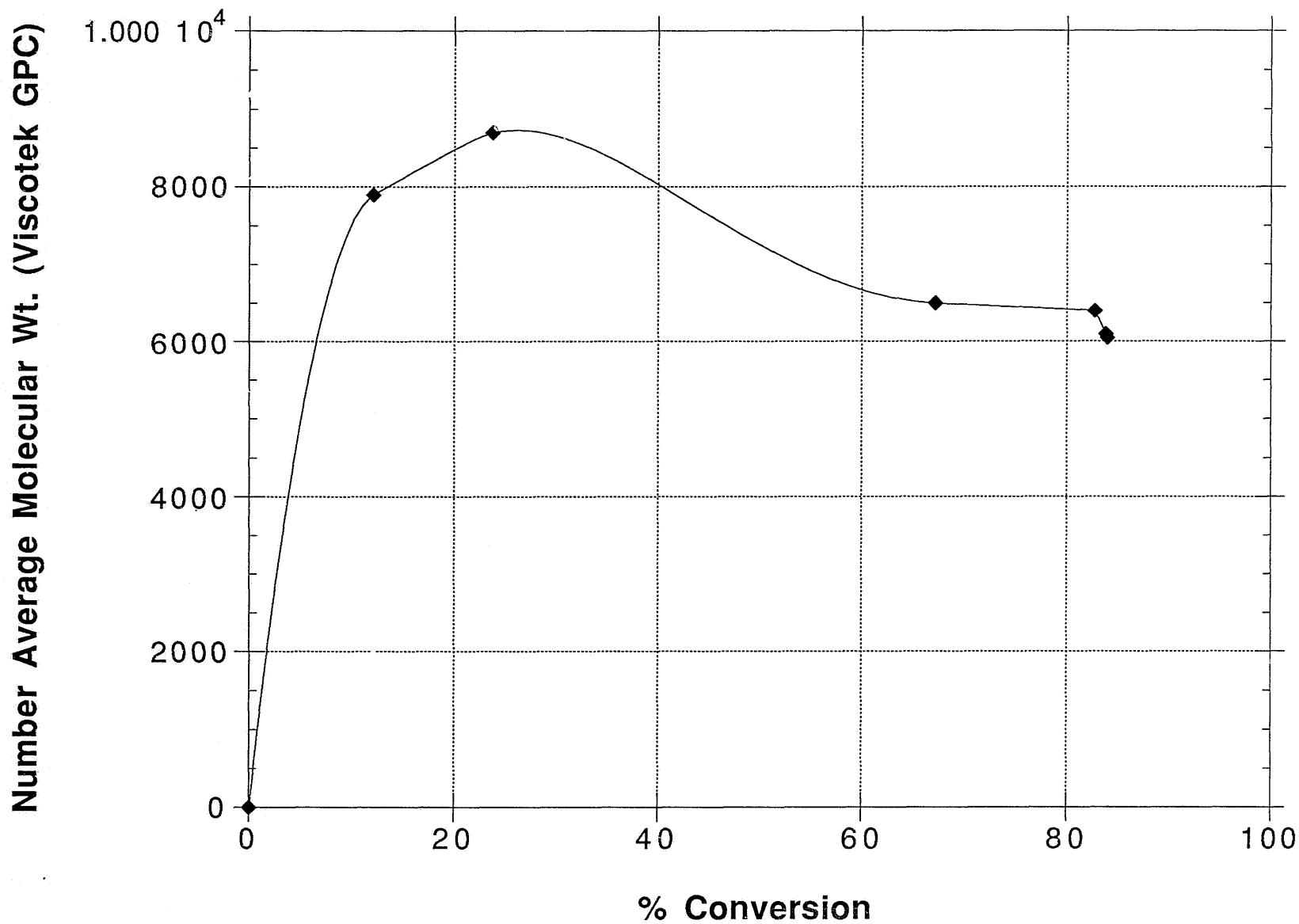
J-3169-179

**Figure 8b.**  
**% Conversion vs. Time Plot for**  
**(ANiTFA)<sub>2</sub>/TMS-CHD System at 50 °C in PhCl**  
**([monomer] = 0.7 M; m:cat. ratio = 7)**



J-3169-m110

Figure 8c.  
Molecular Weight vs % Conversion for  
 $[(\eta^3\text{-allyl})\text{NiO}_2\text{CCF}_3]_2/(\text{TMS-CHD})$  in PhCl  
(50 °C; [monomer] = 0.7 M; monomer:cat. = 75)



J-3169-m11

Experiment	Equiv. of Fresh Monomer Added	Mn (Viscotek)	DP	PDI	Mark-Houwink Coeff. (a)
91DLG035/1	75	1.778 E4	69	2.062	0.572
91DLG035/2	70	3.307 E4	129	1.890	0.722
91DLG035/3*	247	5.140 E4	200	2.031	0.773

• **Successive additions of monomer to the system; [monomer] = 0.7 M (constant).**

\* **Excess monomer required near the end due to gelling problems.**

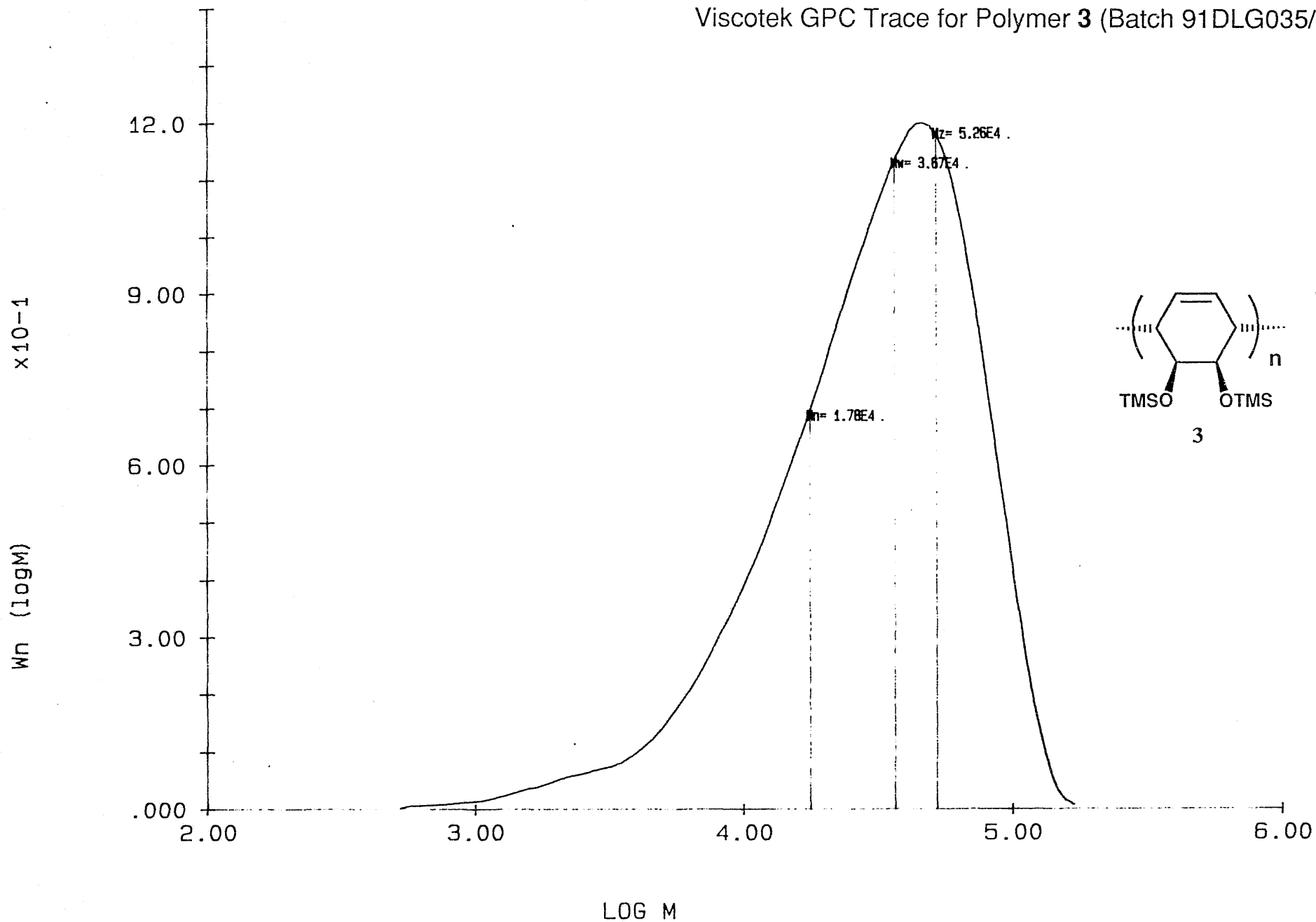
Figure 8d. Mol. Wt. as a Function of Blocking for (ANiTFA)<sub>2</sub> and Monomer 2 System.

J-3169-m12

424-01

91DLG035/1

Figure 9a. Representative Viscotek GPC Data from ICI:  
Viscotek GPC Trace for Polymer 3 (Batch 91DLG035/1).



J-3169-1113

J-3169-m14

UNICAL SUMMARY REPORT

=====  
424-01 ENDED: 07/08/91 11:40: 91DLG035/1  
=====

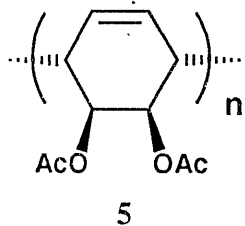
PARAMETERS		MOLECULAR WEIGHT VALUES		
CONCENTRATION (mg/ml)	6.900	Mn (avg) =	1.778E	4
INJECTION VOLUME (ml)	.200	Mw (avg) =	3.667E	4
DPT SENSITIVITY (mv/Pa)	1.000	Mz (avg) =	5.258E	4
INLET PRESSURE (KPa)	20.145	Mp =	3.854E	4
FLOW RATE (ml/min)	1.000	Mv (avg) =	3.343E	4
VISCOMETER OFFSET (ml)	-.121	POLYDISPERSITY RATIOS		
ACQ. START TIME (min)	5.000	Mw/Mn =	2.062	
ACQ. STOP TIME (min)	33.333	Mz/Mn =	2.957	
DATA INTERVAL (sec)	3.400	SKEWNESS OF DISTRIBUTION		
SIGMA (ml)	.150	SKEW(n) =	1.745	
TAU (V)	.126	SKEW(w) =	1.299	
TAU (C)	.087			
THRESHOLD	.020			

METHOD:	UCAL-BROAD	INTEGRATED DETECTOR SIGNALS	BASELINE	X	Y	
CAL FILE	LC10591	CONC (mv-ml) =	24.77	L. VISC	148	316.75
		VISC (mv-ml) =	33.84	R. VISC	235	329.88
MARK-HOUWINK CONSTANTS		IV (dl/gm)	.049	L. CONC	149	773.38
ALPHA	.572	VISCOTEK MODEL#	200	R. CONC	234	782.13
LOG K	-3.928					

Figure 9b. Summary Report for Viscotek GPC Analysis of Polymer 3  
(Batch 91DLG035/1).

J-3169-m15

## Characterization of



400 MHz  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):

$\delta$  5.6-6.0 (2H);  $\delta$  5.0-5.4 (2H);  $\delta$  2.5-2.9 (2H);  $\delta$  1.8-2.2 (6H)

100 MHz  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):

$\delta$  169 (C=O);  $\delta$  127 (C=C);  $\delta$  71 (C-OR);  $\delta$  36 (C-C=C);  $\delta$  21 ( $\text{CH}_3$ )

Elemental Analysis  $\text{C}_{10}\text{H}_{12}\text{O}_4$ :

calculated (%):	C: 61.22	H: 6.16
found (%):	C: 60.45	H: 6.14

IR Analysis (thin film on NaCl):

• characteristic absorptions ( $\text{cm}^{-1}$ ):	1745	$\nu$ (C=O)
	1233	
	1054	$\nu$ (C-O-C)
	1024	

Powder X-Ray Diffraction:

• two amorphous halos centered at 10.4 and 18.9 Å.



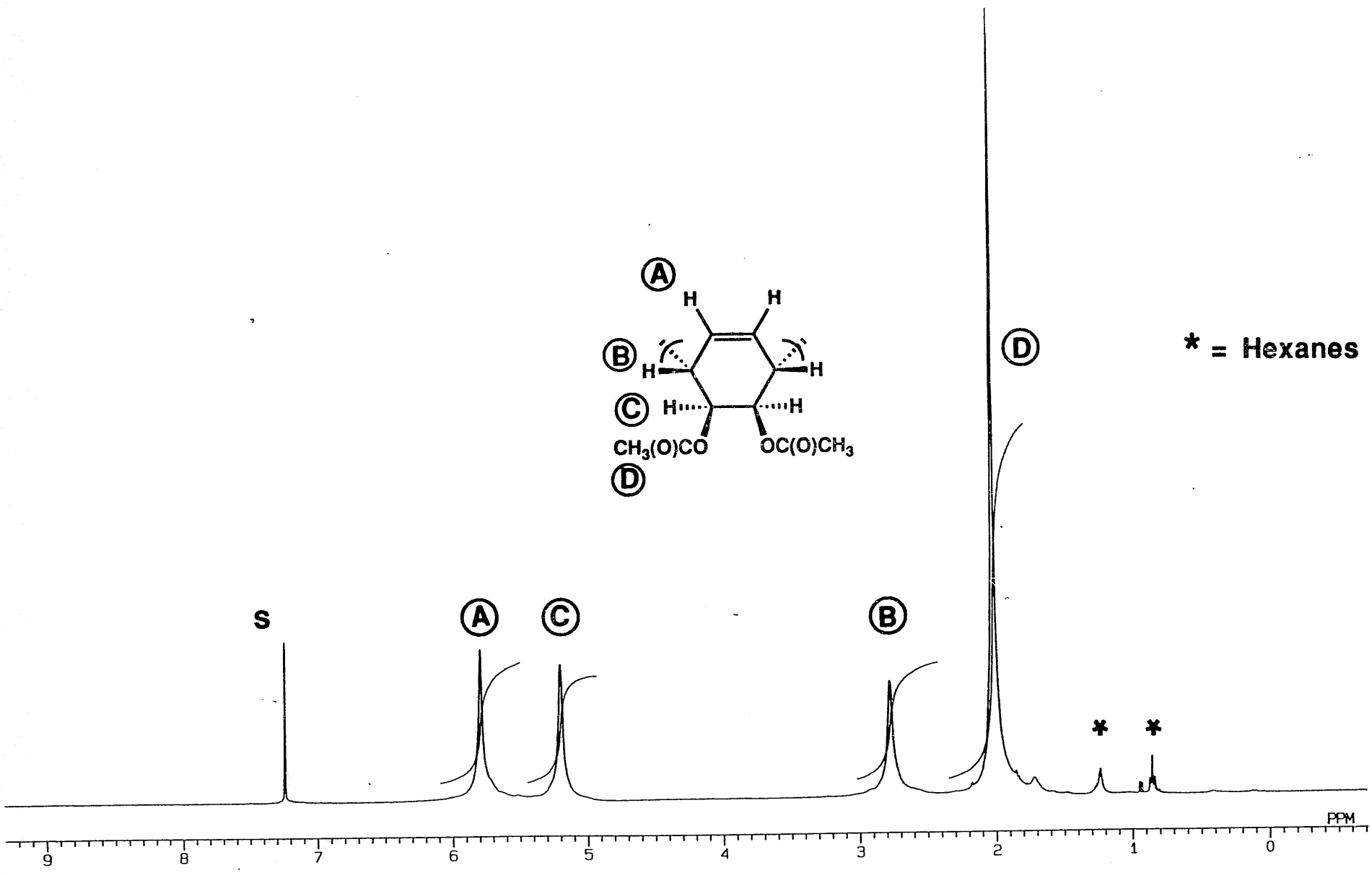


Figure 10a. 400 MHz <sup>1</sup>H NMR Spectrum of Polymer 5 in CDCl<sub>3</sub>.

J-3169-m14

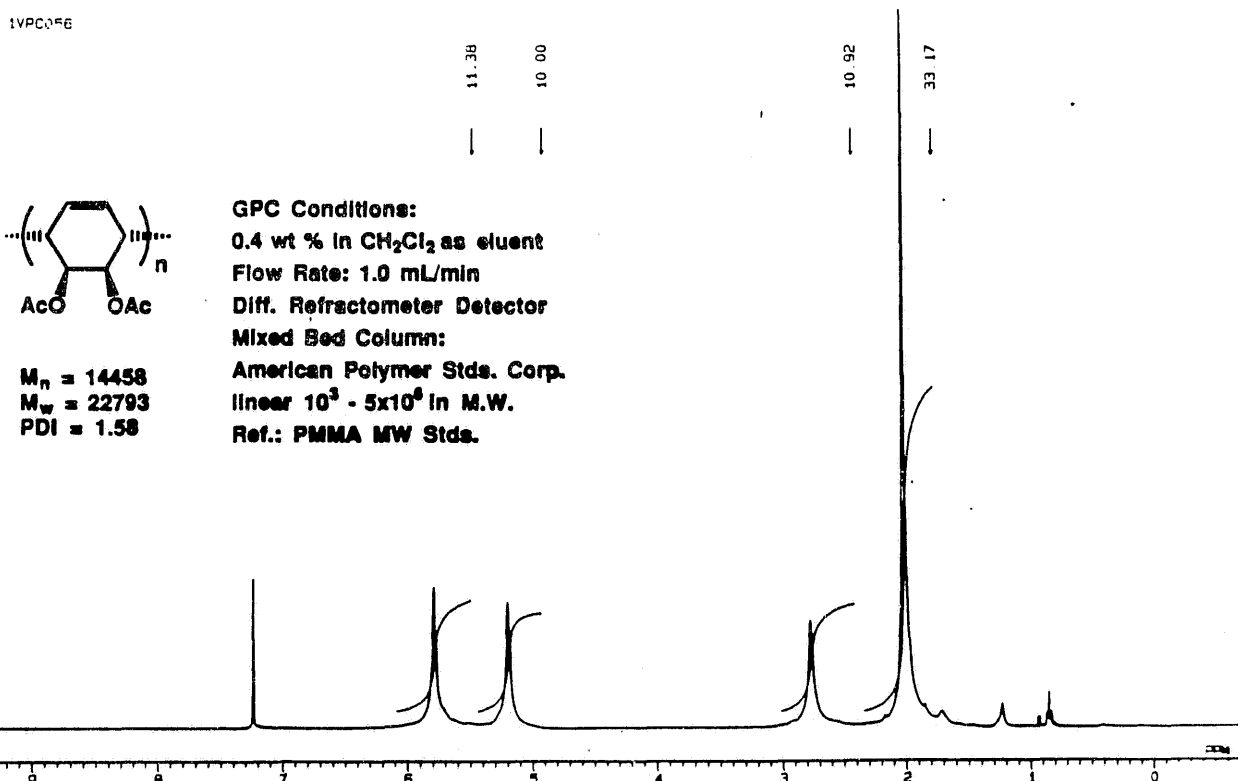
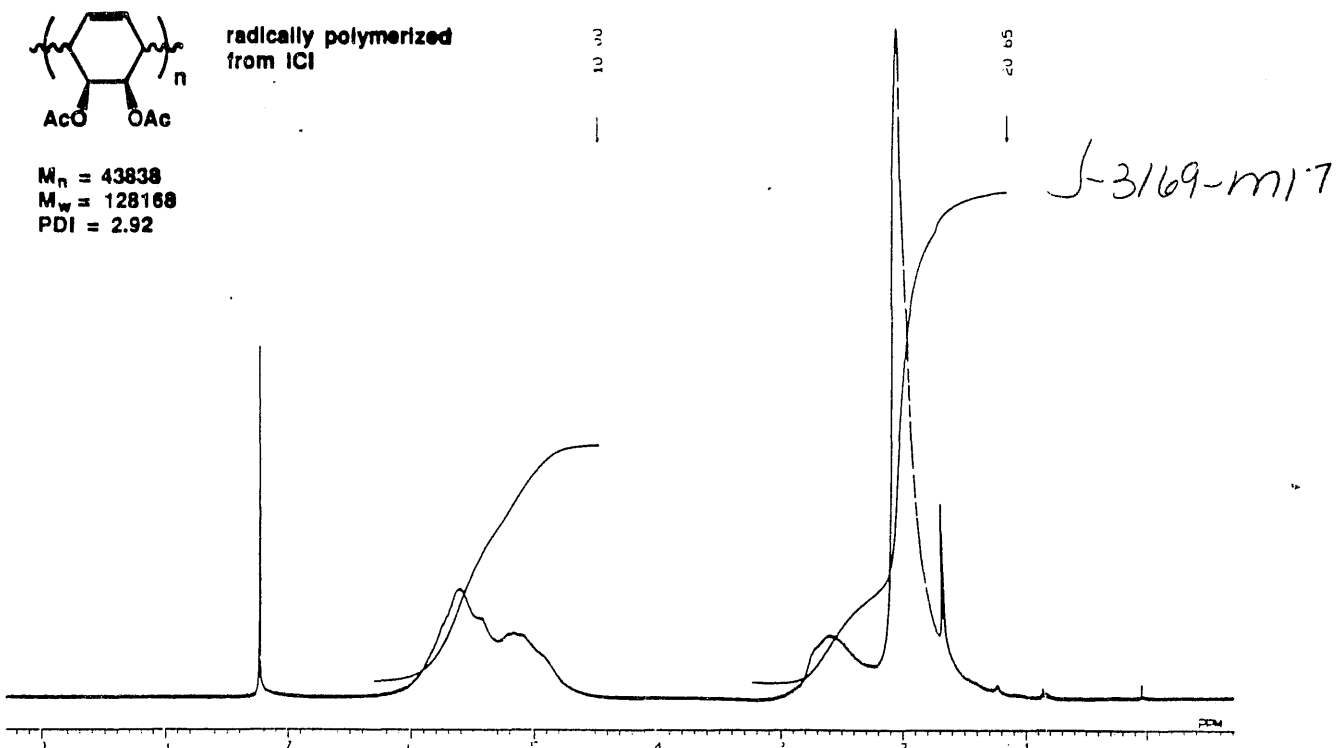
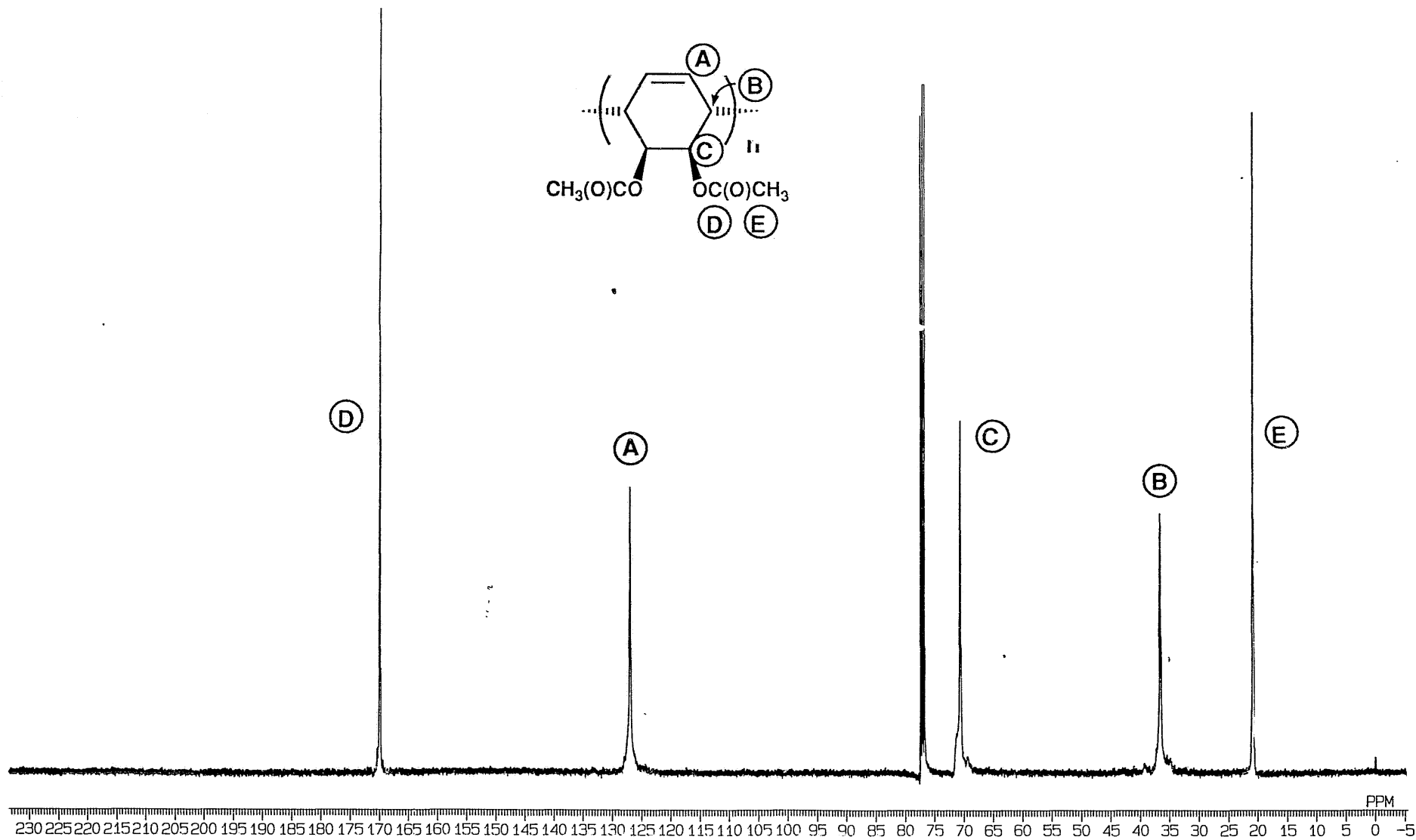


Figure 10b. Comparative 400 MHz  $^1H$  NMR Spectra of Polymer 5 and Its Radically Polymerized Analogue.

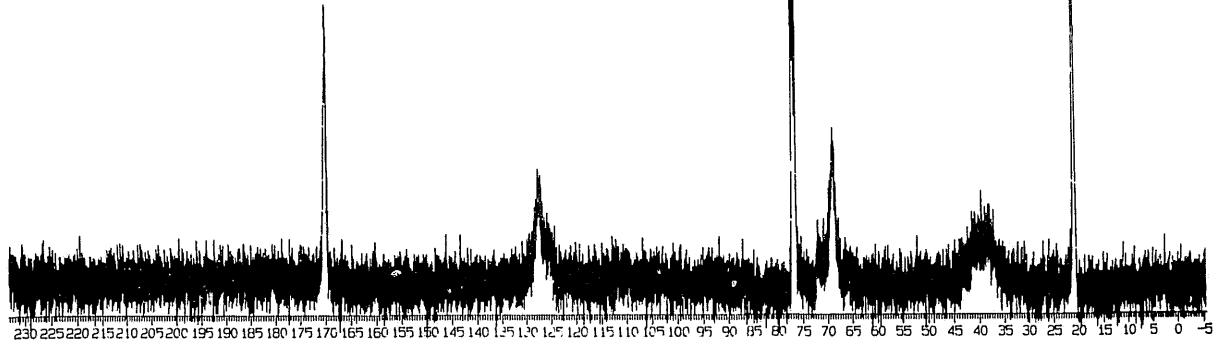
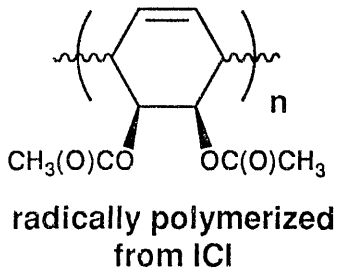


J-3169-1118

Figure 11a. 100 MHz <sup>13</sup>C NMR Spectrum of Polymer 5 in CDCl<sub>3</sub>.

POLY (DA-DH)

J-3169-m19



POLY (DA-DH)

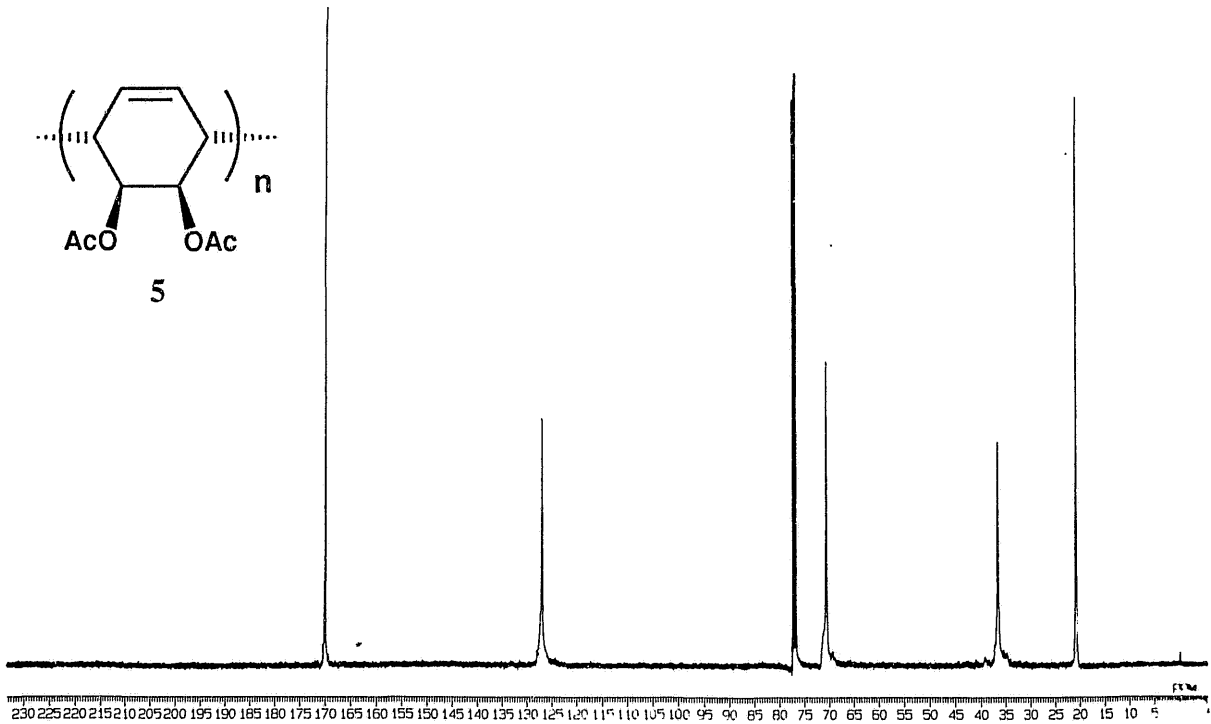
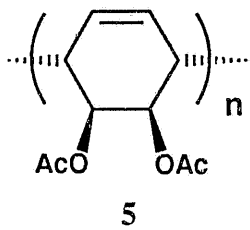
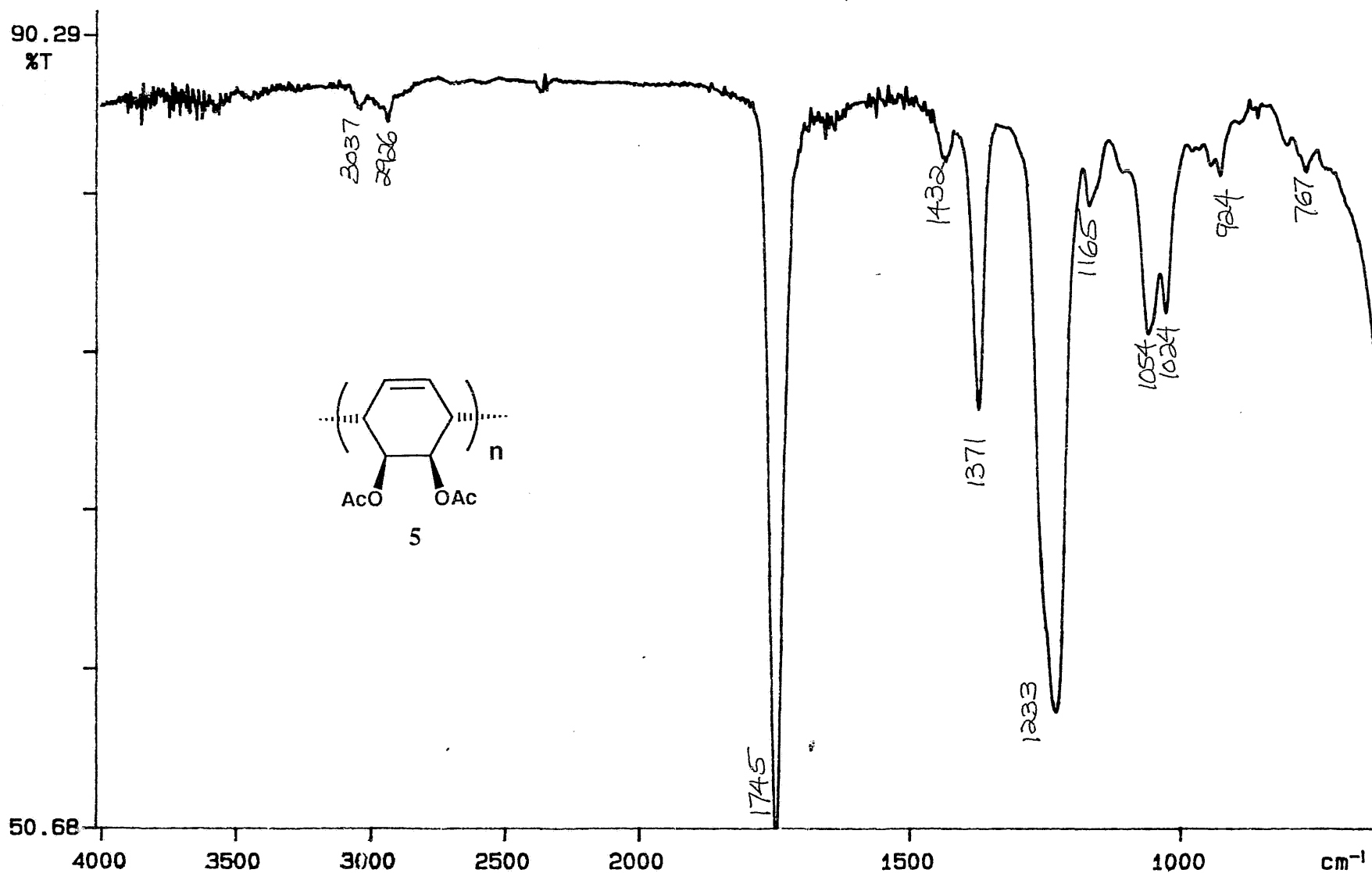


Figure 11b. Comparative 100 MHz <sup>13</sup>C NMR Spectra of Polymer 5 and Its Radically Polymerized Analogue.

P-E



91/04/27 23:30  
Y: 16 scans, 4.0 $\text{cm}^{-1}$ , flat

IVACOS

Figure 12. IR Spectrum of Polymer 5 on NaCl.

J-3169-m30

J 3169-1721

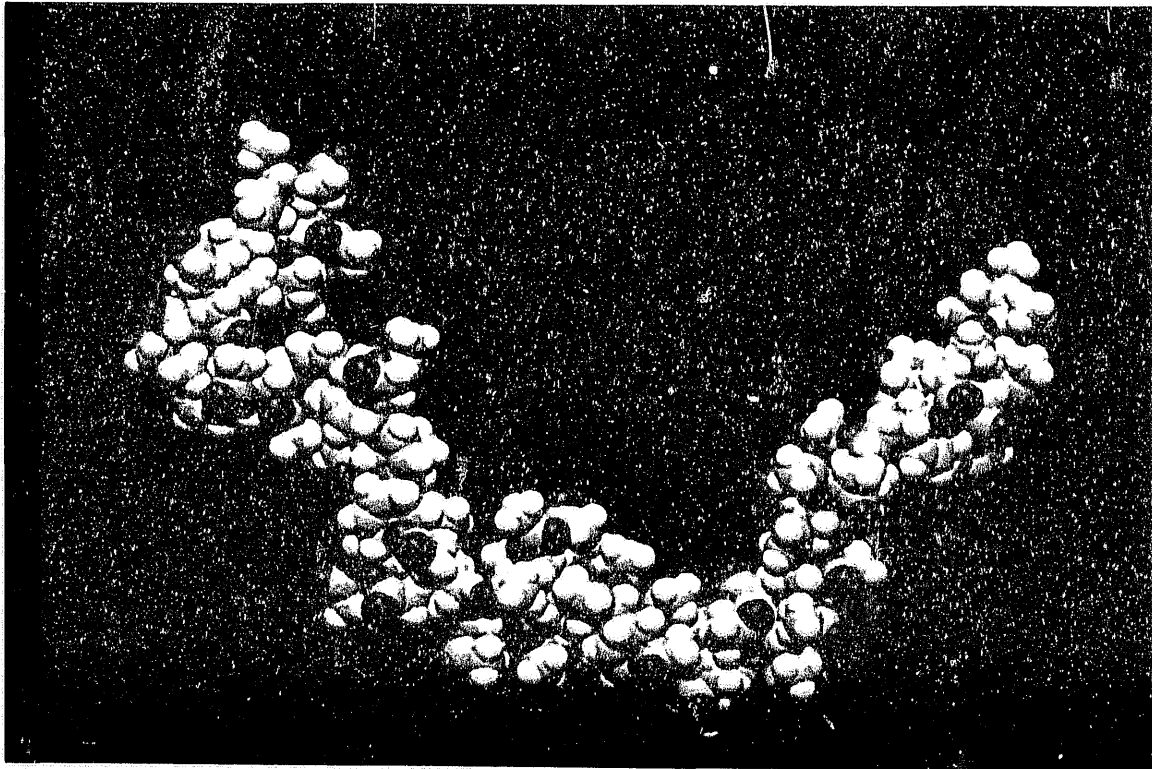


Figure 13. Biograf Computer Model of a 32-Unit Chain of Polymer 5.

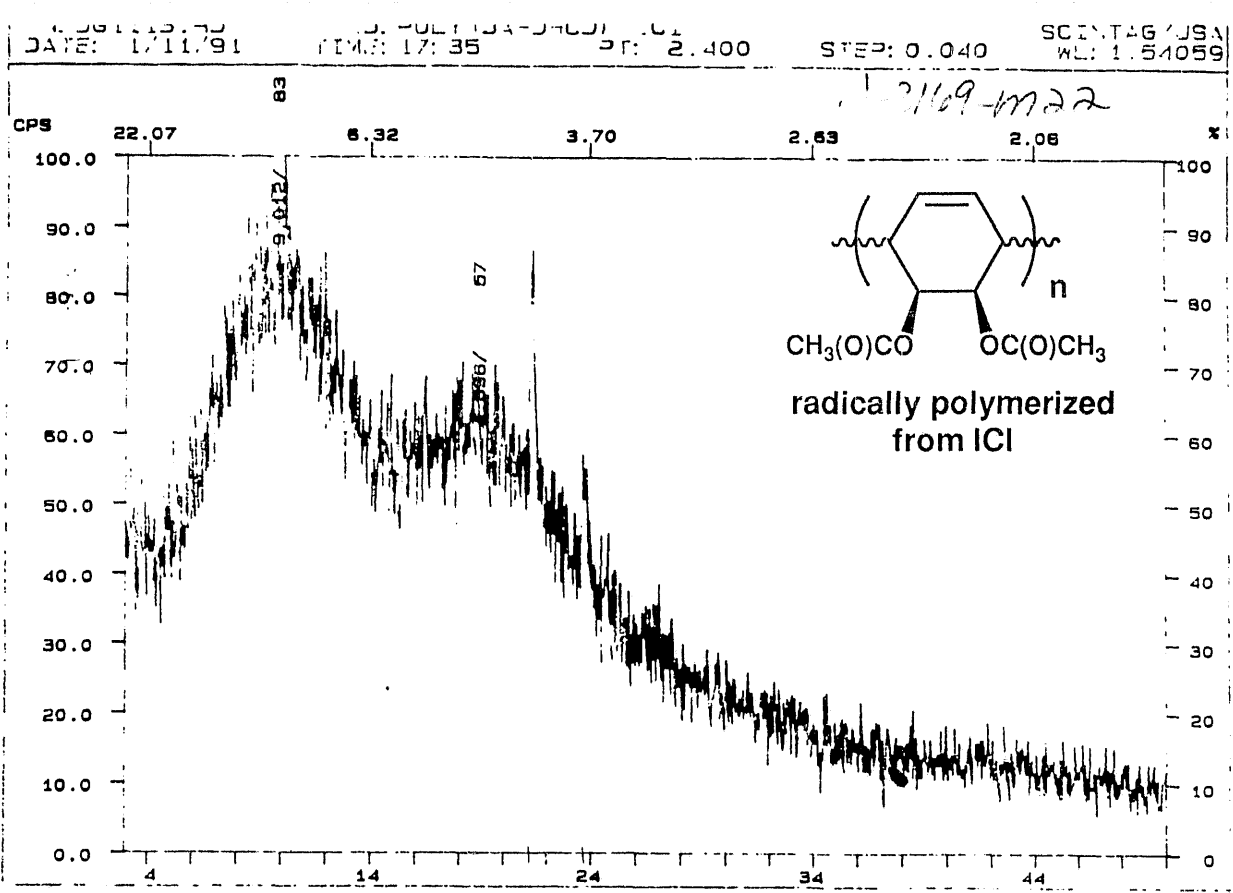
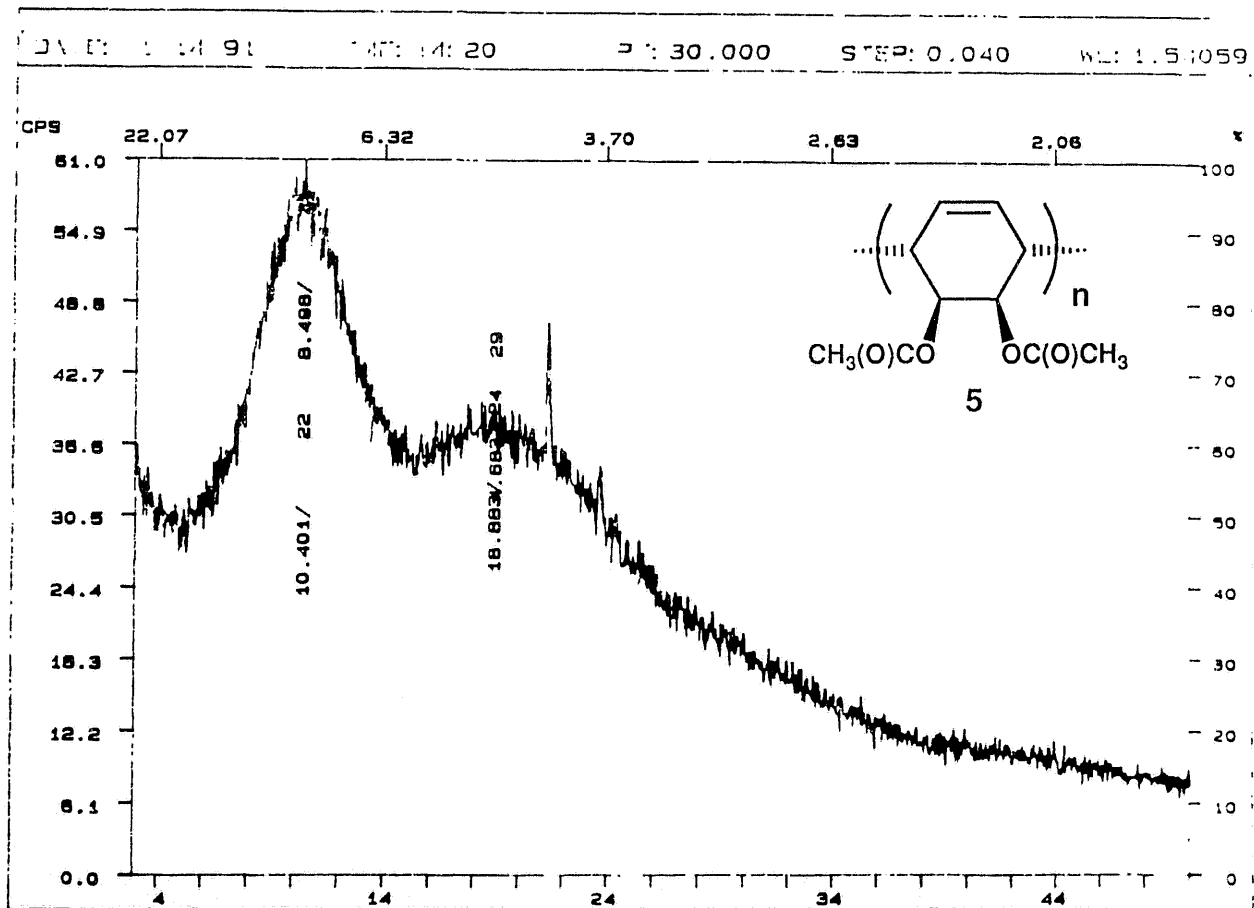


Figure 14. Comparative Powder X-Ray Diffractograms of Polymer 5 and Its Radically Polymerized Analogue.



J-3169-m23

Elution Volumes:

20.00	20.50	21.00	21.50	22.00
22.50	23.00	23.50	24.00	24.50
25.00	25.50	26.00	26.50	27.00
27.50	28.00	28.50	29.00	29.50
30.00	30.50	31.00	31.50	32.00

Slice Heights:

0.05	0.10	0.15	0.20	0.30
0.40	0.55	0.65	0.80	0.85
0.90	0.95	1.00	0.95	0.90
0.80	0.70	0.50	0.40	0.35
0.30	0.20	0.20	0.15	0.15

Molecular Weights:

846106.06	670782.35	531787.90	421594.82	334235.13
264977.45	210070.82	166541.53	132032.05	104673.37
82983.74	65788.48	52156.29	41348.85	32780.86
25988.26	20603.17	16333.93	12949.34	10266.07
8138.82	6452.35	5115.34	4055.38	3215.06

Mn = 26600.724  
Mw = 97139.556  
PDI = 3.65

ICI POLY (AA-DHCA)

GPC Conditions:

0.4 wt. % in CH<sub>2</sub>Cl<sub>2</sub> as eluent.  
Diff. Refractometer Detector.  
Mixed Bed Column:  
American Polymer Standards Corp.  
Linear 10<sup>3</sup>-5x10<sup>6</sup> in M.W.  
Ref.: Polystyrene M.W. Standards.

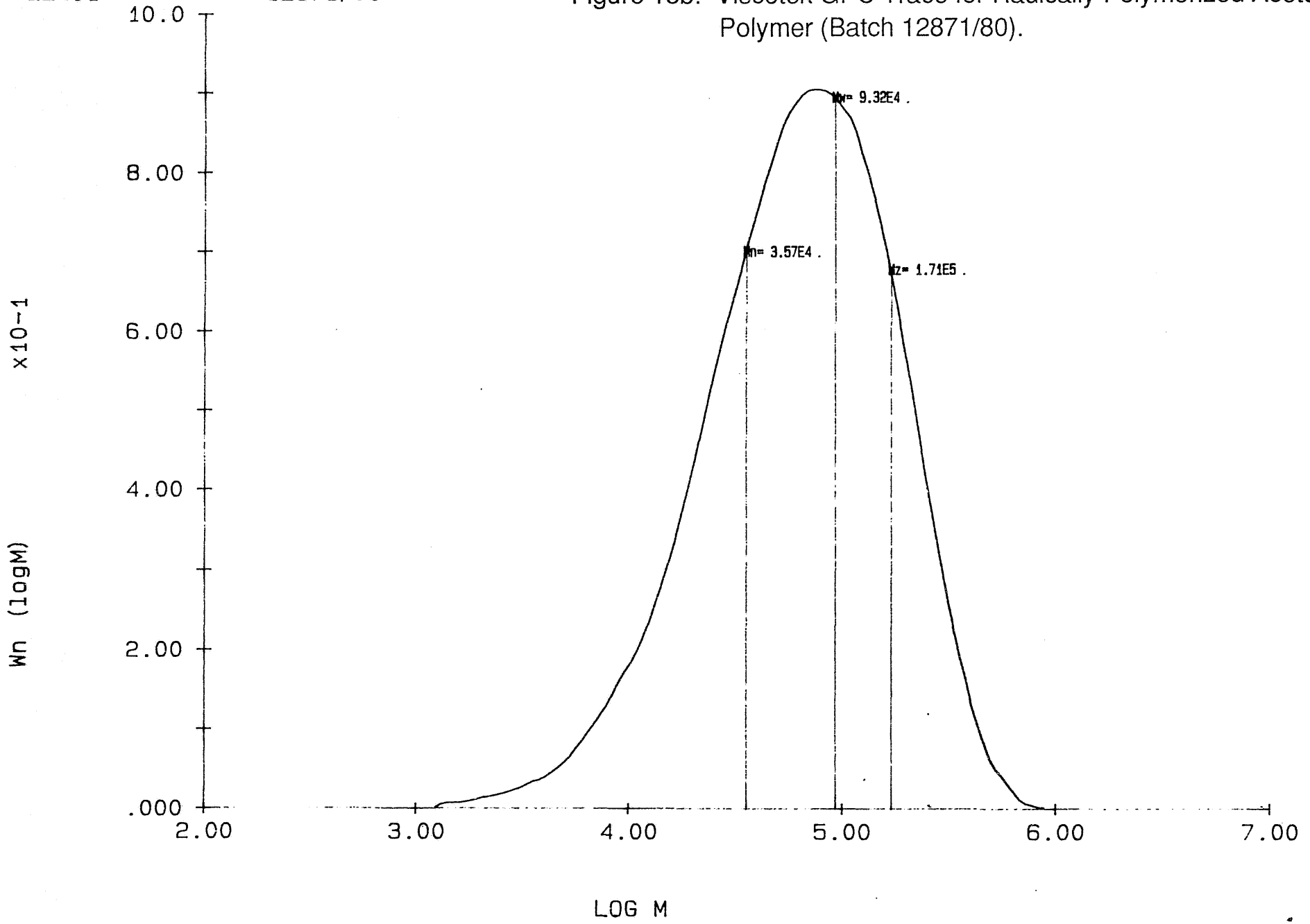
Figure 15a. GPC Data for Radically Polymerized Acetoxy-Polymer (Batch 12871/80), Performed at CIT.



22401

12871/80

Figure 15b. Viscotek GPC Trace for Radically Polymerized Acetoxy-Polymer (Batch 12871/80).



J-3169-m24

J-3169-mas

UNICAL SUMMARY REPORT

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=====
22401      ENDED: 03/26/91 13:54: 12871/80
=====
PARAMETERS
CONCENTRATION (mg/ml)      2.760
INJECTION VOLUME (ml)     0.200
DPT SENSITIVITY (mv/Pa)   1.000
INLET PRESSURE (KPa)      19.588
FLOW RATE (ml/min)        1.000
VISCOMETER OFFSET (ml)    -0.150
ACQ. START TIME (min)     5.000
ACQ. STOP TIME (min)      32.333
DATA INTERVAL (sec)       3.400
SIGMA (ml)                0.225
TAU (V)                   0.121
TAU (C)                   0.020
THRESHOLD                  0.050

MOLECULAR WEIGHTS
Mn (avg) = 3.221E
Mw (avg) = 3.221E
Mz (avg) = 1.705E
Mv (avg) = 1.041E
Mv (avg) = 7.929E

POLYDISPERSITY RATIOS
Mw/Mn = 2.011
Mz/Mn = 4.777

SKEWNESS OF DISTRIBUTION
SKEW(w) = 3.240
SKEW(w) = 1.913

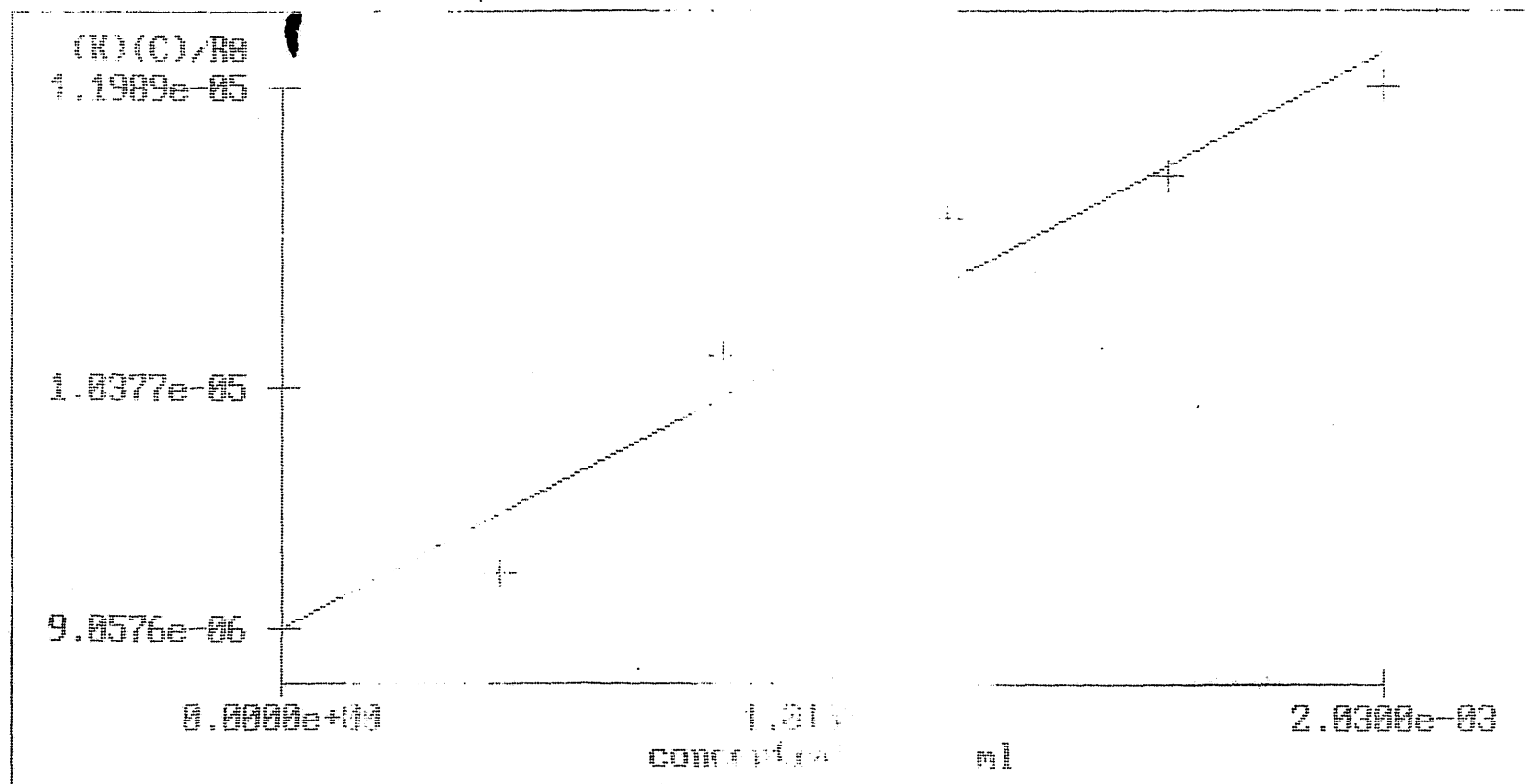
METHOD: UNICAL-BROAD      INTEGRATED DETECTOR SIGNALS      BASELINE
CAL FILE LC26391          CONC (mv-ml) = 46.16             L. VISC 119
MARK-HOUWINK CONSTANTS   VISC (mv-ml) = 55.07            R. VISC 208
ALPHA .552                IV (dl/gm) = .204                L. CONC 120
LOG K -3.407              VISCOTEK MODEL# 200             R. CONC 220
```

Figure 15c. Summary Report for Viscotek GPC Analysis of Radically Polymerized Acetoxy-Polymer (Batch 12871/80)

Figure 15d. LALLS Zimm Plot for Radically Polymerized Acetoxy-Polymer (Batch 12871/80).

Sample 346-01 Ref 12871/80  
THF

STALS v1.0 IDC/Atkinson Roy



Results		<ret>-return to data			
Slope	Std Dev	Intcp	Std Dev	MW	2nd V Co
1.540e-03	2.56e-04	9.058e-06	3.46e-07	1.1040e+05	7.7002e-04

J-3169-1226

Figure 15e. LALLS Summary Report for Radically Polymerized  
Acetoxy-Polymer (Batch 12871/80).

Sample 346-01 - Ref. 12871/80.

THF

STALLS v1.0 LDC/Milton (M)

(esc)-exit

Solvent Rayleigh Factor : 5.27412e-06  
P<sub>0</sub> : 920. P<sub>0</sub> : 40% 1/(n<sup>2</sup>l') or Q(n) : 559.36 D or @ : 4.1600e-09

Polymer Optical Constant : 7.711186e-09  
solvent n : 1.403 dn/dc : 0.0900

Sample Data

conc	D or @	P <sub>0</sub>	P <sub>0</sub>	R <sub>0</sub>	excessR <sub>0</sub>	(K)(C)/R <sub>0</sub>
4.0700e-04	4.1600e-09	900	290	0.6290e-05	3.3546e-06	9.3556e-06
8.1500e-04	4.1600e-09	900	230	1.1247e-05	5.9683e-06	1.0530e-05
1.6300e-03	4.1600e-09	920	150	1.6190e-05	1.0915e-05	1.1515e-05
1.2200e-03	4.1600e-09	910	186	1.3583e-05	8.3280e-06	1.1295e-05
2.0300e-03	4.1600e-09	923	140	1.8331e-05	1.3057e-05	1.1989e-05

conc : <                      D or @ : 4.1600e-09                      P<sub>0</sub> :                      P<sub>0</sub> :

Results (F2)-plot

Slope	Std Dev	Intcp	Std Dev	Cr1	MW	2nd V Co
1.540e-03	2.56e-04	9.050e-06	3.46e-07	0.961	1.1040e+05	7.7002e-04

J 3169-m27

Elution Volumes:

23.60	24.10	24.60	25.10	25.60
26.10	26.60	27.10	27.60	28.10
28.60	29.10	29.60	30.10	30.60
31.10	31.60	32.10	32.60	33.10
33.60				

J-3169-m28

Slice Heights:

0.10	0.30	0.70	1.60	2.90
4.50	5.80	6.80	7.25	7.30
6.80	5.90	4.70	3.20	2.15
1.25	0.70	0.40	0.20	0.10
0.05				

Molecular Weights:

165731.45	132080.78	105262.66	83889.77	66856.51
53281.74	42463.24	33841.36	26970.10	21494.00
17129.78	13651.70	10879.81	8670.74	6910.20
5507.13	4388.94	3497.80	2787.59	2221.59
1770.51				

Mn = 16993.874  
Mw = 29180.119  
PDI = 1.72

1,4-POLY (DA DA) (D)  
1VPC035

BATCH SENT TO ICI FOR LIGHT-SCATTERING ANALYSIS

GPC Conditions:

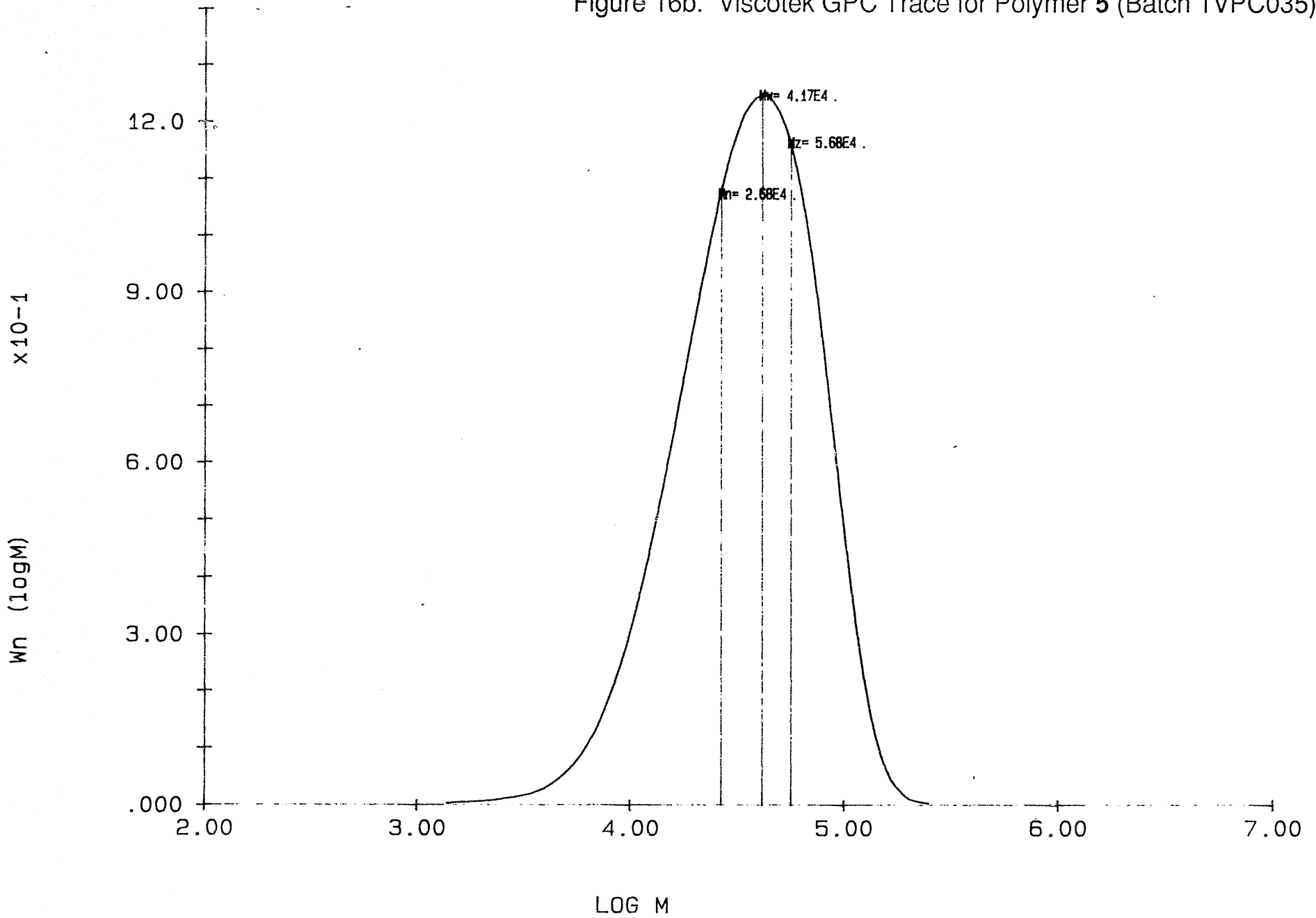
0.4 wt. % in CH<sub>2</sub>Cl<sub>2</sub> as eluent.  
Diff. Refractometer Detector.  
Mixed Bed Column:  
American Polymer Standards Corp.  
Linear 10<sup>3</sup>-5x10<sup>6</sup> in M.W.  
Ref.: Polystyrene M.W. Standards.

Figure 16a. GPC Data for Polymer 5 (Batch 1VPC035), Performed at CIT.

22402

CALTECH

Figure 16b. Viscotek GPC Trace for Polymer 5 (Batch 1VPC035).



J-3169-m29

J-3169-m30

UNICAL SUMMARY REPORT

```

=====
22402      ENDED: 03/26/91 15:11:      CALTECH
=====
PARAMETERS                                MOLECULAR WEIGHT VALUES
CONCENTRATION (mg/ml)                    4.980      Mn (avg) = 2.683E 4
INJECTION VOLUME (ml)                    0.200      Mw (avg) = 4.144E 4
DRT SENSITIVITY (mv/Pa)                  1.000      Mz (avg) = 5.478E 4
INLET PRESSURE (KPa)                     19.595      Nn = 1.79E 4
FLOW RATE (ml/min)                       1.000      Nw = 1.79E 4
VISCOMETER OFFSET (ml)                   0.000
ACQ. START TIME (min)                    5.000
ACQ. STOP TIME (min)                     15.000
DATA INTERVAL (sec)                      4.000
SIGMA (ml)                               0.000
TAU (V)                                  0.000
TAU (C)                                  0.000
THRESHOLD                                 0.050

INTEGRATED DETECTOR SIGNALS              BASELINE
CONC (mv-ml) = 88.94                     L: VISC 141 143.00
VISC (mv-ml) = 42.20                     R: VISC 211 73.00
IV (dl/gm) = 0.087                       L: CONC 140 4674.00
VISCOTEK MODEL# 200                      R: CONC 218 4779.00

METHOD: UCAL-BROAD
CAL FILE LC26391

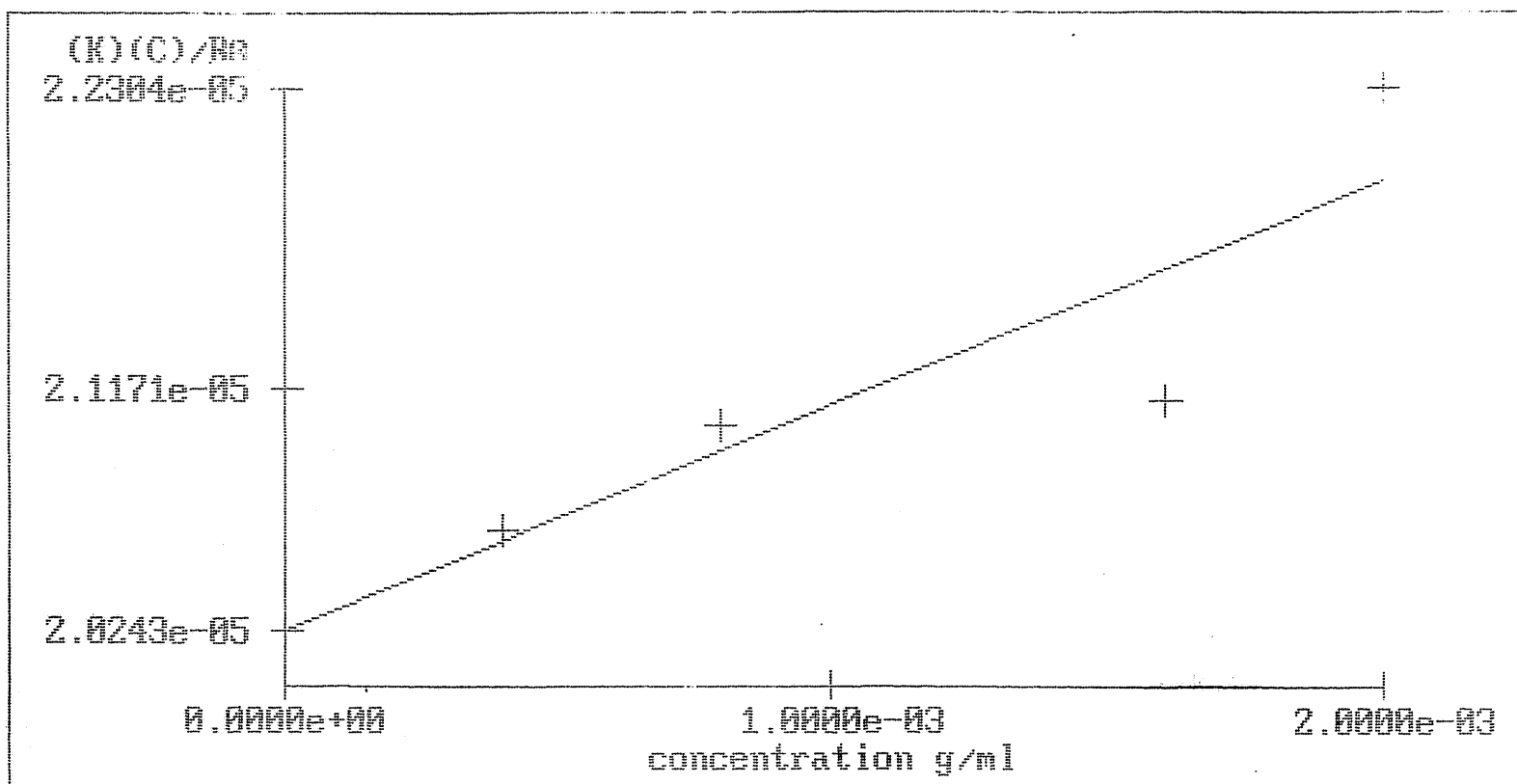
MARK-HOUWINK CONSTANTS
ALPHA 543
LOG K -3.565
  
```

Figure 16c. Summary Report for Viscotek GPC Analysis of Polymer 5 (Batch 1VPC035).

Figure 16d. LALLS Zimm Plot of Polymer 5 (Batch 1VPC035).

Sample 346-02. CAKTECH.  
THF.

STALLS v1.0 LDC/Milton Roy



Results. (ret)-return to data						
Slope	Std Dev	Intcp	Std Dev	Cr1	MW	2nd V Co
8.582e-04	3.42e-04	2.024e-05	4.64e-07	0.871	4.9399e+04	4.2911e-04

J-3169-m31



Figure 16e. LALLS Summary Report for Polymer 5 (Batch 1VPC035).

Sample 346-02 . CALTECH.

THF

STALLS v1.0 LDC/Killer Roy

<esc>-exit

Solvent Rayleigh Factor : 5.38044e-06

P0 : 925 P0 : 478 1/(σ'1') or P0 : 668.36 D or θ : 4.1600e-09

Polymer Optical Constant : 7.711186e-07

solvent n : 1.493 dn/dc : 0.0980

Sample Data

conc	D or θ	P0	P0	RA	excessR0	(K)(C)/R0
4.0000e-04	4.1600e-09	910	368	6.8754e-06	1.4950e-06	2.0633e-05
8.0000e-04	4.1600e-09	900	301	8.3134e-06	2.9330e-06	2.1033e-05
1.6000e-03	4.1600e-09	900	223	1.1221e-05	5.0408e-06	2.1124e-05
2.0000e-03	4.1600e-09	880	199	1.2295e-05	6.9147e-06	2.2304e-05

conc : < D or θ : 4.1600e-09 P0 : P0 :

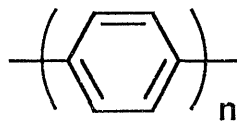
Results <F2>-plot

Slope	Std Dev	Intcp	Std Dev	CrI	NW	2nd V Co
8.582e-04	3.42e-04	2.024e-05	4.64e-07	0.871	4.9399e+04	4.2911e-04

J-3169-m32

J-3169-m33

## Characterization of Thin Films of



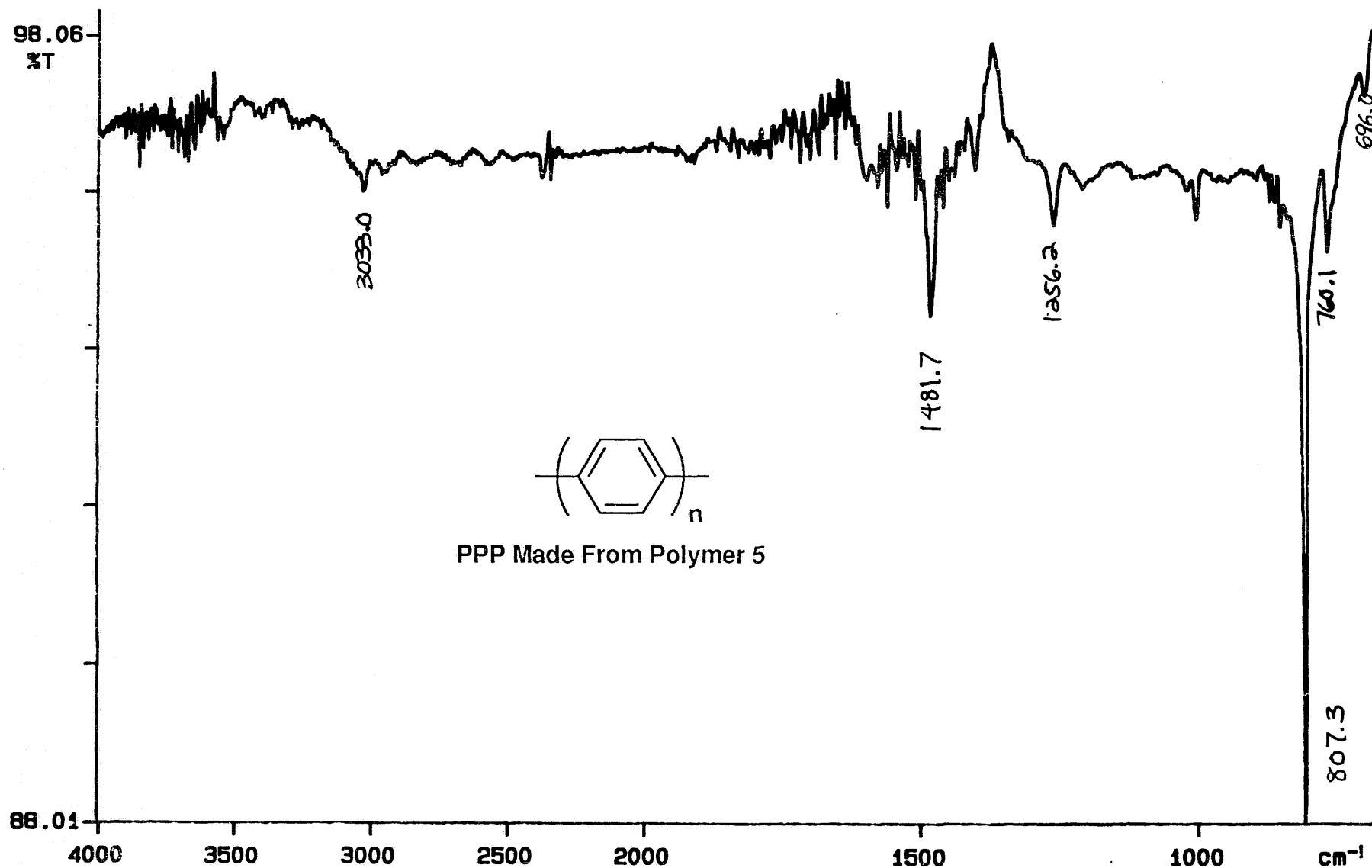
PPP

## on NaCl Crystals, Made From Polymer 5

### IR Analysis:

• characteristic absorptions (cm <sup>-1</sup> ):	3033	$\nu$ (C-H) aromatic
	1482	$\nu$ (C=C) aromatic
	1256	
	807	$\delta$ (C-H) out-of-plane, <i>para</i> -disubstituted aromatic
	760	$\delta$ (C-H) out-of-plane,
	696	monosubstituted aromatic ring

P-E



PPP Made From Polymer 5

91DLG077

91/05/01 13:38

Y: 16 scans, 4.0cm⁻¹, diff, flat

1VPC083 PYROLYZED

Figure 17. Complete IR Spectrum of PPP Film on NaCl, Pyrolyzed From Polymer 5.

J-3169-m34