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SENIOR PROJECT - APPROVAL

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PROJECT TITLE: Materials Property Evaluation of a Molecular Composite.

I have reviewed this completed senior honors thesis with this student and certify that it is a project commensurate with honors level undergraduate research in this field.

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THE UNIVERSITY OF TENNESSEE, KNOXVILLE
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SENIOR HONORS PROJECT

MATERIALS PROPERTY EVALUATION FOR A MOLECULAR COMPOSITE

EVYN CHILDRESS

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ABSTRACT

This project attempts to evaluate macroscopic material properties of a miscible polymer blend. This blend, which incorporates a liquid crystalline polymer and a commodity amorphous polymer, is being developed in the interest of creating a molecular composite that would exhibit extraordinary mechanical properties and excellent processability but at a reduced cost. Previous work investigated miscibility in the blend system, establishing a method for inducing a broad miscibility window. This work has approximately replicated that previous system. The component polymers have been first synthesized and characterized, then blended. An understanding of the miscibility window has been established, and the dynamic mechanical properties evaluated.

INTRODUCTION

Modern complexities and ambitions in technological development fuel a vibrant advance in materials design. Demands for complex combinations of properties while maintaining economic efficiency motivate interest in composite materials.

The domain of polymer blends is among the most significant and active fields of contemporary materials research. Blending polymers facilitates tailoring of properties, particularly for obtaining a combination of properties not exhibited by an individual polymer alone. The blending of poly(methyl methacrylate) with poly(vinylidene fluoride) to form the optically homogeneous (birefringence negative) and moisture insensitive polymer substrate required for ROM (Read Only Memory) is one such example. More specifically, by combining a low viscosity polymer with a high viscosity polymer, a reduction in melt viscosity may be achieved – improving processability. Economically and environmentally, polymer blending is effective for reducing product and fabrication costs, as well as facilitating both post-consumer and inhouse recycling. [1]

The primary challenge with polymer blending is that the properties exhibited by the blend depend on the manner in which the component polymers are dispersed in one another. The system of blended polymers may be immiscible or miscible. If immiscible, which blended polymers often are, the desired properties may not be achieved without a good understanding and or control of the phase morphologies and quality interfacial adhesion

between the phases. However, if the blended system is miscible, the properties typically vary according to composition in a straightforward manner. This relationship between blend property and composition may be additive, synergistic, or nonsynergistic. For an additive relationship, the value of the blend property is intermediate to those of the individual components. For a synergistic relationship, the blend property value is greater than that following from the additive relationship, and for a nonsynergistic relationship the blend property value is less.

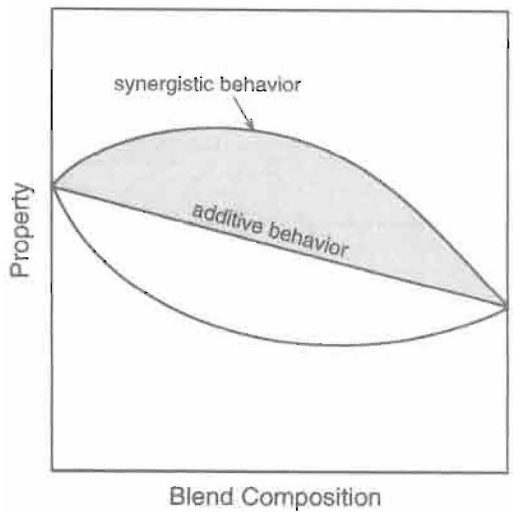


Figure 1. Three types of behavior for the dependence of blend property on composition for a miscible polymer blend. [2]

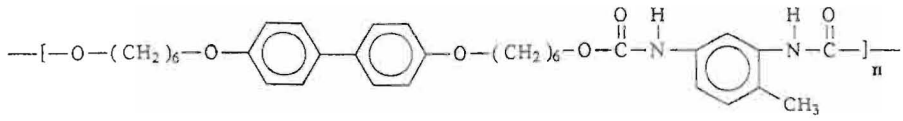
Certain polymers exhibit liquid crystalline behavior. Such behavior may be described as neither truly liquid-like nor truly solid-like but more so as a fluid with ordered regions called mesophases. Polymers exhibiting this behavior may be classed as either thermotropic, meaning they form the ordered phase in the melt or in a particular temperature range, or lyotropic, meaning they form the ordered mesophase under the

influence of solvent. [3] These liquid crystalline polymers (LCPs) exhibit unique and desirable properties including exceptional oxygen and barrier properties, very high thermal stability, high modulus and strength, good dimensional stability, and high chemical and solvent resistance. [2] An especially significant property is the improved (reduced) viscosity which arises from a minimization of frictional drag accompanying the alignment of the rigid mesophases with the flow direction. Also significant is that the ordered arrangement is maintained upon cooling, which is manifested as a great improvement in mechanical properties. An abundance of potential applications are apparent for these polymers as high strength fibers and plastics, despite challenges with tractability and expense. [4] Difficulties with tractability, especially very high melting points and very poor solubility, may be circumvented through chemical modification of the polymers, such as addition of spacers. Expense must be dealt with another way, however.

This project flows out of a proposal aimed at offering a polymer blend of exceptional properties while circumventing this expense challenge – namely, blending an LCP with a commodity amorphous polymer to create a rigid-rod/flexible coil miscible polymer blend with extraordinary mechanical properties and processability. Again, adequate exhibition of properties demands that the rigid-rod polymer be well dispersed in the amorphous/flexible coil polymer matrix, thus the aim for miscibility. The propensity of the LCP to form liquid crystal regimes which exclude the coil polymer levies an additional obstacle for miscibility; however, use of polar interactions, such as hydrogen

bonding, has been found effective. The LCP may not necessarily exhibit liquid crystalline phase behavior after blending, but still behave as a rigid-rod.

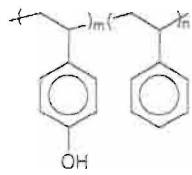
The polymer system chosen incorporates the liquid crystalline polyurethane (LCPU) shown in Figure 2 as the LCP/rigid-rod contributor and poly(styrene-co-4-vinylphenol) (PS-co-VPh) random copolymer as the amorphous/flexible coil contributor (see Figure 3).



Liquid Crystalline Polyurethane
(LCPU)

Figure 2. Structure of the liquid crystalline polyurethane employed in this investigation. [1]

PS-co-VPh was chosen because of commercial feasibility. Its synthesis requires only a simple modification of commodity polymers. The LCPU was chosen because of desires to minimize the complications of transesterification inherent with polyesters and immiscibility inherent with some polyethers.



Poly(styrene-ra-4-vinylphenol)
[PS-co-VPh] Copolymer

Figure 3. Structure of the coil polymer employed in this investigation. [1]

This system was also chosen because of its appropriateness for a miscibility issue investigation. Viswanathan [1] dealt with the miscibility of this system, namely through endeavoring to induce miscibility by optimization of intermolecular hydrogen bonding. This was accomplished by separating the functional groups which participate in hydrogen bonding along the polymer chain, a parameter that is controlled by varying the composition of vinyl phenol in the copolymer. An understanding of the optimum copolymer composition and miscibility window, which gives optimal composition of copolymer in the blend, were also established. The optimum copolymer composition was found to be 20 mol % VPh. As evident in the phase diagram of Figure 4, such a system has the larges miscibility window.

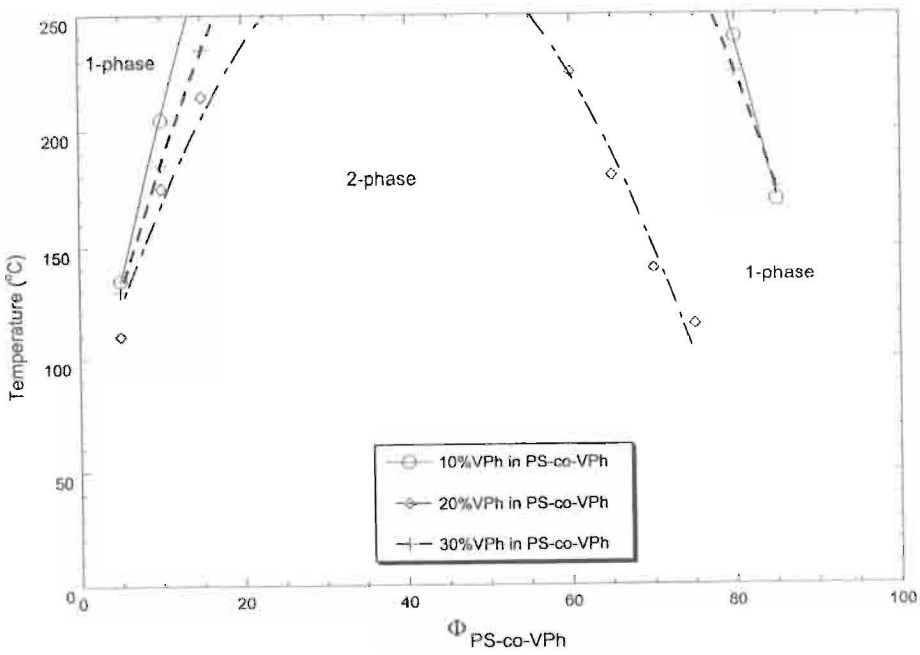


Figure 4. Phase diagram for the LCPU/PS-co-VPh system investigated by Viswanathan [1]

The work of this project fits more immediately within an endeavor to determine the material properties of the blend (macroscopic) and to correlate the results to the microscopic properties involved in inducing miscibility, i.e. to establish that the treatment to induce miscibility was in fact effective for obtaining the blend with the properties desired.

OBJECTIVE

This project has aimed to approximately replicate the previously synthesized system. The component polymers have been synthesized and characterized, then blended. An understanding of the miscibility window for the system has been established, and dynamic mechanical properties evaluated.

EXPERIMENTAL

Materials

4,4'- dihydroxybiphenyl and 2,4-toluene diisocyanate (2,4-TDI) were obtained from TCI America Inc.; styrene, 4-acetoxystyrene, hydrazine hydrate, dioxane, and azobis(isobutyronitrile) (AIBN) were purchased from Aldrich Chemical Co.; and sodium hydroxide, 6-chlorohexanol, methanol, N,N'-dimethylformamide (DMF), and 1-butanol were purchased from Fischer-Acros. DMF was vacuum distilled prior to use in synthesis; all other chemicals were used as received.

Experimental techniques

Molecular weight information was obtained using a Waters gel permeation chromatograph with a PLgel 5 μm MIXED-D column. DMF served as elution solvent for the LCPU and tetrahydrofuran (THF) as elution solvent for PS-co-VPh(20). Narrowly dispersed polystyrene was used as calibration standard for both.

Differential scanning calorimetry was employed to evaluate the thermal transitions of the polymers and blends. These measurements were carried out at 10 °C /min on a Mettler DSC 821 calibrated with indium.

Structure and compositions of the LCPU and PS-co-VPh(20) were evaluated using proton and carbon-13 nuclear magnetic resonance spectroscopy on a 250 MHz Bruker NMR with TMS as internal standard. Deuterated dimethyl sulfoxide was used as solvent for the LCPU and deuterated chloroform as solvent for the PS-co-VPh(20) and other solvents.

Blends of the LCPU and PS-co-VPh(20) of the compositions indicated in Table 1.Each blend was prepared via co-dissolution/co-precipitation of the two component polymers in DMF. LCPU and PS-co-VPh(20) were first co-dissolved in DMF in amounts corresponding to the composition of the blend. The temperature of the mixture was raised to enhance solubility, and the solution was poured into cold methanol for co-precipitation and then refrigerated. The blend solids were then filtered and dried under vacuum.

Table 1. Blend compositions for the LCPU – PS-co-VPh(20) system

	LCPU wt %	PS-co-VPh(20) wt %
80:20	80	20
85:15	85	15
90:10	90	10
95:5	95	5

For use in dynamic mechanical analysis, small rectangular samples having the dimensions indicated in Table 2 were prepared via compression molding. Several samples were prepared for the LCPU, PS-co-VPh(20), and each blend. The blend solids were first crushed with mortar and pestle. The mold cavity was filled with the polymer

solids – typically to overflowing. Even so, because of solid sizes, some spaces remained. These were generally filled during the molding process but occasionally not. The samples were kept at 130 °C and 24 ksi for 30 minutes, then removed to cool and separated from the mold. The samples were then annealed to permit relaxation of residual stresses and the like.

Table 2. DMA sample dimensions

Thickness	1 mm
Width	5 mm
Length	20 mm

Dynamic mechanical analysis was performed on a Rheometrics DMTA V instrument. A calibration check of certain key parameters, namely, a force calibration constant, low frequency phase correction, and air damping constant, was performed prior to each set of experiments. The samples were tested in dual cantilever mode. In this mode, the sample is gripped at both ends and in the middle (see Figure 5). The center grip is in motion, applying a dynamic strain. Both dynamic temperature ramps and frequency ramps were performed to obtain storage modulus, loss modulus, and tan δ as a function of temperature and frequency. Test parameters are listed in Table 2 below. No particular samples apart from those for the LCPU were tested more than once.



Figure 5. Sample loaded in Rheometrics DMTA V dual cantilever fixture. [5]

Table 3. DMA test parameters

	Dynamic temperature ramp	Dynamic frequency ramp (carried out for LCPU only)
Temperature	30 to 150 °C	27 °C
Frequency	1 Hz	0.01 to ~300 Hz
Strain	0.01 %	0.01%, 0.1%, 0.5%
Ramp Rate	2.0 °C/min	-
AutoTension Adjustment	On	On

Phase contrast optical microscopy was performed to characterize the phase behavior of the blends. Very dilute solutions of the blend were prepared in DMF, with heating, and then spotted on a microscope slide. Residual solvent was removed overnight in a vacuum oven at 60 °C. Phase behavior was observed via phase contrast and polarized optical microscopy using an Olympus BH-2 optical microscope with Mettler FP82HT hot stage.

Polymer synthesis and characterization

An Excel spreadsheet *synth.xls* was developed to efficiently calculate required material amounts for the BHHBP and LCPU syntheses according to molar ratios and available quantities. Portions of these spreadsheets are presented in Figures 6 and 7.

BHHBP, a mesogenic diol and LCPU precursor

Synthesis of the mesogenic diol, 4,4'-bis(6-hydroxyhexoxy)biphenyl (BHHBP) was carried out according to the procedure of Stenhouse, et al [4] Using a mechanical stirrer, sodium hydroxide and 4,4'-dihydroxybiphenyl were stirred into ethanol in 1000mL round bottom flask. Sodium hydroxide was added first, followed by ethanol, followed by 4,4'-dihydroxybiphenyl. A thermocouple was positioned between the flask and a heating mantle to monitor the temperature. Using heating mantle, water-cooled condenser, and temperature controller, the resulting slurry was heated under reflux for 24 h, maintaining temperature of about 70 – 80 °C. After reflux, the reaction mixture was poured into cold water and removed to a Buchner funnel for filtration of the precipitated solids. The solids were washed with cold water as they were filtered, and then recrystallized twice, first from a 3:1 mixture of ethanol and DMF and then from 1-butanol. The solids were dried in a vacuum oven at 80 °C for at least 48 hrs. The synthesis was repeated twice giving two batches of material. Molar ratios and amounts employed are presented in the spreadsheet of Figure 6.

NMR and DSC were employed in the characterization of the BHHBP synthesis product. ChemDraw was employed to determine the expected NMR shifts and these as well as those shifts reported by Smyth, et al, [6] were compared with those obtained for the synthesis product. The thermal transitions obtained in DSC analysis were compared with those reported by Stenhouse, et al, [4] and Khan, et al. [7] According to the quality of correlation with expected results, the recrystallizations, filtrations and washings were repeated as needed for purification of the products.

LCPU

Two batches of the LCPU were also synthesized after the procedure of Stenhouse, et al. [4] The complete synthesis, with BHHBP synthesis included, is outlined in Figure 8. DMF solvent was first vacuum distilled. BHHBP was then dissolved in some of the distilled DMF in a heat-dried four-necked reactor fitted with condenser, mechanical stirrer, nitrogen flow access, and addition funnel charged first with 2,4-TDI and then additional DMF. Nitrogen was kept flowing through the system continuously. The 2,4-TDI was to have been added dropwise to the solution and the temperature raised to 80 °C and held there for 20 h. Inadvertently, in the first synthesis, the 2,4-TDI was not added dropwise, but very quickly. In the second synthesis, the 2,4-TCI was added dropwise, as desired. As the reaction proceeded, DMF was added as needed to keep the solution viscosity low enough to permit adequate stirring of the reaction mixture. The hot, viscous solution was poured into cold methanol to precipitate the polymer as a white, fibrous material. The polymer solids were filtered, washed with a bit of fresh methanol,

and dried under vacuum at 90 °C for 72 h. Molar ratios and amounts employed are reported in the spreadsheet of Figure 7.

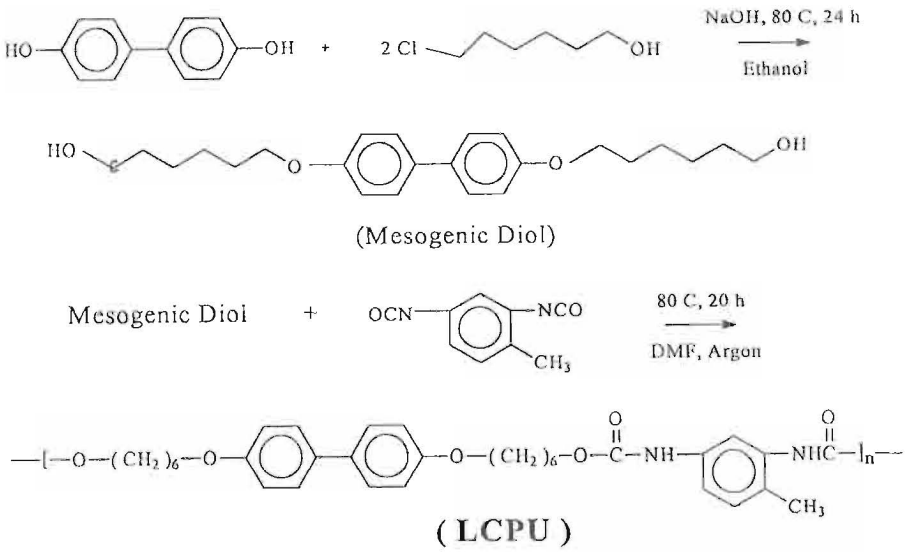


Figure 8. Synthesis of the LCPU employed in this investigation. [1]

NMR and DSC were employed in the characterization of the LCPU synthesis products. NMR shifts were compared with those reported by Stenhouse, et al and Viswanathan [4,1]. Additional characterization of certain solvents facilitated interpretation of the results. Thermal transitions obtained in DSC analysis were also compared with those reported by previous investigators. [8,4] The molecular weight of the LCPU was evaluated using GPC with DMF as elution solvent. After analysis, the LCPU of the second synthesis was chosen for use in the actual blends.

PS-co-VPh(20)

The synthesis of poly(styrene-co-4-vinylphenol) (PS-co-VPh) random copolymers was carried out by a lab partner according to the procedure of Green and Khatri. [9] An outline of the synthesis is depicted in Figure 9. In this procedure, the copolymers are prepared via the free radical polymerization of styrene and 4-acetoxystyrene with AIBN as the initiator. Copolymer containing 20 mol % vinyl phenol was synthesized.

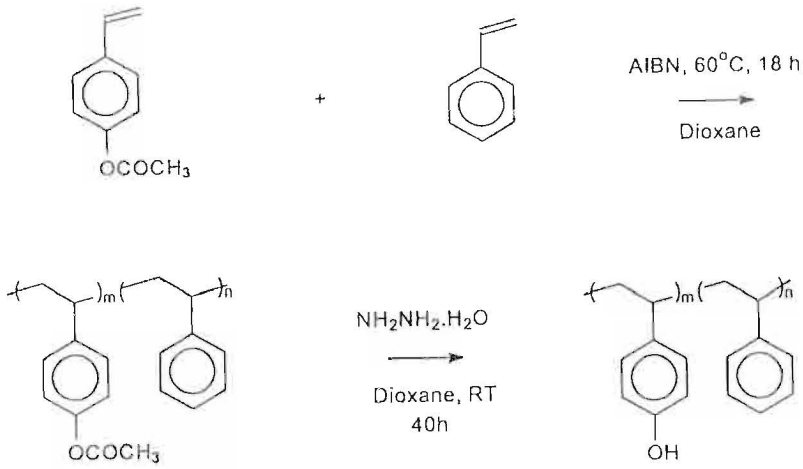


Figure 9. Synthesis of the poly(styrene-co-4-vinyl phenol) employed in this investigation [1]

Characterization of the copolymer was also carried out by this lab partner. The composition of the copolymer was verified using NMR according to the method of Radmard [10] as well as Coleman and Painter. [11] The molecular weight of the copolymer was also evaluated using GPC with THF as elution solvent.

RESULTS AND DISCUSSION

The proton NMR spectra obtained for the synthesized BHHBP, LCPU, PS-co-VPh, and certain solvents are included in the Appendix. Evaluation of the correlations with expected and reported shifts are reported in Table 4. These NMR results indicate that the product for each of these reactions was in fact the BHHBP, LCPU, and PS-co-VPh(20) expected, with possibly certain residual solvents. Following the method of Radmard and Coleman, et al, the composition of the copolymer was confirmed to be 20.5 mol %.

Table 4. Summary of proton NMR results for LCPU

Shifts reported by Stenhouse, et al [4]	Match in spectrum for LCPU1 (first batch)	Match in spectrum for LCPU2 (second batch)	Additional peaks observed	Interpretation
9.51	Possibly	Yes	2.48	d-DMSO
8.75	Possibly	Yes	2.71	DMF ~
7.47	Yes	Yes	2.869	DMF ~
6.96	Yes	Yes	3.138	d-DMSO
3.96	Possibly	Yes	3.155	d-DMSO
2.09	Possibly	Yes	3.336	d-DMSO, methanol ~
1.65	Yes	Yes	4.1	d-DMSO
1.40	Yes	Yes	7.9	DMF

The DSC curves obtained for the synthesized BHHBP and LCPU are displayed in Figures 10 and 11. Thermal transitions are reported in Table 5.

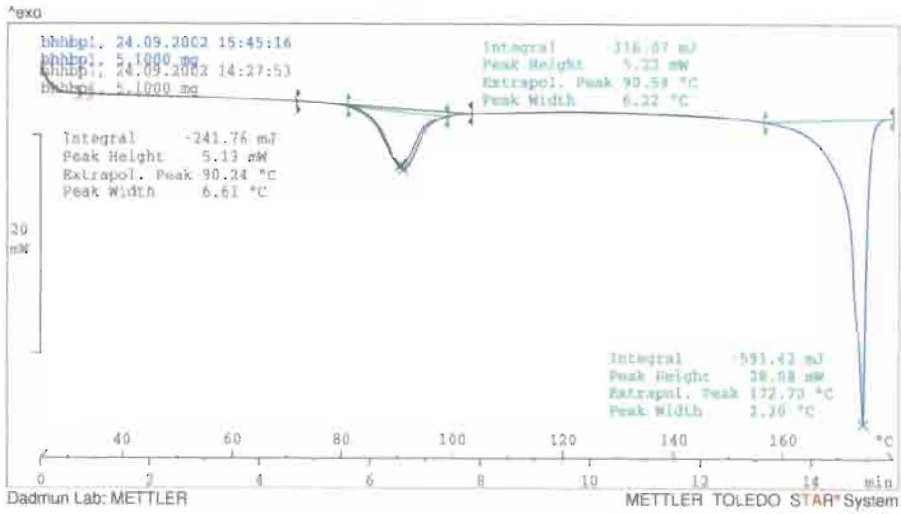


Figure 10. DSC curve for synthesized BHHBP – first batch.

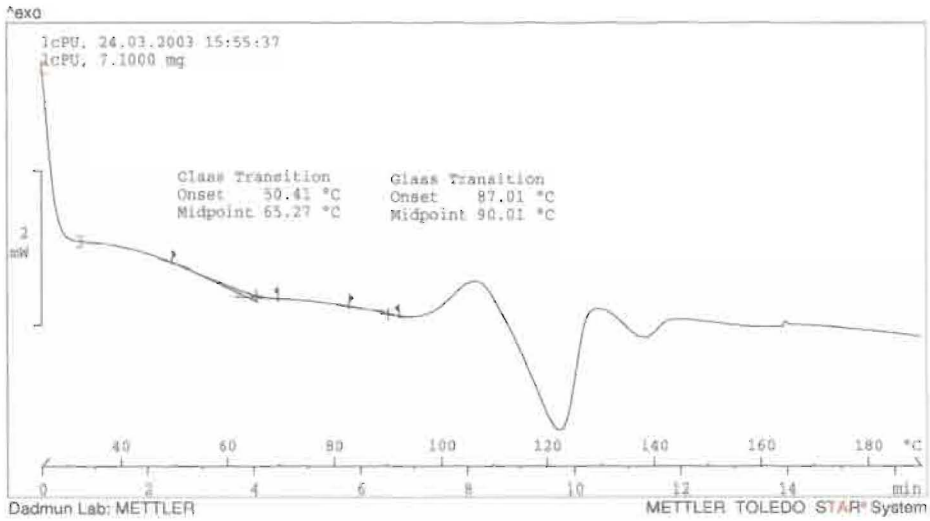


Figure 11. DSC curve for synthesized LCPU – second batch.

The results for the synthesized BHHBP match well with those reported by previous investigators as thermal properties for BHHBP. The curves for the synthesized LCPU are quite bizarre. The expected indications of liquid crystallinity are apparent in the thermal transitions present; however, the transitions are shifted down relative to those reported for the LCPU of the previous system. A molecular weight effect involving broad distribution of several high and low molecular weights was considered as explanation for this.

Table 5. Comparison of thermal transitions for BHHBP and LCPU

	Tg (°C)	Tm (°C)	Ti (°C)
BHHBP – Stenhouse, et al		96	174
BHHBP1 (first batch)		91	173
LCPU – Stenhouse, et al	95	152	166
LCPU – Viswanathan	87	132	160
LCPU2 (second batch)	60*	125*	138*

DSC curves for the blends are also presented in Figure 12. From these data, the behavior of the glass transition temperature as a function of blend composition was obtained.

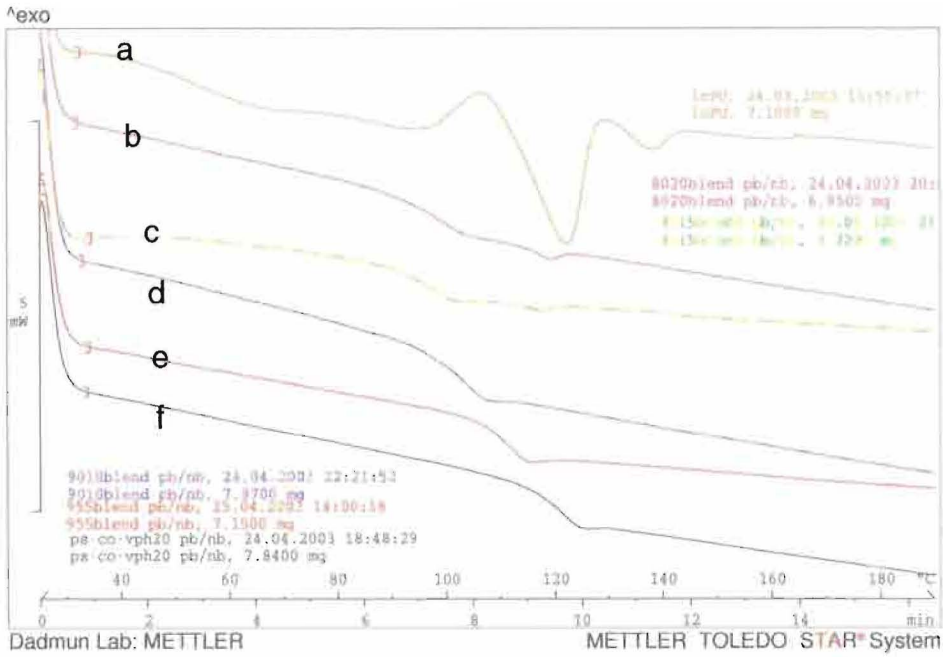


Figure 12. DSC curves for the blends prepared in this study.
(a) pure LCPU (b) 80:20 (c) 85:15 (d) 90:10 (e) 95:5 (f) pure PS-co-VPh

The experimental data were compared with the behavior expected theoretically for a miscible system from the Fox equation, shown in Figure 13. Though the experimental results deviate from those theoretically expected for a miscible system, the DSC curves for the 95:5 and 90:10 blend compositions suggest possible miscibility in that, for each of them, a single glass transition appears, shifted downward in temperature. In addition to a

down-shifted glass transition, a second transition, likely arising from behavior of a second phase, appears in the curves for the 85:15 and the 80:20 blend. With deviation from the theoretical model, miscibility is questionable.

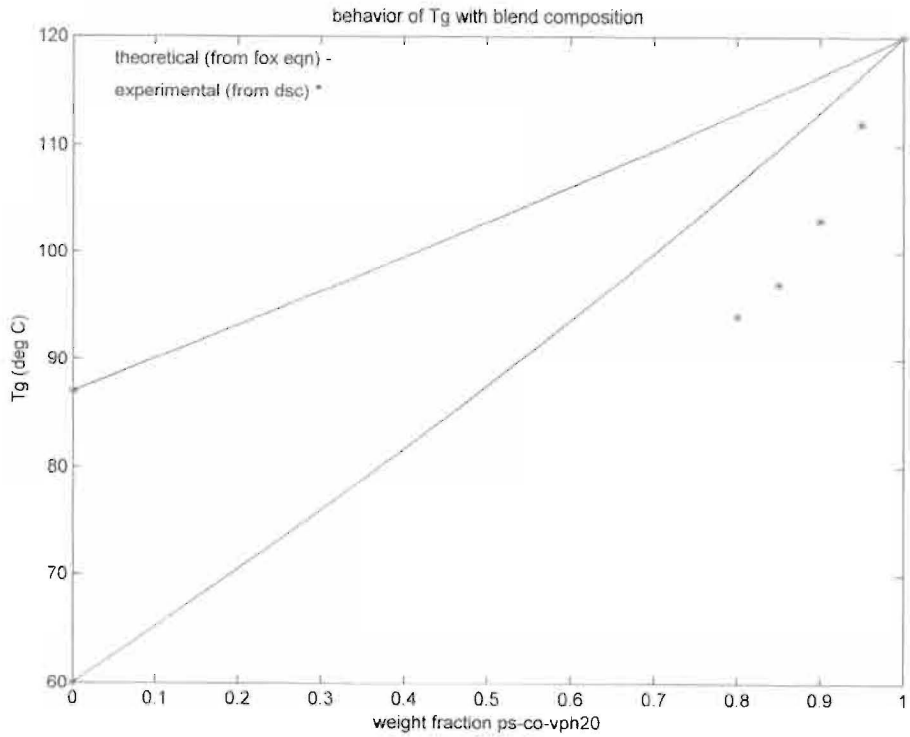


Figure 13. Behavior of Tg with blend composition – theoretical, from Fox equation, and experimental, obtained using DSC. Upper curve is expected with LCPU Tg of 87°C. Lower curve is expected with LCPU Tg of 60°C.

Molecular weight information obtained from the GPC evaluations for the synthesized LCPU and PS-co-VPh(20) is displayed in the curve of Figure 14 the numerical data of Table 6.

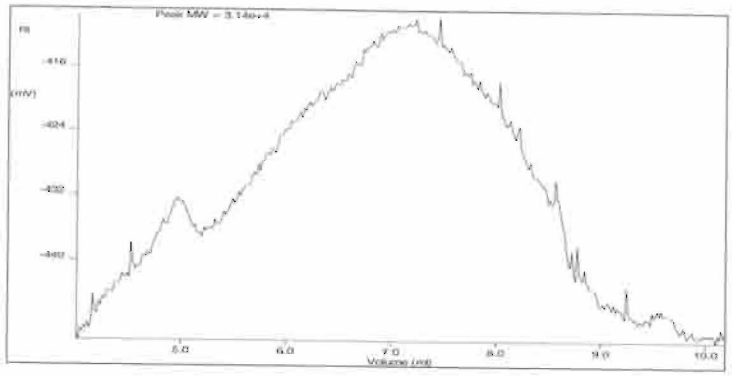


Figure 14. GPC curve for LCPU1 – first batch synthesized

The results for the primary batch of LCPU (second batch) are particularly interesting, indicating a broad distribution of molecular weights, including some values quite low relative to the previously synthesized system. (see Figure 14) A secondary batch of LCPU, actually synthesized first, was found to contain a generous amount of either oligomers or unreacted monomer. This may be a result of the manner of addition of the monomers, which may have been too rapid. Previous investigators reported that increase in molecular weight accompanied an increase in the batch size of the polymer synthesis, likely because of reductions in influence of impurities and side reactions. [4] Their reported polymerization was carried out on quite a large scale, and this scale was replicated in the work of Viswanathan, foundational for this project. However, the polymerizations of this project were carried out on a smaller scale, which may explain the relative reduction in molecular weight. The molecular weight obtained for the PS-co-VPh(20) is high relative to the previously synthesized system.

Table 6. Molecular weight results obtained for the synthesized polymers

	Mn	Mw
LCPU – Viswanathan	35, 000	54, 600
LCPU1 (first batch)	13, 000	60, 000
LCPU2 (second batch)	17, 000	50, 1000
PS-co-VPh(20) - Viswanathan	47, 100	90, 100
PS-co-VPh(20)	140, 000	-

DMA results for the blends and component polymers are displayed in Figures 14 through 19. Additional results are included in the Appendix. The storage modulus obtained for the PS-co-VPh(20) was higher than that obtained for the LCPU. The LCPU exhibited a characteristic retaining of 'solid-like' behavior, exhibited in the values of storage modulus being higher than those of loss modulus over the entire temperature range. The blends exhibited expected transitioning from 'solid-like' to 'liquid-like' behavior, but additionally a transition returning to 'solid-like' behavior. This is again manifest in the relative values of the storage and loss moduli, particularly the points where the curves crossover one another. However, reproducibility was poor for each blend, and thus trends were quite variable and difficult to discern. Generally, storage modulus tended to increase with decreasing LCPU content, and modulus values were intermediate to that for either component.

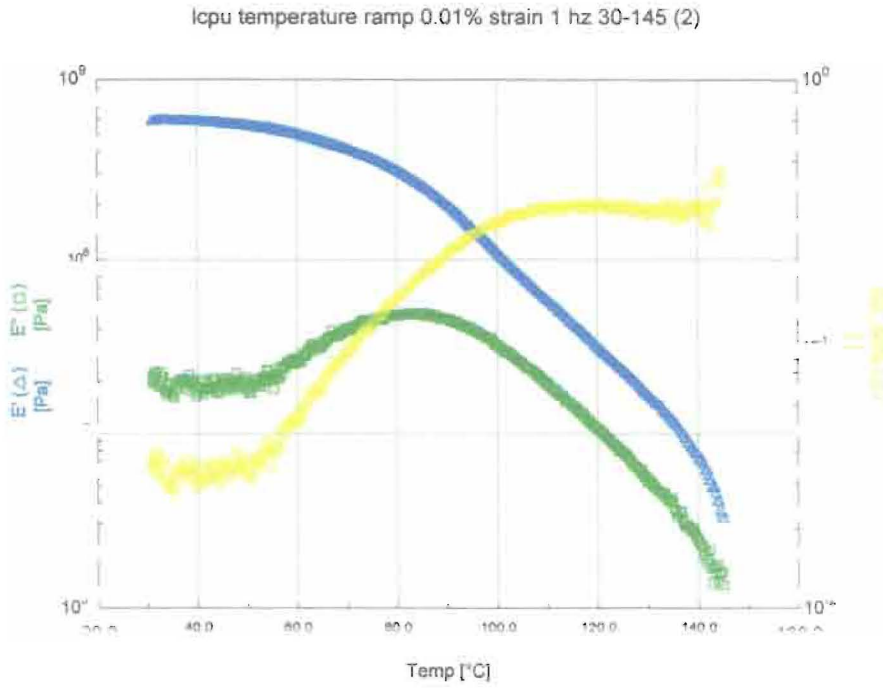


Figure 14. DMA results for pure LCPU

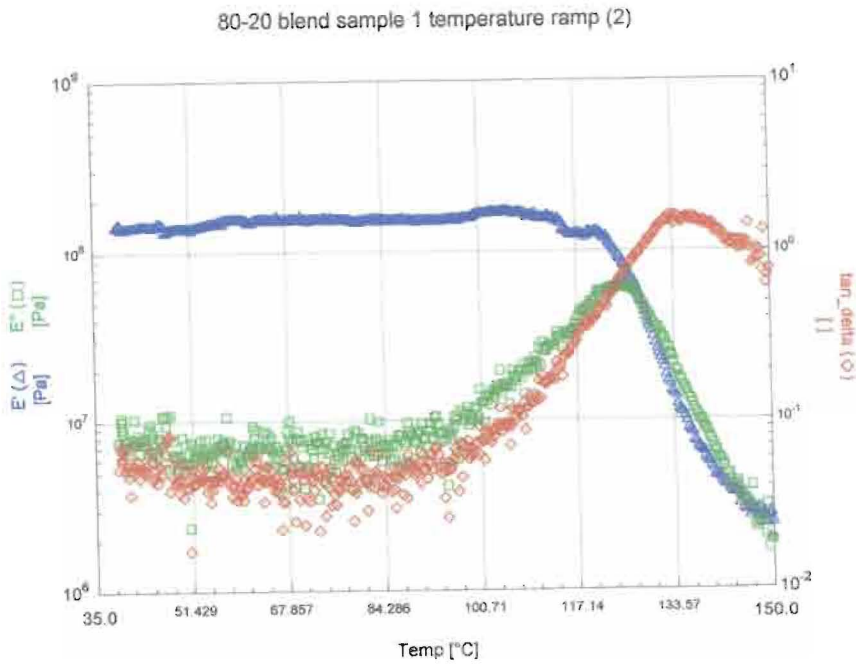


Figure 15. DMA results for 80:20 blend

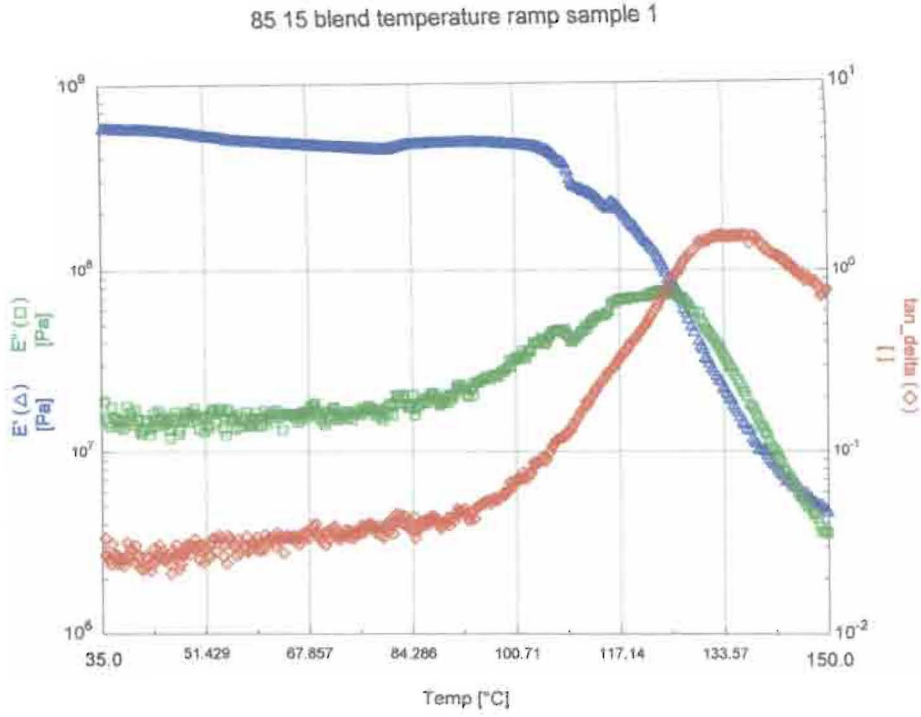


Figure 16. DMA results for 85:15 blend.

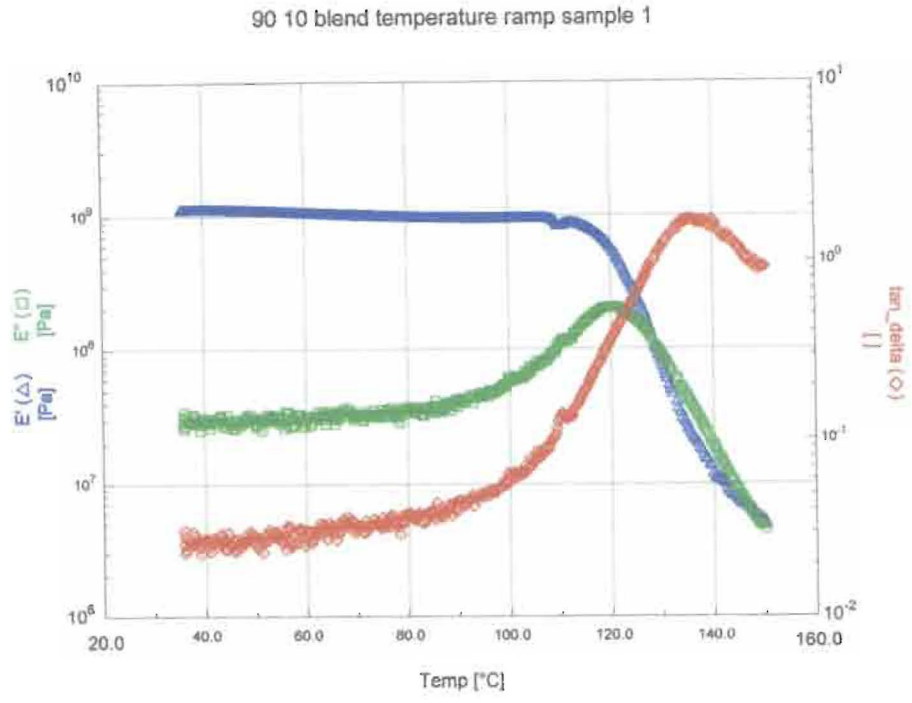


Figure 17. DMA results for 90:10 blend.

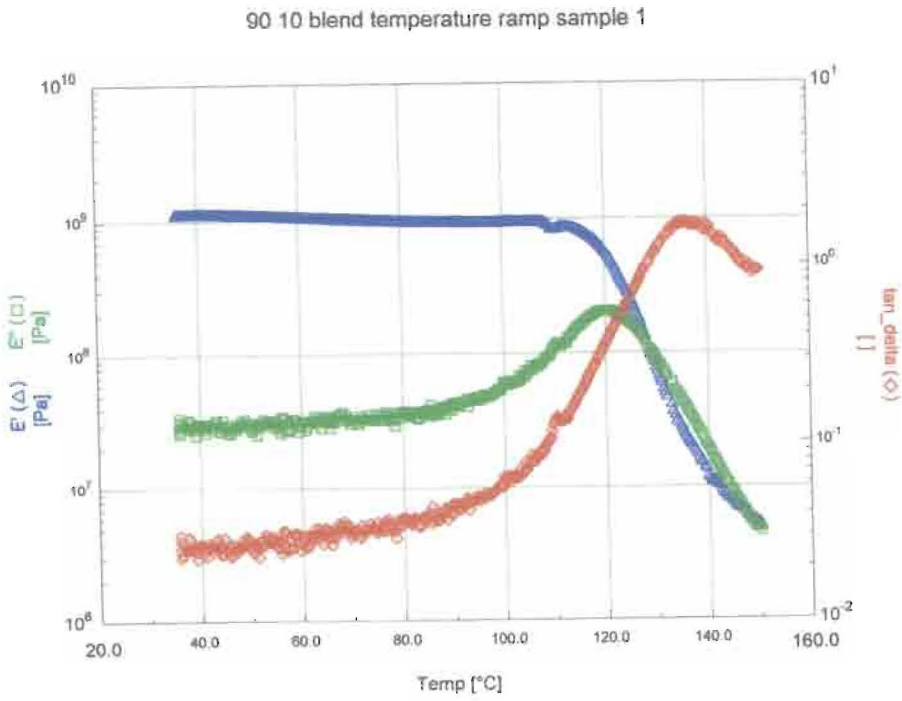


Figure 18. DMA results for 95:5 blend.

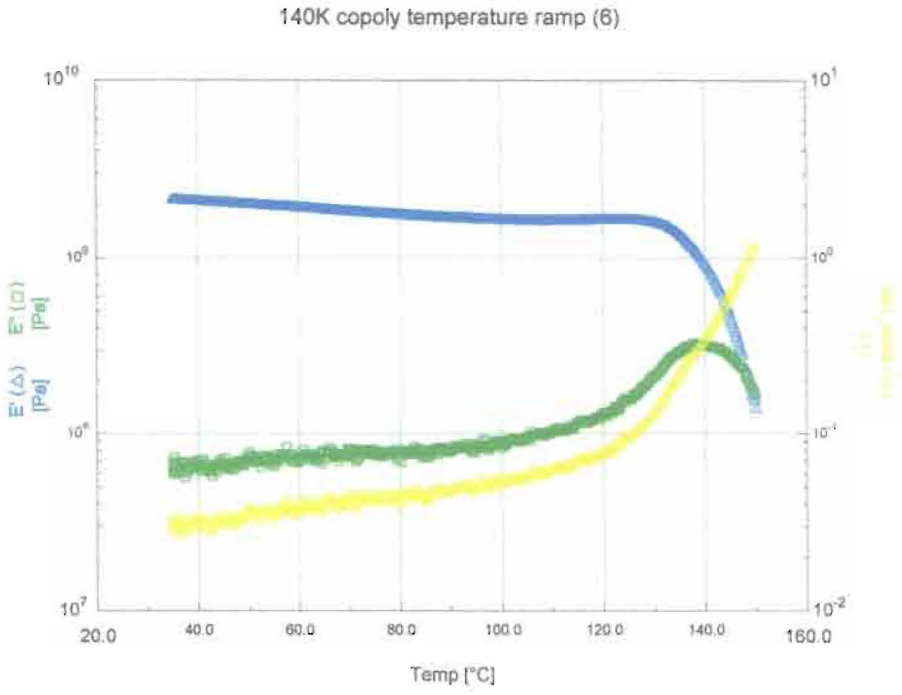


Figure 19. DMA results for PS-co-VPh(20)

The glass transition temperature for each blend was also obtained from the position of the maxima in the loss modulus curve. From these data, the behavior of glass transition temperature as function of composition was evaluated and compared with the theoretically expected values for a miscible system of the two components, calculated from the Fox equation. The results are presented in Figure 20. Apparent deviation from the behavior predicted for a miscible system by the Fox equations raises doubts about the miscibility of the system below the 95:5 blend composition, that is for blends where PS-co-VPh(20) is less than 95 wt%. Comparison with the DSC results yields little insight for a solid conclusion on the miscibility. Phase contrast optical microscopy was performed to more fully understand the miscibility of this system.

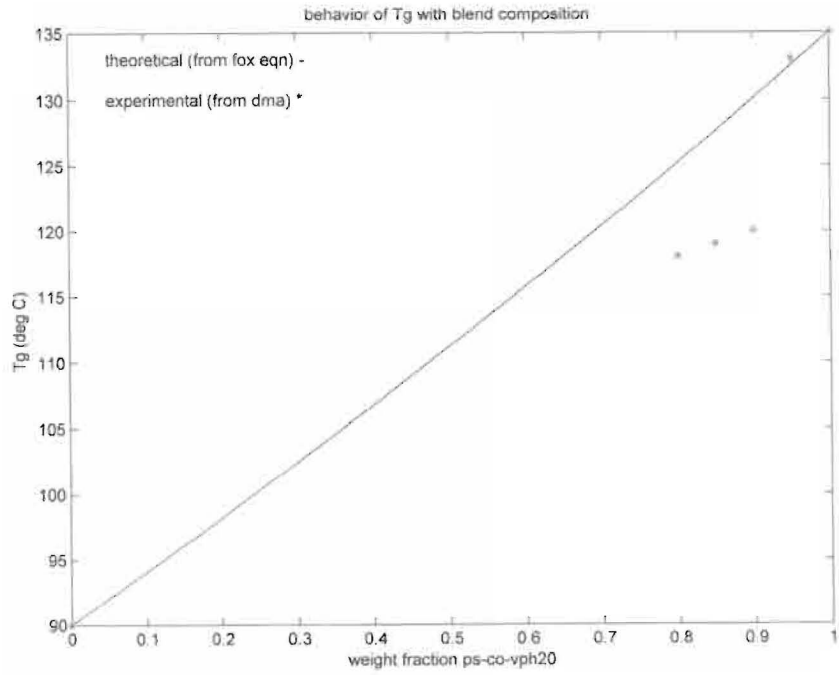


Figure 20. Behavior of Tg with blend composition – theoretical, from Fox equation, and experimental, obtained using DMA.

Via phase contrast optical microscopy, phase separation was observed for even the 95:5 blend, at all temperatures up to 180 °C. It may be that the 2 phase – 1 phase boundary curve to has shifted up and to the right. This observation of the phase behavior confirms that the system is in fact not miscible for this range of compositions.

CONCLUSIONS

From DSC, DMA, and optical microscopy it seems apparent that this particular polymer blend system is not miscible over this range of compositions. This seems to be the result of a molecular weight effect, namely, decreased molecular weight of the LCPU, likely correlated to the scale of the polymerization, and increased molecular weight of the copolymer. It is possible that the high molecular weight of the coil polymer, PS-co-VPh(20), resulted in exclusion of the LCPU from participation in intimate interactions, thus deterring miscibility between the two components. With the system immiscible, the mechanical property evaluation is much less straightforward and less meaningful.

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ACKNOWLEDGEMENTS

Dr. Mark Dadmun, advisor

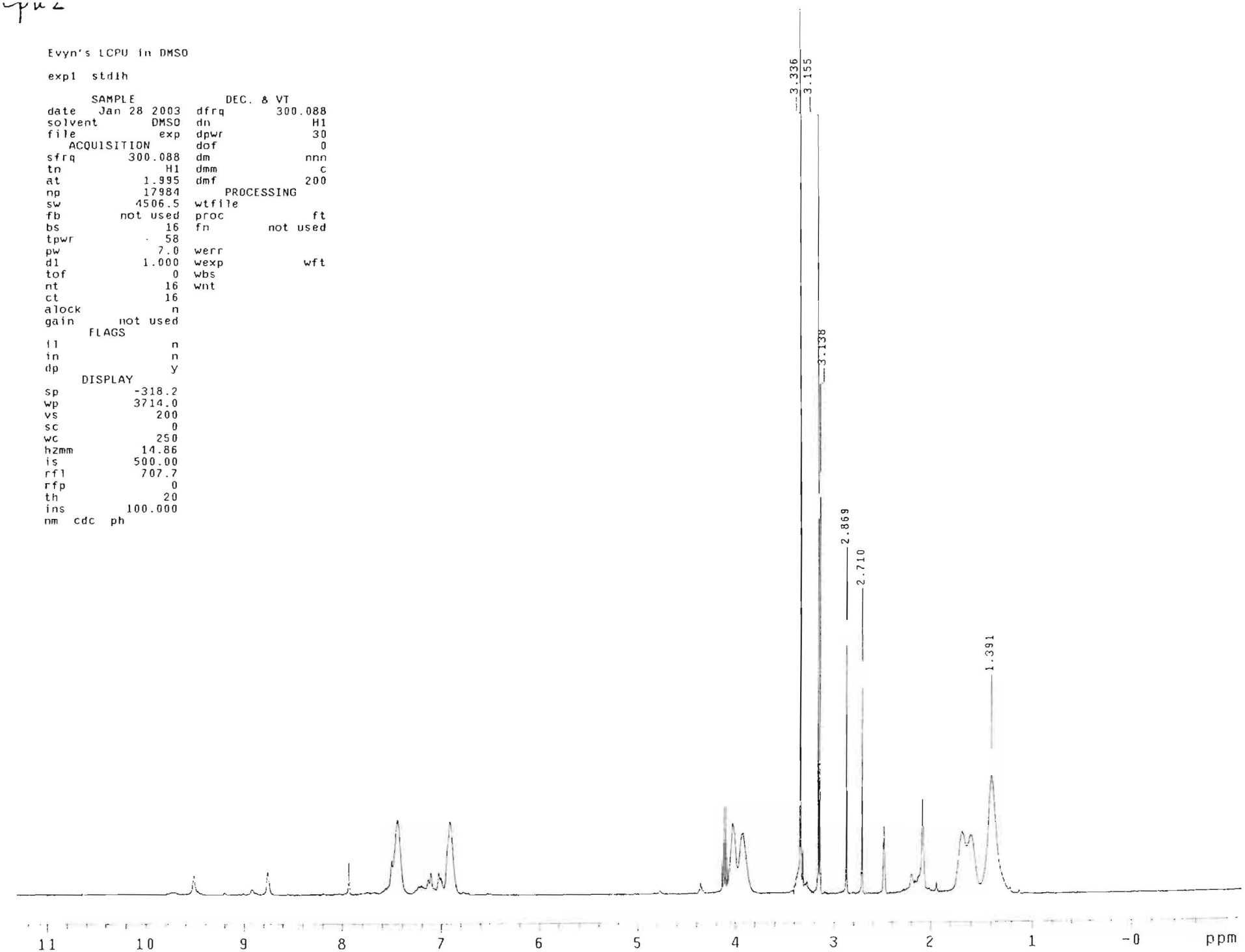
Asif Rasheed, experimental collaborator – copolymer synthesis and characterization

APPENDIX

Evyn's LCPU in DMSO

exp1 stdih

SAMPLE		DEC. & VT	
date	Jan 28 2003	dfrq	300.088
solvent	DMSO	dn	H1
file	exp	dpwr	30
ACQUISITION		dof	0
sfrq	300.088	dm	nnn
tn	H1	dmm	c
at	1.995	dmf	200
np	17984	PROCESSING	
sw	4506.5	wtfile	
fb	not used	proc	ft
bs	16	fn	not used
tpwr	58		
pw	7.0	werr	
d1	1.000	wexp	wft
tof	0	wbs	
nt	16	wnt	
ct	16		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
DISPLAY			
sp	-318.2		
wp	3714.0		
vs	200		
sc	0		
wc	250		
hzmm	14.86		
is	500.00		
rfl	707.7		
rfp	0		
th	20		
ins	100.000		
nm cdc ph			



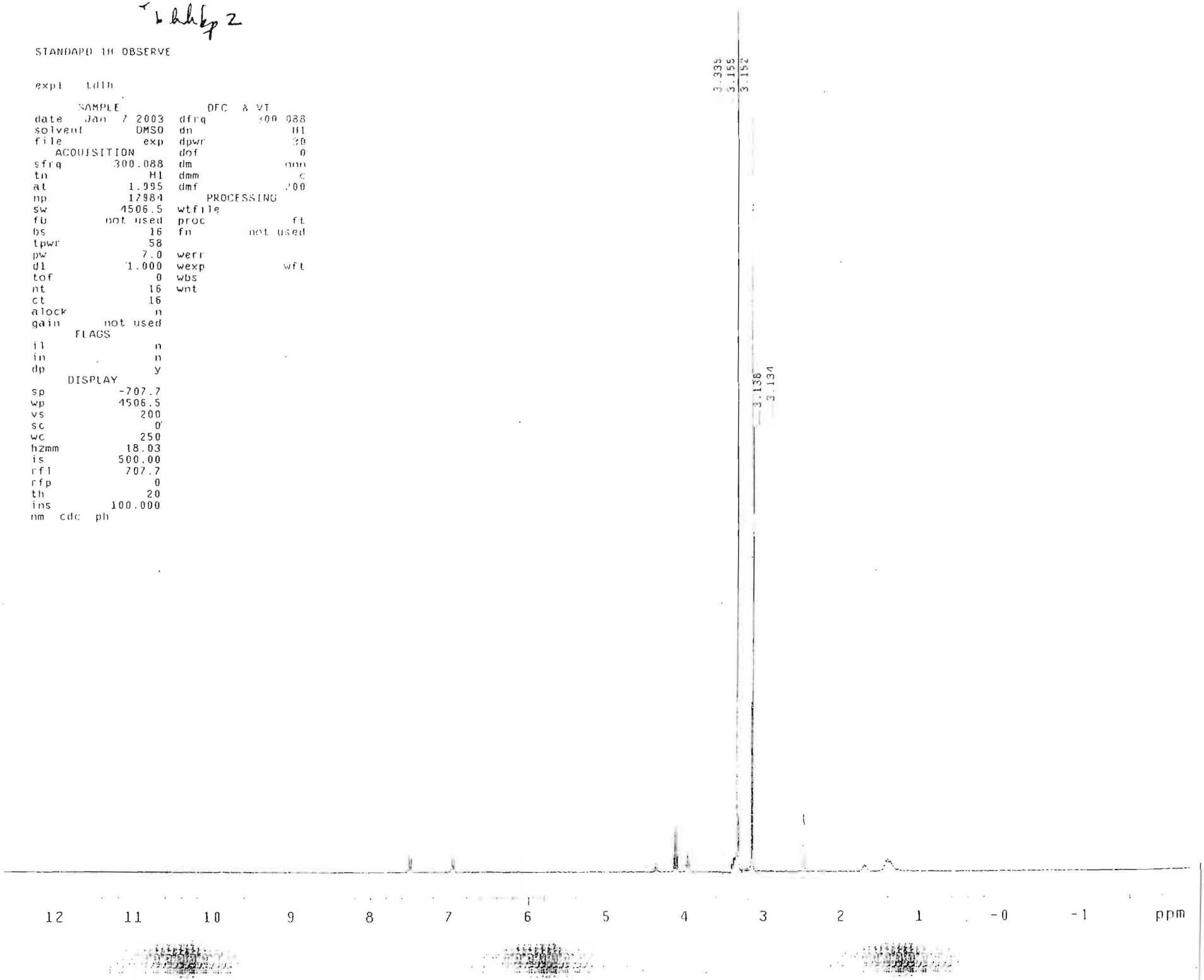
Tldlkp2

STANDARD 1H OBSERVE

expt tdlh

SAMPLE		DEC & VT	
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solvent	DMSO	dn	H1
file	exp	dpwr	30
ACQUISITION		dof	0
sfrq	300.088	dm	nnn
tn	H1	dmm	c
at	1.995	dmf	7000
np	17984	PROCESSING	
sw	4506.5	wtfile	
fb	not used	proc	ft
bs	16	fn	not used
tpwr	58		
pw	7.0	werr	
d1	1.000	wexp	wft
tof	0	wbs	
nt	16	wnt	
ct	16		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
DISPLAY			
sp	-707.7		
wp	4506.5		
vs	200		
sc	0		
wc	250		
hzmm	18.03		
is	500.00		
rfl	707.7		
rfp	0		
th	20		
ins	100.000		

nm cdc ph



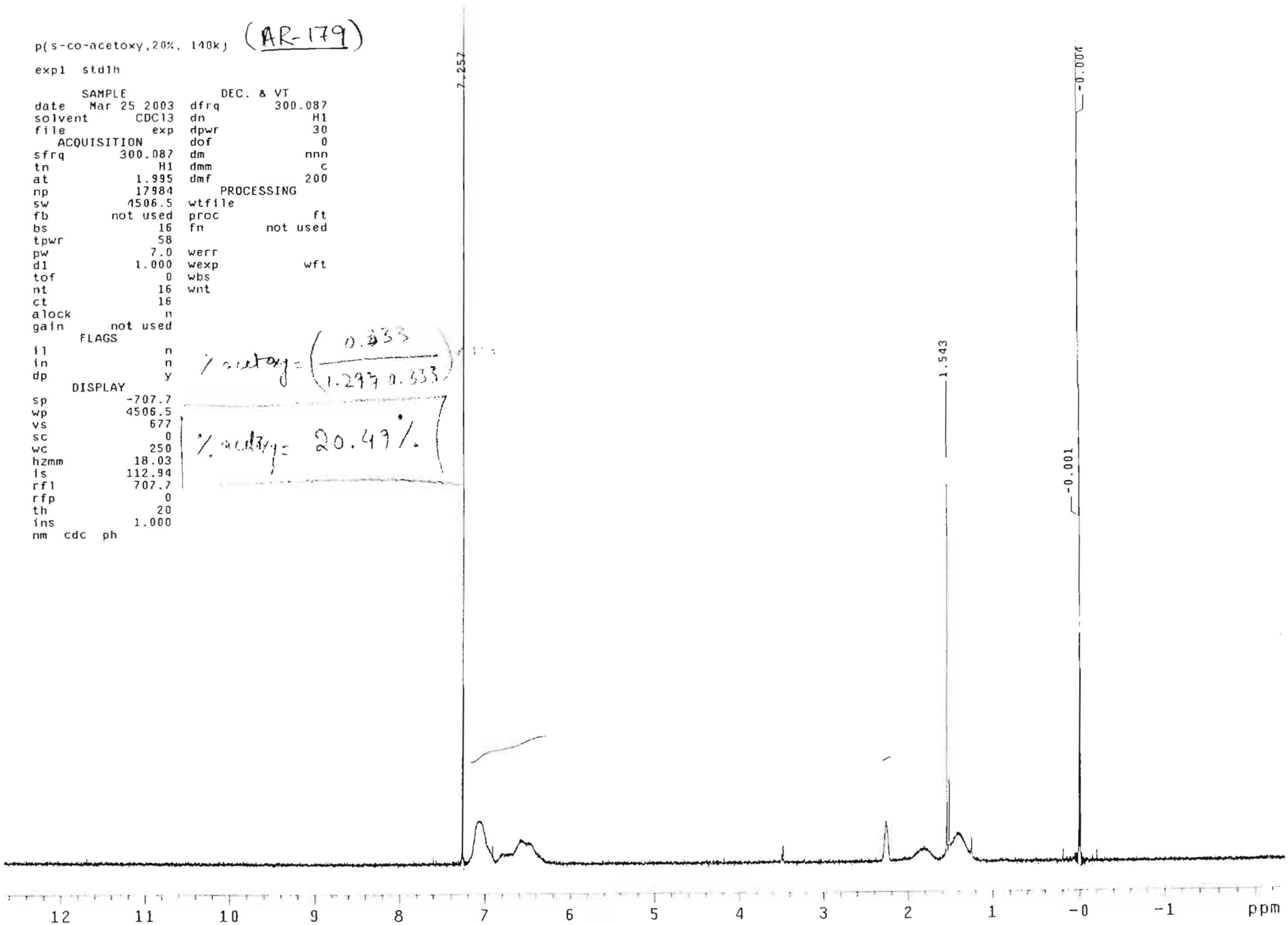
p(s-co-acetoxy,20%, 140k) (AR-179)

exp1 std1h

SAMPLE		DEC. & VT	
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solvent	CDCl3	dn	H1
file	exp	dpwr	30
ACQUISITION		dof	0
sfrq	300.087	dm	nnn
tn	H1	dmm	c
at	1.995	dmf	200
np	17984	PROCESSING	
sw	4506.5	wtfile	
fb	not used	proc	ft
bs	16	fn	not used
tpwr	58		
pw	7.0	werr	
d1	1.000	wexp	wft
tof	0	wbs	
nt	16	wnt	
ct	16		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
DISPLAY			
sp	-707.7		
wp	4506.5		
vs	677		
sc	0		
wc	250		
hzmm	18.03		
is	112.94		
rfl	707.7		
rfp	0		
th	20		
ins	1.000		
nm cdc ph			

% acetoxy = (0.333 / 1.297 + 0.333)

% acetoxy = 20.49 %



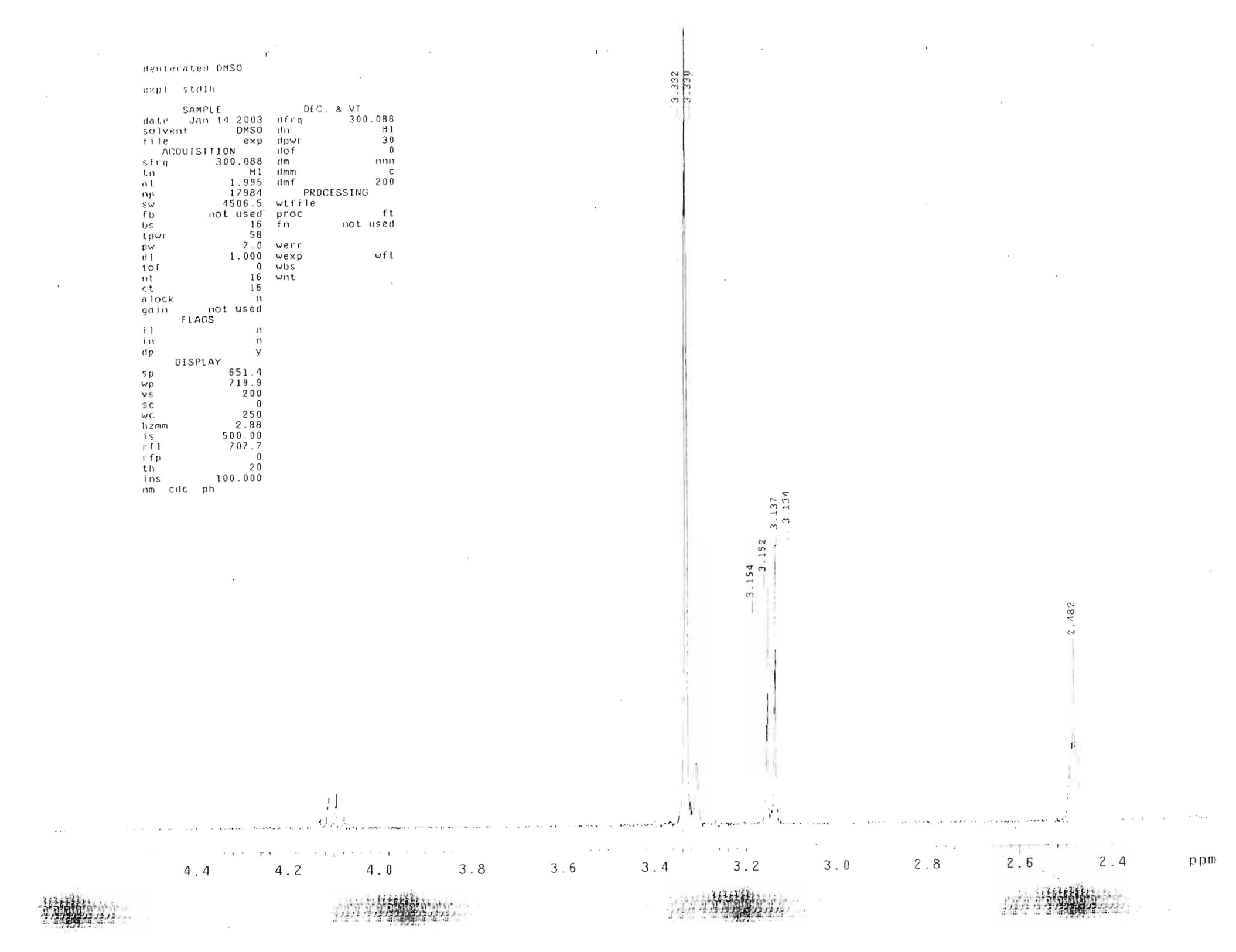
7.29 − 4(0.333) = 1.29

1.00/3 = 0.333

deuterated DMSO

expl std1h

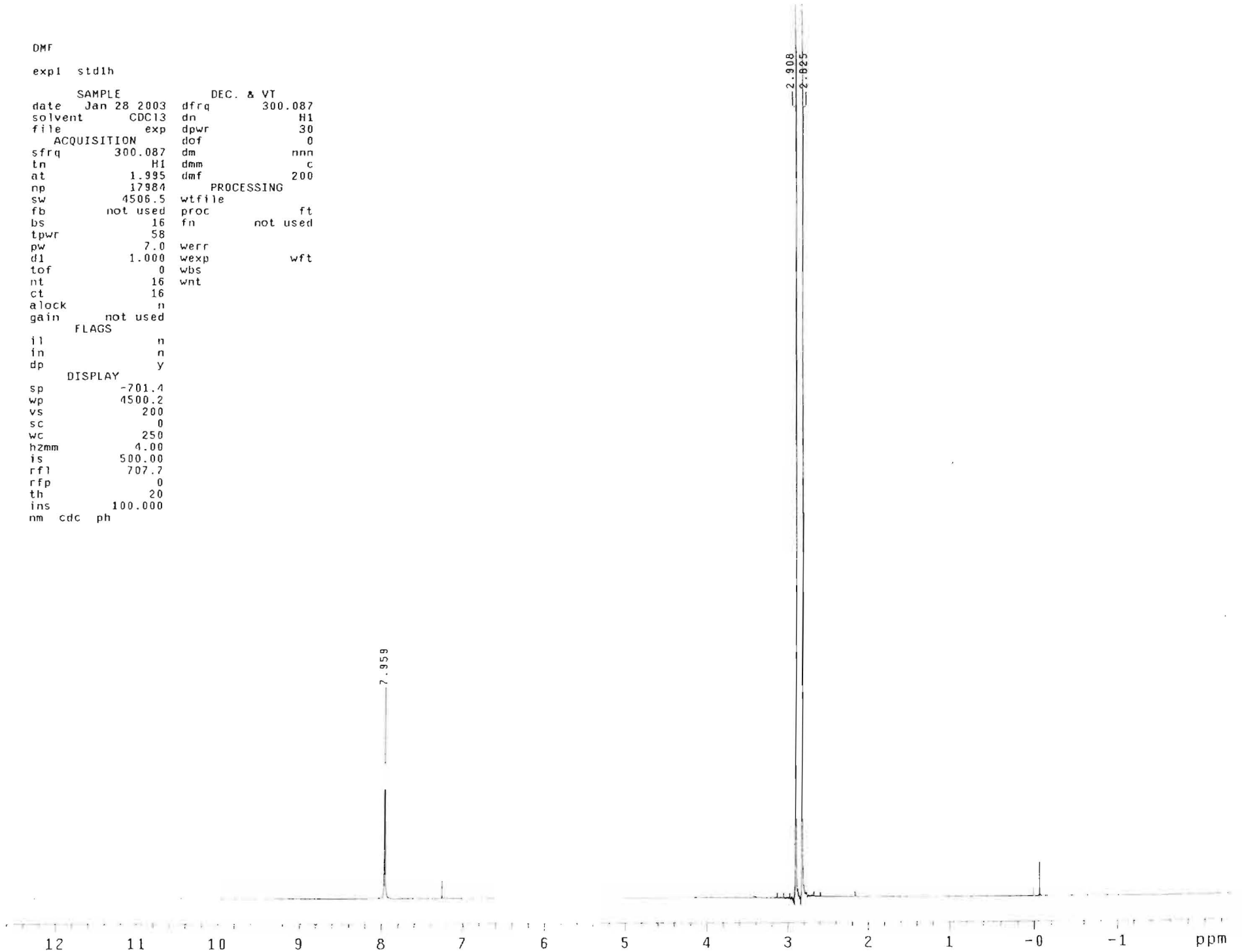
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tn	H1	dmm	c
at	1.995	dmf	200
np	17984	PROCESSING	
sw	4506.5	wtfile	
fb	not used	proc	ft
bs	16	fn	not used
tpwr	58		
pw	7.0	werr	
d1	1.000	wexp	wft
tof	0	wbs	
nt	16	wnt	
ct	16		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
DISPLAY			
sp	651.4		
wp	719.9		
vs	200		
sc	0		
wc	250		
hzmm	2.88		
is	500.00		
rfl	707.7		
rfp	0		
th	20		
ins	100.000		
nm cdc ph			



DMF

expl stdlh

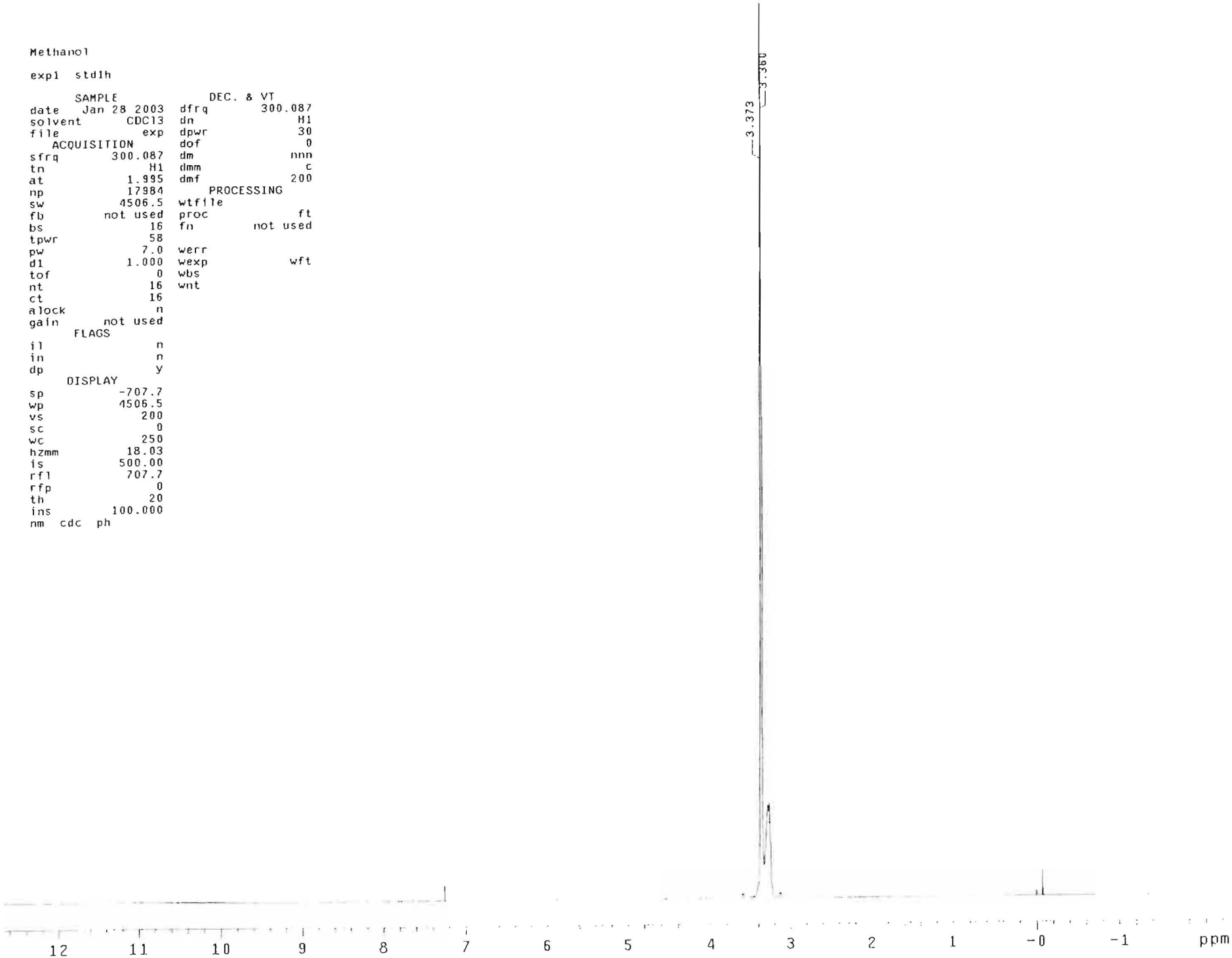
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tn	H1	dmm	c
at	1.995	dmf	200
np	17984	PROCESSING	
sw	4506.5	wtfile	
fb	not used	proc	ft
bs	16	fn	not used
tpwr	58		
pw	7.0	werr	
d1	1.000	wexp	wft
tof	0	wbs	
nt	16	wnt	
ct	16		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
DISPLAY			
sp	-701.4		
wp	4500.2		
vs	200		
sc	0		
wc	250		
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is	500.00		
rfl	707.7		
rfp	0		
th	20		
ins	100.000		
nm cdc ph			

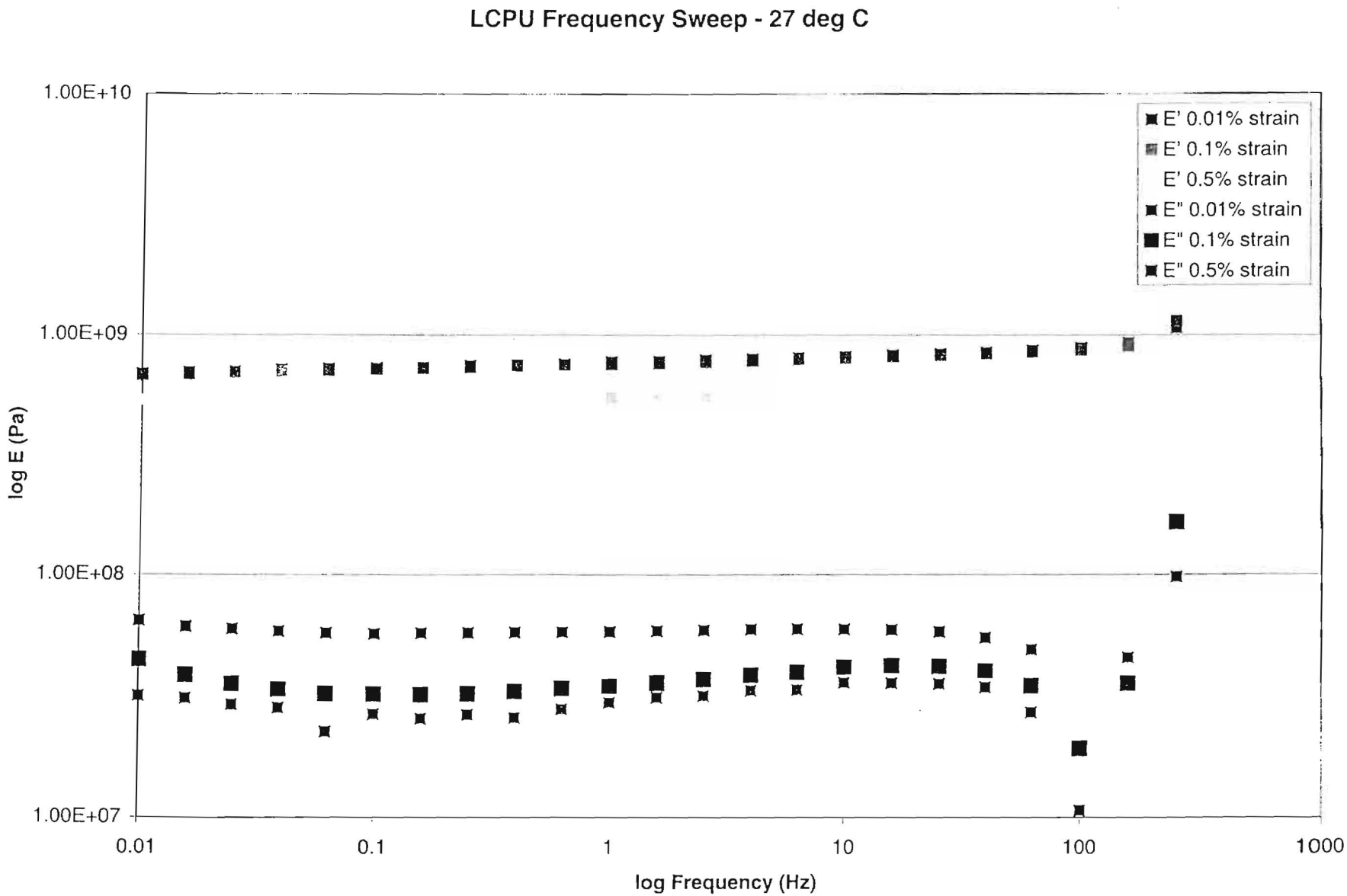


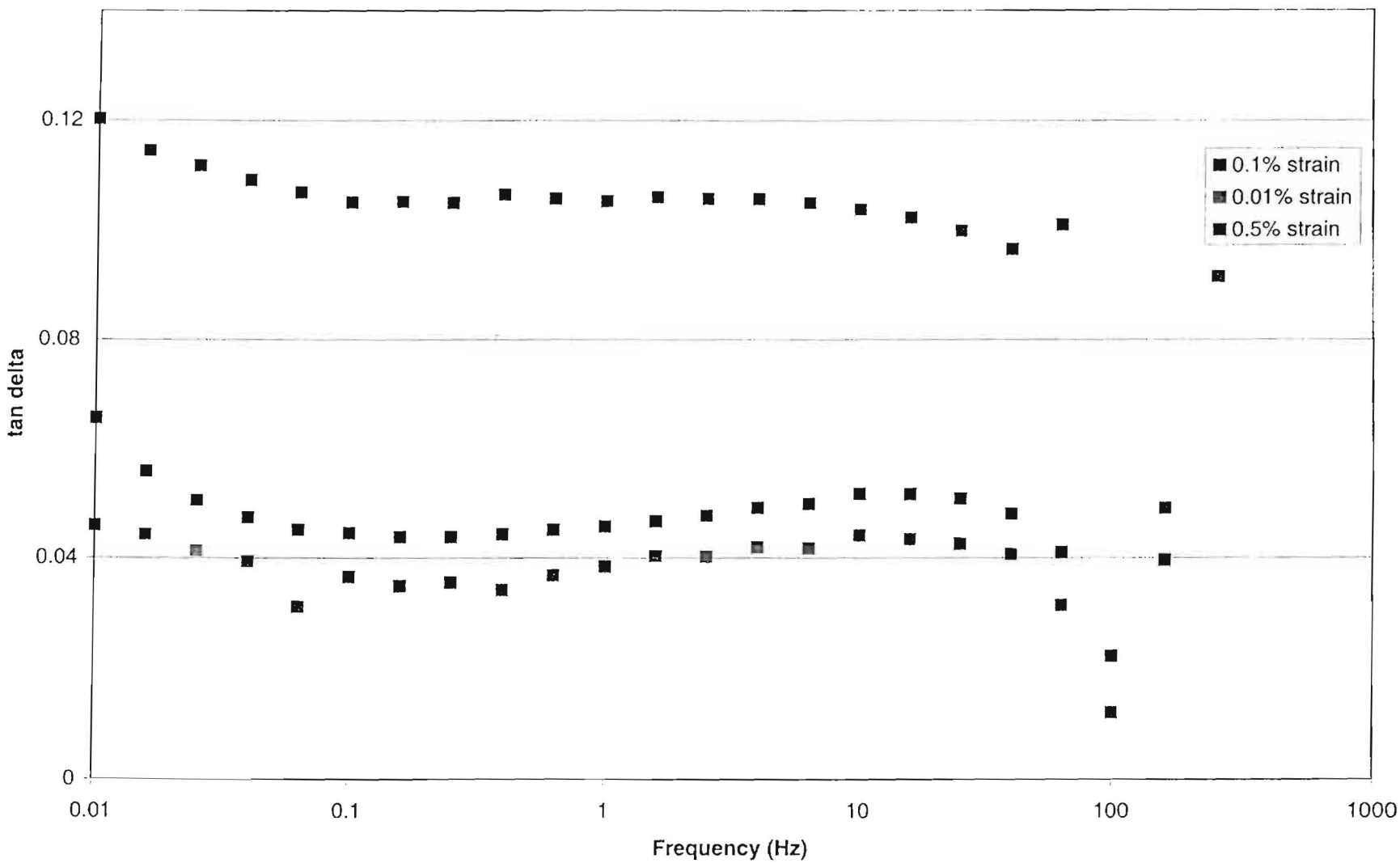
Methanol

expl std1h

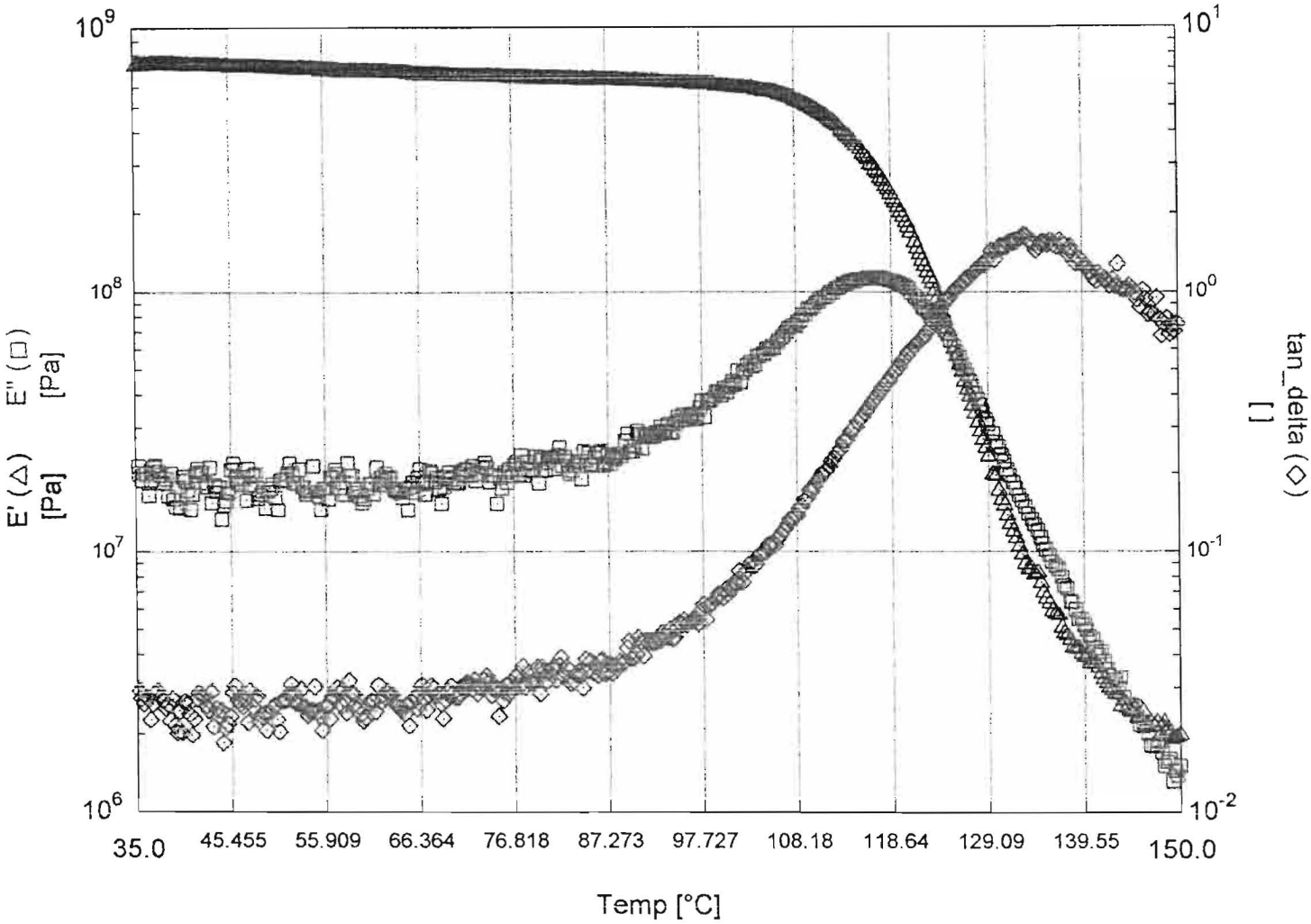
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file	exp	dpwr	30
ACQUISITION		dof	0
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tn	H1	dmm	c
at	1.995	dmf	200
np	17984	PROCESSING	
sw	4506.5	wtfile	
fb	not used	proc	ft
bs	16	fn	not used
tpwr	58		
pw	7.0	werr	
d1	1.000	wexp	wft
tof	0	wbs	
nt	16	wnt	
ct	16		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
DISPLAY			
sp	-707.7		
wp	4506.5		
vs	200		
sc	0		
wc	250		
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is	500.00		
rfl	707.7		
rfp	0		
th	20		
ins	100.000		
nm	cdc ph		

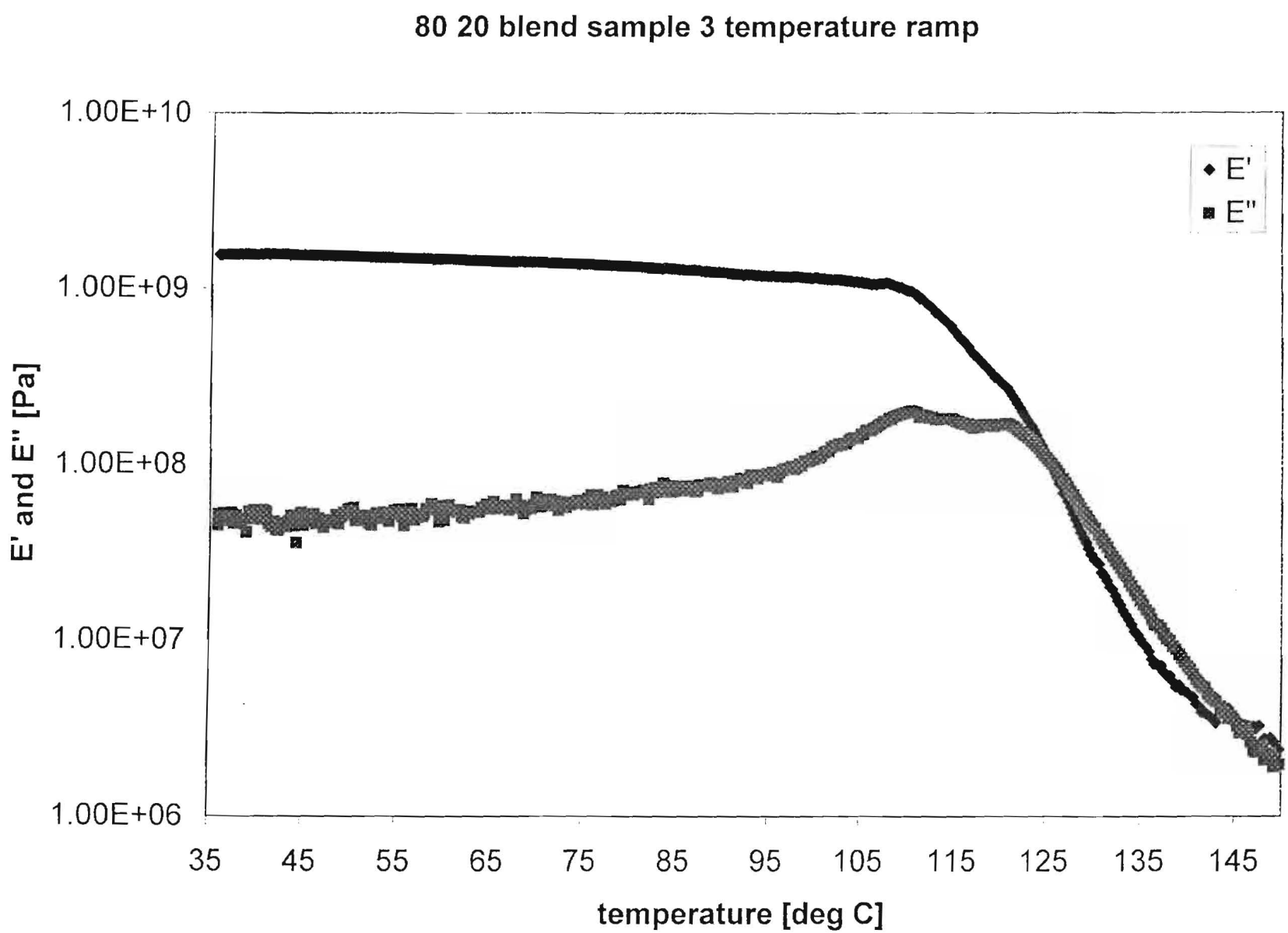


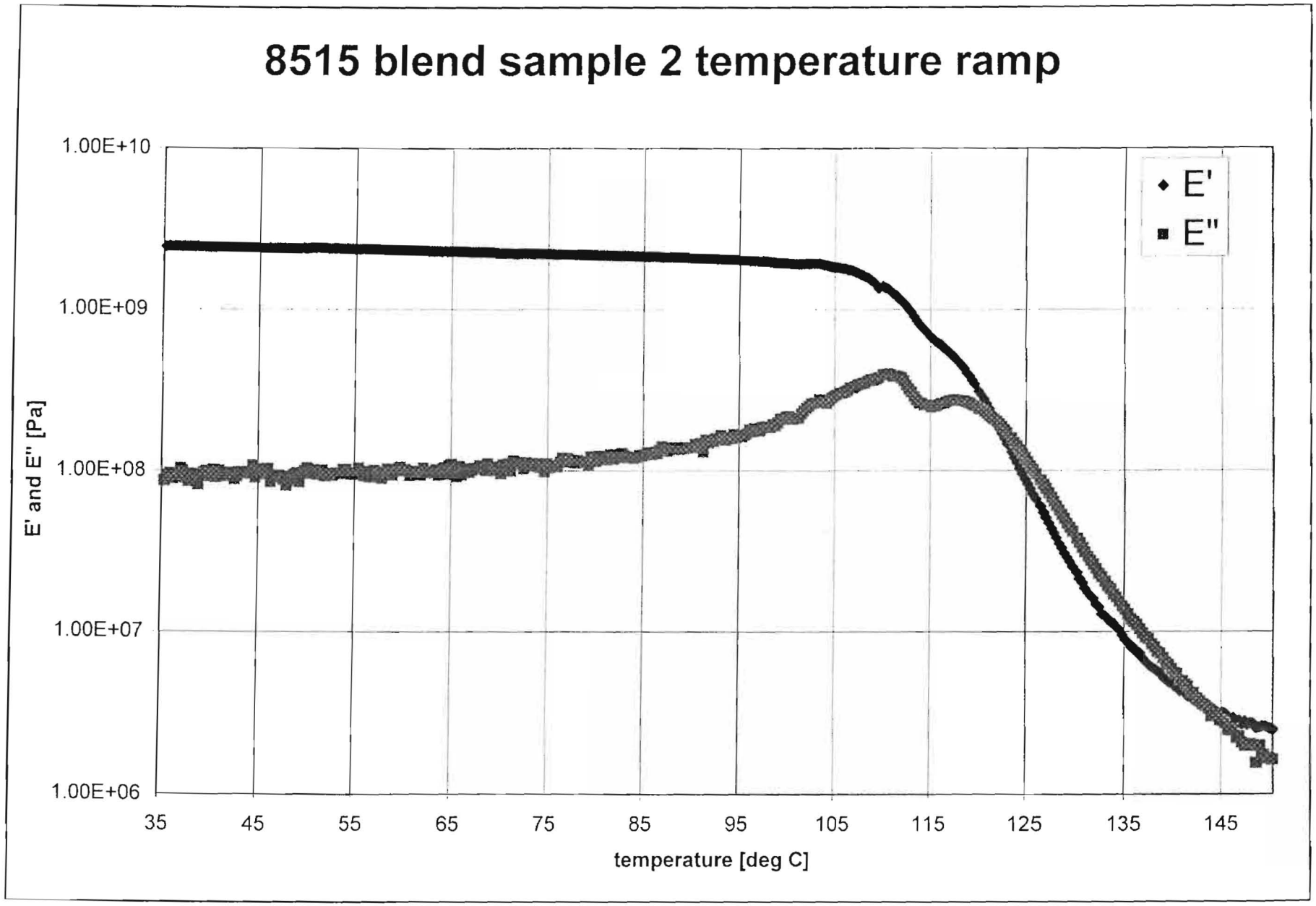

LCPU Frequency Sweep - 27 deg C
1.00E+10
1.00E+09
1.00E+08
1.00E+07
log E (Pa)
0.01
0.1
1
10
100
1000
log Frequency (Hz)
E' 0.01% strain
E' 0.1% strain
E' 0.5% strain
E" 0.01% strain
E" 0.1% strain
E" 0.5% strain

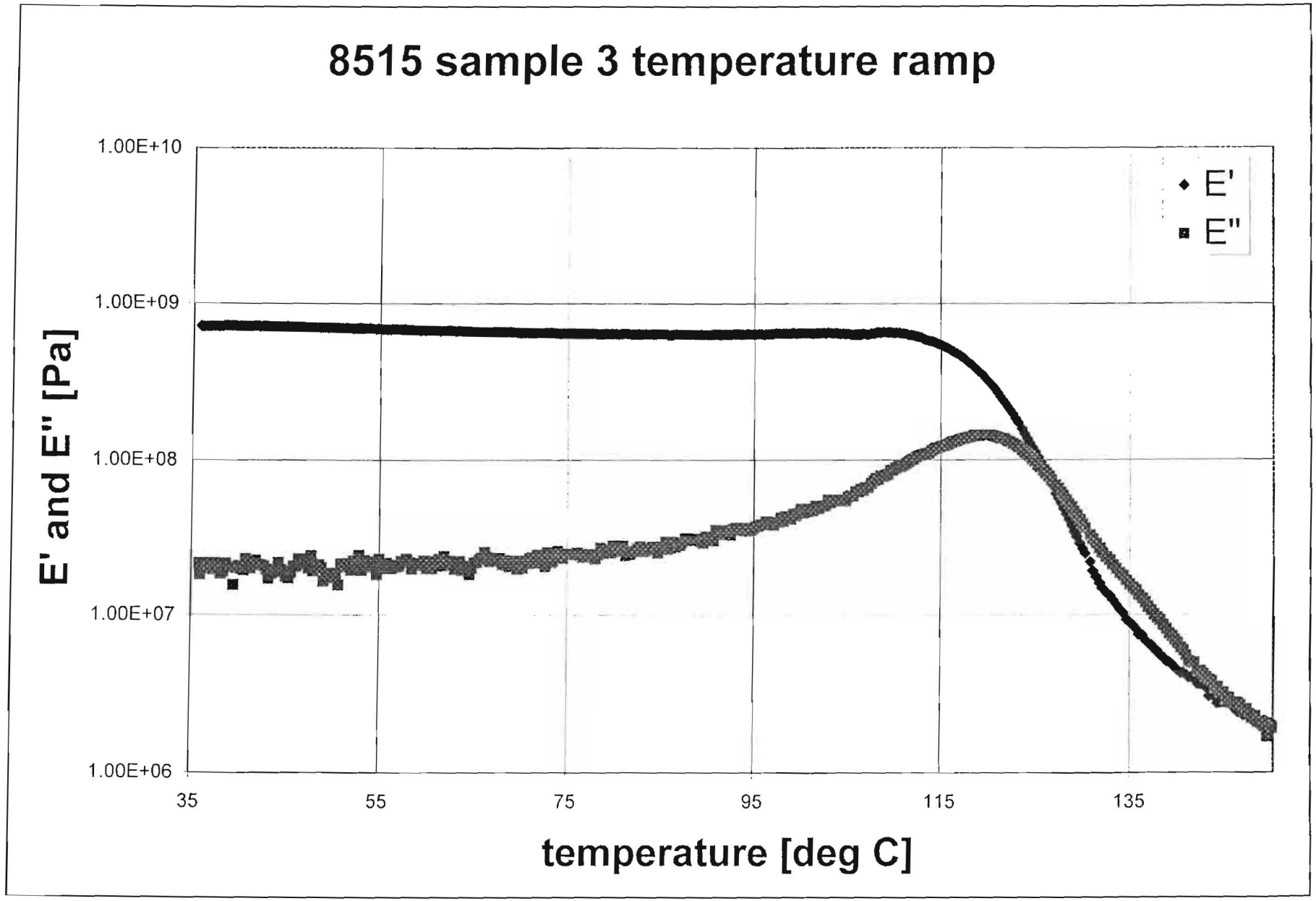

LCPU Frequency Sweep - 27 deg C
0.12
0.08
0.04
0
tan delta
0.01
0.1
1
10
100
1000
Frequency (Hz)
0.1% strain
0.01% strain
0.5% strain

80 20 blend sample 2 temperature ramp




80 20 blend sample 3 temperature ramp
1.00E+10
1.00E+09
1.00E+08
1.00E+07
1.00E+06
E' and E'' [Pa]
E'
E''
35
45
55
65
75
85
95
105
115
125
135
145
temperature [deg C]


8515 blend sample 2 temperature ramp
1.00E+10
1.00E+09
1.00E+08
1.00E+07
1.00E+06
E' and E" [Pa]
35
45
55
65
75
85
95
105
115
125
135
145
temperature [deg C]
E'
E"


8515 sample 3 temperature ramp
1.00E+10
1.00E+09
1.00E+08
1.00E+07
1.00E+06
E' and E" [Pa]
35
55
75
95
115
135
temperature [deg C]
E'
E"

95 5 blend temperature ramp sample 1 (2)

