Evaluation of the Radiaton Stability of SuperLig 639

by

L. N. Oji

Westinghouse Savannah River Company
Savannah River Site
Aiken, South Carolina 29808

D. J. McCabe

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L. N. Oji, 773-43A
D.J. McCabe, 773-43A

Authorized Derivative Classifier

Authorized Reviewing Official

Savannah River Technology Center
Westinghouse Savannah River Company
Aiken, SC 29808

Summary

Samples of SuperLig™ 639 ion exchange resin were irradiated with ^{60}Co gamma source and evaluated for a loss in effectiveness. The resin is manufactured by IBC Advanced Technologies, Inc., and has

been shown to be highly specific for removal of technetium from aqueous waste. The resin was degraded by the radiation, with a 91% lower distribution coefficient after 1.0E9 rad of dose.

Introduction

A method for treatment and disposal of the Hanford High Level Waste has been proposed by BNFL, Inc. In this process, a portion of the Hanford High Level waste will be pretreated to concentrate radionuclides prior to vitrification. The conceptualized process decontaminates radioactive waste by ion exchange removal of Cs^{137} and Tc^{99}, and precipitation of Sr^{90} and transuranic ions. This task examines the stability of one of the ion exchange resins, SuperLig™ 639, toward irradiation. This resin is specific for removal of the pertechnetate ion. These tests were conducted using simulated Hanford High Level Waste containing perrhenate ion as a stand-in for pertechnetate.

Experimental

The stability of irradiated SuperLig™ 639 was evaluated by completely immersing a sample in a solution of simulated salt solution (without perrhenate) and exposing the mixture to a ^{60}Co gamma radiation source. The irradiation flux rate of the gamma source was 1.38E 06 rad/hr. Samples were periodically removed from the gamma source and the distribution coefficients (K_d) were determined. The temperature during irradiation was maintained at 31± 1 ° C.

All chemicals used in the simulant preparation were reagent ACS grade quality. Rhenium was added to the simulant as sodium perrhenate (99.95%). The concentration of the simulant components are summarized in Table 1 below. The simulant was filtered through a 0.2 micron nylon filter after preparation. De-ionized water (conductivity less than 2 µS/cm and pH of 6.8) was used in all preparations. The resin was SuperLig 639, received from IBC Advanced Technologies, Inc., on 6/2/97 as a dry solid.

For irradiation, about 2.0 g of the resin was placed inside a 100 ml Pyrex glass test tube containing 10 ml of the simulant (without rhenium). Five such tubes were prepared and put into a stainless steel (ss) rack configured for the ^{60}Co gamma radiation source. Each test tube was capped with a glass cap containing a small opening for gas release. The ss rack containing the five test tubes was then put into a larger ss jacket, sealed and lowered into the ^{60}Co source inside a pool of water. The test tubes were left in the source for a specified amount of time, Table 2, (7.25, 72.46, 217.39, 458.8 and 724.6 hours) to achieve the required exposure (1.0 E 07, 1.0E 08, 3.0E 08, 6.0E 08 and 1.0E 09 rad, respectively). The reference resin

sample was not exposed to radiation. A continuous stream of high purity argon was used to insure a 24 hours purging of the interior of the ss jacket to remove gases produced as a result of radiolysis. Gases released were neither identified nor quantified. The temperature inside the ss jacket was monitored with a thermocouple.

Table 1. Simulant composition and concentrations

Component	Molar Conc.
$NaNO_3$	0.85
$Al(NO_3)_3.9H_2O$	0.50
KNO_3	0.10
NaCl	0.285
Na_2SO_4 (anhydrous)	4.85E-02
NaOH	3.50
$NaNO_2$	0.46

Preparation of Irradiated Resins for Kd Studies

Periodically (Table 2), the ss jacket was elevated and one of the five test tubes removed. The irradiated resin inside the test tube was washed with about 500 ml of de-ionized water (in 50 ml portions), followed by drying in a vacuum desiccator for 24 hours at room temperature. A known quantity of the dry resin (approximately 0.5 grams, Table 2) was then placed in contact with 10 ml of the perrhenate-containing simulant in a 50 ml polyethylene bottle. The polyethylene bottles were placed in an orbital shaker and the mixture agitated for 24 hours. After the contact time, the samples were filtered with a 0.2 micron nylon filter and the filtrates submitted for rhenium concentration analysis. An identical experiment was also performed with the reference sample (non-irradiated resin). The magnitude of the K_d value was obtained by determining the concentration of rhenium before and after contact and calculating the quantity of rhenium on the resin by difference. Calculation of the K_d was based on the equation below:

$$K_d = ((C_i - C_f)/C_f)(V/(m*F))$$

C_i is the initial rhenium concentration, C_f if the final rhenium concentration after contact, V is the volume of simulant used, m is the resin exchanger mass, and F is the mass of dried resin divided by the mass of as received resin (i.e., the dry weight correction factor). The F-factor was determined to be 1.00 for

this resin as received from IBC. The initial concentration of rhenium was 100 ppm (0.0383 grams of sodium perrhenate in 250 ml of simulant solution).

Table 2. Summary of Distribution Coefficients for Irradiated SuperLig™ 639 Resin

Sample #	Dose (Rad)	Resin wt. (g)	$[Re]_F$ ppm	K_d(ml/g)	Average K_d (ml/g)
93278	No irradiation	0.5013	6.63	289.05	**285.7**
93279	No irradiation	0.5027	6.76	282.32	
93280	1.00E +07	0.5025	6.07	316.8	**298.6**
93281	1.00E +07	0.5063	6.76	280.31	
93282	1.00E +08	0.5060	12.80	138.8	**142.4**
93283	1.00E +08	0.5042	12.28	146.04	
93619	3.00E +08	0.5043	14.08	124.81	**124.1**
93620	3.00E +08	0.5039	14.22	123.48	
93933	6.00E +08	0.5036	23.45	67.11	**65.38**
93934	6.00E +08	0.5036	24.42	63.65	
94465	1.00E +09	0.5030	45.57	24.92	**24.90**
94466	1.00E +09	0.5018	45.69	24.87	

* Simulant volume = 10 ml; $[Re]_i$ ppm = 102.7 ± 0.5

The results of the experiment are also shown in Figure 1. The degradation of the resin was exponential with dose rate. This data set is highly consistent and should provide a good estimate for the performance of the resin with dose. This rapid degradation suggests that the technetium removal columns should be placed after the cesium removal process to minimize radiolytic decomposition of this resin.

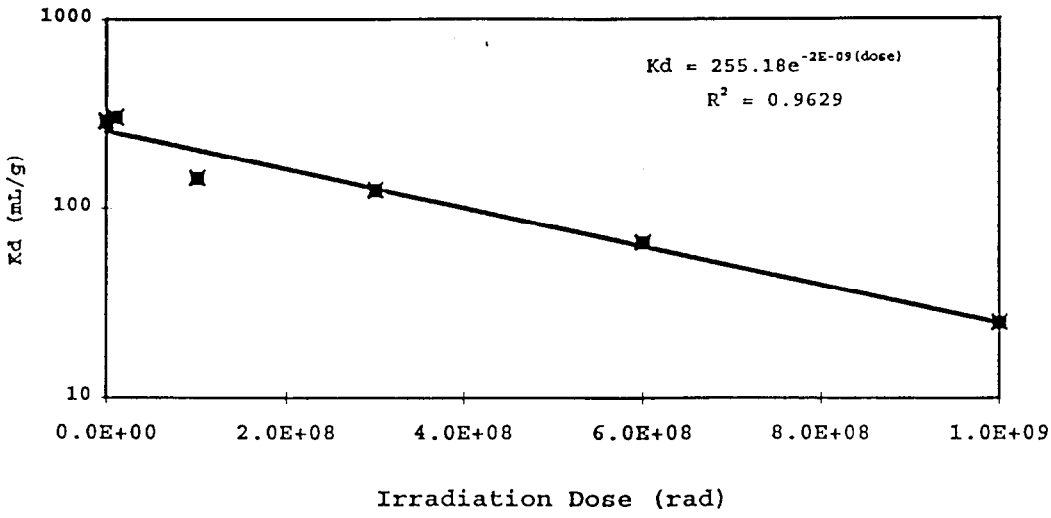


Figure 1. Irradiation of SuperLig™ 639

Results of the Thermal Gravimetric Analysis and Differential Scanning Calorimetry are located in the appendix. The analyses were performed on resin samples that had doses of 0, 6.0E8, and 1.0E9 rad. The results indicate that rapid energetic decompositions do not occur below 600 °C with irradiated resin. Moreover, the resin actually becomes less reactive with irradiation (i.e., the energy release or absorption rate is less rapid). Essentially all of the material was oxidized and had volatized before reaching 450 °C. Based on these data, the resin does not become more reactive after irradiation. If it is shown that the unirradiated material can be safely disposed by vitrification in a glass melter, the irradiated material should be equally safe to vitrify.

Conclusions

The radiolytic decomposition of SuperLig™ 639 has been demonstrated. The data provides a design basis for the change out frequency of the resin beds. The results were very consistent and indicated an exponential degradation in resin performance with dose. Irradiation does not activate the resin toward a material that exhibits more energetic decomposition.

Attachments

Thermal Gravimetric Analysis and Differential Scanning Calorimetry graphs for irradiated and non-irradiated resin.

Approvals

Design Check

M.C. Thompson 8/21/97

M.C. Thompson Date
Chemical and Hydrogen Technology

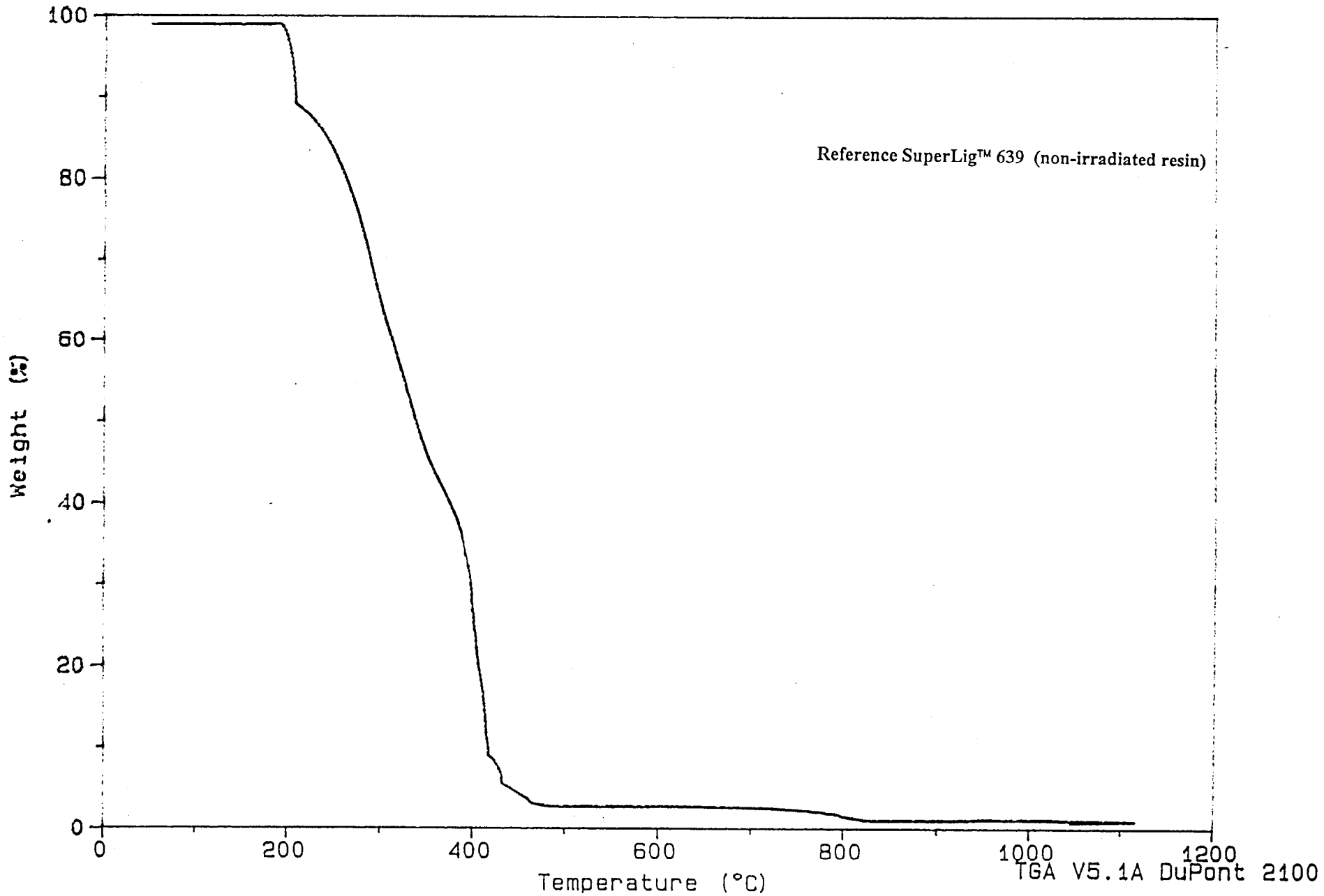
Distribution:

M.E. Johnson, BNFL, Inc.
S.D. Fink, 773-A
H.F. Sturm, 773-A
N.M. Hassan, 773-A
S.T. Wach, 773-A
M.C. Thompson, 773-A
L.M. Nelson, 773-43A

Sample: SG639BNFL
Size: 13.9490 mg
Method: TGA
Comment: OJI

TGA

File: C:INORGRESIN.004
Operator: JWC
Run Date: 13-Aug-97 13:47



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Method: TGA
Comment: OJI

TGA

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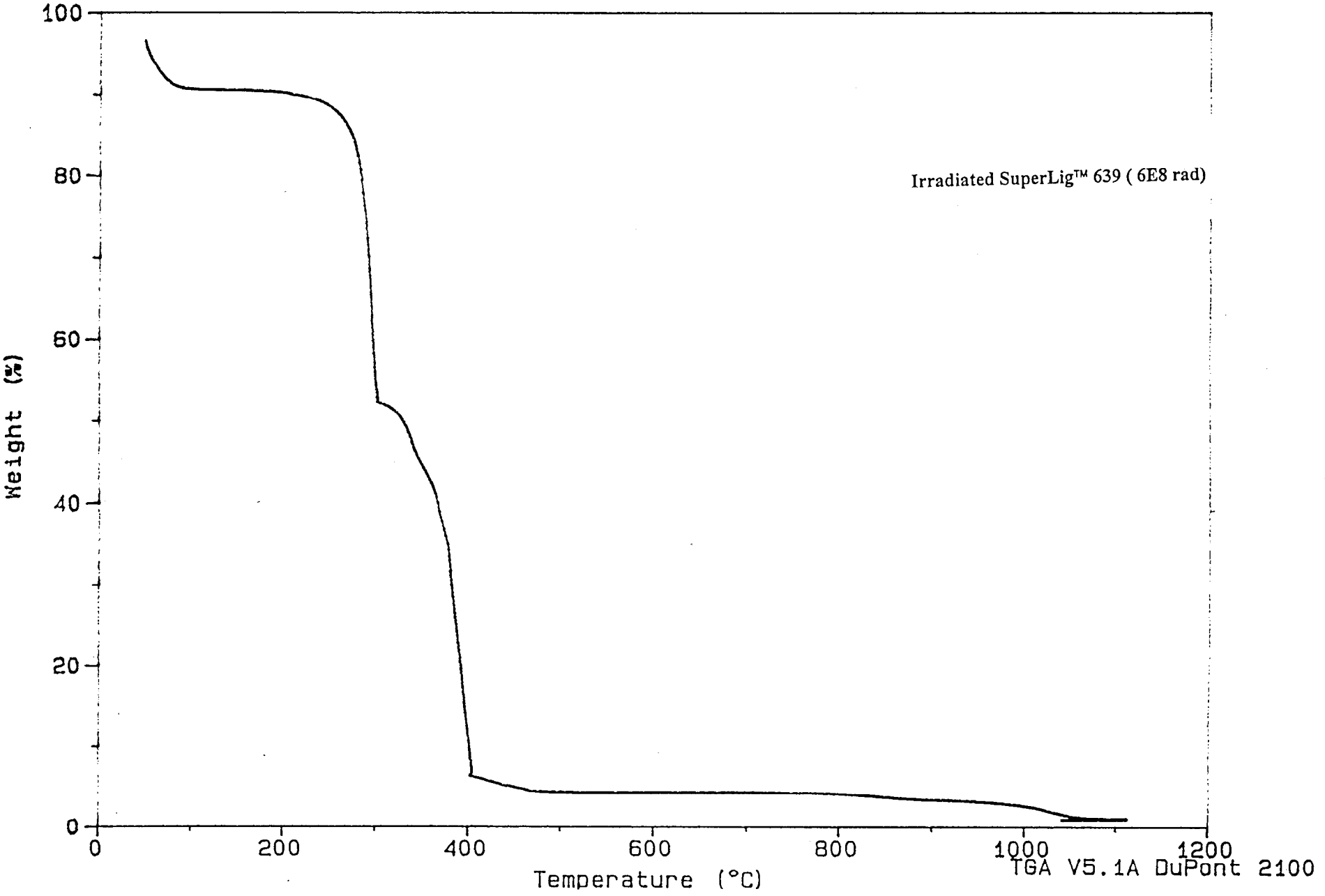

Sample: SG639BNFL31
Size: 11.8940 mg
Method: TGA
Comment: OJI

TGA

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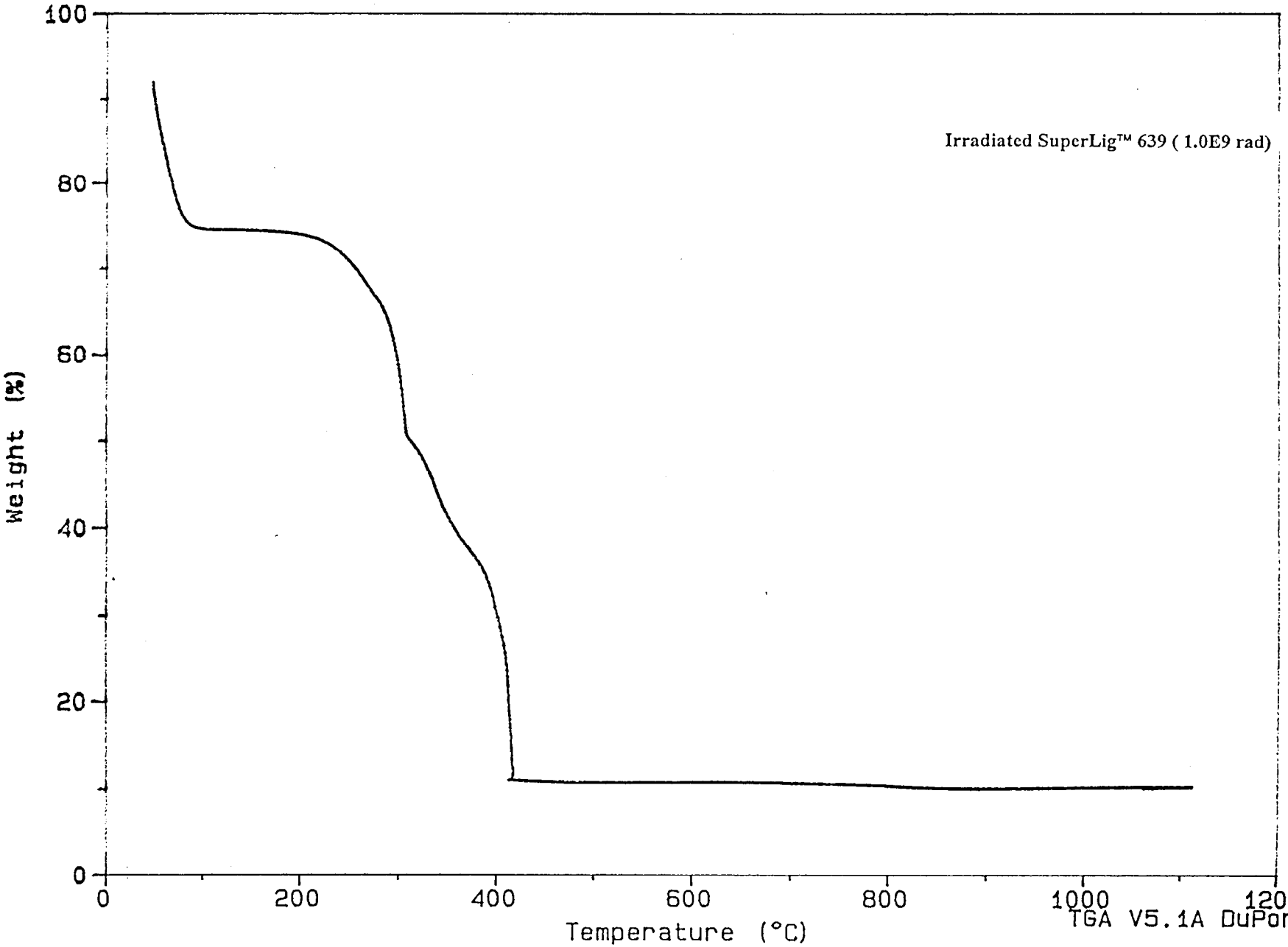

Sample: SG639BNFL
Size: 0.1240 mg
Method: DSC TO 600 C
Comment: OJI

DSC

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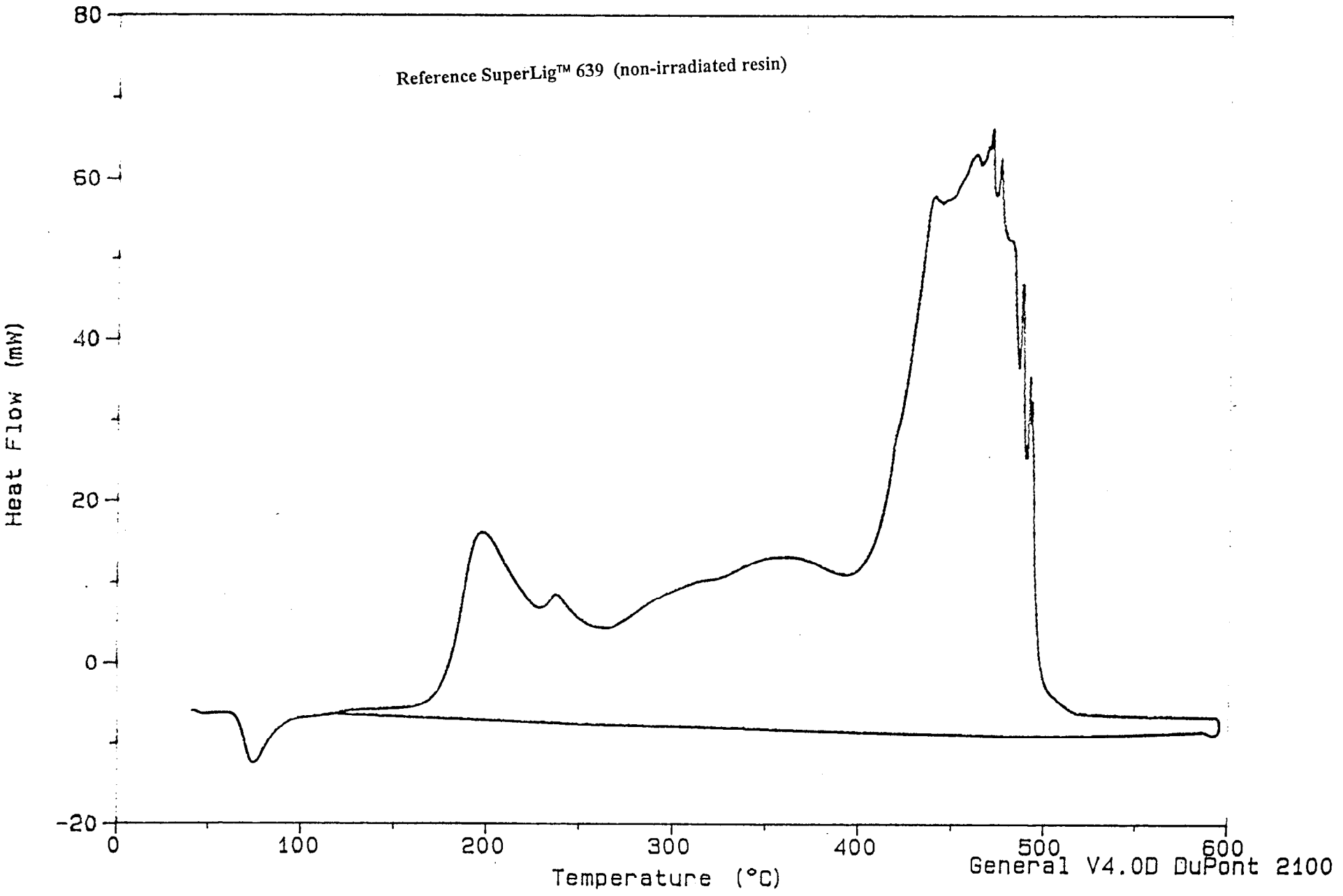

Sample: SG639BNFL19.06
Size: 0.1000 mg
Method: DSC TO 600 C
Comment: OJI

DSC

File: C:INORGRESIN.007
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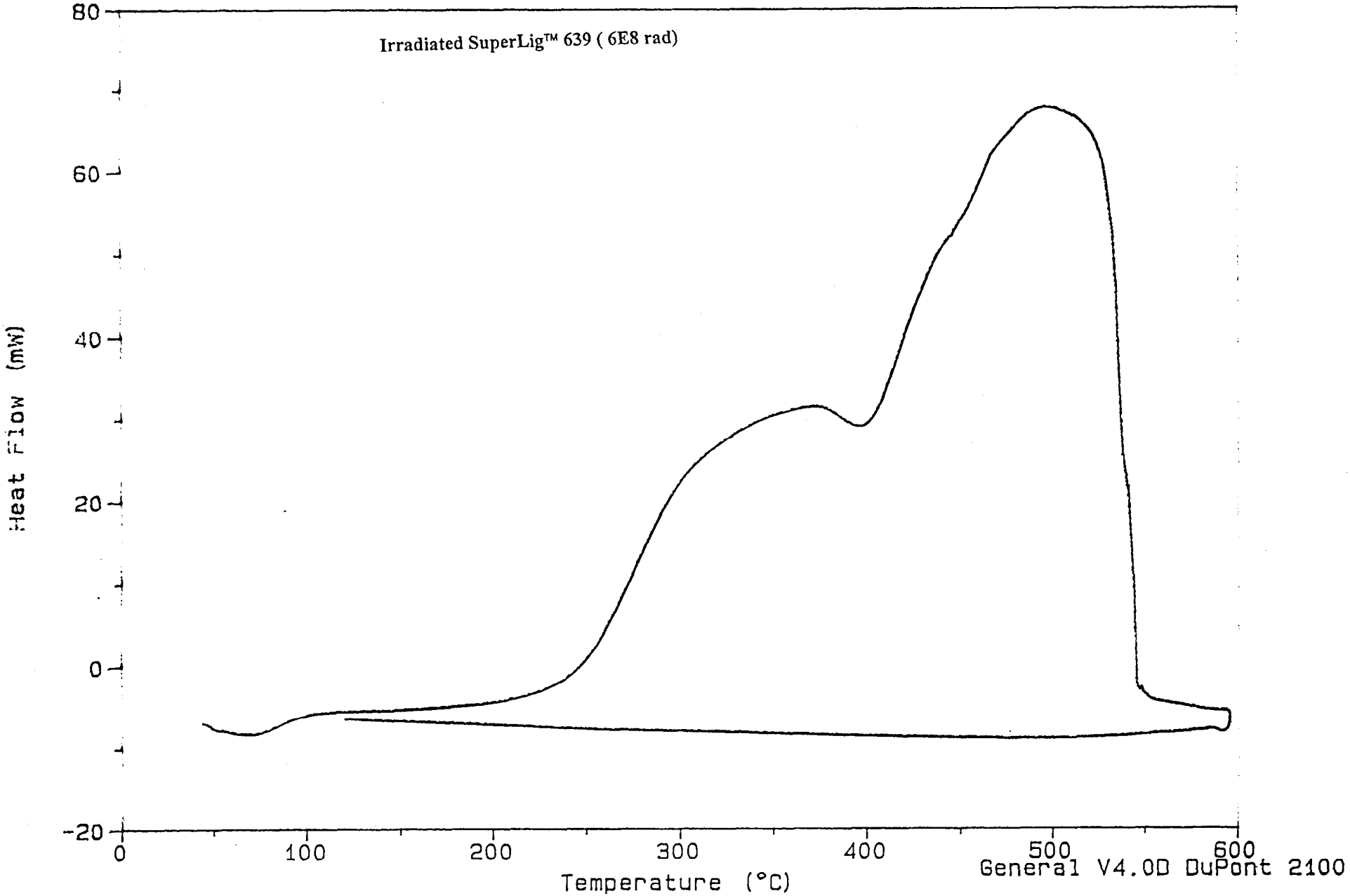

Sample: SG639BNFL31
Size: 0.1000 mg
Method: DSC TO 600 C
Comment: OJI

DSC

File: INORGRESIN.008
Operator: JBL
Run Date: 15-Aug-97 08:31