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**DAYTON
LABORATORY**

DAYTON, OHIO 45407

F.C. #3445

Quarterly Report No. 11
PHYSICAL AND RHEOLOGICAL PROPERTIES OF
NITROSO RUBBERS
25 December 1965 through 24 March 1966

Contract No. DA19-129-AMC-151(N)
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12 April 1966

For

U. S. Army Natick Laboratories
Natick, Massachusetts

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ABSTRACT

Characterization of the trifluoronitrosomethane/tetrafluoroethylene copolymer produced by the Thiokol Chemical Corporation and supplied by the U. S. Army Natick Laboratories was continued. The $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ copolymer was found to be adaptable to elution fractionation in a perfluorocyclic ether and a benzotrifluoride solvent/nonsolvent system. A weight-viscosity distribution consisting of 25 fractions was obtained. A sample (Thiokol XP5702) from which 25% insoluble gel was removed exhibited two dominant molecular weight regions of 2×10^5 and 4×10^6 . The molecular weight of a fraction of the $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ copolymer with a reduced viscosity of 1.37 in perfluorocyclic ether (FC-75) was determined by light scattering to be 2.1×10^6 . The Mark-Houwink Equation for $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ in perfluorocyclic ether at 25°C was determined to be $[\eta] = 2.8 \times 10^{-5} \bar{M}_w^{0.738}$. An amine cured $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ sample was swollen by fourteen solvents and chemicals, including water. No crystallinity was observed in the $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ gum down to -80°C .

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I. INTRODUCTION

The fluorinated nitroso rubber to be characterized in this program is considered to be a highly solvent resistant, stable, low and high temperature rubber. The degree of its worth in these respects can only be determined through a characterization of its basic physical properties. The purpose of the characterization is to describe the rubber for its use and further improvement or modification.

Nine nitroso gum samples, listed as ZR-561-XP5675, XP-5702, XP5812, XP5887, XP5807, XP5704, 0.2 C₂F₃H terpolymer, 0.5 C₂F₃H terpolymer, produced by the Thiokol Chemical Corporation, and a 3M-produced gum, were delivered to Monsanto Research Corporation via the Natick Laboratories for characterization.

Research completed during this period of work includes: elution fractionation of the XP5702 copolymer, determination of a weight-viscosity distribution, molecular weight determinations by light scattering, determination of the constants for the Mark-Houwink Equation, volume swell studies, low temperature differential thermal analysis, and X-ray diffraction analysis.

II. EXPERIMENTAL

A. ELUTION FRACTIONATION OF PURIFIED XP5702 TRIFLUORONITROSO-METHANE/TETRAFLUOROETHYLENE COPOLYMER

A second and third fractionation was performed on the XP5702 copolymer. The elution technique as described in MRC Quarterly Report No. 10 (Ref. 1) was utilized.

The sample was cleaned by putting it into solution in FC-75 solvent (isomers of perfluorocyclic ether), tumbling for 72 hours, heating to 80°C for 20 hours, cooling, filtering through 300 mesh stainless steel screen and No. 1 filter paper, precipitating the clear solution with benzotrifluoride, evaporating the solvent, and recovering the soluble gum. A large portion (49%) was unrecovered. From previous experience (Ref. 1), this unrecovered portion was 25% insoluble gel and 24% loss due to handling. 10.222 grams of polymer was recovered.

1. Fractionation XP5702 - Run No. 2

The above purified gum was again put into solution in FC-75 (1.5000 g in 29 ml) and allowed to sit overnight at 80°C. A solvent/nonsolvent system was then prepared, based on prior determinations of solvent/nonsolvent ratios (Ref. 1). The system consisted of a ratio of 3.6762 g polymer/100 ml FC-75/73 ml benzotrifluoride. Under these conditions, the polymer was all in solution at 70°C and precipitated at 25°C.

The elution column used was described in the MRC Tenth Quarterly Report (Ref. 1) and in Reference 2.

The column was maintained at 78°C by refluxing ethanol in the jacket, and the polymer solution was heated to 80°C prior to pouring on the column for deposition. The actual solution added consisted of 1.500 g XP5702 (purified), 29 ml of FC-75, and 21 ml benzotrifluoride. Following the addition of the solution, the column was cooled slowly in order to cause selective deposition of the polymer on the sand.

Removal of the polymer fractions was performed by eluting with solvent/nonsolvent mixtures of FC-75 and benzotrifluoride. The column was first flushed with 200 ml of benzotrifluoride to remove any impurities and set the polymer to the substrate. The 200 ml benzotrifluoride flush became turbid in passing through the column. The flush solution was then passed over the column three more times to redeposit the polymer from the turbid flush solution. A clear solution indicated that the polymer was all redeposited. A final flush was conducted with a clean benzotrifluoride solution.

Progressive elutions were performed with solvent/nonsolvent mixtures, where the solvent portion was varied from 30% to 60% in 2% volume increments with a final 100% elution. These volume increments were determined from the first fractionation (Ref. 1) which utilized 5% volume increments. The narrower increments were an attempt to provide a more detailed fractionation. The 17 fractions obtained in this run are shown in Table 1 with the corresponding weights and viscosities.

2. Fractionation XP5702 - Run No. 3

A third fractionation was performed in which an identical deposition amount and technique were utilized as in Run 2, with one exception. Following deposition, the column was thoroughly dried by flushing with dry nitrogen for a period of 36 hours.

The column was again flushed with benzotrifluoride to remove impurities and set the polymer to the substrate. This time, no turbidity was encountered. Thus, only one flush was conducted.

Again, to provide a more detailed fractionation, the elution procedure was modified. The jacketing temperature was lowered to 56.5°C (boiling acetone), and the solvent/nonsolvent increments were decreased to 1%. Progressive elutions were performed between solvent/nonsolvent ratios of 35% to 55%, with a final 100% solvent elution. The temperature of the column was raised to 78°C and flushed with 200 ml of FC-75. A nominal amount of 0.0096 g was removed in this final flush. The elutions consisted of 100 ml of the solvent/nonsolvent mixture with an elution time between 20 to 25 minutes. The 24 fractions recovered are shown in Table 2 with the corresponding weights and viscosities. The total and differential weights are plotted in Figure 1 as a function of their viscosity in FC-75.

Specific viscosities were measured in a 0.1% solution in both FC-75 and FC-43 (if sufficient sample was available) and at two temperatures (25°C and 35°C) in FC-75, see Table 2.

The intrinsic viscosities of the whole polymer measured in FC-75 and FC-43 (Table 2) are shown determined in Figure 2.

B. MOLECULAR WEIGHT DETERMINATIONS

The molecular weight of Fraction No. 4 from fractionation XP5702 - Run No. 2 was determined by light scattering measurements in the Brice Phoenix Light Scattering Photometer (Ref. 3). The determinations were made in FC-75 solvent in a manner identical to that described for the evaluation of Sample 3M-9690 (56703-3) in MRC Quarterly Report No. 9 (Ref. 3). The value of $(n-n_0/C)$ was determined on the differential refractometer to be 0.0233 at a wavelength of 436 m μ . The index of refraction reported in the literature (1.281) was again used.

The Zimm plot and a plot of HC/τ (90°) versus concentration for the fraction are shown in Figures 3 and 4. Extrapolation of the Zimm plot to zero concentration indicates a molecular weight of 2.22×10^6 . Applying the 5.5% correction factor (Ref. 3), the molecular weight is 2.1×10^6 . Extrapolation of the 90° plot provides an identical result.

C. INTRINSIC VISCOSITY VS. MOLECULAR WEIGHT FOR CF_3NO/C_2F_4 IN FC-75

The molecular weight and intrinsic viscosities of one fraction each of a Thiokol and a 3M-produced CF_3NO/C_2F_4 gum were measured in FC-75 solvent. The results of the first gum were reported earlier (Ref. 3). The gum examined was 3M Sample 9690 (56703). The second results are reported above (Section B) for a fraction of Thiokol Sample XP5702. The corresponding intrinsic viscosities and molecular weights measured in FC-75 at $25^\circ C$ are as follows:

<u>Sample</u>	<u>$[\eta]$</u>	<u>\bar{M}_w</u>
3M-9690	0.44	4.8×10^5
XP5702 (fraction)	1.30	2.1×10^6

This viscosity-molecular weight relationship is shown in Figure 5. Note that the relationship is based on only two data points. Further data may modify the relationship slightly.

D. PHYSICAL PROPERTIES AND FORMULATIONS OF AMINE CURED TRIFLUORO-NITROSOMETHANE/TETRAFLUOROETHYLENE COPOLYMER

The following master batches of SiO₂ and carbon black filled compositions were prepared:

Master Batch #1 (37566) 100 parts XP5887 gum
1 part carbon black
15 parts Hi Sil-101
1.25 parts TETA
2.25 parts HMDAC

Master Batch #2 (37568) 100 parts XP5887 gum
0.25 part carbon black
15 parts Hi Sil-101
1.25 parts TETA
2.5 parts HMDAC

Master Batch #3 (37572) 100 parts XP5887 gum
15 parts Hi Sil-101
1.25 parts TETA
2.5 parts HMDAC

Thirteen CF₃NO/C₂F₄ rubbers were prepared under the following conditions, utilizing the master batches above. They were:

Sample No. 37566 - Cure No. 1
Cure Conditions: 130°C, 1000 psi, 2 hrs.
Post Cure: 16 hrs. at 50°C, 2 hrs. at 70°C,
2 hrs. at 90°C, 16 hrs. at 95°C
Rubber swell data on above sample.

Sample No. 37566 - Cure No. 2
Cure Conditions: 130°C, 1000 psi, 2 hrs.
Post Cure: 16 hrs. at 50°C, 2 hrs. at 70°C,
3 hrs. at 90°C, 19 hrs. at 95°C
Cracks throughout sample, dull finish on surface.

Sample No. 37566 - Cure No. 3
Cure Conditions: 130°C, 1000 psi, 2 hrs.
Post Cure: 16 hrs. at 50°C, 5 hrs. at 70°C,
19 hrs. at 80°C, 3 hrs. at 90°C

Sample No. 37566 - Cure No. 4
Cure Conditions: 130°C, 1000 psi, 3 1/2 hrs.
Post Cure: 57 1/2 hrs. at 50°C, 3 hrs. at 70°C,
20 hrs. at 80°C, 3 1/2 hrs. at 90°C,
3 1/2 hrs. at 95°C

Sample No. 37566 - Cure No. 5
 Cure Conditions: 130°C, 1000 psi, 3 1/2 hrs.
 Post Cure: 20 hrs. at 50°C, 3 1/2 hrs. at 70°C,
 3 1/2 hrs. at 80°C, 16 hrs. at 90°C,
 8 hrs. at 95°C
 Cracks throughout sample, dull surface finish.

Sample No. 37566 - Cure No. 6
 Cure Conditions: 130°C, 1000 psi, 3 1/2 hrs.
 Post Cure: 16 hrs. at 50°C, 5 hrs. at 70°C,
 3 hrs. at 80°C, 16 hrs. at 90°C,
 5 1/2 hrs. at 95°C

Sample No. 37568 - Cure No. 1
 Cure Conditions: 130°C, 1000 psi, 3 1/2 hrs.
 Post Cure: 20 hrs. at 50°C, 3 1/2 hrs. at 70°C,
 3 1/2 hrs. at 80°C, 16 hrs. at 90°C,
 8 hrs. at 95°C

Sample No. 37568 - Cure No. 2
 Cure Conditions: 130°C, 1000 psi, 3 hrs.
 Post Cure: 20 1/2 hrs. at 50°C, 5 hrs. at 70°C,
 3 hrs. at 80°C, 16 hrs. at 90°C,
 5 1/2 hrs. at 95°C

Sample No. 37568 - Cure No. 3
 Cure Conditions: 130°C, 1000 psi, 3 1/2 hrs.
 Post Cure: 16 hrs. at 50°C, 5 hrs. at 70°C,
 3 hrs. at 80°C, 16 hrs. at 90°C,
 5 1/2 hrs. at 95°C

Sample No. 37568 - Cure No. 4
 Cure Conditions: 120°C, 1000 psi, 5 hrs.
 Post Cure: 1 hr. at 50°C, 1 hr. at 65°C,
 1 hr. at 85°C, 18 hrs. at 100°C

Sample No. 37572 - Cure No. 1
 Cure Conditions: 120°C, 1000 psi, 3 1/2 hrs.
 Post Cure: 17 hrs. at 50°C, 3 hrs. at 70°C,
 5 hrs. at 85°C, 17 hrs. at 95°C,
 5 hrs. at 100°C

Sample No. 37572 - Cure No. 2
 Cure Conditions: 130°C, 1000 psi, 3 1/2 hrs.
 Post Cure: Same as Sample 37572 - Cure No. 1 above.

Sample No. 37572 - Cure No. 3
Cure Conditions: 120°C, 1000 psi, 5 hrs.
Post Cure: 4 hrs. at 50°C, 16 hrs. at 75°C,
3 hrs. at 85°C, 5 hrs. at 95°C
Durometer before post cure 75, after 78, wrinkled surface.

The physical properties of the SiO₂ and carbon black filled, amine cured rubbers are shown in Table 3.

E. SOLVENT AND CHEMICAL RESISTANCE OF AN AMINE CURED CF₃NO/C₂F₄ RUBBER

Sample No. 37566 - Cure No. 1 was molded into a 4 ins. x 4 ins. x 0.02 inch sheet. Specimens approximately 2 ins. x 0.38 ins. x 0.02 inch were cut from this sheet. Their weights and volumes were determined, and the specimens were placed in the 14 solvents and chemicals shown in Table 4. The weights and volumes of the specimens were redetermined at various intervals up to a total of 1128 hours. These and the calculated densities are shown in Table 4 with the corresponding solvent density. Also shown in Table 4 are the results of Cure Sample 9-8 (Ref. 3), immersed in FC-75 up to 1412 hours. This amine cured, SiO₂-filled rubber had exhibited a tensile strength of 267 psi and 420% elongation.

The viscosity of the FC-75 solvent was measured to determine if polymer was being extracted. No significant change was noted.

F. LOW TEMPERATURE DIFFERENTIAL THERMAL ANALYSIS OF CF₃NO/C₂F₄ SAMPLE XP5702

Differential thermal analysis of Sample XP5702 was performed from -100°C up to 100°C. The analysis was similar to previous measurements on this sample (Ref. 1), except that alumina was added to the specimen in an attempt to improve matching of thermal conductivity with the reference. The resulting thermogram is shown in Figure 6.

X-ray diffraction analysis was also performed on the specimen from -80°C up to -20°C. No patterns were seen, indicating the lack of crystallinity.

G. REFERENCES

1. "Physical and Rheological Properties of Nitroso Rubbers," Quarterly Report No. 10, Contract No. DA19-129-AMC-151(N), (O.I. 9115), 12 January 1966.
2. Kenyon, A. S., and Salyer, I. O., "Elution Fractionation of Crystalline and Amorphous Polymers," J. Polymer Sci., 43, 427 (1960).
3. "Physical and Rheological Properties of Nitroso Rubbers," Quarterly Report No. 9, Contract No. DA19-129-AMC-151(N), (O.I. 9115), 12 October 1965.
4. Morneau, G. A., Roth, P. I., and Shultz, A. R., "Trifluoro-nitrosomethane/Tetrafluoroethylene Elastomers, Dilute Solution Properties and Molecular Weight," J. Polymer Sci., 55, 609 (1961).

B. WEIGHT-VISCOSITY DISTRIBUTION OF THE PURIFIED XP5702
TRIFLUORONITROSOMETHANE/TETRAFLUOROETHYLENE COPOLYMER

The viscosities of 17 of the 25 fractions eluted by 1% solvent/nonsolvent increments were determined in FC-75 at 0.1% concentration. The integral and differential weight-viscosity distribution of the purified XP5702 copolymer is shown in Figure 1.

The differential weight-viscosity distribution shows two separate dominant viscosity portions. The two portions have reduced viscosities of ~ 0.2 and ~ 2.3 . The 2.3 viscosity region, however, is most dominant. The nonsymmetry of the weight distribution about the higher viscosity portion is due to the presence of the lower viscosity polymer portion, slight viscosity reversals in the fractionation, and is in all probability real, due to the unusual polymerization process encountered in the formation of the polymer. Fractionation of the polymer with the low viscosity portion removed will be required to establish the reasons for the lack of symmetry which is normally not encountered in polymer distributions.

The similarity of the weight-viscosity distribution to the weight-loss temperature (TGA) spectrum shown in Figure 3 of Monsanto Research Corporation's Tenth Quarterly Report (Ref. 1) is noteworthy. The TGA curve indicates that the low viscosity portion contributes significantly to the nonsymmetry of the polymer weight distribution.

The fact that the reduced viscosities of the various viscosity portions are identical at 35°C to those measured at 25°C (see Table 2) proves that determinations are not being conducted in a critical solubility region of the $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ -FC-75 solution.

C. MOLECULAR WEIGHT DETERMINATIONS

Molecular weight determinations on the $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ copolymer by light scattering were shown to be readily, although tediously, obtainable in the FC-75 solvent.

A molecular weight was obtained on a fraction of the XP5702 sample which had the approximate reduced viscosity of the whole polymer (1.37 in FC-75, see Table 1).

Both extrapolated Zimm and HC/τ (90°) versus concentration plots resulted in a molecular weight determination of 2.22×10^6 . The 5.5% correction factor (Ref. 3) was applied, which reduced this value to 2.1×10^6 .

The improved Zimm plot compared with that determined on the unfractionated 3M gum (Ref. 3, Figure 2) should be noted. Due to the critical nature of even the FC-75 solvent with the CF_3NO/C_2F_4 polymer, Zimm plots are probably obtainable only on narrow, normally distributed fractions.

D. INTRINSIC VISCOSITY VS. MOLECULAR WEIGHT FOR CF_3NO/C_2F_4 IN FC-75 SOLVENT

The relationship of intrinsic viscosity at $25^\circ C$ to molecular weight for CF_3NO/C_2F_4 in FC-75 solvent is shown in Figure 5, based on two determinations. The particular values are:

<u>Sample</u>	<u>$[\eta]$</u>	<u>\bar{M}_w</u>
3M-9690	0.44	4.8×10^5
XP5702 (fraction)	1.30	2.1×10^6

These data may be expressed by the Mark-Houwink Equation:

$$[\eta] = K \bar{M}_w^a$$

Utilizing the data, the values of K and a are:

$$K = 2.8 \times 10^{-5}$$

$$a = 0.738$$

These constants may be compared with the values of Morneau *et al.* (Ref. 4) for FC-43 and Freon 113.

	<u>T, °C</u>	<u>K</u>	<u>a</u>
Perfluorocyclic ether (FC-75)	25	2.8×10^{-5}	0.738
Perfluorotributylamine (FC-43)	25	8.77×10^{-5}	0.66
Trichlorotrifluoroethane (Freon 113)	35	3.80×10^{-4}	0.51

The a value of the FC-75 solvent indicates the improved solubility of the $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ copolymer in this solvent over FC-43 and Freon 113, which are nearer the value of 0.5 for a Flory θ solvent.

Based on the above K and a values for FC-75, the Mark-Houwink Equation, and the intrinsic viscosities of the fractions, the molecular weights of the two dominant regions in the XP5702 distribution are approximately 2×10^5 and 4×10^6 (see Figure 1).

Based on the K and a constants for FC-75 and FC-43, the molecular weight for the XP5702 whole polymer (see Figure 2) is:

<u>[η]</u>	<u>\bar{M}_w</u>
1.42	2.4×10^6
1.19	1.8×10^6

The reason for the 25% difference is unknown.

The K and a values stated above are preliminary, prior to at least a third determination.

E. PHYSICAL PROPERTIES OF AMINE CURED $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ COPOLYMER

As with previous determinations (Ref. 3), no outstanding physical properties were obtained with the amine cured copolymer. SiO_2 -filled compositions, however, were better than the carbon black-filled compositions.

The rubbers were compounded primarily to obtain samples for characterization. Accordingly, little effort was expended to improve properties or establish why better properties were not obtained.

F. SOLVENT AND CHEMICAL RESISTANCE OF AN AMINE CURED $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ RUBBER

The increase (and decrease) of weight and volume of the cured $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ copolymer in 14 solvents and chemicals is shown in Table 3.

The densities of the solvents and chemicals indicate that the volume swell is not due merely to porosity of the rubber and subsequent pick-up of the liquid.

Note that the rubber was swollen by all of the liquids, including the water, indicating that it was poorly crosslinked. The FC-75, FC-43, and Freon 113 swelled the rubber significantly. Extractables were not indicated by a change in viscosity of the solvent. (Further investigation, however, is warranted.)

G. LOW TEMPERATURE DIFFERENTIAL THERMAL ANALYSIS OF CF₃NO/C₂F₄
SAMPLE XP5702

An improved low temperature differential thermogram was obtained by diluting the sample with the alumina reference material. The valley (endotherm) at -45°C with the following exotherm, however, was still not accounted for.

X-ray diffraction analysis down to -80°C did not disclose any crystallinity to account for the valley, which is in addition to the change in slope expected at the glass transition temperature.

The DTA technique would probably be quite useful for studying the curing and degradation of the CF₃NO/C₂F₄ copolymer.

IV. SUMMARY

Elution fractionation of the $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ copolymer, utilizing a perfluorocyclic ether (FC-75)/benzotrifluoride solvent/nonsolvent system, was demonstrated.

The molecular weight distribution of the Thiokol $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Sample XP5702 was described by 25 elution fractions. Two dominant molecular weight regions of 2×10^5 and 4×10^6 were found. At least 25% of the sample was an insoluble gel.

The molecular weight of a fraction of the $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ copolymer with a reduced viscosity of 1.37 in FC-75 solvent was determined by light scattering analysis to be 2.1×10^6 . A usable Zimm plot was obtained.

The K and a constants for the $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ copolymer in perfluorocyclic ether (FC-75) at 25°C were determined to be:

$$K = 2.8 \times 10^{-5}$$

$$a = 0.738$$

The a value of 0.738 indicates the improved solubility of the FC-75 over FC-43 (0.66 at 25°C) and Freon 113 (0.51 at 35°C) as reported by Morneau *et al.*

Utilizing the K and a constants, the Mark-Houwink Equation, and the viscosities in FC-75 and FC-43, the molecular weight of the purified XP5702 copolymer was determined to be 2.4×10^6 and 1.8×10^6 , respectively. The reason for the 25% difference is unknown.

Resistances of an amine cured $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ rubber to 14 solvents and chemicals were determined. Volume swell was exhibited in all the liquids, including water, during a period of as little as 770 hours.

Differential thermal analysis indicated a glass transition of -45°C . Confirmed by X-ray diffraction analysis, no crystallinity was noted down to -80°C .

V. FUTURE PLANS

The $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Sample XP5702 will be refractionated and completely characterized as to molecular weight and distribution. The low molecular weight and gel portions will be characterized. Additional light scattering molecular weight and viscosity measurements will be conducted to validate the Mark-Houwink Equation for $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ in FC-75. The effect of amines on the copolymer gums will be determined by viscosity measurements at 25°C and elevated temperatures. Two $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ gums received from Peninsular Chem. Research will receive preliminary characterization. A final report will be prepared.

VI. TIME AND FINANCIAL STATUS

	<u>Hours to 3/31/66</u>	
George L. Ball III, Research Group Leader*	1,134	
Ival O. Salyer, Research Manager, Polymer Physical Chemistry and Applications	190	
John V. Pustinger, Analytical Group Leader	34	
F. Neil Hodgson, Research Analytical Chemist Professional, unspecified	22	
	<u>478</u>	
Total		1,858
Charlotte D. Fritsch, Research Technician	1,082	
John E. Strobel, Research Technician	57	
Richard L. Evers, Research Technician	24	
Donald Q. Douglas, Research Technician	33	
Margaret J. Ross, Research Technician	294	
Ralph R. Ferguson, Research Technician	33	
Gary A. Clinehens, Research Technician Technical, unspecified	163	
	<u>590</u>	
Total		<u>2,276</u>
Grand Total		4,134 hours

As of 31 March 1966, \$56,035 (including fee) has been spent. The contract is for \$63,488, leaving a balance of \$7,453.

Eighty-seven percent of the work has been completed and 88.3% of the month spent. The time and money remaining on the contract are sufficient.

*Project Leader

VII. APPENDIX

Table 1

**ELUTION FRACTIONATION OF FLUORONITROSO GUM XP5702
FOLLOWING SELECTIVE DEPOSITION - RUN NO. 2**

Fraction	Solvent Mixture ¹		Weight of fraction	Polymer eluted	Cumulative polymer eluted	η_{sp}	η_{sp}/C^1	η_{sp}	η_{sp}/C^1
	PC-75	Benzotrifluoride							
Flush	---	200	0.0722	4.95	4.95	0.009	0.00	---	---
Flush	---	100	0.0485	3.32	8.27	0.003	0.03	---	---
1	30	70	0.0597	4.09	12.36	0.009	0.09	---	---
2	35	65	0.0578	3.96	16.32	0.009	0.09	---	---
3	37	63	0.0151	1.03	17.35	0.040	0.43	---	---
4	39	61	0.3030	20.76	38.11	0.137	1.37	6.122	1.22
5	41	59	0.2013	13.79	51.90	0.171	1.71	---	---
6	43	57	0.2980	20.42	72.32	0.203	2.03	---	---
7	45	55	0.1203	8.24	80.56	0.183	1.83	---	---
8	47	53	0.1116	7.65	88.21	0.222	2.22	---	---
9	49	51	0.0508	3.48	91.69	0.211	2.11	---	---
10	51	49	0.0176	1.21	92.90	0.192	1.92	---	---
11	53	47 ^b	0.0125	.86	93.76	---	---	---	---
12	55	45	0.0027	.19	93.95	---	---	---	---
13	57	43	0.0409	2.80	96.75	0.020	0.20	---	---
14	59	41	0.0105	.72	97.47	---	---	---	---
15	60	40	0.0050	.34	97.81	---	---	---	---
16	100	0	0.0070	.48	98.29	---	---	---	---
17	100	0	0.0249	1.71	100.00	---	---	---	---
Unrecovered	---	---	0.0406	---	---	---	---	---	---
Total			1.5000	100.00					

¹ eluted at 78.5°C
² based on recovered amount of 1.4594
³ 0.1% solution in PC-75 at 25°C
⁴ insufficient to recover or measure
⁵ 0.1% solution in PC-43 at 25°C

Table 2

**ELUTION FRACTIONATION OF FLUORONITROSO GUM XP5702
FOLLOWING SELECTIVE DEPOSITION - RUN NO. 3**

Fraction	Solvent Mixture ⁷		Weight of Fraction	Polymer eluted	Cumulative polymer eluted	η_{sp}^2	η_{sp}/C^2	η_{sp}^4	η_{sp}/C^4	[η] ⁵	[η] ⁶
	FC-75	Benzo-trifluoride									
Flush	0	200	0.0811	5.84	5.84	0.001	0.01	---	---		
1	35	65	0.1426	10.27	16.11	0.001	0.01	---	---		
2	36	64	0.0107	0.77	16.88	0.011	0.11	---	---		
3	37	63	0.0036	0.26	17.14	---	---	---	---		
4	38	62	0.0051	0.37	17.51	---	---	---	---		
5	39	61	0.0036	0.26	17.77	---	---	---	---		
6	40	60	0.0025	0.18	17.95	---	---	---	---		
7	41	59	0.0038	0.27	18.22	---	---	---	---		
8	42	58	0.0123	0.89	19.11	0.016	0.16	---	---		
9	43	57	0.0138	0.99	20.10	0.025	0.25	---	---		
10	44	56	0.0209	1.50	21.60	0.033	0.33	0.037	0.37		
11	45	55	0.0242	1.74	23.34	0.049	0.49	---	---		
12	46	54	0.0401	2.89	26.23	0.060	0.60	---	---		
13	47	53	0.0787	5.67	31.90	0.087	0.87	0.088	0.88		
14	48	52	0.1821	13.11	45.01	0.129	1.29	---	---		
15	49	51	0.3212	23.12	68.13	0.180	1.80	---	---		
16A	50	50	0.2693	19.39	87.52	0.224	2.24	---	---		
17A	Column Dried		0.0891	6.41	93.93	0.237	2.37	0.233	2.33		
16B	50	50	0.0052	0.37	94.30	0.126	1.260	---	---		
17B	51	49	0.0317	2.28	96.58	0.083	0.83	---	---		
18	52	48	0.0151	1.09	97.67	0.102	1.02	---	---		
19	53	47	0.0047	0.34	98.01	---	---	---	---		
20	54	46	0.0047	0.34	98.35	---	---	---	---		
21	55	45	0.0079	0.57	98.92	0.258	2.580	---	---		
22	100	0	0.0023	0.17	99.09	---	---	---	---		
23	100	0	0.0031	0.22	99.31	---	---	---	---		
24	200 ⁸	0	0.0096	0.69	100.00	---	---	---	---		
Unrecovered			0.1110	---	---	---	---	---	---		
Total			1.5000	100.00							
Whole polymer, cleaned up						0.139	1.39	1.418	1.193	1.418	1.193
Whole polymer, as received						0.114	1.14	---	---		

¹ based on recovered amount of 1.3890

² 0.1% solution in FC-75 at 25°C

³ insufficient to recover or measure

⁴ 0.1% solution in FC-75 at 35°C

⁵ in FC-75 at 25°C

⁶ in FC-43 at 25°C

⁷ Eluted at 56.5°C

⁸ Eluted at 78.5°C

Table 3

TENSILE STRENGTH AND ELONGATION OF
AMINE CURED CF₃NO/C₂F₄ RUBBERS

<u>Sample No.</u>	<u>Tensile Strength</u> <u>psi</u>	<u>Elongation</u> <u>%</u>
37566-3	110.4	188
37566-6	78.6	155
37568-1	78.4	115
37568-2	76.2	140
37568-3	97.7	173
37568-4	118	177
37572-1	208	315
37572-2	124	225

Sample thickness and width for tensile test:
0.1" width, 0.06" thick, 1" gage.

Table 4

SOLVENT AND CHEMICAL RESISTANCE OF AN AMINE CURED NITROSO RUBBER
NO. 37566 - CURE NO. 1

Immersion Fluid	Specimen Volume (% Change from Initial)			Specimen Density (gms/cc)			Specimen Wt. (% Change from Initial)												
	24 hr.	144 hr.	295 hr.	24 hr.	144 hr.	295 hr.	Initial	24 hr.	144 hr.	295 hr.	770 hr.	1128 hr.	1128 hr.						
FC-75	1.77	+240.0	+394.0	+335.0	4000.0	+397.5	1.8397	1.4684	1.7125	1.7101	1.6990	1.6634	0.3755	+172.0	+295.0	+304.6	+361.8	+349.8	
FC-43	1.58	+246.0	+272.0	+285.4	+300.3	+302.1	1.8700	1.8890	1.9016	1.8877	1.8627	1.8783	0.3353	+249.0	+279.0	+267.4	+298.8	+304.0	
Freon 113	1.45	+53.9	+80.8	+82.0	70.4	+70.2	1.8466	1.9439	1.9561	1.9518	1.9739	1.9546	0.4022	+28.7	+52.4	+53.1	+45.2	+44.2	
Nitric Acid	1.502			+38.5	+36.7		1.8680				1.7162	1.7535	0.3710				+27.2	+27.1	
Water	1.0			+18.4	+23.3		1.8381				1.6974	1.7108	0.4406				+13.2	+14.8	
D.M.S.O.				+9.0	+10.6		1.8896				1.8191	1.8030	0.4180				+9.0	+7.1	
Chromic/Sulfuric				+6.0	+10.8		1.8528				1.8669	1.8719	0.3852				+5.0	+9.0	
Methyl Chloride	1.4237			+2.2	+5.1		1.8514				1.8827	1.8558	0.3601				+3.9	+3.6	
Benzene	.87901	3.2		-1.4	+4.8		1.8479		1.8171		1.9087	1.7950	0.3330		+1.4		+1.8	+1.5	
M.F.K.	.808			+4.5	+4.5		1.8614				1.8105	1.8045	0.3911				+1.7	+1.3	
Carbon Tetrachloride	1.584			+4.7	+3.3		1.8473				1.8585	1.8535	0.4104				+5.3	+3.6	
Acetone	.792			-2.7	+1.9		1.8364				1.9167	1.8390	0.3695				-1.6	+2.0	
Freon 112		+3.7	+3.0	-2.7	+0.60	-0.15	1.8362	1.8151	1.8172	1.8981	1.8681	1.8566	0.3656	+1.5	+0.9	-1.5	+2.3	+0.9	
Ether				-3.7	-0.50		1.8477				1.8553	1.8365	0.3640				-2.0	-1.9	
FC-75	1.77	362.0	411.4	(456 hr.)	386.4	(1412 hr.)	1.907	1.532	1.518	(1412 hr.)	1.5974			271.3	(456 hr.)	315.1		(1412 hr.)	307.4

NITROSO RUBBER #2-B (Ref. 3)

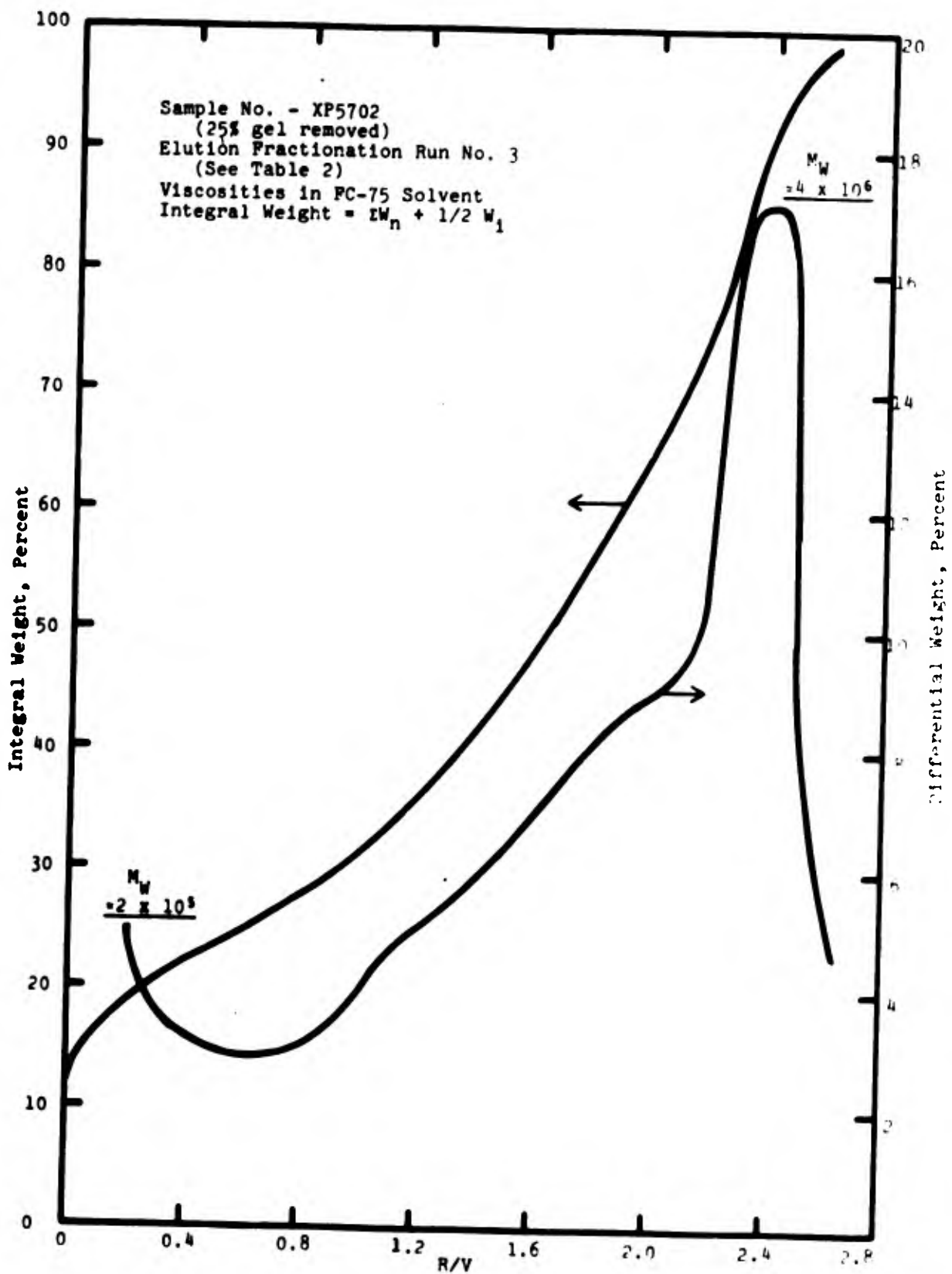


Figure 1. Total and Differential Weights as a Function of Viscosity for the XP5702 Copolymer

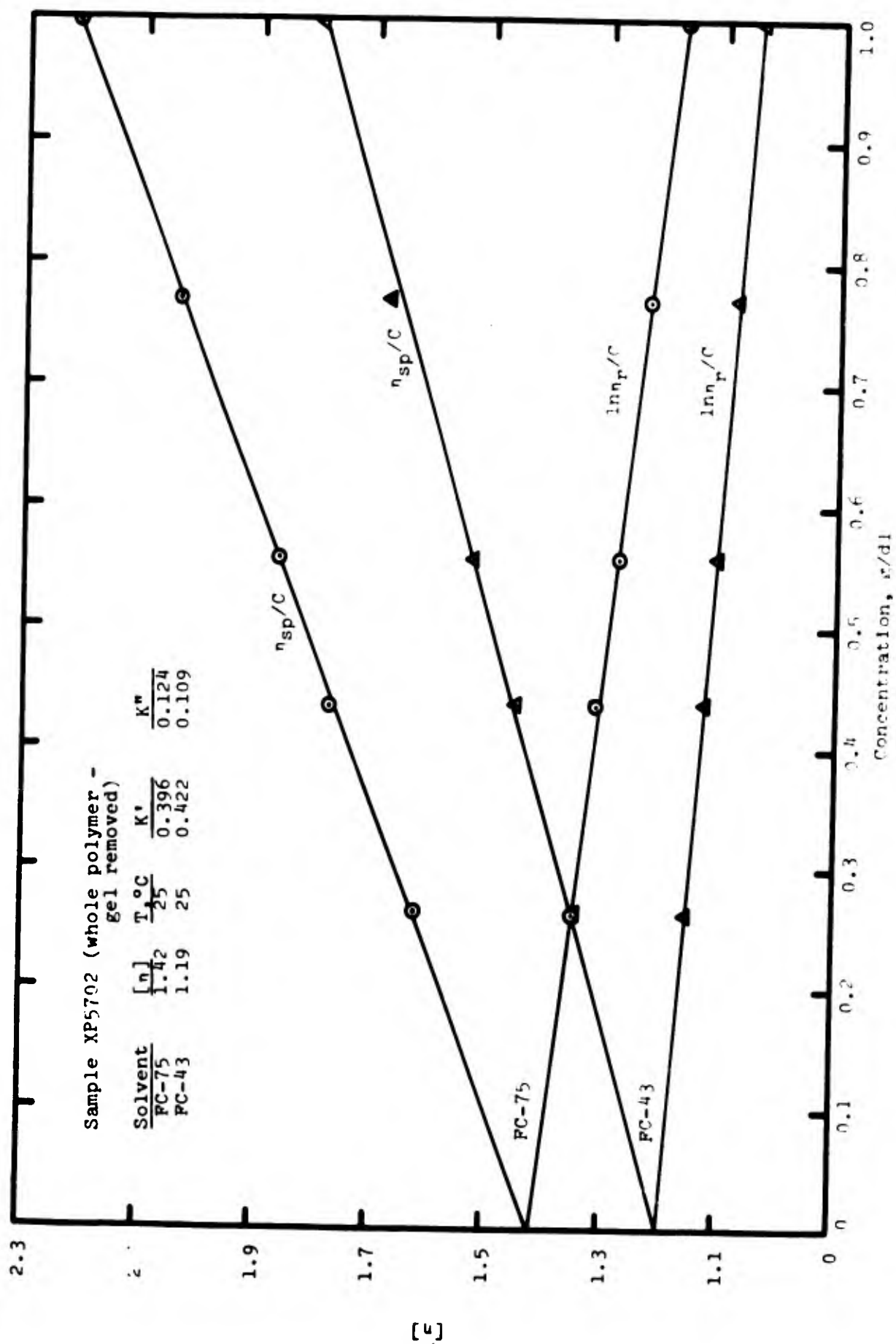


Figure 2. Reduced and Inherent Viscosities of the XP5702 Copolymer in FC-75 and FC-43

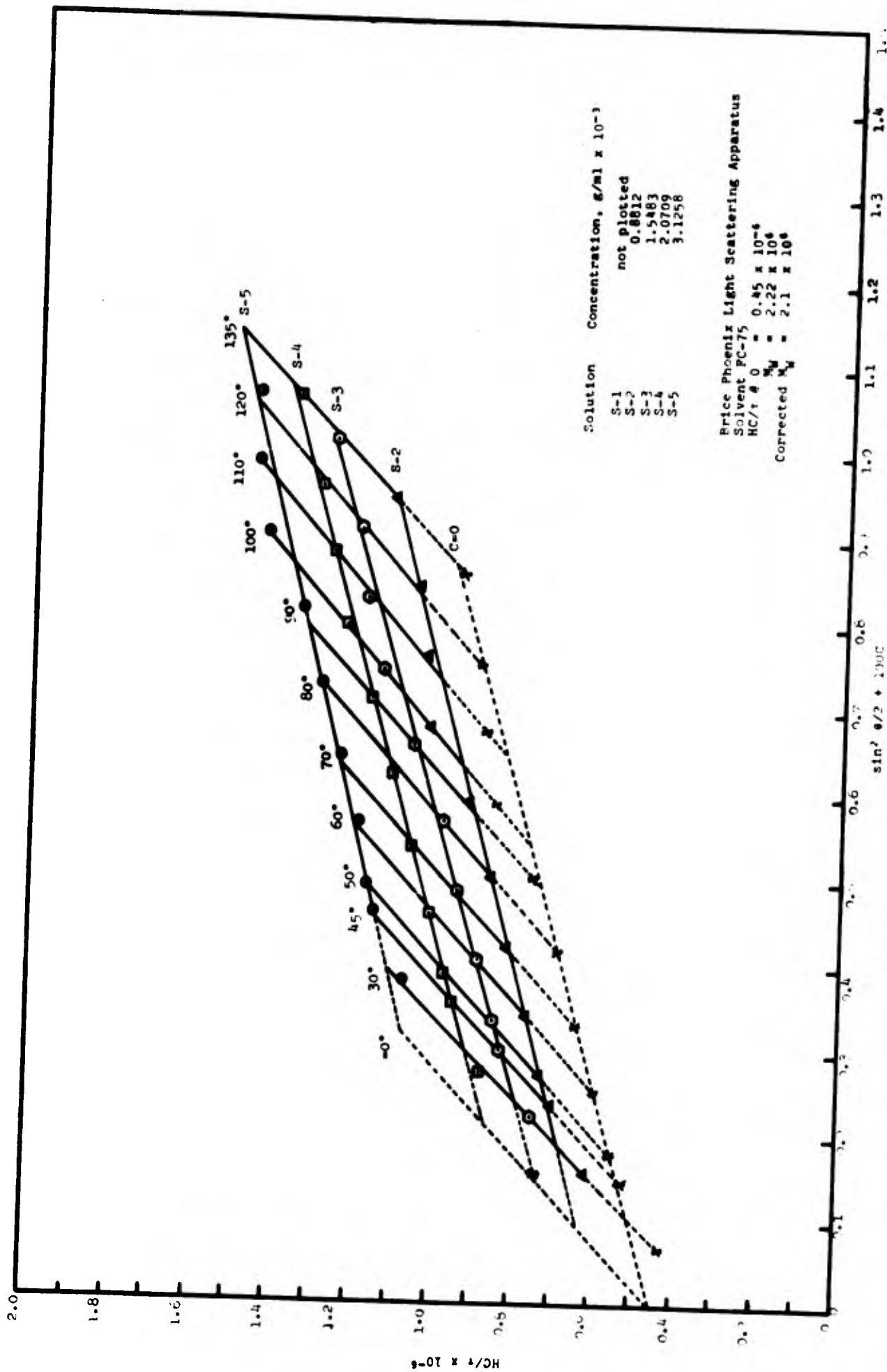


Figure 3. Zimm Plot of CF_3NO/C_2F_4 Copolymer, Fraction No. 4, Run No. 3, Thiokol Sample XP5702

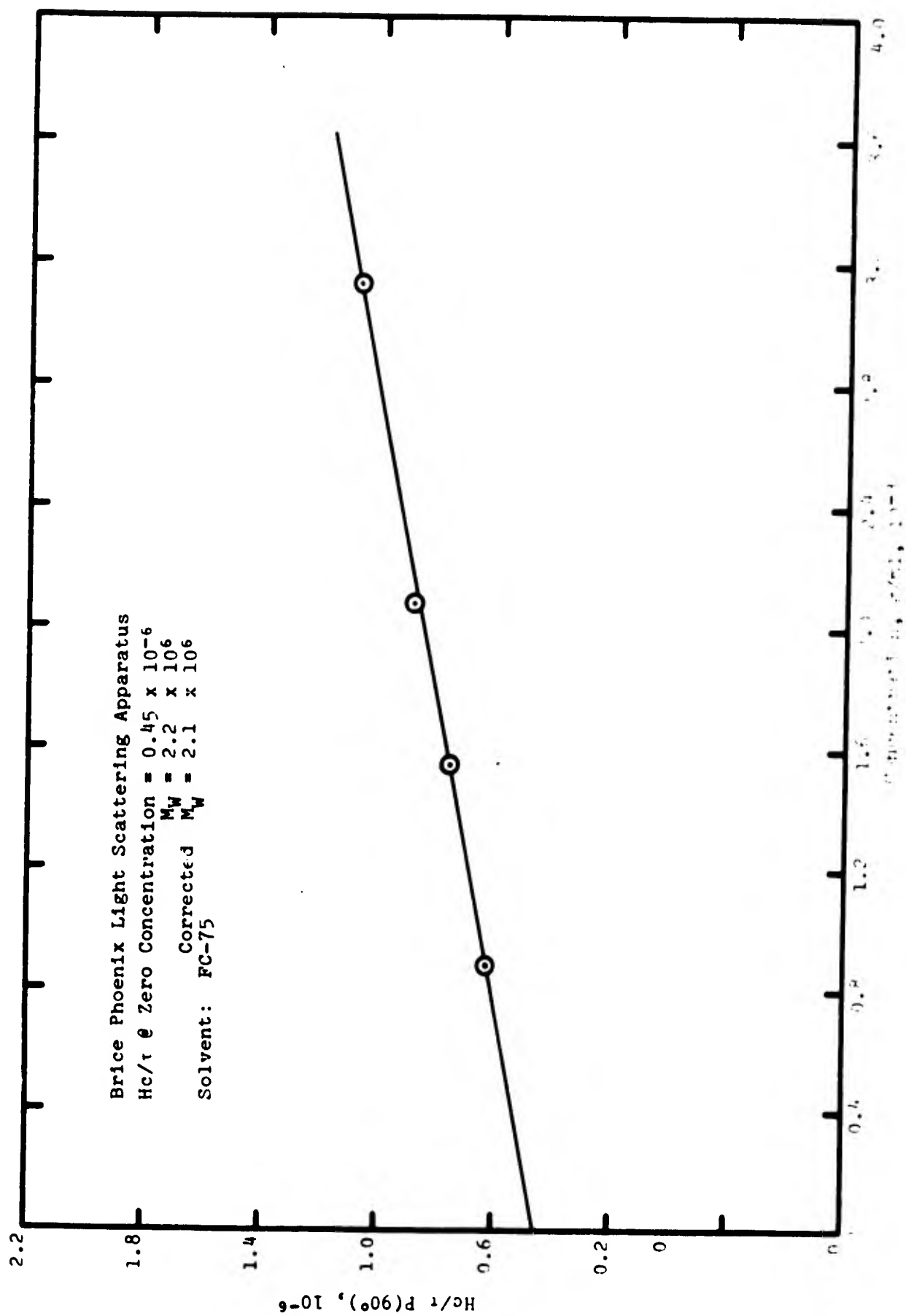


Figure 4. Hc/τ (90°) Versus Concentration for the CF_3NO/C_2F_4 Copolymer, Fraction No. 4, Run No. 3, Thickol Sample XP5702

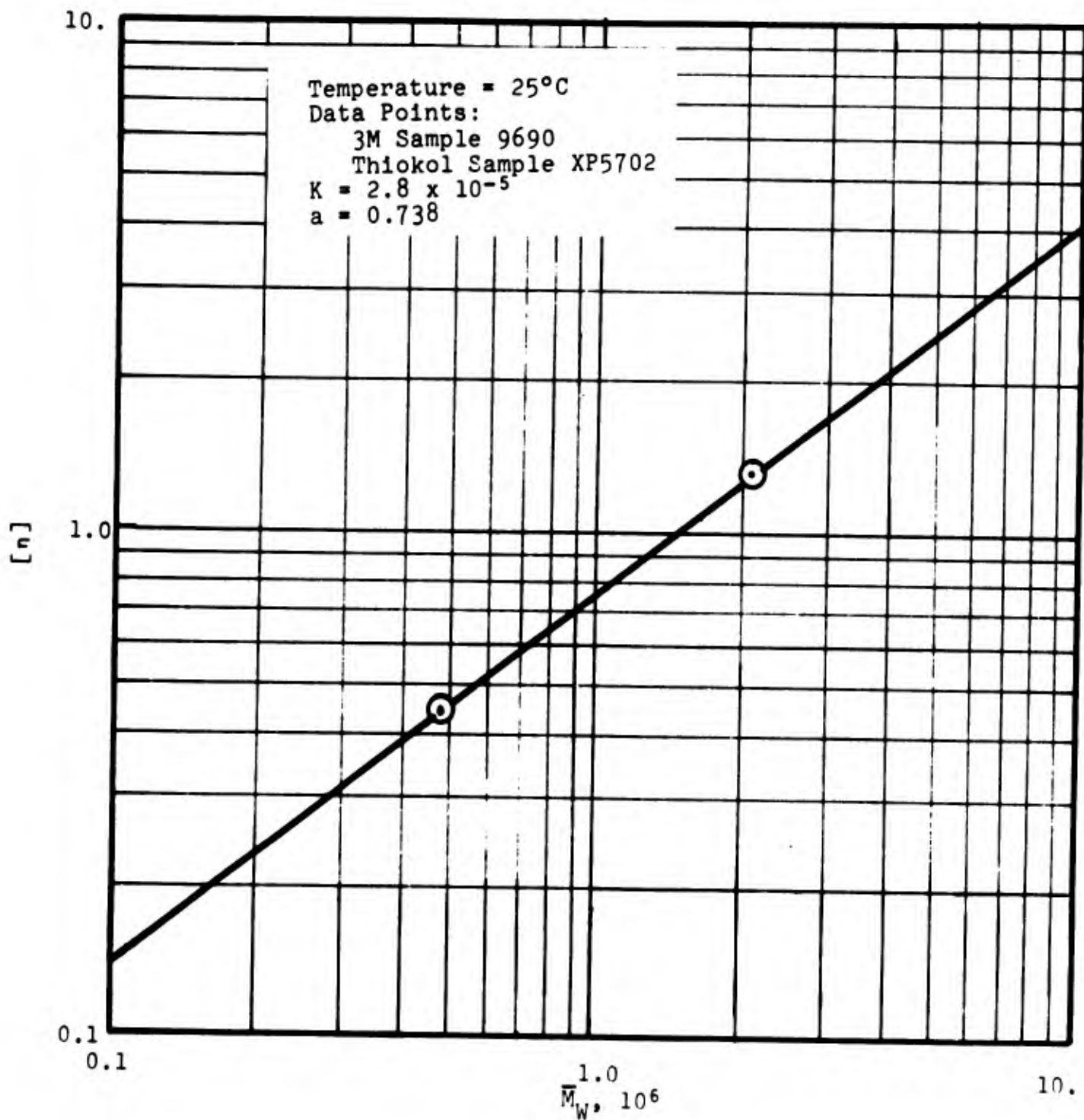


Figure 5. Viscosity-Molecular Weight Relationship of $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ in FC-75 at 25°C

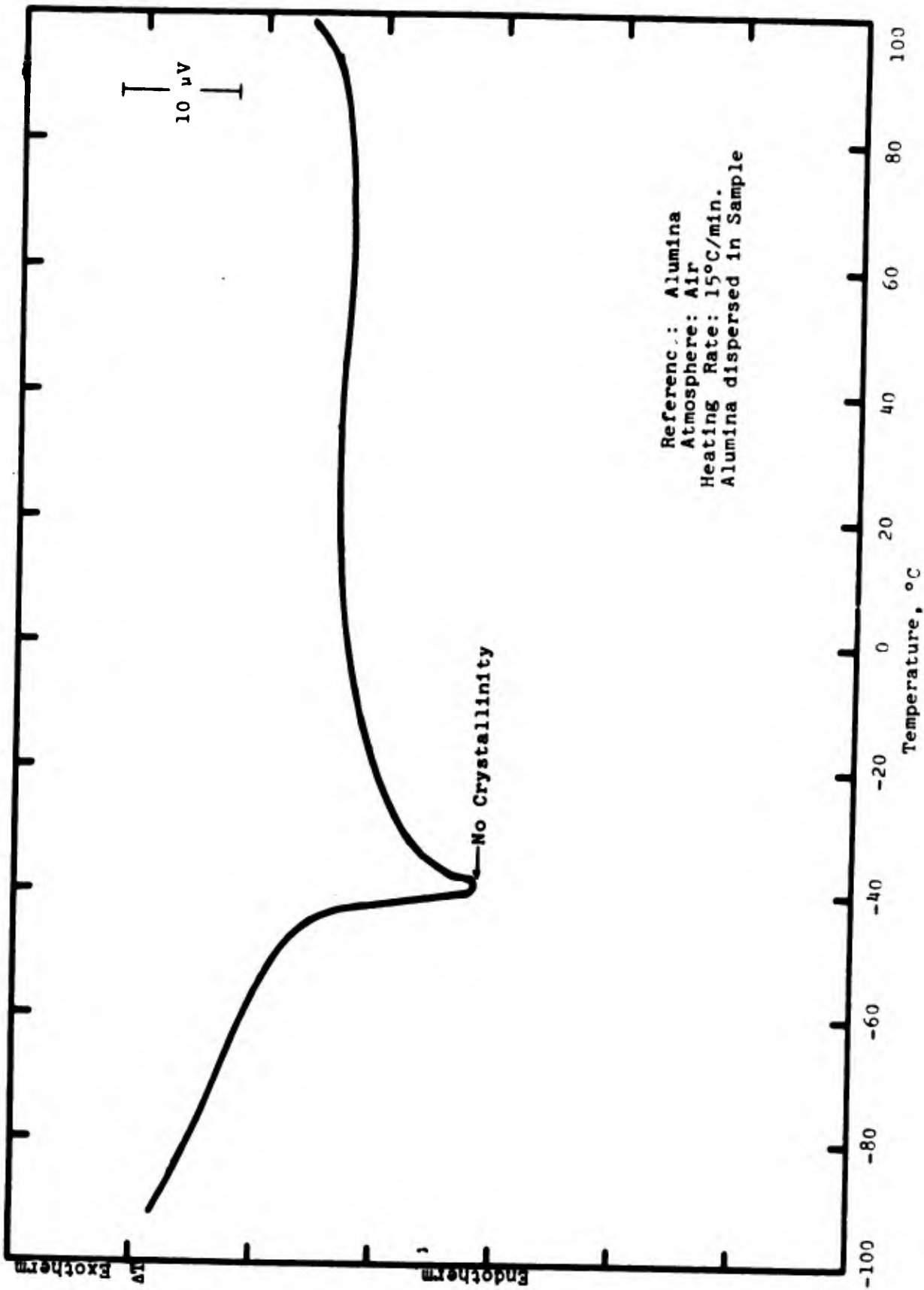


Figure 6. Low Temperature Differential Thermal Analysis of CF_3NO/C_2F_4 Sample XP5702

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Security Classification

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13. ABSTRACT Characterization of the trifluoronitrosomethane/tetrafluoroethylene copolymer produced by the Thiokol Chemical Corporation and supplied by the U.S. Army Natick Laboratories was continued. The CF_3NO/C_2F_4 copolymer was found to be adaptable to elution fractionation in a perfluorocyclic ether and a benzo-trifluoride solvent/nonsolvent system. A weight-viscosity distribution consisting of 25 fractions was obtained. A sample (Thiokol XP5702) from which 25% insoluble gel was removed exhibited two dominant molecular weight regions of 2×10^7 and 4×10^6 . The molecular weight of a fraction of the CF_3NO/C_2F_4 copolymer with a reduced viscosity of 1.37 in perfluorocyclic ether (FC-75) was determined by light scattering to be 2.1×10^6 . The Mark-Houwink Equation for CF_3NO/C_2F_4 in perfluorocyclic ether at 25°C was determined to be $(\eta) = 2.8 \times 10^{-5} M_w^{0.738}$. An amine cured CF_3NO/C_2F_4 sample was swollen by fourteen solvents and chemicals, including water. No crystallinity was observed in the CF_3NO/C_2F_4 gum down to -80°C.			

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Physical properties	8					
Rheology	8					
Nitroso rubber	9					

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