

**POLYMERS AND COPOLYMERS OF
N-1,1-DIHYDROFLUOROALKYL ACRYLAMIDES**

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FOREWORD

This investigation was conducted by the Organic Materials Branch under Project No. 7340, "Rubber, Elastic and Composite Materials", Task No. 73404, "Synthesis and Evaluation of New Polymers", formerly RDO 617-11, "Synthesis and Evaluation of New Polymers". This investigation was initiated under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Mr. F. W. Knobloch acting as project engineer.

This report covers work performed from January 1953 to June 1955.

WADC TR 55-374

A series of six new fluorinated acrylamide monomers have been studied. These included 1,1-dihydrotrifluoroethyl acrylamide, 1,1-dihydroheptafluorobutyl acrylamide and the N-methyl, N-n-butyl, and N-isobutyl derivatives of the latter.

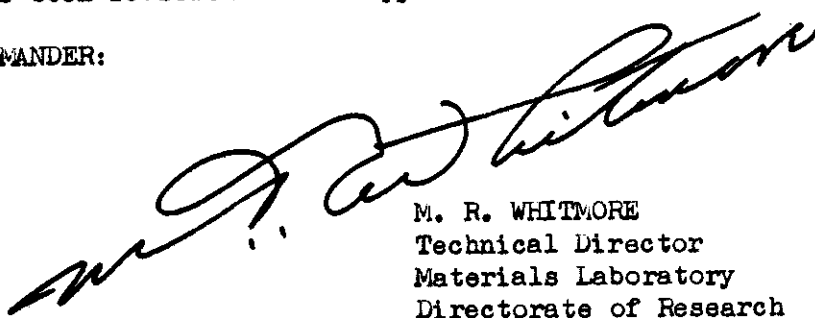
Homopolymerization of the fluoroacrylamide monomers readily proceeded both in bulk and in solution with benzoyl peroxide. Liquid monomers polymerized in emulsion with persulfate initiators. All homopolymers were thermoplastics which could be cast to yield clear transparent films. The electrical, thermal, and dilute solution behavior of some of these materials has been studied.

Copolymerization proceeded with a number of co-monomers which included alkyl acrylates, fluoroalkyl acrylates, vinyl ethers, and several dienes. Essential parameters such as monomer reactivity ratios, intrinsic viscosities and empirical slope constants k' were evaluated for selected copolymers.

PUBLICATION REVIEW

This report has been reviewed and is approved.

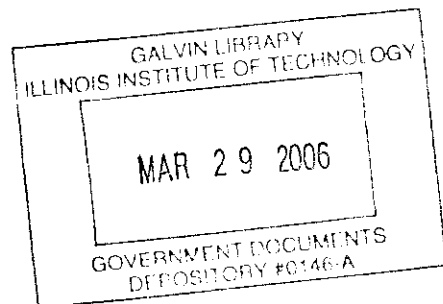
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iii



Contrails

TABLE OF CONTENTS

	Page
INTRODUCTION	v
I. HOMOPOLYMERS	1
A. Polymerization Techniques	1
B. Polymer Characteristics	4
II. COPOLYMERS	6
A. Copolymerization	6
B. Reactivity Ratios	6
1. Discussion	6
2. Experimental	8
C. Copolymerization Curve	10
D. Dilute Solution Studies	10
1. Polymer Fractionation.	10
2. Compositional Heterogeneities.	13
a. Discussion.	13
b. Experimental.	13
3. Molecular Structure Heterogeneities.	16
a. Discussion.	16
b. Experimental.	18
III. SUMMARY OF RESULTS	18
IV. BIBLIOGRAPHY	26

Contrails

INTRODUCTION

There is a need even in today's operational aircraft for materials possessing thermal stabilities above those presently known. New synthetic organic and inorganic polymers are being investigated by the Air Force in an attempt to discover new materials with inherent high thermal stabilities. Aircraft of the future will impose more stringent demands for these compounds, and development of new synthetic materials is an essential prerequisite to the production of future superior air weapons.

This report contains results of an initial investigation related to the polymerization and characterization of a new series of fluorinated acrylamide monomers of potential use for specialized high temperature applications as aircraft materials.

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HOMOPOLYMERS

A. Polymerization Techniques

The six fluorinated acrylamide monomers prepared for use in this investigation are listed in Table 2. The synthesis and physical properties of these monomers have already been reported.^{1*}

The fluorinated acrylamide monomers homopolymerized rapidly to high conversions in either bulk, solution, or emulsion systems. Induction periods of long duration were often encountered. Careful removal of oxygen from the system resulted in almost complete elimination of these induction periods.

The limited quantities of monomers available necessitated the use of small scale polymerizations. Bulk homopolymerizations were run with 0.5 gm. of monomer and 1% benzoyl peroxide as initiator. Solution polymerizations were generally run in benzene with 1 gm. of monomer and 1% benzoyl peroxide as initiator. Emulsion polymerizations and copolymerization of liquid monomers were run with 5 gm. of monomer and potassium persulfate as initiator.

The N-EFBAM Monomer was taken as a representative member of this series and its emulsion polymerization was subjected to a more quantitative study.

The simple emulsion recipe shown in Table 1 was employed.

TABLE 1

EMULSION RECIPE

	Parts
Monomer	100
Water	180
$K_2S_2O_8$	1
Sodium Lauryl sulfate	3
Temperature	50°C

This same recipe was extensively used in emulsion work with the fluorinated acrylamide monomers. A time - conversion graph for the polymerization is presented in Figure 1.

*Numbers refer to Bibliography on Page 26

TABLE 2
FLUORO - ACRYLAMIDE MONOMERS

<u>Monomer</u>	<u>Abbrev.</u>	<u>M.P.</u>
N-1,1-Dihydroperfluoro-acrylamides		
$\text{CH}_2=\text{CH}\overset{\text{O}}{\underset{\text{H}}{\text{C}}}-\text{N}-\text{CH}_2\text{CF}_3$	FEAM	74.5-75.0°C
$\text{CH}_2=\text{CH}\overset{\text{O}}{\underset{\text{H}}{\text{C}}}-\text{N}-\text{CH}_2\text{C}_3\text{F}_7$	FBAM	57.4-57.6°C
N-Alkyl-N-1,1-Dihydroperfluorobutyl Acrylamides		
<u>N-Alkyl Group</u>	<u>Abbrev.</u>	<u>B. F. - Pressure</u>
Methyl	N-MFBAM	79°C 11 mm
Ethyl	N-EBAM	95 15
N-Butyl	N-nBFBAM	112 15
ISO-Butyl	N-iBFBAM	107 15

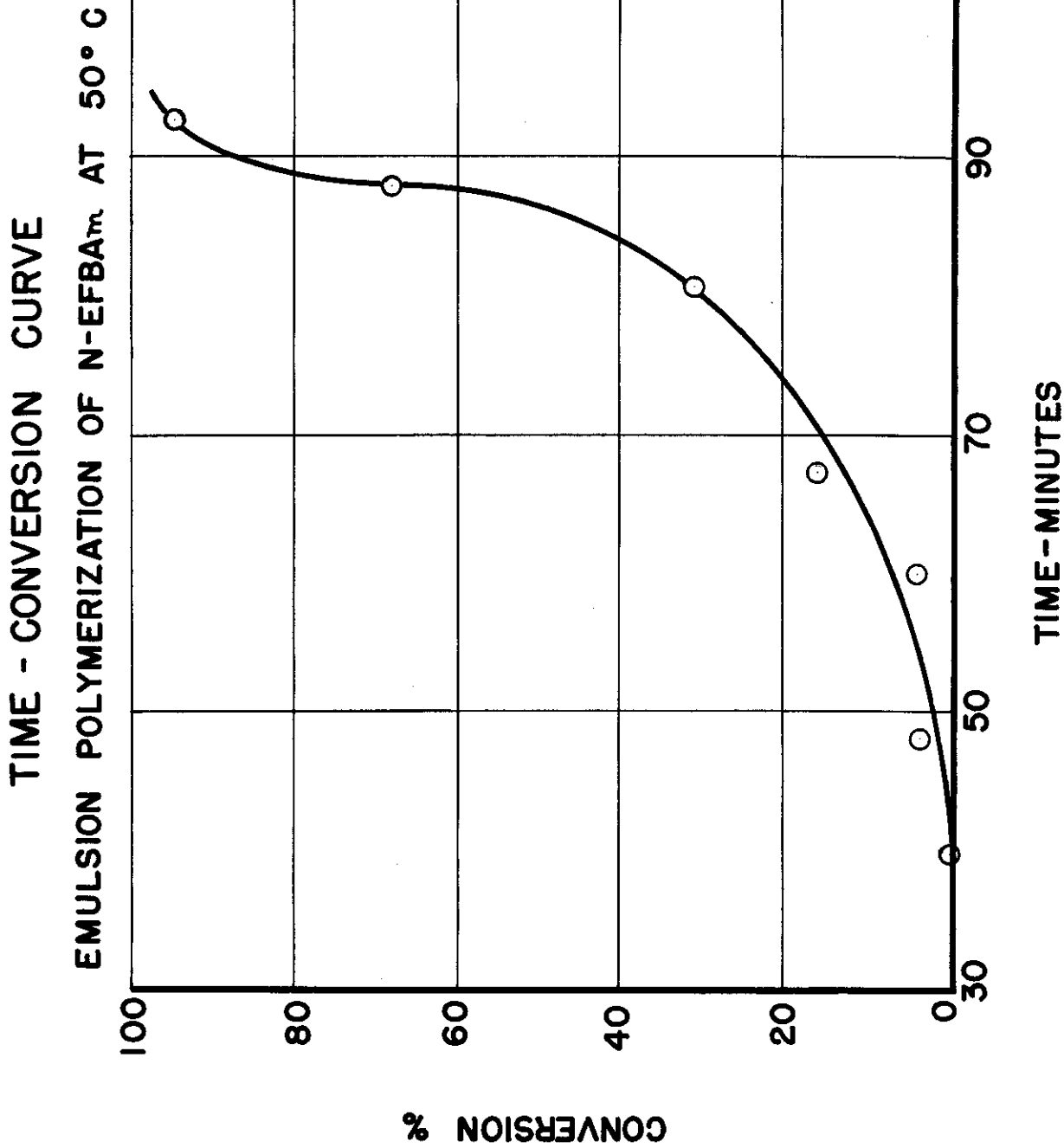


Figure 1

Time - Conversion Curve

Conclusions

An increased rate of polymerization occurred at about 30% conversion. Beyond this point, a plot of concentration vs. time indicated that the polymerization closely followed kinetics of a zero order reaction. This behavior is in keeping with findings for other emulsion polymerizations as is the initial slow rate resulting from the induction period².

It can be noted in Figure 1 that only about 10 minutes were required to complete the major portion of the polymerization (30-95%). This indicates the rapidity of polymerization which was found characteristic of the fluoro-acrylamide monomers.

B. Polymer Characteristics

All of the coagulated polymers whether prepared by emulsion or solution techniques, were exceptionally rubbery. This condition undoubtedly resulted from a plasticizing action of aqueous methanol in the case of emulsion prepared polymers and from benzene in solution prepared polymers. In this plasticized state the polymers exhibited true elastomeric behavior. They possessed a lively snap, considerable strength, and could be elongated several hundred percent.

Upon evaporation of solvent, all polymers in this series were thermoplastic solids which could be cast to yield clear transparent films or drawn from melts or solution into weak fibers.

The poly-fluoro-acrylamides are similar to polyethyl methacrylate in appearance and texture. Flexibility of the polymers did not vary greatly within the series but increased with the length of the alkyl group.

The homopolymers were highly resistant to common organic solvents. (Poly-FEAM, soluble in acetone and swelled greatly by methanol, was an exception.) Fluorinated solvents such as methyl- and ethylperfluorobutyrate were found most effective. Monomeric 1,1-dihydroperfluorobutyl acrylate also dissolved the polymers. Carbon tetrachloride exhibited considerable swelling action and worked well in conjunction with the other fluorinated solvents.

Electrical measurements were made on a sample of linear poly-N-nBFBAM both before and after exposure to gamma radiation. The results, which represent approximate values, are tabulated in Table 3. The sample remained clear and transparent during irradiation. Failure of the irradiated N-nBFBAM to dissolve in methylperfluorobutyrate (a good solvent for the linear polymer) plus the greatly increased brittleness was evidence that exposure to gamma radiation had resulted in appreciable crosslinking.

The behavior of the fluoro-acrylamide polymers on heating was the subject of some study. All observations other than oven tests were made with a small

TABLE 3

ELECTRICAL MEASUREMENTS ON N-nBFBAm

<u>Determination</u>	<u>Before Irradiation</u>	<u>After Gamma 4 x 10⁷r</u>	<u>Frequency</u>
Surface Resistivity	10 ¹⁵ ohms/sq	10 ¹⁵ ohms/sq	
Volume Resistivity	10 ¹⁵ ohms cm	10 ¹⁵ ohms cm	
Dielectric Constant	3.31	3.57	10 ⁶ cycles/sec
Dielectric Loss Tangent	0.0245	0.0228	10 ⁶ cycles/sec

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hot stage heated at a rate of 2°C per minute. The acrylamides of the primary amines began to soften about 140°C; acrylamides of the secondary amines began softening around 100°C. No sharp melting points were exhibited by any of the homopolymers. Continued heating resulted in the formation of rubbery solids which slowly melted to viscous liquids (about 200°C). The thermal stability of these materials was not extensively evaluated but appears to warrant further study. This conclusion was based on some outstanding results observed with two copolymers described below.

A copolymer prepared from 1,1-dihydroheptafluorobutyl acrylate (FBA) and FEAm (25 mole percent charge) was heated to 330°C. Only faint yellowing resulted. This represented approximately 100°C improvement over the darkening and apparent decomposition point for a control sample of poly FBA.

A copolymer of N-nBFBA and trifluoroethyl acrylate (FEA) prepared from equimolar charges lost 5.4% of its weight after oven aging for 72 hours at 350°F. Poly FEA lost over five times this amount (29.1%) in the same test.

SECTION II

COPOLYMERS

A. Copolymerization

Experience has shown that the fluorinated acrylamides copolymerize readily with a variety of monomer types. Comonomer types investigated included dienes, vinyl ethers, alkyl- and fluoroalkyl acrylates. A summary of copolymerizations is presented in Table 4.

B. Reactivity Ratios

1. Discussion

Reactivity ratios r_1 and r_2 are important parameters for characterizing the behavior of individual monomers in copolymerization reactions. Thus r_1 represents the ratio of rate constants for the free radical of monomer one (M_1) with monomer one (M_1) and with monomer two (M_2) respectively. These ratios describe in terms of reaction rates the relative tendency for a particular monomer to homopolymerize compared to its tendency toward copolymerization. The complete theoretical development of this theory is described elsewhere. (3,4)

One convenient method for deriving values for r_1 and r_2 consists of substituting the experimentally determined monomer and copolymer compositions for a single copolymerization run into Equation 1, $F_1 = (r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2) /$

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TABLE 4

COPOLYMERIZATION RUNS

Fluoroacrylamide Monomer	Comonomer and Mole % charged	Polymerization Conditions and Yield	Remarks
FEAm	Homopolymer	Benzene, Bz ₂ O ₂ , * 50°C, 96%	Hard brittle; opaque; thermo-plastic; insol MFB; sol. acetone
	Acrylonitrile 50	Emulsion, K ₂ S ₂ O ₈ , 50°C, 41%	Hard brittle, appeared nonhomogeneous
	Butadiene 50	Emulsion, K ₂ S ₂ O ₈ , 50°C, 100%	White Powder
	Chloroprene 75	Emulsion, K ₂ S ₂ O ₈ , 25°C, 68%	Strong Elastomer
	Ethyl Acrylate 50	Emulsion, K ₂ S ₂ O ₈ , 50°C, 100%	Hard, brittle
	n-Butyl Acrylate 50	Emulsion, K ₂ S ₂ O ₈ , 50°C, 52%	Hard, brittle
	n-Octyl Acrylate 50	Emulsion, K ₂ S ₂ O ₈ , 50°C, 72%	Only slight flexibility
	n-Butyl Vinyl Ether 50	Emulsion, K ₂ S ₂ O ₈ , 50°C, 48%	Brittle, resinous
	FBA 75	" " " 96%	Stiff waxy
	FBA 90	" " " 98%	Strong elastomer
FBAm	Homopolymer	Benzene, Bz ₂ O ₂ , 50°C, 94%	Hard brittle, opaque, thermo-plastic, sol. MFB
	Acrylonitrile 50	Emulsion, K ₂ S ₂ O ₈ , 50°C, 97%	Hard, brittle; powder on grinding
	Chloroprene 75	Emulsion, K ₂ S ₂ O ₈ , 25°C, 57%	Tough elastomer
	n-Butyl Vinyl Ether 50	Emulsion, K ₂ S ₂ O ₈ , 50°C, 75%	Brittle orange-yellow solid
	" " " 75	" " " 42%	Brittle solid
	" " " 10	" " " 30%	Brittle resin; brown
FBA 75	Emulsion, K ₂ S ₂ O ₈ , 50°C, 94%	Tough waxy elastomer	
N-MFBAm	Homopolymer	Benzene, Bz ₂ O ₂ , 50°C -	Brittle, clear polymer
	Homopolymer	Benzene, Bz ₂ O ₂ , 50°C -	Brittle clear transparent
	Homopolymer	Emulsion, K ₂ S ₂ O ₈ , 50°C, 97%	" " "
	MMA * 25-75	Benzene, Bz ₂ O ₂ , 60°C -	Reactivity ratio copolymerizations
N-iBFBAm	Homopolymer	Benzene, Bz ₂ O ₂ , 50°C, 51%	White opaque solid
N-FBFBAm	Homopolymer	Bulk Bz ₂ O ₂ , 100°C -	Yellow transparent plastic
	"	Benzene, Bz ₂ O ₂ , 50°C, 90%	Clear plastic
	"	Emulsion, K ₂ S ₂ O ₈ , 50°C -	White opaque plastic
	FEA * 50 wt	Emulsion, K ₂ S ₂ O ₈ , 50°C, 60%	Tough horny polymer
	VFBE * 50	Emulsion, K ₂ S ₂ O ₈ , 50°C, 84%	Horny, somewhat brittle material
	FBA * 75	Emulsion, K ₂ S ₂ O ₈ , 50°C, 64%	Waxy, tougher than poly FBA
	TAC * 50 wt	Emulsion, K ₂ S ₂ O ₈ , 50°C -	Rubbery at 310°C

*
MFB Methylperfluorobutyrate
Bz₂O₂ Benzoyl Peroxide
FBA 1,1-Dihydroperfluorobutyl acrylate
MMA Methyl methacrylate
FEA Trifluoroethyl acrylate
VFBE 1,1-Dihydroperfluorobutyl vinyl ether
TAC Triallyl cyanurate

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$(r_1 f_1^2 + f_1 f_2^2)$ where F_1 represents the fraction of monomer M_1 in the increment of copolymer at a given stage in the polymerization; f_1 and f_2 represent the mole fractions of monomers M_1 and M_2 in the feed. This is determined for several copolymerizations and r_1 is plotted as a function of r_2 for each case. The average point of intersection represents the best experimental values of r_1 and r_2 .

2. Experimental

Reactivity ratios for the copolymer system methyl methacrylate-N-EFBAM were obtained by the intersection method described above. Copolymerizations were allowed to proceed to between 5 and 10% conversion and the copolymers were isolated and purified. Copolymer composition was determined from nitrogen content (Crippen & Erlich Laboratories, Inc.).

A plot of r_1 as a function of r_2 using Equation 1 is shown in Figure 2.

The small quantities of fluoro-acrylamide monomers allocated for these studies made it necessary to limit the total monomer charge to 5.0 gm per run. A 10% conversion or 0.5 gm of polymer was considered the maximum allowable for the determination. Previous reactivity ratio determinations on this small a scale have not come to our attention.

Copolymerizations were essentially run in bulk although a small amount of benzene was used to wash residual catalyst into polymerization vials. The following recipe was employed:

Monomers	5.0 gm
Benzoyl Peroxide	0.05 gm
Benzene	0.4-0.8 ml
Temperature	66 ± 1°C

The relatively small scale of the polymerizations plus the rapid polymerization rates of the fluoro-acrylamide monomers necessitated that the solutions be carefully watched and quickly coagulated after polymerization commenced. A simple procedure accomplished this. Glass tubing (9 mm) was cut to short lengths and a fragile glass bulb of about 10 cm³ capacity was blown at one end. The ingredients were introduced, frozen in Dry Ice, and sealed in an atmosphere of nitrogen. Vials were agitated just below the surface of a constant temperature bath with the aid of a shaking machine. The small vials were held by merely "plugging" them into a piece of rubber vacuum hose. This facilitated rapid removal for observation and four polymerizations could easily be run concurrently by this procedure. Only a

MONOMER REACTIVITY RATIOS

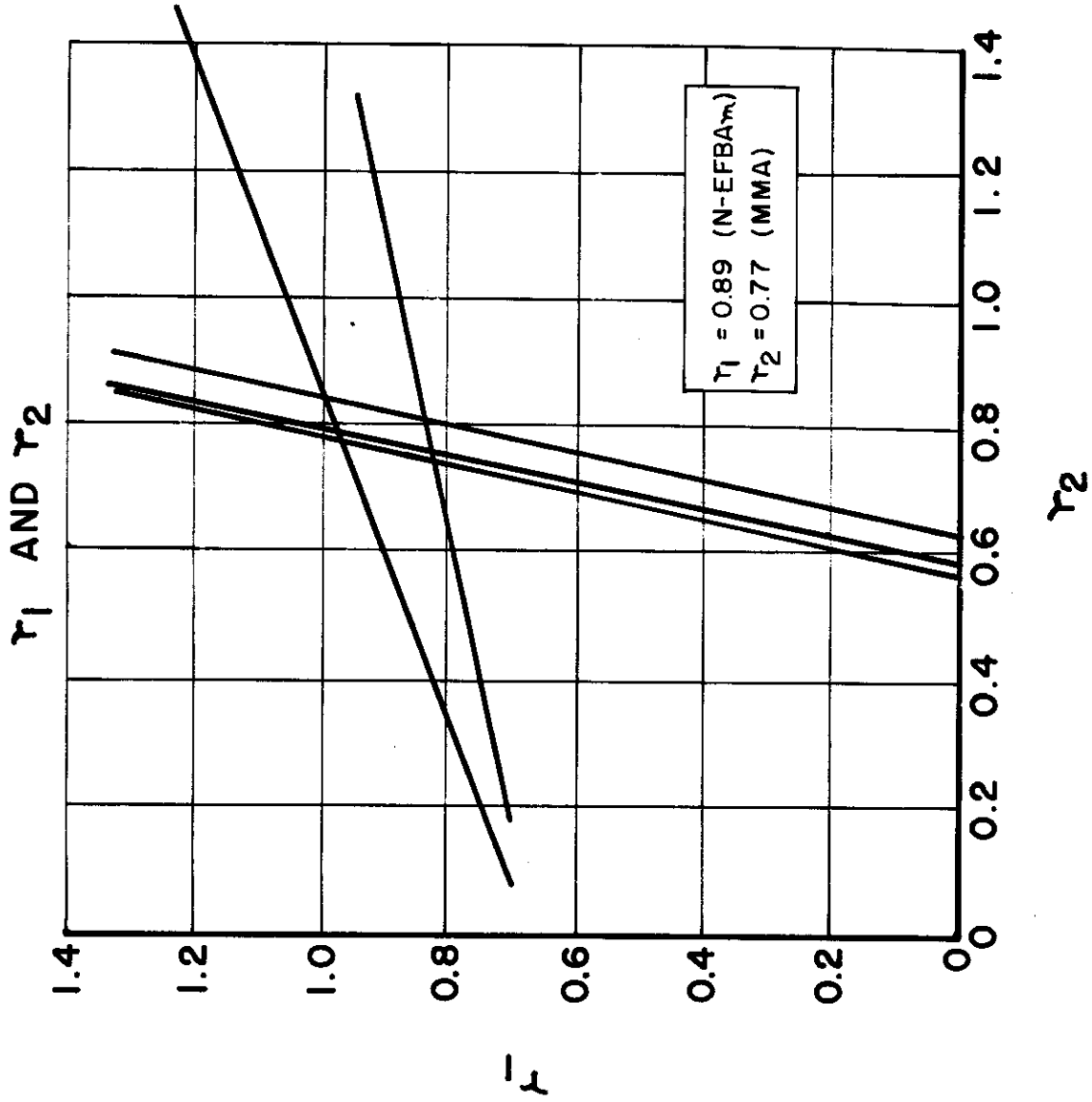


Figure 2

Monomer Reactivity Ratios

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few preliminary runs were required to enable one to determine when polymerization had commenced. After evidence of polymerization was noted, vials were quickly removed and coagulated by crushing the fragile bulb in a beaker of methanol. Polymers thus obtained were subjected to three reprecipitations and two filtrations through glass sintered filters. Results are presented in Table 5.

A value of 0.89 for the reactivity ratio of the N-EFBAM indicates the activated fluorinated acrylamide monomer shows a slightly greater tendency to copolymerize with a methylmethacrylate molecule than to homopolymerize.

C. Copolymerization Curve

Data obtained in reactivity ratio determinations made it possible to construct the copolymerization curve for the N-EFBAM-methylmethacrylate system. Since both reactivity ratios were less than unity a critical concentration or crossover point was known to exist.⁵

The critical concentration point, $(f_1)_c$, at which monomer feed and copolymer have identical composition, was not apparent from experimental data. However setting $F_1 = f_1$ in Equation 1. gives an expression for the critical concentration; $1(f_1)_c = (1-r_2) / (2-r_1-r_2)$ Equation 2. and $(f_1)_c$ was calculated to be 0.687. The copolymerization curve shown in Figure 3 was constructed from the experimental data and the calculated crossover point. From the copolymerization curve it is possible to estimate the ratio monomers are combining to form polymer for any given concentration of monomers. Tailored polymers, with respect to composition, can thus be prepared for any system from a knowledge of the copolymerization curve provided only that monomer concentrations can be maintained constant during the polymerization. It can be seen that in the N-EFBAM-methylmethacrylate system, the combining ratio for the monomers closely approximates monomer concentrations. This is more often not the case and wide variations between monomer concentration and polymer composition frequently exist.

D. Dilute Solution Studies

1. Polymer Fractionation

In cases where little is known about the macromolecular nature of a copolymer, fractional precipitation in conjunction with other determinations often provides valuable indications of the true nature of the copolymers. The theory of polymer fractionation is based on molecular weight differences which exist in the polymer mass; chains with similar molecular weights exhibit similar solubilities. Two complicating factors, however, also affect the fractionation. These are polymer composition⁶

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TABLE 5

DATA FOR DETERMINATION OF REACTIVITY RATIOS

Run No.	Monomer Charge in Mole Fractions		Reaction Time at 60°C in Hours : minutes	Percent Conversion of Copolymer	Nitrogen Content of Copolymer	Copolymer Composition in Mole Fractions	
	N-EFBAM (f_1)	MMA (f_2)				N-EFBAM (F_1)	MMA
1	.1800	.8200	3 : 20	9.6	2.17% 2.14%	.2142	.7858
2	.2037	.7963	3 : 50	5.2	2.21 2.26	.2254	.7747
3	.8160	.1840	1 : 0	7.0	4.55 4.59	.7981	.2020
4	.7324	.2678	1 : 10	7.0	4.41 4.45	.7408	.2592
5	.1921	.8076	1 : 35	8.6	2.23 2.29	.2282	.7719

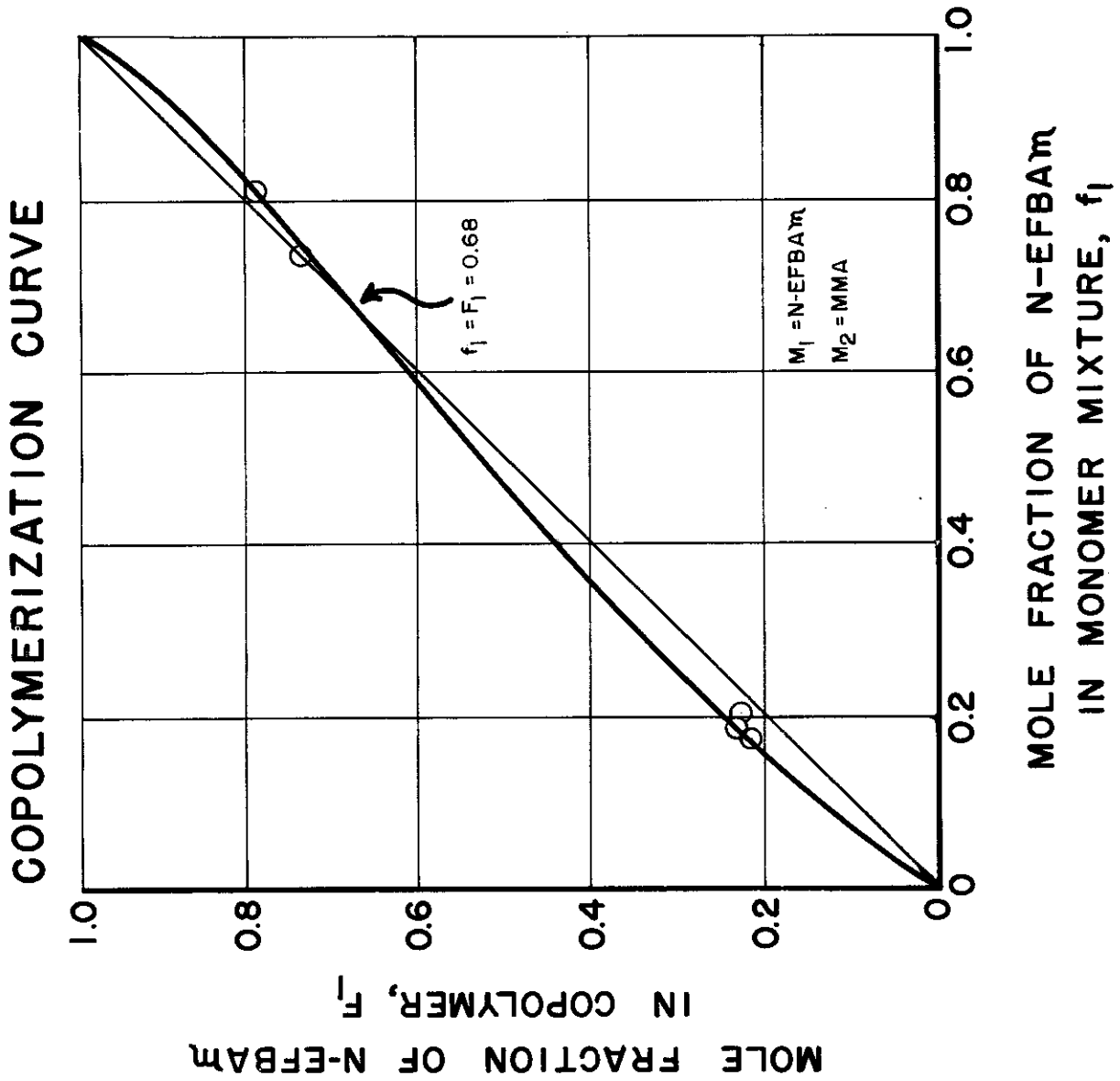


Figure 3
Copolymerization Curve

and molecular structure.⁷

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Two copolymers previously listed in Table 4 were selected for studies related to compositional and molecular structure heterogeneities. These were the n-butyl vinyl ether-FEAm copolymer and the n-butyl acrylate-FEAm copolymer.

2. Compositional Heterogeneities

a. Discussion

The composition of polymer chains varies continuously during the course of almost all copolymerizations as has already been indicated. This inevitably results in heterogeneous comonomer content in the macromolecules. Such compositional heterogeneities are serious obstacles in the evaluation of molecular characteristics for copolymers. The generally accepted methods of evaluating chain length (solubility fractionation and dilute solution viscosity) can be radically affected by these simultaneous changes in composition.

The compositional differences of both copolymers studied were determined by elemental analysis. These are indicated in the inserts of Figures 4 and 5.

The data for the n-butyl vinyl ether-FEAm copolymer indicate fractionation resulted primarily from molecular weight variations. This is substantiated by the fairly constant composition of the polymer fractions and the steady decrease in values for intrinsic viscosities (η) is proportional to molecular weight. See discussion on Page 17.

In contrast, the affect compositional changes played in the fractionation of the n-butyl acrylate-FEAm copolymer can readily be interpreted from the analytical and viscosity data. With only slight deviation, the nitrogen content of fractions increased steadily from a value of 2.70% to 7.79%. Intrinsic viscosity values, after first declining normally, again increased markedly.

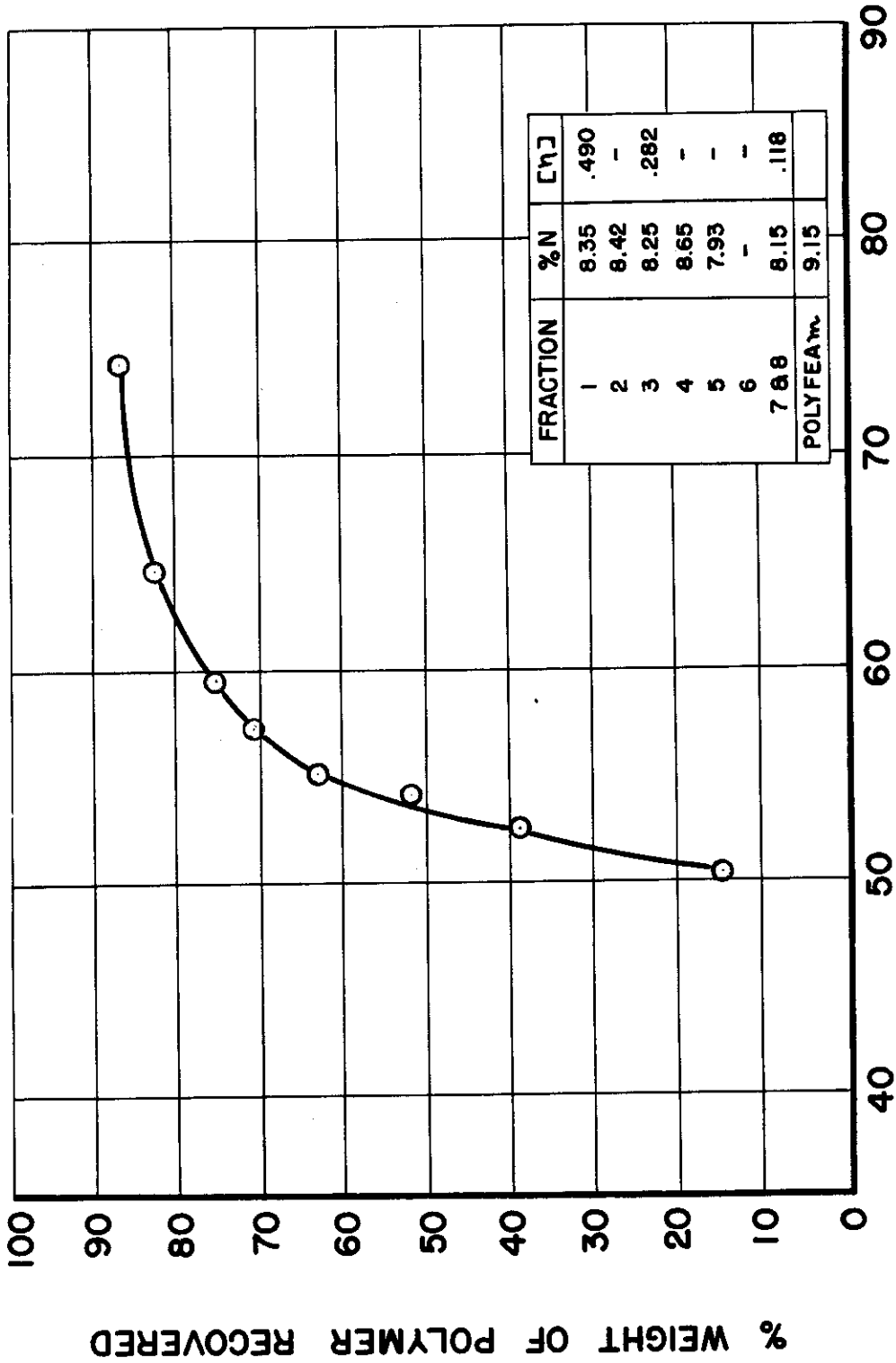
b. Experimental

Fractional precipitation by addition of a nonsolvent to a polymer solution was employed. Conventionally accepted methods⁸ described below were used with the exception that the relatively small volumes of solution made it convenient to employ a large centrifuge to aid in the separations. This resulted in a loss of temperature control for a short period but considerably reduced the difficulty of separating the voluminous precipitate from solution in instances when it was slow to settle.

The two copolymers were both soluble in acetone. Fractionations were made from dilute acetone solutions (concentration of less than 1% polymer)

COPOLYMER FRACTIONATION

FEA_m/*n*-BUTYL VINYL ETHER; MONOMER CHARGE 1:1 (MOLAR)



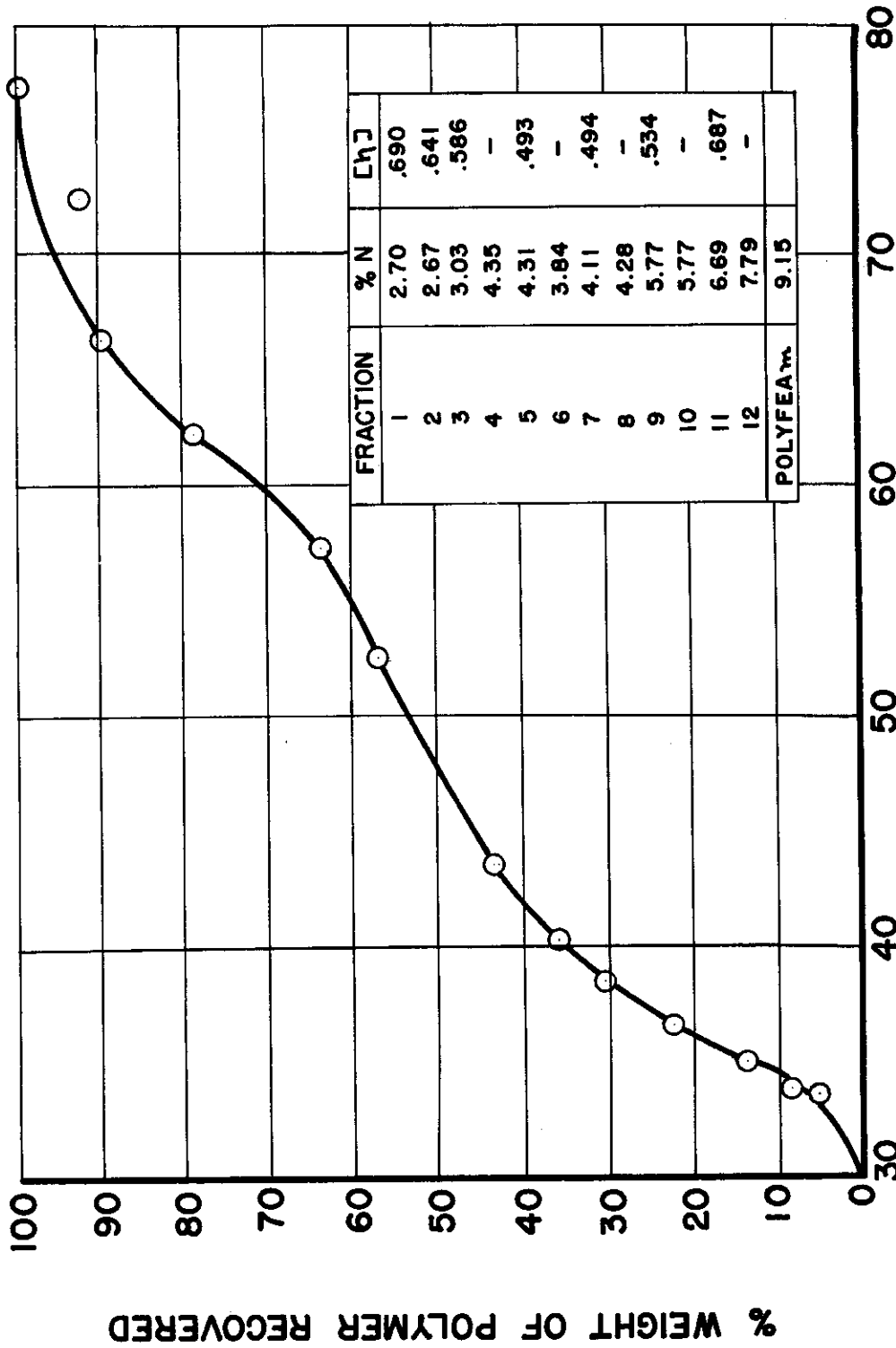
MILLILITERS OF PRECIPITANT

Figure 4

Copolymer Fractionation

COPOLYMER FRACTIONATION

FEA_m / 1/2 - BUTYL ACRYLATE; MONOMER CHARGE 1:1 (MOLAR)



MILLILITERS OF PRECIPITANT

Figure 5

Copolymer Fractionation

using water as a precipitant. The fractionations were performed with small samples; the n-butyl acrylate-FEAM copolymer weighed 2.52 gm; the n-butyl vinyl ether-FEAM copolymer weighed 1.79 gm. In the former case, 12 fractions were obtained of between 0.1 and 0.2 gm; in the latter, 8 fractions of approximately equal size were obtained. Plots of recovered polymer vs. precipitant added are presented in Figures 4 and 5.

Fractions were precipitated by titration with distilled water. Precipitated fractions were warmed and gently agitated until a clear solution was obtained. The solutions were placed in a constant temperature bath (25°C) for at least 12 hours. The solutions were centrifuged for a few minutes and the supernatant liquid removed. Fractions were dried and weighed. Two successive solutions, filtrations and precipitations were employed to sharpen fractions. Fractions were again dried (150°F for 17 hours) and subsequently used for viscosity studies and elemental analyses.

3. Molecular Structure Heterogeneities

a. Discussion

Insight into the nature of molecular structure heterogeneities required more detailed dilute solution studies. Extensive pursuit of such studies can provide valuable indications of intermolecular interactions, molecular weight ranges, and the nature of polymer-polymer and polymer-solvent interaction.

There is considerable evidence⁹ which supports the idea that the structural heterogeneity resulting from chain branching can be detected by a determination of the Huggins' slope constant, k' , found in the equations proposed by Huggins¹⁰

$$\eta_{sp}/c = [\eta] + k' [\eta]^2 c \quad \text{Equation 3}$$

where η_{sp}/c is the reduced viscosity, η the intrinsic viscosity, and c the concentration in gm/100 ml. Branched polymers have been found to yield higher values for k' than unbranched polymers⁹. Several workers have noted such anomalous viscosity behavior and attributed them to the branched species.^{11, 12, 13}

The empirical slope constant k' corresponds to the constant β in the equation of Mead and Fuoss¹⁴.

$$\frac{\ln \eta_r}{c} = [\eta] - \beta [\eta]^2 c \quad \text{Equation 4}$$

where η_r is the relative viscosity.

Curves of η_{sp}/c vs. c and $(\ln \eta_r)/c$ vs. c are linear at very low concentrations and k' and β are evaluated from the limiting slopes ($c \rightarrow 0$) of these equations. The empirical slope constants are related by

$$k' = A - \beta \quad \text{Equation 5}$$

where $A = 1/2.15$

It can be seen from equations 3 and 4 that in the limit as $c \rightarrow 0$, $\eta_{sp}/c = \eta$ and $(\ln \eta_r)/c = \eta$ respectively, hence the intrinsic viscosity, η , can be readily evaluated by extrapolation of either of these curves to infinite dilution using data obtained at finite concentrations. Often both extrapolations are made to pinpoint η with greater accuracy. Because of the nature of the curves it is more convenient, when determining the empirical slope constants, to determine β and compute k' from it using equation 5.

The intrinsic viscosity finds wide use in the characterization of macromolecules. Probably the most significant relationship is in the equation

$$\eta = KM^a$$

where K and a are empirical constants and M is the number average molecular weight. It has been indicated that

$$\eta = \lim_{c \rightarrow 0} (\eta_{sp}/c)$$

where η_{sp} is the specific viscosity. The specific viscosity is defined in terms of the relative viscosity, η_r ,

$$\eta_{sp} = \eta_r - 1$$

Finally the relative viscosity is defined by the solution viscosity, η^s , and the solvent viscosity, η^0 , by the relationship

$$\eta^s/\eta^0 = \eta_r$$

The viscosities η^0 and η^s are experimentally determined from carefully prepared polymer solutions of known concentration.

In many investigations the assumptions are made that density differences (between polymer solution and pure solvent) and kinetic energy corrections are negligible. This allows flow times to be substituted directly in above equations in place of viscosities and $\eta_r = t_r$, $\eta_{sp}/c = t_{sp}/c$, and $[\eta] = [t]$.

b. Experimental

Data obtained in the present investigation are presented in Tables 6 and 7.

Intrinsic viscosities for fractionated FEAM copolymers were determined from plots using both the equation of Huggins and of Mead and Fuoss. These are presented in Figures 6, 7, 8, and 9. The empirical slope constant was calculated and k' determined by use of equation 5.

Normal values for k' range from 0.35 to 0.40¹⁶ Mason and Cragg⁹ have found an appreciable increase in values for k' for polystyrene with an average of one crosslink per 10,000 mers in the polymer chain. On the basis of this information it would appear that the FEAM copolymers were essentially linear in nature.

Viscometer. A modified Ubbelohde viscometer especially constructed for this work incorporated an increased bulb capacity to allow dilutions to be made directly in the viscometer¹⁷. Viscosity determinations were made in a constant temperature bath ($25 \pm .02^\circ\text{C}$) which employed a clamp to assure a standard position for mounting. The flow time for water was 109 seconds.

Solutions. A single "batch" of dimethyl formamide (DMF) was used for all viscosity determinations. The solvent distilled 151.5-152.2°C at 745 mm. ($n_D^{20} = 1.4300$) and was filtered through sintered glass before use. All apparatus used to contain solvents and solutions were treated with hot conc. HNO_3 to remove dust. Polymer solutions were prepared using the completely soluble polymer fractions obtained from the fractionation. Viscosity solutions were prepared in the viscometer by adding a weighed amount of polymer followed by a unit quantity of DMF delivered from a calibrated pipet. The viscometer was capped and gently agitated by fastening to a shaking machine. All samples were shaken overnight to assure complete solution. Successive dilutions were made in the viscometer. The system was allowed to come to equilibrium for at least 10 minutes before any readings were taken. Flow times were measured in triplicate (On a few occasions dust apparently entered the system during dilutions and was recognized by erratic readings. In these cases numerous readings were taken and the shortest flow times used for calculations).

SECTION III

SUMMARY OF RESULTS

Present studies involving the fluorinated acrylamides serve to characterize these new plastics and provide information and technical data to other investigators following parallel courses of research. Significant findings

TABLE 6

Viscosity Data for Fractionated FEAM/n-Butyl Vinyl Ether Copolymer

Fraction	Concentration gm/100 ml	$\frac{\ln \eta}{c}$	Slope	η	β	k'
1	1.0957	.457				
	0.5479	.476	.0301	.490	.125	.37
	.3652	.479				
	.2739	.481				
3	0.8537	.283				
	.4269	.283				
	.2846	.290		.282		
	.2134	.294				
7-8	.1707	.304				
	1.0318	.117		.118		
	0.5159	.119				
	.3439	.116				
	.2580	.117				

TABLE 7

VISCOSITY DATA FOR FRACTIONATED FEAM/n-BUTYL ACRYLATE COPOLYMER

Fraction	Concentration gm/100 ml	$\frac{\ln \eta_r}{c}$	-Slope	η	β	k'
1	0.2901	0.678				
	.1450	.684	.0466	.690	.09 ₈	.44
	.0967	.702				
	.0725	.673				
2	0.3075	.613				
	.1538	.625	.0881	.641	.21 ₄	.32
	.1025	.633				
	.0769	.707				
3	0.9091	.534				
	.4546	.561	.0561	.586	.16 ₇	.33
	.3030	.566				
	.2273	.562				
	.1818	.579				
5	1.2798	.457				
	0.6399	.476				
	.4266	.483	.0281	.493	.11 ₅	.38
	.3200	.484				
	.2560	.483				
	.2133	.484				
7	0.8711	.462				
	.4356	.487				
	.2904	.483	.0333	.494	.13 ₆	.36
	.2178	.484				
	.1742	.486				
	.1452	.483				
9	1.0229	.492				
	0.5115	.514				
	.3410	.517	0.04105	.534	0.14 ₄	0.36
	.2557	.522				
	.2046	.529				
	.1705	.522				
11	1.1692	604				
	0.5846	645				
	.3897	658	0.0684	.687	0.14 ₄	0.36
	.2923	672				
	.2338	680				
	.1949	680				
12	1.1763	608				
	0.5882	645				
	.3921	657	.0629	.682	.13 ₅	.36
	.2941	663				
	.2353	672				
	.1961	672				

Contrails

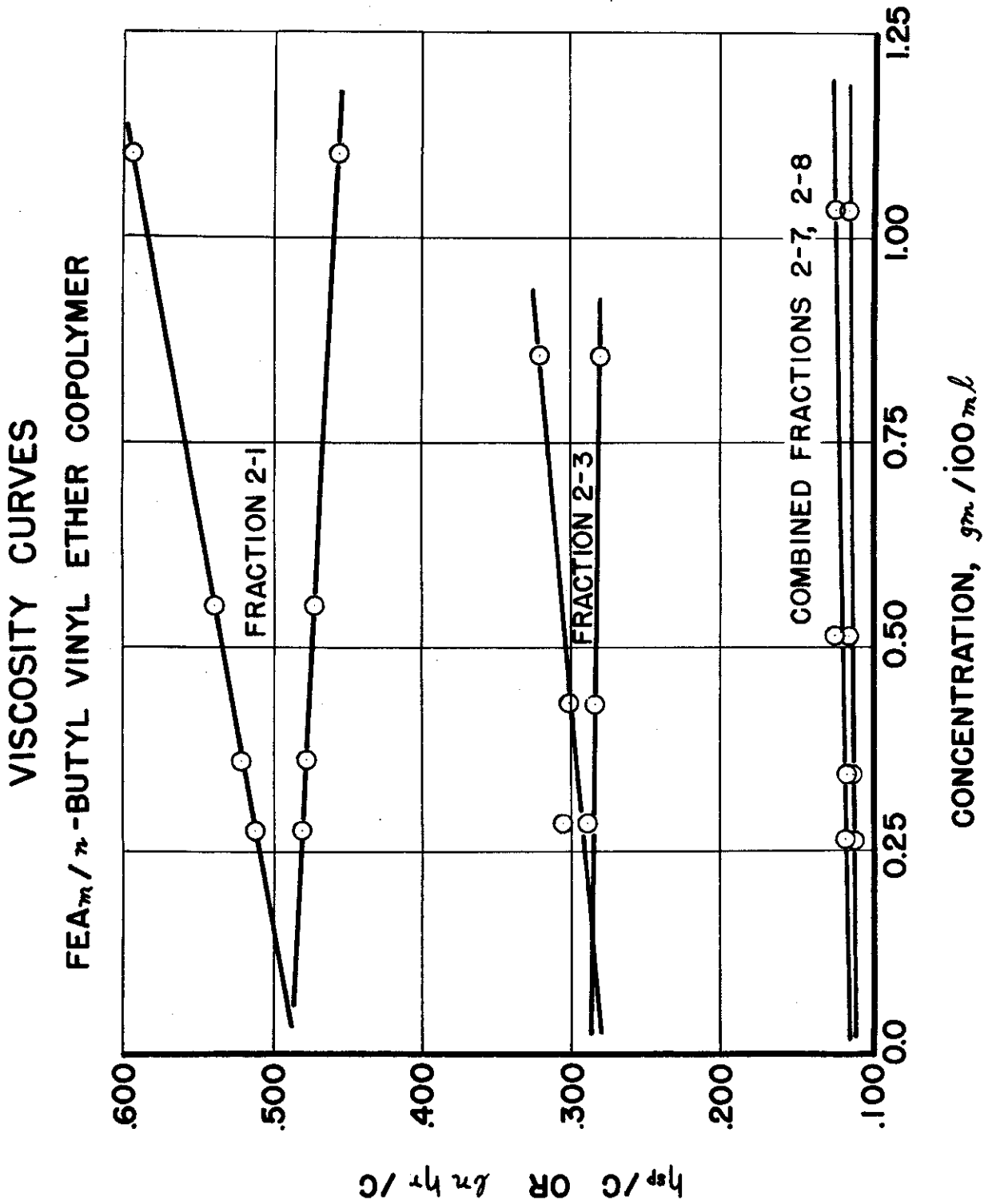


Figure 6

Viscosity Curves

VISCOSITY CURVES
FEA_m/r_n-BUTYL ACRYLATE COPOLYMER

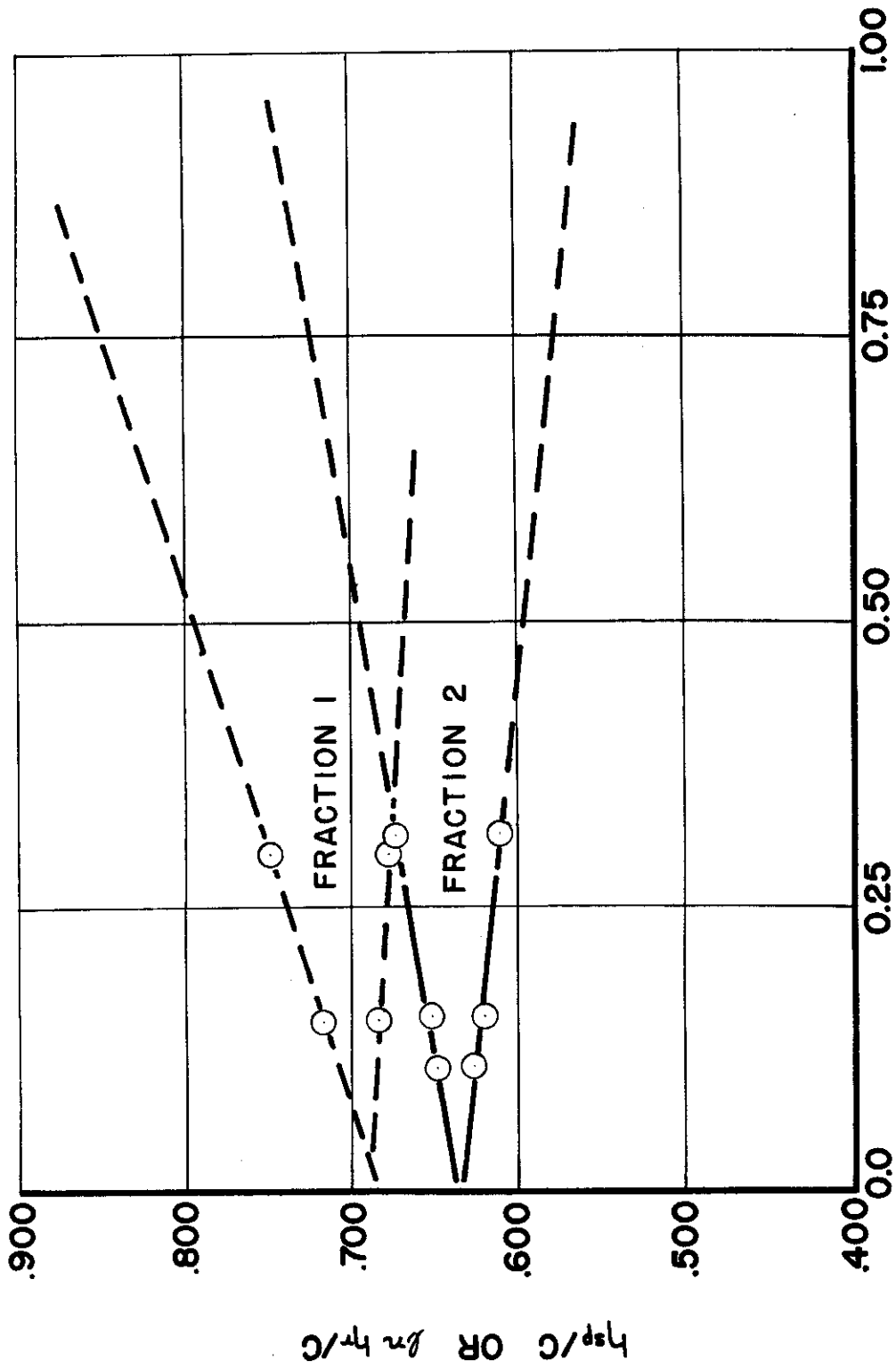


Figure 7
Viscosity Curves

VISCOSITY CURVES
FEA_m/n-BUTYL ACRYLATE COPOLYMER

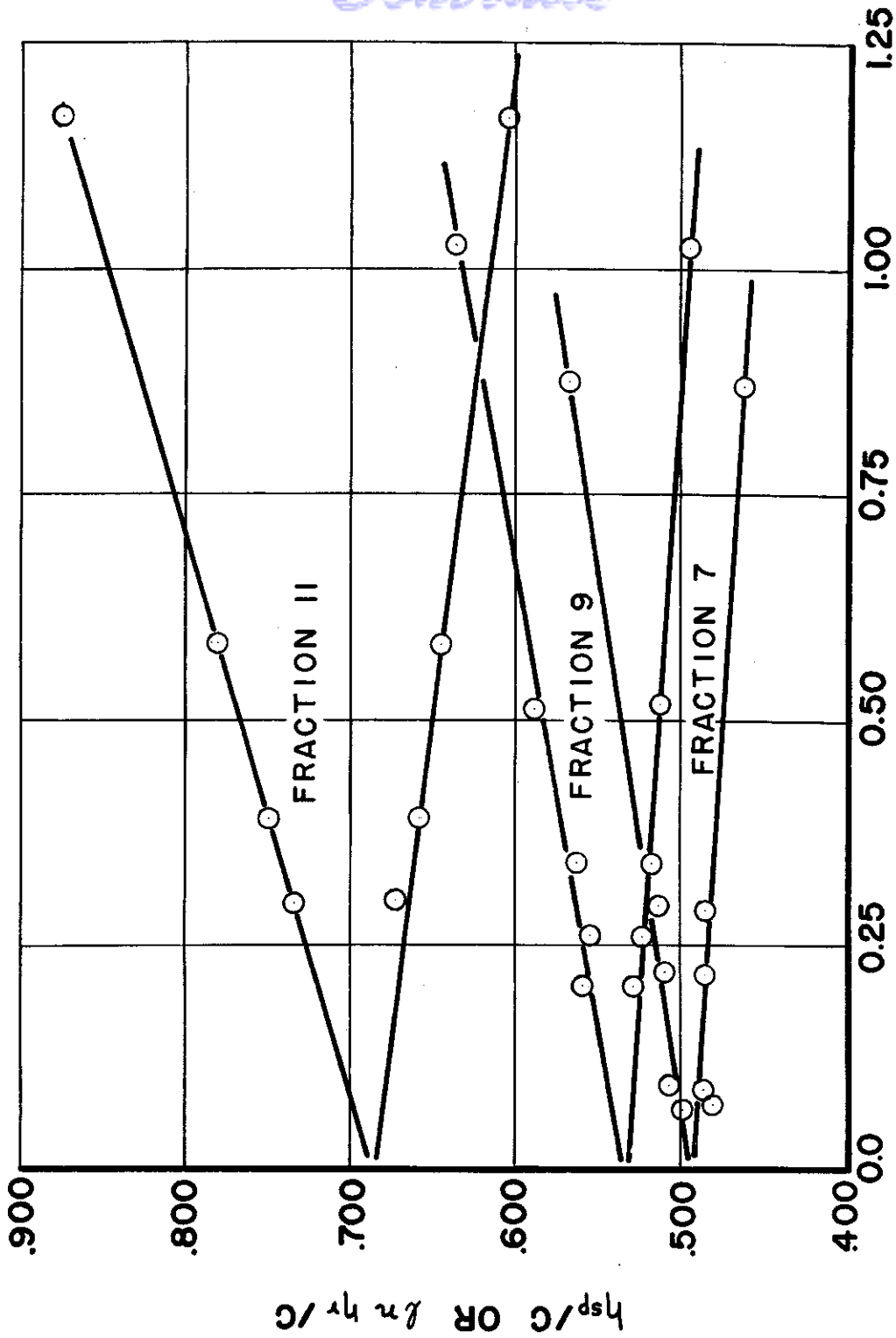


Figure 8
Viscosity Curves

VISCOSITY CURVES
FEA_{m/n}-BUTYL ACRYLATE COPOLYMER

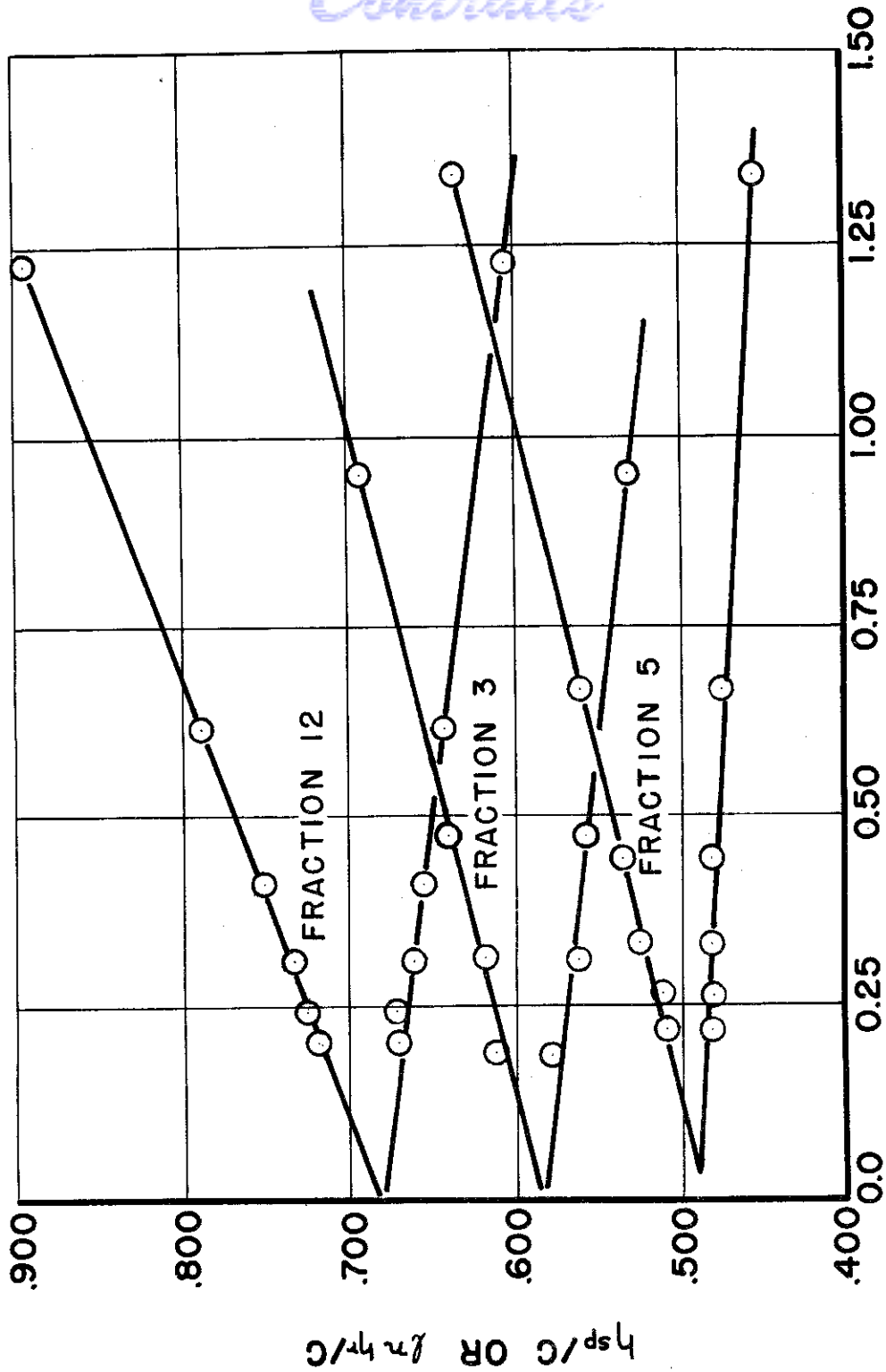


Figure 9
Viscosity Curves

Conclusions

include:

- a. Monomer Reactivity. Reactivity ratios for the system N-EFBAM-methyl methacrylate were experimentally determined. Values of $r_1 = 0.89$ (N-EFBAM) and $r_2 = 0.77$ (methyl methacrylate) indicated the radicals of both monomers showed about equal tendencies toward homo- and copolymerization. A slight preference toward copolymerization is indicated for each of the monomer radicals.
- b. Dilute Solution Behavior. Normal values of the empirical slope constant k' for several copolymers indicated these polymers were essentially linear. Intrinsic viscosities determined in dimethyl formamide for two copolymers ranged from values of $n = 0.118$ to $n = 0.690$.
- c. Thermal Stability. Evidence is presented which indicates some materials may be expected to show improved thermal stability through copolymerization with fluoroacrylamide monomers. Preliminary semi-quantitative data indicated that in two cases thermal stabilities showed somewhat better than marginal improvements.
- d. Plasticization. A unique property of the fluoroacrylamide plastics was their elasticity when plasticized with common solvents such as benzene and methanol. The plasticized polymers possessed strength, lively snap, and elongations of several hundred percent.

Further investigations with these and related monomers may prove of interest. New monomer types incorporating fluoroalkoxy side groups and various combinations of two fluorinated side groups would be expected to yield more flexible polymers of improved solvent resistance and possibly greater thermal stability.

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