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PROJECT IITRI-U6046
PROGRESS REPORT

RESISTANCE OF POLYMERIC STRUCTURES TO NITROGEN TETROXIDE

CALIFORNIA INSTITUTE OF TECHNOLOGY
Jet Propulsion Laboratory
Pasadena, California 91103

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IIT RESEARCH INSTITUTE

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I. INTRODUCTION

The study of polymeric structures resistant to nitrogen tetroxide necessarily involves partial degradation in order to establish the mechanism of attack. It is not surprising, therefore, that conditions and polymers are chosen so as to yield degradation rather than withstand it.

The polyethylene structures varying in degree of branching, unsaturation and molecular weight have been chosen. These offer a range of molecular structures which permit the establishment of the degrees of susceptibility and the mechanism of N_2O_4 attack.

Fluorinated structures are more desirable from the view point of higher resistance to degradation. They, however, have to be examined under more severe conditions in order to obtain the necessary changes for infrared absorption and creep measurements.

This report does not include data on permeation studies. These are being persued with maximum effort in order to compensate for the delay in the delivery of some equipment.

II. INFRARED STUDIES OF POLYETHYLENE AND FLUORINATED STRUCTURES

Polyethylenes with varying molecular weight, degree of branching, and unsaturation were studied. The samples listed on the following page were prepared in 10 mil thick sheets using 12 ton gauge pressures at 325°F followed by quenching in ice water to minimize crystallization.

Fluorinated materials such as TFE (Teflon), FEP (perfluoropropylene ethylene copolymer), the Kel-F series, Fluorel elastomer, and Aclar (fluorinated chlorinated resin) were also studied. The Kel-F series consisted of:

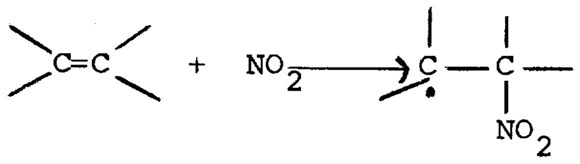
Kel-F 8112	Chlorotrifluoroethylene homopolymer (CTFE)
Kel-F 8205	97% CTFE/3% polyvinylidene fluoride (VF)
Kel-F 827	80% CTFE/20% VF
Kel-F 5500	45% CTFE/55% VF
Kel-F 3700	30% CTFE/70% VF

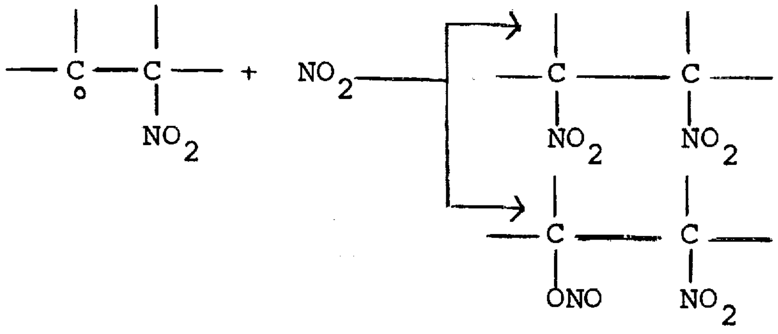
The degradation of polyethylene in nitrogen dioxide was previously studied by means of infrared spectroscopy (Ref. 1,2). The polymers were allowed to react with nitrogen dioxide at 25-120°C. The production of nitro, nitrite ester, nitrate ester, carbonyl and hydroxyl groups in polyethylene was recognized. The nitro and nitrite ester groups were produced early in the reaction by the addition of N_2O_4 to the reaction site (Ref. 1). The nitrite ester groups then decomposed to form nitrate ester, carbonyl, and hydroxyl groups. The following mechanism was considered for the reaction at 25°C (Ref. 2).

Sample	Polymer	Branching	Density	Figure	Curve
46892	Polyethylene	nil	0.96	1	B
46893	Ethylene-butene copolymer	3-4/1000 carbons	0.95	2	B
46894	Ethylene-butene copolymer	7-8/1000 carbons	0.938	2	A

Sample	Polymer	Molecular Weight, wt. avg.	Figure	Curve
46892	Polyethylene	200,000	1	B
46895	Polyethylene	400,000	1	C
46896	Polyethylene	1,000,000	1	D

		Unsaturation %			
Sample	Polymer	Trans	Vinyl	Figure	Curve
46897	Polyethylene (saturated)	0	0	1	A
46893	Ethylene-butene copolymer	0	1.2	2	B
46898	Ethylene-butadiene copolymer	3.7	1.5	2	C





$RONO \longrightarrow RO^{\bullet} \quad + \quad NO$; O—N fission

$RO\bullet \quad + \bullet NO_2 \longrightarrow RONO_2$

$R'CH_2O\bullet \longrightarrow R'CHO \quad + H^{\bullet}$

$R'' \; R'''CHO^{\bullet} \longrightarrow R'R'''CO \; + H^{\bullet}$

$R'' \; R'''CHO^{\bullet} \longrightarrow R''CHO \; + \bullet R'''$

$RO\bullet \; + H\bullet \longrightarrow ROH$

$RONO_2 \longrightarrow RO\bullet \quad + \bullet NO_2$

However, at high temperatures, above 100°C, it was proposed that N_2O_4 also reacts with the methylene chain of polyethylene.

$$RH + \bullet NO_2 \longrightarrow R\bullet + HNO_2$$

$$R\bullet + \bullet NO_2 \longrightarrow RNO_2$$

$$R\bullet + NO_2 \longrightarrow RONO$$

Our study provides additional information on the reaction mechanism of polyethylene degradation by N_2O_4. The polyethylenes were allowed to react with N_2O_4 at 25°C and 75°C for 7 days. After excess N_2O_4 was removed, Attenuated Total Reflectance and absorption spectra of the samples were obtained. The characteristic spectra and spectral changes due to N_2O_4 exposure are shown in Figures 1-3. The experimental results are summarized in Table 1.

The polyethylenes before N_2O_4 exposure had double bonds which could be identified by infrared spectrascopy. The bands at 10.0 and 10.9μ (Figures 1 and 2, Table 1) are assigned to the CH out of plane bending of terminal methylene groups. The band at 10.25μ (Figure 2, Table 1) is due to CH out of plane bending of a trans double bond. These bands disappear after N_2O_4 exposure at 25° and new absorption bands appear (Figure 1, 2). The new absorption bands are assigned to carbonyl, nitro, and nitrate ester groups (Table 1). After N_2O_4 exposure at 75°C, the absorption bands were greatly intensified. Typical results are shown in Figure 3. Since nitrite esters are unstable (Ref. 1, 2), it is not surprising that absorption bands due to this group are not observed.

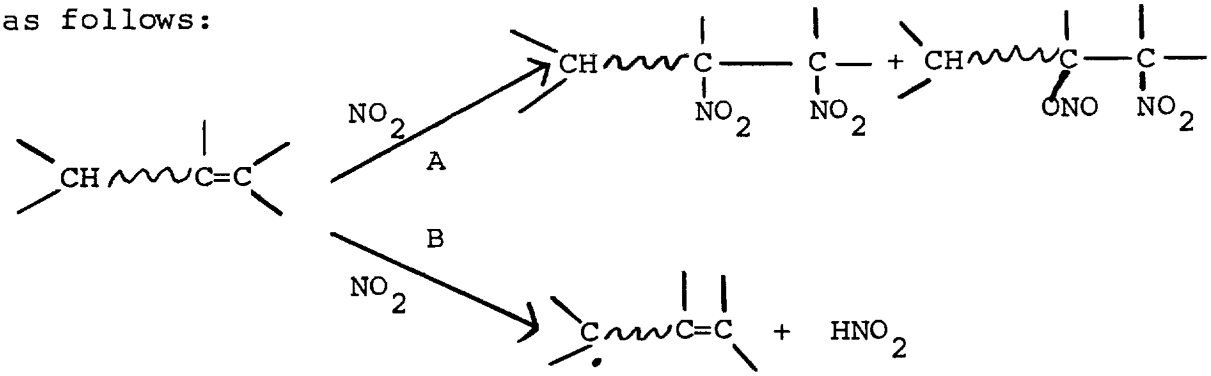
Saturated polyethylene also had absorption bands of the carbonyl, nitro and nitrate ester groups after N_2O_4 exposure (Figure 1, 3). However, these bands were less intense than those formed in the polyethylenes containing double bonds.

Table 1

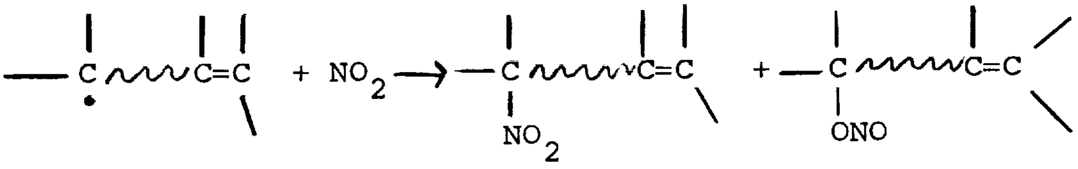
SPECTRAL CHANGES OF POLYETHYLENES
(FIGURES 1 - 3)
AFTER N_2O_4 EXPOSURE

Band, μ	After Exposure	Assignment
5.75	Appear	$>C=O$
6.0	Appear	$RONO_2$
6.35	Appear	RNO_2
7.25	Appear	RNO_2
7.75	Appear	$RONO_2$
10.0	Disappear	$>C=C<$ (vinyl)
10.25	Disappear	$>C=C<$ (trans)
10.9	Disappear	$>C=C<$ (vinyl)
11.45	Appear	RNO_2
11.75	Appear	$RONO_2$

Since both saturated and unsaturated polyethylenes are attacked by N_2O_4, two reaction paths must be possible. It may be concluded that N_2O_4 adds to the double bond which exists originally in polyethylene and also slowly reacts with the methylene chain. Two reaction mechanisms can be written as follows:



Path B
followed by:



The nitrite ester group then could decompose to form nitrate ester, carbonyl, and hydroxyl groups as discussed previously.

The effect of molecular weight, degree of branching and unsaturation was determined by comparing relative intensities of the absorption bands in the polyethylenes during degradation at 25°C (Table 2). The bands used for the studies were 5.75μ (carbonyl), 6.35μ (Nitro), 10.9μ (vinyl) and 11.75μ (nitrate ester).

As the degree of unsaturation increases in samples 46897, 46893, and 46898, the amount of nitro, nitrate ester, and carbonyl groups correspondingly increase during degradation.

The same effect of degree of unsaturation was also illustrated in the series with increasing molecular weight (samples 46892, 46895, and 46896). The degree of unsaturation was reported to decrease with increasing molecular weight (Ref. 3). Our data substantiates this report.

Although the degree of unsaturation is the major factor determining degradation, the degree of branching also is a factor. As can be seen from Table 2, polyethylene 46894 with the greatest degree of branching but lowest degree of unsaturation is degraded more than 46892 which is more unsaturated. This result would be expected if hydrogen abstraction as well as addition to the double bond occurs during degradation.

Hence our results in contrast to those previously reported (Refs. 1, 2) indicate that polyethylenes are degraded

Table 2

EFFECT OF BRANCHING, MOLECULAR WEIGHT, AND UNSATURATION ON POLYETHYLENE DEGRADATION

Sample	Branching	Carbonyl*	Nitro*	Nitrate* ester	Vinyl*
46892	nil	24	40	15	33
46893	3-4/1000 carbons	43	67	37	46
46894	7-8/1000 carbons	34	44	19	22

Sample	Molecular Weight	Carbonyl	Nitro	Nitrate ester	Vinyl
46892	200,000	24	40	15	33
46895	400,000	15	31	9	21
46896	1,000,000	16	18	7	10

	Unsaturation, %				
Sample	Trans	Vinyl	Carbonyl	Nitro	Nitrate Ester
46897	0	0	36	36	16
46893	0	1.2	43	67	37
46898	3.7	1.5	56	77	40

*Absorption change relative units

by N_2O_4 by two reaction paths even at low temperatures. Addition to the double bond predominates but hydrogen abstraction also occurs at 25°C.

The fluorinated materials were allowed to react with N_2O_4 at 25°C for 7 days. After excess N_2O_4 was removed, Attenuated Total Reflectance and Absorption spectra of the samples were obtained. Typical results are shown in Figure 4. The fluorinated materials showed little degradation. However, Fluorel 5500, Kel-F 8205, Kel-F 5500, and Kel-F 3700 had a weak absorbance band at around 6.0μ. Additional work will be required before the nature of this band is understood.

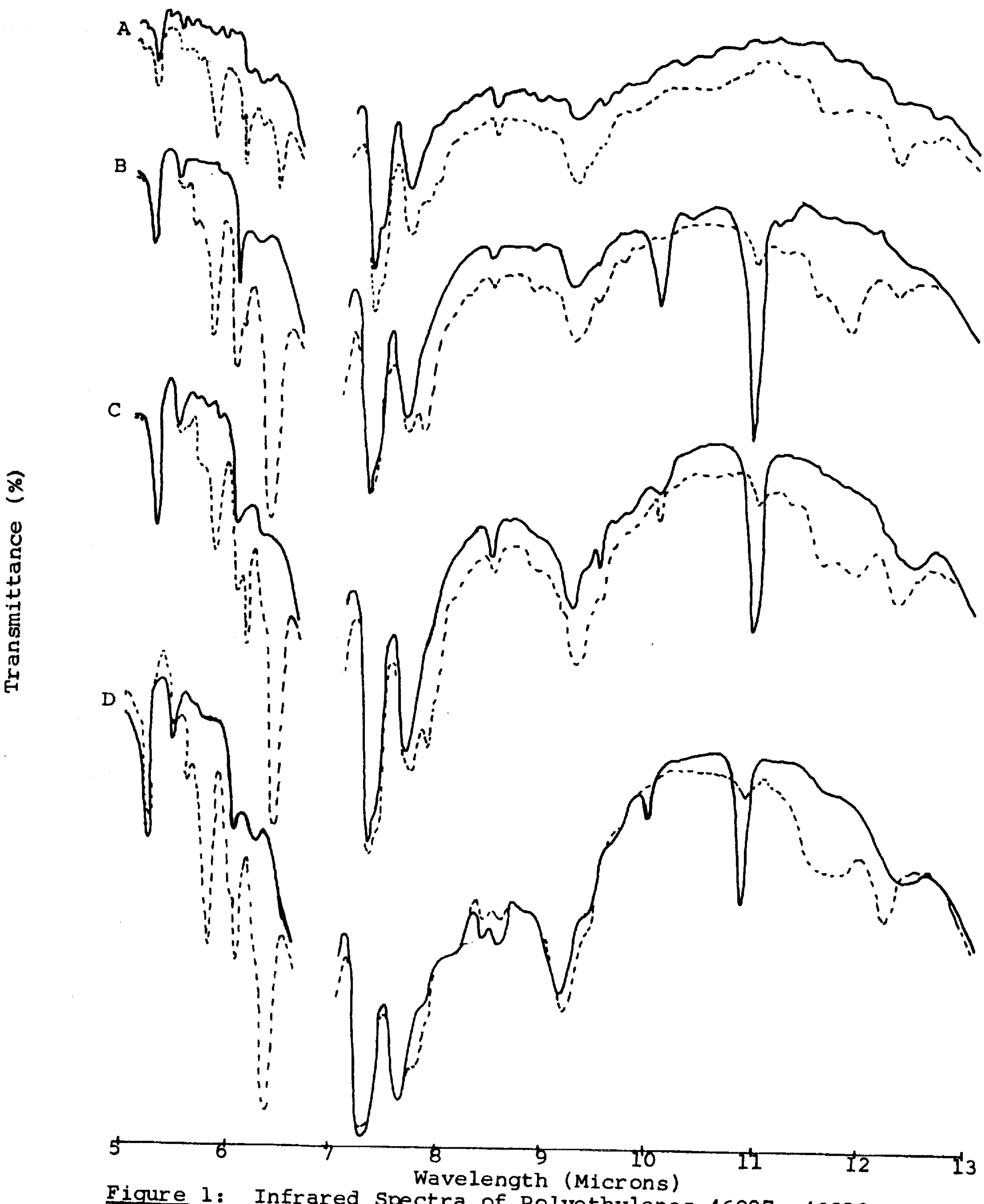


Figure 1: Infrared Spectra of Polyethylenes 46897, 46892, and 46896 (Curves A, B, C, D, respectively); ______ before N_2O_4 exposure, - - - - after N_2O_4 exposure at 25°C.

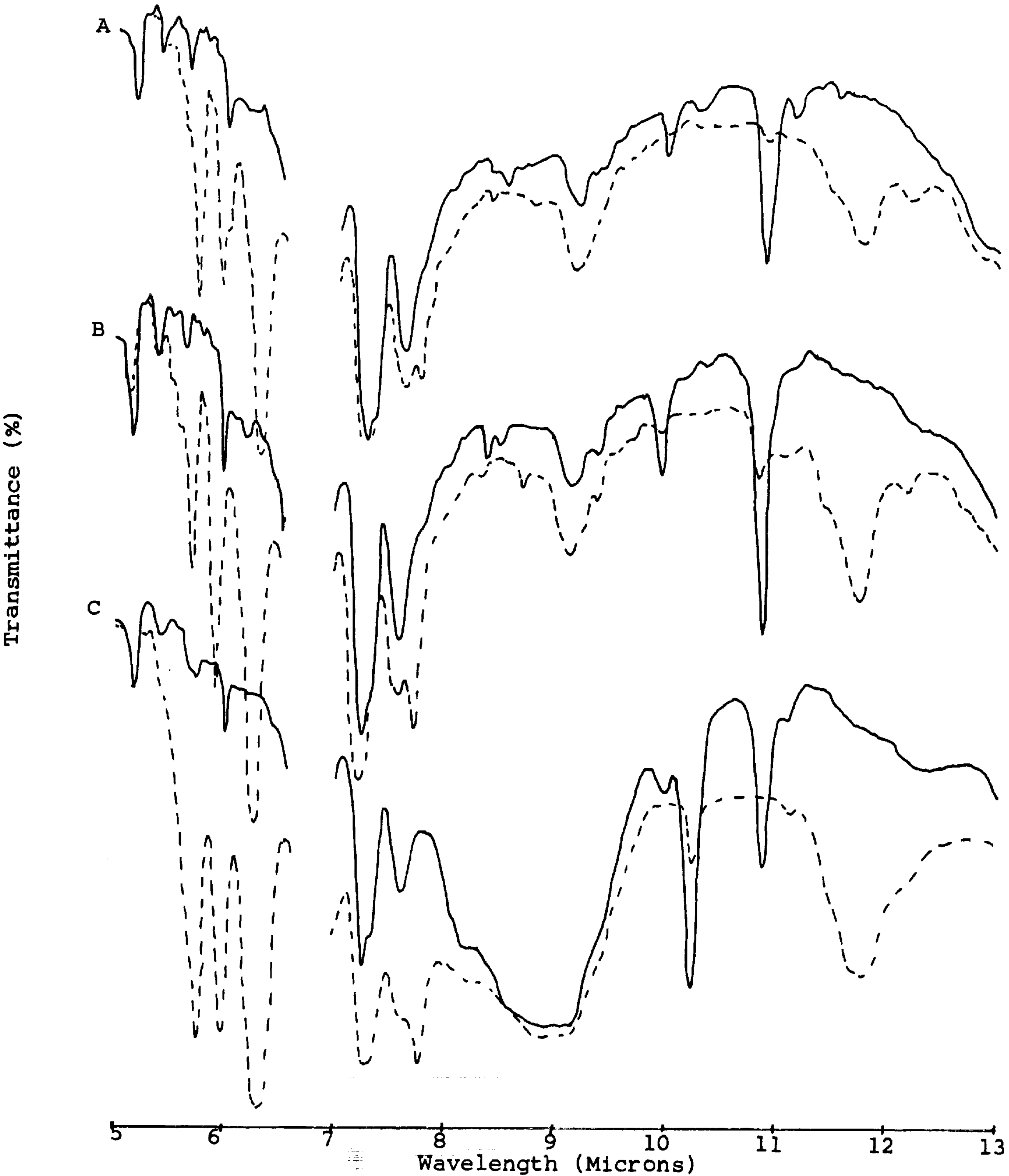


Figure 2: Infrared Spectra of Polyethylenes 46894, 46893, and 46898 (Curves A, B, C respectively); ——— before N_2O_4 exposure, - - - - after N_2O_4 exposure at 25°C

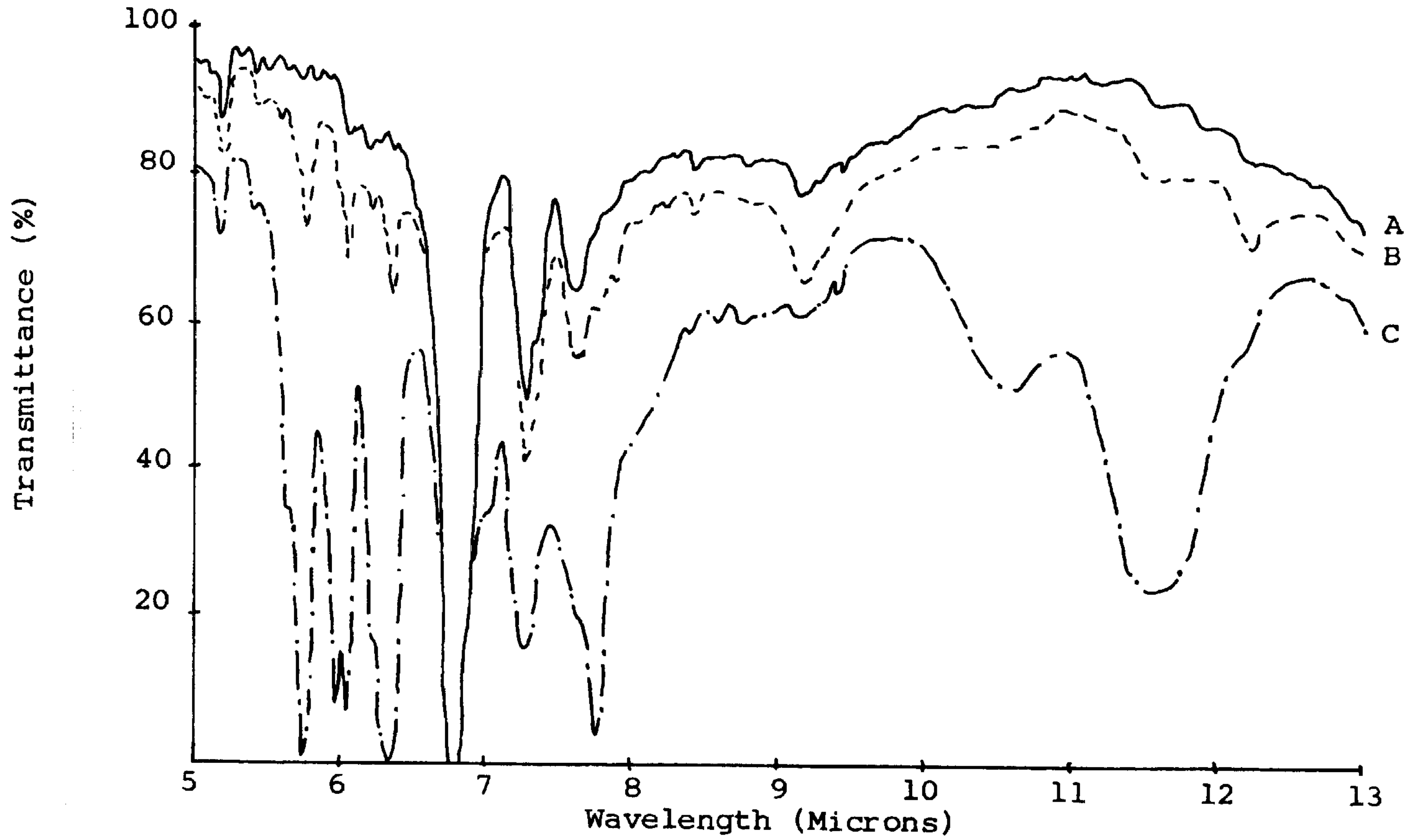


Figure 3: Infrared Spectra of Polyethylene 46897; Curve A, ______ before N_2O_4 exposure, Curve B, - - - - after N_2O_4 exposure at 25°C; Curve C, __ · __ ·, after N_2O_4 exposure at 75°C

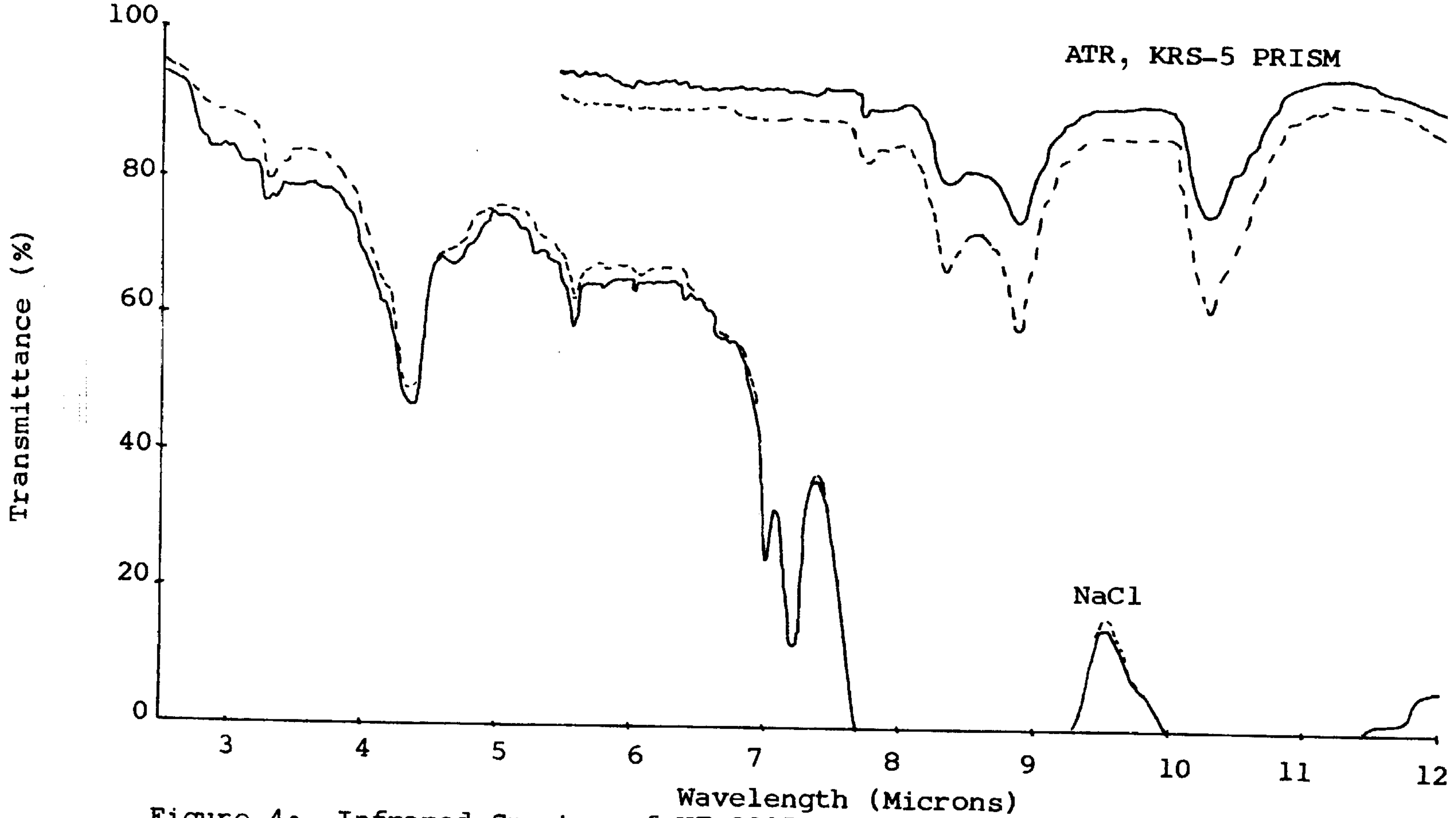


Figure 4: Infrared Spectra of KF-8205, ——— before N_2O_4 exposure, - - - - after N_2O_4 exposure at 25°C

III. CREEP MEASUREMENTS

A. Polyethylene Structures

The series of polyethylenes were studied by measuring the elongation with an applied constant stress as a function of time. The total elongation (ε_t) is recorded after 3000 minutes of stress application or at maximum extension before breaking. Table 3 summarizes the results obtained at 25°C. After exposure to N_2O_4 at 75°C the polyethylenes broke before the 3000 minutes were attained.

It can be seen that the series with different degrees of branching show an increase in elongation and a shorter time before break as the branching increases. This shows that the degree of branching has a definite and measurable effect on the mechanical properties of polyethylene structure.

The greater elongation indicates that chain scission or plasticization is induced by N_2O_4. The decrease in time to break shows a definite embrittlement due to compound formation with N_2O_4. The susceptibility to N_2O_4 increases with increasing degree of branching. This correlates very well with the infrared observations.

The series in which molecular weight is varied indicates that the elongation before exposure is smaller for the higher molecular weight, while after attack by N_2O_4, the elongation is larger for the higher molecular weight polyethylene. In other words, the higher polymer is more susceptible to chain scission.

Table 3

Creep Measurements on Polyethylenes

Sample	Branching		Not Exposed	Exposed to N_2O_4 7 days, 75°C	
			ε_t	ε_t	Minutes before break
46892	ml		1.1	0.7	194
46893	3 to 4/1000		2.3	0.2	85
46894	7 to 8/1000		1.7	1.3	10
			Molecular Weight		
46892	200,000		1.1	0.7	194
46895	400,000		1.0	0.7	>3000
46896	1,000,000		0.2	2.7	0
			Unsaturation		
	trans	vinyl			
46897	0	0	2.5	0	0
46893	0	1.2	2.3	0.2	85
46898	3.7	1.5	0.8	0.8	2

In this case, however, the intermediate molecular weight produces the best resistance to applied load. This can be understood in terms of unsaturation found by infrared measurements. The sample 46892 has greatest content of vinyl groups. It forms larger number of nitro and nitrate ester structures and, therefore, becomes more susceptible to breakage than 46895.

Thus, with respect to molecular weight the most resistant polyethylene is that of intermediate molecular weight.

With varying unsaturation, the polyethylene structure with most extensive unsaturation elongates the least before exposure. The highest unsaturation produces the greatest number of nitro and nitrate ester groups and, therefore, after exposure the trend in elongation is reversed. The time to break does not follow the same trend, because increasing the elongation prevents breakage in that the stress can be dissipated by viscoelastic mechanism. This shows that presence of vinyl unsaturation even though it permits compound formation does not completely degrade the mechanical strength.

In summary, the best mechanical performance with respect is resistance to N_2O_4 of polyethylenes can be expected from those structures containing the least branching, consisting of intermediate molecular weight and containing small amount of vinyl unsaturation.

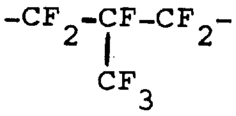
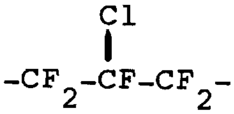
B. Fluorinated Structures

Creep measurements have been performed on the series of fluorinated polymers which indicate a complex behavior with respect to crosslinking and chain scission (Table 4). In particular, it was observed that the two mechanisms may operate simultaneously. With application of small stress the crosslinked structures withstand deformation, while with somewhat higher stress the crosslinks break and indicate chain scission. In other words, the crosslinks are weak and are probably due to nitro groups rather than carbon-carbon bonds.

Attempts are being made to establish this by means of infrared studies. The series of measurements performed did not show sufficiently large changes in structure before and after exposure to N_2O_4 at 25°C. Therefore, these are being performed with exposure at higher temperatures. These results will be discussed in the next report.

Table 4

Creep Measurements
on Fluorinated

Material	Effect*	Not Exposed Et	Not Exposed E_3	Exposed to N_2O_4 7 days, rm. temp. Et	Exposed to N_2O_4 7 days, rm. temp. E_3
Aclar Type 33c, fluorinated chlorinated resin	No Effect	0.6	-0.1	0.7	0
FEP  $-CF_2-\underset{CF_3}{CF}-CF_2-$	Some C. L.	0.5	0	0.5	-0.2
TFE $-CF_2-CF_2-CF_2-$	Some C. S.	3.2	0.7	3.5	1.2
Kel-F (KF8112)  $-CF_2-\overset{Cl}{CF}-CF_2-$ 100% CTFE	Some C. S.	0.2	-0.1	0.6	0.1
Kel-F (KF8205) 97% CTFE 3% VF $-CF_2-CH_2-$	Some C. L.	0.2	-0.2	0.3	-0.5
Kel-F (KF827) (80% CTFE) (20% VF)		40.**		30.	
Kel-F (KF5500) (45% CTFE) (55% VF)	C. S.	25.	3.4	8.8	7.3
Kel-F (KF3700) (30% CTFE) (70% VF)	Some C. S.	21.	0.7	20.	1.0
Fluorel 2141 (20 psi)	Weak C. L.	3.2	0.1	2.6	-0.6
(40 psi)		7.0	0.8	8.6	0.9

*C.S.=Chain scission
C.L.=Crosslinking
**Maximum apparatus extension

IV. Personnel

The infrared work has been performed by J. Hillman of the Polymer Research group.

Respectfully submitted,

A. M. Staké

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Approved:

T. H. Meltzer
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