

ML-TDR-64-151

PART II

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THEORETICAL STUDIES ON THE DEGRADATION OF LADDER POLYMERS

PART II. VAPORIZATION STUDIES

MARTIN M. TESSLER, 1/LT., USAF

TECHNICAL REPORT ML-TDR-64-151, PART II

DECEMBER 1965

AIR FORCE MATERIALS LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

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ML-TDR-64-151
PART II

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OF LADDER POLYMERS**

PART II. VAPORIZATION STUDIES

MARTIN M. TESSLER, 1/LT., USAF

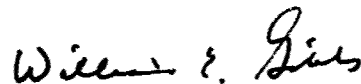
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FOREWORD

This report was prepared by the Polymer Branch of the Nonmetallic Materials Division. The work was initiated under Project No. 7342, "Fundamental Research on Macromolecular Materials and Lubrication Phenomena," Task No. 734203, "Fundamental Principles Determining the Behavior of Macromolecules." It was administered under the direction of the AF Materials Laboratory, Research and Technology Division, 1stLt Martin M. Tessler, project engineer.

This report covers work conducted from January 1964 to December 1964. The manuscript was released by the author in May 1965 for publication as an RTD technical report.

This technical report has been reviewed and is approved.



WILLIAM E. GIBBS
Chief, Polymer Branch
Nonmetallic Materials Division
Air Force Materials Laboratory

ABSTRACT

The random degradation of four and six-membered ring ladder polymers were investigated by means of a digital computer and the results compared to a single chain polymer undergoing degradation under identical conditions. The percent vaporization versus time and the rate of weight loss versus time was plotted and significant differences were obtained. The results indicate that ladder polymers should have increased stability over single chain polymers undergoing random degradation.

TABLE OF CONTENTS

	PAGE
INTRODUCTION	1
MONTE CARLO MODEL	2
RESULTS	4
REFERENCES	5
APPENDIXES I THROUGH V - COMPUTER PROGRAM	11-52

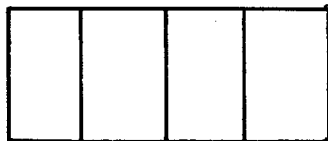
ILLUSTRATIONS

FIGURE	PAGE
1. Ladder Polymer Model	2
2. Plot of Percent Vaporization Versus Time for Simple Case Ladder Polymers Undergoing Random Degradation	6
3. Plot of Percent Vaporization Versus Time for Complex Case Ladder Polymers Undergoing Random Degradation	7
4. Plot of Rate of Weight Loss Versus Time for Simple Case Ladder Polymers Undergoing Random Degradation	8
5. Plot of Rate of Weight Loss Versus Time for Complex Case Ladder Polymers Undergoing Random Degradation	9

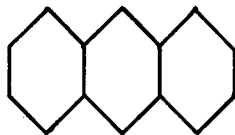
INTRODUCTION

Previously (Reference 1), the thermal stability of a ladder polymer undergoing random degradation was compared with that of a single chain polymer by using a digital computer to set up a statistical (Monte Carlo) model of the degrading system. The change in molecular weight versus time was plotted and significant differences were found in the shapes of the curves for the ladder polymers as compared to a single chain polymer.

A common test for thermal stability of a polymer is to measure its loss of weight upon heating. The previous report (Reference 1) studies the changes in molecular weight of a ladder polymer undergoing random degradation upon heating in a closed system where no weight loss has occurred. The present report discusses the random degradation of a ladder polymer in an open system where, upon heating, small molecular weight fragments of the polymer are vaporized out of the system. Two types of ladder polymers are studied. Type I is a fused four-membered ring and Type II is a fused six-membered ring. All of the results for a four-membered ring are equally applicable to an eight-membered ring.



TYPE I



TYPE II

Initially, a simplified scheme of degradation was considered where a broken bond can break a molecule only if the bond opposite it is broken. The much more realistic scheme of random degradation, where breaks in the crosslinks will result in increased molecule breaks, was also considered. This is called the complex case of degradation.

The following assumptions were made in defining the degrading system:

1. The polymer sample is initially monodisperse; that is, only chains of a single length are present.
2. All bonds in the polymer chain are of equal strength and accessibility, regardless of the length of the chain and the positions of the bonds in the molecule.
3. The rate of bonds breaking is proportional to the number of unbroken bonds in the degrading system.

The simple and complex cases of degradation were studied for Type I and Type II ladder polymers. The percent vaporization at time kt and the rate of weight loss at time kt were calculated and compared with a single chain polymer degrading under identical conditions. The constant, k , is the proportionality constant between the rate of breaking bonds and the number of unbroken bonds in the degrading system. It can only be determined experimentally, so the time factor is kt instead of t , where t is time.

MONTE CARLO MODEL

To construct a Monte Carlo (Reference 2) model for the degradation reaction, a portion of the computer storage is set aside to represent the polymer molecules. Each storage location represents one bond. If a bond is not broken, a zero is placed in the computer storage location corresponding to that bond.

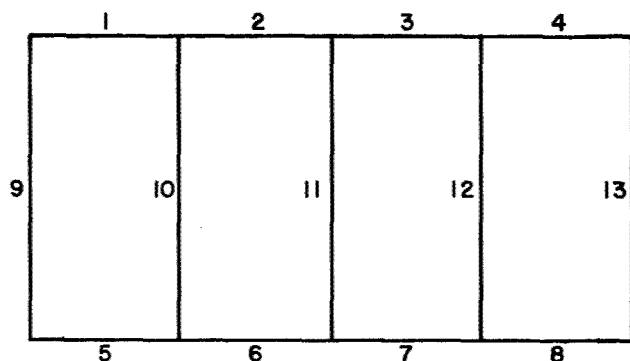


Figure 1. Ladder Polymer Model

In the simple case, when a bond is broken it is set equal to 1 and the opposite bond checked. If the opposite bond is broken, both bonds are set equal to 2. In the complex case, when an isolated bond is broken (bond 3 in Figure 1), it is set equal to 1. If vaporization occurs through the breaking of adjacent side chain bonds only (bonds 1, 10, 11, and 3 in Figure 1 are broken), the side chain bonds are set equal to 2. Since x broken side chain bonds result in $x-1$ atoms vaporizing, all of the broken side chain bonds are set equal to 2 except the last one so that each bond which is set equal to 2 corresponds to a vaporized atom. If two opposite bonds are broken (bond 2 and 6 are broken in Figure 1), they are set equal to 3 except when a bond is broken opposite a bond which has a number 2 in its storage location. The initial broken bond is set equal to 3, but the opposite bond is changed from a 2 to a 5. If two pairs of opposite broken bonds result in vaporization (bonds 1 and 5 and bonds 4 and 8 in Figure 1 are broken), all of the bonds in the vaporized fragment are set equal to 4. If any of the bonds have numbers 2 or 5 in their storage, they are also set equal to 4, but the number of vaporized atoms is reduced by one. This

prevents the same atom from being vaporized twice. If bonds 1, 5, 10, and 6 in Figure 1 are broken and the computer then breaks bond 2, an error will result because only one atom must be vaporized and not two. If the bond opposite the initial broken bond has a number of 3, 4, or 5, the computer checks whether its adjacent bond also has a number of 3, 4, or 5 and if it does, no vaporization of that atom occurs (it has been vaporized previously). If the opposite bond has a number 2 in it, it is set equal to 5 and no vaporization is recorded as described previously.

Initially, all of the storage locations are set to zero. A random number is generated which has the limits of 0 to $B_0 - 1$, where B_0 is the total number of bonds initially present in the system. Each number then represents a particular bond in a particular molecule and the number of molecules and the number of bonds per molecule are selected by the programmer and can readily be altered. The present study investigated a system of 100 molecules with 199 bonds per molecule for ladder polymer Type 1 and 100 molecules with 196 bonds per molecule for ladder polymer Type II. A single chain polymer with the same number of bonds per molecule was degraded in the computer for comparison purposes.

When a random number is generated, the bond which it represents is checked to see whether or not it is broken. If it is already broken, a duplicate is recorded and a new random number generated. If it is not broken, the bond is set equal to one and the opposite bond checked. If the opposite bond is broken, in the simple case both bonds are set equal to 2. The computer then checks the adjacent bonds in both directions until it comes to another pair of opposite bonds with a value of 2 or the end of the molecule. The size of the fragment is measured and if it contains ten atoms or less, vaporization occurs. All of the vaporized bonds are set equal to 2 and the concentration of unbroken bonds is adjusted to account for the vaporized bonds. The size of the fragments which are volatile is arbitrary and can be varied if desired.

Part II

In the complex case, if the opposite bond is broken, both bonds are set equal to 3 except when the opposite bond has a value of 2. The opposite bond is then set equal to 5 and the original broken bond is set equal to 3. The computer then checks the side chain bonds in both directions until it comes to another pair of opposite bonds with a value of 3, 4, or 5 or until it comes to the end of the molecule. The size of the fragment is measured and if it contains ten atoms or less, vaporization occurs. Before the vaporized bonds are set equal to 4, they are checked to see if their value is 0, 2, or 5. The total number of atoms in the fragment minus the number of bonds containing 2 or 5 equals the number of atoms vaporized. The number of bonds which are changed from 0 to 4 is also calculated and the number of unbroken bonds left in the system is reduced by that number of bonds.

If no vaporization occurs or if the opposite bond is not broken, no further work is done in the simple case and a new random number is generated. If the opposite bond is broken and no vaporization occurs in the complex case, the crosslinks are checked to see if broken crosslinks can lead to a broken molecule. The computer checks all of the crosslinks to the left and right until it either comes to an unbroken crosslink or the last crosslink at the end of the molecule. If the computer finds an unbroken crosslink, it then scans all of the side chain bonds on both sides of the ladder polymer from the broken bond produced by the random number generator to the last side chain bond before the unbroken crosslink. If a broken bond is found on the side of the molecule opposite the original broken bond, the computer treats

it exactly as described previously for the case of two opposite bonds breaking. If a broken bond is found on the side of the molecule adjacent to the original broken bond or if all of the crosslinks to the end of the molecule are broken, the computer checks to see if the fragment contains ten or less atoms. If it does, all of the bonds are set equal to 2 and the total number of unbroken bonds remaining in the system is reduced by the number of bonds changed from 0 to 2. If the opposite bond is not broken in the complex case, the computer scans the crosslinks and does all of the calculations previously described.

If the random number generator produces a bond which corresponds to a crosslink, no further work is done in the simple case. In the complex case, the computer checks to see if the broken crosslink will result in a broken molecule. If it does, it then checks to see if the fragments are small enough to be vaporized and adjusts the bond numbers accordingly.

The time factor kt is equal to $\ln(B_0/B)$ where B_0 is the number of bonds present initially and B is the number of unbroken bonds present at time kt . The number of unbroken bonds present at time kt equals the number of bonds present initially minus the number of random numbers generated plus the number of duplicates recorded minus the number of unbroken bonds vaporized out of the system. The computer calculates the number of atoms vaporized out of the system, the percent vaporization, and the rate of vaporization at time kt and prints out the desired data at convenient intervals of kt .

RESULTS

The curves shown for the simple case in Figure 2 and the complex case in Figure 3 are based on computer calculations for the percent vaporization versus kt . As the degrading single chain polymer undergoes a much more rapid decrease in molecular weight when compared to a ladder polymer (Reference 1), we would naturally predict that the single chain polymer would also lose weight at a much faster rate. Examination of Figures 2 and 3 shows quite clearly that this prediction is correct. When 10 percent of the single chain polymer has vaporized, less than 2 percent of the ladder polymer has vaporized in the simple case and less than 4 percent in the complex case. A difference in the shapes of the

curves is also readily apparent. The single chain polymer shows a large initial loss in weight during degradation while the ladder polymers have an induction period during which the loss in weight is very small. As degradation proceeds, the shapes of the curves become identical and merge together. The curves for the rate of weight loss versus kt are shown in Figure 4 for the single case and in Figure 5 for the complex case. The very large initial rate of weight loss for a single chain polymer as compared to a ladder polymer is the major point of interest of these curves. These results indicate that the ladder polymers should have increased thermal stability over single chain polymers.

REFERENCES

1. M. M. Tessler, Technical Documentary Report No. ML-TDR-64-151, July 1964. Research and Technology Division, Wright-Patterson Air Force Base, Ohio.
2. A. S. Householder, G. E. Forsythe, and H. H. Germand, Monte Carlo Method, National Bureau of Standards, Applied Mathematics Series, 12 (1951).

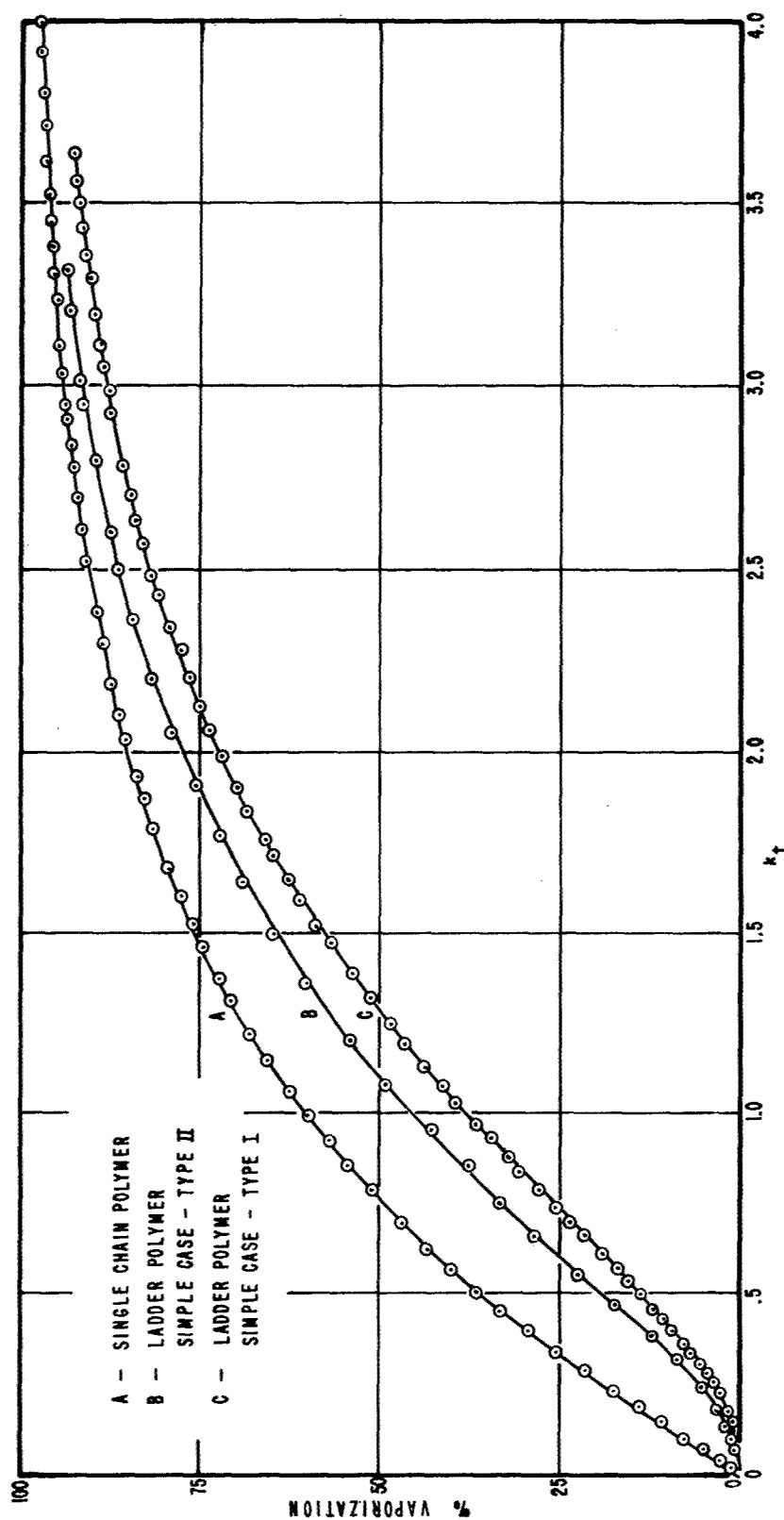


Figure 2. Plot of Percent Vaporization Versus Time for Simple Case Ladder Polymers Undergoing Random Degradation.

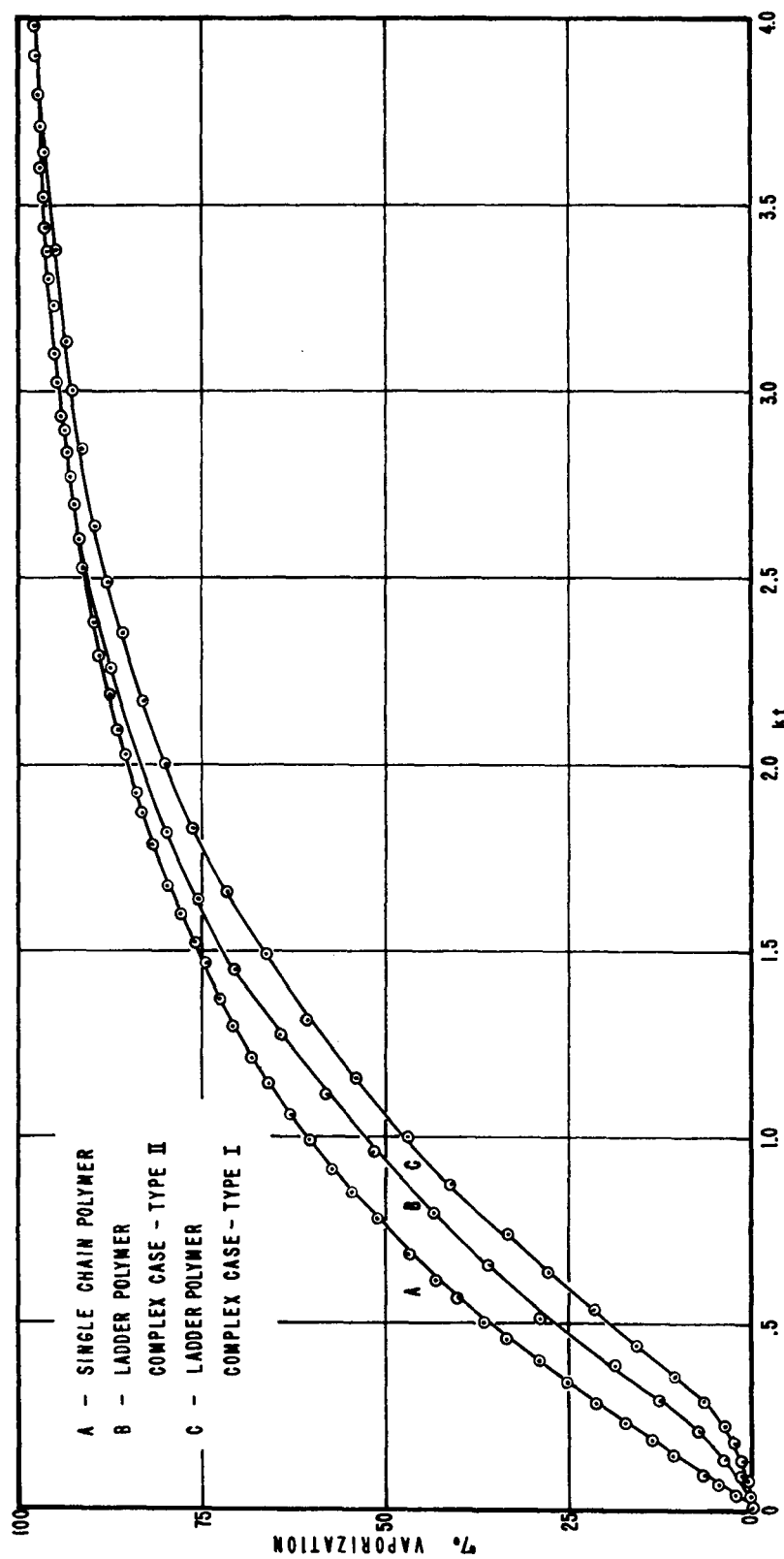


Figure 3. Plot of Percent Vaporization Versus Time for Complex Case Ladder Polymers Undergoing Random Degradation.

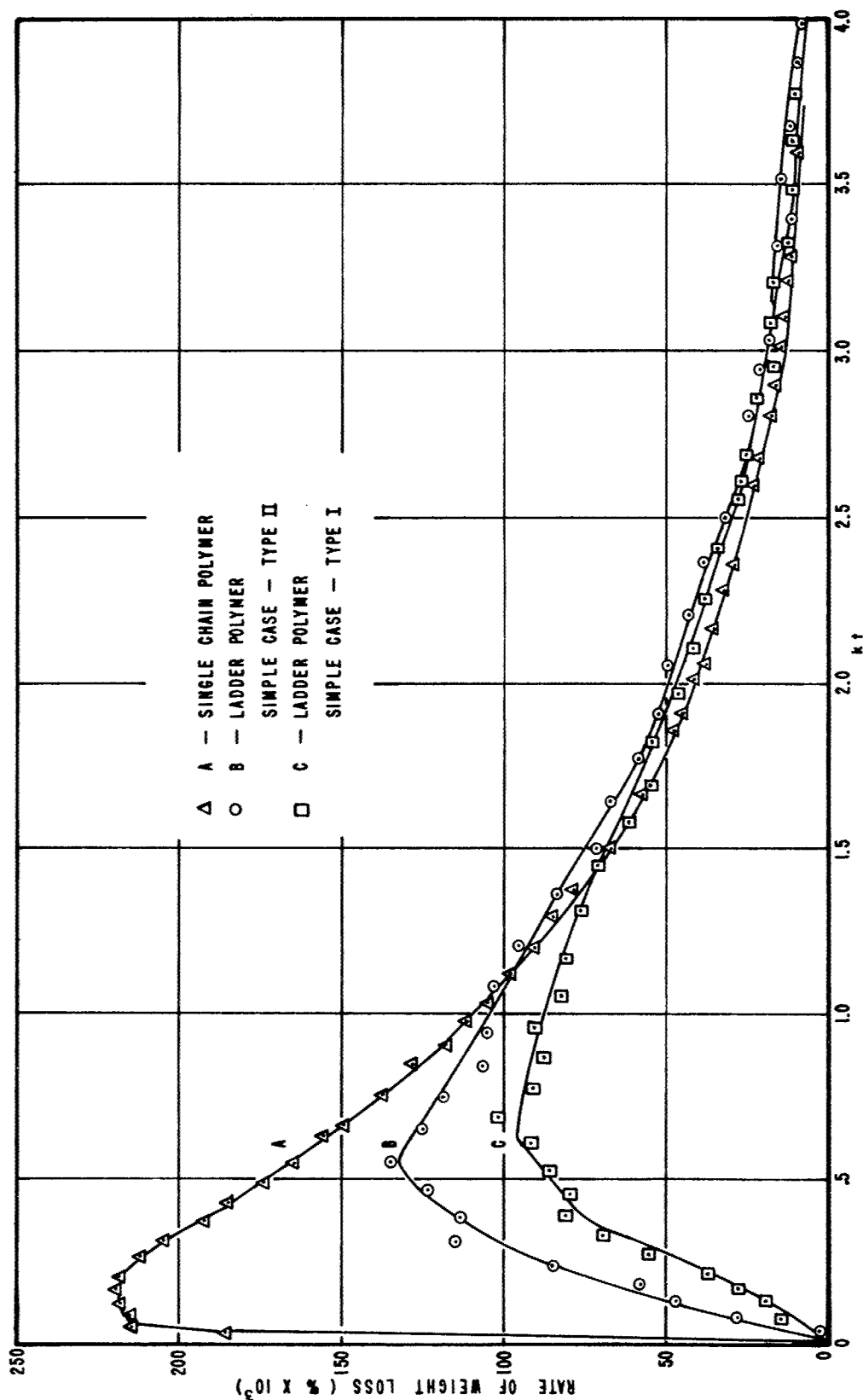


Figure 4. Plot of Rate of Weight Loss Versus Time for Simple Case Ladder Polymers Undergoing Random Degradation.

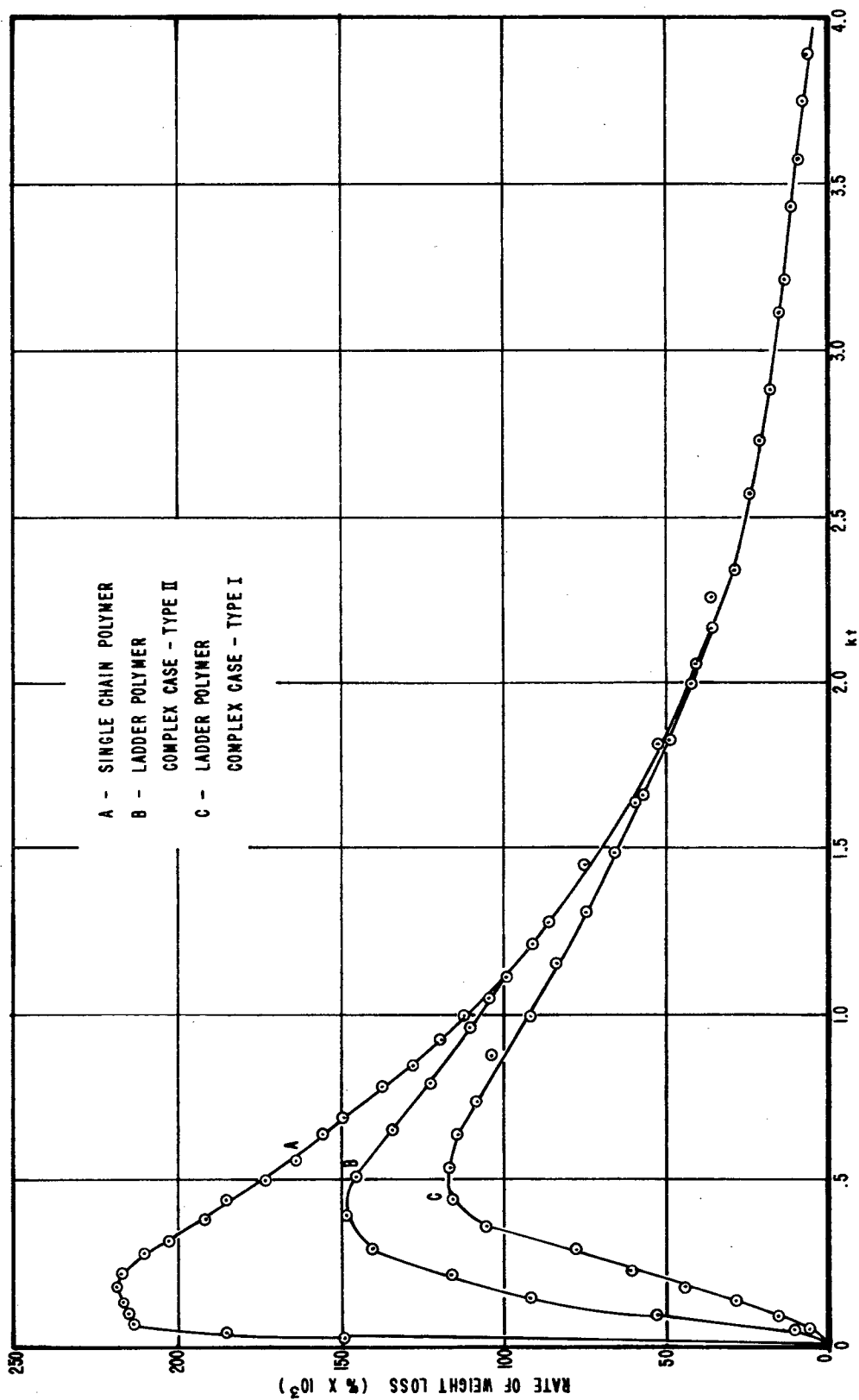


Figure 5. Plot of Rate of Weight Loss Versus Time for Complex Case Ladder Polymers Undergoing Random Degradation.

APPENDIX I
COMPUTER PROGRAM
VAPORIZATION OF SINGLE CHAIN POLYMER

```

C10 VOLATIZATION OF SINGLE CHAIN FROM RANDOM NUMBER GENERATION
DIMENSION L(100,200),E(10)
FREQUENCY 7(5,1,0),110(9,1,1),194(5,1,0),118(1,1,9),196(5,1,0)
1,151(0,1,9),200(0,1,1),204(0,1,1)
DO 25 IX=1,70
DO 24 I=1,200
R=RAND1(Y)*19900.
NR=R
ML=NR/199+1
NB=199*ML-NR
7 IF(L(ML,NB)-1)28,11,11
28 L(ML,NB)=1
C VAPORIZATION OCCURS WHEN CHAIN IS TEN ATOMS OR LESS
DO 103 KW=1,10
110 IF(NB+KW-199)104,104,105
104 NBACKW=NB+KW
194 IF(L(ML,NBACKW)-1)103,105,105
103 CONTINUE
C CHECKED ALL BREAKS TO THE RIGHT
GO TO 150
105 KB=KW
E(KB)=E(KB)+1.
DO 125 KK=1,KW
NBACK=NB+KK
200 IF(1-L(ML,NBACK))125,125,201
201 BVOL=BVOL+1.
125 L(ML,NBACK)=1
C VAPORIZED SEGMENTS REMOVED FROM SYSTEM
150 DO 115 KW=1,10
118 IF(NB-KW)108,108,116
116 NBACKW=NB-KW
196 IF(L(ML,NBACKW)-1)115,108,108
115 CONTINUE
C CHECKED ALL BREAKS TO THE LEFT
GO TO 24
108 KB=KW
E(KB)=E(KB)+1.
DO 126 KK=1,KW
NBACK=NB-KK
204 IF(1-L(ML,NBACK))126,126,205
205 BVOL=BVOL+1.
126 L(ML,NBACK)=1

```

```

C VAPORIZED SEGMENTS REMOVED FROM SYSTEM
  GO TO 24
  NDUP=NDUP+1
  24 CONTINUE
  XI=IX
  DUPN=DUPN
  TIME=LOGF(19900./(19900.-200.*XI+DUPN-BVOL))
C MOLECULAR WEIGHT OF EACH ATOM IS 14
  VOL=E(1)*14.+E(2)*28.+E(3)*42.+E(4)*56.+E(5)*70.+E(6)*84.
  1 +E(7)*98.+E(8)*112.+E(9)*126.+E(10)*140.
  PCVOL=100.*VOL/(200.*1400.)
  DIMENSION A(70),T(70)
  A(IX)=VOL
  T(IX)=TIME
  151 IF(IX-1)152,152,155
  155 IY=IX-1
  DWT=(A(IX)-A(IY))/(T(IX)-T(IY))
  GO TO 153
  152 DWT=A(IX)/T(IX)
  153 WRITE OUTPUT TAPE 3,30,PCVOL,TIME,DWT,NDUP,VOL
  30 FORMAT(IX,3F20.6,I15,F20.2)
  25 CONTINUE
  CALL EXIT
  END
)1 (X- - (G7
  *J -9(NZ5GA 7 -2 -E -G - 3 5- - 97 95 -- 94 78 -- -5 -5 -7 -- 4E -4 -070SQU01
  *U7(P($T 9 -G 5484 -1 -9 -5- - 2(X) - 9 - 070SQU02

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APPENDIX II
COMPUTER PROGRAM
VAPORIZATION OF LADDER POLYMER
SIMPLE CASE - TYPE I

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C9 TYPE I LADDER POLYMER FOUR OR LESS LADDER UNITS VOLATILE
  DIMENSION L(100,200),E(6)
  FREQUENCY 7(1,0,2),8(5,1,1),9(5,1,1),110(9,1,1),194(5,1,0)
  1,118(1,1,9),196(5,1,0),4(1,0,1),10(5,1,1),13(1,1,5),133(9,1,1)
  2,184(5,1,0),140(1,1,9),192(5,1,0),14(5,1,1),150(0,1,9)
  3,200(1,1,3),203(1,1,3),206(1,1,3),210(1,1,3),213(1,1,3)
  4,216(1,1,3),220(1,1,3),223(1,1,3),226(1,1,3),230(1,1,3)
  5,233(1,1,3),236(1,1,3),320(0,1,9),330(0,1,9),360(0,1,9),390(0,1,9)
  6,500(1,1,5),310(1,1,5),600(1,1,5),340(1,1,5),610(1,1,5),370(1,1,5)
  7,620(1,1,5),400(1,1,5)
  DO 25 IX=1, 40
  DO 24 I=1,800
  R=RANDI(Y)*19900.
  NR=R
  ML=NR/199+1
  NB=199*ML-NR
  7 IF(NB-66)8,8,4
  8 IF(L(ML,NB)-1)28,11,11
  28 L(ML,NB)=1
  9 IF(L(ML,NB+66)-1)24,100,100
  100 L(ML,NB)=2
  L(ML,NB+66)=2
  C MOLECULE IS BROKEN
  DO 103 KW=1,5
  110 IF(NB+KW-66)104,104,105
  104 NBAKW=NB+KW
  194 IF(L(ML,NBAKW)-2)103,105,105
  103 CONTINUE
  C CHECKED ALL BREAKS TO THE RIGHT
  GO TO 114
  105 KB=KW
  E(KB)=E(KB)+1.
  KW=KB-1
  320 IF(KW)310,310,300
  300 DO 125 KK=1,KW
  NBAKK=NB+KK
  200 IF(1-L(ML,NBAKK))201,201,202
  202 BVOL=BVOL+1.
  201 L(ML,NBAKK)=2
  NN=NB+66+KK
  203 IF(1-L(ML,NN))204,204,205
  205 BVOL=BVOL+1.

```

```

204 L(ML,NN)=2
    NY=NB+132+KK
206 IF(1-L(ML,NY))125,125,207
207 BVOL=BVOL+1.
125 L(ML,NY)=2
500 IF(1-L(ML,NY+1))501,501,502
502 BVOL=BVOL+1.
501 L(ML,NY+1)=2
310 IF(1-L(ML,NB+133))503,503,504
504 BVOL=BVOL+1.
503 L(ML,NB+133)=2
C VAPORIZED SEGMENTS REMOVED FROM SYSTEM
114 DO 115 KW=1,5
118 IF(NB-KW)108,108,116
116 NBAKW=NB-KW
196 IF(L(ML,NBAKW)-2)115,108,108
115 CONTINUE
C CHECKED ALL BREAKS TO THE LEFT
GO TO 24
108 KB=KW
    E(KB)=E(KB)+1.
    KW=KB-1
330 IF(KW)340,340,350
350 DO 131 KK=1,KW
    NBAKK=NB-KK
210 IF(1-L(ML,NBAKK))211,211,212
212 BVOL=BVOL+1.
211 L(ML,NBAKK)=2
    NN=NB+66-KK
213 IF(1-L(ML,NN))214,214,215
215 BVOL=BVOL+1.
214 L(ML,NN)=2
    NY=NB+133-KK
216 IF(1-L(ML,NY))131,131,217
217 BVOL=BVOL+1.
131 L(ML,NY)=2
600 IF(1-L(ML,NY-1))505,505,506
506 BVOL=BVOL+1.
505 L(ML,NY-1)=2
340 IF(1-L(ML,NB+132))507,507,508
508 BVOL=BVOL+1.
507 L(ML,NB+132)=2

```

```

C VAPORIZED SEGMENTS REMOVED FROM SYSTEM
GO TO 24
4  IF(NB-132)10,10,14
10 IF(L(ML,NB)-1)17,11,11
17 L(ML,NB)=1
13 IF(1-L(ML,NB-66))120,120,24
120 L(ML,NB)=2
    L(ML,NB-66)=2
C MOLECULE IS BROKEN
DO 132 KW=1,5
133 IF(NB+KW-132)134,134,135
134 NBAKW=NB+KW
184 IF(L(ML,NBAKW)-2)132,135,135
132 CONTINUE
C CHECKED ALL BREAKS TO THE RIGHT
GO TO 138
135 KB=KW
    E(KB)=E(KB)+1.
    KW=KB-1
360 IF(KW)370,370,380
380 DO 136 KK=1,KW
    NBAKK=NB+KK
220 IF(1-L(ML,NBAKK))221,221,222
222 BVOL=BVOL+1.
221 L(ML,NBAKK)=2
    NN=NB-66+KK
223 IF(1-L(ML,NN))224,224,225
225 BVOL=BVOL+1.
224 L(ML,NN)=2
    NY=NB+66+KK
226 IF(1-L(ML,NY))136,136,227
227 BVOL=BVOL+1.
136 L(ML,NY)=2
610 IF(1-L(ML,NY+1))509,509,510
510 BVOL=BVOL+1.
509 L(ML,NY+1)=2
370 IF(1-L(ML,NB+67))511,511,512
512 BVOL=BVOL+1.
511 L(ML,NB+67)=2
C VAPORIZED SEGMENTS REMOVED FROM SYSTEM
138 DO 139 KW=1,5
140 IF(NB-KW-66)148,148,142

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ML-TDR-64-151
Part II

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142 NBAKW=NB-KW
192 IF(L(ML,NBAKW)-2)139,148,148
139 CONTINUE
C CHECKED ALL BREAKS TO THE LEFT
GO TO 24
148 KB=KW
E(KB)=E(KB)+1.
KW=KB-1
390 IF(KW)400,400,410
410 DO 149 KK=1,KW
NBAKK=NB-KK
230 IF(1-L(ML,NBAKK))231,231,232
232 BVOL=BVOL+1.
231 L(ML,NBAKK)=2
NN=NB-66-KK
233 IF(1-L(ML,NN))234,234,235
235 BVOL=BVOL+1.
234 L(ML,NN)=2
NY=NB+67-KK
236 IF(1-L(ML,NY))149,149,237
237 BVOL=BVOL+1.
149 L(ML,NY)=2
620 IF(1-L(ML,NY-1))513,513,514
514 BVOL=BVOL+1.
513 L(ML,NY-1)=2
400 IF(1-L(ML,NB+66))515,515,516
516 BVOL=BVOL+1.
515 L(ML,NB+66)=2
C VAPORIZED SEGMENTS REMOVED FROM SYSTEM
GO TO 24
14 IF(L(ML,NB)-1)12,11,11
12 L(ML,NB)=1
GO TO 24
11 NDUP=NDUP+1
24 CONTINUE
XI=IX
DUPN=NDUP
TIME=LOGF(19900./((19900.-800.*XI+DUPN-BVOL)))
C MOLECULAR WEIGHT OF EACH ATOM IS 14
VOL=E(1)*28.+E(2)*56.+E(3)*84.+E(4)*112.+E(5)*140.
PCVOL=100.*VOL/(134.*1400.)
DIMENSION A(70),T(70)

```

```

A(IX)=VOL
T(IX)=TIME
150 IF(IX-1)152,152,155
155 IY=IX-1
DWT=(A(IX)-A(IY))/(T(IX)-T(IY))
GO TO 153
152 DWT=A(IX)/T(IX)
153 WRITE OUTPUT TAPE 3,30,PCVOL,TIME,DWT,NDUP,VOL
30 FORMAT(IX,3F20.6,I15,F20.2)
25 CONTINUE
CALL EXIT
END
)1 (X- - (G7
*J -9(NZ5GA 7 -2 -E -G - 3 5- - 97 95 -- 94 78 -- -5 -5 -7 -- 4E -4 -070SQU00
*U7(P($T 9 -G 5484 -1 -9 -5 - 2(X) - 9 - .070SQU002

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ML-TDR-64-151
Part II

APPENDIX III
COMPUTER PROGRAM
VAPORIZATION OF LADDER POLYMER
SIMPLE CASE - TYPE II

```

C14 TYPE II LADDER POLYMER TWO OR LESS LADDER UNITS VOLATILE
FREQUENCY 7(1,0,2),8(0,1,1),700(1,1,0),40(1,1,5),42(1,1,5)
1,41(1,1,5),43(1,1,5),110(9,1,1),194(9,1,0),320(0,1,9),200(1,1,5)
2,702(1,1,0),703(0,1,5),704(0,1,5),711(9,1,1),714(5,1,0),716(0,1,9)
3,723(1,1,5),731(1,1,5),118(1,1,9),122(5,1,0),330(0,1,9),813(1,1,5)
4,742(1,1,0),743(0,1,5),744(0,1,5),751(1,1,9),757(5,1,0),758(0,1,9)
5,762(1,1,5),770(1,1,5),4(1,0,1),10(0,1,1),400(1,1,0),401(1,1,5)
6,404(1,1,5),402(1,1,5),412(1,1,5),340(9,1,1),343(5,1,0),344(0,1,9)
7,348(1,1,5),350(1,1,0),351(0,1,5),352(0,1,5),361(9,1,1),365(5,1,0)
8,371(0,1,9),374(1,1,5),381(1,1,5),384(9,1,1),387(5,1,0),391(0,1,9)
9,394(1,1,5),600(1,1,0),601(0,1,5),602(0,1,5),611(1,1,9),614(5,1,0)
FREQUENCY 630(0,1,9),634(1,1,5),661(1,1,5),14(5,1,1),690(0,1,9)
1,260(0,1,5),270(0,1,5),281(0,1,5),290(0,1,5)
2,910(1,1,5),900(1,1,0),940(0,1,5),941(0,1,5),947(0,1,1),980(0,1,1)
3,948(0,1,1),951(0,1,1),981(0,1,1),952(0,1,1),960(3,0,1)
DIMENSION L(100,200),E(6)
DO 25 IX=1,60
DO 24 I=1,800
R=RANDI(Y)*19600.
NR=R
ML=NR/196+1
NB=196*ML-NR
960 IF(NB-156)910,910,14
910 IF(1-L(ML,NB))11,11,911
911 NA=NB/2
900 IF(2*NA-NB)940,941,940
940 IF(2-L(ML,NB+1))942,943,942
942 LOP=0
LOPP=0
C LOP=0 MEANS ADJACENT BOND NOT BROKEN///IF LOP=1,ADJACENT BOND BROKEN
C LOPP=0 MEANS NB IS ODD NUMBER///LOOP=1 MEANS NB IS EVEN NUMBER
GO TO 7
943 L(ML,NB)=2
LOP=1
LOPP=0
E(1)=E(1)+1.
GO TO 7
941 IF(2-L(ML,NB-1))944,945,944
944 LOPP=1
LOP=0
GO TO 7
945 LOPP=1

```

```

LOP=1
L(ML,NB)=2
E(1)=E(1)+1.
GO TO 7
7 IF(NB-78)8,8,4
8 IF(1-LOP)947,947,28
947 IF(LOPP)114,114,701
28 L(ML,NB)=1
NA=NB/2
700 IF(2*NA-NB)40,41,40
40 IF(1-L(ML,NB+78))100,100,42
42 IF(1-L(ML,NB+79))101,101,24
101 L(ML,NB+79)=2
GO TO 105
100 L(ML,NB+78)=2
105 L(ML,NB)=2
GO TO 701
41 IF(1-L(ML,NB+78))102,102,43
43 IF(1-L(ML,NB+77))203,203,24
203 L(ML,NB+77)=2
GO TO 104
102 L(ML,NB+78)=2
104 L(ML,NB)=2
C MOLECULE IS BROKEN
701 DO 103 KW=1,5
110 IF(NB+KW-78)106,106,800
106 NBAKW=NB+KW
194 IF(L(ML,NBAKW)-2)103,800,800
103 CONTINUE
C CHECKED ALL BREAKS TO THE RIGHT ON TOP
GO TO 980
800 NA=NB/2
NKW=KW
702 IF(2*NA-NB)703,704,703
703 IF(2-L(ML,NB+78))707,705,707
707 NBA=NB+79
GO TO 706
705 NBA=NB+78
GO TO 706
704 IF(2-L(ML,NB+78))708,709,708
708 NBA=NB+77
GO TO 706

```

```
709 NBA=NB+78
706 DO 710 KV=1,5
711 IF(NBA+KV-156)712,712,715
712 NBAKV=NBA+KV
714 IF(L(ML,NBAKV)-2)710,715,715
710 CONTINUE
      GO TO 980
C CHECKED ALL BREAKS TO THE RIGHT ON BOTTOM
715 E(KV)=E(KV)+1.
      NBAKV=NBA+KV
      KV=KV-1
716 IF(KV)108,108,721
721 DO 722 KK=1,KV
      NBAKK=NBA+KK
723 IF(1-L(ML,NBAKK))722,722,725
725 BVOL=BVOL+1.
722 L(ML,NBAKK)=2
108 KW=NKW
      E(KW)=E(KW)+1.
      KW=KW-1
320 IF(KW)310,310,300
300 DO 125 KK=1,KW
      NBAKK=NB+KK
200 IF(1-L(ML,NBAKK))125,125,202
202 BVOL=BVOL+1.
125 L(ML,NBAKK)=2
310 NW=NB-NB/2+157
      NX=NBAKV-78-(NBAKV-78)/2+157
      KB=NX-NW
260 IF(KB)980,980,251
251 DO 730 KK=1,KB
      NBAKK=NW-1+KK
731 IF(1-L(ML,NBAKK))730,730,733
733 BVOL=BVOL+1.
730 L(ML,NBAKK)=2
C VAPORIZED SEGMENTS REMOVED FROM SYSTEM
980 IF(LOP)114,114,948
948 IF(LOPP)114,114,24
114 DO 115 KW=1,5
118 IF(NB-KW)810,810,121
121 NBAKW=NB-KW
122 IF(L(ML,NBAKW)-2)115,810,810
```

115 CONTINUE
C CHECKED ALL BREAKS TO LEFT ON TOP
GO TO 24
810 NA=NB/2
NKW=KW
742 IF(2*NA-NB)743,744,743
743 IF(2-L(ML,NB+78))747,745,747
747 NBA=NB+79
GO TO 746
745 NBA=NB+78
GO TO 746
744 IF(2-L(ML,NB+78))748,749,748
748 NBA=NB+77
GO TO 746
749 NBA=NB+78
746 DO 750 KV=1,5
751 IF(NBA-KV-79)755,756,756
756 NBAKV=NBA-KV
757 IF(L(ML,NBAKV)-2)750,755,755
750 CONTINUE
GO TO 24
C CHECKED ALL BREAKS TO THE LEFT ON BOTTOM
755 E(KV)=E(KV)+1.
NBAKV=NBA-KV
KV=KV-1
758 IF(KV)120,120,761
761 DO 781 KK=1,KV
NBAKK=NBA-KK
762 IF(1-L(ML,NBAKK))781,781,764
764 BVOL=BVOL+1.
781 L(ML,NBAKK)=2
120 KW=NKW
E(KW)=E(KW)+1.
KW=KW-1
330 IF(KW)760,760,811
811 DO 812 KK=1,KW
NBAKK=NB-KK
813 IF(1-L(ML,NBAKK))812,812,814
814 BVOL=BVOL+1.
812 L(ML,NBAKK)=2
760 NW=NB-NB/2+157
NX=NBAKV-78-(NBAKV-78)/2+157

ML-TDR-64-151
Part II

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KB=NW-NX
270 IF(KB)24,24,252
252 DO 765 KK=1,KB
    NBAKK=NW-KK
770 IF(1-L(ML,NBAKK))765,765,772
772 BVOL=BVOL+1.
765 L(ML,NBAKK)=2
C VAPORIZED SEGMENTS REMOVED FROM SYSTEM
GO TO 24
4 IF(NB-156)10,10,14
10 IF(LOP)29,29,951
951 IF(LOPP)339,339,410
29 L(ML,NB)=1
NA=NB/2
400 IF(2*NA-NB)401,402,401
401 IF(1-L(ML,NB-78))403,403,404
404 IF(1-L(ML,NB-77))405,405,24
405 L(ML,NB-77)=2
GO TO 406
403 L(ML,NB-78)=2
406 L(ML,NB)=2
GO TO 410
402 IF(1-L(ML,NB-78))411,411,412
412 IF(1-L(ML,NB-79))413,413,24
413 L(ML,NB-79)=2
GO TO 420
411 L(ML,NB-78)=2
420 L(ML,NB)=2
C MOLECULE IS BROKEN
410 DO 421 KW=1,5
340 IF(NB+KW-156)341,341,345
341 NBAKW=NB+KW
343 IF(L(ML,NBAKW)-2)421,345,345
421 CONTINUE
C CHECKED ALL BREAKS TO THE RIGHT ON BOTTOM
GO TO 981
345 NA=NB/2
NKW=KW
350 IF(2*NA-NB)351,352,351
351 IF(2-L(ML,NB-78))353,353,353
353 NBA=NB-77
GO TO 360

```

```

354 NBA=NB-78
GO TO 360
352 IF(2-L(ML,NB-78))355,356,355
355 NBA=NB-79
GO TO 360
356 NBA=NB-78
DO 370 KV=1,5
360 IF(NBA+KV-78)362,362,363
361 NBAKV=NBA+KV
362 IF(L(ML,NBAKV)-2)370,363,363
363 CONTINUE
GO TO 981
C CHECKED ALL BREAKS TO THE RIGHT ON TOP
363 E(KV)=E(KV)+1.
NBAKV=NBA+KV
KV=KV-1
371 IF(KV)342,342,373
373 DO 380 KK=1,KV
NBAKK=NBA+KK
374 IF(1-L(ML,NBAKK))380,380,376
376 BVOL=BVOL+1.
380 L(ML,NBAKK)=2
342 KW=NKW
E(KW)=E(KW)+1.
KW=KW-1
344 IF(KW)372,372,346
346 DO 347 KK=1,KW
NBAKK=NB+KK
348 IF(1-L(ML,NBAKK))347,347,349
349 BVOL=BVOL+1.
347 L(ML,NBAKK)=2
372 NW=NB-78-(NB-78)/2+157
NX=NBAKV-NBAKV/2+157
KB=NX-NW
281 IF(KB)981,981,358
358 DO 280 KK=1,KB
NBAKK=NW-1+KK
381 IF(1-L(ML,NBAKK))280,280,383
383 BVOL=BVOL+1.
280 L(ML,NBAKK)=2
C VAPORIZED SEGMENTS REMOVED FROM SYSTEM
981 IF(LOP)339,339,952

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Part II

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952 IF(LOPP)339,339,24
339 DO 390 KW=1,5
384 IF(NB-KW-78)392,392,386
386 NBAKW=NB-KW
387 IF(L(ML,NBAKW)-2)390,392,392
390 CONTINUE
C CHECKED ALL BREAKS TO LEFT ON BOTTOM
GO TO 24
392 NA=NB/2
NKW=KW
600 IF(2*NA-NB)601,602,601
601 IF(2-L(ML,NB-78))603,604,603
603 NBA=NB-77
GO TO 610
604 NBA=NB-78
GO TO 610
602 IF(2-L(ML,NB-78))605,606,605
605 NBA=NB-79
GO TO 610
606 NBA=NB-78
610 DO 620 KV=1,5
611 IF(NBA-KV)612,612,613
613 NBAKV=NBA-KV
614 IF(L(ML,NBAKV)-2)620,612,612
620 CONTINUE
GO TO 24
C CHECKED ALL BREAKS TO THE LEFT ON TOP
612 E(KV)=E(KV)+1.
NBAKV=NBA-KV
KV=KV-1
630 IF(KV)388,388,632
632 DO 640 KK=1,KV
NBAKK=NBA-KK
634 IF(1-L(ML,NBAKK))640,640,635
635 BVOL=BVOL+1.
640 L(ML,NBAKK)=2
388 KW=NKW
E(KW)=E(KW)+1.
KW=KW-1
391 IF(KW)631,631,393
393 DO 399 KK=1,KW
NBAKK=NB-KK

```

Part II

```

394 IF(1-L(ML,NBAKK))399,399,395
395 BVOL=BVOL+1.
399 L(ML,NBAKK)=2
631 NW=NBAKV-NBAKV/2+157
    NX=NB-78-(NB-78)/2+157
    KB=NX-NW
290 IF(KB)24,24,259
259 DO 660 KK=1,KB
    NBAKK=NX-KK
661 IF(1-L(ML,NBAKK))660,660,662
662 BVOL=BVOL+1.
660 L(ML,NBAKK)=2
C VAPORIZED SEGMENTS REMOVED FROM SYSTEM
GO TO 24
14 IF(L(ML,NB)-1)688,11,11
688 L(ML,NB)=1
GO TO 24
11 NDUP=NDUP+1
24 CONTINUE
XI=IX
DUPN=NDUP
TIME=LOGF(19600./((19600.-800.*XI+DUPN-BVOL))
C MOLECULAR WEIGHT OF EACH ATOM IS 14
VOL=E(1)*14.+E(2)*28.+E(3)*42.+E(4)*56.+E(5)*70.
PCVOL=100.*VOL/(158.*1400.)
DIMENSION A(70),T(70)
A(IX)=VOL
T(IX)=TIME
690 IF(IX-1)691,691,692
692 IY=IX-1
    DWT=(A(IX)-A(IY))/(T(IX)-T(IY))
GO TO 695
691 DWT=A(IX)/T(IX)
695 WRITE OUTPUT TAPE 3,30,PCVOL,TIME,DWT,NDUP,VOL
30 FORMAT(1X,3F20.6,I15,F20.2)
25 CONTINUE
CALL EXIT
END
)1 (X- - (G7
*J -9(NZ5GA 7 -2 -E -G - 3 5- - 97 95 -- 94 78 -- -5 -5 -7 --- 4E -4 -070SQU01
*U7(P($ 9 -G 5484 -1 -9 -5 - 2(X) - 9 - 070SQU02

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APPENDIX IV
COMPUTER PROGRAM
VAPORIZATION OF LADDER POLYMER
COMPLEX CASE - TYPE I

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C25 TYPE I COMPLEX-10 ATOMS OR LESS VOLATILE
WRITE OUTPUT TAPE 3,111
111 FORMAT(8X,5HPCVOL,12X,4HTIME,11X,3HDWT,11X,4HNDUP,6X,3HVOL,
1 10X, 4HBVOL,12X,1HE,11X,2HEE,9X,2HXI)
DIMENSION L(100,200)
FREQUENCY 1(0,1,5),2(1,0,2),8(9,1,1),400(0,2,1),404(0,2,1),4(1,0,1
1),480(9,1,1),426(0,2,1),430(0,2,1),482(0,0,9),486(5,1,1),489(5,1,1
2),497(5,1,1),502(0,1,1),503(0,1,1),702(9,0,0),706(5,1,1),511(5,1,1
3),531(5,1,1),541(0,1,1),542(0,1,1),600(0,1,9)
COMMON L,NB,NBA,E,BVOL,IEE,IND,LA,LB,LC,ML,GOG,GAG
DO 25 IX=1,25
DO 24 I=1,600
R=Rand1(Y)*19900.
NR=R
ML=NR/199+1
NB=199*ML-NR
GAG=0
GOG=0
LC=0
C UNBROKEN BOND=0 BROKEN BOND=1 OPPOSITE BROKEN MOLECULE=3
C ADJACENT BROKEN MOLECULE=2 VAPORIZED BOND FROM OPPOS. BROKEN MOL.=4
C WHEN OPPOSITE BOND IS ALREADY 2, IT BECOMES 5 RATHER THAN 3
C IF NBA IS ORIGINALLY 3,4,OR 5 AND NBA+LB-LA IS 3,4, OR 5, THEN GAG=1 AND
C AND IEE=1.
1 IF(1-L(ML,NB))11,11,7
7 L(ML,NB)=1
2 IF(NB-66)8,8,4
C CHECK OPPOSITE BOND
8 IF(L(ML,NB+66)-1)12,13,13
13 L(ML,NB)=3
IF(L(ML,NB+66)-2)711,712,741
712 L(ML,NB+66)=5
GO TO 713
741 GOG=1.
711 L(ML,NB+66)=3
C MOLECULEE IS BROKEN
C IND=0 MEANS NO VAPORIZATION HAS OCCURED. IND=1 MEANS VAPORIZ. OCCURED.
713 NBA=NB+66
C CHECK TO LEFT NEXT
GAG=GOG
CALL MVAP(0,1,0)
400 IF(IND)12,12,402

```

```

12 NBA=NB+66
   GAG=0
   CALL MLNK(0,1,0)
402 NBA=NB+66
   IF(L(ML,NB+66)-1)405,900,900
   C CHECK TO RIGHT NEXT
900 GAG=GOG
   CALL MVAP(1,0,67)
404 IF(IND)405,405,24
405 GAG=0
   CALL MLNK(1,0,67)
   GO TO 24
   4 IF(NB-132)480,480,481
480 IF(L(ML,NB-66)-1)420,421,421
   C CHECKED OPPOSITE BOND
421 L(ML,NB)=3
   IF(L(ML,NB-66)-2)714,715,744
715 L(ML,NB-66)=5
   GO TO 716
744 GOG=1.
714 L(ML,NB-66)=3
   C MOLECULE IS BROKEN
716 NBA=NB-66
   C CHECK TO LEFT NEXT
   GAG=GOG
   CALL MVAP(0,1,0)
426 IF(IND)420,420,428
420 NBA=NB-66
   GAG=0
   CALL MLNK(0,1,0)
428 NBA=NB-66
   C CHECK TO RIGHT NEXT
   IF(L(ML,NB-66)-1)431,901,901
901 GAG=GOG
   CALL MVAP(1,0,67)
430 IF(IND)431,431,24
431 GAG=0
   CALL MLNK(1,0,67)
   GO TO 24
   C BROKEN BOND IS CROSSLINK
481 DO 485 K=1,67
482 IF(NB-K-133)483,484,484
484 NBK=NB-K

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```

486 IF(L(ML,NBK)-1)487,485,485
485 CONTINUE
C ALL CROSSLINKS TO THE LEFT CHECKED
487 DO 488 KK=1,K
    NX=NB-132-KK
489 IF(L(ML,NX)-1)488,490,490
488 CONTINUE
    NB1=0
    GO TO 495
490 NB1=NX
C CHECKED ADJACENT BONDS TO THE LEFT - NB LESS 66
C MUST ALSO CHECK ASSUMED NB FOR GAG WHEN ORIGINAL NB IS CROSSLINK.
C LC=1 IF NB IS 3,4, OR 5 AND NB + LB-LA IS 3,4, OR 5
495 DO 496 KK=1,K
    NX=NB-66-KK
497 IF(L(ML,NX)-1)496,498,498
496 CONTINUE
    NB2=0
    GO TO 500
C CHECKED OPPOSITE BONDS TO THE LEFT - NB MORE THAN 66
498 NB2=NX
500 NBA1=NB
502 IF(NB1)503,503,504
504 NB=NB1
    GAG=0
    IF(L(ML,NB1)-2)640,640,641
640 LC=0
    GO TO 642
641 LC=1
642 CALL MLNK(1,0,67)
503 IF(NB2)800,800,506
506 NB=NB2
    GAG=0
    IF(L(ML,NB2)-2)644,644,645
644 LC=0
    GO TO 646
645 LC=1
646 CALL MLNK(1,0,67)
800 NB=NBA1
    GO TO 24
483 DO 705 K=1,67
702 IF(NB+K-199)703,703,704
703 NX=NB+K

```

```

706 IF(L(ML,NX)-1)710,705,705
705 CONTINUE
C ALL CROSSLINKS TO THE RIGHT CHECKED
704 K=K-1
710 DO 550 KK=1,K
    NX=NB-133+KK
511 IF(L(ML,NX)-1)550,513,513
550 CONTINUE
    NB3=0
    GO TO 530
513 NB3=NX
C CHECKED ADJACENT BONDS TO THE RIGHT - NB LESS 66
530 DO 551 KK=1,K
    NX=NB-67+KK
531 IF(L(ML,NX)-1)551,533,533
551 CONTINUE
    NB4=0
    GO TO 540
C CHECKED OPPOSITE BOND TO THE RIGHT - NB MORE THAN 66
533 NB4=NX
540 NBA1=NB
541 IF(NB3)542,542,543
543 NB=NB3
    GAG=0
    IF(L(ML,NB3)-2)780,780,781
780 LC=0
    GO TO 782
781 LC=1
782 CALL MLNK(0,1,0)
542 IF(NB4)544,544,545
545 NB=NB4
    IF(L(ML,NB4)-2)790,790,791
790 LC=0
    GO TO 792
791 LC=1
792 CALL MLNK(0,1,0)
544 NB=NBA1
    GO TO 24
11 NDUP=NDUP+1
24 CONTINUE
    XI=IX
    DUPN=NDUP
    TIME=LOGF(19900./(19900.-600.*XI+DUPN-BVOL))

```

```

EE=IEE
VOL=14.*(E-EE)
PCVOL=100.*VOL/(1400.*134.)
DIMENSION A(70),T(70)
A(IX)=VOL
T(IX)=TIME
600 IF(IX-1)601,601,602
602 IY=IX-1
DWT=(A(IX)-A(IY))/(T(IX)-T(IY))
GO TO 603
601 DWT=A(IX)/T(IX)
603 WRITE OUTPUT TAPE 3,30,PCVOL,TIME,DWT,NDUP,VOL,BVOL,E,EE,XI
30 FORMAT(1X,3F16.6,110,5F12.1)
25 CONTINUE
CALL EXIT
END
SUBROUTINE MVAP(LAD,LBD,LCD)
DIMENSION L(100,200)
FREQUENCY 30(1,1,9),33(1,0,1),39(1,1,9),44(5,1,1),801(5,1,1),
152(1,0,1),802(5,1,1),59(1,0,1),363(5,1,1)
COMMON L,NB,NBA,E,BVOL,IEE,IND,LA,LB,LC,ML,GOG,GAG
LA=LAD
LB=LBD
C CHECK IF BROKEN MOLECULE RESULTS IN VAPORIZATION
DO 29 K=1,7
30 IF((LB-LA)*NB+(LA-LB)*K*(1-2*LA)+67*LA+66*(NB/67)*(LA-LB))35,35,32
32 NBK=NB+(LA-LB)*K
33 IF(L(ML,NBK)-2)29,29,35
29 CONTINUE
C CHECKED FOR BROKEN MOLECULE ON ADJACENT SIDE
GO TO 45
35 LN=K
DO 38 K=1,7
39 IF((LB-LA)*NBA+(LA-LB)*K*(1-2*LA)+67*LA+66*(NBA/67)*(LA-LB))
1 43,43,41
41 NBK=NBA+(LA-LB)*K
42 IF(L(ML,NBK)-2)38,38,43
38 CONTINUE
GO TO 45
C CHECKED FOR BROKEN MOLECULE ON OPPOSITE SIDE
43 LN1=K
44 IF(LN+LN1-10)46,46,45

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```

45 IND=0
RETURN
46 IF(LN-1)946,901,946
901 IF(LC)946,946,902
902 IF(LB-LA)*NB+(LA-LB)* (1-2*LA)+67*LA+66*(NB/67)*(LA-LB)
1 920,920,905
905 NLN=NB+LB-LA
IF(L(ML,NLN)-2)946,946,920
946 DO 50 K=1,LN
C MOLECULE HAS VAPORIZED
NLN=NB+(LA-LB)*K+LB-LA
801 IF(L(ML,NLN)-1)51,52,52
51 BVOL=BVOL+1.
52 IF(L(ML,NLN)-2)54,50,54
54 IF(L(ML,NLN)-5)800,50,800
800 E=E+1.
50 L(ML,NLN)=4
C VAPORIZED ADJACENT BONDS
920 IF(LN1-1)756,721,756
721 IF(GAG)756,756,725
725 IF(LB-LA)*NBA+(LA-LB)*(1-2*LA)+67*LA+66*(NBA/67)*(LA-LB)780,
1780,758
758 NLN=NBA+LB-LA
IF(L(ML,NLN)-2)756,756,780
756 DO 57 K=1,LN1
NLN=NBA+(LA-LB)*K+LB-LA
802 IF(L(ML,NLN)-1)58,59,59
58 BVOL=BVOL+1.
59 IF(L(ML,NLN)-2)60,80,60
60 IF(L(ML,NLN)-5)811,80,811
811 E=E+1.
80 L(ML,NLN)=4
C VAPORIZED OPPOSITE BONDS
NYY=NB+132+LB+(LA-LB)*K-(NB/67)*(66)
363 IF(L(ML,NYY)-1)63,57,57
63 BVOL=BVOL+1.
57 L(ML,NYY)=4
C VAPORIZED CROSSLINKS
780 IND=1
RETURN
END
SUBROUTINE MLNK(LAD,LBD,LCD)
DIMENSION L(100,200)

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ML-TDR-64-151
Part II

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FREQUENCY 100(1,1,9),106(5,1,1),107(0,1,1),810(5,1,1),811(0,1,1),
1105(0,1,2),815(5,1,1),133(5,1,1),156(5,1,1),161(5,1,1),163(6,1,1),
2152(0,1,1)
COMMON L,NB,NBA,E,BVOL,IEE,IND,LA,LB,LC,ML,GOG,GAG
LA=LAD
LB=LBD
C CHECK IF BROKEN CROSSLINKS GIVE BROKEN MOLECULE
DO 104 K=1,11
  NY=NB+132+LB+(LA-LB)*K-(NB/67)*(66)
  100 IF(200*LA+(LB-LA)*NY-132*LB)105,105,106
  106 IF(L(ML,NY)-1)107,104,104
  104 CONTINUE
  K=11
  GO TO 109
  107 IF(K-1)108,108,109
  108 RETURN
  109 K=K-1
  DO 110 KK=1,K
    NBA=NB+ 66+(LA-LB)*KK-(NB/67)*(132)
    810 IF(L(ML,NBA)-1)110,150,150
    110 CONTINUE
    C CHECKED IF OPPOSITE BOND IS BROKEN TO GIVE BROKEN MOLECULE
    GO TO 151
    150 L(ML,NB)=3
    IF(L(ML,NBA)-2)717,718,747
    718 L(ML,NBA)=5
    GO TO 719
    747 GAG=1.
    717 L(ML,NBA)=3
    719 CALL MVAP(LA,LB,LC)
    C MOLECULE IS BROKEN
    NBAA=NBA
    811 IF(IND)151,151,152
    105 IF(K-1)130,130,131
    130 RETURN
    131 K=K-1
    DO 120 KK=1,K
      NLN=NB+(LA-LB)*KK+(LB-LA)
      815 IF(L(ML,NLN)-1)132,133,133
      132 BVOL=BVOL+1.
      133 IF(L(ML,NLN)-2)134,135,120
      135 IEE=IEE+1

```

```

134 E=E+1.
    L(ML,NLN)=2
120 CONTINUE
    RETURN
C VAPORIZED ADJACENT BONDS
151 DO 155 KK=1,K
    NBA=NB+(LA-LB)*KK
156 IF(L(ML,NBA)-1)155,158,158
155 CONTINUE
    IF(L(ML,NB)-3)650,152,650
C CHECKED IF ADJACENT BOND IS BROKEN TO GIVE BROKEN MOLECULE
158 DO 168 K=1,KK
    NBA=NB+(LA-LB)*K+LB-LA
161 IF(L(ML,NBA)-1)162,163,163
162 BVOL=BVOL+1.
163 IF(L(ML,NBA)-2)164,165,166
165 IEE=IEE+1
164 E=E+1.
    L(ML,NBA)=2
C VAPORIZED ADJACENT BONDS
    GO TO 168
166 E=E+1.
168 CONTINUE
    IF(L(ML,NB)-3)650,152,650
C IF MOLECULE IS BROKEN,CHECK BOTH DIRECTIONS
152 IF(LA)200,200,201
200 LA=1
    LB=0
    LC=67
    GO TO 210
201 LA=0
    LB=1
    LC=0
210 NBA=NBAA
    CALL MVAP(LA,LB,LC)
650 RETURN
END
)1 (X- - (G7
*J -9(NZ5GA 7 -2 -E -G - 3 5- - 97 95 -- 94 78 -- -5 -5 -7 -- 4E -4 -070SQU01
*U7(P($T 9 -G 5484 -1 -9 -5 - 2(X) - 9 - 070SQU02

```

APPENDIX V
COMPUTER PROGRAM
VAPORIZATION OF LADDER POLYMER
COMPLEX CASE - TYPE II

```

C26 TYPE II COMPLEX - 10 ATOMS OR LESS VOLATILE
      WRITE OUTPUT TAPE 3,111
111  FORMAT(8X,5HPCVOL,12X,4HTIME,11X,3HDWT,11X,4HNDUP,6X,3HVOL,10X,
      14HBVOL,12X,1HE,11X,2HEE,9X,2HXI)
      DIMENSION L(100,200)
      FREQUENCY 1(0,1,5),2(1,0,2),700(1,1,0),40(1,1,5),42(1,1,5),701(1,0
      1,1),802(1,0,1),41(1,1,5),721(1,1,5),724(1,0,1),722(1,0,1),400(0,1,
      21),404(0,1,1),4(1,0,1),740(1,1,0),741(1,1,5),743(1,1,5),745(1,0,1)
      3,751(1,0,1),756(1,1,5),758(1,1,5),760(1,0,1),765(1,0,1),770(0,1,1)
      4,773(0,1,1),482(0,1,9),486(5,1,1),489(9,1,1),497(5,1,1),502(0,1,1)
      5,801(1,0,1),503(0,1,1),803(1,0,1),702(9,1,0),706(5,1,1),511(5,1,1)
      6,531(5,1,1),541(0,1,1),805(1,0,1),542(0,1,1),806(1,0,1),600(0,1,9)
      COMMON L,NB,NBA,E,BVOL,IEE,IND,LA,LB,LC,ML,GOG,GAG
      DO 25 IX=1,25
      DO 24 I=1,600
      R=RANDI(Y)*19600.
      NR=R
      ML=NR/196+1
      NB=196*ML-NR
      GAG=0
      GOG=0
      LC=0
      IF(1-L(ML,NB))11,11,7
      L(ML,NB)=1
      IF(NB-78)8,8,4
      C CHECK OPPOSITE BOND
      NA=NB/2
      700 IF(2*NA-NB)40,41,40
      40 IF(1-L(ML,NB+78))100,100,42
      42 IF(1-L(ML,NB+79))101,101,21
      100 L(ML,NB)=3
      701 IF(L(ML,NB+78)-2)711,712,841
      712 L(ML,NB+78)=5
      GO TO 713
      841 GOG=1.
      711 L(ML,NB+78)=3
      C MOLECULE IS BROKEN
      713 NBA=NB+78
      NNBA=NBA
      GO TO 200
      101 L(ML,NB)=3
      802 IF(L(ML,NB+79)-2)715,716,717

```

```

716 L(ML,NB+79)=5
   GO TO 718
717 GOG=1.
715 L(ML,NB+79)=3
C MOLECULE IS BROKEN
718 NBA=NB+79
   NNBA=NBA
   GO TO 200
41 IF(1-L(ML,NB+78))720,720,721
721 IF(1-L(ML,NB+77))722,722,21
720 L(ML,NB)=3
724 IF(L(ML,NB+78)-2)725,726,727
726 L(ML,NB+78)=5
   GO TO 728
727 GOG=1.
725 L(ML,NB+78)=3
C MOLECULE IS BROKEN
728 NBA=NB+78
   NNBA=NBA
   GO TO 200
722 IF(L(ML,NB+77)-2)730,731,732
731 L(ML,NB+77)=5
   GO TO 733
732 GOG=1.
730 L(ML,NB+77)=3
C MOLECULE IS BROKEN
733 NBA=NB+77
   NNBA=NBA
   GAG=GOG
   CALL MVAP(0,1,0)
400 IF(IND)12,12,402
12 NBA=NNBA
   GAG=0
   CALL MLNK(0,1,0)
402 NBA=NNBA
C CHECK TO RIGHT NEXT
   GAG=GOG
   CALL MVAP(1,0,67)
404 IF(IND)405,405,24
405 GAG=0
   CALL MLNK(1,0,67)
   GO TO 24
21 NBA=NB+78

```

ML-TDR-64-151
Part II

```

GAG=0
CALL MLNK(0,1,0)
GAG=0
NBA=NB+78
CALL MLNK(1,0,67)
GO TO 24
IF(NB-156)480,480,481
NA=NB/2
IF(2*NA-NB)741,756,741
740 IF(1-L(ML,NB-78))742,742,743
741 IF(1-L(ML,NB-77))744,744,22
742 L(ML,NB)=3
743 IF(L(ML,NB-78)-2)746,747,748
744 L(ML,NB+78)=5
745 GO TO 750
746 GOG=1.
747 L(ML,NB-78)=3
748 C MOLECULE IS BROKEN
749 NBA=NB-78
750 NNBA=NBA
GO TO 201
751 L(ML,NB)=3
752 IF(L(ML,NB-77)-2)752,753,754
753 L(ML,NB-77)=5
754 GO TO 755
755 GOG=1.
756 L(ML,NB-77)=3
757 C MOLECULE IS BROKEN
758 NBA=NB-77
759 NNBA=NBA
GO TO-201
760 IF(1-L(ML,NB-78))757,757,758
761 IF(1-L(ML,NB-79))759,759,22
762 L(ML,NB)=3
763 IF(L(ML,NB-78)-2)761,762,763
764 L(ML,NB-78)=5
765 GO TO 764
766 GOG=1.
767 L(ML,NB-78)=3
768 C MOLECULE IS BROKEN
769 NBA=NB-78
770 NNBA=NBA
GO TO 201

```

```

759 L(ML,NB)=3
765 IF(L(ML,NB-79)-2)766,767,768
767 L(ML,NB-79)=5
GO TO 769
768 GOG=1.
766 L(ML,NB-79)=3
C MOLECULE IS BROKEN
769 NBA=NB-79
NNBA=NBA
201 GAG=GOG
CALL MVAP(0,1,0)
770 IF(IND)771,771,772
771 NBA=NNBA
GAG=0
CALL MLNK(0,1,0)
772 NBA=NNBA
C CHECK TO RIGHT NEXT
GAG=GOG
CALL MVAP(1,0,67)
773 IF(IND)774,774,24
774 GAG=0
CALL MLNK(1,0,67)
GO TO 24
22 NBA=NB-78
GAG=0
CALL MLNK(0,1,0)
GAG=0
NBA=NB+78
CALL MLNK(1,0,67)
GO TO 24
C BROKEN BOND IS A CROSSLINK
481 DO 485 K=1,40
482 IF(NB-K-157)483,484,484
484 NBK=NB-K
486 IF(L(ML,NBK)-1)487,485,485
485 CONTINUE
C ALL CROSSLINKS TO THE LEFT CHECKED
487 K=2*K
DO 488 KK=1,K
NX=NB-156-KK+NB-157
489 IF(L(ML,NX)-1)488,490,490
488 CONTINUE
NB1=0

```

```

GO TO 495
490 NB1=NX
C CHECKED ADJACENT BONDS TO THE LEFT-NB LESS 78
C MUST ALSO CHECK ASSUMED NB FOR GAG WHEN ORIGINAL NB IS CROSSLINK
C LC=1 IF NB IS 3,4,OR,5 ANDNB+LB-LA IS 3,4,OR,5
495 DO 496 KK=1,K
    NX=NB-156-KK+NB-157-78
497 IF(L(ML,NX)-1)496,498,498
496 CONTINUE
    NB2=0
GO TO 500
C CHECKED OPPOSITE BONDS TO THE LEFT-NB MORE THAN 78
498 NB2=NX
500 NBA1=NB
502 IF(NB1)503,503,504
504 NB=NB1
    GAG=0
801 IF(L(ML,NB1)-2)640,640,641
640 LC=0
    GO TO 642
641 LC=1
642 CALL MLNK(1,0,67)
503 IF(NB2)800,800,506
506 NB=NB2
    GAG=0
803 IF(L(ML,NB2)-2)644,644,645
644 LC=0
    GO TO 646
645 LC=1
646 CALL MLNK(1,0,67)
800 NB=NBA1
    GO TO 24
483 DO 705 K=1,40
702 IF(NB+K-196)703,703,704
703 NX=NB+K
706 IF(L(ML,NX)-1)710,705,705
705 CONTINUE
C ALL CROSSLINKS TO THE RIGHT CHECKED
704 K=K-1
710 K=2*K
    DO 550 KK=1,K
    NX=NB-157+KK+NB-157
511 IF(L(ML,NX)-1)550,513,513

```

```

550  CONTINUE
      NB3=0
      GO TO 530
513  NB3=NX
      C CHECKED ADJACENT BONDS TO THE RIGHT-NB LESS 66
530  DO 551 KK=1,K
      NX=NB-79+KK+NB-157
531  IF(L(ML,NX)-1)551,533,533
551  CONTINUE
      NB4=0
      GO TO 540
      C CHECKED OPPOSITE BOND TO THE RIGHT-NB MORE THAN 66
533  NB4=NX
540  NBA1=NB
541  IF(NB3)542,542,543
543  NB=NB3
      GAG=0
805  IF(L(ML,NB3)-2)780,780,781
780  LC=0
      GO TO 782
781  LC=1
782  CALL MLNK(0,1,0)
542  IF(NB4)544,544,545
545  NB=NB4
806  IF(L(ML,NB4)-2)790,790,791
790  LC=0
      GO TO 792
791  LC=1
792  CALL MLNK(0,1,0)
544  NB=NBA1
      GO TO 24
11   NDUP=NDUP+1
24   CONTINUE
      XI=IX
      DUPN=NDUP
      TIME=LOGF(19600./(19600.-600.*XI+DUPN-BVOL))
      EE=IEE
      VOL=14.*(E-EE)
      PCVOL=100.*VOL/(1400.*158.)
      DIMENSION A(70),T(70)
      A(IX)=VOL
      T(IX)=TIME

```

```

600 IF(IX-1)601,601,602
602 IY=IX-1
   DWT=(A(IX)-A(IY))/(T(IX)-T(IY))
   GO TO 603
601 DWT=A(IX)/T(IX)
603 WRITE OUTPUT TAPE 3,30,PCVOL,TIME,DWT,NDUP,VOL,BVOL,E,EE,XI
30  FORMAT(IX,3F16.6,I10,5F12.1)
25  CONTINUE
   CALL EXIT
   END
   SUBROUTINE MVAP(LAD,LBD,LCD)
   DIMENSION L(100,200)
   FREQUENCY 30(1,1,5),33(1,0,1),39(1,1,5),42(1,0,1),44(5,1,1),46(0,1
1,5),901(0,1,1),902(1,1,5),410(1,0,1),801(3,1,1),52(1,0,1),54(1,1,0
2),920(0,1,5),721(0,1,1),725(1,1,5),420(1,0,1),802(5,1,1),59(1,0,1)
3,60(1,1,0),363(2,1,1)
   COMMON L,NB,NBA,E,BVOL,IEE,IND,LA,LB,LC,ML,GOG,GAG
   LA=LAD
   LB=LBD
C CHECK IF BROKEN MOLECULE RESULTS IN VAPORIZATION
   DO 29 K=1,7
30  IF((LB-LA)*NB+(LA-LB)*K*(1-2*LA)+79*LA+78*(NB/79)*(LA-LB))35,
135,32
32  NBK=NB+(LA-LB)*K
33  IF(L(ML,NBK)-2)29,29,35
29  CONTINUE
C CHECKED FOR BROKEN MOLECULE ON ADJACENT SIDE
   GO TO 45
35  LN=K
   DO 38_K=1,7
39  IF((LB-LA)*NBA+(LA-LB)*K*(1-2*LA)+79*LA+78*(NBA/79)*(LA-LB))
143,43,41
41  NBK=NBA+(LA-LB)*K
42  IF(L(ML,NBK)-2)38,38,43
38  CONTINUE
   GO TO 45
C CHECKED FOR BROKEN MOLECULE ON OPPOSITE SIDE
43  LN1=K
44  IF(LN+LN1-10)46,46,45
45  IND=0
   RETURN
46  IF(LN-1)946,901,946
901 IF(LC)946,946,902

```

```

902 IF((LB-LA)*NB+(LA-LB)*(1-2*LA)+79*LA+78*(NB/79)*(LA-LB))920,
1920,905
905 NLN=NB+LB-LA
410 IF(L(ML,NLN)-2)946,946,920
946 DO 50 K=1,LN
C MOLECULE HAS VAPORIZED
NLN=NB+(LA-LB)*K+LB-LA
801 IF(L(ML,NLN)-1)51,52,52
51 BVOL=BVOL+1.
52 IF(L(ML,NLN)-2)54,50,54
54 IF(L(ML,NLN)-5)800,50,800
800 E=E+1.
50 L(ML,NLN)=4
C VAPORIZED ADJACENT BONDS
920 IF(LN1-1)756,721,756
721 IF(GAG)756,756,725
725 IF((LB-LA)*NBA+(LA-LB)*(1-2*LA)+79*LA+78*(NBA/79)*(LA-LB))
1780,780,758
758 NLN=NBA+LB-LA
420 IF(L(ML,NLN)-2)756,756,780
756 DO 57 K=1,LN1
NLN=NBA+(LA-LB)*K+LB-LA
802 IF(L(ML,NLN)-1)58,59,59
58 BVOL=BVOL+1.
59 IF(L(ML,NLN)-2)60,80,60
60 IF(L(ML,NLN)-5)811,80,811
811 E=E+1.
80 L(ML,NLN)=4
C VAPORIZED OPPOSITE BONDS
57 CONTINUE
KA=LN1/2
KB=NB/2
KAA=LN1-2*KK
KBB=NB-2*KB
KC=K/2+KAA*KBB*LB+KAA*(1-KBB)*LA
DO 400 K=1,KC
NYY=NB+LB+156-NB/2-(NB/79)*39+(LA-LB)*K
363 IF(L(ML,NYY)-1)63,400,400
63 BVOL=BVOL+1.
400 L(ML,NYY)=4
C VAPORIZED CROSSLINKS
780 IND=1

```

```

RETURN
END
SUBROUTINE MLNK(LAD,LBD,LCD)
  DIMENSION L(100,200)
  FREQUENCY 100(1,1,5),107(0,1,5),600(0,1,1),810(5,1,1),610(1,0,1),
  1811(0,1,1),105(0,1,5),815(5,1,1),133(1,0,1),156(5,1,1),620(1,0,1),
  2161(5,1,1),163(1,0,1),630(1,0,1),152(0,1,1)
  COMMON L,NB,NBA,E,BVOL,IEE,IND,LA,LB,LC,ML,GOG,GAG
  LA=LAD
  LB=LBD
  C CHECK IF BROKEN CROSSLINK GIVES BROKEN MOLECULE
    DO 104 K=1,6
      NY=NB+LB+156-NB/2-(NB/79)*39+(LA-LB)*K
      100 IF(197*LA+(LB-LA)*NY-156*LB)105,105,106
      106 IF(L(ML,NY)-1)107,104,104
      104 CONTINUE
      K=6
      GO TO 109
      107 IF(K-1)108,108,109
      108 KA=NB/2
      KB=NB-2*K
      600 IF(LB*(1-KB)+LA*KB)40,41,40
      41 RETURN
      40 NY=NB+LA-LB
      IF(L(ML,NY)-1)240,241,241
      240 RETURN
      241 L(ML,NB)=2
      E=E+1
      RETURN
      109 KA=NB/2
      KB=NB-2*K
      K=2*K+LB*(1-KB)+LA*KB
      DO 110 KK=1,K
      NBA=NB+78+(LA-LB)*KK-(NB/79)*156
      810 IF(L(ML,NBA)-1)110,150,150
      110 CONTINUE
      C CHECKED IF OPPOSITE BOND IS BROKEN TO GIVE BROKEN MOLECULE
      GO TO 151
      150 L(ML,NB)=3
      610 IF(L(ML,NBA)-2)717,718,747
      718 L(ML,NBA)=5
      GO TO 719
      747 GAG=1

```

```

717 L(ML,NBA)=3
719 CALL MVAP(LA,LB,LC)
C MOLECULE IS BROKEN
  NBAA=NBA
811 IF(IND)151,151,152
105 IF(K-1)130,130,131
130 RETURN
131 KA=NB/2
  KB=NB-2*KA
  K=K-1
  K=2*K+LB*(1-KB)+LA*KB
  DO 120 KK=1,K
    NLN=NB+(LA-LB)*KK+(LB-LA)
815 IF(L(ML,NLN)-1)132,133,133
132 BVOL=BVOL+1.
133 IF(L(ML,NLN)-2)134,135,120
135 IEE=IEE+1
134 E=E+1.
  L(ML,NLN)=2
120 CONTINUE
  RETURN
C VAPORIZED ADJACENT BONDS
151 DO 155 KK=1,K
  NBA=NB+(LA-LB)*KK
156 IF(L(ML,NBA)-1)155,158,158
155 CONTINUE
620 IF(L(ML,NB)-3)650,152,650
C CHECKED IF ADJACENT BOND IS BROKEN TO GIVE BROKEN MOLECULE
158 DO 168K=1,KK
  NBA=NB+(LA-LB)*K+LB-LA
161 IF(L(ML,NBA)-1)162,163,163
162 BVOL=BVOL+1.
163 IF(L(ML,NBA)-2)164,165,166
165 IEE=IEE+1
164 E=E+1.
  L(ML,NBA)=4
C VAPORIZED ADJACENT BONDS
  GO TO 168
166 E=E+1.
168 CONTINUE
630 IF(L(ML,NB)-3)650,152,650
C IF MOLECULE IS BROKEN,CHECK BOTH DIRECTIONS

```

```

152 IF(LA)200,200,201
200 LA=1
    LB=0
    LCC=67
    GO TO 210
201 LA=0
    LB=1
    LCC=0
210 NBA=NBAA
    CALL MVAP(LA,LB,LCC)
650 RETURN
    END
)1 (X- - (G7
*J -9(NZ5GA 7 -2 -E -G - 3 5- - 97 95 -- 94 78 -- -5 -5 -7 -- 4E -4 -070SQU00
*U7(P($T 9 -G 5484 -1 -9 -5 - 2(X) - 9 - 070SQU01
                                070SQU02

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UNCLASSIFIED

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DOCUMENT CONTROL DATA - R&D

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1. ORIGINATING ACTIVITY (Corporate author) Nonmetallic Materials Division, Air Force Materials Laboratory, Research and Technology Division, Air Force Systems Command, Wright-Patterson AFB, Ohio		2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED	
		2b. GROUP --	
3. REPORT TITLE THEORETICAL STUDIES ON THE DEGRADATION OF LADDER POLYMERS. Part II. Vaporization Studies			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Summary Report (January 1964 to December 1964)			
5. AUTHOR(S) (Last name, first name, initial) Tessler, 1/Lt. Martin M.			
6. REPORT DATE		7a. TOTAL NO. OF PAGES 52	7b. NO. OF REFS 2
8a. CONTRACT OR GRANT NO.		9a. ORIGINATOR'S REPORT NUMBER(S) ML-TDR-64-151, Part II	
b. PROJECT NO. 7342			
c. Task No. 734203		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
d.			
10. AVAILABILITY/LIMITATION NOTICES DISTRIBUTION OF DOCUMENT IS UNLIMITED			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Nonmetallic Materials Division, Air Force Materials Laboratory, Research & Technology Division, Air Force Systems Command, WPAFB, OH	
13. ABSTRACT The random degradation of four and six-membered ring ladder polymers were investigated by means of a digital computer and the results compared to a single chain polymer undergoing degradation under identical conditions. The percent vaporization versus time and the rate of weight loss versus time was plotted and significant differences were obtained. The results indicate that ladder polymers should have increased stability over single chain polymers undergoing random degradation.			

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Ladder Polymers Degradation Digital Computer Studies						

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