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THEORETICAL STUDIES ON THE THERMAL DEGRADATION OF LADDER POLYMERS

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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, Lt. Martin M. Tessler, project engineer.

This report covers work accomplished January 1963 to December 1963.

ABSTRACT

The random thermal degradation of four- and six-membered ring ladder polymers were investigated and results compared to a single chain polymer undergoing degradation under the identical conditions. The change in molecular weight versus time was plotted and significant differences were found in the shapes of the curves.

Similar studies were conducted with imperfect ladder polymers which had single bonds along the backbone of the polymer.

This technical documentary report has been reviewed and is approved.

William E. Gibbs

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INTRODUCTION

Interest in the development of thermally stable materials has produced much research into new and novel types of polymers. One area of investigation is the preparation of a ladder or double-strand polymer. The first successful synthesis of a ladder polymer was reported by Brown and co-workers (Reference 1). They prepared the double-chain polyphenylsilesquioxane in which the polymer backbone is completely inorganic. Attempts to synthesize a ladder polymer with an organic backbone from vinyl isocyanate (Reference 2) poly-3,4-isoprene (Reference 3) and conjugated dienes (Reference 4) have recently been reported. These polymers have segments of fused rings, but they are not completely fused into the desired ladder structure.

This report compares the thermal stability of a ladder polymer undergoing random degradation with that of a single chain polymer. A digital computer is used to set up a statistical (Monte Carlo) (Reference 5) model of the degrading system. The following assumptions are made in defining the degrading system:

1. The polymer sample is initially homogeneous; that is, only chains of one length are present.
2. All bonds in the polymer chain are of equal strength and equal accessibility, regardless of their positions in the molecule and the length of the chain.
3. The rate of breaking of bonds is proportional to the number of bonds present in the degrading system.
4. The system is closed; that is, no fragments can leave the system.

The ratio of the number average molecular weight (at time kt) to the initial number average molecular weight is obtained directly from the computer, where k is the proportionality constant between the rate of breaking bonds and the number of bonds present in the system at time t .

MODEL LADDER STRUCTURES

Two types of ladder polymers were studied. Type I is a fused four-membered ring and Type II is a fused six-membered ring. All the conclusions reached 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. In this simple case, a broken bond can break a molecule only if the bond opposite it is broken. The fact that a broken crosslink will increase the probability of a molecule breaking is ignored. This type of degradation is shown in Figure 1. The complex case of degradation is shown in Figure 2 where breaks in the crosslinks will result in increased molecule breaks. This is a much more realistic picture of random degradation than the simple case.

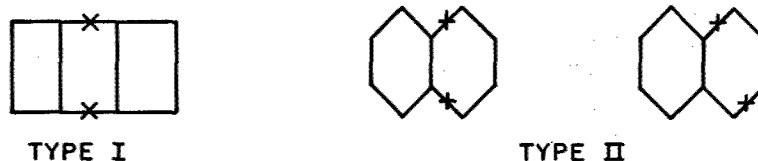


Figure 1. Different Ways a Molecule Can Break - Simple Case

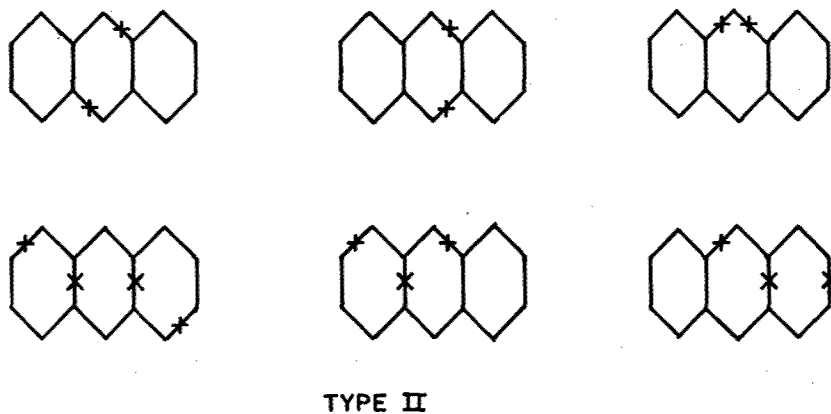
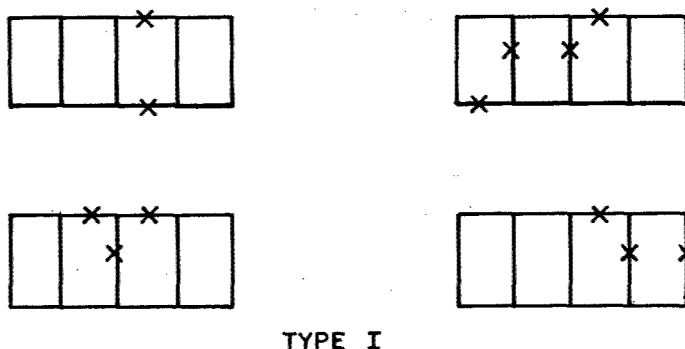


Figure 2. Different Ways a Molecule Can Break - Complex Case

MONTE CARLO MODEL

To construct a Monte Carlo 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 broken, the number one is stored in its location and if it is not broken, a zero is stored there. Initially, all the storage locations are set to zero.

A random number is generated which has the limits of 0 and $B_0 - 1$, 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 can be varied at will with the limiting factor being the size of the computer storage. In the present study, a system of 100 molecules with 199 bonds per molecule for ladder polymer Type I and 100 molecules with 196 bonds per molecule for ladder polymer Type II were chosen. Simultaneously, 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 if it is broken or not. 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, a broken molecule is recorded and a new random number is then generated. If the opposite bond is not broken, no further work is done in the simple case and a new random number is generated. In the complex case, the computer checks all 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 last crosslink is broken, a broken molecule is recorded and a new random number generated. 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 generation to the last side chain bond before the unbroken crosslink. If any of the side chain bonds are broken, a broken molecule is recorded and a new random number is then generated. If none of the side chain bonds are broken, a new random number is generated. The computer keeps track at all times of the number of duplicates recorded. The number of bonds which are broken is equal to the number of random numbers generated minus the number of duplicates.

The number of molecules present in the system (at time kt) is equal to the number of molecules initially present plus the number of broken molecules since each broken molecule produces one more fragment. 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 bonds present at time kt . The ratio of the number average molecular weight at time kt , to the initial number average molecular weight is equal to $100/(100 + \text{number broken molecules})$. All of these quantities are readily calculated during the course of the degradation and the computer prints out the desired data at any convenient interval of kt .

The subprogram by which the computer generates a random number makes use of an equation in which multiplication and division are used, the output being the remainder after division. Several different sets of random numbers were used to check the accuracy of the method. The random number generator appears to be very accurate and reliable.

RESULTS FOR PERFECT LADDER POLYMERS

The curve for the ratio of the number average molecular weight at time kt to the initial number average molecular weight versus kt is shown for ladder polymer Type I in Figure 3 and for ladder polymer Type II in Figure 4. Both the simple case and the complex case are shown as well as the analogous single chain polymer. The proportionality constant k is not known and it probably will have different values for different polymers.

This will shift the curves, but the significant fact is the shapes of the curves. The single chain polymer shows a very sharp drop in molecular weight as soon as degradation begins. The ladder polymer has an induction period where the molecular weight hardly changes and then it drops much more slowly than the corresponding single chain polymer. As degradation proceeds, both curves merge together. These results indicate that the ladder polymers should have increased thermal stability over single chain polymers, but the extent of this stability can only be determined by studying the chemistry of these compounds.

IMPERFECT LADDER POLYMERS

Ladder polymers are of interest because of their potential stability at high temperatures. The double-chain polyphenylsilsesquioxane, synthesized by Brown and co-workers (Reference 1) has an inorganic ladder structure and the silicon-oxygen bonds rearrange at elevated temperatures. The reported attempts to synthesize ladder polymers with an organic ladder structure (References 2, 3 and 4) have all used the same general approach. A polymer is first prepared which has pendant nonconjugated 1,6 unsaturation along the chain of the molecule. Overberger and co-workers (Reference 2) polymerized vinyl isocyanate through the vinyl group or the isocyanate group to get the starting polymer. Angelo (Reference 3) prepared poly-3,4-isoprene and Gaylord and co-workers (Reference 4) used butadiene, isoprene and chloroprene to obtain the desired polymer. Cyclization of the pendant nonconjugated 1,6 unsaturated polymer with suitable catalysts produces a ladder structure.

The problems in preparing a completely perfect ladder polymer are enormous. Imperfect ladder polymers can result from isolated unreactive groups, from alternative cyclizations or isomerizations, from crosslinking and from chain scission reactions. Extremely dilute solutions must be used to prevent crosslinking. Another problem is that as the ladder polymer is being synthesized, its solubility is decreasing rapidly and it may precipitate out of solution before ring closure is complete. If the polymer with the pendant nonconjugated 1,6 unsaturation is not structurally perfect, complications will arise in the cyclization step. For example, the poly-3,4-isoprene used by Angelo contained up to 10 percent of 1,4 structural units.

The difficulty in preparing perfect double-chain polymers raises the question as to how the thermal stability of an imperfect ladder polymer compares with that of a single chain polymer. A partial solution to this problem can be obtained by setting up in the storage of a digital computer, an imperfect ladder polymer. Each storage location will correspond to a different bond and a random number generator will be used to locate the bond which is being broken during degradation. An unbroken bond will be represented by a zero and a broken bond by a one. If all the bonds are initially set equal to zero, we will have a perfect ladder polymer. If we initially set a bond equal to one at prescribed intervals along the chain we will have an imperfect ladder polymer with the "broken bonds" corresponding to missing bonds in an imperfectly synthesized ladder polymer. If the random number generator should produce a number corresponding to one of these missing bonds, a duplicate will be recorded and a new random number will be generated without any further calculations. It is assumed that the polymer sample is homogeneous, all bonds in the polymer have an equal probability of being broken, the rate of breaking bonds is proportional to the number of bonds present in the degrading system and no fragments can leave the system.

The Monte Carlo calculations are identical to those described previously.

Four- (Type I) and six- (Type II) membered ring ladder polymers were studied and both the simple and complex cases of degradation examined. A single chain polymer with the same number of bonds per molecule was degraded simultaneously in the computer for comparison purposes.

Type I ladder polymers were studied with single bonds first at every sixth and then at every twelfth bond along the chain. Type II ladder polymers were studied with single bonds first at every twelfth and then at every twenty-fourth bond along the chain.

RESULTS FOR IMPERFECT LADDER POLYMERS

The introduction of single bonds along the chain of the ladder polymer results in a sharp decrease in molecular weight, as degradation occurs, compared to a perfect ladder polymer. The stability of the imperfect ladder polymer is still much greater than that of an analogous single chained polymer. The shape of the curves when the ratio of the number average molecular weight at time kt to the initial number average molecular weight is plotted against kt is very interesting. With a small number of single bonds within the ladder chain, the curves still have an induction period where the change of molecular weight is relatively small. It then drops very rapidly, although not as fast as a single chain polymer. As the number of single bonds are increased, the induction period disappears and the shape of the curve is the same as that of the single chain polymer although the molecular weight still does not decrease as fast. With a suitable value of k , it is possible that the curves will become superimposable and that the imperfect ladder polymer will have no increased advantage in thermal stability over a single chain polymer. The answer to this problem must await the synthesis and characterization of imperfect ladder polymers and a study of their chemical behavior when undergoing thermal degradation.

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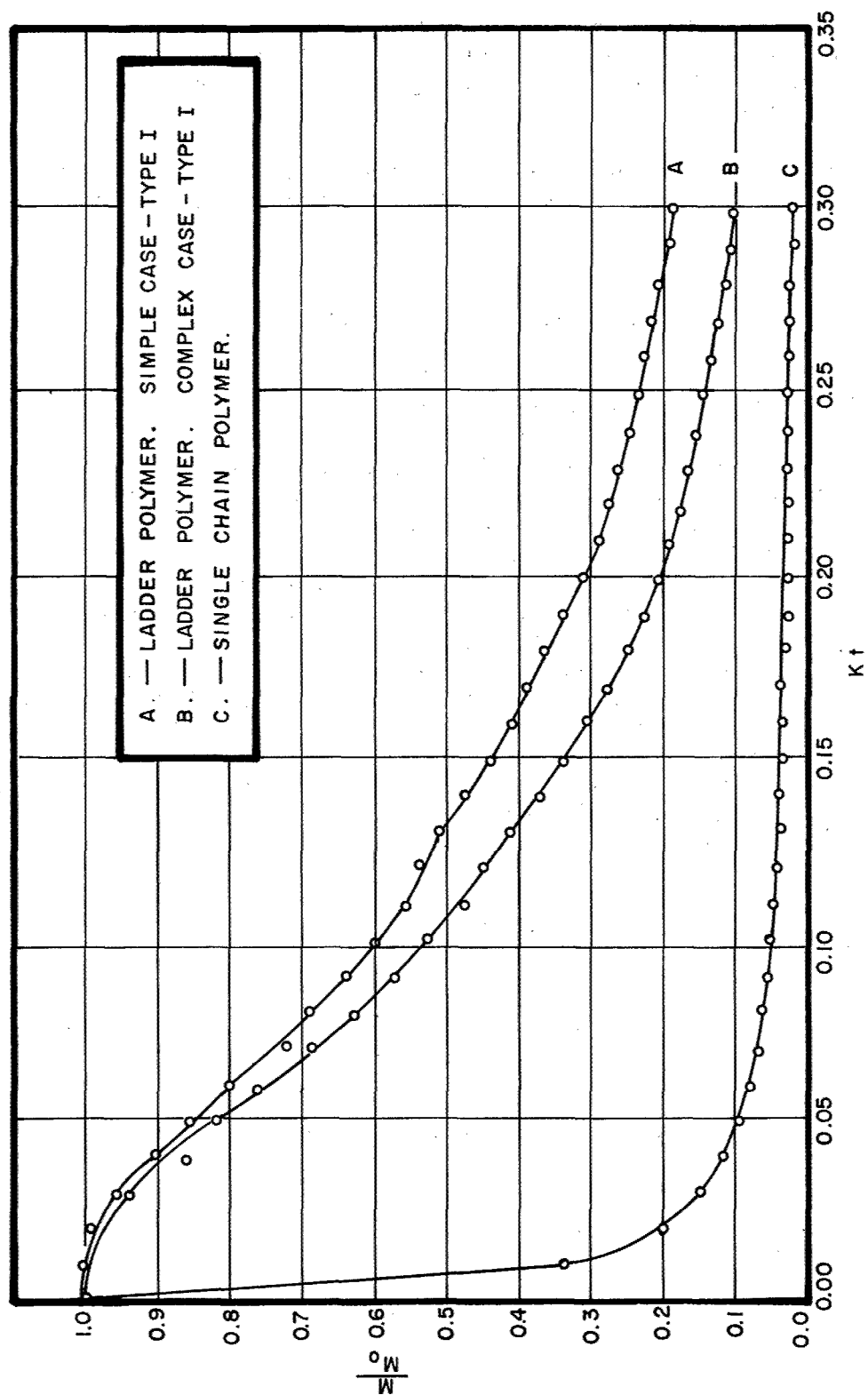


Figure 3. Plot of the Ratio of Molecular Weight to Initial Molecular Weight Versus Time for Different Polymers Undergoing Random Thermal Degradation

- A. Ladder Polymer, Simple Case - Type I
- B. Ladder Polymer, Complex Case - Type I
- C. Single Chain Polymer

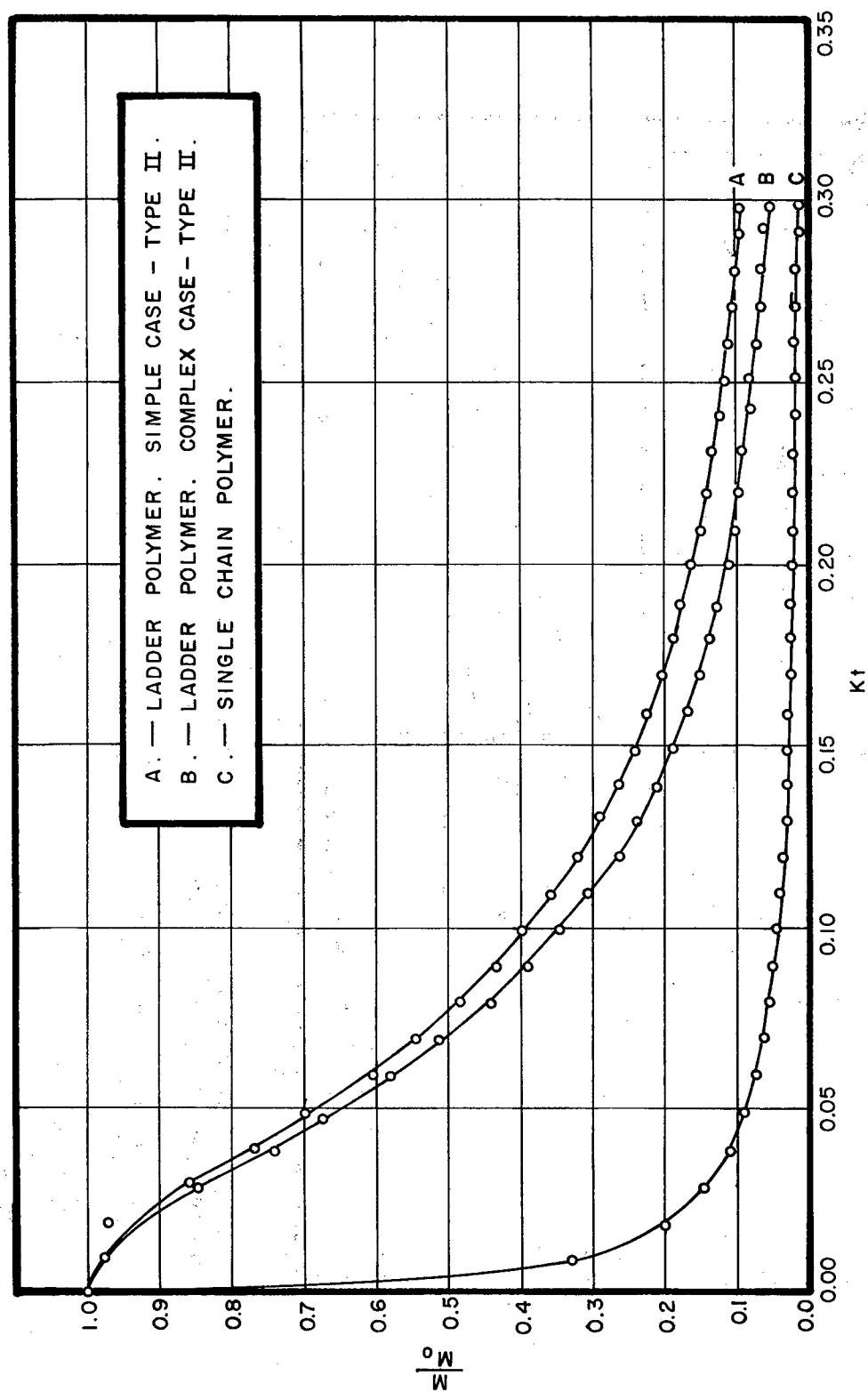


Figure 4. Plot of the Ratio of Molecular Weight to Initial Molecular Weight Versus Time for Different Polymers Undergoing Random Thermal Degradation

- A. Ladder Polymer, Simple Case - Type II
- B. Ladder Polymer, Complex Case - Type II
- C. Single Chain Polymer

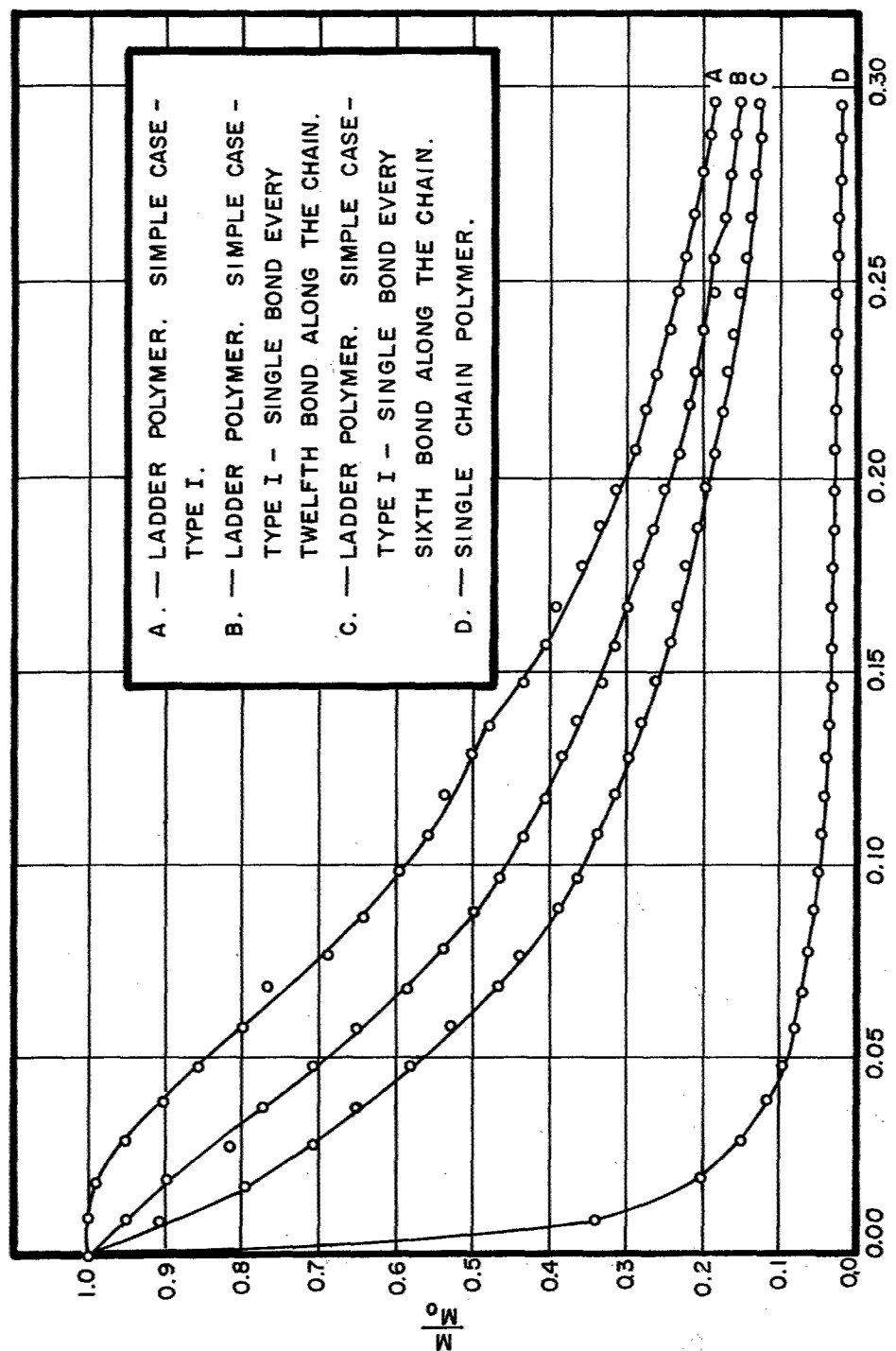


Figure 5. Plot of the Ratio of Molecular Weight to Initial Molecular Weight Versus Time for Different Polymers Undergoing Random Thermal Degradation

- A. Ladder Polymer, Simple Case - Type I
- B. Ladder Polymer, Simple Case - Type I - Single bond every twelfth bond along the chain
- C. Ladder Polymer, Simple Case - Type I - Single bond every sixth bond along the chain
- D. Single Chain Polymer

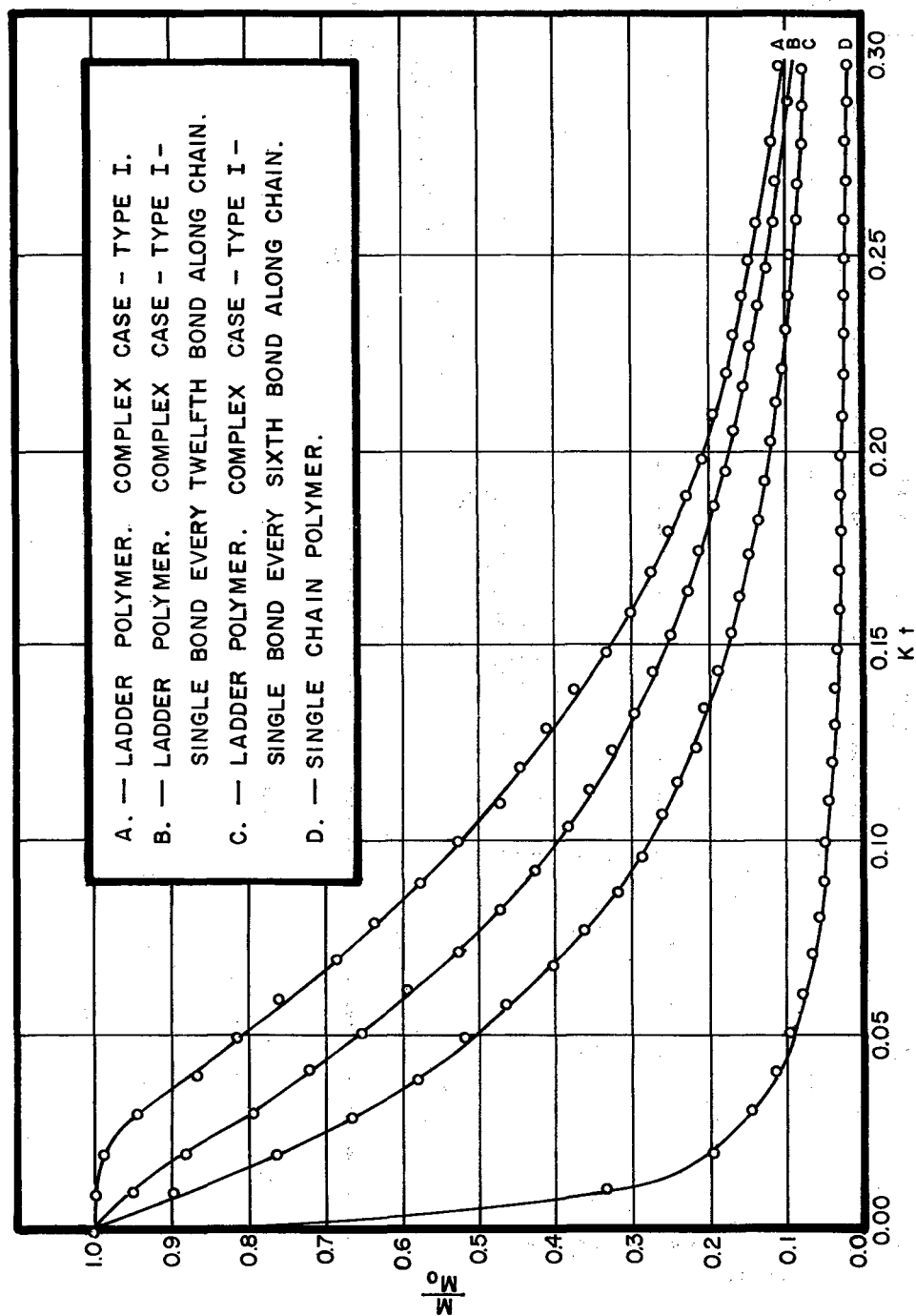


Figure 6. Plot of the Ratio of Molecular Weight to Initial Molecular Weight Versus Time for Different Polymers Undergoing Random Thermal Degradation

- A. Ladder Polymer. Complex Case - Type I
- B. Ladder Polymer. Complex Case - Type I - Single bond every twelfth bond along chain
- C. Ladder Polymer. Complex Case - Type I - Single bond every sixth bond along chain
- D. Single Chain Polymer

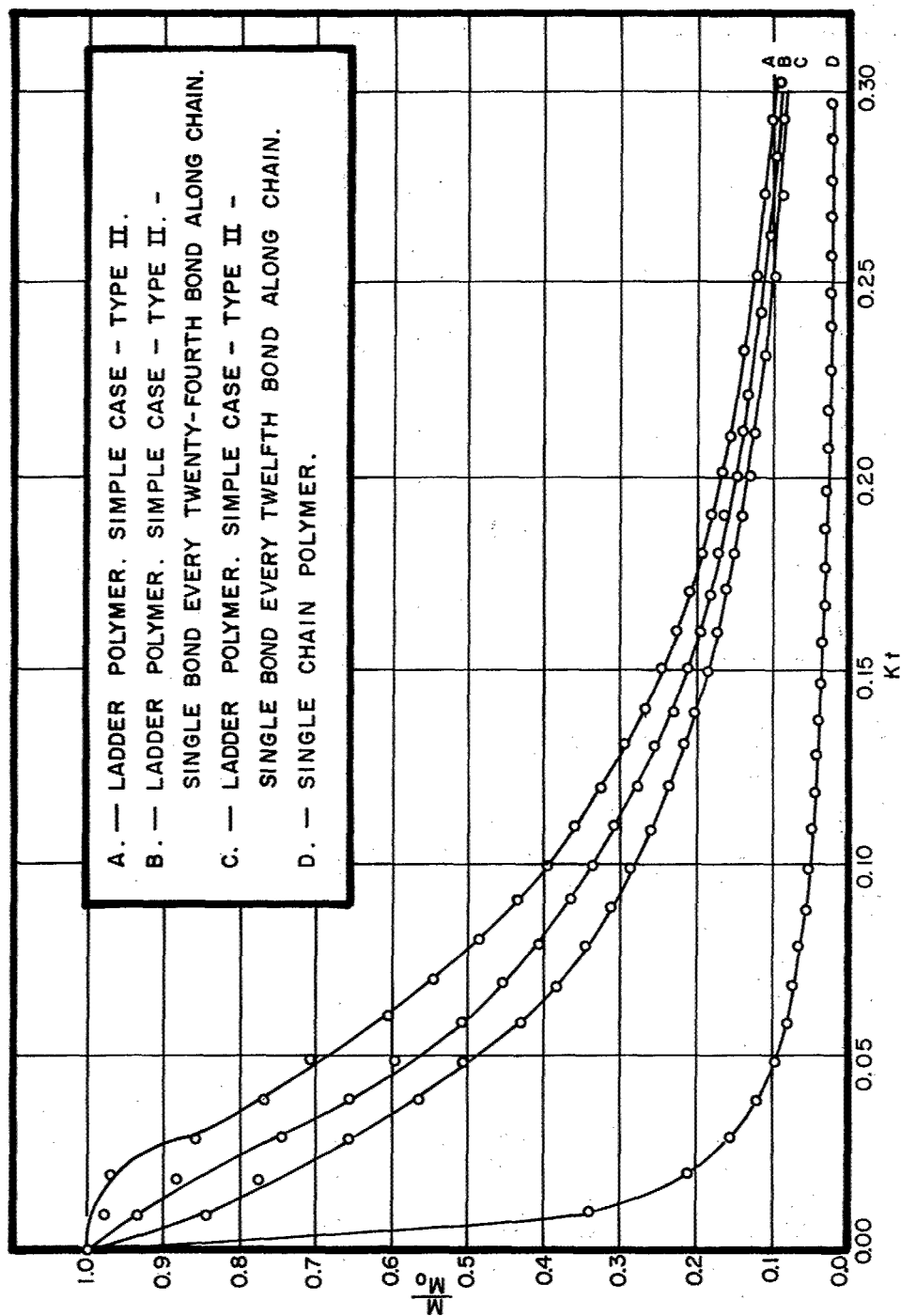


Figure 7. Plot of the Ratio of Molecular Weight to Initial Molecular Weight Versus Time for Different Polymers Undergoing Random Thermal Degradation

- A. Ladder Polymer. Simple Case - Type II
- B. Ladder Polymer. Simple Case - Type II - Single bond every twenty-fourth bond along chain
- C. Ladder Polymer. Simple Case - Type II - Single bond every twelfth bond along chain
- D. Single Chain Polymer

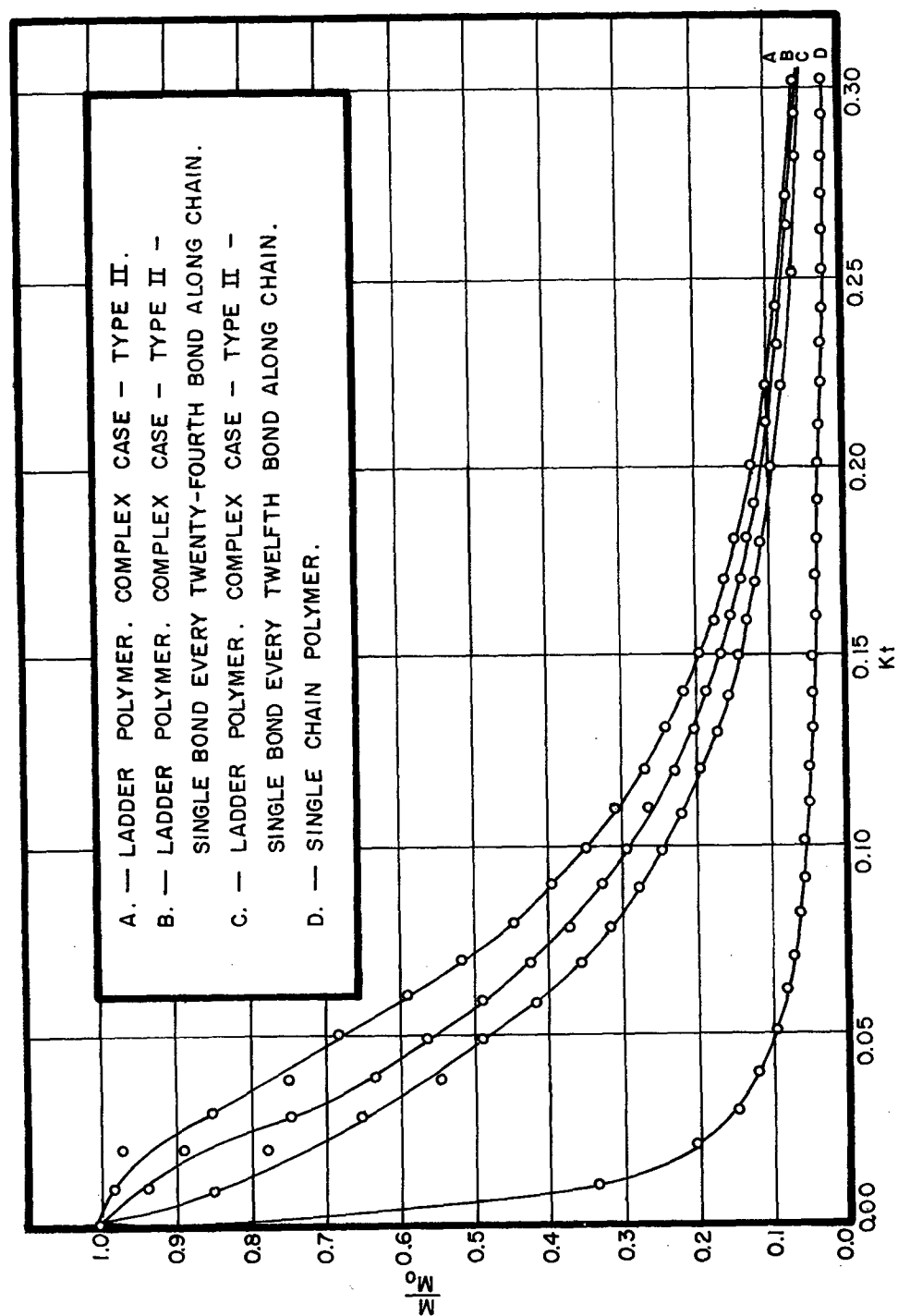


Figure 8. Plot of the Ratio of Molecular Weight to Initial Molecular Weight Versus Time for Different Polymers Undergoing Random Thermal Degradation

- A. Ladder Polymer, Complex Case - Type II
- B. Ladder Polymer, Complex Case - Type II - Single bond every twenty-fourth bond along chain
- C. Ladder Polymer, Complex Case - Type II - Single bond every twelfth bond along chain
- D. Single Chain Polymer

APPENDIX I
COMPUTER PROGRAM
SIMPLE CASE. TYPE I

C TESSLER LADDER POLYMER DEGRADATION

```

    DIMENSION L(100,200)
    FREQUENCY 7(1,0,2),8(9,1,0),9(0,1,9),4(1,0,1),10(9,1,0),13(0,1,9)
    1,14(9,1,0)
    NBRK=0
    NDUP=0
    NLNK=0
    DO 25 IX=1,30
    DO 24 I=1,200
    R=RAND1(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)28,11,28
    28  L(ML,NB)=1
    9   IF(1-L(ML,NB+66))24, 5,24
    4   IF(NB-132)10,10,14
    10  IF(L(ML,NB)-1)17,11,17
    17  L(ML,NB)=1
    13  IF(1-L(ML,NB-66))24,5,24
    14  IF(L(ML,NB)-1)12,11,12
    12  L(ML,NB)=1
    NLNK=NLNK+1
    GO TO 24
    5   NBRK=NBRK +1
    GO TO 24
    11  NDUP=NDUP+1
    24  CONTINUE
    BRK=NBRK
    ANMW=100./((100.+BRK)
    XI=IX
    DUPN=NDUP
    TIME=LOGF(19900./((19900.-200.*XI+DUPN))
    ASMW=100./((100.+200.*XI-DUPN)
    WRITE OUTPUT TAPE 3,30, NBRK,NDUP,NLNK,ANMW,ASMW,TIME
    30  FORMAT (1X,3I10,3F20.5)
    25  CONTINUE
    CALL EXIT
    END

```

APPENDIX II
COMPUTER PROGRAM
SIMPLE CASE. TYPE II

C TESSLER LADDER POLYMER DEGRADATION FUSED 6 MEMBERED RING

```

*      XEQ
      DIMENSION L(100,200)
      FREQUENCY 7(1,0,2),8(9,1,0),23(1,1,0),40(0,1,9),42(0,1,9)
      1,41(0,1,9),43(0,1,9),4(2,0,1),10(9,1,0),21(1,1,0),47(0,1,9)
      2,49(0,1,9),48(0,1,9),50(0,1,9),14(0,1,9)
      NBRAK=0
      NDUP=0
      NLNK=0
      DO 25 IX=1,30
      DO 24 I=1,200
      R=RANDI(Y)*19600.
      NR=R
      ML=NR/196+1
      NB=196*ML-NR
      7 IF(NB-78)8,8,4
      8 IF(L(ML,NB)-1)28,11,28
      28 L(ML,NB)=1
      NA=NB/2
      23 IF(2*NA-NB)40,41,40
      40 IF(1-L(ML,NB+78))42,5,42
      42 IF(1-L(ML,NB+79))24,5,24
      41 IF(1-L(ML,NB+78))43,5,43
      43 IF(1-L(ML,NB+77))24,5,24
      4 IF(NB-156)10,10,14
      10 IF(L(ML,NB)-1)17,11,17
      17 L(ML,NB)=1
      NC=NB/2
      21 IF(2*NC-NB)47,48,47
      47 IF(1-L(ML,NB-78))49,5,49
      49 IF(1-L(ML,NB-77))24,5,24
      48 IF(1-L(ML,NB-78))50,5,50
      50 IF(1-L(ML,NB-79))24,5,24
      14 IF(1-L(ML,NB))12,11,12
      12 L(ML,NB)=1
      NLNK=NLNK+1
      GO TO 24
      5 NBRAK=NBRAK+1
      GO TO 24
      11 NDUP=NDUP+1
      24 CONTINUE
      BRK=NBRAK
      ANMW=100./((100.+BRK)
      XI=IX
      DUPN=NDUP
      TIME=LOGF(19600./((19600.-200.*XI+DUPN))

```

```

      ASMW=100./((100.+200.*XI-DUPN)
      WRITE OUTPUT TAPE 3,30,NBRAK,NDUP,NLNK,ANMW,ASMW,TIME
      30 FORMAT(1X,3I10,3F20.5)
      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(ST 9 -G 5484 -1 -9 -5 - 2(X) - 9 - 070SQU01
070SQU02

```

APPENDIX III
COMPUTER PROGRAM
COMPLEX CASE. TYPE I

C TESSLER LADDER POLYMER DEGRADATION WHERE BRAK LNKS CAN YIELD BRAK

```

*      XEQ
      DIMENSION L(100,200)
      FREQUENCY 7(1,0,2),8(9,1,0),9(0,1,9),31(1,1,9),81(0,1,9),84(0,9,1)
1,93(0,1,9),54(0,1,9),69(9,1,1),42(0,1,9),44(0,9,1),46(0,1,9)
2,48(0,1,9),4(1,0,1),32(9,1,0),6(0,1,9),97(1,1,9),35(9,1,0)
3,36(0,9,1),60(0,1,9),62(0,1,9),68(9,1,1),20(0,1,9),21(0,9,1)
4,91(0,1,9),27(0,1,9),13(9,1,0),190(1,1,9),191(9,1,0),107(9,1,0)
5,109(9,1,0),                      111(9,1,1),194(9,1,0),118(9,1,0)
6,120(9,1,0)
      NBRK=0
      NDUP=0
      MLNK=0
      DO 25 IX=1,30
      DO 24 I=1,200
      K=RAND1(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)28,11,28
28     L(ML,NB)=1
9      IF(1-L(ML,NB+66))80,5,80
C OPPOSITE BOND CHECKED
80     DO 51 IC=1,67
        NW=NB+133-IC
31     IF(NW-133)5,81,81
81     IF(1-L(ML,NW))84,51,84
51     CONTINUE
C ALL CROSSLINKS TO THE LEFT CHECKED
84     IF(IC-1)85,75,85
85     IO=IC-1
        DO 52 KA=1,IO
        NX=NB+66-KA
93     IF(1-L(ML,NX))53,5,53
C ALL OPPOSITE SIDE LINKS CHECKED
53     NY=NB-KA
54     IF(1-L(ML,NY))52,5,52
C ALL ADJACENT SIDE LINKS CHECKED
52     CONTINUE
75     DO 17 IC=1,67
        NW=NB+132+IC
69     IF(NW-199)42,42,5
42     IF(1-L(ML,NW))44,17,44
17     CONTINUE
C ALL CROSSLINKS TO THE RIGHT CHECKED

```

```

44 IF(IC-1)45,24,45
45 IO=IC-1
   DO 19 KA=1,IO
   NX=NB+66+KA
46 IF(1-L(ML,NX))47,5,47
C ALL OPPOSITE SIDE LINKS CHECKED
47 NY=NB+KA
48 IF(1-L(ML,NY))19,5,19
C ALL ADJACENT SIDE LINKS CHECKED
19 CONTINUE
   GO TO 24
4 IF(NB-132)32,32,13
32 IF(L(ML,NB)-1)33,11,33
33 L(ML,NB)=1
6 IF(1-L(ML,NB-66))34,5,34
C OPPOSITE BOND CHECKED
34 DO 90 IC=1,67
   NW=NB+67-IC
97 IF(NW-133)5,35,35
35 IF(L(ML,NW)-1)36,90,36
90 CONTINUE
C ALL CROSSLINKS TO THE LEFT CHECKED
36 IF(IC-1)37,38,37
37 IO=IC-1
   DO 39 KA=1,IO
   NX=NB-66-KA
60 IF(1-L(ML,NX))61,5,61
C ALL OPPOSITE SIDE LINKS CHECKED
61 NY=NB-KA
62 IF(1-L(ML,NY))39,5,39
C ALL ADJACENT SIDE LINKS CHECKED
39 CONTINUE
38 DO 63 IC=1,67
   NW=NB+66+IC
68 IF(NW-199)20,20,5
20 IF(1-L(ML,NW))21,63,21
63 CONTINUE
C ALL CROSSLINKS TO THE RIGHT CHECKED
21 IF(IC-1)22,24,22
22 IO=IC-1
   DO 23 KA=1,IO
   NX=NB-66+KA
91 IF(1-L(ML,NX))26,5,26
C ALL OPPOSITE SIDE LINKS CHECKED
26 NY=NB+KA
27 IF(1-L(ML,NY))23,5,23

```

C ALL ADJACENT SIDE LINKS CHECKED

```

23 CONTINUE
   GO TO 24
13 IF(L(ML,NB)-1)29,11,29
29 L(ML,NB)=1
   NLNK=NLNK+1
   DO 100 IC=1,67
190 IF(NB-IC-133)104,102,102
102 IP=NB-IC
191 IF(L(ML,IP)-1)105,100,105
100 CONTINUE

```

C ALL CROSSLINKS TO THE LEFT CHECKED

```

105 DO 106 IW=1,IC
   NX=NB-IW-132
107 IF(L(ML,NX)-1)108,104,104
108 NY=NB-IW-66
109 IF(L(ML,NY)-1)106,104,104
106 CONTINUE
   GO TO 24

```

C CHECKED ALL SIDELINKS TO THE LEFT

```

104 DO 110 IC=1,67
111 IF(NB+IC-199)112,112,5
112 IP=NB+IC
194 IF(L(ML,IP)-1)116,110,116
110 CONTINUE

```

C ALL CROSSLINKS TO THE RIGHT CHECKED

```

116 DO 117 IW=1,IC
   NX=NB+IW-133
118 IF(L(ML,NX)-1)119,5,119
119 NY=NB+IW-67
120 IF(L(ML,NY)-1)117,5,117
117 CONTINUE

```

C CHECKED ALL SIDELINKS TO THE RIGHT

```

   GO TO 24
5   NBRAK=NBRAK+1
   GO TO 24
11  NDUP=NDUP+1
24  CONTINUE
   BRK=NBRAK
   ANMW=100./((100.+BRK)
   XI=IX
   DUPN=NDUP
   TIME=LOGF(19900./((19900.-200.*XI+DUPN))
   ASMW=100./((100.+200.*XI-DUPN)
   WRITE OUTPUT TAPE 3,30,NBRAK,NDUP,NLNK,ANMW,ASMW,TIME
30  FORMAT(1X,3I10,3F20.5)

```

```

25 CONTINUE
   CALL EXIT
   END

```

APPENDIX IV
COMPUTER PROGRAM
COMPLEX CASE. TYPE II

C8 TYPE II WHERE CROSSLINK BREAK LEADS TO ADDITIONAL SIDE LINK BREAKS

```

* XEQ
  DIMENSION L(100,200)
  FREQUENCY 7(1,0,2),8(9,1,0),92(1,1,0),93(0,1,9),95(0,1,9)
  1,94(0,1,9),96(0,1,9),31(1,1,9),81(0,1,9),84(0,9,1),73(0,1,9)
  2,54(0,1,9),69(9,1,1),42(0,1,9),44(0,9,1),46(0,1,9),48(0,1,9)
  3,4(1,0,1),32(9,1,0),100(1,1,0),98(0,1,9),101(0,1,9),99(0,1,9)
  4,102(0,1,9),97(1,1,9),35(9,1,0),36(0,9,1),60(0,1,9),62(0,1,9)
  5,68(9,1,1),20(0,1,9),21(0,9,1),91(0,1,9),27(0,1,9),13(9,1,0)
  6,190(1,1,9),191(9,1,0),107(9,1,0),109(9,1,0)
  7,111(9,1,1),194(9,1,0),118(9,1,0),120(9,1,0)
  NBRAK=0
  NDUP=0
  NLNK=0
  DO 25 IX=1,30
  DO 24 I=1,200
  R=RANDI(Y)*19600.
  NR=R
  ML=NR/196+1
  NB=196*ML-NR
  7 IF(NB-78)8,8,4
  8 IF(L(ML,NB)-1)28,11,28
  28 L(ML,NB)=1
  NA=NB/2
  92 IF(2*NA-NB)93,94,93
  93 IF(1-L(ML,NB+78))95,5,95
  95 IF(1-L(ML,NB+79))80,5,80
  94 IF(1-L(ML,NB+78))96,5,96
  96 IF(1-L(ML,NB+77))80,5,80
C BOTH OPPOSITE BONDS CHECKED
  80 DO 51 IC=1,41
  NW=NB-NB/2+157-IC
  31 IF(NW-157)5,81,81
  81 IF(1-L(ML,NW))84,51,84
  51 CONTINUE
C ALL CROSSLINKS TO THE LEFT CHECKED
  84 IF(IC-1)85,75,85
  85 IO=(IC-1)*2
  DO 52 KA=1,IO
  NX=((NB+1)/2)*2+77-KA
  73 IF(1-L(ML,NX))53,5,53
C ALL OPPOSITE SIDE LINKS CHECKED
  53 NY=NX-78
  54 IF(1-L(ML,NY))52,5,52
C ALL ADJACENT SIDE LINKS CHECKED
  52 CONTINUE

```

```

75 DO 17 IC=1,41
   NW=NB-NB/2+156+IC
69 IF(NW-196)42,42,5
42 IF(1-L(ML,NW))44,17,44
17 CONTINUE
C ALL CROSSLINKS TO THE RIGHT CHECKED
44 IF(IC-1)45,24,45
45 IO=(IC-1)*2
   DO 19 KA=1,IO
   NX=((NB+1)/2)*2+78+IO
46 IF(1-L(ML,NX))47,5,47
C ALL OPPOSITE SIDE LINKS CHECKED
47 NY=NX-78
48 IF(1-L(ML,NY))19,5,19
C ALL ADJACENT SIDE LINKS CHECKED
19 CONTINUE
   GO TO 24
4 IF(NB-156)32,32,13
32 IF(L(ML,NB)-1)33,11,33
33 L(ML,NB)=1
   NC=NB/2
100 IF(2*NC-NB)98,99,98
98 IF(1-L(ML,NB-78))101,5,101
101 IF(1-L(ML,NB-77))34,5,34
99 IF(1-L(ML,NB-78))102,5,102
102 IF(1-L(ML,NB-79))34,5,34
C OPPOSITE BONDS CHECKED
34 DO 90 IC=1,41
   NW=NB-NB/2+118-IC
97 IF(NW-157)5,35,35
35 IF(L(ML,NW)-1)36,90,36
90 CONTINUE
C ALL CROSSLINKS TO THE LEFT CHECKED
36 IF(IC-1)37,38,37
37 IO=(IC-1)*2
   DO 39 KA=1,IO
   NX=((NB+1)/2)*2-79-KA
60 IF(1-L(ML,NX))61,5,61
C ALL OPPOSITE SIDE LINKS CHECKED
61 NY=NX+78
62 IF(1-L(ML,NY))39,5,39
C ALL ADJACENT SIDE LINKS CHECKED
39 CONTINUE
38 DO 63 IC=1,41
   NW=NB-NB/2+117+IC
68 IF(NW-196)20,20,5

```

```

20 IF(1-L(ML,NW))21,63,21
63 CONTINUE
C ALL CROSSLINKS TO THE RIGHT CHECKED
21 IF(IC-1)22,24,22
22 IO=(IC-1)*2
DO 23 KA=1,IO
NX=((NB+1)/2)*2-78+KA
91 IF(1-L(ML,NX))26,5,26
C ALL OPPOSITE SIDE LINKS CHECKED
26 NY=NX+78
27 IF(1-L(ML,NY))23,5,23
C ALL ADJACENT SIDE LINKS CHECKED
23 CONTINUE
GO TO 24
13 IF(L(ML,NB)-1)29,11,29
29 L(ML,NB)=1
NLNK=NLNK+1
DO 200 IC=1,41
190 IF(NB-IC-157)104,202,202
202 IP=NB-IC
191 IF(L(ML,IP)-1)105,200,105
200 CONTINUE
C ALL CROSSLINKS TO THE LEFT CHECKED
105 IBA=2*IC
DO 106 IW=1,IBA
NX=2*(NB-156)-1-IW
107 IF(L(ML,NX)-1)108,104,104
108 NY=NX+78
109 IF(L(ML,NY)-1)106,104,104
106 CONTINUE
GO TO 24
C CHECKED ALL SIDELINKS TO THE LEFT
104 DO 110 IC=1,41
111 IF(NB+IC-196)112,112,5
112 IP=NB+IC
194 IF(L(ML,IP)-1)116,110,116
110 CONTINUE
C ALL CROSSLINKS TO THE RIGHT CHECKED
116 IBA=2*IC
DO 117 IW=1,IBA
NX=2*(NB-157)+78+IW
118 IF(L(ML,NX)-1)119,5,119
119 NY=NX-78
120 IF(L(ML,NY)-1)117,5,117
117 CONTINUE
C CHECKED ALL SIDELINKS TO THE RIGHT

```

```

      GO TO 24
5  NBRAK=NBRAK+1
      GO TO 24
11  NDUP=NDUP+1
24  CONTINUE
      BRK=NBRAK
      ANMW=100./((100.+BRK)
      XI=IX
      DUPN=NDUP
      TIME=LOGF(19600./((19600.-200.*XI+DUPN))
      ASMW=100./((100.+200.*XI-DUPN)
      WRITE OUTPUT TAPE 3,30,NBRAK,NDUP,NLNK,ANMW,ASMW,TIME
30  FORMAT(1X,3I10,3F20.5)
25  CONTINUE
      CALL EXIT
      END
)1 (X- - (G7 070SQU00
*.J -9(NZ5GA 7 -2 -E -G - 3 5- - 97 95 -- 94 78 -- -5 -5 -7 -- 4F -4 -070SQU01
*U7(P($T 9 -G 5484 -1 -9 -5 - 2(X) - 9 - 070SQU02

```

APPENDIX V
COMPUTER PROGRAM
SIMPLE CASE, TYPE I
SINGLE BOND EVERY SIXTH BOND

```

C15 EVERY SIXTH BOND IS SINGLE CHAIN BOND CALCULATE NAMW CHANGE
C CASE 1 SIMPLE PROBABILITY FOR ALL BONDS BREAKING IS EQUAL
      DIMENSION L(100,200)
      FREQUENCY 7(1,0,2),8(9,1,0),9(0,1,9),4(1,0,1),10(9,1,0),13(0,1,9)
      1,14(9,1,0)
      NBRAK=0
      NDUP=0
      NLNK=0
      DO 810 MA=1,100
      DO 820 IB=6,66,6
820  L(MA,IB)=1
810  CONTINUE
      DO 25 IX=1,30
      DO 24 I=1,200
      R=RAND1(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)28,11,28
      28 L(ML,NB)=1
9      IF(1-L(ML,NB+66))24, 5,24
      4 IF(NB-132)10,10,14
      10 IF(L(ML,NB)-1)17,11,17
      17 L(ML,NB)=1
      13 IF(1-L(ML,NB-66))24,5,24
      14 IF(L(ML,NB)-1)12,11,12
      12 L(ML,NB)=1
      NLNK=NLNK+1
      GO TO 24
      5 NBRAK=NBRAK +1
      GO TO 24
      11 NDUP=NDUP+1
      24 CONTINUE
      BRK=NBRAK
      ANMW=100./((100.+BRK)
      XI=IX
      DUPN=NDUP
      TIME=LOGF(18800./((18800.-200.*XI+DUPN))
      ASMW=100./((100.+200.*XI-DUPN)
      WRITE OUTPUT TAPE 3,30, NBRAK,NDUP,NLNK,ANMW,ASMW,TIME
      30 FORMAT (1X,3I10,3F20.5)
      25 CONTINUE
      CALL EXIT
      END

```

APPENDIX VI
COMPUTER PROGRAM
SIMPLE CASE. TYPE I
SINGLE BOND EVERY TWELFTH BOND

```

C CASE I SIMPLE-PROBABILITY FOR ALL BONDS BREAKING IS EQUAL
C16 EVERY TWELVTH BOND IS SINGLE CHAIN BOND -CALCULATE NAMW CHANGE
  DIMENSION L(100,200)
  FREQUENCY 7(1,0,2),8(9,1,0),9(0,1,9),4(1,0,1),10(9,1,0),13(0,1,9)
  1,14(9,1,0)
  NBRAK=0
  NDUP=0
  NLNK=0
  DO 810 MA=1,100
  DO 820 IB=12,66,12
820 L(MA,IB)=1
810 CONTINUE
  DO 25 IX=1,30
  DO 24 I=1,200
  R=RAND1(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)28,11,28
  28 L(ML,NB)=1
  9 IF(1-L(ML,NB+66))24, 5,24
  4 IF(NB-132)10,10,14
  10 IF(L(ML,NB)-1)17,11,17
  17 L(ML,NB)=1
  13 IF(1-L(ML,NB-66))24,5,24
  14 IF(L(ML,NB)-1)12,11,12
  12 L(ML,NB)=1
  NLNK=NLNK+1
  GO TO 24
  5 NBRAK=NBRAK +1
  GO TO 24
  11 NDUP=NDUP+1
  24 CONTINUE
  BRK=NBRAK
  ANMW=100./((100.+BRK)
  XI=IX
  DUPN=NDUP
  TIME=LOGF(19400./((19400.-200.*XI+DUPN))
  ASMW=100./((100.+200.*XI-DUPN)
  WRITE OUTPUT TAPE 3,30, NBRAK,NDUP,NLNK,ANMW,ASMW,TIME
  30 FORMAT (1X,3I10,3F20.5)
  25 CONTINUE
  CALL EXIT
  END

```

APPENDIX VII
COMPUTER PROGRAM
SIMPLE CASE. TYPE II
SINGLE BOND EVERY TWELFTH BOND

C19 CASE II SIMPLE EVERY TWELVTH BOND IS SINGLE CHAIN BOND
 C PROBABILITY FOR ALL BONDS BREAKING IS EQUAL-CALCULATE NAMW CHANGE

```
*
  XEQ
  DIMENSION L(100,200)
  FREQUENCY 7(1,0,2),8(9,1,0),23(1,1,0),40(0,1,9),42(0,1,9)
  1,41(0,1,9),43(0,1,9),4(2,0,1),10(9,1,0),21(1,1,0),47(0,1,9)
  2,49(0,1,9),48(0,1,9),50(0,1,9),14(0,1,9)
  NBRK=0
  NDUP=0
  NLNK=0
  DO 810 MA=1,100
  DO 820 IB=12,78,12
820  L(MA,IB)=1
810  CONTINUE
  DO 25 IX=1,30
  DO 24 I=1,200
  R=RAND1(Y)*19600.
  NR=R
  ML=NR/196+1
  NB=196*ML-NR
  7 IF(NB-78)8,8,4
  8 IF(L(ML,NB)-1)28,11,28
28  L(ML,NB)=1
  NA=NB/2
  23 IF(2*NA-NB)40,41,40
  40 IF(1-L(ML,NB+78))42,5,42
  42 IF(1-L(ML,NB+79))24,5,24
  41 IF(1-L(ML,NB+78))43,5,43
  43 IF(1-L(ML,NB+77))24,5,24
  4 IF(NB-156)10,10,14
  10 IF(L(ML,NB)-1)17,11,17
  17 L(ML,NB)=1
  NC=NB/2
  21 IF(2*NC-NB)47,48,47
  47 IF(1-L(ML,NB-78))49,5,49
  49 IF(1-L(ML,NB-77))24,5,24
  48 IF(1-L(ML,NB-78))50,5,50
  50 IF(1-L(ML,NB-79))24,5,24
  14 IF(1-L(ML,NB))12,11,12
  12 L(ML,NB)=1
  NLNK=NLNK+1
  GO TO 24
  5 NBRK=NBRK+1
  GO TO 24
  11 NDUP=NDUP+1
  24 CONTINUE
```

```

BRK=NBRAK
ANMW=100./((100.+BRK)
XI=IX
DUPN=NDUP
TIME=LOGF(19000./((19000.-200.*XI+DUPN))
ASMW=100./((100.+200.*XI-DUPN)
WRITE OUTPUT TAPE 3,30,NBRAK,NDUP,NLNK,ANMW,ASMW,TIME
30 FORMAT(1X,3I10,3F20.5)
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
070SQU00

```

APPENDIX VIII
COMPUTER PROGRAM
SIMPLE CASE. TYPE II
SINGLE BOND EVERY TWENTY-FOURTH BOND

C20 CASE II SIMPLE EVERY TWENTY FOURTH BOND IS SINGLE CHAIN BOND
 C PROBABILITY FOR ALL BONDS BREAKING IS EQUAL - CALCULATE NAMW CHANGE

```
*
  XEQ
  DIMENSION L(100,200)
  FREQUENCY 7(1,0,2),8(9,1,0),23(1,1,0),40(0,1,9),42(0,1,9)
  1,41(0,1,9),43(0,1,9),4(2,0,1),10(9,1,0),21(1,1,0),47(0,1,9)
  2,49(0,1,9),48(0,1,9),50(0,1,9),14(0,1,9)
  NBRAK=0
  NDUP=0
  NLNK=0
  DO 810 MA=1,100
  DO 820 IB=24,78,24
820  L(MA,IB)=1
810  CONTINUE
  DO 25 IX=1,30
  DO 24 I=1,200
  R=RAND1(Y)*19600.
  NR=R
  ML=NR/196+1
  NB=196*ML-NR
  7 IF(NB-78)8,8.4
  8 IF(L(ML,NB)-1)28,11,28
28  L(ML,NB)=1
  NA=NB/2
  23 IF(2*NA-NB)40,41,40
  40 IF(1-L(ML,NB+78))42,5,42
  42 IF(1-L(ML,NB+79))24,5,24
  41 IF(1-L(ML,NB+78))43,5,43
  43 IF(1-L(ML,NB+77))24,5,24
  4 IF(NB-156)10,10,14
  10 IF(L(ML,NB)-1)17,11,17
  17 L(ML,NB)=1
  NC=NB/2
  21 IF(2*NC-NB)47,48,47
  47 IF(1-L(ML,NB-78))49,5,49
  49 IF(1-L(ML,NB-77))24,5,24
  48 IF(1-L(ML,NB-78))50,5,50
  50 IF(1-L(ML,NB-79))24,5,24
  14 IF(1-L(ML,NB))12,11,12
  12 L(ML,NB)=1
  NLNK=NLNK+1
  GO TO 24
  5 NBRAK=NBRAK+1
  GO TO 24
  11 NDUP=NDUP+1
  24 CONTINUE
```

```

BRK=NBRAK
ANMW=100./((100.+BRK)
XI=IX
DUPN=NDUP
TIME=LOGF(19300./((19300.-200.*XI+DUPN))
ASMW=100./((100.+200.*XI-DUPN)
WRITE OUTPUT TAPE 3,30,NBRAK,NDUP,NLNK,ANMW,ASMW,TIME
30 FORMAT(1X,3I10,3F20.5)
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 - 070SQU01
070SQU02

```

APPENDIX IX
COMPUTER PROGRAM
COMPLEX CASE. TYPE I
SINGLE BOND EVERY SIXTH BOND

```

C17 CASE 1 COMPLEX-EVERY SIXTH BOND IS SINGLE CHAIN BOND
C PROBABILITY FOR ALL BONDS BREAKING IS EQUAL - CALCULATE NAMW CHANGE
*   XEQ
    DIMENSION L(100,200)
    FREQUENCY 7(1,0,2),8(9,1,0),9(0,1,9),31(1,1,9),81(0,1,9),84(0,9,1)
    1,93(0,1,9),54(0,1,9),69(9,1,1),42(0,1,9),44(0,9,1),46(0,1,9)
    2,48(0,1,9),4(1,0,1),32(9,1,0),6(0,1,9),97(1,1,9),35(9,1,0)
    3,36(0,9,1),60(0,1,9),62(0,1,9),68(9,1,1),20(0,1,9),21(0,9,1)
    4,91(0,1,9),27(0,1,9),13(9,1,0),190(1,1,9),191(9,1,0),107(9,1,0)
    5,109(9,1,0),          111(9,1,1),194(9,1,0),118(9,1,0)
    6,120(9,1,0)
    NBRK=0
    NDUP=0
    NLNK=0
    DO 810 MA=1,100
    DO 820 IB=12,66,12
820  L(MA,IB)=1
810  CONTINUE
    DO 25 IX=1,30
    DO 24 I=1,200
    R=RAND1(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)28,11,28
    28  L(ML,NB)=1
    9   IF(1-L(ML,NB+66))80,5,80
C OPPOSITE BOND CHECKED
80   DO 51 IC=1,67
    NW=NB+133-IC
    31  IF(NW-133)5,81,81
    81  IF(1-L(ML,NW))84,51,84
    51  CONTINUE
C ALL CROSSLINKS TO THE LEFT CHECKED
84   IF(IC-1)85,75,85
    85  IO=IC-1
    DO 52 KA=1,10
    NX=NB+66-KA
    93  IF(1-L(ML,NX))53,5,53
C ALL OPPOSITE SIDE LINKS CHECKED
53   NY=NB-KA
    54  IF(1-L(ML,NY))52,5,52
C ALL ADJACENT SIDE LINKS CHECKED
52   CONTINUE
75   DO 17 IC=1,67

```

```

        NW=NB+132+IC
69      IF(NW-199)42,42,5
42      IF(1-L(ML,NW))44,17,44
17      CONTINUE
C ALL  CROSSLINKS TO THE RIGHT CHECKED
44      IF(IC-1)45,24,45
45      IO=IC-1
        DO 19 KA=1,IO
        NX=NB+66+KA
46      IF(1-L(ML,NX))47,5,47
C ALL  OPPOSITE SIDE LINKS CHECKED
47      NY=NB+KA
48      IF(1-L(ML,NY))19,5,19
C ALL  ADJACENT SIDE LINKS CHECKED
19      CONTINUE
        GO TO 24
4      IF(NB-132)32,32,13
32      IF(L(ML,NB)-1)33,11,33
33      L(ML,NB)=1
6      IF(1-L(ML,NB-66))34,5,34
C OPPOSITE BOND CHECKED
34      DO 90 IC=1,67
        NW=NB+67-IC
97      IF(NW-133)5,35,35
35      IF(L(ML,NW)-1)36,90,36
90      CONTINUE
C ALL  CROSSLINKS TO THE LEFT CHECKED
36      IF(IC-1)37,38,37
37      IO=IC-1
        DO 39 KA=1,IO
        NX=NB-66-KA
60      IF(1-L(ML,NX))61,5,61
C ALL  OPPOSITE SIDE LINKS CHECKED
61      NY=NB-KA
62      IF(1-L(ML,NY))39,5,39
C ALL  ADJACENT SIDE LINKS CHECKED
39      CONTINUE
38      DO 63 IC=1,67
        NW=NB+66+IC
68      IF(NW-199)20,20,5
20      IF(1-L(ML,NW))21,63,21
63      CONTINUE
C ALL  CROSSLINKS TO THE RIGHT CHECKED
21      IF(IC-1)22,24,22
22      IO=IC-1
        DO 23 KA=1,IO

```

```

          NX=NB-66+KA
    91   IF(1-L(ML,NX))26,5,26
C ALL OPPOSITE SIDE LINKS CHECKED
    26   NY=NB+KA
    27   IF(1-L(ML,NY))23,5,23
C ALL ADJACENT SIDE LINKS CHECKED
    23   CONTINUE
        GO TO 24
    13   IF(L(ML,NB)-1)29,11,29
    29   L(ML,NB)=1
        NLNK=NLNK+1
        DO 100 IC=1,67
    190   IF(NB-IC-133)104,102,107
    102   IP=NB-IC
    191   IF(L(ML,IP)-1)105,100,105
    100   CONTINUE
C ALL CROSSLINKS TO THE LEFT CHECKED
    105   DO 106 IW=1,IC
        NX=NB-IW-132
    107   IF(L(ML,NX)-1)108,104,104
    108   NY=NB-IW-66
    109   IF(L(ML,NY)-1)106,104,104
    106   CONTINUE
        GO TO 24
C CHECKED ALL SIDELINKS TO THE LEFT
    104   DO 110 IC=1,67
    111   IF(NB+IC-199)112,112,5
    112   IP=NB+IC
    194   IF(L(ML,IP)-1)116,110,116
    110   CONTINUE
C ALL CROSSLINKS TO THE RIGHT CHECKED
    116   DO 117 IW=1,IC
        NX=NB+IW-133
    118   IF(L(ML,NX)-1)119,5,119
    119   NY=NB+IW-67
    120   IF(L(ML,NY)-1)117,5,117
    117   CONTINUE
C CHECKED ALL SIDELINKS TO THE RIGHT
        GO TO 24
    5    NBRAK=NBRAK+1
        GO TO 24
    11   NDUP=NDUP+1
    24   CONTINUE
        BRK=NBRAK
        ANMW=100./((100.+BRK)
        XI=IX

        DUPN=NDUP
        TIME=LOGF(18800./((18800.-200.*XI+DUPN))
        ASMW=100./((100.+200.*XI-DUPN)
        WRITE OUTPUT TAPE 3,30,NBRAK,NDUP,NLNK,ANMW,ASMW,TIME
    30   FORMAT(1X,3I10,3F20.5)
    25   CONTINUE
        CALL EXIT
        END

```

ML TDR 64-151

APPENDIX X
COMPUTER PROGRAM
COMPLEX CASE. TYPE I
SINGLE BOND EVERY TWELFTH BOND

C18 CASE I COMPLEX EVERY TWELVTH BOND IS SINGLE CHAIN BOND

C PROBABILITY FOR ALL BONDS BREAKING IS EQUAL - CALCULATE NAMW CHANGE

```

*      XEQ
      DIMENSION L(100,200)
      FREQUENCY 7(1,0,2),8(9,1,0),9(0,1,9),31(1,1,9),81(0,1,9),84(0,9,1)
      1,93(0,1,9),54(0,1,9),69(9,1,1),42(0,1,9),44(0,9,1),46(0,1,9)
      2,48(0,1,9),4(1,0,1),32(9,1,0),6(0,1,9),97(1,1,9),35(9,1,0)
      3,36(0,9,1),60(0,1,9),62(0,1,9),68(9,1,1),20(0,1,9),21(0,9,1)
      4,91(0,1,9),27(0,1,9),13(9,1,0),190(1,1,9),191(9,1,0),107(9,1,0)
      5,109(9,1,0),                      111(9,1,1),194(9,1,0),118(9,1,0)
      6,120(9,1,0)
      NBRAK=0
      NDUP=0
      NLNK=0
      DO 810 MA=1,100
      DO 820 IB=6,66,6
820    L(MA,IB)=1
810    CONTINUE
      DO 25 IX=1,30
      DO 24 I=1,200
      R=RAND1(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)28,11,28
      28   L(ML,NB)=1
      9    IF(1-L(ML,NB+66))80,5,80
C OPPOSITE BOND CHECKED
      80   DO 51 IC=1,67
          NW=NB+133-IC
      31   IF(NW-133)5,81,81
      81   IF(1-L(ML,NW))84,51,84
      51   CONTINUE
C ALL CROSSLINKS TO THE LEFT CHECKED
      84   IF(IC-1)85,75,85
      85   IO=IC-1
          DO 52 KA=1,10
          NX=NB+66-KA
      93   IF(1-L(ML,NX))53,5,53
C ALL OPPOSITE SIDE LINKS CHECKED
      53   NY=NB-KA
      54   IF(1-L(ML,NY))52,5,52
C ALL ADJACENT SIDE LINKS CHECKED
      52   CONTINUE
      75   DO 17 IC=1,67

```

```

        NW=NB+132+IC
69      IF(NW-199)42,42,5
42      IF(1-L(ML,NW))44,17,44
17      CONTINUE
C ALL  CROSSLINKS TO THE RIGHT CHECKED
44      IF(IC-1)45,24,45
45      IO=IC-1
        DO 19 KA=1,IO
        NX=NB+66+KA
46      IF(1-L(ML,NX))47,5,47
C ALL  OPPOSITE SIDE LINKS CHECKED
47      NY=NB+KA
48      IF(1-L(ML,NY))19,5,19
C ALL  ADJACENT SIDE LINKS CHECKED
19      CONTINUE
        GO TO 24
4      IF(NB-132)32,32,13
32      IF(L(ML,NB)-1)33,11,33
33      L(ML,NB)=1
6      IF(1-L(ML,NB-66))34,5,34
C OPPOSITE BOND CHECKED
34      DO 90 IC=1,67
        NW=NB+67-IC
97      IF(NW-133)5,35,35
35      IF(L(ML,NW)-1)36,90,36
90      CONTINUE
C ALL  CROSSLINKS TO THE LEFT CHECKED
36      IF(IC-1)37,38,37
37      IO=IC-1
        DO 39 KA=1,IO
        NX=NB-66-KA
60      IF(1-L(ML,NX))61,5,61
C ALL  OPPOSITE SIDE LINKS CHECKED
61      NY=NB-KA
62      IF(1-L(ML,NY))39,5,39
C ALL  ADJACENT SIDE LINKS CHECKED
39      CONTINUE
38      DO 63 IC=1,67
        NW=NB+66+IC
68      IF(NW-199)20,20,5
20      IF(1-L(ML,NW))21,63,21
63      CONTINUE
C ALL  CROSSLINKS TO THE RIGHT CHECKED
21      IF(IC-1)22,24,22
22      IO=IC-1
        DO 23 KA=1,IO

```

```

      NX=NB-66+KA
91   IF(1-L(ML,NX))26,5,26
C ALL OPPOSITE SIDE LINKS CHECKED
26   NY=NB+KA
27   IF(1-L(ML,NY))23,5,23
C ALL ADJACENT SIDE LINKS CHECKED
23   CONTINUE
      GO TO 24
13   IF(L(ML,NB)-1)29,11,29
29   L(ML,NB)=1
      NLNK=NLNK+1
      DO 100 IC=1,67
190  IF(NB-IC-133)104,102,102
102  IP=NB-IC
191  IF(L(ML,IP)-1)105,100,105
100  CONTINUE
C ALL CROSSLINKS TO THE LEFT CHECKED
105  DO 106 IW=1,IC
      NX=NB-IW-132
107  IF(L(ML,NX)-1)108,104,104
108  NY=NB-IW-66
109  IF(L(ML,NY)-1)106,104,104
106  CONTINUE
      GO TO 24
C CHECKED ALL SIDELINKS TO THE LEFT
104  DO 110 IC=1,67
111  IF(NB+IC-199)112,112,5
112  IP=NB+IC
194  IF(L(ML,IP)-1)116,110,116
110  CONTINUE
C ALL CROSSLINKS TO THE RIGHT CHECKED
116  DO 117 IW=1,IC
      NX=NB+IW-133
118  IF(L(ML,NX)-1)119,5,119
119  NY=NB+IW-67
120  IF(L(ML,NY)-1)117,5,117
117  CONTINUE
C CHECKED ALL SIDELINKS TO THE RIGHT
      GO TO 24
5    NBRAK=NBRAK+1
      GO TO 24
11   NDUP=NDUP+1
24   CONTINUE
      BRK=NBRAK
      ANMW=100./(100.+BRK)
      XI=IX

      DUPN=NDUP
      TIME=LOGF(19400./((19400.-200.*XI+DUPN)))
      ASMW=100./((100.+200.*XI-DUPN))
      WRITE OUTPUT TAPE 3,30,NBRAK,NDUP,NLNK,ANMW,ASMW,TIME
30   FORMAT(1X,3I10,3F20.5)
25   CONTINUE
      CALL EXIT
      END

```

APPENDIX XI
COMPUTER PROGRAM
COMPLEX CASE. TYPE II
SINGLE BOND EVERY TWELFTH BOND

C21 CASE II COMPLEX EVERY TWELVTH BOND IS SINGLE CHAIN BOND
 C PROBABILITY FOR ALL BONDS BREAKING IS EQUAL - CALCULATE NAMW CHANGE

```
*      XEQ
      DIMENSION L(100,200)
      FREQUENCY 7(1,0,2),8(9,1,0),92(1,1,0),93(0,1,9),95(0,1,9)
1,94(0,1,9),96(0,1,9),31(1,1,9),81(0,1,9),84(0,9,1),73(0,1,9)
2,54(0,1,9),69(9,1,1),42(0,1,9),44(0,9,1),46(0,1,9),48(0,1,9)
3,4(1,0,1),32(9,1,0),100(1,1,0),98(0,1,9),101(0,1,9),99(0,1,9)
4,102(0,1,9),97(1,1,9),35(9,1,0),36(0,9,1),60(0,1,9),62(0,1,9)
5,68(9,1,1),20(0,1,9),21(0,9,1),91(0,1,9),27(0,1,9),13(9,1,0)
6,190(1,1,9),191(9,1,0),107(9,1,0),109(9,1,0)
7,111(9,1,1),194(9,1,0),118(9,1,0),120(9,1,0)
      NBRK=0
      NDUP=0
      NLNK=0
      DO 810 MA=1,100
      DO 820 IB=12,78,12
820   L(MA,IB)=1
810   CONTINUE
      DO 25 IX=1,30
      DO 24 I=1,200
      R=RAND1(Y)*19600.
      NR=R
      ML=NR/196+1
      NB=196*ML-NR
      7 IF(NB-78)8,8,4
      8 IF(L(ML,NB)-1)28,11,28
28   L(ML,NB)=1
      NA=NB/2
      92 IF(2*NA-NB)93,94,93
      93 IF(1-L(ML,NB+78))95,5,95
      95 IF(1-L(ML,NB+79))80,5,80
      94 IF(1-L(ML,NB+78))96,5,96
      96 IF(1-L(ML,NB+77))80,5,80
C BOTH OPPOSITE BONDS CHECKED
      80 DO 51 IC=1,41
      NW=NB-NB/2+157-IC
      31 IF(NW-157)5,81,81
      81 IF(1-L(ML,NW))84,51,84
      51 CONTINUE
C ALL CROSSLINKS TO THE LEFT CHECKED
      84 IF(IC-1)85,75,85
      85 IO=(IC-1)*2
      DO 52 KA=1,IO
      NX=((NB+1)/2)*2+77-KA
      73 IF(1-L(ML,NX))53,5,53
```

```

C ALL OPPOSITE SIDE LINKS CHECKED
  53 NY=NX-78
  54 IF(1-L(ML,NY))52,5,52
C ALL ADJACENT SIDE LINKS CHECKED
  52 CONTINUE
  75 DO 17 IC=1,41
      NW=NB-NB/2+156+IC
  69 IF(NW-196)42,42,5
  42 IF(1-L(ML,NW))44,17,44
  17 CONTINUE
C ALL CROSSLINKS TO THE RIGHT CHECKED
  44 IF(IC-1)45,24,45
  45 IO=(IC-1)*2
      DO 19 KA=1,IO
          NX=((NB+1)/2)*2+78+IO
  46 IF(1-L(ML,NX))47,5,47
C ALL OPPOSITE SIDE LINKS CHECKED
  47 NY=NX-78
  48 IF(1-L(ML,NY))19,5,19
C ALL ADJACENT SIDE LINKS CHECKED
  19 CONTINUE
      GO TO 24
  4 IF(NB-156)32,32,13
  32 IF(L(ML,NB)-1)33,11,33
  33 L(ML,NB)=1
      NC=NB/2
  100 IF(2*NC-NB)98,99,98
  98 IF(1-L(ML,NB-78))101,5,101
  101 IF(1-L(ML,NB-77))34,5,34
  99 IF(1-L(ML,NB-78))102,5,102
  102 IF(1-L(ML,NB-79))34,5,34
C OPPOSITE BONDS CHECKED
  34 DO 90 IC=1,41
      NW=NB-NB/2+118-IC
  97 IF(NW-157)5,35,35
  35 IF(L(ML,NW)-1)36,90,36
  90 CONTINUE
C ALL CROSSLINKS TO THE LEFT CHECKED
  36 IF(IC-1)37,38,37
  37 IO=(IC-1)*2
      DO 39 KA=1,IO
          NX=((NB+1)/2)*2-79-KA
  60 IF(1-L(ML,NX))61,5,61
C ALL OPPOSITE SIDE LINKS CHECKED
  61 NY=NX+78
  62 IF(1-L(ML,NY))39,5,39

```

```

C ALL ADJACENT SIDE LINKS CHECKED
39 CONTINUE
38 DO 63 IC=1,41
   NW=NB-NB/2+117+IC
68 IF(NW-196)20,20,5
20 IF(1-L(ML,NW))21,63,21
63 CONTINUE
C ALL CROSSLINKS TO THE RIGHT CHECKED
21 IF(IC-1)22,24,22
22 IO=(IC-1)*2
   DO 23 KA=1,IO
   NX=((NB+1)/2)*2-78+KA
91 IF(1-L(ML,NX))26,5,26
C ALL OPPOSITE SIDE LINKS CHECKED
26 NY=NX+78
27 IF(1-L(ML,NY))23,5,23
C ALL ADJACENT SIDE LINKS CHECKED
23 CONTINUE
   GO TO 24
13 IF(L(ML,NB)-1)29,11,29
29 L(ML,NB)=1
   NLNK=NLNK+1
   DO 200 IC=1,41
190 IF(NB-IC-157)104,202,202
202 IP=NB-IC
191 IF(L(ML,IP)-1)105,200,105
200 CONTINUE
C ALL CROSSLINKS TO THE LEFT CHECKED
105 IBA=2*IC
   DO 106 IW=1,IBA
   NX=2*(NB-156)-1-IW
107 IF(L(ML,NX)-1)108,104,104
108 NY=NX+78
109 IF(L(ML,NY)-1)106,104,104
106 CONTINUE
   GO TO 24
C CHECKED ALL SIDELINKS TO THE LEFT
104 DO 110 IC=1,41
111 IF(NB+IC-196)112,112,5
112 IP=NB+IC
194 IF(L(ML,IP)-1)116,110,116
110 CONTINUE
C ALL CROSSLINKS TO THE RIGHT CHECKED
116 IBA=2*IC
   DO 117 IW=1,IBA
   NX=2*(NB-157)+78+IW

```

```

118 IF(L(ML,NX)-1)119,5,119
119 NY=NX-78
120 IF(L(ML,NY)-1)117,5,117
117 CONTINUE
C CHECKED ALL SIDELINKS TO THE RIGHT
GO TO 24
5 NBRAK=NBRAK+1
GO TO 24
11 NDUP=NDUP+1
24 CONTINUE
BRK=NBRAK
ANMW=100./(100.+BRK)
XI=IX
DUPN=NDUP
TIME=LOGF(19000./(19000.-200.*XI+DUPN))
ASMW=100./(100.+200.*XI-DUPN)
WRITE OUTPUT TAPE 3,30,NBRAK,NDUP,NLNK,ANMW,ASMW,TIME
30 FORMAT(1X,3I10,3F20.5)
25 CONTINUE
CALL EXIT
END
)1 (X- - (G7 070SQU00
*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 XII
COMPUTER PROGRAM
COMPLEX CASE. TYPE II
SINGLE BOND EVERY TWENTY-FOURTH BOND

C22 CASE II COMPLEX - EVERY TWENTY FOURTH BOND IS SINGLE CHAIN BOND
 C PROBABILITY FOR ALL BONDS BREAKING IS EQUAL - CALCULATE NAMW CHANGE

```

*      XEQ
      DIMENSION L(100,200)
      FREQUENCY 7(1,0,2),8(9,1,0),92(1,1,0),93(0,1,9),95(0,1,9)
1,94(0,1,9),96(0,1,9),31(1,1,9),81(0,1,9),84(0,9,1),73(0,1,9)
2,54(0,1,9),69(9,1,1),42(0,1,9),44(0,9,1),46(0,1,9),48(0,1,9)
3,4(1,0,1),32(9,1,0),100(1,1,0),98(0,1,9),101(0,1,9),99(0,1,9)
4,102(0,1,9),97(1,1,9),35(9,1,0),36(0,9,1),60(0,1,9),62(0,1,9)
5,68(9,1,1),20(0,1,9),21(0,9,1),91(0,1,9),27(0,1,9),13(9,1,0)
6,190(1,1,9),191(9,1,0),107(9,1,0),109(9,1,0)
7,111(9,1,1),194(9,1,0),118(9,1,0),120(9,1,0)
      NBRK=0
      NDUP=0
      NLNK=0
      DO 810 MA=1,100
      DO 820 IB=24,78,24
820  L(MA,IB)=1
810  CONTINUE
      DO 25 IX=1,30
      DO 24 I=1,200
      R=RAND1(Y)*19600.
      NR=R
      ML=NR/196+1
      NB=196*ML-NR
      7 IF(NB-78)8,8,4
      8 IF(L(ML,NB)-1)28,11,28
28  L(ML,NB)=1
      NA=NB/2
82  IF(2*NA-NB)93,94,93
83  IF(1-L(ML,NB+78))95,5,95
85  IF(1-L(ML,NB+79))80,5,80
84  IF(1-L(ML,NB+78))96,5,96
86  IF(1-L(ML,NB+77))80,5,80
C BOTH OPPOSITE BONDS CHECKED
80 DO 51 IC=1,41
      NW=NB-NB/2+157-IC
81 IF(NW-157)5,81,81
81 IF(1-L(ML,NW))84,51,84
51 CONTINUE
C ALL CROSSLINKS TO THE LEFT CHECKED
84 IF(IC-1)85,75,85
85 IO=(IC-1)*2
      DO 52 KA=1,IO
      NX=((NB+1)/2)*2+77-KA
73 IF(1-L(ML,NX))53,5,53

```

```

C ALL OPPOSITE SIDE LINKS CHECKED
  53 NY=NX-78
  54 IF(1-L(ML,NY))52,5,52
C ALL ADJACENT SIDE LINKS CHECKED
  52 CONTINUE
  75 DO 17 IC=1,41
      NW=NB-NB/2+156+IC
  69 IF(NW-196)42,42,5
  42 IF(1-L(ML,NW))44,17,44
  17 CONTINUE
C ALL CROSSLINKS TO THE RIGHT CHECKED
  44 IF(IC-1)45,24,45
  45 IO=(IC-1)*2
      DO 19 KA=1,IO
          NX=((NB+1)/2)*2+78+IO
  46 IF(1-L(ML,NX))47,5,47
C ALL OPPOSITE SIDE LINKS CHECKED
  47 NY=NX-78
  48 IF(1-L(ML,NY))19,5,19
C ALL ADJACENT SIDE LINKS CHECKED
  19 CONTINUE
      GO TO 24
  4 IF(NB-156)32,32,13
  32 IF(L(ML,NB)-1)33,11,33
  33 L(ML,NB)=1
      NC=NB/2
  100 IF(2*NC-NB)98,99,98
  98 IF(1-L(ML,NB-78))101,5,101
  101 IF(1-L(ML,NB-77))34,5,34
  99 IF(1-L(ML,NB-78))102,5,102
  102 IF(1-L(ML,NB-79))34,5,34
C OPPOSITE BONDS CHECKED
  34 DO 90 IC=1,41
      NW=NB-NB/2+118-IC
  97 IF(NW-157)5,35,35
  35 IF(L(ML,NW)-1)36,90,36
  90 CONTINUE
C ALL CROSSLINKS TO THE LEFT CHECKED
  36 IF(IC-1)37,38,37
  37 IO=(IC-1)*2
      DO 39 KA=1,IO
          NX=((NB+1)/2)*2-79-KA
  60 IF(1-L(ML,NX))61,5,61
C ALL OPPOSITE SIDE LINKS CHECKED
  61 NY=NX+78
  62 IF(1-L(ML,NY))39,5,39

```

```

C ALL ADJACENT SIDE LINKS CHECKED
39 CONTINUE
38 DO 63 IC=1,41
   NW=NB-NB/2+117+IC
68 IF(NW-196)20,20,5
20 IF(1-L(ML,NW))21,63,21
63 CONTINUE
C ALL CROSSLINKS TO THE RIGHT CHECKED
21 IF(IC-1)22,24,22
22 IO=(IC-1)*2
   DO 23 KA=1,IO
   NX=((NB+1)/2)*2-78+KA
91 IF(1-L(ML,NX))26,5,26
C ALL OPPOSITE SIDE LINKS CHECKED
26 NY=NX+78
27 IF(1-L(ML,NY))23,5,23
C ALL ADJACENT SIDE LINKS CHECKED
23 CONTINUE
   GO TO 24
13 IF(L(ML,NB)-1)29,11,29
29 L(ML,NB)=1
   NLNK=NLNK+1
   DO 200 IC=1,41
190 IF(NB-IC-157)104,202,202
202 IP=NB-IC
191 IF(L(ML,IP)-1)105,200,105
200 CONTINUE
C ALL CROSSLINKS TO THE LEFT CHECKED
105 IBA=2*IC
   DO 106 IW=1,IBA
   NX=2*(NB-156)-1-IW
107 IF(L(ML,NX)-1)108,104,104
108 NY=NX+78
109 IF(L(ML,NY)-1)106,104,104
106 CONTINUE
   GO TO 24
C CHECKED ALL SIDELINKS TO THE LEFT
104 DO 110 IC=1,41
111 IF(NB+IC-196)112,112,5
112 IP=NB+IC
194 IF(L(ML,IP)-1)116,110,116
110 CONTINUE
C ALL CROSSLINKS TO THE RIGHT CHECKED
116 IBA=2*IC
   DO 117 IW=1,IBA
   NX=2*(NB-157)+78+IW

```

```

118 IF(L(ML,NX)-1)119,5,119
119 NY=NX-78
120 IF(L(ML,NY)-1)117,5,117
117 CONTINUE
C CHECKED ALL SIDELINKS TO THE RIGHT
GO TO 24
5 NBRAK=NBRAK+1
GO TO 24
11 NDUP=NDUP+1
24 CONTINUE
BRK=NBRAK
ANMW=100./((100.+BRK)
XI=IX
DUPN=NDUP
TIME=LOGF(19300./((19300.-200.*XI+DUPN))
ASMW=100./((100.+200.*XI-DUPN)
WRITE OUTPUT TAPE 3,30,NBRAK,NDUP,NLNK,ANMW,ASMW,TIME
30 FORMAT(1X,3I10,3F20.5)
25 CONTINUE
CALL EXIT
END
)1 (X- - (G7 070SQU00
*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

```