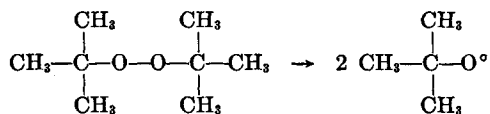




The initial free radicals  $R^\circ$  are often generated by the thermal decomposition of initiators (often referred to inaccurately as catalysts). The most commonly used free-radical initiators are organic peroxides, such as di-*tert*-butyl peroxide, *tert*-butyl perbenzoate, benzoyl peroxide, etc. Butyl peroxide, e.g., decomposes under heating as follows:



where a molecule of peroxide produces two free radicals.

Organic peroxides also decompose in part by a self-induced mechanism whereby radicals from the thermal decomposition attack other peroxide molecules. This induced decomposition is not considered in this program although the equations and program could be readily modified to take it into account. At the low initiator concentrations commonly used in polymerizations the induced decomposition is of secondary importance.

The rate of generation of free radicals is primarily of the first order:

$$d[R]/dt = -2 d[C]/dt = k_d [C] \quad (1)$$

where  $C$  is the initiator concentration in molar equivalents, and  $k_d$  = the rate constant. The factor 2 is included since every initiator molecule splits into two free radicals.  $k_d$  is a function of temperature following the well-known Arrhenius equation:

$$k_d = A e^{-E/RT} \quad (2)$$

where  $A$  is the frequency factor,  $E$  is the activation energy,  $R$  the gas constant, and  $T$  the absolute temperature. The initiator concentration, as derived from (1), drops exponentially:

$$[C] = [C_0] e^{-k_d t} \quad (3)$$

where  $C_0$  is the initial initiator concentration.

By substituting (2) into (3) we obtain the initiator concentration in function of both time and temperature:

$$[C] = [C_0] \exp \{ -A e^{-E/RT} t \} \quad (4)$$

and by substituting (4) into (1) we obtain:

$$d[R]/dt = 2 A e^{-E/RT} [C_0] \exp \{ -A e^{-E/RT} t \}$$

Or more generally:

$$\frac{d[R]}{dt} = \sum_{i=1}^{i=n} 2 A_i e^{-E_i/RT} [C_{0,i}] \exp \{ -A_i e^{-E_i/RT} t \} \quad (5)$$

where the summation sign is added for the case of more than one initiator from one to  $n$ .

We now ask the computer for the proper temperature or time relationship, which will keep eq. (5) constant.

## COMPUTER SOLUTION

### Procedure

Direct calculation of the temperature–time function which will maintain a constant rate of generation of free radicals is not possible. To solve this function between some given initial conditions and a given maximum terminal temperature, a very simple adaptation of Euler's method was programmed for the IBM System 360. The solution is based on the assumption that, for very small time periods, the entire system of variables is linear.

For each time period,  $\Delta t$ , between times  $t_i$  and  $t_{i+1}$ , the following iterations are applied. The temperature is assumed constant for  $\Delta t$  at the level computed for  $t_i$ . The rate constant,  $k_d$ , is therefore also constant for  $\Delta t$  from (2), and the concentration at  $t_{i+1}$  is computed by (3). The rate of generation of free radicals is then computed by (1) using the average concentration during  $\Delta t$ . If this rate is within acceptable limits from the initial rate,  $t_{i+1}$  becomes  $t_i$  for the next time period. If the calculated rate is below acceptable limits, the temperature is incremented by some small amount and the entire set of computations is repeated for the period. Incrementation of the temperature followed by recomputation will continue until the computed rate of generation of free radicals equals the initial rate; then and only then does computation proceed with the next period. The program ends when a given maximum temperature is reached (see Fig. 1).

### Discussion of Accuracy

Accuracy depends on the size of the time period over which linearity is assumed. The smaller the time period, the more accurate the computations. The sample program sets  $\Delta t$  equal to 0.01 hr. Rather than perform rigorous analysis,  $\Delta t$  was modified to 0.1 hr. and the program was rerun. At 37 hr. the temperature differed by 0.1°C. from that calculated with  $\Delta t$  set to 0.01. We feel justified in the inference that computation with  $\Delta t$  equal to 0.01 will yield results well within the limits of practical temperature control.

### SAMPLE CASES

In the first sample case a temperature/time curve is calculated for a polymerization reaction containing a mixture of three peroxides. The three peroxides are benzoyl peroxide, tertiary butyl perbenzoate, and dicumyl peroxide. For each peroxide the activation energy was taken from the literature.<sup>1</sup> The Arrhenius constants were calculated from the first-order rate constants given in the same publication.<sup>1</sup>

The results obtained are given in Table I.



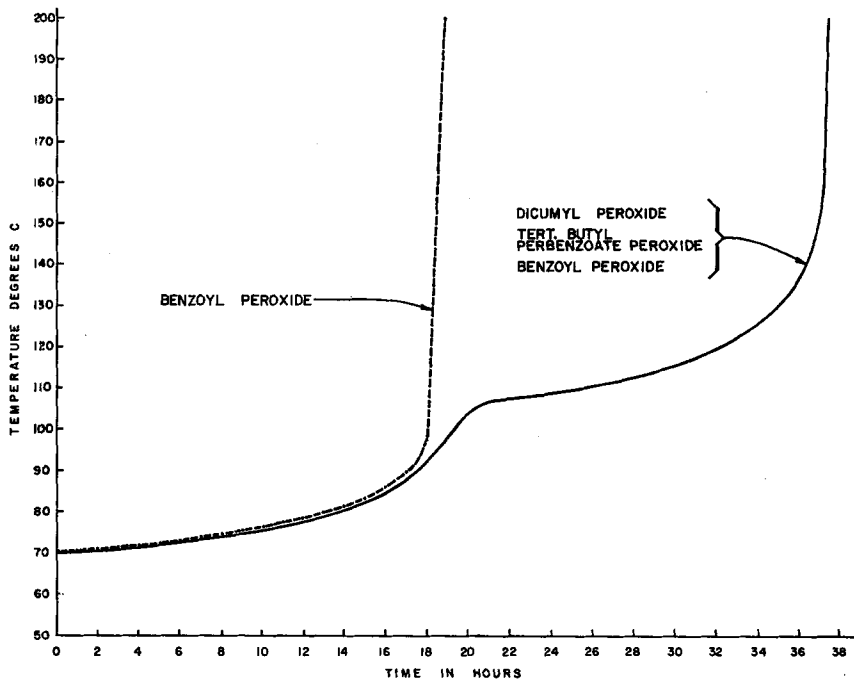


Fig. 2. Temperature-time relationship for constant free-radical production.

Table I also shows the concentrations used in the first sample case.

In the second sample case the temperature/time curve for a polymerization initiated with a single peroxide is calculated.

Benzoyl peroxide is being used at a concentration of  $0.12 \times 10^{-2}$  moles/l. The absolute amount of initiator does, of course, not affect the calculation of the temperature/time relationship, it merely affects the rate of radical

TABLE I

Peroxide	Activation energy, kcal./mole	A, per hr.	1st Case conc., moles/l.
Dicumyl peroxide	40.7	$0.46233 \times 10^{22}$	$0.2 \times 10^{-2}$
<i>tert</i> -Butyl perbenzoate	34.7	$0.81128 \times 10^{19}$	$0.4 \times 10^{-2}$
Benzoyl peroxide	29.6	$0.37995 \times 10^{18}$	$0.6 \times 10^{-2}$

production to be kept constant by that relationship. But in a case of a mixture of initiators, the relative concentrations of these initiators do indeed influence the outcome of the temperature/time relationships.

The code listings are given in the printout and the solutions to the sample cases are shown in Figure 2.

As can be seen, a mixture of peroxides allows one to effect a polymerization reaction at a lower temperature over a longer period of time. This is

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PAGE 001

DATA BEGIN LOADING

STORAGE MAP
IBCON AT LOCATION 001000
PRAIN AT LOCATION 002480
MAIN AT LOCATION 002980
CGTU AT LOCATION 002C70
WEXP AT LOCATION 002C48
EXP AT LOCATION 002C4C

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BEGIN COMPILATION

S.0001 DIMENSION C(5),C(5),E(5),A(5),DK(5)
S.0002 I=1
S.0003 KOUNT=3
S.0004 10 WRITE(KOUNT,W00)
S.0005 WRITE(KOUNT,W05)
S.0006 WRITE(ADDY,W10)
S.0007 DT=W-01
S.0008 I=1
S.0009 READ(RIN,W15)H,T,A
S.0010 T=TA\*273.1
S.0011 DO 15 J=1,N
S.0012 READ(RIN,W20)C1,J,E(J),A(J)
S.0013 WRITE(KOUNT,W20)C1,J,E(J),A(J)
S.0014 C1J=C1/J\*100.
S.0015 C2J=C1/J
S.0016 15 E1J=E(J)\*1000.
S.0017 TR=W-
S.0018 N=1.9865
S.0019 100 DO 110 J=1,N
S.0020 105 DK(J)=A(J)\*EXP(-E(J)/TR\*11)
S.0021 GO TO 110,120,1
S.0022 110 DNG.
S.0023 DO 115 J=1,N
S.0024 115 D=D+DK(J)+C(J)
S.0025 I=2
S.0026 SW=D-0
S.0027 WRITE(KOUNT,W50)SWD
S.0028 WRITE(ADDY,W55)
S.0029 GO TO 137
S.0030 120 DO 121 J=1,N
S.0031 IF(C1J-I-E-201123,123,124
S.0032 124 IF(DK1)9,1-100,112,122,125
S.0033 126 C1J=C1J\*WEXP1-061JDKD1
S.0034 GO TO 121
S.0035 123 C1J=0
S.0036 C1J=0
S.0037 121 CONTINUE
S.0038 D=0
S.0039 DO 125 J=1,N
S.0040 125 D=DK1J+I(C2J)+C1J/2.1+0
S.0041 IF(D-SW)9,10,130,135,137
S.0042 130 IF(D-SW)9,1140,135,135
S.0043 135 KOUNT=KOUNT+1
S.0044 IF(KOUNT-100)136,137,137
S.0045 136 DO 136 J=1,N
S.0046 136 C1J=C2(J)
S.0047 GO TO 120
S.0048 137 KOUNT=0
S.0049 137 TA=T-273.1
S.0050 WRITE(KOUNT,W60)TR,TA
S.0051 TR=TR\*DT\*100-
S.0052 GO TO 136
S.0053 140 T=1.5
S.0054 IF(T-473.11100,143,143
S.0055 145 KOUNT=KOUNT
S.0056 TR=TR\*(KOUNT-100.1)\*0.95
S.0057 TA=T-273.1
S.0058 WRITE(KOUNT,W60)TR,TA
S.0059 PAUSE

BP5 FORTRAN IV D COMPILER VERSION 2 LEVEL 1 MAR 1964

PAGE 002

S.0060 GO TO 10
S.0061 900 FORMAT(15,'+',115,'\*POLYMER RESEARCH//218,'INPUT DATA//')
S.0062 905 FORMAT(1,'PERCENT//226,'\*CONCENTRATION//46E,'%',14,'A')
S.0063 910 FORMAT(1,' NAME//127,'\*MOLES/LITER//154,'\*KCAL/MOLE PER HOUR//')
S.0064 915 FORMAT(14,F10.0)
S.0065 920 FORMAT(29)
S.0066 930 FORMAT(177,'ZIN RADICALS PRODUCED AT E14.7,' \*M/L PER HOUR//')
S.0067 935 FORMAT(172H,' TIME TEMPERATURE//21H HOURS DEGREES C//')
S.0068 940 FORMAT(18,'(F11.1)')
S.0069 END

STORAGE MAP VARIABLES (TAG C = COMMON, E = EQUIVALENT)

Table with columns: NAME, TAG, REL. ADR, NAME, TAG, REL. ADR, NAME, TAG, REL. ADR, NAME, TAG, REL. ADR. Rows include C, N, D, TA, KOUNT.

EXTERNAL REFERENCES

Table with columns: NAME, REL. ADR, NAME, REL. ADR, NAME, REL. ADR, NAME, REL. ADR. Row includes EXP, 00012C.

CONSTANTS

Table with columns: NAME, REL. ADR, NAME, REL. ADR, NAME, REL. ADR, NAME, REL. ADR. Rows include 00000005, 00000004, 42640000, 29148888, 90707083.

IMPLIED EXTERNAL REFERENCES

Table with columns: NAME, REL. ADR, NAME, REL. ADR, NAME, REL. ADR, NAME, REL. ADR. Rows include IBCOM, 000328, CGTU, 00032C.

Table with columns: STATEMENT NUMBER, REL. ADR, STATEMENT NUMBER, REL. ADR, STATEMENT NUMBER, REL. ADR, STATEMENT NUMBER, REL. ADR. Rows include 00010, 00122, 00130, 00137, 00008, 00930.

END OF COMPILATION MAIN SIZE OF COMMON 00000 PHOGRAM 01978

## POLYMER RESEARCH

## INPUT DATA

PEROXIDE NAME	CONCENTRATION MOLES/LITER	E KCAL/MOLE	A PER HOUR
DICUMYL	0.200E-02	40.700	0.44233E 22
TERY BUTYL PERBENZATE	0.400E-02	34.700	0.81128E 19
BENZOYL	0.600E-02	29.600	0.37995E 18

RADICALS PRODUCED AT 0.3165156E-05 M/L PER HOUR

TIME HOURS	TEMPERATURE DEGREES C
0.0	70.0
1.0	70.5
2.0	71.0
3.0	71.5
4.0	72.0
5.0	72.5
6.0	73.0
7.0	74.0
8.0	74.5
9.0	75.5
10.0	76.0
11.0	77.0
12.0	78.0
13.0	78.5
14.0	81.0
15.0	82.5
16.0	85.0
17.0	88.0
18.0	92.0
19.0	96.5
20.0	105.0
21.0	107.0
22.0	107.5
23.0	108.5
24.0	109.0
25.0	110.0
26.0	111.0
27.0	112.0
28.0	113.0
29.0	114.5
30.0	116.0
31.0	118.0
32.0	120.5
33.0	123.0
34.0	126.0
35.0	130.5
36.0	136.0
37.0	154.5
37.2	200.0
PAUSE	00000

C.T.A.C

PEROXIDE NAME	CONCENTRATION MOLES/LITER	E KCAL/MOLE	A PER HOUR
BENZOYL	0.120E-02	29.600	0.37995E 18

RADICALS PRODUCED AT 0.6277879E-06 M/L PER HOUR

TIME HOURS	TEMPERATURE DEGREES C
0.0	70.0
1.0	70.5
2.0	71.0
3.0	71.5
4.0	72.0
5.0	72.5
6.0	73.0
7.0	74.0
8.0	74.5
9.0	75.5
10.0	76.5
11.0	77.5
12.0	78.5
13.0	80.0
14.0	81.5
15.0	83.5
16.0	86.0
17.0	90.0
18.0	98.0
18.8	200.0

well known. The computer program given in this article allows one to take optimum advantage of this knowledge.

In practice, one would program the temperature in function of time as given by the calculated relationship for as long as possible or until limited by other factors not considered in our computer program. These other factors may be several, such as excessive temperature or the Trommsdorff<sup>2</sup> effect. Excessive temperature is self-explanatory: for some reason, a given polymerization temperature should not be exceeded in certain polymerizations, either because the rate of depolymerization equals that of polymerization (ceiling temperature) or because side-reactions start taking an effect on either monomer or polymer. The Trommsdorff<sup>2</sup> effect is related to an increase in viscosity which causes the chain-termination reaction to slow down. Thereby the concentration of free radicals increases—hence also the rate of polymerization. Furthermore, the slowdown of the termina-

tion reaction results in the production of higher molecular weight polymers. For these and other reasons, the temperature/time relationship will usually not be followed during the entire course of a polymerization reaction. However, the relationship will still prove useful for optimum control of the initial and intermediate stages of polymerizations and the production of sharper molecular weight distributions.

### References

1. O. L. Mageli, S. D. Bukata, and D. J. Bolton, *Evaluation of Peroxides from Half-Life Data*, publ. of Lucidol Div. of Wallace & Tiernan, Inc., Buffalo, N. Y.; D. F. Doehnert and O. L. Mageli, *Mod. Plastics*, No. 6, 142 (1959).
2. E. Trommsdorff, *BIOS Report*, No. 363, Item No. 22; E. Trommsdorff, H. Kohle, and P. Lagally, *Makromol. Chem.*, 1, 169 (1947).

### Résumé

Une méthode est décrite pour mettre au point grâce à un calculateur digital un programme de température qui, appliqué à la polymérisation, permet de garder la formation de radicaux libres constante tout le long de la partie principale de la réaction.

### Zusammenfassung

Eine Digitalcomputermethode zur Aufstellung eines Temperaturprogrammes wird beschrieben, das eine Konstanthaltung der Radikalnachlieferung während des Hauptteils der Reaktion in einem Polymerisationsansatz gewährleistet.

Received October 7, 1966

Prod. No. 1516