

## Predicting Chain Length Distribution in Step Growth Polymerization by Monte Carlo Method

Wahyudi Budi Sediawan<sup>1</sup>, Megawati<sup>2\*</sup>

<sup>1</sup>Chemical Engineering, Faculty of Engineering, Gadjah Mada University  
Jl. Grafika 2, Yogyakarta 55281, Indonesia

<sup>2\*</sup>Chemical Engineering, Faculty of Engineering, Semarang State University  
Bldg. E1, Sekaran, Gunungpati, Semarang 50229, Indonesia

Tel.: +62 24 8508009; Fax: +62 24 8508009; E-mail add.: megawatie@yahoo.com

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**Abstract**— Chain length distribution is an important factor affecting the polymer product properties. A Monte Carlo method was applied to predict the chain length distribution in the step growth polymerization product under isothermal condition. The results for small time of polymerization were compared to the results of kinetics modeling. It was observed that Monte Carlo method can quantitatively well predict the chain length distribution. The Monte Carlo method was then applied to predict the chain length distribution for large times. It is observed that the Monte Carlo method was relatively easy to be applied until relatively high degree of polymerization.

**Keywords** —Chain length distribution, kinetic modeling, Monte Carlo method, step growth polymerization

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### I. INTRODUCTION

Step growth polymerization is an important process for producing polymer materials, such as epoxy, silicone, nylon, kevlar, polycarbonates, polyurea, polyanhydride, polyester, polyamides, polyurethanes, etc. Properties of polymer materials produced are highly dependent of the chain length distribution (CLD) of the polymer molecules. For example, the higher the chain length, the higher the material strength would usually be.[1] Hence, it is obvious that the prediction and control of chain length is very important in polymerization processes, including step growth polymerization. Various calculation methods have been developed to predict the CLD of step growth polymerization. A number of simplified models result in the average number of the CLD, while kinetics models via simultaneous differential equations predict the CLD. Recently, the average number of the CLD is considered unsatisfactory to predict the properties of materials.[2] Meanwhile, the kinetics model via simultaneous differential equations is considered too complicated.[3] The complexity of the kinetics model via simultaneous differential equations is due to the large number and the length of the simultaneous differential equations to be solved. On the other hand, Monte Carlo (MC) method has been shown to be a simple and useful technique in studying polymerization, since it does not need to solve complicated equations.[4-20]

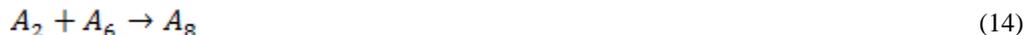
In a number of papers, MC simulation has been applied to predict the CLD of the products of different polymerization processes, such as free-radical [12–17] and living free-radical [18–20]. In fact, MC simulation requires only imagination of the phenomena occur and simple programming utilizing random number generators. For step growth polymerization, the methods are based on the simulated occurrence of reaction via probability concept and random number generation. Another advantage of MC simulation is that this method can be easily applied for other mechanism of step growth polymerization as well as other reactions.

In the present contribution, we compare the resulted CLD from a simple MC model and the one from simultaneous differential equations approach of a hypothetical step growth polymerization at a relatively small time (low degree of polymerization), in which the simultaneous differential equations approach is still not too complicated to be solved numerically. And then, the proposed MC simulation approach is also used to predict the CLD at large times reaction (high degree polymerization). This work will organize as follows. It starts with formulating/generating the kinetics of the step growth polymerization reaction at a relatively small time of reaction via simultaneous differential equation (monomer to octamers). The differential equation was solved numerically using Runge-Kutta method. In the next, the MC simulation scheme and program was generated based on the imagination of the phenomena of the step growth polymerization reaction. And then, the population number of the MC simulation result was compared to the Runge-Kutta results, in which the MC simulation was repeated a number of time, using increasing number of simulated molecules, until the error of the population number was considered small. Finally, the MC simulations were performed for relatively large chain lengths, to study whether or not the MC method be feasible for relatively high degree of polymerization and the results was then compared with the theories.

## II. METHODS OF SIMULATION

### 1. The Step Growth Polymerization Kinetics

For the purpose of comparison of methods, the MC simulation and kinetics model via simultaneous differential equations, we considered a simple case, in which the step growth polymerization is assumed to follow the mechanism shown in equations (1) to (16). Avoiding mathematical complexity, we only observed the reactions at a relatively short time, so that the molecules consisting of more than 8 monomers have not been formed.



The rate of reactions are assumed to be proportional to the numbers of each reactants' molecules (this assumption is equivalent to second order reaction with the reaction rate constant  $k$ , and the value of  $k$  be independent of the degree of polymerization). Therefore, based on material balances, the progress of reactions (1) to (16) can be described mathematically by a system of simultaneous differential equations as follows:

$$\frac{dA_1}{dt} = -kA_1(2A_1 + A_2 + A_3 + A_4 + A_5 + A_6 + A_7) \quad (17)$$

$$\frac{dA_2}{dt} = k(A_1^2 - A_2(A_1 + 2A_2 + A_3 + A_4 + A_5 + A_6 + A_7 + A_8)) \quad (18)$$

$$\frac{dA_3}{dt} = k(A_1A_2 - A_3(A_1 + A_2 + 2A_3 + A_4 + A_5 + A_6 + A_7 + A_8)) \quad (19)$$

$$\frac{dA_4}{dt} = k(A_1A_3 + A_2^2 - A_4(A_1 + A_2 + A_3 + 2A_4 + A_5 + A_6 + A_7 + A_8)) \quad (20)$$

$$\frac{dA_5}{dt} = k(A_2A_3 + A_1A_4 - A_5(A_1 + A_2 + A_3 + A_4 + 2A_5 + A_6 + A_7 + A_8)) \quad (21)$$

$$\frac{dA_6}{dt} = k(A_1A_5 + A_2A_4 + A_3^2 - A_6(A_1 + A_2 + A_3 + A_4 + A_5 + 2A_6 + A_7 + A_8)) \quad (22)$$

$$\frac{dA_7}{dt} = k(A_1A_6 + A_2A_5 + A_3A_4 - A_7(A_1 + A_2 + A_3 + A_4 + A_5 + A_6 + 2A_7 + A_8)) \quad (23)$$

$$\frac{dA_8}{dt} = k(A_1A_7 + A_2A_6 + A_3A_5 + A_4^2 - A_8(A_1 + A_2 + A_3 + A_4 + A_5 + A_6 + A_7 + 2A_8)) \quad (24)$$

The kinetic equations (17) to (24) were solved numerically using Runge-Kutta method with appropriate boundary conditions, in which at time equals to zero, the concentration of monomer be  $C_0$ , while the ones of the polymers be zero. In this simulation, the initial monomer concentration ( $C_0$ ) was taken to be 2 mole/L, while the reaction rate constant ( $k$ ) be 0.005 mole/L/min. The numerical solution was conducted using  $\Delta t = 0.1$  min. Based on the Runge-Kutta results (concentrations of monomer and polymers at various times), the total mole of polymerization products at certain time ( $C_{total}$ ), the reaction yields of each chains (the ratio of  $C_{poly}$  to  $C_0$ ) as well as the CLD population (the ratio of  $C_{poly}$  to  $C_{total}$ ) can be then calculated.

## 2. Monte Carlo Simulation

Imagination of the step growth polymerization process as the basis of the MC simulation is schematically shown in Fig. 1. The input data are same with the Runge-Kutta method ( $C_0 = 2$  mole/L,  $k = 0.005$  mole/L/min and  $N_{GRID} = 8$ ).  $N_{GRID}$  represents the maximum degree of polymerization to be observed. Macroscopic phenomenon of second order reaction with reaction rate constant,  $k$ , leads to the microscopic phenomenon that for  $N$  molecules in volume of  $V$ ,  $k N_2/V$  or  $k N C_A$  reactions per unit of time occur. It means that for  $N$  molecules, the time needed for each reaction is  $V/kN_2$  or  $1/kN/C_A$ . The average time for one reaction within  $N_{MONO}$  molecules with surrounding concentration  $C_0$  is:

$$\Delta t = \frac{1}{k C_0 N_{MONO}} \quad (25)$$

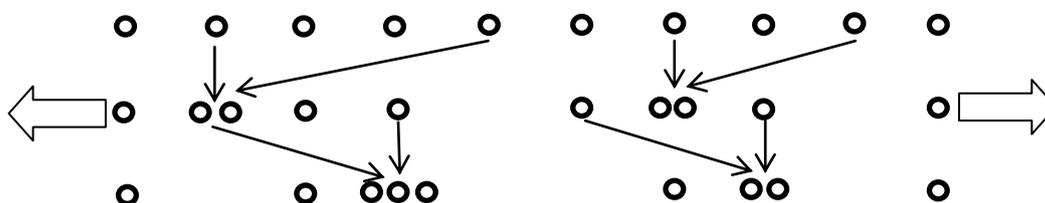


Figure 1 Imagination of the step growth polymerization process.

When the number of molecule in volume of  $V$  is  $N$ , the probability of a reaction occurs in the time interval of  $\Delta t$  would be  $(N/N_{MONO})^2$ . According to the imagination proposed, the MC simulation was conducted with the following steps.

1. Taken a number of monomer molecules ( $N_{MONO}$ ), and assigned indexes for each molecules (1, 2, 3, ...).
2. Set the degree of polymerization of each molecule (1, 2, 3, ...; 0 means the molecule does not exist anymore)
3. Randomly picked-up a molecule, say index  $i$ .
4. Randomly picked-up another molecule, say index  $j$ .
5. If  $j=i$ , back to step 4, if  $j \neq i$  forward to step 6.
6. Added the degree of polymerization of molecules  $i$  and  $j$ , and assigned to molecule  $i$ , while the degree of polymerization of the other molecule ( $j$ ) is set to be zero (molecule vanished). If the degree of polymerization molecule  $i$  or  $j$  be zero, automatically the degree of polymerization does not change (no reaction)
7. Calculated the value of the yield to each chain length as well as the population distribution.
8. Set: time = time +  $\Delta t$  and back to step 3
9. Steps 1 to 8 are repeated until  $N_{SIM}$  times, in which  $N_{SIM}$  is the total time of simulation divided by  $\Delta t$ .

By conducting simulation for a number of time interval, and observing the degrees of polymerization of each molecules, the CLD of polymerization at various time can be calculated. The program of MC simulation is presented as follows.

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C BATCH STEP GROWTH POLYMERIZATION
C MONTE CARLO METHOD
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      DIMENSION NPOLI(800000),FMOL(100)
C      NUMBER OF MONOMER (BEWARE OF THE DIMENSION OF NPOLY,
C          BOTH IN MAIN PROGRAM AND SUBROUTINE)
      NMONO=40000
C      INITIAL CONCENTRATION OF MONOMER, MOL/L
      C0=2.
C      REACTION RATE CONSTANT, MOL/L/MIN
      AK=0.005
C      REACTION TIME, MIN
      DELT=1./AK/C0/FLOAT(NMONO)
C      TIME OF SIMULATION, MIN
      TEND=200.
C      NUMBER OF SIMULATION STEPS
      NSIM=INT(TEND/DELT+0.001)
C      TIME OF SIMULATION UNTIL PRINT
      TPRINT=10.
      NEVAL=INT(TPRINT/DELT+0.001)
C      NUMBER OF GRID OF DISTRIBUTION
      NGRID=20
C      INITIAL CONDITION (DEGREE OF POLYMERIZATION)
      DO 30 I=1,NMONO
      NPOLI(I)=1
30 CONTINUE
C      SIMULATION STARTS HERE
      ISIM=0
      IEVAL=0
C      INDEX OF FIRST MOLECULE
      40 IREAC1=1+INT(RANDOM()*FLOAT(NMONO-1))
C      INDEX OF SECOND MOLECULE
      50 IREAC2=1+INT(RANDOM()*FLOAT(NMONO-1))
      IF(IREAC2 .EQ. IREAC1) GOTO 50
C      NEW DEGREE OF POLYMERIZATION
      NPOLI(IREAC1)=NPOLI(IREAC1)+NPOLI(IREAC2)
      NPOLI(IREAC2)=0
      ISIM=ISIM+1
      IEVAL=IEVAL+1
      IF(IEVAL .EQ. NEVAL) GOTO 90
      GOTO 40
      90 CALL POPULATION(NGRID,NMONO,NPOLI,FMOL)
      WRITE(*,250) ISIM*DELT
      WRITE(*,255)
      WRITE(*,260)
      WRITE(*,270)
      TOTAL=0.
      DO 120 I=1,NGRID
      TOTAL=TOTAL+FMOL(I)
120 CONTINUE
      DO 130 I=1,NGRID
      X=1.-FMOL(I)
      POP=X**(I-1)*(1.-X)
      WRITE(*,280) I,FMOL(I),FMOL(I)/TOTAL,POP
130 CONTINUE
      WRITE(*,270)
      IEVAL=0
      IF(ISIM .LT. NSIM) GOTO 40
250 FORMAT(/2X,'TIME = ',F7.2,' MIN')
255 FORMAT(2X,'-----')
260 FORMAT(4X,'NPOLY',4X,' CI/C0 ',4X,' POP(I) ',4X,'THEORY')
270 FORMAT(4X,'-----',4X,'-----',4X,'-----',4X,'-----')
280 FORMAT(5X,I4,5X,F6.4,6X,F6.4,5X,F6.4)
      STOP
      END

      SUBROUTINE POPULATION(NGRID,NMONO,NPOLI,FMOL)
C      CALCULATING DISTRIBUTION BASED ON COUNTED NUMBER DATA
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C      MAY 21, 2012
      DIMENSION NPOLI(800000), JSUM(100), FMOL(100)
      DO 640 I=1, NGRID
        JSUM(I)=0
640    CONTINUE
      DO 700 I=1, NMONO
        J=1
680    IF(NPOLI(I).EQ. J) GOTO 690
        IF(J .EQ. NGRID) GOTO 700
        J=J+1
        GOTO 680
690    JSUM(J)=JSUM(J)+1
700    CONTINUE
      DO 720 I=1, NGRID
        FMOL(I)=FLOAT(JSUM(I))/FLOAT(NMONO)
720    CONTINUE
      RETURN
      END
    
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### III. RESULTS

The results of the MC simulation and the Runge-Kutta method for the step growth polymerization at the reaction times of 10 and 40 minutes, with initial number of monomer ( $N_{\text{MONO}}$ ) = 20000, and  $N_{\text{GRID}} = 8$  are shown at Fig. 2 to 3. Fig. 2 shows that the CLD predicted by both methods agree very well for the small reaction times. At the reaction times longer, however, there are small deviations, but noticeable, at the CLD resulted by the MC simulation and the kinetic model via simultaneous differential equations, as seen at the reaction time of 40 minutes (Fig. 3). This is most likely because at the large time, the number of molecules remaining becomes relatively small, so the simulation runs at small number of molecules. To improve the results, the number of the initial monomers should be taken to be larger. To prove the argument and also to show the application of MC simulation at relatively large time of reaction, MC simulations were then conducted until 200 minutes at various values of initial number of monomers. The results are shown in figure 4. It can be observed that oscillation of the result appear at small value of  $N_{\text{MONO}}$ . These suggest that MC simulation should be done a number of times with the increasing number of  $N_{\text{MONO}}$ , until good stability obtained and oscillation vanishes.

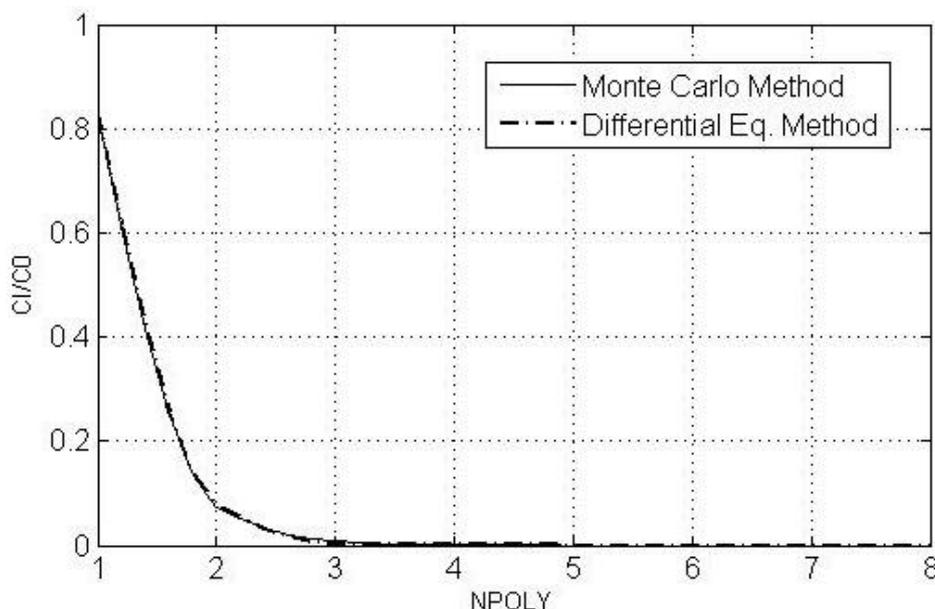


Fig. 2. The CLD of addition polymerization by the kinetic model via simultaneous differential equations (solid line) as well as the Monte Carlo method (spotted line) at reaction time of 10 min. The kinetic model was solved by Runge-Kutta method with input data of  $C_0 = 2$  mole/L,  $k = 0.005$  mole/L/min, and  $N_{\text{GRID}} = 8$ . The Monte Carlo method was solved with initial data that are same with Runge-Kutta method, initial number of monomer ( $N_{\text{MONO}} = 20000$ ), and interval time for simulation ( $\Delta t = 1/k/C_0/N_{\text{MONO}}$ ).

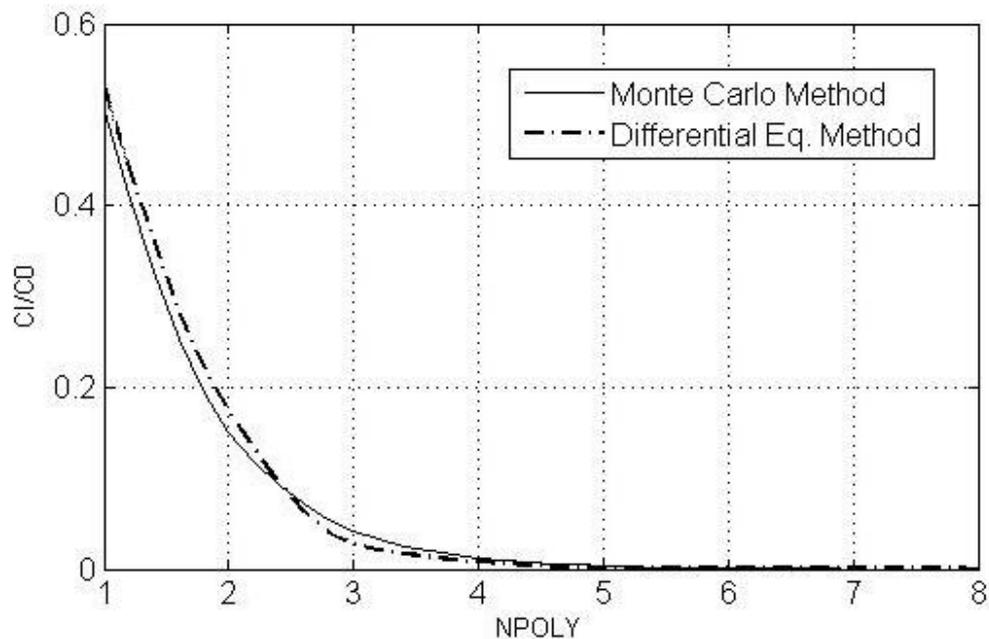


Fig. 3. The CLD of addition polymerization by the kinetic model via simultaneous differential equations (solid line) as well as the Monte Carlo method (spotted line) at reaction time of 40 min. The kinetic model was solved by Runge-Kutta method with input data of  $C_0 = 2$  mole/L,  $k = 0.005$  mole/L/min, and  $N_{GRID} = 8$ . The Monte Carlo method was solved with initial data that are same with Runge-Kutta method, initial number of monomer ( $N_{MONO}$ ) = 20000, and interval time for simulation ( $\Delta t$ ) =  $1/k/C_0/N_{MONO}$ .

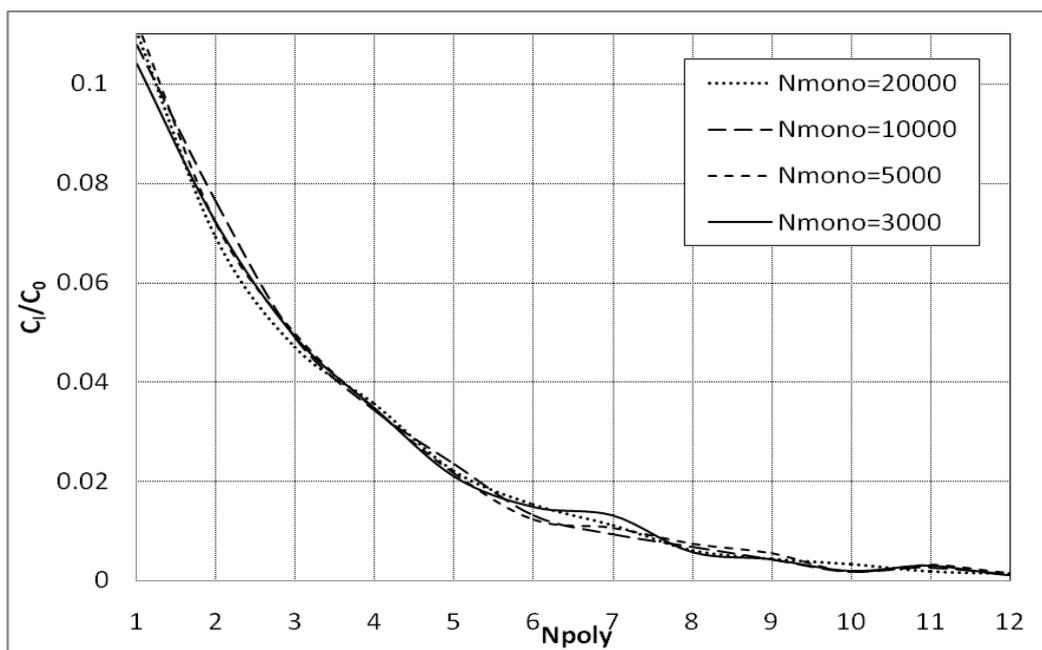


Fig. 4. The CLD of addition polymerization by the Monte Carlo method at reaction time of 200 min, with  $C_0 = 2$  mole/L,  $k = 0.005$  mole/L/min,  $N_{GRID} = 20$ , interval time for simulation ( $\Delta t$ ) =  $1/k/C_0/N_{MONO}$ , resulted from different values of initial number of monomer ( $N_{MONO}$ ).

#### IV. CONCLUSION

The Monte Carlo simulation method has been shown to be a potential tool for the prediction of chain length distribution of step growth polymerization. Moreover, a simple Monte Carlo simulation results presented are in good agreement with the kinetics model via simultaneous differential equations solved numerically using Runge-Kutta method. It was also shown that the Monte Carlo simulation can be easily applied to calculate the chain length distribution for large times of reaction (high degree of polymerization). Furthermore, the scheme of the Monte Carlo simulation and the computer program listed suggest that Monte Carlo simulation can be relatively easy to be applied to other mechanisms of step growth polymerization as well as other reactions.

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