

## Kinetic Model for the Copolymerization of Methyl Acrylate and Propylene

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**ABSTRACT:** *A copolymer from propylene and methyl acrylate would produce an alternating copolymer of highly desirable properties for paint and allied chemical industries; indicative of the properties of the individual homopolymers. In this work, a kinetic model was developed for the copolymerization of propylene and methyl acrylate. A radical initiator was used for the initiation to form a couple and subsequent propagation steps presented. Transfer specie used for the termination step. The various rate expressions and subsequent kinetic models were presented, thereby showing the relationship between various polymerization parameters with time. Such parameters includes: concentration of initiator, concentration of growing polymer chain and concentration of dead polymer chain. The models developed will prove invaluable if annexed in the design, control and optimization of the polymer production process.*

**Keywords:** Alternating Copolymerization, Methyl Acrylate, Propylene, Polymerization Steps and Kinetic Model  
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### INTRODUCTION

In the world of polymer science and engineering, more researches are needed in order to source for more polymers of highly rated physical and chemical properties that could substitute the existing ones. Over the years, polymethyl acrylate has been found useful as a paint pigment, especially in emulsion paint formulation. However, there are indications of improved surface activity and surface finishing when the acrylate monomer is copolymerized with olefins (Codd, 1973). Polypropylene is a rigid, light crystalline thermoplastic polymer of melting point 165- 170°C. It has a favourable strength/weight ratio. Tensile and notch impact strength of respectively 300 - 400kg/cm<sup>2</sup> and 5- 10kg-cm/cm<sup>2</sup>; which allows it to be pulled to produce tough fibers. It has high chemical and electrical resistance although it shows little oxidation sensitivity. Polymethyl acrylate is a very brittle, light polymer of melting point of 245°C and glass transition temperature of

12.5°C (Codd, 1973; Kirk-Othmer, 1982; Parker, 1989).

The copolymerization of methyl acrylate and propylene would provide flexibility to the polymer chain, which has a wide variety of applications. Owing to the insensitivity of the copolymer to earth alkalis (provided by propylene), it will be very important in paint and allied chemical industry. They can also be used as thickeners in toothpaste, creams, brilliantine and shampoos. The production of emulsion paints can be carried out using a copolymer of methyl acrylate and propylene as a vehicle. Enamel vanishes prepared with methyl acrylate copolymers show excellent adhesion to metals (Codd, 1973; George, 1984).

Whilst there are sufficient literatures on polypropylene and associated products, polymethyl acrylate and associated products; there are scarce literatures on the copolymer of propylene and methyl acrylate amidst its

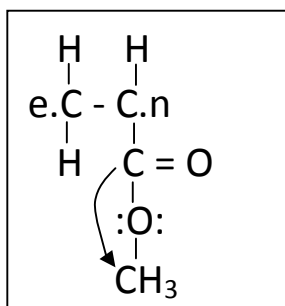
promising physical and chemical properties, if explored. For instance, Ojinnaka (2000) presented a detail survey of products derived from polypropylene and their usefulness. Also, Uppal (2005) gave a comprehensive review of products obtained from Polymethyl acrylate, their usefulness and properties. Hence, this study is geared towards developing a kinetic model for the copolymerization of propylene and methyl acrylate, which is the first step in the design, control and simulation of the polymerization reaction.

## METHODOLOGY

The kinetic models were developed for initiation, chain propagation and termination steps for the copolymerization of propylene and methyl acrylate. However, the reaction rate constants for the polymerization steps were obtained from literature (Wauton, 1999).

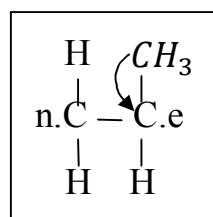
## MODEL FORMULATION

In the copolymerization of methyl acrylate and propylene, the polymerization steps; initiation step, propagation step, and termination steps will be considered, based on the characters of the monomers. For the purpose of this study, .e and .n are used to express the excited state of molecule; e. represents electrophilic end whereas n. is the nucleophilic end.



**Figure 1: Excited Methyl Acrylate Monomer**

The characters of methyl acrylate as shown in Figure 1 are: two active centres, -O-CH<sub>3</sub> is election withdrawing, it has no ionic centres but possess electrostatic charges and transfer species: it is an electrophile.



**Figure 2: Excited Propylene Monomer**

The structural formula of excited propylene monomer is as shown in Figure 2. Based on the structure, it has one active centre, no polar group, -CH<sub>3</sub> group is election pushing, it has no ionic centres but posses electrostatic charges and transfer species: it is a nucleophile.

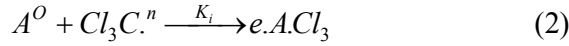
## Initiation Step

The initiation route that will favour the copolymerization of methyl acrylate and propylene must be that, that is natural to the route. The ionic route of initiation will not favour the initiation because of the electrostatic forces of repulsion between the carbon and oxygen centres ( Ferdinand, 1983; Odian, 1997 ; Peter, 1986) . However, the initiation will be favoured radically. Propylene and methyl acrylate will alternate because their substituents have opposite polarity.

The initiation of the methyl acrylate will be favoured by a nucleophilic radical. A good choice of a nucleophilic radical solvent will be tetrachloromethane. The tetrachloromethane catalyst will radically exist as (Peter, 1986)



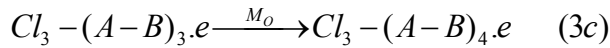
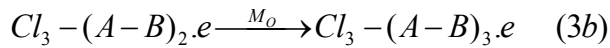
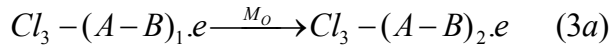
$\cdot CCl_3$  is nucleophilic and  $K_d$  is the rate constant for the dissociation of tetrachloromethane. The active centre which acts as a chain carrier is created by the reaction of the  $\cdot CCl_3$  radical and methyl acrylate as



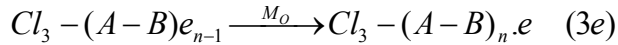
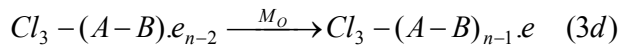
Where  $A^o$  is the activated methyl acrylate molecule,  $Cl_3C.^n$  is the nucleophilic radical initiator from the dissociation of tetrachloromethane,  $K_i$  is the rate constant of the initiation reaction and  $e.AC l_3$  is the active chain carrier (or first monomer growing chain).

**Propagation Steps**

In this step, more activated monomers are added linearly to the growing chain. The activated propylene is added to the chain carrier to form a couple, a larger radical,  $R_i$ , which adds to other couples to generate still larger radical alternately, and so on. This is represented in equation (3).



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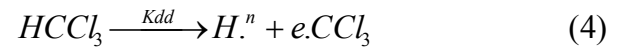


Where  $M_o$  is the activated couple,  $Cl_3-(A-B)e$  to  $Cl_3-(A-B)_n$  are the polymer growing chain which is represented by  $R_i$  (i.e.  $Cl_3-(A-B)_1$  to  $Cl_3-(A-B)_n$ , A and B are methyl acrylate and propylene comonomers. The reaction rate constants for equations (3a) to (3e) are represented by  $k_{pi}$  (i.e.  $k_{p1}$  to  $k_{pn}$ ).

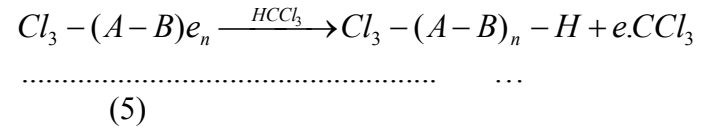
**Termination Steps**

In order stop the growing polymer chain from endless polymerization, transfer specie is used to terminate the polymerization reaction to produce a dead polymer. Transfer species are obtained from foreign agents and trichloromethane is a good choice (Odian, 1991; Peter, 1986).

Trichloromethane dissociates to produce a nucleophilic radical as



Where  $K_{dd}$  is the rate constant for dissociation of trichloromethane; the transfer specie suffer H-abstraction by the growing polymer chain, thereby terminating the reaction to form a dead polymer as



The rate constant for the termination reaction is  $K_t$ .  $Cl_3-(A-B)_n-H$  is the dead polymer of methyl acrylate and propylene.

**KINETIC MODEL**

**Initiation Rate**

The rate of initiation, I (from equation 2) is given as

$$I = K_i [A^o] [Cl_3C.^n] \quad (6)$$

And from equation 1,

$$\frac{d[Cl_3C.^n]}{dt} = K_d [CCl_4] - K_i [A^o] [Cl_3C.^n]$$

.....

(7)

Since  $Cl_3C.^n$  radical is transient in existence, the phenomenon of pseudo-steady state hypothesis could be applied (Cowie, 1991; Levenspiel, 2006), therefore,

$$\frac{d[Cl_3C^n]}{dt} = 0 \tag{8}$$

Hence, equation (7) yields

$$[Cl_3C^n] = \frac{K_d [CCl_4]}{K_i [A^o]} \tag{9}$$

Substituting equation (9) into (6) yields

$$I = K_d [CCl_4] \tag{10}$$

From equation (1),

$$\frac{d[CCl_4]}{dt} = -K_d [CCl_4] \tag{11}$$

Integrating equation (11) with the boundary conditions;

$$t = 0; [CCl_4] = [CCl_{4o}]$$

And  $t = t; [CCl_4] = [CCl_4]$

We have  $[CCl_4] = [CCl_{4o}] \exp(-K_d t)$  ..... (12)

Substituting equation (12) into equation (10) yields

$$I = K_d [CCl_{4o}] \exp(-K_d t) \tag{13}$$

By introducing an efficiency factor,  $f$ , we have

$$I = f K_d [CCl_{4o}] \exp(-K_d t) \quad , 0 \leq f \leq 1$$
 ..... (14)

**Propagation Steps**

The rate of production and consumption of the first growing chain is given as

$$\frac{d[R_1]}{dt} = I - K_{p1} [M_o] [R_1] \tag{15}$$

The rate of production and consumption of the growing polymer chain from  $R_2$  up to  $n-1$  is given as

$$\frac{d[R_n]}{dt} = K_{pn-1} [M_o] [R_{n-1}] - K_{pn} [M_o] [R_n]$$
 ..... (16)

Where  $2 \leq n \leq n-1$

In addition, the rate of production of the final couple,  $R_n$  is

$$\frac{d[R_n]}{dt} = K_{pn-1} [M_o] [R_{n-1}] \tag{17}$$

By adding equation (15), (16) and (17), and adding an efficiency factor,  $f$  we have

$$\frac{d \left[ \sum_{n=1}^{n-1} [R_n] \right]}{dt} = I = f K_d [CCl_{4o}] \exp(-K_d t)$$
 ..... (18)

Integrating equation (18) with the boundary conditions:

$$t = 0; R_n = 0$$

$$t = t; R_n = R_o$$

We have

$$[R_o] = f [CCl_{4o}] [1 - \exp(-K_d t)] \dots \tag{19}$$

Where  $[R_o]$  is the growing polymer chain. Therefore, the rate of polymerization can be evaluated as

$$R_p = K_{p1} [M_o] [R_1] + K_{p2} [M_o] [R_2] + \dots + K_{pn} [M_o] [R_{n-1}]$$
 ..... (20)

$$= M_o \left\{ \sum_{n=1}^{n-1} K_{pn} [R_n] \right\} \tag{21}$$

**Termination Steps**

The dead polymer of methyl acrylate and propylene is formed using transfer specie,  $H^n$  to terminate the polymerization reaction. The rate of polymerization is given by

$$R_t = K_t \sum_{n=2}^n [R_n] [H^n] = K_t [R_o] [H^n] \tag{22}$$

Equation (22) can be written as

$$\frac{d \sum_{n=1}^{n-1} R^l}{dt} = K_t [R_o] [H.^n] \quad (23)$$

Where  $R^l$  is the concentration of dead polymer chain and  $K_t$  is the rate constant for the termination step. Substituting eq.19 into eq.23 yields

$$\frac{d \sum_{n=1}^{n-1} R^l}{dt} = K_t f [CCl_{4o}] \{1 - \exp(-K_d t)\} [H.^n] \quad (24)$$

From equation (4),  $H.^n = K_{dd} \frac{[HCCl_3]}{[e.CCl_3]}$  and

by assuming that,

$$K^{ll} = \frac{K_t [CCl_{4o}] K_{dd} [HCCl_3]}{[e.CCl_3]}$$

Equation (24) becomes

$$\frac{d \sum_{n=1}^{n-1} R^l}{dt} = f K^{ll} \{1 - \exp(-K_d t)\} \quad (25)$$

Integrating equation (25) with the boundary conditions:

$$t = 0; R^l = 0$$

$$t = t; R^l = R^l$$

We have

$$\sum_{n=1}^{n-1} [R^l] = f K^{ll} \left\{ t - \frac{1}{K_d} + \frac{\exp(-K_d t)}{K_d} \right\} \quad (26)$$

## RESULTS AND DISCUSSIONS

### Concentration of Initiator during Polymerization

Figure 3 shows the concentration of initiator with time in the copolymerization of propylene and methyl acrylate.

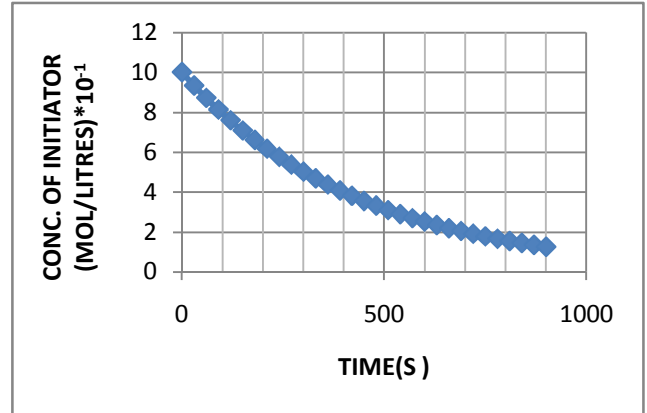


Figure 3: Plot of Concentration of Initiator against Time

The graph shows that the concentration of the initiation decreases exponentially with time; decreases from an initial concentration of 1mol/litres and tends towards zero. The shape is an indication of a high rate of initiation for the polymerization reaction; typical of initiation steps in polymerization reactions (Ferdinand, 1983; Foggler, 2005).

### Concentration of Growing Polymer Chain

Figure 4 depicts that the concentration of the growing polymer chain increases exponentially from zero to 0.6667mol/litres in 30 seconds; typical of polymerization reactions (Foggler, 2005; Dara, 2006).

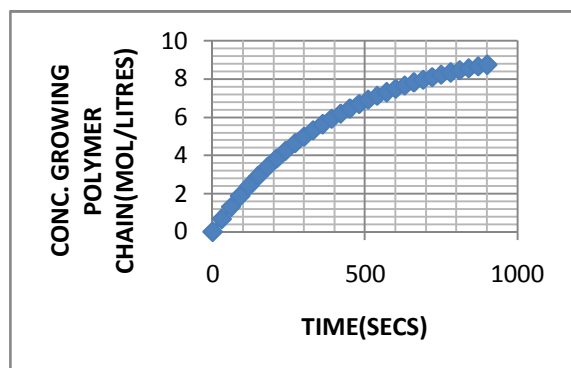


Figure 4: Plot of Conc. of Growing Polymer Chain against Time

### Concentration of Dead Polymer Chain

The concentration of the dead polymer chain in the copolymerization propylene and methyl acrylate is as shown in Figure 5. The concentration of the dead polymer increases exponentially from zero at a very fast rate; consistent with literatures (O dian, 1991; Cowie, 1991; Foggler, 2005).

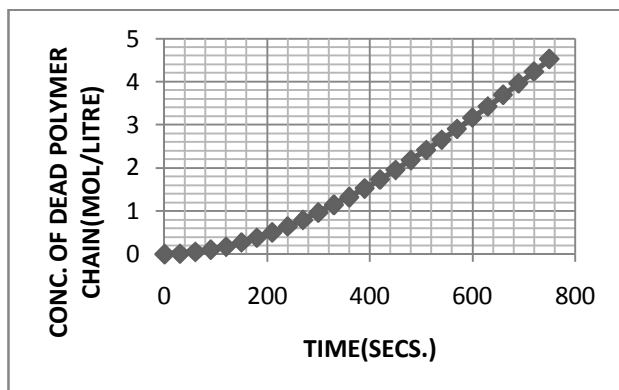


Figure 5: Plot of Conc. OF Dead Polymer against Time

### CONCLUSION

The models developed shows clearly that the polymerization parameters such as concentration of initiator, growing polymer chain and dead polymer chain for the copolymerization of propylene and methyl acrylate are all functions of time. This is in line with what has been reported in

literatures (O dian, 1991; Foggler, 2005). The substituent groups in propylene (-CH<sub>3</sub>) and methyl acrylate (-COOCH<sub>3</sub>) are electron pushing and electron withdrawing respectively (Ojinnaka, 2000; Dara, 2006). This is an indication that the copolymer formed must be an alternating polymer. Also, the polymerization of propylene and methyl acrylate takes place at a very fast rate; a clear indication that it is a chain copolymerization. When a reaction proceeds through more than one step, the slowest step determines the rate of the overall reaction (Ojinnaka, 2000; Levenspiel, 2006). The determination of the rate determining step is the focus for further studies. From this study, it could be deduced that the production of alternating copolymer of propylene and methyl acrylate will certainly introduce a polymer of highly desirable quality for paint and allied chemical industry, and possibly the oil industry. The models developed will prove invaluable if annexed in the design, control and optimization of the polymer production process. However, the experimental validation of models before usage is imperative.

### NOMENCLATURE

$K_d$  = Rate constant for catalyst dissociation, Sec<sup>-1</sup>

$K_i$  = Rate constant for initiation step, Litre/mol/Sec

$K_{pi}$  = Rate constant for propagation steps, Litre/mol/Sec

$A^o$  = Activated methyl acrylate molecule

$R_i$  = Growing couple chain

$M_o$  = Couple

$K_{dd}$  = Rate constant for dissociation of trichloromethane, Sec<sup>-1</sup>

$K_t$  = Rate constant for termination step,  
Litre/mol/Sec

$R^l$  = Concentration of dead polymer  
chain, mol/Litre

$K''$  = Multiple constant,  $\text{Sec}^{-1}$

$f$  = Efficiency Factor,  $0 \leq f \leq 1$

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