ผลกระทบของสภาวะในการหล่อแบบที่มีต่อเลนส์พลาสติกย้อมสี

นาย ชัยวัฒน์ จิตติคุณ

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IMPACTS OF CASTING CONDITION ON TINTING PLASTIC LENS

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การศึกษานี้ได้ทำการศึกษาเกี่ยวกับผลกระทบของการผลิตเลนส์พลาสติกโดยวิธีการหล่อแบบที่มีต่อเลนส์พลาสติกย้อมสี ตัวแปรที่ทำการศึกษาคือ ความเข้มข้นของตัวเริ่มต้นปฏิกิริยา สภาวะของอุณหภูมิและเวลาในการหล่อแบบ โดยทำการศึกษาถึงอัตราการย้อมสีโดยใช้สี HOYA SUNGLASS BLACK จากผลการศึกษาพบว่าอัตราการย้อมสีจะแปรผกผันกับค่าความเข้มข้นของตัวเริ่มต้นปฏิกิริยา,อุณหภูมิ และ เวลาที่ใช้ในการหล่อแบบ นอกจากนั้นการศึกษาเกี่ยวกับการควบคุมคุณภาพของผิวหน้าเลนส์ซึ่งพบว่าในการผลิตจะต้องควบคุมสภาวะในการผลิตให้เหมาะสมเพื่อรักษาคุณภาพของผลิตภัณฑ์ จากการย้อมสีโดยวิธีมาตรฐานของ HOYA พบว่าสำหรับในประเภทที่ 1 ควรใช้ความเข้มข้นของสารตั้งต้นปฏิกิริยา ในช่วง 3.5% ถึง 3.6% และควรใช้อุณหภูมิในขั้นตอนเริ่มต้นจะควบคุมที่ 40 ถึง 46 องศาเซลเซียส ในส่วนของอุณหภูมิในขั้นตอนสุดท้ายควรควบคุมไว้ที่ 80 ถึง 85 องศาเซลเซียส โดยกำหนดระยะเวลาในการผลิตขั้นตอนสุดท้ายไม่ต่ำกว่า 30 นาที จนถึง 90 นาที สำหรับในประเภทที่ 2 ควรใช้ความเข้มข้น ของตัวเริ่มต้นปฏิกิริยา ในช่วง 2.7% ถึง 2.9% สำหรับรูปแบบของการผลิตพบว่า สภาวะ C1 ถึง C4 สามารถ ใช้ในการผลิตได้โดยกำหนดระยะเวลาในการผลิตขั้นตอนสุดท้ายไม่ต่ำกว่า 30 นาทีจนถึง 180 นาที

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สาขาวิชา วิศวกรรมเคมี ลายมือชื่ออาจารย์ที่ปรึกษา...............................
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KEY WORD: DIETHYLENE GLYCOL BIS(ALLYL CARBONATE) / CR39 / DIISOPROPYL PEROXYDICARBONATE / CASTING / TINTING / RATE OF TINTING / DYEING

CHAIWAT CHITTIKUN : IMPACTS OF CASTING CONDITION ON TINTING PLASTIC LENS THESIS ADVISOR : ASSOCIATE PROFESSOR URA PANCHAROEN, D.Eng.Sc. THESIS COADVISOR : MR. SHINJI MORIKAWA , 131 pp. ISBN 974-13-0494-3

This study was study about the impact of plastic lens production by casting method on tinting plastic lens. Factors in this study are initiator concentration, temperature condition and casting processing time. By the study of rate of tinting use HOYA SUNGLASS BLACK, the result found that rate of tinting is inverse proportional to initiator concentration, temperature condition and casting processing time. Although the study of surface quality control found that in production must control these condition in suitable for keep the quality of product. From tinting follow by HOYA standard method found that for Type I, initiator concentration should be in range 3.5% to 3.6% and should be control starting temperature at 40 to 46 °C, final step temperature should control at 80 to 85 °C by set final step process time at least 30 min to 90 min. For Type II, initiator concentration should be in range of 2.7% to 2.9%. For production pattern found that condition C1 to C4 polymerization pattern can use in production by set final step processing time at least 30 min to 180 min.

Department Chemical Engineering Student's signature……………………………………

Field of study Chemical Engineering Advisor's signature……………………………………

Academic year 2000 Co-advisor's signature………………………………

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CHAPTER 1

INTRODUCTION

1.1 History and problems

Optical lenses are optical tools that purposed to correct human vision that has disorder in vision field. In pass time, lens was made by mineral substance called "glass lens". Manufacturing process of glass lens employs material melting process. Although it can use for main purpose of visual correction but some user was disappoint it because of its weight and difficulty to keep. Density of glass lens is too high then made it so heavy that uncomfortable to use. Also, the impact resistance is low properties when drop to rigid place that will make it broke.

For these disadvantages point, optical plastic material was improved. Lighter and better impact resistance are appreciate for user. However, some disadvantage points of plastics lens if compared with glass lens is abrasion resistance. Mineral lens is very good abrasion property. It's too difficult to happen of the scratch on its surface. For improvement plastic lens has surface treatment technique. By hard coating with high abrasion resistance resin films the abrasion resistance of plastic lens is becoming better (called hard coated lens). Some hard coat materials give us abrasion result as well as mineral lens get.

Lightweight, good impact resistance and good abrasion resistance (after hard-coating treatment) are important factors for user. In present, plastics lens is well known for consumers. Marketing of plastics lens is higher than mineral lens. In present situation, the marketing competition is very strong. Then manufactures must improve their product to better properties and strictly in quality control.

One of advantage point of plastic lens compare with mineral lens is easy tintable substrate. The objective of tinting lens is use for protect the light intensity come to eyes, well known example is sunglasses that usually use in outdoor. In present market, the purpose of tinting lens that not only for protects the light intensity but support for fashion too. Numerous type of tinting lens is come from color itself and the color density. The color of tinted lens is usually depends on the customer satisfactions which depend on skin color and weather.

The color density that usually depends on using conditions, for strong light, dark color (high color density, low transparency) is selected, such as driving case or outdoor sport. On the other hand, the light color is major use for indoor using or as use in fashion of young people.

The tinting process of plastic lens business usually uses dye-tinting technique for processing. The dye tinting method is put the normal lens into dye bath then the diffusion of dye molecule in solution is penetrated into surface of substrate and move to under the bulk, however almost at near surface volume. The diffusion of dye molecule is depending on surface properties. The effect of casting condition is study via the surface property by tinting method.

Diethylene glycol bis (allyl carbonate), CR-39, is well known plastic lens monomer. It is highly successful commercial resin use in application where high optical transparency. The other products that produced by CR-39 are safely glasses and guards, watch crystal, and instrument windows. Initially it used for window of fuel and deicer-fluid gauge and in glass fiber laminate for wiry reinforcement of B-17 bombers. The most recent use is in the detection of nuclear radiation (Delgado, 1994). Structure and properties of Diethylene glycol bis (allyl carbonate) is shown in figure 1.1 and table 1.1 respectively.

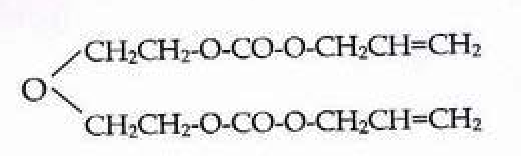


Figure 1.1 Chemical Structure of CR39

Table 1.1 Properties of CR39 resin (W.R. Dial; 1955)

Molecular weight	274.6
Specific gravity, 20°C / 4°C	1.143
Reflective index	1.4503
Surface tension, dyne/cm	35
Viscosity, cp at 25°C	9
Boiling point, °C	160
Melting point, °C	-4 ~ 0
Flash point, °C	177

Diethylene glycol bis (allyl carbonate) are homopolymerized via a free radical mechanism using an initiator. Benzoic peroxide, di-sec-butyl percarbonate and diisopropyl peroxy bicarbonate are commercial use initiation. The initiator used in the present study was diisopropyl peroxy bicarbonate, IPP.

1.1.1 Manufacturing

Diethylene glycol bis (allyl carbonate) can produce by casting process. It's thermosetting plastics that change from monomer to polymer via heating process. Radical polymerization is polymerization mechanism. However the main processing is employed common process of ordinary casting process.

Thermoplastic resin casting process, fluid plastic resin at near room temperature is poured in various types of molds. Curing through the heat is use to produce the thermosetting resin undergo and irreversible reaction via cross-linking reaction.

Benefit of casting process has its commercial value in prototyping and low volume production. Machine cost related with annual volume is too low that compare with the expense related to injection mold tooling.

Advantages of this processing method include:

- Lower expense for mold, since the largely pressureless processing means that the mechanical loads on the mold are low so that the mold need not be built as ruggedly;
- Simpler machine requirements for mold part production
- More economical production of small quantities.
- The particularly homogeneous and isotropic structure of cost parts

The following advantages, however, must also be taken into consideration:

- With thermosetting resin, air is often incorporated during mixing and under certain circumstance can no longer escape because of the increase in viscosity as a result of curing reaction; casting of bubble-free parts thus requires that the mold be evacuated
- The cross link reaction of casting resin is exothermic in many cases, so that in the absence of adequate heat removal excessive heating of the inferior of the molded part, and thus cracking, may occur because reaction take place too rapidly;
- With very thick walled parts, the curing time is very long because of the heat of reaction, which in turn lead to longer cycle times and the need for several molds to achieve economical production so that the advantage of lower mold costs is offset in part;

The casting production of HOYA LENS THAILAND LTD is follow by normal procedure. The monomer is mixed in low temperature then filled in the cavity between mold and gasket.

The concentration of initiator is one of distribution of product. This problem is not usually found in normal processing except the mistaken of operator in sometime. The concentration of initiator is control to the polymerization mechanism that occurs in radical polymerization. Degree of polymerization depends on its concentration in CR39. Such this case the polymeric characteristic is different even if the concentration of initiator was changes. Surface property study via tinting method is use to study. That is one of properties different that can get from initiator different cases.

After that polymerization process is started by input in polymerization oven that have 2 type, conveyor type and batch oven type. The different of operation of each type is depending on characteristic of machine. For conveyor type the controller for each distance is fixed and the polymerization period controlled by driving motor speed. Then the conveyor type is usually steady in processing like the continuous processing. The other type is batch oven that controlled the temperature by programmable controller. The polymerization pattern is install to controller then control to temperature control device as heater and cooler, i.e. cooling water.

The disorder of each type of oven is different. Conveyor type oven is usually open at input and output stage, with out shutter, that very easy to processing by direct input but the heat lost from oven at first zone that important to product properties distribution that cause from polymerization temperature distribution. Also the last zone of polymerization that usually high temperature, the heat loss form polymerization to surrounding is greater than first zone. The gap of temperature is great driving force of loss for this evidence. This study was study for the different of surface character of polymer that different in first step and final step in case of polymerization temperature.

For another type, batch oven, that important point in control of polymerization temperature by temperature controller. The temperature controller function is like normal character of each control loop. Feedback, feed forward or each of patterns of controller can use for aim of operation of temperature control. The signal from thermal sensor to processor is very important factor of batch oven. The source of different signal may come from many cases as, touching of sensor to frame of oven or full load heated air flowing inside oven and etc. These evidences cause of different output signal to final control element that give the different in level of present polymerization temperature. However the batch oven type is usually close chamber unit then the different of temperature is not so different, look like close systems. Then this study is also study in different of temperature effect on distribution of surface property via tinting method.

1.1.2 Tinted Lenses

Tinted Lenses (or fibers) are used to protect the eyes from glare or harmful radiation. The action is being to intercept a proportion of light or radiation energy would otherwise enter the eyes.

Suitable tint requires careful consideration. Three of physical properties are prescribes suitable tint product.

- Transmission is various important regions of the spectrum.
- The overall tinted depth (formerly known as integrated visible transmission).
- Tinting color.

An adequate understanding of these properties requires some knowledge of the optics of reflection, absorption, and transmission.

Lens tinting method

Tinted lens may be process in three different ways.

Integral Tints: Tinting material have been linked during the course manufacture. Various oxides were added to the batch material to give the specific color in glass lens. Thickness effect is action on percentage of light transmitted.

Surface Coating: Glass lens can be tint in a vacuum chamber. Transmission of light is uniform over the whole lens area, whatever the power and thickness of lens. The vacuum tint does not occur as the energy is reflected that eliminating the possibility of irradiation.

Dye Tinting: Apply to use for resin lenses by immersion in a colored liquid, which permeates into the surface.

In this study, the CR-39 resin lens was tinted by dye tinting process. The disperse dyestuff solution is use to processing.

Dye Tinting

Resin lenses can be tinted by dipping in the dye bath (the tank or container of dye solution). Penetration of dyestuff molecule into the lens substrate will become a part of lens. During the Processing time, which the lens remain in the dye solution, is effects to percentage of light transmitted. Dye bath is normally housed in a unit that allows heat to be transfer to the dye.

From dyes of the three preliminary colors, red, yellow and blue, it is possible to make all the other colors that require. For example, green color is a mixture of blue and yellow dyes. Brown is a mixture of red and blue with perhaps a little yellow.

Dyestuff can be purchased in either powder or liquid form, which is then mixed with either, demonized water or water that has been previously boiled to remove any chloride.

Dye tinting can be produced in two type of product

Solid color: The lenses which uniform of transmission is uniform over the whole lens area.

Gradient color: The lens which transmission is not uniform over the whole lens area. The transmission is decrease or increase in some direction that desired.

High index resin material exhibits different characteristics that prevent them from being tinted to the dark shade (low percent of transmission). Some resin material such as polycarbonate is not tintable in acceptable sense. It's called tint limitation.

As the major of lenses supplied to uses are of a resin material, dye tinting is most convenient and popular method. Tinted lens is common to combination with hard coating, UV protector and AR coating because dyestuff are absorbed into both surfaces convex and concave equally. They are not affected by power of lens and with therefore have and even tint regardless of prescription.

Problems in dye tinting

In the process of dye tinting, a pair of lens is proceeding in dyebath. Unfortunately it is not able to predict the product result. Even though both ways is of the same material and indeed from the same manufacturer, the ‘take up’ rate between the right and the left may be different. This can be due to a number of factors.

How can ensure to a pair of lens that tinted in some time? This is the main problem of tinting product. One choice that tries to reduce problem to minimize is to make sure for their manufacturer. If they came from some manufacturer then can reduce level of tinting problems. Each manufacturer has unique technology. Components, processing facilities and processing details is always different. It’s safer to use product to tint. Otherwise, different of storage is some time effect to tinting product, too. These points have effect on how a pair of lens will react when introduce to a tint.

In this case, main problem is surface condition of resin lens. Many factories are effect to the surface characteristic. This study tried to find out some of factors that can influence to tinted process. All of factor does not in tinting process but come from manufacturing condition of substrate, resin lens.

1.2 Objective

1. Study the effective of different of initiator concentration in casting process on tinting process of diethylene glycol bis (allyl carbonate) plastic lens

2. Study the effective of polymerization program parameter, temperature and process time of casting process on tinting process of diethylene glycol bis (allyl carbonate) plastic lens

3. Study of surface quality control of diethylene glycol bis (allyl carbonate) product

1.3 Scope of study

1. Type I

   1.1 Study of initiator concentration (% by weight) between 3.43 – 3.60

   1.2 Study of polymerization program of Type I

$$T1 \xrightarrow{1:30} T2 \xrightarrow{1:30} 48 \xrightarrow{1:50} 51 \xrightarrow{1:30} 55 \xrightarrow{1:15} 60 \xrightarrow{0:50} 67 \xrightarrow{1:05} T3 \xrightarrow{t} T4 \quad \overset{\text{Hr:min}}{{}^{\circ}\text{C}}$$

Table 1.2 Setting temperature items for Type I

Items	T1	T2	Items	T3	T4
A1	46	47	B1	85	85
A2	40	46	B2	80	80
A3	35	45	B3	75	75

Table 1.3 Final step process time variable for Type I

Items	t1	t2	t3	t4
Min	0	30	60	90

2. Type II

   2.1 Study of initiator concentration (% by weight) between 2.60 –2.90

   2.2 Study of polymerization program of Type II

$$Q0 \xrightarrow{14:00} Q1 \xrightarrow{2:00} Q2 \xrightarrow{2:30} Q3 \xrightarrow{2:00} Q4 \xrightarrow{0:30} Q5 \xrightarrow{0:50} Q6 \xrightarrow{t} Q7 \quad \overset{\text{Hr:min}}{^{\circ}\text{C}}$$

Table 1.4 Setting temperature items for Type II

Items	Q0	Q1	Q2	Q3	Q4	Q5	Q6	Q7
C1	43	54	58	73	88	88	83	83
C2	41	52	56	71	86	86	81	81
C3	40	51	55	70	85	85	80	80
C4	39	50	54	69	84	84	79	79
C5	37	48	52	67	82	82	77	77

Table 1.5 Final step process time variable for Type II

Items	t1	t2	t3	t5	T6
Min	0	30	60	120	180

CHAPTER 2

THEORY

2.1 Polymerization of Diethylene Glycol Bis (Allyl Carbonate)

Diethylene glycol bis(allyl carbonate) polymer, also known as CR 39 resin, is wildly monomer for optical plastic lens production. It is a clear liquid that homopolymerized via free radical mechanism by using specified initiation.

Bulk polymerization of diethylene glycol bis(allyl carbonate) results in clear, colorless abrasion resistance casting polymer. The polymerization studies indicated show polymerization at first with increasing conversion and relation, and then polymerization is accelerated.

Diethylene glycol bis(allyl carbonate) does not undergoes thermal polymerization radically on heating without radical initiator, and the monomer has relatively good stability on storage (A. Qurohi; 1995)

Casting process of diethylene glycol bis(allyl carbonate) is an ordinary casting process. Low temperature of catalyst Homo-monomer is pouring into the mold with separation around the edge by flexible gasket of vinyl resin. However this process is only “back-bone” for each of application. In many manufacturing of plastic lens have employed different of details such as polymerization pre-grown or mold material. The processing is developed in several decades with different experiences and conditions of each manufacturing.

In plastic lens processing, casting mold is unique from another transparent product. Optical knowledge must be use to calculate the curvature of upper mold and lower mold to produce a corrected “optical power” for correction of human vision. However this calculation is depend on the reflective in day of using polymer. For CR39, the reflective in day of product, after polymerization is approximately 1.5 which is the basis of parameter for mold calculation. Anyway this study does not concern with this point (tinted properties is independent from power of lens).

Polymerization of CR39 was discussed in topic of radical polymerization in previous study. Several kinds of radical initiator were used to cast. The details of processing with different radical initiator were different by its nature. The kinetics studies show the rate of polymerization of each initiator was different. This is one of the varieties in CR39 manufacturing condition.

The free radical polymerization of CR39 has been the subject of several previous study in which the conversion of monomer was determined by variety of technique via titration of double bond, dilatometry, mid range IR spectroscopy, precipitation of polymer, Raman spectroscopy and electron spin resonance technique [DJ. T. Hill, 1900]. For another investigation technique have been studied by FTIR and DMA technique (D.J. T. Hill; 1997).

Benzoyl peroxide is well known initiator for casting CR39. Many experiments for study of properties of CR39 had used BPO. W.R. Dial used 3% benzoyl peroxide act as initiator and polymerization under constant temperature condition, 70° C. Under this condition, the good yields of perfect costing are achieved. However 60 to 70 hours of casting time is required to develop essentially full cure. If used constant temperature condition at 115°C then the processing time will reduce to 2 hours (W.R. Dial; 1955)

J.H. O'Donnell has studied the polymerization of CR 39 with benzoyl peroxide initiator, between 70 and 85°C. The rate of vinyl bond consumption (as rate of reaction) could be approximated by 1st order kinetic in using lesser Raman spectroscopy. Kinetic studies of cross linking vinyl polymerization only applicable to the initial stage of the reaction, prior to the gel point, due to the subsequent insolubility of polymer and the great increase in viscosity (J.H. O'Donnell; 1981)

The polymerization study under reaction with benzoyl peroxide at 85°C, time dependent of conversion of double bonds has been monitor by near infrared spectroscopy and that the radical concentration by electron spin resonance spectroscopy. The result shown that dominating radical species in early stages of the polymerization is allyl radical. Beyond 60% conversion, the terminate rate, termination step, decrease rapidly but the rate of polymerization decrease presumably because the

“Free monomer” concentration is small and the diffusion of double bonds is restricted by the matrix (D.J.T. Hill; 1990)

However the limitation of this initiator is processing temperature because benzoyl peroxide is rapidly decomposed in condition of temperature over 100°C (M. Frounchi; 1994).

Commercially use of initiator is diisopropyl peroxydicarbonate. About 3% to 3.3% have been found the optimum in polymerization with CR39. Advantage of this initiator is lower polymerization temperature, can generally be cast at 25°C. Thus CR39 can be cast at 45°C in constant temperature process. Some of the changes in physical properties, which occur when initiated with 3% of isopropyl peroxydicarbonate at a constant temperature of 45°C, are listed in table 4-1. These data were collected by analyzed of under cure gel (W.R. Dial; 1955). The reaction order show of 0.79 but increasing slightly with initiator concentration.

The sample of casting CR39 has used diisopropyl peroxydicarbonate act as initiator. Chemical structure of diisopropyl peroxydicarbonate is shown in figure 2.1.

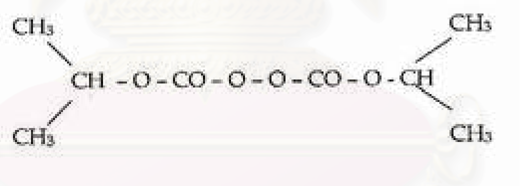


Figure 2.1 Chemical structure of diisopropyl peroxydicarbonate

The polymerization of diethylene glycol bis(allyl carbonate) initiated by peroxide initiator such as diisopropyl peroxydicarbonate and benzoyl peroxide, was investigated more than 40 years ago. Analysis of the result was made on assumption that polymerization rate was proportional to the square root of the initiator concentration. However a dependent on the initiator concentration was more common in allyl polymerization.

Table 2-1 Properties of Undercured Gels Prepared by Polymerization of Diethylene Glycol Bis (Allyl Carbonate) at a Constant Temperature (Diisopropyl peroxydicarbonate catalyst, 3.0%; oven temperature, 45°C.) (W.R. Dial; 1955).

Time of Heating at 45°C., Hours	Density	Diisopropyl Peroxydicarbonate Remaining,%	Acetone Insoluble Content, %
0	1.150	3.0	0
3.5	1.180	2.4	35.4
4.0	1.192	2.3	…
5.0	1.203	2.1	42.8
6.0	1.206	2.1	52.8
6.5	1.211	2.0	53.0
9.7	1.229	1.7	62.0
28	1.284	0.7	95.2
30	1.294	0.6	91.0
35	1.297	0.5	93.5
40	1.304	…	100.0
44	1.309	…	…
50	1.309	0.3	99.4
75	1.309	…	100.00

For another initiator, Di-sec-butyl peroxydicarbonate and tert-butoxyl radical were studied in polymerization of CR39. Di-sec-butyl peroxydicarbonate, similar functional as diisopropyl peroxydicarbonate, was found as the kinetic order of polymerization with respect to initiator between 0.5 to 1.0. The interesting result is that the molecular weight of polymer is almost independent of initiator concentration (E. Schnarr; 1980).

The initiation step of polymerization mechanism of Cr39 with tert-butoxyl radical was studied by using 1,1,3,3-tetra methyl isoindolinyl-2-oxyl as radical scavenger. The study was discovered that the first formed carbon centered radical is not at the allylic region as it has postulated over the years, but is in fact at C8, figure a. This is due to the α oxygen effect and may be due to β oxygen effect (A. Qureshi; 1995). The confirmed result was shown that C8 is carbon center radical (A. Qureshi; 1996).

For kinetic study, the important steps in polymerization of allyl monomer have been identified as (D.J.T. Hill, 1997)

Initiation	I	$\rightarrow$	$2I^{\circ}$
	$I^{\circ}+M$	$\rightarrow$	M°
Propagation	$M^{\circ}+M$	$\rightarrow$	P°
Chain Transfer	$P^{\circ}+M$	$\rightarrow$	$P+A^{\circ}$
Reinitiation	$A^{\circ}+M$	$\rightarrow$	M°
Termination	$A^{\circ}+A^{\circ}$	$\rightarrow$	$A\text{-}A$

Chain transfer step was found to be independent of conversion, but at very high conversions. The reinitiating rate constant was found to be zero. The terminate rate constant decreased with conversion where as for propagation the rate constant remained constant until 80% conversion.

The viscoelastic behavior of CR39 has been studied. The standard linear model was used to describe for simulated viscoelastic model. Mathematics solution for sinusoidal loading of a standard linear solid model that represented in figure 2.2 (M. Frourchi, 1994).

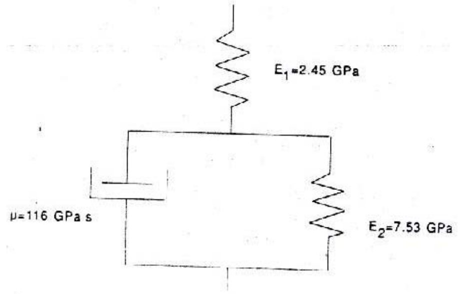


Figure 2.2 Standard solid model of CR39 (M. Frounchi; 1994)

The thermal condition of polymerization of CR39 resin is natural material. CR39 resin is one of the thermosetting polymers that contain the highly exothermic nature of reaction. Thus, polymerization of CR 39 resin often led to difficulties due to its nature.

In the production of high optical product, control of polymerization during casting process is necessary to prevent overheating due to the exothermic heat developed during polymerization. If such overheating occur, it leads to more rapid polymerization and addition liberation of heat. The unpredictable rapid curing mass then fracture from the high shear force developed because of excessive temperature, the polymerization initiator is not used efficiently (WR. Dial; 1955).

The thermal nature of polymerization is effect to select the processing facilities. Temperature removal system is required when polymerization reaction occurred. Circulation of heat is helpful for two points, provides protection for the over heating case and makes the balance of temperature in polymerization chamber.

In several previous studies of CR39 polymerization, especially with benzoyl initiation, using constant temperature process at 70°C and 85°C under the constant temperature process condition, the exothermic heat can be removed by ordinary circulating air oven and good yields of perfect casting can be obtained.

Although the casting of very good quality can be obtained in such a constant temperature process but the processing time required is long. 60 to 72 hours are required in previous study (W.R. Dial; 1955). Thus the shorter process would be desirable. In application of initiator with known diisopropyl peroxydicarbonate can obtain a better result in low temperature. Both reasons with kinetics studies were derived to generate the alternative processing, constant rate polymerization.

In these types of polymerization treatment, constant rate polymerization, the heat development is serious only at the beginning of the curving process. A constant rate of polymerization and constant rate of peroxide decomposition was desired that would result in a constant rate of exothermic heat evolution. The heat evolved conveniently dissipated by curving oven.

The first step in developing a constant rate of polymerization heating cycle of CR39 data was collected on the change in monomer and initiator concentration during polymerization. Assumption of calculation was assumed that unsaturated monomer was present. The basis of calculation was developed from constant temperature experiment. The concentration of remaining monomer is a linear function of content of un-decomposed catalyst as figure 2.3

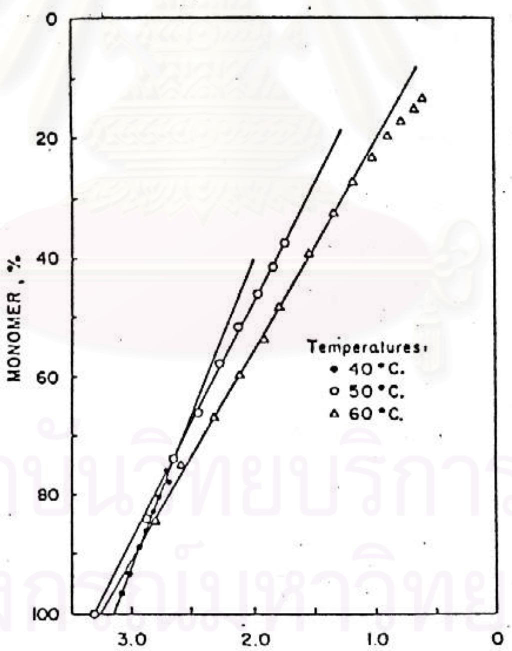


Figure 2.3 Decomposition of IPP in CR39 (W.R. Dial; 1955)

The slightly different slopes of the straight lines at different temperature show that the efficiency of utilization of the initiator is lost at higher temperature, in constant polymerization temperature process.

From experiment result was used to derive to calculate heating cycle for a constant rate of polymerization. Since the rate of change of monomer concentration was proportional to the rate of change of initiator concentration (W.R. Dial; 1955).

From calculation of polymerization cycle, the time above 75% of processing time equation (12) has no real solution. However it was known from previous experience with this initiator that the final temperature should be about 90^{o}C to completely decompose the final trace of initiator, the remaining portion of the cycle was obtain by extrapolating to 90^{o}C.

By using these polymerization cycles can be effected successfully in 1/8 to 1/4 the time required by constant temperature technique. In all case the polymer are finished by giving them a short post curing treatment after removed from the mold. This decomposes traces of remaining initiator and stabilizes the product against dimensional change upon aging.

Automatic program controller has been used for oven control in carry out these constant polymerization cycles with satisfactory results.

2.2 Chemistry of Dyeing [basis of Tinting lens principle]

Dyeing is one of the most ancient techniques in long history that can be traced back at least four thousand years. Coloration of cloth was developed together with human history. Until the middle last century all dyes were natural products extracted in most cases from variety of plants, but few from animal sources. In present, textile industry is large industry then the consumption of dye is increased. Synthesis dye is an organic compound which have coloring application. It's support is to present the consumption in present industry.

In optical lens industry, substrate of system is plastic lens substitute from textile in textile industry. However the nature of dyeing in both industries have same technique. Substrate, water dye and dyebath assistants are usually common in dyeing system. The interactions between components in dyeing system is show in figure 2.4

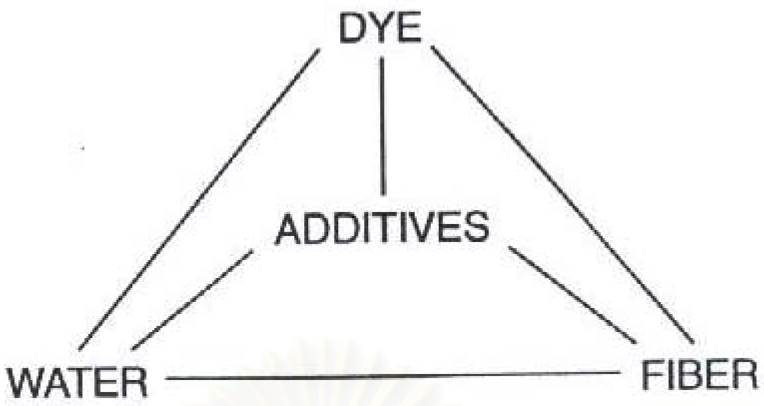


Figure 2.4 Interaction between component in a dyeing system (W.S.Perkins; 1996)

Dyestuff need in tinting lens industry is the applications of disperse dye. Disperse dyestuff is hydrophobic organic substance. It doesn’t soluble in water or a little solubility in aqueous phase. However if it does not soluble then the tinting process does not occur. The application of dyebath assistance is solution for these problems. Dispersion agent, one of dyebath assistance, is use to dyestuff dispersion condition in dyebath. Thus the tinting process is possible under the dyebath condition of interaction between disperse dye, dispersion agent and water.

Mass transfer is general mechanism of tinting process. Driving force of system is the gradient of concentration between dyebath and substance (plastic lens). Fick’s Law of diffusion can explain for diffusion phenomena. However the variation of tinting system, refer to figure 4-3, are made different of tinting result. Variations of substrate is major topic in this study, another variation is controlled.

Dispersion concept has 2 major concepts that use to explain the dyeing in present, monomolecular diffusion mechanism and solid solution mechanism. The former theory is suggest the aqueous phase mechanism that only monomolecular dye is difference in substrate lattice. The latter theory explains to the interaction between dye-hydrophobic substrate. There is a little difference between them that will discuss in the topic below.

Thermodynamic and kinetic were studied to explain the dyeing phenomena. Thermodynamic of dyeing is explained for model of dyeing mechanism that can be generated. Molecular Dispersion Concept and Solubility Parameter Concept are attempted to explain the dispersion phenomenon of dye into substance.

In tinting work, interesting point of worker is intended to rate of dyeing. Kinetic study of dyeing can explains the speed of dyeing progression. Processing Time of dyeing is important to tinting lens work because the transmittance is reduced time by time by diffusion of dyestuff into lens material. Then the kinetic study is important to estimate the reaction time that point to purpose %T.

However, the tinting parameters in actual work were studied because the diffusion system was changed when there are changes in working environment. Temperature, dye-bath assistant and dye particle effect one important parameter. Not only these parameter but the variables of system are important too. The variable of substance, preparation is effect to tinting result. These parameters will be discussed in the following topic.

2.2.1 Disperse dye

In present, various products in world market are dyeing products. The great number of consumption made need of dyestuff. At first, dyestuff was from natural product but the product is not enough for demand. Then in present, most of dyestuff is synthetic dyestuff from organic synthesis. First of commercial synthetic dye was produce in 1856 by W. H. Perkin. Manveine was prepared by accident when he attempted to make quinine. Then the world of synthetic dye production was set up on that time until present.

Intense Color

Most of organic dye is essentially unsaturated compounds having certain substituent groups, chromophore and auxochrome. Chromophore is chemical grouping which present in an aromatic compound. Auxochrome is the chemical grouping which present in electron – doner or electron – acceptor compound. Usually chromophore absorbs most energy at short wavelength in the region of ultraviolet and appeared in colorless. When auxochrom is present, the wavelength increases in region of visible spectrum. Thus cause of compound appear the color. Chromophore acts as the backbone of molecule and auxochrome and choice of dye maker to select the variation of its color.

Solubility.

Normal tinting process is work in aqueous solution then the dye must contain substituent groups conferring solubility in water. The solubility of dye in aqueous phase may need temporary. During process, dyestuff in aqueous phase is diffused into hydrophobic surface of material and soluble in matter. The soluble groups use in dye molecule are summarized in table 2.2.

Table 2.2 Soluble group of disperse dyes (C.H. Giles, 1974)

Group		Types of dye
Permanent	- SO$_3$Na (or – COONa)	Direct; acid; Chrome mordant; reactive; 1:1 metal-
	- NH$_3$Cl, - NR$_3$Cl	Basic dyes for cellulose, wool, silk, and acrylic fiber
	- OH, - NH$_2$, - SO$_2$NH$_2$	Disperse dyes for cellulose acetate, nylon, polyester fiber;
Temporary	- ONa	Dyes for cellulose, i.e. naphthols for subsequent azo coupling on the fiber; vat dyes
	Onium group	Phthalocyanine dyes for cellulose
	- SO$_3$Na	Solubilised vat dyes

In class of interesting dye, disperse dye, is very slightly soluble in water then the dispersing agent is required. Dispersing agent have main purpose to make dispersion of dye molecule in water and maintain a stable dispersion during dyeing (S. M. Burkinsaw; 1995).

Substantivity

Substantivity is ability of dye to be absorbed and retained by substance (i.e. lens material). The presence of one or more specific groups in dye molecule determines its substantivity for any given type of material and its method of application.

Fastness.

Fastness of dyestuff is determines for resistance of the color to one number of agencies. That's means the resistant of dyestuff in material turns to fading state after use of test in specific environment.

Generally, disperse dye is defined as a substantially water insoluble or relatively low water soluble dye having substantivity for one or more hydrophilic polymer or fiber. Even if it is almost insoluble but it must applied as a fine dispersion in water. It is required to be relatively small, planar molecules to allow the dyes to penetrate between the polymer chain and into the bulk of polymer (R. M. Christie; 2000).

Disperse dyes are usually derivertives of azo, anthraquinove, diphenylamine and other compounds. In dispersing agent, particle size of dyestuff is distributed between 0.5~2μm which produce a dispersion (as soluble) in dyebath [Pornchai, 1993]. It may have tendency to volatile, and prone to sublimation out of polymer surface at high temperature or degraded with uncontrolled pH condition. However it have not changes in chemical structure between dyeing process.

2.2.2 Interaction of Dyeing System

As the configuration of dyeing system in figure 2.4 that show the relation and interaction of system which composed of dyestuff, substrate, water and additive. In this topic, the application of addictive is negligible. The interaction of 3 components is mainly in usual tinting process.

Dye-water interaction

As explain in previous topic, usually the disperse dye is almost water-insoluble and solubility is occur when dispersing agent added in system. However the important point of dye-water interaction is dispersion condition of dye stuff in dye bath must be excellent. Disperse dyes are nonionic dyes which manufactured to have very small particle size and formulated with surfactants so that they are easily dispersible in water.

Substrate-water interaction

Polyethylene glycol bis(allyl carbonate) is hydrophobic polymer, however a small quantity of humidity can immerse into surface of product. It does not swell much in water. Although, water is usual dyeing medium and the interaction between substrate and water has a major role in application of many dyes (J.W. Perkin; 1996).

Such as this case, water plays a less activity for dyeing process. It requires some additive for helping the dyeing mechanism. However it may still be need as major media to disperse the dye that is small enough to diffuse into hydrophobic polymer surface. It also serves as heat transfer medium in dyeing process.

Dye - substrate interaction

Dye and substrate are applied usually that have an inherent interaction between them. This natural condition promotes the diffusion (mass transfer) of dye from dyebath to substrate and sometimes important to holding the dye in fiber.

The natural force of all matter that held together is attraction force. The force operated within molecules was termed intermolecular force that represents for individual molecular stability. On the other side, molecules are attacked to one another by set of forces which are termed intermolecular force.

Due to the disperse dye are non-polar molecules. The interaction force between dyes and substrate that support to dyeing is explained by no-polar force or Van der Waals force (C.H. Giles; 1974) or dispersion force [R.M. Christie; 2000]. The another intermolecular forces covalent force, ionic forces, dipolar force and hydrogen bonding. Non-polar force is the weakest compare with the others. Because the another forces are applied to substrate with strong attraction but for non-polar is only dispersion force of dye molecule only. Non-polar molecule is no overall charge dispersion. The electrons are in constant motion then small instant dipoles are presented. These instantaneous dipoles in turn induce oppositely-oriented dipoles in neighboring molecules and weak attraction between the molecules result. However, there is no real consistency in the literature concerning the use of term Van de Waal force, since it is

Also the presense of water to dispersion and diffusion of dye stuff in water and insubstrate because hydrocarbon groups tend to escape from water and associate together. This effect is known as ‘hydrophilic bonding’ (C.H. Gills; 1974).

2.2.3 Mechanism of Dyeing

The mechanism of dyeing involves several distinct indentfiable evens take place in the dyeing of a substrate material. The events are as follows (W.S. Perkin; 1996).

- Diffusion in solution: Dye must move or diffuse through the dyebath in order to establish contact with the substrate material being dyed.
- Absorption on substrate-surface: Dye molecules are attracted to substrate and are initially deposited on substrate surface.
- Diffusion in the substrate: Dye deposited on the surface creates a concentration gradient which is the driving force for movement of dye from the surface to the interior of the fiber. During diffusion, dye molecules migrate from place to place on the substrate. This migration tends to have a level effect on the dye application. Dye which migrate readily are easy to apply uniformly.
- Dissolution of dye in the dyebath: Dyes which are only sparingly soluble in water may have to dissolve from a dispersion of highly aggregated particles in order to be small enough to diffuse into the substrate.

Dyeing mechanism of disperse dye interacts with substrate has attended with 2 hypothesis, aqueous phase transfers and solid solution mechanism. Aqueous phase transfer mechanism is explained as molecular diffusion in aqueous solution form but the other is explained for system which presence with dispersing agent that positive charged dye molecule attach to the substrate.

The nature of non-polar interaction, as disperse dye interaction, was studies since 1920s. Interaction of disperse dyes with hydrophobic polymeric surface is generally accepted that the mechanism of the aqueous transfer. The dye solution is ideal separation in 2 levels. Inner level is around polymeric surface, is represented as the aqueous solution of dyestuff, and outer level is represented as bulk dispersion, as show in figure 2.5

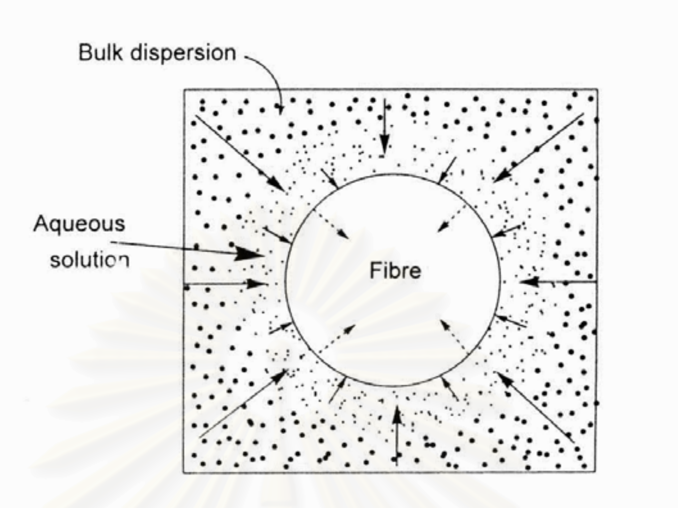


Figure 2.5 Aqueous transfer of disperse dye (S.M.Burskinshaw; 1995)

When dyeing occurs, monomolecular dyes are absorbed on to the surface of substrate and diffuse into interior substrate. Thus, the dye concentration in aqueous phase layer is reduced. As, the material balance dye particles from bulk suspension are dissolve (or monomolecular disperse) in the depleted aqueous dye solution. This process continues until either the dye bath is exhausted of dye or the substrate is saturated with dye.

Solid solution mechanism, debate with monomolecular diffusion mechanism, was proposed which demonstrated that when dyeing was carried out in present of dispersing agent. Dispersing agent is produce positive charge on dye molecule, then attack to substrate. Then this mechanism is proposed about important of dispersing agent action in dyeing system.

From above two theories that explain about the interaction between dye and substrate with different function of dispersion agent. Former theory proposed function of dispersing agent as distribution associated to produce monomolecular distribution in inner shell of solution near substrate surface. Latter theory proposes the action dispersion agent that made charred molecule then diffuse in substrate. The result of dyeing is same and dispersing agent is necessary in dyeing system.

2.2.4 Kinetic of dyeing

Kinetic study of dyeing with disperses dye studied via the rate of dyeing. The result of dyeing was detected in several Term such as % T, Abs, dye on fiber (%) or % exhaustion with processing time. That was showed the penetration speed of dye into substrate.

The rate of dyeing is important to any dyeing process because the dye-bath condition and substrate information is parameter to get the dyeing rate result. For specified parameter, dyeing rate is unique.

The rate of dyeing is corresponding with the dyeing mechanism that the concentration gradient is important driving force for dyeing process. At first, the dyeing rate is very high because a lot of dyestuffs are diffused through the surface. Later, the dyeing rate is decrease because the surface concentration is proceeding to equilibrium with dye-bath concentration.

Time of half dyeing (t 1/2) is one of preferable term that use to expressed the time required to reach 50% of final, i.e. equilibrium. Figure 2.6 is showed the time of half-dyeing with % dye of fiber. Figure 2.7 is showed rate of dyeing curve of different dyeing temperature that show the different time of half dyeing.

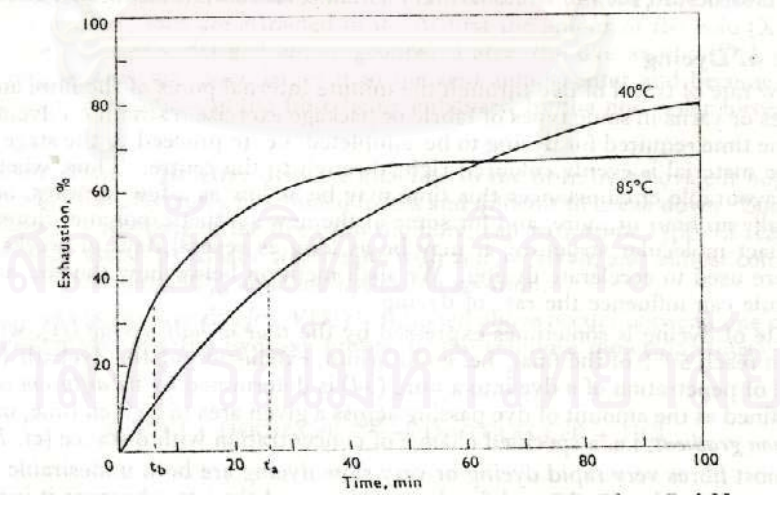


Figure 2.6 Time of Half dyeing (C.H.Giles; 1974)

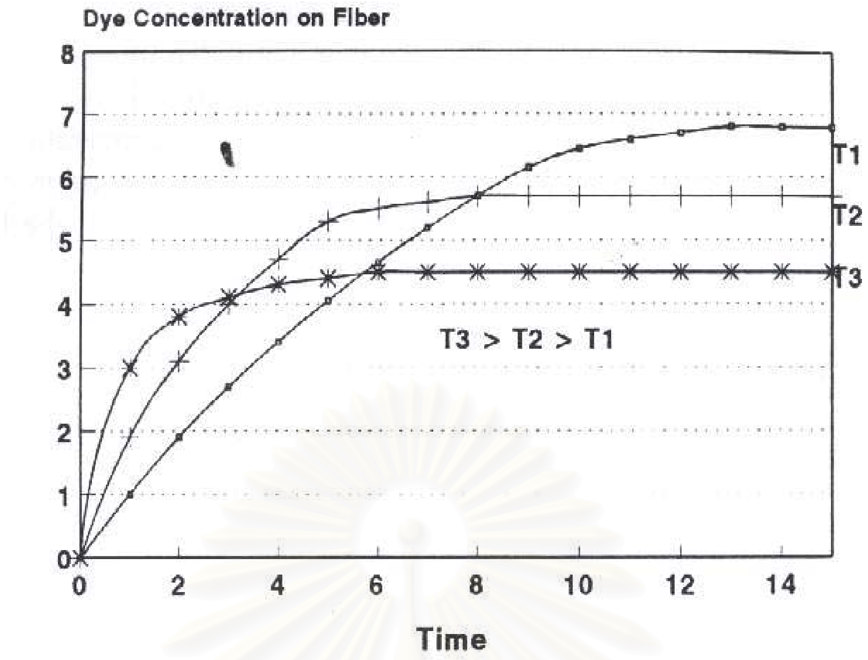


Figure 2.7 Rate of dyeing curve of different dyeing temperature (W.S.perkins; 1996)

The speed of penetration of dye into substrate is determined by it diffusion coefficient. Which may be defined as the amount of dye passing across given area in a given time, under a specified concentration gradient (C.H. Giles; 1974), figure 2.6 However the apparent diffusion coefficients are decreased with increasing time of dyeing.

Another expression to describe dyeing rate was proposed as empirical rate of dyeing equation by which the rate of dying of disperse dyes can be described in terms of a rate constant. Equation (2.1) is concluded by Patterson and Sheldon (S.M.BURKINSHAW; 1995) which express in the initial stage of dyeing.

$$Qt = \text{Const}\ C_b\ t^{1/2} \qquad (2.1)$$

Where Qt is dye uptake at time t

C_b is dye-bath concentration

The kinetic of dyeing PET, Ceqarra and Puente concluded as Equation (2.2) (S.M.BURKINSHAW,1995)

$$\frac{M_t}{M_\infty} = \left[1-\exp\left(\frac{2k'}{M_\infty^2}\right)t\right]^{\frac{1}{2}} \tag{2.2}$$

Where M_t = mass of dye absorbed at time t

M_∞ = mass of dye absorbed at equilibrium

K' = Velocityconstant

Usually in aqueous dye-bath system with disperse dye., the disperse dyeing systems may follow are of there main types of kinetic behavior, i.e. finite, infinite and transitional. If the dye-bath is initially unsaturated, then the solution of Fick's equation for finite dye-baths is appropriates whereas for an initially saturated dye-bath, then either infinite or transitional kinetics operates. The dyeing at high depth of shade with dyes of low aqueous solubility, the dye-bath may remain saturated throughout the course of dyeing and thus infinite dye-bath kinetics can be employed, whilst in the cause of dyes of high water solubility when applied at low concentration or at high liquor ratios, finite kinetics are appropriate (S.M.Burkinshaw; 1985).

2.2.5 Dyeing Parameter

Temperature effect

Temperature is usually parameter to studies in each chemical process. Dyeing temperature is used to study of adsorption of disperse dye on substrate. Temperature change affects dyeing in at least three distinct ways; thus a rise in temperature (C.H.Giles, 1975)

- Increase the speed of dyeing
- Decrease the amount of dye which substrate can absorb hence the exhaustion of the bath
- Increase the speed with which the dye can redistribute

In order to explain the effect of temperature on the distribution of disperse dye between water and hydrophobic substrate it is firstly necessary to consider that the partition coefficient (K) is constant, then the standard affinity ($\Delta\mu^\circ$) of the dye at temperature, T. K is given by equation (3.3) where in K is the partition coefficient and R, the gas constant

$$-\Delta\mu^{\circ} = RT \ln K \qquad (2.3)$$

When the temperature increase, partition coefficient K is decreased. Equation (3.3) show that the affinity of the disperse dye also decrease with increase in application temperature. This phenomenon is usually occur for two reasons (S.M.Burkindhaw; 1995).Firstly, since dye absorption is generally exothermic process, then an increase in temperature will reduce standard affinity. Secondary, the standard affinity comprises both the heat (ΔH°) and the entropy (ΔS°) of dyeing in equation (3.4)

$$-\Delta\mu^{\circ} = \Delta H^{\circ} - T\,\Delta S^{\circ} \qquad (3.4)$$

Combining equation (2.3) and (2.4) give equation (2.5)

$$-\Delta\mu^{\circ} = RT \ln K = \Delta H^{\circ} - T\,\Delta S^{\circ} \qquad (3.5)$$

Thus

$$\ln K = -(\Delta H^{\circ}/RT) + \Delta S^{\circ}/R \qquad (2.6)$$

From equation (2.6) shows, when temperature is increase with constant ΔH°Thus ΔH /RT approaches to zero and the partition coefficient is approximates to $\Delta S/R$. Since the absorption of dye molecule from the dye-bath on to substrate becomes less probable than desorption of the dye into dye-bath so that the partition coefficient and thus standard affinity both decrease.

From figure 2.6, it shows the different of reaction curve of dyeing with different temperature. % Exhaustion of direct dye C.I. Direct Red88 was detected. The two curve cross, and therefore if dyeing are inspected at this time exhaustion will be the same for both temperature. At first stage, the exhaustion was greater at the higher temperature. However, at equilibrium stage (longer application time), more dye will always be found on the lower temperature.

However the rate of dyeing in fact increases very considerably with rise in temperature; e.g., a rise form 60 to 100°C may increase the rate more than twenty-fold (C.H.Giles; 1975). Figure 2.9 show at the same exhaustion time, 85°C sample was under equilibrium after application time about 40 min but at 100 min 40°C sample was not equilibrate. Anyhow, the maximum exhaustion was on 40°C sample.

The effect of temperature on dyeing can be further explained in context of the various enthalpy terms relevant to dyeing, figure 2.10. The discussion concerned the determination of three enthalpy terms namely, the standard heats of dissolution of the dye in water ($\Delta H^{\circ}sw$), dyeing ($\Delta H^{\circ}wf$) and dissolution of the solid dye on substrate ($\Delta H^{\circ}sf$).

If the absolute heat changes involved increased in the order $\Delta H^{\circ}sf < \Delta H^{\circ}wf < \Delta H^{\circ}sw$ from which it can be concluded that since $\Delta H^{\circ}sw$ are greater than $\Delta H^{\circ}SF$ then the rate of dissolution of the dye in water was greater than the rate of dissolution in substrate with the effect that the partition coefficient, K, decrease with increasing temperature. Since transfer of dye from the water to the substrate was, an exothermic process then will decrease with increase temperature thereby further supporting the observation that K decreases with increasing temperature. (S.M.Burkinshaw; 1995)

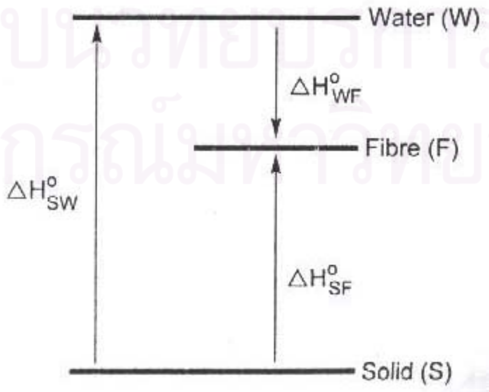


Figure 2.8 Enthalpy diagrams (S.M.Burskinshaw; 1995)

Rate of dyeing isotherms shows some inherent characteristic of dyeing system, figure 2.7. An increase in dyeing temperature causes an increase in the initial rate. The slope of the curve decrease is show less dye is adsorbed per unit of time. That depends on concentration different between dye-bath and substrate. The higher temperature increases the dyeing rate but decreases the ultimate exhaustion if the dyeing time is long enough. Dye absorbs to a greater degree at lower temperature because the dyeing is exothermic.

$$\text{Dye} + \text{Substrate} \;\; ==== \;\text{Substrate-dye} \qquad (2.7)$$

At higher temperature raised, the system driving the equilibrium to separately dye and substrate left side. Since the amount of substrate in the system is constant, some dye must leave from substrate and enter the dye-bath if temperature is raised.

Dye-path assistance effect

Disperse dye is hydrophilic substance that very poor solubility in aqueous phase. However, processing needs to use aqueous solution that is considerable economy. Dye-bath assistance is chemical assistant which its function is use to help the process and it is introduced in dye-bath. For this case, dispersing agent is preferably use to distribute the dye uniformly in dye-bath.

The dispersing agent is commonly anionic, ligninsulphonates or polycondensates of aryl sulphonic acid (S.M.Burkinshaw; 1995) .It facilities millinery by preventing agglomeration of dye particles and enables the dye to be prepared in powder or liquid form.

Dispersing agents increase the aqueous solubility of disperse dyes. Several dye at 80° was increased the solubility in presence of the dispersing agent to an extent which depended on dispersion agent used as table 2.3

Table 2.3 Solubility at 80°c of pure disperse dye in water and 0.5% dispersing agent (Lissapol C (ICI) [Sodium oleyl sulphate]; Dispersal VL (ICI) [Fatty alcohol-ethylene oxide condensate]) (S.m.burkinshaw; 1995)

CI Disperse	Solubility (mg/dm^3) at 80°c			
	Water	Sodium acetate	Lissapol C	Dispersel VS
Red I	7.0	240	104	41.0
Orange 3	9.5	60	31	29.0
Orange 1	0.5	46	18	21.5
Violet 1	17.0	57	36	27.5
Red 11	11.0	49	36	20.0
Blue 24	5.5	40	17	8.0

Dispersing agents also effect both the rate and extents of uptake of disperse dyes on hydrophobic substrate. The exhaustion of several commercial disperse dyes on cellulose diacetate at 80°c decreased with increasing concentration of sodium 1oleyl-4-anisidine-2-sulphonate and that the equilibrium partition coefficient of CI Disperse Red 1 on secondary cellulose acetate at 80° decreased with increasing concentration of the pure dispersing agent. The rate uptake of CI Disperse Blue 24 on cellulose acetate at 80° increased with increasing concentration of anionic dispersing agent. This as attributed to the surfactant having increased the rate of solubilisation of the particles of this low aqueous solubility dye. (S.M. Burkinshaw; 1995)

For another dye, the dye-bath assistant are use and classified as (C.H. Giles; 1975)

- Acids; used in dyeing protein fiber and nylon with acid dyes.
- Alcali; used in dyeing cellulose fiber, with azonic, vot or sulpher dye.
- Salts; used in dyeing with acid dyes and in all form of dyeing of cellulose.
- Surface-active leveling agent; use with vat dyes, disperse dyes and certain acid dyes.
- Carrier; used in dyeing some of the newer synthetic polymer fiber.

- Organic Solvent; use sometimes in dyeing wool and some synthetic polymer fiber.
- Reducing agent.

Dye particle effect [S.M.Burkinshaw, 1995]

Dye particle is important point of study that effect to dyeing to dyeing process. Suitable dye particle size and good dispersion in aqueous phase is required in dyeing. The dispersing level was explained in effect of dispersion agent already in previous topic. The range of particle sizes present in dye is shown in figure 2.9.

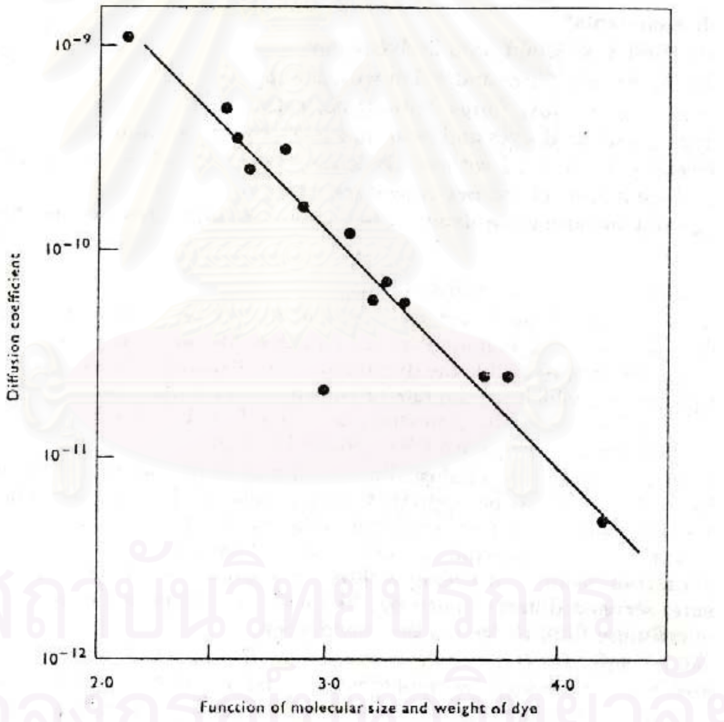


Figure 2.9 The Influence of due particle size on rate of dyeing (C.H.Giles; 1974)

In case of particle size, crystal forms of dye and particle distribution are discussed.

Five different crystal forms of aminopyrazole yellow dye on cellulose diacetate at 80°c was studied in presence of anionic dispersing agent. The saturation uptake increased with decreasing thermodynamic stability of the crystal form of the dye and proposed that these results were applicable to palyester fiber that show in table 2.4.

Table 2.4 Saturation values of different crystal forms of aminopyrazole yellow dye. On cellulose diacetate at 80°c

Crystal Form	Saturation Value (g dye/100g fiber)
α	0.77
β	1.0
γ	2.13
δ	3.07
ε	5.5

Table 2.4 shown that the different of saturation value of identical dye depending on crystal form. That is attributable to difference in solubility of the various form of dye in both the water and the substrate. Thus, the different solubility will be lowest for the mast stable crystalloqraphic form of the dye since the lowest energy content.

During dyeing, it is probable that a metastable form of disperse dye is transformed into a more stable, less soluble form, with some exceptions, the effect of the various modifications on the dyeing properties of the dyes is small in comparison to the charaeteristics imparted to the dye dispersion by milling and formulation. The transformation of the γ form of an aminopyzole yellow dye to β form is occurred during heat of aqueous solution with non-ionic dispersing agent. In amionic dispersing agent. Usage, the β formation is converse to α form in heating process. The type of dispersing agent is influence to control the crystal form is one point of important that affect to product.

Particle size and its distribution is important to uniform of Dye in dye bath. The greater solubility of small particles may cause the solution become supersaturated with respect to large particle size also the crystallization of dye occurs on the surface of the large particle.

The solubility of disperse dye in aqueous solution is depend on particle size. The aqueous solution of disperses dye particle in a dispersion increase with decreasing particle size. An increase in milling decrease the particle size, there by enhancing the solubility and hence dye uptake.

In dyeing process, temperature is important to control the particle size and its distribution. During processing, if the application temperature decreased than the recrystallization of disperse dye occurs. The growth of crystal made the particle size increase and its dispersion property is poor. This phenomena affects to dyeing because the dye distribution is lack to be uniform of dispersing agent can help this situation. The aggromerate may be redispersed at lower temperatures owing to the corresponding increase in efficiency of the dispersing agent at lower temperature.

The shape and size of a dye molecule have important effect on its dyeing properties as (C.H.Giles; 1975)

- Substantivity; Flatness or planarity of dye molecule has mentioned for influence on dyeing propertied. Disperse dye which seriously disturbs the overall planarity and introduces a twist into the molecule greatly reduce the amount of the dye can be taken up or dye ability
- Rate of dyeing; figure 2.9 show that the particle size of dye effects to diffusion coefficient. Increasing of particle size is decreases the diffusion coefficient that means the rate of dyeing is decreased.
- Fastness; Light fastness of dye may cause from same shape of dye molecule, especially flat molecule. However, so many factors influence light fastness that these differences may be due to others causes.

2.2.6 Variable in dyeing. (WS. Perkins, 1996)

The interaction in dyeing process is complex interaction of many variables. Dyers who want to get the high quality dyeing must control these variables. Variables in dyeing may be several types including substrate variations, variations in chemical (including water), variations in preparation of the substrate for dyeing and procedural variations.

Substrate Variations

Several types of substrate variations may cause variation in dye ability. The chemical nature of each material is also the variation of raw material that can have a major effect on dye ability.

The surface of substrate with different in chemical nature have different in diffusion properties. For mixed dye, combined of red blue and yellow, the dyeing result of each substrate is individual result as permeable surface. The affinity of dye is interaction between dye and substrate that made the specific dye for specific type of substrates.

In polymeric substrates, especially thermosetting plastic lens, The specific dye ability of substrates is depending on their material. Hight index product have lower dye ability than low index product that come from nature of urethane resin and CR-39 resin respectively in same batch of dyeing. In this case, specific dye for each product was produce for each type because the processing time is important for economic volume. Thus the variables in substrate nature are important to dyers must be study the relative between dye and substrate.

Variations in chemical

Variation in water or auxiliary chemicals used in the dyeing process can cause dyeing defects. In addition, the dye itself is probably the best example of a possible chemical variation. Dyes can very in strength, a measure of the color depth per unit of dye used, or hue.

In dyeing system, dechlorinated water is recommended to used. The residual chlorine has been known to react with and decolorized some dye in dye-bath that influence for dyeing product especially color line.

Variation in Preparation

Consistent preparation of the substrate for dyeing is critical to consistent dye application. This variation often cannot be corrected in dyeing and cause of defects or off-quality product.

The different in heat history or energy history of substrate is subject to the variation in dye ability results. In fiber, yarn or fabric manufacturing, a few degrees of different temperature can cause of dyeing rate that become to increase process time or cause of defect.

Stress or tension that remains in some part on substrate surface can be made the dyeing defect. During the processing of substrate preparation, if the critical condition occur, as suddenly change of temperature or strong force action, its made the stress on surface that dye ability result is different. The energy history of substrate is important for this case. Uneventint on same part of substrate is cannot treated anymore that become loss in processing.

Procedural variations

Procedural variations must be closely controlled in dyeing. Mixing ratio of dye and chemical must be correct even if the water is controlled. Reproduction of dyeing cycle time, dyeing temperature, rate of dyeing, rate of temperature rise, and agitation of substrate and dye-bath must all controlled for dyeing to be successful.

2.2.7 Mass Transfer and Diffusion of Dyeing

Mass Transfer is the net movement of component from one location to another location at different concentration, that is movement of chemical species from high concentration region to low concentration region. Chemical species' concentration gradient is basic driving force of this phenomena.

Mass transfer of dyeing process is the transfer of dye molecule from the dye aqueous solution to the substrate in a uniform and efficient manner. At first dyestuff concentration in the substrate is zero. On the other side, in dye bath, the dyestuff concentration is indicated by mixing ratio, greater too much when compare with substrate surface. This different in concentration of these two region is the great driving force when starting the process. The initial stage of mass diffusion, concentration gap made diffusion of dyestuff pass trough the film of aqueous film (stagnant of surface) the diffuse (penetrate) from surface to bulk polymer. When processing time pass, the concentration in bulk is rose up, the different concentration between dye solution and substrate surface is reduced (concentration gap is narrow time by time). Thus the driving force from concentration gap is smaller than initial stage, the diffusion rate is decreased. Until the process undergo to equilibrium, the mass diffusion to bulk and leave the bulk of substrate is equal (driving force = 0). The mass diffusion is seem to stop, but in real mechanism rate of input is equal to rate of output at steady state of equilibrium.

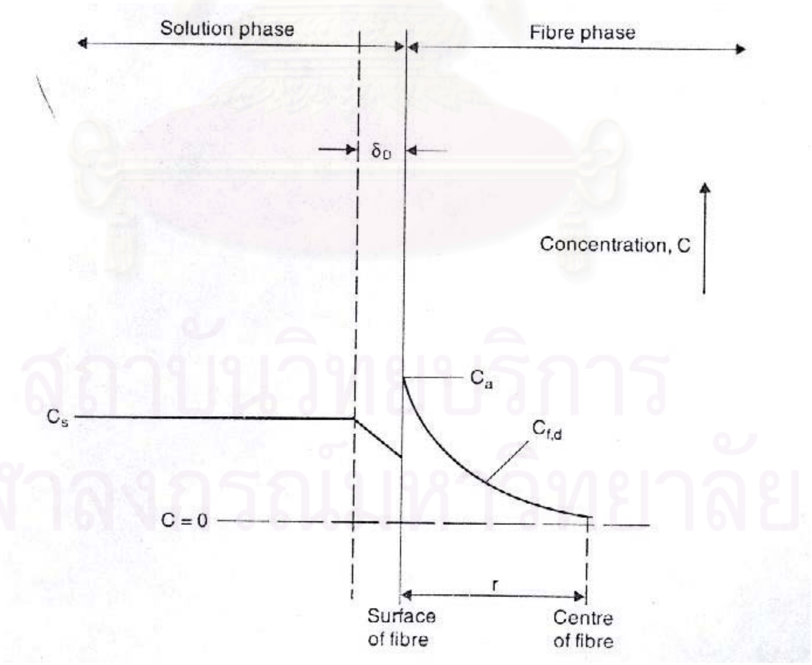


Figure 2.10 Diffusion phenomena of dyestuff (R.M. Christie; 2000)

Figure 2.10 show the schematic of mass transfer process of dyeing. It show the concentration different between bulk solution, substrate and concentration profile in bulk substrate. Mass transfer species (dye molecule) is passing through the stagnant film with thickness δD. This film is resistance of transfer process. Then in dye system, it is most readily influenced by the designed of the dyeing machine in order to minimize the thickness of the diffusional boundary layer, an effective flow of solution around the substrate is required.

The concentration of dye in bulk substrate is smaller than at substrate surface. Also the concentration gradient between surface an inner bulk of substrate is driving force of dyeing transfer process. The Flux of dye is decribed in term of Fick's Law which Flux is proportional to concentration gradient.

$$DQ/dt = J = -D\,(\partial C/\partial X) \tag{2.8}$$

Equation(3.8) shown the Fick's first law of diffusion which the equation states that diffusion species diffuses in the direction of decreasing mole fraction of diffusion species. This expression is written in term of molar diffusion flux, J (R.B. Bird; 1996) where equal to dQ/dt, the quantity of material crossing unit area during the time interval. However at steady state operation dQ/dt is zero that mass flux, transferred, is zero. From fick's law show that the gradient of concentration is function of direction as show by figure 2.10.

One of important parameter of diffusion process is diffusion coefficient, D, that measure of the speed with which the dye molecule move under the action of unit force. This coefficient is a function of temperature, pressure and composition system. That is the dyeing of different condition and also the system composition made the different result of dyeing. This is one of variable in dyeing that explain in previous topic.

For dyeing of polymeric system, the diffusion of transfer species is highly dependent on type of polymer, weather it be crystalline or amorphous and, if the latter, glassy or rubbery. All condition of polymer is effect to the diffusion coefficient that working as selective membrane. (J.D. Seader; 1998)

In many case of dyeing system such as plastic lens works, the mass transfer process is usually or never done until equilibrium stage because the result is control at unique value. These works, can called 'Unsteady state work', study for a unsteady state diffusion that driving force of system control the result. That is mainly study in rate of dyeing corresponding to mass transfer.

2.2.8. Light and Transmission Data

Three necessary components for this part are light, object and vision (or observer). Visible light consists of the narrow band of the electromagnetic spectrum having wavelength in the range of 380-780 nm. The color of each band in spectrum is show in Table 2.5.

Table2.5 Colors of the visible spectrum.

Color Perceived	Wavelength (nm)
Red	700~610
Orange	610~590
Yellow	590~570
Green	570~480
Blue	480~430
Violet	430-390

When the light applied on object one or more pertinent can happen as following (W.S. Perkins, 1996).

- Transmission; Light pass through without change of direction. The object is said to be transparent. It is said to be transmitted through the material, which is described as transparent object, see figure 6
- Scatter; Light waves bounce of at various angles. This is call scattering or diffuse reflection. If all of the incident light is reflected, scattered and absorbed, and no light is transmitted, the object is said to be translucent.

- Absorption; Light is transformed to some other form of energy, Typically heat. In addition to being Transmitted, light may be absorbed, or lost of visible light. The fundamental lam of light absorption state that equal amounts of absorption result when light pass through equal thickness of material.
- Reflection; Light bounce off at an angle equal to the angle of incidence in specular reflection. If certain wavelengths of light are reflected to greater than other wavelengths the object has color as opposed to being white. If no light is reflected by the object, the object is black.
- Refraction; Speed of light change as light pass through an object resulting is bending of the waves. Reflection is responsible for the appearance of dividing line between two immiscible liquids in contact with one another and for the apparent of a stick at the point that it is submergedin water.

Observer

First image of the observer is human but an electronic instrument also satisfies this requirement. For human sense, the sensitivityy of the eye is low near both end of normal range of visible spectrum (380~780 nm), so the visible region is often said to be from 400~700 nm. Nerves in retina send signals to the brain so that the observer perceives an image.

In electronical devices, artificial to human system, Figure 3-2 show in diagram of scanning spectrophotometers.

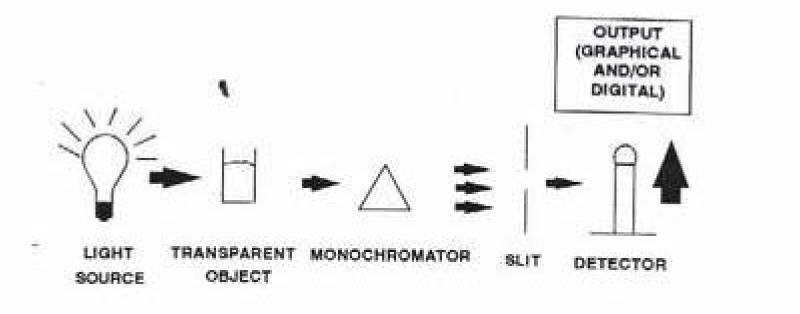


Figure 2.11 Schematic diagram of spectrophotometer for measuring transmittance (W.S.Perskin; 1996)

In this case, the system to resulting is same as human by mean of comparison, detector as human eye and also output signal (passed processor; like brain) as image in human vision.

Transmission and its data

In plastic lens property, the light must be transmits through the material. Then the light action on substrate is interesting in transmission data. For normal plastic lens, assume that the light absorption is equal to zero only reflection occure about 7.5% ~80% (for Diethylene glycol bis (allyl carbonate)). Then the transmittance of incidence light pass through to user about 92.0~92.5%.

For tinting lens, the dye stuff material that pass of product, is different manner. Dye material is assumed to only absorption function, no reflection. Then the absorption is product is occur by dyestuff contained. The transmission result is reduced by concentration and by difference manner of dyestuff.

Lambert-Beer's Law is useful for explain this phenomena. Light absorption property of material is proportional to chemical nature (absorption coefficient), part length and concentration. However, the variation of internal transmittance, T, with thickness, b of layer and concentration, c, can write in conventional equation as.

$$T = e^{-c\varepsilon_b} \qquad (2.9)$$

Where K1 is the absorption coefficient for unit of concentration and ε is the base of Naperian logarithms For c = 1, it is known as Bouguer's law. For thickness, b, constant it is known as Beer's law. [D.B.Judd, 1952]

The Lambert-Beer's law is usually written in the form.

$$A = \varepsilon bc \tag{2.10}$$

This law is usually valid only when monochromatic light is used. Any now , the Lambert-Beer's law is described for absorption then the relation between absorption and transmission is described by the equation

$$A = \log (100/\%T) \tag{2.11}$$

When %T is the percentage of incident light that pass through the solution.

In practical use, color density is described for the resistance for the transmission and its relation by this equation

$$D = 100 - \%T \tag{2.12}$$

Then color density is related to absorption, or obtical density, can rewrite as

$$A = \log (100/(100-D)) \tag{2.13}$$

Thus the relation between dye concentration and color density of substrate can written by

$$\varepsilon bc = \log (100/(100-D)) \tag{2.14}$$

$$c = 1/\varepsilon b * \log(100/(100-D)) \tag{2.15}$$

That’s mean the color density can explain to concentration by using information of absorption coefficient and its thickness.

CHAPTER 3

EXPERIMENT

3.1 Material

- Diethylene glycol bis (allyl carbonate), CR39, is product from PPG industry, Japan
- Diisopropyl peroxydicarbonate, IPP, is product from NOF Corporation, Japan
- Hoya marron dyestuff from Hoya corp., Japan
- Hoya sunglass black dyestuff from Hoya corp., Japan
- Dispersing agent; Nicca sunsolt 7000, from Nicca Chemical Co.,Ltd., Japan
- Acetone

3.2 Tools and Instruments

- Batch oven for polymerization with temperature controller: Tonetsu batch oven, Model TN80 with Temperature Controller: Chino KP 1000
- Hoya tinting bath from Hoya corp., Japan
- Density meter: Asahi density meter model 321s
- Balance: Precisa Model1 PRE 310C
- Stirring motor with propeller
- Tinting rack
- Measuring cylinder
- Timer
- Wiping paper
- Acetone container

- Glass mold for casting sample
- Gasket
- Polymerization tray
- Monomer filling bottle with nozzle
- Digital thermometer

3.3 Preparation of casting sample

3.3.1 Preparation of Type I casting sample

Mixing initiator (diisopropyl peroxy dicarbonate) in diethylene glycol bis (allyl carbonate), CR39, by weight percentage of 3.4, 3.45, 3.5, 3.55, and 3.6. The calculation of mixing ratio is related to weight (g) of initiator per 100 g of CR39. After introduce initiator into CR39, the monomer was mixed with stirrer for 1 hr, in mixing temperature setting at 0 ± 5 °C, before use.

After finish mixing of monomer, fill the monomer in filling bottle. Monomer was filled into the cavity of mold and gasket then put in polymerization tray. After finished, input polymerization tray in to batch oven for casting the resin monomer.

The pattern of polymerization program is shown in figure 3.1 and the temperature setting for each step is shown in table 3.1. Also the final step processing time is indicated in table 3.2.

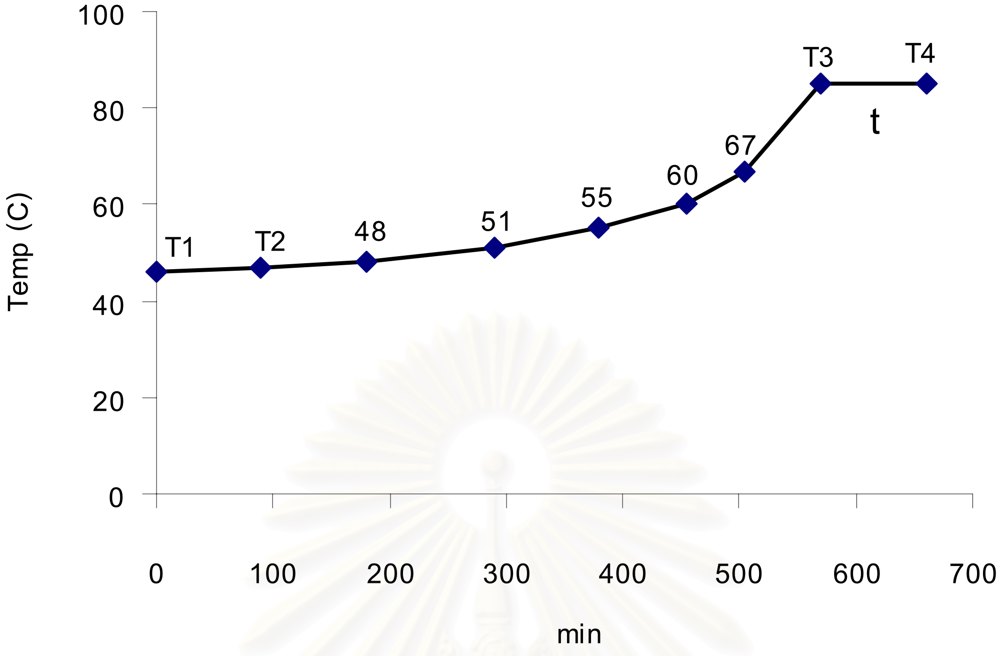


Figure 3.1 Pattern of Type I polymerization program

Table 3.1 Temperature (^{o}c) setting for each step of Type I polymerization program

Temp Patterns	T1	T2	48	51	55	60	67	T3	T4
A1B1	46	47	48	51	55	60	67	85	85
A1B2	46	47	48	51	55	60	67	80	80
A1B3	46	47	48	51	55	60	67	75	75
A2B1	40	46	48	51	55	60	67	85	85
A2B2	40	46	48	51	55	60	67	80	80
A2B3	40	46	48	51	55	60	67	75	75
A3B1	35	45	48	51	55	60	67	85	85
A3B2	35	45	48	51	55	60	67	80	80
A3B3	35	45	48	51	55	60	67	75	75

Table 3.2 Final step processing time (min) for Type I

Items	Process time (min)
t1	0
t2	30
t3	60
t4	90

For example, the casting sample item 3.55A3B1t3 is means this sample have 3.55% initiator concentration, cast by polymerization condition with temperature condition item A3B1 with final step processing time of 60 min

3.3.2 Preparation of Type II casting sample

Mixing initiator (diisopropyl peroxy dicarbonate) in diethylene glycol bis (allyl carbonate), CR39, by weight percentage of 2.6, 2.7, 2.8, and 2.9. The calculation of mixing ratio is related to weight (g) of initiator per 100 g of CR39. After introduce initiator into CR39, the monomer was mixed with stirrer for 1 hr, in mixing temperature setting at 0 ± 5 °C, before use.

Same as Type I, after finish mixing of monomer, fill the monomer in filling bottle. Monomer was filled into the cavity of mold and gasket then put in polymerization tray. After finished, input polymerization tray in to batch oven for casting the resin monomer.

The pattern of polymerization program is shown in figure 3.2 and the temperature setting for each step is shown in table 3.3. Also the final step processing time is indicated in table 3.4.

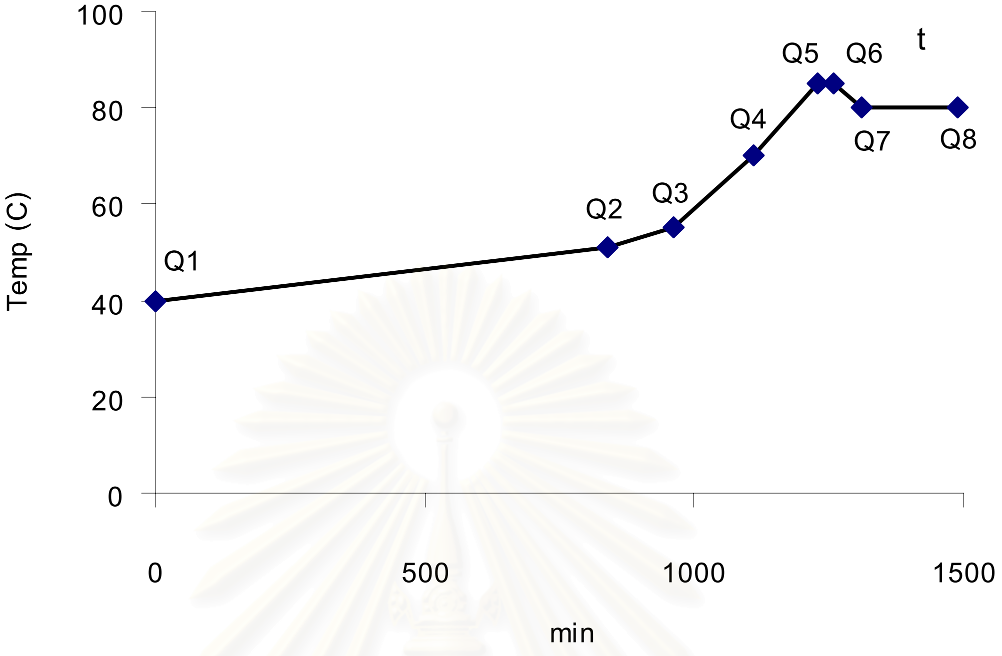


Figure 3.2 Pattern of Type II polymerization program

Table 3.3 Temperature (^{o}c) setting for each step of Type II polymerization program

Step Items	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8
C1	43	54	58	73	88	88	83	83
C2	41	52	56	71	86	86	81	81
C3	40	51	55	70	85	85	80	80
C4	39	50	54	69	84	84	79	79
C5	37	48	52	67	82	82	77	77

Table 3.4 Final step processing time (min) for Type II

Items	Process time (min)
t1	0
t2	30
t3	60
t5	120
t6	180

For example, the casting sample item 2.6C5t5 is means this sample have 2.6% initiator concentration, cast by polymerization condition with temperature condition item C5 with final step processing time of 120 min.

3.4 Preparation of tinting solution (dyestuff solution)

3.4.1 Preparation of Hoya sunglass black solution

Preparing 85 ± 1 °C de-chlorinated water for 10 liters in Hoya tinting bath. Introducing 20 ml of dispersing agent (Nicca sunsolt 7000) into prepared water.

Hoya Sunglass Black dyestuff is measured at 50 ± 0.5 g then take into prepared dispersing aqueous solution. Keep dyestuff solution for 8 hr before use.

3.4.2 Preparation of Hoya marron solution

Preparing 81 ± 1 °C de-chlorinated water for 10 liters in Hoya tinting bath. Introducing 20 ml of dispersing agent (Nicca sunsolt 7000) into prepared water.

Hoya Marron dyestuff is measured at 50 ± 0.5 g then take into prepared dispersing aqueous solution. Keep dyestuff solution for 8 hr before use.

3.5 Determination of rate of dyeing for tinting sample

Study of rate of dyeing (tinting rate) use application of 5g/L Hoya Sunglass Black dyestuff solution at 85±1 °C. Casting sample that use for tint is prepare by Type I and Type II from section 3.2.

For casting sample, before tinting, have measuring value from density meter. This value is assumed only reflection phenomena. Light absorption of casting sample is assumed to zero. From result, the reflection data from density meter is 7.0.

3.5.1 Tinting procedure

Prepare casting sample by wiping with acetone then setting in the tinting rack. Stir the dyestuff solution with stirring rod for good distribution. Check the solution temperature by digital thermometer if temperature keep steady at 85 ± 1 °C then put the prepared casting sample into dyestuff solution.

For study of rate of tinting sample is varies in different tinting time as 0.5, 1, 2, 4, 9, 16, 25, 36, 49 and 64 min (in product use processing time with in 60 min). Cleaning tinted sample with water and wiping by acetone. Measure the result in term of color density at 550 nm that defined as

$$\text{Color density (\%D)} = 100 - \%T \qquad (3.1)$$

Where %T is % transmittance at 550 nm

However the density meter, Asahi model 321s, is special device for use in tinted lens field. The result of measuring is display in value of color density then it do not calculation as equation 3.1. The function of density meter is use for one wavelength measurement, in study use 550 nm for commercial product and in practical of control used.

3.5.2 Determination of rate constant

Rate of dyeing is related to equation 2.1. The general form is

$$Abs = K\sqrt{t} \qquad (3.2)$$

where $Abs = -\log T = \varepsilon bC$

t = time (min)

K = Rate constant ($\text{min}^{-1/2}$)

From equation 3.2, the absorbance value is follow by Beer's law that related with concentration of substance in substrate with specified ε, molar absorbtivity, at one part length. Also the Beer's law is validated for only one wavelength that this study uses as commercial at 550 nm.

While the density meter is indicated color density and the effect of non-tinted reflection density of casting sample. Assumption for this study is supported by the reflection value at 7.7 constant of non-tinted lens. The equation 3.2 is explained for the rate of constant because the diffusion of dye molecule into plastics lens sample. The linear equation must be point on the origin at zero min. then the reflection of non- tinted lens, value 7.7 from density meter at 550 nm, must be displaced in equation 3.1. The equation 3.2 is rearrange as

$$Abs = -\log\left(\frac{107.7 - D}{100}\right) \qquad (3.3)$$

Where D = %color density

From equation 3.3 is show the absorbance at 550 nm that came from only absorption of 550 nm without the reflection phenomena. Then the study of diffusion of dyestuff into substrate is leave another point and concentrate only the rate of diffusion that made concentration in substrate is grown up in processing time pass.

The limitation of measurement by density meter that use in tinted plastics lens measurement is the range of machine from 0.0% color density to 100% color density. The 0.0% is calibrated of air. However that value of 100% is not means as no light pass the lens but the %T is less than the machine detector can detect. That is accepted for tinting lens measurement.

The relation of Abs and %T (or %color density) is explained in figure 3.3 and figure 3.4.

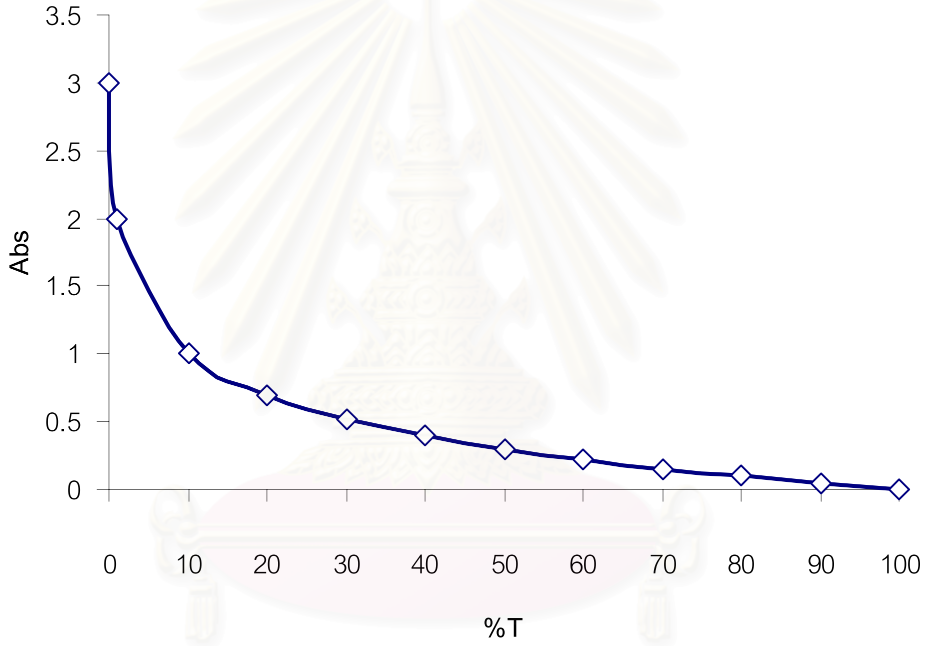


Figure 3.3 Relationship between %T and Abs

From figure 3.3 shown the relation of %T versus the Abs that show the high value of Abs (high concentration from Beer's law) gives the low %T, a little transparency material. On the other hand, sample is measured high %T. It is means the low value of Abs or low dyestuff concentration in the sample.

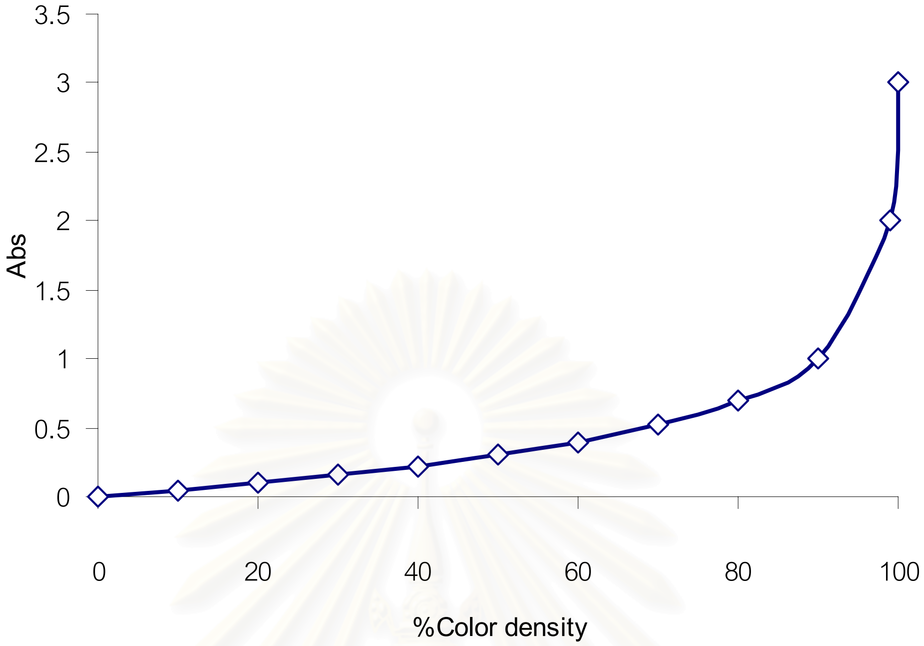


Figure 3.4 Relationship between %Color density and Abs

From figure 3.4 shown the relationship between %Color density and Abs that show the high value of color density give high Abs value. From Beer's law, it is means that sample is high concentration. On the other hand, some tinted sample has low %color density then the ABS is low or low dyestuff concentration in substrate.

From equation 3.2, Abs is linear relation versus $\sqrt{t}$ with slope K. from the experiment Abs can get by equation 3.3 that related to % color density data, shown the relation in figure 3.4. Then the rate constant K is explained for the rate of tinting in each case of casting sample.

Slope of linear plot between $\sqrt{t}$ versus Abs show the rate of dyeing that explain how speed of tinting progression. For example, if compare between 2 cases of tinting and plot the relationship as shown in figure 3.5

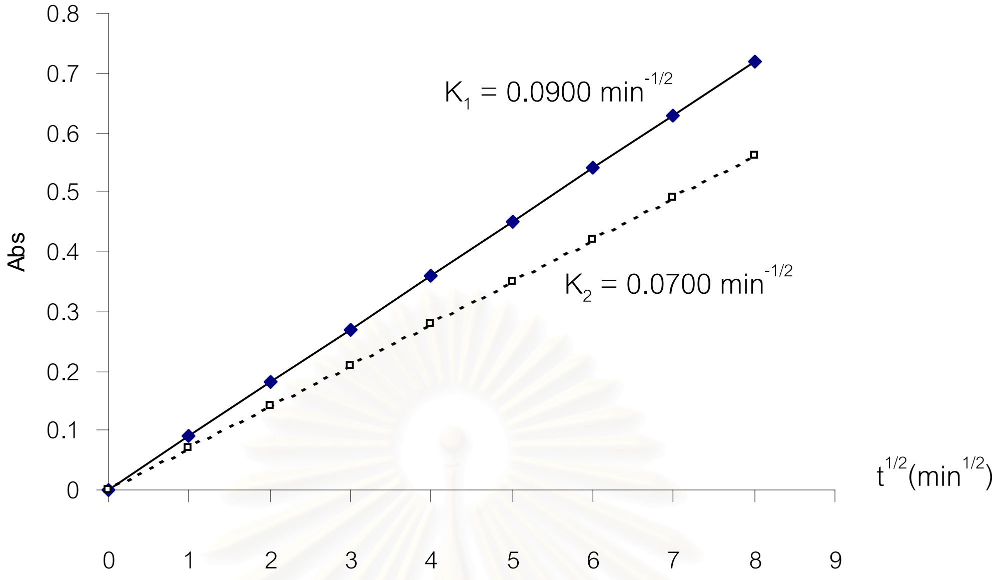


Figure 3.5 Relationship between $t^{1/2}$ versus Abs with different slope K_i

Form figure 3.5 shown the relationship between $t^{1/2}$ versus Abs with different slope K_i. Solid line is described for the rate of tinting with rate constant, K_1, at 0.900 $min^{-1/2}$ compared with dotted line for the rate of tinting with rate constant, K_2, at 0.700 $min^{-1/2}$. This figure shown the rate of tinting depended on rate constant at tinting time. If the rate constant is high then the rate of tinting is high. On the other hand, if the rate constant in low then the rate of tinting is low.

The substrate, which contain the character of high rate constant give the higher rate of tinting, higher speed of tinting or diffusion into substrate, that compare with substrates that contain the character of lower rate constant. Like wise,

In analysis of casting condition effect on tinting process is study to how effect of casting condition on rate of tinting via rate constant comparison that will effect to processing time. However the rate of tinting cannot determine the value of product but will explain for the factors that effect on. The most important for production control is how range is suitable for production that can control the product within standard (discussed below).

3.6 Study the effect of different of initiator concentration on tinting process

From result of rate of tinting study, plot the relation ship between initiator concentration versus rate constant (K; min$^{-1/2}$) for each related item in polymerization condition of Type I and Type II. The rate constant is related to tinting processing time (discussed in previous topic). If the rate constant is high then get the short processing time. On the other hand, if rate constant is low then get the long processing time.

From the study will discuss the effect of concentration on surface property of casting material in case of diffusion phenomena.

3.7 Study of effective of polymerization condition on tinting process.

As same as study in topic 3.6 but in this study is plot the relationship between temperature condition and processing time (related to final stage processing time) versus rate constant (K; min$^{-1/2}$) for each item of initiator concentration of Type I and Type II. The evaluation is same as in topic 3.6. If the rate constant is high then get the short processing time. On the other hand, if rate constant is low then get the long processing time.

However in this study is shown how the polymerization condition effect on surface property in case of diffusion phenomena.

3.8 Study of surface quality control

This study is related to the standard of production control in HOYA LENS THAILAND. The specific dye stuff, method, and specification is shown in table 3.5.

Table 3.5 The surface quality control method and specification

Dyestuff	Hoya Marron Dyestuff
Tinting temperature	81± 1 °C
Tinting time	10 min
Specification	50 ± 5 %D (by density meter model 321s)

Tinting solution preparation was explain in section 3.1.2.

From the result of Hoya marron dyestuff, the tinting result (%D) is compared with Hoya specification of casting product. In this case, for company application, this study will recommend for suitable casting condition. The display method will use shading table to recommend for suitable condition.

CHAPTER 4

DISCUSSION

4.1 Study the effective of different of initiator concentration in casting process on tinting process of diethylene glycol bis(allyl carbonate) plastic lens.

The study of effect of initiator is considering between initiator concentrations versus rate of tinting via tinting rate constant (K; min$^{-1/2}$) in same polymerization condition. However the effect of polymerization condition and casting process time will discuss in section 4.2.

In radical polymerization the initiator concentration that effect to initiation step. The different of initiator concentration give the different rate of initiation step. Thus the polymer characteristic should be different manner. Not only bulk characteristic but surface characteristic of polymer in different of initiator concentration should be different too. The surface reaction as diffusion phenomena (as tinting process) is studied from this point.

However for Type I and Type II polymerization was study in different range of initiator concentration that corresponding to polymerization condition. Type I study, the initiators are distribution from 3.4% to 3.6% with 0.05% gap. For Type II study, the initiators are distributed from 2.6% to 2.9% with 0.1% gap.

4.1.1 Study of initiator concentration for Type I

In this study the Type I polymerization, initiator concentration is setting for 3.4, 3.45, 3.5, 3.55 and 3.60. In each figure, the polymerization condition (temperature condition) is same that different in initiator concentration and shown in different casting process time (corresponding with the different of final step process time).

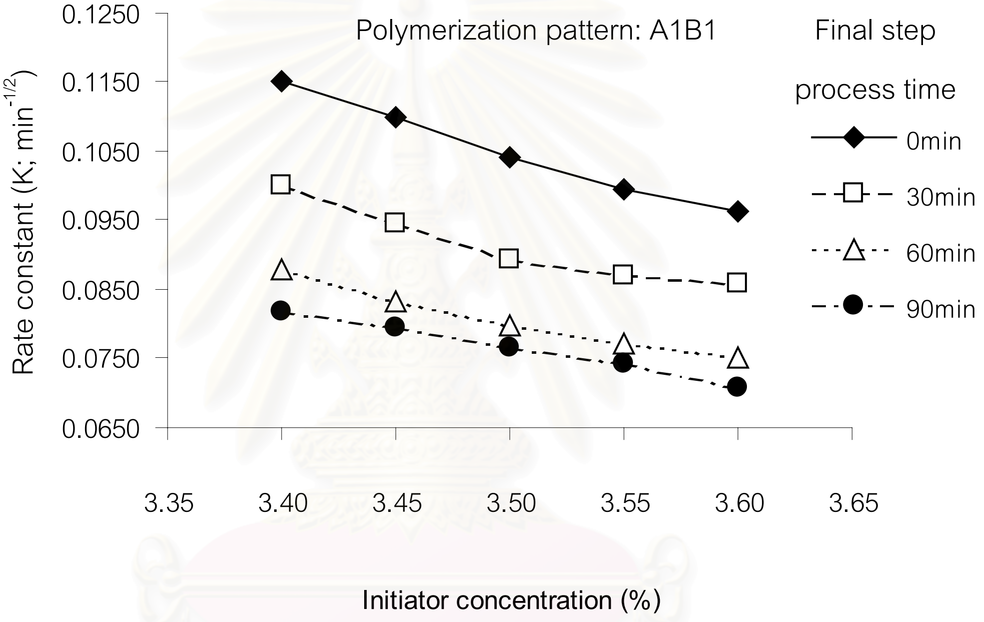


Figure 4.1: Relationship between initiator concentrations versus rate constant (Polymerization pattern A1B1 with different final step process time)

From figure 4.1 show the initiator concentrations that effect to the surface property of casting sample. The tinting result of these samples show different in rate constant of dyeing. The higher initiator concentration made lower value of rate constant. Sample of 3.4% of initiator concentration get easy to low transmission when compare with 3.6% sample in same polymerization condition. The progression of rate constant corresponding to initiator concentration is shown in curve when final step process time is less than 60 min but shown more linear since 60 min of the final step process time. That's mean the different in final step process time is influence to the rate constant of tinting not only value but influence in shape of curve change too (discussed in below section).

The different in tinting rate constant shows the diffusion phenomena of dyestuffs into casting sample is different. The diffusion process due to 2 main parts first is driving force of different in concentration between bulk solution and substrate and second is diffusion coefficient of casting sample which depend on structure and nature of substrate especially at surface. In this study, the tinting solution is controlled by dyestuff concentration and assume to constant along the test period. Thus the first case that depends on the different dyestuff concentration between solution and substrate is negligible.

From this study, the initiator concentration is varied then the different in tinting rate result should be related to. The diffusion coefficient of substrate is different from the initiator concentration then the diffusion phenomena (mass transfer) are different result too. The second factor of diffusion coefficient in system is corresponding with this study. The different of initiator concentration may control the polymerization level that influence to the properties of both cases, bulk polymer properties and surface property.

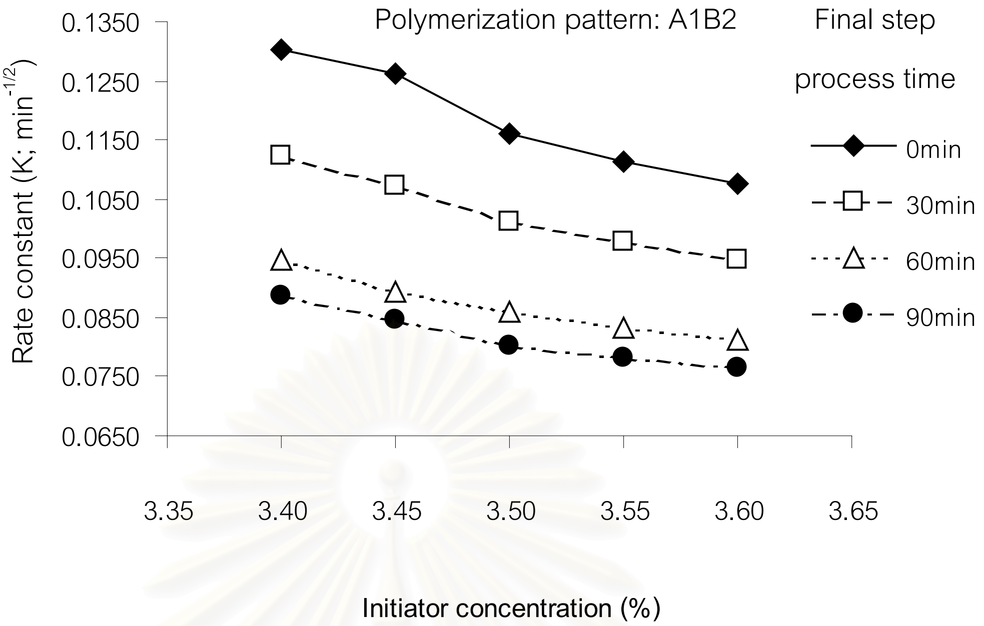


Figure 4.2: Relationship between initiator concentrations versus rate constant (Polymerization pattern A1B2 with different final step process time)

From figure 4.2, the relationship result have similar trend as figure4.1. The different in rate constant value that depend on initiator concentration. The trend of evidence is shown in inverse proportional relationship between initiator concentration and tinting rate constant.

Anyhow the rate constant from figure 4.2 is higher than rate constant from figure 4.1 for each point of concentration that influence from polymerization condition. The condition of A1B2 has lower final stage temperature than A1B1 (80°C and 85°C respectively).

From this different, the shape of line is different form figure 4.1. In figure 4.1 the progression of rate constant curve was more linear when final step process time over than 60 min. For figure 4.2, the sample of final step process time at 90 min is show in curve relationship along studied initiator concentration. In this case should be refer to the casting temperature that lower in final step process if compare with figure 4.1. It is means when the condition getting more mild condition of polymerization (lower temperature and shorter final step process time give the curve relationship between initiator concentration versus rate constant. then the hardest condition in this study (A1B1t4 that shown in figure 4.1) was shown the linear relationship between initiator concentration versus tinting rate constant.

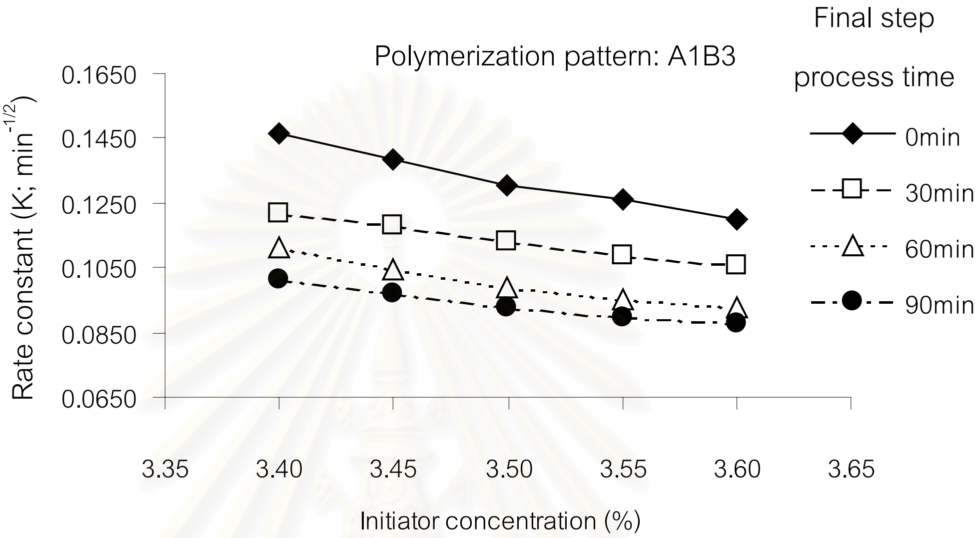


Figure 4.3: Relationship between initiator concentrations versus rate constant (Polymerization pattern A1B3 with different final step process time)

From figure 4.3 shows similar trend as figure 4.1 and 4.2 only different in rate constant vale that effect from final step temperature at 75°C.

The trend of initiator concentration effect of A1 series i.e. A1B1, A1B2 and A1B3 are same trend all but the different of rate constant value depend on the polymerization condition. For the polymerization condition effect will discuss in following section.

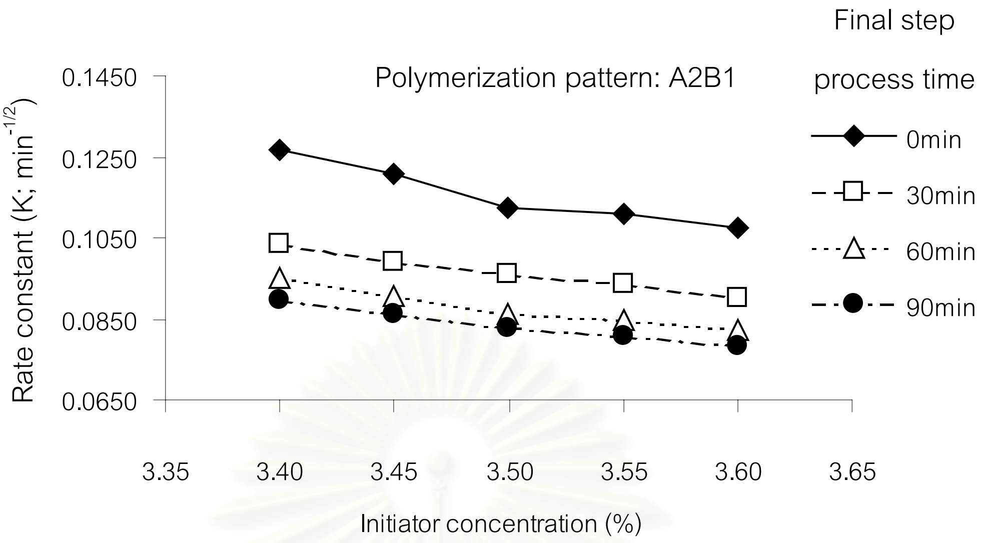


Figure 4.4: Relationship between initiator concentrations versus rate constant (Polymerization pattern A2B1 with different final step process time)

From figure 4.4 the effect of initiator concentration is same trend with previous figures. Compare with this figure with figure 4.1, the result of rate constant came from different in first step temperature, 46°C for pattern A1B1 and 40°C for pattern A2B1. The figure show, first step temperature is effect to rate constant of tinting process. The lower first step temperature made higher value of rate constant. In practical, if a pairs of sample, one from A1B1 and the other from A2B1, the result after tint in same period will give us different result of transparent. A2B1 sample give darker color density (low transparency) than A1B1 sample.

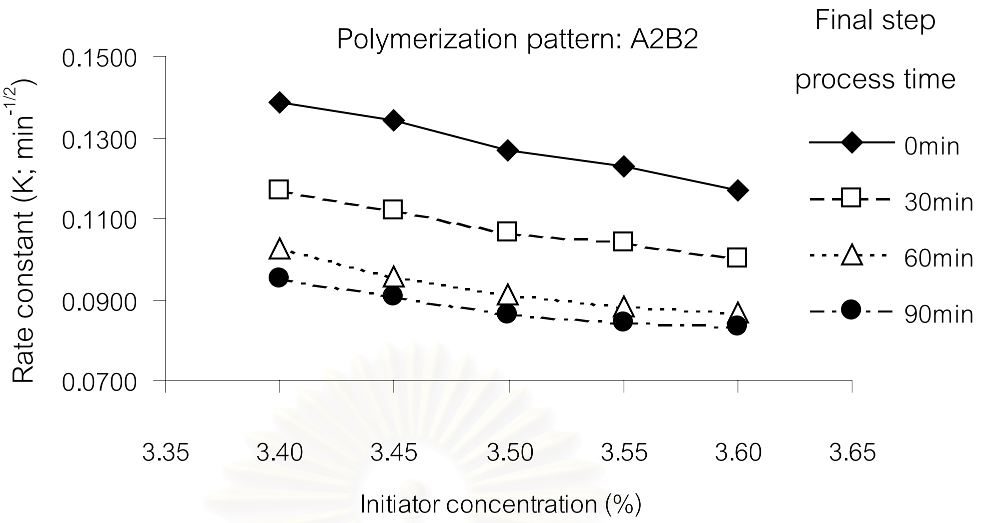


Figure 4.5: Relationship between initiator concentrations versus rate constant (Polymerization pattern A2B2 with different final step process time)

From figure 4.5 shows the effect of initiator concentration is similar trend as previous figures. However, consider the comparison between 2 groups. First group is figure 4.1 versus figure 4.2 and the second group is figure 4.4 versus figure 4.5. The different of final step temperature is effect to tinting result as explained in previous figure.

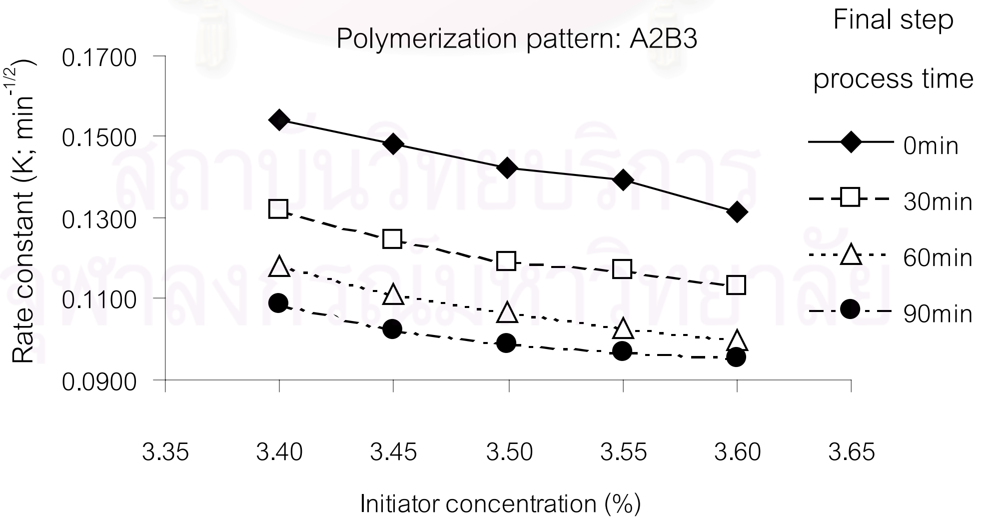


Figure 4.6: Relationship between initiator concentrations versus rate constant (Polymerization pattern A2B3 with different final step process time)

From figure 4.6, the effect of initiator concentration is same trend as previous figures. Also, the same comparison of final step temperature at 75°C have discussed in figure 4.3 already.

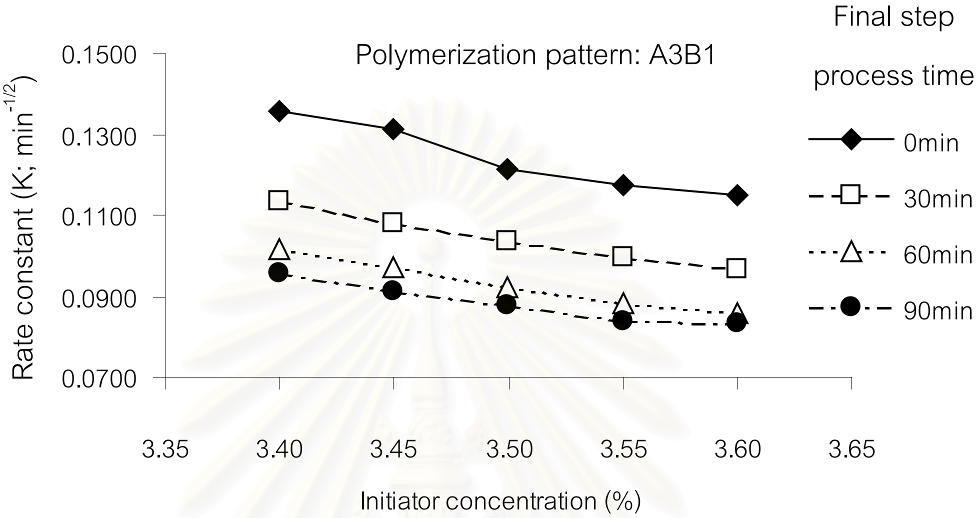


Figure 4.7: Relationship between initiator concentrations versus rate constant (Polymerization pattern A3B1 with different final step process time)

From figure 4.7, the rate constant of tinting sample is depending on initiator concentration of casting sample. Trend of rate constant versus initiator concentration is similar as previous figures.

However the value of rate constant in this figure is depending on polymerization pattern of them. The first stage temperature is A3, 35°C, that different from figure 4.1 and 4.4 (46°C and 40°C respectively). This figure is confirmed for temperature effect of polymerization pattern that effective for the rate constant and rate of tinting.

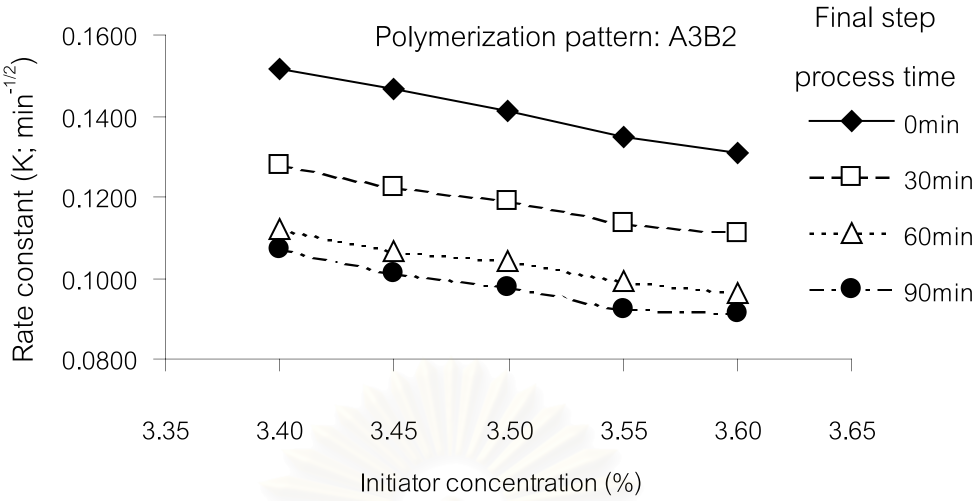


Figure 4.8: Relationship between initiator concentrations versus rate constant (Polymerization pattern A3B2 with different final step process time)

From figure 4.8 shows similar trend as figure 4.7 only different in rate constant vale that effect from final step temperature at 80°C

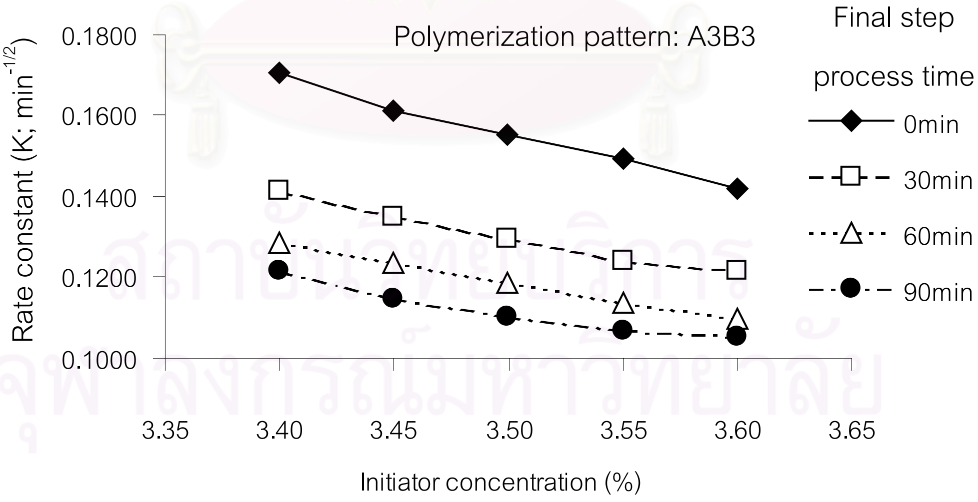


Figure 4.9: Relationship between initiator concentrations versus rate constant (Polymerization pattern A3B3 with different final step process time)

From figure 4.9 shows similar trend as figure 4.7 and figure 4.8 only different in rate constant vale that effect from final step temperature at 75°C

From figure 4.1 to 4.9 the relationship of initiator concentration versus rate constant of tinting have same trend of changes. The initiator concentration is important to casting product properties one of them is surface property. Casting product with different in initiator concentration give different manner of tinting result.

Rate of tinting is defined for speed of dyeing diffuse into substrate. Form Type I study, the initiator concentration range of 3.4 to 3.6 gave interesting phenomena. Speed of tinting is inverse proportion with initiator concentration. 3.4% of initiator concentration sample have easy to tint more than 3.6% initiation concentration sample.

4.1.2 Study of initiator concentration for Type II

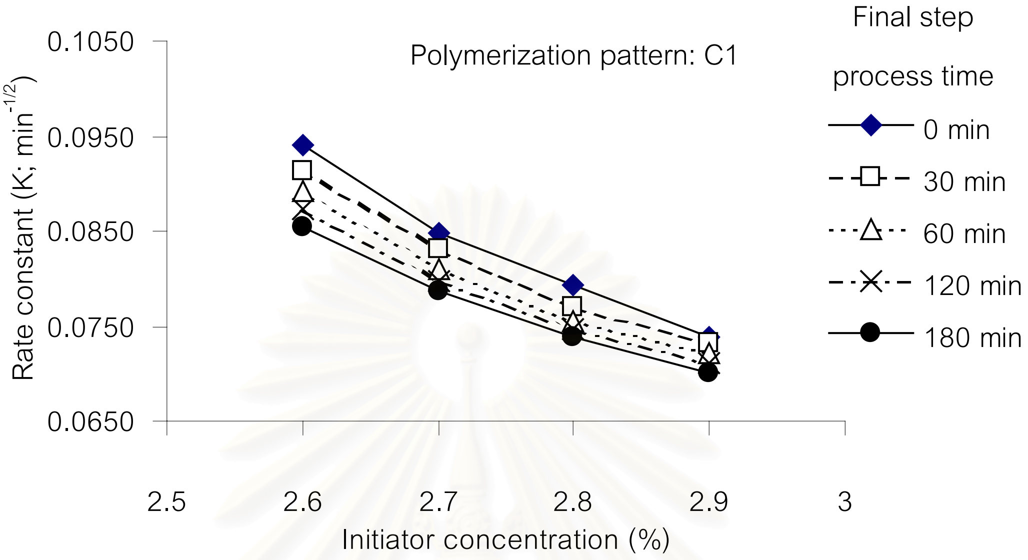


Figure 4.10: Relationship between initiator concentrations versus rate constant (Polymerization pattern C1 with different final step process time)

From figure 4.10 show the relationship between initiator concentrations versus rate constant of polymerization pattern C1 of Type II. Initiator concentration effect is similar as in topic 4.1.1. Rate constant of tinting is inverse proportional to initiator concentration from 2.6% to 2.9% in same polymerization pattern with different processing time.

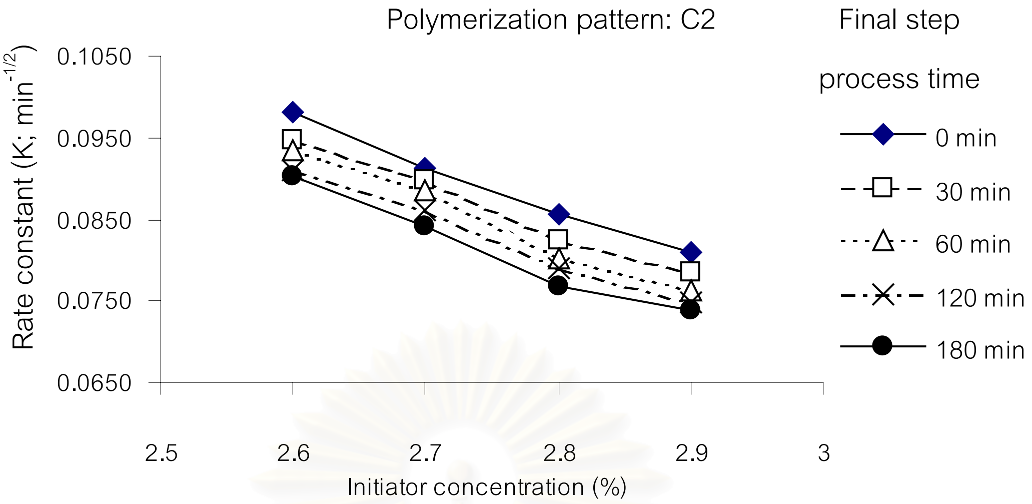


Figure 4.11: Relationship between initiator concentrations versus rate constant (Polymerization pattern C2 with different final step process time)

From figure 4.11 shows similar trend as figure 4.10 only different in rate constant value that effect from polymerization pattern C2

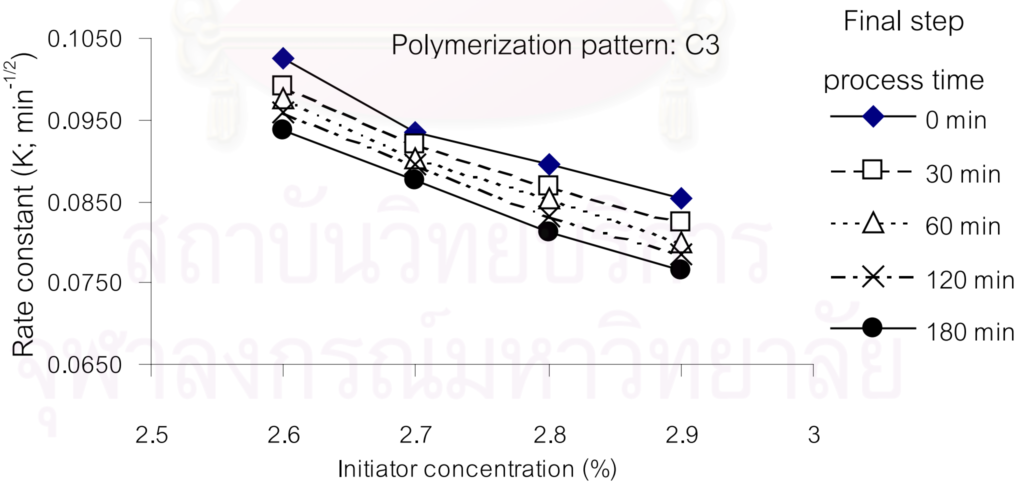


Figure 4.12: Relationship between initiator concentrations versus rate constant (Polymerization pattern C3 with different final step process time)

From figure 4.12 shows similar trend as figure 4.11 only different in rate constant value that effect from polymerization pattern C3

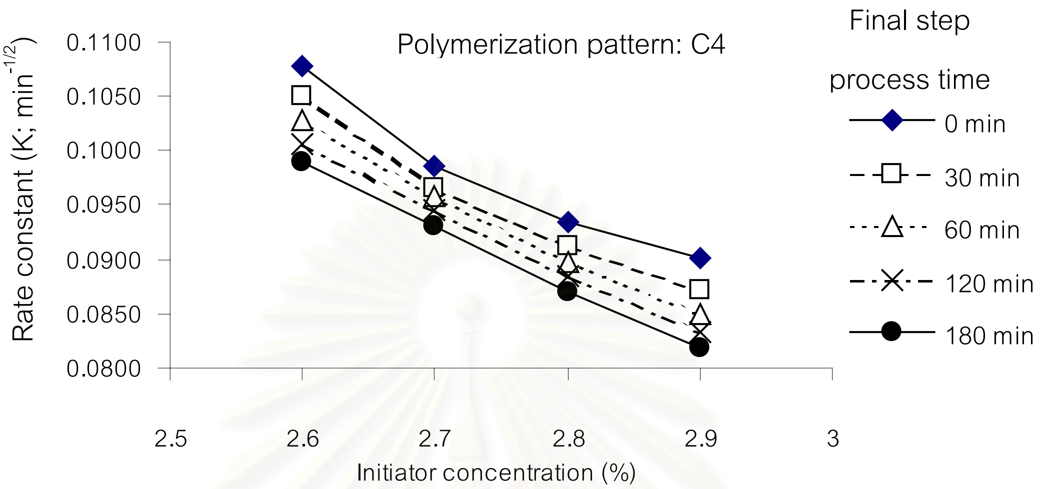


Figure 4.13: Relationship between initiator concentrations versus rate constant (Polymerization pattern C4 with different final step process time)

From figure 4.13 shows similar trend as figure 4.12 only different in rate constant value that effect from polymerization pattern C4

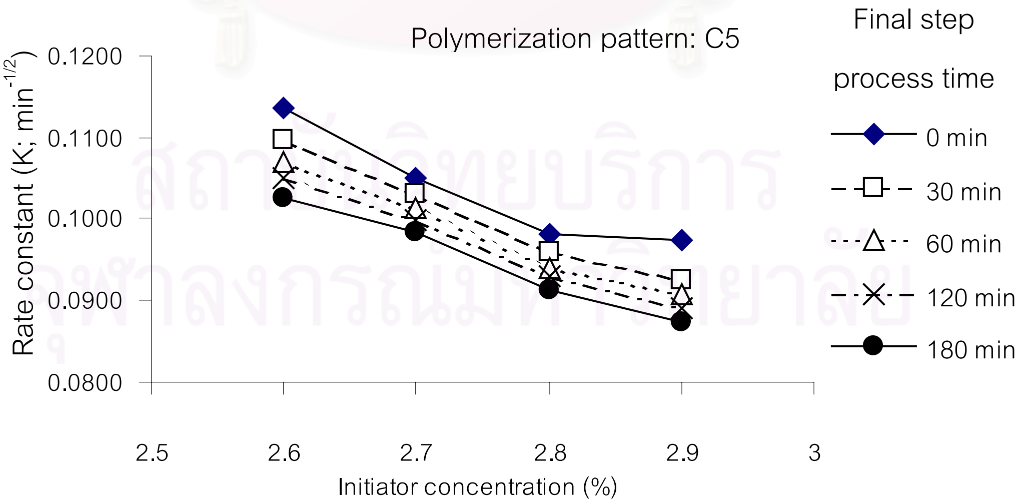


Figure 4.14: Relationship between initiator concentrations versus rate constant

(Polymerization pattern C5 with different final step process time)

From figure 4.14 shows similar trend as figure 4.13 only different in rate constant value that effect from polymerization pattern C5

Figure 4.10 to 4.14 show the relationship between initiator concentrations versus rate of tinting of Type II polymerization. The rate of tinting is inverse proportional to initiation concentration, similar as Type I, in range of 2.6 to 2.9. Higher initiator concentration gave lower rate constant of tinting. That is means a pairs of tinting sample that employ different in initiator concentration, but cast in same of polymerization pattern will give different result of color density result. The higher initiator concentration will give lower color density result. In the other word, if color density is fixed by order, the 2.6% sample must spend long tinting time than 2.4% sample.

Initiator concentration is one of important factor to polymer property. The casting sample with different initiator concentration have different manner of property. Initiator concentration has influences all of bulk of polymer and surface property. Such as tintability, ability to tint, of sample with different in initiator concentration give different result of rate of tinting via value of rate constant.

Initiator concentration effect is influences to tinting process because of the different in tinting rate. If a pairs of CR39 lens with different initiator concentration is tint in same time with respected color density but the result show different in color density at finish. That has at least 3 cases in tinting result.

First, if one of them has under specification (needed color density), operator must more tint this piece for reach to required specification. The processing time of production is lost in two points, one is rework time for complete color density. The other is time to produce new pairs of product.

Unfortunately, if the specified color density is very high (close to 100%), some of initiator concentration cannot reach to target then it must be rejected. However, the production was spent processing time and rework time with out product. It is very un-appreciate to production.

Second, if one of them has over specification, it is means operator must spend processing time to decrease color density back to respected target. The rework time is spent to operate. Also the new pairs processing time is spent too. If the result of first tint is very higher than respected target and cannot reach back then that lens must be rejected.

Third, if one of them lower than target but the other one higher than target, the working time will lost for two rework process. One to reach forward to target and the other one reach back to target. Unfortunately, in this case, the risk to lost of processing time and product will growth to twice.

Then the initiator concentration of casting sample should be control as specification with some small range. That will give a little deviation in surface property of casting product then the chance to lost of processing time and lost of product will reduce then the tinting production can run more smooth.

Study of effect of initiator concentration on tinting process, both Type I and Type II, can summarized as

$$Rate\ of\ tinting \propto \frac{1}{initiator\ concentrat\ ion} \qquad (4.1)$$

also

$$Tinting\ process\ time \propto initiator\ concentrat\ ion \qquad (4.2)$$

Because tinting process time is depend on rate of tinting. The higher rate of tinting gives faster (or shorter) tinting processing time. Then equation 4.2 is follow and get the inverse relationship with initiator concentration as equation 4.1.

4.2 Study the effective of polymerization program parameter, temperature and process time of casting process on tinting process of diethylene glycol bis(allyl carbonate) plastic lens.

From the study of rate of tinting, in section 4.1 the initiator concentration effect was discussed. However for this study the initiator doesn’t one of variable. The polymerization program that including with temperature condition and final step process time is study too.

4.2.1 Study of polymerization program parameter for Type I

For Type I polymerization the temperature is varied in first step and final step. The study of first and second step temperature is setup the temperature of A1,A2 and A3 condition. Deviation of final step is setup for B1,B2 and B3 condition (constant at 85, 80 and 85 respectively). For all case of temperature deviation, The final step processing time was varied from 0 min to 90 min.

From section 4.1, the initiator concentration effect is known that influence to tinting rate constant. Then in this section the discussion will not displayed for all chart.

The discussion will do on effect of variable to rate of tinting. For another chart is displayed in Appendix.

4.2.1.1 Effect of starting temperature of polymerization

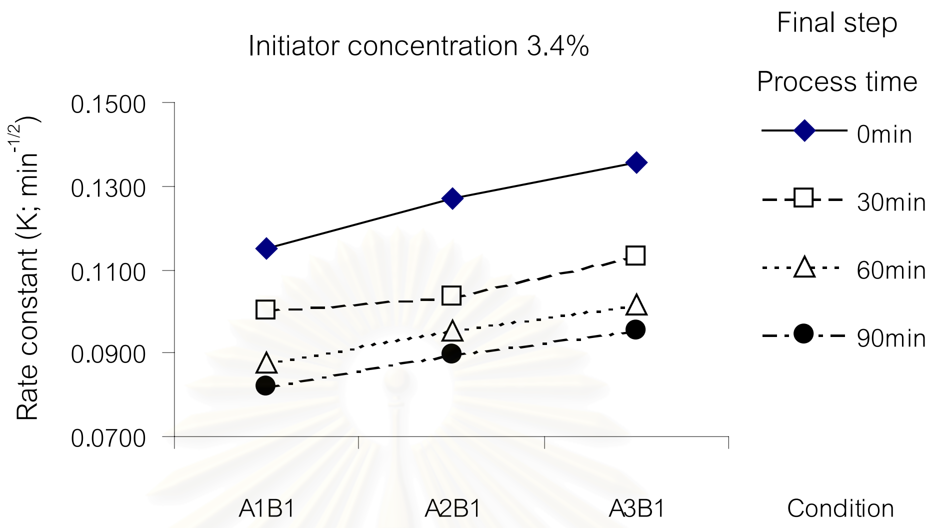


Figure 4.15a: Relationship between starting temperature condition versus rate constant

(Initiator concentration 3.4% with final step temperature condition B1)

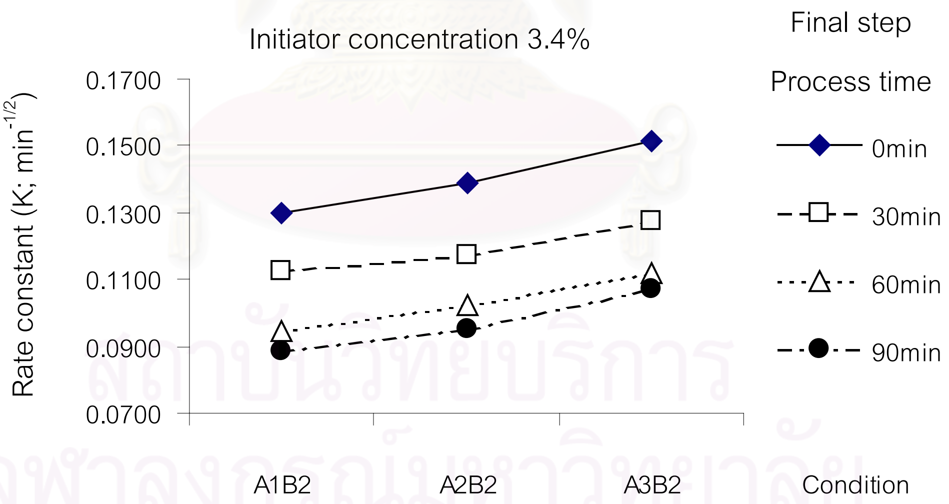


Figure 4.15b: Relationship between starting temperature condition versus rate constant

(Initiator concentration 3.4% with final step temperature condition B2)

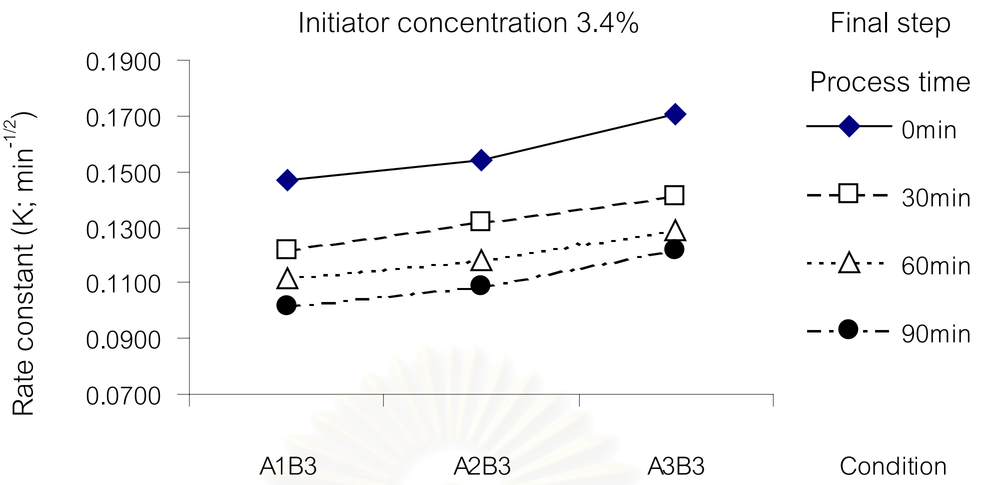


Figure 4.15c: Relationship between starting temperature condition versus rate constant

(Initiator concentration 3.4% with final step temperature condition B3)

From figure 4.15a, 4.15b and 4.15c show the relationship between starting temperature condition A1, A2 and A3 of 3.4% initiator concentration. The three figures show the same trend of rate constant change when starting temperature is changes.

In experiment, the temperature setting of A1 is higher than A2 and A2 is higher than A3. Then the temperature is decrease from A1 to A3. The rate constant result shown that higher starting temperature has lower rate of tinting. It is means A1 sample has lower rate constant than A3 sample with another controlled variable.

The starting temperature is related to polymerization of casting process. CR39 resins is exothermic reaction then the different of starting temperature has influence to polymerization.

From the result can summarized the relationship as

$$Rate\ \ of\ \ tint\,ing \quad \propto \quad \frac{1}{starting\ \ temperatur\ e\ \ of\ \ polymeriza\ tion} \qquad (4.3)$$

Also

$$\textit{Tinting process time} \propto \textit{starting temperature of polymerization} \quad (4.4)$$

For another initiator concentrations is similar trend as figure 4.15a, 4.15b, and 4.15c except the rate constant value that depend on initiator concentration that discussed in section 4.1

4.2.1.2 Effect of final step temperature of polymerization

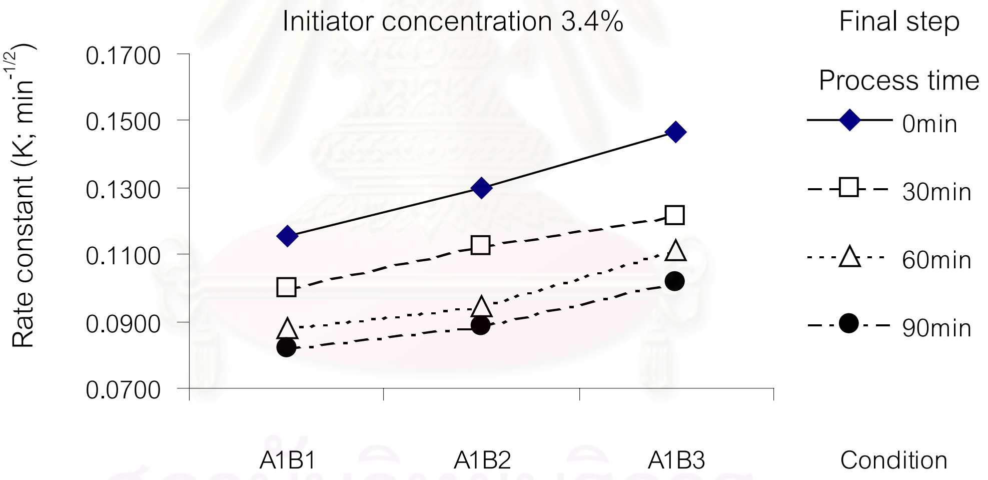


Figure 4.16a: Relationship between final step temperature condition versus rate constant (Initiator concentration 3.4% with starting temperature condition A1)

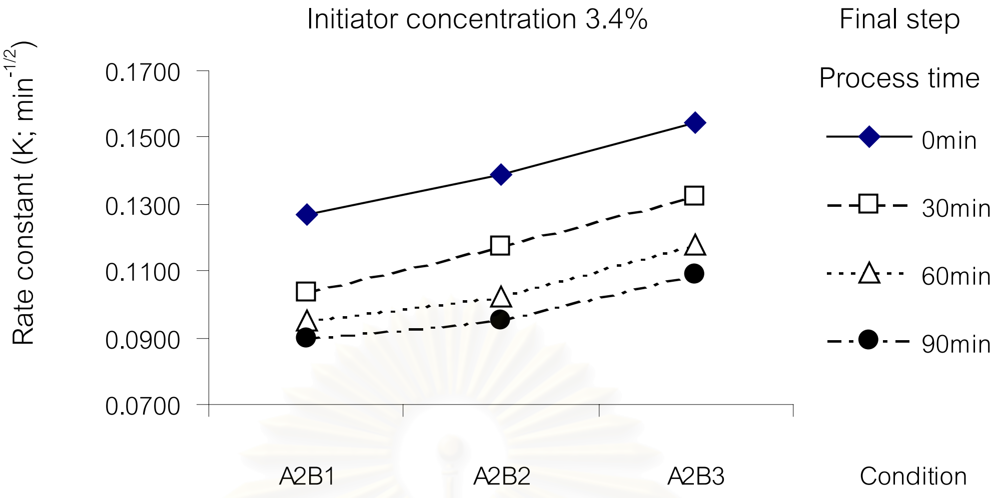


Figure 4.16b: Relationship between final step temperature condition versus rate constant (Initiator concentration 3.4% with starting temperature condition)

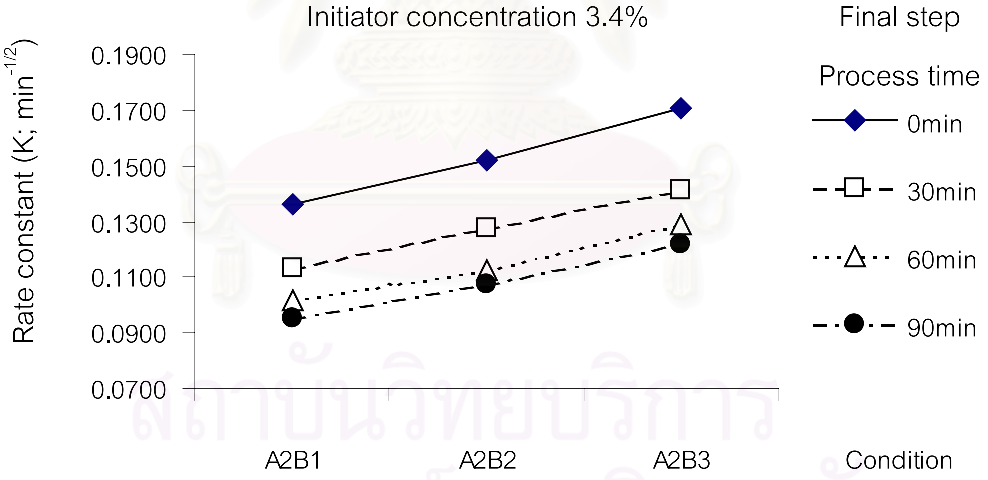


Figure 4.16c: Relationship between final step temperature condition versus rate constant (Initiator concentration 3.4% with starting temperature condition A3)

Figure 4.16a, 4.16b and 4.16c show relation ship between final step temperature conditions versus rate constant of 3.4% initiator concentration. The three figures show the same trend of rate constant change when starting temperature is changes.

From the result can summarized the relationship as

$$Rate\ \ of\ \ tinting \quad \propto \quad \frac{1}{final\ \ step\ \ temperature\ \ of\ \ polymerization} \qquad (4.5)$$

Also

$$Ttinting\ \ process\ \ time \quad \propto \quad final\ \ step\ \ temperature\ \ of\ \ polymerization \qquad (4.6)$$

For another initiator concentrations is similar trend as figure 4.16a, 4.16b, and 4.16c except the rate constant value that depend on initiator concentration that discussed in section 4.1

4.2.1.3 Effect of final step process time of polymerization

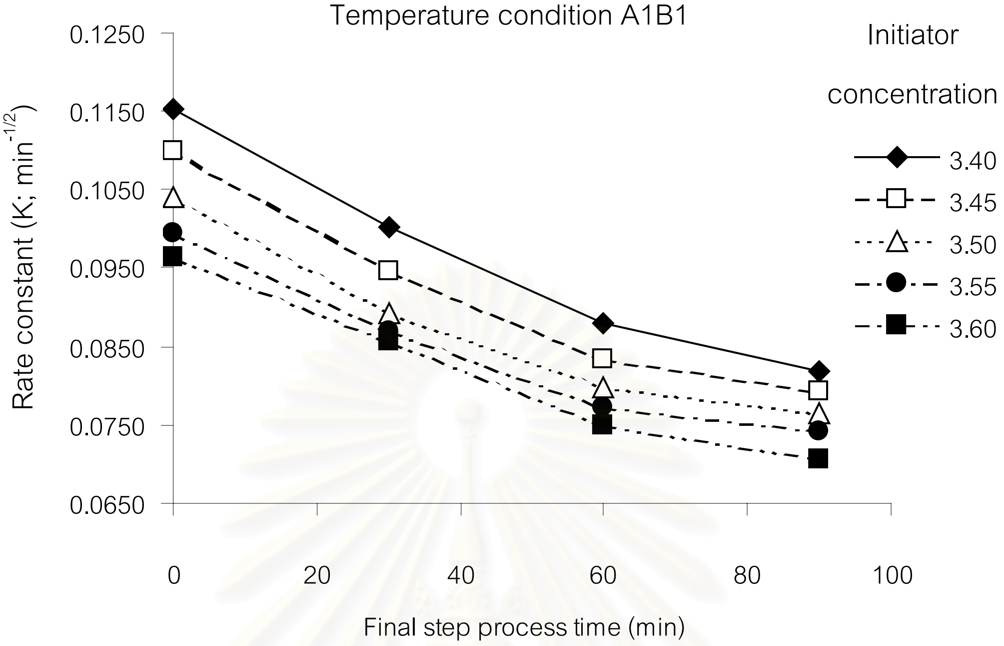


Figure 4.17: Relationship between final step process time of polymerization versus rate constant (temperature condition A1B1)

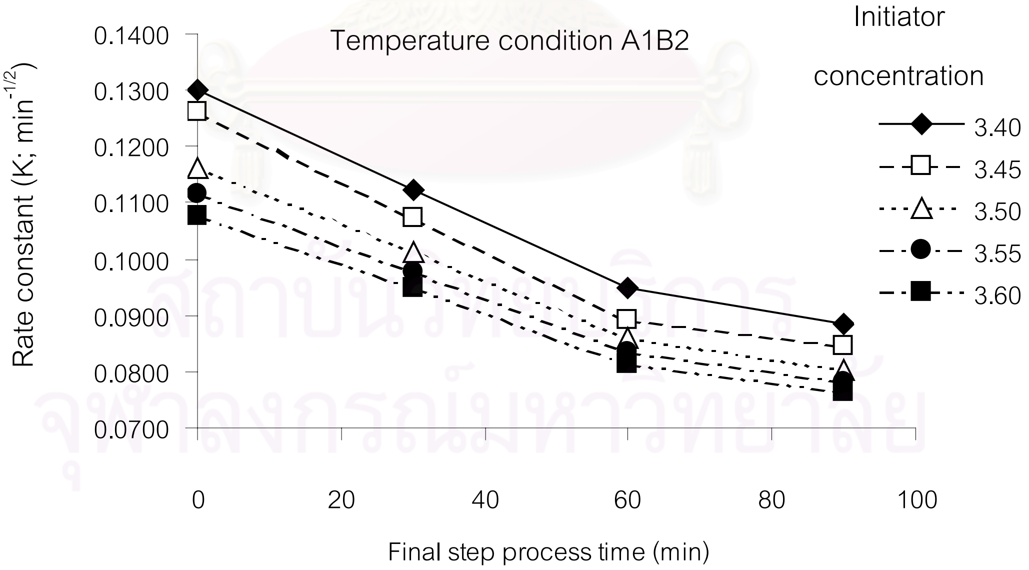


Figure 4.18: Relationship between final step process time of polymerization versus rate constant (temperature condition A1B2)

Figure 4.17 and 4.18 show relation ship between final step processing time versus rate constant of A1B2 temperature condition. The figures show the same trend of rate constant change when starting temperature is changes.

From the result can summarized the relationship as

$$Rate\ \ of\ \ ti\,nt\,ing \quad \propto \quad \frac{1}{t_{final\ \ step}} \tag{4.7}$$

Where $t_{\text{final step}}$ is final step processing time

Also

$$Tti\,nt\,ing\ \ process\ \ \ time \quad \propto \quad t_{final\ \ step} \tag{4.8}$$

4.2.2 Study of polymerization program parameter for Type II

4.2.2.1 Effect of process temperature

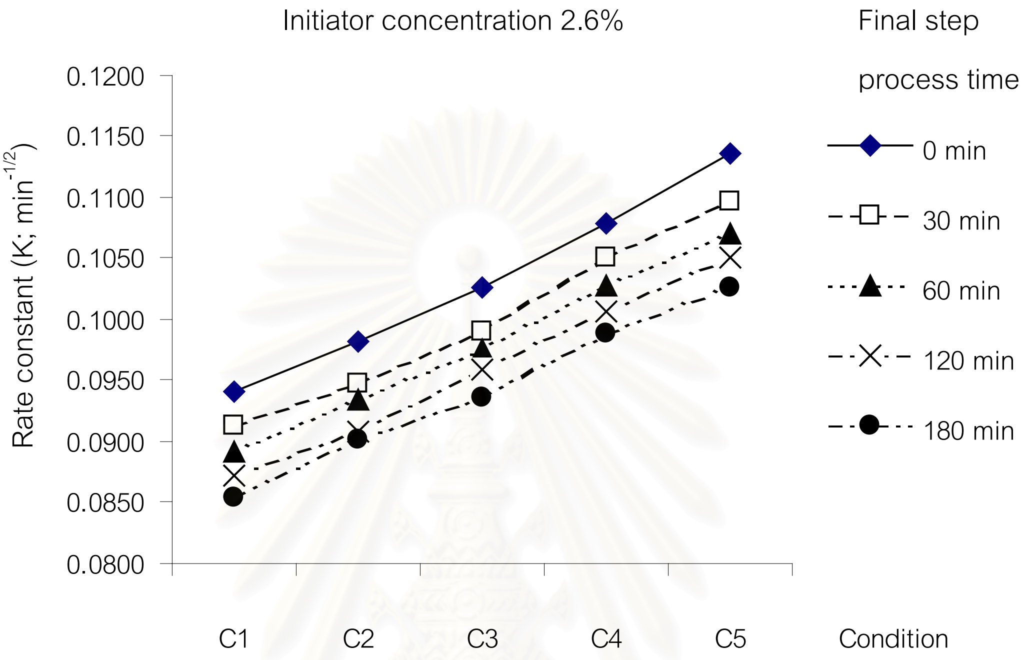


Figure 4.19: Relationship between polymerization patterns of temperature versus rate constant (Initiator concentration 2.6%)

From figure 4.19 show the relationship of between polymerization patterns of temperature versus rate constant. The polymerization pattern is different in temperature in each step. However pattern temperature is set as C1>C2>C3>C4>C5 then can summarized the relation ship as

$$\text{Rate of tinting} \propto \frac{1}{\text{Polymerization temperature}} \qquad (4.9)$$

or

$$\text{Tinting process time} \propto \text{Polymerization temperature} \qquad (4.10)$$

4.2.2.2 Effect of final step process time

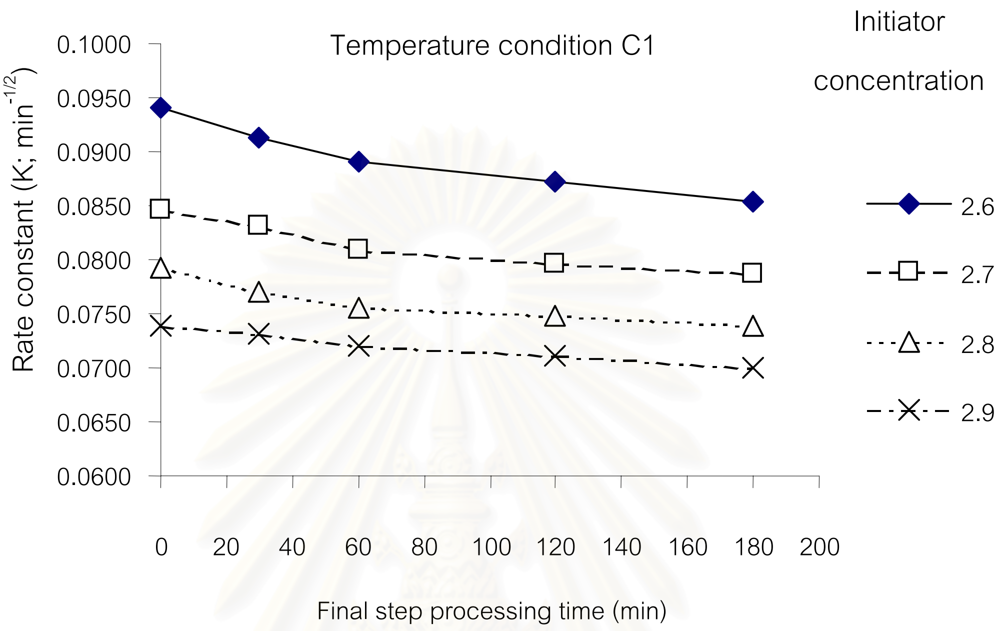


Figure 4.20: Relationship between final step process times of polymerization versus rate constant (temperature condition C1)

Figure 20 show relation ship between final step processing time versus rate constant of C1 temperature pattern of polymerization. The three figures show the same trend of rate constant change when starting temperature is changes.

From the result can summarized the relationship as

$$Rate\ of\ tinting \propto \frac{1}{t_{final\ step}} \qquad (4.11)$$

Where $t_{final\ step}$ is final step processing time

Also

$$Ttinting\ process\ time \propto t_{final\ step} \qquad (4.12)$$

4.3 Study of surface quality control of diethylene glycol bis(allyl carbonate) product

The surface quality control of diethylene glycol bis(allyl carbonate) product of HOYA is qualifies via tinting method. From the result of section 4.1 and 4.2, the different condition of casting since initiator concentration and polymerization condition (temperature and process time) are effect to tinting process as different rate of dyeing. That will influence to customer to use for tinting product. Rate of tinting is defined by result of tinting (%color density) changes along tinting process. But the checking method of product quality control is a little bit different by fixed the tinting time. Then the HOYA standard to checking the product was setup to control the production by this method. The tinting parameters as temperature (81C), dyestuff (Hoya marron dyestuff) and its concentration (5g/l), tinting time (10 min) are controlled for check the different of surface condition of product.

The tinting result of diethylene glycol bis(allyl carbonate) product is compared with HOYA standard, 50±5 %color density. The out of tolerance result shows that process must be check and action for counter measure.

In this study, the sample that set at different in chemical information and processing condition is checked by this method for reference of data.

4.3.1 Study of surface quality control for Type I

In study of type I, the concentration of mixing monomer was setting as in Chapter 3. The suitable condition that pass Hoya specification is displayed in shade area of table 4.1

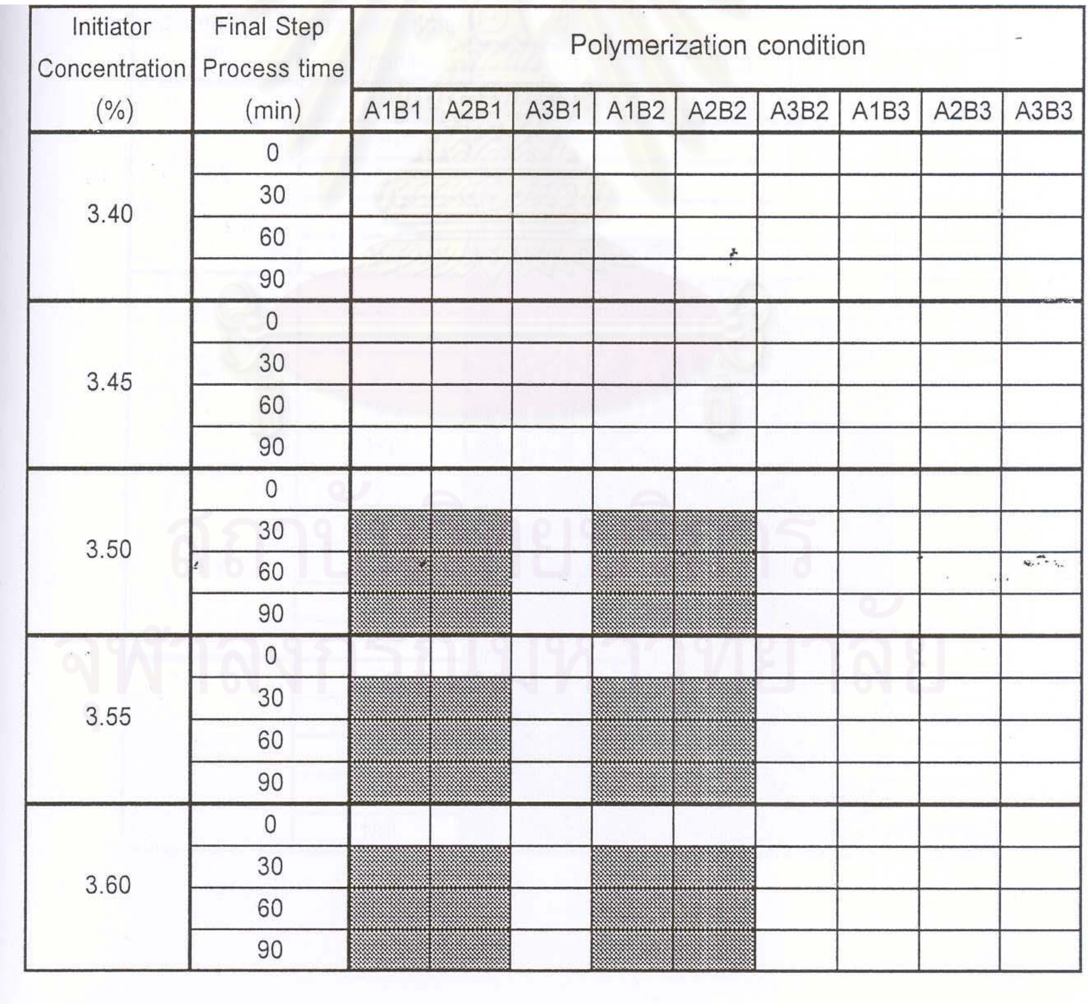
Table 4.1: Suitable condition for casting of CR39 with Type I polymerization (displayed in shade area)

Initiator Concentration (%)	Final Step Process time (min)	Temperature condition								
		A1B1	A2B1	A3B1	A1B2	A2B2	A3B2	A1B3	A2B3	A3B3
3.40	t1									
	t2	🟩								
	t3	🟩	🟩	🟩	🟩	🟩				
	t4	🟩	🟩	🟩	🟩	🟩		🟩	🟩	
3.45	t1									
	t2	🟩								
	t3	🟩	🟩	🟩	🟩	🟩		🟩		
	t4	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	
3.50	t1									
	t2	🟩	🟩	🟩	🟩	🟩				
	t3	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	
	t4	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	
3.55	t1									
	t2	🟩	🟩	🟩	🟩	🟩				
	t3	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	
	t4	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	
3.60	t1	🟩			🟩					
	t2	🟩	🟩	🟩	🟩	🟩			🟩	
	t3	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	
	t4	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩

From table 4.1 the suitable condition for pass specification is initiator concentration from 3.5% to 3.6% with some polymerization pattern. The suitable polymerization pattern is point for final step temperature and final step process time. The final step temperature should be higher than 80°C except the condition A3B2 does cannot use. For final step processing time, the product must be output at least 30 min passed of final step processing time.

The conclusion is displayed in shade area in table 4.2

Table 4.2 Control condition for casting of CR39 with Type I polymerization (displayed in shade area)



Initiator Concentration (%)	Final Step Process time (min)	Polymerization condition								
		A1B1	A2B1	A3B1	A1B2	A2B2	A3B2	A1B3	A2B3	A3B3
3.40	0									
	30									
	60									
	90									
3.45	0									
	30									
	60									
	90									
3.50	0									
	30	▨	▨		▨	▨				
	60	▨	▨		▨	▨				
	90	▨	▨		▨	▨				
3.55	0									
	30	▨	▨		▨	▨				
	60	▨	▨		▨	▨				
	90	▨	▨		▨	▨				
3.60	0									
	30	▨	▨		▨	▨				
	60	▨	▨		▨	▨				
	90	▨	▨		▨	▨				

4.3.2 Study of surface quality control for type II

In study of type I, the concentration of mixing monomer was setting as in chapter 3. The suitable condition that pass Hoya specification is displayed in shade area of table 4.2

Table 4.2: Suitable condition for casting of CR39 with Type II polymerization (displayed in shade area)

Initiator Concentration (%)	final step process time (min)	Temperature condition				
		C1	C2	C3	C4	C5
2.6	T1	🟩				
	T2	🟩				
	T3	🟩				
	T5	🟩				
	T6	🟩	🟩			
2.7	T1	🟩	🟩	🟩		
	T2	🟩	🟩	🟩	🟩	
	T3	🟩	🟩	🟩	🟩	
	T5	🟩	🟩	🟩	🟩	
	T6	🟩	🟩	🟩	🟩	
2.8	T1	🟩	🟩	🟩	🟩	
	T2	🟩	🟩	🟩	🟩	
	T3	🟩	🟩	🟩	🟩	
	T5	🟩	🟩	🟩	🟩	
	T6	🟩	🟩	🟩	🟩	
2.9	T1	🟩	🟩	🟩	🟩	
	T2	🟩	🟩	🟩	🟩	
	T3	🟩	🟩	🟩	🟩	
	T5	🟩	🟩	🟩	🟩	
	T6	🟩	🟩	🟩	🟩	🟩

From table 4.2 the suitable condition for pass specification is initiator concentration from 2.7% to 2.9% with some polymerization pattern. The suitable polymerization pattern is point for polymerization temperature pattern and final step process time. The suitable polymerization patterns is all case except C5 pattern. For final step processing time, the product must be output at least 30 min passed of final step processing time.

The conclusion is displayed in shade area in table 4.4

Table 4.4 Control condition for casting of CR39 with Type II polymerization (displayed in shade area)

Initiator concentration (%)	Final step process time (min)	Polymerization condition				
		C1	C2	C3	C4	C5
2.6	0					
	30					
	60					
	120					
	180					
2.7	0					
	30	▨	▨	▨	▨	
	60	▨	▨	▨	▨	
	120	▨	▨	▨	▨	
	180	▨	▨	▨	▨	
2.8	0					
	30	▨	▨	▨	▨	
	60	▨	▨	▨	▨	
	120	▨	▨	▨	▨	
	180	▨	▨	▨	▨	
2.9	0					
	30	▨	▨	▨	▨	
	60	▨	▨	▨	▨	
	120	▨	▨	▨	▨	
	180	▨	▨	▨	▨	

CHAPTER 5

CONCLUSION

The conclusions for this study are

1. The concentration of initiator, diisopropyl peroxydicarbonate, in casting of diethylene glycol bis(allyl carbonate) is influence on rate of tinting. The rate constant is inverse proportional to initiator concentration. This evidence was happening both of Type I and Type II.

2. For Type I, polymerization temperature condition in casting process is influence on rate of tinting. Starting and final process temperatures are both effects to surface property of product.

3. For Type II, pattern of temperature in polymerization is influence on rate of tinting. The rate constant is inverse proportional to temperature in polymerization process.

4. Processing time is influence on rate of tinting. . The rate constant is inverse proportional to processing time.

5. For Type I processing time is much influence to rate of tinting more than Type II. That came from the temperature program of Type II was passed the highest of temperature. Then the processing time is less effect than Type I that output between highest temperature step.

6. The suitable condition for Type I is control for initiator concentration at 3.5% to 3.6%. For temperature condition, final temperature should be higher than 80°C for all condition of starting temperature condition. The suitable output is more than 30 min of final step. However for starting temperature of 40°C with final step temperature of 80°C, the product must be output at least 1 hr of final step processing time.

7. The suitable condition for Type II is control for initiator concentration at 2.7% to 2.9%. For temperature condition, from C1 to C4 condition is suitable for production. The suitable output is more than 30 min of final step.

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APPENDIX

APPENDIX A

RESULTS OF EXPERIMENT

A1 Rate of tinting result for Type I

Polymerization condition	Final step Process time (min)	Initiator concentration				
		3.40	3.45	3.50	3.55	3.60
A1B1	0	0.1153	0.1101	0.1042	0.0995	0.0964
	30	0.1002	0.0947	0.0894	0.0870	0.0858
	60	0.0880	0.0834	0.0797	0.0772	0.0751
	90	0.0819	0.0794	0.0765	0.0743	0.0707
A1B2	0	0.1301	0.1263	0.1162	0.1114	0.1077
	30	0.1124	0.1074	0.1012	0.0978	0.0949
	60	0.0949	0.0894	0.0860	0.0834	0.0813
	90	0.0886	0.0845	0.0804	0.0783	0.0765
A1B3	0	0.1468	0.1386	0.1304	0.1261	0.1200
	30	0.1216	0.1183	0.1130	0.1086	0.1059
	60	0.1115	0.1044	0.0989	0.0955	0.0927
	90	0.1017	0.0973	0.0929	0.0895	0.0879
A2B1	0	0.1268	0.1208	0.1123	0.1109	0.1073
	30	0.1038	0.0992	0.0963	0.0936	0.0900
	60	0.0953	0.0908	0.0865	0.0849	0.0824
	90	0.0898	0.0864	0.0828	0.0810	0.0786
A2B2	0	0.1389	0.1342	0.1270	0.1229	0.1168
	30	0.1171	0.1121	0.1066	0.1042	0.1003
	60	0.1025	0.0957	0.0913	0.0885	0.0868
	90	0.0950	0.0906	0.0863	0.0845	0.0832
A2B3	0	0.1542	0.1482	0.1423	0.1393	0.1314
	30	0.1321	0.1248	0.1189	0.1171	0.1133
	60	0.1181	0.1113	0.1068	0.1028	0.1001
	90	0.1089	0.1022	0.0987	0.0971	0.0956
A3B1	0	0.1359	0.1313	0.1215	0.1173	0.1148
	30	0.1133	0.1078	0.1037	0.0994	0.0969
	60	0.1015	0.0970	0.0923	0.0882	0.0858
	90	0.0955	0.0914	0.0878	0.0840	0.0832
A3B2	0	0.1517	0.1467	0.1411	0.1346	0.1307
	30	0.1277	0.1224	0.1189	0.1137	0.1111
	60	0.1121	0.1066	0.1043	0.0994	0.0965
	90	0.1072	0.1014	0.0979	0.0924	0.0912
A3B3	0	0.1708	0.1613	0.1553	0.1494	0.1418
	30	0.1414	0.1353	0.1294	0.1242	0.1219
	60	0.1287	0.1237	0.1186	0.1136	0.1097
	90	0.1216	0.1147	0.1106	0.1069	0.1055

A2 Rate of tinting result for Type II

Polymerization condition	Final step Process time (min)	Initiator concentration			
		2.6	2.7	2.8	2.9
C 1	0	0.0941	0.0847	0.0793	0.0739
	30	0.0913	0.0832	0.0770	0.0732
	60	0.0892	0.0810	0.0756	0.0721
	120	0.0873	0.0797	0.0748	0.0712
	180	0.0855	0.0787	0.0739	0.0700
C 2	0	0.0982	0.0913	0.0857	0.0810
	30	0.0947	0.0898	0.0825	0.0785
	60	0.0934	0.0885	0.0803	0.0764
	120	0.0909	0.0862	0.0789	0.0749
	180	0.0902	0.0843	0.0769	0.0738
C 3	0	0.1026	0.0936	0.0895	0.0854
	30	0.0991	0.0920	0.0869	0.0825
	60	0.0976	0.0902	0.0853	0.0801
	120	0.0959	0.0896	0.0832	0.0786
	180	0.0936	0.0877	0.0812	0.0767
C 4	0	0.1078	0.0987	0.0935	0.0902
	30	0.1051	0.0966	0.0912	0.0872
	60	0.1028	0.0959	0.0898	0.0850
	120	0.1006	0.0946	0.0886	0.0834
	180	0.0989	0.0932	0.0870	0.0819
C 5	0	0.1137	0.1050	0.0982	0.0974
	30	0.1097	0.1031	0.0960	0.0926
	60	0.1071	0.1015	0.0941	0.0907
	120	0.1052	0.1000	0.0929	0.0892
	180	0.1026	0.0984	0.0914	0.0873

APPENDIX B
ANALYSIS RESULT
(ADDITION FOR CHAPTER 4. SECTION 4.2)

B1: study of polymerization program parameter for Type I (section 4.2.1)

B1.1: Effect of starting temperature of polymerization

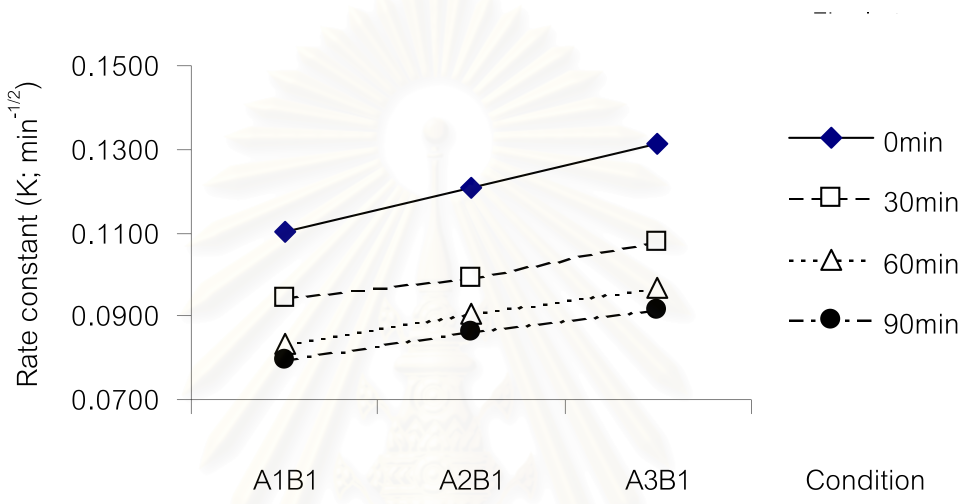

Figure B.1: Relationship between temperature condition versus rate constant (initiator concentration 3.45% with final step temperature condition B1)

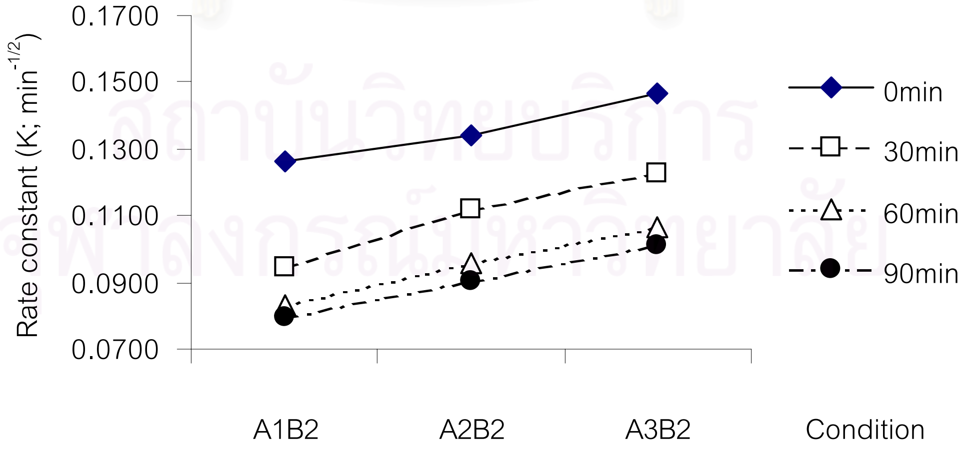

Figure B.2: Relationship between temperature condition versus rate constant (initiator concentration 3.45% with final step temperature condition B2)

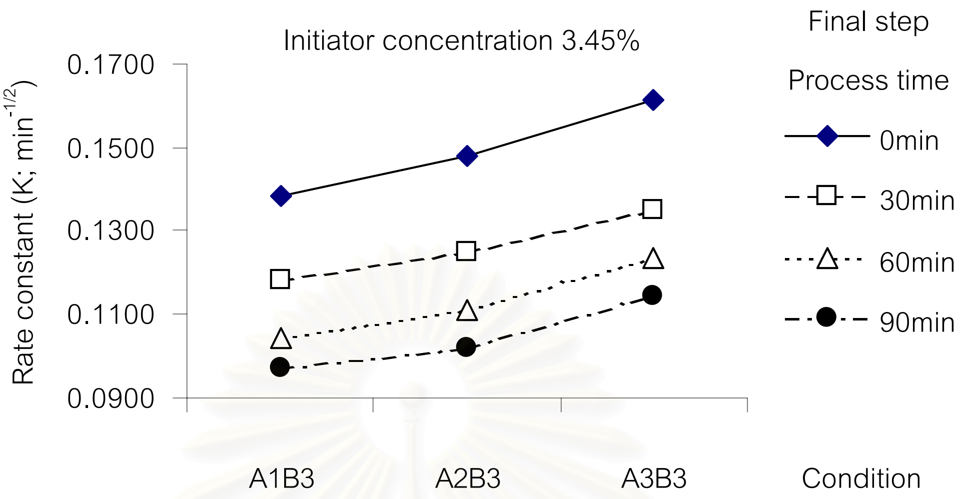

Figure B.3: Relationship between temperature condition versus rate constant (initiator concentration 3.45% with final step temperature condition B3)

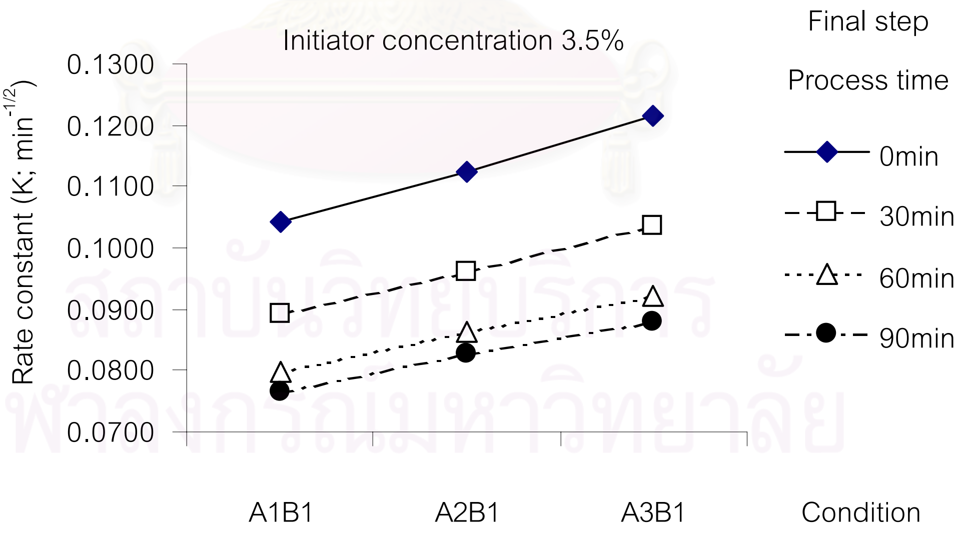

Figure B.4: Relationship between temperature condition versus rate constant (initiator concentration 3.5% with final step temperature condition B1)

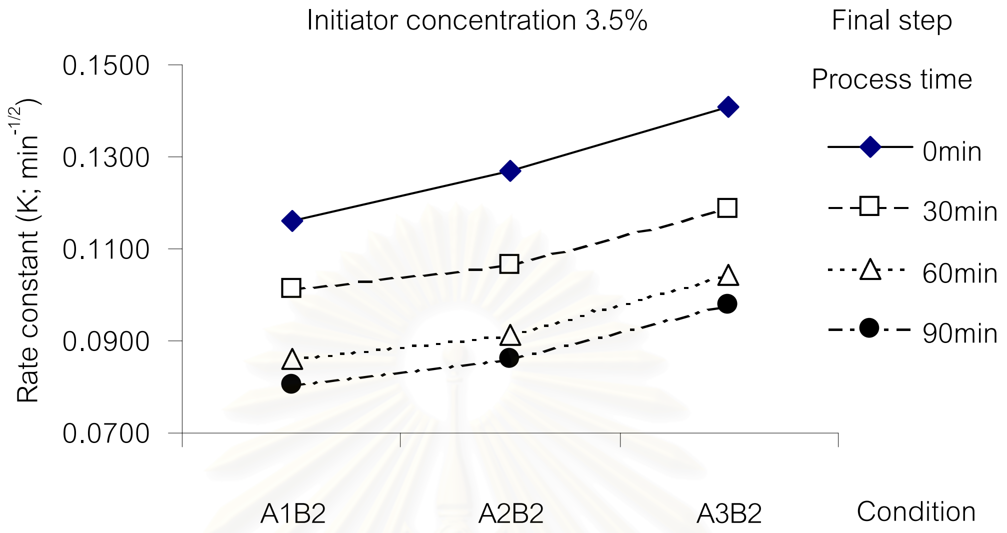

Figure B.5: Relationship between temperature condition versus rate constant (initiator concentration 3.5% with final step temperature condition B2)

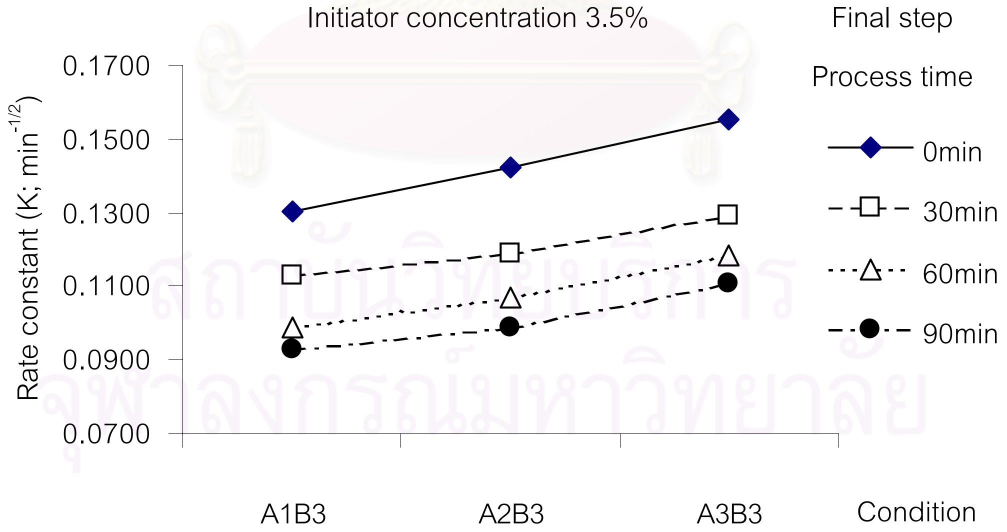

Figure B.6: Relationship between temperature condition versus rate constant (initiator concentration 3.5% with final step temperature condition B3)

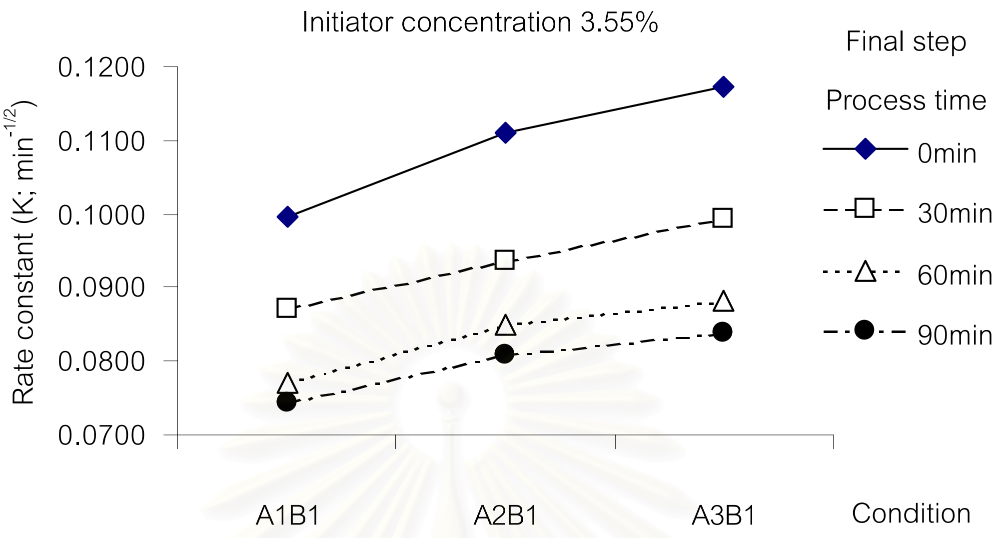

Figure B.7: Relationship between temperature condition versus rate constant (initiator concentration 3.55% with final step temperature condition B1)

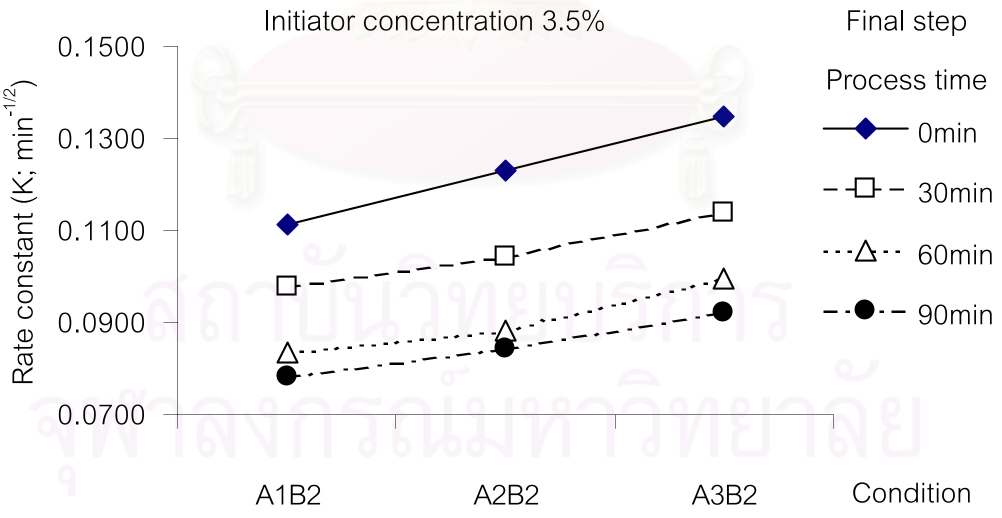

Figure B.8: Relationship between temperature condition versus rate constant (initiator concentration 3.55% with final step temperature condition B2)

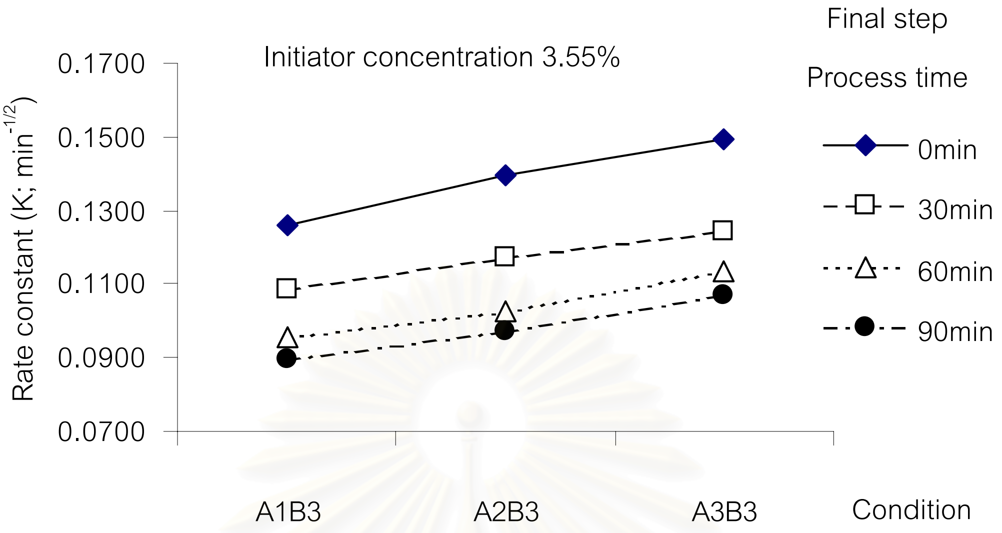

Figure B.9: Relationship between temperature condition versus rate constant (initiator concentration 3.55% with final step temperature condition B3)

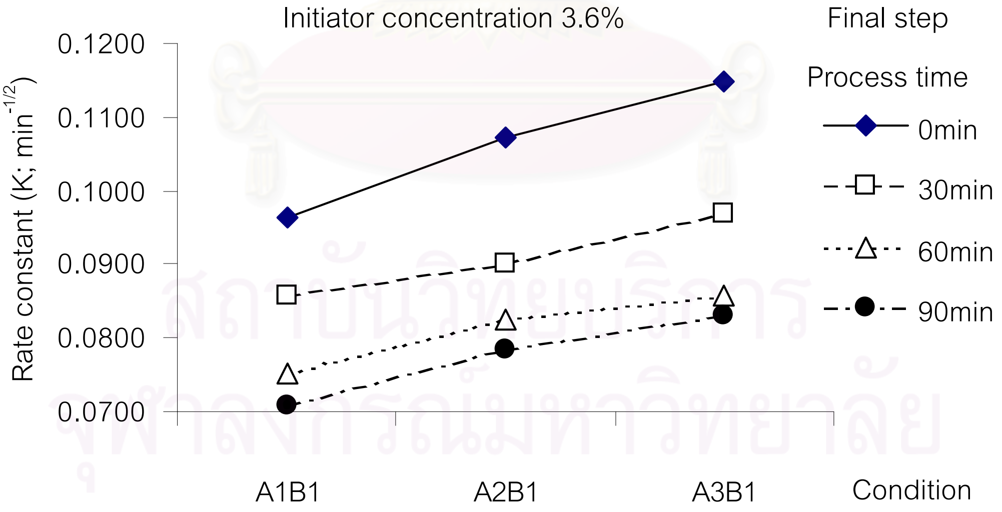

Figure B.10: Relationship between temperature condition versus rate constant (initiator concentration 3.6% with final step temperature condition B1)

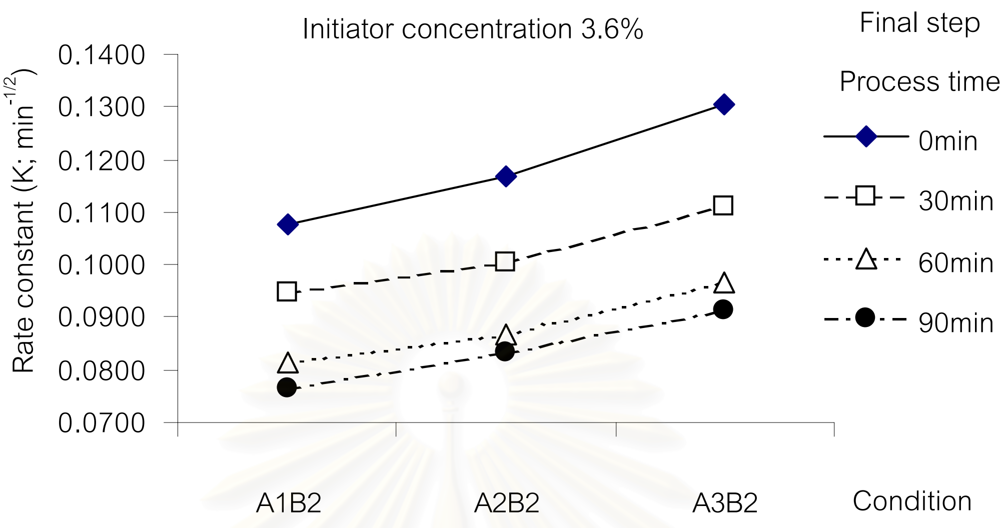

Figure B.11: Relationship between temperature condition versus rate constant (initiator concentration 3.6% with final step temperature condition B2)

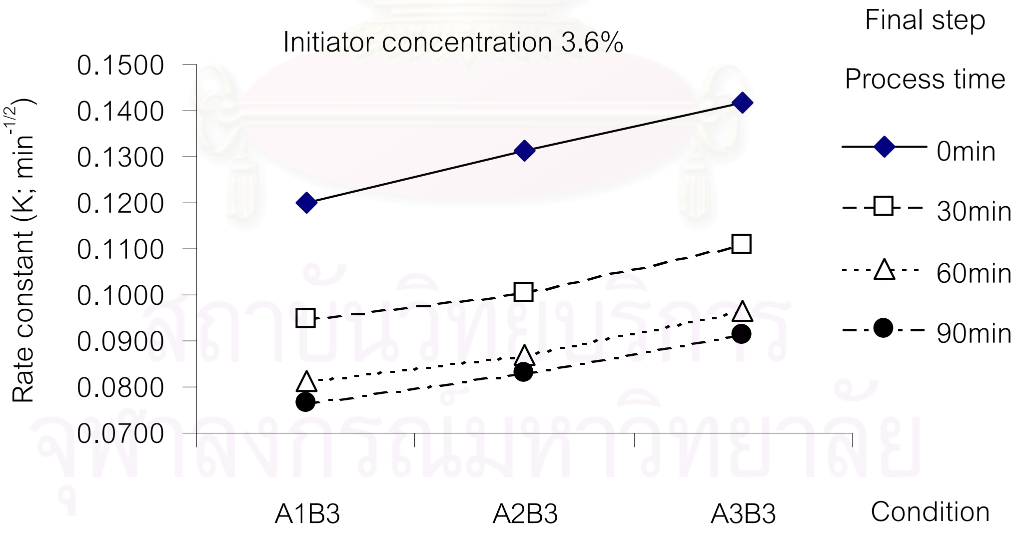

Figure B.12: Relationship between temperature condition versus rate constant (initiator concentration 3.6% with final step temperature condition B3)

B1.2: Effect of final step temperature of polymerization

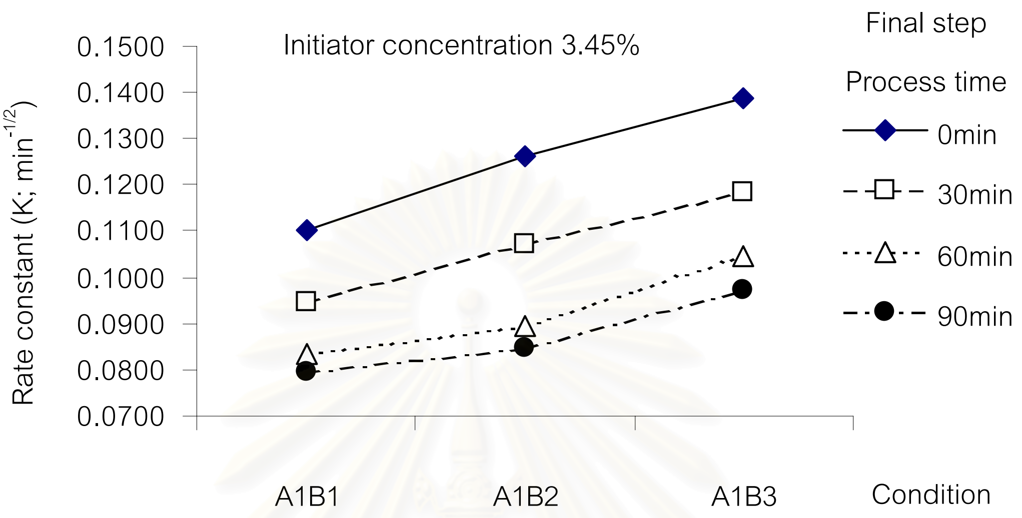

Figure B.13: Relationship between temperature condition versus rate constant (initiator concentration 3.45% with starting temperature condition A1)

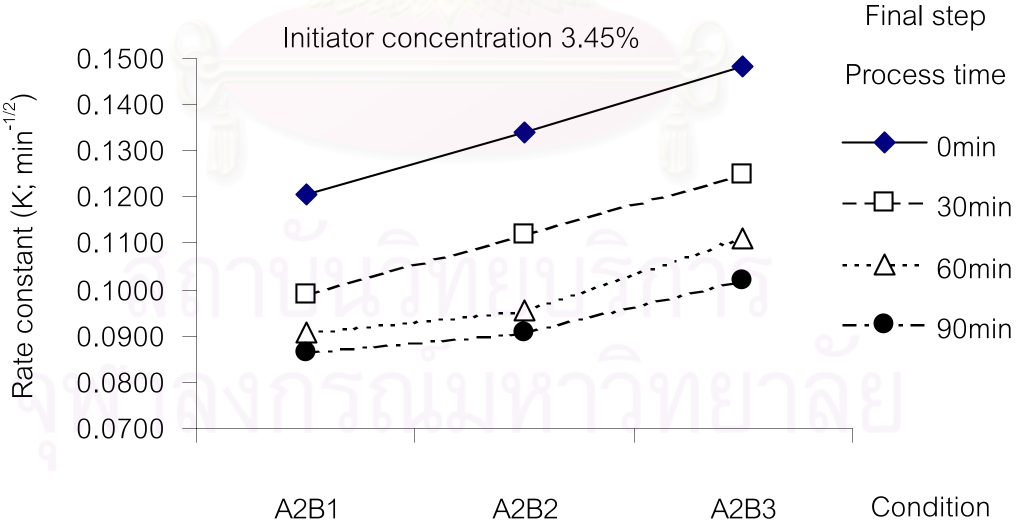

Figure B.14: Relationship between temperature condition versus rate constant (initiator concentration 3.45% with starting temperature condition A2)

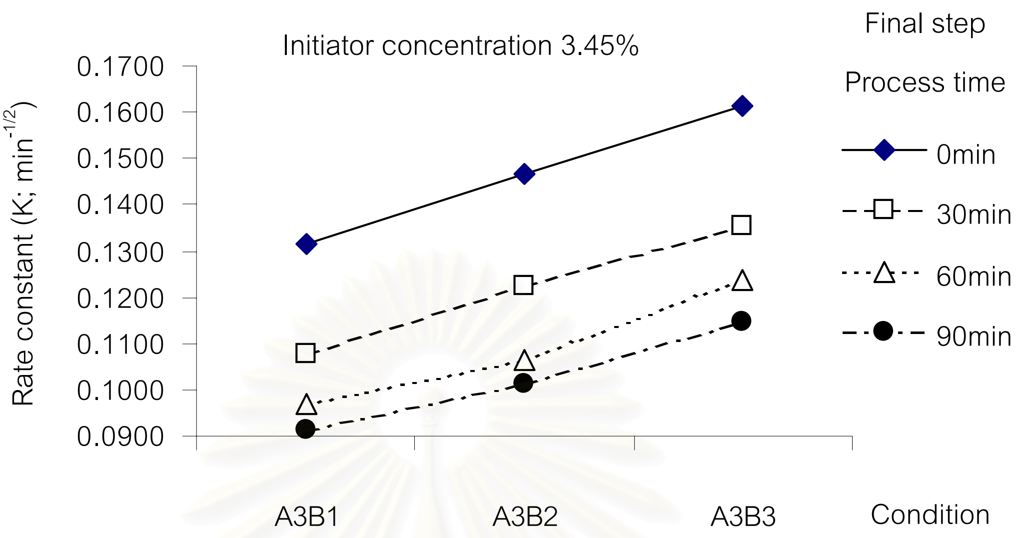

Figure B.15: Relationship between temperature condition versus rate constant (initiator concentration 3.45% with starting temperature condition A3)

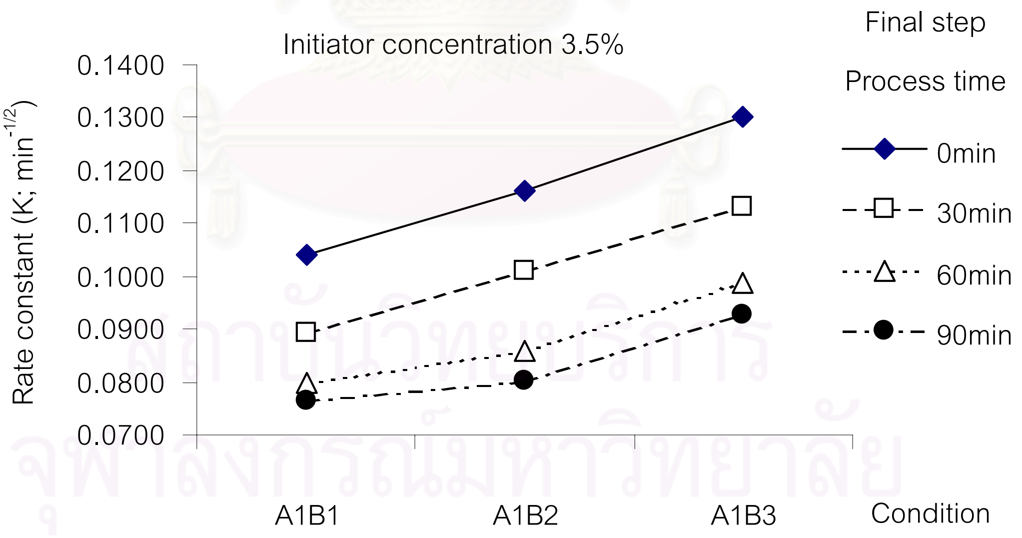

Figure B.16: Relationship between temperature condition versus rate constant (initiator concentration 3.5% with starting temperature condition A1)

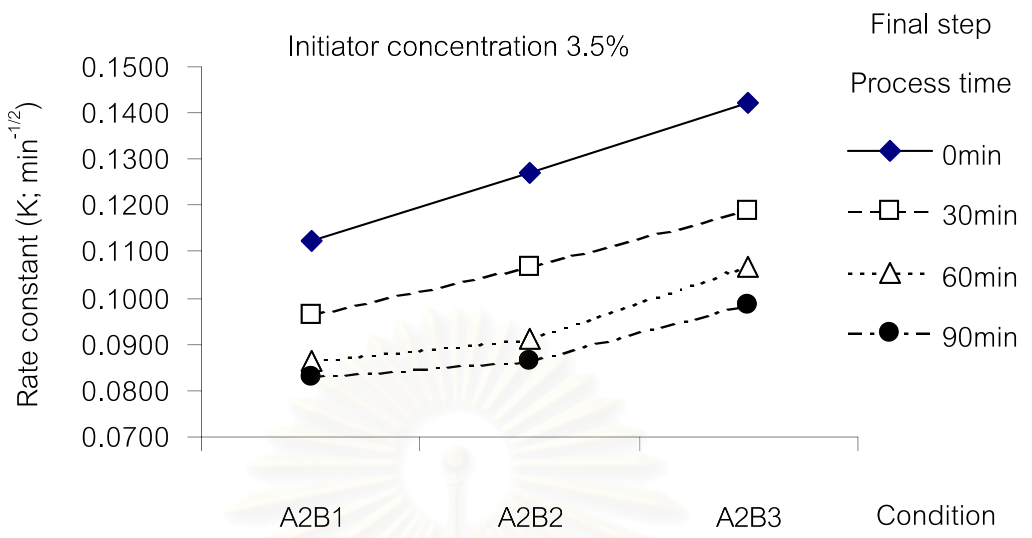

Figure B.17: Relationship between temperature condition versus rate constant (initiator concentration 3.5% with starting temperature condition A2)

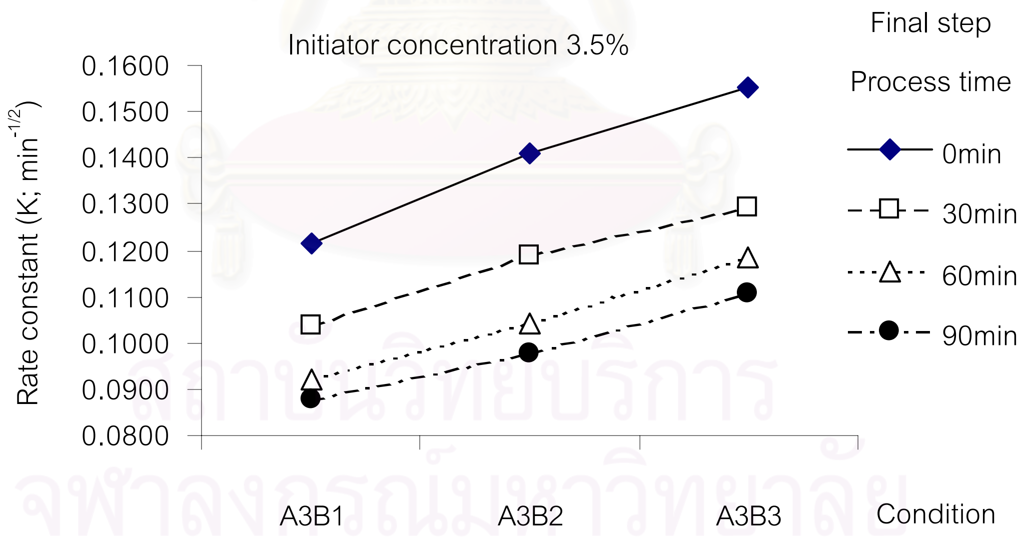

Figure B.18: Relationship between temperature condition versus rate constant (initiator concentration 3.5% with starting temperature condition A3)

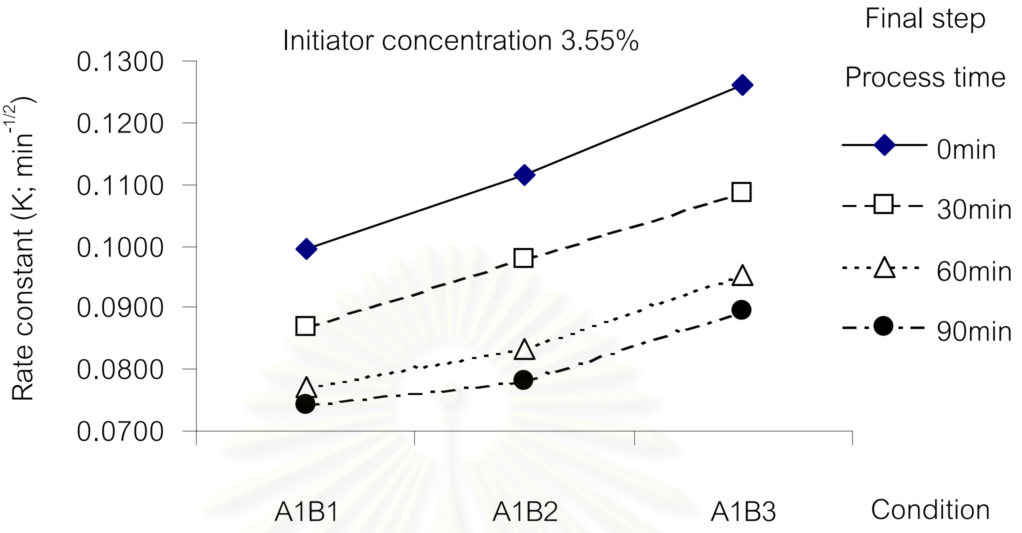

Figure B.19: Relationship between temperature condition versus rate constant (initiator concentration 3.55% with starting temperature condition A1)

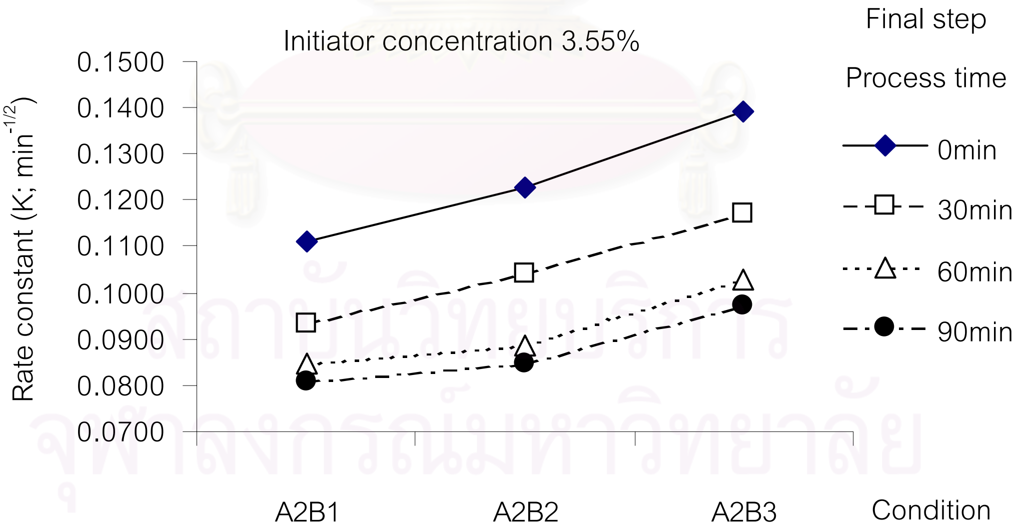

Figure B.20: Relationship between temperature condition versus rate constant (initiator concentration 3.55% with starting temperature condition A2)

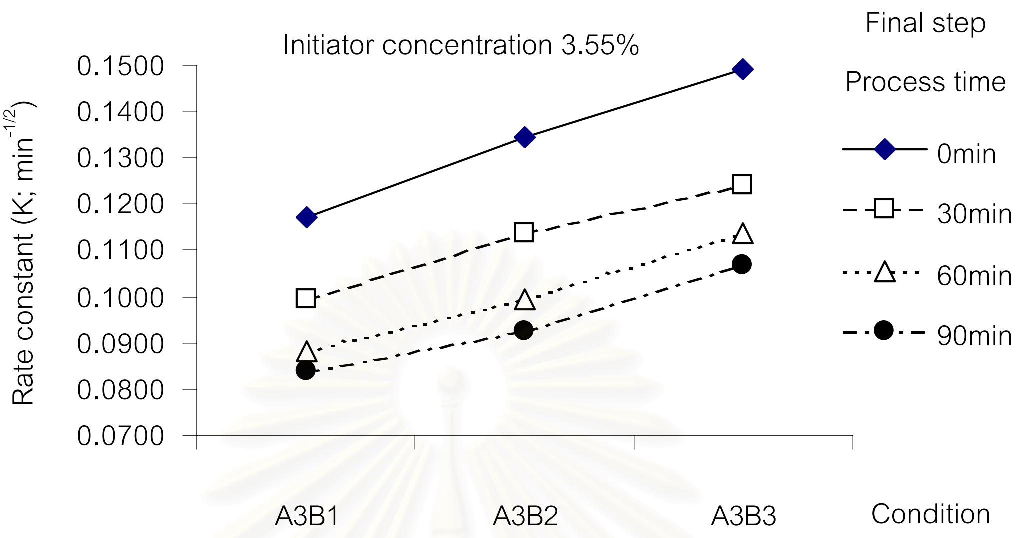

Figure B.21: Relationship between temperature condition versus rate constant (initiator concentration 3.55% with starting temperature condition A3)

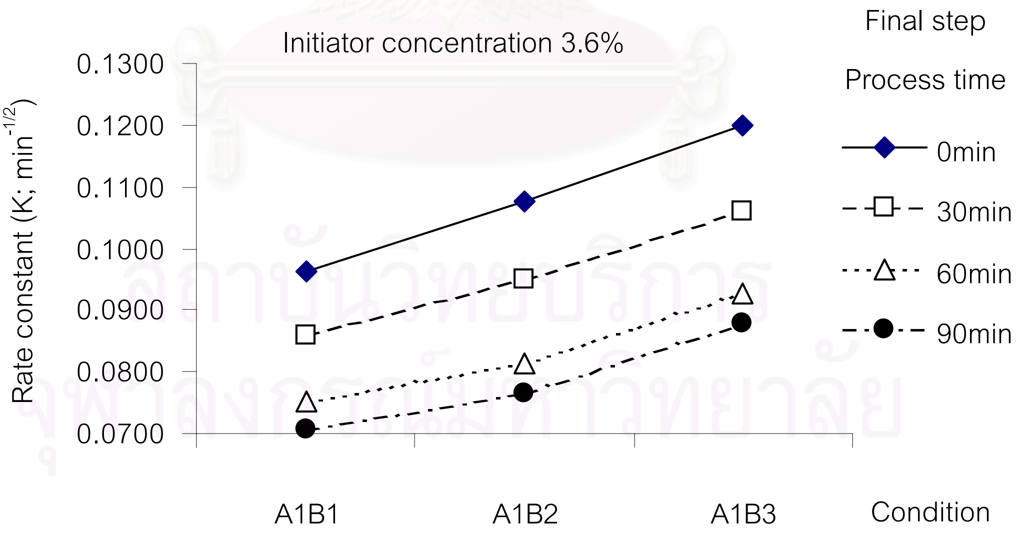

Figure B.22: Relationship between temperature condition versus rate constant (initiator concentration 3.6% with starting temperature condition A1)

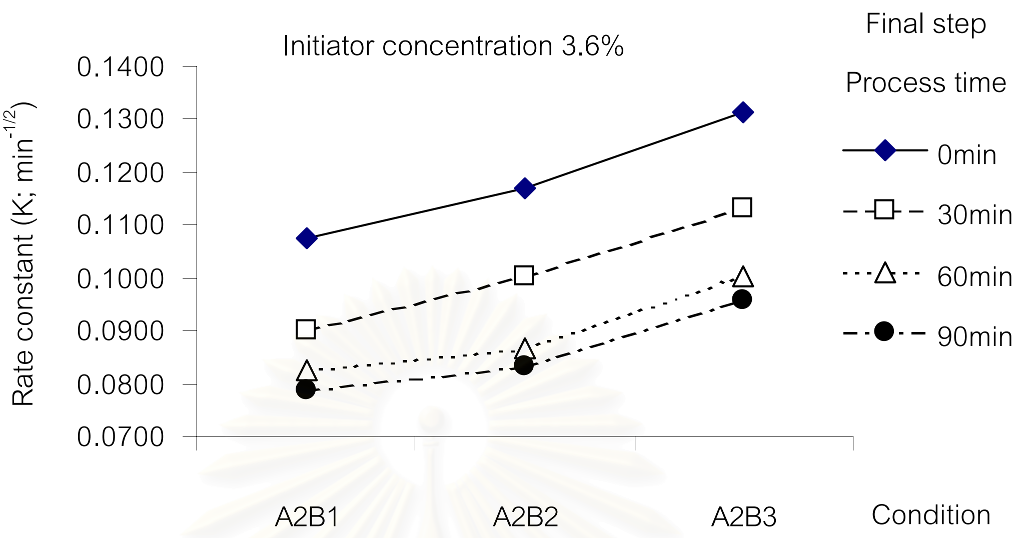

Figure B.23: Relationship between temperature condition versus rate constant (initiator concentration 3.6% with starting temperature condition A2)

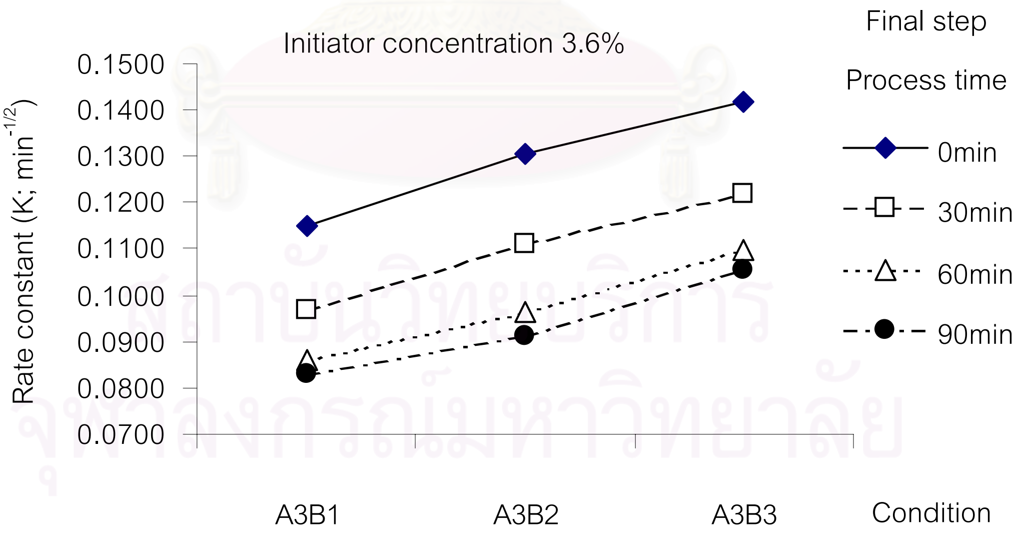

Figure B.24: Relationship between temperature condition versus rate constant (initiator concentration 3.6% with starting temperature condition A3)

B1.3: Effect of final step process time of polymerization

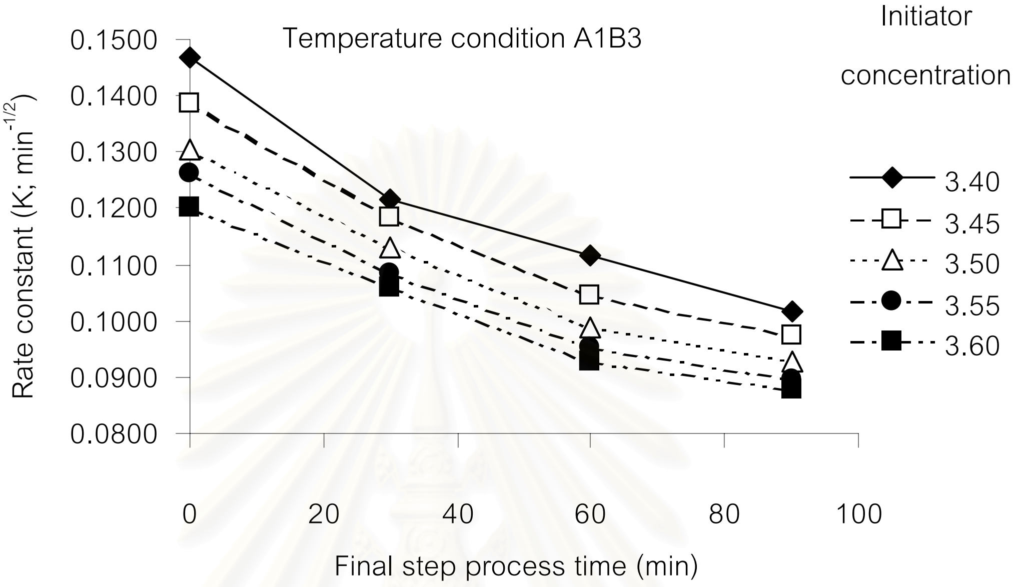

Figure B.25: Relationship between final step process time of polymerization versus rate constant (temperature condition A1B3)

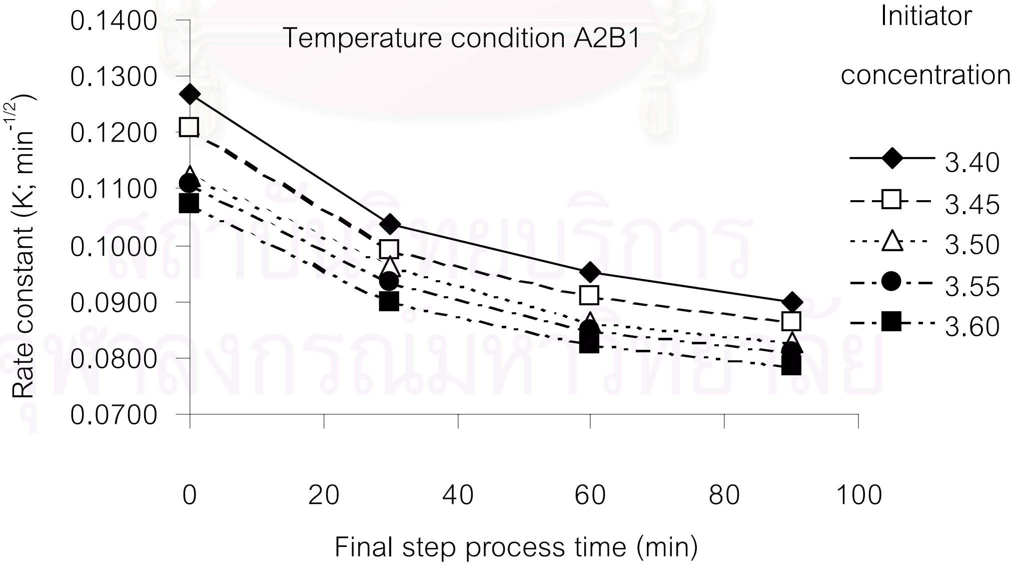

Figure B.26: Relationship between final step process time of polymerization versus rate constant (temperature condition A2B1)

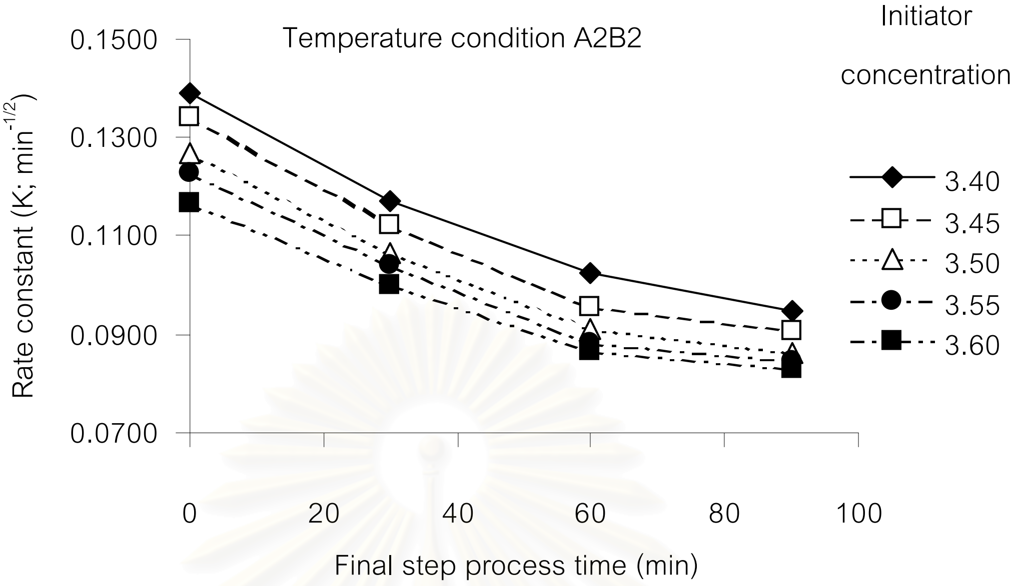

Figure B.27: Relationship between final step process time of polymerization versus rate constant (temperature condition A2B2)

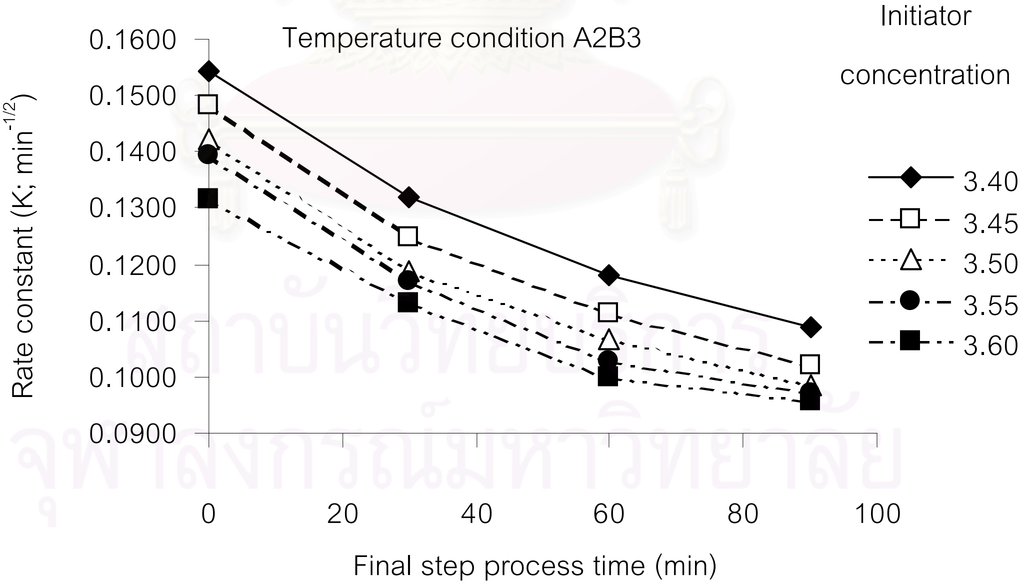

Figure B.28: Relationship between final step process time of polymerization versus rate constant (temperature condition A2B3)

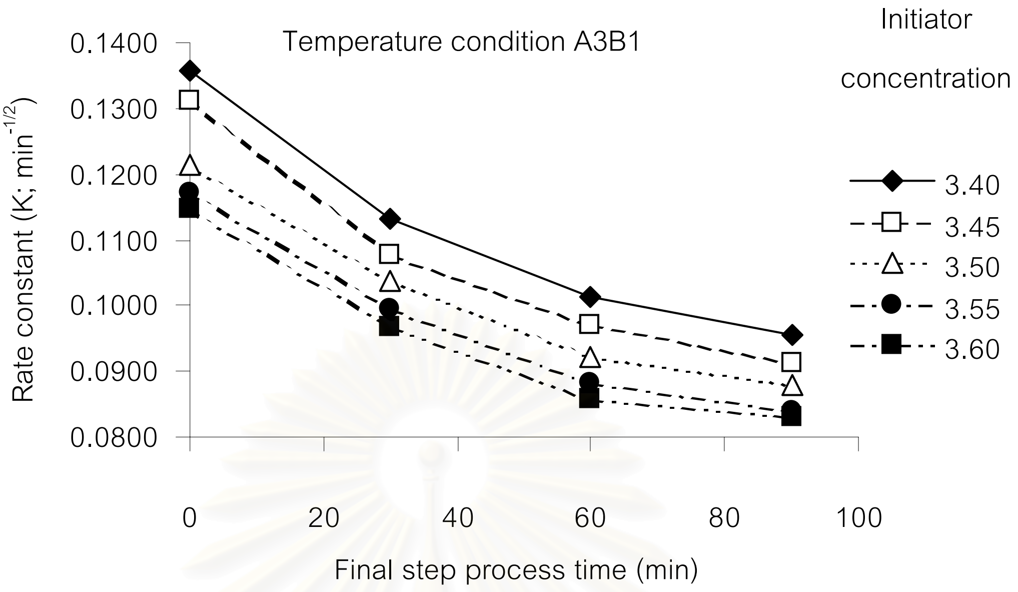

Figure B.29: Relationship between final step process time of polymerization versus rate constant (temperature condition A3B1)

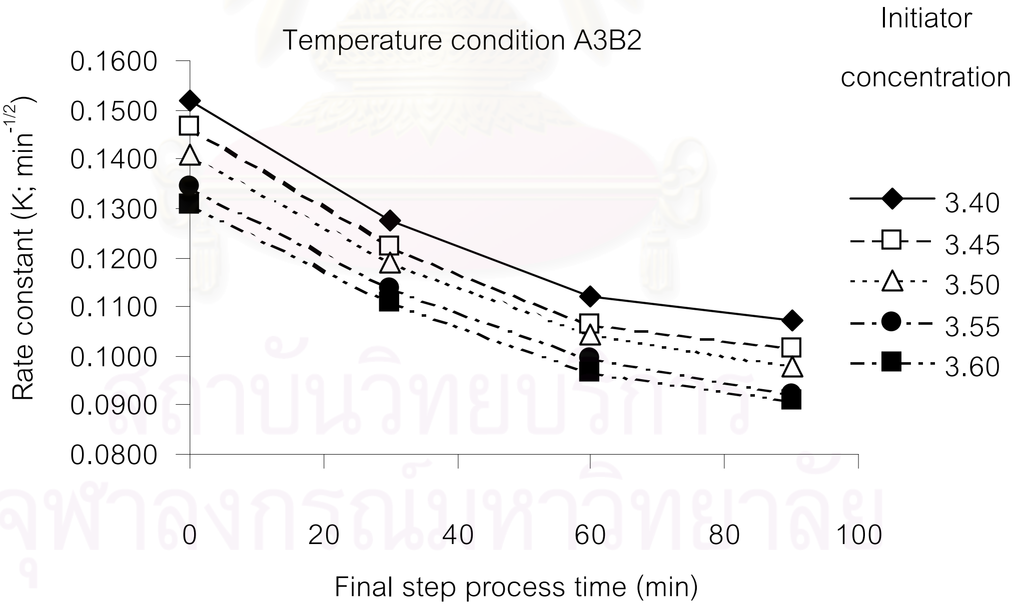

Figure B.30: Relationship between final step process time of polymerization versus rate constant (temperature condition A3B2)

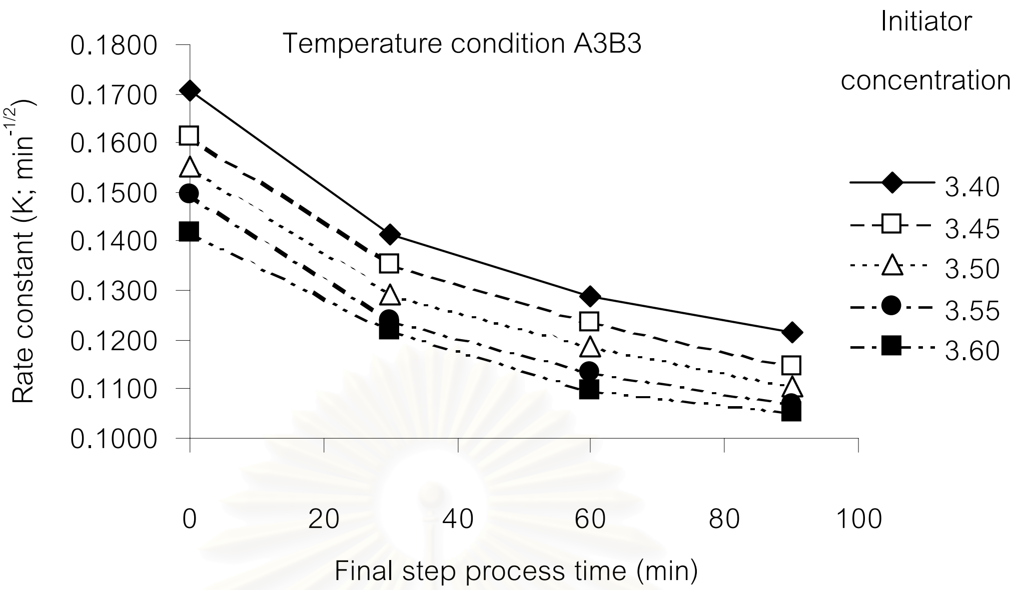

Figure B.31: Relationship between final step process time of polymerization versus rate constant (temperature condition A3B3)

B2: Study of polymerization program parameter for Type II (section 4.2.2)

B2.1: Effect of process temperature

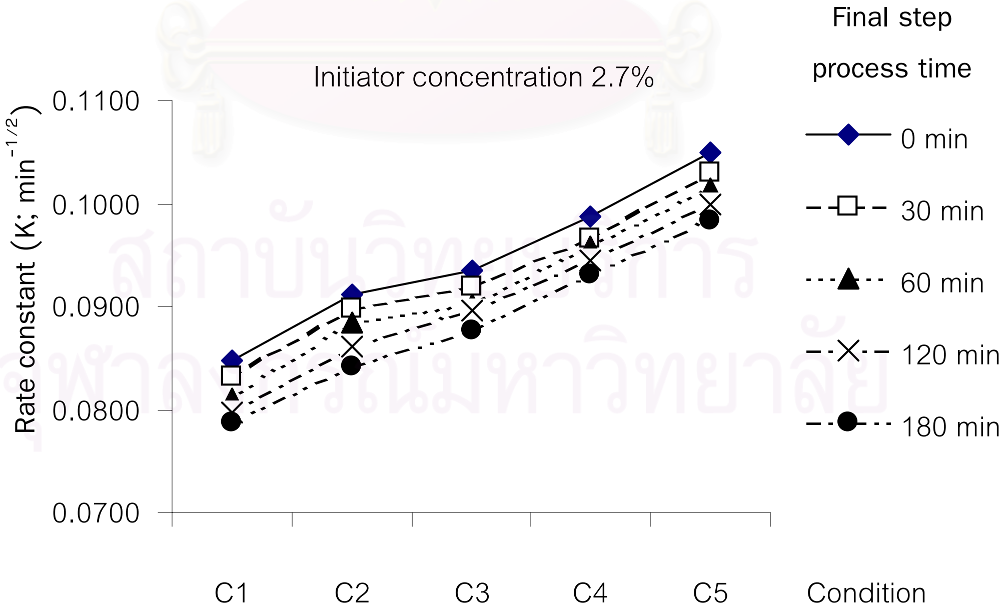

Figure B.32: Relationship between polymerization patterns of temperature versus rate constant (Initiator concentration 2.7%)

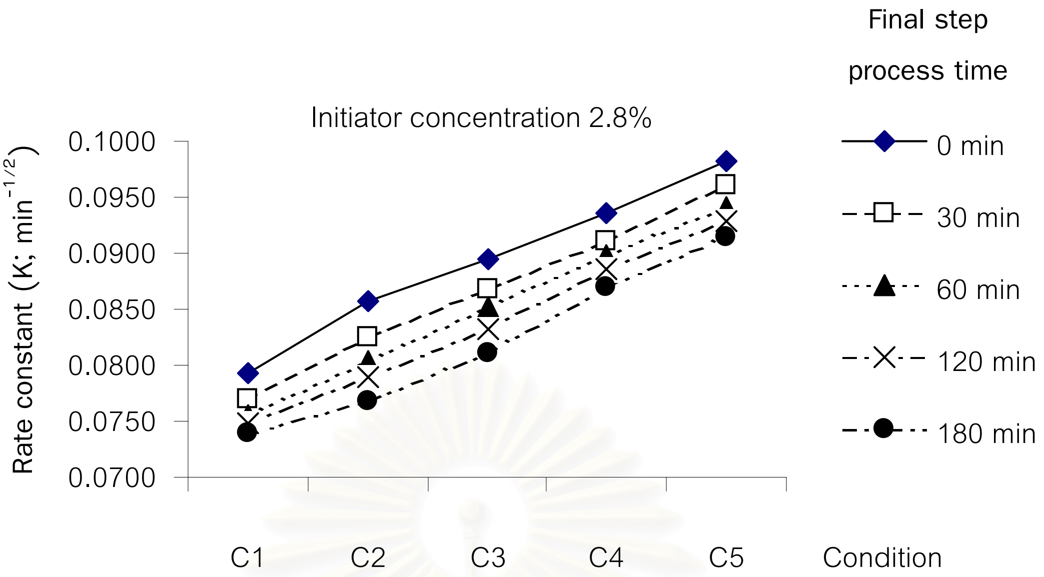

Figure B.33: Relationship between polymerization patterns of temperature versus rate constant (Initiator concentration 2.8%)

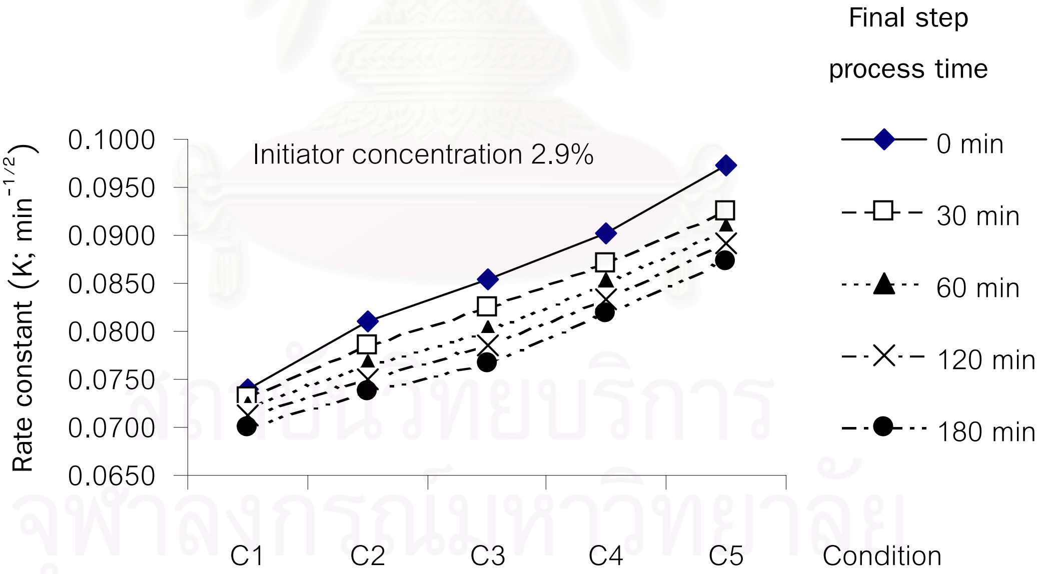

Figure B.34: Relationship between polymerization patterns of temperature versus rate constant (Initiator concentration 2.9%)

B2.2: Effect of final step process time

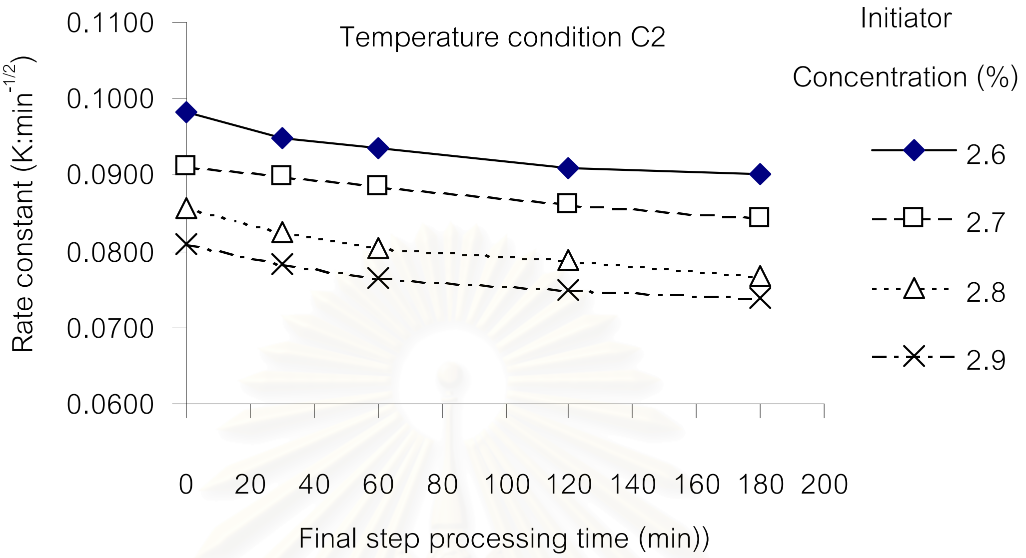

Figure B.35: Relationship between final step process times of polymerization versus rate constant (temperature condition C2)

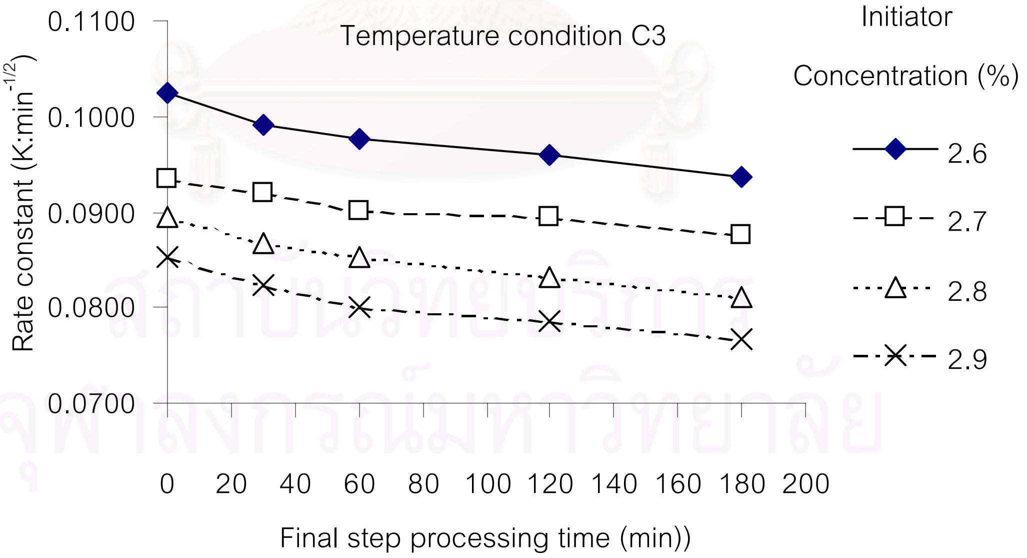

Figure B.36: Relationship between final step process times of polymerization versus rate constant (temperature condition C3)

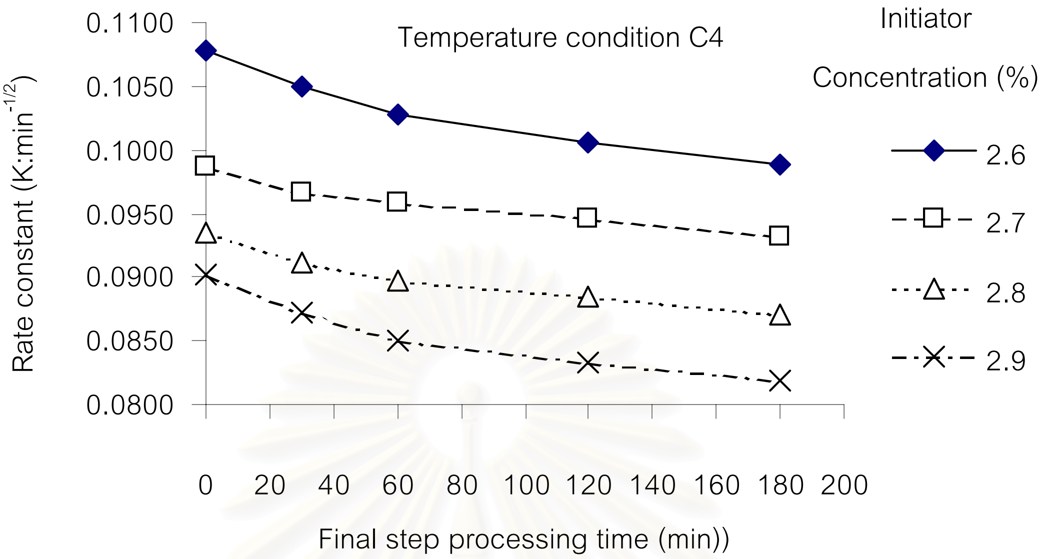

Figure B.37: Relationship between final step process times of polymerization versus rate constant (temperature condition C4)

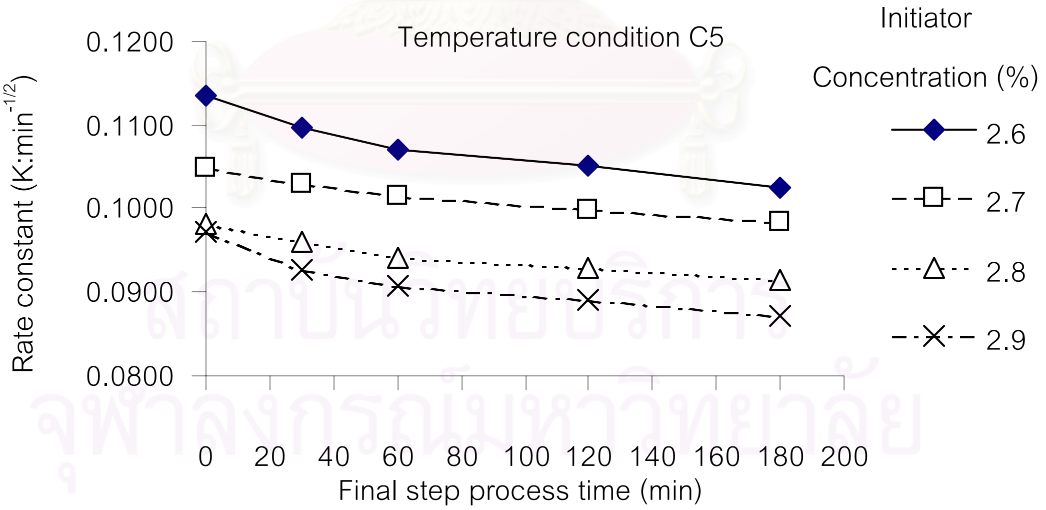

Figure B.38: Relationship between final step process times of polymerization versus rate constant (temperature condition C5)

APPENDIX C

RESULTS OF SURFACE QUALITY CONTROL

C1 result for Type I

Initiator Concentration (%)	Polymerization Pattern	Final step process time (min)			
		0	30	60	90
3.4	A1B1	63.6	54.6	50.6	50.2
	A1B2	65.6	55.8	52.1	51.5
	A1B3	70.6	62.8	55.2	53.6
	A2B1	65.3	55.6	52.5	51.6
	A2B2	68.2	58.6	53.4	52.0
	A2B3	72.0	65.4	56.4	55.2
	A3B1	67.7	57.0	54.9	54.2
	A3B2	71.3	61.6	58.3	55.8
	A3B3	74.1	69.0	61.6	59.4
3.45	A1B1	60.3	52.5	48.1	46.5
	A1B2	64.7	55.7	51.0	48.0
	A1B3	68.8	61.4	54.3	50.3
	A2B1	63.7	55.4	49.8	48.3
	A2B2	65.5	56.6	51.8	50.8
	A2B3	71.4	64.5	56.1	52.4
	A3B1	65.3	56.5	53.9	53.3
	A3B2	70.6	61.0	58.0	54.6
	A3B3	73.6	68.3	59.9	58.2
3.5	A1B1	57.6	49.3	47.1	46.0
	A1B2	62.5	54.0	48.8	46.9
	A1B3	67.9	60.9	52.9	48.9
	A2B1	60.9	51.1	48.3	47.2
	A2B2	63.5	54.8	50.4	47.8
	A2B3	69.0	59.6	53.3	50.5
	A3B1	63.9	54.9	52.6	50.9
	A3B2	70.3	57.5	53.8	52.7
	A3B3	73.0	65.9	58.9	56.7
3.55	A1B1	55.1	47.1	45.4	45.3
	A1B2	58.4	52.5	48.3	45.9
	A1B3	65.3	58.3	50.3	47.9
	A2B1	58.9	50.6	47.8	46.5
	A2B2	60.7	53.5	49.1	47.5
	A2B3	66.8	58.9	51.3	49.1
	A3B1	63.0	53.6	51.5	50.7
	A3B2	69.4	56.9	53.6	51.3
	A3B3	72.7	64.5	58.0	55.5
3.6	A1B1	53.1	46.4	45.1	44.5
	A1B2	55.1	50.9	48.1	45.6
	A1B3	63.8	56.3	49.7	47.5
	A2B1	57.3	48.4	46.0	43.9
	A2B2	58.7	51.2	46.7	44.8
	A2B3	65.0	58.1	50.8	46.4
	A3B1	62.5	53.0	51.1	49.9
	A3B2	68.8	56.1	52.1	50.3
	A3B3	71.9	63.6	55.5	54.4

C2 Result for Type II

Initiator concentration	Polymerization pattern	Final step process time (min)				
		0	30	60	120	190
2.6	C1	54.9	54.5	54.1	54.0	53.9
	C2	56.3	55.9	55.5	55.6	55.4
	C3	56.7	56.3	55.8	55.7	55.6
	C4	57.4	56.9	56.2	56.1	55.9
	C5	59.9	59.3	58.5	57.9	57.6
2.7	C1	52.7	52.4	52.3	52.1	51.9
	C2	54.7	53.8	53.5	53.4	53.4
	C3	54.7	54.0	53.8	53.5	53.4
	C4	55.1	54.6	54.2	54.0	54.0
	C5	58.6	58.1	57.7	56.8	56.5
2.8	C1	51.2	51.2	50.8	50.8	50.5
	C2	53.0	52.6	52.7	52.2	52.2
	C3	53.5	53.2	52.7	52.6	52.6
	C4	54.3	54.1	53.9	53.6	53.4
	C5	57.3	57.1	56.1	55.7	55.5
2.9	C1	50.2	50.0	49.7	49.4	49.3
	C2	51.7	51.0	50.6	50.2	50.4
	C3	52.0	51.4	51.1	50.7	51.0
	C4	52.5	52.5	52.0	52.0	51.9
	C5	56.0	55.9	55.1	54.2	54.4

APPENDIX D

EXAMPLE OF CALCULATION OF RATE CONSTANT

Example for 3.4A1B1t1 sample

Table D1: Tinting result of 3.4 A1B1t1 sample with HOYA sunglass black dyestuff at 85°C (measured by Asahi density meter, 321s, at 550 nm)

Time (min)	0	0.5	1	2	4	9	16	25	36	49	64
D	7.7	20.7	23.7	32.3	45.6	58.2	71.2	79.3	86.5	93.0	96.9

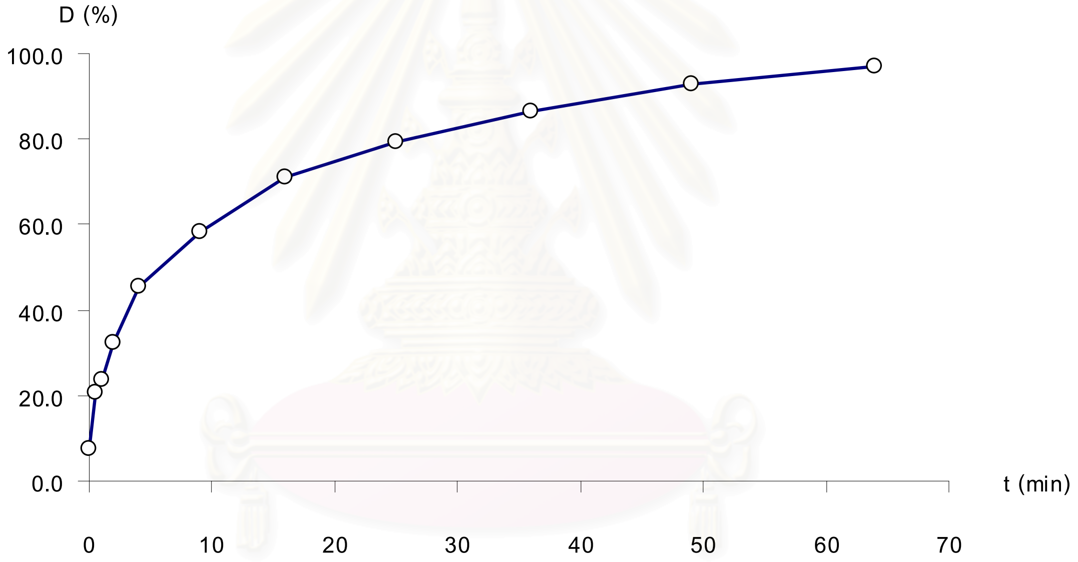

Figure D1: Tinting curve of HOYA Sunglass Black dyestuff in 3.4A1B1t1 samples (% color density from Asahi density meter , 321s, at 550 nm)

Calculation above data with Equation 3.3 and plot the linear relation with Equation 3.2 then can get the data as table D2.

Table D2: Adjusted tinting result of 3.4 A1B1t1 sample with HOYA sunglass black dyestuff at 85°C (Abs calculated by equation 3.3)

Time$^{1/2}$ (min$^{1/2}$)	0.0	0.7	1.0	1.4	2.0	3.0	4.0	5.0	6.0	7.0	8.0
Abs	0.00	0.06	0.08	0.12	0.21	0.31	0.44	0.55	0.67	0.83	0.97

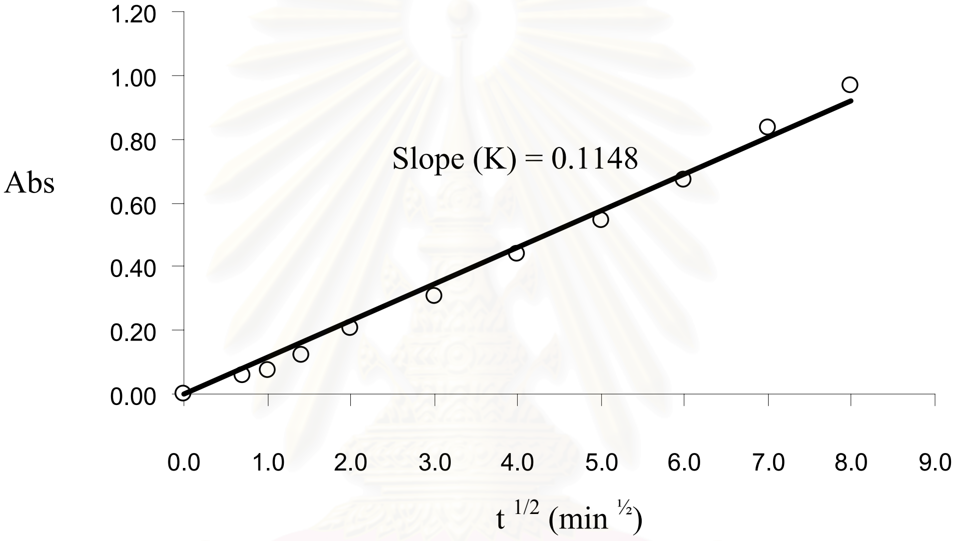

Figure D2: Relationship between t$^{1/2}$ versus Abs

From figure D2 shown the relationship between t$^{1/2}$ Versus Abs that get the linear relation with equation

$$Abs = 0.1148\ t^{1/2}$$

Compare with equation 3.2 then tinting rate constant (K) is 0.1148 min$^{-1/2}$

APPENDIX E

TINTING RAW DATA

E1 Tinting result of Type I polymerization

Table E1 Color density data of A1B1 polymerization condition

Initiator Concentration (%)	Final step process time (min)	First set											Second set										
		Tinting process time (min)											Tinting process time (min)										
		0	0.5	1	2	4	9	16	25	36	49	64	0	0.5	1	2	4	9	16	25	36	49	64
3.40	0	7.7	20.7	23.7	32.3	45.6	58.2	71.2	79.3	86.5	93.0	96.9	7.7	20.9	24.3	32.3	43.7	58.1	71.4	79.0	86.9	93.3	96.5
	30	7.7	19.3	22.4	31.3	41.0	52.5	66.7	75.3	82.8	88.8	92.6	7.7	19.2	22.4	31.3	40.7	52.9	66.8	75.9	82.4	88.7	92.9
	60	7.7	18.7	20.4	28.6	36.2	46.9	60.5	70.0	76.3	84.5	89.8	7.7	18.3	20.9	28.6	36.4	47.6	62.4	70.4	76.9	84.9	89.9
	90	7.7	17.4	19.9	27.3	35.5	46.2	59.2	67.2	75.6	83.3	87.6	7.7	18.0	20.0	27.3	35.0	46.7	58.7	65.1	76.0	81.0	86.4
3.45	0	7.7	20.5	22.7	29.2	39.2	52.2	67.3	78.4	85.9	92.4	96.0	7.7	20.5	23.0	29.2	40.0	54.5	67.9	78.4	85.5	92.5	95.7
	30	7.7	18.9	21.9	28.4	37.7	48.7	63.1	74.2	80.3	88.3	91.2	7.7	18.8	22.2	28.4	37.5	51.2	63.5	74.5	80.0	86.4	91.4
	60	7.7	18.0	19.6	26.9	34.7	46.5	59.2	69.0	76.0	84.1	86.5	7.7	18.1	19.4	26.9	34.4	47.0	59.5	68.7	75.4	83.7	87.0
	90	7.7	17.6	18.8	25.8	33.4	42.8	55.8	66.1	74.0	82.3	85.6	7.7	18.0	19.3	25.8	33.8	44.0	56.2	66.0	74.1	82.0	85.7
3.50	0	7.7	20.3	22.4	27.9	38.1	50.5	65.7	76.4	83.3	91.2	94.8	7.7	20.5	23.0	27.8	38.3	50.8	65.0	76.5	83.0	91.0	94.5
	30	7.7	18.3	21.4	26.9	36.9	46.7	59.6	71.7	78.4	85.3	90.6	7.7	18.4	21.5	26.5	36.7	45.5	59.4	71.3	78.4	85.2	90.0
	60	7.7	17.7	19.3	24.8	33.9	44.4	55.8	67.0	73.2	82.5	86.0	7.7	17.7	19.4	24.3	33.6	44.5	55.5	67.4	73.1	82.7	86.3
	90	7.7	17.4	18.6	24.1	32.2	40.7	54.8	65.0	72.8	81.0	85.2	7.7	17.4	18.8	23.6	32.1	40.5	54.8	65.3	72.7	80.7	84.6
3.55	0	7.7	19.5	22.3	27.4	37.1	50.0	65.3	75.1	83.0	88.7	93.0	7.7	19.9	22.2	27.0	37.0	50.4	64.9	75.5	82.0	89.9	92.6
	30	7.7	17.4	21.5	26.3	35.8	44.1	58.7	71.3	77.7	84.2	89.3	7.7	17.6	21.0	26.2	35.7	44.7	58.4	70.9	77.5	84.5	89.5
	60	7.7	16.8	19.2	24.0	33.3	43.9	54.7	65.8	71.6	82.0	84.5	7.7	17.1	19.2	23.6	33.0	43.7	55.0	66.2	72.0	81.8	84.9
	90	7.7	16.8	18.8	23.5	31.7	40.4	54.0	64.3	71.4	80.1	83.3	7.7	16.9	18.5	23.2	31.0	39.9	53.5	64.1	71.4	80.4	84.0
3.60	0	7.7	18.0	21.3	26.0	36.3	49.3	64.3	74.8	81.3	88.9	91.7	7.7	18.3	21.5	26.3	36.0	49.6	64.0	74.9	81.0	88.4	91.4
	30	7.7	17.1	20.0	25.5	35.0	44.0	57.4	71.1	76.8	83.6	88.3	7.7	17.2	20.0	25.6	35.0	44.0	67.1	72.0	76.5	83.7	88.0
	60	7.7	16.0	18.5	23.1	32.7	43.5	54.4	65.5	71.3	80.5	83.4	7.7	16.0	18.9	23.4	32.4	43.2	54.3	65.4	71.2	80.1	84.0
	90	7.7	15.9	17.3	22.4	30.1	39.0	53.0	61.1	70.1	78.7	82.0	7.7	15.5	17.6	22.7	29.9	38.8	52.9	61.0	70.5	79.0	81.4

Table E2 Color density data of A1B2 polymerization condition

Initiator Concentration (%)	Final step process time (min)	First set											Second set										
		Tinting process time (min)											Tinting process time (min)										
		0	0.5	1	2	4	9	16	25	36	49	64	0	0.5	1	2	4	9	16	25	36	49	64
3.40	0	7.7	21.5	26.2	35.5	46.8	59.3	73.3	83.8	91.2	97.6	99.5	7.7	22.0	26.1	35.5	46.9	59.6	73.7	84.0	91.4	96.8	99.1
	30	7.7	20.6	24.3	31.8	42.2	55.5	69.4	78.6	85.6	92.5	96.5	7.7	20.4	24.5	31.8	43.5	55.4	69.1	78.7	85.7	93.0	96.6
	60	7.7	18.7	22.8	30.7	38.8	49.8	62.9	72.5	79.7	87.3	91.9	7.7	18.8	22.4	30.7	38.9	49.4	62.8	72.7	80.1	87.4	92.2
	90	7.7	17.3	21.3	29.6	36.0	48.7	61.5	69.5	78.7	84.2	89.6	7.7	17.4	21.3	29.6	36.0	48.7	60.5	69.9	79.0	84.5	90.0
3.45	0	7.7	20.9	25.3	32.5	45.1	56.0	71.5	83.8	90.1	97.2	98.3	7.7	21.5	25.1	32.5	45.5	57.5	71.5	83.0	90.0	96.8	98.9
	30	7.7	19.8	24.2	30.3	42.2	53.0	67.4	77.6	85.0	92.0	94.2	7.7	20.0	24.5	30.3	42.4	55.1	67.4	77.5	85.1	92.5	94.4
	60	7.7	18.3	21.4	27.0	35.5	47.2	59.8	71.0	78.8	86.8	89.3	7.7	18.1	21.7	27.0	35.3	47.4	59.4	71.3	78.4	86.6	89.1
	90	7.7	17.8	18.9	26.3	34.6	45.2	59.0	68.5	76.4	83.8	88.2	7.7	17.4	20.0	26.3	34.8	46.0	58.3	68.3	76.7	83.5	88.5
3.50	0	7.7	20.6	24.8	30.3	44.3	53.8	69.5	81.8	87.7	94.3	96.8	7.7	20.8	24.5	30.5	44.3	53.5	69.8	81.4	87.6	93.7	96.7
	30	7.7	19.3	24.1	29.6	42.0	52.1	64.7	76.7	83.3	90.1	92.8	7.7	19.5	23.5	29.4	41.5	50.0	64.3	76.6	83.4	90.5	92.0
	60	7.7	17.7	20.9	26.4	33.8	45.1	57.3	70.0	77.5	85.6	88.0	7.7	17.5	21.0	26.1	33.6	44.7	57.7	70.3	77.1	85.5	88.2
	90	7.7	17.6	19.5	25.0	33.7	42.3	55.5	67.6	74.4	82.9	86.5	7.7	17.3	19.7	25.0	33.0	42.5	55.5	67.4	73.9	82.7	86.6
3.55	0	7.7	20.5	24.4	29.3	43.3	53.5	68.3	80.8	86.3	92.4	95.4	7.7	20.0	24.3	29.5	43.4	53.0	68.4	80.5	86.6	92.7	95.7
	30	7.7	19.2	22.5	27.7	39.8	49.0	63.0	75.2	81.9	89.4	92.0	7.7	18.9	23.9	28.0	40.2	50.3	63.3	75.5	82.4	88.8	91.5
	60	7.7	17.4	20.8	25.1	32.5	43.3	56.0	69.8	76.0	84.2	87.2	7.7	17.0	20.6	25.4	32.7	44.5	55.6	69.7	76.1	84.5	87.2
	90	7.7	16.7	20.0	24.1	31.7	41.4	54.5	66.7	73.0	82.2	85.4	7.7	16.8	19.5	24.4	32.5	41.5	54.3	66.4	73.5	81.7	86.0
3.60	0	7.7	18.8	23.2	28.4	41.9	52.0	67.3	79.3	85.5	91.5	94.3	7.7	19.7	23.7	28.5	42.3	52.5	67.6	79.5	85.5	92.0	94.6
	30	7.7	17.5	23.0	27.0	38.2	48.6	61.4	75.1	81.4	88.0	90.4	7.7	17.3	23.0	27.3	38.6	48.1	61.8	75.0	82.0	88.3	90.5
	60	7.7	16.8	21.1	24.0	31.8	42.4	56.8	68.6	75.4	83.5	86.3	7.7	17.0	22.5	24.1	31.8	42.8	52.7	68.9	75.0	83.2	86.8
	90	7.7	16.2	19.0	23.1	31.4	40.5	54.4	65.3	72.7	81.1	84.8	7.7	16.3	21.0	23.5	30.9	41.0	54.9	65.0	72.8	81.0	85.0

Table E3 Color density data of A1B3 polymerization condition

Initiator Concentration (%)	Final step process time (min)	First set											Second set										
		Tinting process time (min)											Tinting process time (min)										
		0	0.5	1	2	4	9	16	25	36	49	64	0	0.5	1	2	4	9	16	25	36	49	64
3.40	0	7.7	22.7	27.1	38.9	51.0	63.1	81.9	87.4	94.9	100.0	100.0	7.7	22.0	27.4	38.9	51.5	63.3	81.5	87.7	95.2	99.9	100.0
	30	7.7	21.3	25.1	34.5	45.6	56.6	72.8	79.8	87.5	95.5	98.6	7.7	21.0	25.2	34.5	45.5	56.8	74.2	80.1	87.8	95.4	98.4
	60	7.7	19.8	24.6	33.3	41.3	54.0	67.6	76.7	85.6	93.3	96.8	7.7	19.8	24.5	33.3	41.2	54.5	71.6	76.8	85.5	91.5	96.6
	90	7.7	18.8	23.6	30.7	40.1	52.6	65.5	73.4	82.8	89.9	94.1	7.7	18.4	23.3	30.7	40.3	52.4	65.6	73.4	82.4	90.1	94.0
3.45	0	7.7	21.3	25.9	34.3	48.4	58.6	76.4	86.7	93.7	99.3	100.0	7.7	21.3	25.4	34.3	48.6	60.4	76.8	86.0	93.5	99.1	100.0
	30	7.7	20.1	24.6	29.8	43.6	52.4	71.9	82.5	87.3	94.6	97.5	7.7	20.3	24.9	29.8	43.5	54.5	71.7	82.4	87.6	94.7	97.0
	60	7.7	18.7	23.0	28.6	39.4	48.7	65.0	78.1	84.3	91.3	93.6	7.7	19.1	22.9	28.6	40.0	52.5	65.3	77.7	84.5	91.4	93.8
	90	7.7	18.2	21.8	28.0	38.4	47.5	63.7	72.6	81.8	88.9	92.2	7.7	18.5	21.3	28.0	38.4	49.6	63.8	72.3	81.9	89.0	92.8
3.50	0	7.7	21.6	25.5	32.0	46.6	57.0	72.5	84.6	92.2	97.8	99.4	7.7	21.5	25.4	32.0	46.4	56.5	72.3	84.5	92.3	96.5	99.2
	30	7.7	20.0	23.6	28.1	41.3	51.7	66.0	80.6	85.7	94.0	96.5	7.7	20.1	23.0	28.3	41.5	52.0	66.7	81.7	85.4	93.6	96.6
	60	7.7	18.4	22.0	27.5	38.3	47.8	63.1	76.0	81.9	89.9	92.7	7.7	18.5	22.1	27.1	37.8	46.8	63.0	76.1	81.5	89.8	92.4
	90	7.7	17.9	21.2	26.7	37.0	46.8	60.8	71.5	80.4	87.0	91.4	7.7	18.0	21.4	26.6	36.6	46.3	61.0	71.4	80.6	86.9	91.5
3.55	0	7.7	21.1	26.6	31.0	45.4	55.3	72.0	83.4	91.1	96.5	98.5	7.7	21.0	26.4	31.1	45.7	56.5	71.6	83.5	91.5	96.6	98.2
	30	7.7	19.4	22.3	27.3	40.6	51.0	65.6	79.5	85.3	92.3	95.3	7.7	19.6	22.2	27.5	40.1	50.7	65.2	79.0	85.0	92.7	95.5
	60	7.7	18.0	21.8	26.5	37.4	46.5	62.3	74.8	81.1	88.2	91.1	7.7	18.0	21.5	26.6	37.1	46.4	62.0	75.2	81.0	88.7	91.6
	90	7.7	17.8	20.4	25.3	36.4	45.3	59.8	71.3	79.8	84.3	90.0	7.7	17.5	20.9	25.6	36.1	45.6	59.9	71.0	79.5	85.8	90.4
3.60	0	7.7	20.0	25.4	30.5	44.6	54.1	70.2	82.6	90.4	95.0	97.6	7.7	20.4	25.5	30.4	44.9	35.5	70.5	82.7	90.6	94.7	97.4
	30	7.7	18.8	21.3	26.4	39.3	50.0	64.1	78.4	84.1	92.0	94.2	7.7	18.5	23.4	26.7	39.0	51.0	64.3	78.0	84.5	92.3	94.8
	60	7.7	17.1	20.4	25.4	36.8	45.5	61.0	74.1	80.0	87.1	90.1	7.7	17.3	22.7	25.3	36.5	45.7	61.5	73.9	80.1	88.0	90.7
	90	7.7	16.9	20.0	24.3	35.3	44.2	59.1	70.1	78.6	85.5	89.3	7.7	16.7	21.4	23.8	35.4	44.7	59.5	70.4	78.9	85.1	89.4

Table E4 Color density data of A2B1 polymerization condition

Initiator Concentration (%)	Final step process time (min)	First set											Second set										
		Tinting process time (min)											Tinting process time (min)										
		0	0.5	1	2	4	9	16	25	36	49	64	0	0.5	1	2	4	9	16	25	36	49	64
3.40	0	7.7	20.5	25.4	33.6	47.2	58.4	71.6	83.9	91.0	96.7	98.3	7.7	21.9	25.5	33.6	46.9	58.4	71.3	84.0	91.2	96.5	98.5
	30	7.7	19.2	23.5	32.5	42.1	52.0	62.5	75.0	84.7	91.2	93.4	7.7	20.4	23.6	32.5	43.5	53.0	62.7	75.1	85.0	91.4	93.9
	60	7.7	18.7	21.8	29.4	39.3	47.4	61.4	72.3	79.3	88.9	91.8	7.7	18.7	21.9	29.4	39.5	49.6	61.6	72.3	79.7	88.9	91.7
	90	7.7	18.2	21.3	27.9	36.8	46.6	60.5	70.1	77.2	86.8	90.1	7.7	18.6	20.8	27.9	37.3	48.4	60.0	70.6	77.4	86.3	90.5
3.45	0	7.7	21.8	23.9	32.5	45.1	56.2	70.5	82.8	90.4	95.2	97.0	7.7	21.3	24.2	32.5	45.6	58.5	70.3	82.4	89.6	95.0	97.3
	30	7.7	19.6	22.6	30.8	40.5	51.2	61.5	73.3	82.6	90.0	92.5	7.7	19.3	23.0	30.8	40.5	53.5	61.7	74.6	82.0	89.9	92.6
	60	7.7	18.5	21.0	28.5	39.5	46.4	59.9	70.0	78.7	88.4	90.2	7.7	18.8	21.4	28.5	39.0	47.1	59.6	70.4	77.9	87.3	89.8
	90	7.7	18.0	19.8	26.5	35.8	45.5	59.1	69.6	76.6	86.0	89.0	7.7	18.3	20.5	26.5	35.4	46.3	58.4	68.9	75.9	85.4	88.4
3.50	0	7.7	20.5	23.5	30.8	44.0	54.7	68.5	81.4	89.1	93.0	94.7	7.7	20.4	23.3	30.5	44.1	54.5	67.5	82.0	89.3	92.0	94.3
	30	7.7	18.2	22.5	29.3	40.5	49.4	61.4	74.1	81.5	87.2	91.2	7.7	18.2	22.6	29.1	40.6	49.6	62.3	74.5	82.7	88.7	92.0
	60	7.7	18.0	20.3	27.8	37.5	45.7	58.7	69.0	76.5	85.0	88.8	7.7	18.1	20.4	28.0	38.6	45.6	59.4	69.0	75.9	84.9	89.5
	90	7.7	17.6	19.6	25.9	36.2	44.4	57.7	67.8	75.3	83.7	87.1	7.7	17.7	19.9	25.5	36.3	44.0	58.3	68.0	75.1	83.8	87.4
3.55	0	7.7	19.7	23.5	30.1	43.3	53.3	67.3	80.5	88.3	92.8	94.1	7.7	20.2	23.3	30.0	43.2	53.5	67.2	80.4	88.0	92.7	94.8
	30	7.7	18.1	22.7	29.7	40.0	48.8	61.4	72.5	80.7	88.3	91.0	7.7	17.8	22.4	28.5	39.6	48.7	61.5	72.2	80.0	87.8	90.0
	60	7.7	17.7	20.0	27.4	36.9	45.3	57.0	68.4	75.5	85.0	88.7	7.7	17.5	20.1	26.7	37.0	45.0	57.4	68.2	75.7	84.5	88.4
	90	7.7	17.0	19.5	25.3	35.4	44.1	56.3	67.7	75.0	83.7	86.4	7.7	17.2	19.4	25.7	35.0	43.7	56.5	66.6	74.4	83.3	85.9
3.60	0	7.7	18.7	22.5	29.0	42.4	52.1	65.8	79.5	87.7	92.0	92.9	7.7	19.5	22.0	29.3	42.7	52.5	66.3	79.4	87.3	91.6	93.7
	30	7.7	17.7	21.4	27.5	38.8	48.5	61.0	71.3	79.0	86.5	89.4	7.7	17.3	21.1	27.0	38.9	48.0	60.6	71.4	79.3	86.4	89.0
	60	7.7	16.5	19.3	25.9	36.0	44.1	56.9	67.5	74.5	83.4	87.4	7.7	16.7	19.0	26.0	36.4	44.0	56.6	67.3	75.0	83.8	87.7
	90	7.7	16.4	18.4	24.9	34.8	43.0	54.1	65.5	73.6	82.6	85.5	7.7	16.6	18.5	24.8	34.3	42.8	55.0	65.9	73.7	82.7	85.0

Table E5 Color density data of A2B2 polymerization condition

Initiator Concentration (%)	Final step process time (min)	First set											Second set										
		Tinting process time (min)											Tinting process time (min)										
		0	0.5	1	2	4	9	16	25	36	49	64	0	0.5	1	2	4	9	16	25	36	49	64
3.40	0	7.7	22.1	28.4	35.9	47.1	61.5	76.0	86.3	93.7	99.0	100.0	7.7	22.0	28.6	35.9	47.0	61.8	76.3	86.5	93.7	99.3	100.0
	30	7.7	20.4	24.5	33.0	43.8	57.1	71.1	82.0	89.1	93.6	96.0	7.7	20.6	23.3	33.0	43.9	57.6	71.0	82.3	89.4	93.9	96.3
	60	7.7	19.3	22.6	31.7	41.5	52.3	65.6	75.7	83.9	89.5	93.6	7.7	18.7	26.5	31.7	41.6	53.3	64.9	75.7	84.1	89.5	94.0
	90	7.7	18.6	21.5	30.0	40.0	51.0	64.5	73.6	82.1	86.6	90.6	7.7	18.4	21.8	30.0	40.6	51.2	64.1	73.4	82.5	87.0	90.9
3.45	0	7.7	21.5	26.4	34.3	45.8	60.2	74.8	84.8	93.0	98.3	99.6	7.7	21.6	27.2	34.3	46.0	62.6	74.5	85.1	92.6	98.2	99.4
	30	7.7	19.3	24.5	31.6	42.6	54.1	70.3	81.0	87.9	92.7	94.4	7.7	19.9	23.9	31.6	42.7	56.0	70.0	80.8	88.0	93.8	94.2
	60	7.7	18.5	21.7	29.0	39.7	50.8	63.7	74.2	83.1	88.0	89.9	7.7	18.8	21.5	29.0	40.0	52.3	63.7	73.8	82.8	87.4	91.0
	90	7.7	18.2	20.6	28.5	37.4	49.5	61.3	72.3	81.3	85.6	88.8	7.7	18.4	20.9	28.5	37.1	50.0	60.8	71.8	81.4	85.3	89.3
3.50	0	7.7	20.9	26.3	32.6	44.8	59.1	72.4	82.4	91.1	97.1	98.5	7.7	20.5	26.5	32.1	45.0	57.9	72.5	83.0	91.6	96.8	98.3
	30	7.7	19.0	23.1	31.5	42.1	52.8	68.6	78.9	86.1	91.2	93.1	7.7	19.3	23.8	30.7	42.8	51.4	69.1	78.5	86.0	91.3	94.0
	60	7.7	18.0	20.7	28.5	37.6	48.3	61.9	73.8	81.6	86.8	88.6	7.7	18.4	21.0	27.4	35.4	47.6	60.9	74.0	81.5	87.1	87.9
	90	7.7	18.1	19.6	27.6	37.1	47.1	60.1	70.7	79.4	84.6	87.1	7.7	17.9	19.5	26.7	34.1	46.5	60.0	70.3	80.0	83.9	87.2
3.55	0	7.7	20.8	26.3	32.1	44.4	58.6	72.5	82.0	90.4	96.3	97.7	7.7	20.5	26.2	31.9	43.9	58.2	71.5	81.7	90.0	96.0	97.3
	30	7.7	19.0	23.4	31.7	41.1	52.1	67.8	78.0	85.5	91.7	92.5	7.7	18.7	23.0	30.6	41.3	52.0	67.7	78.0	84.9	91.2	92.0
	60	7.7	18.0	20.1	28.8	36.9	47.3	61.4	72.5	80.1	85.3	87.6	7.7	17.6	20.6	27.4	36.8	47.5	61.0	72.1	80.4	85.6	87.4
	90	7.7	17.7	19.5	27.0	36.0	47.0	59.3	69.0	79.0	83.4	86.0	7.7	17.3	19.4	26.7	36.0	46.5	59.4	70.2	79.5	83.8	86.3
3.60	0	7.7	19.3	24.9	31.3	43.0	56.4	70.5	81.3	89.4	93.5	96.7	7.7	19.7	25.3	31.0	43.1	57.1	70.9	81.0	89.4	93.2	96.4
	30	7.7	18.0	22.7	29.5	40.3	50.3	66.8	77.5	84.5	89.0	91.5	7.7	19.8	22.4	29.9	40.6	51.3	67.1	77.0	84.1	89.4	91.3
	60	7.7	16.8	20.0	26.6	37.0	46.9	61.4	71.4	80.0	84.9	86.8	7.7	17.2	19.5	26.4	36.5	47.3	60.0	71.5	79.7	85.0	86.5
	90	7.7	16.4	19.1	25.8	35.8	45.3	58.4	69.3	78.3	83.4	86.0	7.7	16.5	18.8	26.0	35.0	45.9	58.9	69.3	78.8	82.8	85.6

Table E6 Color density data of A2B3 polymerization condition

Initiator Concentration (%)	Final step process time (min)	First set											Second set										
		Tinting process time (min)											Tinting process time (min)										
		0	0.5	1	2	4	9	16	25	36	49	64	0	0.5	1	2	4	9	16	25	36	49	64
3.40	0	7.7	24.3	28.4	37.0	52.0	64.6	81.0	90.9	97.6	100.0	100.0	7.7	24.5	28.4	37.0	51.5	64.7	81.3	91.5	97.7	100.0	100.0
	30	7.7	21.3	26.1	34.1	47.2	58.9	75.5	85.7	92.9	96.3	99.2	7.7	22.1	26.3	34.1	47.6	59.3	75.9	86.6	93.1	97.0	99.4
	60	7.7	20.0	25.6	32.1	44.3	54.3	73.5	82.4	88.2	93.1	97.1	7.7	19.9	25.4	32.1	44.4	55.4	72.1	83.0	88.1	93.5	97.8
	90	7.7	19.5	25.4	31.5	40.6	54.0	70.9	79.8	86.5	91.2	94.6	7.7	18.8	24.8	31.5	40.7	53.9	70.3	79.7	86.5	91.0	94.5
3.45	0	7.7	22.0	26.5	35.7	50.7	63.9	79.9	90.5	96.9	99.3	100.0	7.7	22.4	27.0	35.7	51.1	65.9	79.7	90.3	97.0	99.6	100.0
	30	7.7	20.5	24.3	32.4	45.3	57.4	74.5	84.8	92.1	95.5	97.0	7.7	21.1	25.5	32.4	45.4	58.5	73.9	84.6	91.5	95.3	97.8
	60	7.7	19.5	23.9	30.9	42.7	52.9	68.8	81.0	86.3	92.8	94.8	7.7	20.0	24.2	30.9	42.8	53.5	69.4	81.3	87.4	92.6	95.0
	90	7.7	19.5	23.3	30.6	39.4	51.3	66.7	78.4	85.8	89.0	91.5	7.7	19.7	23.8	30.6	40.2	52.2	67.1	78.1	85.0	90.1	92.4
3.50	0	7.7	21.6	26.0	34.3	48.9	62.6	78.6	89.3	95.6	98.9	100.0	7.7	21.7	26.5	34.4	49.0	63.0	78.4	89.4	95.5	98.5	100.0
	30	7.7	20.3	23.8	31.8	44.1	55.4	72.9	83.3	91.0	94.0	95.7	7.7	20.4	24.0	31.8	44.8	56.6	73.1	83.6	91.3	94.2	95.5
	60	7.7	19.2	22.5	30.0	41.5	51.6	67.3	79.6	85.0	91.8	93.6	7.7	20.0	22.3	29.8	42.6	53.3	67.7	79.9	85.3	92.5	93.1
	90	7.7	19.0	22.3	29.1	38.8	50.6	66.0	77.1	84.3	88.5	90.3	7.7	19.2	22.0	29.0	40.0	50.9	66.3	76.5	84.7	89.3	90.5
3.55	0	7.7	21.5	26.5	33.3	48.4	61.4	76.8	88.3	94.9	98.5	100.0	7.7	21.2	26.0	33.5	48.0	61.7	76.8	88.1	94.5	99.3	99.0
	30	7.7	20.0	23.3	30.1	43.6	54.4	71.1	82.8	90.1	93.4	96.5	7.7	20.0	23.7	30.9	43.1	54.3	70.8	82.5	89.7	93.6	96.0
	60	7.7	18.7	22.1	29.4	40.7	50.3	68.3	78.9	84.7	90.3	92.4	7.7	18.8	22.4	29.1	40.3	50.7	66.1	78.5	84.5	90.5	92.0
	90	7.7	18.4	22.0	29.1	38.5	49.1	64.2	76.9	84.0	87.6	90.0	7.7	18.5	22.3	28.0	38.0	49.4	64.8	76.2	83.5	88.0	91.5
3.60	0	7.7	20.4	25.7	32.9	47.1	61.0	76.8	87.1	93.7	96.1	98.4	7.7	20.5	25.3	32.6	47.1	61.2	76.3	87.4	93.5	96.5	98.2
	30	7.7	19.3	23.5	30.5	42.0	52.5	70.3	81.4	88.7	93.2	95.0	7.7	19.5	23.0	30.5	42.5	53.4	70.4	82.0	88.6	92.4	95.3
	60	7.7	18.0	21.5	28.7	39.5	50.0	65.5	78.3	83.6	90.0	91.4	7.7	18.3	22.0	28.3	39.9	50.5	65.0	77.5	83.5	89.7	91.4
	90	7.7	17.5	21.3	27.5	37.1	49.1	64.4	75.6	82.5	87.4	91.0	7.7	17.5	21.6	27.0	37.1	48.3	64.5	75.4	82.6	87.1	90.7

Table E7 Color density data of A3B1 polymerization condition

Initiator Concentration (%)	Final step process time (min)	First set											Second set										
		Tinting process time (min)											Tinting process time (min)										
		0	0.5	1	2	4	9	16	25	36	49	64	0	0.5	1	2	4	9	16	25	36	49	64
3.40	0	7.7	21.8	27.0	36.7	50.7	62.7	75.1	85.5	93.5	98.2	99.6	7.7	22.0	26.6	36.7	49.5	62.7	75.6	85.1	93.6	97.8	99.7
	30	7.7	19.8	24.0	32.9	44.5	56.1	67.9	78.4	86.6	93.4	96.4	7.7	19.8	24.1	32.9	43.3	56.3	67.7	78.5	86.3	93.0	96.0
	60	7.7	19.2	22.5	31.2	41.3	52.8	63.1	75.3	84.3	90.2	93.5	7.7	19.1	22.7	31.2	42.1	52.8	63.5	74.6	83.0	90.0	93.6
	90	7.7	18.8	21.8	28.6	39.0	51.5	60.0	72.2	81.4	88.8	92.7	7.7	18.3	21.6	28.6	38.9	51.3	60.4	70.7	79.5	88.1	92.7
3.45	0	7.7	21.1	25.3	33.5	48.3	60.0	74.3	84.5	92.8	97.0	98.7	7.7	21.5	25.8	33.5	47.6	62.8	73.9	84.4	92.4	97.4	99.4
	30	7.7	19.3	23.1	30.0	42.7	53.0	65.8	77.1	85.2	92.5	95.1	7.7	19.5	22.8	30.0	41.8	55.5	65.4	77.3	85.1	92.1	94.8
	60	7.7	19.0	20.6	29.3	40.8	50.0	61.2	71.5	81.5	89.4	92.0	7.7	19.1	21.5	29.3	40.8	51.6	61.4	73.9	82.2	89.1	91.8
	90	7.7	19.0	20.5	27.0	39.6	49.3	59.8	71.3	78.9	88.2	89.6	7.7	18.8	20.8	27.0	40.1	51.0	58.8	72.0	78.4	87.3	90.0
3.50	0	7.7	20.8	24.9	31.0	45.1	57.8	72.3	83.5	91.6	95.4	96.6	7.7	21.0	25.3	31.4	45.3	58.3	72.7	82.9	92.4	93.3	96.7
	30	7.7	19.0	22.3	28.0	40.7	49.8	63.5	75.7	83.9	90.5	94.3	7.7	19.3	22.4	27.7	41.4	49.0	63.8	73.4	84.3	90.7	95.5
	60	7.7	18.5	20.5	28.4	39.8	47.6	59.5	70.4	79.9	87.3	90.4	7.7	18.1	20.7	27.8	39.3	46.8	60.1	70.1	80.1	88.1	91.3
	90	7.7	18.3	20.2	26.3	38.6	46.7	57.9	69.0	78.0	86.2	88.6	7.7	18.1	20.0	26.0	38.7	46.0	58.3	69.3	78.5	86.0	89.3
3.55	0	7.7	20.0	24.0	30.3	44.0	57.3	71.4	82.7	90.1	94.0	95.3	7.7	20.5	24.5	30.1	44.3	57.0	71.3	82.5	90.4	94.3	95.4
	30	7.7	18.4	22.5	27.4	38.7	48.1	62.2	74.0	82.7	90.0	93.5	7.7	18.3	22.2	27.3	39.5	48.3	62.4	74.3	83.0	89.4	92.8
	60	7.7	18.0	20.1	26.3	36.8	46.6	59.9	69.0	78.8	86.1	89.5	7.7	18.2	20.6	26.6	38.6	46.3	58.9	69.2	78.6	86.0	88.6
	90	7.7	18.0	19.5	25.4	36.0	46.0	56.5	67.7	77.3	84.4	87.3	7.7	17.9	19.6	25.3	36.5	45.5	57.0	68.0	77.2	84.1	87.5
3.60	0	7.7	19.5	23.5	29.1	43.5	56.1	70.4	81.4	89.6	93.5	95.3	7.7	19.8	23.7	29.5	43.7	57.1	70.7	81.8	89.4	93.6	94.6
	30	7.7	17.3	21.5	26.5	38.3	47.5	63.5	73.5	82.4	88.4	92.0	7.7	17.5	21.4	26.3	38.3	47.9	62.3	73.7	82.3	88.8	92.2
	60	7.7	17.2	19.7	25.4	37.6	45.6	58.4	68.6	77.5	85.1	88.3	7.7	17.5	19.5	25.7	37.4	46.0	58.3	68.8	77.9	85.0	87.8
	90	7.7	17.0	18.6	24.6	36.8	44.9	56.5	67.4	76.6	84.7	86.9	7.7	17.0	18.7	24.4	37.2	44.9	56.7	67.1	76.7	84.4	86.7

Table E8 Color density data of A3B2 polymerization condition

Initiator Concentration (%)	Final step process time (min)	First set											Second set										
		Tinting process time (min)											Tinting process time (min)										
		0	0.5	1	2	4	9	16	25	36	49	64	0	0.5	1	2	4	9	16	25	36	49	64
3.40	0	7.7	24.8	30.3	40.2	52.7	67.6	77.6	90.5	96.8	100.0	100.0	7.7	25.0	30.2	40.2	52.5	67.7	77.7	90.1	97.1	100.0	100.0
	30	7.7	20.6	24.9	35.2	43.7	58.0	73.1	84.2	90.8	96.1	98.9	7.7	20.4	24.4	35.2	45.4	58.3	72.8	84.3	90.8	96.6	99.2
	60	7.7	20.3	25.9	32.8	42.5	56.5	68.7	79.4	86.9	93.4	95.3	7.7	20.6	25.7	32.8	42.8	56.1	71.0	79.2	87.5	93.6	95.5
	90	7.7	19.8	24.7	32.6	41.7	55.5	66.7	76.7	85.9	91.9	94.0	7.7	20.0	24.9	32.6	41.9	55.8	67.8	76.9	85.7	92.0	94.1
3.45	0	7.7	22.8	27.9	36.6	48.5	62.3	76.5	89.2	96.1	100.0	100.0	7.7	23.2	28.1	36.6	48.9	64.5	75.9	89.4	95.5	100.0	100.0
	30	7.7	20.6	23.6	31.5	42.5	54.8	72.3	83.1	89.6	95.1	98.4	7.7	20.0	24.3	31.5	43.1	56.4	72.7	83.5	89.9	95.5	98.5
	60	7.7	20.1	24.0	31.3	40.4	51.8	65.4	78.9	86.0	92.5	93.3	7.7	19.7	23.8	31.3	40.7	52.9	66.7	78.7	86.3	92.1	93.0
	90	7.7	19.3	23.4	30.7	39.3	50.5	63.5	74.7	85.2	91.0	92.1	7.7	18.8	23.1	30.7	39.9	51.6	63.9	74.3	84.8	91.4	91.8
3.50	0	7.7	21.8	27.3	34.9	47.0	60.9	74.8	87.6	94.8	99.6	100.0	7.7	22.0	27.0	35.3	47.4	61.7	74.3	87.4	95.2	99.8	100.0
	30	7.7	19.9	23.0	30.7	42.3	53.6	71.0	81.9	88.7	94.3	97.2	7.7	21.7	235.0	31.1	42.5	54.0	71.0	82.1	89.1	94.4	98.0
	60	7.7	19.1	22.9	30.3	39.2	49.5	63.8	77.5	85.3	91.9	92.9	7.7	20.0	23.3	30.8	39.9	50.2	63.3	77.8	86.4	92.3	92.4
	90	7.7	18.8	22.0	29.9	38.3	48.3	61.5	73.6	83.8	89.5	91.3	7.7	19.8	23.0	29.9	38.7	49.0	60.8	74.9	83.8	89.7	91.7
3.55	0	7.7	21.2	27.4	33.4	46.3	60.7	73.3	86.8	93.5	98.0	99.5	7.7	21.2	27.1	34.0	46.2	60.0	73.8	86.0	93.9	98.3	99.0
	30	7.7	20.0	22.3	29.9	41.7	53.1	68.7	81.1	86.6	93.5	96.3	7.7	19.5	22.7	29.6	41.5	53.0	68.9	81.0	87.5	94.0	95.7
	60	7.7	18.7	21.7	28.3	37.4	48.5	62.5	76.7	84.5	89.9	91.6	7.7	18.8	22.0	29.1	38.1	48.8	62.7	76.3	84.2	90.6	90.8
	90	7.7	18.3	21.5	27.4	36.6	47.1	61.0	72.4	83.0	87.8	88.8	7.7	18.5	21.6	28.9	37.2	47.2	60.5	72.6	82.6	87.1	89.1
3.60	0	7.7	20.8	26.3	33.4	45.4	59.3	73.3	85.5	93.4	97.0	98.6	7.7	20.3	26.3	33.1	45.4	59.1	73.0	85.3	93.1	97.4	98.5
	30	7.7	18.7	22.0	30.0	40.3	53.5	68.1	80.2	86.7	93.0	95.3	7.7	18.5	21.8	29.0	40.7	52.4	68.3	80.1	86.8	92.3	95.0
	60	7.7	18.0	21.4	28.9	37.1	48.1	62.0	75.3	83.4	88.4	90.5	7.7	18.3	21.5	28.1	37.1	48.3	62.3	75.5	83.1	88.7	91.2
	90	7.7	17.5	20.6	28.2	36.5	46.4	59.4	71.7	81.7	87.5	89.4	7.7	17.6	20.7	27.6	36.4	46.9	59.9	72.0	81.6	87.1	88.5

Table E9 Color density data of A3B3 polymerization condition

Initiator Concentration (%)	Final step process time (min)	First set											Second set										
		Tinting process time (min)											Tinting process time (min)										
		0	0.5	1	2	4	9	16	25	36	49	64	0	0.5	1	2	4	9	16	25	36	49	64
3.40	0	7.7	26.0	32.4	40.9	53.9	69.9	86.7	94.1	100.0	100.0	100.0	7.7	26.3	33.5	40.9	54.1	69.5	86.5	94.3	100.0	100.0	100.0
	30	7.7	22.6	28.3	36.4	48.1	63.5	78.5	87.6	95.8	98.4	100.0	7.7	22.5	28.3	36.4	48.3	64.0	78.8	87.7	95.8	98.5	99.9
	60	7.7	21.2	27.4	34.9	44.7	58.6	73.1	83.9	93.1	96.9	98.4	7.7	21.0	27.1	34.9	44.4	58.4	73.0	84.1	92.3	96.5	98.5
	90	7.7	20.3	25.9	33.0	43.4	55.8	71.3	83.1	91.1	95.0	97.2	7.7	20.5	25.8	33.0	43.5	55.9	71.5	82.7	90.5	94.8	97.5
3.45	0	7.7	25.2	28.8	39.2	52.8	67.6	83.0	92.6	99.3	100.0	100.0	7.7	25.3	28.1	39.2	52.4	68.9	83.4	93.0	99.5	100.0	100.0
	30	7.7	21.5	26.9	36.8	46.5	60.4	77.4	86.1	94.8	98.0	98.7	7.7	21.4	27.4	36.8	47.0	60.6	77.5	86.2	94.6	97.8	98.8
	60	7.7	20.8	24.8	32.7	44.3	57.5	69.9	82.4	92.6	96.0	97.2	7.7	20.5	24.6	32.7	45.1	54.7	71.3	82.3	92.6	96.2	97.0
	90	7.7	20.2	24.2	32.0	40.3	53.6	68.8	81.5	89.1	94.2	95.0	7.7	20.0	23.5	32.0	41.0	53.8	68.8	81.4	89.4	94.1	95.3
3.50	0	7.7	24.5	28.0	37.8	51.6	65.3	81.0	91.1	98.1	100.0	100.0	7.7	23.9	28.1	37.8	51.3	65.0	81.3	91.5	98.2	100.0	100.0
	30	7.7	20.7	25.5	35.6	45.3	57.5	74.7	85.5	94.6	96.9	97.8	7.7	22.0	24.9	35.5	45.5	57.1	75.2	85.9	92.1	96.6	98.0
	60	7.7	19.9	23.7	31.4	43.1	52.6	69.0	81.6	91.5	94.8	95.7	7.7	19.9	23.9	32.0	43.3	52.5	68.7	81.9	91.3	95.0	96.6
	90	7.7	19.6	23.3	30.9	41.3	51.3	67.9	79.9	88.6	93.3	94.5	7.7	19.8	23.5	31.4	42.1	50.8	68.0	79.7	87.9	92.3	94.4
3.55	0	7.7	24.5	27.4	37.4	50.4	64.3	79.5	90.4	97.4	100.0	100.0	7.7	24.1	27.7	37.0	50.7	64.5	79.8	90.3	97.0	99.5	100.0
	30	7.7	20.0	25.2	34.3	44.4	56.5	73.5	85.0	92.3	96.0	97.0	7.7	20.3	25.4	34.5	44.5	56.4	73.1	84.8	91.5	95.6	96.6
	60	7.7	19.1	22.8	30.4	42.1	52.3	68.0	80.8	90.7	93.6	94.6	7.7	19.5	23.2	30.6	42.0	51.8	68.1	80.8	90.3	93.7	94.5
	90	7.7	18.8	22.4	28.8	40.3	50.9	66.7	79.0	86.4	92.4	93.7	7.7	19.0	23.0	29.8	40.5	50.5	67.0	78.7	87.0	91.9	93.1
3.60	0	7.7	22.9	27.5	36.5	50.1	63.3	78.6	89.4	96.4	98.7	99.8	7.7	23.4	27.0	36.4	50.0	61.5	79.3	89.7	94.3	98.5	99.7
	30	7.7	19.7	24.3	33.4	44.4	65.6	72.3	84.3	91.0	94.5	97.0	7.7	19.4	24.6	33.9	43.5	54.6	72.5	84.0	90.6	94.9	96.7
	60	7.7	18.8	22.1	29.8	41.3	51.7	67.5	80.1	88.4	92.3	94.0	7.7	18.7	22.5	30.0	41.0	51.3	67.3	80.0	88.1	92.5	94.2
	90	7.7	18.1	22.0	28.8	39.8	50.3	66.0	78.0	86.3	91.2	93.5	7.7	18.3	22.3	29.4	39.3	48.6	66.7	78.3	86.6	91.2	93.6

E2 Tinting result of TypeII polymerization

Table E10 Color density data of C1 polymerization condition

Initiator Concentration (%)	Final step process time (min)	First set											Second set										
		Tinting process time (min)											Tinting process time (min)										
		0	0.5	1	2	4	9	16	25	36	49	64	0	0.5	1	2	4	9	16	25	36	49	64
2.60	0	7.7	19.1	23.0	27.9	36.5	50.5	62.6	73.9	81.0	87.6	89.8	7.7	19.0	22.8	27.5	37.0	52.5	63.0	74.1	80.5	86.9	91.3
	30	7.7	18.5	22.6	27.8	36.3	50.3	61.8	73.6	80.2	86.5	88.6	7.7	18.4	22.5	27.3	36.7	52.4	62.3	73.3	79.3	86.5	89.5
	60	7.7	18.5	22.1	27.7	36.1	50.0	61.5	72.4	79.5	85.3	88.4	7.7	18.3	22.3	27.0	36.5	52.0	61.7	72.1	78.6	85.7	88.3
	120	7.7	18.3	22.0	27.7	35.9	49.9	61.0	71.3	78.2	84.2	87.9	7.7	18.0	22.3	26.8	36.3	51.5	61.4	71.8	78.0	84.3	88.0
	180	7.7	17.8	21.7	27.3	35.7	49.6	61.0	70.6	77.6	83.5	87.0	7.7	17.4	21.7	26.6	36.0	51.3	61.0	71.6	77.0	83.2	87.3
2.70	0	7.7	18.8	21.0	27.0	34.9	49.3	59.3	69.0	77.0	83.2	87.9	7.7	18.5	21.0	26.5	35.5	49.0	59.2	69.3	76.7	83.5	87.5
	30	7.7	18.4	20.7	26.3	34.5	48.6	58.5	68.5	76.4	82.6	86.9	7.7	18.2	20.9	26.4	34.7	48.2	59.1	69.3	76.6	83.0	86.7
	60	7.7	17.9	20.5	26.0	34.0	48.0	58.3	68.1	75.7	81.9	85.5	7.7	17.9	20.9	26.3	33.8	47.6	58.5	68.4	75.5	82.0	85.7
	120	7.7	17.3	20.4	25.9	33.8	47.5	57.6	67.6	75.3	81.5	85.0	7.7	17.4	20.7	26.1	33.1	47.3	58.1	68.1	75.4	81.6	84.4
	180	7.7	17.1	19.9	25.5	32.9	47.1	56.5	67.3	74.8	80.7	84.6	7.7	16.9	20.7	26.0	32.6	47.0	58.1	67.9	75.1	81.0	84.0
2.80	0	7.7	18.4	20.7	24.6	31.9	46.3	55.7	66.8	74.8	81.6	85.3	7.7	17.6	20.8	24.7	32.0	48.0	55.5	67.0	74.3	81.6	85.6
	30	7.7	16.8	20.1	24.6	31.8	45.5	54.6	64.5	72.6	81.0	84.9	7.7	17.0	20.3	24.3	31.6	46.8	54.0	65.5	73.3	80.8	84.7
	60	7.7	16.8	20.0	24.4	31.4	45.0	53.3	65.3	72.6	80.5	83.6	7.7	17.0	19.7	24.3	31.5	46.0	53.3	64.8	72.0	80.5	84.0
	120	7.7	16.5	19.7	24.1	31.1	44.8	53.0	65.3	72.7	80.0	83.4	7.7	16.8	19.6	24.2	30.3	45.0	52.8	64.4	71.8	79.9	83.5
	180	7.7	16.5	19.6	23.7	30.9	44.0	52.7	64.2	71.4	79.4	83.3	7.7	16.5	19.4	24.0	30.7	44.4	52.4	64.0	71.5	79.7	83.4
2.90	0	7.7	16.9	20.3	23.3	31.4	42.5	53.2	65.0	73.0	78.8	83.5	7.7	17.3	20.2	23.3	31.5	42.7	53.0	63.8	71.3	78.6	83.7
	30	7.7	16.7	19.9	23.0	31.3	42.5	53.0	64.7	72.3	78.4	83.0	7.7	17.0	19.8	23.0	31.2	42.5	52.5	64.5	72.0	78.6	82.5
	60	7.7	16.6	19.6	22.8	30.9	42.3	52.4	64.0	71.7	77.7	82.4	7.7	16.8	19.7	22.9	30.3	42.5	52.1	63.4	70.9	77.8	83.0
	120	7.7	16.4	19.3	22.8	30.3	42.1	51.6	63.2	70.9	77.2	82.3	7.7	16.5	19.7	22.8	29.8	42.2	51.2	63.1	70.4	77.8	82.5
	180	7.7	15.5	19.0	22.5	30.0	41.9	50.9	62.9	70.0	77.0	81.4	7.7	15.8	19.2	22.8	29.8	41.5	50.5	62.5	69.6	77.5	81.8

Table E11 Color density data of C2 polymerization condition

Initiator Concentration (%)	Final step process time (min)	First set											Second set										
		Tinting process time (min)											Tinting process time (min)										
		0	0.5	1	2	4	9	16	25	36	49	64	0	0.5	1	2	4	9	16	25	36	49	64
2.60	0	7.7	20.2	22.6	28.9	38.7	51.7	64.5	75.6	83.5	88.2	91.2	7.7	20.0	23.6	29.1	38.3	55.4	65.1	75.3	83.0	88.6	91.4
	30	7.7	19.7	22.5	28.8	37.9	51.3	64.1	74.7	81.6	86.5	90.0	7.7	19.0	22.8	28.8	37.9	55.0	64.7	74.5	82.2	86.8	90.6
	60	7.7	18.9	22.5	28.6	37.8	51.1	64.0	73.6	80.4	86.8	89.8	7.7	18.3	22.6	28.3	37.3	54.5	64.0	73.6	81.1	86.5	90.2
	120	7.7	18.8	22.1	28.2	37.6	51.0	63.4	73.6	80.0	85.5	88.8	7.7	18.2	22.6	27.9	36.9	53.3	63.5	73.3	80.5	85.5	88.6
	180	7.7	18.6	22.4	28.6	37.5	50.5	64.4	73.6	79.9	85.3	88.4	7.7	17.9	21.9	27.5	36.5	52.8	63.3	72.9	80.0	85.3	88.2
2.70	0	7.7	19.3	21.8	27.9	35.6	50.5	61.6	72.5	80.6	85.9	89.7	7.7	19.4	21.8	27.8	35.4	50.4	61.7	73.0	80.3	86.2	89.3
	30	7.7	18.6	21.4	27.3	34.9	50.3	61.0	72.0	79.9	85.6	89.1	7.7	18.9	21.7	27.6	35.1	50.0	61.2	72.2	79.2	85.8	89.0
	60	7.7	18.1	21.2	27.2	34.6	49.7	60.7	71.4	78.6	85.0	89.8	7.7	18.7	21.5	27.3	34.6	49.7	60.7	70.8	78.4	85.3	88.3
	120	7.7	17.6	21.0	26.9	34.2	49.0	60.0	70.9	78.0	84.6	87.4	7.7	18.5	21.4	27.2	34.3	49.3	60.0	70.3	77.9	84.0	87.9
	180	7.7	17.5	20.5	26.8	34.1	48.8	59.5	70.0	77.1	83.8	87.2	7.7	18.3	20.8	26.9	33.8	48.6	59.8	69.4	76.4	83.0	87.0
2.80	0	7.7	19.7	22.0	26.4	34.8	48.3	59.2	71.1	78.4	83.7	87.0	7.7	18.5	21.6	26.0	33.5	48.5	59.2	71.3	78.3	83.9	87.5
	30	7.7	19.0	21.0	25.8	32.8	48.0	57.6	69.4	77.3	82.1	86.0	7.7	17.7	21.0	25.4	33.5	47.7	57.9	69.6	77.3	82.4	86.3
	60	7.7	18.9	20.8	25.7	32.6	47.9	57.2	69.0	75.7	81.8	85.2	7.7	17.5	20.9	25.3	33.3	47.2	57.2	69.0	75.5	81.7	84.6
	120	7.7	18.8	20.7	25.7	32.6	47.5	56.7	68.7	75.3	80.8	84.5	7.7	17.3	20.5	25.2	33.1	46.9	57.0	68.3	75.1	81.0	83.9
	180	7.7	18.2	20.4	25.1	32.1	45.6	55.8	67.0	74.8	79.6	83.1	7.7	17.1	20.4	24.8	32.6	45.3	56.0	67.4	74.4	80.0	83.9
2.90	0	7.7	17.8	21.5	25.2	34.0	46.8	55.5	68.5	76.1	82.8	85.6	7.7	19.2	21.0	25.0	33.8	46.8	55.7	68.3	76.0	82.5	85.3
	30	7.7	17.4	21.3	24.6	33.3	45.5	54.7	67.0	75.5	81.6	84.6	7.7	18.4	20.9	24.9	33.5	45.5	54.3	67.0	75.4	81.0	84.3
	60	7.7	17.4	20.8	24.0	32.9	44.9	54.0	66.7	75.0	80.9	83.7	7.7	17.8	20.7	24.2	33.0	45.0	53.5	66.3	73.0	80.1	83.2
	120	7.7	17.1	20.3	24.0	32.7	44.4	53.6	66.1	73.4	79.5	83.1	7.7	17.4	20.6	24.1	32.5	44.6	53.3	65.9	72.4	79.4	83.0
	180	7.7	16.8	20.3	23.9	32.4	44.0	53.1	65.8	72.6	79.0	82.5	7.7	17.2	20.2	23.9	32.4	44.2	52.9	65.5	72.3	78.8	82.2

Table E12 Color density data of C3 polymerization condition

Initiator Concentration (%)	Final step process time (min)	First set											Second set											
		Tinting process time (min)											Tinting process time (min)											
		0	0.5	1	2	4	9	16	25	36	49	64	0	0.5	1	2	4	9	16	25	36	49	64
2.60	0	7.7	20.8	23.7	30.1	40.3	53.6	67.1	76.8	84.0	89.6	92.8	7.7	21.0	24.0	30.3	40.5	57.5	66.9	77.1	84.3	89.9	92.6
	30	7.7	20.1	23.5	29.9	39.6	53.1	66.1	76.4	82.5	88.4	91.6	7.7	19.9	23.4	30.0	39.7	56.3	66.0	76.6	82.6	88.8	91.5
	60	7.7	19.9	23.4	29.9	39.0	52.7	66.4	75.6	82.1	88.0	91.2	7.7	19.5	23.0	29.3	39.5	55.4	65.3	75.9	82.4	88.2	91.0
	120	7.7	19.3	23.1	29.6	38.9	51.2	65.9	75.1	81.7	87.5	90.6	7.7	19.2	22.8	28.4	39.2	54.2	64.6	75.0	81.9	87.9	90.4
	180	7.7	19.4	22.3	27.0	36.8	50.6	64.4	74.5	80.7	86.2	89.9	7.7	19.0	22.2	28.0	39.0	53.7	64.1	74.8	80.7	87.0	90.0
2.70	0	7.7	19.7	22.6	28.0	36.0	52.4	63.1	73.5	81.4	86.4	90.3	7.7	19.5	22.7	28.0	35.6	53.2	63.0	73.7	81.1	86.9	90.1
	30	7.7	19.2	22.5	27.8	35.8	51.8	62.7	72.9	80.3	86.0	89.9	7.7	19.2	22.4	27.7	35.2	51.6	61.7	73.0	80.5	86.4	89.9
	60	7.7	19.0	22.0	27.5	35.0	51.5	61.5	72.4	78.8	85.3	89.7	7.7	19.0	22.3	27.4	35.1	50.7	61.5	72.2	79.1	85.8	89.5
	120	7.7	18.6	21.6	27.3	34.8	50.5	60.9	71.6	78.4	86.0	89.5	7.7	18.8	21.9	27.2	34.9	50.3	61.5	71.6	79.0	85.4	89.2
	180	7.7	18.5	21.0	26.8	34.8	50.0	59.8	71.0	77.4	84.8	88.8	7.7	18.5	21.6	27.0	34.6	49.4	61.4	71.6	77.5	84.6	89.0
2.80	0	7.7	18.5	21.0	26.2	33.3	48.9	60.0	72.0	79.4	86.1	88.8	7.7	19.3	22.2	26.2	34.5	49.2	60.5	72.3	79.4	86.0	89.0
	30	7.7	17.9	20.8	25.2	32.8	47.8	58.4	71.2	78.7	85.5	87.6	7.7	19.0	21.4	25.8	34.0	48.4	58.0	71.4	78.8	85.3	87.6
	60	7.7	17.7	20.5	25.1	32.4	47.7	58.0	70.9	79.0	85.3	86.9	7.7	18.9	20.9	25.3	33.2	47.8	58.3	70.6	78.3	84.0	86.4
	120	7.7	17.6	20.4	24.9	32.3	47.7	57.3	70.0	77.2	83.2	87.5	7.7	18.7	20.5	25.1	33.0	47.1	57.1	70.4	77.7	83.5	84.7
	180	7.7	17.2	20.0	24.5	32.0	46.4	57.0	68.5	75.3	82.5	86.8	7.7	18.4	20.5	25.0	33.0	46.9	56.9	68.9	75.6	82.3	85.2
2.90	0	7.7	18.6	21.9	25.5	34.4	47.8	57.8	70.7	77.3	84.0	88.0	7.7	18.3	20.5	25.2	35.1	47.5	57.6	70.2	77.1	84.5	87.7
	30	7.7	17.8	21.9	24.8	33.6	47.0	56.8	68.9	75.7	83.6	86.6	7.7	18.1	20.0	24.5	35.1	46.0	56.8	68.4	75.9	83.4	86.5
	60	7.7	17.3	20.9	24.5	33.1	45.9	55.5	67.5	74.5	82.2	86.3	7.7	17.7	19.7	24.1	33.8	44.8	55.1	67.8	74.3	82.0	86.0
	120	7.7	17.3	20.8	24.2	33.0	45.2	54.4	67.5	73.1	81.0	85.5	7.7	17.0	19.6	23.9	32.9	44.6	54.5	67.2	73.5	81.7	86.0
	180	7.7	17.5	20.5	24.1	32.8	44.5	53.9	67.0	73.0	80.4	84.0	7.7	16.8	19.5	23.8	32.7	44.0	54.1	66.7	73.1	80.7	84.5

Table E13 Color density data of C4 polymerization condition

Initiator Concentration (%)	Final step process time (min)	First set											Second set										
		Tinting process time (min)											Tinting process time (min)										
		0	0.5	1	2	4	9	16	25	36	49	64	0	0.5	1	2	4	9	16	25	36	49	64
2.60	0	7.7	21.6	25.7	32.3	42.4	55.8	70.3	79.8	85.9	91.0	93.5	7.7	21.5	25.6	32.5	41.9	60.5	70.6	78.9	85.7	91.4	93.5
	30	7.7	21.0	24.6	31.0	41.5	54.8	67.4	78.9	85.2	90.0	92.1	7.7	20.8	24.8	32.0	41.5	59.3	68.5	78.7	85.0	90.7	93.8
	60	7.7	20.9	24.5	30.5	41.2	53.6	67.2	77.6	84.4	89.5	92.0	7.7	20.6	24.7	31.0	41.0	58.0	68.9	77.5	84.6	89.9	92.5
	120	7.7	20.3	23.9	30.5	40.4	53.4	67.2	76.7	83.9	89.0	91.6	7.7	20.2	23.8	30.8	39.7	57.4	67.3	76.9	83.5	89.0	91.9
	180	7.7	20.2	23.5	30.3	39.7	52.4	66.6	76.1	83.3	88.4	91.0	7.7	20.0	23.5	30.4	39.5	57.0	67.0	76.4	83.3	88.6	91.1
2.70	0	7.7	20.6	23.6	28.9	37.0	53.7	64.1	75.8	83.5	88.8	91.4	7.7	20.7	23.6	28.2	36.8	53.3	63.9	76.0	84.0	89.1	91.1
	30	7.7	20.4	23.3	28.5	36.6	52.5	63.9	75.3	83.0	87.0	90.9	7.7	20.4	23.6	27.9	36.0	52.5	63.7	75.6	82.3	88.8	90.9
	60	7.7	20.3	23.3	27.9	36.0	51.7	63.0	75.0	82.4	87.6	90.3	7.7	20.4	23.6	27.8	35.9	52.1	63.1	75.3	83.0	88.4	90.6
	120	7.7	19.7	22.9	27.2	35.3	51.1	62.6	74.9	81.3	87.4	89.9	7.7	19.8	23.2	27.7	35.5	51.8	62.9	75.0	83.0	88.1	89.6
	180	7.7	19.5	22.4	26.8	35.0	50.8	62.4	74.7	80.6	86.6	89.5	7.7	19.7	22.9	27.4	35.1	50.5	62.3	74.8	80.8	88.1	89.8
2.80	0	7.7	20.1	23.0	26.0	34.3	51.7	63.0	74.3	81.1	87.4	89.6	7.7	20.1	23.0	26.8	34.5	51.5	62.4	74.5	81.4	87.0	90.0
	30	7.7	19.4	22.5	25.5	33.7	50.8	62.2	74.2	80.5	86.0	88.8	7.7	19.8	22.0	25.4	33.6	50.3	62.0	74.4	80.3	86.3	89.1
	60	7.7	19.2	22.3	25.4	33.6	49.9	61.3	74.0	79.5	85.8	88.3	7.7	19.5	21.5	25.3	33.3	49.5	61.5	74.0	80.0	85.5	88.7
	120	7.7	18.9	22.2	25.4	33.5	48.6	61.1	74.0	79.1	85.0	88.3	7.7	19.3	21.3	25.0	33.1	49.0	60.8	73.8	79.2	84.8	88.2
	180	7.7	18.8	21.8	25.0	33.3	48.0	60.4	72.6	78.2	84.5	87.7	7.7	18.6	21.0	25.0	33.1	48.4	60.3	73.0	78.6	84.1	87.9
2.90	0	7.7	19.0	22.2	26.0	34.8	49.4	61.7	72.8	79.4	86.6	88.8	7.7	19.2	21.9	26.2	34.4	49.2	61.7	72.6	79.6	86.3	88.7
	30	7.7	18.7	22.0	26.0	34.2	48.4	60.0	72.6	78.3	85.7	87.8	7.7	19.0	21.5	26.0	34.2	48.3	59.7	70.5	78.5	85.0	87.5
	60	7.7	18.5	22.0	25.8	34.0	47.9	59.5	72.0	77.7	84.0	87.4	7.7	18.9	21.4	25.5	33.6	47.7	59.3	69.8	77.6	83.6	86.6
	120	7.7	18.3	21.5	25.4	33.5	47.6	58.3	70.9	76.8	83.2	86.3	7.7	18.4	21.3	24.4	33.4	47.1	58.8	70.5	77.6	83.0	86.0
	180	7.7	18.0	21.4	24.4	33.3	47.3	57.5	70.0	76.5	82.7	85.9	7.7	18.4	21.2	24.4	33.1	47.1	57.9	69.8	76.3	82.1	85.5

VITA

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Table E14 Color density data of C5 polymerization condition

Initiator Concentration (%)	Final step process time (min)	First set											Second set										
		Tinting process time (min)											Tinting process time (min)										
		0	0.5	1	2	4	9	16	25	36	49	64	0	0.5	1	2	4	9	16	25	36	49	64
2.60	0	7.7	21.6	25.9	32.8	43.4	58.6	73.5	81.3	86.9	92.0	96.5	7.7	22.0	26.7	33.0	43.8	61.7	73.3	81.5	87.0	92.2	94.3
	30	7.7	21.5	25.0	32.1	42.1	58.1	69.9	80.4	85.6	91.6	94.6	7.7	21.6	25.9	32.4	43.0	61.1	71.4	80.2	86.5	91.4	93.9
	60	7.7	20.8	24.9	31.5	41.9	57.5	69.3	79.7	85.0	90.2	94.0	7.7	21.5	24.9	32.0	42.1	60.3	69.7	79.5	85.9	90.5	93.5
	120	7.7	20.8	24.4	31.2	41.9	57.3	69.2	79.0	84.9	89.5	93.3	7.7	21.3	24.5	31.5	41.9	60.0	69.3	79.0	84.8	89.9	93.0
	180	7.7	20.3	24.0	30.6	40.5	56.4	68.9	77.5	84.4	89.2	93.0	7.7	20.8	24.4	31.0	41.0	58.7	69.1	78.1	84.6	87.1	92.5
2.70	0	7.7	21.2	24.8	30.5	40.5	55.3	69.0	79.2	85.4	90.2	93.3	7.7	21.0	24.6	30.1	40.1	59.3	68.7	79.0	85.5	90.9	91.9
	30	7.7	21.0	24.5	29.7	40.0	55.0	68.5	78.4	84.3	89.5	93.1	7.7	20.7	24.0	29.7	39.4	56.8	68.2	78.4	83.2	90.5	91.8
	60	7.7	20.7	24.5	29.4	39.2	54.3	68.0	77.3	83.1	89.3	93.0	7.7	20.4	23.8	29.1	39.1	55.2	67.1	78.1	83.0	90.2	91.8
	120	7.7	20.3	23.8	29.0	38.8	54.1	66.7	76.9	82.7	88.9	92.5	7.7	20.2	23.4	28.8	37.8	54.2	66.0	77.3	82.6	89.4	91.0
	180	7.7	20.0	23.4	28.7	37.3	53.9	66.5	76.5	82.0	88.3	92.1	7.7	19.9	23.1	28.4	37.8	54.2	65.9	76.4	82.0	88.4	90.8
2.80	0	7.7	20.3	23.5	27.3	36.0	54.2	66.2	77.4	82.9	89.1	91.1	7.7	20.4	24.1	27.5	36.0	53.0	64.4	77.7	82.6	89.5	91.5
	30	7.7	19.6	23.3	26.7	35.0	52.6	65.0	76.8	82.4	87.2	90.6	7.7	20.3	24.0	26.5	35.4	52.6	63.5	76.7	82.0	87.0	90.9
	60	7.7	19.4	23.1	25.8	34.7	51.3	63.1	75.1	81.9	86.7	90.3	7.7	20.3	23.6	25.9	35.0	52.3	62.0	75.3	81.7	86.3	90.5
	120	7.7	19.2	23.0	25.8	33.8	50.9	62.7	75.0	81.4	85.6	90.0	7.7	19.9	23.4	25.6	34.6	51.5	61.3	75.3	81.0	85.8	90.7
	180	7.7	19.0	22.5	25.6	33.7	50.4	62.4	74.0	80.5	85.4	89.6	7.7	19.3	22.8	25.3	34.3	49.7	61.9	74.1	80.8	85.1	90.0
2.90	0	7.7	19.5	22.8	26.5	35.3	52.5	63.0	75.5	82.0	89.8	91.0	7.7	19.2	23.0	26.2	35.2	51.7	62.8	75.1	82.3	89.0	90.8
	30	7.7	19.3	22.9	25.9	35.0	50.8	62.4	74.9	81.6	87.4	89.5	7.7	18.9	22.8	26.1	35.2	51.1	61.8	74.6	80.3	85.4	89.9
	60	7.7	19.0	22.7	25.5	35.0	49.9	61.5	74.4	80.4	85.3	89.3	7.7	18.7	22.0	26.1	34.4	50.4	61.8	74.0	79.9	84.9	89.5
	120	7.7	18.9	22.4	25.0	34.6	48.9	60.3	74.0	79.0	85.0	88.6	7.7	18.6	21.6	25.1	34.1	48.6	60.7	73.5	79.1	84.8	89.4
	180	7.7	18.4	21.8	25.0	34.1	48.3	59.7	73.8	78.5	84.4	88.0	7.7	18.4	21.5	24.9	34.0	47.8	59.2	71.8	78.9	84.0	88.5