

CHAPTER IV

EXPERIMENTS

The experimental results that used to fit data was obtained from the temperature jump experiment. The data are the intensities at various angles and various time of the sample at the specific temperature.

There are two sets of experimental results used in this study. The first set is the system of tetramethyl-bisphenol-A polycarbonate (TMPC)/polystyrene(PS) blends at five temperature jumps. Three compositions (30, 50, 70 %w TMPC/PS BLENDS) of this blend were prepared by solvent casting, while 50%w TMPC/PS BLENDS was prepared by melt mixed. This set of experimental results was obtained from the study of Thongyai, S [Thongyai, 1994]. The second set is system of polystyrene co maleic anhydride(SMA)/polymethyl methacrylatem(PMMA) blends at one temperature jump. Three compositions (20, 30, 40 %w SMA) of this blend were used. This set of experimental results was obtained from the study of Rojanapitayakorn, P.

Experimental results were performed using light scattering apparatus. The equipment is schematically shown in Fig.4.1. An aerotech model 1105P He/Ne laser of 5 mW ($\lambda=632.8$ nm) is used as light source incidented on a sample inside a temperature controlled sample holder. The scattered light was detected by a photo diode array, mounted on an arc between 5-67 degrees at 2-degree intervals. The signal is then converted in a multi-channel analogue/digital converter. Control and data collection are both implemented using a PC.

The wave vector q can be expressed as a function of the wave length of the laser λ and the scattered angle θ ;

$$q = \frac{4n\pi}{\lambda} \sin\left(\frac{\theta}{2}\right) \quad (4.1)$$

Light scattering is the instrument that can indirectly measure the concentration fluctuations of a polymer blend. It measures the scattered light intensity at various angles and times that results from the changes in the refractive indices of the sample. When the phase separation occurs, the two different phases induce a difference in refractive index which results from an increasing in the concentration fluctuations of the polymer blend.

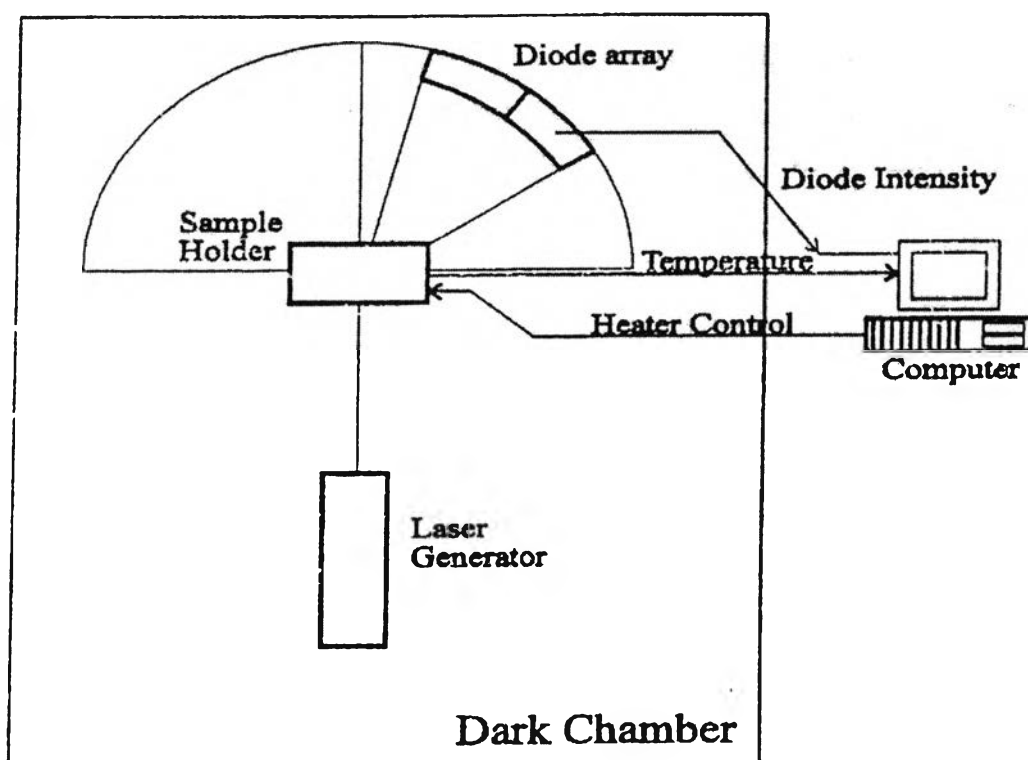


Fig. 4.1 Small Angle Light Scattering Machine [Thongyai, 1994]

4.1 Test of Cahn-Hilliard's Theory

According to the Cahn-Hilliard's theory, the intensity can be calculated from equation (3.2.27).

$$S(q,t) = S_x(q) + (S(q,o) - S_x(q)) \exp(2R(q)t) \quad (4.1.1)$$

The data are the intensities at various angles and times of the sample at a specific temperature. The intensity-time curve can be fitted by taking $\ln(I)$ of Intensity and fitting it with a straight line. The data obtained is the growth rate $R(q)$. The $R(q)$ are obtained from half of the slope of the fitted line.

Where the term $S_x(q)$ is the thermal noise that is very small and often negligible, and $S[q,o] - S_x(q)$ is the intensity factor.

We use the equation (3.2.27) to calculate the intensity data of Cahn-Hilliard's theory at constant q and different time. Then, we compare calculated intensity data with experimental data received from Thongyai, S and Rojanapitayakorn, P.

4.2 Test of Langer, Bar-on, and Miller's Theory

From Langer, Bar-on and Miller's theory, we will use equation (3.3.21) to find the intensity data.

$$\frac{\partial S(q,t)}{\partial t} = -2Mq^2 [Kq^2 + A(t)] S(q,t) \quad (3.3.21)$$

This equation is more complicated than the normal Cahn-Hilliard equation, but this theory can be explained the beginning of the spinodal decomposition process.

The term $A(t)$ in equation (3.3.21) can be solved by using the power law, which can be expanded as,

$$A(t) = a + bt + ct^2 + dt^3 \quad (4.2.1)$$

When we substitute equation (4.2.1) in to equation (3.3.21), we will obtain

$$\frac{\partial S(q,t)}{\partial t} = -2Mq^2 [Kq^2 + a + bt + ct^2 + dt^3] S(q,t) \quad (4.2.2)$$

The equation (4.2.2) can be rewritten as,

$$\frac{1}{S(q,t)} \partial S(q,t) = -2Mq^2 [Kq^2 + a + bt + ct^2 + dt^3] \partial t \quad (4.2.3)$$

Then, we can solve this equation by integrating both side of the equation as,

$$\ln(S(q,t)) - \ln(S(q,0)) = -2Mq^2 [Kq^2 t + at + bt^2 + ct^3 + dt^4] \quad (4.2.4)$$

$$\ln(S(q,t)) = -2MKq^4 t + q^2 (a't + b't^2 + c't^3 + d't^4) + E \quad (4.2.5)$$

When q is given as a constant, we can write equation (4.2.5) in the simple form as

$$\ln(S(q,t))_q = (E + At + Bt^2 + Ct^3 + Dt^4)_q \quad (4.2.6)$$

When A, B, C and D are the total coefficients of any q at different time, and E is the intensity factor. The equation (4.2.6) is the basic equation that can be used to fit experimental data at constant q and different time by using MATHEMATICA program. From fit data, we get the total coefficients and the intensity factor. Then, we substitute these values in equation (4.2.6) at different

time to calculate the new intensity data of Langer, Bar-on and Miller's theory. Finally, we compare results between the intensity data form calculation and the experiment data.

Langer, Bar-on and Miller's theory differs from the other theories by factor $A(t)$ which was expanded using the power law to simplify the equation (3.3.21) for calculation. The intensities were calculated using only exponential from fitted equation.

4.3 Test of Akcasu's Theory

We obtains the equation of Akcasu's theory from equation (3.4.20), that can be used to calculate the intensity $I(q,t)$

$$\frac{dI(q,t)}{dt} = -2R(q)I(q,t)[1 + Z(q,t)] + C(q) \quad (3.4.20)$$

From equation (3.4.20), when q is constant then the term of $Z(q,t)$ can be expanded by using power law as,

$$Z(q,t)_q = a' + B't + C't^2 + D't^3 \quad (4.3.1)$$

After we substituted equation (4.3.1) in equation (3.4.20), we will obtain the intensity equation as in equation (4.3.2).

$$\frac{dI(q,t)}{dt} = -2R(q)I(q,t)\left[1 + a' + B't + C't^2 + D't^3\right] + C(q) \quad (4.3.2)$$

When divided equation (4.3.2) by $-2R(q)I(q,t)$, we can write as,

$$\left(\frac{dI(q,t)}{-2R(q)I(q,t)dt} \right)_q = \left[1 + a' + B't + C't^2 + D't^3 \right]_q + \left(\frac{C(q)}{-2R(q)I(q,t)} \right)_q \quad (4.3.3)$$

We can write equation (4.3.3) in a different form as,

$$\left(\frac{I(q,t+\Delta t) - I(q,t)}{-2R(q)I(q,t)\Delta t} \right)_q = \left[1 + a' + B't + C't^2 + D't^3 \right]_q + \left(\frac{C(q)}{-2R(q)I(q,t)} \right)_q \quad (4.3.4)$$

From equation (4.3.4), the term $C(q)/(-2R(q)I(q,t))$ can be neglected because $C(q)$ is very small and often negligible. So we can rewrite equation (4.3.4) as,

$$\left(\frac{I(q,\Delta t) - I(q,t)}{-2R(q)I(q,t)\Delta t} \right)_q = \left[A' + B't + C't^2 + D't^3 \right]_q \quad (4.3.5)$$

When $A' = 1 + a'$ and A', B', C', D' are coefficients of equation.

We use the experiment results to calculate value of the left-hand side term of equation (4.3.5), then we use this value to find the coefficients of the right-hand side term. The equation from fitting data can be used to calculate the intensity of Akcasu's theory. We must rearrange equation (4.3.5) to calculate intensity, and can be written as,

$$I(q,\Delta t)_q = I(q,t)_q - 2R(q)I(q,t)\Delta t \left[A' + B't + C't^2 + D't^3 \right]_q \quad (4.3.6)$$

After we calculated intensity from equation (4.3.6), we use this calculated results to compare with experiment results.

Akcasu's theory differs from the other theories by factor $Z(q,t)$. Akcasu's theory differs from that of Langer, Bar-on and Miller's theory in the way the fluctuations are treated in the nonlinear theory, and in the details of calculations arising from the polymer effect (factor $Z(q,t)$). The term $Z(q,t)$ was expanded using the power law to simplify the equation(3.4.20) at q constant. The calculated data of fitting equation differ from the other theories. These calculated data were calculated from the term of left hand side of equation (4.3.5) by using $R(q)$, step time (Δt) and intensities data of experiments.

4.4 Test of Nauman's Theory

From equation (3.5.18), it can be rewritten as,

$$\frac{\partial a(x,t)}{\partial t} = D_{AB} \nabla a(x,t) (1 - a(x,t)) \left[g'' \nabla a(x,t) - \kappa \nabla^3 a(x,t) \right] \quad (4.4.1)$$

Where $a(x,t)$ is mole fraction. For the sake of simplicity, considering one dimension of x , one can obtain

$$\frac{\partial a(x,t)}{\partial t} = D_{AB} \frac{\partial}{\partial x} a(x,t) (1 - a(x,t)) \left[g'' \frac{\partial}{\partial x} a(x,t) - \kappa \frac{\partial^3}{\partial x^3} a(x,t) \right] \quad (4.4.2)$$

This equation can be modified by Fourier transform to relate it with structure function, and substitution of $\partial/\partial x$ by iq . The Fourier transform of equation (4.4.2) can be written as,

$$\frac{\partial a(q,t)}{\partial t} = D_{AB} (iq) a(q,t) (1 - a(q,t)) \left[g'' (iq) a(q,t) - \kappa (iq)^3 a(q,t) \right] \quad (4.4.3)$$

The equation (4.4.3) then can be modified.

$$\frac{\partial a(q,t)}{\partial t} = D_{AB}a(q,t)(1-a(q,t)) \left[-\left(g'' q^2 a(q,t) \right) - \left(\kappa q^4 a(q,t) \right) \right] \quad (4.4.4)$$

$$\frac{\partial a(q,t)}{\partial t} = D_{AB} \left(-g'' q^2 - \kappa q^4 \right) \left(a^2(q,t) - a^3(q,t) \right) \quad (4.4.5)$$

We have the definition of the structure function ($S(q,t)$) below,

$$S(q,t) = \left\langle |a(q,t)|^2 \right\rangle = \langle a(q,t)a(-q,t) \rangle \quad (4.4.6)$$

Differentiating the structure function as below,

$$\frac{\partial S(q,t)}{\partial t} = a(-q,t) \frac{\partial a(q,t)}{\partial t} + a(q,t) \frac{\partial a(-q,t)}{\partial t} \quad (4.4.7)$$

From equation (4.4.5) and (4.4.7), the structure function then can also be written as,

$$\frac{\partial S(q,t)}{\partial t} = \left\{ \begin{aligned} & a(-q,t) D_{AB} \left(-g'' q^2 - \kappa q^4 \right) \left(a^2(q,t) - a^3(q,t) \right) + \\ & + a(q,t) D_{AB} \left(-g'' q^2 - \kappa q^4 \right) \left(a^2(q,t) - a^3(q,t) \right) \end{aligned} \right\} \quad (4.4.8)$$

It showed be noted that a does not depend on the sign of q , i.e., or $da(q,t)/dt$ equal $da(-q,t)/dt$, so equation (4.4.8) can be written as below.

$$\frac{\partial S(q,t)}{\partial t} = \left\{ \begin{aligned} & D_{AB} \left(-g'' q^2 - \kappa q^4 \right) \left(a^3(q,t) - a^4(q,t) \right) + \\ & + D_{AB} \left(-g'' q^2 - \kappa q^4 \right) \left(a^3(q,t) - a^4(q,t) \right) \end{aligned} \right\} \quad (4.4.9)$$

We will obtain the structure equation as in equation (4.4.10).

$$\frac{\partial S(q,t)}{\partial t} = 2D_{AB} \left(-g'' q^2 - \kappa q^4 \right) \left[S(q,t)a(q,t) - S^2(q,t) \right] \quad (4.4.10)$$

From equation (4.4.10), it can be written as,

$$\frac{1}{[S(q,t)a(q,t) - S^2(q,t)]} \frac{\partial S(q,t)}{\partial t} = 2D_{AB} \left(-g'' q^2 - \kappa q^4 \right) \quad (4.4.11)$$

And we can rearrange it as,

$$\frac{1}{S(q,t)[a(q,t) - S(q,t)]} \frac{\partial S(q,t)}{\partial t} = 2D_{AB} \left(-g'' q^2 - \kappa q^4 \right) \quad (4.4.12)$$

It is assumed that the a value is the mole fraction and very small ($a < 1$) so it can be neglected when compare with the structure function. Then, we can write the equation as,

$$\frac{1}{-S^2(q,t)} \frac{\partial S(q,t)}{\partial t} = 2D_{AB} \left(-g'' q^2 - \kappa q^4 \right) \quad (4.4.13)$$

Because the structure function is directly proportional to the intensity, so we can calculate the intensity $I(q,t)$ and the equation (3.5.28) can be rewritten as,

$$\frac{1}{-I^2(q,t)} \frac{dI(q,t)}{dt} = 2D_{AB} \left(-g'' q^2 - \kappa q^4 \right) \quad (4.4.14)$$

From equation (4.4.14), when t is constant but q is varied, we can arrange this equation to fit data as,

$$\frac{1}{-I^2(q,t)} \frac{dI(q,t)}{dt} = \left(A'' q^2 + B'' q^4 \right) \quad (4.4.15)$$

When A'', B'' are the coefficients of time constant at different q . We can write equation (4.4.15) in a different form as,

$$\frac{I(q + \Delta q, t) - I(q, t)}{-I^2(q, t)\Delta t} = \left(A'' q^2 + B'' q^4 \right) \quad (4.4.16)$$

We use the experimental results to find the coefficients A'', B'' . In order to calculate the intensity at constant q and different time, we shall insert those coefficients in the equation (4.4.16). So, we can be rewritten equation (4.4.16) in a form of

$$\frac{I(q, t + \Delta t) - I(q, t)}{-I^2(q, t)\Delta t} = \left(A'' q^2 + B'' q^4 \right) \quad (4.4.17)$$

$$I(q, t + \Delta t) = I(q, t) - I^2(q, t)\Delta t \left(A'' q^2 + B'' q^4 \right) \quad (4.4.18)$$

The coefficients parameter; A'', B'' , were expanded by using power law as

$$A'' = f + ht + jt^2 + lt^3 \quad (4.4.19)$$

$$B'' = f' + h't + j't^2 + l't^3 \quad (4.4.20)$$

It was made in order to consider A'', B'' parameters as the function of time. These coefficients at one angle were fitted with equation (4.4.19) and (4.4.20) using MATHEMATICA program. From fit data, we obtain the coefficients parameter; f, h, j, l, f', h', j' and l' . So, we can be rewritten equation (4.4.18) as,

$$I(q, t + \Delta t)_q = I(q, t)_q - I^2(q, t)\Delta t \left[\left(f + ht + jt^2 + lt^3 \right) q^2 + \left(f' + h't + j't^2 + l't^3 \right) q^4 \right] \quad (4.4.21)$$

From equation (4.4.21), it can be calculated the intensity data of Nauman's theory by substituting the coefficients. Then, we compare calculated intensity with experimental data.

Nauman's theory differs from the Cahn-Hilliard's theory by factor of $a(1 - a)$ and differs from that of the other theories in the way are treated in structure function $(S(q, t))$ and in the details of calculations arising from equation (4.4.5). The equation (4.4.5) was used to calculate the simulation data. Inserting time step (Δt) and intensity values $(I(q + \Delta q, t), I(q, t))$ from experiment into equation (4.4.6) can provide coefficient parameters; A, B using MATHEMATICA program. After these coefficient parameters were expanded using power law. These coefficient parameters fitted with equation (4.2.9) and (4.2.10) can provide new coefficient parameters; f, h, j, l, f', h', j' and l' .