CHAPTER VII

STATIC AND DYNAMIC LIGHT SCATTERING STUDY OF POLYBENZOXAZINE IN DIOXANE

7.1 Abstract

Static and dynamic light scattering methods (SLS and DLS, respectively) are utilized to characterize poly(BA-had) and to study its sol–gel transition, molecular weight (M_w), radius of gyration (R_g), and hydrodynamic radius (R_h). The benzoxazine solution transforms to gel as function of time. Intermolecular and intramolecular crosslinking reactions in poly(BA-hda) result in changes of M_w, R_g, and R_h with time. Highly crosslink occurs after 24 h.

Keywords: static light scattering; dynamic light scattering; polybenzoxazine

7.2 Introduction

In the past decade, the sol–gel transition using dynamic light scattering (DLS) and static light scattering (SLS) techniques has attracted much attention from many scientists since these techniques can provide important polymer characteristics, namely, molecular weight (M_w), radius of gyration (R_g), and hydrodynamic radius (R_h) [1-4]. DLS (photon correlation spectroscopy or quasi-elastic light scattering) is used to measure the size distribution profile and to study the behavior of polymer in solution whereas SLS (an optical technique) is used to determine the intensity of the scattered light in dependence of the scattering angle. The advantages of both techniques are relatively inexpensive, do not emit harmful radiation, and do not require special solvents.

Although, recently, we discovered a novel synthesis method of polybenzoxazines with highly cross–linked via sol–gel process called quasi-solventless and their applications [5-7], we still concern their important characteristics and its sol–gel transition to understand what going on in polymer solution as function of time. Moreover, polybenzoxazines have been continuously and vigorously studied in recent years because of their wide range in many different research areas. Most importantly, various polybenzoxazines can be synthesized using different aromatic/aliphatic amines, mono/diphenols, and formaldehyde as starting materials. In the present work, we thus prepared polybenzoxazine from hexa-methylenediamine (hda), bisphenol-A, and formaldehyde, abbreviated as poly(BA-hda), in dioxane solution through the Mannich condensation and the ring-opening polymerization and studied both dynamic and static properties in sol–gel transition of poly(BA-hda) to determine its M_w, R_g, and R_h and observe the changes as a function of time.

7.3 Experimental

7.3.1 Materials

Analytical grade 1,4-dioxane, formaldehyde (analytical grade, 37 %wt. in water) and potassium chloride (KCl) were purchased from Fisher Scientific.

Bisphenol-A (BPA, 97 % purity) and hexa-methylenediamine (hda, 98 % purity) were obtained from Aldrich, Germany. All chemicals were used as received.

7.3.2 Measurements

Differential refractive index (dn/dc) measurement was conducted on a Brice-Phoenix differential refractometer. The dn/dc of polybenzoxazine solution was obtained from web-posted instructions written by Russo [8].

Static Light scattering was analyzed using a Stabilite Ar^+ laser emitting vertically polarized light at λ= 632.8 nm with a power output of 15 mW. The scattering angle was increasing in $10°$ increments between $50°$ and $100°$ and the experiment was carried out at room temperature. Molecular weight determination was calibrated by using polystyrene of known molecular weight. The specific equation used to determine the M_w and R_g via Zimm plot are

$$\frac{Kc}{\Delta R} = \frac{1}{M_w} + 2A_2c + 3A_3c^2 + \cdots \qquad (7.1)$$

and

$$\ln \frac{Kc}{\Delta R} = \ln \frac{1}{M_w} + \frac{q^2(R_g)^2}{3} \qquad (7.2)$$

where $q = \left(\frac{4\pi n}{\lambda}\right)\sin\theta$, $K = \frac{4\pi^2 n^2 \left(\frac{dn}{dc}\right)^2}{N_A \lambda^4}$, ΔR is the excess Rayleigh ratio, q is the scattering vector, c is concentration, and K is an optical constant computed using the differential refractive index.

Dynamic light scattering was examined using the same equipment as SLS technique at 25 °C and 90° scattering angle. The CONTIN software was used to determine R_h of polybenzoxazine in dioxane solution.

7.3.3 Sample preparation

The poly(BA-hda) precursor was prepared by mixing bisphenol-A, formaldehyde, and the hda diamines at a mole ratio of 1:1:4, respectively [5]. Bisphenol-A was first dissolved in 1,4-dioxane in a 50 mL glass bottle and stirred until a clear solution was obtained. A formaldehyde solution was then added to the bisphenol-A solution. The temperature was kept under 10 °C by using an ice bath. The solution of hda in dioxane was then added dropwise into the mixture while

continuously stirring for approximately 1 h and heat treatment at 100°C for 3 h was required to accelerate the reaction. The bezoxazine precursor was then purified by washing with a 0.1 M NaHCO₃ solution (200 mL) before solvent removal by evaporation and drying under vaccum. The purified synthesized benzoxazine was then characterized using ^{1}H-NMR. The polymer solution was prepared by dioxane as solvent in concentration from 5 g/L to 25 g/L and was also used to study sol–gel transition by DLS and SLS technique as function of time from 0–48 h. All of the solutions were filtered through a 0.45 μm nylon filter before using SLS and DLS technique.

7.4 Results and Discussion

The polybenzoxazine was synthesized from hda, bisphenol-A and formaldehyde by following the procedure generalized in Scheme 7.1. The benzoxazine rings were created in the first time and then polymerized via ring opening polymerization. The ^{1}H NMR result was used to identify the successful synthesized benzoxazine polymer as shown, in Figure 7.1. The characteristic peaks of methyl proton of oxazine ring were observed at approximately 4.80 to 4.82 and 3.90 to 3.94 ppm. The peaks at 1.55–1.57 ppm were assigned to the methyl protons of bisphenol-A. The methylene protons of the ring-opened benzoxazine were examined at 2.85 ppm. These results strongly agree with the results reported from Takeichi et al. [9] and Ning et al. [10].
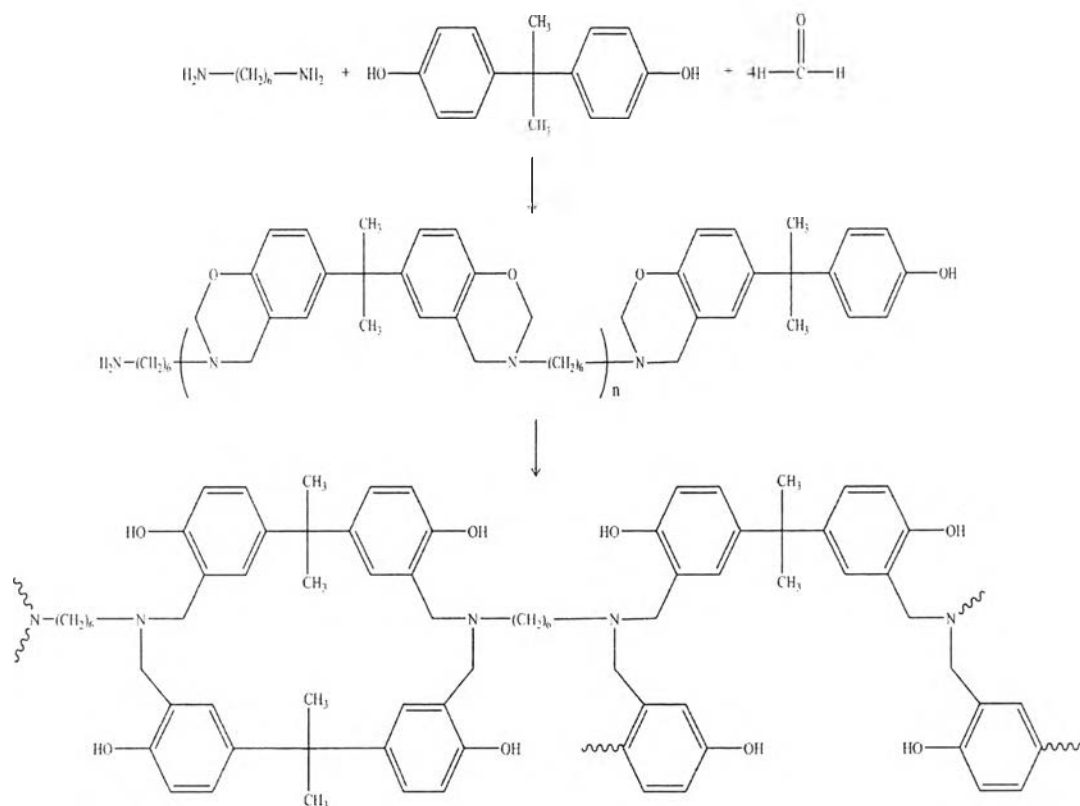
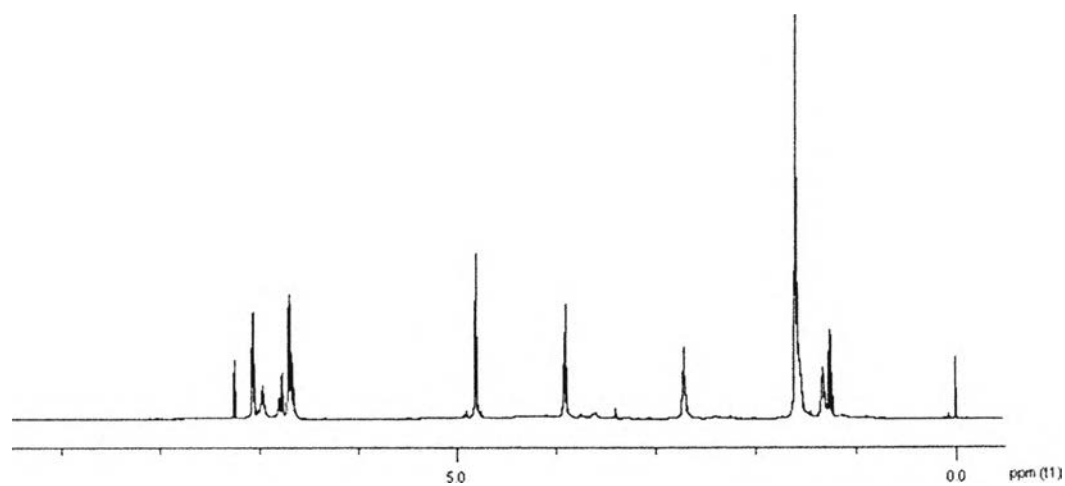**Scheme 7.1** Synthesis of poly(BA-hda)

Figure 7.1 ^{1}H NMR spectrum of poly(BA-hda)

Prior to the molecular weight determination of benzoxazine polymer, the dn/dc of poly(BA-hda) was determined using Brice-Phoenix differential refractometer calibrated against KCl solution at three different wavelengths (436, 546, and 589 nm). The dn/dc results were plotted against $1/\lambda^2$, as shown in Figure 7.2, to obtain dn/dc = 0.0925 mL/g at 632.8 nm.
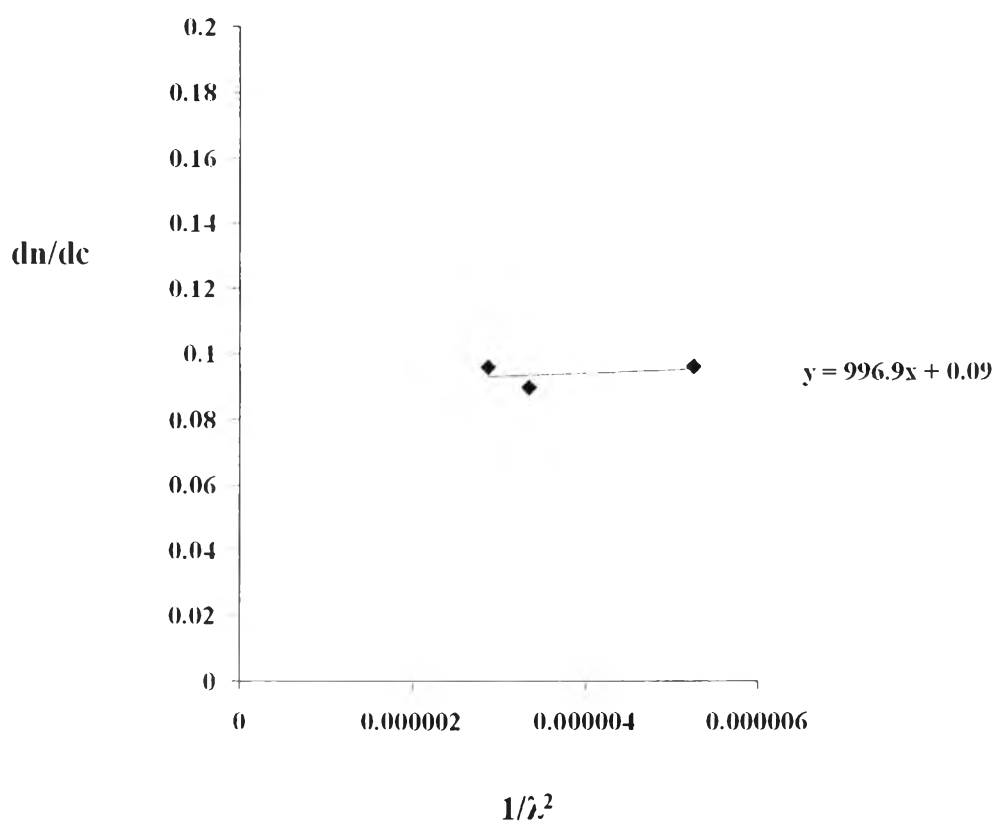

Figure 7.2   Differential refractive index versus $1/\lambda^2$

The molecular weight, M_w, of poly(BA-hda) as a function of time was studied using the Zimm plot analyzed from both the dn/dc and the static light scattering data. The angular dependence of the excess scattered light from different polybenzoxazine solutions in dioxane was experimentally determined, as shown in Figure 7.3.
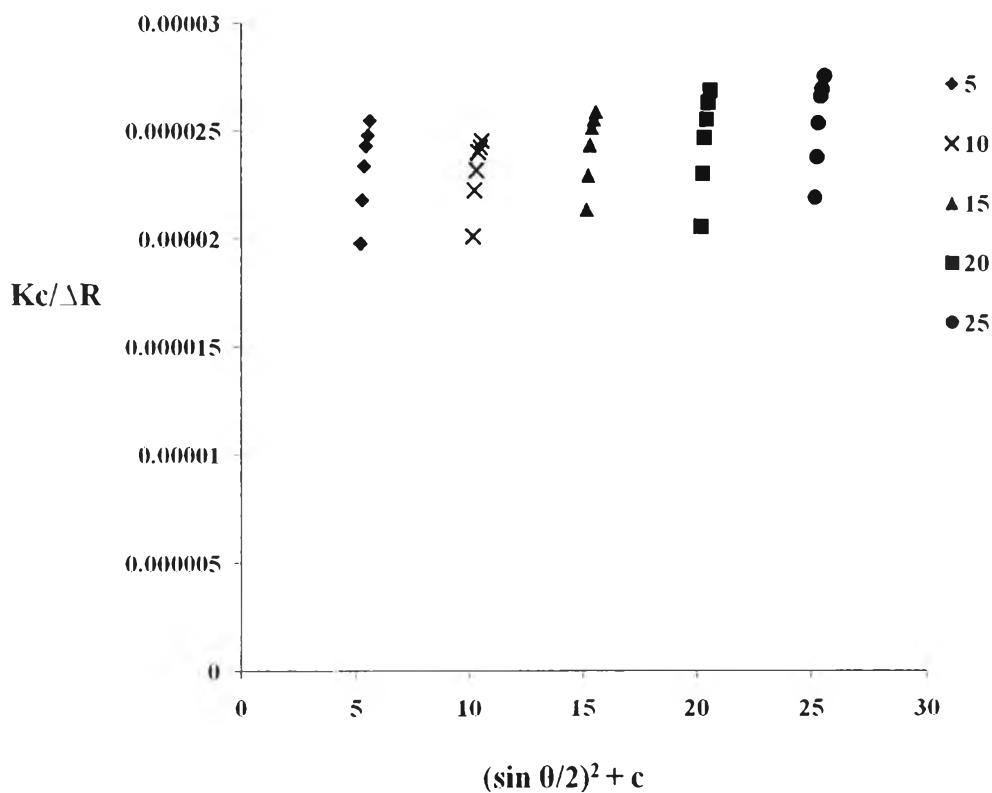
Figure 7.3 Zimm plot of poly(BA-hda) at 48 h.

The Zimm plot of poly(BA-hda) at 48 h with a series of concentrations from 5 to 25 g/L of benzoxazine polymer in dioxane shows no downturn at low angles. The radius of gyration was determined from the average slopes of $Kc/\Delta R$ versus $(\sin\theta/2)^2+c$. Both M_w and R_g of poly(BA-hda) obtained from the Zimm plot at varied time and room temperature are concluded in Table 7.1. The M_w plotted as a function of time (h) in Figure 7.4 indicated that the M_w of poly(BA-hda) slightly increased at time lower than 24 h, however, it strongly increased after 24 h because the reaction could continually occur to polymerize by the active groups and there was also the crosslinked polymer derived from the main chain oxazine ring, as also reported by Andrey C. *et al.* [11]. The possible crossinking reactions are shown in Scheme 7.2.

Table 7.1 Molecular weight, M_w, Radius of gyration, R_g, and hydrodynamic radius, R_h, of poly(BA-hda)

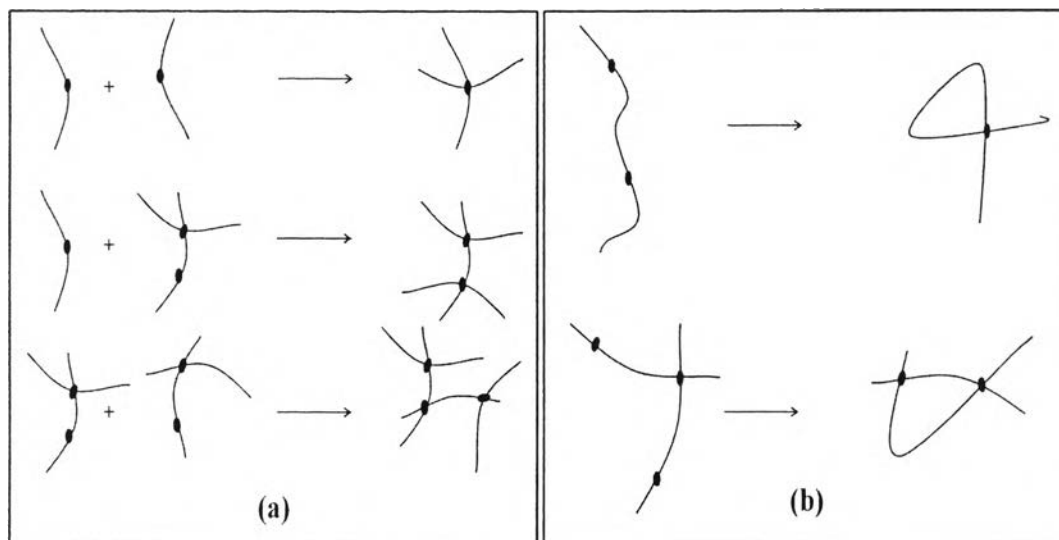| Time (h)	$M_w \times 10^4$ (g/mol)	R_g (nm)	R_h (nm)
0	2.19 ±0.27	67.12 ± 5.83	19.28 ± 0.33
12	2.39 ± 0.34	63.19 ± 5.61	19.27 ± 0.57
24	2.58 ± 0.28	61.49 ± 4.49	17.15 ± 0.44
36	3.90 ± 0.35	50.51 ± 3.95	16.37 ± 0.78
48	4.99 ± 0.39	50.14 ± 3.97	15.49 ± 0.46

Time (h)
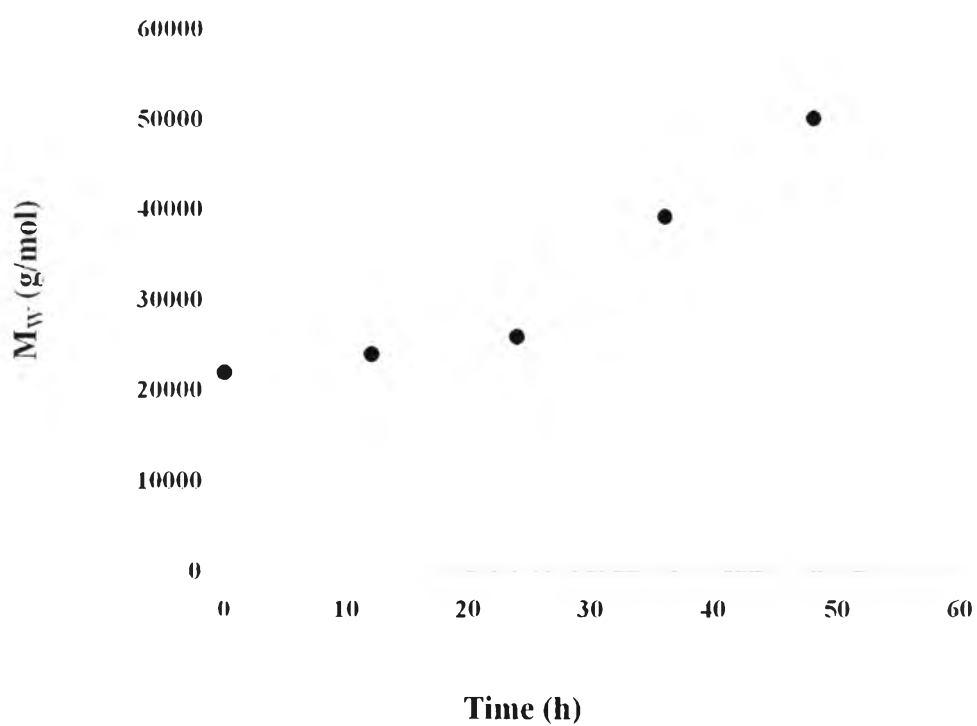
Figure 7.4 Molecular weight of poly(BA-hda) versus time

Scheme 7.2 The possible crosslinks in poly(BA-hda): (a) intermolecular and (b) intramolecular crosslinking reactions.

Since both intermolecular and intramolecular crosslinking reactions were present in benzoxazine polymer, an increase of the molecular weight was mainly caused by the intermolecular crosslinking. The slight decrease in the radius of gyration (R_g) and the hydrodynamic radius (R_h), as shown in Table 7.1, resulted from the intramolecular crosslinking reaction causing the collapse of a linear or branched polymer chain. Because there are some active groups, such as H^+ and OH^- in the chain [12,13]. The hydrodynamic radius of poly(BA-hda) was determined from the DLS method, also used to study the sol–gel transition of poly(BA-hda), as presented in Figures 7.5–7.6. The correlation functions were obtained from experiments at a scattering angle θ = 90° for various times (0–48 h). The intensity of correlation functions was increased with time and after 24 h, a good correlation function was achieved which showed a longer time tail, indicating a system closed to the sol-gel transition. The results were consistent with the study from Lin *et al.* [14]
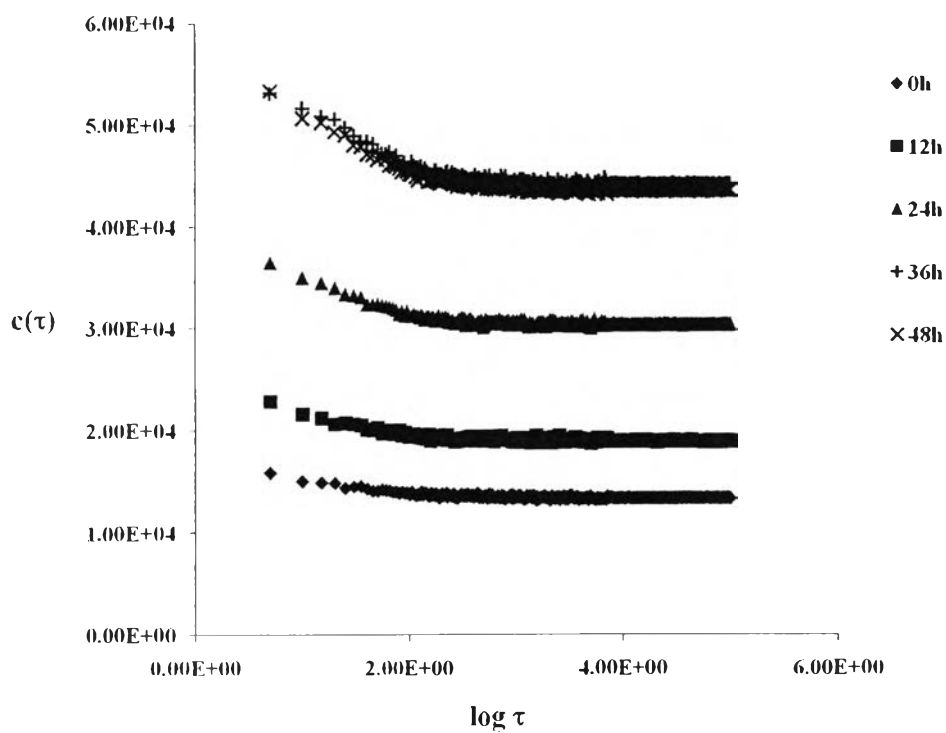
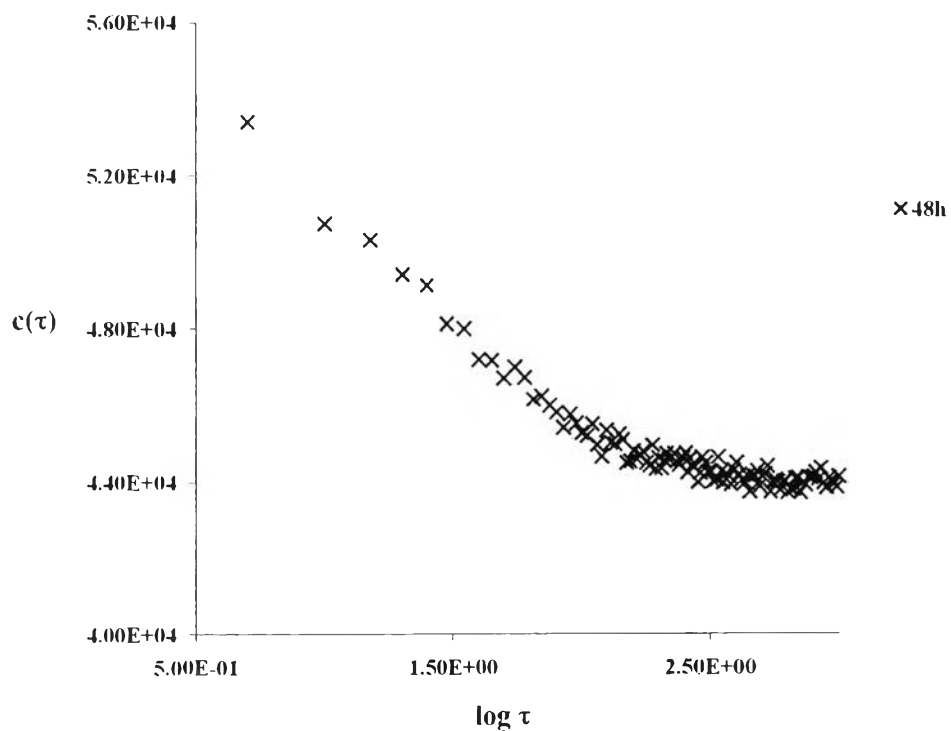**Figure 7.5** Correlation functions of poly(BA-hda) for various times.

Figure 7.6 Correlation function of poly(BA-hda) at 48 h.

7.5 Conclusions

Sol–gel transition of poly(BA-hda) was studied by static (SLS) and dynamic (DLS) light scatterings. Molecular weight, radius of gyration, and hydrodynamic radius with time were obtained. Molecular weight was increased with time due to intermolecular crosslinking reaction whereas radius of gyration and hydrodynamic radius were slightly decreased because of intramolecular crosslinking reaction.

7.6 Acknowledgements

7.7 References

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