CHAPTER 2: EXPERIMENTAL

2.1 Materials

Oleic acid (purity 99.5%) and glycerol (purity 99.5%) were supplied by Emery Oleochemicals Sdn. Bhd., a local palm oleochemicals manufacturer. Phthalic anhydride (PA) was purchased from P.T. Petrowidada Indonesia.

Methyl methacrylate monomer (MMA) , butyl acrylate (BA), benzoyl peroxide (BPO), ethanol (denatured ethanol 95%), methanol (99.5%), diethyl ether, potassium hydroxide, sodium hydroxide, potassium hydrogen phthalate (KHP), and phenolphthalein indicator were reagent grade chemicals from Merck, and they were used as received. Toluene (R&M chemical grade) was distillation before using.

BPO which was supplied with 25% moisture, was recrystallized from ethanol, followed by drying in a vacuum oven at 30°C and kept in the fridge before use.

2.2 Procedure of macromers synthesis

Three unsaturated macromers synthesized from 65, 40, and 28 wt% of oleic acid. They were formulated according to the procedure of Patton's gel point calculation [99] using a pre-weighed PA, oleic acid and glycerol. The formulations were shown in Table 2.1. The samples were labeled as AlkOA65 (long oil length), AlkOA40 (medium oil length) and AlkOA28 (short oil length).

Table 2.1 : Composition of oleic acid, PA and glycerol used in preparation of macromers

Compositions/properties	**Alk65OA**	**AlkOA40**	**AlkOA28**
Oleic Acid(g)	460	400	452
Phthalic Anhydride(g)	103	338	700
Glycerol (g)	145	256	456
Color	Light brownish	Brownish	Dark brownish
Estimated OH number (mg KOH/g macromer)	143.2	142.2	142.3

For each macromer, the required ingredients were charged into a 2-L four-neck round bottomed glass reactor equipped with a condenser, thermometer, mechanical stirrer and a Dean-Stark decanter for separating the water evolved during the reaction. The mixture was stirred and heated to 160-180°C for 1 h. The temperature was subsequently raised and maintained at 220-240°C when the reaction could carry on readily with evolving of water. The reactions were completed after the collected by product water of reaction was as predicted in the formulation. Progress of the polycondensation reaction, during the synthesis of macromer, was monitored by periodic checking of the acid number of the reflux mixture which was sampled from the reaction flask throughout period of the reaction. All three macromers were synthesized by using the same apparatus as shown in Figure 2.1.

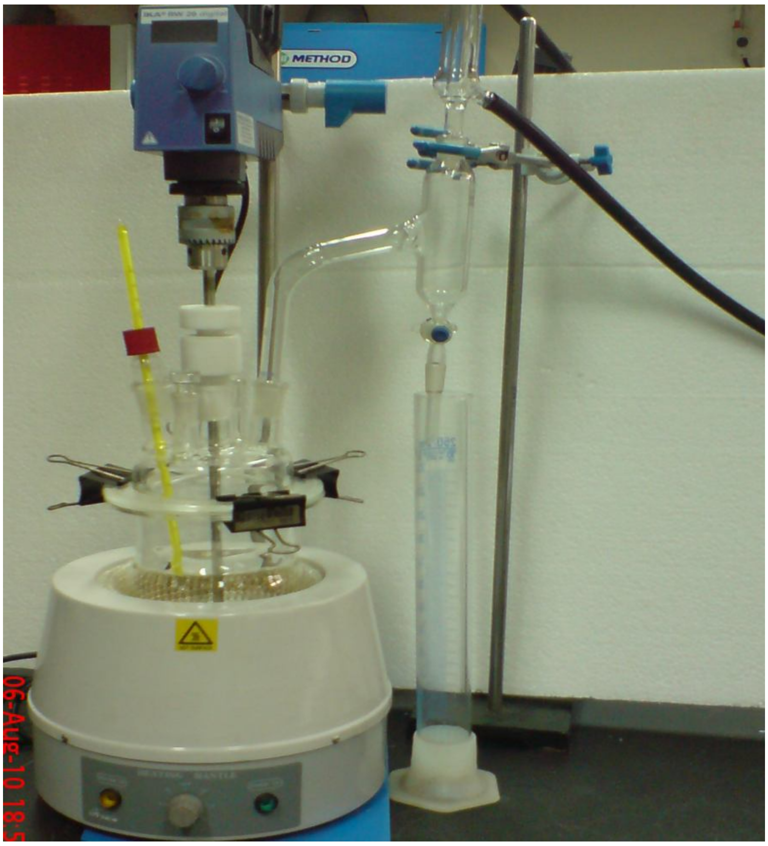

Figure 2.1 : Representation of set up used in polyesterification of macromers including reaction flask; Dean-Stark decanter; Condenser; Stirrer motor; Stainless steel rode of stirrer and Thermometer.

2.2.1 Procedure of determination of acid number

Progress of the macromers polycondensation reactions was monitored by periodically checking acid number, a procedure adapted from ASTM D1980-87. According to this test, the acid number is defined as number of milligrams of potassium hydroxide necessary to neutralize the free acidic groups in 1 g sample. To achieve this test, two stages are required. The initial stage is to prepare test reagents and standardization of the ethanolic KOH solution. The next stage is titration of the sample and the blank.

2.2.2 Standardization of potassium hydroxide

KOH solution used was prepared with concentration of 0.05 N. This solution was prepared by dissolving 2.8 g of KOH in 1000 mL of ethanol. The solution was then standardized by using KHP ($KHC_8H_4O_4$). Around 2 g KHP was dried in the oven at 110ºC for 2 h and was cooled in desiccators before use. About 0.5 g of KHP was weighed directly into a conical flask and 50 mL of distillate water and a few drops of 1.0% phenolphthalein indicator were added. The mixture was swirled until the salt has dissolved completely. It was then titrated with ethanolic potassium hydroxide solution (0.05 N) in a burette to the first appearance of a permanent pink colour. The pink colour must persist for at least 10 s. The normality of KOH solution was calculated as in equation [2.1]:

$$\text{Normality of KOH} = \frac{W_{KHP}}{0.2042 \times V_{KOH}} \qquad [2.1]$$

where, W_{KHP} is weight of potassium hydrogen phthalate and V_{KOH} refers to the volume of KOH solution used to neutralizing of KHP.

2.2.3 Sample and blank titration

About 3-4 g of sample (macromer) was taken from reaction flask and was weighed accurately into a conical flask followed by dissolving in 50 mL of solvent mixture which consists of ethanol and toluene in a ratio of 2:3 respectively. The mixture was swirled by stirrer slowly until the sample dissolved in the solvent. The blank solution was prepared by dissolving 0.5 mL of phenolphthalein indicator in 50 mL of the solvent mixture. The sample solution having 0.5 mL indicator and the blank solution were shaken while titrating separately with KOH solution in the burette to the end point of the indicator which was a permanent pink colour. The acid number was determined as following equation:

$$\text{Acid number} = \frac{56.1 \times N \times (V - V_b)}{W} \qquad [2.2]$$

where, N is the normality of KOH solution, V and V_b refer to the volumes of KOH solution necessary to titrating sample and blank, respectively.

2.2.4 Procedure of determination of hydroxyl number

The hydroxyl number was determined according to the standard test method as described under ASTM D4274-94, test method B. This test method measures the hydroxyl groups in the polyesters and polyols. According to this test method, the hydroxyl number is defined as number of milligrams of sodium hydroxide equivalent to the hydroxyl content in 1 g of sample.

This test method comprises of two reactions: in the first reaction, the hydroxyl groups in the alkyd are reacted with PA reagent to form ester and the next reaction is to neutralize the remained PA by using the standard sodium hydroxide solution. In order to achieve to these reactions, this test was carried out in two stages; the initial stage was to prepare test reagents and standardize the sodium hydroxide solution while next stage is to titrate the sample and blank.

2.2.5 Preparation of test reagents

The reagents necessary involved redistilled pyridine, PA reagent, phenolphthalein indicator solution and sodium hydroxide solution. The reagents referred above were prepared as follows:

1) Pyridine was redistilled by distilling pyridine from PA. The fraction with boiling point 114 to 115°C was collected and stored in a brown glass bottle.

2) For preparation of PA reagent, 115 g of PA was dissolved into a 700 mL of redistilled pyridine in a brown glass bottle and shook vigorously by using an orbital shaker until dissolved. The prepared reagent was left to stand overnight at room temperature before use. It must be discarded if it develops a colour.

3) A solution (1% w/v) of phenolphthalein indicator was prepared by dissolving 0.1 g of phenolphthalein in 10 mL of redistilled pyridine.

4) The sodium hydroxide solution was prepared by dissolving 10 g of NaOH in 500 mL of distilled water to achieve a standard solution with concentration of 0.5 N. Before use this solution must be standardized as follows:

About 10 g of KHP was dried in the oven at 110˚C for 2 h and was then placed in desiccators to cool down. About 4 to 5 g of dried KHP was weighed accurately and transferred into a 500 mL conical flask containing 200 mL of distilled water and was with nitrogen gas being flowed through for a few minutes to remove free carbon dioxide. After dissolving the sample, 4 drops of phenolphthalein indicator was added into the flask. The mixture was then titrated with 0.5 N NaOH solution in a burette to get a permanent pink colour. The normality of NaOH solution was calculated as follows:

$$\text{Normality of NaOH} = \frac{W_{KHP}}{0.2042 \times V_{NaOH}} \qquad [2.3]$$

where, W_{KHP} is the weight of KHP and V_{NaOH} refer to NaOH required for titration of the KHP.

2.2.6 Titration of sample and blank

Before sample titration, sample was placed in an oven at 110˚C for 2 h to eliminate excess water in the sample which can interrupt the esterification reagent during titration. The sample size required for the test was obtained as equation [2.4]:

$$\text{Sample size} = \frac{561}{\text{Estimated hydroxyl number}} \qquad [2.4]$$

The sample size obtained from the formula was dissolved in 25 mL PA reagent into a conical flask and was then closed with stopper. In order to prepare the blank solution, 25 mL PA reagent was transferred into conical flask which was closed by a stopper. The sample and blank solution were clamped in oil bath at 98-100˚C and left to heat for 2 h. After the flasks were removed from the oil bath to cooling down at room temperature, 50 mL of distilled pyridine and 0.5 mL of phenolphthalein indicator were added to both the sample and blank solutions. The solutions were then titrated with standardized NaOH solution in a burette to get the first appearance of permanent pink colour. Two important points to note: In the blank titration, 25 mL PA reagent should consume 95-100 mL of 0.5 N standard solution and the net titration (V_b-V) of the sample should be between 18-22 mL. If the titration results did not agree with these requirements, the sample and blank titrations need to be repeated by readjusting the sample size. The hydroxyl number of the sample was determined using following equation:

$$\text{Hydroxyl number} = \frac{56.1 \times N \times (V_b - V)}{W} \qquad [2.5]$$

where, V and V_b refer to the volume of NaOH required to titrate sample and blank, respectively, W is the amount the sample (sample size) and N refers the normality of the NaOH solution.

The average of the results was reported by double titration of sample and blank solutions.

2.3 Preparation of macromer-methyl methacrylate copolymers (MMC)

Copolymerization of macromer and MMA monomer was carried out in a four neck glass reactor equipped with a condenser, mechanical stirrer, digital thermometer and dropping funnel, as shown in Figure 2.2.

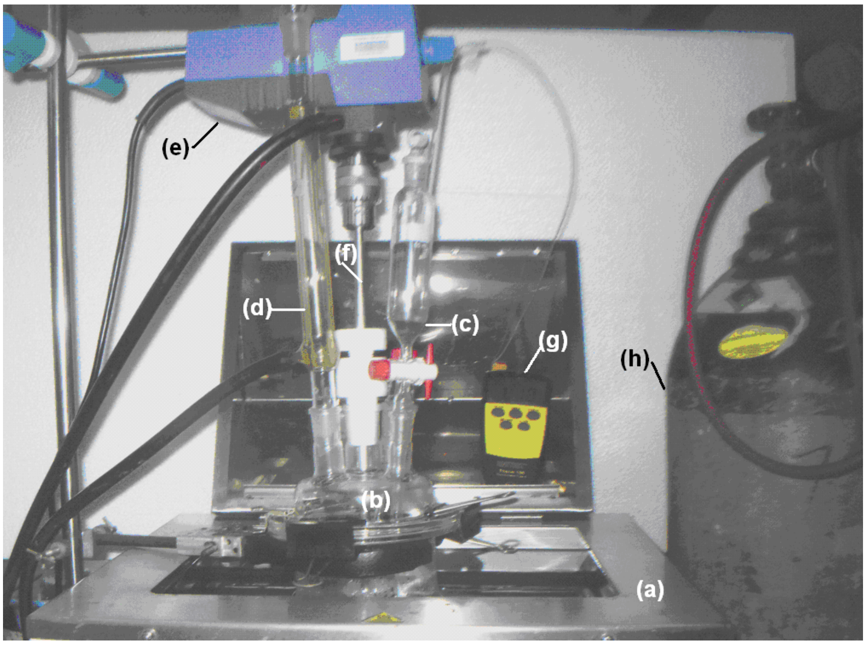

Figure 2.2 : Representation of apparatus set up for copolymerization of the macromer with MMA [(a) Oil bath; (b) reaction flask; (c) Dropping funnel; (d) Condenser; (e) Stirrer motor; (f) Stainless steel rod of stirrer; (g) Digital thermometer and (h) Nitrogen cylinder]

Initially the reactor was charged with known weight of macromer in 100 g toluene with the specified amount of MMA. The system was purged with nitrogen gas for 5 min, heated to 90°C and stirred at 250 rpm. The pre-weighed BPO initiator dissolved in 20 g toluene was introduced into the reactor through the dropping funnel within approximately 8 min. to start the reaction. The temperature was maintained at 95-100°C for 8 h. The effect of the AlkOA/MMA ratio on conversion was determined gravimetrically. As a control, PMMA homopolymer was synthesized under the same conditions. Resulting copolymers with different compositions from three different kinds of macromers were synthesized in the same manner and the same set up using MMA and macromer in three different ratios. The composition recipes and designation codes of the copolymers are tabulated in Table 2.2.

Table 2.2 : Composition recipes and designation codes of the copolymers

Macromer	Copolymer	AlkOA/MMA	AlkOA (g)	MMA(g)	BPO(g)	Toluene(g)
AlkOA65	AL1	50/50	30	30	3	120
	AL2	35/65	21	39	3	120
	AL3	20/80	12	48	3	120
AlkOA40	AM1	50/50	30	30	3	120
	AM2	35/65	21	39	3	120
	AM3	20/80	12	48	3	120
AlkOA28	AS1	50/50	30	30	3	120
	AS2	35/65	21	39	3	120
	AS3	20/80	12	48	3	120

2.4 The modification of copolymers using butyl acrylate (BA) monomer (MMBC)

The copolymers described in Section 2.3 were modified by incorporating a small amount of BA as a co-monomer. Copolymerization reaction was carried out using the same procedure and the same set up as in Section 2.3. Three series of acrylated macromers were prepared using MMA, three kinds of macromers and BA. (BA monomer was replaced with 10 wt.% of acrylate amount). In the case of AlkOA28 macromer, BA used was 5 wt.% and 10 wt.% of the acrylate proportion. During the copolymerization reaction, the percentage conversion was determined gravimetrically using the same procedure as in Section 2.3. The composition recipes and designation codes of the copolymers are summarized in Table 2.3.

Table 2.3 : Composition of modified copolymers using 5 wt.% and 10 wt.% BA

Macromer	Copolymer	AlkOA/Acrylate	AlkOA (g)	MMA (g)	BA (g)	BPO (g)	Toluene (g)
AlkOA65	AL1B	50/50	30	27.0	3.0	3	120
	AL2B	35/65	21	35.1	3.9	3	120
	AL3B	20/80	12	43.2	4.8	3	120
AlkOA40	AM1B	50/50	30	27.0	3.0	3	120
	AM2B	35/65	21	35.1	3.9	3	120
	AM3B	20/80	12	43.2	4.8	3	120
AlkOA28	AS1B (10%)	50/50	30	27.0	3.0	3	120
	AS2B (10%)	35/65	21	35.1	3.9	3	120
	AS3B (10%)	20/80	12	43.2	4.8	3	120
	AS1B (5%)	50/50	30	28.5	1.5	3	120
	AS2B (5%)	35/65	21	37.0	2.0	3	120
	AS3B (5%)	20/80	12	45.6	2.4	3	120

2.5 Conversion (%) of polymerization

During the copolymerization, the conversion (%) was determined gravimetrically. Aliquots of the sample were taken from the reaction mixture by a syringe at regular intervals of 35 min up to 8 h and subsequently weighted and dropped immediately into excess methanol to precipitate the copolymer. The copolymer was isolated by filtration and dried in oven at 60°C and weighed. The conversion (%) for each sample was calculated using following equation:

$$\text{Conversion (\%)} = \frac{\text{C}}{\text{A} \times \text{B}} \times 100 \qquad [2.6]$$

where, A = total weight of macromer and MMA per g of reaction mixture and B is weight of reaction mixture taken from the reactor at t time (min), and C refer to dried weight of copolymer obtained. The conversion here reflects the amount of the monomers (macromer and MMA) that has been converted to copolymer.

2.6 Solid content

In order to calculate solid content of copolymer sample, the final sample at the end of reaction was taken from the reactor and immediately weighed and the copolymer was isolated by precipitation in excess methanol. The precipitated copolymer was filtered and dried in the oven under 60˚C for 24 h. The dried sample was weighed again. The results were displayed as percentage of solid content. Solid content for each sample was calculated using equation [2.7].

$$\text{Solid content} = \frac{\text{Ds}}{\text{Fs}} \times 100 \qquad [2.7]$$

where, Fs and Ds refer to the weight of final sample taken from reactor at the end of the reaction and weight of the dried sample after precipitation in methanol respectively.

2.7 Solvent extraction

Diethyl ether was chosen as it is a good solvent for the macromers and bad solvent for the polyacrylate. About 5 g of product from the copolymerization reaction (before precipitate in the methanol) was put in the oven at 100°C for 2 h to dry and remove the solvent. The dried sample was then put into the soxhlet extractor apparatus with diethyl ether under continued reflux for 2 days at 35°C. Then remained sample was removed from the soxhlet extractor for characterization.

2.8 Swelling test

The extent of swelling of a copolymer sample by immersing in toluene was expressed as the percentage by weight of toluene that could be held by swollen gel of the copolymer. This test was carried out by copolymer sample which was dried in oven under 100˚C for 24 h. Pre-weighted sample was immersed in toluene and the state of swollen gel was periodically checked up to 6 h. The percentage of swelling was reported at sixth hour. For each sample two determinations were carried out.

2.9 Characterization methods

The prepared copolymer samples were characterized as described in the following parts.

2.9.1 Fourier Transform Infrared analysis (FTIR)

Infrared spectroscopy is an important analytical tool to identify and study the presence of functional groups in a molecule. Also, one can use absorption bands to recognize and verify a pure compound or specific impurities in a compound, typically from the functional groups and hydrogen bonding.

FTIR spectra were recorded on a Perkin Elmer FTIR RX1 spectrometer at room temperature, with 4 scans from 4000 to 400 cm^{-1} and resolution of 4 cm^{-1}. Background effects due to carbon dioxide, atmospheric water were subtracted. Thin liquid film of the macromer was cast directly on the sodium chloride cell for recording its spectrum. In the case of copolymers, a small sample was first dissolved in a minimum amount of toluene and a thin layer of the viscous solution was spread onto the sodium chloride cell. The solvent was removed by blowing with hot air.

2.9.2 Nuclear Magnetic Resonance (^{1}H-NMR and ^{13}C-NMR))

Nuclear Magnetic Resonance is a powerful non-selective analytical tool that allows molecular structure characterization including relative configuration, relative and absolute concentrations, and even intermolecular interactions.

Sample was dissolved in deuterated chloroform at concentration of around 10 mg mL^{-1} for ^{1}H-NMR and 100 mg mL^{-1} for ^{13}C-NMR. The ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a JNM–GSX270 Fourier Transform Spectrometer operating at 270 MHz. The chemical shifts were referenced against TMS as 0 ppm, and the deuterated solvent; chloroform-d$_1$ ($CDCl_3$) showed a typical peak at δ value of 7.26 ppm for ^{1}H-NMR and 77 ppm for ^{13}C-NMR due to trace $CHCl_3$ in the deuterated solvent.

2.9.3 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry is a powerful analytical technique that allows determination glass transition temperature (T_g). T_g is defined as a change in the heat capacity as the polymer matrix pass from the glass state to the rubber state. In other words, the T_g is the softening region of a plastic. In fact, it refers to the amorphous region of semicrystalline materials or to amorphous materials whereby the materials becomes flexible as it is heated due to the molecular motion. When a material is heated to this point and beyond, molecular motion around single bonds suddenly becomes significantly easier.

The glass transition demonstrates a thermodynamic second-order transition because at the T_g there is a heat capacity jump, but this increment of the heat capacity take places in a range of temperature not at a definite temperature [100]. In DSC, T_g is represented graphically in the thermal curve as a shift in the baseline. A quite amorphous polymer does not exhibit crystallization temperature (T_c) or melting point (T_m). Figure 2.3 shows the diagram of DSC instrument parts with two pans, sample pan and the other is reference pan (empty).

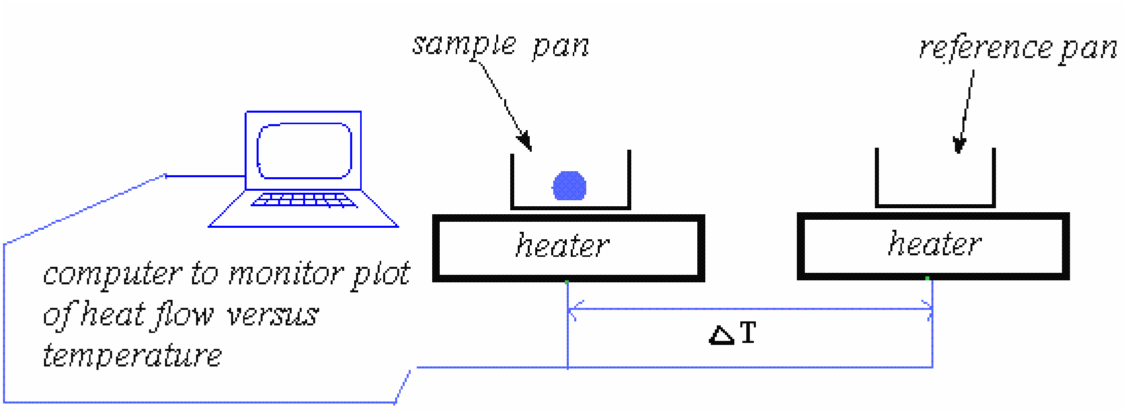

Figure 2.3 : Simple diagram of DSC instrument

Each pan is placed on top of a heater. The heating rate is exactly the same for two pans throughout the experiment. The extra material in sample pan means that it will absorb more heat to keep the temperature of the sample pan increasing at the same rate as the reference pan.

In a DSC plot, y-axis discloses difference in heat output of the two heaters at a given temperature and x-axis exhibits temperature. After a certain temperature, the plot will shift to a higher level rapidly. This means the polymer is sample gets more heat flow and subsequently reveals an increase in the heat capacity of polymer. Total heat needed to take a certain temperature is the heat capacity (C_p).

DSC thermograms in nitrogen atmosphere were obtained with a Perkin Elmer Pyris 6 DSC analyser calibrated with Indium at a scan rate of 5°C min^{-1} in a temperature range of 35 to 190°C. An Intercooler 2P cooling system was used for samples having sub-ambient T_g, and measurement was made from -50°C to 120°C at scan rate of 5°C min^{-1} under nitrogen atmosphere. For the macromers about 3-4 mg and for copolymers about 8-10 mg of samples were weighed and encapsulated in a standard aluminum sample pans. The same empty pan was utilized as a reference. The first scan was to remove the thermal history of the sample. Thermal data were acquired based on the second heating run.

2.9.4 Thermogravimetry analysis (TGA)

Thermogravimetry analysis (TGA) is used primarily for determining thermal stability of substance as a technique defines that weight change of material heated at a controlled rate recorded as a function of temperature or time on a thermobalance (a sensitive balance) as sample temperature is increased in an inert atmosphere or in air. Such analysis is based on a high degree of accuracy in three measurements: weight, temperature, and temperature change. Data are recorded as thermogram of weight versus temperature referred to as the thermogravimetry TG curve and a plot of the weight loss against temperature which is referred as derivative thermogravimetric curve or DTG. As many weight loss curves look similar, a derivative weight loss curve can be used to tell the point at which weight loss is most apparent. This is known as non-isothermal TGA. The non-isothermal technique should be used when the degradation temperature is unknown [101].

Thermal stability studies are the major application of TGA; however TGA is capable to determine compositional analysis of materials, decomposition temperatures, activation energy and oxidative stability as well. Weight loss may result from evaporation of residual moisture, component or solvent, but at higher temperatures it results from polymer decomposition. Isothermal TGA technique is to record weight loss with time at a constant temperature.

In this study thermal stability of macromers and synthesized copolymers were studied using a Perkin Elmer Pyris 6 system under a steady flow of nitrogen atmosphere 20 mL min^{-1} at a heating rate of 10°C min^{-1} from 30 to 900°C. The sample weight used was between 16 and 17 mg.

2.9.5 Gel-permeation chromatography (GPC)

Determination of molecular weight and its molecular weight distribution, MWD (M_w/M_n), is one of the basic characteristics of polymers. These two characteristics have influences on thermal stability and other properties of polymer. Therefore, measurements of the molecular weight and MWD are extremely important in estimating the quality of raw materials and products, analysing quality in production processes. Also, since a polymer is a mixture of different molecules in molecular weight, the value of a measurement obtained by such methods is a statistical mean value assuming the polymer to be of a single molecular composition [102].

GPC uses porous particles to separate molecules of different sizes. Molecules larger than the pore size can not enter the holes and elute together as the first peak in the chromatogram. Molecules that can enter the pores will have an average residence time in the particles that depends on the size and shape of the molecules. Different molecules therefore have different total transit times through the column. This portion of a chromatogram is called the selective permeation region. Molecules that are smaller than the pore size can enter all pores, and have the longest residence time on the column and elute together as the last peak in the chromatogram. This last peak in the chromatogram determines the total permeation limit. Thus, if the same average molecular weight is shown for two samples, the MWD between them may be very different, and the polymers may then represent different properties. Therefore, determination of molecular weight by GPC is a useful method for better understanding of the true nature of a polymer.

The MWD of the macromer and its copolymers were determined with the GPC setup consisting of a Water 600 controller, Water 717 Auto sampler, and Water 2414 Refractive Index detector. Tetrahydrofuran (THF) was used as eluent at a flow rate of 1 mL min^{-1}. The calibration of the GPC column was performed with monodispersed polystyrene (PS) standards. Sample was dissolved in THF at around 2 mg mL^{-1}.

2.9.6 Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis, an important technique in the modern polymer laboratory, is used to study and characterize materials. This method provides information about the viscoelastic behaviour and mechanical properties of sample under sinusoidal, oscillating force as a function of temperature and time. A sinusoidal stress is applied and a corresponding strain (deformation) in the material is measured, allowing one to determine the modulus.

The analytical parameters in dynamic mechanical tests are the amplitudes of the deformation, stress and the time displacement between deformation and stress. All these parameter are used to determine the sample characteristics.

The storage modulus E' depicts the stiffness of a viscoelastic material and is proportional to the energy stored during a loading cycle. The loss modulus E'' is defined as being proportional to the energy dissipated during one loading cycle. It shows energy lost as heat, and is a measure of vibration energy that has converted during vibration and that cannot be recovered [103]. Modulus values are expressed in MPa. The phase angle δ is the phase difference between the dynamic stress and the dynamic strain in a viscoelastic material exposed to a sinusoidal oscillation. The loss factor tan δ is the ratio of loss modulus to storage modulus. It is a measure of the energy lost, expressed in terms of the recoverable energy and shows mechanical damping or internal friction in a viscoelastic system.

The loss factor is depicted as dimensionless number. A high tan δ value is indicative of a material that has a high, non elastic strain component, while a low value indicates one that is more elastic. According to the above definitions for the sinusoidal stress and the corresponding strain response, the phase angle δ can be expressed as following:

$$\tan \delta = E''/E'$$

The dynamic mechanical behaviour of the copolymer samples was determined using DMA (TA instrument DMA Q800) in liquid nitrogen. The tests were run with oscillation frequency of 1 Hz and in the dual cantilever mode with a rectangular powder clamp (12.78 mm×3.19 mm×35 mm). Analyses were carried out at heating rate of 3°C min^{-1} from -60°C to 110°C and the strain amplitude was 15 μm. It should be noted that samples AL1 and AL1B were run up to 75°C because these two samples were too sticky and may damage the clamp.