CHAPTER 2

EXPERIMENTAL

2-EXPERIMENTAL

2.1. MATERIALS

The chemical structures, as well as the physicochemical properties of the materials used to prepare and characterize the oil sorbers in this work are as follow:

2.1.1. Monomeric Compounds

- **Cinnamoyl chloride**

$$C_6H_5CH=CHCOCl$$

It is obtained from Aldrich Chemical Co. with the following specifications:

Density g/cm^3	:	1.028
M.Wt.	:	166.61
m.p, °C	:	35-37
b.p, °C	:	256-258

- **Isooctyl acrylate (IOA)**

$$H_2C=CH\ COO\ (CH_2)_5CH\text{-}(CH_3)_2$$

It is obtained from Aldrich Chemical Co. with the following specifications:

Density g/cm^3	:	0.880
M.Wt.	:	184.25
b.p, °C	:	125 /20mm.Hg

- **Dodecyl acrylate (DDA)**

$$H_2C=CH\ COO(CH_2)_{11}CH_3$$

It is obtained from Aldrich Chemical Co. with the following specifications:

Density g/cm^3	:	0.884
M.Wt.	:	240.39
m.p, °C	:	-6
b.p, °C	:	314

• **Octadecyl acrylate (ODA)**

$$H_2C{=}CH\ COO(CH_2)_{17}CH_3$$

It is obtained from Aldrich Chemical Co. with the following specifications:

Density g/cm^3	:	0.800
M.Wt.	:	324.55
m.p, °C	:	32-34

• **Ethylene glycol (EG)**

$$HO\text{-}CH_2CH_2OH$$

It is obtained from Aldrich Chemical Co. with the following specifications:

Density g/cm^3	:	1.189
M.Wt.	:	62.07
m.p, °C	:	-13
b.p, °C	:	196-198

• **Diethylene glycol (DEG)**

$$H\text{-}(O\text{-}CH_2CH_2)_2OH$$

It is obtained from Aldrich Chemical Co. with the following specifications:

Density g/cm^3	:	1.118
M.Wt.	:	106.12
m.p, °C	:	-10
b.p, °C	:	245

• **Triethylene glycol (TEG)**

$$H\text{-}(O\text{-}CH_2CH_2)_3OH$$

It is obtained from Aldrich Chemical Co. with the following specifications:

Density g/cm^3	:	1.125
M.Wt.	:	150.17
m.p, °C	:	-7
b.p, °C	:	285

• **Tetraethylene glycol (TeEG)**

$H-(O-CH_2CH_2)_4OH$

It is obtained from Aldrich Chemical Co. with the following specifications:

Density g/cm^3	:	1.125
M.Wt.	:	194.23
m.p, °C	:	-6
b.p, °C	:	314

• **Polyethylene glycol$_{400}$ (PEG_{400})**

$H-(O-CH_2CH_2)_9OH$

It is obtained from Aldrich Chemical Co. with the following specifications:

Density g/cm^3	:	1.127
M.Wt.	:	400
m.p, °C	:	-6

• **2-hydroxyethyl methacrylate (HEMA)**

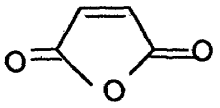
$CH_2=C(CH_3)-COO-CH_2-CH_2-OH$

It is purchased from Aldrich Chemical Co. with the following specification:

Density g/cm^3	:	1.073
M.Wt.	:	130.14
m.p, °C	:	-
b.p, °C	:	67/3.5mmHg

HEMA was purified by washing with 5% aqueous sodium hydroxide, dried over anhydrous $CaCl_2$ and distilled under vacuum.

• **Maleic anhydride (MA)**



It is produced from B.D.H. CO. Ltd.(U.K.) with the following specifications:

M.Wt. : 98.06

m.p, °C : 54-56

b.p, °C : 200

2.1.2. Polymeric Compound

- Polyisobutylene$_{1000}$

$$[-CH_2-C(CH_3)_2-]_{23}$$

It is pruchased from B.D.H. CO. Ltd.(U.K.) with the following specifications:

Density g/cm^3 : 0.920

M.Wt. : 1000

2.1.3. Crosslinking Agents

a- 1,1,1-Trimethylolpropane trimethacrylate (TPT$_m$)

$$CH_3-CH_2-C[CH_2-O-CO-C(CH_3)=CH_2]_3$$

It is obtained from Aldrich Chemical CO. Ltd.(U.K.) with the following specifications:

Density g/cm^3 : 1.06

M.Wt. : 338.4

b- 1,1,1-Trimethylolpropane triacrylate (TPT)

$$CH_3\text{-}CH_2\text{-}C[CH_2\text{-}O\text{-}CO\text{-}CH{=}CH_2]_3$$

It is obtained from Aldrich Chemical CO. Ltd.(U.K.) with the following specifications:

Density g/cm^3 : 1.10

M.Wt. : 296.32

2.1.4. Thermal Initiators

a- Benzoyl Beroxide (BPO)

$$(C_6H_5CO)_2O_2$$

It is purchased from Aldrich Chemical CO. Ltd.(U.K.) with the following specifications:

M.Wt. : 242.23

m.p, °C : 104-106

b- 2,2`azobisisobutyronitrile (AIBN)

$$(CH_3)_2C(CN)\text{-}N{=}N\text{-}C(CH_3)_2CN$$

It is obtained from Aldrich Chemical CO. Ltd.(U.K.) with the following specifications:

M.Wt. : 164.21

m.p, °C : 103-105

ABIN, recrystallized from ethanol was used as a thermal polymerization initiator.

2.1.5. Solvents

Methyl ethyl ketone, chloroform, acetone, triethyl amine (TEA) and toluene were obtained from Aldrich Chem. Co., Germany. Tetrahydrofuran was obtained from Adweic Chem. Co., Egypt.

Petroleum crude oil was obtained from PETROBEL, Egypt with specifications listed in **Table (2.1).**

Table(2.1): Physicochemical Properties of the Used Petroleum Crude Oil.

Test	Method	Value
Specific gravity at 60 F	IP 160/87	0.875
API gravity	Calculated	21.70
Pour Point (°C)	IP 15/67(86)	14.00
Kinematic Viscosity (60F) (Cst)	IP 71	762.8
Wax content (wt%)	UOP 46/64	2.45
Asphaltene content (wt%)	IP 143/84	8.80

2.2. PREPARATION OF LINEAR AND CROSSLINKED COPOLYMERS

2.2.1 Synthesis of cinnamoyloxyethyl methacrylate monomer (CEMA)

The reaction was carried out in four neckd reaction flask fitted with mechanical stirrer, reflux condenser, thermometer and dropping funnel. The reaction flask is represented in **Figure (2.1)**. A solution of 66 mmol of HEMA and 66 mmol of TEA was refluxed in 100 THF for 2h in absence of air or moisture, and then the clear solution was cooled to 0 °C in an ice bath. Then, 79 mmol of cinnamoyl chloride was added dropwisely with vigorous stirring for 2h at 0°c and for 4h at room temperature. The formed triethylamine hydrochloride salt was filtered out and the filtrate was concentrated on a rotary evaporator. The concentrated solution was slowly added to 500 ml of n-hexane. The precipitate was filtered out and the solvent was distilled off using cuprous chloride to inhibit polymerization.

2.2.2. Low Conversion Copolymerization (Synthesis of Linear Acrylates Copolymers).

The detailed procedures to synthesize linear CEMA/IOA, CEMA/DDA or CEMA/ODA copolymers are described as follows: A mixture of IOA, DDA or ODA and CEMA with different monomer feed ratios [mole % CEMA / mole % acrylate) viz, 90/10, 70/30, 50/50, 30/70 and 10/90]was dissolved in 100 ml toluene and the solution was poured into a round-bottom flask under N_2 atmosphere. The monomers were mixed together with ABIN initiator 0.02 %(w/w). The solution was then heated to 70 °C. until≈10 % of low conversion copolymerization was obtained. The products were poured into excess methanol with stirring.

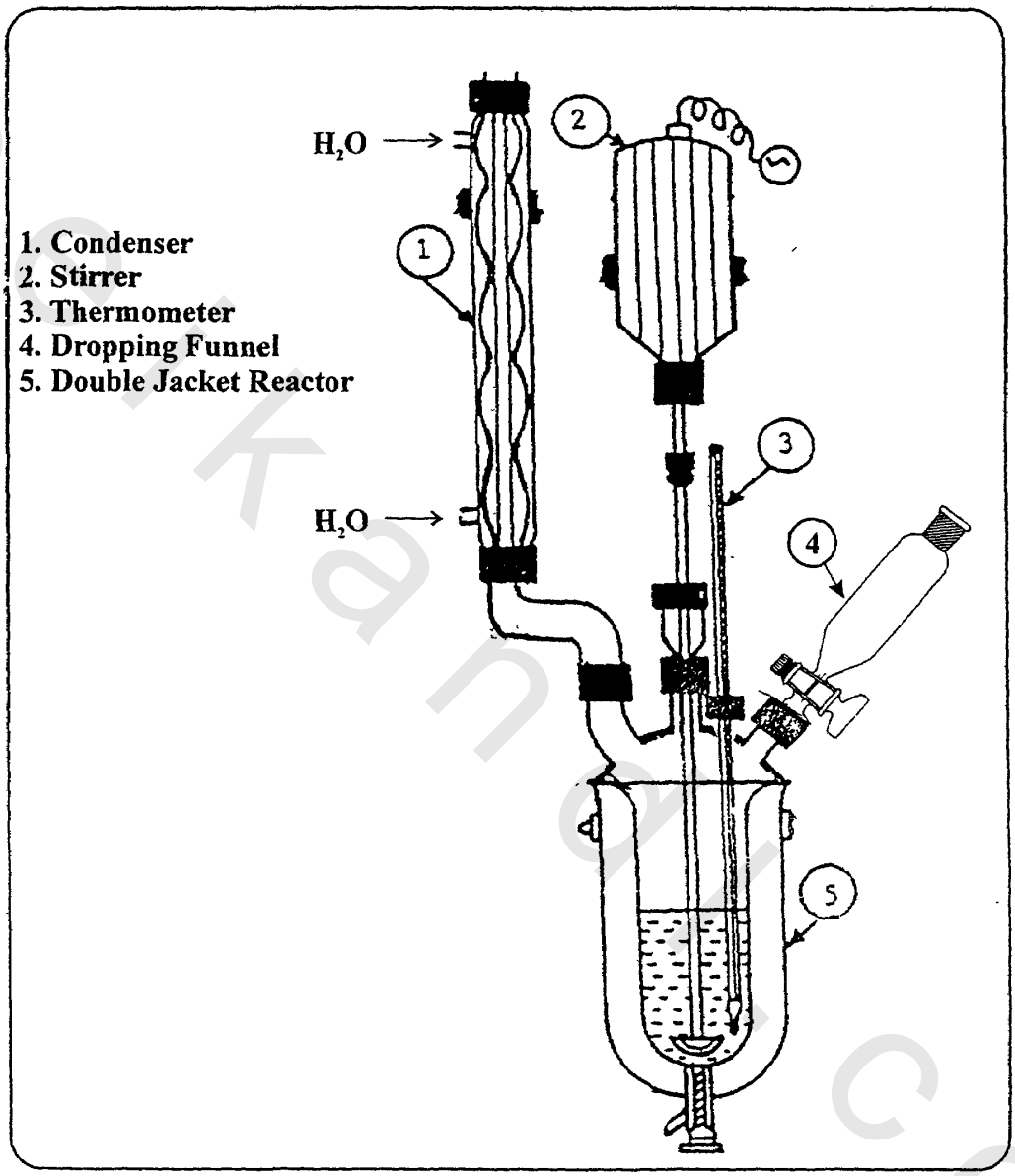


Figure (2.1): Diagrammatic Sketch for the Kettle used for Esterification Reactions.

The obtained precipitate was filtered and dried in vacuum at 30 °C to a constant weight .

The time required for low conversion was estimated by monitoring the weight of the linear copolymer precipitated in excess methanol after different time intervals.

2.2.3. High Conversion Copolymerization (Synthesis of Crosslinked Acrylates Copolymers).

The crosslinked copolymers of CEMA/IOA, CEMA/DDA and CEMA/ODA were performed through bulk polymerization. The monomers were mixed together with ABIN initiator 0.02 %(w/w), and different weight ratios of TPT or TPT_m crosslinker ranging from 0-4%(w/w) and the mixture were bubbled with nitrogen. This procedure was repeated with different monomer feed ratios (mol % CEMA / mol% acrylate) viz. 90/10, 70/30, 50/50, 30/70 and 10/90 to prepare different compositions of crosslinked copolymers. The copolymerization reactions were performed in siliconized test tubes at 333K for 3h. The time of reaction was extended to assure complete reaction of all monomers. The constituents of the synthesized crosslinked copolymers are listed in **Table (2.2).**

The test tubes were thoroughly cleaned and completely dried. The internal surface was rendered hydrophopic by prior siliconisation using dimethyldichlorosilane(DDS). About $1\mu m^3$ from a solution of 2% DDS in1,1,1-trichloroethane was syringed into each of the clean test tubes and spread allover the internal surface. The surplus of solution was poured off leaving a thin film. The tubes were then left in the oven for

Table(2.2): Constituents of the Prepared CEMA/ Acrylate Crosslinked Copolymers.

Systematic name of the copolymer	Designation	Compositions (mole%)		Crosslinker content(wt%)	
		CEMA	Alkyl acrylate	TPT	TPT_m
Cinnamoyloxy ethyle methacrylate-isooctyl acrylate copolymers	CEMA / IOA	90	10	1	1
		70	30	1	1
		50	50	0.5	0.5
				1	1
				2	2
				4	4
		30	70	1	1
		10	90	1	1
Cinnamoyloxy ethyle methacrylate-dodecyl acrylate copolymers	CEMA / DDA	90	10	1	1
		70	30	1	1
		50	50	0.5	0.5
				1	1
				2	2
				4	4
		30	70	1	1
		10	90	1	1
Cinnamoyloxy ethyle methacrylate-octadecyl acrylate copolymers	CEMA/ ODA	90	10	1	1
		70	30	1	1
		50	50	0.5	0.5
				1	1
				2	2
				4	4
		30	70	1	1
		10	90	1	1

at least four hours at 343K. The ampules were then rinsed with water to remove any traces of HCl and dried in an air oven at 308K. This treatment of the internal surface of the test tubes allows an easy dislodge the polymerized rods.

The crosslinked copolymer rods were post cured at 378K in air oven. The rods were cut to thin discs that were used for determining the soluble fraction (SF) and swelling parameters.

2.3. SYNTHESIS OF CROSSLINKED REACTIVE POLYMERS

2. 3.1- Synthesis of cinnamate esters

The reaction were carried out in the reaction flask as represented in **Figure (2.1)**. Cinnamoyl chloride (1 mole) is reacted with 2 moles of each of five different glycols namely, ethylene glycol, diethylen glycol, triethylene glycol, tetraethylene glycol and polyethylene glycol 400 to produce five different compounds of hydroxy alkyloxy cinnamate. The reactions were carried out by adding 1 mole of cinnamoyl chloride dropwise at temperature below 25 °C to 2 moles of the individual glycol in presence of pyridine as a catalyst for 1 hour.

The reaction was continued for another 1 hour at 25 °C. Then, the reaction mixture was poured into water to dissolve the formed pyridinium salt. The products were extracted by adding the chloroform. The chloroform layer was washed with water diluted with sulfuric acide H_2SO_4, and aqueous magnesium sulfate to remove any unreacted materials. Chloroform was then removed by distillation under reduced pressure in a rotary evaporator. The designation and constitution of the prepared cinnamate esters are listed in **Table (2.3)**.

Table (2.3): Designation and Constitution of the Prepared Cinnamate esters.

Systematic name	Glycols	acid chloride	Abbreviation
hydroxyethyl Cinnamate	Ethylene glycol	Cinnamoyl chloride	CM_1
hydroxy butyloxy Cinnamate	Diehylene glycol	Cinnamoyl chloride	CM_2
hydroxy hexyloxy Cinnamate	Triethylene glycol	Cinnamoyl chloride	CM_3
hydroxy octyloxy Cinnamate	Tetraethylene glycol	Cinnamoyl chloride	CM_4
hydroxy octadecyloxy Cinnamate	Polyethylene glycol 400	Cinnamoyl chloride	CM_9

2.3.2. Synthesis of Maleic Anhydride/Polyisobutylene Adduct (PIB-MA)

Polyisobutene (1 mol), having an average molecular weight of 1000, was placed in a three-neck flask equipped with thermometer, mechanical stirrer, and reflux condenser, was heated from 200 to 240°C and maleic anhydride (2 mols) was added in small amounts over the course of 6 h in such a way that the temperature was maintained without further heating. The mixture was diluted with hexane and poured in excess methyl ethyl ketone. The polyisobutenylsuccinic anhydrides were obtained as a colorless oil. Reaction yielded nearly 90% polyisobutenylsuccinic anhydride.

The product was filtered out by decantation and subjected to spectral analysis and stored in refrigerator.

2.3.3. Reaction of Cinnamate Ester Monomers With PIB-MA Adduct

To 1 mole. dm^{-3} pyridine solution of PIB-MA adduct, two mole of individual cinnamate ester were added. The reaction was carried out at 75°C for 21 hour. The resulting mixture was poured in excess acetone to extract the products. The products were stored under nitrogen atmosphere in a refrigerator.

The product was designed as **PIB-MA-CM_1, PIB-MA-CM_2, PIB-MA-CM_3, PIB-MA-CM_4 and PIB-MA-CM_9** and used to prepare crosslinked polymers when reacts with acrylate monomers.

2.3.4. Synthesis of Crosslinked PIB-MA-CM_n /ODA Copolymers

Copolymerization and crosslinking of each **(PIB-MA-CM)** polymer and ODA monomer were performed through bulk polymerization. The

monomers were mixed together with benzoyl peroxide initiator 0.02 %(w/w), cobalt octoate as activator. 0.02%, different weight ratio of TPT crosslinker ranging from 1 to 4%(w/w) and the mixture was bubbled with nitrogen. The copolymerization reactions were performed in siliconized test tubes at 333K for 1.5h and the crosslinked copolymer rods were post cured at 378K in air oven. The rods were cut to thin discs that were used for determining the soluble fraction (SF) and swelling parameters.

2.4. CHARACTERIZATION OF THE PREPARED COPOLYMERS

2.4.1. FTIR spectroscopy

Some of the prepared oil sorbers were analyzed by using FTIR (Mattson-infinity series bench tab 961) as aspectroscopic technique for elucidating the structure.

2.4.2. ^{1}HNMR Spectroscopy

The prepared copolymers were analyzed using ^{1}HNMR spectrometer as another spectroscopic technique for determining the chemical structure. Also, the compositions of the prepared linear CEMA/ acrylate copolymers were established by calculating reactivity ratio from ^{1}HNMR spectroscopy data. All ^{1}HNMR spectra were obtained at 300 MHz on a Varion NMR 300 spectrometer (Jeol NMR spectrometer model JNM-EX) using $CDCl_3$ as a solvent and TMS as an internal reference.

2.5. EVALUATION OF CROSSLINKED POLYMERS

2.5.1. Extraction of Soluble Fraction Materials (SF)

The polymer rods were post cured at 378K in an air oven for 24 hours to ansure complete polymerization. These rods were cut to thin discs and exhaustively dried in vacuum at 308K to a constant weight. The soluble fractions of these polymeric materials were determined via Soxhlet extraction technique. In this respect, the dried xerogel discs were transferred into an extraction thimble and were subjected to Soxhlet extraction with chloroform. Normally three or four discs were used per soxhlet. A preliminary test was performed to establish the required time for complete extraction of the soluble fractions. Based on this test, 24 hr of extraction time was adopted for all samples. After extraction, the samples were dried in the atmospheric pressure for several hours and then dried to a constant weight in vacuum oven at 308K.

The soluble fraction (SF) was expressed as the fractional loss in weight of xerogel **[Atta, 2002 and Atta and arndt, 2003]**. SF values were calculated according to the following equation

$$SF\ \% = ((W_0 - W)\ X\ 100/\ W_0) \qquad \textbf{(2.1)}$$

where W_0 and W are the weight of discs before and after extraction respectively

2.5.2. Oil Absorption Test

Oil absorbency of synthesized crosslinked copolymers with either TPT or TPT_m were determined at different temperatures, viz., 298, 303, 308 and 313K through ASTM (F726-81): 0.1g polymer was put in a pure stainless steel mesh (4x4x2 cm) that had been immersed in pure

toluene or with crude oil diluted with toluene, 10% oil, and weighted beforehand. The sample and the mesh were together picked up from oil, drained for 30 s, tapped with filter paper to remove excess oil from the bottom of the mesh, and then weighed on a balance. The oil absorbency (Q) and equilibrium toluene content (ETC) were calculated by following equations:

$$Q\ (g/g) = \frac{\text{weight of absorbed oil in sample}}{\text{weight of sample before oil absorbency}} \quad (2.2)$$

$$ETC\ \% = ((\text{wt of gel} - \text{wt. of xergel})/\ \text{wt. of gel}) \times 100 \quad (2.3)$$

The volume fraction of polymer within a xerogel (Φp) is given, at a particular temperature, by:

$$\Phi_p = (Do/D)^3 \quad (2.4)$$

Where, Do and D are the diameters of dry and swollen discs, respectively. Do was measured at 298 K with a micrometer. Values of D were obtained at different temperatures within the range 298-313K. Φ_p can also be calculated on the basis of Q measurements where $\Phi_p = 1/Q$ when the crosslinking polymerization of homopolymers and copolymers were carried out in bulk or in absence of organic solvents.

2.5.3. Swelling Kinetics of Oil Absorption

The swelling kinetics of oil absorption was studied by repeating the previous measurements at different time intervals. The swelling parameters, Q and ETC, of the prepared gels were calculated from five repeated measurements. Also, the maximum oil absorbency was determined by allowing the tests to stand for 24h. To study the kinetics

of swelling, gel samples in triplicate, were immersed in crude oil. After equilibration-swollen gel samples were placed into oven at 318 °K for 12 h, for gels deswelling. The deswelling was then followed by weighing the gel at various times to constant weight. The reversibility of swelling and deswelling was determined using the same samples for consecutive swelling and deswelling experiments.

2.5.4. Network Parameters of Gels

Network parameters of crosslinked polymers include the theoretical crosslink density ν_t, Flory-Huggins type interaction parameter χ, effective crosslink density ν_e, and molar mass between crosslinks (M_c). From the temperature dependence of transport coefficients, attempts were made to predict the activation parameters, Flory-Huggins type interaction parameter (χ) and molar mass between crosslinks (M_c) of the polymer and effective crosslink density υ_e of the polymer. Also, the theoretical crosslink density ν_t has been calculated from:

$$\nu_t = Cf/2 \qquad (2.5)$$

where, C (mol dm^{-3}) is the concentration of crosslinking agent of functionality f. For TPT and TPT_m, f = 6. The value of C was determined from the weight concentration of TPT and TPT_m and the density ρ of the xerogel. The latter was determined by direct weighing and micrometrically measured dimensions of the dried discs and pellets used.

The Flory-Rehner swelling mode[**Flory and Rehner 1943, Flory, 1950, Flory, 1953**] has been used in the literature to predict the molar mass between crosslinks (M_c). This needs accurate values of Flory-Huggins type interaction parameter χ. Several researchers [**Takahashi, 1983, Gupta et al., 1987, Bristow and Watson 1987**] have attempted

to compute it from the solubility parameter concept as developed by Hildebrand **[Hildebrand, 1962]**. This approach being strictly empirical which sometimes leads to wrong predictions for χ. Also, for some penetrants it would be cumbersome to find reliable literature **[Crank, 1975]** solubility parameters data of solvents. Instead, we suggest using an alternative phenomenological theory to calculate χ. Thus, starting from the Flory-Rehner equation **[Flory and Rehner 1943, Flory, 1950 and Flory, 1953]**, the temperature coefficient of volume fraction ($d\Phi_p/dT$) may be obtained as:

$$(d\Phi_p/d\,T) = \chi\Phi_p\,T^{-1}\{2\Phi_p\chi - \Phi p(1 - \Phi_p) - [\ln(1 - \Phi_p) + \Phi_p + \chi\Phi_p^2]N\}^{-1} \quad \textbf{(2.6)}$$

where,

$$\mathbf{N = (1/3\,\Phi_p^{2/3} - 2/3)(\Phi_p^{1/3} - 2/3\,\Phi_p)^{-1}} \quad \textbf{(2.7)}$$

Solving equation (2.6) we get the value of χ as follow:

$$\chi = [\Phi_p(1 - \Phi_p)^{-1} + N\ln(1 - \Phi_p) + N\Phi_p] \times [2\,\Phi_p - \Phi_p^{2}N - \Phi_p^{2}T^{-1}(d\,\Phi_p/dT)^{-1}]^{-1} \quad \textbf{(2.8)}$$

The molar mass between crosslinks can then be estimated as :

$$M_c = -\rho_p\,v_s\,\Phi_p^{1/3}[\ln(1 - \Phi_p) + \Phi_p + \chi\,\Phi_p^{2}]^{-1} \quad \textbf{(2.9)}$$

Where, v_s is the molar volume of solvent, ρ_p is the density of polymer. The υ_e was calculated from equation (2.11) **[Flory, 1953]**:

$$ln(1 - \Phi_p) + \Phi_p + \chi\,\Phi_p^{2} + \nu_e\,v_s\,(\Phi_p^{1/3} - 2\,\Phi_p\,f^{-1}) = 0 \quad \textbf{(2.10)}$$

where v_s (mol dm^3) is the molar volume of toluene at different temperatures T and obtained from :

$$v_s = 10^{-3}[\text{MWt of toluene} + 3.6 \times 10^{-3}\,(T - 298)] \quad \textbf{(2.11)}$$

Determination of χ thus allowed the effective crosslinking density (υ_e) to be evaluated, thereby yielding the molar mass between crosslinks (Mc) via:

$$M_c = \rho_p/\nu_e \quad \textbf{(2.12)}$$