



EXPERIMENTAL

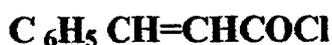
2. EXPERIMENTAL

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



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

Density g/cm^3	: 1.028
M.Wt.	: 166.61
m.p, $^\circ\text{C}$: 35-37
b.p, $^\circ\text{C}$: 256-258

- Isooctyl acrylate (IOA)



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

Density g/cm^3	: 0.880
M.Wt.	: 184.25
b.p, $^\circ\text{C}$: 125 /20mm.Hg

• Dodecyl acrylate (DDA)

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)

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

• 2-hydroxyethyl methacrylate (HEMA)

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

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

HEMA was purified by washing with 5% aqueous sodium hydroxide, dried over anhydrous CaCl₂ and distilled under vacuum.

2.1.2. Reagents for synthesis of Crosslinking Agents

a- Melamine: $C_3H_6N_6$

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

Assay: $\geq 99\%$

FW: 126.12

mp : $> 300\text{ C}$ (lit) References

Melamine is used as it is received.

b- Acryloyl Chloride: $CH_2=CH-COCl$

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

Synonym: 2-Propenoyl chloride

Assay: $\geq 98\%$

FW: 90.51

Density: 1.114 g/mL at $25\text{ }^\circ\text{C}$ (lit.)

Vapor pressure: 1.93 psi ($20\text{ }^\circ\text{C}$)

Refractive index: $n_{20/D}$ 1.435(lit.)

Bp: $72-76\text{ }^\circ\text{C}$ (lit.)

Fp: $61\text{ }^\circ\text{F}$

It is used as received.

c- Methacryloyl Chloride: $CH_2=C(CH_3)-COCl$

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

Assay: $\geq 97.0\%$ (GC)

Molecular Weight: 104.53

Refractive index: $n_{20/D}$ 1.442(lit.)

bp: 95-96 °C(lit.)

Density: 1.08 g/mL at 20 °C, 1.07 g/mL at 25 °C (lit.)

Storage temp.: 2-8°C

It is used as received.

2.1.3. Thermal Initiators

a- Benzoyl Peroxide (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)



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.

2.1.4. Solvents

1-methyl-2-pyrrolidinone (NMP), n-hexane, chloroform, acetone, triethylamine (TEA), and toluene were analytical reagents obtained from Aldrich Chem. Co., USA. 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 SYNTHESIS AND PURIFICATION OF CROSSLINKERS

2.2.1. Synthesis and purification of N-melamine acrylamide crosslinkers

As previously described elsewhere [Atta and Arndt, 2005], the crosslinkers were prepared as follows. Melamine (0.1 Mol) was dissolved in NMP (100 ml) at room temperature for 24 h. The solution was transferred into a four-necked flask fitted with a mechanical stirrer, thermometer, Nitrogen inlet and dropping funnel. Triethyl amine (0.3mol) was added to the solution. Acryloyl chloride or methacryloyl chloride (0.3 Mol) was added dropwise at room temperature for 2 h. The reaction temperature was not increased above 10 °C for 6 h. precipitate of the triethylamine hydrochloride appeared immediately. The reaction mixture was stirred for 48 h at room temperature and the precipitate was removed by filtration. The filtrate was diluted with THF and the unreacted melamine was removed from the aqueous layer by addition of saturated hot NaCl aqueous solution. THF was evaporated from the filtrate under vacuum. The remaining products were added to toluene and the precipitate was removed by filtration. The final viscous products were recovered after evaporation of toluene and NMP under vacuum through the use of a rotary evaporator. The products of reaction between AC or MC with melamine are designated here as MAA_m and MMA_m, respectively.

2.3. PREPARATION OF LINEAR AND CROSSLINKED COPOLYMERS

2.3.1 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 and 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.

2.3.2. Low Conversion Copolymerization (Synthesis of Linear Acrylate Copolymers)

The detailed procedures to synthesize linear CEMA/ODA copolymers are described as follows: A mixture ODA and CEMA with different monomer feed ratios [mole % CEMA / mole % Octa decyl 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 N₂ 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. The obtained precipitate was filtered and dried in vacuum at 30 °C to a constant weight.

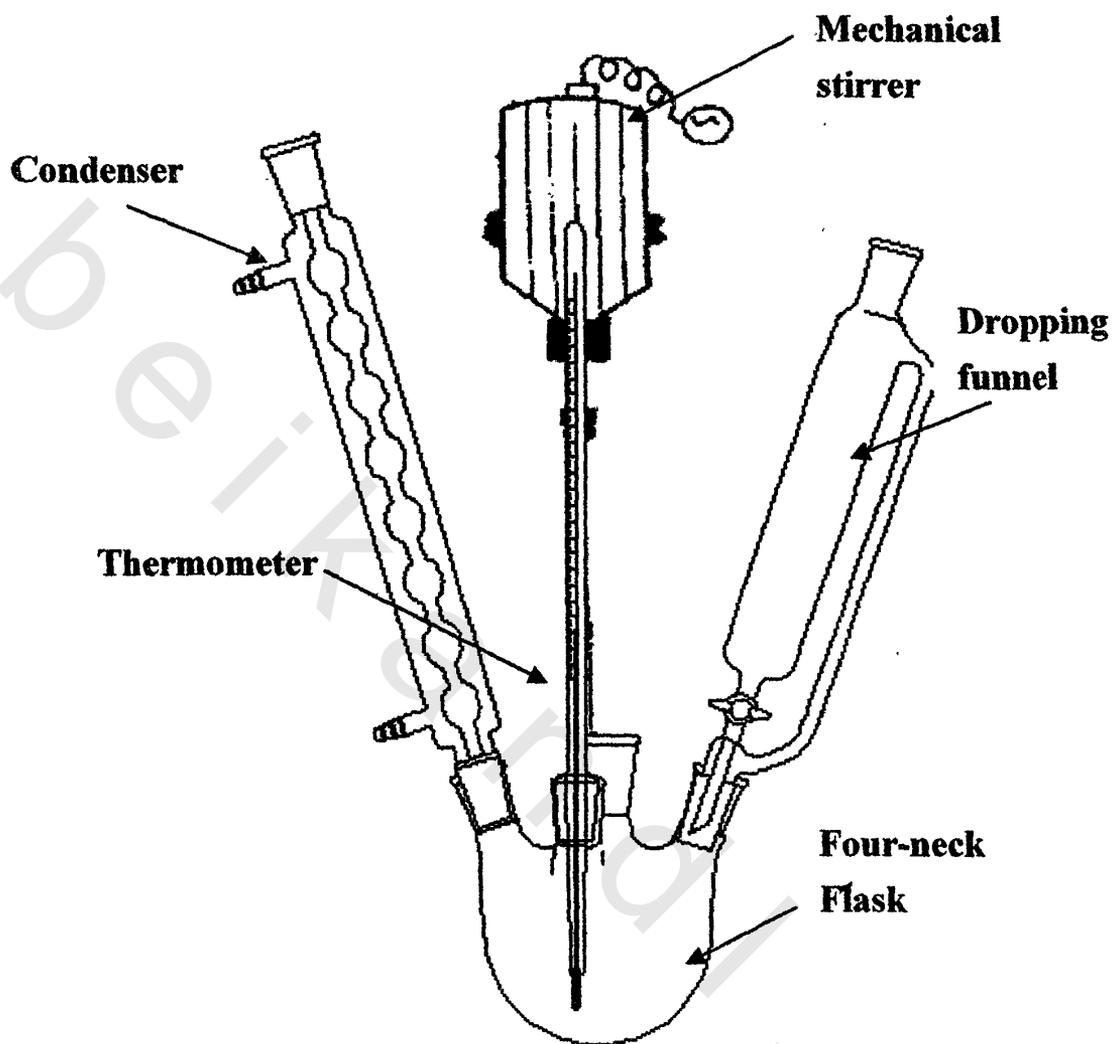


Figure (2.1): Diagrammatic Sketch for the Apparatus used for synthesis of CEMA, MAA_m and MMA_m

2.3.3. 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 MAA_m or MMA_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 hydrophobic by prior siliconisation using dimethyldichlorosilane(DDS). About 1 μm^3 from a solution of 2% DDS in 1,1,1-trichloroethane was syringed into each of the clean test tubes and spread all over the internal surface. The surplus of solution was poured off leaving a thin film. The tubes were then left in the oven for 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

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	MAA _m	MMA _m
Cinnamoyloxy ethyl 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		

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.

2.4. COPOLYMERIZATION AND CROSSLINKING OF CEMA/ALKYL ACRYLATE ONTO PET NONWOVEN FIBER (NWF)

2.4.1 Thermally

For preparation of thermally crosslinked CEMA and Alkyl acrylate (IOA, DDA or ODA) onto PET nonwoven fiber (NWF) , CEMA and Alkyl Acrylate monomers were mixed together with ABIN initiator 0.02 %(w/w) and different weight ratios of MAA_m or MMA_m crosslinker ranging from 0.5-4%(w/w). The mixture was bubbled with nitrogen, then cast over one gram of PET NWF. This procedure was performed with monomer feed ratios 50/50 mol % of CEMA/Alkyl acrylate. The copolymerization and crosslinking 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 prepared crosslinked copolymers are listed in **Table (2.3)**.

2.4.2. Photochemically

Photochemically crosslinked CEMA and Alkyl acrylate (IOA, DDA or ODA) onto PET nonwoven fiber (NWF) were prepared as follows: mixtures of CEMA and Alkyl Acrylate monomers with different weight ratios of MAA_m or MMA_m crosslinker ranging from 0-4%(w/w) were cast over one gram of PET NWF. The PET NWF treated with CEMA/

Alkyl acrylate was irradiated with the wavelength of 365 nm using a 100 watts high intensity UV lamp (Blak-Ray B100A). The irradiated PET NWF was extracted with THF to remove the uncrosslinked part of the polymer which is soluble in THF and dried in vacuo at 30°C until a constant weight. The constituents of the prepared crosslinked copolymers are listed in Table (2.3) also.

2.5. UV CROSSLINKING OF LINEAR COPOLYMERS ONTO PET NONWOVEN FIBER

One gram of linear copolymer of CEMA/Octadecyl acrylate having different composition (90/10, 70/30, 50/50, 30/70 and 10/90) was dissolved in 9 ml of THF and then the solution was cast over 1 g PET NWF at room temperature under an air atmosphere. The treated PET was irradiated with UV having wavelength 365 nm using a 100 watts high intensity UV lamp (Blak-Ray B100A). The irradiated PET was extracted with THF to remove the uncrosslinked part. The PET was dried in vacuo at 30 °c until constant weight.

2.6. CHARACTERIZATION OF THE PREPARED COPOLYMERS

2.6.1. FTIR spectroscopy

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

Table(2.3): Constituents of PET NWF Thermally and Photochemically Treated with CEMA/Acrylates in presence of crosslinkers

Sample	Designation	Compositions (mole%)		Crosslinker content(wt%)	
		CEMA	Alkyl acrylate	MAA _m	MMA _m
PET NWF Crosslinked with CEMA/IOA	PET-CEMA/IOA	50	50	0.5	0.5
				1	1
				2	2
				4	4
PET NWF Crosslinked with CEMA/DDA	PET-CEMA/DDA	50	50	0.5	0.5
				1	1
				2	2
				4	4
PET NWF Crosslinked with CEMA/ODA	PET-CEMA/ODA	50	50	0.5	0.5
				1	1
				2	2
				4	4

Table(2.4): Constituents of PET NWF Photochemically Treated with linear CEMA/Octadecyl acrylate.

Sample	Designation	Compositions (mole%)	
		CEMA	ODA
PET NWF Photocrosslinked with liner CEMA/ODA	PET-L-CEMA/ODA	90	10
		70	30
		50	50
		30	70
		10	90

2.6.2. ¹HNMR Spectroscopy

The prepared copolymers were analyzed using ¹HNMR 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 ¹HNMR spectroscopy data. All ¹HNMR spectra were obtained at 300 MHz on a Varion NMR 300 spectrometer (Jeol NMR spectrometer model JNM-EX) using CDCl₃ as a solvent and TMS as an internal reference.

2.6.3. Thermogravimetric Analysis (TGA)

The thermal properties of the prepared copolymers were determined using Perkin Elmer TGA 7. The samples are heated from 25°C to 600 °C in N₂ flow (20 cm min⁻¹) at a heating rate 10 C/min.

2.6.4. Dynamic Mechanical Analysis (DMA)

Dynamic mechanical measurement, DMA, on dried discs of crosslinked polymers were carried out using a Perkin Elmer model DMA 7e from -50 °C to 100 °C at Heating rate of 5 °C /min, 1 Hz. sinusoidal frequency and measuring system parallel plates- disc.

2.6.5. Scan Electron Microscopy (SEM)

The morphology of the prepared crosslinked copolymer, PET NWF treated and untreated were characterized by a JEOL JSM-5800 Scanning electron Microscope at 15 Kev. Dried crosslinked polymers were cut to expose their inner structure, coated with a thin layer of palladium gold alloy.

2.7. EVALUATION OF CROSSLINKED POLYMERS

2.7.1. Extraction of Soluble Fraction Materials (SF)

The polymer rods were post cured at 378K in an air oven for 24 hours to ensure 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:

$$\text{SF \%} = ((W_0 - W) \times 100 / W_0) \quad (2.1)$$

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

2.7.2. Oil Absorption Test

Oil absorbency of synthesized crosslinked copolymers with either MAA_m or MMA_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:

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

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

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

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

Where, D_o and D are the diameters of dry and swollen discs, respectively. D_o 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.

2.7.3. 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 318K 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.

2.7.4. 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 ν_e of the polymer. Also, the theoretical crosslink density ν_t has been calculated from:

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

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 [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:

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

where,

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

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

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

The molar mass between crosslinks can then be estimated as :

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

Where, v_s is the molar volume of solvent, ρ_p is the density of polymer.

The v_e was calculated from equation (2.11) [Flory, 1953]:

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

where v_s (mol dm³) is the molar volume of toluene at different temperatures T and obtained from :

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

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

$$M_c = \rho_p / v_e \quad (2.12)$$