CHAPTER 3

RESULTS AND DISCUSSION

3. RESULTS AND DISCUSSIONS

Despite the nation's best efforts to prevent spills, 14,000 oil spills, are reported each year, mobilizing thousands of specially trained emergency response personnel and challenging the best-laid contingency plans. There are different methods can be used to control these spills, i.e, oil spills skimmers, manual clean up, dispersants, in-situ burning, bioremediation and sorbents. Sorbents come in two basic types: natural organic materials like peat moss and sawdust; and synthetic organic sorbents like polypropylene, polyester foam, polystyrene and polyurethane. Many kinds of polymers have been widely used to absorb oil spilled on water. Among them, alkyl acrylate and aromatic polymers have been attracting much attention of scientific and applied research groups. In the present research, the aim is directed to synthesize new oil sorbers based on hydrophobic monomers (alkyl acrylates and cinnamate moiety) and reactive polymer (chemical modification of polyisobutylene) through copolymerization to control the environmental pollution. Accordingly, the present investigation are divided into the following sections:

- Synthesis and structural confirmation of cinnamoyloxy ethyl methacrylate monomer (CEMA).
- Low conversion copolymerization of CEMA with alkyl acrylate monomers like, IOA, DDA or ODA. Calculation of the reactivity ratios of linear CEMA/acrylates copolymers. Calculation of statistical distribution of monomers and monomer mean sequences of the synthesized linear CEMA/acrylates copolymers.
- Synthesis of crosslinked copolymers of CEMA with each of, IOA, DDA or ODA with high conversion by bulk polymerization in presence of ABIN initiator and two different hexafunctinal

crosslinkers [1,1,1-Trimethylolpropane triacrylate (TPT) or 1,1,1-Trimethylolpropane trimethacrylate (TPT_m)] to produce crosslinked CEMA/acrylates copolymers (oil sorbers).

- Synthesis of reactive polymers based on PIB-MA adducts. Confirming the structure of the prepared polymers by IR and ^{1}HNMR spectroscopic analyses.
- Crosslinking the synthesized reactive polymers with ODA in presence of benzoyl peroxide as initiator, cobalt octoate as activator and TPT as crosslinker to produce crosslinked reactive polymer/ODA graft copolymers (oil sorbers).
- Evaluating the efficiency of the synthesized sorbers by measuring swelling and network parameters of the prepared sorbers in crude oil and toluene.

3.1. COPOLYMERIZATION of ALKYL ACRYLATE MONOMERS WITH CEMA

It is well known that oil sorbers should have hydrophobic character to swell in oil medium. The present work aims to synthesis new monomer based on hydrophobic moieties such as alkyl or phenyl groups. It is well established that, HEMA monomer contains both hydrophilic and hydrophobic moieties. So, it is important to convert it to hydrophobic monomers which will be obtained by reaction of its hydroxyl group. This was carried out by reaction of HEMA with cinnamoyl chloride, as described in experimental section, to add phenyl moiety as hydrophobic group. The chemical structure of the obtained monomer, CEMA, can be evaluated from IR and ^{1}HNMR analyses. In this respect, IR and ^{1}HNMR spectra were represented in **Figures (3.1& 3.2)**, respectively. The IR spectrum of CEMA, **Figure (3.1)**, exhibits characteristics

absorption bands at 2926 cm^{-1} (stretching vibration of the aliphatic C-H bond), 1730 cm^{-1} (stretching vibration of the C=O), 1620 cm^{-1} (stretching vibration of the C=C), 1149 cm^{-1} (stretching of C-O), and 900 – 650cm^{-1} (out of plane rotational vibration of aromatic C-H). The disappearance of a band at 3200-3500cm^{-1} confirms the completion of the esterification reaction between OH of HEMA and cinnamoyl chloride. In the ^{1}HNMR spectrum, **Figure (3.2)**, the peaks of CEMA indicated aromatic protons at 7.2 - 7.8 ppm, vinyl protons at 5.6-6.6 ppm, and methyl protons at 1.9 ppm.

The radical polymerization mechanism is frequently employed for preparation of copolymers. The overall reaction scheme for radical copolymerization is very similar to the one for homopolymerization: initiation, propagation, termination and transfer reactions are again involved. However, the chemical nature of both monomers plays a role in a number of ways. It is not possible just to mix two monomers, add an initiator, and expect a copolymer to form. While copolymerization may closely follow the kinetics of homopolymerization of the component monomers which are very similar to each other, a small amount of a monomer that is totally different, the copolymerization may proceed much faster than the homopolymerization. Sometimes two monomers that would not homopolymerize can form a copolymer. On the other hand, a small amount of a monomer may totally inhibit the polymerization of the second monomer. A major difference between homopolymerization and copolymerization is in the propagation step. This difference is based on the nature of the ultimate unit carrying the free radical and the reactivity of this radical. Accordingly, knowledge of the reactivity ratios is the key to predict the composition of a copolymer.

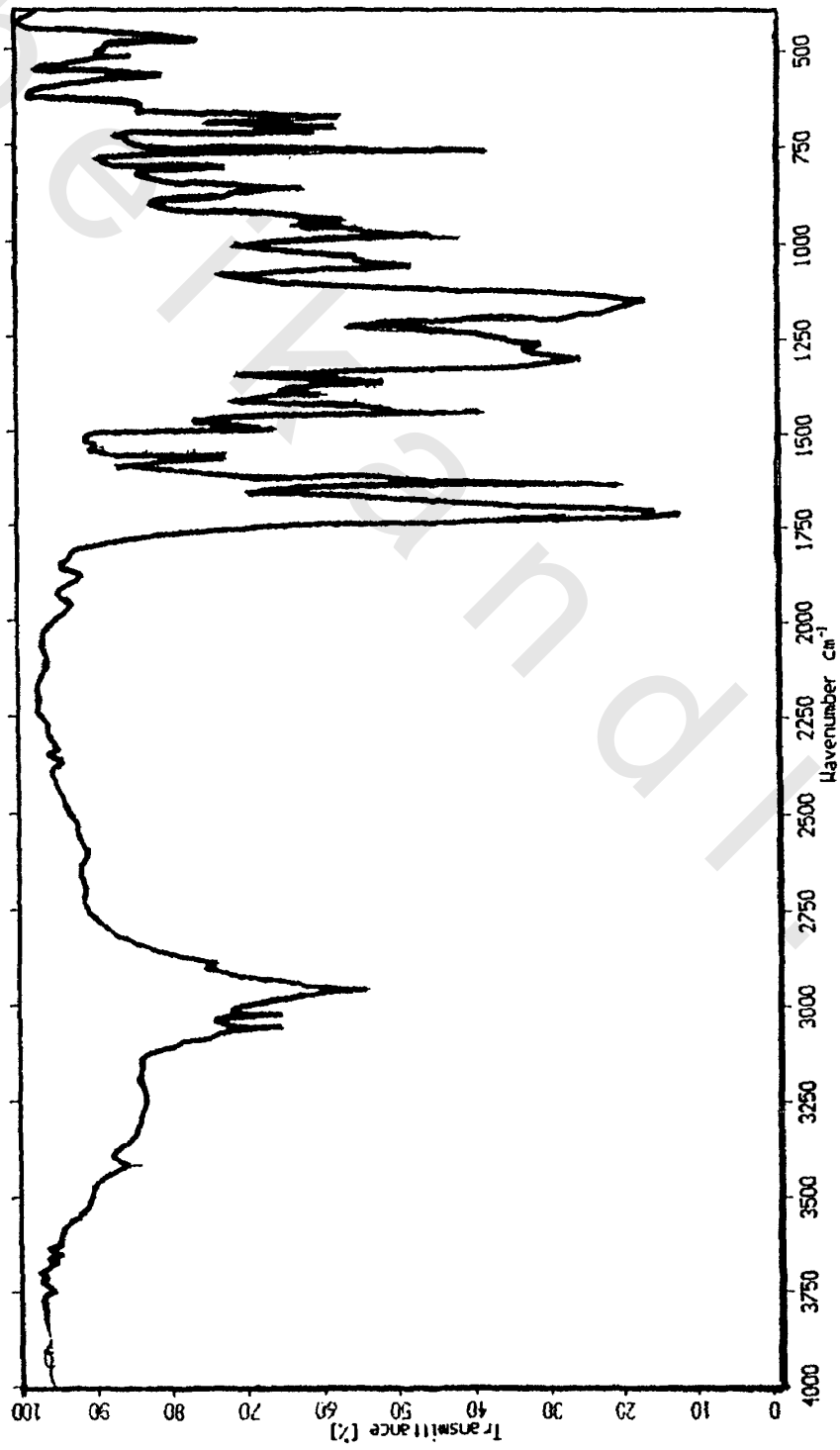


Figure (3.1) RTIR Spectrum of the Prepared CEMA Monomer.

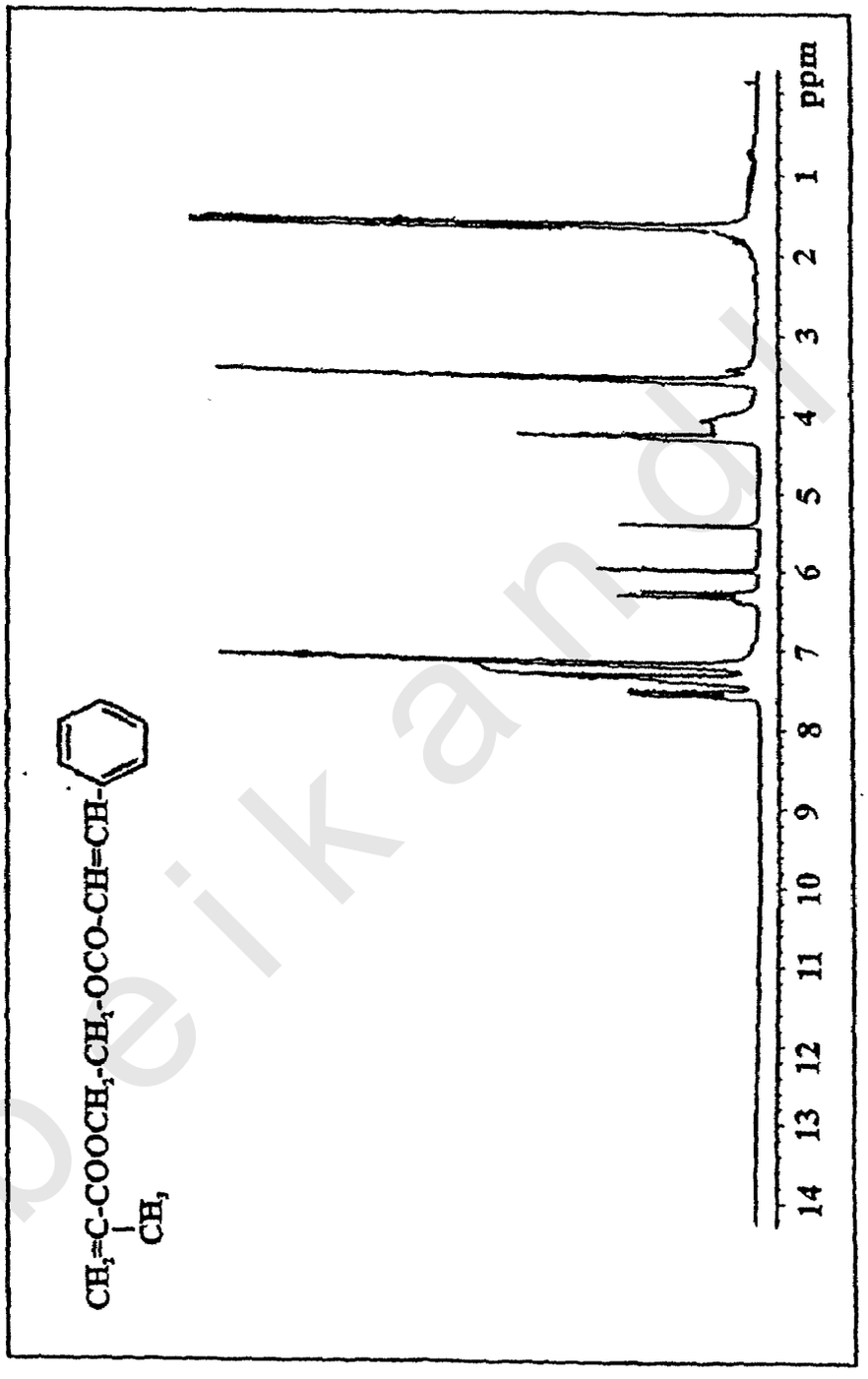


Figure (3.2) ^{1}HNMR Spectrum of the Prepared CEMA Monomer.

It is therefore very desirable to measure these ratios in order to predict the structure of the produced copolymer. Normally the two monomers will polymerize at different rates, so that the composition of a copolymer is completly dependant on the relative reactivity of the first monomer versus the second one. Spectroscopic methods are now widely used in the polymer field as an analytical tool to probe structure and to obtain information on physico-chemical changes occurring in polymers and polymer additives. Spectroscopy utilizes the interaction of radiation with matter to provide details of molecular energy levels, energy state life times and transition probabilities. This information in turn may be applied in studying chemical structure, molecular environment, polymer tacticity and conformation, and monitoring changes in these properties follow external perturbations. In the present study, CEMA monomer has been copolymerized with IOA, DDA or ODA in the presence of benzene at 343K using the procedure described in the experimental section. The structure of the prepared linear copolymers was confirmed by ^{1}HNMR analysis. In this respect the ^{1}HNMR spectra of different compositions of CEMA /alkyl acrylate copolymers were represented in **Figures (3.3-3.5).** The ^{1}HNMR spectroscopic analysis of the synthesized copolymers afforded similar spectra, which show bands at 1.1, 7.2-7.8 and 6.4-6.8 ppm that represent, methyl protons in the polymer backbone, aromatic protons of CEMA and vinyl proton in the cinnamoyl moiety, respectively. The appearance of methylene protons band at 1.9 ppm together with the disappearance of vinyl protons in the acryloyl group at 5.6–6.2 ppm indicate the incorporation of alkyl acrylate and CEMA in copolymerization backbone. Accordingly, low conversion linear copolymers (≤10%) were obtained and their structures were confirmed by ^{1}HNMR and their reactivity ratios can be calculated.

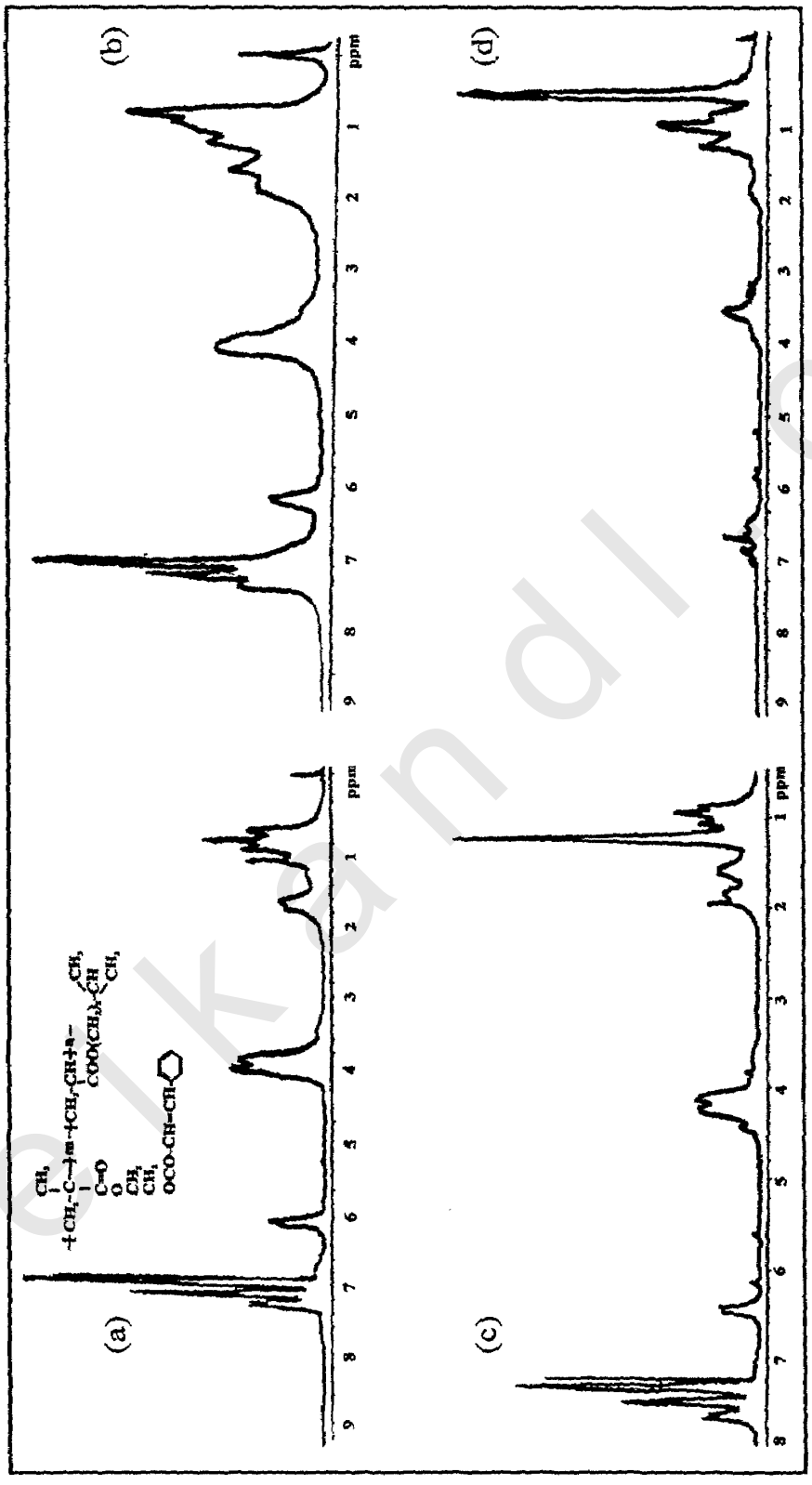


Figure (3.3): ^{1}HNMR Spectra of CEMA / IOA Linear Copolymers Having Different Compositions (a) 90/10 (b) 70/30 (c) 50/50 (d) 10/90

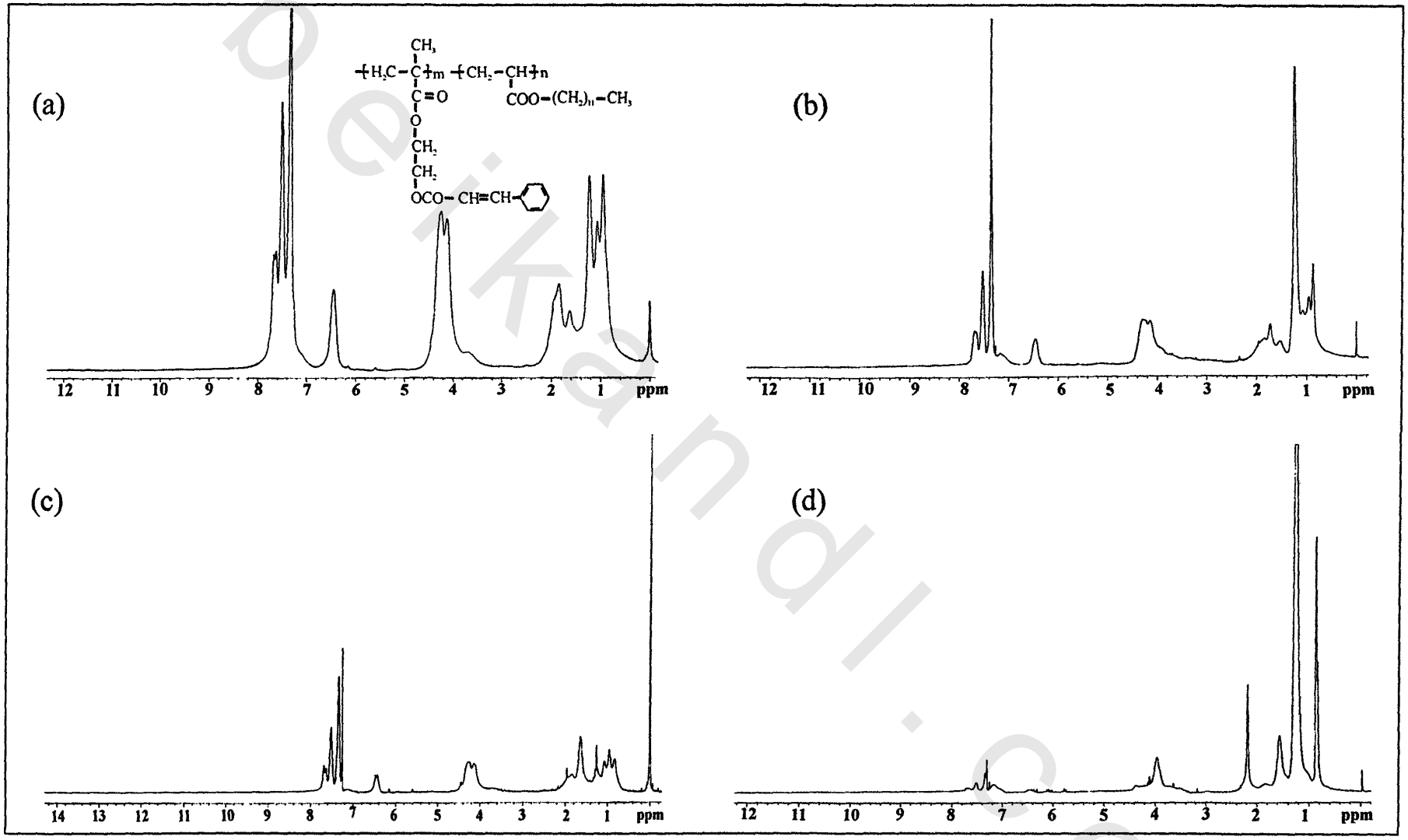


Figure (3.4): ^{1}HNMR Spectra of CEMA / DDA Linear Copolymers Having Different Compositions
(a) 90/10 (b) 70/30 (c) 50/50 (d) 10/90

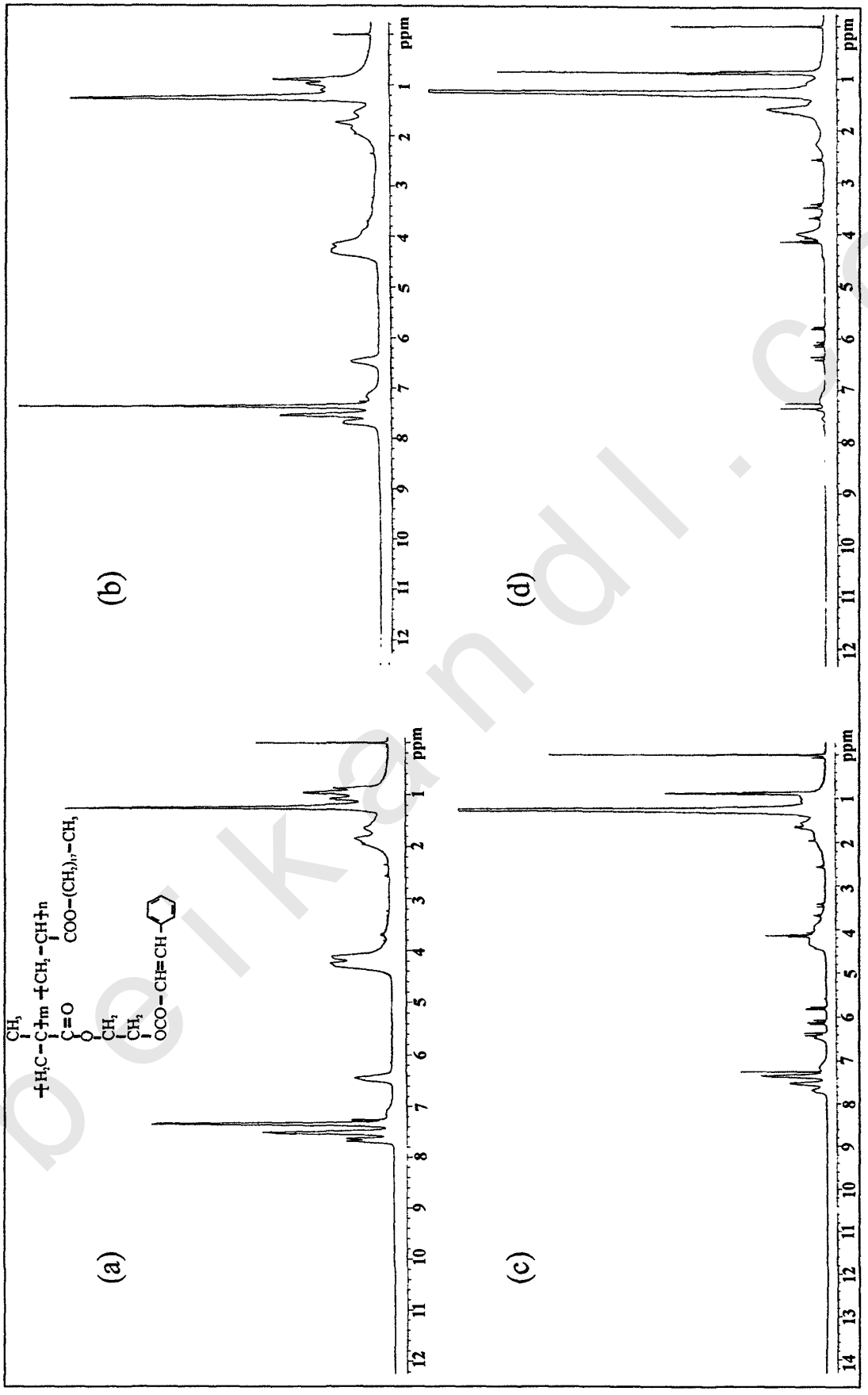


Figure (3.5): ^{1}HNMR Spectra of CEMA / ODA Linear Copolymers Having Different Compositions
(a) 90/10 (b) 70/30 (c) 50/50 (d) 10/90

3.1.1. Reactivity Ratio Studies

Composition drift is an issue in batch copolymerizations when one monomer is incorporated into the polymer chain more rapidly than the other. In the typical case, the composition of the copolymer is different than the monomer mixture from which it is formed; thus, both compositions are drifted as conversion of monomer to copolymer proceeds.

This leads to a distribution of composition of the copolymer chains in the sample, which may affect the physical properties observed. In general, it is preferable to minimize the composition distribution by limiting the conversion of the copolymerization to low levels or by performing the reaction in a continuous process where the monomer and copolymer compositions do not change with time or throughout the reaction. These approaches are not always convenient. Of course, for monomers of sufficiently similar structures, relative reactivities may be close enough to avoid such measures, i.e. when the reactivity ratios, r_1 and r_2, are approximately equal to unity. However, a prior prediction of such assumption validity is not always reliable. Recently, Mogri and Paul **[Mogri and paul, 2000]** reported on the gas transport properties of various side-chain crystalline polymers including a brief study of octadecyl and tetradecyl acrylate copolymers.

It is imperative that the composition of copolymers be uniform in order to attribute correct properties to structure and composition. Most copolymer studies for alkyl acrylate systems have assumed the compositions of the copolymers were the same as that of the monomer reaction mixtures **[Alfrey and Greenberg, 1948 and Jordan et al., 1971]**, i.e. the monomer reactivity was assumed not to vary among n-alkyl acrylates with different side-chain length.

Several techniques have been developed to determine the reactivity ratios of monomers **[Leary and Paul, 2004]**. The most frequently cited methods are that of Fineman-Ross **[Fineman and Ross, 1950]** and Kelen-Tudos **[Kelen and Tudos, 1975]** methods, where monomer feed mixtures of varying composition are polymerized to low conversion and the resultant polymer composition is measured. Knowledge of the reactivity ratios is the key to predict the composition of the copolymer. It is therefore very desirable to be able to measure these ratios to predict the structure of the produced copolymer. Determination of reactivity ratios is based mainly on the analysis of the components making up the copolymer molecule. Previous publications demonstrated several techniques used for determining the percentage of the constituents of the copolymers e.g., elemental analysis **[Neoh et al., 1989 and Sailaja and Kumar, 1995]**, ^{13}CNMR **[Gorda et al., 1990, Cho et al., 1994, Cengiz and Ibrahim, 2003 and Thomas et al., 2003]**, ^{1}HNMR **[Kim et al., 2003, Wamsley et al., 2004, Cengiz and Ibrahim, 2004 and Nanjundan et al., 2005]** and FTIR **[Liu et al., 1996. Mohammed et al., 1998 and Senthilkumar et al., 2003]**. Quantification of the diad and triad fractions of copolymers by ^{1}HNMR is also a useful method to obtain the reactivity ratios. In the present investigation, reactivity ratios of CEMA/IOA, CEMA/DDA or CEMA/ODA copolymers were calculated using ^{1}HNMR analysis to determine the copolymer compositions. The analysis was carried out by comparing the integrated intensities of resonance signals with chemical shifts, 1.96-2.5 ppm assigned to the –CH terminating proton of IOA or –CH backbone proton of ODA or DDA repeating unit with that at 6-7ppm corresponding to the CH=CH protons of the cinnamate moiety of CEMA repeating unit. The monomer ratios in the feed and in the

copolymers, obtained from ^{1}HNMR, together with conversion % and reaction time conditions are listed in **Tables (3.1-3.3).**

a- Reactivity ratio of CEMA(M_1) /IOA(M_2)

It is very desirable to measure the reactivity ratios of participating monomers in order to predict the structure of the produced copolymer **[Rim, 1985]**. Fineman-Ross **[Fineman and Ross, 1950]** and Kelen-Tudos **[Kelen and Tudos, 1975]** methods were used to determine reactivity ratios at low conversion. Fineman-Ross plot based on F(f-1)/f (G ordinate) vs. F^2/f (H abscissa), where F, f are mol fractions of monomers and copolymer respectively. Fineman-Ross plot for the copolymerization of CEMA (M_1) and IOA (M_2) is represented in **Figure (3.6)**. In this figure the relation is straight line, with slope and intercept r_1 and - r_2, respectively, where r_1 and r_2 represent the reactivity ratios for the monomer pair M_1 and M_2. Results from the graphical evaluation for CEMA/IOA yields values of r_1 = 1.04 and r_2 = 2.579. From Kelen-Tudos approach, relation between E vs N where E= H/(α+H)and N= G/(α +H), it was likewise used for graphical evaluation of reactivity ratio for the same monomer pair **(Figure 3.7)**. Here α is calculated from the maximum and minimum values of H as $\alpha = (H_{max} . H_{min})^{0.5}$. Extrapolation to E=0 and E=1 affords the values of $N = -r_2/\alpha$ and r_1, respectively. In this respect, values of 1.00 and 2.55 were obtained for r_1 and r_2, respectively.

Excellent agreement was found between Fineman-Ross and Kelen-Tudos methods.

Table (3.1): Reaction parameters for the copolymerization of CEMA (M_1) with IOA (M_2)

Sample	Feed ratio M_1/ M_2 Mole%/mole%	Time (hr)	Conversion %	$[M_1]^a$	$[M_2]^a$
1	90/10	3	4.45	89	11
2	70/30	2.5	6.33	60	40
3	50/50	1.5	11.8	40	60
4	10/90	1	10.94	4	96

[a]From ^{1}HNMR

Table (3.2): Reaction parameters for the copolymerization of CEMA (M_1) with DDA (M_2)

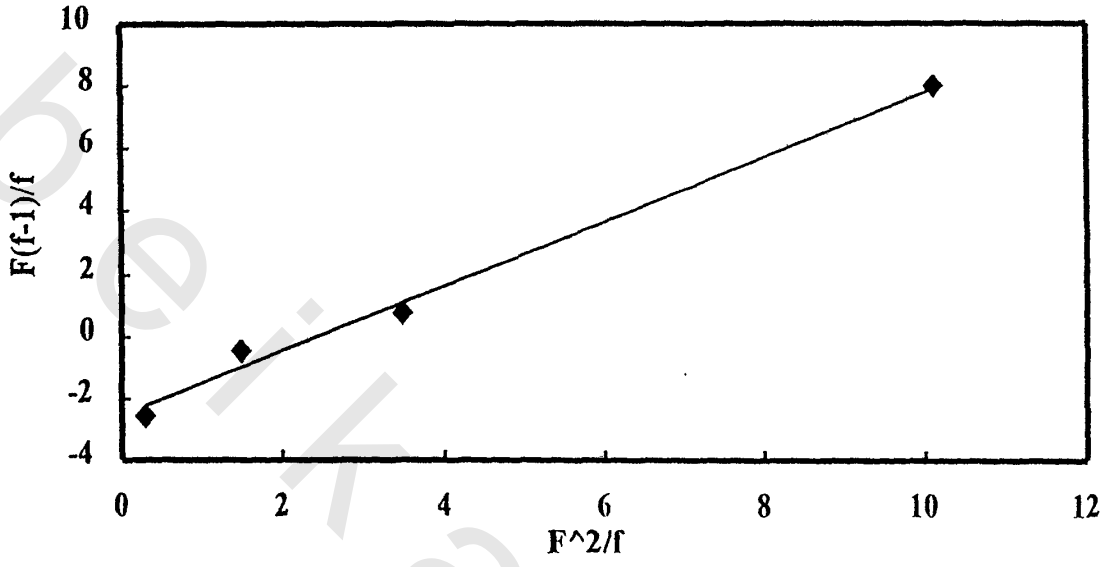
Sample	Feed ratio M_1/ M_2 Mole%/mole%	Time (hr)	Conversion %	$[M_1]^a$	$[M_2]^a$
1	90/10	2.5	8.28	88	12
2	70/30	2	8.30	60	40
3	50/50	1.5	7.82	46	54
4	10/90	1	9.27	3	97

[a]From ^{1}HNMR

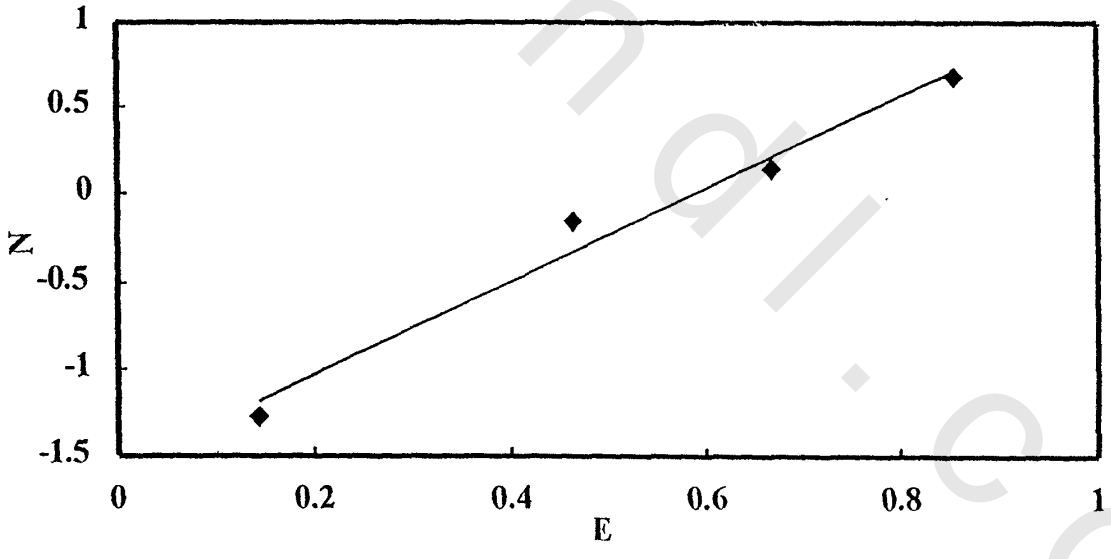
Table (3.3): Reaction parameters for the copolymerization of CEMA (M_1) with ODA (M_2)

Sample	Feed ratio M_1/ M_2 Mole%/mole%	Time (hr)	Conversion %	$[M_1]^a$	$[M_2]^a$
1	90/10	2	9.11	73	37
2	70/30	1.5	6.80	57	43
3	50/50	1	8.30	49	51
4	10/90	1	8.00	6	94

[a]From ^{1}HNMR



Figure(3.6): Fineman-Ross Plot for the Copolymerization of CEMA (M1) and IOA (M2).



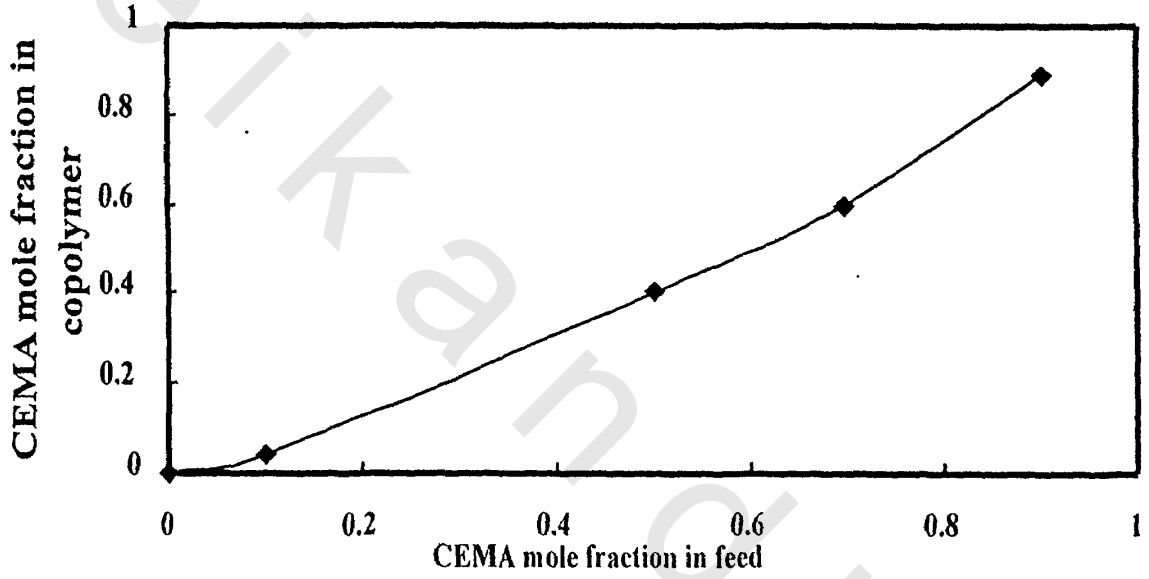
Figure(3.7):Kelen-Tudos plot for the copolymerization of CEMA (M1) and IOA (M2).

In a copolymerization reaction, when r_1 and r_2 values are greater than unity each monomer group prefers to react with itself and not with the other monomer. In case of r_1 =1, a growing chain ending with M_1 group reacts equally with M_1 or M_2. On the other hand, it is observed that, the graphical plot of Kelen-Tudos showed a straight line. This behavior indicates that the copolymerization of (CEMA/IOA) follows the conventional copolymerization kinetics based on the fact that only the terminal monomer unit determines the reactivity of a polymer radical **[Iwatsuki et al., 1984]**. Meanwhile, the product of the average values of r_1 r_2 equals 2.615 (r_1 and r_2 are relatively close to unity) indicates that the CEMA/IOA copolymer prepared under these condition will have a random distribution of the monomer units along the copolymer chains.

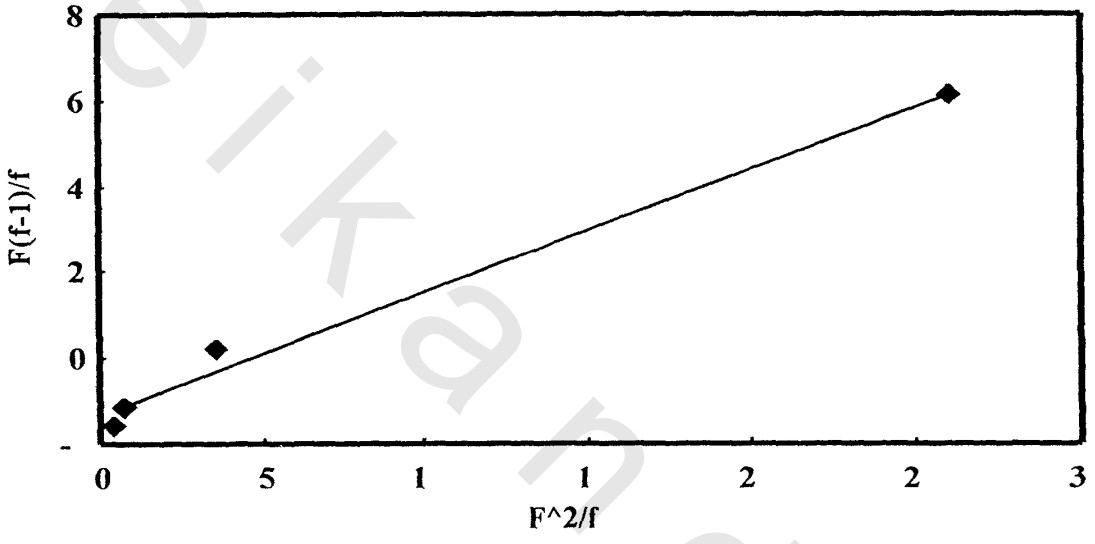
Figure (3.8) shows the copolymer composition (m) as determined from ^{1}HNMR as a function of feed composition (M) for the copolymerization reaction of CEMA/IOA. It is observed that, there is no point where m = M, i.e., no azeotropic copolymer is expected to be formed through the copolymerization of CEMA and IOA monomers.

b- Reactivity ratio of CEMA(M_1)/DDA(M_2)

The above mentioned methods for determining the reactivity ratio were used to measure the reactivity ratio of CEMA (M_1), and DDA (M_2). The linear plot of F(f-1)/f (G ordinate) vs. F^2/f (H abscissa) (Fineman-Ross plot) affords r_1 and $-r_2$, respectively from the slope and the intercept. The data are illustrated in **Figure (3.9)**. The obtained values of r_1 and r_2, from this figure, are 0.2825 and 1.29, respectively. Consequently the product of r_1 r_2 is 0.36491.



Figure(3.8):Copolymer Composition as a Function of Feed Composition for the Copolymerization Reaction of CEMA/IOA.

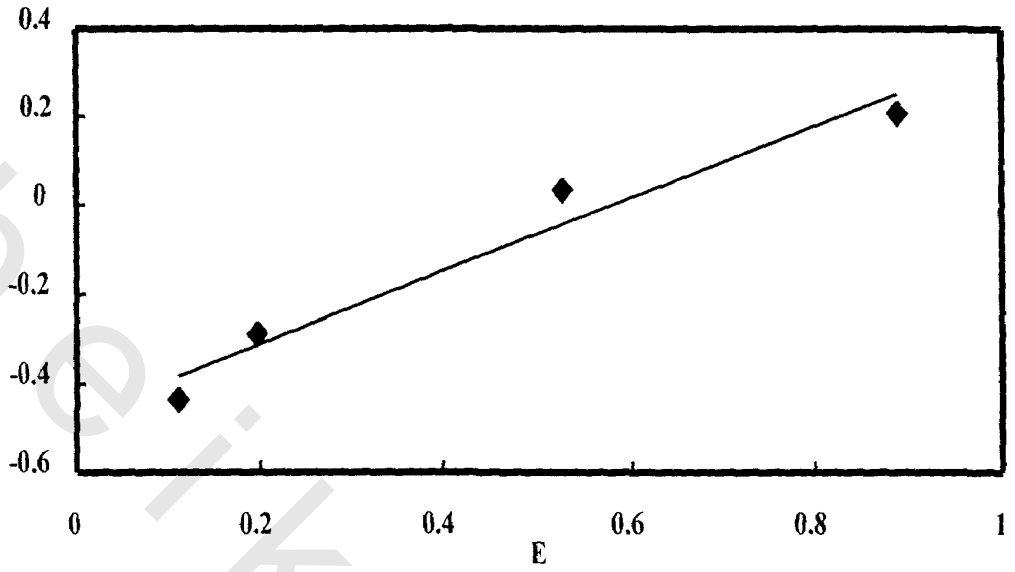


Figure(3.9): Fineman-Ross Plot for the Copolymerization of CEMA (M1) and DDA (M2).

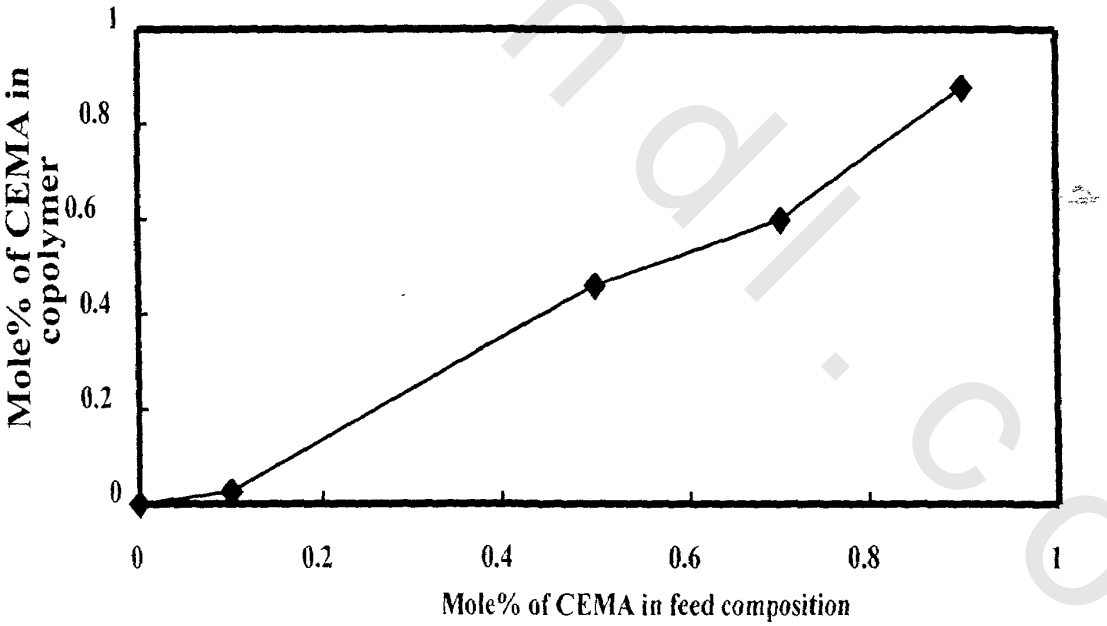
The linear plot of N vs. E (Kelen and Tudos method) is shown in **Figure (3.10).** The values of r_1 and r_2 obtained from this figure were found to be 0.3 and 1.48, respectively. The product of r_1 r_2 = 0.444. Accordingly, the average values of r_1, r_2 and r_1 r_2 are 0.29, 1.385 and 0.406, respectively. The obtained values of r_1, r_2 and r_1 r_2 indicate that the produced copolymer has random distribution. The high value of r_2 of DDA confirms the high incorporation of DDA in copolymer when compared with that of CEMA. The relationship between mole fraction of CEMA incorporated into the copolymers (m_1), and that in comonomer feed ratio (M_1) is shown in **Figure (3.11).** It is obvious that, there is no point where $m_1 = M_1$, i.e., no azeotropic copolymer is expected to be formed through the copolymerization of CEMA and DDA monomer.

c- Reactivity ratio of CEMA(M_1)/ODA(M_2)

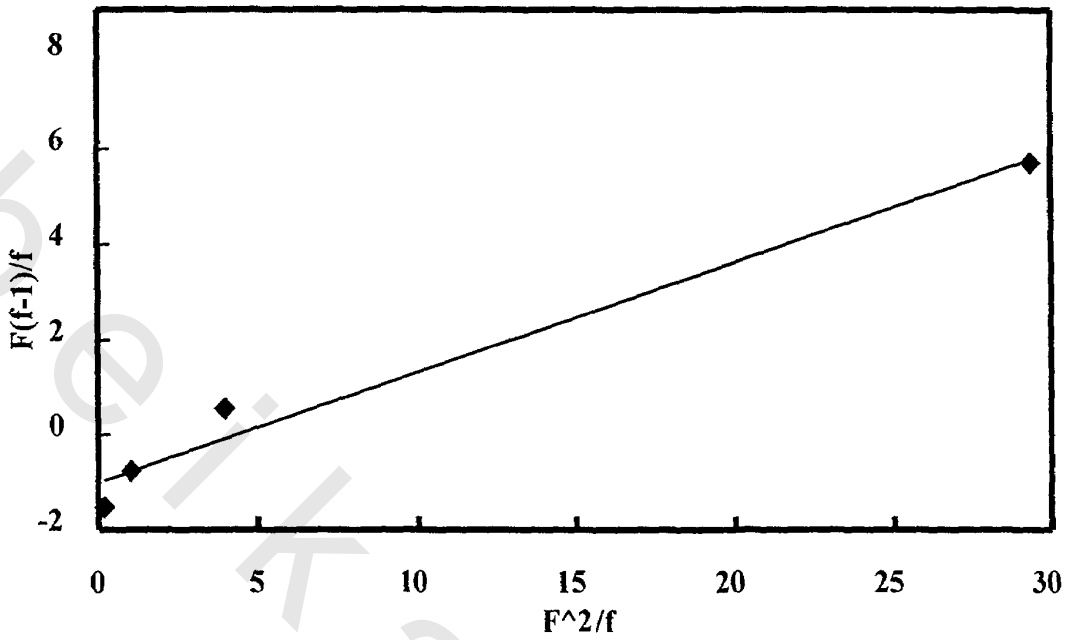
The monomer reactivity ratios for the copolymerization of CEMA (r_1) with ODA (r_2) were determined also through Fineman-Ross method **Figure (3.12)** and Kelen-Tudos method **Figure (3.13).** The obtained values of r_1 and r_2 from **Figure (3.12)**, are 0.2349 and 0.9797 respectively, and consequently r_1 r_2=0.23. The values of r_1 and r_2 from Kelen-Tudos plot are 0.3 and 0.986 respectively, and consequently r_1 r_2 =0.2958. The average values of r_1, r_2 and r_1 r_2 are 0.265, 0.982 and 0.2629, respectively. The reactivity of growing radicals to react with CEMA unit, as measured by $1/r_1$ seems to be higher towards ODA less CEMA units than in the feed. The product of r_1 and r_2 suggests random distribution with longer sequence of ODA units in the copolymer chain. These results run in harmony with the reactivity ratio data observed by Nanjundan et al.,**[Nanjundan et al., 2005]**.



Figure(3.10): Kelen-Tudos Plot for the Copolymerization of CEMA (M1) and DDA (M2).



Figure(3.11): Copolymer Composition as a Function of Feed Composition for the Copolymerization Reaction of CEMA/DDA.



Figure(3.12): Fineman-Ross Plot for the Copolymerization of CEMA (M1) and ODA (M2).

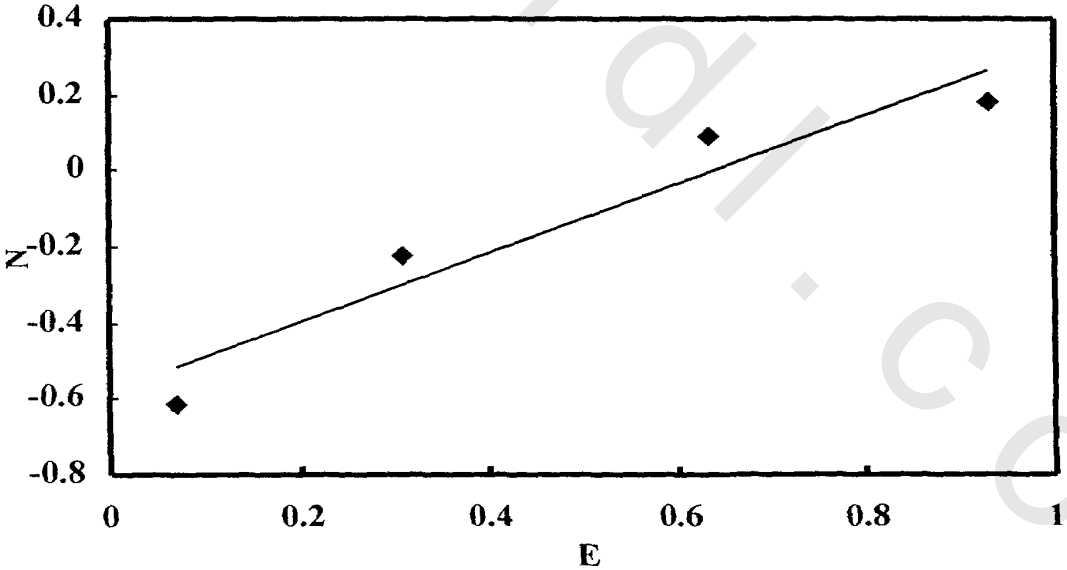


Fig. (3.13): Kelen-Tudos Plot for the Copolymerization of CEMA (M1) and ODA (M2).

They found that the reactivity ratio (r_1) for 4-benzyl methacrylate(BPM) is higher than unity and (r_2) for glycidyl methacrylate (GMA) monomer is lower than unity. However, the product of r_1 and r_2 is less than 1, which suggests a random distribution of monomer units.

Figure (3.14) shows the copolymer composition as determined from ^{1}HNMR as a function of feed composition for the copolymerization reaction of CEMA/ODA. It is observed that, there is a point where m = M, i.e., azeotropic point was observed at a molar ratio for the copolymerization of CEMA/ODA of 50/50 mole % composition.

Compairing the reactivity ratio (r_2) for the different alkyl acrylates incorporated in the copolymers, r_2 for IOA was 2.615 while for DDA was 1.385 and that for ODA was 0.982. these values give an indication of more active IOA incorporation into the copolymer chain than that of DDA which inturn is more active than ODA.

3.1.2. Copolymer microstructure

the microstructure of the prepared copolymers is of great utility in predicting their properties.The statistical distribution **[Igarashi, 1963, Harwood, 1968, Pyun, 1970 and Georgiev, 1978,]** of monomer sequences, M_1- M_1, M_2- M_2 and M_1- M_2 may be calculated utilizing the following equations:

$$X = \varphi_1 - 2\varphi_1(1-\varphi_1) / [1 + [(2\varphi_{1-1})^2 + 4 r_1 r_2 \varphi_1 (1-\varphi_1)]^{0.5}] \quad (3.1)$$

$$Y = (1-\varphi_1) - 2\varphi_1(1-\varphi_1) / [1 + [(2\varphi_{1-1})^2 + 4 r_1 r_2 \varphi_1 (1-\varphi_1)]^{0.5}] \quad (3.2)$$

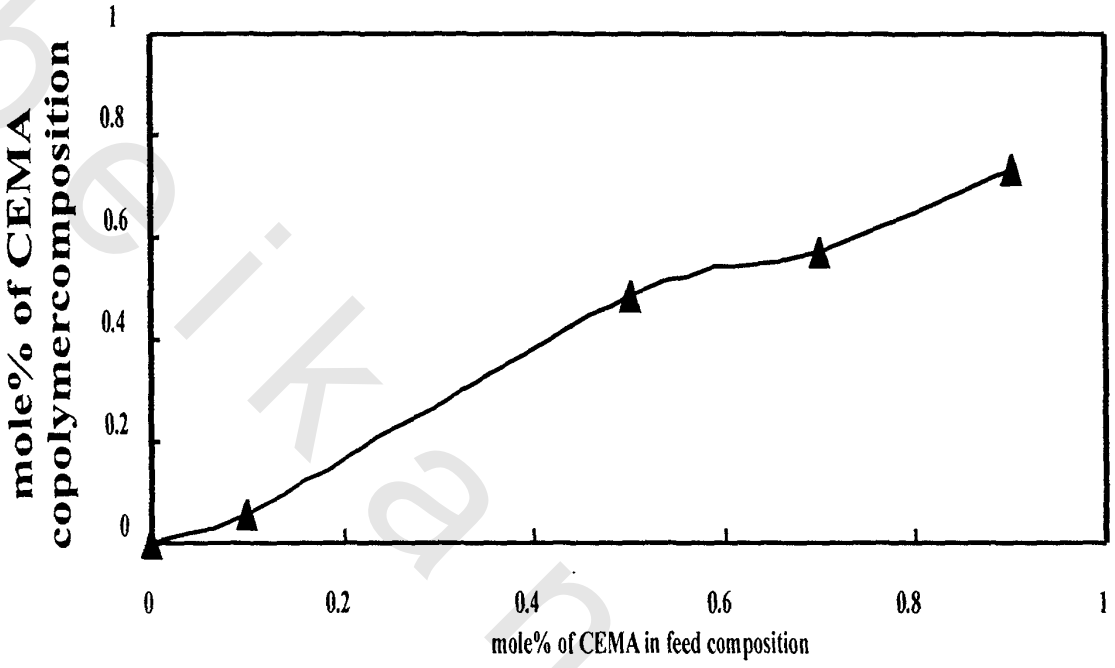


Fig. (3.14): Copolymer Composition as a Function of Feed Composition for the Copolymerization Reaction of CEMA-ODA.

$$Z = 4\varphi_1 (1- \varphi_1) / [1+ [(2 \varphi_{1-1})^2 + 4 r_1 r_2 (1- \varphi_1)]^{0.5}] \quad (3.3)$$

Where X, Y and Z are the mole fractions of M_1- M_1, M_2- M_2 and M_1-M_2 sequences in the copolymer. While φ_1 is the copolymer composition and r_1 and r_2 are the reactivity ratios of the respective monomer pairs.

Also, the mean sequence lengths, μ_1 and μ_2, can be calculated **[Igarashi, 1963]** utilizing the following equations:

$$\mu_1 = 1+ r_1 [M_1] / [M_2] \quad (3.4)$$

$$\mu_2 = 1+ r_2 [M_2] / [M_1] \quad (3.5)$$

The structural data for different compositions of CEAM/IOA copolymers are listed in **Table (3.4).** The calculated mole percentage of poly(CEMA/IOA) linkage in each copolymer composition was relatively low, indicating a definite random tendency. It is noticeable that the mean sequence length of CEMA (μ_{CHEM}), varies from 9.253 – 1.04 as the mole percentage of CEMA in the copolymer decreases from 90 – 10 mol%, while that of IOA (μ_{IOA}) increases from 1.316 – 62.44 for increased IOA molar percentage in copolymer from 10 – 90 mol%. The relatively low mean sequence lengths of CEMA and high values for IOA afford a further indication of the random tendency in CEMA/IOA copolymer.

The inter monomer linkages and mean sequence length distributions for different compositions of CEAM/DDA copolymers are listed in **Table (3.5).** Also, the calculated mole percentage of poly(CEMA/DDA) linkage in each copolymer was relatively low, indicating a definite random tendency. For CEMA/DDA copolymers the mean sequence length of CEMA (μ_{CHEM}), varies from 3.09 at 90 mole ratio of CEMA/DDA in the copolymer to 1.00 with a 10 mole ratio. While that

Table(3.4): Structural data for CEMA/IOA copolymers.

Sample	[a]Blockiness (mole%)		[a]Alternation (mole%)	Mean sequence length	
	CEMA/CEMA	IOA/IOA	CEMA/IOA	μ_{CEMA}	μ_{IOA}
1	78.800	0.072	20.549	9.25	1.35
2	32.536	12.536	54.927	2.53	2.89
3	12.536	32.536	54.927	1.68	5.26
4	0.089	92.089	7.8207	1.04	62.44

[a]Statstically calculated from reactivity ratios

Table(3.5): Structural data for CEMA/DDA copolymers.

Sample	[a]Blockiness (mole%)		[a]Alternation (mole%)	Mean sequence length	
	CEMA/CEMA	IOA/IOA	CEMA/IOA	μ_{CEMA}	μ_{IOA}
1	76.616	0.600	22.767	3.095	1.175
2	30.450	10.450	59.099	1.4287	1.860
3	15.085	23.085	61.818	1.2434	2.514
4	0.034	94.034	5.931	1.008	42.710

[a]Statstically calculated from reactivity ratios

of DDA (μ_{DDA}) increases from 1.17 – 42.71 for increased DDA molar percentage in copolymer from 10–90 mol%. Similar resuls of microstructural data were found for CEMA/DDA affording an indication of the random tendency in copolymer.

The structural data for different compositions of CEAM/ODA copolymers are listed in **Table (3.6)**. The alternation mole percentage of poly (CEMA/ODA) linkage in each copolymer composition was relatively low, indicating a definite random tendency.

It is remarkable that the mean sequence of CEMA (μ_{CHEM}), varies from 1.60 – 1.01 as the mole percentage of CEMA in the copolymer decreases from 90 – 10 mol%, while that of ODA (μ_{ODA}) increases from 1.36 – 16.34 for increased ODA molar percentage in copolymer from 10 – 90 mol%. Similar values of μ_{CHEM} and μ_{ODA} at different copolymer compositions afford a n indication of the random tendency.

Comparing the mean sequence lengthes of the different alkyl acrylates incorporated in the copolymer structure, they decreas with increasing the alkyl chain length (i.e from IOA to DDA to ODA). Thes results confirm the previously mentioned reactivity sequence of different alkyl acrylates towards copolymerization with CEMA.

3.2. SYNTHESIS OF PIB-MA GRAFTS

Polyisobutylene, PIB, is one of the most important polymers that have large industrial application. It is prepared through cationic polymerization using BF3 as a catalyst and in presence of organic solvent. It was proved that the polymer chains are ended with olefinic double bond. Maleic anhydride, MA, easily adds to polyisobutylene at high temperature or in presence of radical catalyst.

Table(3.6): Structural data for CEMA/ODA copolymers.

Sample	[a]Blockiness (mole%)		[a]Alternation (mole%)	Mean sequence length	
	CEMA/CEMA	IOA/IOA	CEMA/IOA	μ_{CEMA}	μ_{IOA}
1	48.770	2.770	48.459	1.626	1.3623
2	24.215	10.215	65.569	1.307	1.739
3	15.230	17.230	67.538	1.222	2.019
4	0.091	88.091	11.817	1.014	16.348

[a]Statstically calculated from reactivity ratios

Syntheses of a variety of useful telechelic polyisobutylenes (PIBs) carrying reactive termini have been reported during the past 15 years **[Sawamoto, 1991, kennedy and Ivfin, 1992, Ivfin, 1993, Gandini, 1992 and Ivfin and Kennedy, 1993]**. The so-called inifer method **[Kennedy and Smith, 1980]** led to the preparation of telechelic PIBs with tert-chlorine end groups upon quenching the polymerization with methanol. Quenching living polymerizations of isobutylene with excess nucleophiles also yielded tert-chlorine end groups **[Faust and Kennedy, 1987, Mishra and Kennedy, 1987, Ivfin and Kennedy, 1988 and Ivfin and Kennedy, 1990]**. Quantitative dehydrochlorination of the *tert-chlorine* end by a strong base, such as t-BuOK **[Kennedy et al., 1979]** or CH_3ONa **[Mishra et al., 1985]**, was claimed to yield 2-methyl-2-propenyl (isobutenyl)-telechelic P1Bs.

Another type of olefin-terminated polymers, allyl-telechelic PIBs, were obtained by allylation of *tert-chlorine*-terminated PIBs **[Wilczek and Kennedy, 1987]** and later by one-pot end quenching of living PIB chains by allyltrimethylsilane (ATMS) **[Ivfin and Kennedy, 1988 and Ivfin and Kennedy, 1990]**. The polymer purification followed by dehydrochlorination of *tert-chlorine-telechelic* PIBs were done by refluxing in dry tetrahydrofuran (THF) for a relatively long time (16-20 h) in order to obtain isobutenyl termini, allyl end quenching is a simpler, faster and more economic process to prepare olefin-ended PIB **[Kennedy and Ivfin, 1992]**. Both the isobutenyl and allyl end groups can be quantitatively converted into hydroxyl-telechelic PIBs by regioselective hydroboration followed by oxidation **[Ivfin and Kennedy, 1988, Ivfin and Kennedy, 1990 and Ivfin et al., 1980]**. The desired reaction product between 2-chloro 2,4,4-trimethyl pentane

TMPC1 and isobutenyltrimethyl silane(IBTMS), 2,4,4,6,6-pentamethyl-l-heptene (PMH) is expected to provide ^{1}HNMR signals similar to that characteristic of the isobutenyl-ended PIB obtained by dehydrochlorination of *tert-chlorine-terminated* chains **[Kennedy et al., 1979 and Mishra et al., 1985]**. It was found that olefin signals at 4.52 and 4.78 ppm corresponding to the isobutenyl groups (-CH_2-$C(CH_3)$=CH_2) appear in the presence of both BCl_3 and TiCl4. However, only a negligible signal was observed at 1.38 ppm characteristic of the methylene protons next to the isobutenyl group (-CH_2-$C(CH_3)_2$-$C(CH_3)$ =CH_2), when the reaction was carried out in the presence of $BC1_3$. In contrast, good correlation was obtained between the ^{1}HNMR, signals of these methylene protons and the olefinic protons in the isobutenyl group in the presence of $TiCl_4$. Thus the results of model experiments indicated that the functionalization reaction with IBTMS for P1B should be carried out in the presence of $TiCl_4$.

Walsh and Gaymans **[Walsh and Gaymans, 1994]** prepared anhydride terminated polyisobutylene (PIB) oligomers in a one- or two-step process from chlorine-terminated oligomers. In the one-step process, chlorine functional oligomers were just heated in the presence of maleic anhydride (MA) for 12 h at 190°C without a catalyst. In the two-step process, the chlorine end functional groups were first converted by selective dehydrochlorination to isopropenyl polyisobutylene end groups with t-BuOK by refluxing in tetrahydrofuran for 16h. In a second step, MA was coupled to the PIB with unsaturated end groups by reacting the oligomer with MA for 12 h at 190°C.

With anionic polymerization, it is possible to obtain well-defined end groups. This is also true for some cationic polymerizations **[Sawamoto et al., 1987]**. With the living PIB synthesis, chlorine end groups are

nearly always obtained. Termination of living PIB with EtN_3, pyridine and methanol gave solely chlorine end groups **[Faust and Kennedy, 1987]**. The same occurs with other nucleophiles like esters, anhydrides, ethers, ketones, dimethylsulfoxide and N,N-dimethyl- acetamide **[Ivfin and Kennedy, 1990]**. There are only a few exceptions. It has been shown that it is possible to link anisole to the living end **[Mishra et al., 1986]**. Also, allyl end groups were introduced in one step by terminating with allyltrimethylsilane **[Ivfin and Kennedy, 1990]** or an allylstannate.

The chlorine end group of PIB-Cl can be converted to obtain functional groups **[Kennedy, 1983 and Kennedy, 1984]** suitable for further copolymers. Some of these polymers have characteristic polymerization. By elimination of HCl from the chain end, a PIB oligomer with an unsaturated end group is obtained (PIB-U). The elimination is carried out by heating the PIB-Cl where two kinds of unsaturated groups are formed: one with a double bond inside the polymer chain at a 2,3-position ('endo') and one with the double bond outside the chain at the 1,2-position ('exo'). The exo form is preferred because it has a higher reactivity **[Hoffman et al., 1986]**. It can be obtained quantitatively by abstracting the HCl with a sterically hindered base such as t-BuOK **[Kennedy et al., 1979 and Solomons, 1988]** or even with EtONa **[Mishra et al., 1985]**. The exo double bond can be used to add a variety of compounds to the chain end **[Kennedy, 1983]**. One of the possibilities is the addition of an unsaturated anhydride group **[Hill and Barger, 1965 and Tessier and Marrchal, 1984]** by an ene reaction. With this type of reaction only one monomer is added. This anhydride group will give a telechelic that is reactive towards alcohol and amine groups. The addition of acrylic acids is not

favourable as their rate of reaction of an ene type is too slow, and a radical or ionic reaction will not stop after one addition. Other possibilities for the conversion of the double bond are hydroboration, hydrosilation, free radical addition of thiols and reaction with chlorobenzoic acid.

PIB absorbs very weakly in the IR region. Large amounts of PIB could be used so that strong absorption bands of the end groups could be obtained. IR spectrum of PIB-U is not represented here for brevity. The unsaturated end groups of PIB-U absorb strongly at 890 and 1640 cm^{-1}. The band at 890 cm^{-1} is particularly clear, even at low levels of unsaturation. Unsaturated end groups could be traced with IR at concentrations that were too small to detect with ^{1}HNMR. PIB-U has a rather simple ^{1}HNMR spectrum (**Figure 3.15**). The main chain of PIB shows two single peaks at 1.11 and 1.42 ppm. Also there are some small-unknown peaks in the 1.0-2.3 ppm range. The end groups and the bulk part of the chain have reasonably different peak positions so that the end groups of the telechelics can be examined and compared with the bulk. The appearance of peaks at 4.85, 4.65, 1.78 and 2.00 ppm that represent olefinic protons, methyl and methylene proton attached to olefinic protons (**Figure 3.15**) indicates that the end double bond have a 1,2-bond (exo).

The addition of maleic anhydride (MA) to PIB-U was studied by Tessier and Marrchal **[Tessier and Marrchal, 1984 and Tessier and Marrchal, 1990]**. They reacted poly(maleic anhydride) which are not soluble in hexane with telechelic PIB as well as model compounds and analyzed the products with ^{1}HNMR. It appeared that the MA reacted by means of an ene reaction with PIB-U.

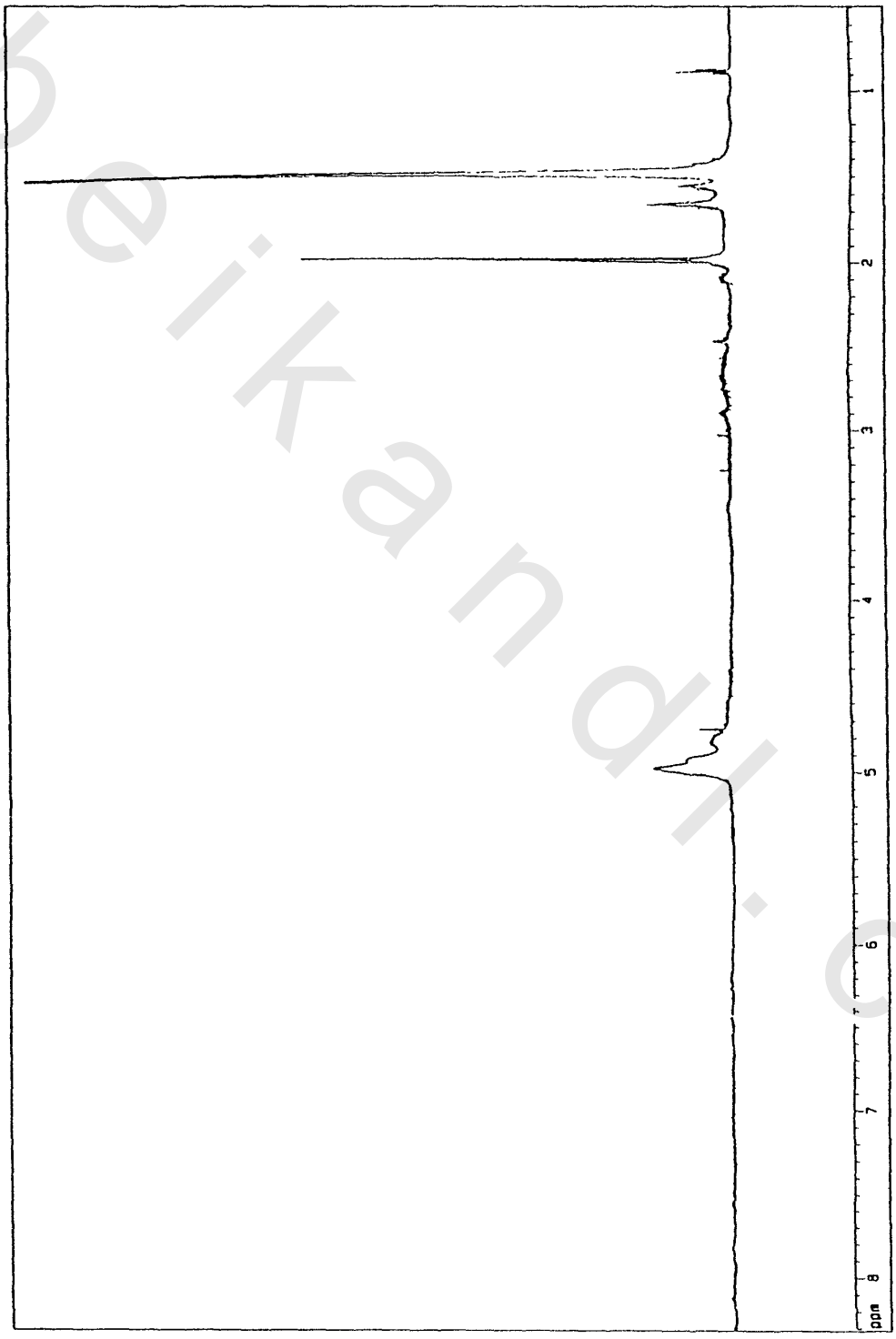


Figure (3.15): ^{1}HNMR Spectrum of PIB-U

In the present system, the reaction of MA onto PIB-U can be illustrated in **Figure (3.16),** to take place by the ene cyclo-addition reaction at high temperatures or by a hydrogen abstraction reaction on the α-CH2. The radical addition reaction yielded products that had many complicated structures and the large portion of the products become insoluble. But in the present system, the products were soluble, and no insoluble product was obtained. The chemical structures of the produced PIB-MA adduct can determined by IR and ^{1}HNMR analyses. IR spectrum of PIB-MA adduct, which represented in **Figure (3.17)** shows two strong anhydride bands at 1790 and 1830 cm $^{-1}$ and a minor band at 715 cm $^{-1}$ were found. Although the anhydride was present only in the end groups, it had an absorbance of the same order of magnitude as the strong bands in the PIB main chain. The unsaturated band seen at 890 cm^{-1} in the case of PIB-U, had disappeared completely in the IR spectrum of PIB-MA. According to the reaction mechanism, a new double bond was formed but this could not be observed with IR. It is possible that the band is shifted 30 cm^{-1} and is obscured behind the adjacent C--C stretching band.

^{1}HNMR analysis can be used to determine the chemical structure of PIB-MA adduct. In this respect, the ^{1}HNMR spectrum of PIB-MA adduct was represented in **Figure (3.18).** The presence of the anhydride groups is difficult to be observed by ^{1}HNMR, because the two protons give several small peaks distributed over a broad range that lies around 2.5 ppm. Only the newly formed unsaturated group gives one clearly visible peak at 4.91 ppm. On the other hand the peaks corrosponding to the unsaturated bond at 4.85 and 4.65ppm have disappeared**[Tessier and Marrchal, 1990, Tessier and Marrchal, 1983 and Tessier and Marrchal, 1986]**.

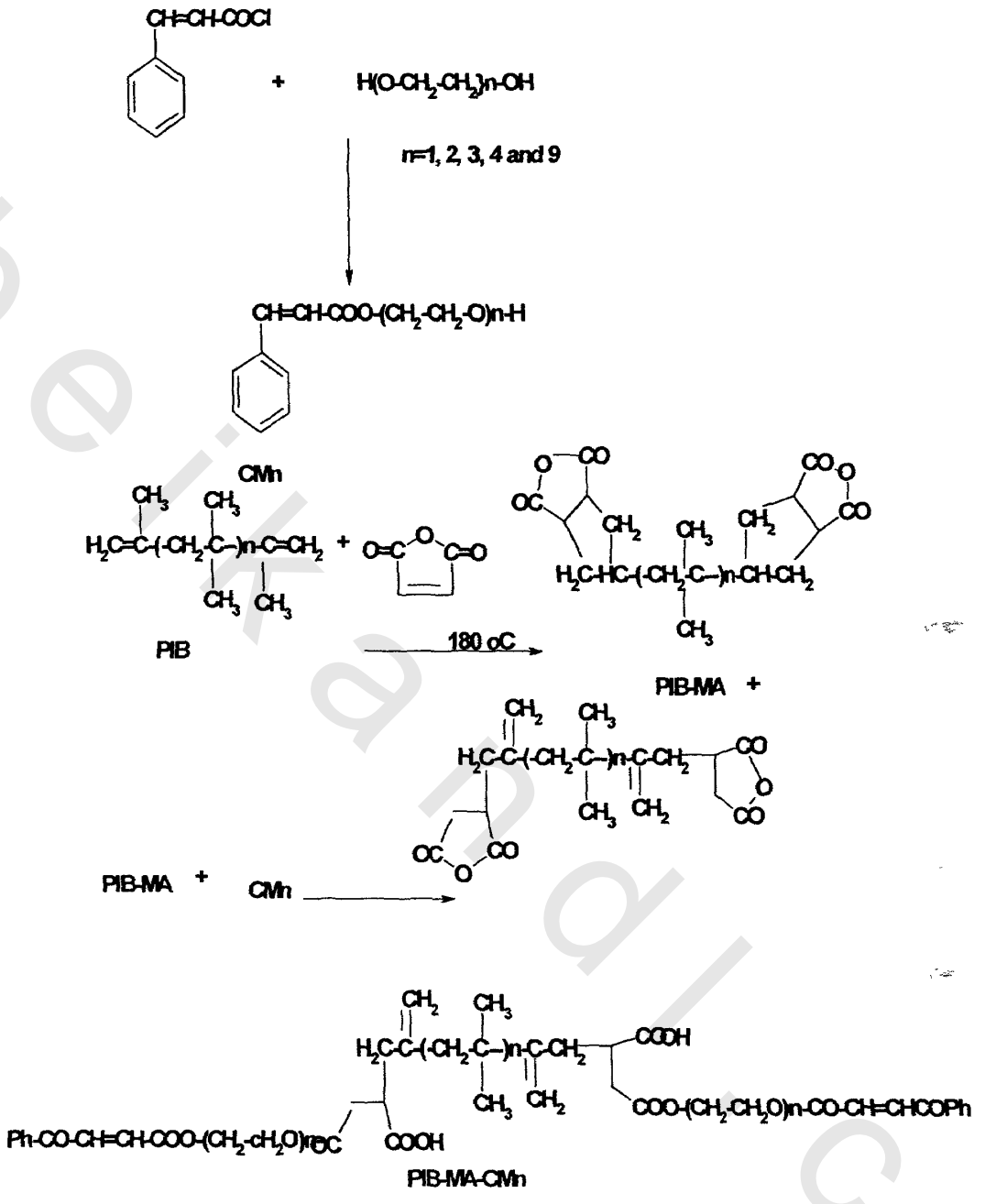


Figure (3.16): Reaction Scheme of the Synthesized Reactive Macromonomers.

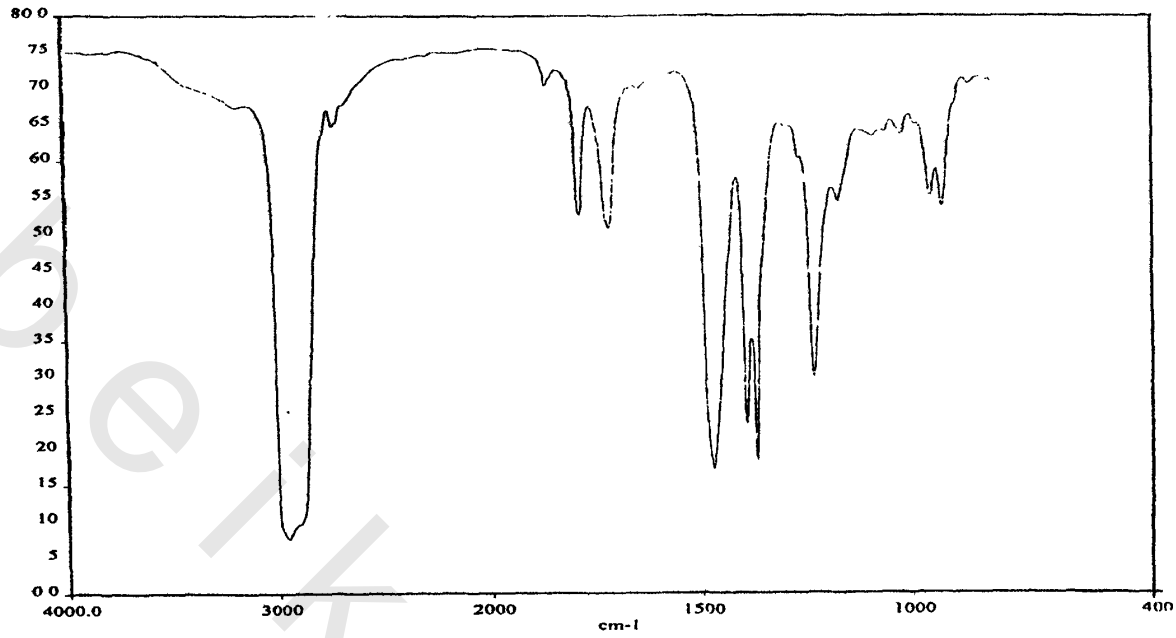


Figure (3.17) FTIR spectrum of the PIB-MA adduct

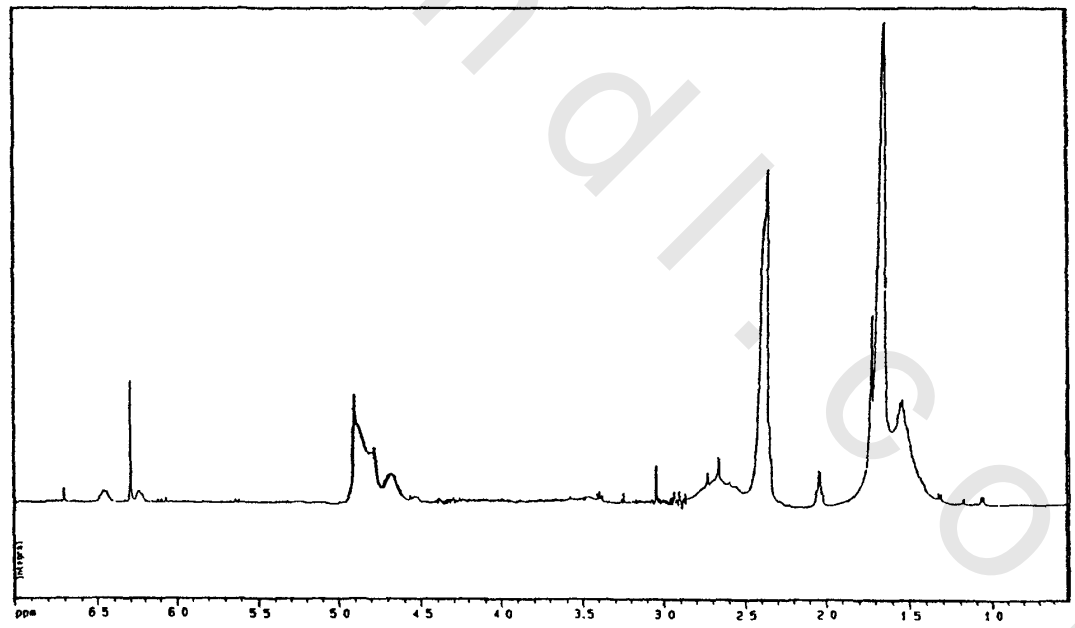


Figure (3.18) ^{1}HNMR of PIB-MA adduct

3.2.1. Synthesis of Hydroxyalkyloxy Cinnamate (CM_n)

In this work CM_n ester derivatives were synthesized by the reaction of cinnamoyl chloride with different glycols in presence of triethyl amine (TEA) as a catalyst. The reaction scheme was represented in **Figure (3.16)**. The chemical structure of CM esters was illustrated using IR analysis. The IR spectrum of CM ester with PEG_{400} was selected and represented in **Figure (3.19)**. The appearance of two new strong bands at 1735 and 1145cm-^{1} represent C=O and C-O stretching of ester group, indicates the formation of ester group when cinnamoyl chloride was reacted with glycol. On the other hand the appearance of strong band at 3445 cm^{-1} for OH stretching, indicates that the chemical structures of CM esters have terminal hydroxyl groups. The bands at 1620 and 900-650 cm^{-1} that represent C=C stretching vibration, and out-of-plane rotational vibration of aromatic C-H, respectively indicate the incorporation of cinnamate group in the structure of CM_n esters.

3.2.2. Synthesis of PIB-MA–CM Macromonomers.

The present study aims to modify PIB with maleic anhydride followed by reaction with cinnamoyl moieties to introduce aromatic moieties to increase its solubility in crude oil. In this respect, PIB having an average molecular weight of 1000, reacts with maleic anhydride through an ene reaction resulting in a polyalkenylsuccinic anhydride, which further reacts with each hydroxyalkyloxy cinnamate ester to give the respective polyalkenylsuccinate macromonomers (reactive polymer). The advantage of cinnamate groups are: stability for long storage, polymerization is not affected by oxygen and antioxidants and its ability to copolymerize either by thermal or photo polymerization

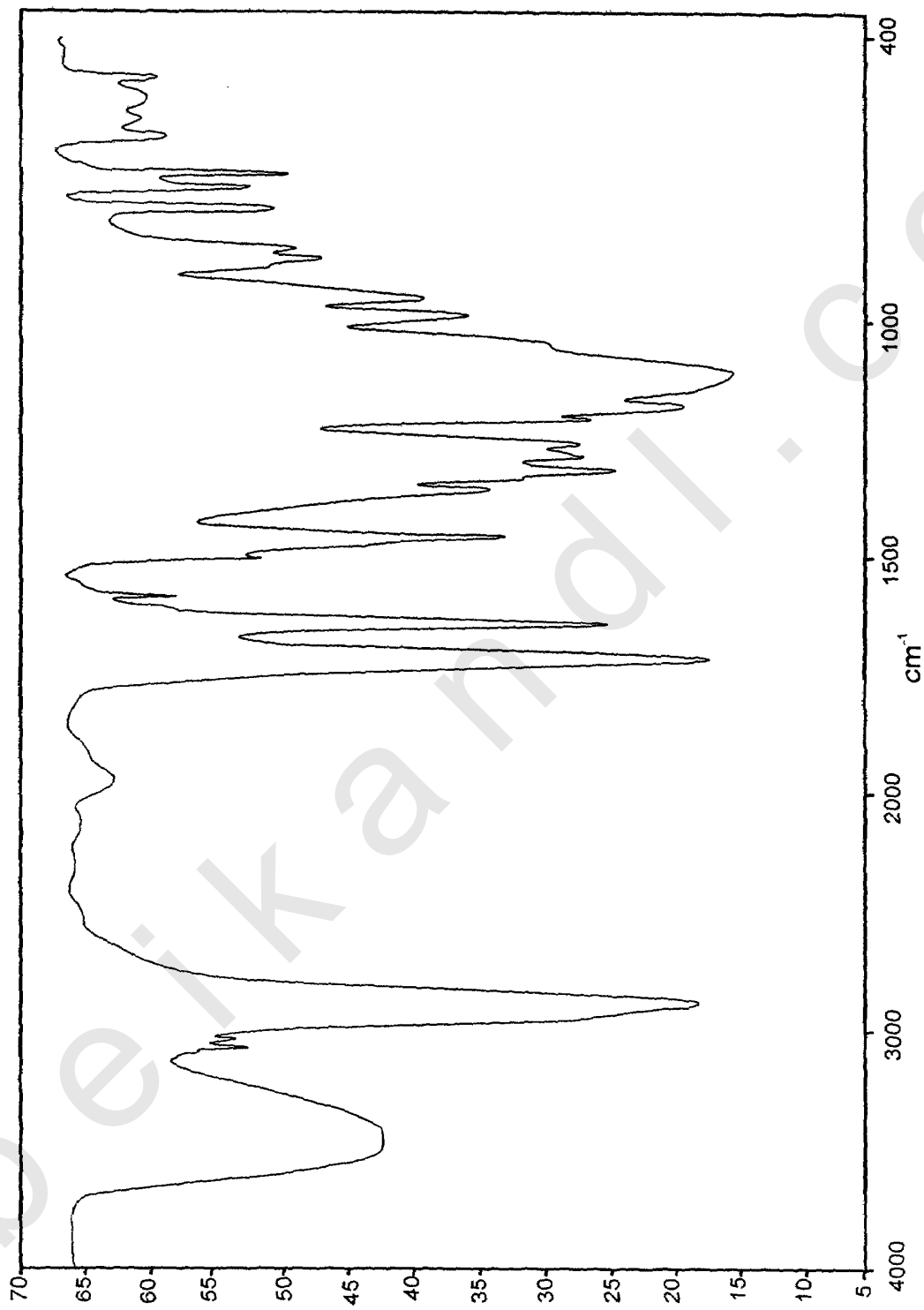


Figure (3.19): FTIR Spectrum of CM_9 Ester.

[Azuma et al., 1980]. Therefore, it is desirable to synthesis crosslinked rubbers containing cinnamate groups, which may have the advantages of both polyisobutylene and cinnamate groups. An attempt had been made in order to obtain cyclized polyisoprene- MA adduct **[Azuma et al., 1983]** to form modified polyisoprene with substituted succinic anhydride groups. These groups were converted by reaction with hydroxyalkyloxy cinnamate to cinnamate groups.

The aim of this work was to synthesize new oil-absorptive polymers containing hydrophobic chain in presence of different types of crosslinkers by chemical initiation. Accordingly, the present section aims to modify PIB-MA adduct with cinnamate moieties to introduce polymerizable aromatic moieties in order to obtain crosslinked PIB having high oil absorptivitiy to be used in the field of oil sorbers. The base materials for oil absorbent are as follows: fast oil absorption rate, high absorption oil capacity, good absorption selectivity of oil over water and low density compared to water to float with or without absorbed oil.

The reaction between PIB-MA and CM_n was carried out according to the procedure described in the experimental section. The reaction scheme was represented in **Figure (3.16).** In this respect, the succinic anhydride group of PIB-MA was apparently converted to mono (β-cinnamoyl oxyalkyl) succinate groups. The products were confirmed by ^{1}HNMR analysis. The ^{1}HNMR spectra of **PIB-MA-CM_1, PIB-MA-CM_2, PIB-MA-CM_3 and PIB-MA-CM_9** were illustrated in **Figure (3.20 a-d),** respectively. The peaks of cinnamate group were observed at 7.2-7.8 ppm for aromatic protons and 5.6-6.6 ppm for vinyl proton in all spectra. The peak at 3.8 ppm indicates the presence of OCH2-CH2O

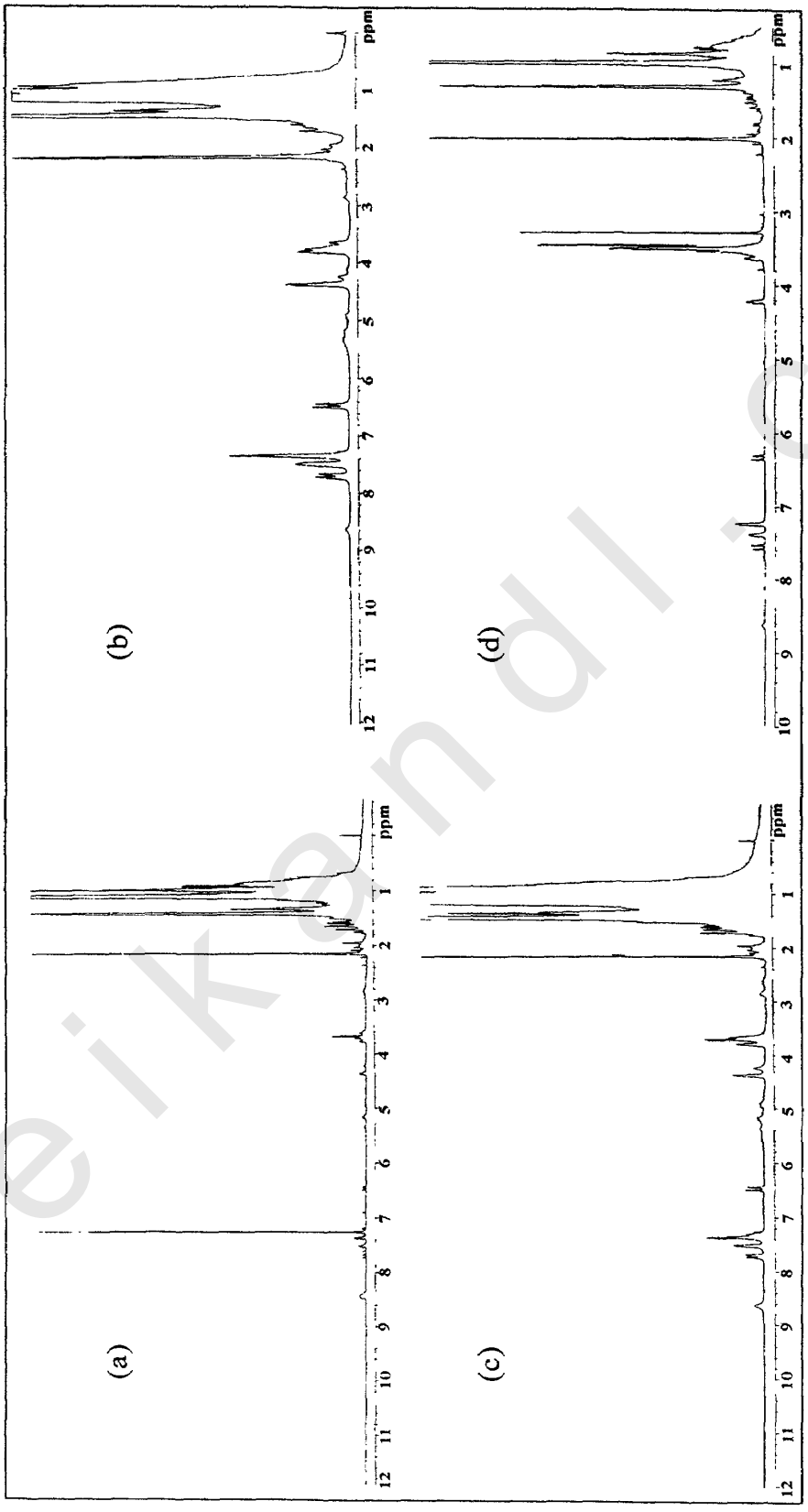


Figure (3.20): ^{1}HNMR Sectra of (a) PIB-MA-CM_1 (b) PIB-MA-CM_2 (c) PIB-MA-CM_3 (d) PIB-MA-CM_9 Reactive Macromonomer.

protons and their intensities are based on type of the used glycols. The peak at 8.9 ppm that represent COOH proton confirms the monoester formation between CM_n and PIB-MA. Therefore, it was confirmed that the succinic anhydride group in PIB-MA was completely condensed to the cinnamate group by the reaction with hydroxylalkyloxy cinnamate.

3.3. HIGH CONVERSION COPOLYMERIZATION

Crosslinking is responsible for the three-dimensional network structure that is important for oil to be swelled into sorbers rather to dissolve in it. Elasticity and swelling properties are attributed to the presence of physical or chemical crosslinks within polymer chains. Hydrophobic network polymers are used as absorbents of oil as well as some organic solvents spilled on water in the field of environment.

High conversion polymerization was performed for preparing different crosslinked copolymers. The crosslinked copolymers of CEMA/IOA, CEMA/DDA and CEMA/ODA copolymers were prepared via bulk polymerization in presence of 0.02% ABIN as initiator and different weight percentage of two different crosslinkers TPT and TPT_m ranging from 0.5 % to 4%. Different molar ratios of CEMA with each alkyl acrylates viz. 90/10, 70/30, 50/50, 30/70 and 10/90 (mole%/mole%) were used in each copolymer.

3-3-1 Crosslinked copolymers

A wide variety of vinyl crosslinkers has been used to form crosslinked networks. The choice of the crosslinkers is quite broad in bulk and solution polymerization. The crosslinker concentrations usually about 0.05-1% are used to provide super absorbents with high swelling capacity and low soluble polymer content. Many side reactions, such as

intrachain cyclization -decrease the efficiency of the crosslinker and result in a gel point later in the polymerization than would be predicted by theory- and less crosslinked networks than would be predicted from the number of potential crosslinking sites. This deviation from theory can be significant at high crosslinker levels, such as used in styrene divinylbenzene copolymers where intramolecular cyclization is believed to occur. Intramolecular cyclization increases with low monomer content and high copolymer conversion. Because of the high monomer content and low crosslinker levels used in typical gel processes, there is a reduced probability of this inefficient side reaction, especially during the initial part of the polymerization process. To understand the distribution of crosslinks in the network, the reactivity of the various double bonds in the system must be determined. This includes the reactions between double bonds of CEMA and each of alkyl acrylate, the initial double bonds of the crosslinker, and the various double bonds that are pendant to the polymer chain after incorporation of the crosslinker.

The present copolymeric system is composed essentially of CEMA with varying amounts of IOA, DDA or ODA comonomer to give certain hydrophibicity, which improves oil affinity. The yield of crosslinking reaction increases very rapidly at some extent of the reaction as the reaction proceeds, and the reaction product begins to form an infinite molecular weight network called gel point. In the gel state, chemical reaction can proceed and chains form the network by crosslinking. The crosslink density or degree of crosslinking is a measure of the total links between chains in a given mass of substrate. In a crosslinking system, there are soluble portions and insoluble portions, the former can be extracted with suitable solvents and the

latter cannot be extracted with any solvent due to crosslinking. It only swells in good solvent to give a gel. According to Flory's swelling theory **[Flory, 1953]**, swelling behavior is affected by rubber elasticity, affinity to solution and crosslinking density. The swelling behavior of gels with different amounts of the crosslinkers was studied. Generally, the crosslinker concentrations used are at levels ranging from 0.01-4% usually about 0.05 –1% to provide super absorbents with high swelling capacity and low soluble polymer content.

3.3.2 Soluble Fraction

Some polymer chains are not attached to the infinite network can be extracted from the gel fraction. The effect of these chains is difficult to treat, and usually neglected in the theories. These chains do not contribute to the modulus but can be solvated and contribute to the swelling. Therefore, it is desirable to eliminate or minimize the content of these extractable molecules. The percentage of this extractble fraction (soluble fraction) depends on: (a) the type and concentration of the monomers, and (b) the type and concentration of crosslinking agent **[Kossmehl et al., 1994]**.

In the present investigation the polymer rods were post cured at 378K in an air oven for 24 hours to assure complete polymerization. The sol 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. After extraction for 24h, the samples were dried in atmosphere for several hours and then dried to a constant weight in vacuum oven at 308K. However, no further extraction was

found after 24hours, and this soxhlet extraction time was adopted for all samples.

In the present work, the reactivity of a crosslinker containing acrylate group (TPT) and that with methacrylate group (TPT_m) towards (CEMA-IOA), CEMA-DDA) and (CEMA-ODA) copolymer was investigated from polymerization conversion and SF measurements in chloroform.

The total conversion of monomers to cross-linked polymers was estimated using equation (3.6):

$$\text{Total conversion (\%)} = W \times 100 / W_0 \qquad \textbf{(3. 6)}$$

Where, W and W_0 are total weight of cross-linked polymers after post curing at 105°C and weight of reactants, respectively. The data of total conversion% for copolymerization of CEMA and IOA, DDA or ODA monomers crosslinked by either TPT or TPT_m crosslinker were determined and listed in **Table(3.7).** The data show the variation of conversion% for all composition of CEMA and IOA, DDA or ODA monomers with 1% crosslinker and with different crosslinker weight content for 50% mole (CEMA) and 50% mole alkyl acrylate. It was found that the crosslinking conversion precentages increase as the amount of alkyl acrylate increases. This indicates that the efficiency of crosslinking was increased with increasing alkyl acrylate contents.

On the other hand, determined SF% values are listed in **Tables (3.8-3.10).** The effect of crosslinker concentrations on SF values was determined through crosslinking of CEMA (50 mol%) / each alkyl acrylate (50 mol%) copolymer with different contents of TPT or TPT_m viz. 0.5, 1, 2 and 4% (w/w). From data it's obvious that, the percentage of SF for crosslinked copolymers is reduced when crosslinker content

Table (3.7): The Percentage Conversion Of The Prepared CEMA/Alkylacrylate Sorbers Crosslinked by Either TPT or TPT_m Crosslinker.

Xerogel Compositions	Crosslinker Weight %	Conversion %					
		CEMA/IOA		CEMA/DDA		CEMA/ODA	
		TPT	TPT_m	TPT	TPT_m	TPT	TPT_m
90/10	1	94.4	95.4	92.9	92.9	89.1	90.9
70/30	1	95.4	96.3	93.8	93.1	90.8	93.5
50/50	0.5	93.8	94.5	92.8	93.8	91.8	91.9
	1	95.7	95.9	94.7	94.4	92.1	92.1
	2	94.5	96.1.	94.4	94.9	92.8	93.1
	4	96.5	97.2	95.6	95.2	93.5	93.9
30/70	1	97.5	97.8	94.7	95.5	91.9	92.2
10/90	1	98.2	98.8	95.1	96.1	92.1	93.5

Table (3.8): Soluble Fraction of the Crosslinked CEMA/IOA Copolymers Having Different Crosslinker Contents.

Xerogel composition of (CEMA/IOA)	Crosslinker content (wt%)	SF % of Crosslinked gels in chloroform	
		TPT	TPTm
90/10	1	31.60	30.66
70/30	1	24.32	23.14
50/50	0.5	23.00	20.32
	1	18.78	16.33
	2	15.76	13.54
	4	11.32	10.53
30/70	1	12.35	9.02
10/90	1	10.89	8.89

Table (3.9): Soluble Fraction of the Crosslinked CEMA/DDA Copolymers Having Different Crosslinker Contents.

Xerogel composition of (CEMA/IOA)	Crosslinker content (wt%)	SF % of Crosslinked gels in chloroform	
		TPT	TPTm
90/10	1	35	33.52
70/30	1	24.96	21.32
50/50	0.5	30.919	27.2181
	1	22.13	20.331
	2	15.88	13.23
	4	12.03	10.22
30/70	1	18.28	16.79
10/90	1	11.433	9.42

Table (3.10): Soluble Fraction of the Crosslinked CEMA/ODA Copolymers Having Different Crosslinker Contents.

Xerogel composition of (CEMA/IOA)	Crosslinker content (wt%)	SF % of Crosslinked gels in chloroform	
		TPT	TPT_m
90/10	1	39.57	36.53
70/30	1	32.55	30.55
50/50	0.5	32.91	30.21
	1	30.98	27.98
	2	17.6	15.68
	4	14.11	12.33
30/70	1	20.57	18.22
10/90	1	13.25	11.58

increases from 0.5% to 4% (w/w). This indicates that high content of TPT or TPT_m crosslinkers reduces the probability of side reactions, which affect the crosslinking activity. It is also observed that SF% values for each of the prepared CEMA-alkyl acrylate copolymer crosslinked with TPT_m are lower than those crosslinked with TPT. This may be attributed to the differences in reactivity ratios of both crosslinkers with the produced polymer **[Atta and Arndt, 2001]**, where the presence of methyl groups in TPT_m would allow it to enter in the crosslinking reaction of CEMA-alkyl acrylate comonomer system more readily than TPT. Also, the effect of copolymer compositions on SF% values were determined by crosslinking different compositions of CEMA-alkyl acrylate copolymer using 1%(w/w) of either TPT or TPT_m crosslinkers and 0.02% (w/w) AIBN as initiator. Regarding the data shown in **Tables (3.8-3.10)**, it is obvious that, for copolymers crosslinked with either crosslinkers TPT or TPT_m, SF % decrease with increasing alkyl acrylate percentage in the copolymer composition. This may be referred to the higher reactivity of alkyl acrylate homopolymer towards either crosslinkers than that of CEMA/alkyl acrylate copolymer. In other words, the alkyl acrylate polymers are used up before a significant number of CEMA would incorporate in the network structure. It is also observed that, SF % increases as length of alkyle acrylate increases this may be attributed to the lower reactivity of longer alkyl acrylate towards either crosslinkers than that of CEMA/alkyl acrylate copolymer.

3.3.3. Swelling Behavior of the Crosslinked Copolymers

Water clean up implies recovering oils and hydrocarbon oils from water, among other pollutants. Among the main existing techniques, the

use of a sorbent, seems to be interesting because its function is to induce separation of oil and water so that the oil can easily be recovered **[Pete, 1992]**.

In this respect, the sorbent should have a high oleophilic and hydrophobic property. The sorption capacity is measured by the liquid sorption ratio. It is increased if the sorbent has the capability of drawing the oil into the material matrix, which implies a porous structure. Besides, the faster the oil is trapped, the less likely it will disperse and get away, and the easier the recovery operation will be. Sorbents buoyancy and durability in aqueous media are high; it should not retain water or react like a hydrophilic product. Their oil retention capability should also be high, so that the sorbed oil should not drain too quickly. It should rather be reusable and non-toxic for environment if not reused **[Browers, 1982 and Desphande et al., 2003]**.

It has been reported that, the excellent oil absorptivitiy of materials depends on the bulkiness and length of the alkyl substituents **[Kim et al., 1999]** and especially the porosity of the microstructure, which can be controlled by crosslinking. Because the driving force for oil absorption is caused mainly by the vander Waals force between the material and the oil, therefore, the materials with the proper porosity can effectively contain oil in their structures.

The oil used in this experiment is diluted with toluene (10 %). For the real application to clean up an oil spill, the oil absorption test has to be operated using not only light or medium oil but also heavy oil, because the spilt crude oil has a high viscosity. On the other hand, the materials used to absorb the oil do not have a sponge like structure with open pores. It has only a network structure, which formed by the crosslinking reaction. Therefore, heavy oil with high viscosity, like Belayium crude

oil, cannot easily diffuse from the surface of the samples into the internal space of network. On the other hand, toluene is the most applicable solvent that used to dissolve asphaltene of crude oil. For these reasons, we have used diluted crude oil with toluene in this experiment so that the swelling behavior of the samples could be easily evaluated. The swelling characteristics of crosslinked networks are controlled by a balance of opposing forces, swelling forces driven by osmotic pressure, and restoring forces from a variety of physical, covalent, or ionic crosslinks. The crosslinks are typically incorporated during the polymerization by the use of copolymerized multifunctional crosslinkers.

(a)- Oil absorbencies for CEMA/IOA crosslinked copolymers

The swelling curve is based on plotting the relation between oil absorbancies versus immersion times. In this respect, upon using pure toluene, **Figures (3.21& 3.22)** show the oil absorbencies for CEMA–IOA copolymers with different mole ratios of CEMA to IOA as a function of immersion time crosslinked by either TPT or TPT_m crosslinker respectively. **Figures (3.23 & 3.24)** show the oil absorbencies for CEMA–IOA copolymers with different compositions of CEMA to IOA as a function of immersion time upon using 10% crude as an oil medium crosslinked by either TPT or TPT_m crosslinker, respectively. In these figures, it is obvious that the oil absorbency increases with increasing the immersion time and leveled off at 3h. Also, it is clear that, the higher the IOA content is the higher the oil absorbency. This may be explained on the basis that, the increase in acrylate ratio in the crosslinked

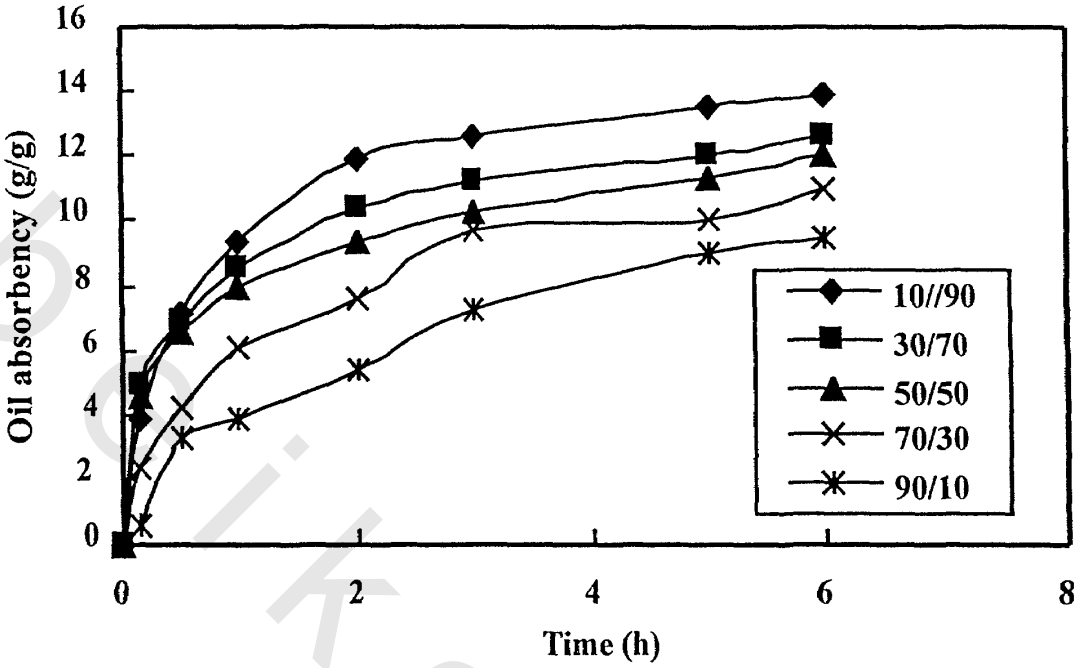


Figure (3.21):Oil Absorbencies for CEMA/IOA Copolymers in Pure Toluene With Different Mole Ratios of CEMA to IOA as a Function of Immersion Time Using 1%TPT Crosslinker at 298K..

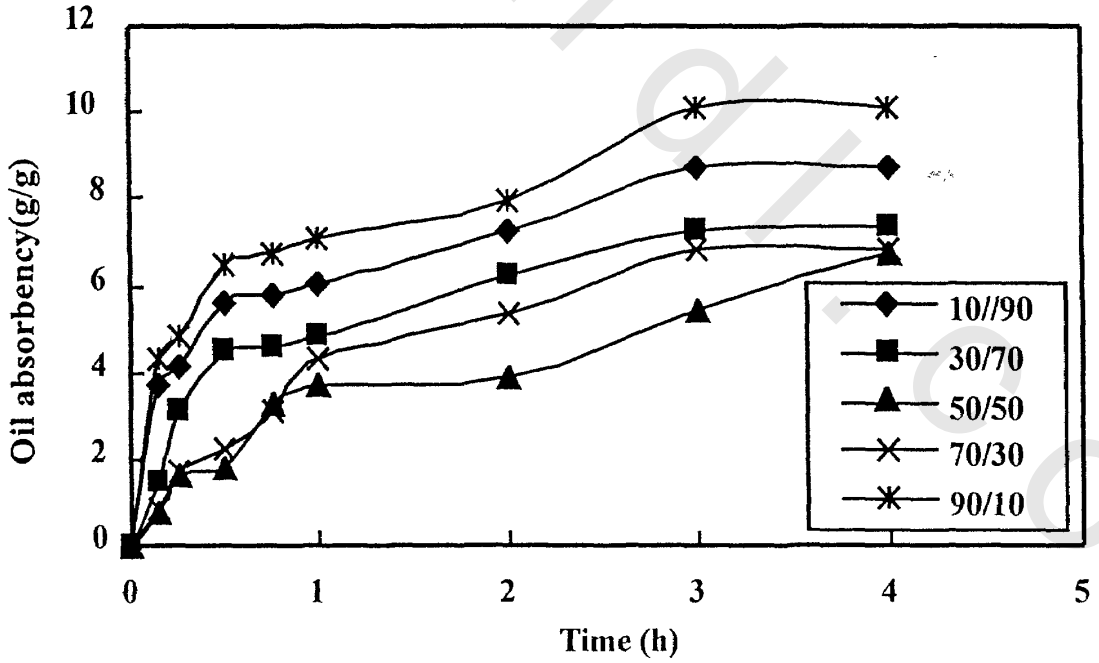
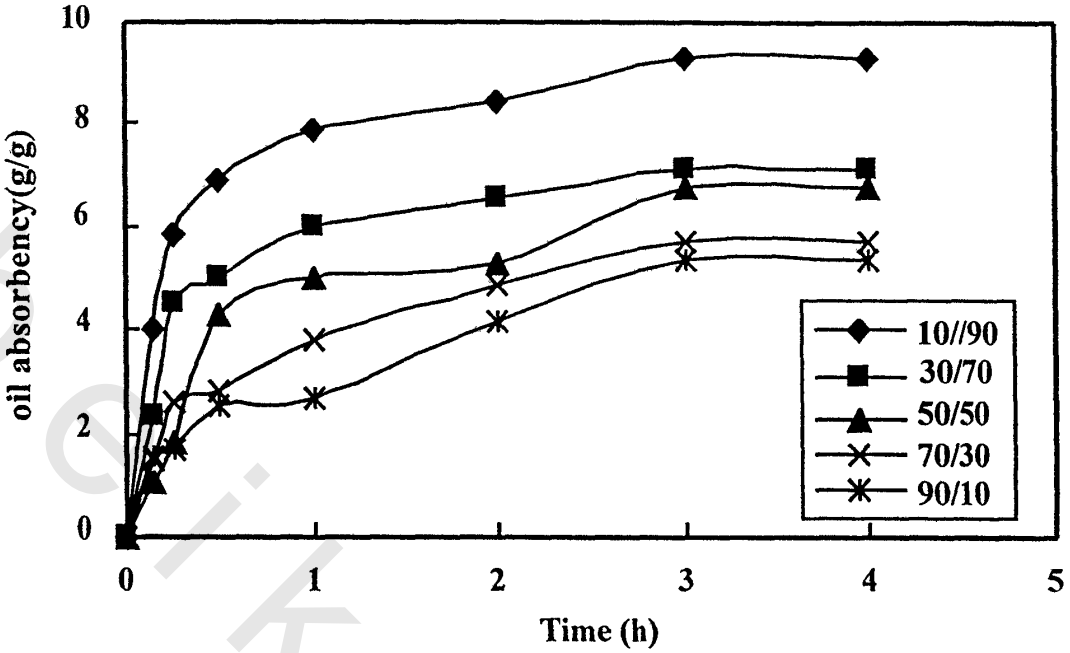


Figure (3.22):Oil Absorbencies for CEMA/IOA Copolymers in Pure Toluene With Different Mole Ratios of CEMA to IOA as a Function of Immersion Time Using 1%TPT_m Crosslinker at 298K



Figure(3.23): Oil Absorbencies for CEMA/IOA Copolymers in 10% Crude Oil With Different Mole Ratios of CEMA to IOA as a Function of Immersion Time Using 1%TPT Crosslinker at 298K.

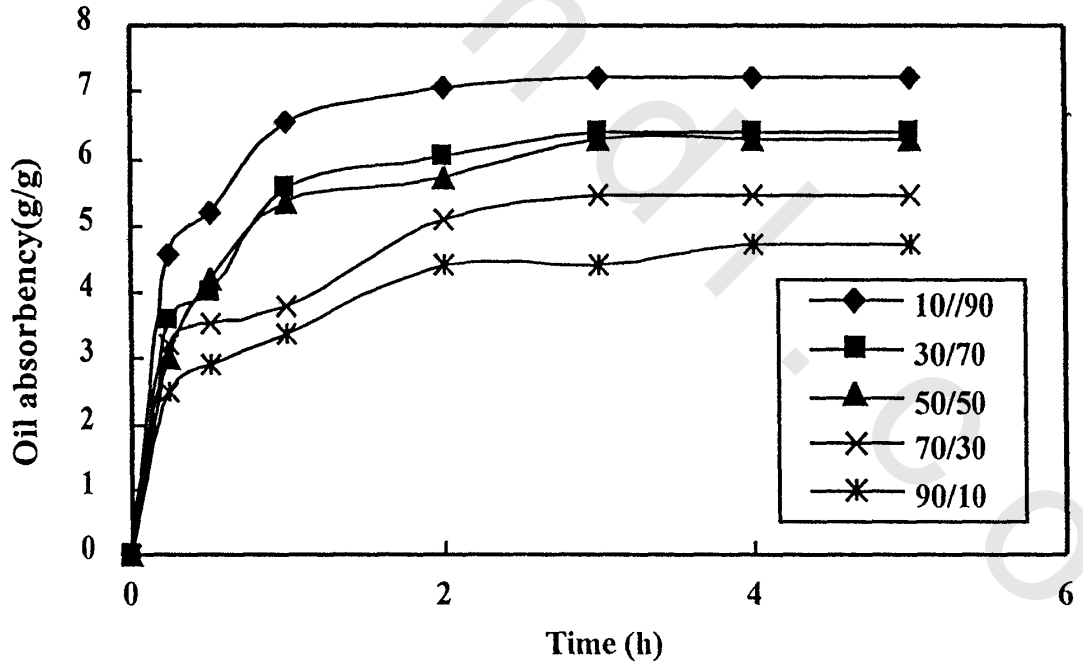


Figure (3.24): Oil Absorbency for CEMA/IOA Copolymer in 10% Crude Oil With Different Mole Ratios of CEMA to IOA as a Function of Immersion Time Using 1wt% TPTm at 298K..

copolymer will increase the hydrophibicity of crosslinked network. It is also observed that, the oil absorbency decreases slightly upon using 10% crude instead of pure toluene. This may be explained as follow, the swelling process of polymer networks may be primarily due to the oil solution penetration into polymeric gel through capillary and diffusion. Therefore, crude oil with higher viscosity cannot easily diffuse from external surface of the sample into the internal space of networks **[Jang and Kim, 2000]**.

Figures (3.25-3.26) represent the oil absorbencies of poly(CEMA/IOA) xerogels at 50/50 mol% of CEMA/IOA in the presence of different crosslinker contents immersed in pure toluene and 10% crude oil, respectively. It is found that, the oil absorbency decreased with increasing the amount of TPT or TPT_m crosslinker. The increment in the amount of the crosslinking agent forms denser network of the copolymer and reduces M_c (the average molecular weight between crosslinks) **[Flory and Rehner, 1943]** i.e., restricted relaxation of the polymeric chain. Generally, the higher M_c increases the swelling ratio **[peppas and Merrill, 1976]**.

By comparing the maximum oil absorbency Q_{max} of poly(CEMA/IOA) crosslinked by TPT and those crosslinked by TPT_m, it is found that TPT crosslinked sorbers give higher Q_{max} than those of TPT_m–based. This is mainly due to lower crosslinking density with TPT. **Tables (3.11 & 3.12)** list absorption characteristics of the crosslinked CEMA/IOA copolymers upon using pure toluene or diluted crude oil medium respectively, different CEMA/IOA molar compositions with TPT or TPT_m crosslinker, respectively.

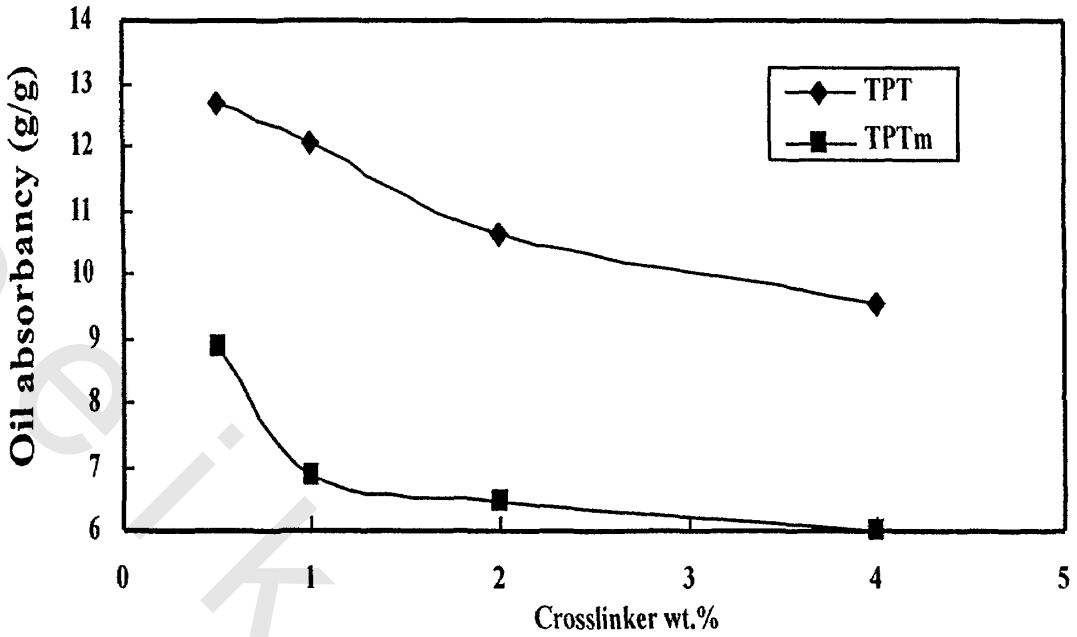


Fig. (3.25): Oil Absorbency of CEMA/IOA Xerogels in Pure Toluene at 50mole% of CEMA to 50 Mole%IOA as a Function of Crosslinker wt%.

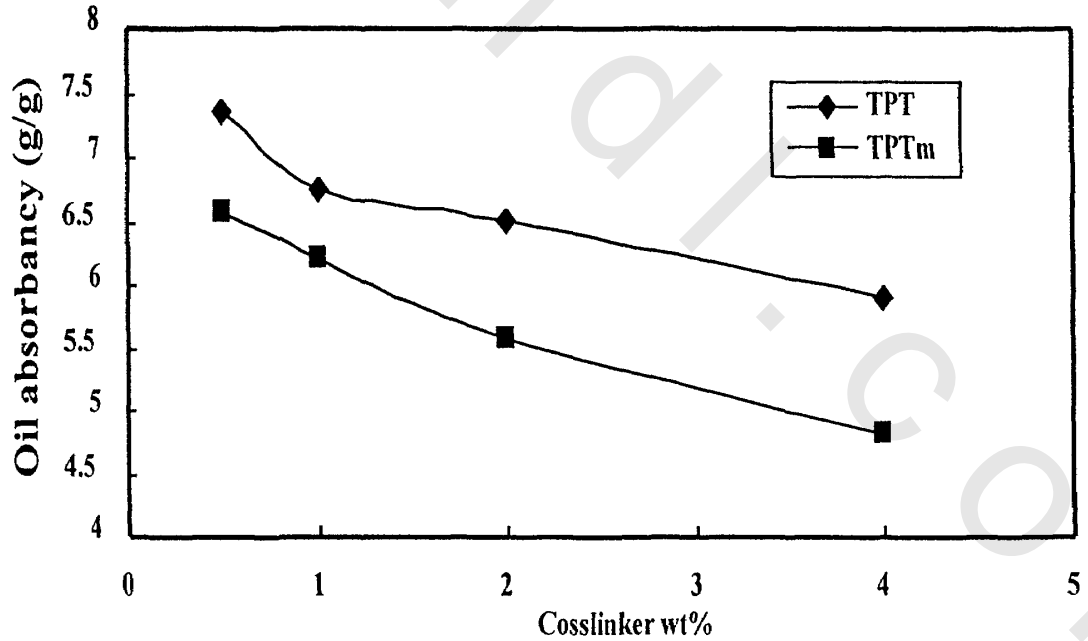


Fig. (3.26): Oil Absorbency of CEMA/IOA Xerogels in 10% Crude Oil at 50Mole% of CEMA to 50 Mole%IOA as a Function of Crosslinker wt%.

Table (3.11): Absorption Characteristics of the *CEMA/IOA Copolymers* Crosslinked With TPT Crosslinker at 298 K.

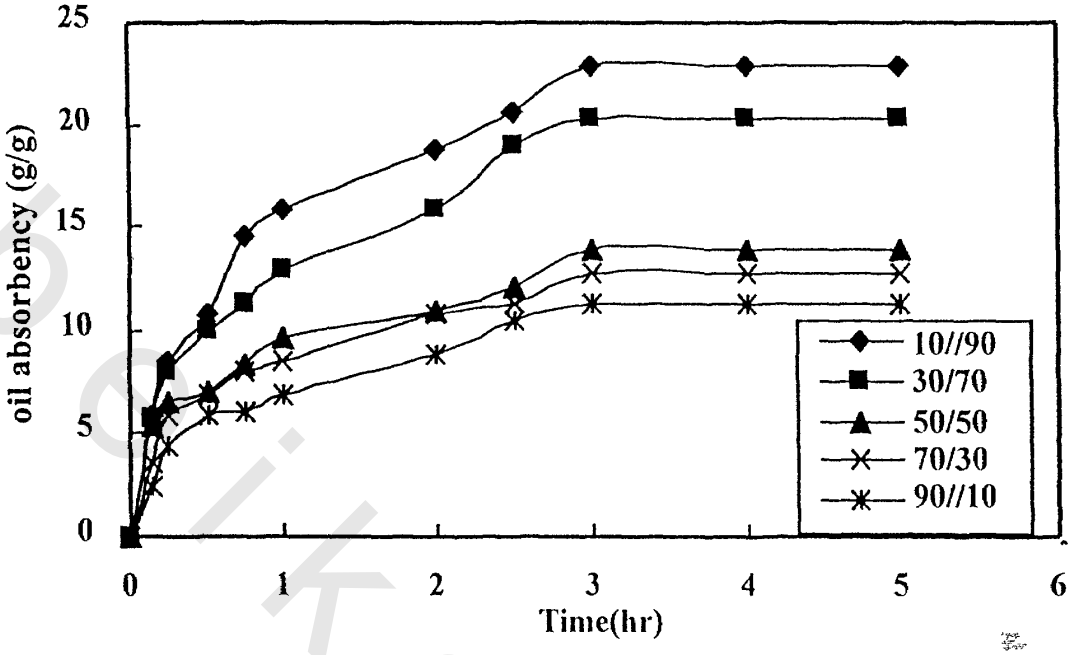
Xerogel composition	Crosslinker Content (wt%)	Q_{max} (g/g)		ETC		Q (g/g)		T (h)		K (h^{-1})	
		Toluene	crude oil	Toluene	crude oil	Toluene	crude oil	Toluene	crude oil	Toluene	crude oil
90/10	1	9.45	5.32	90.43	84.17	5.97	3.36	1.2	1	0.499	0.999
70/30	1	10.98	5.76	91.65	85.14	6.93	3.64	1.25	1	0.799	0.999
50/50	0.5	12.71	7.35	92.70	88.02	8.02	4.64	1	0.6	1.66	2.499
	1	12.08	6.76	92.35	87.11	7.60	4.27	0.75	0.5	1.42	2.221
	2	10.62	6.53	91.39	86.71	6.71	4.12	0.7	0.45	1.33	1.999
	4	9.56	5.91	90.53	85.52	6.04	3.73	0.6	0.4	0.99	1.666
30/70	1	12.57	7.12	92.63	87.68	7.94	4.49	0.90	0.25	1.11	3.98
10/90	1	13.94	9.29	93.3	90.28	8.80	5.87	0.75	0.25	1.33	3.99

Table(3.12): Absorption Characteristics of the CEMA/IOA Copolymers Crosslinked With TPT_m Crosslinker at 298 K.

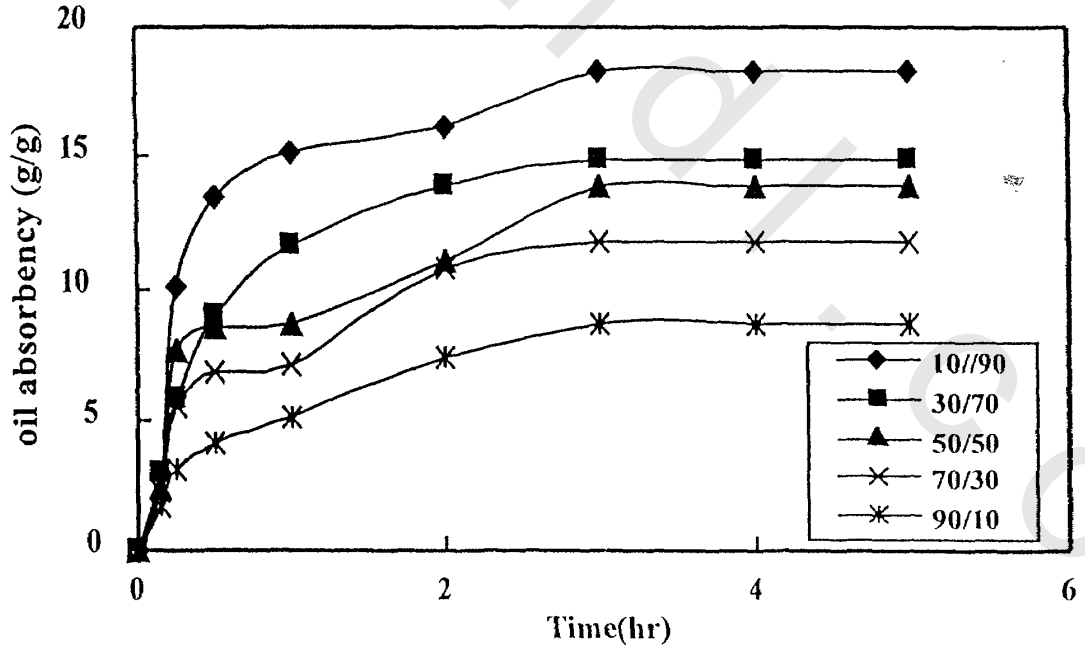
Xerogel Composition	Crosslinker Content (wt%)	Q_{max} (g/g)		ETC		Q (g/g)		T (h)		K (h^{-1})	
		Toluene	crude oil	Toluene	crude oil	Toluene	crude oil	Toluene	crude oil	Toluene	crude oil
90/10	1	5.66	4.71	84.98	82.48	3.57	2.97	2.5	1	0.399	0.99
70/30	1	6.83	5.43	87.30	89.44	4.31	3.43	2.5	0.75	0.399	1.33
50/50	0.5	8.869	6.58	89.86	86.80	5.60	4.15	1.5	0.75	2.499	3.33
	1	6.83	6.21	87.23	86.13	4.31	3.95	1.25	0.6	0.999	1.99
	2	6.45	5.58	86.65	84.80	4.07	3.52	1	0.5	0.799	1.66
	4	6.02	4.87	85.87	82.96	3.80	3.07	0.4	0.3	0.666	1.33
30/70	1	7.42	6.41	88.12	86.13	4.68	4.05	0.5	0.4	1.99	2.49
10/90	1	8.69	7.22	89.68	87.83	5.49	4.56	0.5	0.25	1.99	3.99

(b)- Oil absorbencies for CEMA/ linear alkyl acrylat (DDA or ODA) crosslinked copolymers

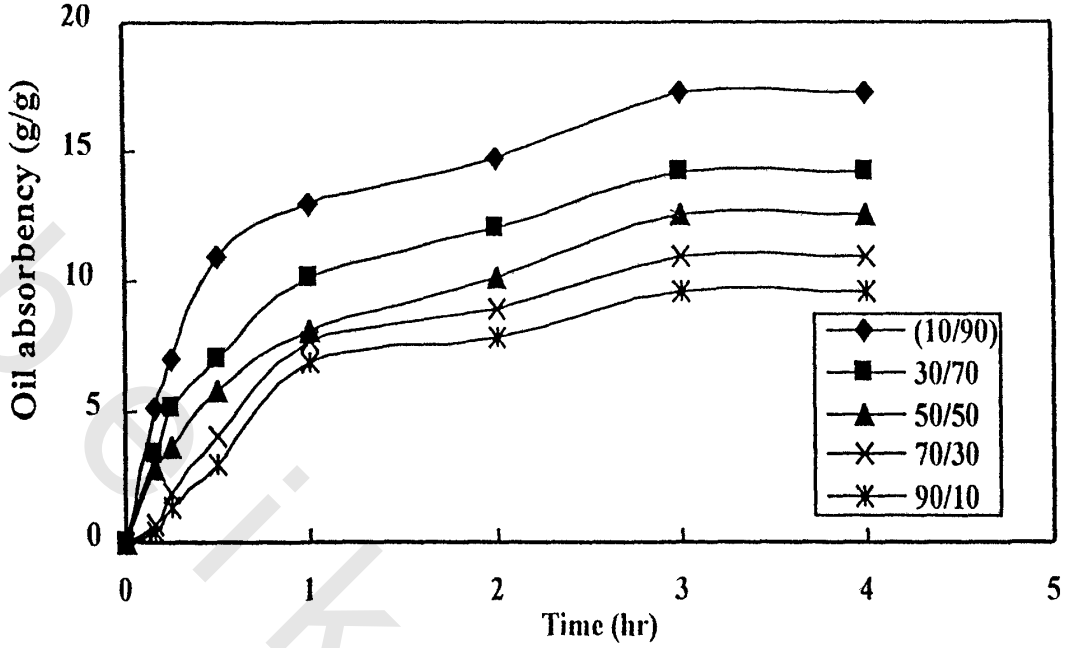
The oil absorbencies of different crosslinked copolymer compositions with either TPT or TPT_m as a function of immersion time upon using pure toluene or 10% crude as an oil medium for of CEMA/DDA were represented in **Figures (3.27-3.30)** an that for of CEMA/ODA were represented in **Figures (3.31-3.34)**. In these figures, it is observed that the oil absorbency increases with increasing the immersion time and attain the maximium swelling values during 3h for CEMA/DDA and CEMA/ODA copolymers. Also It can be observed that, Q_{max} values for all CEMA/ODA compositions are usually higher than those observed for CEMA/DDA compositions upon using 1% of either crosslinker. Also, it is observed that the higher the alkyl acrylate content is, the higher the oil absorbency. This may be explained on the basis that, the increase in acrylate ratio in the crosslinked copolymer will increase the hydrophibicity of crosslinked network. This indicates that, the swelling capacities are affected by the hydrophobicity of copolymers. On the other hand, Q_{max} values are largely affected by the sorption medium. It is noticed that, the oil absorbency decreases slightly upon using 10% crude instead of pure toluene. This could be due to the higher viscosity of crude oil which can cause two opposite effects: decreased sorption during the penetration through interior of network and improved sorption since the oil is better adhered to the material **[Choi and Cloud, 1992]**. **Figuers (3.35–3.38)** show a comparison of Q_{max} between CEMA/DDA and CEMA/ODA crosslinked with TPT or TPT_m as afunction of crosslinker content. It is found that the crosslinked sorbers with TPT have higher Q_{max} than that crosslinked with TPT_m.



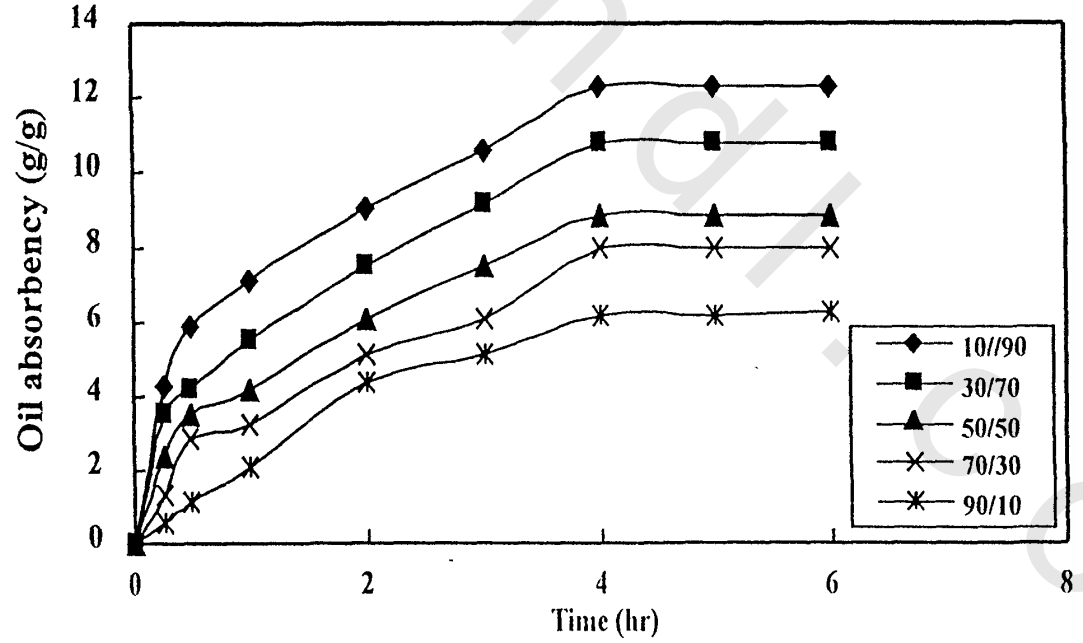
Figure(3.27): Oil Absorbencies for CEMA–DDA Copolymers in Pure Toluene with Different Mol Ratios of CEMA to DDA as a Function of Immersion Time Using 1%TPT Crosslinker at 298K



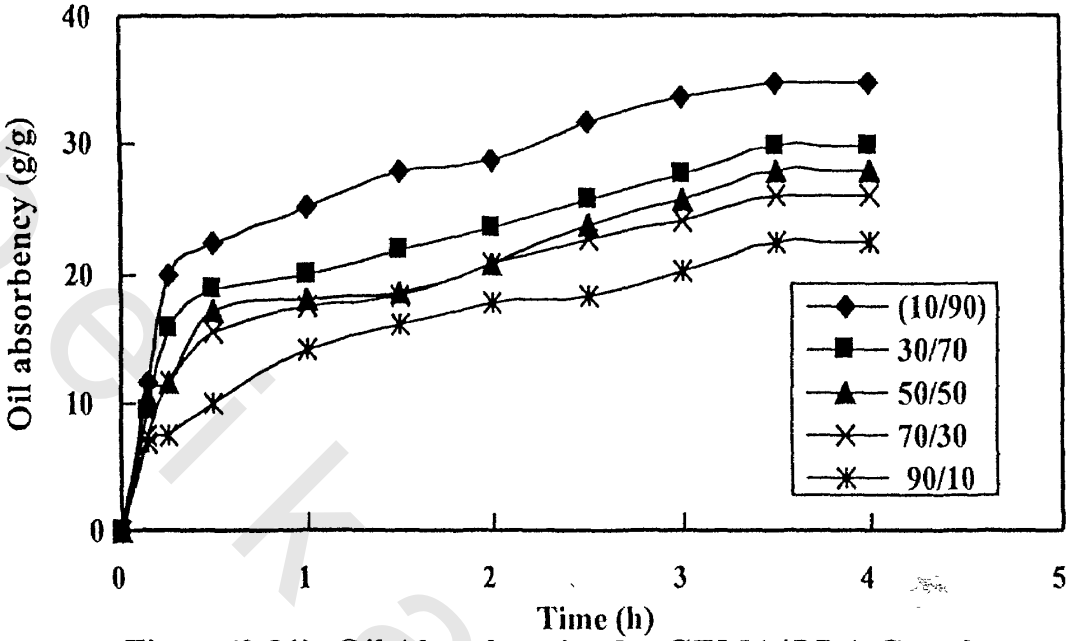
Figure(3.28): Oil Absorbencies for CEMA–DDA Copolymers in Pure Toluene With Different Mole Ratios of CEMA to DDA as a Function of Immersion Time Using 1%TPTm Crosslinker at 298K.



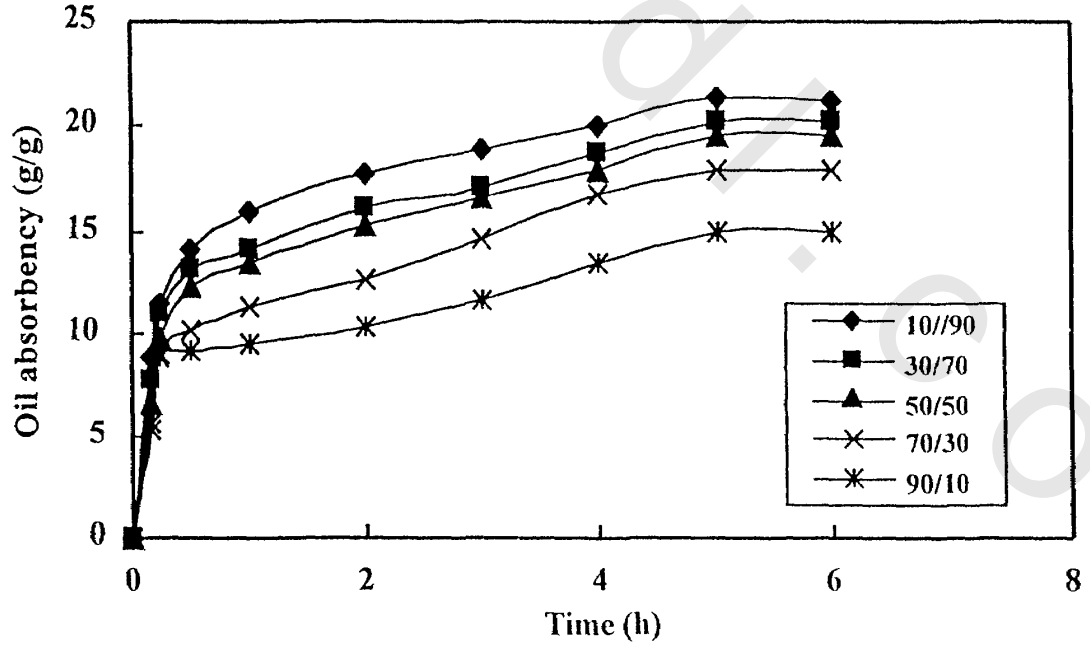
Figure(3.29): Oil Absorbencies for CEMA–DDA Copolymers in 10% Crude Oil With Different Mol Ratios of CEMA to DDA as a Function of Immersion Time Using 1%TPT Crosslinker at 298K.



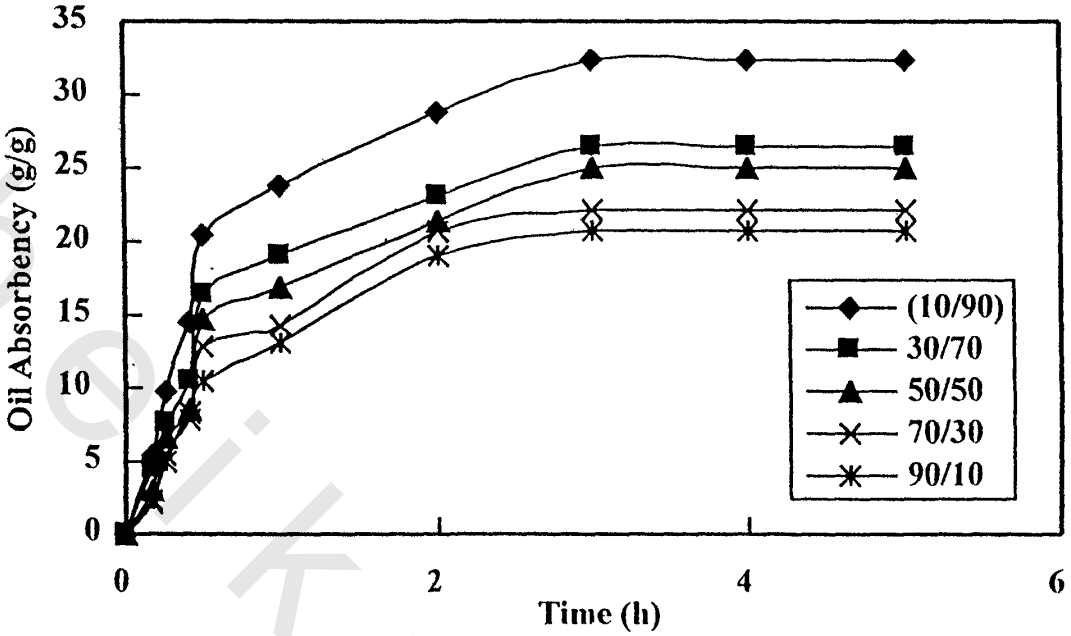
Figure(3.30): Oil Absorbencies for CEMA/DDA Copolymers in 10% Crude Oil With Different Mol Ratios of CEMA to DDA as a Function of Immersion Time Using 1%TPTm Crosslinker at 298K.



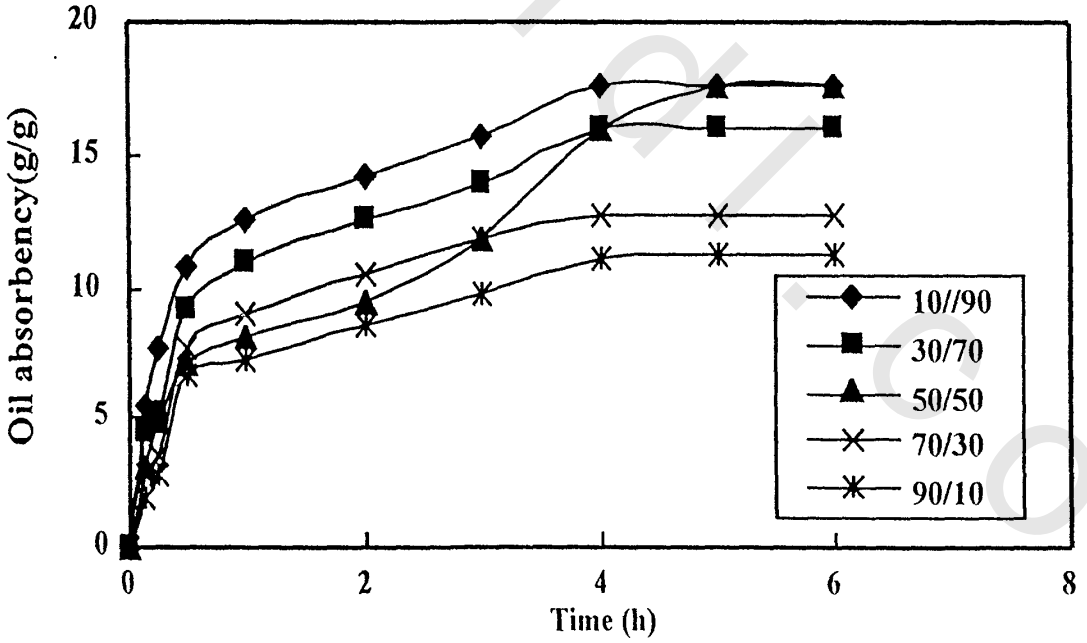
Figure(3.31): Oil Absorbencies for CEMA/ODA Copolymers in Pure toluene With Different Mol Ratios of CEMA to ODA as a Function of Immersion Time Using 1%TPT Crosslinker at 298K.



Figure(3.32): Oil Absorbencies For CEMA/ODA Copolymers in Pure Toluene With Different Mole Ratios of CEMA to ODA as a Function of Immersion Time Using 1%TPTm Crosslinker at 298K.



Figure(3.33): Oil Absorbencies For CEMA/ODA Copolymers in 10% Crude Oil With Different Mol Ratios of CEMA to ODA as a Function of Immersion Time Using 1%TPT Crosslinker at 298K.



Figure(3.34): Oil Absorbencies for CEMA/ODA Copolymers in 10% Crude Oil With Different Mol Ratios of CEMA to ODA as a Function of Immersion Time Using 1%TPTm Crosslinker at 298K.

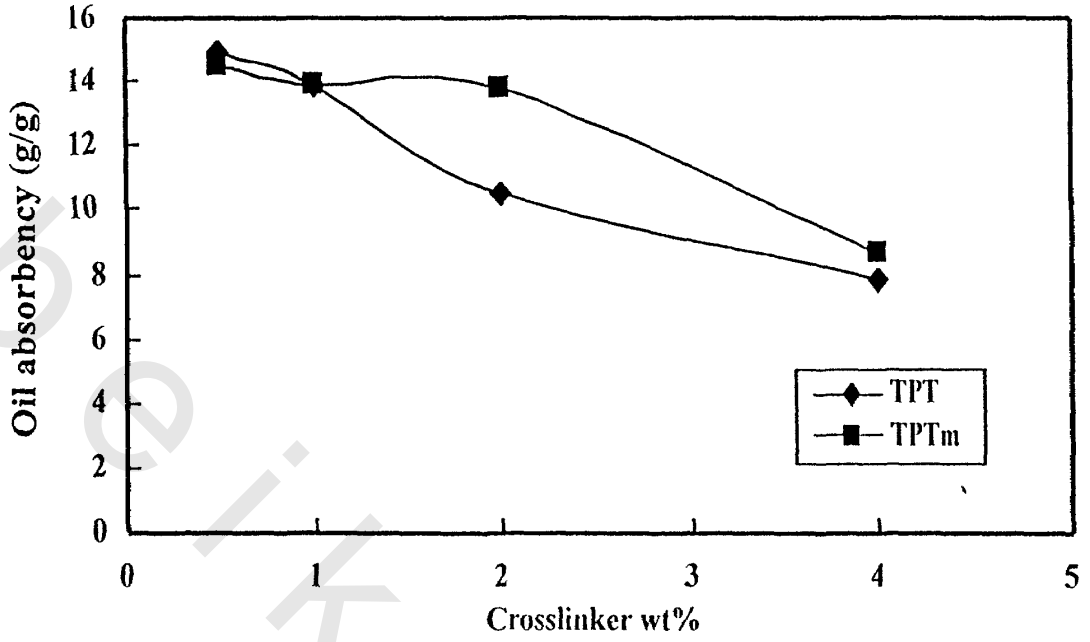


Figure (3.35)Oil Absorbency of CEMA/DDA Xerogels in Pure Toluene at 50Mole% of CEMA to 50 Mole%DDA as a Function of Crosslinker wt% at 298K.

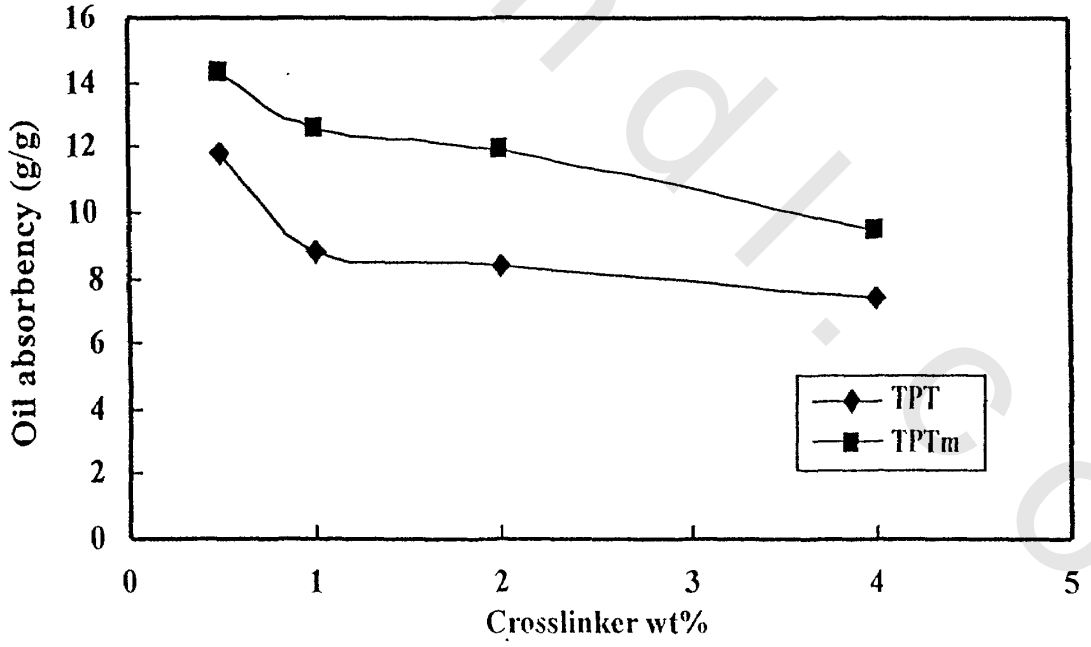


Figure (3.36): Oil Absorbency of CEMA-DDA Xerogels in 10% Crude Oil at 50Mole% of CEMA to 50Mole%DDA as a Function of Crosslinker wt%.

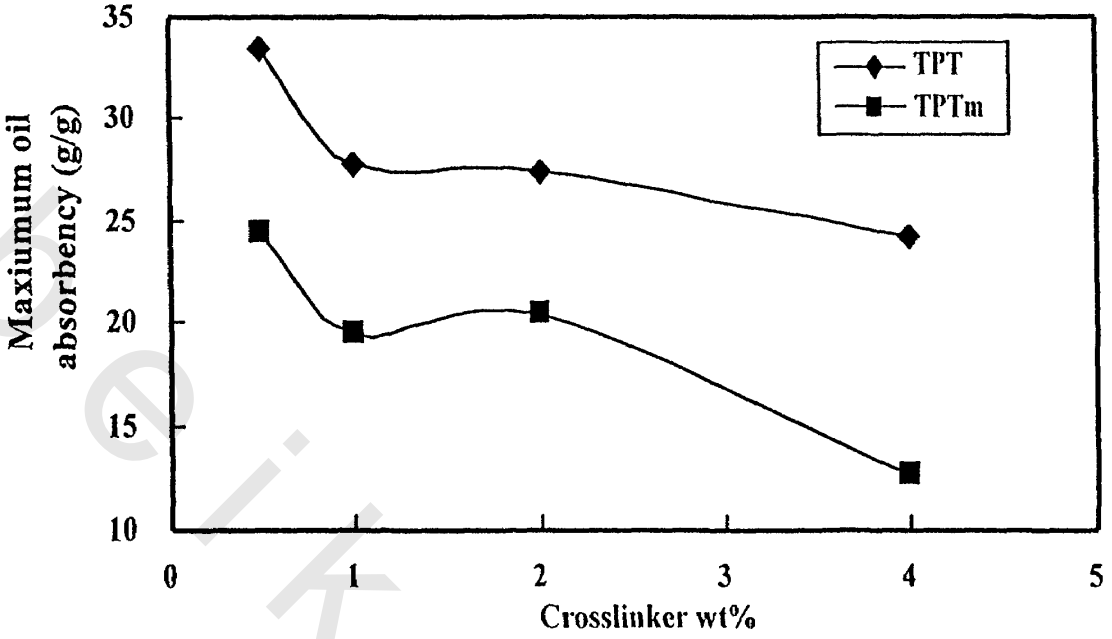


Figure (3.37): Oil Absorbency of CEMA/ODA Xerogels in Pure Toluene at 50Mole% of CEMA to 50 Mole%ODA as a Function of Crosslinker wt% at 298K.

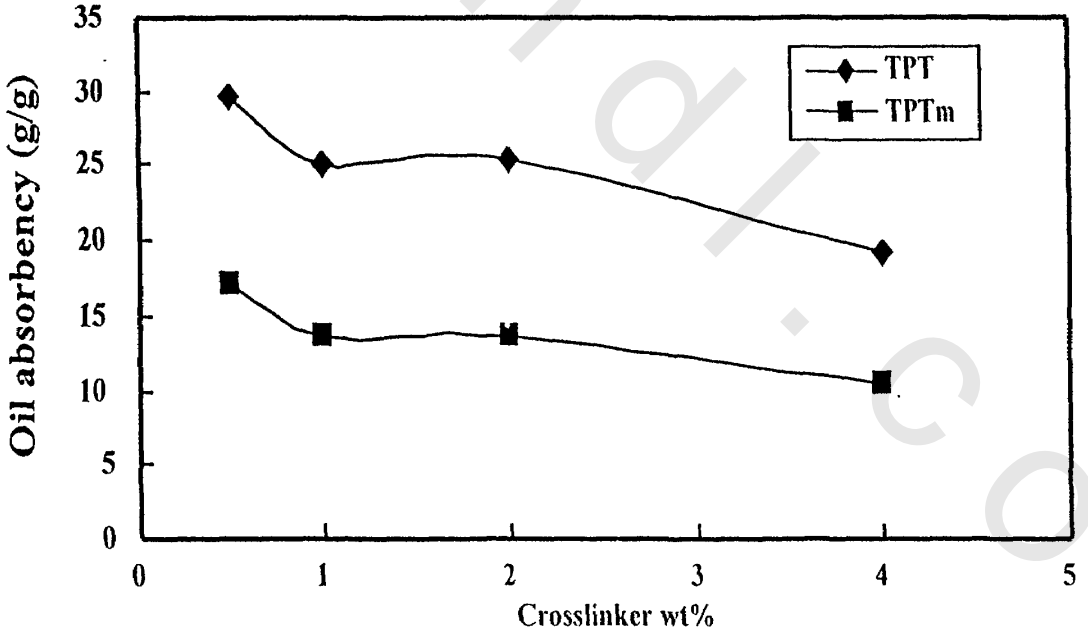


Figure (3.38): Oil Absorbency of CEMA/ODA Xerogels in 10% Crude oil Toluene at 50Mole% of CEMA to 50 Mole% ODA as a Function of Crosslinker wt% at 298K.

This is mainly due to lower crosslinked density network when TPT is used as crosslinker. These results run in harmony with SF% data which confirm that TPT_m is more efficient as a crosslinker than TPT.

This was also noticeable in **Tables (3.13-3.16)** which lists the absorption characteristics of the crosslinked CEMA/DDA and CEMA/ODA copolymers upon using pure toluene or diluted crude oil medium, with different CEMA/ alkyl acrylate molar compositions and with either TPT or TPT_m crosslinkers. Regarding the data listed in **Tables (3.11-3.16)** it is observed that, the oil absorbency is found to be in the order CEMA/ODA > CEMA/DDA> CEMA/IOA. Finally, it can be concluded that oil absorbency increases with increasing the length of alkyl groups. It can be easily explained that the longer the aliphatic side group exists, the more hydrophobic property can be introduced to the copolymer and hence promotes the oil absorption capacity **[Jang and Kim, 2000]**.

3.3.4. Swelling kinetics of the synthesized crosslinked CEMA/ alkyl acrylate copolymers

The sorption and diffusion of organic solvents through crosslinked polymer networks has been a subject of great interest **[Errede, 1986, Poh etal., 1987, Berens and Hopfenbergh, 1978]**. The sorption behavior gives an idea about the permeability and diffusion coefficient of pentrant through polymers, which are used in various applications such as, gel permeation chromatography, ion-exchangers and controlled-release of drugs. Consequently, there is a growing interest in the study of the kinetics of gel swelling.

Swelling kinetics of the prepared crosslinked copolymers were determined according to **[Yao and Zhou, 1994]** in which the swelling

Table(3.13): Absorption Characteristics of the CEMA/DDA Copolymers Crosslinked with TPT Crosslinker at 298 K.

Xerogel Composition	Crosslinker Content (wt%)	Q_{max} (g/g)		ETC		Q (g/g)		T (h)		K (h^{-1})	
		Toluene	crude oil	Toluene	crude oil	Toluene	crude oil	Toluene	crude oil	Toluene	crude oil
90/10	1	11.220	9.56	91.087	89.539	7.091	6.041	1.5	1	0.666	0.999
70/30	1	12.711	10.895	92.132	90.546	8.033	6.885	1.4	0.90	0.714	1.110
50/50	0.5	14.500	14.235	93.103	92.975	9.164	8.996	1	0.50	0.999	1.999
	1	13.866	12.563	92.788	92.040	8.763	7.939	1.2	0.85	0.833	1.176
	2	13.791	11.876	92.7485	91.579	8.715	7.505	1.3	0.9	0.768	1.110
	4	8.660	9.418	88.452	89.382	5.473	5.952	1.4	1	0.714	0.999
30/70	1	20.335	14.235	95.082	92.975	12.851	8.996	1	0.75	0.999	1.332
10/90	1	22.898	17.235	95.632	94.198	14.471	10.892	0.75	0.5	1.332	1.999

Table(3.14): Absorption Characteristics of the CEMA/DDA Copolymers Crosslinked with TPT_m Crosslinker at 298 K.

Xerogel Composition	Crosslinker Content (wt%)	Q_{max} (g/g)		ETC		Q (g/g)		T (h)		K (h^{-1})	
		Toluene	crude oil	Toluene	crude oil	Toluene	crude oil	Toluene	crude oil	Toluene	crude oil
90/10	1	8.615	6.321	88.39	84.179	5.444	3.994	1.3	2	0.77	0.499
70/30	1	11.790	7.986	91.518	87.478	7.451	5.047	1.2	2	0.83	0.499
50/50	0.5	15.00	11.76	93.33	91.496	9.48	7.432	1	1	0.999	0.999
	1	13.885	8.856	92.797	88.708	8.77	5.596	1	1.7	0.999	0.588
	2	10.495	8.36	90.462	88.038	6.62	5.283	1.5	1.8	0.666	0.550
	4	7.875	7.456	87.301	86.587	4.97	4.712	1.9	2	0.526	0.499
30/70	1	14.885	10.728	93.281	90.678	9.40	6.780	0.6	1.5	1.666	0.666
10/90	1	18.250	12.288	94.520	91.861	11.534	7.766	0.35	1.2	2.856	0.833

Table(3.15): Absorption Characteristics of the CEMA/ODA Copolymers Crosslinked with TPT Crosslinker at 298 K.

Xerogel Composition	Crosslinker Content (wt%)	Q_{max} (g/g)		ETC		Q (g/g)		T (h)		K (h^{-1})	
		Toluene	crude oil	Toluene	crude oil	Toluene	crude oil	Toluene	crude oil	Toluene	crude oil
90/10	1	22.260	20.662	95.507	95.160	14.068	13.058	1	0.9	0.999	1.11
70/30	1	26.030	22.034	96.158	95.461	16.450	13.925	0.75	0.8	1.33	1.249
50/50	0.5	33.556	29.572	97.019	96.618	21.207	18.689	0.5	0.4	1.99	2.499
	1	27.8	24.982	96.402	95.997	17.569	15.788	0.6	0.75	1.66	1.33
	2	27.398	24.342	96.350	96.053	17.315	16.016	0.7	0.80	1.428	1.249
	4	24.242	19.214	95.874	94.795	15.320	12.143	0.75	0.85	1.333	1.176
30/70	1	29.812	26.356	96.645	96.205	18.841	16.656	0.5	0.6	1.99	1.666
10/90	1	34.832	32.472	97.129	96.920	22.013	20.522	0.4	0.5	2.499	1.999

Table(3.16): Absorption Characteristics of the CEMA/ODA Copolymers Crosslinked with TPT_m Crosslinker at 298 K.

Xerogel Composition	Crosslinker Content (wt%)	Q_{max} (g/g)		ETC		Q (g/g)		T (h)		K (h^{-1})	
		Toluene	crude oil	Toluene	crude oil	Toluene	crude oil	Toluene	crude oil	Toluene	crude oil
90/10	1	15.037	11.191	93.349	91.064	9.503	7.072	1	1	0.999	0.999
70/30	1	17.912	12.672	94.417	92.667	11.320	8.009	1	0.8	0.999	1.249
50/50	0.5	24.412	17.225	95.903	94.194	15.428	10.886	0.235	0.5	3.075	1.999
	1	19.564	13.637	94.888	92.667	12.364	8.618	0.4	075	2.499	1.332
	2	20.450	13.646	95.110	92.671	12.924	8.624	0.5	1	1.999	0.999
	4	12.732	10.475	92.146	90.453	8.0469	6.620	0.5	2	1.999	0.499
30/70	1	20.256	16.017	95.063	93.756	12.801	10.123	0.4	0.75	2.499	1.332
10/90	1	21.218	17.653	95.287	94.335	13.410	11.156	0.325	0.6	3.0759	1.666

rate can be described by the following experimental equation:

$$\frac{dQ}{dT} = K (Q_{max} - Q) \quad (3.7)$$

where Q_{max} and Q are the maximum and the characteristic oil absorbency, respectively, while K is the swelling kinetic constant. Integration of eq.(3.7) gives:

$$-\ln (Q_{max} - Q) = Kt + C \quad (3.8)$$

where, t is the characteristic swelling time and C is the integration constant.

As a consequence of $t = 0$, $Q = 0$, and $-\ln Q_{max} = C$, therefore

$$\ln(Q_{max} / (Q_{max} - Q)) = kt \quad (3.9)$$

For an example, the characteristic swelling time is defined as

$Q = 0.632\ Q_{max}$ **[Lee and Wu, 1996]**.

Swelling kinetic constant values (k), listed in **Tables (3.11-3.16)**, increase with decreasing either crosslinker wt.%. This result may be explained by the fact that the more crosslinker content, the stiffer the crosslinked polymer is, and the smaller cavities produced. Considering that the swelling kinetics may be dependent not only on the surfaces of the polymer but also on the number and volume of the pores in the polymer. The larger cavities will provide larger absorption surfaces, which give higher swelling rate of the polymeric network, namely larger value of k. In other words, the polymer with higher swelling rate may have suitable structure for oil absorption **[Zhou and Ha, 2001]**. On the other hand, k values increase with increasing alkyl acrylate mole ratio and using TPT_m rather TPT. Also, it is obvious that k values increase with increasing the alkyl acrylate chain length i.e. CEMA/ODA > CEMA/DDA > CEMA/IOA. This may be attributing to

the longer the aliphatic side group exists, the more hydrophobic property can be introduced to the copolymer and hence promotes the oil absorption capacity rate. These results lead us to confine the subsequent sorber syntheses on ODA as alkyl acrylate and TPT as crosslinker.

The equilibrium toluene content (ETC), listed in **Tables (3.11-3.16),** increases with increasing alkyl acrylates mol%. This high oil absorptivity of the polymer depends on the blockness of the alkyl constituent. These results agree with blockness values listed in **Tables (3.4-3.6)**.

The ability of the swelled gels to undergo several cycles of swelling and deswelling is shown in **Figure (3.39)**. In this respect, the swelling behavior of poly(CEMA –IOA) xerogels in both toluene and crude oil, at 50/50 mol% of CEMA to IOA crosslinked with 1 % TPT crosslinker, was selected as representative sample. We can see that after the first cycle the gel did not achieve the original swollen state but that in all of the following cycles it swelled back to its previous swollen state. This indicates that small amount of soluble fractions still remains in the crosslinked gels which could have leached out upon deswelling, reducing the degree of successive swelling **[Atta, 2002]**.

3.3.5. Network parameters of crosslinked CEMA/acrylate copolymers.

The theoretical crosslinking density υ_t is given in terms of concentration C (mol dm^{-3}) of crosslinking agent of functionality f as explained in experimental section (equation 2.5). The values of C were calculated from the known weights (mc) of crosslinkers TPT or TPT_m in the feed mixture, the mass (mx) of xerogel, in conjunction with the

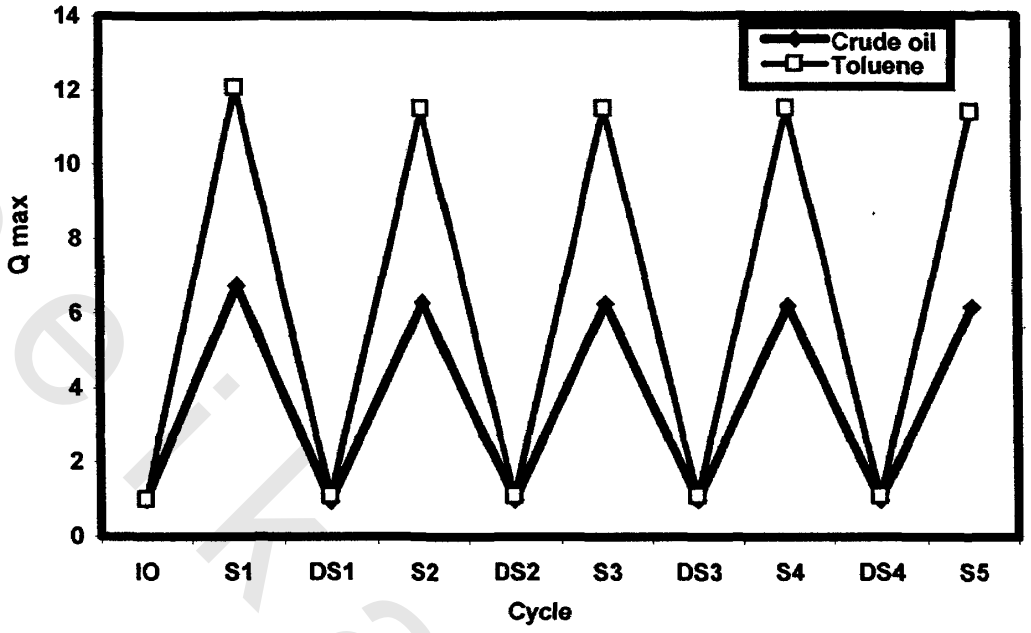


Figure (3.39): Reversibility of CEMA (50%)/ IOA (50%) Copolymer Crosslinked with 1% of TPT Gel Swelled in Toluene and Crude Oil: IO Indicates Initial Condition, S1-5 = Swelling Cycle Equilibrium Condition and DS 1-4 = DeSwelling Cycle Equilibrium Condition.

density ρ ($kgdm^{-3}$) of xerogel. This value of ρ is the average of densities obtained from direct weights and micrometrically measured dimensions of all the dried discs and pellets used. C is given by the following Eqn. (3.10):

$$C = mc/Mw(mx/\rho) \quad \textbf{(3.10)}$$

The value of density was virtually independent of the concentration of crosslinker over the range used here. Their values were calculated for crosslinked CEMA and alkyl acrylate copolymers with either TPT or TPT_m crosslinkers. The network parameters υ_e, M_c and χ were determined from the swelling measurements of copolymers with pure toluene or 10% crude oil and listed in **Tables (3.17-3.28).** As described in the experimental section, from the values of υ_e and ρ_p the molar mass per crosslinked unit (M_c) was calculated. Before considering the network parameters it will be useful at this juncture to supplement on the basis of Eqn. (2.10). Isolation of χ depends mainly on the mixing contribution, i.e. the three terms of Eqn. (2.10). Numerically, it is found that the elastic contribution, i.e. remaining terms, have only a slight effect on the derived value of χ. Because in the present system where in Φ_p and v_e are small, this is especially true and Eq. (2.10) can be reduced as follows to an excellent approximation:

$$\ln(1-\Phi_p) + \Phi_p + \chi\Phi_p^{\,2} \approx 0 \quad \textbf{(3.11)}$$

Expansion of the logarithmic series, followed by function of terms in $\Phi_p^{\,4}$, $\Phi_p^{\,5}$ and $\Phi_p^{\,6}$ etc. and rearrangement yields

$$\chi = 1/2 + \Phi_p^{\,1/3} \quad \textbf{(3.12)}$$

Of course full implementation of Eq. (2.10) does allow in principle the values of χ to be <0.50. However, Eq. (3.11) indicates that $\chi > 0.5$. In

Table(3.17): Network Parameters of Different Compositions CEMA/IOA Copolymers Crosslinked with Various Concentrations of TPT Crosslinker at 298K.

Xerogel Composition	Crosslinker Content (wt%)	υ_t mol/dm^3	$\upsilon_e \times 10^3$ (mol/dm^3)		M_c (g/mole)		χ	
			Toluene	Crude oil	Toluene	Crude oil	Toluene	Crude oil
90/10	1	0.86	78.22	841.577	10.866	1.010	0.46	0.728
70/30	1	0.81	50.06	577.569	15.979	1.385	0.449	0.627
50/50	0.5	0.78	60.00	304.639	12.86	2.527	0.374	0.467
	1	0.79	61.48	316.647	12.80	2.463	0.393	0.519
	2	0.80	61.69	373.33	12.68	2.116	0.441	0.535
	4	0.82	63.84	450.118	12.53	1.727	0.471	0.599
30/70	1	0.78	39.68	247.305	19.653	3.153	0.43	0.500
10/90	1	0.75	34.15	132.083	21.963	5.678	0.413	0.416

Table(3.18): Follow Network Parameters of Different Compositions CEMA/IOA Copolymers Crosslinked with Various Concentrations of TPT Crosslinker at 298K.

Xerogel Composition	Crosslinker Content (wt%)	Density (ρ_p) Kg/dm^3	Φ_p		G_T MN.m^{-2}	
			Toluene	Crude oil	Toluene	Crude oil
90/10	1	0.85	0.105	0.187	89.755	1169.4
70/30	1	0.8	0.091	0.173	54.643	781.62
50/50	0.5	0.77	0.0786	0.136	62.37	380.09
	1	0.78	0.082	0.147	65.01	406.25
	2	0.79	0.0941	0.153	68.09	484.53
	4	0.80	0.1046	0.169	72.97	603.94
30/70	1	0.78	0.0795	0.140	41.408	311.84
10/90	1	0.75	0.0717	0.107	34.421	152.42

Table(3.19): Network Parameters of Different Compositions CEMA/IOA Copolymers Crosslinked with Various Concentrations of TPT_m Crosslinker at 298K.

Xerogel Composition	Crosslinker Content (wt%)	υ_t mol/dm^3	$\upsilon_e \times 10^3$ (mol/dm^3)		M_c (g/mole)		χ	
			Toluene	Crude oil	Toluene		Toluene	Crude oil
90/10	1	0.868	698.87	860.28	1.40	1.14	0.65	0.82
70/30	1	0.842	101.05	701.28	9.40	1.35	0.54	0.68
50/50	0.5	0.833	66.09	402.74	14.22	2.33	0.49	0.53
	1	0.842	66.85	428.91	14.20	2.21	0.54	0.56
	2	0.851	67.70	550.47	14.17	1.74	0.55	0.64
	4	0.859	68.98	667.49	14.06	1.45	0.56	0.74
30/70	1	0.817	84.85	665.37	10.84	1.38	0.52	0.54
10/90	1	0.799	88.71	222.22	10.14	4.05	0.47	0.50

Table(3.20): Follow Network Parameters of Different Compositions CEMA/IOA Copolymers Crosslinked with Various Concentrations of TPT_m Crosslinker at 298K.

Xerogel Composition	Crosslinker Content (wt%)	Density (ρ_p) Kg/dm^3	Φ_p		G_T MN.m^{-2}	
			Toluene	Crude oil	Toluene	Crude oil
90/10	1	0.98	0.176	0.212	951.31	1244.9
70/30	1	0.95	0.146	0.184	129.20	967.89
50/50	0.5	0.94	0.112	0.152	77.46	521.37
	1	0.95	0.146	0.161	85.47	566.07
	2	0.96	0.155	0.179	88.23	752.87
	4	0.97	0.166	0.205	91.99	955.28
30/70	1	0.92	0.134	0.156	105.53	868.92
10/90	1	0.90	0.115	0.138	104.67	278.92

Table(3.21): Network Parameters of Different Compositions CEMA/DDA Copolymers Crosslinked with Various Concentrations of TPT Crosslinker at 298K.

Xerogel Composition	Crosslinker Content (wt%)	υ_t mol/dm^3	$\upsilon_e \times 10^3$ (mol/dm^3)		M_c (g/mole)		χ	
			Toluene	Crude oil	Toluene		Toluene	Crude oil
90/10	1	0.744	59.777	64.388	12.295	11.415	0.42	0.47
70/30	1	0.757	45.924	44.307	16.265	16.859	0.41	0.46
50/50	0.5	0.708	45.989	23.039	15.220	30.382	0.35	0.44
	1	0.730	47.480	26.405	15.164	27.266	0.37	0.463
	2	0.745	48.474	32.790	15.160	22.414	0.37	0.461
	4	0.750	48.984	44.329	15.106	16.693	0.47	0.49
30/70	1	0.801	16.919	23.039	46.691	34.289	0.38	0.44
10/90	1	0.760	13.190	15.166	56.857	49.452	0.37	0.436

Table(3.22): Follow Network Parameters of Different Compositions CEMA/DDA Copolymers Crosslinked with Various Concentrations of TPT Crosslinker at 298K.

Xerogel Composition	Crosslinker Content (wt%)	Density (ρ_p) Kg/dm^3	Φ_p		G_T MN.m^{-2}	
			Toluene	Crude oil	Toluene	Crude oil
90/10	1	0.735	0.089	0.104	64.776	73.597
70/30	1	0.747	0.078	0.091	47.737	48.493
50/50	0.5	0.700	0.069	0.070	45.752	23.062
	1	0.720	0.072	0.079	47.945	27.555
	2	0.735	0.073	0.084	49.037	34.866
	4	0.740	0.097	0.106	54.704	50.923
30/70	1	0.79	0.049	0.070	15.038	23.062
10/90	1	0.75	0.043	0.058	11.268	14.243

Table(3.23): Network Parameters of Different Compositions CEMA/DDA Copolymers Crosslinked with Various Concentrations of TPT_m Crosslinker at 298K.

Xerogel Composition	Crosslinker Content (wt%)	υ_t mol/dm^3	$\upsilon_e \times 10^3$ (mol/dm^3)		M_c (g/mole)		χ	
			Toluene	Crude oil	Toluene		Toluene	Crude oil
90/10	1	0.771	91.603	698.93	9.497	1.244	0.48	0.55
70/30	1	0.735	36.065	125.189	23.013	6.629	0.456	0.487
50/50	0.5	0.726	50.788	36.297	16.145	22.591	0.32	0.456
	1	0.735	51.727	67.911	16.045	12.22	0.358	0.489
	2	0.744	52.514	83.317	15.995	10.08	0.459	0.495
	4	0.762	54.079	102.191	15.900	8.145	0.523	0.518
30/70	1	0.692	20.841	46.135	37.424	16.906	0.44	0.46
10/90	1	0.666	13.447	32.549	55.772	23.042	0.43	0.45

Table(3.24): Follow Network Parameters of Different Compositions CEMA/DDA Copolymers Crosslinked with Various Concentrations of TPT_m Crosslinker at 298K.

Xerogel Composition	Crosslinker Content (wt%)	Density (ρ_p) Kg/dm^3	Φ_p		G_T MN.m^{-2}	
			Toluene	Crude oil	Toluene	Crude oil
90/10	1	0.87	0.116	0.158	108.400	917.00
70/30	1	0.83	0.085	0.125	38.440	151.93
50/50	0.5	0.82	0.066	0.085	49.959	38.721
	1	0.83	0.072	0.112	52.210	79.628
	2	0.84	0.095	0.119	58.187	99.587
	4	0.86	0.126	0.134	65.940	126.89
30/70	1	0.78	0.067	0.093	20.554	50.745
10/90	1	0.75	0.055	0.081	12.390	34.218

Table(3.25): Network Parameters of Different Compositions CEMA/ODA Copolymers Crosslinked with Various Concentrations of TPT Crosslinker at 298K.

Xerogel Composition	Crosslinker Content (wt%)	υ_t mol/dm^3	$\upsilon_e \times 10^3$ (mol/dm^3)		M_c (g/mole)		χ	
			Toluene	Crude oil	Toluene		Toluene	Crude oil
90/10	1	0.658	16.453	19.271	39.505	33.728	0.353	0.355
70/30	1	0.628	11.909	16.810	52.059	36.880	0.349	0.353
50/50	0.5	0.607	9.211	9.217	65.135	65.096	0.298	0.346
	1	0.628	9.765	12.951	63.491	47.870	0.358	0.350
	2	0.648	10.054	13.660	63.358	46.850	0.359	0.351
	4	0.689	11.11	21.053	61.183	32.298	0.382	0.368
30/70	1	0.608	9.070	11.612	66.149	51.669	0.346	0.349
10/90	1	0.547	7.935	9.106	68.049	59.301	0.312	0.314

Table(3.26): Follow Network Parameters of Different Compositions CEMA/ODA Copolymers Crosslinked with Various Concentrations of TPT Crosslinker at 298K.

Xerogel Composition	Crosslinker Content (wt%)	Density (ρ_p) Kg/dm^3	Φ_p		G_T MN.m^{-2}	
			Toluene	Crude oil	Toluene	Crude oil
90/10	1	0.65	0.0449	0.0483	14.189	17.037
70/30	1	0.62	0.0384	0.0453	9.748	14.546
50/50	0.5	0.60	0.0298	0.0338	6.928	7.230
	1	0.62	0.0359	0.0400	7.820	10.747
	2	0.64	0.0365	0.0411	8.091	11.434
	4	0.68	0.0412	0.0520	9.316	19.069
30/70	1	0.60	0.0335	0.0379	7.0966	9.466
10/90	1	0.54	0.0287	0.0307	5.898	6.924

Table(3.27): Network Parameters of Different Compositions CEMA/ODA Copolymers Crosslinked with Various Concentrations of TPT_m Crosslinker at 298K.

Xerogel Composition	Crosslinker Content (wt%)	υ_t mol/dm^3	$\upsilon_e \times 10^3$ (mol/dm^3)		M_c (g/mole)		χ	
			Toluene	Crude oil	Toluene		Toluene	Crude oil
90/10	1	0.700	47.728	72.925	16.551	10.832	0.334	0.404
70/30	1	0.664	38.792	51.958	19.333	14.434	0.284	0.396
50/50	0.5	0.691	33.890	34.621	23.010	22.529	0.107	0.329
	1	0.709	35.415	41.333	22.588	19.35	0.255	0.398
	2	0.744	37.352	43.037	22.488	19.51	0.211	0.393
	4	0.76	38.016	88.718	22.358	9.58	0.441	0.408
30/70	1	0.621	30.773	29.345	22.746	23.853	0.271	0.385
10/90	1	0.577	27.799	23.549	23.381	27.601	0.269	0.382

Table(3.28): Follow Network Parameters of Different Compositions CEMA/ODA Copolymers Crosslinked with Various Concentrations of TPT_m Crosslinker at 298K.

Xerogel Composition	Crosslinker Content (wt%)	Density (ρ_p) Kg/dm^3	Φ_p		G_T MN.m^{-2}	
			Toluene	Crude oil	Toluene	Crude oil
90/10	1	0.79	0.066	0.0665	46.910	79.092
70/30	1	0.75	0.056	0.0558	35.968	54.065
50/50	0.5	0.78	0.041	0.0409	28.348	32.521
	1	0.80	0.051	0.0511	31.885	41.970
	2	0.84	0.0489	0.0489	33.136	43.690
	4	0.85	0.0815	0.0815	40.000	98.364
30/70	1	0.70	0.0493	0.0493	27.387	28.241
10/90	1	0.65	0.0471	0.0471	24.361	21.940

fact the use of Eqn. (3.12) in conjunction with the values of Φ_p affords values of χ that lie in close accord with those listed in **Tables (3. 17 – 3.28)**. It should be noted that the application of equation (3.12) **[Huglin and Rego, 1991, Flory, 1953]** is based on the acceptance that the entropy of mixing is given entirely by the configurational entropy; this assumption implies that other contributions to the entropy derived from specific interaction between neighbouring components are neglected. The values of χ are all <0.500 and toluene remains a moderately good thermodynamically solvent over the whole temperature region. χ comprises enthalpic (χH) and entropic (χS) components:

$$X = \chi H + \chi S$$

$$\chi H = -T\, d\chi/dT$$

$$\chi S = \chi + T\, d\chi/dT$$

At $d\chi/dT = 0$, it follows that $\chi = \chi S$ and the swelling process is entropically dominated, which lends support to the previously mentioned comment on the assumptions implicit in Eq. (3.12). It is interesting to note that for protein gels the situation is entirely different and the swelling is enthalpically controlled **[Clark and Ross-Murphy, 1987]**.

The compression moduli G_T values were obtained via following Eqn.

$$G_T = RT\, \upsilon_e\, \Phi p^{1/3} (Vu/Vf)^{2/3} \qquad \textbf{(3.13)}$$

Where, R is the gas constant, T is absolute temperature.

For the present systems, a solvent was included within the reaction medium and hence the correction factor $(Vu/Vf)^{2/3}$ is required **[Davis and Huglin 1990]** in Eq. (3.13), where Vu and Vf are the volumes of the dry unstrained xerogel and the network at its formation (i.e. the feed mixture) respectively.

The value of Vu was calculated from Eq.

$$Vu = (mt/\rho)\,\theta \qquad (3.14)$$

Where, mt and θ are the weight of total monomers in the feed and fractional conversion in preparation of xerogel, respectively. Alternatively, Vu can be calculated as Vu = mx/ ρ. Vf can be obtained directly by using a volumetric cylinder; Vf can also be obtained from a calibration curve of [total monomers (g)/solvent (g)] against [total volume (ml) of solution/volume of solvent (ml)]. In the present system, water was included within the reaction medium and therefore Vu < Vf. Note that if no solvent is used, Vu/Vf = 1. In this respect G_T values were calculated for the copolymeric gels and listed in **Tables (3.17-3.28)** It is well known that the lower G_T values indicate that the prepared gels have elastic network **[Toblosky et al., 1961]**. This increase the interaction between toluene and the copolymer networks. Bestide et al. **[Bestide et al, 1979]** showed that the presence of dangling chains or pendant chains in the polymeric network affected the compression moduli of elasticity. They found that the values of moduli decrease drastically when the proportion of pendant chains increase. The lower values of G_T and υ_e for crosslinked copolymers by TPT than that crosslinked with TPT_m crosslinkers, listed in **Tables (3.17-28)**, indicate the formation of dangling chain that was increased by using TPT than TPT_m crosslinker. For the same reason, values of G_T and υ_e decrease with increasing the alkyl acrylate proportion in the copolymer composition and increase with increasin the crosslinker weight content. This can be proved from measuring polymer-solvent interaction parameter (χ). The values of χ were calculated for all copolymers and listed in **Tables (3.17-28).** The data of χ values for crosslinked copolymers by TPT show lower values of than that determined for crosslinked copolymers by TPT_m crosslinker. The

decreasing of χ values indicates the good interaction between the crosslinked copolymers with toluene. This indicates that crosslinking with TPT introduces dangling hydrophobic groups to network at crosslinking **[Atta and Arndt, 2003, Mehnert et al., 1993 and Atta and Arndt, 2001]**.

From the values of υ_t and υ_e listed in **Tables (3.17-3.28)** υ_e varies with υ_t according to follwing Eqn.

$$\upsilon_e = \alpha + \beta\, \upsilon_t \qquad (3.15)$$

The parameter α is a measure of the effective crosslinking in the absence of any included chemical crosslinker which may arise from physical crosslinking or crosslinking induced when γ-irradiation is used in the synthesis. The parameter β is a measure of crosslinking efficiency ($\beta = \upsilon_e/\upsilon_t$ when $\alpha = 0$) and its magnitude is usually **[Davis and Huglin, 1990, Huglin et al., 1987, Davis and Huglin, 1989 and Collett et al., 1981]** ≤ 1.0, although one unusual case has been reported **[Davis and Huglin, 1990]** where $\beta \geq 1$.

Plots (not reproduced here) according to Eq. (3.15) display linearity for the prepared organogels of CEMA and alkyl acrylate copolymers. The values of α and β were calculated and listed in **Table (3.29)**. In this respect, α values for CEMA/ODA copolymer crosslinked with different concentrations of TPT or TPT_m have very low values ranging from 0.0004 to 0.0007. While CEMA/IOA copolymers possess high α values than other copolymers. It is well known that poly(acrylates) and their copolymers have a high tendency to crosslink under irradiation **[Atta and Abdel-Azim,1998, Chapiro, 1975 and Huglin and Richard 1980]** and moreover, acrylic acid undergoes chain transfer and crosslinking when polymerized by irradiation **[Huglin and Richard 1980]**. So, CEMA deactivates the crosslinking efficiency of ODA >

Table(3.29):The Values of β and α for CEMA/alkyl Acrylat Copolymer Crosslinked with Different wt.% of Either TPT or TPT_m Crosslinker Using Pure Toluene as Swelling Medium.

COPOLYMERS	α		β		Correlation coefficient	
	TPT	TPT_m	TPT	TPT_m	TPT	TPT_m
CEMA/IOA	0.023	0.0165	0.0472	0.0595	0.91	0.94
CEMA/DDA	0.0016	0.0083	0.0434	0.0579	0.96	0.99
CEMA/ODA	0.0007	0.0004	0.0137	0.0488	0.97	0.98

DDA >IOA polymers in absence of crosslinkers. On the other word, this can be also referred to the increasing probability of crosslinking in bulk system due to increment in the rate of chain transfer of the polymerization and crosslinking reactions. The crosslinking and polymerization of the present systems were carried out in bulk without diluent. This agrees with the finding that the crosslinking decreases with decreasing content of diluent **[Janacek and Hasa, 1966]**. So, the ability of copolymers to form physical crosslinks increases with IOA > DDA >ODA copolymers. Accordingly, the oil swelling is the highest for CEMA/ODA copolymers due to their low affinity to form physical crosslinks. It was also observed that the β values for crosslinking of CEMA/alkyl acrylate were decreased when ODA was used instead of IOA and DDA copolymers. This finding reveals that the reactivity of TPT or TPT_m crosslinkers is less efficient for crosslinking of CEMA/ODA copolymers. On the other hand, crosslinked CEMA/ alkyl acrylate copolymers with TPT_m have higher β values than that crosslinked with TPT crosslinker. Comparing β values obtained from using TPT in CEMA/alkyl acrylate with that crosslinked with TPT_m organogels, the crosslinking efficiency is much higher for TPT_m. This indicates that there is still quite large proportion of TPT waste during the crosslinking polymerization, probably due to a low reactivity ratio of TPT with CEMA/alkyl acrylate.

This conclusion is supported by the data of M_C for the crosslinked copolymer by both crosslinkers. **Tables (3.17-3.28)**, show that M_C values of TPT_m networks are always smaller than the corresponding values when TPT is used as the crosslinking agent. Since M_C is used to determine the distance between two successive crosslinks, the smaller its value the higher the crosslinking density networks. As the

crosslinking density increases, the oil sorber capacities are reduced **(see Tables 3.17-28)**. It was also observed that the β values are less than unity. It is due to the fact that toluene is a better swelling agent for this system. This is because β is not only a measure of chemical crosslinking but also of physical interaction between the chains when the values are greater than unity **[Yokota et al., 1978]**.

3.4- SYNTHESIS OF CROSSLINKED PIB-MA-CM_n/ODA COPOLYMERS.

Polyisobutylene could be crosslinked by irradiation after chlorine had been introduced into its macromolecules. Carbon-chlorine bonds act both as radiation-sensitive groups and reaction species in the radiation process of chlorinated polyisobutylene. In general, controlled crosslinking may lead in some cases to beneficial changes, but radiation degradation always causes a steady decrease in most of the valuable properties of polymers. Polyisobutylene (PIB), which is expected to undergo chain scission rather than crosslinking, cannot form an insoluble three-dimensional network under radiation without the presence of multifunctional monomers **[Alexander et al., 1955, Charlesby and Steven, 1979, Chapiro, 1962 and Dole, 1973]**. However, as reported previously, **[Zhao et al., 1992]** it is found that PIB could be crosslinked to some extent by irradiation if it was blended with a suitable radiation-crosslinkable polymer. PIB could be dissolved in toluene, but when irradiated under vacuum, it could not be dissolved completely. The gel content of PIB, is determined by solvent extracting. It can be seen that the gel content increases with increasing radiation dose; this indicates that PIB undergoes crosslinking rather than chain scission.

In a previous section (3.2), we have reported on esterification of hydroxy alkoxycinnamate with polyisobutylene succinate adduct. Depending on the high effictive swelling properties obtained upon using ODA and TPT, they were selected to be used as the alkyl acrylate moiety and crosslinker, respectively in this section. The products were reacted with ODA monomer in presence of TPT, cobalt octoeate (CO) and BPO as crosslinker, activator and initiator, respectively. Accordingly, we suggest a new way to crosslink PIB by chemical method through introducing cinnamoyl derivatives into its macromolecular chains.

3.4.1. Soluble Fraction of Crosslinked Reactive Polymers

The crosslinking efficiencies of PIB-MA-CM_n/ODA copolymers were determined from the SF values which was determined from soxhlet extraction of the prepared xerogels with chloroform after 24h of extraction. The extraction period of 24h was confirmed to be enough to remove all the oil extractable materials from the gels. The unreacted fractions that fail to incorporate to the network were leached and their values were determined. In the following section, the reactivity of TPT crosslinker was investigated from SF measurements in chloroform. In this respect, the results obtained via soxhlet extraction for the crosslinked (50mol%) BIP-MA-CM_n/(50mol%) ODA (where n= 1,2,3,4 or 9) with 1,2 and 4% TPT crosslinker were listed in **Table (3.30)**. It's obvious that, the percentage of SF for crosslinked copolymers decreased with increasing the TPT weight % from 1 to 4%. This indicates that high crosslinker content reduces the probability of side reactions that affects crosslinking activity. It is also observed that,

Table(3.30). Soluble Fraction of the Crosslinked PIB-MA-CM_n/ODA Copolymers Having Different Crosslinker Contents.

Copolymers	Soluble Fraction (SF %)		
	1% wt TPT	2% wt TPT	4% wt TPT
PIB-MA-CM_1/ODA	41.53	40.13	38.45
PIB-MA-CM_2/ODA	38.63	34.43	32.65
PIB-MA-CM_3/ODA	34.73	32.83	30.85
PIB-MA-CM_4/ODA	32.98	31.86	30.11
PIB-MA-CM_9/ODA	26.62	24.76	20.15

SF % values for PIB-MA-CM_n/ODA decreases from n=1 to n= 9. This may be attributed to the difference in the reactivity of the crosslinker towards the copolymers. This indicates that increasing number of ethylene oxide units for PIB-MA-CM_n macromonomers increases their ability to crosslinking with TPT. This can be referred to increasing compatibility between the reactants, which affects on polymerization and crosslinking conversion. Accordingly, the crosslinking efficiency of ODA with reactive macromonomers increases in the order PIB-MA-CM_9 > PIB-MA-CM_4 > PIB-MA-CM_3 > PIB-MA-CM_2 > PIB-MA-CM_1. Comparing SF% values for the reactive copolymers with those of CEMA/ODA copolymers, it is obvious that high SF% values are higher for the former. This may be due to lower expected collisions of reactants in the case of reactive copolymers.

3.4.2. Oil absorbency of crosslinked reactive macromonomers

However, the phenomenological laws of diffusion are applicable to all systems. The molecular mechanism of solvent transfer is dependent on the properties of the components. The large mass, chain structure and flexibility of macromolecules affect the nature of diffusion in polymer-solvent systems. The properties of the system are function not only of the nature of the components but also of their composition. Mixing of a polymer with a solvent involves change in the energy of interaction and in the number of direct contacts between the polymer chains. Intermolecular interaction changes little when polymer-polymer contacts are replaced by polymer-solvents contacts, but the mobility of the segments of the polymer molecules increases. The thermal motion of molecules under the influence of a concentration gradient is associated with cooperative movement of neighbouring molecules.The

probability of this process is dependent on the mobility of the molecules of the medium. The higher the solvent content of the system the greater is the mobility and the less the energy required for movement of the diffusing molecules. Assuming an exponential dependence of this energy on composition it is possible to find the relationship connecting the unidirectional coefficient of diffusion with the solvent concentration **[Vasenin, 1960]**. When a molecule moves under the influence of a concentration gradient the molecule is orientated in the direction of movement [Aitkken and Barrer, 1955], and is subjected to two types of resistances **[Vasenin, 1964]**, namely "lateral" and "frontal" resistances. The first is determined by the amount of movement that the moving molecule transmits to the surrounding medium. It is dependent on the interaction of the medium molecules with the diffusing molecules, and is proportional to the size or to the first approximation of mass of the molecule. The second is associated with the necessity for movement of the molecules of the diffusion medium for the formation of gaps of the required dimensions. This resistance is on the one hand proportional to the minimal cross-sectional area of the diffusing molecule, i.e. it is determined by its structure. Also, it is dependent on the molecular interaction between the molecules of the medium and on the compressibility of the latter. Both types of resistance are determined to a considerable extent by the viscosity of the medium.

Radetic et al. **[Radetic et al., 2003]** reported the sorption capacity for recycled wool-based for nonwaven material as a natural fiber for oil spill clean up. The experiments showed that for 10% crude oil sample the dry wool-based nonwaven sample sorbs 11.2g/g sample. Deschamps et al **[Deschamps et al., 2003]** also observed the sorption

capacity of different cotton-based materials. They found a maximum sorption of 23g/g sample for raw cotton and 19g/g sample for treated cotton in 28% fuel (v/v%) at 20°C. In other words, lower capacities were accomplished by synthetic fibers than by natural ones. Choi and co-workers **[Choi et al., 1993, Choi and Cloud, 1992)** demonstrated that cotton, milkweed and kenef have 1.5-3 times better sorption properties than polypropylene fibers. Zhou et al. **[Zhou et al., 2001]** reported that, the highest Q_{max} observed for 4-tert butylstyrene-SBR-divinylbenzene was 57.76g/g polymer at a solvent amount of 15.0 ml/g after being immersed in oil solution for 48h. The oil absorbency studied for 4-tert-butylstyrene-ethylene-propylene-diene-divinylenzene (PBED) graft terpolymer was reported by Zhou and Cho **[Zhou and Cho, 2002]**. They get maximum oil absorbency for the treated PBED of 84.0-g/g polymer.

In our investigation the oil absorbency of the crosslinked PIB-MA-CM_n /ODA were determined according to **ASTM F726-81** using toluene and 10% crude oil. The tested samples were crosslinked with 1, 2 and 4-wt% of TPT crosslinker. **Figures (3.40-3.41)** represent swelling kinetic curves for PIB-MA-CM_1/ODA in either toluene or 10% crude oil as representative. The data of the maximum oil absorbency Q_{max}, equilibrium swelling time (T_{max}) for all reactive crosslinked macromonomer sorbers -in either pure toluene or 10% crude oil media- are listed in **Tables (3.31-3.32)**. As shown from the data, the maximum oil absorbency decreases with increasing the crosslinker concentration from 1 to 4-wt% in both media. This behavior can be attributed to more restricted polymeric chains upon using higher crosslinker concentration. The increase in the crosslinker concentration causes an

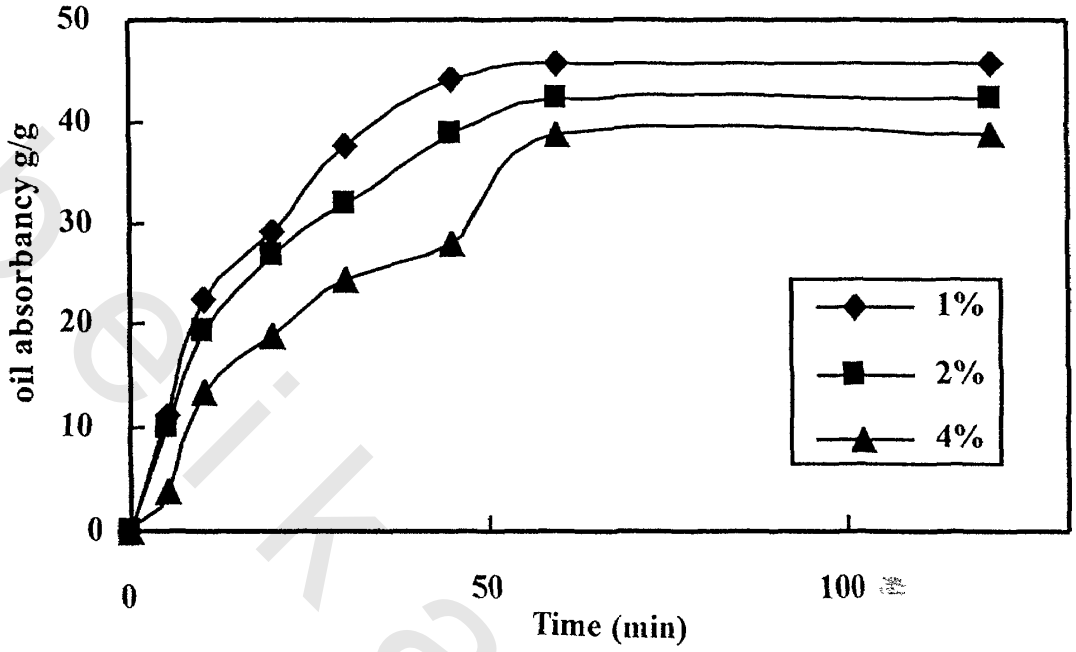


Figure (3.40): Oil absorbency for (50%mol)PIB-MA-CM$_1$/ODA (50%mole) Crosslinked reactive Copolymer in Pure Toluene as a Function of Immersion Time Using 1, 2 or 4wt% TPT.

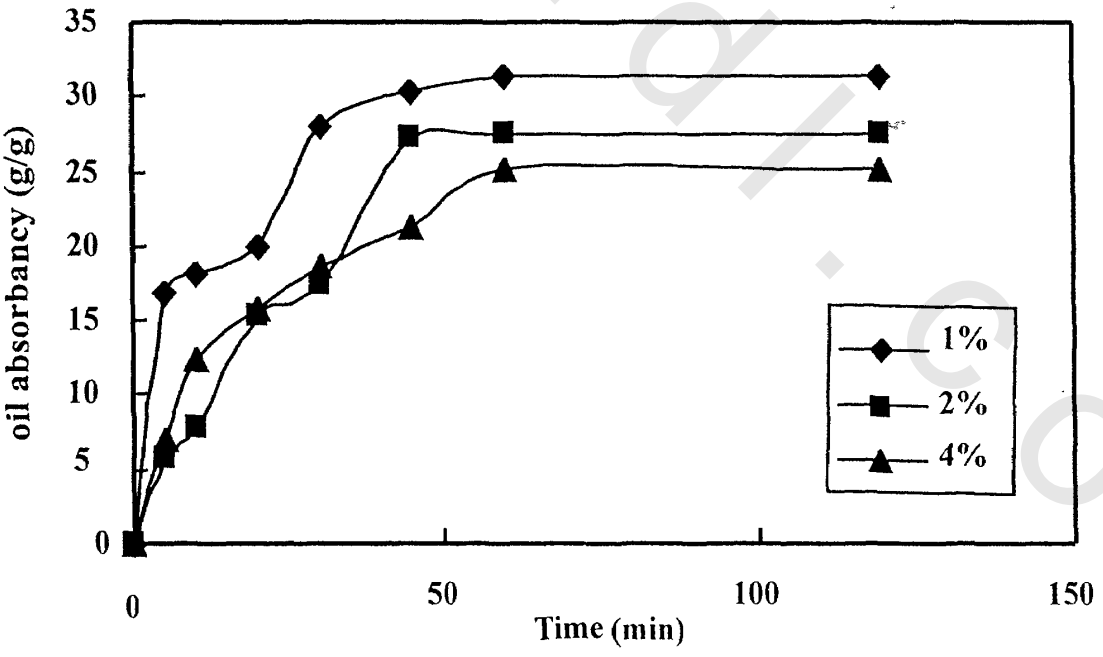


Figure (3.41): Oil absorbency for (50%mol)PIB-MA-CM$_1$/ODA (50%mole) Crosslinked reactive Copolymer in 10% Crude Oil as a Function of Immersion Time Using 1, 2 or 4wt% TPT.

Table(3.31):Absorption Characteristics of the Crosslinked PIB-MA-CM_n/ODA Copolymers Having Different Crosslinker Weight Contents in Toluene at 298K.

Sample	Crosslinker Content (wt%)	Q_{max}(g/g)	Q(g/g)	ETC	T	T_{max}	k (h^{-1})
PIB-MA-CM_1/ODA	1	45.90	29.008	97.82	0.25	1	3.99
	2	42.22	26.683	97.63	0.33	1	2.99
	4	38.70	24.458	97.41	0.5	1	1.99
PIB-MA-CM_2/ODA	1	35.55	22.467	97.18	0.3	1	3.33
	2	33.50	21.172	97.01	0.4	1	2.49
	4	32.50	20.54	96.92	0.5	1	1.99
PIB-MA-CM_3/ODA	1	28.05	17.731	96343	0.33	2	3.00
	2	26.90	17.00	96.28	0.42	2	2.39
	4	26.23	16.577	96.18	0.58	2	1.71
PIB-MA-CM_4/ODA	1	26.99	17.062	96.29	0.33	2	3.029
	2	25.30	15.989	96.04	0.45	2	2.22
	4	25.05	15.830	96.00	0.75	2	1.33
PIB-MA-CM_9/ODA	1	24.30	15.362	95.88	0.33	2	2.99
	2	23.10	14.599	95.67	0.5	2	1.99
	4	22.86	14.44	95.62	0.75	2	1.33

Table(3.32):Absorption Characteristics of the Crosslinked PIB-MA-CM_n/ODA Copolymers Having Different Crosslinker Weight Contents in 10% Crude Oil at 298 K.

Sample	Crosslinker Content (wt%)	Q_{max}(g/g)	Q(g/g)	EOC	T	T_{max}	k (h^{-1})
PIB-MA-CM_1/ODA	1	31.46	19.88	96.82	0.33	1	2.99
	2	27.37	17.301	96.34	0.40	1	2.49
	4	25.02	15.81	96.00	0.45	1	2.22
PIB-MA-CM_2/ODA	1	25.34	17.34	96.35	0.40	1	2.49
	2	23.28	14.71	95.70	0.50	1	1.99
	4	20.11	12.71	95.03	0.50	1	1.99
PIB-MA-CM_3/ODA	1	24.45	15.45	95.92	0.50	2	1.99
	2	23.132	14.61	95.67	0.50	2	1.99
	4	19.56	12.36	94.88	0.50	2	1.99
PIB-MA-CM_4/ODA	1	24.534	15.50	95.91	0.33	2	1.99
	2	21.82	13.79	95.41	0.50	2	1.99
	4	17.31	10.93	94.22	0.50	2	1.99
PIB-MA-CM_9/ODA	1	19.406	12.26	94.84	0.60	2	1.66
	2	18.046	11.40	94.22	0.60	2	1.66
	4	17.022	10.75	94.13	0.75	2	1.33

increase in the crosslink density. A consequent result of the increased crosslink density is the decrease in the diffusion of solvent molecules to penetrate through the network. These results run in harmony with the data of swelling which was observed by Zhou et al., **[Zhou et al, 2001]**. They found that the oil sorption (Q_{max}) decreases upon increasing the crosslinker molar ratio for 4-tert-butystyrene-styrene butadiene rubber - divinyl benzene system.

Another factor, the influence of surrounding medium on the sorption capacity was also studied. From the listed data, the sorption capacity of all tested crosslinked copolymers for pure toluene is always higher than for 10% oil medium. As an example Q_{max} for PIB-MA-CM_1/ODA in toluene is 45.9 g/g sample while in 10% oil is 31.46 g/g sample. This behavior could be due to higher viscosity of 10% oil as compared to pure toluene. High viscosity of the sorption media can cause a decrease of sorption through the penetration to the interior of the copolymer. This increased restriction can be also illustrated in the average molecular weight between crosslinks M_c as will be discussed in following section.

We suggest that the low rate of diffusion of toluene at room temperature and the high energy of activation for this process is associated with the structure of the toluene molecule and the nature of its interaction with polyisobutylene macromolecules. There is some indication that the energy of interaction between toluene and polyisobutylene is small **[Tager et al., 1963]**. It is probable that the introduction of cinnamoyl groups into polyisobutylene slightly disturbs the local ordering of the polymer chains.

The effect of alkyloxy chain length were introduced namely n= 1, 2, 3,4 and 9 into crosslinked PIB-MA-CM_n/ODA copolymer. The data

presented in **Table (3-31)** show that, upon increasing the ethyloxy chain length a remarkable decrease in the sorption capacity was observed. While the sorption capacity in toluene for PIB-MA-CM_1/ODA (1%mole) crosslinked with 1% TPT is 45.9g/g polymer, PIB-MA-CM_9/ODA (1%mole) crosslinked with 1% TPT is 24.3 g/g polymer.The same behavior was observed for the sorption capacity in 10% crude oil regarding the data shown in **Table (3.32).** Maximum sorption of 10% crude oil observed by PIB-MA-CM_1/ODA crosslinked with 1%TPT is 31.46g/g polymers, compared by 19.40g/g polymer attained by PIB-MA-CM_9/ODA crosslinked with 1% TPT at same conditions. This phenomenon may be attributed to prevailing of the nature of the ethyloxy chain through its ethereal bond. This hydrophilicity contradicts with the hydrophobic nature of the oil medium (toluene and 10% crude oil).

3.4.3. Swelling Kinetics of Crosslinked Reactive Polymer

According to Yao and Zhou **[Yao and Zhou, 1994]**, the swelling kinetic of the investigated reactive crosslinked polymers PIB-MA-CM_n/ODA was studied. The swelling parameters were determined from the swelling curves, **Figures (3.40-3.41)** as arepresentative, listed in **Tables (3.31-3.32).** These tables show the equilibrium toluene or oil content, (ETC) or (EOC), characteristic time required for the swelling (T), maximum swelling time (T_{max}) required to reach equilibrium and swelling kinetic constant (k) for the prepared reactive crosslinked copolymers. Regarding T_{max} values in either oil medium cases (toluene and 10% crude oil), it is noticeable that generally as the ethyloxy chain length increases the T_{max} increase. This behavior can be explained easily by considering the increase in the hydrophilic nature of the

polymer matrix by increasing the ethyloxy chain length. **Tables (3.31 & 3.32)** show also that the swelling rate constant (k) decreases with increasing the crosslinker (TPT) concentration from 1 to 4%. This result may be explained by the fact that the higher TPT content, the stiffer the crosslinked polymer is, and the smaller the cavities produced. On the other hand, the rate constant values decrease with increasing the ethyloxy chain length from n= 1 to 9. This may be explained on the basis of swelling mode. The swelling process of polymeric networks is primarily due to oil solution penetrating into the polymeric gel through diffusion. Here, increasing the ethyloxy chain length increases the hydrophilicity of the polymeric networks, thus increasing the difficulty of oil diffusion. In other words, low compatibility between oil and the polymeric networks hinders oil diffusion. The swelling rate constant for PIB-MA-CM_1/ODA is only 2.99(h^{-1}) swelled in 10% crude oil where that swelled in pure toluene is 3.99(h^{-1}). Comparing the swelling rate constants between the gels swelled in 10% crude oil and those swelled in pure toluene, the latter always show higher values. This behavior can be easily explained on the basis of different viscosity of either pure toluene and 10% crude oil which cannot easily diffuse from the surface of the gels into the internal space of the network.

A comparison of rate constant values for the crosslinked reactive polymer with those of CEMA/ODA copolymers crosslinked with the same crosslinker content in toluene was held. As an example, k= 3.99h^{-1} for PIB-MA-CM_1/ODA, whereas k=1.66h^{-1} for CEMA/ODA. This show increased absorption rate capacity for reactive polymers than that for CEMA/ODA copolymer. This behavior can be easily explained on the basis of, in case of crosslinked reactive polymer more hydrophobic

chain nature due to PIB moiety enhances oil diffusion than that of CEMA/ODA copolymer (less hydrophobic).

3.4.4. Network Parameters of the Reactive Polymers

Tables (3.33 & 3.34) show effective crosslink density (υ_e), theoretical crosslink density (υ_t), molecular weight of the chains between two successive crosslinks (M_c), polymer-solvent interaction parameter (χ), volume fraction of the polymeric material in the xerogels (Φ_p), equilibrium moduli of elasticity for xerogels (G_T), and density of the xerogels. The Flory-Rehner swelling model **[Flory and Rehner, 1943, Flory, 1950]** has been used in the literature to predict the molar mass between crosslinks (M_c). To do this we need to have accurate values of (χ). Several researchers **[Takahashi, 1983, Gupta et al., 1987, Bristow and Watson, 1987]** have attempted to compute χ from the solubility parameter concept. This approach being strictly empirical sometimes leads to wrong predictions for χ also, for some penetrates it would be cumbersome to find reliable literature data on solubility parameters of solvents. Instead, it was suggested by Aithal and Aminabhavi **[Aithal and Aminabhavi, 1990]** using an alternative phenomenological theory to calculate χ. This approach starts from Flory-Rehner equations in experimental section. Where the temperature coefficient of polymer volume fraction (d Φp/dT) was determined and utilized to calculate χ. As shown in **Tables (3.33,3.34)**, χ have values always < 0.3 for PIB-MA-CM_n/ODA at 1% crosslinker, where χ = 0.124 for PIB-MA-CM_1/ODA whereas for PIB-MA-CM_9/ODA χ = 0.192 at the same crosslinker concentration where the samples are swelled in Toluene. However, the lower the values of χ, the higher the polymer-solvent interaction. This behavior runs in harmony with the equilibrium

swelling results, where Q_{max} values are shifted to higher values as χ decreases. In other words, toluene is a thermodynamically good solvent for these polymers when χ is always less than 0.3. It is also observed from **Tables (3.33 & 3.34)** that, the lowest value of χ (=0.124) was exhibited at the lowest TPT (crosslinker) content for PIB-MA-CM_1/ODA polymer swelled in toluene. A similar behaviour for χ parameter and its effects was observed for samples swelled in 10% crude oil. A comparison of χ parameter values of the reactive polymer with those of CEMA/ODA copolymers crosslinked with the same crosslinker content in toluene was held. As an example, χ = 0.124 for PIB-MA-CM_1/ODA, whereas χ =0.358 for CEMA/ODA where either were crosslinked with 1% TPT. This show increased polymer-solvent interaction for reactive polymers than that for CEMA/ODA copolymer. This in turn affects on the swelling behaviour of either cases. In reactive polymers the swelling is shifted to higher values of Q_{max} for PIB-MA-CM_1/ODA= 45.9g/g polymer where as for CEMA/ODA Q_{max}= 27.8g/g polymer upon using 1% TPT. This increased swelling efficiency may be attributed to the compositional drift of the reactive polymer (hydrophobic and the elastic nature of the polyisobutylene moiety).

Values of Φ_p listed in **Table (3.33)** measured at 298K using pure toluene as oil medium increases with increasing content of crosslinking agent (from1 to 4 wt%). Also, Φ_p increase with increasing ethyloxy chain length moiety which may be explained as previously mentioned explaination for χ values. Increase in Φ_p values are also observed upon using 10% crude oil instead of pure toluene **Table (3.34)**.

The densities of the prepared PIB-MA-CM_n/ODA sorbers (ρ_p) crosslinked with 1,2 or 4wt % TPT crosslinker were determined and

Table(3.33): Network Parameters from Swelling Measurements of the Crosslinked PIB-MA-CM_n/ODA Copolymers in Toluene With Various Concentrations of TPT Crosslinker at 298K.

Sample	Crosslink. Content (wt%)	υ_t mol/dm^3	$\upsilon_e \times 10^3$ (mol/dm^3)	M_c (g/mole)	χ	Φ_p	G_T MN.m^{-2}	Density (ρ_p) Kg/dm^3
PIB-MA-CM_1/ODA	1	0.581	9.043	63.361	0.124	0.0217	6.120	0.573
	2	0.667	10.620	61.956	0.125	0.0236	7.390	0.658
	4	0.719	11.557	61.433	0.156	0.0258	8.279	0.710
PIB-MA-CM_2/ODA	1	0.735	13.655	53.093	0.157	0.2812	10.062	0.725
	2	0.790	14.909	52.314	0.168	0.0298	11.206	0.78
	4	0.821	15.599	51.926	0.173	0.0307	11.843	0.81
PIB-MA-CM_3/ODA	1	0.757	21.011	35.552	0.175	0.0356	16.752	0.747
	2	0.807	22.576	35.258	0.181	0.0371	18.256	0.796
	4	0.831	23.337	35.136	0.187	0.0381	19.032	0.82
PIB-MA-CM_4/ODA	1	0.791	22.406	34.811	0.181	0.0370	18.097	0.78
	2	0.811	23.286	34.354	0.212	0.0395	19.219	0.80
	4	0.821	23.693	34.186	0.213	0.0399	19.620	0.81
PIB-MA-CM_9/ODA	1	0.902	27.031	32.924	0.192	0.0411	22.610	0.89
	2	0.922	27.839	32.687	0.2180	0.0432	23.685	0.91
	4	0.943	28.470	32.665	0.2182	0.0437	24.303	0.93

Table(3.34): Network Parameters from Swelling Measurements of the Crosslinked PIB-MA-CM_n/ODA Copolymers in 10% Crude oil With Various Concentrations of TPT Crosslinker at 298K.

Sample	Crosslink. Content (wt%)	$\upsilon_e \times 10^3$ (mol/dm^3)	M_c (g/mole)	χ	Φ_p	G_T MN.m^{-2}	Density (ρ_p) Kg/dm^3
PIB-MA-CM_1/ODA	1	17.426	32.881	0.158	0.0317	13.375	0.573
	2	21.772	30.221	0.180	0.0365	17.504	0.658
	4	26.270	27.026	0.1817	0.0399	21.763	0.71
PIB-MA-CM_2/ODA	1	25.574	28.348	0.1815	0.0394	21.096	0.725
	2	29.636	26.319	0.1934	0.0429	25.146	0.78
	4	38.052	21.286	0.2173	0.0497	33.900	0.81
PIB-MA-CM_3/ODA	1	26.699	27.977	0.1926	0.0409	22.289	0.747
	2	29.051	27.399	0.2041	0.0432	24.705	0.796
	4	40.517	20.238	0.2179	0.0511	36.435	0.820
PIB-MA-CM_4/ODA	1	23.007	33.902	0.2350	0.0407	19.184	0.780
	2	31.824	25.137	0.2158	0.0458	27.595	0.800
	4	43.916	18.444	0.2749	0.0577	41.134	0.810
PIB-MA-CM_9/ODA	1	38.286	23.245	0.2396	0.0515	34.521	0.890
	2	41.839	21.849	0.2630	0.0554	38.473	0.910
	4	45.670	20.363	0.2754	0.0587	43.017	0.930

listed in **Tables (3.33 & 3.34).** The listed data show that the densities of xerogels are all less than unity. This indicates that the prepared xerogels can floate on sea surface.

The most important property of an absorbent polymer is its sorption capacity. On the basis of Flory-Rehner theory **[Flory and Rehner, 1943]** the key variables, which control this property are crosslink density υ_e, average molecular weight between crosslinks M_c, equilibrium moduli of elasticity G_T.

The values of υ_e and υ_t for PIB-MA-CM_n/ODA sorbers crosslinked with 1, 2 or 4wt % TPT crosslinker using pure toluene or 10% crude oil are listed in **Tables (3.33 & 3.34).** The data show that, υ_e increases with increasing ethyloxy chain length from n=1 to n=9.

This runs in harmoney with Q_{max} values obtained by PIB-MA-CM_n/ODA. This may be explained by increased possibility of physical crosslinks with increasing the alkyloxy chain length, from n = 1 to n = 9. Also, υ_e increases with increasing crosslinker weight content (increased chemical crosslinks). This conclusion is supported by the data of M_c for the crosslinked reactive polymer by different weight content of TPT crosslinker using toluene or 10% crude oil **Tables (3.33 & 3.34)**. The data show that M_c values decrease as crosslinker weight content increase and with increaseing ethyloxy chain length for PIB-MA-CM_n/ODA crosslinked reactive polymer. The reason may be that the increase in the amount the crosslinking agent led to formation of a denser network of the crosslinked reactive copolymer and reduce M_c (average molecular weight between successive crosslinks). In other words, the smaller M_c value indicates the higher crosslinking density network. On the other hand, the crosslinking density increase, the oil sorber capacity reduced.

The effective and theoretical crosslinking densities of the prepared crosslinked reactive polymer are rarely equal to each other, the dependence of the former on the latter usually being of the following form: $\upsilon_e = \alpha + \beta \upsilon_t$. Where β is a measure of crosslinking efficiency and α results from crosslinks induced even in absence of any added crosslinking agent. The values of β and α are listed in **Table (3.35)** for PIB-MA-CM_n (1%mole)/ODA (1%mole) sorbers crosslinked with 1, 2 or 4 wt % TPT crosslinker using pure toluene as swelling medium. The data reveal that, α values ranging from 0.0002 to 0.0054 as ethyloxy chain length increase from n=1 to n=9. This indicates that, the efficiency of PIB-MA-CM_n/ODA crosslinked reactive polymer to form physical crosslinks at zero crosslinker increase from n= 1 to n= 9 (as ethyloxy chain length increase). With regard to β values in **Table (3.35)** it was found that, β increase from 0.0153 to 0.0239 as ethyloxy chain length increase from n=1 to n=9. This indicates that, the efficiency of TPT crosslinker towards PIB-MA-CM_n reactive macromonomer and ODA monomer increases from n= 1 to n= 9 i.e., ethyloxy chain length increase. The values of υ_e are uniformly less than $\upsilon_t/10$, which is indicative of inefficient crosslinking as ethyloxy chain decrease. The high soluble fraction for PIB-MA-CM_n/ODA prepared in presence of 1% TPT varied from 41.53 to 26.62wt% as ethyloxy chain length increase from n=1 to n=9, reflects the inefficient crosslinking and thus an inhomogeneous network. It was also observed that β values are always less than unity, a property exhibited due to fact that toluene is good swelling agent for this system. The values of equilibrium moduli of elasticity (G_T) for PIB-MA-CM_n/ODA sorbers crosslinked with 1, 2 or 4 wt % TPT crosslinker using pure toluene or 10% crude oil are listed in **Tables (3.33 & 3.34)**. The data show that, G_T increases with

Table(3.35): Values of β and α for PIB-MA-CM_n/ODA Sorbers crosslinked with 1, 2 or 4 wt % TPT crosslinker using pure toluene.

Copolymers	α	β	Correlation coefficient
PIB-MA-CM_1/ODA	0.0002	0.0153	0.9808
PIB-MA-CM_2/ODA	0.0008	0.0175	0.996
PIB-MA-CM_3/ODA	0.0009	0.0269	0.9877
PIB-MA-CM_4/ODA	0.001	0.0271	0.9903
PIB-MA-CM_9/ODA	0.0054	0.0239	0.9780

increasing ethyloxy chain length and by increasing crosslinker weight content.This may be due to, the decreased probability of forming dangling chain or pendant groups as ethyloxy chain length increase and with increased crosslinker weight content. The presence of pendant chains or dangling chains in the polymeric network affectes the compression moduli. The values of moduli decrease drastically when the proportion of pendant chains increase **[Bastide et al., 1979]**. The lower G_T and υ_e values for PIB-MA-CM_n/ODA crosslinked reactive polymer indicate that the prepared gel have elastic network. This will increase interaction between toluene and prepared networks and hence increased absorption capacity for PIB-MA-CM_n/ODA crosslinked reactive polymer.