

# Crosslinking of Reactive $\alpha$ -Olefins and Maleic Anhydride Copolymers as Oil Sorbers

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**ABSTRACT:** Octene (OC) and tetradecene (TD) monomers were copolymerized with maleic anhydride (MA) with a low conversion (<10% conversion) to determine their reactivity ratios. The monomers were copolymerized with different molar percentages of MA and OC or TD (90/10, 70/30, 50/50, and 10/90) with benzoyl peroxide as an initiator to produce MA/ $\alpha$ -olefin copolymers of different compositions. Fourier transform infrared was used to determine the copolymer compositions. The monomer reactivity ratios of the MA/OC and MA/TD copolymers were determined with the Fineman–Ross and Kelen–Tudos methods. Crosslinked MA/TD and MA/OC (50 : 50 mol/mol) copolymers were prepared by the condensation of

the prepared linear copolymers with different glycols. The crosslinked copolymers were evaluated for oil absorbency applications. The effects of the glycol type, composition, crosslinker weight percentage, and type of oil on the swelling properties of the crosslinked polymers were studied with oil absorption tests. The swelling parameters, such as the maximum oil absorbency, characteristic oil absorbency, characteristic swelling time, and swelling rate constant, were evaluated for the synthesized sorbers. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 871–881, 2007

**Key words:** copolymerization; crosslinking; esterification; FT-IR; gelation; graft copolymers; kinetics (polym.); swelling

## INTRODUCTION

Spilled oil contributes an undesirable taste and odor to drinking water and causes severe environmental damage.<sup>1–3</sup> The most urgent technique for the elimination of the emergency spread of oil and petroleum products is collecting thin layers from the water surface with the help of sorbents. Sorbents should have oleophilic or hydrophobic characteristics to be used as the sole cleanup method in small spills. Once sorbents have been used to recover oil, they must be removed from the water and properly disposed of or cleaned for reuse.<sup>4,5</sup> It is known that an effective means of obtaining an oil absorbent is to synthesize a crosslinked polymer that does not dissolve in oil.<sup>6</sup> Despite the development of polymers for oil absorption, there have been few reports on the synthesis of such polymers. The synthesis of an ethylene–propylene–diene polymer containing an aromatic moiety has been reported.<sup>7</sup> Other kinds of polymers have been widely used to absorb oil spilled into water.<sup>8,9</sup> Among them, alkyl acrylate and aromatic polymers, which have hydrophobicity and gel-type structures consisting of an elastic network and interstitial space, have

been attracting much interest in the field of environmental science.<sup>10–15</sup>

The synthesis and characterization of linear and crosslinked octadecene-*alt*-maleic anhydride copolymers for oil absorbency applications have been studied previously.<sup>16</sup>

In this research, we aimed to synthesize new oil sorbers based on hydrophobic monomers ( $\alpha$ -olefin monomers) through copolymerization with maleic anhydride (MA) to produce reactive polymers that crosslinked in the presence of ethylene glycol (EG) and poly(ethylene glycol) (PEG) to control environmental pollution. In this respect, the copolymerization and crosslinking of octene (OC) and tetradecene (TD) with MA were the main goals of this study. On the other hand, we aimed to use the MA moiety to introduce glycolic moieties to increase the solubility in crude oil and to increase the oil swelling capacities. The determination of the swelling and kinetic parameters of the prepared gels was another goal of this work.

## EXPERIMENTAL

### Materials

OC, TD, and MA were obtained from Aldrich Chemical Co. (Germany). OC and TD were purified through washing with 5% aqueous sodium hydroxide, dried over anhydrous CaCl<sub>2</sub>, and distilled *in vacuo*. MA was

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refluxed with chloroform and filtered to remove any traces of maleic acid. The product was then crystallized three times from chloroform to yield white needles. MA was purified by sublimation. EG, poly(ethylene glycol)<sub>600</sub> (PEG<sub>600</sub>), poly(ethylene glycol)<sub>2000</sub> (PEG<sub>2000</sub>), and poly(ethylene glycol)<sub>6000</sub> (PEG<sub>6000</sub>) were obtained from Aldrich Chemical. Benzoyl peroxide recrystallized from ethanol was used as a thermal polymerization initiator. The Belayium crude oil and condensates were produced by Petrobel Co. and Rashid Petroleum Co. (Cairo, Egypt), respectively.

### Synthesis of the MA/OC and MA/TD copolymers

The detailed procedures used to synthesize the linear MA/OC and MA/TD copolymers were as follows. OC or TD and MA were mixed with different monomer feed ratios (MA/OC or MA/TD) of 90/10, 70/30, 50/50, 30/70, and 10/90 mol/mol. The reactants were dissolved in 100 mL of toluene, and the mixture then was poured into a round-bottom flask under an N<sub>2</sub> atmosphere in the presence of benzoyl peroxide as an initiator [0.02% (w/w)]. The solution was then heated to 70°C until a low-conversion copolymerization of approximately 10% was obtained. The products were poured into an excess of methanol with stirring. The obtained precipitate was filtered and dried in a vacuum oven at 30°C to a constant weight. The time required for the low conversion was estimated by the monitoring of the weight of the linear copolymer that precipitated in excess methanol after different time intervals.

### Synthesis of the crosslinked MA/OC and MA/TD copolymers

The crosslinked MA/OC and MA/TD copolymers were produced through stepwise polymerization. The copolymers (50/50 mol/mol) were mixed together with calculated weight percentages of EG and PEG with different weight ratios of polyurethane (PU) foam. The stepwise polymerization reactions were performed in Petri dishes at 373 K for 3 h. The reaction time was extended to ensure the complete reaction of all the monomers. The constituents of the synthesized crosslinked copolymers were calculated according to the molar ratios. The crosslinked copolymer foams were postcured at 378 K in an air oven. The foams were cut into thin discs, which were used to determine the soluble fractions (SFs) and swelling parameters.

### Characterization of the prepared polymers

The chemical structures of the MA/OC and MA/TD copolymers were determined from Fourier transform infrared (FTIR) data. FTIR spectra were obtained with

a Mattson Infinity Series bench top 961 model using KBr discs.

For the crosslinked xerogel discs, SFs were extracted with chloroform until constant weights were achieved.<sup>16</sup>

### Oil swelling measurements

The oil absorbency of the crosslinked copolymers was determined according to ASTM F726-81: 0.1 g of the polymer was put in a stainless steel mesh (4 × 4 × 2 cm<sup>3</sup>). The sample was immersed in pure toluene, a petroleum condensate, or a crude oil solution (crude oil diluted with toluene, 10% oil). The sample and the mesh were together picked up from oil, drained for 30 s, tapped with filter paper to remove excess oil from the bottom of the mesh, and then weighed. The characteristic oil absorbency (Q) and equilibrium toluene content (ETC) were calculated as described in a previous article.<sup>16</sup>

The swelling kinetics of oil absorption were studied by the repetition of the previous measurements at different time intervals. The swelling parameters, Q and ETC, of the prepared gels were calculated from five measurements as follows:

$$Q(\text{g/g}) = \frac{\text{Weight of the absorbed oil in the sample}}{\text{Weight of the sample before oil absorbency}} \quad (1)$$

$$\text{ETC} (\%) = \left[ \frac{\text{Weight of the gel} - \text{Weight of the xerogel}}{\text{Weight of the gel}} \right] \times 100 \quad (2)$$

Also, the maximum oil absorbency ( $Q_{\text{max}}$ ) was determined by the tests being allowed to stand for 24 h. To study the kinetics of swelling, gel samples in triplicate were immersed in crude oil. After equilibration-swollen gel samples were placed in an oven at 318 K for 12 h, the gels deswelled. The deswelling was then followed by the weighing of the gels at various times.

## RESULTS AND DISCUSSION

Many kinds of polymers have been widely used to absorb oil spilled in water. It is well known that oil sorbers should have hydrophobic characteristics to swell in an oil medium. This work was aimed at the synthesis of new copolymers based on MA and hydrophobic moieties such as alkyl groups. Because of its bifunctionality, MA is both an interesting compound for scientific investigations and an important building block for commercial polymers. In this research, we tried to synthesize new oil sorbers based on hydrophobic monomers ( $\alpha$ -olefin monomers) through copolymerization with MA to produce reactive polymers that crosslinked in the presence of EG and PEG to control

TABLE I  
Reaction Parameters for the Copolymerization of MA ( $M_1$ ) with OC or TD ( $M_2$ )

Molar fraction of OC or TD ( $M_2$ )	Molar fraction of MA ( $M_1$ )	Conversion (%)	Time (h)	$M_1/M_2$ feed ratio (mol/mol)	Sample
5	95	4.45	3	90/10	MA/OC
15	85	8.28	2.5	90/10	MA/TD
20	80	6.33	2.5	70/30	MA/OC
40	60	8.3	2	70/30	MA/TD
35	65	11.8	1.5	50/50	MA/OC
68	32	7.82	1.5	50/50	MA/TD
62	38	10.94	1	30/70	MA/OC
80	20	9.27	1	30/70	MA/TD
85	15	8.5	1	10/90	MA/OC
95	5	10	1	10/90	MA/TD

environmental pollution. Accordingly, this work was based on the preparation of low-conversion copolymers from MA with  $\alpha$ -olefin monomers such as OC and TD. The calculation of the reactivity ratios for the prepared linear MA/ $\alpha$ -olefin copolymers was used to detect the distribution of the monomers of the synthesized linear copolymers. The synthesis of crosslinked copolymers was accomplished by the reaction of linear copolymers with EG and PEG in the presence of PU foam, which was used as a carrier to produce crosslinked copolymers (oil sorbers). The oil absorbance efficiency of the synthesized sorbers was determined by the calculation of the swelling parameters of the prepared sorbers on Egyptian crude oil and paraffin condensates.

### Reactivity ratio studies

Several techniques have been developed to determine the reactivity ratios of the monomers.<sup>17</sup> The most frequently cited methods are the Fineman–Ross<sup>18</sup> and Kelen–Tudos methods.<sup>19</sup> Monomer feed mixtures of various compositions are polymerized to low conversions, and the resultant polymer composition is measured. Knowledge of the reactivity ratios is key to predicting 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. In this investigation, the FTIR technique was used to determine the percentage of MA in the MA/OC and MA/TD copolymers. This could be achieved by the monitoring of the intensity of the absorption band at  $1760\text{ cm}^{-1}$  for the vibration stretching of the anhydride (CO—O—CO—) group of MA. The method was based on the blending of a constant weight of the MA monomer (0.05 g) with KBr to determine the absorbance of the anhydride group with 100 mol % MA ( $A_1$ ). The same weight of the low-conversion copolymers was blended with KBr discs to obtain the absorbance of the anhydride group of the copolymers ( $A_2$ ). The MA molar percentage in the copolymers

was determined as follows: MA molar percentage =  $A_2(100)/A_1$ . The data are listed in Table I. FTIR spectra of the MA/OC linear copolymers were selected and are presented in Figure 1. These ratios were used to calculate the reactivity ratios. The monomer reactivity ratios for the copolymerization of MA ( $r_1$ ) and OC ( $r_2$ ) were determined with the Fineman–Ross method and Kelen–Tudos method, as presented in Figure 2(a,b), respectively. The Fineman–Ross plot was based on  $F(f - 1)/f$  ( $G$  ordinate) versus  $F^2/f$  ( $H$  abscissa), where  $F$  and  $f$  are the molar fractions of the monomers and copolymer, respectively. The Fineman–Ross plot for the copolymerization of MA ( $M_1$ ) and OC ( $M_2$ ) is presented in Figure 2(a). There is a straight line with a slope and intercept of  $r_1$  and  $r_2$ , respectively, where  $r_1$  and  $r_2$  represent the reactivity ratios for the monomer pair  $M_1$  and  $M_2$ . The results from the graphical evaluation of the MA/OC yield values of  $r_1 = 2.045$  and  $r_2 = 0.792$ . From the Kelen–Tudos approach, the relationships between  $E$  and  $N$  were  $E = H/(\alpha + H)$  and  $N = G/(\alpha + H)$ ; they were likewise used for the graphical evaluation of the reactivity ratio for the same two monomers presented in Figure 2(b). Here  $\alpha$  was calculated from the maximum and minimum values of  $H$  as  $\alpha = (H_{\max} \times H_{\min})^{0.5}$ . Extrapolation to  $E = 0$  and  $E = 1$  afforded the values of  $N = -r_2/\alpha$  and  $r_1$ , respectively. In this respect, values of 2.05 and 0.79 were obtained for  $r_1$  and  $r_2$ , respectively. Excellent agreement was found between the Fineman–Ross and Kelen–Tudos methods. In a copolymerization reaction, when the  $r_1$  and  $r_2$  values are greater than unity, each monomer group prefers to react with itself and not with the other monomer. In the case of  $r_1 = 2.05$ , a growing chain ending with an  $M_1$  group reacts with  $M_1$  more than  $M_2$ . On the other hand, the Kelen–Tudos graphical plot shows a straight line. This behavior indicates that the copolymerization of MA and OC follows conventional copolymerization kinetics because only the terminal monomer unit determines the reactivity of a polymer radical. Meanwhile, the product of the average values

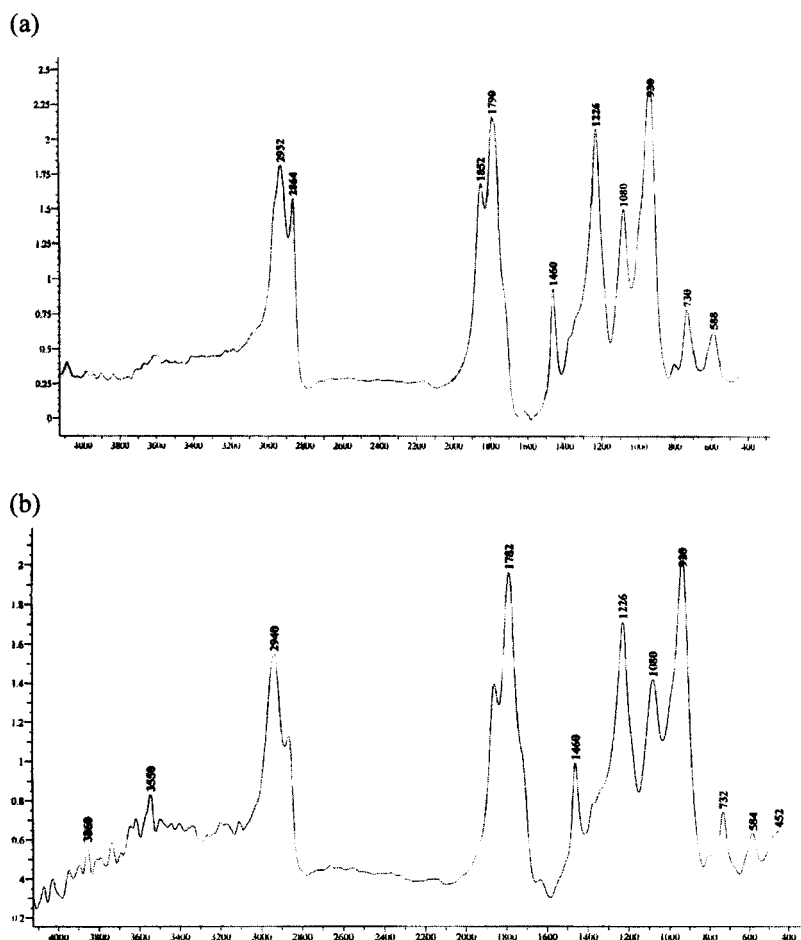


Figure 1 FTIR spectra for MA/OC samples with ratios of (a) 10/90 and (b) 30/70.

of  $r_1$  and  $r_2$  was 1.619 ( $r_1$  and  $r_2$  were relatively close to unity), indicating that the MA/OC copolymer prepared under these conditions had a random distribution of the monomer units along the copolymer chains having high MA contents.

The aforementioned methods for determining the reactivity ratios were used to measure the reactivity ratios of MA ( $M_1$ ) and TD ( $M_2$ ). The linear plot of  $F(f - 1)/f$  ( $G$  ordinate) versus  $F^2/f$  ( $H$  abscissa) (Fineman–Ross plot) afforded  $r_1$  and  $-r_2$ , respectively from the slope and the intercept. The data are illustrated in Figure 3(a). The obtained values of  $r_1$  and  $r_2$ , from this figure, were 0.65 and 2.045, respectively. Consequently, the product of  $r_1$  and  $r_2$  was 1.329. The linear plot of  $N$  versus  $E$  (the Kelen–Tudos method) is shown in Figure 3(b). The obtained values of  $r_1$ ,  $r_2$ , and  $r_1r_2$  indicate that the produced copolymer had a random distribution. The high value of  $r_2$  of TD confirmed the high incorporation of TD in the copolymer compared with that of MA.

The relationship between the molar fraction of MA incorporated into the copolymers ( $m_1$ ), determined by FTIR analyses, and that in the feed ratio of the comonomer ( $M_1$ ), is shown in Figure 4. It is obvious

that there is no point at which  $m_1$  is equal to  $M_1$ ; that is, no azeotropic copolymer is expected to be formed through the copolymerization of MA with OC and TD monomers.

### Copolymer microstructure

The statistical distribution<sup>20</sup> of monomer sequences  $M_1$ – $M_1$ ,  $M_2$ – $M_2$ , and  $M_1$ – $M_2$  can be calculated with the following equations:

$$X = \phi_1 - 2\phi_1(1 - \phi_1)/[1 + [(2\phi_{1-1})^2 + 4r_1r_2\phi_1(1 - \phi_1)]^{0.5}] \quad (3)$$

$$Y = (1 - \phi_1) - 2\phi_1(1 - \phi_1)/[1 + [(2\phi_{1-1})^2 + 4r_1r_2\phi_1(1 - \phi_1)]^{0.5}] \quad (4)$$

$$Z = 4\phi_1(1 - \phi_1)/[1 + [(2\phi_{1-1})^2 + 4r_1r_2(1 - \phi_1)]^{0.5}] \quad (5)$$

where  $X$ ,  $Y$ , and  $Z$  are the molar fractions of the  $M_1$ – $M_1$ ,  $M_2$ – $M_2$ , and  $M_1$ – $M_2$  sequences in the copolymer, respectively, whereas  $\phi_1$  is the molar fraction of MA

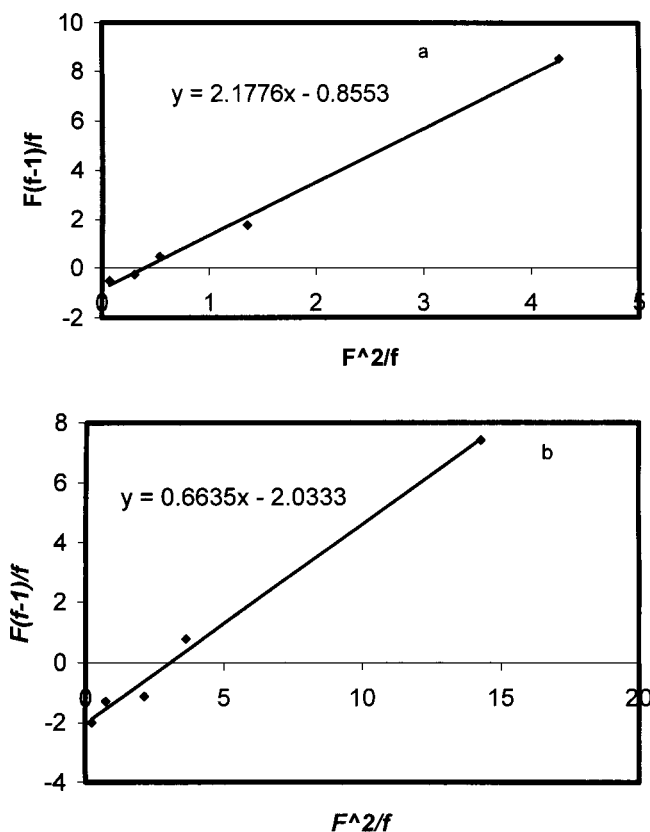


Figure 2 Fineman-Ross plots of (a) MA/OC and (b) MA/TD copolymers.

and  $r_1$  and  $r_2$  are the reactivity ratios of the respective monomer pairs.

Also, the mean sequence lengths,  $\mu_1$  and  $\mu_2$ , can be calculated with the following equations:

$$\mu_1 = 1 + r_1[M_1]/[M_2] \quad (6)$$

$$\mu_2 = 1 + r_2[M_2]/[M_1] \quad (7)$$

The structural data for MA/OC and MA/TD copolymers of different compositions are listed in Table II. The calculated molar percentage of the poly(MA/OC) linkage in each copolymer was relatively low, indicating a definite random tendency. It is noticeable that the mean sequence of MA ( $\mu_{MA}$ ) varied from 5.47 to 1.04 as the molar percentage of MA in the copolymer decreased from 90 to 10 mol %, whereas the mean sequence of OC ( $\mu_{OC}$ ) increased from 1.316 to 39.95 as the OC molar percentage increased in the copolymer from 10 to 90 mol %. The relatively low  $\mu_{MA}$  values and high values for OC afford a further indication of the random tendency in the MA/OC copolymer.

The structural data for MA/TD copolymers of different compositions are listed in Table II. The calculated molar percentage of the poly(MA/TD) linkage in each copolymer was relatively low, indicating a

definite random tendency. It is noticeable that  $\mu_{MA}$  varied from 39.85 to 1.36 as the molar percentage of MA in the copolymer decreased from 90 to 10 mol %, whereas the mean sequence of TD ( $\mu_{TD}$ ) increased from 1.03 to 4.68 as the TD molar percentage in the copolymer increased from 10 to 90 mol %. The relatively high  $\mu_{MA}$  values and low values of TD afford a further indication of the random tendency in the MA/TD copolymer.

### High conversion and crosslinked copolymerization

Crosslinking is responsible for the three-dimensional network structure that is important for oil swelling into sorbers rather than dissolving in them. The elasticity and swelling properties are attributed to the presence of physical or chemical crosslinks within polymer chains. Hydrophobic network polymers are

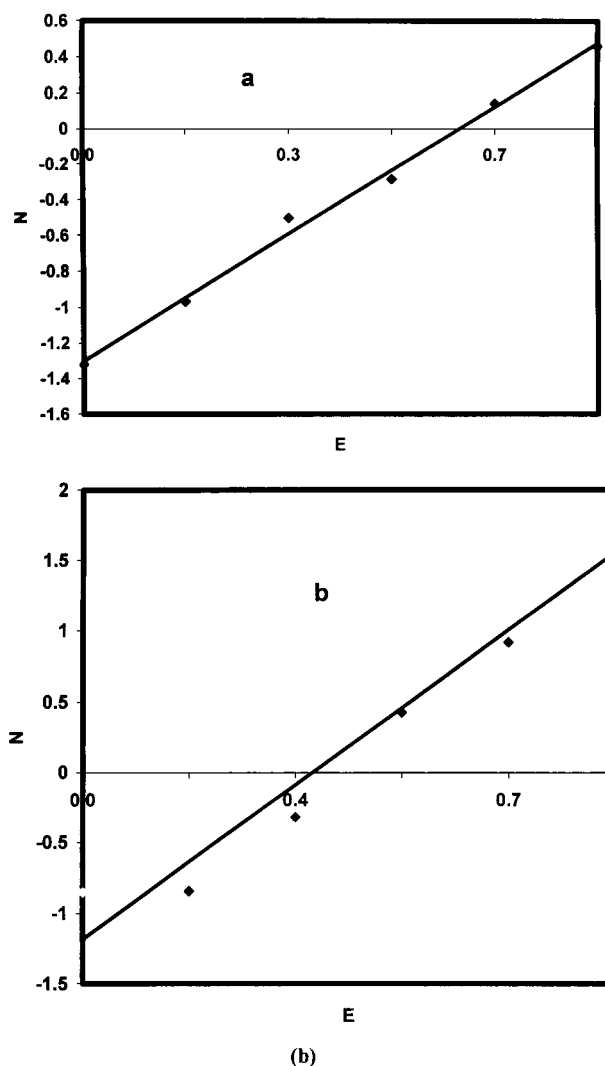


Figure 3 Kelen-Tudos plots of (a) MA/OC and (b) MA/TD copolymers.

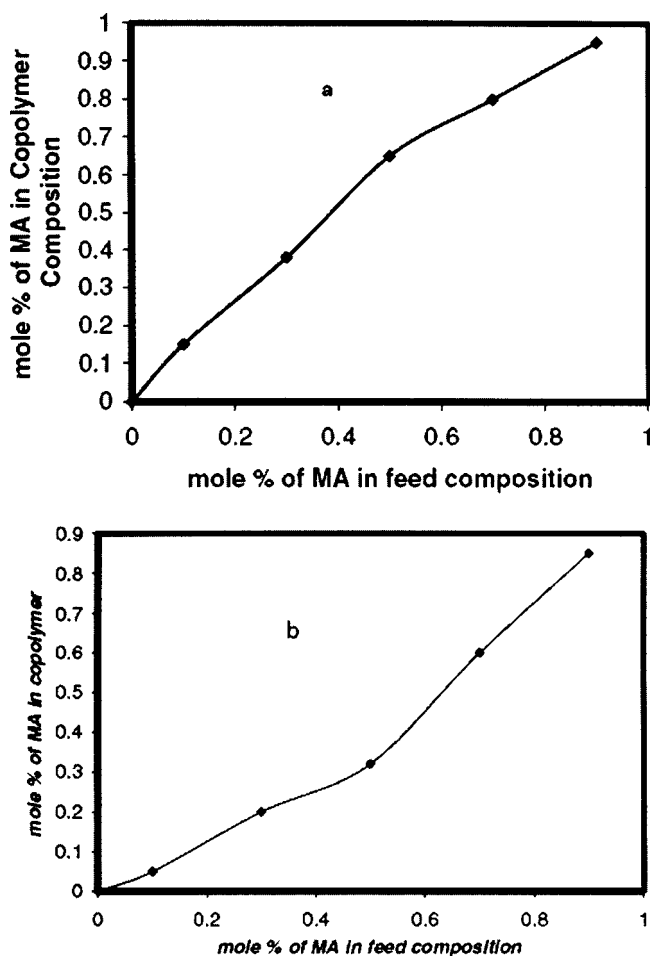


Figure 4 Copolymer compositions as a function of the feed composition for the copolymerization reaction of (a) MA/OC and (b) MA/TD copolymers.

used as absorbents of oil as well as some organic solvents spilled into water in the environment.

High-conversion polymerizations were performed to prepare different crosslinked copolymers. The crosslinked MA/OC and MA/TD (50/50 mol/mol) copolymers were prepared via bulk polymerization in the presence of 0.02% benzoyl peroxide as an initiator. EG and PEG with different molecular weights were used to form crosslinked polymers through

esterification reactions between the hydroxyl groups of PEG and the anhydride groups of the prepared copolymers. The reaction of the prepared crosslinked copolymers is presented in Figure 5.

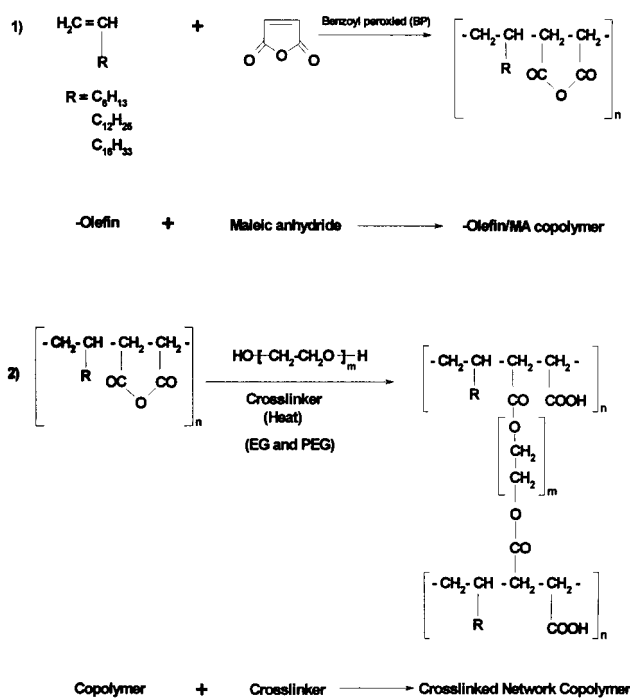
The composite technique is one of the available methods for reinforcing oil sorbers.<sup>21</sup> Fibers, sponges, and nonwoven fabrics are used as reinforces. Sponges are used with two different techniques. The first technique is based on immersion during the polymerization of monomers. The second technique is based on the coating of sponges with polymer solutions. In this respect, the reaction was conducted on PU foam by the second technique, as described in the Experimental section. 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 because of crosslinking. It only swells in a good solvent to give a gel. According to Flory's swelling theory,<sup>22</sup> the swelling behavior is affected by the rubber elasticity, the affinity to the solution, and the crosslinking density. Generally, the crosslinker concentrations affect the swelling capacity and soluble polymer fractions.

## SF

Some polymer chains that are not attached to the infinite network can be extracted from the gel fraction. The effect of these chains is difficult to determine and is usually neglected in 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 extractable fraction (SF) depends on (1) the type and concentration of the monomer and (2) the type and concentration of the crosslinking agent.<sup>23</sup> In this investigation, the polymers were postcured at 378 K in an air oven for 24 h to ensure complete polymerization. The sol fractions of these polymeric materials were determined via a Soxhlet extraction technique. In this respect, the dried crosslinked polymers were transferred into an extraction thimble and were subjected to Soxhlet extraction

TABLE II  
Structural Data for the MA/OD and MA/TD Copolymers

MA/TD mean sequence length		MA/OC mean sequence length		Alternation (mol %)		MA/TD blockiness (mol %)		MA/OC blockiness (mol %)		Sample
$\mu_{TD}$	$\mu_{TD}$	$\mu_{OC}$	$\mu_{MA}$	MA/TD	MA/OC	TD/TD	MA/MA	OC/OC	MA/MA	
1.03	1.03	1.36	5.47	90.32	73.12	0.32	9.35	3.12	23.75	MA/ $\alpha$ -olefins
1.16	1.16	2.25	2.28	64.76	41.13	4.76	30.47	17.13	41.72	MA/ $\alpha$ -olefins
1.30	1.30	4.80	1.42	47.60	14.78	11.60	40.78	44.78	40.43	MA/ $\alpha$ -olefins
1.97	1.97	9.20	1.19	17.64	5.33	37.64	44.70	65.33	29.33	MA/ $\alpha$ -olefins
4.68	4.68	39.95	1.04	2.74	0.38	72.74	24.51	90.38	9.23	MA/ $\alpha$ -olefins



Where; EG = Ethylene Glycol  
 PEG = Polyethylene Glycol

Where as;

$\text{R} = \text{C}_{16}\text{H}_{33}$ , the copolymer is MA/OD [EG, PEG<sub>600</sub>, PEG<sub>2000</sub> and PEG<sub>6000</sub>].

**Figure 5** Synthesis of the crosslinked network copolymers.

with chloroform. After extraction for 24 h, the samples were dried in the atmosphere for several hours and then dried to a constant weight in a vacuum oven at 308 K. However, no further extraction was found after 24 h, and this Soxhlet extraction time was adopted for all samples. The determined SF values for the MA/OC copolymer with EG, PEG<sub>600</sub>, PEG<sub>2000</sub>, and PEG<sub>6000</sub> were determined to be 30.66, 23.14, 20.32, and 16.33%, respectively. The SF values for the MA/TD copolymers were 35.66, 28.96, 26.92, and 22.33%, respectively. The SF values for the MA/OC and MA/TD copolymers crosslinked with EG were higher than the values of those crosslinked with PEG. This could be attributed to the lower affinity of EG to crosslink MA/OC and MA/TD copolymers. This may be attributed to the differences in the reactivities of both the EG and PEG crosslinkers with the produced polymer.<sup>24</sup> On the other hand, SF increased with an increasing  $\alpha$ -olefin percentage in the copolymer composition. This may have been due to the higher reactivity of the MA/ $\alpha$ -olefin copolymers, which had short chain lengths, and the MA/OC copolymers toward crosslinking because of increasing active sites and the MA contents, as described in the section on reactivity ratios. In other words, the MA

moieties were used before a significant amount of OC was incorporated into the network structure. This may also be attributed to the lower reactivity of longer  $\alpha$ -olefins toward either crosslinker because of the steric effect of the bulk groups, which reduced the reactivity of EG and PEG to form crosslinked polymers.

### Swelling behavior of the crosslinked copolymers

The excellent oil absorbability of materials depends on the bulkiness and length of the alkyl substituents<sup>25</sup> and especially on the permeability of the microstructure, which can be controlled by crosslinking. Because the driving force for oil absorption is caused mainly by the van der Waals force between the material and the oil, materials with the proper permeability can effectively absorb more oil in their structures.

The oil used in this experiment was diluted with toluene (10% oil). For a real application to cleaning up an oil spill, the oil absorption test had to be operated with not only light or medium oil but also heavy oil because spilled crude oil has a high viscosity. On the other hand, the materials used to absorb the oil did not have a spongelike structure with open pores. They had only a network structure, which was formed by the crosslinking reaction. Therefore, heavy oil with a high viscosity, such as Belayium crude oil, cannot easily diffuse from the surface of samples into the internal space of the network. Therefore, toluene is the most applicable solvent used to dissolve asphaltene of crude oil. For these reasons, crude oil diluted by toluene was used in this experiment. As a result, 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. In this investigation, the oil absorbency of the crosslinked MA/OC or MA/TD foam composites crosslinked with EG and PEG were determined according to ASTM F726-81 with paraffin condensates and 10% crude oil. The  $Q_{\text{max}}$  values of the composites containing different crosslinked polymers versus the foam content were calculated and are recorded in Tables III–VI. On the other hand, the swelling curve is based on plotting the relation between the oil absorbency and immersion time. In this respect, the oil absorbency for the MA/OC and MA/TD foam composites crosslinked with EG and PEG with 10% crude as an oil as a function of the immersion time was also calculated and is listed in Tables III–VI. This relation was also represented with the use of the paraffin condensate and crude oil, as shown in Figure 6. The oil

**TABLE III**  
**Swelling Characteristics of the MA/OC and MA/TD Copolymers Crosslinked with the EG Crosslinker**

$K$ ( $\text{h}^{-1}$ )		$T_{\text{max}}$ (h)		EOC (%)		ECC (%)		$Q$ (g/g)		$Q_{\text{max}}$ (g/g)		XCLP/PU
Oil	Condensate	Oil	Condensate	Oil	Condensate	Oil	Condensate	Oil	Condensate	Oil	Condensate	
1.501	1.200	0.66	0.833	97.55	97.46	25.160	24.280	39.8	38.419	1 : 1	MA/OC	
1.999	1.714	0.5	0.583	97.82	97.57	28.421	25.361	44.971	40.129	1 : 1	MA/TD	
1.091	0.999	0.91	1	97.52	97.38	25.082	23.529	39.6	37.230	1 : 3	MA/OC	
1.501	1.200	0.66	0.833	97.71	97.45	26.964	24.129	42.6	38.178	1 : 3	MA/TD	
0.857	0.749	1.16	1.333	97.39	97.29	23.554	22.678	37.2	35.884	1 : 5	MA/OC	
0.999	0.857	1.00	1.166	97.58	97.42	25.416	23.854	40.2	37.744	1 : 5	MA/TD	
0.666	0.600	1.5	1.666	97.26	97.23	22.398	22.115	35.4	34.993	1 : 10	MA/OC	
0.749	0.666	1.33	1.5	97.42	97.32	23.900	22.99	37.8	36.378	1 : 10	MA/TD	
0.545	0.499	1.83	2	97.08	96.97	20.872	20.218	31.9	33.026	1 : 15	MA/OC	
0.600	0.545	1.66	1.833	97.22	97.14	22.195	21.66	35.1	34.273	1 : 15	MA/TD	

absorbency obviously increased with an increasing immersion time and leveled off at 3 h. Moreover, the oil absorbency decreased slightly with the use of the condensate instead of the 10% crude toluene solution. This may be explained as follows. The swelling process of polymer networks may be primarily due to the oil solution penetrating the polymeric gel through a capillary effect and diffusion. Therefore, crude oil diluted with toluene can be easily diffused from the external surface of a sample into the internal space of the networks.<sup>26</sup> 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 the diffusion in polymer–solvent systems. The properties of the systems are functions not only of the nature of the components but also of their compositions. Mixing a polymer with a solvent involves a change in the energy of interaction and in the number of direct contacts between the polymer chains. Intermolecular interactions change little when polymer–polymer contacts are replaced by polymer–solvent 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 the cooperative movement of neigh-

boring molecules. The probability of this process is dependent on the mobility of the molecules of the medium. The higher the solvent content is of the system, the greater the mobility is and the less energy is required for the movement of the diffusing molecules. Assuming an exponential dependence of this energy on the composition, we can find the relationship connecting the unidirectional coefficient of diffusion with the solvent concentration.<sup>27</sup> When a molecule moves under the influence of a concentration gradient, the molecule is oriented in the direction of the movement<sup>28</sup> and is subjected to two types of resistance, namely, lateral and frontal resistance. 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 first approximation of the 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; that is, it is determined by its structure. Also, it is dependent on the molecular interaction between the molecules of the medium and

**TABLE IV**  
**Swelling Characteristics of the MA/OC and MA/TD Copolymers Crosslinked with the PEG<sub>600</sub> Crosslinker**

$K$ ( $\text{h}^{-1}$ )		$T_{\text{max}}$ (h)		EOC (%)		ECC (%)		$Q$ (g/g)		$Q_{\text{max}}$ (g/g)		XCLP/PU
Oil	Condensate	Oil	Condensate	Oil	Condensate	Oil	Condensate	Oil	Condensate	Oil	Condensate	
1.333	1.091	0.75	1.0	94.85	94.68	11.641	11.257	18.4	17.811	1 : 1	MA/OC	
1.501	1.333	0.66	0.75	95.3	95.2	12.722	12.622	20.1	19.971	1 : 1	MA/TD	
0.779	0.706	1.25	1.333	94.51	94.35	10.889	10.546	17.2	16.687	1 : 3	MA/OC	
0.923	0.799	1.08	1.25	94.79	94.6	11.488	11.165	18.1	17.666	1 : 3	MA/TD	
0.545	0.479	1.83	2.083	94.41	94.21	10.671	10.282	16.8	16.269	1 : 5	MA/OC	
0.600	0.522	1.66	1.916	94.66	94.51	11.214	10.881	17.7	17.216	1 : 5	MA/TD	
0.462	0.414	2.16	2.516	94.12	93.92	10.108	9.759	15.9	15.441	1 : 10	MA/OC	
0.499	0.444	2	2.25	94.25	94.06	10.351	9.996	16.3	15.817	1 : 10	MA/TD	
0.375	0.353	2.58	2.66	93.35	93.33	8.864	8.843	14.0	13.992	1 : 15	MA/OC	
0.399	0.375	2.50	2.666	93.45	93.39	9.021	8.923	14.2	14.119	1 : 15	MA/TD	



**TABLE V**  
**Swelling Characteristics of the MA/OC and MA/TD Copolymers Crosslinked with the PEG<sub>2000</sub> Crosslinker**

$K$ ( $h^{-1}$ )		$T_{max}$ (h)		EOC (%)		ECC (%)		$Q$ (g/g)		$Q_{max}$ (g/g)		XCLP/PU
Oil	Condensate	Oil	Condensate	Oil	Condensate	Oil	Condensate	Oil	Condensate	Oil	Condensate	
1	0.857	1	1.166	94.38	94.18	10.616	10.231	16.7	16.189	1 : 1	MA/OC	
1.091	1	0.91	1	94.77	94.57	11.459	11.001	18.1	17.407	1 : 1	MA/TD	
0.666	0.60	1.5	1.666	94.19	94.0	10.242	9.899	16.2	15.663	1 : 3	MA/OC	
0.75	0.666	1.33	1.5	94.61	94.44	11.094	10.587	17.5	16.751	1 : 3	MA/TD	
0.48	0.40	2.08	2.5	94.04	93.83	9.978	9.606	15.7	15.199	1 : 5	MA/OC	
0.522	0.444	1.91	2.25	94.34	94.05	10.540	9.993	16.6	15.812	1 : 5	MA/TD	
0.40	0.364	2.5	2.75	93.78	93.55	9.531	9.160	15.0	14.493	1 : 10	MA/OC	
0.429	0.4	2.33	2.5	93.96	93.72	9.838	9.428	15.5	14.917	1 : 10	MA/TD	
0.343	0.316	2.91	3.166	93.23	92.91	8.708	8.288	13.7	13.114	1 : 15	MA/OC	
0.353	0.333	2.83	3	93.32	93.02	8.835	8.428	13.9	13.336	1 : 15	MA/TD	

on the compressibility of the latter. Both types of resistance are determined to a considerable extent by the viscosity of the medium.<sup>27</sup>

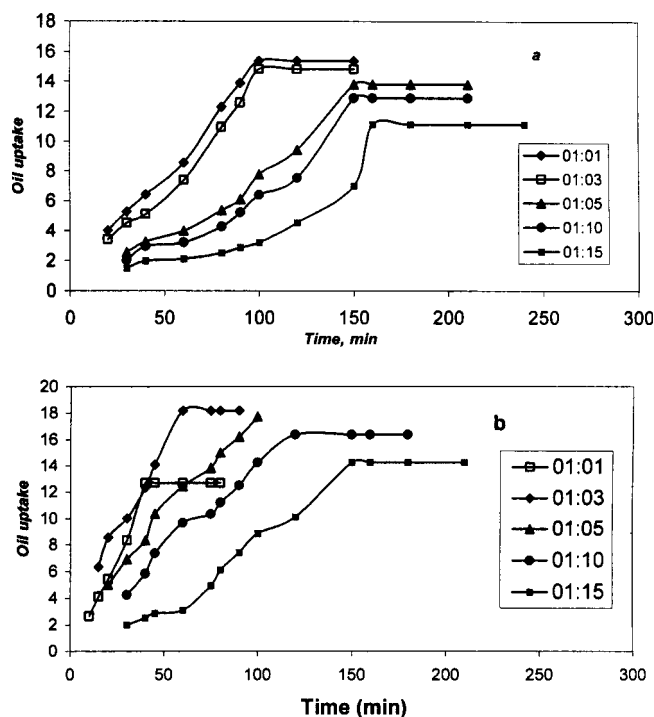
A careful inspection of the listed data in Tables III–VI, with respect to the effect of the crosslinker type on the oil absorbency of MA/OC and MA/TD foam composites, showed that the oil absorbency decreased with the increasing molecular weight of the crosslinkers. This can be attributed to the increasing probability of the formation of a highly crosslinked polymer when the molecular weight of PEG increased; that is, the relaxation of the polymeric chain was restricted.<sup>29</sup> By comparing  $Q_{max}$  of MA/OC or MA/TD foam composites crosslinked with EG and those crosslinked with PEG<sub>6000</sub>, we found that the crosslinked sorbers with EG had higher  $Q_{max}$  values than those crosslinked with PEG<sub>600</sub>, PEG<sub>2000</sub>, and PEG<sub>6000</sub>. This was mainly due to the lower crosslinking density with EG. These results agree with SF data, which confirm that PEG<sub>6000</sub> is more efficient as a crosslinker than EG. On the other hand, this can be also attributed to the decreasing hydrophobicity of the polymeric network when the molecular weight of PEG was increased. This indicates that the swelling capacities increased with the increasing hydrophobicity of the copolymers and vice versa with increasing hydro-

philicity. According to the data listed in Tables III–VI, the oil absorbency was in the order of MA/TD > MA/OC. This can be attributed to the reactivity ratios between the monomers and crosslinkers and to the hydrophobicity of the copolymers. The reactivity ratios of the copolymers, as discussed previously, indicated that MA was incorporated into the copolymers in the order of OC > TD. Accordingly, the probability of the reaction of EG and PEG could be arranged in the same order, but the steric hindrance of the C-14  $\alpha$ -olefin inhibited the reaction of PEG with TD. Accordingly, the order of crosslinking could be arranged in the order of OC > TD, which agreed with the swelling characteristics of the crosslinked copolymers, which indicated higher oil absorption of the MA/TD copolymers than the MA/OC copolymers. On the other hand, the hydrophobicity of the copolymers could arrange in the same order. Finally, it can be concluded that the oil absorbency increased with the increasing length of the alkyl groups. It can be easily explained that the longer the aliphatic side group was, the more hydrophobicity could be introduced into the copolymer, and this promoted the oil absorption capacity.<sup>26</sup>

The effect of the ratios of the foam to the crosslinked copolymers on the oil absorbance capacities

**TABLE VI**  
**Swelling Characteristics of the MA/OC and MA/TD Copolymers Crosslinked with the PEG<sub>6000</sub> Crosslinker**

$K$ ( $h^{-1}$ )		$T_{max}$ (h)		EOC (%)		ECC (%)		$Q$ (g/g)		$Q_{max}$ (g/g)		XCLP/PU
Oil	Condensate	Oil	Condensate	Oil	Condensate	Oil	Condensate	Oil	Condensate	Oil	Condensate	
0.803	0.706	1.25	1.416	93.27	93.05	8.762	8.456	13.8	13.379	1 : 1	MA/OC	
0.923	0.8	1.08	1.25	94.09	93.89	10.060	9.718	15.9	15.376	1 : 1	MA/TD	
0.571	0.522	1.75	1.916	92.93	92.71	8.313	8.036	13.1	12.715	1 : 3	MA/OC	
0.632	0.571	1.58	1.975	93.86	93.68	9.669	9.367	15.2	14.821	1 : 3	MA/TD	
0.414	0.375	2.41	2.666	92.54	92.20	7.844	7.472	12.4	11.823	1 : 5	MA/OC	
0.444	0.40	2.25	2.50	93.49	93.25	9.077	8.729	14.3	13.811	1 : 5	MA/TD	
0.363	0.333	2.75	3	92.07	91.61	7.341	6.904	11.6	10.924	1 : 10	MA/OC	
0.4	0.375	2.50	2.666	92.93	92.80	8.307	8.148	13.1	12.892	1 : 10	MA/TD	
0.324	0.308	3.08	3.25	90.56	91.01	6.856	6.400	10.8	10.127	1 : 15	MA/OC	
0.324	0.308	3.08	3.083	3.166	92.11	91.75	7.380	11.6	11.127	1 : 15	MA/TD	



**Figure 6** Oil swelling for (a) the OC/MA-PEG<sub>600</sub> copolymer in the paraffin condensate and (b) the OC/MA-PEG<sub>600</sub> copolymer in the paraffin crude oil with different polymer/PU ratios.

was determined from Tables III–VI. The best swelling ratios were obtained when the ratio of the foam to the crosslinked copolymers was 1 : 1, and they decreased when the weight percentage of the crosslinked copolymers increased to 1 : 15 wt %. This phenomenon can be explained as follows. The oil absorption of the composites was probably synergized by the supporter. Too much of the crosslinked copolymers probably stuffed many pores that existed in the sponge and gave a large specific surface area. In contrast, the crosslinked polymers in the pores may not have swelled freely.<sup>30</sup>

### Swelling kinetics of the synthesized crosslinked copolymers

The sorption and diffusion of organic solvents through crosslinked polymer networks have been subjects of great interest.<sup>31</sup> The sorption behavior gives an idea about the permeability and diffusion coefficients of a penetrant through polymers, which are used in various applications such as gel permeation chromatography, ion exchange, and the controlled release of drugs. Consequently, there is growing interest in the study of the kinetics of gel swelling. The swelling kinetics of the prepared crosslinked copolymers were determined according to ref. 32. The swelling rate can be described by the following experimental equation:

$$dQ/dT = K(Q_{\max} - Q) \quad (8)$$

where  $K$  is the swelling kinetic constant. The integration of eq. (9) gives

$$-\ln(Q_{\max} - Q) = Kt + C \quad (9)$$

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

For  $t = 0$ ,  $Q = 0$ , and  $-\ln Q_{\max} = C$ , we obtain

$$\ln[Q_{\max}/(Q_{\max} - Q)] = kt \quad (10)$$

For example,  $t$  is defined at

$$Q = 0.632Q_{\max} \quad (11)$$

According to Yao and Zhou,<sup>32</sup> the swelling kinetics of the investigated crosslinked MA/ $\alpha$ -olefin polymers were studied. The swelling parameters were determined from the swelling curves, which are not presented here for brevity. Tables III–VI show the equilibrium condensate content (ECC), the equilibrium oil content (EOC), the characteristic time required for the swelling ( $T$ ), the maximum swelling time ( $T_{\max}$ ) required to reach equilibrium, and the swelling kinetic constant ( $k$ ) for the prepared reactive crosslinked copolymers. The  $k$  values are also listed in Tables III–VI. The  $k$  values increased with the decreasing molecular weight of the crosslinker (EG and PEG) and with the increasing alkyl chain length of the  $\alpha$ -olefin monomers. This may have been due to the increase in the crosslinker (wt %), which stiffened the obtained crosslinker polymers; further small swelling was obtained because of the resulting low polymer–solvent interaction. The swelling kinetics may depend not only on the surfaces of the polymer but also on the elasticity of the polymer network. A more elastic network will provide larger absorption surfaces, which lead to higher swelling rates of the polymeric network, that is, large values of  $k$ . In other words, a polymer with a higher swelling rate may have a suitable structure for oil absorption. On the other hand, the  $k$  values increase with increasing alkyl chain length, that is, MA/TD copolymers > MA/OC copolymers. This can be attributed to the fact that the longest aliphatic side group increases the hydrophobicity that can be introduced into the copolymer and hence promotes the oil absorption capacity rate.

Regarding  $T_{\max}$  values in either an oil medium or a condensate (a condensate and a 10% diluted crude oil toluene solution), generally it is noticeable that as the ethyloxy chain length of the crosslinker increases,  $T_{\max}$  increases. This behavior may be due to the increase in the molecular weight of PEG, which leads to an increase in the hydrophilic nature of the polymer matrix.  $k$  decreases with the increasing molecular

weight of the PEG crosslinkers, as shown in Tables III–VI. This may be explained on the basis of the swelling mode, which indicates that the swelling process of the polymeric networks is primarily due to the oil solution penetrating 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 the oil and the polymeric networks hinders oil diffusion. Comparing the swelling rate constants of the gels swollen in 10% crude oil and those swollen in a condensate, we find that the former always shows higher values than the latter. This behavior can be easily explained on the basis of different viscosities of the 10% diluted crude oil with toluene and the condensate, which cannot easily diffuse from the surface of the gels into the internal space of the network.

### CONCLUSIONS

The conclusions of this work can be collected from the previous results in the following points:

1. Low conversions of linear copolymers from  $\alpha$ -olefins with MA in different molar ratios were prepared to detect the reactivity ratios.
2. Crosslinked copolymers were prepared by the reaction of the linear copolymers with EG and PEG having different molecular weights (600, 2000, and 6000) as crosslinker agents.
3. The prepared crosslinked copolymers exhibited a higher absorption capacity for crude oil than those obtained for the paraffin condensate.
4. The swelling capacity was increased as the type of  $\alpha$ -olefin changed.
5. The PU foam was used as a supporter for the crosslinked copolymers. The 1 : 1 ratio of the PU foam to the crosslinked copolymers exhibited the maximum oil absorption capacity.
6. The data indicate that the copolymers crosslinked with EG exhibited higher absorption effi-

ciency than those crosslinked with PEG. Meanwhile, low-molecular-weight PEG<sub>600</sub> exhibited higher absorption than PEG<sub>2000</sub> and PEG<sub>6000</sub>.

### References

1. Johnson, R. F.; Manjrekar, T. G.; Halligan, J. E. *Environ Sci Technol* 1973, 7, 439.
2. Blumer, M. In *Oil on the Sea*; Hoult, D. P., Ed.; Plenum: New York, 1969; p 6.
3. Morita, M.; Higuchi, M.; Sakata, I. *J Appl Polym Sci* 1987, 34, 1013.
4. Shimizu, T.; Koshiro, S.; Yamada, Y.; Tada, K. *J Appl Polym Sci* 1997, 65, 179.
5. Jang, J.; Kim, B. S. *J Appl Polym Sci* 2000, 77, 903.
6. Liu, Y.; Mao, R.; Huglin, M. B.; Holmes, P. A. *Polymer* 1996, 37, 1437.
7. Davis, S. C.; Hellens, W. V.; Zahalka, H. A. In *Polymeric Materials Encyclopedia*; Salamone, J. C., Ed.; CRC: New York, 1996; Vol. 4, p 2264.
8. Bertrand, P. A. *J Mater Res* 1993, 8, 1749.
9. Anthony, W. S. *Appl Eng Agric* 1994, 103, 357.
10. Atta, A. M.; Arndt, K. F. *J Appl Polym Sci* 2005, 97, 80.
11. Atta, A. M.; Rasha, A. M.; Farag, R. K.; El-Kafrawy, A. F.; Abdel-Azim, A. A. *Polym Int* 2005, 547, 1088.
12. Zhou, M. H.; Cho, W. J. *Polym Int* 2000, 49, 17.
13. Champ, S.; Xue, W.; Huglin, M. B. *Polymer* 2001, 42, 6439.
14. Sayil, C.; Okay, O. *Polymer* 2001, 42, 7637.
15. Saito, S.; Kanno, M.; Inomoto, H. *Adv Polym Sci* 1993, 109, 207.
16. El-Hamouly, S. H.; Al Sabagh, A. M.; Gabr, M. M.; Atta A. M. *J Appl Polym Sci*, submitted.
17. Leary, K. O.; Paul, D. R. *Polymer* 2004, 45, 6575.
18. Fineman, M.; Ross, S. *J Polym Sci* 1950, 52, 259.
19. Kelen, T.; Tudos, F. *J Macromol Sci Chem* 1975, 9, 1.
20. Georgiev, G. S. *J Macromol Sci Chem* 1978, 12, 1175.
21. Zhou, M. H.; Cho, W. J. *Polym Int* 2001, 50, 1193.
22. Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, New York, 1953; Chapter 13.
23. Kossmehl, T. M.; Abdel-Bary, E. M.; Sarhan, A. A.; Abdelaal, M. *Angew Makromol Chem* 1994, 215, 59.
24. Atta, A. M.; Arndt, K. F. *Polym Int* 2001, 50, 1360.
25. Kim, S.; Chung, I.; Ha, C.; Kim, K.; Cho, W. *J Appl Polym Sci* 1999, 73, 2349.
26. Jang, J.; Kim, B. S. *J Appl Polym Sci* 2000, 77, 914.
27. Vasenin, R. M. *Vysokomole* 1960, 2, 885.
28. Aitkin, A.; Barrer, R. *Trans Faraday Soc* 1955, 5, 116.
29. Flory, P. J.; Rehner, J. *J Chem Phys* 1943, 11, 512.
30. Zhou, M. H.; Hao, C. S.; Cho, W. J. *J Appl Polym Sci* 2001, 81, 1277.
31. Poh, B. T.; Adachi, K.; Kotaka, T. *Macromolecules* 1987, 20, 2563.
32. Yao, K. J.; Zhou, W. J. *J Appl Polym Sci* 1994, 53, 1533.