

Swelling and Network Parameters of High Oil-Absorptive Network Based on 1-Octene and Isodecyl Acrylate Copolymers

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ABSTRACT: Crosslinked 1-octene-isodecyl acrylate copolymers were synthesized and evaluated for oil-absorbency applications. The copolymer was crosslinked at different concentrations of ethylene glycol diacrylate (EGDA) and EG dimethacrylate (EGDMA) crosslinkers via catalytic initiation or by electron-beam irradiation at a dose rate 80 kGy. The concentration of both crosslinkers was varied from 0.5 to 2%. The effects of the crosslinking conditions such as crosslinker concentration, method of polymerization and monomer concentrations on the conversion and gel fraction were examined through oil-absorption tests using petroleum crude oil. It was found that the oil absorbency was influenced mainly by the degree of crosslinking and the

hydrophobicity of the copolymer units. The final equilibrium oil content, volume fraction of the polymer, and swelling capacity were determined at 298 K. The effective crosslinking density, average molecular weight between the crosslinks, and polymer-toluene interaction parameter were determined from stress-strain measurements. The crosslinking efficiencies of EGDA and EGDMA toward copolymers were determined. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 80–91, 2005

Key words: oil sorbers; copolymerization; acrylate crosslinker; chemical initiation; electronbeam irradiation; network parameters

INTRODUCTION

Crosslinked polymers are important in chemical research and practice, because of their wide range of applications. Water treatments, chromatographic techniques, biomedical and biochemical applications, solid-phase organic synthesis, enzyme immobilization, soil conditioning, solvent and ion separation, and oil sorbers use crosslinked polymers as the principal substrate. As environmental pollution from oil spills increases, oil absorbents have gained considerable interest.^{1–5} The base materials for oil absorbents are as follows: a fast oil absorption rate, high oil-absorption capacity, good absorption selectivity of oil over water, and lower density compared to water to float with or without oil absorbed.

Crosslinking is responsible for the 3-dimensional network structure that characterizes these materials. The elasticity and swelling properties are attributed to the presence of physical or chemical crosslinks within polymer chains. Various polymers have been widely used to absorb spilled oil on water. The existing oil

absorbents (polypropylene fiber, melt-blown polyesters, and polyurethane foam sheets) have unsatisfactory oil-absorbing capabilities. Among them, alkyl acrylate and aromatic polymers have been attracting much interest in the environmental field.^{6–14} Hydrophobic network polymers are used as absorbents of oil or some organic solvents spilled on water in this field. However, long-chain alkyl acrylate polymers have a tendency to be in a crystalline state. In this case, their oil-swelling properties are reduced. To control this undesirable effect, the copolymerization of alkyl acrylate monomers with another monomer is used to obtain amorphous copolymers. The aim of this work was to synthesize new oil-absorptive copolymers containing alkyl acrylate in the presence of different types of crosslinkers by chemical initiation or by the irradiation technique. In previous publications^{15,16} the copolymerization of acrylate monomers was carried out by electron-beam irradiation at different dose rates. Furthermore, the crosslinking of these polymers at a high dose of electron-beam irradiation in the presence of crosslinkers was studied. In the present investigation, the swelling properties of crosslinked 1-octene/isodecyl acrylate copolymers are measured in both toluene and petroleum crude oil. The influence of the synthetic variables of the crosslinked copolymers (monomer feed ratio, amount and types of crosslinking agents, and techniques of polymerization) on the oil-absorp-

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TABLE I
Physicochemical Properties of Tested Petroleum Crude Oil

Test	Method	Value
Specific gravity at 60°F	IP 160/87	0.875
API gravity	Calculated	21.7
Pour point (°C)	IP 15/67(86)	14
Kinematic viscosity (60°F, cs)	IP 71	762.8
Wax content (wt %)	UOP 46/64	2.45
Asphaltene content (wt %)	IP 143/84	8.8

tion capacity was examined for oil-absorbency applications. In this respect, the copolymerization of 1-octene and isodecyl acrylate in the presence of ethylene glycol diacrylate (EGDA) and EG dimethacrylate (EGDMA) as crosslinkers was achieved via radical initiation and by electron-beam irradiation. In addition, the influence of polymerization techniques and types of crosslinkers on the network parameters in toluene are another goal of the present study.

EXPERIMENTAL

1-Octene and isodecyl acrylate obtained from Aldrich (St. Louis, MO) were used as received. EGDA (Nakara Chemical Ltd.) and EGDMA (Aldrich) were used as crosslinkers without purification. Azobisisobutyronitrile (AIBN, Aldrich) was used as a radical initiator. Toluene (Aldrich) was used to measure the swelling capacities of the prepared gels. Petroleum crude oil was obtained from PETROBEL. Its physicochemical characteristics are given in Table I.

Methods

Synthesis of crosslinked copolymers via chemical initiation

The crosslinking of 1-octene with isodecyl acrylate was conducted by bulk polymerization in the presence of 0.02% AIBN initiator and different weight percentages of both EGDMA and EGDA crosslinkers ranging from 0 to 2%. Monomer ratios of 90/10, 70/30, 50/50, 30/70, and 10/90 (mol/mol %) were used to prepare crosslinked 1-octene/isodecyl acrylate copolymers. The copolymerization reactions were performed in siliconized test tubes at 333 K. The polymer rods were postcured at 378 K in an air oven for 24 h to ensure complete polymerization and to estimate the total conversion of monomers. The rods were cut to thin disks to determine the sol fraction (SF) and swelling parameters.

Purification of the linear copolymers (0 content of both EGDA and EGDMA crosslinkers) was carried out at the end of each reaction period by cooling the reaction mixture and precipitation from benzene solu-

tion into excess methanol with stirring, followed by filtration. Further purification was carried out and the solid products were dried at 40°C for 4 h.

Synthesis of crosslinked copolymers via electron-beam irradiation

Different monomer feed ratios of 1-octene and isodecyl acrylate were mixed in a flask with different weight ratios of EGDMA or EGDA ranging from 0 to 2%. The solutions were bubbled with nitrogen for 4 h. After that time the flask was filled with nitrogen and sealed. The solutions were subjected to electron-beam irradiation in Petri dishes covered with Parafilm®. The irradiation experiments were performed using a linear electron accelerator (ELV-2, Bruker Institute for Nuclear Physics, Novosibirsk, Russia) with an electron voltage of 1 MeV. An irradiation dose of 80 kGy was used to obtain crosslinked copolymers. The obtained gels were cut to thin cylindrical disks that were used to determine SF and swelling parameters.

Characterization of prepared polymers

The copolymerization of 1-octene/isodecyl acrylate monomers in the absence of crosslinker was characterized by ¹H-NMR analysis. The spectra were recorded on a 270-MHz spectrometer (Bruker W-P-270 SY). The chemical shifts (ppm) were reported downfield from 0 to 10 ppm using tetramethylsilane and CDCl₃ as the internal reference and solvent, respectively. Peak areas were determined by spectrometer integration.

The total conversion of monomers to crosslinked polymers was estimated using eq. (1):

$$\text{total conversion(\%)} = W \times 100/W_0 \quad (1)$$

where W and W_0 are the total weight of crosslinked polymers after postcuring at 378 K and the weight of monomers, respectively.

The probable SF percentage (SF %) in the crosslinked xerogel disks was extracted with toluene at 393 K. A preliminary test was performed to establish the required time for complete extraction. Based on this test, a 24-h extraction time was adapted for all samples. Detailed techniques of measuring as well as the equations used for calculating the SF are described in previous articles.^{15,16} The SF values are calculated according eq. (2):

$$\text{SF (\%)} = (W_0 - W) \times 100/W_0 \quad (2)$$

where W_0 and W are the weights of the disks before and after extraction, respectively.

The oil absorbency of the crosslinked polymers was determined by ASTM F726-81: 0.1 g of the polymer

was put in a stainless steel mesh with $4 \times 4 \times 2$ cm dimensions, which had been immersed in an oil solution (crude oil diluted with toluene, 10% oil). The sample and the mesh were picked up together from the oil, drained for 20 s, tapped with filter paper to remove excess oil from the bottom of the mesh, and then weighted on a balance. The oil absorbency (Q) was calculated by eq. (3):

$$Q = W/W_0 \quad (3)$$

where W and W_0 are the weights of the gels after and before oil absorption, respectively. To study the kinetics of oil absorption, the previous measurements were repeated from time to time using thin disks (0.2×11 mm). The test was allowed to stand for 4 days at constant temperature (298 K) to determine the maximum oil absorbency.

Stress–strain measurements

These measurements were conducted by uniaxial compression at 298 K for the swollen cylindrical disks (10×11 mm) while they were immersed in toluene. The stress–strain measurements were performed on the swollen disks after they attained their equilibrium toluene content (ETC) using an apparatus designed in our institute. The ETC values of the gels were calculated from the following relation:

$$\text{ETC} = (W - W_0) \times 100/W_0 \quad (4)$$

where W and W_0 are the weights of the gels after and before swelling in toluene, respectively. The swelling capacity in toluene (q_T) was calculated as described for oil. The polymer volume fraction (φ_p) was calculated from the reciprocal of the q_T values.

RESULTS AND DISCUSSION

The irradiation of acrylate and methacrylate monomers with electrons having energies between 120 and 300 kV leads to nearly instantaneous curing by the formation of radicals starting both the polymerization and crosslinking. However, apart from these two main reactions, electron-induced side reactions such as chain scission can occur simultaneously, leading to radiolytic degradation processes in the polymer network.¹⁷ Crosslinking and degradation of polymers are competing processes. They depend on the kinetic rate constants of both the crosslinking and degradation reactions. The rate constants are influenced in a complex manner by several factors such as the chemical structure of the polymer, the presence of sensitizing or desensitizing additives, and irradiation dose rates.¹⁸ In order to find the optimum irradiation conditions for achieving maximum conversion of the methacrylate

functionalities and avoid extensive radiolytic degradation, the dose dependence of the crosslinking process was studied. In our previous work,^{15,16,19} the effect of the dose rate of electron-beam irradiation on gelation of acrylate monomers was investigated. It was found that 80 kGy is the optimum dose rate of irradiation to obtain crosslinked acrylate polymers without chain scission degradation. In the present work, the copolymerization of 1-octene/isodecyl acrylate copolymers was carried out in the absence of EGDA and EGDMA crosslinkers. It was found that the copolymerization was completed to obtain linear polymers without gelation. The chemical structure of the obtained copolymers at a dose rate of 80 kGy was studied by ¹H-NMR analysis. The purified copolymers, obtained from radical polymerization of 1-octene and isodecyl acrylate monomers, were also subjected to ¹H-NMR analysis. In this respect, the spectra of 1-octene (50 mol %)/isodecyl acrylate (50 mol %) copolymers were selected as representative samples to study the effect of irradiation on copolymerization reactions. The ¹H-NMR spectra of 1-octene/isodecyl acrylate copolymers prepared by radical initiation and electron-beam irradiation are shown in Figure 1 (a, b). The disappearance of olefinic protons of both 1-octene/isodecyl acrylate monomers at δ 4.9–5.1 ppm (attributed to CH_2 —protons) 5.8–5.9 ppm (attributed to —CH protons of 1-octene), and 6.4 ppm (attributed to —CHC—O of isodecyl acrylate group) indicates the completion of the copolymerization of both 1-octene and isodecyl acrylate monomers. The disappearance of olefinic protons of two monomers through copolymerization via electron-beam irradiation indicates that the copolymerization was completed between monomers through their double bonds only without capture of other bonds. Figure 1 of the copolymer demonstrates the chemical shifts of the methyl protons of isodecyl and 1-octene groups as an intense signal at δ 0.87 ppm. The methylene protons of octene [$(\text{CH}_2)_6$] and isodecyl [$(\text{CH}_2)_6$] are recognized from the intense broad signals at δ 1.1–1.4 ppm. The comparatively downfield triplet in the δ 3.85–5.4 ppm region is assigned to the methylene protons bonded to the ester carbonyl of the acrylate monomer in the copolymer. The polymerization of 1-octene with isodecyl acrylate was evidenced by the appearance of multiplet signals at δ 2.05 ppm, which corresponds to CH_2 protons of the copolymer backbone. It is therefore quite obvious that both methods of copolymerization (radical initiation and electron-beam irradiation) produce the same copolymer structures and indicate that both monomers existed in the copolymer structure without any chain scission degradation by electron-beam irradiation at 80 kGy.

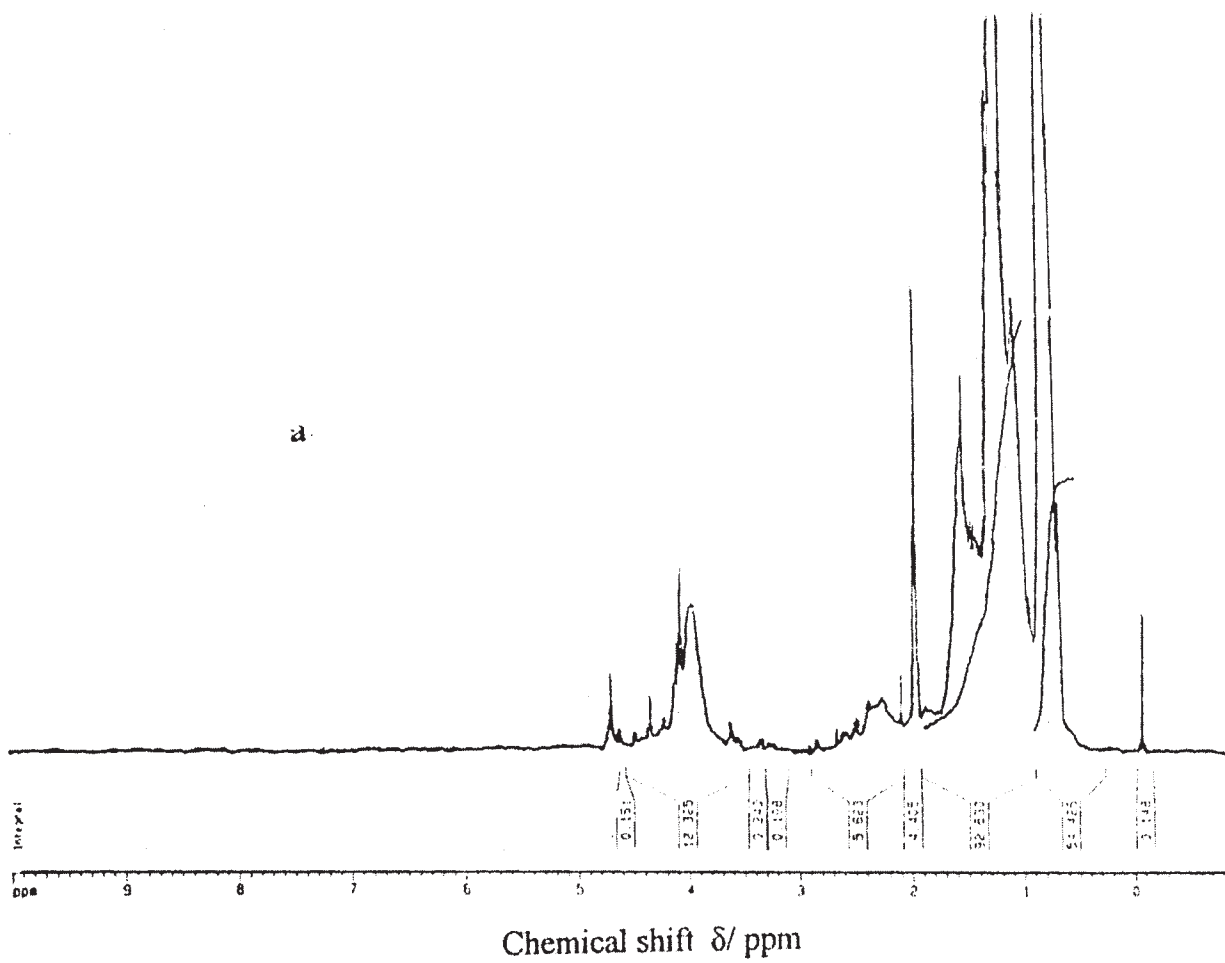
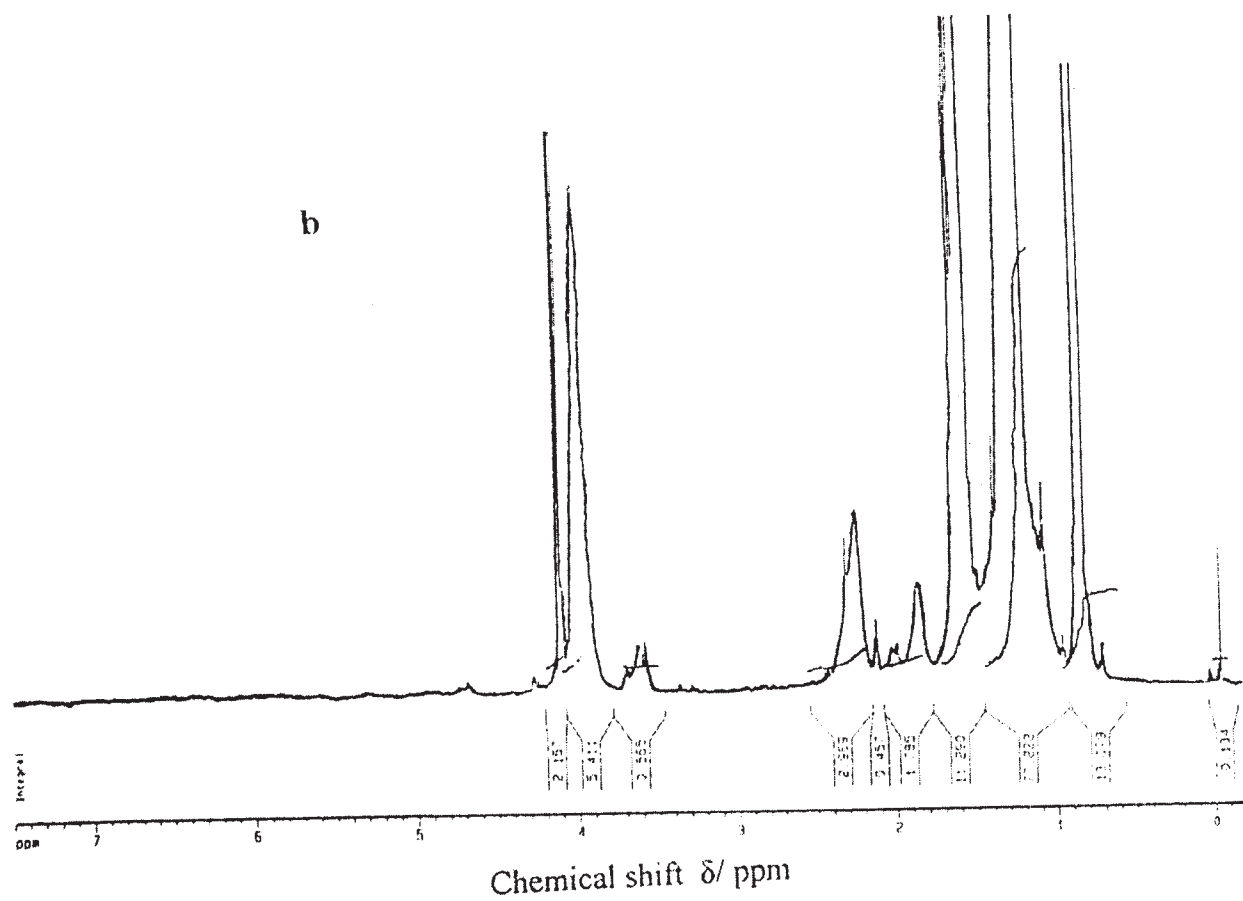


Figure 1 $^1\text{H-NMR}$ spectra of (a) 1-octene/isodecyl acrylate copolymers prepared in the presence of AIBN and (b) 1-octene/isodecyl acrylate copolymers prepared by electron-beam irradiation.

TABLE II
Conversion and SF values of Different Compositions of 1-Octene/Isodecyl Acrylate Copolymers Crosslinked with 1% EGDA or EGDMA Crosslinkers by AIBN Initiator or E-Beam Irradiation at 80-kGy Dose Rate

Xerogel comp. 1-octene/isodecyl acrylate	Crossl. (%)	SF of crossl. gels by chem. init.		SF of crossl. gels by e-beam irradiat.		Conversion (%) of crossl. gels by chem. init.		Conversion (%) of crossl. gels by e-beam irradiat.	
		EGDA	EGDMA	EGDA	EGDMA	EGDA	EGDMA	EGDA	EGDMA
90/10	1	30.2	27.6	19.1	16.3	93.25	94.23	95.12	96.1
	0					90.08	91.21	93.11	95.4
70/30	1	25.9	23.2	17.2	14.9	94.45	95.5	96.2	97.8
	0					92.02	93.12	95.4	97.2
50/50	1	21.3	19.3	15.3	13	95.1	96.9	98.95	99.4
	0					94.4	94.32	98.4	98.3
30/70	1	17.6	13.9	12.5	8.3	96.8	97.7	99.2	99.6
	0					96.2	96.1	99.12	99.1
10/90	1	3.4	10.7	8.0	5.1	98.3	98.8	99.5	99.8
	0					97.1	97.23	99.4	99.3

Crosslinked 1-octene/isodecyl acrylate copolymers

A wide variety of vinyl crosslinkers have been used to form crosslinked networks. The choice of the crosslinkers is quite broad in bulk and solution polymerization. Crosslinker concentrations of about 0.05–1% are usually used to provide superabsorbents with high swelling capacity and low soluble polymer content. The Flory–Stockmayer theory has been used to predict the gel network buildup of a crosslinking polymerization.^{20,21} Many side reactions, such as interchain cyclization, decrease the efficiency of the crosslinker. This can be significant at high crosslinker levels, such as used in styrene divinylbenzene copolymers where intramolecular cyclization is believed to occur. At very high levels of crosslinker and at high conversion, pendant vinyl groups were found to be less reactive and not utilized in forming the network. Local steric effects and lack of chain mobility were proposed for their lack of reactivity.²² Okay et al.²³ determined that almost half of the pendant double bonds in a mixture of EGDMA in methyl methacrylate (MMA) were consumed by internal cyclization reactions when the mole fraction of EGDMA 0.126–0.256 wt %. However, Landin and Macosko²⁴ showed that the rate of intramolecular cyclization was very low at low levels of EGDMA in MMA polymerization. In this respect, crosslinked 1-octene/isodecyl acrylate copolymers were obtained at low level of crosslinker contents of 0.5–2 wt %. Moreover, the crosslinking of these copolymers was completed in the presence of tetrafunctional crosslinkers such as EGDMA and EGDA to decrease the affinity to side reactions of cyclization that occurred when hexafunctional crosslinkers, such as trimethylolpropane-trimethacrylate, were used to prepare crosslinked copolymers.^{25–27} To understand the distribution of crosslinks in the network, the reactivity of the various double bonds in the system must be determined. This in-

cludes the reactions between double bonds of isodecyl acrylate and octene, the initial double bonds of the crosslinker, and the various double bonds that are pendant to the polymer chain after incorporation of the crosslinker. In the present work, the reactivity of crosslinkers toward isodecyl acrylate/octane copolymers were investigated from polymerization conversion (oven recovery) and SF measurements in toluene.

All the produced polymer rods and films prepared via chemical initiation and electron-beam irradiation were postcured at 378 K to ensure that no monomer residue was left in the xerogel. The data of total conversion (%) for copolymerization of 1-octene and isodecyl acrylate monomers in the presence and absence of crosslinkers were determined and are listed in Tables II and III.) The data show the variation of conversion (%) for all compositions of 1-octene and isodecyl acrylate monomers with and without 1% crosslinkers. It was found that the conversion increases as the amount of isodecyl acrylate increases with using AIBN and slightly increases as the amount of isodecyl acrylate increases using the irradiation technique. This indicates that the irradiation with electron-beam irradiation is useful to obtain 1-octene and isodecyl acrylate polymers. However, the incorporation of crosslinkers did not have a pronounced effect on conversion. The effect of the crosslinker concentrations on the SF values was estimated from the crosslinking of octene (50 mol %)/isodecyl acrylate (50 mol %) copolymer with different contents of EGDA and EGDMA (0.5–2 wt %). The effect of copolymer compositions on SF values was also evaluated from crosslinking of different compositions of 1-octene/isodecyl acrylate copolymers with 1 wt % EGDA or EGDMA crosslinkers. Moreover, the effect of the crosslinking technique on the SF values was studied from SF measurements of crosslinked 1-octene/isodecyl acrylate copolymers by radical initiation or electron-beam irradiation. In

TABLE III
Conversion and SF values of 1-Octene (50%)/Isodecyl (50%) Acrylate Copolymers Crosslinked with Various Concentrations of EGDA or EGDMA by AIBN Initiator or E-Beam Irradiation at 80-kGy Dose Rate

Crossl. content (wt %)	SF ^a		SF ^b		Conversion (%) ^a		Conversion (%) ^b	
	EGDA	EGDMA	EGDA	EGDMA	EGDA	EGDMA	EGDA	EGDMA
0	—	—	—	—	94.4	94.32	98.4	98.3
0.5	23.7	21.2	19.8	17	94.3	95.6	98.6	98.4
1	21.3	19.3	15.3	13	95.1	96.9	98.95	99.4
1.5	15.8	13.1	12.4	10.9	95.8	97.2	99.1	99.5
2	10.9	9.3	7.6	6.3	96.2	97.8	99.2	99.7

^a Xerogels crosslinked by AIBN.

^b Xerogels crosslinked by electron-beam irradiation at an 80-kGy dose rate.

this respect, the results obtained via Soxhlet extraction for the crosslinked copolymers with 1 wt % both EGDA and EGDMA via radical initiation or electron-beam irradiation techniques are given in Table II. The SF values for crosslinked 1-octene (50 mol %)/isodecyl acrylate (50 mol %) having different EGDA or EGDMA contents are listed in Table III. It is obvious that the percentage of SF for crosslinked copolymers is reduced when the crosslinker content increases from 0.5 to 2 wt %. This indicates that a low content of both EGDA and EGDMA crosslinkers is suitable for crosslinking of 1-octene and isodecyl acrylate copolymers. The reduction of the SF (%) with increasing contents of both EGDA and EGDMA crosslinkers suggests that the obtained networks contain either highly crosslinked copolymer or more of the linear copolymer chains are linked into the gel network. It was also observed that the crosslinked 1-octene/isodecyl acrylate copolymers with EGDMA have lower SF values than those determined for crosslinked copolymers with EGDA. This can be attributed to the differences in the reactivity ratios of both crosslinkers with the produced polymer.¹⁹ It was also observed that the SF values increase with decreasing isodecyl acrylate in the polymer composition. This can be referred to as the higher reactivity of isodecyl homopolymer toward vinyl crosslinkers than 1-octene/isodecyl acrylate copolymers. The effect of EGDMA on the crosslinking and the SF values of 1-octene/isodecyl acrylate copolymers contradicts the data based the basis of the reactivity of EGDMA with MA polymers.²⁸ It was found that the reactivity of EGDMA towards or acrylate groups may promote the reaction rate initially because of a crosslinking-facilitated gel effect but it may retard the diffusion of reactants and leave unreacted vinyl groups (trapped free monomers or pendants) within the system at the later stage. This behavior agrees with our data about high SF values of crosslinked copolymers with EGDA. It was also noted that the crosslinked copolymers prepared by electron-beam irradiation have lower SF values than copolymers prepared by thermal initiation. This is explained by the restriction of the expansion of the network structure

resulting from the increase of the crosslinking density.¹⁹ This can be also assigned more incorporation of 1-octene monomer in the crosslinked gels by irradiation than by thermal initiation.

Oil absorbency

According to Flory swelling theory,²⁰ swelling behavior is affected by three factors: rubber elasticity, affinity to the solution, and crosslinking density. In this respect, the swelling behavior of crosslinked gels with different amounts of EGDA and EGDMA crosslinkers was studied. Various copolymers were crosslinked with different amounts of EGDA and EGDMA crosslinkers (from 0.5 to 2% of the total monomers weight). In addition, different copolymer compositions based on 1-octene/isodecyl acrylate were crosslinked with 1% EGDA or EGDMA crosslinkers. The oil absorptivities of copolymer gels (having different 1-octene compositions) in 10% crude oil diluted with toluene are summarized in Table IV. The data of the swelling parameters of crosslinked octene (50 mol %)/isodecyl acrylate (50 mol %) copolymers crosslinked with different percentages of EGDA or EGDMA crosslinkers are listed in Table V. The data of the oil absorbencies of 1-octene (50 mol %)/isodecyl acrylate (50 mol %) crosslinked with different concentrations of EGDA by thermal initiation and electron-beam irradiation were correlated with the swelling time (selected as representative samples) and are represented in Figures 2 and 3. These figures show that the gels attain their maximum (Q) at different times ranging between 24 and 96 h, based on the percentage of EGDA crosslinker. It was observed that the gels having lower crosslinker content produce gels with higher oil absorbency with increasing immersion time. In addition, the highest oil absorbency was produced from the copolymers crosslinked via electron-beam irradiation and they attained maximum swelling capacities at low content of EGDA crosslinker after 4-h immersion in oil solution. This behavior can be related to the fact that the swelling increases when decreasing the crosslinking densities of networks.²⁹ However, the

TABLE IV
Swelling Parameters for Different Compositions of 1-Octene/Isodecyl Acrylate Copolymers
Crosslinked with 1% EGDA or EGDMA in Crude Oil and Toluene

Xerogel comp. 1-octene/isodecyl acrylate	Crossl. types	Swelling parameters ^a				Swelling parameters ^b			
		Q	ETC	q	Φ_p	Q	ETC	q	Φ_p
90/10	EGDA	25.60	95.05	20.2	0.049	35	96.85	31.7	0.032
	EGDMA	20.20	94.38	17.8	0.056	30	96.38	27.6	0.036
70/30	EGDA	35.20	96.63	29.7	0.034	48	97.54	40.6	0.025
	EGDMA	25.31	95.78	23.7	0.042	43	97.19	35.6	0.028
50/50	EGDA	40.41	97.20	35.7	0.028	55	97.94	48.6	0.021
	EGDMA	35.70	96.69	30.2	0.033	50	97.68	43.1	0.023
30/70	EGDA	55.1	97.94	48.6	0.021	68	98.38	61.7	0.016
	EGDMA	48.2	97.66	42.8	0.023	65	98.29	58.4	0.017
10/90	EGDA	67.7	98.42	63.2	0.016	85	98.74	79.3	0.012
	EGDMA	59.3	98.16	54.3	0.018	75	98.58	70.2	0.014

^a Xerogels crosslinked by AIBN.

^b Xerogels crosslinked by electron-beam irradiation at an 80-kGy dose rate.

oil-absorption rate for 1-octene/isodecyl acrylate copolymer crosslinked via thermal initiation has lower values than that crosslinked via electron-beam irradiation. This phenomenon can be referred to as high conversion of monomers and low SF values for copolymers crosslinked via electron-beam irradiation (Tables II, III). The data indicate that 1-octene monomer was introduced in the network structure via electron-beam irradiation. The high content of 1-octene or isodecyl acrylate in the copolymer network increases the oil uptake into the gel network. This result may be explained by the fact that the crosslinked gels produced via electron-beam irradiation are stiffer than those crosslinked with chemical initiation. The stiffer crosslinked polymers have small cavities. At the same time, the smaller cavities will provide larger absorption surfaces, which give higher swelling rates of the polymeric network.³⁰ It has been reported³¹ that excellent oil absorptivity of materials depends on the bulkiness and length of the alkyl constituents, especially the porosity of the microstructure, which can be

controlled by crosslinking techniques. The measured Q values listed in Tables IV and V indicate the high oil absorption of gels at high isodecyl acrylate content and lower contents of both EGDA and EGDMA crosslinkers. This can be attributed to the fact that isodecyl acrylate groups have long alkyl chains (more hydrophobic character), which is reflected in the high Q values. At the same time, high EGDA or EGDMA content forms a denser network of the copolymer and decreases the swelling ratio.

It is of interest to compare our swelling data with that obtained from crosslinked styrene-alkyl acrylate copolymers.^{6,7} These studies are based on crosslinking of 2-ethylhexyl-, lauryl-, and stearyl-acrylates/styrene copolymers to investigate their oil-swelling capacities. It was observed that the maximum swelling capacities in toluene are not increased more than 15 g/g, even at very low crosslinker contents. In the present investigation, the swelling capacities of the prepared copolymers in toluene are not below 20 g/g. Therefore, a highly oil-absorbing property can be obtained by con-

TABLE V
Swelling Parameters of 1-Octene (50%)/Isodecyl Acrylate (50%) Copolymers Crosslinked with Various
Concentrations of EGDA or EGDMA in Crude Oil and Toluene at 25°C

Crossl. concn.	Crossl. types	Swelling parameters ^a				Swelling parameters ^b			
		Q	ETC	q	Φ_p	Q	ETC	q	Φ_p
0.5	EGDA	56.1	97.95	48.7	0.021	66	98.28	58.3	0.017
	EGDMA	50.1	97.64	42.3	0.024	59	98.06	51.6	0.019
1	EGDA	40.4	97.20	35.7	0.028	55	97.94	48.6	0.021
	EGDMA	35.7	96.69	30.2	0.033	50	97.68	43.1	0.023
1.5	EGDA	38.7	96.69	30.2	0.033	48	97.54	40.7	0.025
	EGDMA	36.1	96.47	28.3	0.035	41	97.17	35.3	0.028
2	EGDA	33.4	96.11	25.7	0.035	40	97.16	35.2	0.028
	EGDMA	28.3	95.02	20.1	0.05	38	96.85	31.7	0.032

^a Xerogels crosslinked by AIBN.

^b Xerogels crosslinked by electron-beam irradiation at an 80-kGy dose rate.

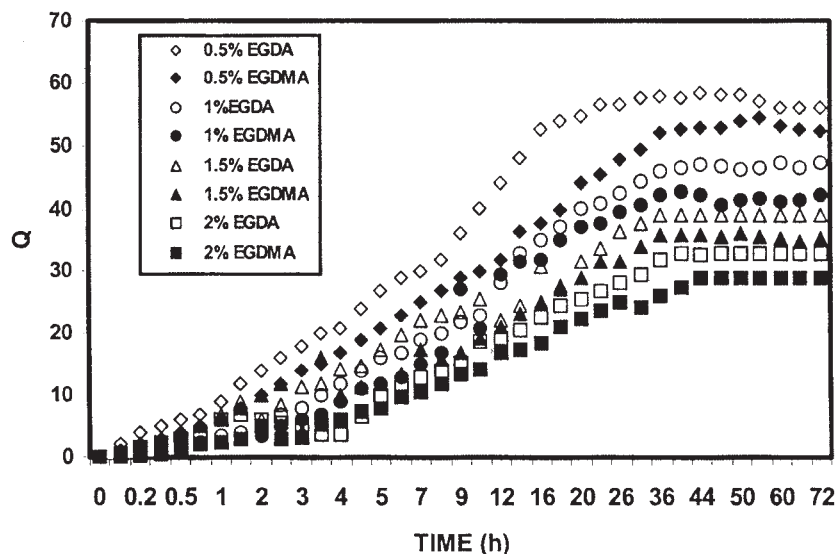


Figure 2 Oil-swelling curves of 1-octene (50 mol %)/isodecyl acrylate (50 mol %) copolymers crosslinked with different ratios of EGDA and EGDMA crosslinkers in the presence of AIBN at 298 K.

trolling the composition and crosslinking density of the copolymer. Thus, octene and isodecyl acrylate were chosen as hydrophobic monomers to prepare superior oil sorbers.

Network crosslink density

The swelling process of 1-octene/isodecyl acrylate xerogels was investigated in pure toluene. The toluene contents were calculated and are listed in Table IV. Toluene contents for 1-octene (50 mol %)/isodecyl acrylate (50 mol %) crosslinked with different contents of both EGDA and EGDMA crosslinkers are listed in

Table V. The data indicate that the same swelling behaviors of gel in diluted crude oil were observed in pure toluene. All organogel disks swelled at equilibrium in pure toluene were evaluated on the compression test as described in the Experimental section to determine the network parameters. The Young's moduli of elasticity (E) were obtained as the slopes of linear plots of stress (τ) versus strain ($\lambda - 1$), where λ is the ratio of the deformed length (L) of the hydrogel to its undeformed length (L_0). The relations between stress and strain for crosslinked 1-octene (50 mol %)/isodecyl acrylate (50 mol %) crosslinked with different ratios (0.5–2%) of EGDA and EGDMA crosslinkers

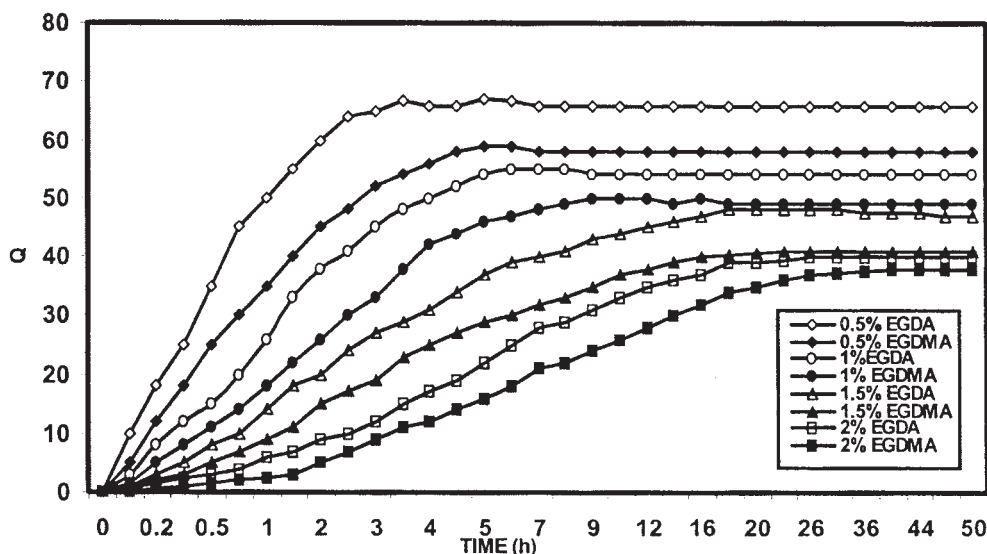


Figure 3 Oil swelling curves of 1-octene (50 mol %)/isodecyl acrylate (50 mol %) copolymers crosslinked with different ratios of EGDA and EGDMA crosslinkers by electron-beam irradiation at 298 K.

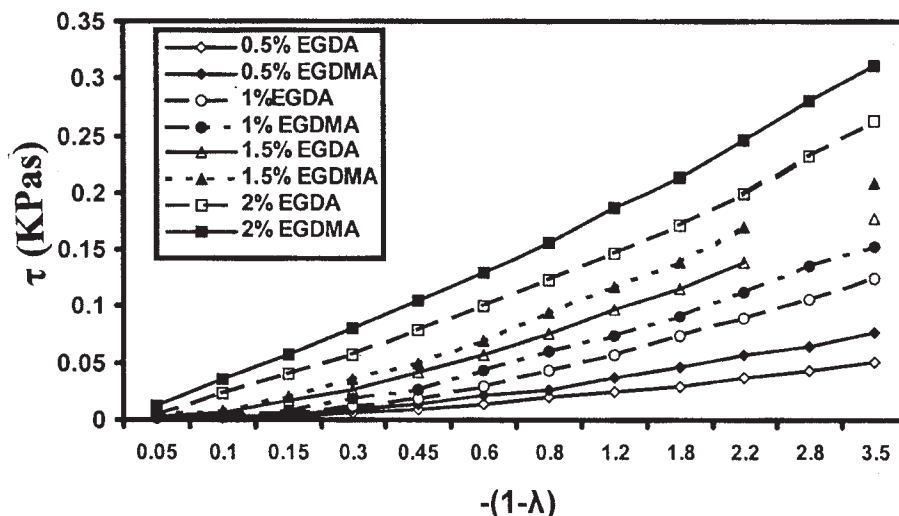


Figure 4 Plots of the stress–strain at 298 K for 1-octene (50 mol %)/isodecyl acrylate (50 mol %) copolymers crosslinked with different ratios of EGDA and EGDMA crosslinkers in the presence of AIBN.

were selected as representative samples to show the linear relation between stress and strain, and the results are plotted in Figures 4 and 5. The compression moduli of elasticity (G) was obtained by linear regression analysis of the slopes of τ versus $(\lambda - \lambda^{-2})$. The effective crosslinking density (V_e) can be calculated from eq. (5):

$$G = RTV_e\varphi_p^{-1/3} \quad (5)$$

where RT carries its normal meaning, which is $R = 8.14$ and $T = 298$ K.³² The volume fraction (φ_p) of copolymers in the swollen pellets were obtained from measurements conducted on their corresponding disks having measured diameters in the dry (d_0) and swollen (d) states at equilibrium in toluene via $\varphi_p = (d_0/d)^3$. The values of G , E , and V_e were determined and are listed in Tables VI and VII. The ratio of E/G was frequently found in all systems to be >3 .

It was also noted that the G , E , and V_e values show continuous increases with increasing concentrations of EGDA or EGDMA crosslinkers. In contrast, the produced gels have lower E and G values of <0.1 MPa. The lower the E values ($E = 0.002$ – 0.4 MPa) indicates that the prepared gels have an elastic network.³² This increases the interaction between toluene and the copolymer networks. Bestide et al.³³ showed that the presence of dangling chains or pendant chains in the polymeric network affected the compression moduli. They found that the moduli values decrease drastically when the proportion of pendant chains increases. The lower values of E , G , and V_e for crosslinked copolymers by electron-beam irradiation than that crosslinked by chemical initiators (Table VI) indicate the formation of dangling chains that were more increased by irradiation than chemical initiation. This can be proved from measuring polymer–solvent interaction parameter

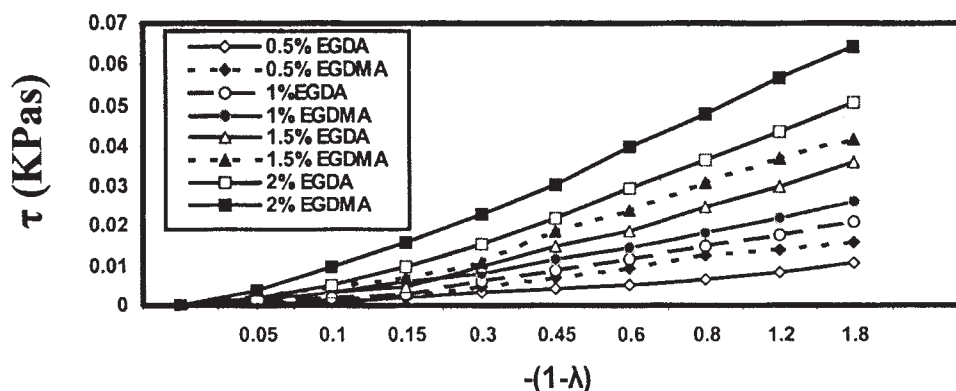


Figure 5 Plots of the stress–strain at 298 K for 1-octene (50 mol %)/isodecyl acrylate (50 mol %) copolymers crosslinked with different ratios of EGDA and EGDMA crosslinkers by electron-beam irradiation.

TABLE VI
Stress–Strain Measurements for Different Compositions of 1-Octene/Isodecyl Acrylate Copolymers Crosslinked with 1% EGDA or EGDMA by AIBN Initiator or E-Beam Irradiation at 80-kGy Dose Rate

Xerogel comp. 1-octene/isodecyl acrylate	Crossl. types	Network parameters ^a				Network parameters ^b			
		$E \times 10^3$ (MPa)	$G \times 10^3$ (MPa)	$V_e \times 10^3$ (mol/dm ³)	χ	$E \times 10^3$ (MPa)	$G \times 10^3$ (MPa)	$V_e \times 10^3$ (mol/dm ³)	χ
90/10	EGDA	10.01	3.28	5.3	0.532	6.04	1.87	3.3	0.487
	EGDMA	14.24	4.67	7.34	0.58	7.59	2.49	4.25	0.512
70/30	EGDA	13.61	4.29	6.4	0.492	10.29	3.34	5.45	0.451
	EGDMA	26.77	8.58	12.43	0.547	12.44	4.04	6.47	0.493
50/50	EGDA	40.95	13.41	18	0.432	19.75	6.31	9.42	0.413
	EGDMA	71.15	22.15	28.43	0.473	27.29	8.69	12.59	0.458
30/70	EGDA	81.74	25.19	31.7	0.412	32.52	10.49	14.78	0.408
	EGDMA	156.1	50.5	59.38	0.451	50.15	15.6	21.13	0.432
10/90	EGDA	249.3	78.4	88	0.401	63.71	19.38	25.73	0.392
	EGDMA	396.83	131.4	141.5	0.437	96.67	30.21	37.68	0.412

^a Xerogels crosslinked by AIBN.

^b Xerogels crosslinked by electron-beam irradiation at an 80-kGy dose rate.

(χ). On the basis of Flory–Rehner theory³⁴ χ is calculated from the following equation.

$$V_e = - \frac{\ln(1 - \varphi_p) + \varphi_p + \varphi_p^2 \chi}{[V_T(\varphi_p)^{1/3} - 2\varphi_p/F]} \quad (6)$$

where V_T is the molar volume of toluene (0.1067 dm³/mol at 298 K) and F is the functionality of crosslinkers, which equals 4. The values of χ were calculated for all copolymers and are listed in Tables VI and VII. The data for χ values for crosslinked copolymers by electron-beam irradiation show lower values than those determined for crosslinked copolymers by chemical initiation. The decreasing χ values indicate good interaction between the crosslinked copolymers with toluene. This indicates that electron-beam irradiation introduces hydrophobic groups to network at crosslinking.^{16–19}

The theoretical crosslink density (V_t) of xerogels is given by the following:³⁵

$$V_t = CF/2 \quad (7)$$

where C and F are the concentration and the functionality of the crosslinking agent, respectively. The value of C (mol dm⁻³) in each case was calculated on the basis of the molar mass of the crosslinker and the density of the xerogel (P_p). In this respect, the density was calculated from the volume of the tested sample (measured using a micrometer) and its weight according to the method described by Huglin and Zakaria.³⁶ The values of V_t and P_p were determined and are listed in Tables VIII and IX. The values of the molecular weight of the chain between crosslinks (M_C) can be calculated from eq. (8):

$$M_C = P_p/V_e \quad (8)$$

The determined values of M_C are listed in Tables VIII and IX with regard to the V_e , which frequently differs in magnitude from V_t . The dependence of V_e on V_t for

TABLE VII
Stress–Strain Measurements for 1-Octene (50%)/Isodecyl Acrylate (50%) Copolymers Crosslinked with Various Concentrations of EGDA or EGDMA Crosslinkers by AIBN Initiator or E-Beam Irradiation at 80-kGy Dose Rate

Crossl. content (wt %)	Crossl. types	Network parameters ^a				Network parameters ^b			
		$E \times 10^3$ (MPa)	$G \times 10^3$ (MPa)	$V_e \times 10^3$ (mol/dm ³)	χ	$E \times 10^3$ (MPa)	$G \times 10^3$ (MPa)	$V_e \times 10^3$ (mol/dm ³)	χ
0.5	EGDA	20.46	6.6	9.8	0.421	11.62	3.81	6.1	0.407
	EGDMA	30.13	9.72	13.88	0.462	15.70	5.06	7.8	0.417
1	EGDA	40.95	13.41	18	0.432	19.75	6.31	9.42	0.413
	EGDMA	71.15	22.15	28.43	0.473	27.29	8.69	12.59	0.458
1.5	EGDA	68.89	21.53	27.64	0.451	32.43	10.23	14.4	0.438
	EGDMA	84.13	26.29	33.1	0.481	45.98	14.37	19.48	0.467
2	EGDA	107.34	35.08	42.6	0.478	44.13	13.62	18.47	0.442
	EGDMA	233.47	74.83	83.65	0.492	60.77	18.75	24.85	0.473

^a Xerogels crosslinked by AIBN.

^b Xerogels crosslinked by electron-beam irradiation at an 80-kGy dose rate.

TABLE VIII
Network Parameters from Stress–Strain Measurements for Different Compositions of 1-Octene/Isodecyl Acrylate Copolymers Crosslinked with 1% EGDA or EGDMA by AIBN Initiator or E-Beam Irradiation at 80-kGy Dose Rate

Xerogel Comp. 1-octene/isodecyl acrylate	Crossl. types	Network parameters ^a			Network parameters ^b		
		$V_t \times 10^3$ (mol/dm ³)	$M_C \times 10^{-3}$ (g/mol)	P_p (kg/dm ³)	$V_t \times 10^3$ (mol/dm ³)	$M_C \times 10^{-3}$ (g/mol)	P_p (kg/dm ³)
90/10	EGDA	84	135.47	0.716	76	197.3	0.65
	EGDMA	74	99.13	0.728	76	176.7	0.751
70/30	EGDA	86	113.73	0.748	88	136.69	0.745
	EGDMA	94	74.75	0.929	82	125.66	0.813
50/50	EGDA	139	65.61	1.18	91	77.3	0.728
	EGDMA	117	40.91	1.16	85.6	71.42	0.899
30/70	EGDA	119	31.93	1.012	116	66.84	0.988
	EGDMA	117	19.48	1.165	106	49.69	1.05
10/90	EGDA	129	12.47	1.097	119	22.4	1.01
	EGDMA	120	8.38	1.186	111	12.4	1.1

^a Xerogels crosslinked by AIBN.

^b Xerogels crosslinked by electron-beam irradiation at an 80-kGy dose rate.

1-octene/isodecyl acrylate gels (not shown) is found to be linear. The linear dependencies of V_e and V_t for both crosslinkers (EGDA and EGDMA) were obtained by least square analysis. The linear interrelation between V_e and V_t follows eq. (9):

$$V_e = \alpha + \beta V_t \quad (9)$$

where α is the crosslinking coefficient at zero crosslinker content and β is the efficiency of the crosslinking coefficient. In this respect, α values for 1-octene (50 mol %)/isodecyl acrylate (50 mol %), crosslinked with different concentrations of EGDA and EGDMA by chemical or irradiation initiation, have very low values ranging from 0.0006 to 0.0008. It is well known that polyacrylates and their copolymers have a high tendency to crosslink under irradiation.^{26,37,38} Moreover, acrylic acid undergoes chain transfer and crosslinking when polymerized by irradiation.³⁸ Thus, 1-octene deactivates the

crosslinking efficiency of isodecyl acrylate in the absence of crosslinkers when electron beams were used for irradiation. This can also be referred to as the increasing probability of crosslinking in a bulk system that is due to an 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.³⁵ It was also observed that the β values for crosslinking of 1-octene/isodecyl acrylate by EGDA and EGDMA crosslinkers via chemical initiation and electron-beam irradiation are 0.2954, 0.5235, 0.1054, and 0.14, respectively. This finding reveals that EGDMA is more efficient than EGDA for crosslinking of 1-octene/isodecyl copolymers. This conclusion is supported by the data of M_C for the crosslinked copolymer by both crosslinkers. Ta-

TABLE IX
Network Parameters from Stress–Strain Measurements for 1-Octene (50%)/Isodecyl Acrylate (50%) Copolymers Crosslinked with Various Concentrations of EGDA or EGDMA Crosslinker by AIBN Initiator or E-Beam Irradiation at 80-kGy Dose Rate

Crossl. content (wt %)	Crossl. types	Network parameters ^a			Network parameters ^b		
		$V_t \times 10^3$ (mol/dm ³)	$M_C \times 10^{-3}$ (g/mol)	P_p (kg/dm ³)	$V_t \times 10^3$ (mol/dm ³)	$M_C \times 10^{-3}$ (g/mol)	P_p (kg/dm ³)
0.5	EGDA	71	122.4	1.199	49	136.23	0.831
	EGDMA	60	84.89	1.18	49	123.4	0.963
1	EGDA	139	65.61	1.18	91	77.3	0.728
	EGDMA	117	40.91	1.16	85.6	71.42	0.899
1.5	EGDA	142	29.13	0.805	127	50.1	0.721
	EGDMA	128	25.52	0.842	135	45.69	0.891
2	EGDA	188	18.74	0.789	169	38.64	0.714
	EGDMA	196	11.75	0.982	177	35.61	0.885

^a Xerogels crosslinked by AIBN.

^b Xerogels crosslinked by electron-beam irradiation at an 80-kGy dose rate.

bles VIII and IX show that M_C values of EGDMA networks are always smaller than the corresponding values when EGDA is used as the crosslinking agent, because M_C is used to determine the distance between two successive crosslinks. The smaller value indicates higher crosslinking density networks. As the crosslinking density increases, the oil-sorber capacities are reduced (see Table V). It was also observed that the β values are less than unity, which is due to the fact that toluene is a better swelling agent for this system. This is because β is a measure not only of chemical crosslinking but also of physical interactions between the chains when the values are greater than unity.³⁹ It is of interest to observe that the crosslinked copolymers by electron-beam irradiation at an 80-kGy dose rate have lower β values than those crosslinked by chemical initiator.

CONCLUSIONS

The conclusions of this work can be selected from the previous results and discussions arranged in the following points:

- Initiation by electron-beam irradiation at an 80-kGy dose rate is a convenient method for performing high conversion bulk polymerization and crosslinking of 1-octene/isodecyl acrylate with EGDA and EGDMA.
- Crosslinked 1-octene/isodecyl acrylate copolymers have low SF values when prepared by electron-beam irradiation.
- Irradiation of copolymers in the presence of EGDA or EGDMA crosslinkers by electron beams at an 80-kGy dose rate gives crosslinked polymers with high oil absorbency that is due to the formation of small cavities at the surface of the crosslinked polymers.
- The oil-swelling capacities of the crosslinked copolymers were increased by decreasing crosslinker and 1-octene contents.
- Compression measurements indicate the formation of dangling chains when 1-octene/isodecyl acrylate copolymers are crosslinked under the influence of electron-beam irradiation at a dose rate of 80 kGy.
- The data of M_C for the crosslinked copolymer by both EGDA and EGDMA crosslinkers is in the order EGDMA > EGDA.

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