

Preparation of Ethylene Copolymers Containing Pendant Unsaturation for Radiation Crosslinking

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SYNOPSIS

The work presented here suggests that the radiation crosslinking of particular ethylene copolymers can markedly be enhanced by introduction of pendant radiation-sensitive functional groups and that reactive melt processing offers an attractive alternative to introduce the pendant groups. *m*-Isopropenyl- α,α -dimethylbenzyl isocyanate was found to react in high yields (> 80%) during a few minutes of reactive mixing with an ethylene hydroxyethyl methacrylate copolymer, and no residual monomers were found in the polymer after 10 min of mixing. Copolymers that contained from 0.1 to 1.2 mol % of pendant unsaturation were prepared. The functionalized copolymer, which contained 1.2 mol % of pendant unsaturation, formed 90% gel after having received a radiation dose of 100 kGy. The corresponding value for the unfunctionalized copolymer was 25% gel. Furthermore, ethylene copolymers containing 0.3–1.4 mol % of acrylate or 0.1–0.4 mol % of methacrylate side groups were prepared by mixing an ethylene vinyl alcohol copolymer with acrylic acid or by mixing an ethylene acrylic acid copolymer with glycidyl methacrylate. Although the conversion of these esterification reactions was low, the amount of incorporated pendant unsaturation was sufficient to crosslink the polymers to high gel contents (> 80%) already at a radiation dose of 10 kGy. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

In 1952 Charlesby¹ investigated polymer radiation chemistry and showed that irradiation could change polyethylene into a crosslinked and insoluble material. A number of papers and reviews^{2,3} followed after this, describing the effects of radiation on different kinds of polymers. Still there is a worldwide interest in radiation-induced modifications of polymers.^{4,5}

The radiation crosslinking of polymers, and in particular polyethylene, is today a rather well-understood phenomenon that proceeds through the recombination of macroradicals.⁶ On the other hand, the radiation crosslinking of polymers in the presence of polyfunctional monomers^{7–9} has gained a great deal of interest because these monomers can act as crosslinking promoters and allow crosslinking

to be brought about at reduced doses compared to those normally required. The monomers are thought to react with free radicals on polyethylene chains, thus forming a three-dimensional crosslinked network. However, up to this date there are no spectroscopic data available showing the existence of this covalent coupling. Thus the preparation of polymers that can be transformed into dense and crosslinked networks at low irradiation doses are still of interest.

Acrylates and other unsaturated compounds readily polymerize at low irradiation doses.¹⁰ The introduction of pendant unsaturated functional groups to polymers would therefore result in highly radiation-sensitive polymers that could easily be crosslinked upon irradiation. A few studies have been reported with an interest in introducing side groups of the general formula $\text{CH}=\text{CR}-\text{COO}-$ ($\text{R}=\text{H}$ or CH_3) to ethylene copolymers.^{11,12} A thermoplastic resin having a dispersed rubber phase and good impact strength, weather, and ozone resistance was prepared by copolymerizing vinyl or vinylidene monomers (such as styrene, α -methyl styrene) in

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the presence of a functionalized ethylene vinyl acetate copolymer having methacrylate $[\text{CH}=\text{C}(\text{CH}_3)-\text{COO}-]$ side groups to activate the polymer for graft copolymerization with the vinyl or vinylidene monomers.¹¹ No efforts to cure the material with ionizing radiation were done.

Pastes, cliches, and photoresists that can be photopolymerized were prepared by reacting glycidyl methacrylate to an ethylene copolymer containing acrylic acid and *n*-butyl acrylate or 2-ethylhexyl acrylate as constitutional repeating units. 2-Dimethylaminopyridin or *n*-methyl-imidazole were suggested as suitable catalysts for the esterification. The esterification reaction was carried out either by dissolving the polymer in a suitable solvent and adding the monomer and the catalyst or by a reactive processing in a mixer or a twin-screw extruder.¹²

Reactive melt processing offers unique opportunities to incorporate new side groups to polymers by *in situ* chemical reactions.^{13,14} A polymer processing equipment may be considered as a chemical reactor, although one major distinction is apparent. The time of reaction is generally limited during polymer processing, particularly during a continuous mixing in an extruder. Furthermore, it is necessary to eliminate by-products, particularly true for say a reversible esterification reaction.

In this work we report the radiation crosslinking of functionalized ethylene copolymers that contain pendant unsaturation. These polymers are prepared by *in situ* reaction of radiation-sensitive monomers and ethylene copolymers in a laboratory-scale internal mixer as a reactor. Regarding the functionalization reactions chosen in this study, the esterification between an epoxide and a carboxylic acid and the reaction between an alcohol and an isocyanate are virtually irreversible and the direct esterification of an alcohol and a carboxylic acid is reversible producing water as a by-product. One objective of this study was, therefore, to determine which reaction is most suitable for reactive processing, i.e., which one has the highest conversion and the highest rate of reaction. Another objective was to assess the degree of crosslinking as a function of irradiation dose for the functionalized polymers.

EXPERIMENTAL

Materials

Three different copolymers were used in this study. An ethylene acrylic acid copolymer (EAA) containing 3 wt % acrylic acid was used as received from

Dow Chemical Co. (Primacor 3150) and an ethylene hydroxyethyl methacrylate copolymer (EHEMA) containing 10 wt % hydroxyethyl methacrylate was used as received from NESTE Chemicals (NTR-354). An ethylene vinyl alcohol copolymer (EVOH) containing 16 wt % vinyl alcohol was purchased from Bayer (Levasint S-31) and used as received.

Glycidyl methacrylate (GMA) and acrylic acid (AA) were purchased from Aldrich, and *m*-isopropenyl- α,α -di-methylbenzyl isocyanate (TMI) was received from American Cyanamid. All monomers were used without any further purification.

Tributylamin (TBA, Merck) was used as catalyst during esterification of the ethylene acrylic acid copolymer.

A calibration curve from the mixture of 2-ethylhexyl acrylate (2-EHA, Fluka) and polyethylene (NCPE-7518, Neste Chemicals) was used for quantitative FTIR measurements.

Sample Preparation

The esterification of EAA with GMA was carried out by reactive mixing in a Haake Buchler 50-cm³ mixer at 150 and 200°C at 60 rpm. The polymer was allowed to melt for 1 min before a stoichiometric amount of GMA was added to the mixer. The conversion of the reaction was followed as a function of time, and the effect of catalyst was evaluated by addition of 10 mol % of TBA to the melted polymer before addition of GMA.

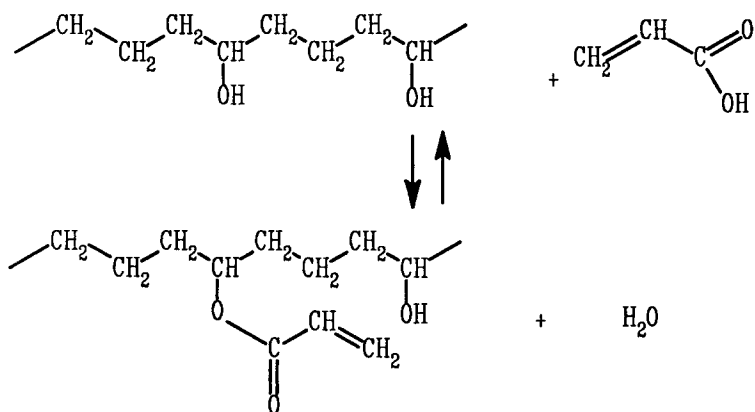
The functionalization of EHEMA with TMI was carried out by mixing EHEMA with various amounts of TMI (0.9, 1.9, and 7.2 wt %) as described earlier. The reaction, however, was carried out at 180 and 200°C and the conversion of the reaction was determined as a function of time.

EVOH was esterified with a stoichiometric amount of AA in a mixer as described above and the esterifications were carried out at 190°C and 50 rpm, and the time of the esterifications varied from 5 to 20 min.

The functionalized polymers were compression molded to approximately 150- μm thin films at 120°C. The films of the esterified EAA and EVOH samples were further placed in a vacuum oven at 50°C for 12 h to remove residual monomers.

Irradiation

The polymer films were irradiated using an Electrocurtain[®] electron accelerator (Energy Sciences Inc.). Irradiation was carried out under nitrogen at-



Scheme 1

mosphere ($< 300 \text{ ppm O}_2$) at an acceleration voltage of 175 kV.

Analysis

The conversion of the reactions were determined by acquiring Fourier-transformed infrared spectra on a Perkin-Elmer 1710 spectrometer. A Lab Calc™ (Galactic Industries Corp.) program was used to resolve overlapping peaks and to calculate peak areas.

The amount of esterified acrylic acid repeating units of esterified EAA was determined both by titration of unreacted acrylic acid repeating units and by FTIR. The titration was done according to ASTM D-4094.

The degree of crosslinking was determined according to ASTM D-2765. However, divergent from the standard method, the time of extraction was extended to 24 h and no antioxidant was added to the solution.

RESULTS AND DISCUSSION

Functionalization of EVOH with AA (EVOH-AA)

The esterification of EVOH with AA is a reversible reaction that follows the general reaction (Scheme 1). To achieve a high yield of ester groups, the reaction should be displaced toward the product side

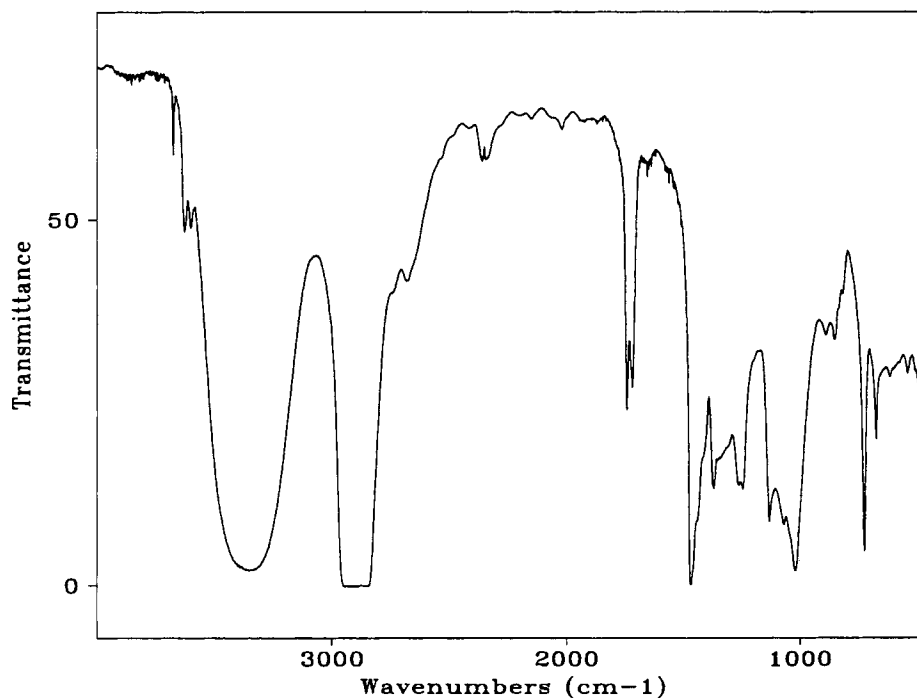


Figure 1 FTIR spectrum of EVOH.

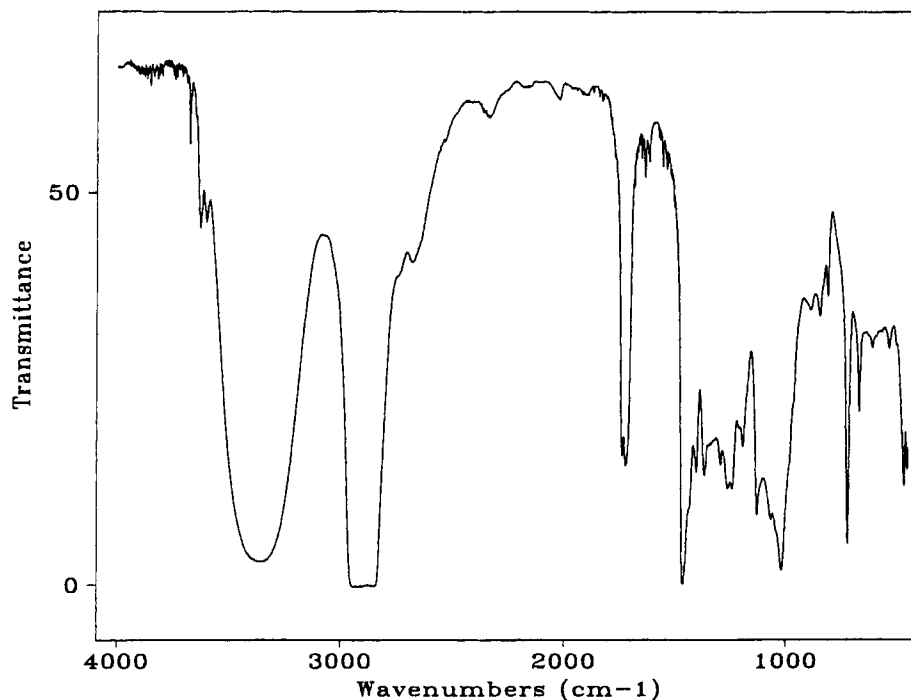


Figure 2 FTIR spectrum of EVOH-AA functionalized with AA for 20 min at 190°C.

by removal of water or by use of an excess of one of the reactants. However, in practice, it is difficult to remove water during melt processing at 190°C without losing large amounts of AA at the same time, and the use of a large excess of AA causes practical problems.

The yield of pendant acrylate groups of functionalized EVOH may be determined by comparing FTIR spectra of EVOH-AA at different times of esterification to the FTIR spectrum of EVOH presented in Figure 1. The characteristic band observed in the spectrum of EVOH is the broad band in the 3000–3500 cm^{-1} region that results from the O—H stretching of hydrogen-bonded hydroxyl groups. A small amount of unhydrolyzed vinyl acetate repeating units are present in EVOH, since the spectrum shows absorption at 1717 and 1740 cm^{-1} , originating from the carbonyl group.

In addition to the bands found for EVOH the spectrum of EVOH mixed with acrylic acid for 20 min (Fig. 2) reveals four new bands at 1400, 1200, 1100, and 940 cm^{-1} and a broadening of the absorption band in the region 1700–1780 cm^{-1} . A curve fit analysis of this region [Fig. 3(a)] reveals that the band consists of three different bands; a band at 1725 cm^{-1} that corresponds to the C=O stretching vibration of the pendant acrylate group and the two absorption bands of unhydrolyzed vinyl acetate repeating units.

Since the absorption at 1725 cm^{-1} is due to the ester group formed during functionalization of EVOH with AA, the absorption can be utilized to calculate the amount of the incorporated pendant acrylate groups. A quantitative determination is possible by using the calibration curve in Figure 4. This calibration curve was obtained by acquiring FTIR spectra of films of polyethylene containing known amounts of 2-ethylhexyl acrylate and plotting the peak area of 1731 cm^{-1} divided with the film sample thickness as a function of the amount of 2-ethylhexyl acrylate. The linear function representing the calibration curve was found to be $Y = 10.2 \times X$.

The amounts of pendant acrylate groups formed when EVOH is mixed with AA for various lengths of time, as determined from the calibration curve, are presented in Table I. The peak area at 1725 cm^{-1} was obtained by subtracting the sum of the peak area at 1717 and 1740 cm^{-1} , derived from the FTIR spectrum of EVOH [Fig. 3(b)], from the sum of the areas of the peaks at 1717, 1725, and 1740 cm^{-1} of the esterified samples. All peak area values were divided with the sample thickness to correct for differences in thickness.

The values given in Table I are the amount of pendant acrylate groups incorporated, during the esterification of 40 g of EVOH with a stoichiometric amount of AA. The functionalized EVOH will have three constitutional repeating units with the molar

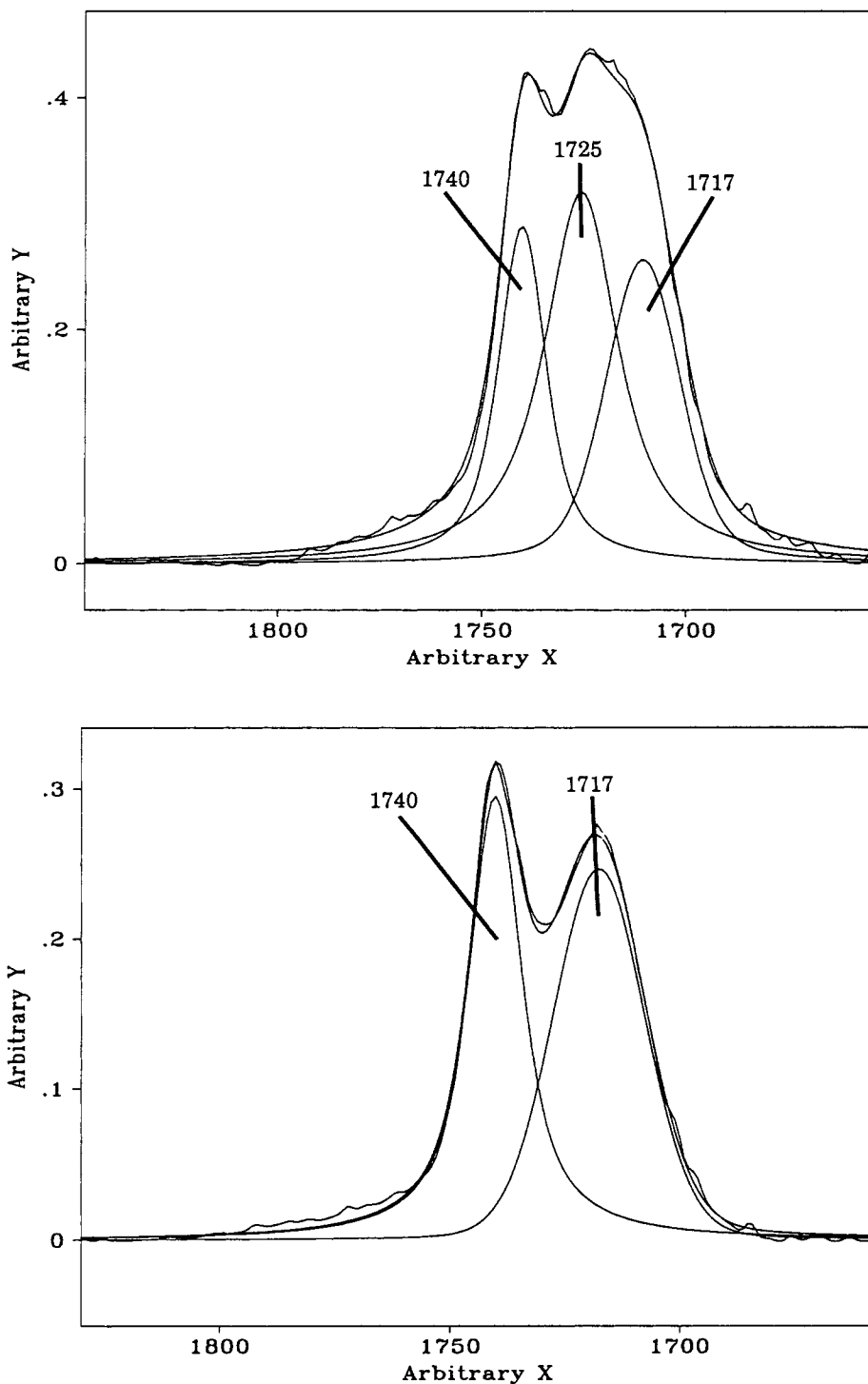


Figure 3 (a) FTIR spectrum of EVOH-AA functionalized with AA for 20 min at 190°C. Curve fit analysis of the region 1650–1800 cm^{-1} . (b) FTIR spectrum of EVOH. Curve fit analysis of the region 1650–1800 cm^{-1} .

masses of 28, 44, and 98 g/mol, the latter molar mass representing the molar mass of the repeating unit containing the pendant unsaturation. Thus, the

amounts of comonomers, expressed in grams, can be calculated with the value obtained from the calibration curve.

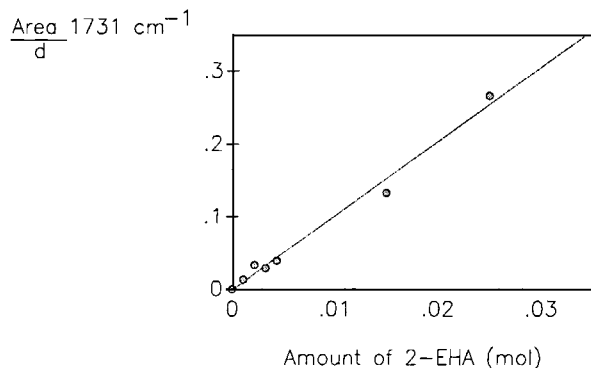


Figure 4 Calibration curve with 2-ethylhexyl acrylate mixed with polyethylene.

Furthermore, the weight of the polymer sample will increase due to the esterification. The increase, Δw , is given by

$$\Delta w = \text{amount of ester groups (mol)} \times (M_{AA} - M_{H_2O})$$

where M_{AA} = molar mass of acrylic acid and M_{H_2O} = molar mass of water, and since the final sample weight is given by $40 \text{ g} + \Delta w$, the values derived above allows the calculation of the composition of the functionalized EVOH. By varying the time of esterification from 1 to 20 min, polymers with different amounts of pendant acrylate groups, ranging from 0.8 to 4.6 wt %, can be prepared. However, the conversion of the reaction is low ($\sim 13\%$) even at prolonged reaction times.

Functionalization of EAA with GMA (EAA-GMA)

In principle, EAA-GMA can be prepared by reacting a stoichiometric amount of GMA to EAA. The general course of the reaction is illustrated by Scheme 2a. The addition reaction is exothermic and the ring-

opening reaction is preferably catalyzed by addition of bases, which increases the rate of the reaction by increasing the concentration of carboxylate ions (Scheme 2b).^{15,16}

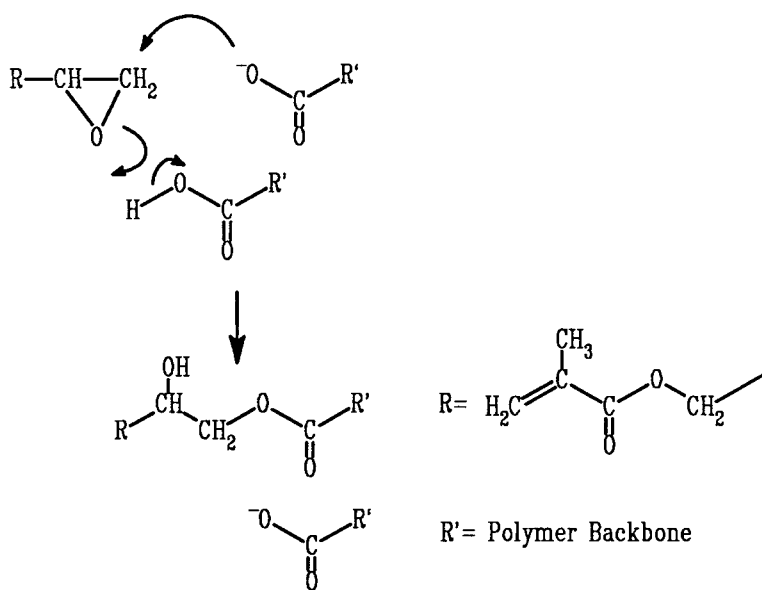
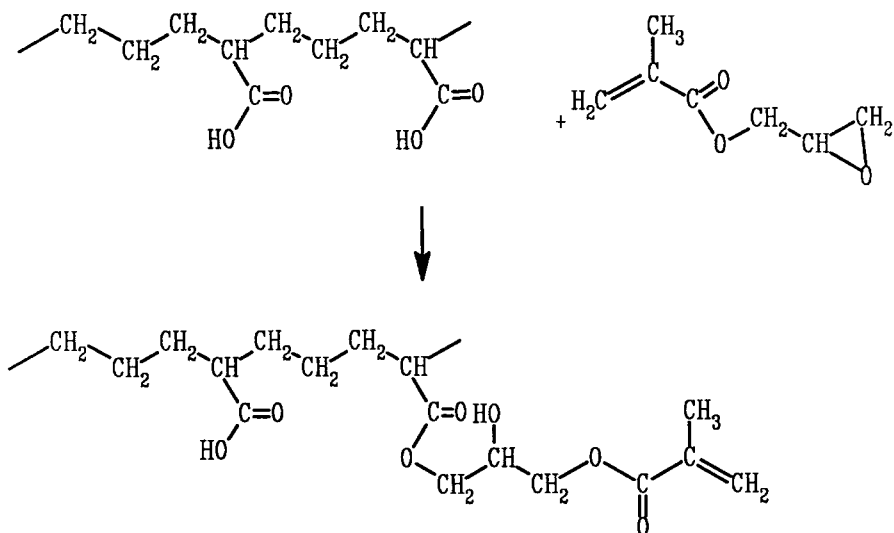
Both FTIR measurements and titration of unreacted acrylic acid repeating units were used to determine the conversion of the functionalization reaction of EAA with GMA, and it is obvious from Table II that determination of the conversion by titration results in higher values than values determined by FTIR. However, the titration procedure includes dissolution of the sample in a hot solution of xylene and *n*-butanol and titrating while the sample solution is still hot. This procedure allows further esterification to continue during the determination. Since the sample preparation for FTIR measurements involves only a short heat treatment during the compression molding of the polymer into films, one may conclude that the true conversion values are derived from the FTIR measurements.

Four different FTIR spectra, which represent the functionalization at different reaction times, are compiled and shown in Figure 5. There are seven abundant peaks that originates from the EAA-GMA, but the new broad absorption at $3200\text{--}3500 \text{ cm}^{-1}$ and the new peak centered at 1727 cm^{-1} represents the best bands to characterize the esterification reaction. The former absorption results from the O—H stretching of hydrogen-bonded hydroxyl groups, which are formed during the ring-opening of the epoxy group (Scheme 2), while a curve fit analysis of the latter absorption band reveals that there are three overlapping peaks present (Fig. 6). The peak centered at 1705 cm^{-1} originates from the carboxylic acid group of unreacted acrylic acid repeating units, while the peak centered at 1727 cm^{-1} originates from the carbonyl group conjugated with the double bond of the methacrylate group, and the absorption at 1742 cm^{-1} is due to the ester group formed during reaction of GMA and EAA. The

Table I Conversion and Amount of Pendant Acrylate Groups of EVOH-AA at Different Esterification Times

Time (min)	Area/d	Amount of Pendant Acrylate Groups				Conversion (%)
		mmol ^a	g	Wt %	Mol %	
5	0.036	3.5	0.3	0.8	0.3	2.4
10	0.139	13.6	1.3	3.2	1.0	9.4
15	0.149	14.6	1.4	3.4	1.1	10.0
20	0.193	18.9	1.9	4.6	1.4	13.0

^a Derived from the calibration curve.



functionalization will lead to a decrease in the amount of free carboxylic acid groups of EAA, and a quantitative determination of the conversion of the reaction as a function of time can therefore be determined by calculating the ratio of the area of the peak at 1705 cm^{-1} and the area of the reference peaks at 721 and 730 cm^{-1} (the $(\text{CH}_2)_n$ rocking band). This value, determined at different times of esterification, is in turn compared to the ratio value derived from the FTIR spectrum of EAA to obtain the conversion value.

At 150°C the conversion of the reaction is low (10%), and no significant improvements are achieved by prolonged mixing time (see Table II).

At 200°C the reaction is faster and 26% of GMA is converted to ester after 15 min. On the other hand, the same conversion is achieved by adding TBA as catalyst at 150°C , while adding the same catalyst at 200°C increases the conversion to 33% after 15 min.

The composition of the functionalized EAA can be calculated from the conversion values in Table II. For example, when 40 g of EAA is mixed with a stoichiometric amount of GMA at 150°C for 10 min in the presence of 10 mol % TBA, 28%, i.e., 0.34 g (4.7 mmol), of the acrylic acid repeating units were converted to ester. The functionalization will result in a polymer (Scheme 2) with three constitutional repeating units with the molar masses 28, 72, and

Table II Conversion of Functionalization Reaction of EAA With GMA at Different Reaction Times and Conditions

Sample	Temp. (°C)	Time (min)	Catalyst ^a	Conv. ^b (%)	Conv. ^c (%)
EAA-GMA 1	150	3		9.3	7.1
		6		10.7	10.3
		10		11.3	11.0
		15		14.7	11.3
EAA-GMA 2	150	3	X	19.0	18.0
		6	X	42.6	22.3
		10	X	52.7	27.5
		15	X	53.0	32.2
EAA-GMA 3	200	3		10.7	11.5
		6		26.3	15.8
		10		40.3	23.0
		15		57.7	25.9
EAA-GMA 4	200	3	X	18.7	19.1
		6	X	41.3	27.0
		10	X	50.3	30.2
		15	X	65.0	33.4

^a 10 mol % tributyl amine used as catalyst, when marked with X.

^b Determined by titration of unreacted acrylic acid repeating units.

^c Determined from FTIR data.

214 g/mol. The latter molar mass is the molar mass of the repeating unit containing the pendant unsaturation and consequently the amount of this mono-

mer is 1.0 g ($0.0047 \text{ mol} \times 214 \text{ g/mol}$). The final sample will thus have the following composition: 0.9 g AA, 1.0 g GMA, and 38.8 g polyethylene (PE).

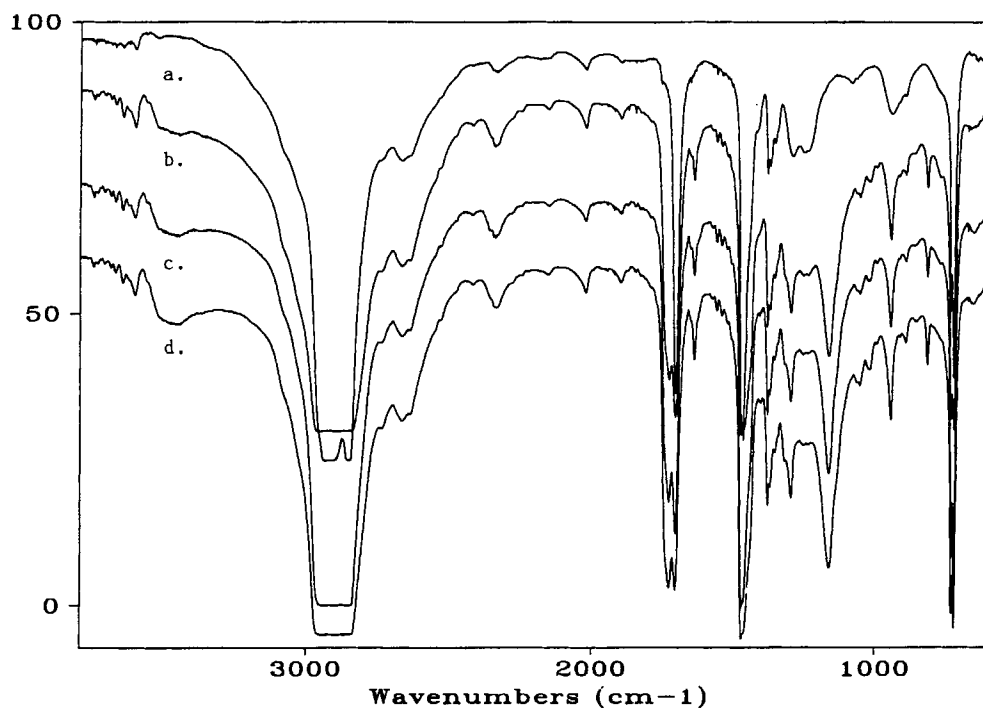


Figure 5 FTIR spectrum of EAA at (a) 0 min, and spectra of the reaction mixture EAA-GMA representing the functionalization at (b) 3, (c) 10, and (d) 15 mins.

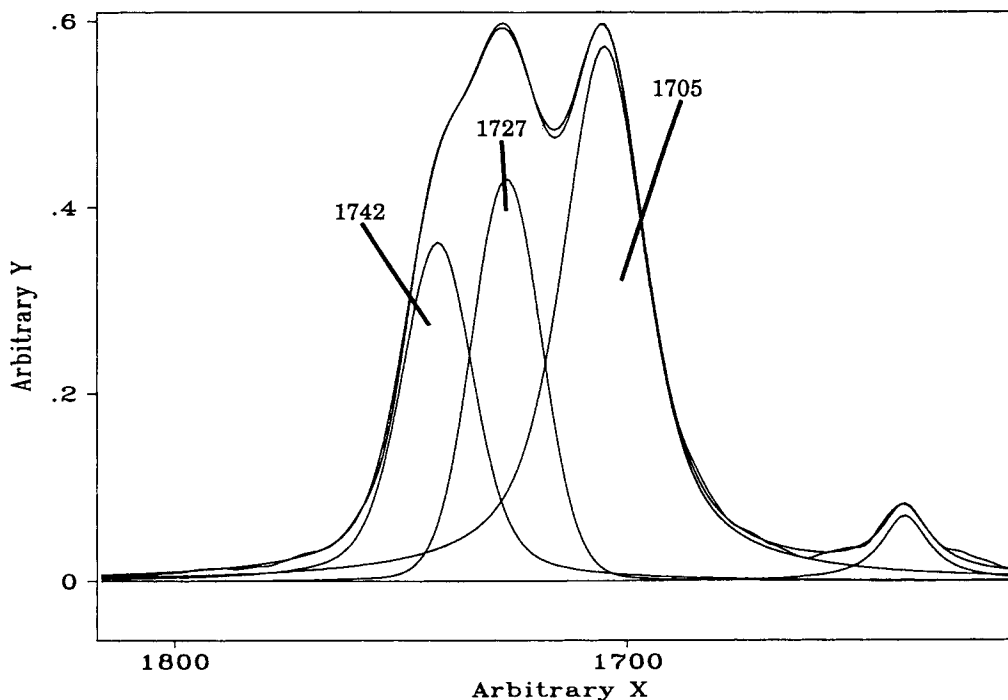


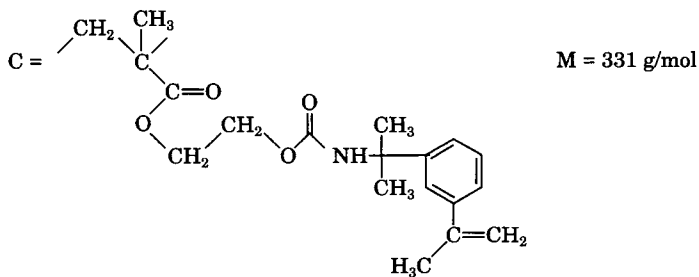
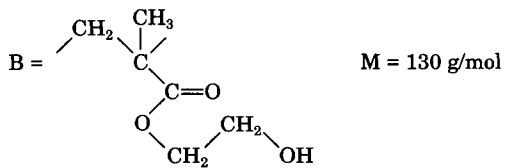
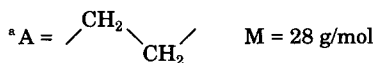
Figure 6 FTIR spectrum of EAA-GMA. Curve fit analysis of the region 1650–1800 cm^{-1} .

Due to the esterification the sample weight has increased with 0.66 g, and the percentage comonomer composition of the polymer is 2.1 wt % AA (0.9 mol

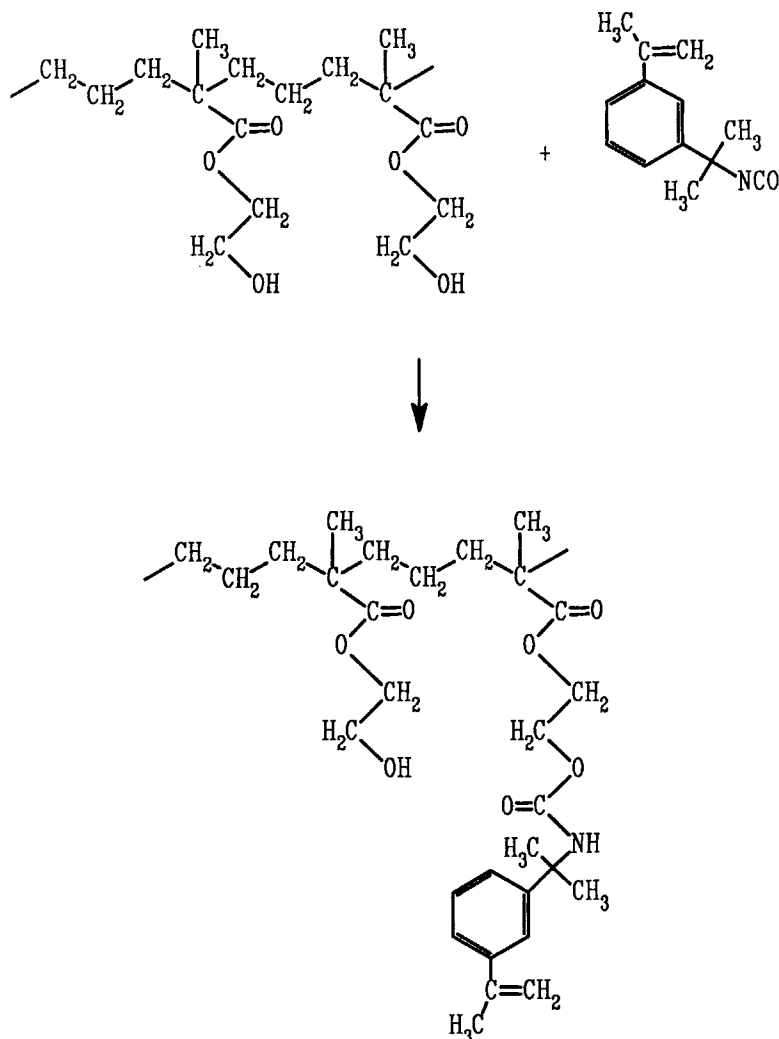
%), 2.5 wt % methacrylic acid, 2,3-dihydroxypropyl ester, 3-acrylate [MDPA (0.3 mol %)], 95.4 wt % ethylene (98.8 mol %).

Table III Composition of EHEMA-TMI Functionalized with Different Amounts of TMI

Amount of Added TMI to 40 g EHEMA		A ^a		B ^a		C ^a		Weight ^b (g)
wt %	mmol	wt %	mol %	wt %	mol %	wt %	mol %	
0.9	1.9	89.2	97.7	9.3	2.2	1.5	0.1	40.4
1.9	3.8	88.3	97.7	8.6	2.0	3.1	0.3	40.8
7.2	15.4	83.5	97.7	4.7	1.1	11.8	1.2	43.1



^b Weight of the final sample after the functionalization.



Scheme 3

Functionalization of EHEMA with TMI (EHEMA-TMI)

The preparation of EHEMA-TMI follows the reaction course presented in Scheme 3, and the reaction of an isocyanate and an alcohol is usually considered to be a fast reaction, especially at elevated temperatures. Figure 7 depicts the disappearance of the TMI monomer as a function of time when EHEMA is mixed with 1.9 wt % of the monomer at 180 and 200°C. The disappearance of TMI was monitored by acquiring FTIR spectra of films of the reaction mixture at different times and calculating the ratio of the peak area of the cumulated double bond (-N=C=O) stretch vibration centered at 2258 cm^{-1} and the sum of the area of the reference peaks at 721 and 730 cm^{-1} . The value of the absorbance representing the reaction mixture at 0 min of reaction time was obtained by extrapolation of the

function $y = 4.8 \times 0.6^x$, obtained from regression analysis of the data collected from the functionalization reaction at 180°C, to 0 min. Figure 8 shows

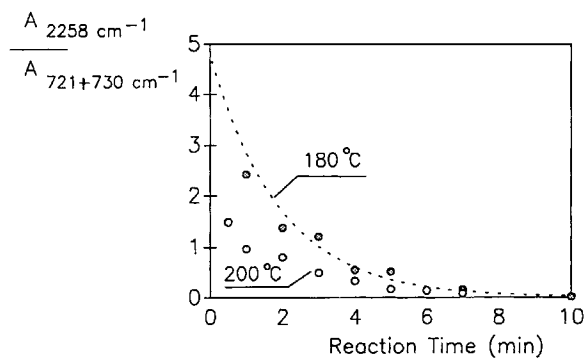


Figure 7 The disappearance of the -N=C=O vibration of the TMI monomer as a function of time during functionalization of EHEMA.

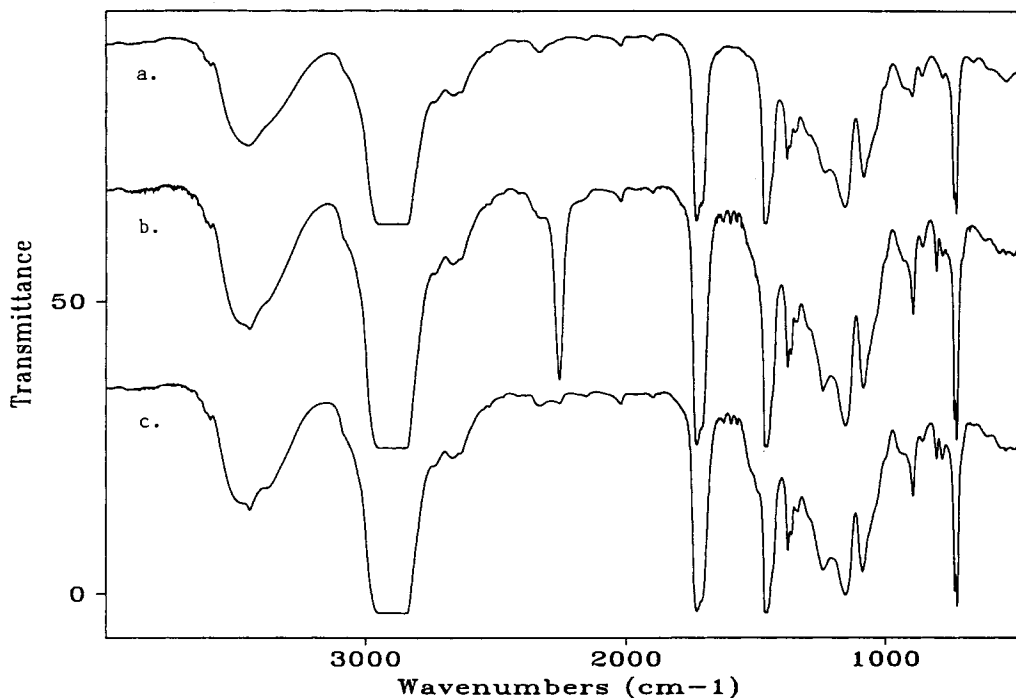


Figure 8 FTIR spectrum of (a) EHEMA and spectra of the reaction mixture EHEMA-TMI at (b) 3 min (c) and 10 min.

the FTIR spectrum of EHEMA (spectrum a) and two FTIR spectra of the reaction mixture at 3 min (spectrum b) and 10 min (spectrum c). The most abundant differences between the spectra are the disappearance of the —N=C=O stretch vibration at 2258 cm^{-1} with increasing time of reaction and the appearance of new bands due to both hydrogen-bonded (3370 cm^{-1}) and “free” (3450 cm^{-1})

—N—H stretch vibrations and, finally, a new band centered at 1246 cm^{-1} due to either —C—O—C— or —C—N stretch vibrations or probably a combination of both.

It is obvious from Figure 7 that only a few minutes of mixing time is required to react approximately 80% of the TMI monomers to EHEMA, however, a mixing time of 10 min is required for preparation of a sample that is free of residual TMI monomers.

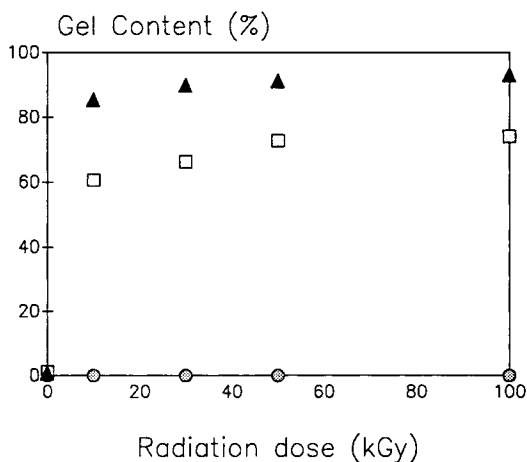


Figure 9 The Gel Content as a function of radiation dose: ●, EVOH; ■, EVOH-AA containing 0.3 mol % of pendant acrylate groups; ▲, EVOH-AA containing 1.4 mol % of pendant acrylate groups.

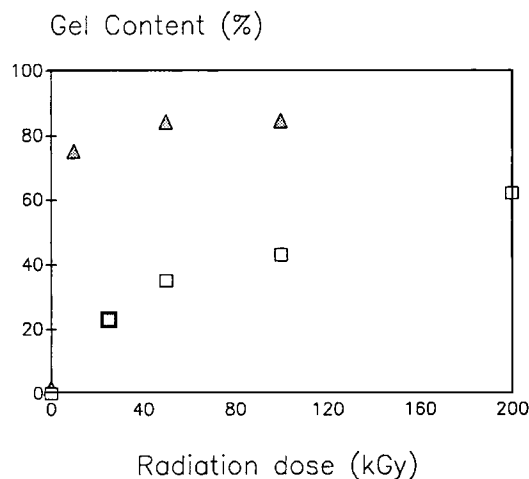


Figure 10 The gel content as a function of radiation dose: ■, EAA; ▲, EAA-GMA containing 0.3 mol % of pendant methacrylate groups.

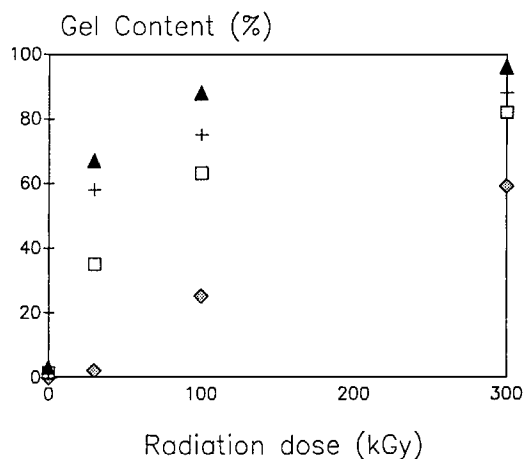


Figure 11 Gel content as a function of radiation dose: ♦, EHEMA; ■, EHEMA-TMI containing 0.1 mol % of pendant unsaturation; +, EHEMA-TMI containing 0.3 mol % of pendant unsaturation; ▲, EHEMA-TMI containing 1.2 mol % of pendant unsaturation.

The reactive mixing of EHEMA with 0.9, 1.9, or 7.2 wt % TMI for 10 min at 200°C will result in polymers that have the composition presented in Table III, i.e., polymers containing pendant isopropenyl unsaturation that range from 0.1 to 1.2 mol %.

Degree of Crosslinking

Depending on the amount of pendant unsaturated groups, the polymers will behave in quite different ways upon irradiation, and even though the amount of pendant acrylate groups are low, the polymers readily crosslink at low irradiation doses. Figure 9 depicts the formation of gel as a function of irradiation dose for EVOH and EVOH-AA containing either 0.3 or 1.4 mol % of pendant acrylate groups. Irradiation of EVOH will not result in any formation of gel, while irradiation of EVOH-AA will result in high gel contents already at an irradiation dose of 10 kGy. Approximately 42% more gel is obtained at 10 kGy by increasing the amount of pendant acrylate groups from 0.3 to 1.4 mol %.

The gel content as a function of radiation dose for the polymer containing 0.3 mol % of pendant methacrylate groups is presented in Figure 10 along with the gel content for original EAA. The functionalized EAA-GMA sample behaves in the same manner as the EVOH-AA samples upon irradiation. Approximately 80% gel is formed already at an irradiation dose of 10 kGy.

The corresponding gel contents as a function of radiation dose for the functionalized EHEMA-TMI polymers are presented in Figure 11 together with the data obtained for the original EHEMA sample. The EHEMA sample has a low sensitivity to radiation, and only 25% gel is formed at a radiation dose of 100 kGy. On the other hand, when EHEMA is functionalized with TMI, high gel contents are obtained at 100 kGy. Increasing the amount of pendant isopropenyl unsaturation from 0.1 to 1.2 mol % increases the gel content at 100 kGy from 64 to 88%. The formation of ~90% gel of EHEMA-TMI containing 1.2 mol % of pendant isopropenyl unsaturation requires a radiation dose of 100 kGy, while the corresponding value for EVOA-AA containing 1.4 mol % of pendant acrylate groups is 30 kGy. Thus, the radiation sensitivity of EHEMA-TMI is not as high as the functionalized EVOH-AA or EAA-GMA.

CONCLUSIONS

Ethylene copolymers that contain 0.1–1.4 mol % of pendant unsaturation are readily radiation crosslinked to high gel contents at reduced doses compared to those normally required. Furthermore, introduction of pendant unsaturation to ethylene vinyl alcohol copolymers allows radiation crosslinking of a polymer that otherwise is impossible to radiation crosslink.

Compared to traditional copolymerization processes, reactive melt processing offers the flexibility of tailoring polymer properties for specific applications, for instance, the functionalization of polymers for improved radiation processing. However, the reactants should be carefully chosen in order to achieve the desired properties, and our study shows that the reaction of an isocyanate and a hydroxy-functional polymer is fast enough to give a high yield of reaction product after only a few minutes of processing.

Finally, Fourier-transformed infrared spectroscopy has proven to be a convenient and suitable method to characterize functionalized ethylene copolymers and to follow changes of the reaction mixture as a function of time during a functionalization.

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