Electrical Conductivities of Photochemically Prepared Polyethylene Glycol Dimethacrylate, Reacted with Iodine and Lithium Perchlorate Dopants and Activation Energy Determination for Polymer-Dopant Interaction

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ABSTRACT: Conductive polymers were obtained by using a new polymerization method where UV-light was used as a photochemical initiator. To obtain high percent conversion optimum irradiation times were determined. Since it was observed in a previous work that conductivity of some polymeric materials can be improved by the addition of dopants (Ramelow et al., Mat Res Innovat 2001, 5, 40; Ma et al., Tr J Chem 1997, 21, 313), in this work, the effect of dopants on conductivity of the polyethylene glycol dimethacrylate (PEGDM) was studied by using lithium perchlorate ($LiClO_4$) and iodine (I_2). The most effective dopant concentration was determined by measuring the conductivities. The conductivity change at various temperatures was traced during the reaction of PEGDM with dopant Lithium perchlorate ($LiClO_4$) and the activation energy of dopant-polymer interactions was calculated. A method was developed to follow the kinetics of polymerization reactions by tracing conductivity changes with time at different temperatures. The polymerization pathway of ethylene glycol dimethacrylate was given in a previous work, and the mechanism was studied by using NMR and relaxation time method (Ramelow et al., J Appl Polym Sci 2006, 100, 5087). In this work, the suggested pathway was confirmed by additional calculations. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 1916–1926, 2009

Key words: UV-irradiation; dopant; conductivity; semiconductor; polyethylene glycol dimethacrylate

INTRODUCTION

The development of conducting polymers can be traced to mid-1970s when researchers at the University of Pennsylvania reported that films of polyacetylene became conducting by doping reactions.[1,2]

A major discovery was that certain polymers such as polysulfonitride[3] and polyacetylene[4] can be made highly conducting in the presence of certain additives called dopants.[5]

Although the mechanism of conduction remains incompletely understood, it is believed that certain structural features influence the level of conductivity; they include delocalization (charge may be transferred through pendant groups); doping (by additional groups rearranging double bonds into a conjugated conducting mode)[6]; and morphology (configurational and conformational factors).[7]

Improved resin grades will result in more intensive use of electronics, appliances, electrostatic spray painting of automotive and industrial parts. Conductive polymers will control the high levels of static electricity developed by moving parts as well as EMI/RFI emissions, and they will be effective in protecting sensitive electronic devices from static discharge during production, transportation, and storage.

Conductive polymers are of great interest because of their applications in rechargeable batteries,[8] electronic devices,[9] gas separation membranes,[10] and enzyme immobilization,[11,12] owing to their electrical properties. Their conductivity can be improved by addition of dopants,[13,14] and by developing their poor mechanical and physical properties with chemical and electrochemical blending.[15–17] Solvents used during the polymerization process also have an importance in increasing the conductivity of the polymer.[18]

Semiconductors are used in solid-state electronic devices, such as transistors, light-emitting diodes (LED's) and laser diodes. A CD player, for example uses transistors for its electronic circuits as well as laser diode to read a compact disk. Basic component of most of these electronic devices is silicon a metalloid. Metalloid is a semiconducting element, which
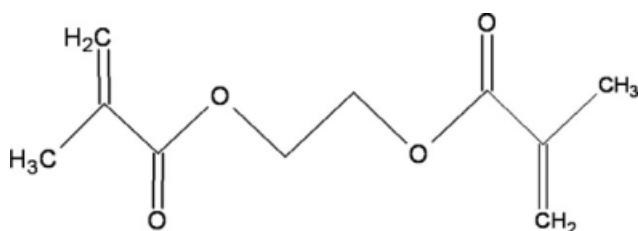
Figure 1 Ethylene glycol dimethacrylate monomer (EGDM).

has low electrical conductivity at room temperature, but increases as the temperature increases. Metals are good electrical conductors but their conductivity decreases with temperature

EXPERIMENTAL/MATERIALS AND METHODS

Materials

Ethylene glycol dimethacrylate (EGDM) monomer (Fig. 1) was a product of Aldrich Chemical Company (Milwaukee, WI). It was purified from inhibitor by vacuum distillation at 60–80°C at 30 mmHg pressure. 2-2'-Azobisisobutyronitrile (AIBN) initiator (Polysciences Inc., Warrington, PA) was a product of Polyscience Inc, and was purified from methanol before use. Lithium perchlorate (LiClO$_4$) was obtained from Mallinckrodt Chemical Works (Phillipsburg, NJ) and was used directly after dissolving in THF. Iodine was also a product of Mallinckrodt Chemical Works Company and was dissolved as a solid directly in (THF) solution during EGDM polymerization.

For UV-irradiation, a Phillips (Turnhout, Belgium) HPR, 125W Mercury vapor UV-lamp was used with a maximum wavelength of 254 nm. For conductivity measurements of the polymer solutions, an Omega CDB-420 conductivity meter was used (Omega Engineering, Inc., Stanford, CT). A constant temperature water bath with a thermoregulator circulator combination (Fisher Scientific, Pittsburg, PA, Mode 70, Bioamp immersion circulator) was used to study the temperature effect on the conductivity of the polymer.[18]

All samples were degassed and irradiated in quartz tubes of 12-cm height and 2.8-cm diameter. A high vacuum system (10^{-4} to 10^{-5} mmHg) was used for evacuating monomer solutions.

Preparation of polymers

About 5 mL distilled EGDM, 10 mL THF, and 1.0% initiator (AIBN) were put in quartz tubes, which was sealed with a septum, and connected to the high vacuum system with syringe needles and degassed to 10^{-4} to 10^{-5} mmHg pressure for 5–6 h.

The degassed tubes were then irradiated by UV-rays at 25°C under a mercury vapor lamp with wavelength of 254 nm. The tubes were then irradiated in a horizontal position at a distance of 20 cm from the light source. After irradiation for the required time of polymerization the obtained polymer was dissolved in THF, which is a good solvent for both monomer and polymer, and precipitated in methanol. The obtained polymer was then filtered and dried in a vacuum oven at room temperature to a constant weight. When dopant addition is required, different concentrations of dopant was incorporated with the monomer solution system before polymerization or it was added to the polymer solution after polymerization. The polymerization pathway of EGDM was shown in a previous work.[19] The mechanism was determined by an NMR study.[19]

The suggested mechanism for polymerization is given in Figure 2 (with the corresponding ppm values).[19] NMR signals imply that polymerization takes place by a free radical process where the possible pathways are across the C—CH$_3$ bond (Path A) and the —CH$_2$—CH$_2$— bond (Path B).[19] Figures 3 (Path A) and 4 (Path B) present the mechanism of two possible pathways. These two processes are both possible for free radicalic polymerization of EGDM, as summarized in Figure 5. To find the most probable pathway, corresponding bond-breaking energies were calculated for the C—CH$_3$ and —CH$_2$—CH$_2$— bonds. The UV-light energy at 254 nm was calculated as 78×10^{-20} J/mol. The energies required to break the C—CH$_3$ and —CH$_2$—CH$_2$— bonds were calculated as 61.16×10^{-20} J/mol and 57×10^{-20} J/mol, respectively.[19] Therefore, it was concluded that UV-light is capable of breaking both bonds, but since the —CH$_2$—CH$_2$ bond-breaking energy is much smaller than the energy required to break the C—CH$_3$ bond, it was decided that free radical polymerization through the —CH$_2$·radical (stabilized by resonance) after breaking the —CH$_2$—CH$_2$ bond seems to be more probable and polymerization proceeding via Pathway B is more likely.[19]

By using the relaxation time method, activation energies of dopant (I$_2$)—polymer interactions at 4.3 ppm (CH$_2$—CH$_2$ bond) and 2.4 ppm (C—CH$_3$ bond) were calculated as 64.43 kJ/mol and 165.764 kJ/mol, respectively.[19] Since the activation energy for 4.3 ppm interaction is much lower than the activation energy for 2.4 ppm, it provides additional evidence that the dopant attack occurs on the —CH$_2$—CH$_2$— bond rather than the —C—CH$_3$ bond.

Conductivity measurement

About 0.125 g of the obtained polymer was dissolved in 12.5 mL THF solution and the conductivity
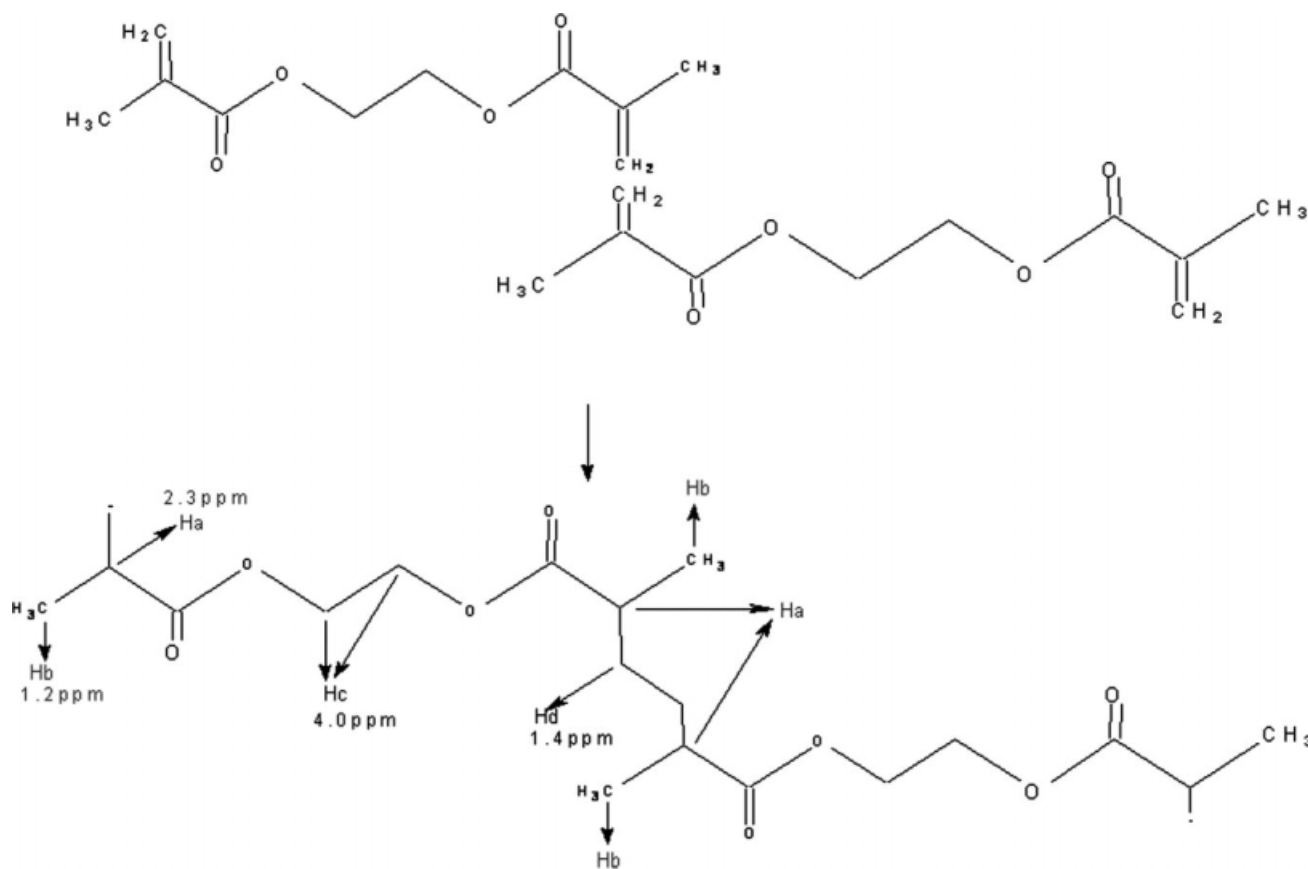
Figure 2 Suggested polymerization pathway of EGDM.[19]

was measured directly with the conductivity meter, by using a probe immersed in the polymer solution.

THEORY

Semiconductors are used widely in rectifiers and transistors: In a sold-state electronic device a *p*-n junction consists of a *p*-type semiconductor joined to an *n*-type semiconductor. It can function as a rectifier. A rectifier is a device that allows current to flow in one direction only.

If the wire connections are reversed, positive holes are attracted to the negative wire and electrons are attracted to the wire. The region of the junction becomes depleted in charge carriers, so the *p*-n junction becomes nonconducting and no current can flow. Nonconducting *p*-n junctions of semiconductors are used as transistors. The latest computer chips have microscopic electrical circuits integrated with as many as a million transistors per square centimeter of surface area. This work shows that conducting polymers can potentially be used to control the current in electrical devices via temperature change.

During formation of bonds in molecular orbitals, the overlap of *s* orbitals gives rise to an *s* bond and
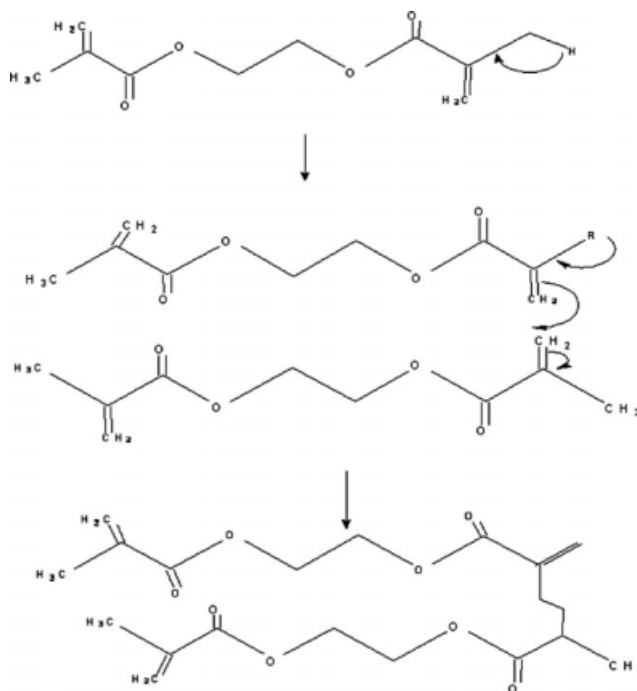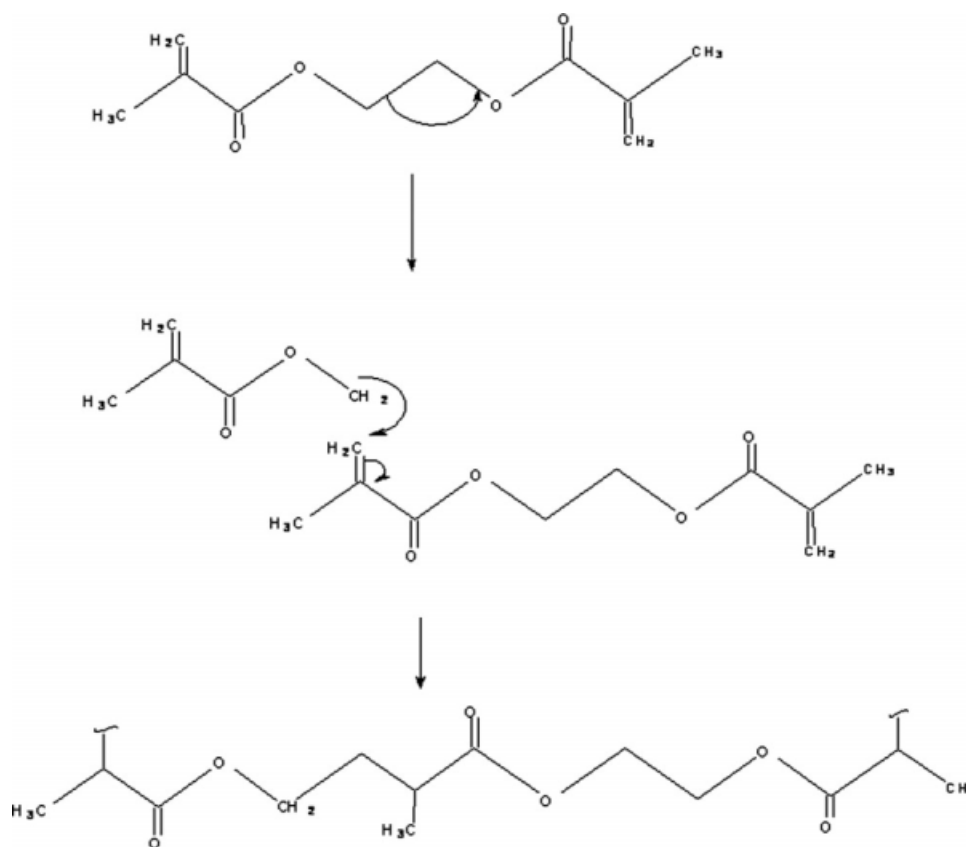

Figure 3 Path A: Breakage across the C—CH₃ bond.[19]

Figure 4 Path B: Breakage across the H_2C—CH_2 bond.[19]

the overlap of p orbitals gives rise to a p bond. The spacing between s and p orbitals is called bond gap.

Conductors have half-filled valence bands, as seen in the Fermi Dirac equation where P indicates the population of the given orbital in the following equation[13,14,20]:

$$P = 1/(e^{E-E_f} + 1) \quad (1)$$

where E_f is the Fermi energy at the level for which $P = 1/2$. For the energies well above the Fermi energy, the 1, the unity in the denominator, can be neglected, so that eq. (2) is obtained[14,20]:

$$P \approx e^{-(E-E_f)/kT} \quad (2)$$

The population now resembles a Boltzman distribution, decaying exponentially with increasing energy and increases exponentially with increasing temperature. Ironically, the electrical conductivity of metallic solids (conductors) decreases with increasing temperature, even though more electrons are excited into the empty orbitals. Conductors have half-filled orbitals which allow maximum in and out transportation. The increase in temperature causes more vigorous thermal motion of the atoms causing collisions between moving electrons and atoms. Electrons are scattered out of their paths and are less

efficient at transporting charge[13,20]; as a result, conductivity decreases with temperature.

Semiconductors have filled valence bands but the energy gap is small between the valence and conduction bands. Thermal excitation produces a few electrons in the upper band and a few holes in the lower band, and conductivity increases with increasing temperature. At higher temperatures electrons populate the levels of the upper conduction band at the expense of the filled valence band. Therefore, for semiconductors one method of increasing the conductivity is to increase the temperature, and another method is to increase the number of charge carriers by incorporating foreign atoms (dopants) to function as a donor band or acceptor band. Even though semiconductors certain full valence bands, with the introduction of dopants electrons are either removed
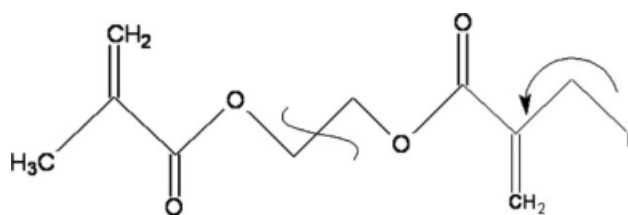

Figure 5 The two possible pathways for free radical polymerization of EGDM.[19]
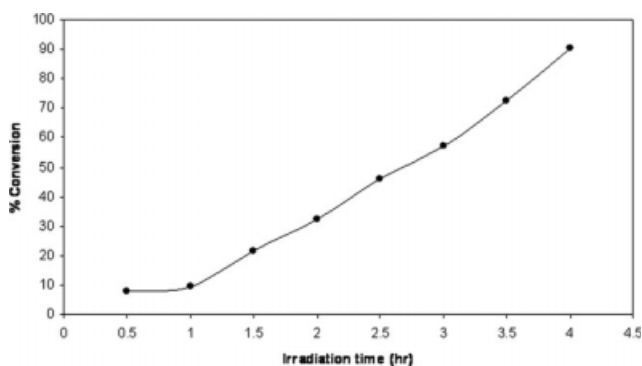
Figure 6 Percent conversion of PEGDM (without dopant) at different irradiation times.

from the valence band or added to the conduction band, in both cases electrons become mobile and conductivity increases with temperature. This work is based on their simple premises.

The purpose of this study was to obtain a new conductive polymer, polyethylene glycol dimethacrylate (PEGDM) by using photochemical methods (UV-irradiation), and to obtain high percent conversions by determination of the optimum irradiation time and studying the temperature effect on the conductivity of the obtained polymer. Furthermore, to increase the conductivity of the polymer, incorporate the polymer with some dopant substances such as iodine and lithium perchlorate either before or after the irradiation (after obtaining the polymer) and by tracing the conductivity while changing the dopant concentrations to find the most effective concentrations for each dopant.

The measurement of conductivity change with time provides an excellent way to follow the kinetics of the reaction. Even though one does not know the rate law for a chemical reaction, it is possible to use the Arrhenius equation to calculate the effect of temperature on reaction rate. When conductivity changes were measured by time immediately after the addition of dopant, sudden increase in the conductivity during polymer-dopant reaction slows down and reaches a constant value at the end of the reaction.

Suppose the time required to reach a certain extent of reaction at two different temperatures, T_1 and T_2, are denoted by τ_1 and τ_2, respectively, then[14,21] by using the Arrhenius equation at two different rate constants and assuming that $k_2/k_1 \propto \tau_1/\tau_2$. The faster the reaction time, the shorter the time to complete it; therefore, they are inversely proportional, and the following equation was calculated as:

$$\tau_1/\tau_2 = e^{-E_a/RT_2}/e^{-E_a/RT_1} \tag{3}$$

and

$$\ln \tau_1/\tau_2 = (E_a/R)(1/T_1 - 1/T_2) \tag{4}$$

are obtained.[14,21] From eq. (4), the activation energy E_a for the reaction of PEGDM with perchlorate ion is determined.

EXPERIMENTAL RESULTS AND DISCUSSION

The effect of dopant on conductivity was studied by using Lithium perchlorate (LiClO$_4$) and iodine (I$_2$). The most effective dopant concentration for each case was determined by measuring the conductivities at different dopant concentrations incorporated with monomer before irradiation or with polymer after irradiation.

Percent conversion

The percent conversion of PEGDM was determined by irradiating monomer and initiator-solvent systems at different time intervals. After each irradiation time, obtained polymer was dissolved in THF and precipitated in methanol solution. The obtained polymer was then filtered, dried, and weighed for percent conversion determination.

Figure 6 shows the percent conversion of (PEGDM) at different irradiation times when no dopant was introduced into the monomer solution. Figure 7 shows the percent conversion results at different irradiation times when dopant was incorporated (0.347M lithium perchlorate) into the monomer solution before irradiation. In both cases within 4.0 h of irradiation about 90% conversion values were reached. However, Figure 7 gives an S-shaped curve that indicates auto-acceleration (Norrish-Smith effect) during polymerization.

Conductivity measurement

For conductivity measurement, about 0.125 g of the obtained polymer was dissolved in 12.5 mL THF and conductivity was measured directly with the
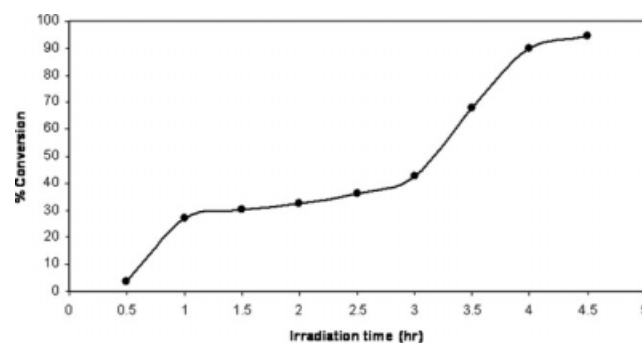

Figure 7 Percent conversion of PEGDM at different irradiation time when dopant LiClO$_4$ was added before polymerization.

TABLE I
Conductivity Change of PEDGM Prepared without Dopant (0.125 g EGDM + 12.5 mL THF)

Conductivity (μS)	Irradiation time (h)
0	0.5
0.15	1.0
0.35	1.5
0.70	2.0
1.11	2.5
1.24	3.0
1.12	3.5
1.13	4.0

Figure 8 Conductivity change of PEGDM without addition of dopant.

conductivity meter by using a probe immersed into the solution.

Without dopant

Poly-EGDM was prepared at different irradiation times when no dopant was added in monomer solutions and the conductivity was measured. Table I shows the conductivity measurements and Figure 8 indicates the conductivity change of PEGDM prepared without dopant, by irradiating at different time intervals. Maximum conductivity without dopant was observed to be 1.24 μS at 3.0 h of irradiation. At 4.0 h of irradiation, about 1.13 μS conductivity value was observed.

With dopant

Perchlorate ion effect on conductivity of PEGDM. Dopant added before polymerization: The monomer solution was first incorporated with dopant (0.347M (LiClO$_4$) + 5.0 mL monomer + 10.0 mL THF + 1% AIBN) and irradiated at different time intervals with UV-light after degassing at high vacuum. Obtained polymer was then dissolved in THF and precipitated in
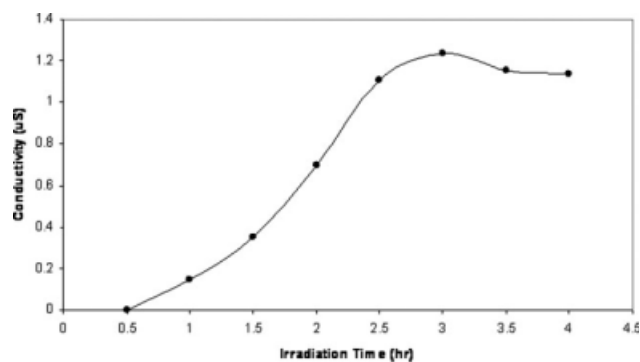
methanol, filtered and dried. Dried solid polymers were dissolved in THF (0.125 g PEGDM + 12.5 mL THF) and conductivity values were measured for each time of irradiation. Figure 9(B) shows the conductivity change of PEGDM prepared at different irradiation times when dopant was added before polymerization. After 3.0 h of irradiation sudden jump in conductivity was observed and at 4.0 h of irradiation, it was about 2.75 mS and polymer still shows increasing conductivities at further irradiation times. When there was no dopant added this value at 4.0 h was only 1.15 μS (1.15 $\times$ 10^{-3} mS) [Figs. 8 and 9(C)]. Dopant addition increases the conductivity values of about 2000 times (2434 times at 4 h).

Dopant added after polymerization: After obtaining polymers with certain irradiation times each were dried in vacuum oven dissolved in THF and incorporated with lithium perchlorate (0.125 g PEGDM + 12.5 mL THF + 0.347M LiClO$_4$). Figure 9(A) shows the conductivity changes of such polymer with irradiation times. After 3.0 h of irradiation maximum conductivity was obtained at 3.15 mS. Similar values are obtained for polymer-dopant system (dopant
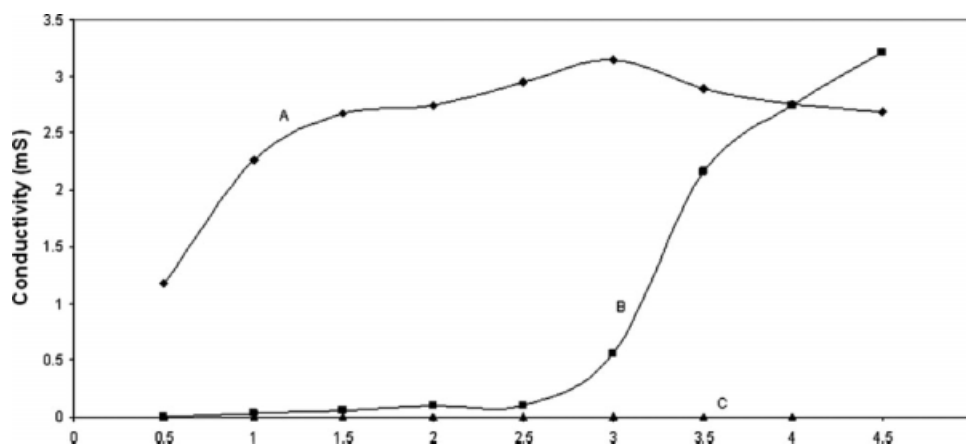

Figure 9 Conductivity change of PEGDM. (A) Dopant added after polymerization, (B) dopant added before polymerization, and (C) without dopant.

TABLE II
Conductivity Change of PEGDM After Reacting with LiClO₄ Dopant When Added after Polymerization (0.125 g PEGDM + 12.5 mL THF + 0.347M LiClO₄)

Conductivity (mS)	Irradiation time (h)
1.18	0.5
2.26	1.0
2.68	1.5
2.74	2.0
2.95	2.5
3.15	3.0
2.90	3.5
2.75	4.0
2.70	4.5

TABLE III
Conductivity Change of PEGDM After Reacting with LiClO₄ Dopant When Added Before Polymerization (5.0 mL EGDM + 10.0 mL THF + 1% AIBN + 0.347M LiClO₄)

Conductivity (mS)	Irradiation time (h)
0	0.5
0.04	1.0
0.05	1.5
0.01	2.0
0.12	2.5
0.56	3.0
2.16	3.5
2.75	4.0
3.21	4.5

added before irradiation), however, in this case after 3.0 h of irradiation conductivity values start to decrease. Figure 9 shows all the three results when the conductivities measured at different irradiation time intervals and expresses on the same mS scale. Figure 9(A) shows when dopant was added after polymerization [Table II and Fig. 9(A)]. Figure 9(B) shows when it was added before polymerization [Table III and Fig. 9(B)]; and Figure 9(C) shows when polymers were obtained without any addition of dopant [Table I and Fig. 9(C)]. Figure 9(C) was given in the µS region as well as in Figure 8.

The highest conductivity values were obtained when dopant was added after polymerization. Maximum value was 3.15 mS at 3.0 h of irradiation. When dopant was added before irradiation, it showed no significant increase in conductivity for the first 3.0 h; however after 3.0 h, acceleration was observed, and at 4.0 h of irradiation they both gave the same conductivity value of 2.75 mS.

Dopant concentration effect: To see the most effective dopant concentration, two sets of experiments were prepared: dopant added before polymerization and dopant added after polymerization, both were

examined at different concentrations using the same irradiation time (2 h).

Dopant added before polymerization: Dopant was added in different concentrations to monomer solutions (5.0 mL EGDM + 10.0 mL THF + 1% AIBN + various concentrations of LiClO₄ dopant). After obtaining the polymer, the conductivity values were determined. Figure 10 shows the conductivity changes of PEGDM prepared with changing molar concentrations of lithium perchlorate. For each case 2.0 h of irradiation time was applied. The most effective concentration was obtained at 0.3M LiClO₄ with a conductivity value of 35.4 µS.

Dopant added after polymerization: After obtaining polymer samples (each obtained with 2.0 h of irradiation), the dopant (LiClO₄) was added to samples at different molar concentrations (0.125 g PEGDM + 12.5 mL THF + different concentrations of LiClO₄ dopant) and the conductivity values were determined. The obtained conductivities were much higher than the ones obtained when the dopant was added before (Fig. 11). Similarly, the most effective concentration of dopant (LiClO₄) was found to be 0.3M and the corresponding conductivity value in
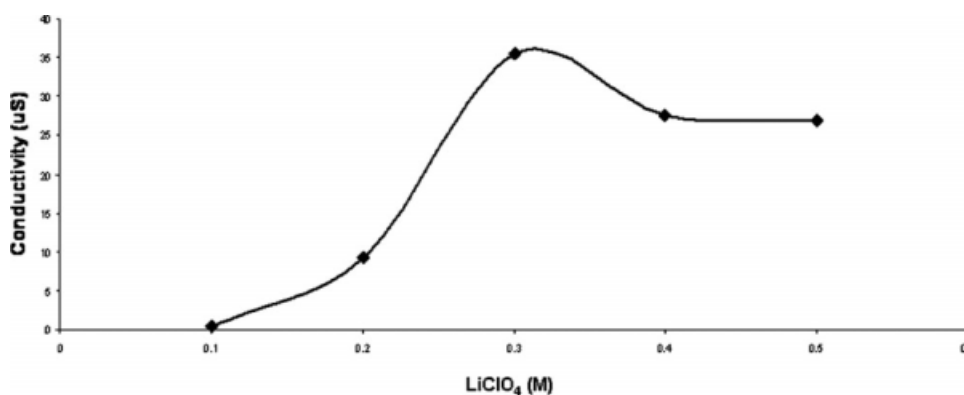

Figure 10 Conductivity change of PEGDM after reacting with different concentrations of LiClO₄ when dopant was added before polymerization at 2 h of irradiation time.
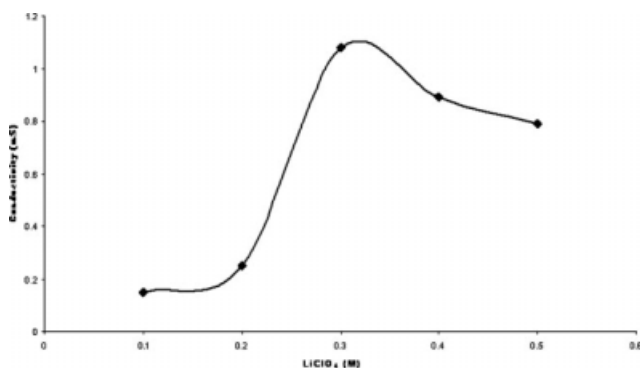
Figure 11 Conductivity change of PEGDM reacting with different concentrations of LiClO$_4$ when dopant was added after polymerization at 2 h of irradiation time.

this case was 1.08 mS (about 30 times bigger than the previous one).

When these two results were shown on the same graph using the same conductivity scale, for comparison; the effect of dopant addition after polymerization becomes more pronounced (Fig. 12). When no dopant was added, conductivity measure only 1.15 μS (1.15 × 10^{-3} mS) after 4 h of irradiation [Figs. 8 and 9(C)]. Perchlorate dopant addition before polymerization increased this value to 2.75 mS after 4 h of irradiation [Fig. 9(B)]. Perchlorate dopant addition increased the conductivity values by a factor of about 2500. Dopant addition after polymerization enhances this value even more to 3.15 mS after 3 h of irradiation [Fig. 9(A)], which is a factor of about 2800.

After combining all the results given in the Experimental section, it can be concluded that the perchlorate ion increases the conductivity values of the polymer to about 2800 times and when it was incorporated with polymer after completion of polymerization it gave much higher conductivity values. The
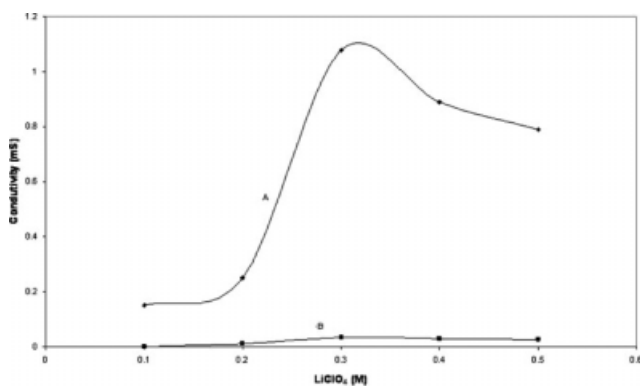
most efficient concentration of the dopant, lithium perchlorate, was found to be 0.3*M*.

Iodine dopant effects on conductivity of EGDM. The Iodine (I$_2$) was used as another dopant to increase the conductivity of PEGDM.

Dopant added before polymerization: Iodine was added into the monomer mixture (5.0 mL EGDM + 10.0 mL THF + 1% AIBN + 0.5*M* I$_2$) before irradiation. However, there was no polymer obtained when I$_2$ was introduced before irradiation. This is attributed to the following mechanism as given in equations:

Reactions can be summarized as follows[19]:

$$\mathbf{M} \xrightarrow{hv} \mathbf{M}^{\bullet} \tag{5}$$

$$\mathbf{I_2} \xrightarrow{hv} 2\,\mathbf{I}^{\bullet} \tag{6}$$
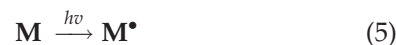
$$\mathbf{M}^{\bullet} + \mathbf{I}^{\bullet} \xrightarrow{\text{termination}} \mathbf{M} - \mathbf{I} \tag{7}$$

where **M** is the EGDM molecule, **M**$^{\bullet}$ is the EGDM monomer, and **I**$^{\bullet}$ is the iodine radical.

Here, although the monomer radical is forming by UV-irradiation, at the same time iodine radicals are formed. UV-light forms iodine radicals that cause termination in the polymerization reaction. As a result no polymer was obtained.[19] Therefore, it was decided to add iodine to the obtained polymer dissolved in a solvent.

Dopant added after polymerization: To find out the most effective dopant concentration using I$_2$ as a dopant, obtained polymer solutions were prepared at different I$_2$ concentrations (0.125 g PEGDM + 12.5 mL THF + different concentrations of I$_2$) and conductivity values were measured at different concentrations (Fig. 13). The most effective I$_2$ concentration was found to be 0.5*M*, with maximum conductivity of 192.1 μS (Fig. 13). The most effective irradiation time was determined by measuring the
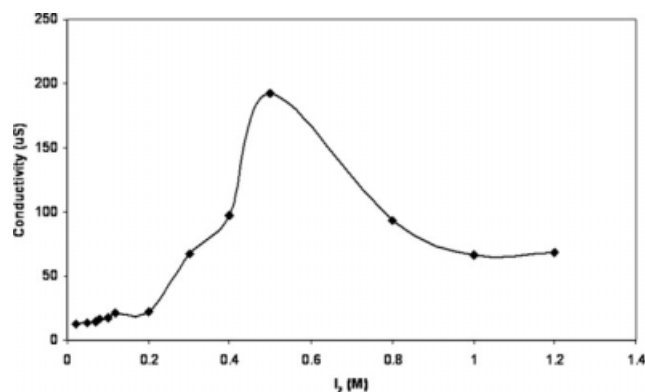

Figure 12 Conductivity change of PEGDM after reacting with different concentrations of LiClO$_4$ at 2 h of irradiation time. (A) Dopant added after polymerization and (B) dopant added before polymerization.

Figure 13 Conductivity change of PEGDM after reacting with different concentrations of I$_2$ when dopant was added after polymerization at 3 h of irradiation time.
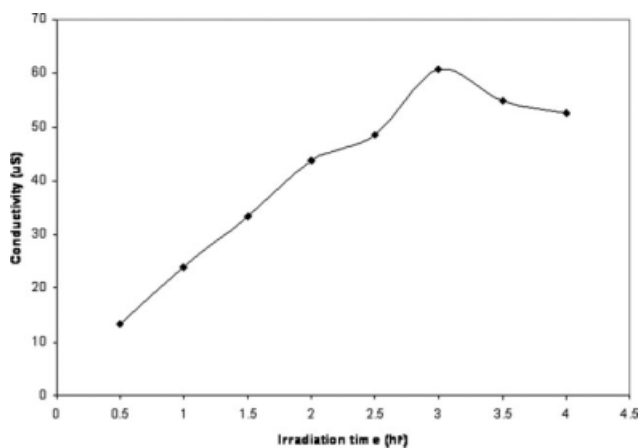
Figure 14 Conductivity change of PEGDM after reacting with iodine at room temperature when dopant was added after polymerization.

conductivities of PEGDM samples incorporated with iodine dopant after polymerization. Figure 14 shows these results. The maximum conductivity was reached after 3.0 h of irradiation with a value of 60.8 μS.

For comparison, conductivity values were shown on the same scale for both the polymers obtained without dopant and dopant added on the samples after polymerization [Fig. 15(B,A), respectively]. The polymers obtained using the same irradiation time without any dopant showed a maximum conductivity value of 1.24 μS [Figs. 8 and 15(B)]. Iodine addition, therefore, increased the conductivity about 60 times. The most effective I_2 concentration was found to be 0.5M (Fig. 13) with a most effective radiation time of 3.0 h. By comparing all the results, it shows that the perchlorate ion is more effective. It increases the conductivity by about 2500–2800 times
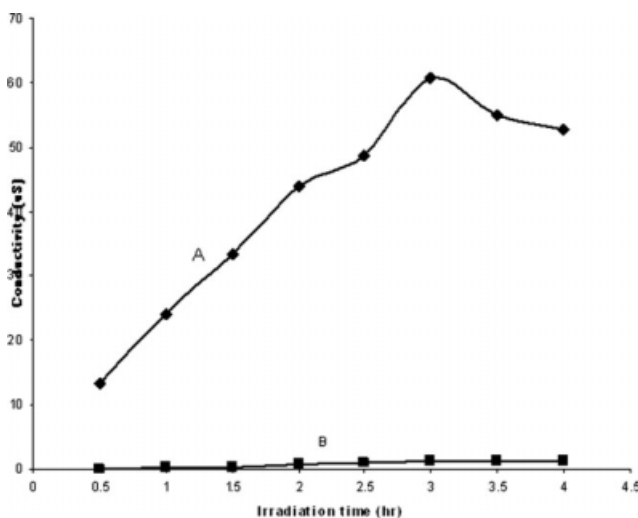

Figure 15 Conductivity change of PEGDM versus irradiation time. (A) Dopant added after polymerization and (B) without addition of dopant.

when compared with the 60-fold improvement with iodine.

Activation energy determination for the reactions of PEGDM with lithium perchlorate

The measurement of conductivity change with time provides an excellent way to follow the kinetics of the reaction. Even though one does not know the rate law for a chemical reaction, it is possible to use the Arrhenius expression to calculate the effect of temperature on reaction rate. When conductivity changes were measured by time right after the addition of the dopant, sudden increase in the conductivity during polymer-dopant reactions slows down and reaches a constant value at the end of the reaction. By considering the time required to reach a certain extent of reaction at two different temperatures T_1 and T_2, denoted by $\cdot_1$ and $\cdot_2$, respectively, as shown in eqs. (3) and (4), the activation energy E_a for the reaction of PEGDM with perchlorate ion is determined.

Figure 16(A,B) show the conductivity change of PEGDM during the reaction with $LiClO_4$ at two different temperatures, 32.6 and 4°C, respectively. The sudden increase in conductivity after dopant addition finally becomes constant after completion of the reaction (220 min at 32.6°C and 30 min at 4°C). By using eq. (4), the activation energy for this reaction was calculated as −49.06 kJ/mol. Activation energy was calculated as −43.714 kJ/mol by using the same equation between −4 and 18.2°C.

For the same system reaction, completion times were determined at several different temperatures and, results were shown [Table IV and Fig. 17]. Activation energy determined by using any two temperatures and reaction completion times gives approximately the same value, −40 kJ/mol. Figure 17 indicates that it takes a longer time to complete the reaction because as the temperature increases, the rate slows down. This can be explained as follows: when the temperature is increased, the kinetic energy increases. Consequently, electron transfer
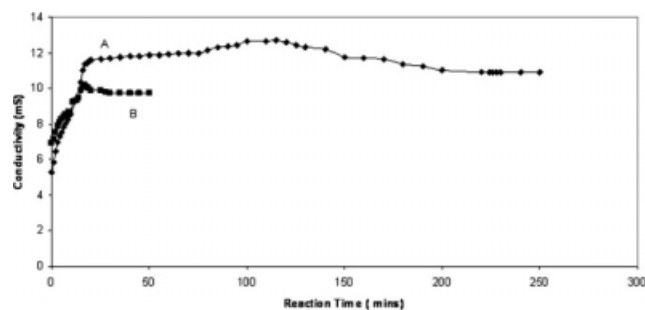

Figure 16 Conductivity change of PEGDM during the reaction with $LiClO_4$. (A) At 32.6°C and (B) at 4°C.

TABLE IV
Measurement of Conductivity Change of PEGDM with LiClO₄ Dopant with Reaction Completion Time at Different Temperatures (0.125 g PEDGM + 12.5 mL THF + 0.347M LiClO₄)

Temperature (°C)	Reaction completion time (min)	Conductivity (σ)
35.0	276	12.3
32.6	220	10.9
26.0	96	9.0
18.2	62	6.7
4.0	30	9.8
−4.0	14	12.0

Figure 18 Plot of conductivity versus temperature with (LiClO₄) when dopant was added after polymerization (1 h irradiation time).

and settling down of electrons to a steady condition takes a longer time due to collisions of fast-moving electrons and atoms. This is consistent with the negative value of activation energy of interaction obtained where as temperature increases, the rate of the reverse reaction increases. This indicates that this addition is an exothermic reaction. According to thermodynamics, $\Delta E = Ea_f - Ea_r$ is equal to the internal energy change Δu. Since $\Delta u = \Delta H + P \Delta v$, this value is also equal to the ΔH of the reaction at constant pressure since there is no volume change ΔV. The ΔH value being negative indicated that these reactions are exothermic.

When conductivity values were drawn versus temperature, Figure 18 was obtained. This figure gives a peculiar plot that shows first a decrease in conductivity with increasing temperature, then after certain temperature (18.2°C) it shows and increase with further increase in temperature, indicating that conducting polymer first acts as a conductor, then it becomes a semiconductor. This can be explained with Fermi-dirac equation, as given in eq. (1).

Conductors have half-filled orbitals (valence band) that provides the maximum number of electron in and out transportation. The population, P, of the orbitals is given by the Fermi-Dirac distribution [eq. (2)]. For energies well above the Fermi Level (population is half filled), the 1 in the denominator can be
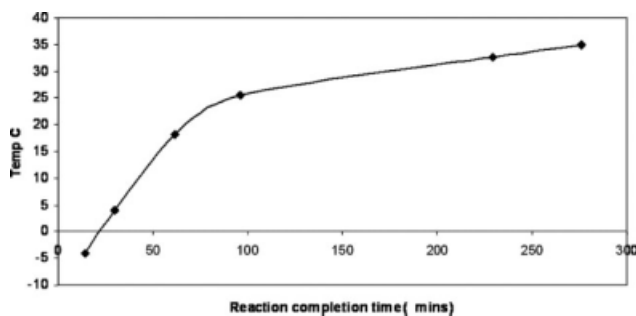

Figure 17 Plot of temperature versus reaction completion time of PEGDM with LiClO₄ when dopant was added after polymerization (1 h irradiation time).
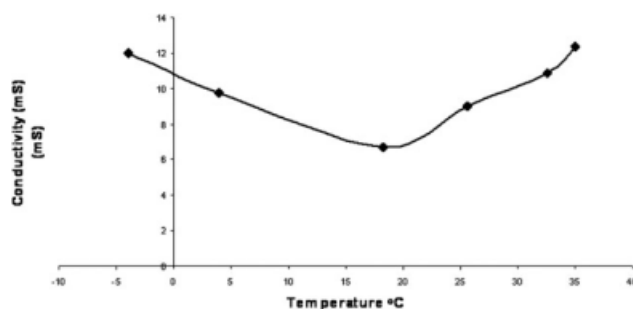
neglected, and the equation resembles a Boltzman distribution, decaying exponentially with increasing energy and increasing exponentially with temperature. However, conductivity of metallic solids decreases with increasing temperature even though more electrons are excited into empty orbitals with temperature.[13,18] The reason for this was explained in the Theory section.

First, the system has incomplete bands (half-filled or less) and behaves as a conductor. As the temperature increases, electrons populate the empty orbitals of the upper band. They are now mobile and the solid is an electric conductor, and conductivity decreases with temperature due to the reason given in the theory section.

Electrical conductivity depends on the number of electrons that are promoted across the gap. As temperature increases, jump frequency and kinetic energy increase. At one temperature electrons reach the energy to overcome the collision factor with the atoms that cause them to be ineffective and start filling an empty conductance band. If the gap is small, the number increases as the temperature is raised; as a result, conductivity increases. This explains the conductivity increase after 18.2°C; at that temperature the conduction band starts to be filled.

The behavior of conductivity change with temperature, as shown in Figure 18, has a potential importance that can be used in industry. Future work will study the conductivity changes of other polymers with temperature change to find out if they show the same kind of behavior as observed in Figure 18.

In this work, a new method was developed to obtain conductive polymers by photochemical initiation. The novel methodology is much faster and less expensive than other processes used to obtain these materials. By adding selective dopants, the conductivities of the polymeric materials were increased by a factor approaching 2500 (with lithium perchlorate) and about 60 (with iodine). Also, a method was developed to follow the kinetics of the reactions by using conductimetric techniques.

The results have the potential to benefit the technological development and applications of these conductive polymers in solid-state devices, such as rectifiers, LEDs, sensors, laser diodes, and transistors. The results shown in Figure 18, in particular, indicate that these polymers can potentially be used to control the current in electrical devices via temperature changes (novel thermal switch technology) instead of using high voltages. These polymers can also be used in thermocouples to replace metals that are more easily corroded and more expensive. The application of these methods to electrical instruments is a promising new technology.

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