Spectrofluorometric Analysis and Electrical Conductivities of Styrene and Methyl Methacrylate Polymers

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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 molecular weights, optimum irradiation times were determined. The luminescence properties of polymers have been found to be useful for their identification. The use of luminescence spectroscopy as an analytical technique for polymer identification involves the measurement of fluorescence emission spectrum, which is obtained by exciting the polymer with UV-radiation. Fluorescence emission spectra of polystyrene (PS) and polymethyl methacrylate (PMMA) samples were taken at room temperature at excitation wavelengths at 290 nm and 292 nm, respectively. PPMA was prepared with different molecular weights, and the intensity of the fluorescence emission was correlated with polymer chain length. Conductivity versus molecular weight relation was established for each polymer. The plots obtained between conductivities and molecular weights can be used as a calibration curve. From the plot of emission intensity against polymer molecular weights, the molecular weights of unknown polymeric samples can be determined. The most efficient irradiation times were determined by using conductivity versus irradiation time plots. Conductivity versus temperature change of the polymeric samples at different temperatures was determined. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 1469–1476, 2011

Key words: conductivity; UV-irradiation; spectrofluorometry; styrene; methyl methacrylate

INTRODUCTION

Luminescence properties of polymers can be correlated with their conductivities since these properties of polymers are used for their identification.[1,2] Conductive polymers are of great deal of interest because of their applications in electrical devices,[3] gas separation membranes,[4] rechargeable batteries,[5] and enzyme immobilization.[6,7] Their conductivity can be improved by addition of dopants[8–10] and by developing their poor mechanical and physical properties with chemical and electrochemical blending.[11,12] Solvents used for the polymerization process also have importance in increasing the conductivites.[13]

Although the mechanism of conduction remains incompletely understood, it is believed that certain structural features influence the level of conductivity; they include: doping (by additional groups rearranging double bonds into a conjugated form[14]), morphology (configurational and conformational factors;[15] e. g., conductivity of *trans*-polyacetylene is greater than its *cis* form),[16,17] and delocalization (charge transferred through pendant groups). Doping may also affect the rearrangement of the double bonds of nonconjugated polymers (e. g. polyisoprene) into a conjugated conducting mode.[14] The dopant forms a charge-transfer complex with the polymer that is believed to give rise to highly delocalized cation radicals or anion radicals, depending on whether the dopant is an electron acceptor or a donor, respectively.[18] According to one theory of polyacetylene conductivity, the delocalized regions are called solitons and they extend about 15 bond lengths. The energy gain arises from lengthening of double bonds and shortening of single bonds apparently outweighs the stabilization arising from delocalization.[18] Conduction is believed to involve movement of electrons intramolecularly and intermolecularly via the positive or negative solitons.

There is no previous study reported to show the correlations between the conductivity values and molecular weights of polymers. Only, conductivity change with irradiation time (which is directly related to molecular weight) was studied for ethyleneglycoldimethacrylate (PEGDM) polymer in a previous work.[10] However, fluorescence intensity change with molecular weight is given for some polymers such as polystyrene.[19–21] Therefore, polystyrene is one of the polymers chosen to correlate the conductivity, molecular weight, and fluorescence intensity relationships. The intensity of fluorescence and phosphorescence emissions from various synthetic polymers has been related to polymer chain length.[20,21] In general, the intensity of the fluorescence emission from a polymer decreases with an increase in its molecular weight.[20,21]

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An extended conjugated system is usually necessary for backbone conductivity; however, charge may be transferred in some cases through pendant groups such as poly-N-vinyl carbazole.[22] Electrical conductivities of ethylvinyl ketone (EVK) and methylvinyl ketone (MVK) polymers were determined also in our earlier study.[9] Previously, the reaction of polyalkylvinyl ketones with active chloride such as phosphoryl chloride ($O=PCl_3$ used as a dopant) to obtain the corresponding polyacylacetylenes and the changes in the conductivities have been described.[23–25] Through a process of hydrogen atom abstraction of phosphoryl chloride from the monomer molecule, the medium becomes acidic and a double bond is transferred to the main chain and conjugation, which is responsible for the increase in conductivity, is maintained.[9]

Semiconductors are used in electronic devices, such as transistors, light emitting diodes (LEDs), and laser diodes. A CD player 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. A metalloid is a semi conductive element which has low conductivity at room temperature, but increases as the temperature increases. Metals are good electrical conductors but their conductivity decreases with temperature. The conductivities of the polymers in this work were determined at different temperatures. Conductive polymers have extended delocalized bonds when charge carriers (from the addition or removal of electrons) are introduced into conduction or valence bonds, the electrical conductivity increases dramatically. Delocalization can be accomplished by forming a conjugated backbone of continuous overlapping orbitals, for example alternating single or double C—C bonds, which leaves a continuous path of overlapping which leaves a continuous path of overlapping p-orbitals. This continuous string of orbitals creates degeneracy in the frontier molecular orbitals, which leads to the filled (electron containing) and unfilled (valence and conduction) bonds, respectively, that defines a semi conductor. A conductive polymer does not become highly conductive until an electron is removed from the valence band (p-doping) or added to the conduction band (n-doping, which is far less common). Doping (p or n) generates charge carriers which move in an electric field. Positive charges (holes) or negative charges (electrons) move to opposite electrodes. This movement of charge is what is actually responsible for electrical conductivity.[26] Increasing conductivity values with molecular weight can be explained by increasing conjugation on the backbone structure.

In this study, the effect of molecular weights and irradiation times on the conductivity was studied for the photochemically prepared polymeric samples.

A relationship between conductivity and molecular weight was established for the first time.

EXPERIMENTAL MATERIALS AND METHODS

Materials

Styrene was obtained from Sigma-Aldrich Chemical Company (Milwaukee, WI). The 4-TBC inhibitor was removed by washing three times with 10% NaOH solution, then, several times with deionized water, dried over anhydrous sodium sulfate and distilled at 30 torr between 32 and 35°C. Styrene samples with different molecular weights were supplied as standards from Sigma-Aldrich Chemical Company (Milwaukee, WI) and used directly for conductivity measurements.

Methyl methacrylate was a product of Sigma-Aldrich Chemical Company (Milwaukee, WI) and inhibited with 10 ppm MEHQ. The inhibitor was removed by washing with 10% NaOH solution and deionized water, dried over anhydrous sodium sulfate, and distilled at 30 torr between 40 and 43°C.

2–2′-Azobis isobutyronitrile (AIBN) catalyst (Polyscience, Warrington, PA) was purified from methanol before use as follows: A solution was prepared in methanol and cooled; the crystals were collected on a fritted glass, filtered, and dried under vacuum at room temperature.

All solvents were reagent grade and used without further purification.

For UV-irradiation, a Entela Model UV GL-58 Mineral light lamp, multiband UV-254/ 366 nm, 115 V, 60 Hz, 0.16 Amp mercury UV-lamp (Entela, Upland, CA) was used with a maximum wavelength of 254 nm.

Molecular weights were determined at 25°C by using Ubbelohde viscometer.

All samples were degassed at 10^{-5} mm Hg Pressure and irradiated in quartz tubes of 12 cm height and 2.8 cm diameter. A high vacuum system was used for evacuating monomer solutions.

For conductivity measurements of the polymer solutions, an Omega CDB-420 conductivity meter was used (Omega Engineering, Stanford, CT). A constant temperature bath with thermo-regulator circular combination (Fisher Scientific, Pittsburgh, PA, Model 70, Bioamp Immersion Circulator) was used to study the temperature effect on the conductivity of the polymers.

For spectrofluorometric analysis, a Fluoromax-4 spectrofluorometer (Horiba Jobin Yvon, Edison, NJ) was used.

Preparation of polymers

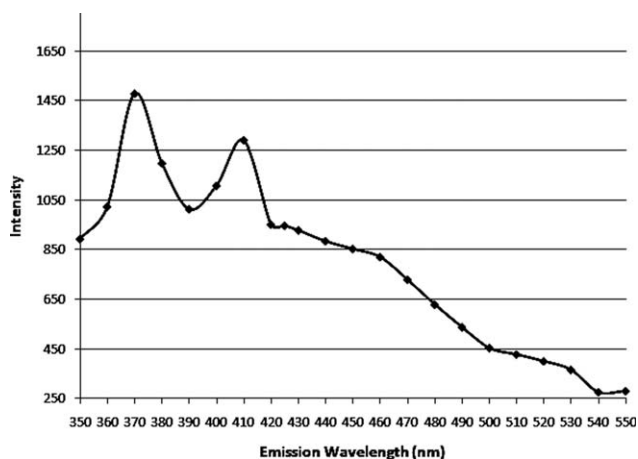Both styrene and methyl methacrylate polymers were prepared by applying the same method. About

Figure 1 Fluorescence intensity versus emission wavelength of PS. Molecular weight $= 0.5 \times 10^5$, 0.125 g PS in 25 mL chloroform. Excitation wavelength: 290 nm.

Figure 3 Fluorescence intensity versus emission wavelength of PS. Molecular weight $= 8.6 \times 10^5$, 0.125 g PS in 25 mL chloroform. Excitation wavelength: 290 nm.

5 mL of distilled monomer and 1% AIBN initiator (0.05 g) were put in a quartz tube. The tube was sealed with rubber septum and connected to the manifold of the vacuum system with syringe needle and degassed to 10^{-4}–10^{-5} mmHg pressure for 5–6 h. The tube was then irradiated by UV rays at 254 nm for different time intervals, then, the resultant polymer was dissolved in chloroform and precipitated in methanol, filtered and dried at room temperature in a vacuum oven to a constant weight.

For spectrofluorometric analysis of PS, 0.125 g polymer samples were dissolved in 25 mL chloroform, and excitation wavelength was taken as 290 nm. For spectrofluorometric analysis of PMMA, 0.125 g polymer samples were dissolved in 25 mL chloroform, and excitation wavelength was taken as 292 nm.

THEORY

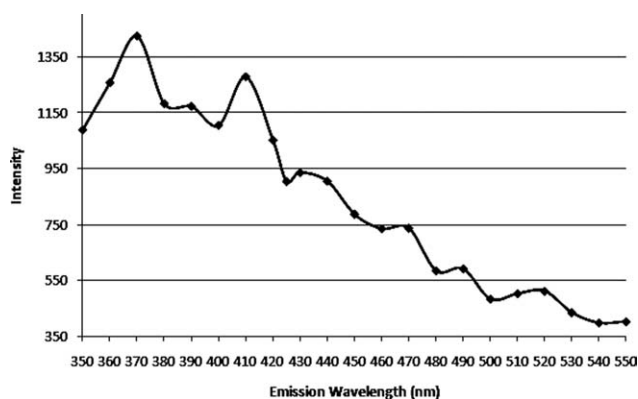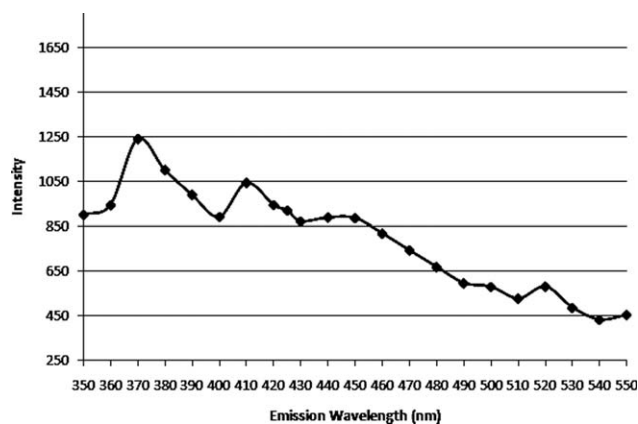The purpose of the present study is to prepare styrene and methyl methacrylate polymers by using photochemical methods (UV irradiation) and to see the effect of irradiation times on molecular weights and conductivities by using spectrofluorometric analysis.

To correlate the relation between the molecular weights and conductivities, determine first the optimum irradiation time and obtain the emission spectra of each polymer by using a spectrofluorometer. To find out the relationship between conductivity and molecular weight and between irradiation times and molecular weight, the molecular weights must first be determined by using viscosity measurements, then, the conductivities are determined at different temperatures. To study the fluorescence intensity change of both polymers with different molecular weights, first the emission spectra are taken and the intensity change of main peaks for these polymers are determined.

In a solid state electronic device, p-type semiconductor is joined to an n-type semiconductor. It can function as a rectifier which allows current to flow in one direction only. Non conducting p-n junctions
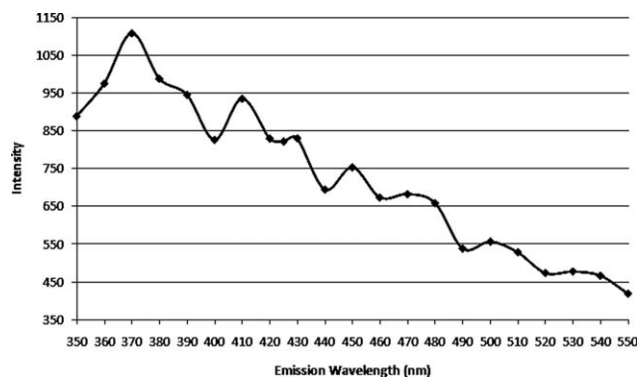

Figure 2 Fluorescence intensity versus emission wavelength of PS. Molecular weight $= 1.6 \times 10^5$, 0.125 g PS in 25 mL chloroform. Excitation wavelength: 290 nm.

Figure 4 Fluorescence intensity versus emission wavelength of PS. Molecular weight $= 20 \times 10^5$, 0.125 g PS in 25 mL chloroform. Excitation wavelength: 290 nm.

TABLE I
Emission Intensity Change of PS at Different Molecular Weights

M_w of PS (10^5)	Intensity of peak at 370 nm	Intensity of peak at 410 nm
0.51	1477	1355
1.60	1425	1279
8.60	1238	1042
20.00	1111	937

Excitation wavelength: 290 nm.

TABLE II
Conductivity Change of PS with Molecular Weight at 25°C

Polystyrene molecular weight ($M_w \times 10^5$)	Conductivity (μS) 10^{-2}
0.51	5.1
1.60	5.8
8.60	7.8
20.00	9.1

of semiconductors are used as transistors. Computer chips have microscopic circuits integrated with millions of transistors. This work shows that conducting polymers can be used to control the current in electrical devices by using temperature change instead of using high voltages of electricity.

Conductors have half filled orbitals which allow maximum in and out transportation. The increase in temperature causes thermal motion of the atoms, thus causing collisions between moving electrons and atoms. Electrons scatter out of their paths and become less effective in transporting charge. As a result, conductivity decreases with temperature.

Although semiconductors have filled valence bonds, the energy gap is much smaller between the valence band and conduction bands. Thermal excitation causes some electrons to jump into the conduction band producing a few electrons in the upper band and a few holes in the lower band, thereby increasing conductivity with temperature. Therefore, for semiconductors there are two methods to increase the conductivity either by increasing the temperature or by increasing the number of charge carriers by incorporating foreign atoms (dopants) to function as a donor band or acceptor band. Even though semiconductors contain full valence bands, with dopants electrons are either removed from the valence band or added to the conduction band, in both cases as a result of increasing mobility of electrons, conductivity increases.
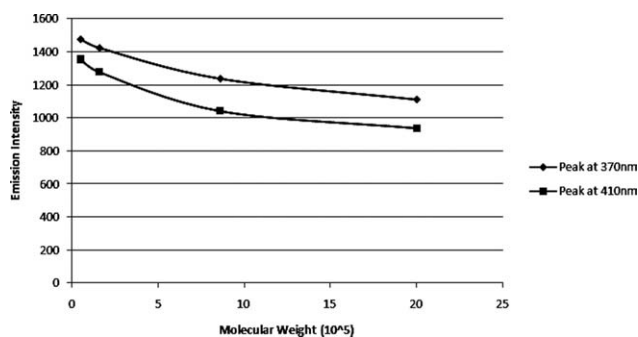
Molecular weights were determined by using Mark-Houwink-Sakurada equation:[18]

$$[\eta] = K M^{\alpha} \tag{1}$$

where $[\eta]$ is the intrinsic viscosity, and K and α are empirical constants determined experimentally.

By using the Ubbelohde viscometer, flow times, η_{sp} and $\frac{\eta_{sp}}{c}$ values can be calculated. A plot of $\frac{\eta_{sp}}{c}$ versus C (g/100ml) gives $[\eta_{int}]$ viscosity values at the y intercept, and by using eq. (1), molecular weights are calculated.

EXPERIMENTAL RESULTS AND DISCUSSION

Spectrofluorometric analysis of PS

About 0.125 g of the prepared polymer samples at different molecular weights were dissolved in 25 mL chloroform and spectra were taken. Excitation wavelength was taken as 290 nm. Figures 1–4 show spectra of four different samples of PS at molecular weights 0.51×10^5, 1.6×10^5, 8.6×10^5, and 20×10^5, respectively. They all gave two main emission peaks at 370 nm and 410 nm. Table I shows the intensity of emission peaks (370 and 410 nm) for the corresponding molecular weights of PS samples.

When emission intensity values for each peak were plotted against corresponding wavelength, it was observed that both peak heights decrease with
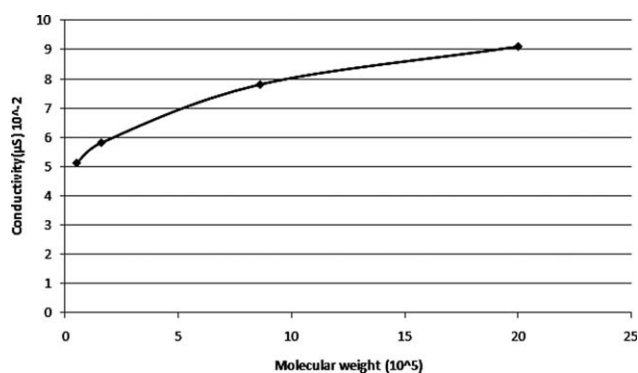
Figure 5 Fluorescence intensity change of PS with molecular weight.

Figure 6 Conductivity change of PS with molecular weight (at 25°C).

TABLE III
Conductivity (µS) Change of Different Molecular Weights of PS with Temperature

Temperature (°C)	$M_w = 0.51 \times 10^5$	$M_w = 1.60 \times 10^5$	$M_w = 8.60 \times 10^5$	$M_w = 20.00 \times 10^5$
0	0.129	0.138	0.160	0.16
5	0.078	0.089	0.101	0.114
10	0.041	0.051	0.070	0.07
15	0.021	0.028	0.035	0.045
20	0.029	0.039	0.049	0.058
25	0.051	0.058	0.078	0.091
30	0.089	0.130	0.13	0.148

the increasing molecular weight as shown in Figure 5. However, from this plot, it can be observed that by finding the emission intensity of a polymeric sample (whose molecular weight is not known), at one of these wavelengths, it is possible to determine the exact molecular weight.

Conductivity measurement of PS

For conductivity measurements, about 0.125 g of PS (P.S) samples of different molecular weights were dissolved in 25 mL chloroform and the conductivity of each determined at 25°C in a constant temperature bath. Table II shows these results. Figure 6 shows the conductivity change of PS samples with different molecular weights at 25°C. It was observed that conductivity increases directly with the increase of molecular weight, giving almost a linear relationship.

To study the effect of temperatures on conductivity, the PS samples with different molecular weights were put in constant temperature bath, and conductivities were measured at different temperatures. Table III shows conductivity values of different molecular weights of PS samples at different temperatures. Figure 7 shows the plots of conductivity versus temperature change of PS at differ-
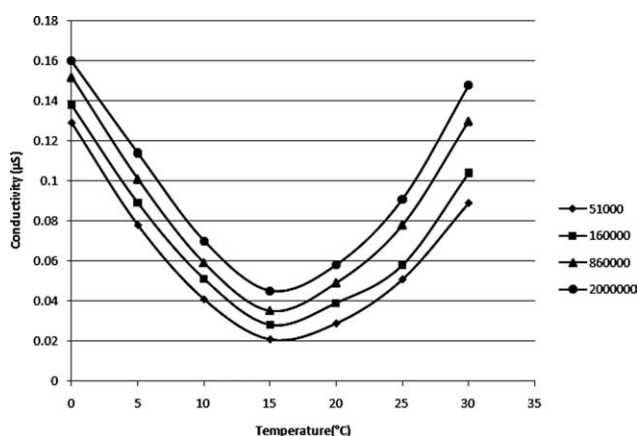
ent molecular weights. They all showed a minimum around 15°C. These curves are similar to the one obtained in previous studies for the ethyleneglycol dimethacrylate (EGDMA) polymer.[10] This figure indicates that these polymers can potentially be used to control the current in electrical devices via temperature change (novel thermal switch technology) instead of using high voltages. These polymers can also be used in thermocouples to replace metals.

Spectrofluorometric analysis of polymethyl methacrylate

Methyl methacrylate polymers (PMMA) were prepared at different irradiation times between 1 and 5 h. About 0.125 g of polymer samples were dissolved in chloroform and emission-spectra were taken at excitation wavelength 292 nm. Figure 8 shows the spectrum of these samples prepared at 1–5 h irradiation times. All samples gave two main emission peaks at 375 nm and 425 nm. Figure 8 shows all the results together. Table IV shows the spectrofluorometric analysis results of polymethyl methacrylate samples and indicate the changes on both peaks for the polymers obtained by different irradiation times. Figure 9 shows the plot of emission intensity versus irradiation times for both peaks at 375 and 425 nm.
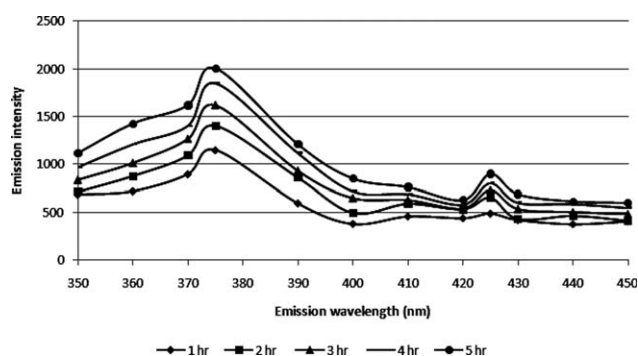

Figure 7 Conductivity versus temperature change of PS at different molecular weights.

Figure 8 Spectrofluorometric analysis of PMMA obtained at different irradiation times. Excitation wavelength: 292 nm.

TABLE IV
Spectrofluorometric Analysis of PMMA

Irradiation time (h)	Intensity of peak at 375 nm	Intensity of peak at 425 nm
1	1150	484
2	1401	590
3	1619	732
4	1848	804
5	2003	898

PMMA (0.125 g) in 25 mL chloroform.
Excitation wavelength = 292 nm.

Figure 9 Fluorescence emission intensity of PMMA versus irradiation time. Excitation wavelength: 292 nm.

Conductivity measurment of PMMA

For conductivity measurement, each polymer (0.125 g) was dissolved in 25 mL chloroform and conductivities at different temperatures were determined in a constant temperature bath. Table V shows the results. Figure 10 shows the conductivity versus temperature change of PMMA samples obtained by 1, 2, 3, 4, and 5 h of irradiation times, respectively. They all show the same kind of plot where conductivity decreases with temperature first and they all give the same minimum value at 17.0°C. This figure is similar to the one obtained for PS in Figure 7, which gave a minimum value at around 15°C. Figure 11 shows a plot for the conductivities of PMMA samples at 25°C prepared at different irradiation times. Four hours of irradiation gives the maximum conductivity.

Molecular weight determination of PMMA samples

The molecular weights of PMMA samples were determined at 25°C in a constant temperature bath. About 0.125 g of sample was dissolved in 25 mL of acetone and flow times were determined by using Ubbelohde viscometer. Viscosity determinations are very important in the study of polymers. By the use of simple viscosity measurements, an average molecular weight can be determined for the polymer and certain information can be obtained afterwards as to the general form and structure of macromolecules in solution.
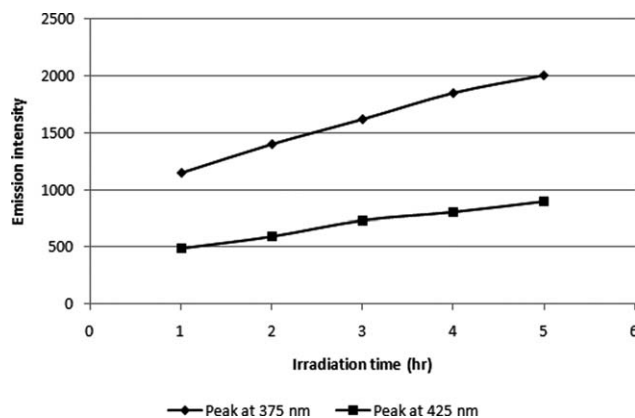
The viscosity of a polymer solution, at constant temperature depends on the concentration of solute, its molecular weight and the shape of solute molecule. For PMMA samples at 25°C, the K and α constants of 6.76×10^{-5} and 0.71, respectively (acetone as solvent) were taken from a table.[27]

The η_{sp}/C values were drawn for each polymer versus concentration C (g/100 mL) and $[\eta_{int}]$ values were calculated from the y intercept. Table VI shows all the results. Table VII shows the relation between molecular weights and conductivity values measured at 25°C. Figure 12 shows the molecular weight versus irradiation time plot for PMMA, which gives exactly the same shape as it was obtained in Figure 11, conductivity versus irradiation time plot. It indicates a direct relationship between conductivity and molecular weights. Figure 13 shows this linear relation, indicating that as molecular weight increases conductivity of PMMA samples also increases. This result is identical to PS samples as shown in Figure 6. Figures 11 and 12 indicate that 4 h of irradiation give maximum conductivity and molecular weight. Most probably, after 4 h of irradiation, degradation starts in the backbone structure which decreases the molecular weight, and consequently decreases the conjugation.

TABLE V
Conductivity (µS) Change of PMMA Samples (Prepared at Different Irradiation Times) with Temperature

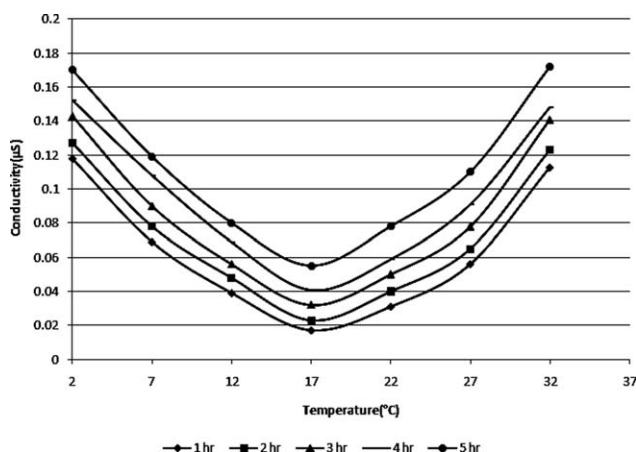| Irradiation time (h)	Irradiation temperature (°C)						
	2	7	12	17	22	27	32
1	0.118	0.069	0.039	0.017	0.031	0.056	0.113
2	0.127	0.078	0.048	0.023	0.040	0.065	0.123
3	0.143	0.090	0.056	0.032	0.050	0.078	0.141
4	0.152	0.108	0.069	0.041	0.059	0.091	0.148
5	0.170	0.119	0.080	0.055	0.078	0.11	0.172

Figure 10 Conductivity versus temperature change of PMMA at different irradiation times.

In this work, a new method was applied to obtain conductive polymers by photochemical initiation. The new methodology is much faster and less expensive than other processes used to obtain these materials. The effect of molecular weight on conductivity is observed for the polymers obtained at different irradiation times. Fluorescence emission intensity peaks were determined for different wavelengths using a spectrofluorometer, for both polymers. For PS, peak intensities at two different wavelengths decreased by increasing molecular weights (Fig. 5). However, for PMMA it shows linear, increasing values of intensities with irradiation times (or molecular weights) (Fig. 9). When conductivities were determined both for PS and PMMA, conductivity values increased by increasing molecular weights for both polymers and showed a linear relationship (Figs. 6 and 13). Both PS and PMMA gave the same shape of plots when conductivity values were drawn versus temperatures (Figs. 7 and 10, respectively); PS shows a minimum at 15.0°C while the minimum for PMMA is at 17.0°C. These plots show first a decrease in conductivity with increasing
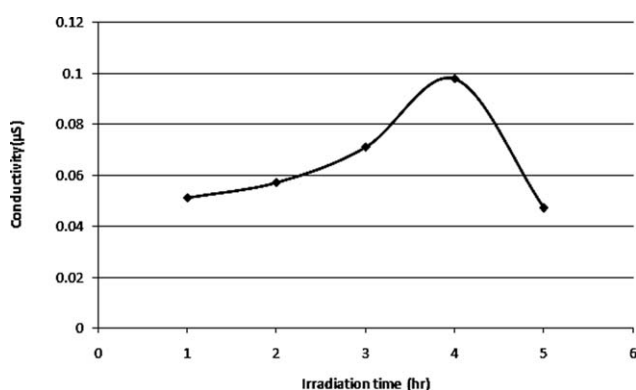
temperature. Then after certain temperature, they show an increase with further increase in temperature, indicating that conducting polymer first acts as a conductor, then, it becomes a semi-conductor. After 15°C or 17°C, sharp decreases in declining curves of conductivity versus temperature for both PS and PMMA indicate the conformation changes owing to either crankshaft-type motion about the chain or owing to rotation of methyl groups. Thermal energy is converted into electronic excitation after these points.

The results have the potential to benefit the technological development and applications of these conductive polymers in solid state devices such as sensors, laser diodes, transistors, and rectifiers. The results shown in Figures 7 and 10, in particular,
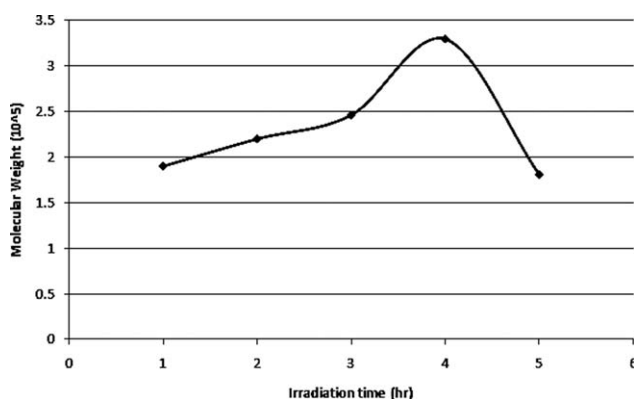
TABLE VI
Irradiation Time versus Molecular Weight of PMMA

Irradiation time (h)	η_{int}	Molecular weight (10^5)
1	0.378	1.9000
2	0.420	2.2010
3	0.455	2.4640
4	0.560	3.3010
5	0.365	1.8065

Excitation wavelength: 292 nm.

TABLE VII
Conductivity Change of PMMA of Different Molecular Weights at Different Irradiation Times (at 25°C)

Irradiation time (h)	Molecular weight (10^5)	Conductivity (µS)
1	1.9000	0.051
2	2.2010	0.057
3	2.4640	0.071
4	3.3010	0.098
5	1.8065	0.047

0.125 g in 25 mL chloroform.

Figure 11 Conductivity versus irradiation time of PMMA.

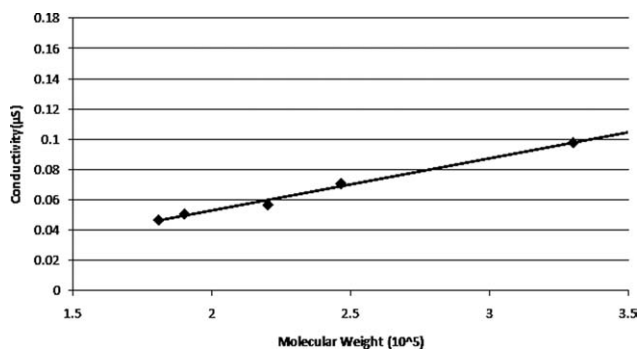**Figure 12** Molecular weight versus irradiation time of PMMA.

Figure 13 Conductivity versus molecular weight of PMMA.

indicate that these polymers can be used to control the current in electrical devices via temperature changes (thermal switch technology) instead of using high voltages.

Conductivity versus irradiation times plots for PMMA samples indicate that 4 h of irradiation gives the maximum conductivity (Fig. 11). When molecular weights of PMMA samples were plotted versus irradiation time (Fig. 12), it gives exactly the same shape of curve with 4 h of irradiation giving maximum molecular weight. Therefore, when conductivity values were drawn versus molecular weight, a linear relationship was obtained, where conductivity increases directly with the molecular weight (Fig. 13). This plot can be used as a reference for determining molecular weights of PMMA samples by using their measured conductivity values. Conductivity versus molecular weight plot for PS (Fig. 6) also gives a linear relationship, as was observed with PMMA. This plot in future can also be used as a reference curve for molecular weight determination of PS samples by directly measuring conductivities. Increasing the conductivity values, both for PS and PMMA, with molecular weight can be explained by increasing conjugation on the backbone structure of the polymer chain.

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