Spectrofluorometric Analysis and Electrical Conductivities of Styrene and Methylmethacrylate Polymers by Adding Symmetrical Polymethine Dyes

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ABSTRACT: To see the effect of conjugation on molecular weight and conductivity, three symmetrical polymethine dyes are added in polymers either before or after polymerization. Dyes have conjugated bonds between nitrogen atoms. Among three dyes, it was observed that as conjugation increases, the conductivity also increases. Previous study with polyethylvinylketone and polymethylvinylketone support the idea that increased conjugation will increase the molecular weight and conductivity. For these polymers also, the dopant, phosphorylchloride increased the conductivities due to the double bond being transferred to the main chain and increased conjugation. The same method developed in this work can be applied to methyl methacrylate and styrene polymers to see the relationship between molecular weight, conductivity, and fluorescence intensity. When dyes were added to methylmethacrylate and styrene monomers before polymerization, much higher conductivities were obtained. Conductivity values are directly proportional to the irradiation times and molecular weights. Four-hour irradiation time results in a maximum molecular weight of 6.4×10^5 and a maximum conductivity of 2.25 µS for MMA polymers. Spectrofluorometric analysis of methyl methacrylate polymers indicates that as molecular weight of the dyes increases, the emission intensities at 375 and 425 nm also increases. In the same way, increased molecular weight of polymer also results higher emission intensities. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 2278–2286, 2011

Key words: fluorescence; conducting polymers; conjugated polymers; irradiation; polystyrene

INTRODUCTION

The intensity of fluorescence and phosphorescence emission from various synthetic polymers has been related to polymer chain length (molecular weight) with varying success.[1,2] Increased conjugation in the molecular structure will increase the molecular weight and conductivity.[3] Luminescence properties of polymers can be correlated with their conductivities, and these properties used for their identifications. Conductive polymers are of great interest because of their applications in electrical devices,[4] gas separation membranes,[5] rechargeable batteries,[6] and enzyme immobilization.[7,8] Their conductivities can be improved by addition of dopants[3,9,10] and by developing their poor mechanical and physical properties with chemical and electrochemical blending.[11,12] There is no previous study reported to show the correlation between conductivity values and molecular weights of polymers. Only, conductivity change with irradiation time (which is directly related to molecular weight) was reported for ethylene glycol dimethacrylate polymer in one of our previous studies.[10] However, fluorescence intensity change with molecular weights has been determined for some polymers, such as polystyrene.[12,13] Therefore, in this work, polystyrene is one of the polymer chosen to correlate the relationship among conductivity, molecular weight, and fluorescence intensity. An extended conjugated system is usually necessary for backbone conductivity; however, charge may be transferred in some cases through a pendant group such as poly(N-vinyl carbazole).[14] Also, for ethyl vinyl ketone and methyl vinyl ketone polymers, dopant ($O=PCl_3$) additions increased the conductivity.[3,15–17]

By hydrogen atom obstruction of phosphoryl chloride ($O=PCl_3$) from the monomer molecule, the medium becomes acidic and a double bond is transferred to main chain and conjugation, which is responsible for the increase in conductivity, is maintained, as it was explained by equations given in our previous work.[3]

The intensity of fluorescence and phosphorescence emission from various synthetic polymers has been related to polymer chain length (molecular weight) with varying success.[1,2] To support the idea that

conjugation is responsible for increasing molecular weight and conductivity, in this study, three symmetrical polymethine dyes were added to polymers. Dyes have conjugated bonds between nitrogen atoms, and it has been found that with the increasing molecular weight of the dyes, the conjugation increases between nitrogen atoms and thus conductivity of the polymer to which they are added.

Conductive polymers have extended delocalized bonds when charge carriers (from 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 (alternating single or double C=C bonds), 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 semiconductor. It is not until an electron is removed from the valence bond (p-doping) or added to the conduction band (n-doping) that a conducting polymer becomes highly conductive. Doping generates charge carriers, which move in an electric field. Positive charges (holes) or negative charges (extra electrons) move to opposite directions. This movement of charge is what is responsible for electrical conductivities. The increasing conductivity with molecular weight can also be explained by increasing conjugation in the backbone structure.

EXPERIMENTAL

Styrene was obtained from Sigma Aldrich Chemical Company. The 4-tertiary-butylcatechol (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 and used directly for conductivity measurements.

Methyl methacrylate was a product of Sigma Aldrich Chemical Company and inhibited with 10 ppm hydroquinone monomethyl ether (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 was a product of Polyscience and 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.

Three different dyes: 1,1′-diethyl-2,2′-dicarbocyanine iodide (MW = 506.43), 1,1′-diethyl carbocyanine iodide (MW = 480.39), and 1,1′-diethyl 2,2′-cyanine iodide (MW = 454.36) were obtained from Sigma Aldrich Chemical Company and used directly.

All solvents were reagent grade and used without further purification.

For UV-irradiation, a Entela Model UV 6L-58 Mineral light lamp, multiband UV-254/366 nm, 115 V, 60 Hz, and 0.16 amp mercury UV-lamp was used with a maximum wavelength of 254 nm.

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

All samples were degassed at 10^{-5} mmHg 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. A constant temperature bath with thermoregulator circular combination (Fisher-scientific, Model 70, Bioamp immersion circulator) was used to study the temperature effect on the conductivity of the polymers.

Conductivities were measured in solution. For this purpose, the probe of the conductivity meter was inserted into the solution and kept in a constant temperature bath. The probe read both conductivity and temperature simultaneously. When the temperature reached an adjusted constant value, the conductivity reading was recorded.

Conductivities were all measured in solution rather than in the solid state as films because casting polymer samples as film is a difficult and time-consuming procedure. Also, the casting method is applied to polymers with much higher conductivities. In the solid state, the conductivity of polymer films are directly measured with the van der Pauw (four-probe) method or by coating a fabric surface with polymer, then using the four-probe method.[3,9]

For spectrofluorometric analysis, a spectrofluorometer (Jobin Yvon Horiba Fluoromax-4) was used. For chain-length determination of the dye samples, the maximum absorption wavelengths were determined with a Milton Roy Spectronic 20 spectrophotometer.

RESULTS

Spectrofluorometric analysis of polystyrene

About 0.125 g amount of the prepared polymer samples at different molecular weights were dissolved in 25-mL chloroform, and fluorescence spectra were taken at excitation wavelength 290 nm. Four different samples of polystyrene with molecular weights between 0.51×10^5, and 20×10^5, respectively, were used. All samples gave two main emission peaks at

Figure 1 Structures of the three dyes.

a) 1,1'-diethyl-2,2'-cyanine iodide
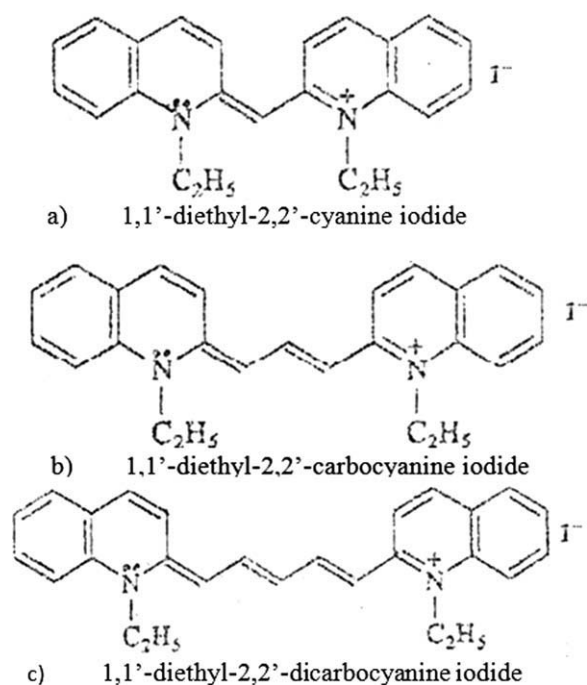
b) 1,1'-diethyl-2,2'-carbocyanine iodide

c) 1,1'-diethyl-2,2'-dicarbocyanine iodide

370 and 410 nm. In a previous study, the intensity of emission peaks for the corresponding molecular weights of polystyrene samples were determined.[18,19] It was observed that both peak heights decrease with the increasing molecular weight of polystyrene (PS).

To see the effect of increasing conjugation, some symmetrical polymethine dyes were added to polystyrene samples. In these cyanine dyes, the polymethine chain forms a conjugated chain extending from the nitrogen atom on one end of the molecule to the opposite nitrogen atom plus one carbon atom (on the ethyl group), as shown in Figure 1.

About 0.125-g PS samples were dissolved in 25-mL chloroform, and dyes were added to make a $1.25 \times 10^{-4} M$ concentration in the solution. Polystyrenes
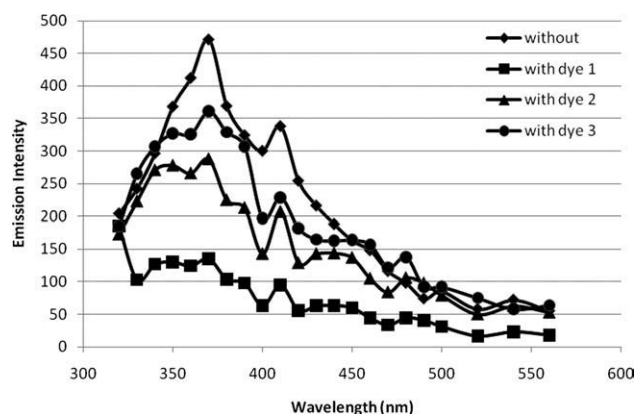

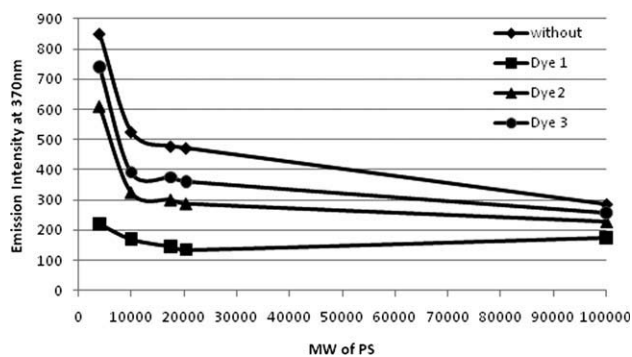Figure 2 Spectrofluorometric analysis of PS (MW = 20,400) with different dyes. Excitation Wavelength: 290 nm

Figure 3 Emission Intensity vs. different MW of PS with dyes at 370 nm. Excitation Wavelength: 290 nm

with molecular weights of 20,400, 17,500, 10,000, and 4000 were studied. Figure 2 shows the spectrofluorometric analysis of different PS samples with a molecular weight of 20,400, incorporated with three different dyes. Figure 3 shows the emission intensity versus molecular weight of different dyes at 370 nm. Table I summarizes the results at 370 nm.

Conductivity measurement of PS samples with dyes

For conductivity measurements, about 0.125-g amounts of PS samples were dissolved in 25-mL chloroform, and conductivities for each were determined at 25°C in a constant temperature bath. Figure 4 shows the conductivity versus molecular weight of PS with different dyes. Dyes were added after polymerization ($1.25 \times 10^{-4} M$). Table II summarizes the conductivity measurements of PS samples at different molecular weights after addition of three different dyes.

Conductivity measurement of polymethyl methacrylate

For conductivity measurement, MMA polymer (0.125 g) was dissolved in 25-mL chloroform, and

TABLE I
Emission Intensity versus Molecular Weight of PS with different dyes at 370 nm

Molecular weight of PS (g/mol)	Emission intensity at 370 nm			
	Without dye	Dye 1	Dye 2	Dye 3
4000	850	220	600	740
10,000	525	170	325	390
17,500	477	146	301	375
20,400	471	135	288	361
100,000	285	175	228	257

Excitation wavelength: 290 nm.
Dye 1 MW = 454.36.
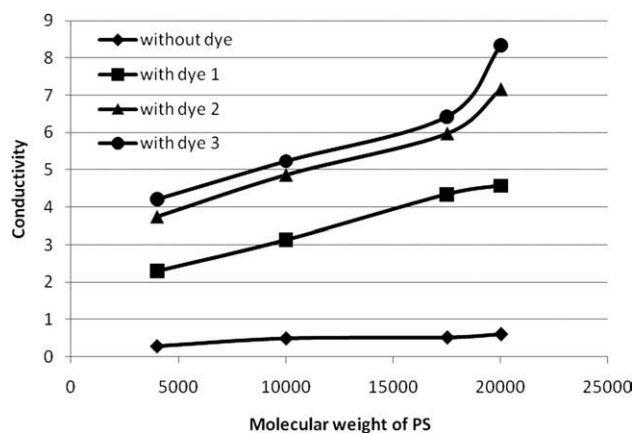Dye 2 MW = 480.39.
Dye 3 MW = 506.43.

Figure 4 Conductivity vs. Molecular weights PS with different dyes (at 25°C).

conductivities at different temperatures were determined in a constant temperature bath.

In this study, different molecular weights of PMMA samples were incorporated with dyes to see the effect of conjugation on conductivities. About 0.125-g polymer samples were dissolved in 25-mL chloroform, and each dye was added to be $1.25 \times 10^{-4}M$ in the solution. Conductivities were measured in a constant temperature bath at 25°C.

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 taken at excitation wavelength 292 nm. All samples gave two main emission peaks at 375 and 425 nm.[18,19] (Fig. 5)

To see the effect of conjugated dyes on PMMA samples, different molecular weights of PMMA samples were incorporated with dyes before and after polymerization (irradiation).

Dyes added after polymerization

About 0.125-g PMMA samples (with molecular weights 33,200, 48,600, and 160,000) were dissolved

TABLE II
Conductivity Change of Different Molecular Weights of PS with Dyes

Molecular weight of PS (g/mol)	Conductivity (µS)			
	Without dye	Dye 1	Dye 2	Dye 3
4000	0.287	2.30	3.75	4.21
10,000	0.494	3.13	4.87	5.23
17,500	0.521	4.34	5.98	6.43
20,000	0.606	4.57	7.17	8.34

Dye 1 MW = 454.36.
Dye 2 MW = 480.39.
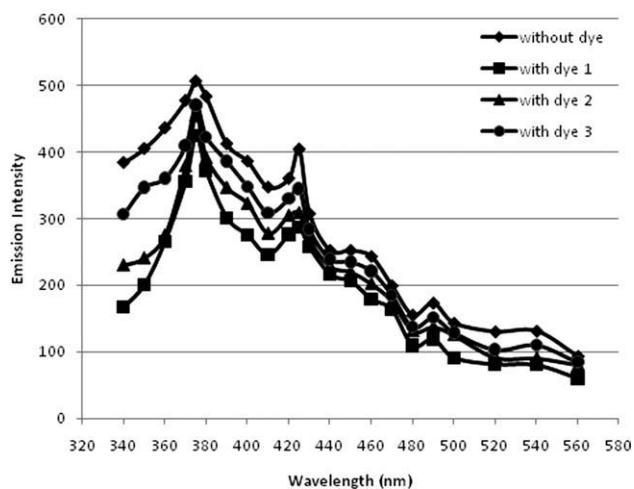Dye 3 MW = 506.43.

Figure 5 Spectrofluorometric Analysis of PMMA (molecular weight: 33200) with different dyes (Dyes added after polymerization). Excitation wavelength: 292 nm.

in chloroform and dyes added to make a concentration of $1.25 \times 10^{-4}M$ in each solution. Figure 5 shows the emission intensity versus wavelength of PMMA with molecular weight 33,200. Figure 6 shows the emission intensity of PMMA samples of different molecular weights with dyes at 375 nm. Conductivities were measured in a constant temperature bath at 25°C. Results for different molecular weights of PMMA samples with three different dyes are given in Figure 7, and the results are summarized in Table III.

Dyes added before polymerization

For this purpose, about 5 mL of distilled monomer and 1% AIBN initiator (0.05 g) and dye were added
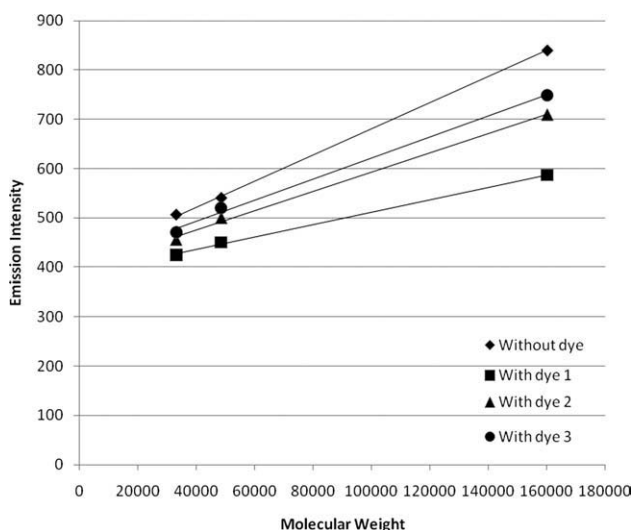

Figure 6 Emission intensity of different molecular weights of PMMA with dyes at 375 nm (Dyes added after polymerization). Excitation wavelength: 292 nm.
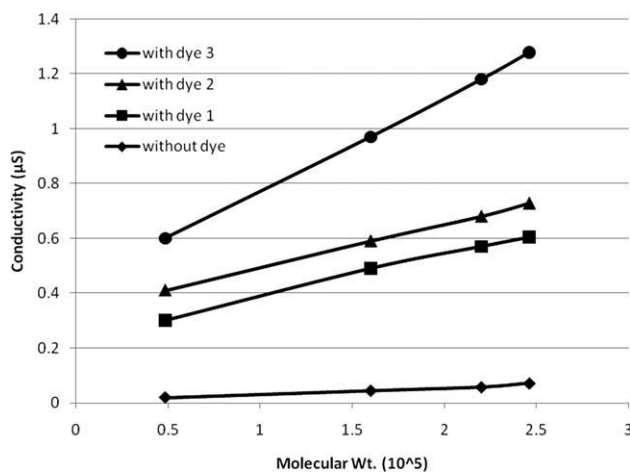
Figure 7 Conductivity change of different molecular weights PMMA with dyes (at 25°C) (Dyes added after polymerization).

in a quartz tube (dyes added to make a concentration of $1.25 \times 10^{-4}M$). The tube was sealed with rubber septum, 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. 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. Emission spectra were taken at an excitation wavelength of 292 nm. Figure 8 shows the spectrofluorometric emission spectra of polymers irradiated for 5 h. Two main peaks were obtained at 375 and 425 nm.

Figure 9 shows the emission intensity change of different molecular weights of PMMA with dyes at 375 nm at different irradiation times.

Molecular weight determination of polymethyl methacrylate

The molecular weights of PMMA samples were determined at 25°C in a constant temperature bath.

TABLE III
Conductivity Change of Different Molecular Weights of PMMA with Dyes at 25°C (Dyes added after polymerization)

Molecular weight of PMMA (10^5) (g/mol)	Conductivity (μS)			
	Without dye	Dye 1	Dye 2	Dye 3
0.49	0.02	0.30	0.41	0.60
1.60	0.04	0.49	0.59	0.97
2.20	0.06	0.57	0.68	1.18
2.46	0.07	0.60	0.73	1.28

Dye 1 MW = 454.36.
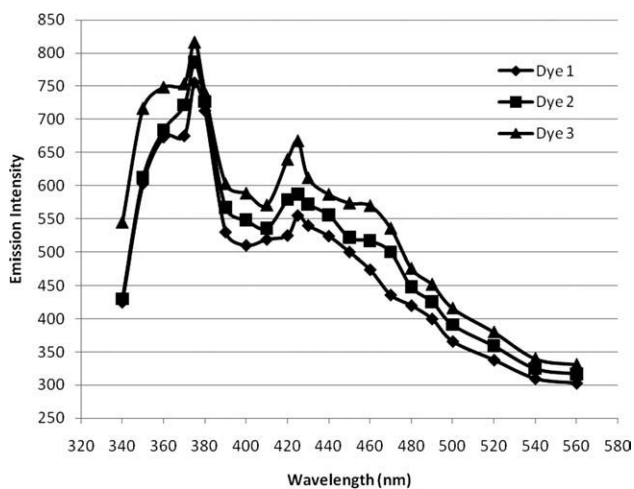Dye 2 MW = 480.39.
Dye 3 MW = 506.43.

Figure 8 Spectrofluorometric analysis of PMMA with different dyes (Dyes added before polymerization, Irradiation time: 5 h).

About 0.125-g amount of samples were dissolved in 25 mL of acetone, and flow times were determined by using a Ubbelohde viscometer. Molecular weight was calculated by using the Mark Houwink equation ($[\eta] = K M^\alpha$ where $[\eta]$ is the intrinsic viscosity, and K and α are empirical constants determined experimentally) with K constant to be 6.76×10^{-5} and α 0.71.[18–20]

Table IV shows the results for the emission intensity change of PMMA with dyes at 375 nm when the MMA and dye samples were polymerized at different irradiation times. Molecular weights for PMMA samples polymerized with different dyes were determined at different irradiation times and listed in Table V.

Figure 10 shows the emission intensity versus molecular weight of PMMA with dyes at 375 nm (dyes added before polymerization), respectively. As the molecular weight of PMMA increases, emission
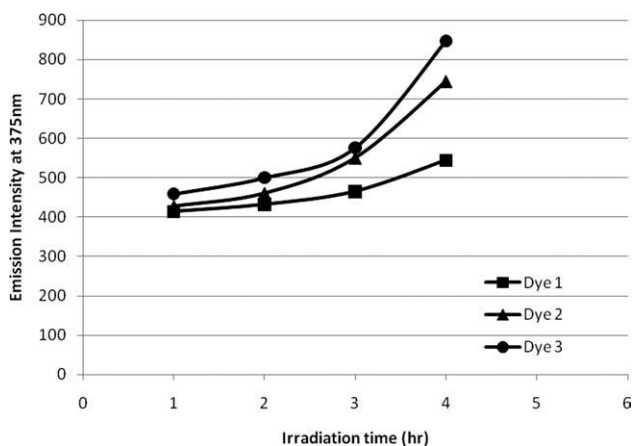

Figure 9 Emission intensity with different molecular weights of PMMA with dyes at 375 nm (Dyes added before polymerization). Excitation wavelength: 292 nm.

TABLE IV
Emission Intensity Change of PMMA with Dyes at Different Irradiation Times at 375 nm

Irradiation time (h)	Emission intensity at 375 nm		
	Dye 1	Dye 2	Dye 3
1.0	414	427	459
2.0	432	460	500
3.0	465	550	576
4.0	544	745	847
5.0	755	786	817

Dye 1 MW = 454.36.
Dye 2 MW = 480.39.
Dye 3 MW = 506.43.

intensities increase. Also, as the molecular weight of the dye increases, intensities increase as well.

Conductivities of the PMMA samples were determined as explained in the experimental section. Table V summarizes the results and change of conductivities for PMMA samples with irradiation time (consequently with different molecular weights) when they were incorporated with Dyes 1, 2, and 3, respectively, before irradiation. Figure 11 shows the conductivity change of different molecular weights of PMMA samples in the presence of different dyes. Dye 1 has a molecular weight of 454.36 g/mol, Dye 2 has a weight of 480.39 g/mol, and Dye 3 has a weight of 506.43 g/mol. Results are summarized in Table VI where conductivities were measured when dyes were added before and after polymerization for different molecular weights of PMMA samples.

For the corresponding molecular weights, without dyes, the conductivities are lowest. When dyes were added before polymerization (irradiation) at each corresponding molecular weight, the conductivity values are higher than when dyes were added after polymerization. Each dye indicates the same result. It is also apparent that for the molecular weight range between 0.49 and 2.46 × 10⁵, as the molecular weight increases, conductivity increases. Figure 12 shows plots of conductivity values versus irradiation time for PMMA samples when dyes were added before polymerization. Figure 12 and Table V indicate that 4 h of irradiation gives maximum conduc-

TABLE V
Molecular Weight versus Conductivity of PMMA at 25°C with Dyes (Dyes added before Polymerization)

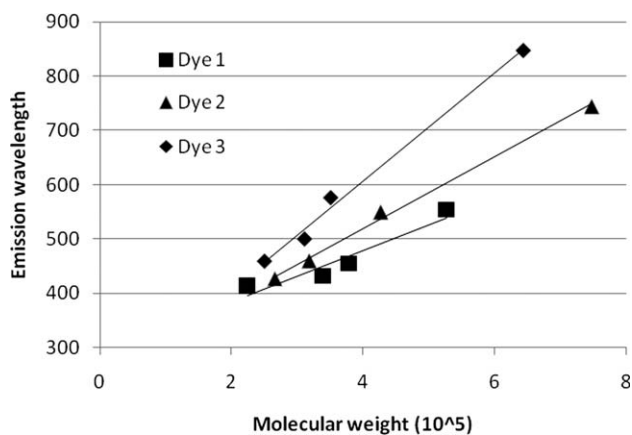| Irradiation time (h)	Molecular weight (10^5) (g/mol)			Conductivity (μS)		
	Dye 1	Dye 2	Dye 3	Dye 1	Dye 2	Dye 3
1	2.24	2.50	2.66	0.34	0.62	1.05
2	3.38	3.11	3.18	0.52	0.89	1.32
3	3.79	3.51	4.26	0.61	1.04	1.57
4	5.26	6.44	7.47	0.85	1.69	2.25
5	2.78	2.89	3.01	0.41	0.81	1.16

Figure 10 Emission intensity vs. molecular weight of PMMA with Dyes at 375 nm (Dyes added before polymerization). Excitation wavelength: 292 nm.

tivities and maximum molecular weights of PMMA when incorporated with dyes before irradiation. Decreasing conductivity values after 4 h can be attributed to degradation of the growing chains with high radiation.

Chain length determination of dyes by using spectrophotometric analysis

A spectrophotometer was used for the maximum wavelength determination of these three dyes in concentrations of $1.25 \times 10^{-4}M$ in methanol. From the maximum absorption wavelength, the chain length L is calculated by using the equation given below:[21–25]

$$L = (N + 1)^{1/2}.\lambda^{1/2} (0.01744) \text{ nm} \qquad (1)$$

where, N is the total number of π electrons between nitrogen atoms, and λ is the maximum wavelength.
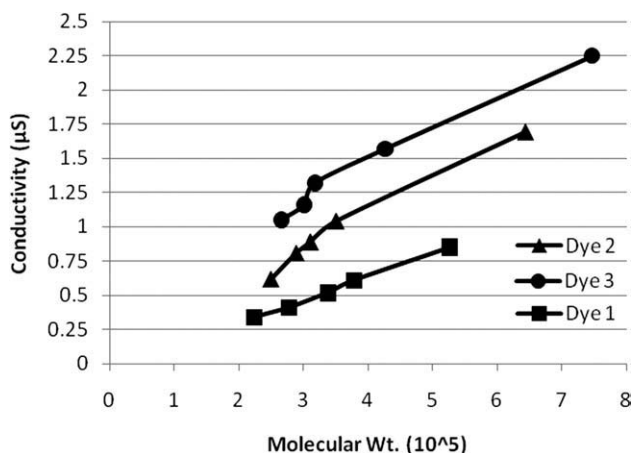

Figure 11 Conductivity of PMMA with Dyes at 25°C (Dyes added before polymerization) with different molecular weights.

TABLE VI
Conductivity versus Molecular Weight of PMMA with Different Dyes (Dyes Added before/after Polymerization)

Molecular weight (10^5) (g/mol)	Conductivity (μS)						
	Without dye	With dye 1		With dye 2		With dye 3	
		Before	After	Before	After	Before	After
0.49	0.02	0.30	0.02	0.41	0.20	0.60	0.55
1.6	0.04	0.49	0.23	0.59	0.45	0.97	0.87
2.2	0.06	0.57	0.31	0.68	0.59	1.18	1.00
2.46	0.07	0.60	0.35	0.73	0.70	1.28	1.10

Dye 1 MW = 454.36.
Dye 2 MW = 480.39.
Dye 3 MW = 506.43.

Table VII gives the results. Theoretical chain lengths were calculated by using particle in box theory and by using eq. (2):[21]

$$L = 0.139 \times Np \qquad (2)$$

where 0.139 is the C—C chain length in nm, and Np is equal to $p + 3$ in which p is the number of C atoms between nitrogen atoms, and 3 is the total number of π electrons coming from two nitrogen atoms in the chain. For the chain shown in Figure 1(a), p is 3 and $Np = 3 + 3 = 6$ (the N atom on the left provides two electrons, whereas the N atom on the right provides one electron (total three π electrons). The N value is also expressed as the length of zigzag chain between nitrogen atoms plus one bond distance to either side; therefore, for a dye molecule given in Figure 1(a), N is equal to 6, or by other equation $Np = p + 3 = 6$. As C—C chain length is 0.139 nm, total chain length L is calculated by using eq. (2) to be 0.834 nm. For the dyes in Figures 1(b,c), the chain lengths were calculated with the same methods and

found to be 1.112 and 1.393 nm, respectively (Table VII).

CONCLUSIONS

Polystyrene shows two main fluorescence emission peaks at 370 and 410 nm. The intensity of the peaks increased when PS was incorporated with dyes, according to increasing molecular weights of the dyes. However, PS itself without any dye addition shows the highest intensities for these peaks. This is consistent with a previous study that showed that peak intensities of PS at two different wavelengths decreased with increasing molecular weights of its own.[19,20] As the molecular weight of the dye samples increases, the emission intensities both at 370 and 410 nm show increasing values. (Table I and Fig. 3 show the results at 370 nm.)

When the dyes are added to PS, conductivity also increases with the increasing molecular weight of the dye due to the increasing conjugation on the backbone structure of the polymer supplied by dye molecules (Figs. 1 and 4). An extended conjugated system is usually necessary for backbone conductivity.[15–17] In Figure 1(c), the dye contains the longest chain length and highest conjugation between nitrogen atoms; consequently, it gives the highest conductivity (Fig. 4).

The chain length between nitrogen atoms for these three different dyes was calculated by using both theoretical and experimental methods. The results are listed in Table VII. Both methods gave consistent results. For experimental calculations, a spectrophotometer was used to find the maximum absorption wavelength. Chain length was calculated by using eq. (1). Theoretical chain length was calculated with eq. (2). Increasing chain length increases conjugation, which is also responsible for the increase in conductivity. The effect of conjugation on increasing conductivity values was explained in the theory section. Figure 4 also shows that with increasing molecular weight of PS, conductivities for all dye cooperated
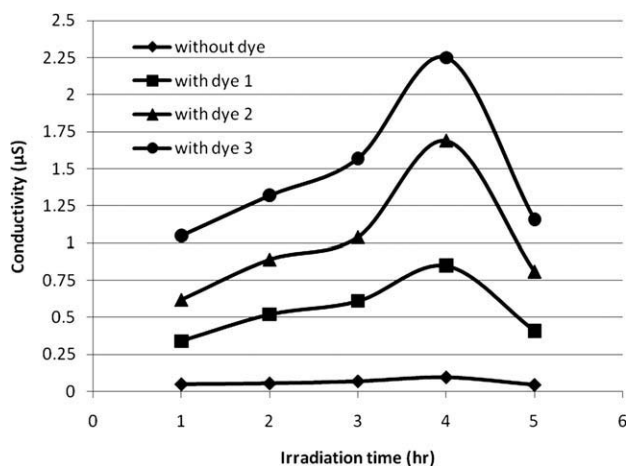

Figure 12 Conductivity of PMMA with Dyes at 25°C (Dyes added before polymerization) at different irradiation times.

TABLE VII
Chain Length Determination of Dyes by Using Spectrophotometric Analysis

Dye	Color	Molar weight (g/mol)	Maximum absorbance, λ (nm)	Theoretical length (nm)	Experimental length (nm)
1	Red	454.36	510	0.834	1.042
2	Blue	480.39	570	1.112	1.249
3	Tea	506.43	600	1.393	1.420

Dye 1 MW = 454.36 (1,1' diethyl 2,2' cyanine iodide).
Dye 2 MW = 480.39 (1,1' diethyl 2,2' carbocyanine iodide).
Dye 3 MW = 506.43 (1,1' diethyl, 2,2' dicarbocyanine iodide).

samples also increases. Therefore, two main factors are influencing the increase in conductivity of PS:

1. Molecular weight of the polymer
2. Molecular weight of the dye added (affecting the increasing conjugation on the chain length)

Polymethyl methacrylate samples also showed the same trends as observed for PS samples. PMMA samples gave two main peaks at 375 and 425 nm. Both peaks increase in intensity with increasing molecular weights of the polymer samples. When dyes were added to PMMA, both peaks exhibited increasing intensity values with increasing molecular weight of the dyes. However, the highest intensity values were observed for PMMA alone, when not incorporated with dyes (Fig. 6). The same trend is observed as shown for PS when polymer samples were incorporated with dyes. Figure 7 shows that as the molecular weights of the PMMA itself increase, conductivity values increases; also, if the molecular weight of the dye increases, so does the conductivity (when dyes were added after polymerization). When the dyes are added before polymerization of MMA samples, the molecular weight of PMMA increases with increasing irradiation time and emission intensity increases (Fig. 9).

The results obtained for PS and PMMA samples prove that addition of polymethine dyes increases the conductivity of both polymer samples. Among these three dyes, as conjugation between nitrogen atoms increases, the conductivity increases. The intensity of fluorescence and phosphorescence emission from synthetic polymers is related to the polymer chain length.

The conductivity values are all higher for the PMMA polymers when the dyes are added before polymerization than the ones added after polymerization (Table V and Fig. 11). The highest conductivity values were obtained for three different dyes incorporated with MMA at 4 h of irradiation (Fig. 12). Conductivities are directly proportional to the molecular weights of PMMA and dyes. The increasing conductivity of polymers with increasing molecular weight of the dyes added is attributed to the increasing conjugation between nitrogen atoms, and increasing N—N

chain length in the dye molecules. This study shows a correlation between conjugation, molecular weight, conductivity, and fluorescence intensity values for styrene and methyl methacrylate polymers. Conductivity values increases for both PS and PMMA as the molecular weight increases. The conductivity values also increase as the molecular weights of the dyes increases. Table V and Figure 12 indicate that both conductivity and molecular weight of the PMMA samples decrease after 4 h of irradiation. This suggests that degradation of PMMA molecular structure begins after 4 h of irradiation.

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