Miscibility study of polymer blends by a novel phosphorescent quenching system

Lin Qiao

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Miscibility Study of Polymer Blends by a Novel Phosphorescent Quenching System

Lin Qiao

August, 1998

THESIS

Submitted in partial fulfillment of the requirements for the degree of Master of Science in Chemistry

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Miscibility Study of Polymer Blends by a Novel Phosphorescent Quenching System

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Abstract

In this study, a novel phosphorescent quenching system was developed to investigate the phase miscibility of binary polymer blends. The system consists of a benzophenone derivative as the chromophore, and an iodobenzene derivative as the quenching agent. The phosphorescent benzophenone derivative, 4-vinylbenzophenone, was synthesized by the Grignard reaction of bromostyrene and benzonitrile. The vinyl-functionalized iodobenzene, N-(4-iodophenyl)maleimide, was synthesized from iodoaniline and maleic anhydride. The polymers, containing less than 5 wt% of either phosphorescent chromophore or phosphorescent quenching agent, were synthesized by free radical copolymerization of styrene, or methyl methacrylate, with 4-vinylbenzophenone, or N-(4-iodophenyl)maleimide in benzene solution, initiated with AIBN at 70°C. Thermal analysis demonstrated that the small amount of dye groups incorporated in the polymer chains did not significantly affect the glass transition temperature nor thermal stability of the homopolymers.

Miscibility of polymer blends, which are composed of 50 wt% chromophore-containing polymer and 50 wt% quencher-containing polymer, was studied by time-resolved and steady state phosphorescence. Results showed that phosphorescent signal was quenched in homogeneous blend whereas it did not change in phase-separated system. Time-resolved phosphorescence indicated that the triplet exciton of benzophenone has a quenching radius of 14 Å. Thus, the phosphorescent chromophore/quencher pair could be used as a sensitive probe to determine polymer-polymer miscibility at molecular level.
Acknowledgement

I would like to express my deep appreciation to my advisor, Professor Andreas Langner, for his guidance, support, and patience throughout my graduate study at the Rochester Institute of Technology. His valuable comments and suggestions have been inspirational and indispensable to the successful conclusion of this work. Special acknowledgements are due to Professors Gerald A. Takacs, Terence C. Morrill, Massoud Miri, and Paul Craig for their interest in my work as well as their advice. Thanks are extended to my classmates and the staff members of the chemistry stockroom for their help.
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I. Introduction

For many years, a primary focus of polymer science and technology was developing new polymers and chemical variations of existing ones. This approach is expensive, and it has been realized that new or different chemical structures may not always be required to achieve the intended purpose. Polymer blends, which are made by mixing two or more polymers, with no covalent bonds between them, often give the desired properties. However, when two polymers are combined, a major feature encountered is that the components tend to phase-separate to form heterogeneous mixtures, resulting in blends which do not exhibit enhanced properties. Therefore, the miscibility behavior of polymer blends has evolved into a major area for current polymer science research.\(^1\)\(^2\)

The equilibrium state of a mixture of high molecular weight polymers may not be as obvious, by visual inspection, as is an analogous mixture of low molecular weight materials. Thus, it normally requires special techniques to examine the nature of this state and the properties of the macromolecular mixture. A number of methods have been proposed to probe polymer blends and to determine whether they are homogeneous (monophase) or heterogeneous (multiphase). Among them, optical clarity is the simplest test. This is only convenient when both the difference in the refractive index of the polymers of the mixture is large enough, and the heterogeneity is at a scale larger than 100 nanometer. The most commonly used techniques are the measurement of the glass transition temperature, \(T_g\) (e.g. by differential scanning calorimetry or dynamic mechanical
analysis) and the direct imaging of the morphology (e.g. by optical or electron microscopy).

The techniques based on the measurement of $T_g$ rely on the fact that each component of the blend has a characteristic glass transition temperature. If the blend is a homogeneous mixture, a single $T_g$ is observed. A binary immiscible polymer mixture exhibits two $T_g$ values, characteristic of the individual components. A partially miscible system also displays two glass transition temperatures, which may be shifted closer to one another on the temperature scale. A very large variety of physical measurements have been proposed for the determination of glass transition temperatures. They may be classified into the following categories: (a) calorimetric determination of heat capacities as a function of temperature (e.g. differential scanning calorimetry, differential thermal analysis), (b) dynamic mechanical (low strain) measurements of complex modulus as a function of temperature (e.g. dynamic mechanical analysis), (c) dielectric relaxation spectroscopy, and (d) dilatometry.

A drawback of glass transition determination methods is that they invariably involve non-equilibrium conditions, typically temperature is swept at 2 to 20°C/minute. The results then reflect a combination of the state of the blend at its preparation temperature and at the measurement temperature. Also, these methods cannot detect the phase separation if the heterogeneous domains are less than 10 nm in size or if the polymers have similar $T_g$s.

For the detailed characterization of the phase morphology in the blends, microscopy is unmatched by any other technique. Modern shape analysis techniques increase the accuracy of size, shape, and orientation determination. For instance, good
optical microscopes are capable of the resolution of 200 nm if the optical contrast is sufficient. The electron microscope is capable of much higher resolution than the optical microscope. Of the two, transmission electron microscopy (TEM) has seen as much application to blends as the easier-to-use scanning electron microscope (SEM). A drawback of these techniques is that they require altering the sample by staining with heavy metals, etching, etc., which sometimes introduce additional structure even in single-component systems. 1

In recent years, nanostructured materials have aroused much interest in both academia and industry. A great deal of attention is paid to novel techniques able to probe multicomponent systems on the molecular scale, for example, X-ray and neutron scattering, 4 solid-state NMR, 5,6 and fluorescence quenching techniques. 7-10 Among these new tools, fluorescence quenching techniques are most often used owing to their greater sensitivity. The technique is based on the fact that, the characteristic fluorescence signal of dye molecules attached to polymers will be influenced by the phase miscibility of a specific blend system. The probe molecule, dye, is designed such that one or more of its photophysical properties is directly dependent on some aspect of its local environment. The supreme advantage of these methods is that local molecular environments, at the sub-nanometer level, can be elucidated. Thus, they may be employed to determine the phase diagram of blends more precisely, and to obtain information at earlier stages of phase separation than the other techniques used in polymer blend work.

Before discussing the application of fluorescence techniques, a brief introduction to photophysics of molecules will be presented. The ground states of most organic molecules are singlets, with electrons paired in the highest occupied molecular orbital
(HOMO), as shown in Figure 1. Absorption of light by the molecule results in a promotion of an electron from the HOMO into an orbital normally unoccupied in the ground state, the lowest unoccupied molecular orbital (LUMO). The resulting excited state is designated

Figure 1 Jablonskii diagram showing fates of polyatomic molecules upon photoexcitation
S\textsubscript{1}, in Figure 1. Promotion of elections from the HOMO to other than LUMO must produce a higher energy state than S\textsubscript{1}, shown in Figure 1 as S\textsubscript{n}. All states, S\textsubscript{n}, are singlet states since singlet to triplet transitions are "forbidden" transitions.

The energy of a photon (E = hc/\lambda, where E is the energy, h is Planck constant, c is the speed of light, and \lambda is the wavelength of the light) required to produce any type of photoexcitation is the energy difference between molecules in the excited state and that in the ground state. The actual photoexcitation time, which is the time required for a molecule to go from one electronic state to another, is very short, approximately 10\textsuperscript{-15} seconds. Therefore, according to the Born-Oppenheimer approximation, the geometry and electronic environment of a molecule is static during electronic transition.\textsuperscript{11}

Once a molecule is promoted to an excited state, one of two processes can occur: the molecule may emit the absorbed photon from the vibrational level to which it was initially excited, or it may undergo changes in vibrational levels prior to deexcitation. The dominant process depends on the vibrational level of the excited molecule. The molecule raised to an upper vibrational level of any excited state is rather unstable and it may rapidly lose its excess of vibrational energy by collisions with surrounding molecules. Vibrational levels are represented by the unlabeled horizontal lines of Figure 1. Molecules in higher electronic excited states (S\textsubscript{n}) other than S\textsubscript{1} will undergo a process known as internal conversion, whereby the molecules pass from a low vibrational level of the upper state to a high vibrational level of the lower state having the same total energy. Once internal conversion has occurred, the molecule again loses its excess vibrational energy through collisions with other molecules. The net result of all these processes is that molecules
raised to levels higher than the lowest vibrational level of the first excited state rapidly fall to this level ($10^{-12}$ S).

The molecule in the $S_1$ excited state will lose its energy by several means. It may emit light (fluorescence) and return to the ground state, form an excimer or exciplex with other molecules, or convert to a triplet state through intersystem crossing. It should be mentioned that, due to loss of vibrational energy, the fluorescence emission spectrum is shifted to longer wavelengths, relative to the absorption spectrum. The possible processes for molecules in their first excited state are listed in the following:

Fluorescence: \[ ^1 \text{M}^* \rightarrow M + \text{hv} \]

Intersystem Crossing: \[ ^1 \text{M}^* \rightarrow ^3 \text{M}^* \]

Internal Conversion: \[ ^1 \text{M}^* \rightarrow M \]

Excimer: \[ M + ^1 \text{M}^* \rightarrow ^1 (\text{MM}^*) \]

Exciplex: \[ ^1 \text{M}^* + D \rightarrow ^1 (\text{MD})^* \]

Luminescence Quenching: \[ ^1 \text{M}^* + Q \rightarrow \text{Quenching} \]

where, $M$ is the molecule in the ground state, $^1 \text{M}^*$ is the molecule in the first singlet state, $^3 \text{M}^*$ is the molecule in the triplet state, $D$ is a donar molecule in the ground state, $Q$ is a quenching molecule in the ground state, $^1 (\text{MM}^*)$ is an excimer, and $^1 (\text{MD})^*$ is an exciplex.

The intersystem crossing from a singlet state results in populating molecules to the triplet excited state, which can then deexcite by phosphorescent emission. Since direct population of the triplet state by absorption is spin forbidden, most phosphorescent
emission will arise as a result of intersystem crossing from the excited singlet state. When the lowest vibrational level of a triplet state is situated energetically below that of the lowest excited singlet state, but its vibrational levels reach to the bottom of the singlet level, the intersystem crossing can occur by the molecule crossing over to one of these upper vibrational levels of the triplet state. From here the molecule rapidly loses its excess vibrational energy and falls to the lowest vibrational level of the lowest triplet state.\textsuperscript{12} This process can be visualized by means of the following potential energy diagram (Figure 2).

The curve MN represents the potential energy of the system in the ground state, curve XY represents the potential energy in the excited state, and curve TV represents the
potential energy of the lowest triplet state. The lowest vibrational level of the TV curve is situated below that of the excited singlet state, and the curves for the two excited states will cross at some point O.

Light absorption raises the molecule from the ground state to an upper vibrational level of the excited singlet state (vertical line EP). The molecule in the excited singlet state rapidly loses its excess of vibrational energy, passing down the curve XY until it reaches the point O. At this point the positions and momenta of the atomic nuclei are identical with those corresponding to a molecule in the lowest triplet state and the molecule can at this point cross over to the corresponding vibrational level of the triplet state, provided there is sufficient spin-orbit coupling to do so.

Similar to the case of chromophores in excited singlet states, chromophores in excited triplet states may lose their energy by many processes. The main photophysical processes are the following: \(^{13}\)

Phosphorescence: \( ^3\text{M}^* \rightarrow ^1\text{M} + \text{hv} \)

Nonradiative Decay: \( ^3\text{M}^* \rightarrow ^1\text{M} \)

Triplet Energy Transfer: \( ^3\text{M}^* + ^1\text{B} \rightarrow ^1\text{M} + ^3\text{B}^* \)

Triplet Quenching: \( ^3\text{M}^* + \text{Q} \rightarrow ^1\text{M} + \text{Q} \)

The probability of triplet energy transfer from \( \text{M}^* \) to \( \text{B} \) is proportional to the spectral overlapping between the phosphorescent emission band of the donar, \( \text{M}^* \), and the absorption band of the acceptor, \( \text{B} \); this is known as the Dexter Formalism. Triplet quenching is thought to be collisional quenching and thus can take place only if the two moieties approach each other so closely that they may be considered to be in molecular
contact. Therefore, the latter process is controlled by diffusion of the quencher. This process also requires a change in spin state, which is facilitated by the large spin-orbit coupling of heavy atoms such as iodine. Because of the significantly long lifetime of the triplet state, molecules in this state are subject to more such interactions. Thus, the intensity of the phosphorescence signal is highly sensitive to the presence of added quencher molecules in the polymer matrix.

The fluorescence quenching techniques probe the different quenching processes between pairs of chromophore (F) molecules in the excited state and quencher (Q) molecules in the ground state. All the quenching processes are dependent on the distance between the chromophore/quencher pairs. Relative orientation may also be important. The sensitivity of each quenching process to intermolecular distance and orientation depends upon the quenching mechanism. For instance, energy transfer by dipole coupling (Forster energy transfer) can occur over distance of up to 100 Å, electron transfer can occur at 15 Å to 20 Å, whereas quenching by paramagnetic species requires orbital overlap and is a short range process. A convenient way of classifying these processes is to define a distance parameter $R_o$ at which the quenching rate (for randomly oriented F/Q pairs) equals the unquenched decay rate of the excited chromophore, $F^*$. The value $R_o$ will depend upon the details of the quenching mechanism and the particular F/Q pair under consideration. A selection of $R_o$ ranges for different quenching processes is collected in Table 1.
Table 1. Bimolecular Excited State Quenching Processes

<table>
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<th>interaction mechanism</th>
<th>Effective distance \textsuperscript{a,b}, ( R_o )</th>
</tr>
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<tbody>
<tr>
<td>1. Energy transfer by</td>
<td></td>
</tr>
<tr>
<td>dipole coupling</td>
<td>10 Å to 100 Å</td>
</tr>
<tr>
<td>electron exchange</td>
<td>4 Å to 15 Å</td>
</tr>
<tr>
<td>reabsorption</td>
<td>as far as emission reaches</td>
</tr>
<tr>
<td>2. Electron transfer</td>
<td>4 Å to 25 Å</td>
</tr>
<tr>
<td>3. Exciplex formation</td>
<td>4 Å to 15 Å</td>
</tr>
<tr>
<td>4. Excimer formation</td>
<td>ca. 4 Å</td>
</tr>
<tr>
<td>5. Non-emissive self-quenching</td>
<td>4 Å to 15 Å</td>
</tr>
<tr>
<td>6. Heavy atom effect</td>
<td>ca. 4 Å</td>
</tr>
<tr>
<td>7. Chemical bond formation</td>
<td>ca. 2 Å to 4 Å</td>
</tr>
</tbody>
</table>

a. The minimum interaction distance is arbitrarily taken to be 4 Å except where new chemical bonds are formed.

b. Each pair of chromophores, for each interaction mechanisms, has its own characteristic distance \( R_o \). These values are estimates of the range of \( R_o \) for randomly oriented non-diffusing pairs of species.

\( R_o \) is the only important distance scale for mechanisms in which diffusion is unimportant. For the diffusion-controlled quenching process, this distance will be determined by the diffusion of F or Q on a time scale of the F\(^*\) lifetime. The chromophores with longer excited-state lifetime may transfer farther than the ones with shorter lifetimes. Quenching experiments could detect large separated phase domains if chromophores with long excited-state lifetimes are used. Since the lifetime of a chromophore in the singlet state is far shorter than that in the triplet state,
phosphorescence quenching techniques are expected to probe larger phase domains (size about 15–20 Å) than fluorescence quenching techniques.

As early as 1978, Morawetz, et. al. \(^9(a)\) introduced a nonradiative energy transfer (NRET) technique to investigate the miscibility of polymer blends in the solid state. In this technique, the first polymer was labeled with a fluorescent substituent (the donor) and the second polymer with another fluorescent group (the acceptor), chosen so that the emission spectrum of the donor overlaps the absorption spectrum of the acceptor. The efficiency of the nonradiative energy transfer, after the photoexcitation of the donor, depends upon the average distance between the donor and acceptor molecules. Measurements of the relative emission intensities of the donor and acceptor, characterized by their emission intensity ratio, indicate the extent of interpenetration of the chains, thus giving information about the miscibility of the polymer blends. If two polymers are immiscible, the donor and acceptor labels will be too far from each other for efficient energy transfer, leading to a large donor emission. The ratio of donor and acceptor emission intensities will exhibit a decrease as the two phases mix on a segment level (one phase). The high sensitivity of fluorescence spectroscopy makes it possible to carry out such experiments with very small label concentrations (\(10^5\) M) so that the properties of the polymers are not appreciably altered.

Amrani, et. al. \(^9(b)\) studied phase-separated mixtures of carbazole-labeled poly(styrene-co-acrylonitrile) with anthracene-labeled poly(methyl methacrylate). As the acrylonitrile content of the copolymer was varied, the change in degree of mixing or miscibility of the two polymers was monitored by measuring the acceptor-donor fluorescence ratio, they demonstrated that this technique may probe polymer phase
behavior on a scale of about 3 nm. This technique has also been used effectively by Albert, et. al. for the study of PVC blends with syndiotactic PMMA \(^\text{10}\). The phase separation increases smoothly with an increasing content of s-PMMA in the blends, going through a maximum at a weight fraction 0.8 of s-PMMA. Instead of attaching the donor to one polymer and the acceptor to the other polymer, Zhao, et. al. \(^\text{14}\) attached fluorescence donor and acceptor molecules to the same polymer component (but to different chains) to study blends of PVC and PMMA. They found that this technique is sensitive to the extent of random dispersion of polymer chains in a miscible blend. In the case of block copolymers, the blocks can be individually labeled, so that NRET data provided information about the mixing of the labeled block with the second component of the blend. This approach was used to study blends of polystyrene/poly(styrene-tertbutylstyrene) \(^\text{9(d)}\), poly(vinyl chloride)/ polystyrene-poly(methyl methacrylate) \(^\text{15}\), and polyisoprene/poly(styrene-isoprene) \(^\text{16}\). Results demonstrated that this technique is also very sensitive to the phase behavior of blends of random copolymers with homopolymers.

Another fluorescence quenching phenomenon, which is employed for the study of polymer compatibility, involves excimer formation \(^\text{7}\). An excimer is a complex between a photo-excited and a ground-state chromophore which typically includes two aromatic residues lying approximately parallel to each other at a spacing of 3-4 Å. In a polymer containing closely spaced chromophores, an excimer may form either by the interaction of adjacent groups on the same chain, or on different chains. Thus, in mixtures of fluorescent and nonfluorescent polymers, excimer emission will be favored by phase separation. In 1981, Gashgari and Frank \(^\text{7b}\) demonstrated that excimer fluorescence could be used to detect phase separation in polymer blends at an earlier stage than is possible by
measurements of optical clarity or differential scanning calorimetry. Later, by studying spinodal decomposition in polystyrene-polyvinylmethylether (PS-PVME) blends, Gelles, et. al. 7c,d developed a two phase model to describe the relationship between the ratio between excimer and monomer fluorescence intensities, $I_E/I_M$, and the compositions of PS-rich and PS-lean phases. More recently, Tsai, et. al. 17 studied the phase separation behavior of oligomeric polystyrene/polybutadiene using optical density methods and excimer fluorescence. They achieved an excellent agreement between the equilibrium compositions determined from the optical method and that obtained from an interpretation of the fluorescence measurements using Gelles-Frank model.

Since phase separation behavior is simpler in the earliest stages of the process, well before the appearance of the coarsening process, it is advantageous to follow the kinetics when the system is subjected to very small thermodynamic stresses. It has been demonstrated that the kinetics in the initial stages of phase separation cannot be followed accurately by the nonradiative energy transfer fluorescence method. Halary, et. al. 8 developed a new fluorescence technique which is claimed to have the capacity to overcome this problem. This method is based on the non-diffusive quenching of the fluorescence emission of anthracene-labeled polystyrene (PS*) by PVME. The phenomenon occurs in miscible blends but tends to cease as phase separation develops, leading to a sharp increase of fluorescence intensity. They investigated both the spinodal decomposition mechanism in the unstable one-phase region, and the nucleation and growth mechanism in the metastable regions, on a series of mixtures covering the entire composition range of the PS-PVME blends. The results showed excellent agreement with that predicted by relevant theories. Later, they studied the miscibility of PVME with
random copolymers of styrene and methyl methacrylate. Since they couldn’t label the copolymer with anthracenic groups directly, a small amount (around 0.5 wt%) labeled PS* was added to the blends. The results indicated that the presence of methyl methacrylate (MMA) groups did not generate any noticeable synergy effect, which had been claimed by some other researchers using cloud-point measurements. Rather, as a consequence of the corresponding change in the friction coefficient, the MMA units significantly decreased the phase-separation rate.

Phosphorescence has also been used successfully to study the molecular interactions in solution between small molecule-small molecule \(^{18}\), polymer-small molecule\(^{19,20}\), and polymer-polymer \(^{21}\). However, there is no report regarding miscibility studies of solid state polymer blends using phosphorescent probes. As discussed earlier, phosphorescence quenching techniques could monitor large phase domains (size about 15–20 Å). Therefore, phosphorescent quenching techniques may have the capacity to bridge the gap between thermo-mechanical techniques and fluorescent methods. In this study, we investigate the feasibility of studying phase miscibility of solid-state polymer blends, using a new phosphorescence quenching system.

Benzophenone has been extensively used as an effective phosphorescent sensitizer in biochemistry to study protein interactions \(^{22-24}\), due to its high intersystem-crossing yield and long phosphorescent lifetime. It was found in our laboratory that benzophenone could be quenched by 4-iodoaniline. Thus, this pair was selected as our phosphorescence quenching system and attached to the polymer chains. The miscibility of the polymeric blends of styrene/styrene-co-maleimide, MMA/MMA-co-maleimide, and phase-separated PS/PMMA will be studied using this new phosphorescence quenching system.
The objectives of this project are: 1) design, synthesis, purification, and characterization of vinyl monomers modified by chromophore/quencher pairs, 2) synthesis and characterization of copolymers with a controlled chromophore/quencher content, 3) study the phosphorescent behavior of the chromophore-containing copolymers for known miscible and immiscible blends.
II. Synthesis and Characterization

II-1. Materials and Purification

All the chemicals in this study were purchased from Aldrich Chemical Company. 4-iodoaniline (98%), iodomethane (99.5%), 4-bromostyrene (98%), benzonitrile (99.9%), 2,2'-azobisisobutyronitrile (AIBN, 98%), magnesium powder (~50 mesh, 99+%), sodium acetate (99%), acetic anhydride (99+%), sulfuric acid (99%), chloroform (99.9%), acetone (99.5%), tetrahydrofuran (99.9%), benzene (99%), and petroleum ether were used as received.

Methyl methacrylate (99%) and styrene (99%) were purified by inhibitor remover column (Aldrich, column for styrene is 1344-28-1 and that for MMA is 9003-70-7) to get rid of the polymerization inhibitors. These inhibitor free monomers were then stored in a refrigerator until they were needed for polymerization. Maleic anhydride (99%) was purified by sublimation at atmospheric pressure. The sublimation process was carried out by placing the crude maleic anhydride in a beaker and heating the beaker with an oil bath at 48°C, the sublimed, needle-like maleic anhydride crystals were collected on a glass cover and stored in a glass desiccator for use.
II-2. Synthesis

All the reactions were conducted in a 100 ml three-necked round-bottom flask, of which the first neck was mounted with a glass addition tube, the middle neck was fitted with a cold water condenser, and the third was utilized as a dry nitrogen inlet. An oil bath was used to maintain the desired temperature and a magnetic agitation system was employed to stir the reactants in the flask.

**Synthesis of N-(4-iodophenyl)maleimide**

The synthesis of N-(4-iodophenyl)maleimide (NIPMI) was carried out by a two-step reaction, following the method developed by Searle. The first step yielded N-(4-iodophenyl)maleamic acid (NIPMA). The NIPMI was prepared by dehydration of NIPMA in a second step (shown in Figure 3). To 0.9806 g (10 mmol) of maleic anhydride in 10 ml of chloroform, 2.1903 g (10 mmol) of 4-iodoaniline, dissolved in 10 ml chloroform, was added slowly under vigorous stirring. The reaction was kept at 0-4°C in a ice-water bath for 30 minutes. The resulting NIPMA was filtered, washed twice with chloroform, recrystallized from acetone, and dried in a vacuum oven at 40°C for 24 hours. A total of 3.024 g (yield 95.3%) of fine yellow powder was produced. The measured melting point of NIPMA was 184°C.

In the imidization step, 0.9130 g (2.88 mmol) of NIPMA was treated with 0.1182 g (1.44 mmol) of anhydrous sodium acetate and 2.964 g (28.8 mmol) of acetic anhydride in 10 ml of chloroform at 70 °C for 2 hours. Then, the products were poured into a large
amount of water. After twice recrystallizing from cyclohexane the product was dried in vacuum oven at 40°C for 24 hours. A total of 0.8077 g rectangular, prismatic NIPMI crystals were obtained (yield 93.8%). The melting point was 160-161°C.

![Chemical structure](image)

Figure 3. Synthetic route for NIPMI (Ref 25)

**Synthesis of 4-vinylbenzophenone**

4-vinylbenzophenone (VBP) was synthesized according to the method of Braun, et. al. (as shown in Figure 4). In a nitrogen-protected flask, 2.43 g (0.1 mol) of magnesium powder in 18 ml absolute tetrahydrofuran (THF), was activated by slowly adding 0.2 g of iodomethane. Once the magnesium was activated, 18.39 g (0.1 mol) of bromostyrene, in 10 ml of THF, was added dropwise to the system at room temperature. After the addition of bromostyrene, the temperature of the reaction was increased to 60°C, and maintained there for 30 minutes. Then, 10.13 g (0.1 mol) of benzonitrile, in 15 ml of
THF, was added to the reaction mixture. The reaction was completed after another 30 minutes.

The products were poured into 60 ml of ice water, with 10 ml of 98% sulfuric acid. The resulting solution was diluted with 100 ml petroleum ether and transferred to 250 ml separatory funnel. The mixture in the separatory funnel was shaken well and then allowed 30 minutes for separation. The upper ether layer was filtered to remove oligomers and other impurities. The filtrate was separated using a silica gel (Merck 7734) column and ethylene chloride as an eluant. The separation of benzonitrile, bromostyrene, and 4-VBP was confirmed using their UV absorption spectra. Yellow 4-VBP crystals were obtained after evaporation of the solvent. They were purified by recrystallization from a solvent mixture of methanol/water (67:33 by volume). The total yield was 30% with a melting point of 51°C (lit.29 50.5°C).

Figure 4 Synthetic route for VBP
Copolymer Synthesis via Free Radical Polymerization

Chemical modification of base homopolymers with chromophores was realized by copolymerization of the above vinyl-functionalized dyes with styrene or methyl methacrylate. The dyes were attached to different copolymer chains, i.e. some molecules of copolymers contained the benzophenone moiety, whereas others had iodophenyl group. Four types of copolymers were made, poly(MMA-co-NIPMI), poly(MMA-co-VBP), poly(St-co-NIPMI), and poly(St-co-VBP).

The copolymers were synthesized by free radical polymerization of vinyl monomers in benzene solution (shown in Figure 5 and 6). Monomer compositions in the feed were listed in Table 2 and 3. The monomers in 100 ml benzene, were added into flask and the oxygen in the reactor was removed by bubbling with dry nitrogen for 20 minutes. Then, the reactants were brought to and equilibrated at 75°C. 0.020 g (1.2x10^-4 mol) initiator of 2,2'-azo-bis-isobutyronitrile (AIBN) was added to start polymerization. After reaction for 8 hours, the resulting polymer was precipitated from the solvent by pouring the reactant into a large amount of cold methanol. After filtering, the filter cake was washed with methanol three times. Then it was redissolved in 20 ml benzene. The polymer, in benzene solution, was precipitated once again by adding the solution dropwise into 800 ml cold methanol, under agitation. The precipitated polymer was filtered, washed twice with fresh methanol, and dried in vacuum oven at 40°C for 12 hours.
<table>
<thead>
<tr>
<th></th>
<th>MMA (mol)</th>
<th>NIPMI (mol)</th>
<th>VBP (mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA1</td>
<td>0.1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>PMMA2</td>
<td>0.1</td>
<td>0</td>
<td>0.0038</td>
</tr>
<tr>
<td>PMMA3</td>
<td>0.1</td>
<td>0.0012</td>
<td>0</td>
</tr>
<tr>
<td>PMMA4</td>
<td>0.1</td>
<td>0.003</td>
<td>0</td>
</tr>
<tr>
<td>PMMA5</td>
<td>0.1</td>
<td>0.0055</td>
<td>0</td>
</tr>
<tr>
<td>PMMA6</td>
<td>0.1</td>
<td>0.008</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 3 Monomer composition for the polystyrene copolymers

<table>
<thead>
<tr>
<th></th>
<th>St (mol)</th>
<th>NIPMI (mol)</th>
<th>VBP (mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS1</td>
<td>0.1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>PS2</td>
<td>0.1</td>
<td>0</td>
<td>0.005</td>
</tr>
<tr>
<td>PS3</td>
<td>0.1</td>
<td>0.0006</td>
<td>0</td>
</tr>
<tr>
<td>PS4</td>
<td>0.1</td>
<td>0.0015</td>
<td>0</td>
</tr>
<tr>
<td>PS5</td>
<td>0.1</td>
<td>0.0025</td>
<td>0</td>
</tr>
</tbody>
</table>
Figure 5 Synthesis of poly(methyl methacrylate) copolymers

Figure 6 Synthesis of polystyrene copolymers
II-3. Characterization

Before conducting characterization experiments, the purity of the monomers and copolymers were checked by thin layer chromatography (TLC), using Kodak Silica Gel Chromatography paper and either a benzene-methanol (65:35) or a benzene-ethanol (65:35) mixture as solvent. Melting points were obtained using a standard melting point apparatus or differential scanning calorimetry. Other characterization techniques, such as thermal and spectroscopic analyses, used to evaluate all the compounds and copolymers, are detailed in the following paragraphs.

**Thermogravimetric Analysis**

Thermogravimetric analysis (TGA) was performed on a Seiko TGA/DTA 220 instrument. 6–8 mg sample was loaded into an uncovered aluminum pan. The sample mass and the temperature were measured relative to an empty aluminum pan. The sample was purged with nitrogen for 15 minutes before starting the run and a nitrogen atmosphere was maintained throughout the process (nitrogen flowrate was 300 ml/min). Data was collected from 30–600°C at a heating rate of 10°C per minute.

**Differential Scanning Calorimetry**

Differential scanning calorimetry (DSC) analysis was performed on a Seiko SDM/220C DSC instrument. 4 to 5 mg sample was loaded into a sealed aluminum pan. The sample chamber was purged with nitrogen for 15 minutes before each analysis and a
nitrogen atmosphere was maintained throughout the run (nitrogen flow rate of 50 ml/min). Data was collected from 25 to 200°C at a heating rate of 10°C.

**Fourier Transform Infrared Analysis**

Fourier transform infrared (FT-IR) spectroscopic analyses were conducted with a Perkin-Elmer 1760X spectrometer. Samples to be measured were blended with dry potassium bromide salt powder (Aldrich Chemical Co.) and were molded into small plates. The spectra were recorded in transmission mode, using an air blank, and a resolution of 4 cm⁻¹. The scans were run from 4000 cm⁻¹ to 400 cm⁻¹ with an average of 10 scans being taken for each sample.

**Proton Nuclear Magnetic Resonance**

Proton nuclear magnetic resonance (NMR) measurements were performed using a Bruker 300 spectrometer. Samples were dissolved in deuterated chloroform. The spectra were recorded at a frequency of 299.9 MHz. The chemical shifts were reported in ppm with triple runs for each sample.
II-4. Results and Discussion

The purpose of this section of the thesis was to synthesize polymers with chromophore or quencher moieties. In previous studies by Vandell \(^27\) and DiFelice \(^28\), at this laboratory, the chromophore-containing polymers were synthesized by two different methods. In Vandell's method, \(^27\) the dye-containing vinyl monomers (N-substituted maleimides) were first synthesized by the imidization reaction of an aromatic amine with maleic anhydride. Then, the copolymers were obtained by free radical copolymerization of the maleimide with other vinyl monomers, such as styrene or methyl methacrylate. In DiFelice's method, \(^28\) the chromophore-containing polymers were synthesized by the reaction of aromatic amines with commercially available poly[styrene-co-(maleic anhydride)] copolymers having various styrene/anhydride ratios. However, these commercial poly[styrene-co-(maleic anhydride)] copolymers had different physical properties from polystyrene, because they contained a large fraction of maleic anhydride (8–50%). As stated earlier, the dye content in the copolymers should be less than 5% to assure that the physical properties of the modified copolymers are the same as those of the homopolymers. This problem was solved in the present study by synthesizing low dye-content copolymers in the laboratory, using Vandell’s method.

Synthesis of N-(4-iodophenyl) maleimide

The synthesis of the quencher compound N-(4-iodophenyl)maleimide (NIPMI) from maleic anhydride and 4-idoaniline was performed in a two-step reaction. In the first step, the maleamic acid, NIPMA, was formed. This is believed to be a result from
nucleophilic attack of the amino group on the anhydride carbonyl. However, because of the alkalinity of the amine, excess amine may form a salt with the carboxylic acid groups of the generated maleamic acid. The salt formation prevents further reaction of amine groups with the anhydride. Rather than forming a diamide, the reaction is designed to convert 4-iodoaniline and maleic anhydride to a maleimide. The second, dehydration, step of the reaction scheme combines NIPMA in acetic anhydride, with sodium acetate as the catalyst, to give the final product, NIPMI. Both of these reactions involve a proton transfer process as viewed in the reaction mechanisms, given in Figure 7.

Figure 7. Reaction mechanism of 4-iodoaniline and maleic anhydride to produce maleimide
Figure 8(a) is the FT-IR transmission spectrum of the first reaction product, NIPMA. It exhibits absorption peaks of typical amides, with an N-H stretching band at 3291 cm$^{-1}$ and an N-H bending band at 1543 cm$^{-1}$. The conversion of the NIPMA amide to the NIPMI imide, in subsequent imidization reaction was confirmed by the disappearance of these N-H absorption bands (see Figure 8(b)). The IR spectra of NIPMI are similar to those of N-(bromophenyl)maleimide. The weak absorption bands at 3117 cm$^{-1}$ are assigned to the stretching vibrations of the =C-H bonds of the imide ring. The strong absorption at 1773 cm$^{-1}$ can be attributed to the stretching vibration of the imide carbonyls. The absorption at 1580 cm$^{-1}$ has been assigned to the stretching vibration of the C=C bond of the maleimide ring, since it was only observed with monomeric maleimides, not with their polymers. Pronounced absorptions in the range of 690-830 cm$^{-1}$ may be attributed to the out-of-the-plane -CH vibrations of aromatic ring. Table 4 lists the characteristic absorption bands of NIPMA and NIPMI.

The proton NMR spectrum of the imidized product, taken after purification by recrystallization form cyclohexane, also confirmed the formation of NIPMI. It is given in Figure 9. The singlet at 7.05 ppm supports the presence of the two olefinic hydrogen atoms of the symmetrical imide. The $^1$H-NMR chemical shifts, $\delta$, of the NIPMI spectrum, taken in deuterium chloroform (CDCl$_3$), are listed in Table 5. The integral ratio of these three proton resonance peaks is 1:1:1.
Table 4 Characteristic IR bands of NIPMA and NIPMI

<table>
<thead>
<tr>
<th>Compound</th>
<th>Functionality</th>
<th>Absorption (cm(^{-1}))</th>
<th>Peak Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>NIPMA</td>
<td>Aromatic C-H</td>
<td>3076</td>
<td>Medium</td>
</tr>
<tr>
<td></td>
<td>Carboxyl Carbonyl</td>
<td>1702</td>
<td>Strong</td>
</tr>
<tr>
<td></td>
<td>Amide Carbonyl</td>
<td>1635</td>
<td>Medium</td>
</tr>
<tr>
<td></td>
<td>Amide N-H</td>
<td>3291</td>
<td>Weak</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1543</td>
<td>Strong</td>
</tr>
<tr>
<td>NIPMI</td>
<td>Aromatic C-H</td>
<td>3087</td>
<td>Medium</td>
</tr>
<tr>
<td></td>
<td></td>
<td>690-830</td>
<td>Strong</td>
</tr>
<tr>
<td></td>
<td>Imide Carbonyl (asym)</td>
<td>1717</td>
<td>Strong</td>
</tr>
<tr>
<td></td>
<td>Imide Carbonyl (sym)</td>
<td>1773</td>
<td>Weak</td>
</tr>
<tr>
<td></td>
<td>Olefinic C=C</td>
<td>1580</td>
<td>Weak</td>
</tr>
<tr>
<td></td>
<td>Olefinic C-H</td>
<td>1492</td>
<td>Weak</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3117</td>
<td>Weak</td>
</tr>
</tbody>
</table>

Table 5 Proton NMR Data for N-(4-iodophenyl)maleimide

<table>
<thead>
<tr>
<th>Proton</th>
<th>Peak</th>
<th>Type</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>7.05</td>
<td>Singlet</td>
<td>Olefinic</td>
</tr>
<tr>
<td>B</td>
<td>7.35</td>
<td>Doublet</td>
<td>Aromatic</td>
</tr>
<tr>
<td>C</td>
<td>8.00</td>
<td>Doublet</td>
<td>Aromatic</td>
</tr>
</tbody>
</table>

*300 MHz Spectra

* solvent: CDCl\(_3\)
Figure 8 The FTIR spectra of (a) N-(4-iodophenyl)maleamic acid and (b) N-(4-iodophenyl)maleimide
Figure 9 \(^1\text{H} \) NMR spectrum of NIPMI monomer
Synthesis of 4-vinyl benzophenone

Following the successful synthesis of NIPMI, the phosphorescent 4-aminobenzophenone was selected as chromophore because it was easily functionalized with maleic anhydride. However, it turned out that 4-aminobenzophenone was no longer phosphorescent after imidization with maleic anhydride. Therefore, 4-vinylbenzophenone was chosen as the phosphorescent monomer.

The compound 4-vinylbenzophenone (VBP), an aromatic ketone containing a terminal vinyl group, can be synthesized by the Friedel-Crafts acylation of β-bromoethyl-substituted hydrocarbons. This single-stage dehydrobromination is complicated by a series of side reactions and by the formation of a mixture which is difficult to separate. Thus, in this study, VBP was synthesized by the Grignard reaction of 4-bromostyrene and benzonitrile, as described in the experimental section.

The first part of the synthesis involves the preparation of a Grignard reagent from bromostyrene and magnesium. Because free radicals are evolved in this step, the temperature of the reaction system must be precisely controlled to prevent the free radical polymerization of the bromostyrene, and to raise the yield. After extraction of the product with petroleum ether, it is very important to filter the ether solution twice so as to remove oligomers and other impurities. The Whatman filtration paper is used for the first operation and Gelman PTFE acrodisc syringe filter (pore size 0.45 μm) is used for the second operation. Then, VBP was easily separated from the product mixture by column chromatography on silica gel. The crude product could be purified by recrystallization from methanol/water solvent mixture.
The $^1$H-NMR spectrum of VBP in deuterium chloroform (CDCl$_3$) is shown in Figure 10. Chemical shifts are summarized in Table 6. Proton A and B do not have equivalent chemical shift. Proton A ($\delta$ ~5.90 ppm) is deshielded about 25 Hz compared with proton B, because of its relative proximity to the aromatic ring. Proton X ($\delta$ ~6.90ppm) is strongly deshielded by the ring and is split by proton A (J ~17.1 Hz) and by proton B (J ~10.8 Hz). The A proton signal is split by the X proton (J ~17.1Hz) and by the B proton (J ~2.00Hz). The B proton signal is split by the X proton (J ~10.8Hz) and by the A proton (J ~2.00Hz). The integral ratio (9:1:1:1) of all proton resonances provides the evidence for the formation of pure 4-vinyl benzophenone.

<table>
<thead>
<tr>
<th>Proton</th>
<th>Peak</th>
<th>Type</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>5.90</td>
<td>Doublet</td>
<td>Olefinic</td>
</tr>
<tr>
<td>B</td>
<td>5.50</td>
<td>Doublet</td>
<td>Olefinic</td>
</tr>
<tr>
<td>C</td>
<td>7.2-8.0</td>
<td>Multiplet</td>
<td>Aromatic</td>
</tr>
<tr>
<td>X</td>
<td>6.91</td>
<td>Triplet</td>
<td>Olefinic</td>
</tr>
</tbody>
</table>

*300 MHz Spectra

* Solvent: CDCl$_3$
Figure 10 $^1$H NMR spectrum of VBP monomer
Synthesis of Copolymer

Chromophore-containing polymers were obtained by free radical copolymerization of NIPMI or VBP with styrene or methyl methacrylate in benzene, at 75°C, in the presence of AIBN (1.2 x 10^{-3} mol/L) for 8 hours. The crude copolymers were precipitated out of the reaction solvent using a large amount of methanol, and could be collected by vacuum filtration. Purification of the copolymers was achieved by first re-dissolving in a minimal amount of benzene, followed by precipitation out of methanol. The average yield for the copolymerization reaction was around 30%.

The incorporation of VBP or NIPMI into the copolymer was confirmed by the appearance of new peaks in the £H NMR spectra, compared to those of the homopolymers (refer to Appendix A for the NMR spectra). All the peaks of the PMMA homopolymer have chemical shifts less than 4 ppm, and those of the PS homopolymer are less than 7.2 ppm. 31 New peaks, with chemical shifts of 7.2-8.0 ppm, were observed for the poly(St-co-VBP) copolymer and for the poly(MMA-co-VBP) copolymers. These are believed to originate from benzophenone moieties because they match the aromatic peaks of the £H NMR spectra of the VBP monomer. In the poly(MMA-co-NIPMI) and poly(St-co-NIPMI) copolymers, a new peak at chemical shift of 8.0 ppm was observed and was assigned to the α-proton to iodine in NIPMI. The chromophore content in the copolymers was determined from the NMR spectra. Results are listed in Table 7. As can be seen from the table, the chromophore labels at less than 5 mol% in the copolymers were incorporated.

These copolymers had lower dye content than the feed composition, which indicates that the chromophores have smaller reactivity ratios than the counterpart. The
low reactivity ratio of the dyes is probably due to large steric hinderance of the aromatic rings. In the kinetic study of copolymerization of N-(Monohalogenphenyl)maleimides with styrene, Bezdek found that the reactivity ratios of the maleimides are zero and that of styrene is around 0.05. He predicted an alternating copolymer is formed. In Matsumoto’s copolymerization study of N-(Monohalogenphenyl)maleimides with MMA, he found that the reactivity ratios of the maleimides are 20 times lower than that of MMA.

Table 7 Physical properties of photoactive copolymers

<table>
<thead>
<tr>
<th>copolymer</th>
<th>Composition (mol/mol)</th>
<th>Yield WT (g)</th>
<th>Percent (%)</th>
<th>$T_d$ (°C)</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA</td>
<td>100/0.00</td>
<td>3.607</td>
<td>40.4</td>
<td>339</td>
<td>107</td>
</tr>
<tr>
<td>P(MMA-co-VBP)</td>
<td>96.46/3.5</td>
<td>2.588</td>
<td>30.1</td>
<td>338</td>
<td>107</td>
</tr>
<tr>
<td>P(MMA-co-NIPMI)</td>
<td>99.53/0.5</td>
<td>2.547</td>
<td>29.6</td>
<td>337</td>
<td>107</td>
</tr>
<tr>
<td></td>
<td>98.63/1.4</td>
<td>2.639</td>
<td>27.9</td>
<td>338</td>
<td>107</td>
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<td></td>
<td>97.24/2.8</td>
<td>2.486</td>
<td>28.5</td>
<td>338</td>
<td>107</td>
</tr>
<tr>
<td></td>
<td>96.06/3.9</td>
<td>2.504</td>
<td>29.1</td>
<td>337</td>
<td>108</td>
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<tr>
<td>PS</td>
<td>100/0.00</td>
<td>3.642</td>
<td>31.9</td>
<td>397</td>
<td>114</td>
</tr>
<tr>
<td>P(St-co-VBP)</td>
<td>96.06/3.9</td>
<td>3.615</td>
<td>30.0</td>
<td>393</td>
<td>110</td>
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<tr>
<td>P(St-co-NIPMI)</td>
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<td>3.640</td>
<td>32.2</td>
<td>397</td>
<td>112</td>
</tr>
<tr>
<td></td>
<td>97.31/2.7</td>
<td>3.592</td>
<td>30.6</td>
<td>399</td>
<td>115</td>
</tr>
<tr>
<td></td>
<td>95.66/4.3</td>
<td>3.622</td>
<td>30.5</td>
<td>398</td>
<td>114</td>
</tr>
</tbody>
</table>

In order to make sure that the chemical modification did not change the physical properties of the base PS and PMMA homopolymers, glass transition temperature ($T_g$) and thermal decomposition temperature ($T_d$) of the copolymers and homopolymers were measured using differential scanning calorimetry and thermogravimetric analysis.
techniques. Results are listed in Table 7 (Thermograms are shown in Appendix B). Both copolymers and homopolymers exhibited the same glass transition temperature and thermal decomposition temperature. From this we can conclude that the low dye-content of the modified PMMA and PS did not noticeably affect the molecular interactions. The phase miscibility behavior of polymer blends based on these dye-modified copolymers is expected to be similar to the associated homopolymer blends.
III. Phase Miscibility Study of Polymer Blends

III-1. Experiments

Polymer blends were composed of 50 wt% chromophore-containing polymer and 50 wt% quencher-containing polymer. With this formulation, the quencher content in the polymer blend was half of its original value. To make the binary polymer blends, each component was weighed in the given proportions and added to tetrahydrofuran (THF), to produce a solution containing 3 wt% total solids. The solutions were allowed to mix for several days at room temperature to become completely clear, single phase liquids.

Thin solid films were prepared by spin-coating the THF-polymer solution onto quartz substrates at room temperature, followed by drying under vacuum at 323 K for 24 hours to ensure the removal of excess solvent. Film thicknesses of ~2 μm were determined using Tencor Model 200 alpha-step profilometer, which has a resolution of 1 nm. For transmission electron microscopy (TEM) measurements, the thin blend films, spun onto glass substrates, were placed in deionized water, peeled off using a blade, and transferred onto copper grids.

The TEM images were obtained using a JOEL model JEM2000EX instrument at University of Rochester. UV-VIS absorption spectra were measured using a Varian Cary 219 spectrophotometer. Phosphorescence data were obtained using a Perkin-Elmer LS-50B Fluorimeter. Samples were excited at 265 nm in a front-face arrangement to minimize self-absorption. Figure 11 gives a schematic of the optical diagram. Time-resolved
phosphorescent data were recorded at an emission wavelength of 450 nm with 5 ms gate time and a variable delay time.

Figure 11 Schematic diagram showing optics of the phosphorescent measurement. A: Tungsten light source, B: monochrometer, C: sample, and D: phosphorescent signal detector
III-2. Results and Discussion

The UV-VIS absorption spectra of VBP, measured in methanol is shown in Figure 12. The monomer exhibited some strong absorption bands in the wavelength region from 240 to 320 nm with an absorption maximum at 286 nm ($\epsilon=2.63\times10^4$ dm$^3$ mol$^{-1}$ cm$^{-1}$, this agrees with the literature$^{33}$). These transitions are due to $\pi\rightarrow\pi^*$ transitions of the aromatic rings of the molecule. It should also exhibit a weak band ($\epsilon=3\times10^2$ dm$^3$ mol$^{-1}$ cm$^{-1}$) in the wavelength region from 320 to 400 nm due to the $n\rightarrow\pi^*$ transition of the carbonyl group. $^{34}$ However, because the polar methanol solvent is expected to cause a blue shift of the $n\rightarrow\pi^*$ band and a red shift of the $\pi\rightarrow\pi^*$ band, $^{35}$ the $n\rightarrow\pi^*$ transition is probably masked by the $\pi\rightarrow\pi^*$ transition. This $n\rightarrow\pi^*$ transition was not observed in our experiment, but it could be observed in nonpolar solvents (e.g. hexane). $^{35}$

Because the lowest singlet state of 4-vinylbenzophenone is an $n\rightarrow\pi^*$ state localized on the carbonyl group, it should exhibit a very efficient intersystem crossing from the excited singlet state to the $n\rightarrow\pi^*$ triplet state. Usually, this system has a high phosphorescence quantum yield, on the order of 0.1 to 0.5, whereas the phosphorescence quantum yield for the $\pi\rightarrow\pi^*$ triplet states is less than 0.1. $^{36}$ However, no phosphorescence emission signal was observed for VBP in methanol solution, nor when dispersed in PMMA solid films. Tsubakiyama, et. al. $^{35}$ thought that the phosphorescent emission of VBP came from a benzoxy1 derivative, or styrene groups. The rings of VBP are not planar, thus, the molecule looks like a styryl group attached to a benzoxy1 group. Since styrene gives no phosphorescence emission, despite the considerable efficiency of
intersystem crossing (quantum yield is about 0.4), they inferred that the lowest triplet state for VBP was a $\pi,\pi^*$ configuration of the styryl group in contrast to the $n,\pi^*$ configuration for the highly phosphorescent benzophenone. Therefore, after VBP is polymerized with other monomers, the vinyl group becomes saturated. This leaves the $n\rightarrow\pi^*$ state of benzophenone as the lowest state. Consequently, VBP-containing polymers were expected to be phosphorescent.

Figure 13 displays the absorption spectra of poly(MMA-co-VBP) and poly(MMA-co-NIPMI). Poly(MMA-co-NIPMI) has an absorption band around 240 nm. Poly(MMA-co-VBP) exhibits an absorption band around 260 nm, which can be assigned to be a $\pi\rightarrow\pi^*$ transition of the aromatic ring system. The $n\rightarrow\pi^*$ transition of the carbonyl group of benzophenone should appear at 365 nm. This was not observed, probably due to a too low chromophore concentration. The spectrum of the poly(MMA-co-VBP) copolymer was narrower and less structured than the UV absorption spectrum of the VBP monomer (see Figure 12).

Phosphorescent emission spectrum of poly(MMA-co-VBP) is shown in Figure 14. It has three emission maxima at 417, 445, and 474 nm, which are characteristic phosphorescence of benzophenone. Emission spectra of benzophenone dispersed in PMMA solid films are also represented in this figure. Both the copolymer and the PMMA film contain the same concentration of benzophenone groups, to enable a basis for comparison.
Figure 12 UV absorption spectra of VBP in methanol
Figure 13 UV absorption spectra of poly(MMA-co-VBP) and poly(MMA-co-NIPMI)
Figure 14 Phosphorescent emission spectra of poly(MMA-co-VBP) copolymer and a PMMA film containing the same concentration of benzophenone
The emission spectra were normalized by the following:\textsuperscript{39}

\[
I_{\text{norm}} = \frac{I_{\text{exp}}}{1 - 10^{-\text{OD}}}
\]  

(1)

where, \( I_{\text{exp}} \) is the experimental emission intensity of tested samples, OD is the optical density of samples, and \( I_{\text{norm}} \) is the emission intensity after taking the optical density into account. The integral of \( \int I_{\text{norm}}(\nu)d\nu \), representing the area under the emission spectra, is proportional to the quantum yield for light emission. Therefore, for a given absorption band, high emission intensity indicates a large quantum yield. As can be seen in Figure 14, the quantum yield of poly(MMA-co-VBP) is nearly the same as that of benzophenone dispersed in a PMMA matrix. Similar results were obtained in the study of Borkman,\textsuperscript{38} on substituent effects on benzophone phosphorescence, He determined that alkyl substitution had no effect on the phosphorescence of benzophenone.

Figure 15 shows the phosphorescence spectra of poly(MMA-co-VBP)/PMMA and poly(MMA-co-VBP)/poly(MMA-co-NIPMI) 50/50 blends. As can be seen, the phosphorescence of benzophenone in the polymer blends quenched by the NIPMI groups of the poly(MMA-co-NIPMI) copolymers. The phosphorescence quantum yield of these blends was decreased upon an increase of quencher content. Since poly(MMA-co-NIPMI) absorbss below 300 nm (Figure 13), whereas the phosphorescence emission of benzophenone containing polymers is above 350 nm. Therefore, there is no spectral overlap between these bands. Consequently, the phosphorescent signal quenching can be
explained by invoking the non-resonant energy transfer mechanism. Rather, quenching is believed to be a consequence of the heavy-atom-induced quenching by iodine.

Since the introduction of VBP and NIPMI did not affect the physical properties of the parent homopolymers, the poly(MMA-co-VBP)/poly(MMA-co-NIPMI) polymer blends are believed to be miscible under these conditions, the heavy iodine atom of the imide group could lie within the diffusion length, \( R_0 \), of triplet benzophenone. The excited triplet benzophenone may be deactivated to ground state singlet by iodine atom on the route of the triplet exciton diffusion, so the phosphorescence emission decreases (The processes are shown in Figure 16). Quantum yield for phosphorescence \( (\phi_p) \) in the presence of static quenching groups, \( Q \), can be approximately expressed by the Stern-Volmer equation:

\[
\phi_p = \frac{\phi_o}{1 + k_q \tau_o [Q]}
\]  

where, \( \phi_o \) is the quantum yield of phosphorescence in the absence of quencher, \( \tau_o \) is the phosphorescence lifetime without quencher, \( k_q \) is the quenching rate constant, and \([Q]\) is the quencher concentration. From equation (2), it can be seen that a decrease of quantum yield is expected when the quencher concentration is increased.

The time-resolved phosphorescent decay curves, measured at an emission wavelength of 450 nm, for these poly(MMA-co-VBP)/poly(MMA-co-NIPMI) blends are shown in Figure 17. The phosphorescence intensity, \( I(t) \), decreases non-exponentially over the time scale of the experiments. Horie, et. al. \(^{40}\) interpreted that the deviation from
Figure 15 Phosphorescent emission spectra of poly(MMA-co-VBP)/poly(MMA-co-NIPMI) miscible blends with various concentrations of quencher. The NIPMI concentration in the legend indicates the particular poly(MMA-co-NIPMI) used.
Figure 16 Simplified photophysical processes of excited benzophenone, where $S_o$ is the ground state benzophenone, $S_1 (n\pi^*)$ is the benzophenone in the first singlet excited state, $S_n (\pi\pi^*)$ is the benzophenone in the singlet excited state with energy higher than $S_1 (n\pi^*)$, $T (n\pi^*)$ is the benzophenone in the lowest triplet state, $k_p$ is the phosphorescence rate constant of triplet benzophenone, $k_n$ is the non-radiative decay rate constant of triplet benzophenone without the presence of quencher, and $k_q$ is the non-radiative decay rate constant induced by NIPMI.
exponential decay (the Stern-Volmer model) is caused by the dynamic quenching of benzophenone triplets. They proposed that the quenching rate constant contains a time-dependent term representing group diffusion. The expression for the quenching rate constant, \( k_q \), is:

\[
k_q = 4\pi R_o DN (1 + \frac{R_o}{(\pi D t)^{1/2}}) = A + \frac{B}{t^{1/2}} \tag{3}
\]

with \( A = 4\pi R_o DN \) and \( B = 4R_o^2(\pi D)^{1/2}N \). In equation (3), \( D \) is the sum of diffusion coefficients for the carbonyl groups of benzophenone and for the quenching iodophenyl groups in the polymer blends, limited by side-chain rotation and local segmental motion of the polymer chain. \( R_o \) is the critical energy transfer distance between the two groups, and \( N \) is the Avogadro’s number divided by \( 10^3 \).

Since there is NRET in this system, the decay process of triplet benzophenone, \( ^3\text{BP}^* \), is affected by phosphorescent and non-radiative decay and triplet quenching, as depicted in the following equations:

\[
^3\text{BP}^* \xrightarrow{k_o} \text{BP} \tag{4}
\]

\[
^3\text{BP}^* + [Q] \xrightarrow{k_q} \text{BP} + [Q] \tag{5}
\]

where \( k_o = k_p + k_n \) is the rate constant for phosphorescent and non-radiative deactivation.
Figure 17 Semi-logarithmic time-resolved decay curves of benzophenone phosphorescence in the poly(MMA-co-VBP)/poly(MMA-co-NIPMI) blend, the NIPMI concentration in the legend indicates the particular poly(MMA-co-NIPMI) used.
benzophenone triplet. The resulting decay rate of benzophenone triplets is given by

\[ \int dt = (k_0 + A[Q] + B[Q_T]) [3BP^*] \] (6)

Integration of equation (6), gives the dependence of [3BP^*] on time

\[ [3BP^*] = [3BP^*]_0 \exp[-(k_0 + A[Q])t - 2B[Q_T]'t'] \] (7)

where [3BP^*]_0 is the initial concentration of benzophenone triplets immediately after light excitation. The phosphorescence intensity, I(t), is proportional to kp[3BP^*], so we get

\[ \ln I(t) = -k_0 t - A[Q]t - 2B[Q_T]'t + \ln /t \] (8)

where \( k_0 + A[Q] \)

\[ K + A[Q] \]

\[ B = \frac{1}{2} Q_T \] (9)

By fitting the phosphorescence decay curves in Figure 17 with equation (8), the values of reciprocal lifetime, 1/t, and the constant C were obtained. These are listed in
Table 8. The constants A and B were obtained by plotting $1/\tau$ and $\frac{C}{2}\tau^{\frac{3}{2}}$, respectively, versus the quencher concentration, [Q], in the blend. The resulting linear plots are given in Figure 18 and 19. The critical energy transfer distance is calculated as $R_o = \left(\frac{B^2}{4AN}\right)^{\frac{1}{2}} = 14^\circ A$. Within this radius, iodophenyl groups effectively quench the benzophenone phosphorescence. Polymer blends, for which the iodine-benzophenone pair, are determined to be phase separated by this technique.

Table 8  Life-time analysis of benzophenone triplets in PMMA blends

<table>
<thead>
<tr>
<th>[Q] (mol/L)</th>
<th>$1/\tau$ (ms$^{-1}$)</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.24</td>
<td>0.0131</td>
<td>0.160</td>
</tr>
<tr>
<td>0.69</td>
<td>0.0428</td>
<td>0.304</td>
</tr>
<tr>
<td>1.38</td>
<td>0.103</td>
<td>0.492</td>
</tr>
<tr>
<td>1.97</td>
<td>0.163</td>
<td>0.658</td>
</tr>
</tbody>
</table>

The iodine-mediated phosphorescent quenching of excited benzophenone triplets was also observed in the miscible poly(St-co-VBP)/poly(St-co-NIPMI) 50:50 blends. As shown in Figure 20, the phosphorescence signal in these blends decreased significantly in the presence of quencher-containing polymers. This demonstrates the utility of phosphorescent quencher system to study miscible polymer blends in the solid state.
Figure 18 Relationship of benzophenone triplet lifetime with quencher concentration
Figure 19 Determination of diffusion constant $B$, for the poly(MMA-co-VBP)/poly(MMA-co-NIPMI) blends
There is some difference between the phosphorescence emission spectra of the poly(St-co-VBP) blends and the poly(MMA-co-VBP) blends. The emission maxima at 417 nm of poly(St-co-VBP) blends is relatively higher than that of the poly(MMA-co-VBP) blends, and the emissions are not equally quenched in the poly(St-co-VBP) blends. This suggests that the emission of poly(St-co-VBP) blends at 417 nm is a combination of emission of polystyrene segments and benzophenone moieties.

The time-resolved phosphorescent decay curves of these poly(St-co-VBP)/poly(St-co-NIPMI) blends, monitored at an emission wavelength of 450 nm, are not well-fitted with the Horie model (shown in Figure 21). The phosphorescence intensities of the experiments decay slower than that as predicted from Horie model. When samples of these blends were exposed to 265 nm light, both the benzophenone moieties and the polystyrene segments were excited. The fluorescence of singlet polystyrene segments could be quenched by benzophenone moieties, that is, there is an energy transfer process from excited polystyrene segments to benzophenone moieties. These energy-transfer-induced excitons of benzophenones are lagged, compared to the light-excited benzophenones, and are thought to contribute to the slower decay in phosphorescent intensity.

Blends of polystyrene and poly(methyl methacrylate) are immiscible for a 50:50 mass ratio. This is evident from the transmission electron micrograph of the poly(st-co-VBP)/poly(MMA-co-NIPMI) blend. It shows that this blend exhibits a dispersed phase having domains which are several micrometers in diameter (given in Figure 22). In this blend, the phosphorescence signal of the benzophenone triplet should not be quenched, because the distance between the chromophore and the quencher are beyond the critical
Figure 20 Phosphorescent emission spectra of \text{poly(St-co-VBp)/poly(St-co-NIPMI)} miscible blends with various concentration of quencher. The NIPMI concentration in the legend indicates the particular \text{poly(St-co-NIPMI)} used.
Figure 21 Semi-logarithmic time-resolved decay curves of benzophenone phosphorescence in the poly(St-co-VBP)/poly(St-co-NIPMI) blend, the NIPMI concentration in the legend indicates the particular poly(St-co-NIPMI) used.
energy transfer distance. Figure 23 shows that the phosphorescence emission of this blend is almost the same as that of poly(St-co-VBP)/PMMA blend. Thus, the phosphorescence emission of benzophenone in poly(St-co-VBP)/poly(MMA-co-NIPMI) has not quenched, as predicted. The slight decrease in the emission intensity of the blend containing quencher may arise from the proximity of benzophenone and iodophenyl groups at the interface of the phase domains.
Figure 22 TEM picture of poly(St-co-VBP)/poly(MMA-co-NIPMI) 50:50 blend
Figure 23 Phosphoresence emission of poly(St-co-VBP)/PMMA and poly(St-co-VBP)/poly(MMA-co-NIPMI) 50:50 blends
IV. Conclusion

Novel, N-(4-iodophenyl)maleimide (NIPMI) was synthesized by imidizing maleic anhydride with 4-iodoaniline (with high yield 93.8%). The phosphorescent chromophore benzophenone and its quencher, NIPMI, were incorporated into polystyrene and poly(methyl methacrylate) polymers by free radical copolymerization of styrene or methyl methacrylate with 4-vinylbenzophenone or NIPMI. Thermal analysis results revealed that the resulting copolymers, with low chromophore incorporation, exhibited the same physical properties as the base homopolymers.

The sensitivity of phosphorescent signals to quencher concentration allowed us to probe the miscibility of binary polymer blends. Results indicated that for the binary polymer blends containing chromophore/quencher pairs on the same base polymer, the phosphorescent signal was quenched, whereas the signal was not affected by the quencher group in the phase-separated PS/PMMA system. Time-resolved phosphorescence measurements indicated that the triplet exciton can be quenched within a radius of 14 Å. Thus, the phosphorescent chromophore/quencher system could be used to probe polymer-polymer miscibility at the molecular level.
References


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Appendix A

$^1$H NMR Spectra of Polymers
Figure A.1 $^1$H NMR spectrum of poly(St-co-VBP)
Figure A.2 $^1$H NMR spectrum of poly(MMA-co-VBP)
Figure A.3 $^1$H NMR spectrum of poly(St-co-NIPMI)
Figure A.4 $^1$H NMR spectrum of poly(MMA-co-NIPMI)
Appendix B

Thermal Analysis of Polymers
Figure B.1 Differential scanning calorimetry measurement of polystyrene
Figure B.2 Thermogravimetric analysis of polystyrene
Figure B.3 Differential scanning calorimetry measurement of poly(St-co-VBP)
Figure B.4 Thermogravimetric analysis of poly(St-co-VBP)
Figure B.5 Differential scanning calorimetry measurement of poly(St-co-NIPMI)
Figure B.6 Thermogravimetric analysis of poly(St-co-NIPMI)
Figure B.7 Differential scanning calorimetry measurement of poly(methyl methacrylate)
Figure B.8 Thermogravimetric analysis of poly(methyl methacrylate)
Figure B.9 Differential scanning calorimetry measurement of poly(MMA-co-VBP)
Figure B.10 Thermogravimetric analysis of poly(MMA-co-VBP)
Figure B.11 Differential scanning calorimetry measurement of poly(MMA-co-NIPMI)
Figure B.12 Thermogravimetric analysis of poly(MMA-co-NIPMI)