

PHOTOCHEMISTRY AND PHOTOPHYSICS OF POLYMER MATERIALS

Edited by

NORMAN S. ALLEN



WILEY

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CONTENTS

Preface	vii
Contributors	xiii
1 Energy Transfer and Electronic Energy Migration Processes <i>Li-Juan Fan and Wayne E. Jones Jr.</i>	1
2 Optical Properties of Polyelectrolytes <i>Linda Swanson</i>	41
3 Chemiluminescence Processes in Polymeric Materials <i>Teresa Corrales, Carmen Peinado, Concha Abrusci, Norman S. Allen, and Fernando Catalina</i>	93
4 Nonlinear Optical Polymeric Materials <i>Mirko Faccini, David N. Reinhoudt, and Willem Verboom</i>	137
5 Metallodendrimers: Photophysical Properties and Related Applications <i>Grégory Franc and Ashok K. Kakkar</i>	185
6 Photochromic Polymers for Optical Data Storage: Azobenzenes and Photodimers <i>Avtar S. Matharu and P.S. Ramanujam</i>	209
7 Optical and Luminescence Properties and Applications of Metal Complex-Based Polymers <i>Joe A. Crayston and Joanne R. Ritchie</i>	235

8	Photovoltaic Polymer Materials	271
	<i>Hazel Assender and Aaron Barkhouse</i>	
9	Organic Light-Emitting Diodes	309
	<i>Sebastien Forget, Sebastien Chenais, and Alain Siove</i>	
10	Photoinitiators for Free Radical Polymerization Reactions	351
	<i>Jean Pierre Fouassier, Xavier Allonas, Jacques Lalevée, and Céline Dietlin</i>	
11	Photoinitiated Cationic Polymerization: Reactivity and Mechanistic Aspects	421
	<i>Muhammet U. Kahveci, Ali Gorkem Yilmaz, and Yusuf Yagci</i>	
12	Photoimaging and Lithographic Processes in Polymers	479
	<i>Marius Gabriel Ivan and Juan Cesar (Tito) Scaiano</i>	
13	Photografting of Polymeric Materials	509
	<i>Ali Ekrem Muftuoglu, Mehmet Atilla Tasdelen, and Yusuf Yagci</i>	
14	Photoablation of Polymer Materials	541
	<i>Lukas Urech and Thomas Lippert</i>	
15	Photodegradation Processes In Polymeric Materials	569
	<i>Jean-Luc Gardette, Agnès Rivaton, and Sandrine Therias</i>	
16	Photodegradable Polymers	603
	<i>Sahar Al-Malaika, C. Hewitt, and H.H. Sheena</i>	
17	Photostabilisation of Polymer Materials	627
	<i>Pieter Gijsman</i>	
	Index	681

PREFACE

In the last four decades, the photophysics and photochemistry of polymeric materials have evolved from what were essentially esoteric, often topical, basic research specialities into what one would clearly class today as one of the most significant and important industrial fields and specializations of our modern era. In fact, our whole modern industrial world today in terms of electronic devices, computers, solar cells, printing, imaging, copying and recording systems, to name but a few, would not exist without this creative science surrounding light and its interactions with plastics. Furthermore, our modern-day applications of commercial plastics would not exist without sound knowledge and understanding of their degradation and stabilization processes.

Today, this subject embraces many fields of science and technology, all continuing to develop and change rapidly. However, we have reached a stage where now it is important to categorize and collate our knowledge achieved to date on most of the specific areas of industrial significance. Indeed, only recently, some research specializations such as OLED's and plastic solar cells have emerged into new industrial technologies that will make their mark in the forthcoming years. Our current knowledge achieved to date in most of the areas is clear and scientifically sound and this handbook hopes to lay the foundations of such an understanding for future developments. There are always controversies in all fields of research and indeed this will continue as mankind develops ideas and new technologies. The foundations laid in this book will hopefully facilitate such developments for specialists, academics, and industrialists worldwide.

Thus, the theme of this book brings together a wide range of subjects in the field of photophysics and photochemistry of polymers by underpinning the fundamental,

functional, operational, developmental, and application knowledge acquired to date.

The book comprises a total of 17 chapters, each dealing with a specific topic from the basic empirical approach to specific applications in the various fields. The utilization of light energy and its effects is the main theme of the book. Indeed, each chapter interlinks well in terms of the fundamentals, mechanisms, processes, and applications. As one might expect, some of the topics in each chapter interrelate and cross boundaries as many plastics materials have numerous applications.

Chapter 1 on energy transfer and migration processes is indeed the key to the whole operational processes underpinning the interactions of light energy with polymer materials. Light absorption and its dismutation is crucial to all the technologies applicable to polymer materials in terms of their photonic applications. Thus, how the energy is utilized, degraded, and transformed plays a major role in determining the viability of a particular polymer in its application. Here the inherent structural features and morphology of the material control the nature of the photophysical processes that result in energy transformations and potential chemical reactions. All these are dealt with in subsequent chapters. Concurrent with this chapter is Chapter 2 dealing with more complex effects of polymer materials in solution, especially in polyelectrolytic media where important processes for energy transfer can be controlled and made more effective, for example, in light harvesting, enhanced photochemistry, and rheological modifications. Examination of the light emission processes is crucial to our understanding of such processes and their efficiency. In Chapter 3, an extension to light emissive processes is discussed in relation to chemiluminescence. This is light emission in a different context that arises from the inherent features of the polymer itself rather than being light induced. All polymer materials degrade in their lifetime, even during their initial manufacture, and here this technique has attracted much interest worldwide into a specialized field probing the durability of the polymer. In fact, it has become a highly sensitive method of providing rapid information on polymer life expectancies and stabilization efficiency. In the applications area, polymeric electrooptical materials incorporating nonlinear (NLO) chromophores have important commercial potential. Chapter 4 concentrates on the design features of efficient dipolar NLO chromophores via different processes for various electrooptic device applications. This includes guest–host systems, chromophore functionalization, dendritic and cross-linked materials, to name but a few. Here, state-of-the-art technologies are covered with emphasis on high NLO responses and good stability for their long-term future. As an extension to this area, we have novel exploitations in the development of smart devices based on metallodendrimers, and their structure–property relationships are described in detail in Chapter 5. Such metallated macroassemblies show enormous promise with some intriguing architectures for future development. On another front, polymers with photochromic properties have developed and become a major factor in the manufacture of optical storage media. Materials based on azobenzene functionalities are fundamental to this process and are covered in terms of the latest developments in Chapter 6. Cycloaddition reactions and the use of

thiamine as new high-potential devices for high storage capacities are some of the key developments here. Metallopolymers with integrated metal complexes is a further addition to the development of molecular devices, especially with regard to enhanced applications for OLED's and metal complexation of polyconjugated materials. Their role in solar energy devices is becoming an area of significant development. Their optical and luminescence characteristics underpin their efficiency and this is covered in Chapter 7. On the application side, clearly one of the major roles of polymer materials in future optical electronics is their development in solar cell construction as one potential solution for the future energy crisis facing us all. Their development and construction and structure–efficiency relationships are described in some detail in Chapter 8. Here the cost-effective devices with high conversion efficiency that can compete with inorganic devices is the key to their success and this chapter shows the way forward. Another major area closely looked into the previous chapters is the development of OLED polymers that has grown into a major field of commercialization, especially in terms of electronic devices and displays with of course thin flat screen televisions being one of the most significant. Structure LED properties for a range of such polymers is described in depth in Chapter 9 probes the molecular device complexities with light emitting properties and how these may be maximized for effect. Moving on to some different topics, the use of light in synthesis of polymer materials is also an area of significance and has been closely allied to many commercial operations for many years. Polymerization processes being the key to the manufacture of polymeric materials involves a number of mechanisms, some requiring heat while others requiring light or radiation. The latter has some major beneficial advantages over conventional methods. These are controlled reactions, energy efficiency, polydispersity, and *in situ* production of materials, that is, in coatings applications such as electronic devices. These processes are indeed vast in terms of potential mechanisms and methods. Free radical addition polymerization through the use of active light-absorbing initiators is a major field of commercial significance and academic interest. Chapter 10 underpins all the complex mechanistic processes involved in free radical polymerization chemistry covering most of the currently available and topical initiators that have been investigated. On the other front and indeed another closely related manufacturing technology for electronic devices is the use of cationic initiators. Here there are many other advantages over that of conventional free radical initiators such as ring opening reactions, absence of oxygen inhibition, and production of what one can describe as “living polymers” for further extensions. Chapter 11 delves into some depth on the types and mechanisms of such processes in relation to new commercial developments. In the electronic world, the key to circuitry, for example, is the process and technology of imaging science through the use of light energy. Photoimaging, as it is known, is indeed a major field where various polymer materials, monomers, and prepolymers are processed and converted by light into an image. Lithographic printing, for example, is a well-established technology and continues to be developed into newer materials for processing. This takes us into the realms of nanolithography and the adaptability

and use of specific lasers for nanoimaging. All these processes, new technologies, and polymer materials in photoimaging science and lithography are defined and discussed in Chapter 12. The last area in terms of the synthetic polymerizations with light is the field of photografting. Here light is utilized to graft monomers and polymers onto surfaces either to enhance the properties of materials or to develop molecular electronic devices. In this technology, free radical initiation, cationic, and cross-linking processes can all play a role depending on the end use, covered in depth in Chapter 13. In the fabrication of polymeric electrooptical devices, another major field of significance is in the ablation of polymer materials to yield specially designed and fabricated surfaces. This area of photoablation underpins a number of important and established commercial technologies in microdevices and microfluidic channels, to name but a few. The computing and printing industries could not, for example, function well without this modern type of photoapplication. Here the mechanisms and efficacy of photoablation and its applications in the electronics field is described in detail. The key here is to produce effective clear ablative surfaces or holes without contamination, and how to design and modify photochemistry to suit is described in Chapter 14. Remaining with light and its effects on polymer materials, we come to one of the most important fields that one could argue is imperative in terms of the future use and applicability of electronic polymers and that is their stability to the actual light activation itself. Indeed, all organic polymers and for that matter inorganic types undergo some type of photochemically induced reaction in their useful lifetime that can cause a breakdown to varying degrees in their physical and mechanical properties. Such processes are complicated by the nature of the light, environmental effects, and the manufacturing and compositional nature of the polymer material itself. Such processes and their effects are clearly described in Chapter 15 for both conventional thermoplastics through to modern-day electronic and composite materials. An extension to this issue is the usefulness of light-induced degradation processes and its chemistry for the production of environmental polymers where there is widespread application in minimizing, for example, waste and pollution. There are also extensive applications in agriculture for enhanced and controlled crop growth and subsequent degradation and mulching. The area of photodegradable polymers has significant commercial development and applicability from the plastic carrier bag through to agricultural greenhouse films. These topics covering the types of polymers and modes of operation are described in some detail in Chapter 16. In the end, it is important to be able to overcome many of the detrimental processes described here in previous chapters, especially if one is to be able to secure the long-term viability of modern-day polymer materials in the environment. Thus, the role and effectiveness of stabilization technologies is crucial, and Chapter 17 thus covers the structural types and modes of operation of stabilizers and stabilization mechanisms for polymer materials. Hopefully, this will provide an opportunity for the more specialized optical electronic specialists to look into the ways and methods for extending the practical usefulness of their materials.

In conclusion, I hope this book will bring together what has been a series of major developments in the polymer world where light and its energy has been put to valuable use in enhancing the technological developments we find ourselves in today and the future. The book I am sure will provide specialists in the fields concerned with a sound understanding and basis for the future in launching new materials while at the same time having a clearer view and opportunity of related areas for problem solving.

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1

ENERGY TRANSFER AND ELECTRONIC ENERGY MIGRATION PROCESSES

LI-JUAN FAN AND WAYNE E. JONES JR.

- 1.1 Introduction
 - 1.1.1 Foundations of energy transfer and energy migration
 - 1.1.2 Luminescent polymer systems
 - 1.2 Energy transfer and migration processes in conjugated polymers
 - 1.2.1 Light harvesting and fluorescence superquenching
 - 1.2.2 Intramolecular versus intermolecular energy migration
 - 1.2.3 Probing of energy migration in different conjugated systems
 - 1.2.4 Summarizing the characteristics of energy transfer and energy migration in conjugated polymers
 - 1.3 Applications
- References

1.1 INTRODUCTION

1.1.1 Foundations of Energy Transfer and Energy Migration

Photoinduced energy transfer and energy migration processes have been studied extensively in luminescent polymers for several decades and have applications in sensors, optics, and solar energy conversion [1–7]. Energy transfer refers to a photophysical process whereby the excitation energy of an excited luminophore (donor “D”) moves to a chromophore (acceptor “A”). This process can occur by either

a nonradiative process or a radiative process and is typically thermodynamically spontaneous. Within a unimolecular system, including macromolecules and one-dimensional polymer systems, this process is called electronic energy migration. This can occur between identical molecular subunits where no thermodynamic gradient exists or between different structures resulting in an energy transfer gradient. Thus, energy migration is a specific class of energy transfer. Here, the term “energy transfer” will be used to refer to an interaction between two different species (“heterogeneous” transfer) while the term “energy migration” to refer to processes involving the same species (“homogeneous” transfer), unless otherwise noted.

Electronic excitation results in a quasiparticle, termed an “exciton” in a one-dimensional polymer system [8–11]. When an insulator or a semiconductor absorbs light, an electron from the valence band is excited into the conduction band, and the missing electron in the valence band leaves a hole behind. The exciton can be regarded as a bound state of the excited electron and hole. It is an electrically neutral, excited state of the molecule. An exciton is mobile in a homogeneous one-dimensional system resulting in “hopping” of the exciton state among identical particles with equal energy rather than localizing on one chromophore. Therefore, energy migration can also be called “exciton migration” or “exciton hopping.” The energy of a migrating “exciton” is not dissipated during migration; however, the kinetic relaxation of the molecule to the ground state results in a natural lifetime unless the exciton interacts with a lower energy trap site.

There are two nonradiative energy transfer mechanisms that can be described: the Förster mechanism and the Dexter mechanism [8,10]. Both energy transfer mechanisms occur through a radiationless process. Förster energy transfer, also known as through-space or dipole–dipole energy transfer, involves the long-range coupling of the donor and acceptor dipoles. The resonance between the donor dipole moment and the acceptor dipole moment is facilitated by the presence of intervening solvent dipoles. According to Förster, this kind of energy transfer mechanism is mainly affected by three factors: (1) the spectral overlap between the absorption spectrum of the acceptor and the fluorescence spectrum of the donor; (2) the distance between donor and acceptor since both dipole–dipole interaction energy and resonance are distance dependent; and (3) the orientation of the dipoles of the donor and the acceptor molecules and the intervening medium. The Förster energy transfer is favored when donor and acceptor are rigidly held in good alignment, because resonance is maximized when the oscillating dipole of the excited donor and the transition dipole of the acceptor ground state are aligned. The energy transfer rate (k_{ET}) for the Förster mechanism is described by the following relationship:

$$k_{ET}(\text{Förster}) = k \frac{\kappa^2 k_D^0}{R_{DA}^6} J \quad (1.1)$$

where k is a constant determined by experimental conditions such as solvent index of refraction and concentration, κ^2 is related to the interaction between the oscillating donor dipole and the acceptor dipole, which depends on the square of the transition dipole moments for the donor and the acceptor and the orientation of the dipoles in

space, k_D^0 is the pure radiative rate of the donor, J is the spectral overlap integral, and R_{DA} is the distance between donor and acceptor.

Dexter energy transfer is known as through-bond energy transfer and takes place through a double electron exchange mechanism within the molecular orbitals of the donor and the acceptor. The electronic coupling leading to energy transfer requires significant orbital overlap. Therefore, close interaction between the excited donor and the acceptor ground state is necessary. The rate constant of Dexter energy transfer, $k_{ET}(\text{Dexter})$, is shown below:

$$k_{ET}(\text{Dexter}) = KJ e^{(-2R_{DA}/L)} \quad (1.2)$$

where R_{DA} is the distance between donor (D) and acceptor (A) relative to their van der Waals radii L , K is related to the specific orbital interactions, and J is the normalized spectral overlap integral. Thus, the Dexter transfer rate is affected by the spectral overlap and also the separation distance between D and A.

The rates of the Förster energy transfer and Dexter energy transfer depend on the separation distance between the donor and the acceptor, shown qualitatively in Fig. 1.1. The former decreases as the inverse sixth power of the distance, whereas the latter falls off exponentially as the distance increases. Therefore, the Förster energy transfer is able to occur over very large distances, while Dexter energy transfer will give much greater rates at short distances and close contacts.

There is also a radiative energy transfer mechanism termed the “trivial” mechanism of energy transfer. It is accomplished through radiative deactivation of a luminophore donor and reabsorption of the emitted photon by a chromophoric acceptor. There is no direct interaction between the excited donor and the ground

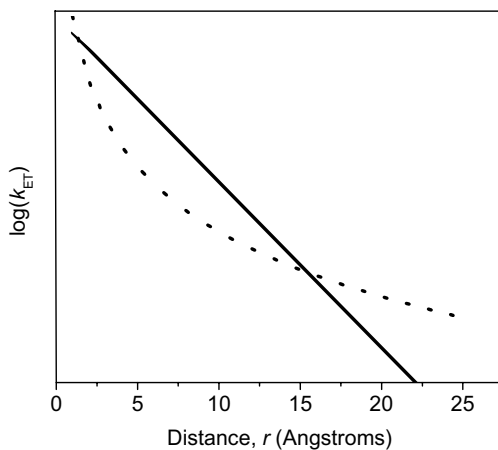


FIGURE 1.1 Plot of $\log(k_{ET})$ versus distance r for both Dexter (solid line) and Förster (dotted line) energy transfer mechanisms, excluding any criterion other than distance. k_{ET} denotes the rate of energy transfer.

state of the acceptor. Thus, the “trivial” energy transfer is a two-step sequence as shown in Equations 1.3 and 1.4, where D^* and D denote the excited and ground states of the donor and A^* and A denote the excited and ground states of the acceptor.



The trivial mechanism is not very efficient given the statistical probability of direct emission and reabsorption. However, the efficiency of this kind of energy transfer can be maximized with high emission quantum yield of the donor, high concentration and high extinction coefficient of the acceptor, and strong overlap between the emission and absorption spectra. In most systems, the trivial process does not contribute significantly compared to the other two mechanisms.

1.1.2 Luminescent Polymer Systems

Excited-state processes in polymer materials strongly depend on their electronic and structural properties. There are several types of polymers that are capable of energy transfer and migration. A polymer with a saturated backbone and pendant chromophores such as naphthalene, anthracene, and commercial dyes can be described as type I polymer [11]. In some cases, the chromophore has also been incorporated as a component of the polymer backbone repeat unit or covalently linked to the polymer as a terminal end group. Typically, introduction of the chromophore is achieved through premodification of the monomers or postfunctionalization of the polymers.

The photophysics of type I polymers is very similar to that of the corresponding small-molecule substituent chromophores that they contain. The polymer can be described as an inert scaffold that restricts the movement and relative distance of the chromophores. As a result, the photophysics of these polymers can be strongly affected by the conformation of the polymer backbone and, to a lesser extent, by the aggregation of the polymers. The basic photophysics and energy migration processes of this type of fluorescent polymers have been studied extensively by Guillet and Webber over the past two decades and have been summarized elsewhere [1,11].

Another type of polymers involves conjugated backbones with extensive electronic coupling and has been classified as type II polymers. These so-called “molecular wire” conjugated polymers have received substantial and growing interest in recent years due to their potential wide application as light emitting diodes (LEDs), photovoltaics, and sensors [3,4,9]. Understanding energy transfer and migration in these polymer systems is critical to their success in these applications. An interesting subset of conjugated polymers is the group known as electrically conducting polymers first discovered in 1977 by MacDiarmid and Coworkers [12]. This Nobel Prize winning work has been described elsewhere and is beyond the scope of this review [13]. Here, focus will exclusively be on the fluorescent conjugated polymers that are typically semiconducting in nature.

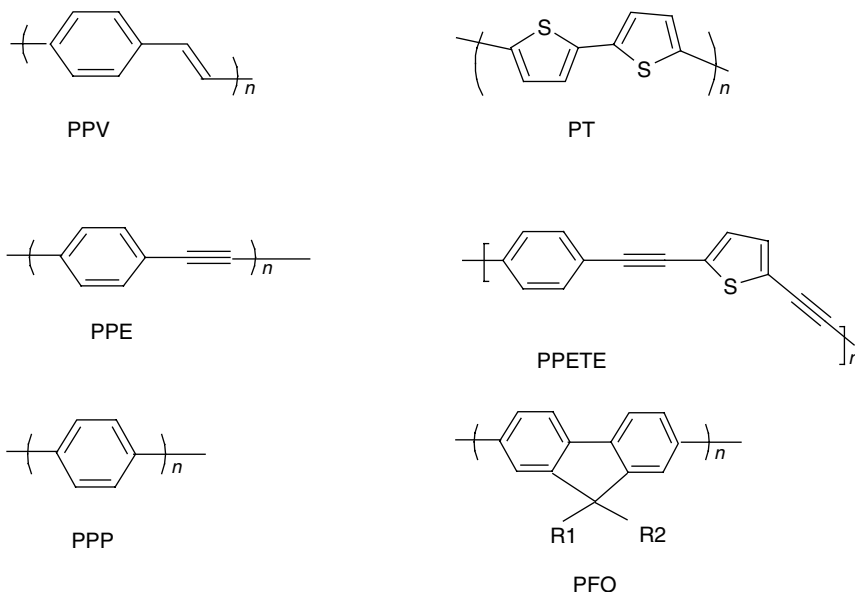


FIGURE 1.2 Basic structures of several fluorescent conjugated polymers.

There are two distinctive characteristics of conjugated polymer fluorophores relative to their small-molecule model compounds. The first is that the initial excited state formed by absorption of a photon is not a localized electron-hole pair. The excitation energy can be described as a delocalized *exciton* that spreads over several repeat units along the polymer backbone. The second characteristic is that the excitation energy can migrate along the polymer backbone. Some representative examples of conjugated polymer backbones are given in Fig. 1.2. They are poly(phenylene vinylene) (PPV), polythiophene (PT), poly[*p*-(phenylene ethynylene)] (PPE), poly[*p*-(phenyleneethynylene)-*alt*-(thienyleneethynylene)] (PPETE), poly(*para*-phenylene) (PPP), and polyfluorenes (PFO).

Compared to type I fluorescent polymers, the conjugated polymer backbone is the active chromophore. The monomer units that make up the polymer might not be inherently fluorescent. The absorption and emission of photons involve electronic transitions between a ground-state singlet (S_0) and a excited-state singlet (typically S_1) as shown in Fig. 1.3. Radiative (k_r) and nonradiative (k_{nr}) transitions result in relaxation to the ground state and the observed kinetic lifetime τ of these systems is governed by the relationship

$$\tau = 1/(k_r + k_{nr}) \quad (1.5)$$

Introduction of transition metal elements might introduce significant spin-orbit coupling into the system that increases intersystem crossing, k_{isc} , and results in population of lower energy triplet states (T_1). The result is phosphorescence between the lowest energy triplet state and the ground-state singlet S_0 .

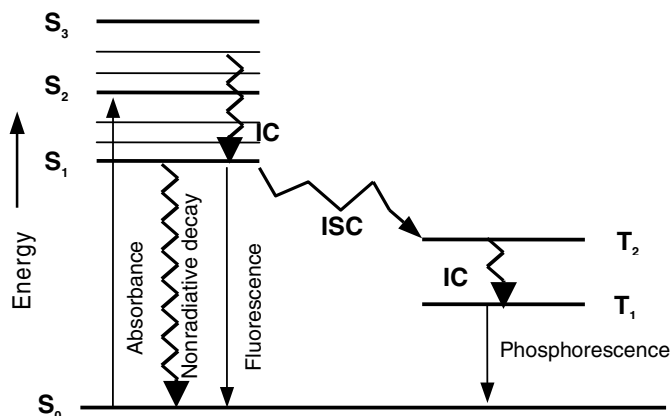


FIGURE 1.3 The Jablonski diagram. k_r , k_{nr} , and k_{isc} denote the rate constants of the deactivating processes from S_1 ; IC indicates the internal conversion process and ISC indicates the intersystem crossing process.

1.2 ENERGY TRANSFER AND MIGRATION PROCESSES IN CONJUGATED POLYMERS

1.2.1 Light Harvesting and Fluorescence Superquenching

Many applications of conjugated polymers take advantage of the facile energy migration that can occur through the extended π -system of the polymer backbone. The process can be represented using an electronic state diagram as shown in Figs. 1.4 and 1.5. The process of exciton migration has been described in the literature as following a random walk between energetically degenerate and equidistant chromophoric sites [9].

Here the natural lifetime of the exciton is not affected by the migration, although changes in polarization are evidence of the migration event. An exception to this

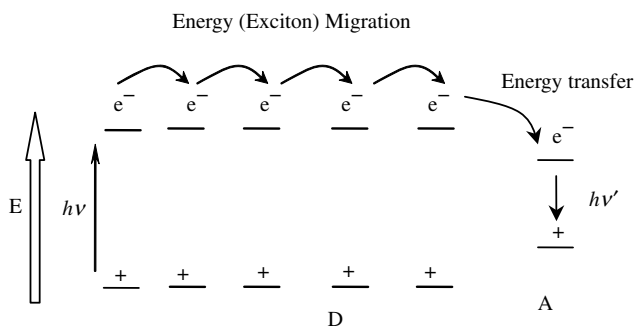


FIGURE 1.4 Illustration of the exciton (bound electron–hole pair) migration process in a conjugated polymer ending with a red-shift emission.

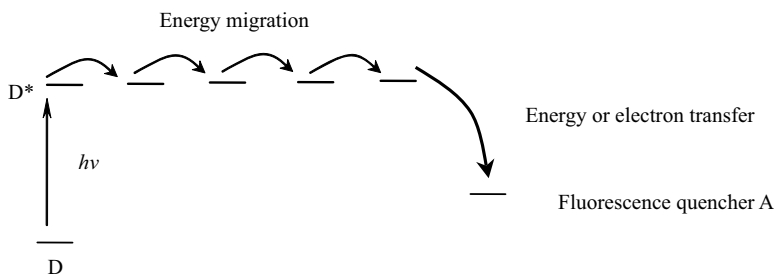


FIGURE 1.5 Illustration of energy migration from a donor state D^* to a fluorescence quenching acceptor site A.

would be when the exciton comes into proximity with an energy quenching site. This site could be a narrow-bandgap chromophore with emission at a long wavelength (Fig. 1.4) or a fluorescence quencher (Fig. 1.5). Two forms of energy transfer are involved in both situations: the energy migration among the identical excitonic sites of the polymer backbone (homotransfer) followed by energy transfer or electron transfer to a quenching acceptor (heterotransfer). Energy migration could occur over very large distances along the polymer chain depending upon the lifetime of the exciton and the relative loading of the acceptor.

The energy transfer situations depicted in Figs. 1.4 and 1.5 represent different models currently discussed in the literature. In the case of Fig. 1.4, the energy migration and transfer efficiency can be characterized by the emission ratio between the polymer backbone donor and the fluorescence from the acceptor group. This phenomenon has been called “light harvesting” since the conjugated polymer captures the incident light efficiently over the entire polymer and dumps the energy out at the lower energy trap site. This is the basis for solar harvesting in photosynthetic cells [1,3,14].

Superquenching of polymer fluorescence can be described based on Fig. 1.5. In this case, energy migration in the polymer and subsequent energy transfer or electron transfer to the acceptor is very efficient. Rapid exciton mobility combined with energy transfer to a trap site can result in million-fold amplification and the “superquenching” phenomenon in sensory system [6,9,15,16]. Superquenching has also been observed with gold nanoparticles in conjugated polymer systems further extending the scope of this phenomenon [17].

1.2.2 Intramolecular Versus Intermolecular Energy Migration

In recent years, there has been growing interest in understanding the energy migration processes that occur in conjugated polymer materials [3]. Many have found that the rate and efficiency of energy migration in conjugated polymers strongly depend on the conformation, aggregation, and electronic structure properties of the polymer. This dependence is due to the fact that energy migration processes can occur both intramolecularly and intermolecularly in different assemblies of the polymer materials.

In the case of a rigid-rod polymer in dilute solution, the system is free of any specific interaction between polymer chains or chain segments. In this case, the exciton usually follows a random walk along the polymer backbone, which is called “intramolecular energy migration process” [9,16]. When the polymer is in an aggregated state, the “intermolecular energy migration process” is the more dominant mechanism, although the intramolecular energy migration could still occur at a slower rate [18,19]. The aggregation state could be in several forms, such as specific interaction induced polymer aggregation in solution, spin-coating film, LB film, and self-assembled polymers onto the surface of a sphere [14,18–23]. Intramolecular energy migration takes place in one dimension, while the intermolecular energy migration takes places in two or three dimensions. Sometimes, polymer segments can fold back to form aggregation with another segment of the same polymer chain. The energy migration between these two segments is still classified as intermolecular here since it is more close to interchain migration as discussed in greater detail below.

Most conjugated polymers form aggregates at high concentration or in the solid state when the chains are in close contact. This aggregation tends to order the polymer chains, increasing p-conjugation and resulting in a red shift in the observed absorption and emission process. In some assemblies, well-packed conjugated chains preserve electronic independence and there is no observed interaction between the polymer chromophores. In other cases, the interaction between the conjugated segments results in the formation of new excited states such as excimers, exciplexes, and charge transfer species. When two adjacent polymer chromophores have π -electron interaction in the excited state but not in the ground state, the excited state is referred to as an excimer if the segments are identical or an exciplex if they are different. These aggregates are more common in the process of energy migration in condensed polymers.

1.2.3 Probing of Energy Migration in Different Conjugated Systems

There is considerable interest in understanding the mechanism and variables related to rate and efficiency for intramolecular and intermolecular energy migration in conjugated polymer systems. Many techniques, other than the room-temperature steady-state spectroscopy, have been used, such as single-molecule spectroscopy, time-resolved fluorescence spectroscopy, and low-temperature fluorescence and emission polarization spectroscopy. In addition, some specific conjugated polymers and assemblies have been designed to facilitate the study of isolated polymers or aggregated polymers with precise conformation or controlled migration. Some theoretical modeling and simulation have also been advanced by some groups for further understanding the experimental phenomena. Poly(arylene ethynylene) (PAE), PPV, and polyphenylene are the most discussed conjugated polymer systems in the literature and will be described in detail here as representative examples.

1.2.3.1 Poly(arylene ethynylene) Systems Energy migration processes in PAE have received great interest due to their relatively rigid structure, photophysical

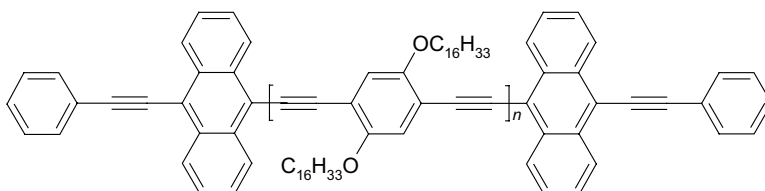


FIGURE 1.6 Structure of PPE endcapped with anthracene.

characteristics, and capability for facile long-range energy migration. Swager and coworkers have devoted considerable effort in this area, along with their outstanding research in the amplification of fluorescence-based chemosensory signal. One creative method for probing energy migration efficiency is to attach low-bandgap termini at the ends of a conjugated polymer chain. This was first demonstrated by Swager et al. in 1995 [24]. They synthesized the highly luminescent PPE polymer and incorporated anthracene into the backbone (Fig. 1.6). In this system, the polymer acted as an antenna that harvested the optical energy and transferred it to the low-energy anthracene group. The energy migration efficiency could be quantified by the emission ratio between anthracene and the polymer backbone. Figure 1.7 shows the absorption and emission spectra for this representative polymer. In this study, the absorption was a composite spectrum of the model PPE without the anthracene endcap and a model small-molecule anthracene chromophore. This suggested that the end group on the polymer produces very little perturbation in the polymer electronic structure. Interestingly, these low-energy termini were found to have a large effect on the emission behavior. Most emissions occurred in a band at 524 nm, which belonged to anthracene, while only a small amount ($<5\%$) of emission at 478 nm was from the polymer backbone. This demonstrated that 95% of the excitation energy was

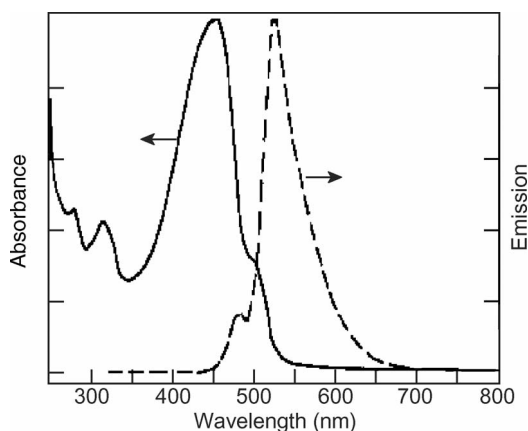


FIGURE 1.7 Absorption and emission spectra of the anthracene-endcapped PPE in dilute solution. For a detailed comparison among the spectra of the model polymer, anthracene, and this polymer, please see the original literature. (Source: Ref. [24].)

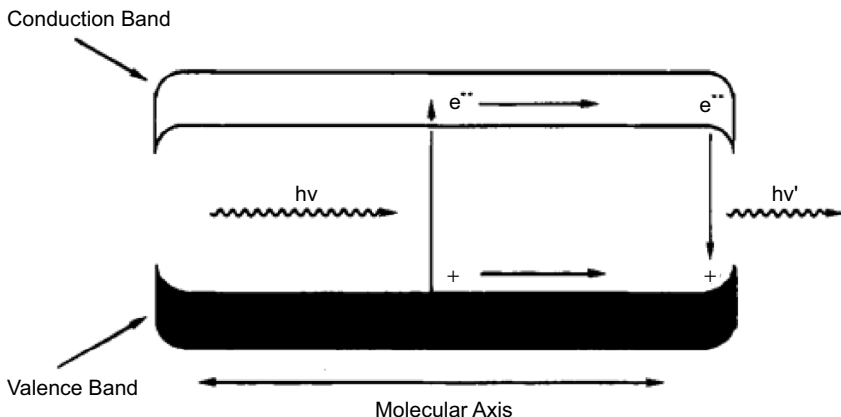


FIGURE 1.8 Schematic illustration of energy migration in a semiconductive molecular wire with a lower bandgap at the terminus. The exciton (the electron-hole pair) is initially generated by the photoexciton, migrates along the conjugated polymer backbone to the terminus, and then recombines with emitting fluorescence. (Source: Ref. [24].)

transferred to the end group and was attributed to facile energy migration in a semiconductive molecular wire with a decrease in the bandgap trap at the end (Fig. 1.8).

The molecular wire concept was first advanced in a chemosensory system by Swager and coworkers in 1995 [16,25]. In this case, energy migration could be classified as intramolecular, one-dimensional random walk since the photophysical study was carried out in dilute chloroform solutions. PPE is a rigid-rod polymer that suggested very little interaction between the polymer chains or segments at low concentrations. The one-dimensional energy migration along the polymer backbone can be described as involving through-bond Dexter energy transfer as a result.

One-dimensional random walks do not always provide for the most efficient energy migration. There are at least two reasons to explain the relatively sluggish one-dimensional energy migration in some systems. First, an excitation might retrace certain portions of the polymer backbone several times before quenching or relaxation. Second, the through-bond Dexter energy transfer process can be limited by orbital overlap as a result of chain defects, or conformational irregularities might exist in certain polymer backbones with more degrees of freedom.

To improve the efficiency of energy migration in chemosensory polymers, Swager et al. extended their interest in designing new conjugated polymers to assemblies capable of two- or three-dimensional random walks [14,18]. The idea was based on the consideration that increased dimensionality might decrease the probability of an excitation retracting a given segment of the polymer. In addition, multidimensional intermolecular energy transfer usually involves more facile Förster-type processes, which depend on the dipolar interaction between donor and acceptor [8,10].

The photophysics and energy transport properties of another PPE (Fig. 1.9) were investigated in highly aligned monolayer and multilayer Langmuir-Blodgett (LB) films as well as in the spin-coating film [18]. The cyclophane pendant group was

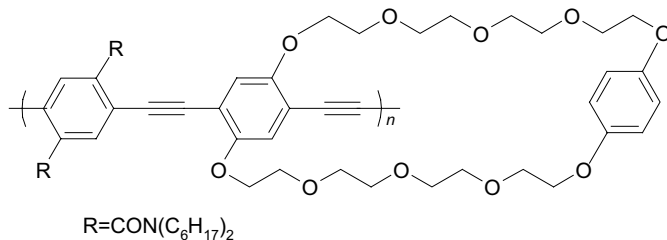


FIGURE 1.9 Structure of a PPE with cyclophane pendant group.

introduced in this case to prevent fluorescence self-quenching in the film due to intermolecular π -stacking between the fluorophores. Compared with fluid polymer solution, all the films displayed some degree of red shift. This was consistent with increased interaction (π -stacking) between the polymer backbones in the aggregated state (Fig. 1.10). The spectral profile in the case of the LB film showed a more limited change compared to the spin-cast film that was red shifted and exhibited a broadening in the spectra. A progression of red shifts in the LB film emission was observed with an increase in the number of layers, indicating more aggregation with increasing number of aligned layers in the films (Fig. 1.11).

Direct evidence of energy migration in the different films was found in polarized fluorescence emission studies. The fluorescence anisotropy indicated that intramolecular energy migration (with a Dexter hopping mechanism) existed in both the solution and spin-cast films. Further energy migration and transfer studies were

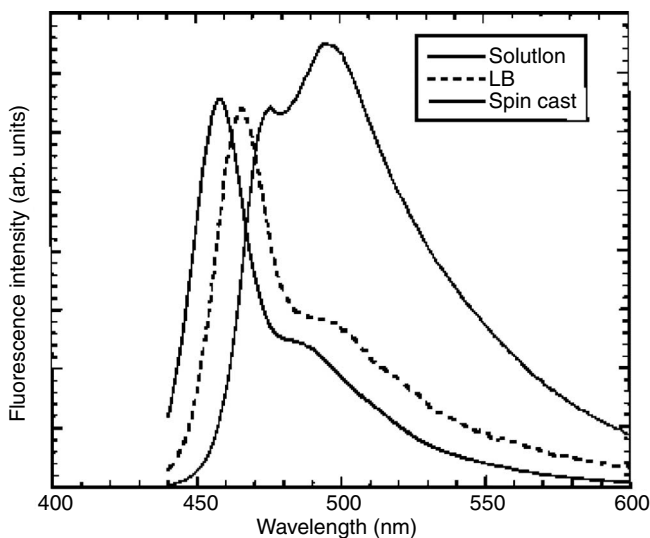


FIGURE 1.10 Comparison of the emission spectra for PPE with cyclophane pendant group (polymer in Fig. 1.9) in solution, as a highly aligned LB film (two layers) and as spin-cast from CHCl_3 . The excitation wavelength was 420 nm. (Source: Ref. [18].)

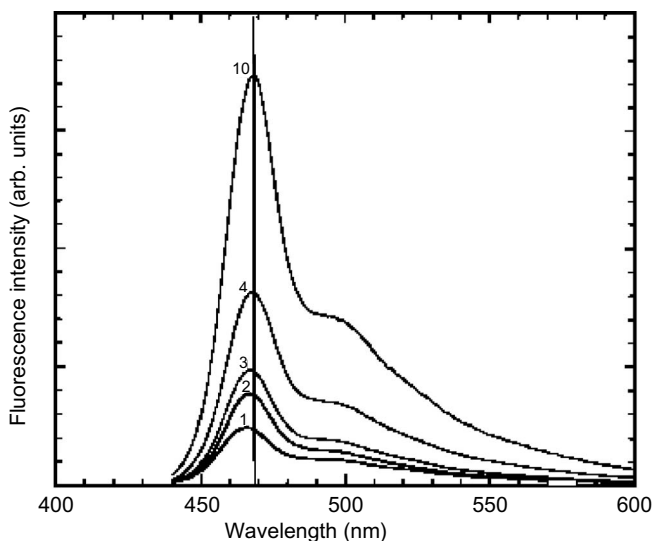


FIGURE 1.11 Emission spectra for LB films of the polymer in Fig. 1.9 containing 1, 2, 3, 5, and 10 aligned layers. The excitation wavelength was 420 nm. (Source: Ref. [18].)

carried out by using a luminescence trap Acridine Orange (AO) located on the polymer surface, which was prepared by dipping the LB film into the AO solution in methanol. As seen in Fig. 1.12, while selectively exciting the chromophoric polymer, the AO emission increases. This is accompanied by a decrease in the polymer

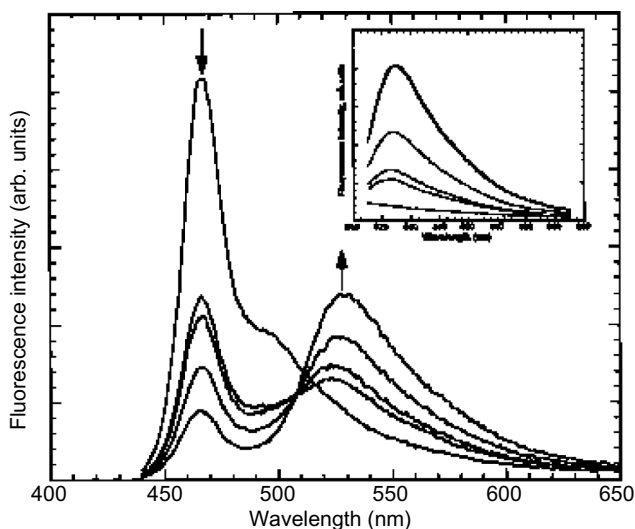


FIGURE 1.12 Emission ($\lambda_{\text{ex}} = 360$ nm) from a bilayer LB film of polymer in Fig. 1.9 treated with increasing concentrations (0 , 8×10^{-8} , 1×10^{-7} , 3×10^{-7} , and 5×10^{-7} M) of AO in MeOH before dipping. The inset shows the emission spectra of the same films excited at 490 nm, where AO was selectively excited. (Source: Ref. [18].)