Handbook of Polymer Science and Technology

Volume 4
Composites and Specialty Applications

Edited by: Nicholas P. Cheremisinoff

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Preface

The *Handbook of Polymer Science and Techonology: Composites and Specialty Applications,* Volume 4 is organized with 14 chapters covering the end-use properties and applications of engineering plastics, polymer blends and alloys, and polymer composites. As has been done throughout this series of handbooks, emphasis is on relating molecular properties to end-use performance in consumer- and engineering-related applications. Chapter 1 relates molecular structure to polymer physical and photochemical properties. Chapters 2 through 4 provide detailed discussions on the preparation and properties of elastomeric blends and plastic blends. The subjects of polymer compatibility, phase separation, crystallization, and the basis for designing polymer alloys and blends and their processing characteristics are treated. Chapter 5 provides an overview of the general properties and conventional applications of vinyl plastics, giving orientation and background for Chapters 6 through 11. Chapters 6 through 9 are devoted to the theory and design of plastic composites for applications in construction. Product-design information, in terms of the proper selection of polymers based on properties and stress mechanics theory for the design of plates and panels, is reviewed in detail. Chapter 10 is devoted to the subject of fiberglass-reinforced plastics. This chapter provides information on selection and application of various resin/catalyst systems for various high-strength applications. Applications such as process vessel design, fluid transport system design, and functional structures based on fiberglass-reinforced plastics are discussed in this chapter. The balance of this volume, Chapters 11 through 14, is devoted to specialty applications presently viewed as emerging technologies. Chapter 11 describes transport properties of polymeric films, with emphasis given to present and potential consumer-oriented applications. Chapter 12 describes charge mosaic membranes. Chapter 13 describes applications of polymers to plasma films. Finally, Chapter 14 covers the application of lithography.

The efforts of nineteen specialists were enlisted in the preparation of this volume. Their devotion of time and effort are gratefully acknowledged. Special thanks is also extended to Marcel Dekker, Inc., for its fine production of this series.

Nicholas P. Cheremisinoff

Contributors

Malcolm Chainey Emulsion Polymers Institute, Sinclair Laboratory, Lehigh University, Bethlehem, Pennsylvania

Nicholas P. Cheremisinoff Polymers Technology Division Exxon, Chemical Company, Linden, New Jersey

Paul N. Cheremisinoff Department of Civil and Environmental Engineering, New Jersey Institute of Technology, Newark, New Jersey

B. D. Favis National Research Council of Canada, Industrial Materials Research Institute, Boucherville, Quebec, Canada

A. Frick Institute of Polymer Testing and Polymer Science, University of Stuttgart, Stuttgart, Federal Republic of Germany

Takashi Fukutomi Department of Polymer Science, Tokyo Institute of Technology, Tokyo, Japan

Kazuyuki Horie Institute of Interdisciplinary Research, University of Tokyo, Tokyo, Japan

R. Hussein Department of Civil Engineering, State University of New York, Syracuse, New York

Norihiro Inagaki Laboratory of Polymer Chemistry, Shizuoka University, Johoku, Hamamatsu, Japan

Takashi Inoue Department of Organic Materials, Tokyo Institute of Technology, Tokyo, Japan

Koji Ishizu Department of Polymer Science, Tokyo Institute of Technology, Tokyo, Japan

J. P. Jog Polymer Science and Engineering Group, National Chemical Laboratory, Pune, India

H. Klamser Institute of Polymer Testing and Polymer Science, University of Stuttgart, Stuttgart, Federal Republic of Germany

M. Morsi Arab Bureau for Design and Technical Consulting, Cairo, Egypt

V. M. Nadkarni Polymer Science and Engineering Group, National Chemical Laboratory, Pune, India

Toshiaki Ougizawa Department of Organic Materials, Tokyo Institute of Technology, Tokyo, Japan

Kyoichi Shibayama LSI Research & Development Laboratory, Mitsubishi Electric Corporation, Itami, Japan

Hideharu Ushiki Tokyo University of Agriculture and Technology, Tokyo, Japan

L. A. Utracki National Research Council of Canada, Industrial Materials Research Institute, Boucherville, Quebec, Canada

About the Editor

NICHOLAS P. CHEREMISINOFF heads the product development group in the Polymers Technology Division of Exxon Chemical Company. He is responsible for directing the research and development of specialty elastomers for the consumer and various industry segment markets, and conducts research on polymer rheology/processing and development of quality control instrumentation for polymer manufacturing. Dr. Cheremisinoff has had extensive experience in the chemical and allied industries, with particular interests in the design and scale-up of multiphase reactors. The author/co-author of over thirty-five books, he received his B.S., M.S., and Ph.D. degrees in chemical engineering from Clarkson College of Technology.

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Influence of Molecular Structure on Polymer Photophysical and Photochemical Properties

Hideharu Ushiki
Tokyo University of Agriculture and Technology
Tokyo, Japan

Kazuyuki Horie
The University of Tokyo
Tokyo, Japan

INTRODUCTION

Present Status of Polymer Photophysical and Photochemical Research

Throughout human history, people have responded to lights, as evidenced by various religions. So far, light has never been used as a destructive force. Future macromolecular research will have to take account of both photophysical and photochemical concepts, but it is not an easy task to regard light as a form of high-grade energy differing macromolecularly from heat.

Recent developments in polymer photophysics and photochemistry include the following:

1. The flash photolysis method was established by Porter and Norrish in 1949.
2. Instrumental analyses of organic molecules were established in the period 1950–1960.
3. Laser apparatus first appeared in 1960, with the Q-switch laser in 1962 and the mode lock laser in 1968.
4. Organic photochemistry was established by Hammond, Zimmerman, Turro, et al. in the period 1960–1970, including the appearance of the Woodward-Hoffman rule in 1965.

Table 1 Trends in Photophysical and Photochemical Research in the Field of Polymers[a]

	Macromolecules (U.S.A.)				J. Polym. Sci. (U.S.A.) Phys. Ed.				J. Polym. Sci. (U.S.A.) Chem. Ed.				Eur. Polym. J. (U.K.)				Polym. J. (Japan)				
	'75	'80	'85	'86	'75	'80	'85	'86	'75	'80	'85	'86	'75	'80	'85	'87	'75	'80	'85	'86	Total
N.P.	206	303	522	570	203	219	208	209	263	334	272	298	156	200	179	176	88	114	148	135	4803
Total	25	41	73	87	10	19	18	15	41	30	21	26	16	29	23	16	9	26	19	12	556
P.P.SS	5	8	13	11	2	4	1	1	1	2	1	9	4	5	2	4	1	2	4	0	80
P.P.TR	4	10	11	24	0	4	1	2	0	1	2	2	1	1	4	0	0	2	1	2	72
P.C.	3	7	19	19	0	0	0	1	33	19	14	11	6	15	10	5	2	5	5	1	175
L.S.	8	3	13	19	7	7	7	7	0	0	0	0	4	2	3	0	3	5	3	5	96
Theory	3	3	4	3	1	2	4	3	0	0	0	0	0	1	0	0	0	0	0	0	24
Others	2	10	13	11	0	2	5	1	7	8	4	4	1	5	4	7	3	12	6	4	109
Australia			1										1		1						3
Belgium	1		2						4			3	1	1				1	1		14
Brazil															1						1
Canada	1	5	6	8	1				2	3		1		1	1	1		1			31
Chile											1			2							3
China											1										1
Czechoslovakia					1	2		1	3				1	3	3	2					16
Denmark										1											1
Egypt													1								1
France	2		6	3		2			1	5	1	1	2	2	1	4		1			31

Germany	2	2	4	1			2	1					1	3	2	2					19
India									5			1		1	1						8
Indonesia												1									1
Israel									1												1
Italy		1	1	3							1		1	1							8
Japan	5	7	18	20	2	4		3	11	8	11	12		2	3	3	8	21	16	12	166
Korea				1																	1
Malaysia															1						1
Mexico			1																		1
New Zealand		1			1											2					4
Nigeria															1						1
Poland			1	1					1	2				1				1			7
Singapore															1						1
South Africa														3							3
Spain							1	2					1		1						5
Sweden			2	5					1					1							9
Switzerland			1																		1
Turkey														1							1
U.K.	1		1		1	4	1		2				6	4	6	2					28
U.S.	13	25	29	43	4	7	14	8	8	10	6	7					1	1	2		178
USSR			1	1					1	2			1	3				1			10
Yugoslavia									2												2

[a]N.P., total number of papers (contained notes and communications); total, total number of photophysical and photochemical research studies; P.P.SS, investigation of photophysical processes by use of steady-state measurement; P.P.TR, investigation of photophysical processes by use of time-resolved measurement; P.C., investigation of photochemical processes; L.S., investigation of polymer by use of light scattering methods (including Raman, Brillouin, and forced Rayleigh scatterings); theory, theoretical or computer calculation approaches for polymer photophysical and photochemical properties; other, investigation of polymers by use of photophysical and photochemical measurement techniques.

Recent trends in photophysical and photochemical research in the field of polymers are shown in Table 1. Although several journals in which polymer photophysics and photochemistry appear (e.g., *J. Amer. Chem. Soc.*, *J. Chem. Phys.*, *J. Phys. Chem.*, *Makromol. Chem.*, etc.) are not listed in Table 1, this table shows the outline of recent trends in polymer photophysical and photochemical research. The number of published reports on polymer photophysics and photochemistry increases each year. This tendency is especially noticeable in the field of macromolecules. Reports on research using both steady-state and time-resolved measurements have increased recently. The number of reports from the United States and Japan combined is more than the total number from all other countries. Much of the work in Japan is connected with applied photochemistry, not as much with systematized photophysics. On the other hand, in Europe most research is concerned with the new systematized polymer photophysics and photochemistry.

Interactions Between Photons and Molecules

Research concerned with light comprises two fields: optics and photophenomena. Photophysics and photochemistry apply to interactions between photons and molecules, optics to the field of light. This chapter deals only with photophenomena (photophysics and photochemistry).

The photophenomena begin with the absorption of light by molecules. The case of no change in molecular structure is classified as a photophysical process; the case of a change in molecular structure is classified as a photochemical process. Therefore, it is important

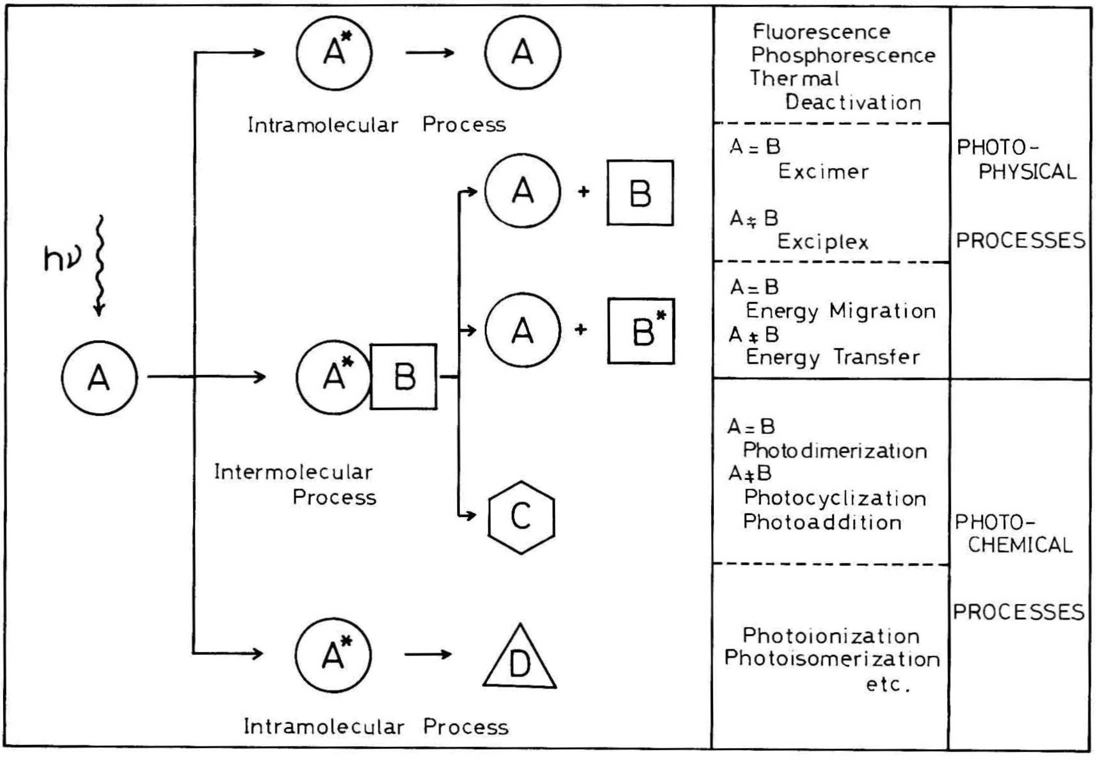

Figure 1 Photophysical and photochemical processes of organic compounds.

to clarify in detail photophysical and photochemical processes after the absorption of light. A diagram of typical photophysical and photochemical processes in organic compounds is shown in Figure 1. Photophysical and photochemical processes are classified in Table 2, together with literature references. Although the table includes light scattering processes, we do not deal with them in this chapter.

An energy diagram of photoprocesses of organic compounds is shown in Figure 2. The remarkable feature of interaction between photons and molecules in the fields of photophysics and photochemistry is that the processes demonstrate discrete energies (quantum, energy pack). In general, organic molecules exist as the singlet ground state (S_0). A molecule is excited to the excited singlet state (S_n) after the absorption of a photon. Then

Table 2 Classification of Books and Reviews for Photophysical and Photochemical Processes

Property	Classification	Ref.
Photophysical	1. Quantum theory of light	1, 2
	2. Various phenomena in light field	
	a. Absorption	3, 4
	b. Light scattering	5, 6
	c. Raman spectroscopy	7, 8
	d. Depolarized light	9
	e. Laser photophysics	10–12
	f. Instruments	13
	3. Photophysical processes of organic molecules	
	a. General	14–16
	b. Charge transfer complex	17
	c. Fluorescence	18
	d. Phosphorescence	19, 20
	e. Excimer	21
	f. Exciplex	22
	g. Energy transfer	23
	h. Thermal deactivation	24
Photochemical	1. General	25–28
	2. Photoisomerization	29
	3. Photoreaction of electron transfer	30
	4. Photocycloaddition reaction	
	a. Photodimerization	31, 32
	b. Photocycloaddition	33
	c. Woodward-Hoffman rule	34
Macromolecular structure	1. General	35–38
	2. Charge transfer complex	39
	3. Fluorescence	40
	4. Excimer and exciplex	41
	5. Energy transfer and migration	42
	6. Photoisomerization	43
	7. Labeled polymer	44
	8. Time-resolved emission techniques	45
	9. Polarized light	46
	10. Polymer dynamics	47, 48
	11. Degradation of polymer chain	49, 50

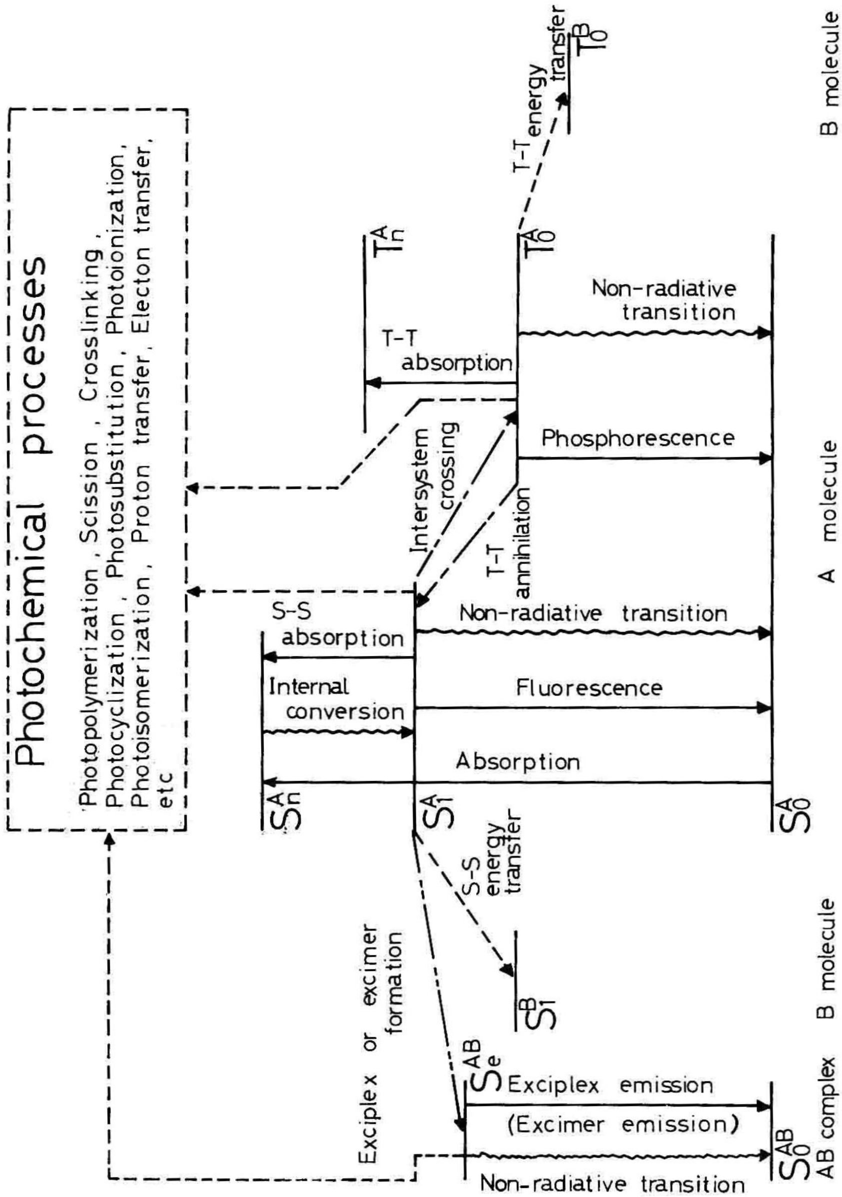

Figure 2 Energy diagrams of photoprocesses of organic compounds.

the molecular state changes to the lowest excited singlet state (S_1) via an internal conversion process. The S_1 state of molecule can be transformed to many other states via photophysical and photochemical processes (fluorescence, intersystem crossing, excimer and exciplex formations, singlet-singlet energy transfer, nonradiative transition, and many photochemical processes). Similarly, the lowest excited triplet state (T_1, spin flip) of a molecule can be transformed to many other states via the photophysical and photochemical processes (phosphorescence, triplet-triplet energy transfer, nonradiative transition, and many photochemical processes). Consequently, it is important to consider photoprocesses in photophysics and photochemistry based on energy diagrams.

The characteristics of polymer photophysics and photochemistry are summarized as follows:

1. Basic photophysical and photochemical processes occur for each functional group in a polymer.
2. The local concentration of functional groups in polymers is higher than that of small molecules. Therefore, it is essential that the polymer photophysical and photochemical properties be fairly influenced by the local structures and local dynamical motions of the polymer chain.

In this chapter we first discuss briefly the photophysical and photochemical processes of monomer units and functional groups. Then the characteristics of polymer photophysical and photochemical processes are dealt with based on the classification of polymer structure as molecular assemblies.

PHOTOPROPERTIES OF MONOMER UNITS AND FUNCTIONAL GROUPS

Photophysical Properties

Absorptions and Emissions

For absorption and emission processes to occur in a molecule, two conditions must be satisfied:

1. There must be a state f with a higher energy level E_f than the initial state i with E_i such that $h\nu = E_f - E_i$.
2. There must be specific interaction between the electric component of the incident radiation and the molecule or functional group, which results in a change in the dipole moment of the molecule during the transition; that is, the transition moment integral, $\langle f|M|i\rangle = M_{if}$ must be nonzero, where i and f are the wavefunctions of the initial and final states of a molecule.

When the electronic transition of a molecule occurs in the solid angle $d\Omega$ of k space, the absorption transition probabilities $W_{ab}\, d\Omega$ per unit time from the i state to the f state in the process of photon absorption (k, v) are determined by

$$W_{ab}\, d\Omega = \left(\frac{e}{mc}\right)^2 \frac{\omega_k n_{kv}}{2\pi\hbar c} |\langle f|\Sigma_j e^{ikr_j} g_{kv} p_j|i\rangle|^2\, d\Omega \tag{1}$$

where

e, r_j, p = electronic charge, vector, and operator that has the form $p_j = i\hbar\nabla_j$, respectively