Shlyapintokh

Photochemical Conversion and Stabilization of Polymers

Victor Ya. Shlyapintokh

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With a Foreword by James E. Guillet

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Prof. Victor Ya. Shlyapintokh
Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow

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Foreword

The increasing utilization of polymeric materials to replace metals in a wide variety of structural applications such as in buildings, automobiles and aircraft, has drawn attention to the importance of light-induced chemical reactions as failure mechanisms which may limit the usefulness of these products. In response to technological demands, the field of polymer photochemistry and photophysics has, during the last two decades, moved from a largely empirical body of accumulated practical knowledge to an increasingly sophisticated science, employing the most advanced techniques of physics and chemistry.

It is therefore particularly valuable to those engaged in these studies to have available in English translation this comprehensive monograph by the distinguished Soviet scientist V. Ya. Shlyapintokh. Shlyapintokh's group in the Institute of Chemical Physics in Moscow is one of the largest working in this field, and is responsible for a number of major advances, both in our understanding of the fundamental principles underlying the photophysical and photochemical processes which occur when polymers are exposed to visible and UV radiation, as well as in the development of new and important stabilizers for a wide variety of polymeric materials.

This book is particularly valuable because it represents an authoritative review of a large body of work carried out in the Soviet Union which has heretofore been unavailable in English translation.

As is the case in any advancing field of science, the interpretations of some of the experiments reported here are often controversial, and have led to much lively and spirited debate at international meetings where these topics have been discussed at length. In my opinion, this can only improve the value of the book, and will no doubt lead to a much deeper understanding of the basic chemistry when these ideas are given the attention they deserve.

Much of the work reported here is from the earlier Russian edition and so does not deal with some of the more recent advances in stabilizer mechanisms. Nonetheless, the book stands on its own merits as an authoritative introduction to an important field of science and technology.

Toronto, Canada
June 1984

James Guillet

Preface to the English Language Edition

This book is an outgrowth of a 15-year experiment on the photodestruction and photostabilization of polymers conducted at the Institute of Chemical Physics of the Academy of Science, USSR. The present state of the art is examined here. The most important results are discussed, as well as ideas and directions for further investigation. Several unresolved problems are noted. This edition includes reference citations of articles that have appeared most recently.

It is the hope of every author to have as many readers as possible. In this connection, I would like to acknowledge the fine collaboration with Carl Hanser Verlag, which was able to overcome the language barrier that limited contacts with a wider audience. I hope the book will prove to be beneficial to new readers and will assist them in attaining solutions to both theoretical and applied problems.

Preface to the Russian Edition

This book considers the recent representations of photoaging mechanisms and the physicochemical bases for light stabilization in polymers. Part One is devoted to photophysical processes, the nature of the kinetics of chemical conversion in solid polymers, photooxidation in certain polymers and the roles of singlet oxygen in these processes. Part Two considers the general principles of light stabilization, mechanisms involved in protective action of various light stabilizers, and other points of their photostability.

This book will be useful to scientific workers, engineering and technical personnel in certain branches of scientific research, people in business and factory laboratories, instructors, students in advanced courses, and those specializing in branches of chemistry, physics, and technology related to polymeric materials.

Introduction

Interest in the photochemistry of polymers has been stimulated by its practical significance in problems associated with increasing the photostability of polymer materials, with polymer modification, and with photoprinting and photoresists, photochromic materials, light-conducting materials, and electrophotography, among others.

The photochemistry of polymers not only includes all the various aspects of low-molecular-weight photochemistry, but also has its own set of problems and specific character. Its peculiarities are related to the complexity of macromolecules and to the dependence of their properties and their reactivity upon configuration. One peculiarity is the restriction of motion of the reactive centers that are part of the composition of high molecular compounds, and (or) are incorporated into the solid polymer matrix. Despite these features, which greatly hamper the interpretation of results, in recent years there has been an increase in the number of studies with a quantitative approach. These studies have been directed toward the photochemistry of polymers and low-molecular-weight compounds in polymer matrices, where both the purely chemical and the photophysical processes were considered, as well as the actual conditions in which they take place.

In this book, polymer photochemistry is examined in conjunction with problems of light stabilization. A monograph on this subject was published in 1975 by B. Ranby and J.F. Rabek. In it there is an excellent survey of photodegradation and photooxidation of various classes of polymers; it fully clarifies the questions concerning the experimental methods of photochemistry, and the testing of light stabilizers. In order to avoid duplication, these topics are only briefly touched upon in this book. For this same reason, we will give our main attention to the literature of recent years, inasmuch as the literature to the end of 1972 has been analyzed in detail by B. Ranby and J.F. Rabek.

In the first part of this book, we consider problems of phototransformation of polymers, photophysical processes, features of the kinetics of

chemical conversion in polymer matrices, the mechanisms of photooxidation in polypropylene and aliphatic polyamides, and the role of singlet oxygen in the photooxidation of polymers. The second part covers the basic principles of light stabilization, the mechanisms of protective action of different light stabilizers, and other questions about their light stability.

The author's area of scientific interest is the mechanism and kinetics of photochemical reactions. His work in polymer photochemistry was conducted in the Laboratory for the Photodegradation and Photostabilization of Polymers, which is part of the Polymer Stabilization Department of the Institute of Chemical Physics, Academy of Sciences, U.S.S.R., headed by N.M. Emanuel, an Academy member. The remarkably creative conditions in the Laboratory and the Department, and the frequent meetings and discussions with friends and colleagues provided an "atmosphere of nourishment" without which this book could not have been achieved.

I would like to thank friends and colleagues: L.M. Postnikov, A.L. Margolin, for writing Chapter 4, M.V. Alfimov, V.M. Anisimov, G.P. Butyagin, P. Yu. Butyagin, E.V. Buistritskaya, E.V. Vichutinskaya, E.T. Denisov, V.B. Ivanov, O.N. Karpukhin, A.V. Kutsenova, R.N. Nurmukhametov, G.B. Pariiskoi, T.S. Repin, V.A. Roginskoi, and E.M. Slobodetskaya for their help and participation in the discussions of various problems.

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Part one

Photoconversion of Polymers

Chapter 1

Photophysical Processes

The transition of molecules to an electronically excited state results in a chance of their electronic configuration. As a consequence, the physical and chemical properties and the reactivity of the molecules are also changed. In the excited state, the molecule's electron affinity and its ability to transfer an electron to another molecule are both increased, and the acid-base properties are altered. Reactions that ordinarily do not occur with thermal activation are now possible.

The kinetics of photochemical reactions is usually examined according to the well-known Jablonski energy-level diagram, a version of which appears in Figure 1.1. This figure shows the energy conversion processes

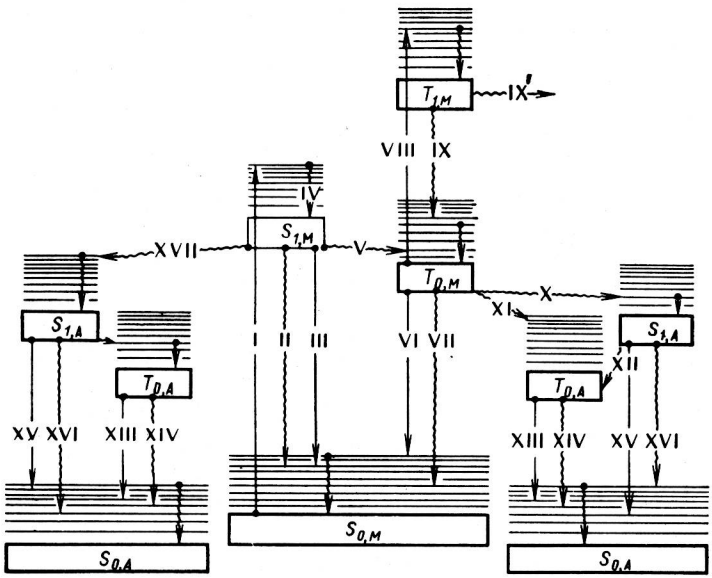

Figure 1.1. Diagram showing the energy levels for molecule M, an energy donor, and A, an energy acceptor. Straight arrows indicate radiation transitions and light absorption; wavy arrows indicate radiationless conversions.

of electron excitation following photon absorption. The rectangles designate the ground state singlet ($S_{0,M}$) and lowest energy triplet ($T_{0,M}$) states of molecule M and the corresponding electronically excited states ($S_{1,M}$ and $T_{1,M}$). The figure also shows the ground state ($S_{0,A}$), lowest energy triplet state ($T_{0,A}$), and electronically excited state for the energy acceptor A. The horizontal lines indicate energy levels, the wavy arrows indicate radiationless conversion, while the straight arrows indicate the remission transitions — fluorescence (III, XV) and phosphorescence (VI, XIII).

In principle, each of the excited particles shown in the diagram can react, whereupon the time spent in the reaction is determined by the lifetimes of excited particles in corresponding states:
$10^{-11} - 10^{-12}$S in a high vibrational level of electronic transition (lifetime of vibrational relaxation); $10^{-7} - 10^{-9}$S at lowest (zero) vibrational levels of electronic transitions $S_{1,M}$, $S_{1,A}$, $T_{1,M}$. from $10^{-5} - 10^{-6}$ to 10 for ground state levels $T_{0,M}$ and $T_{0,A}$.

For photoreactions, as for dark reactions, the rate of chemical conversion is determined by the concentration of excited particles. If, for example, a photochemically active substance is at state $T_{0,M}$, then from Figure 1.1 it follows that for a given intensity I of monochromatic excitation light in the absence of chemical reactions, the concentration of $T_{0,M}$ is

$$[T_{0,M}] = \frac{k_1 k_5 [M] I}{k_6 + k_7 + (k_{10} + k_{11})[A] + k_8 I - \frac{k_8 k_9 I}{k_9 + k_9'[A']}} \cdot \cdot \frac{1}{(k_2 + k_3 + k_5 + k_{17}[A]} \qquad (1.1)$$

or

$$[T_{0,M}] = \tau_{T_{0,M}} \frac{k_1 k_5 [M] I}{k_2 + k_3 + k_5 + k_{17}[A]} \qquad (1.2)$$

where k_1 are the rate constants for the corresponding processes; [M], [A], and [A'] are the concentrations of the energy donor and acceptors; and $\tau T_{0,M}$, the lifetime of state $T_{0,M}$, is

$$\tau_{T_{0,M}} = \frac{1}{k_6 + k_7 + (k_{10} + k_{11})[A] + k_8 I - \frac{k_8 k_9 I}{k_9 + k_9'[A']}}$$