CRC

LASERS *in* POLYMER SCIENCE *and* TECHNOLOGY: APPLICATIONS

Volume I

Jean-Pierre Fouassier
Jan F. Rabek

CRC PRESS

Lasers in Polymer Science and Technology: Applications

Volume I

Editors
Jean-Pierre Fouassier, Ph.D.
Professor
Laboratory of General Photochemistry
Ecole Nationale Superieure de Chimie
University of Haute-Alsace
Mulhouse, France

Jan F. Rabek, Ph.D.
Department of Polymer Technology
The Royal Institute of Technology
Stockholm, Sweden

CRC Press, Inc.
Boca Raton, Florida

Library of Congress Cataloging-in-Publication Data

Lasers in polymer science and technology:applications / editors, Jean
-Pierre Fouassier and Jan F. Rabek.
p. cm.
Bibliography: p.
Includes index.
ISBN 0-8493-4844-7 (v. 1)
1. Polymers--Analysis. 2. Laser spectroscopy. I. Fouassier,
Jean-Pierre, 1947- II. Rabek, J. F.
TP1140.L37 1990
668.9--dc20 89-9822
CIP

Direct all inquiries to CRC Press, Inc., 2000 Corporate Blvd., N.W., Boca Raton, Florida, 33431.

International Standard Book Number 0-8493-4844-7 (v. 1)
International Standard Book Number 0-8493-4845-5 (v. 2)
International Standard Book Number 0-8493-4846-3 (v. 3)
International Standard Book Number 0-8493-4847-1 (v. 4)

Library of Congress Number 89-9822
Printed in the United States

DEDICATION

To our wives, partners through life
Geneviève — Ewelina
and our children
Patrick, Laurence, and Yann — Dominika
for their patience and understanding.

PREFACE

Laser spectroscopy and laser technology have been growing ever since the first laser was developed in 1960 and cover now a wide range of applications. Among them, three groups came into prominence as regards polymer science and technology: molecular gas lasers (notably CO_2 lasers) in the IR region, gas, solid, and dye lasers in the visible and near IR region, and the relatively new group of UV excimer lasers. Lasers are unique sources of light. Many recent advances in science are dependent on the application of their uniqueness to specific problems. Lasers can produce the most spectrally pure light available, enabling atomic and molecular energy levels to be studied in greater detail than ever before. Certain types of laser can give rise to the shortest pulses of light available from any light source, thus providing a means for measuring some of the fastest processes in nature.

Measurements of luminescence (fluorescence and phosphorescence) provide some of the most sensitive and selective methods of spectroscopy. In addition, luminescence measurements provide important information about the properties of excited states, because the emitted light originates from electronically excited states. The measurement of luminescence intensities makes it possible to monitor the changes in concentration of the emitting chemical species as a function of time, whereas the wavelength distribution of the luminescence provides information on the nature and energy of the emitting species.

Such areas as laser luminescence spectroscopy, pico- and nanosecond absorption spectroscopy, CIDNP and CIDEP laser flash photolysis, holographic spectroscopy, and time-resolved diffuse reflectance laser spectroscopy, have evolved from esoteric research specialities into standard procedures, and in some cases routinely applied in a number of laboratories all over the world.

Application of Rayleigh, Brillouin, and Raman laser spectroscopy in polymer science gives information about local polymer chain motion, large-scale diffusion, relaxation behavior, phase transitions, and ordered states of macromolecules.

During the last decade the photochemistry and photophysics of polymers have grown into an important and pervasive branch of polymer science. Great strides have been made in the theory of photoreactions, energy transfer processes, the utilization of photoreactions in polymerization, grafting, curing, degradation, and stabilization of polymers. The progress of powerful laser techniques has not been limited to spectroscopical studies in polymer matrix, colloids, dyed fabrics, photoinitiators, photosensitizers, photoresists, materials for solar energy conversion, or biological molecules and macromolecules; it has also found a number of practical and even industrial applications.

One of the most important applications of lasers is the use of a high intensity beam for material processing in polymers. In these materials, the laser beam can be employed for drilling, cutting, and welding. Lasers can produce holes at very high speeds and dimensions, unobtainable by other processing methods.

Lasers can be successfully used to study surface processes and surface modification of polymeric materials, such as molecular beam scattering, oxidation, etching, annealing, phase transitions, surface mobility, and thin films and vapor phase deposition.

UV laser radiation causes the breakup and spontaneous removal of material from the surface of organic polymers (ablative photodecomposition). The surface of the solid is etched away to a depth of a few tenths of a micron, and the products are expelled at supersonic velocity. This method has found practical applications in photolithography, optics, electronics, and the aerospace industries.

The newest process includes stereolithography, which involves building three-dimensional plastic prototypes (models) from computer-aided designs. Stereolithography is actually a combination of four technologies: photochemistry, computer-aided, laser light, and laser-image formation. The device (which consists in a mechanically scanned, computer driven three-dimensional solid pattern generator) builds parts by creating, under the laser exposure, cross sections of the part out of a liquid photopolymer, then ''fusing'' the sections together until a complete model is formed.

Another new development is technology of micromachines such as gears, turbines, and motors which are 100 to 200 μm in diameter which can be used in a space technology, microrobots, or missile-guidance systems. These micromachines are made by a process of etching patterns on silicon chips. Beside making such micromachines, microscopic tools on a catheter, inserted through a blood vessel, would enable surgeons to do ''closed heart'' surgery. Developing of micromachine technology would not be possible without photopolymers and UV lasers.

The editors went to great lengths in order to secure the cooperation of the most outstanding specialists to complete this monography. A number of invited authorities were not able to accept our invitation, due to other commitments, but all authors who presented their contributions ''poured their hearts out'' in this endeavour. We would like to thank them for their efforts and cooperation. This monography strongly favors the inclusion of experimental details, apparatus, and techniques, thus allowing the neophyte to learn the ''tricks of the trade'' from the experts. This is an effort to show, in compact form, the bulk of information available on applications of lasers to polymer science and technology. The editors are pleased to submit to the readers the state-of-the art in this field.

J.-P. Fouassier and J. R. Rabek

THE EDITORS

Dr. Jean-Pierre Fouassier is head of the Laboratoire de Photochimie Générale, Ecole Nationale Supérieure de Chimie de Mulhouse, and Centre National de la Recherche Scientifique, and Professor of Physical Chemistry at the University of Haute Alsace.

Prof. J. P. Fouassier graduated in 1970 from The National School of Chemistry, Mulhouse, with an Engineer degree and obtained his Ph.D. in 1975 at the University of Strasbourg. After doing postdoctoral work at the Institüt für Makromolekulare Chemie, Freiburg, (West Germany), he was appointed as lecturer. It was in 1980 that he assumed his present position.

Prof. J. P. Fouassier is a member of the Société Française de Chimie, the Groupe Français des Polymères, the European Photochemistry Association, the ACS Polymer Division, and Radtech Europe.

Prof. J. P. Fouassier has been the recipient of research grants from the Centre National de la Recherche Scientifique, the Ministère de la Recherche, the Association Nationale pour la Valorisation et l'Aide à la Recherche, and French and European private industries. He has published more than 100 research papers. His current major research interests include time-resolved laser spectroscopies, excited state processes in photoinitiators and photosensitizers, laser-induced photopolymerization reactions, development of photosensitive systems for holographic recording, and light radiation curing.

Dr. Jan F. Rabek is Professor of Polymer Chemistry in the Department of Polymer Technology, The Royal Institute of Technology, Stockholm, working in the field of polymer photochemistry and photophysics since 1960. His research interests lie in the photodegradation, photooxidation, and photostabilization of polymers, singlet oxygen photooxidation, spectroscopy of molecular complexes in polymers, and recently photoconducting polymers and polymeric photosensors.

Dr. Rabek obtained his D.Sc. in Polymer Technology at the Department of Polymer Technology, Technical University, Wroclaw, Poland (1965) and his Ph.D. in Polymer Photochemistry at the Department of Chemistry, Sileasian Technical University, Gliwice, Poland (1968). He has published more than 120 research papers, review papers, and books on the photochemistry of polymers.

CONTRIBUTORS

Richard D. Burkhart, Ph.D.
Professor
Department of Chemistry
University of Nevada
Reno, Nevada

Michel Clerc, D.Sc.
Research Scientist
CEA
DESICP/DPC
Gif-Sur-Yvette, France

M. Fofana, Ph.D.
Research Fellow
PCSM Laboratory
Ecole Superieure de Physique et
Chimie Industrielle
Paris, France

Curtis W. Frank, Ph.D.
Professor
Department of Chemical Engineering
Stanford University
Stanford, California

Tomiki Ikeda, Ph.D
Research Associate
Research Laboratory of Resources
Utilization
Tokyo Institute of Technology
Yokohama, Japan

K. A. McLauchlan, Ph.D.
Physical Chemistry Laboratory
Oxford University
Oxford, England

Jean-Claude Mialocq, D.Sc.
Research Scientist
Department of Physical Chemistry
CEN Saclay
Gif-Sur-Yvette, France

L. Monnerie, Ph.D.
Professor
PCSM Laboratory
Ecole Superieure de Physique et
Chimie Industrielle
Paris, France

Donald B. O'Connor
Research Assistant
Department of Chemistry
University of California
Riverside, California

David Phillips, Ph.D.
Department of Chemistry
Imperial College of Science,
Technology and Medicine
London, England

Garry Rumbles, Ph.D.
Department of Chemistry
Imperial College of Science,
Technology and Medicine
London, England

Gary W. Scott, Ph.D.
Professor
Department of Chemistry
University of California
Riverside, California

William C. Tao
Department of Chemical Engineering
Stanford University
Stanford, California

Shigeo Tazuke, Ph.D., D.Eng.
Professor
Research Laboratory of Resources
Utilization
Tokyo Institute of Technology
Yokohama, Japan

V. Veissier, Ph.D.
Research Fellow
PCSM Laboratory
Ecole Superieure de Physique et
Chimie Industrielle
Paris, France

J. L. Viovy, Ph.D.
Research Associate
PCSM Laboratory
Ecole Superieure de Physique et
Chimie Industrielle
Paris, France

Mitchell A. Winnik, Ph.D.
Professor
Department of Chemistry
University of Toronto
Toronto, Canada

SERIES TABLE OF CONTENTS

Application of Lasers in the Scattering for the Study of Solid Polymers
Laser Spectroscopy in Life Sciences
Emission and Laser Raman Spectroscopy of Nucleic Acid Complexes
Picosecond Laser Spectroscopy and Optically Detected Magnetic Resonance on Model Photosynthetic Systems in Biopolymers

TABLE OF CONTENTS

Chapter 1

LASERS FOR PHOTOCHEMISTRY

Michel Clerc and Jean-Claude Mialocq

TABLE OF CONTENTS

I. INTRODUCTION

The acronym LASER (light amplification by stimulated emission of radiation) first appeared 30 years ago in a paper by Townes and Schawlow.[1] Stimulated emission had been predicted by Einstein as early as 1917. Lasers are now entering the industrial applications period but they continue to be valuable laboratory instruments. Several publications[2,3] have been devoted to the principle of laser operation, with the fundamental physics treated at very different levels of scientific knowledge. There is a much greater lack of data on the use of lasers, such as the investment costs and operating costs (power consumption and maintenance). It is still too soon to obtain precise practical information for conventional equipment. Lasers are still being extensively developed and new techniques are appearing such as free electron lasers (FELs). In the course of the last 4 years the civilian market for lasers has equaled and then overtaken the military market. This situation allows us to characterize a few types of lasers (among the numerous commercial varieties) which appear to have promise for significant industrial development. The carbon dioxide lasers and the Nd:YAG lasers have already found a place in production units for machining, cutting, soldering, or the thermal treatment of materials. The UV excimer lasers are starting to find applications in this field and have an assured future in photochemistry. The high spatial coherence of lasers makes them irreplaceable in applications where precise geometry in the deposition of energy is of prime importance.

This is the case in the production technique in high implantation density semiconductor circuits. Lasers make possible direct engraving, annealing, and the localized deposition of doping materials by laser chemical vapor deposition. The large investments necessary in the manufacture of integrated circuits do not allow other than a conservative development based on well-tested material. This is why the use of lasers which seems so promising in laboratories is slow in appearing in this industry. On the other hand, the development of medical and surgical applications is very rapid and the working conditions contribute a great deal by their requirements to the reliability of the material.

In chemistry there was previously much discussion of the comparative cost of photons and of usual sources of energy (electricity and oil). The conclusions were a little falsified by the low yields of lasers (10^{-3} and even 10^{-4} in the visible) until the appearance of excimer lasers with yields of the order of 10^{-2}.

The yield is defined as the ratio of the luminous energy measured at the exit of the laser to the electrical energy consumed. This purely energetic reasoning does not leave much chance in photochemistry except in the fields where the conventional techniques required extremely high energy consumption. This is the case, for example, in the separation of uranium isotopes where 2 MeV/separated atom of uranium-235 is used in thermal diffusion. The photochemical and radical polymerization reactions with quantum yields much greater than the inverse of the electrical yield of lasers could also be profitable. Finally it seems that the most promising applications are those where the laser contributes to the manufacture of products with a high intrinsic value. Often the energy cost in the price of these products is not the dominant one. It is also necessary that the specific characteristics of lasers such as spectral selectivity, polarization, and the small divergence are all, or in part, involved in the process considered.

In addition to the lasers already mentioned, metal vapor lasers (copper or gold) are reaching average powers of the order of 100 W, in the visible spectrum wavelengths (570 and 510 nm for copper) and with electrical yields near 1%. The champion of lasers with high electrical yields is the semiconductor laser. This laser was for a long time considered as being limited to the IR and as having very low power; now the average power is > 1W. The semiconductor laser has a yield >10% and a reliability that is measured in thousands of hours.

The wavelengths of semiconductor lasers now extend into the red visible spectrum and the powers obtained in pulsed operation allow us in the short term to envisage frequency doubling owing to the progress now being made in nonlinear crystals.

In this chapter we have chosen to sacrifice a little of the usual treatment of the fundamental physical principles of lasers, which are very well presented in a large number of books.[2-4] We shall devote more effort to the technological description of the lasers that are most likely to have industrial applications in photochemistry. Believing that a simple diagram is worth more than a photograph, we shall base our comments on laser technology on simplified drawings where the most important elements are clearly shown.

II. FUNDAMENTAL PHYSICAL PRINCIPLES

Atoms and molecules have the property of distributing their internal energy in a discontinuous series of energy states.

This distribution of energy takes place at thermodynamic equilibrium according to Boltzmann's law, where the ratios of the energy differences of the quantum levels considered E_i, E_j, and the average thermal energy kT appear in the exponential term. The distribution of the populations N_i/N_j in the states E_i, E_j is given by:

$$N_i/N_j = (g_i/g_j)\exp[-(E_i - E_j)/kT]$$

(g_i and g_j are the multiplicities of the levels i and j)

For an energy difference $[E_i - E_j]$ the photons emitted or absorbed have a frequency such that $[E_i - E_j] = h\nu$. h is Planck's constant ($6.62 \cdot 10^{-34}$ J.s) and k Boltzmann's constant ($1.38 \cdot 10^{-23}$ J. molecule^{-1} .K^{-1}). The temperature is measured in degrees Kelvin : K. The fluorescences of atoms that are subjected to certain electrical or chemical excitations give rise to light spectra which show discrete lines characteristic of the elements. The energy states of the atoms are defined by a set of quantum numbers which describe the state of excitation of an electronic orbit of an electron of the atom. For molecules there are other discrete quantized levels, which are due to vibration and rotation of the atoms which make up the molecule. In addition, for each set of electronically excited atomic states there correspond one or several electronically excited states of the molecule formed by these atoms.

Whatever the type of quantization considered (electronic, vibrational, rotational, or the

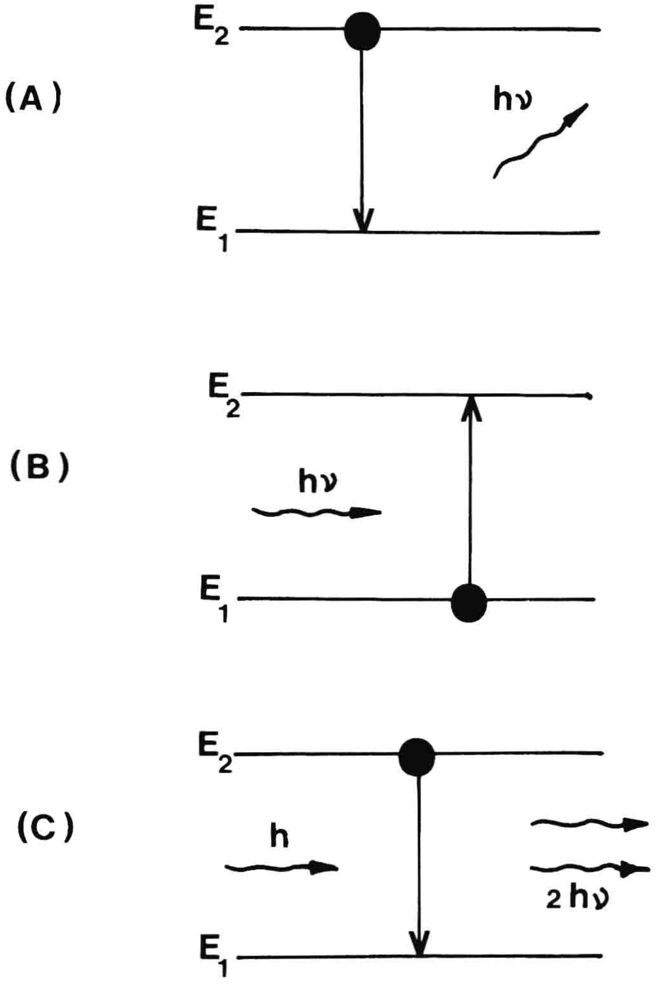

FIGURE 1. (A) Spontaneous emission, (B) absorption, and (C) stimulated emission.

resultant of the three), the transition between two different energy states can be accompanied by the emission or the absorption of a photon whose energy is given by Planck's law, $E = h\nu$.

The energy of a transition can also be dissipated nonradiatively, for example, by collision or by internal energy conversion in the case of a molecular structure with several degrees of freedom.

The spontaneous emission from a state E_2 to a state E_1 (Figure 1A) is characterized by a coefficient ''A'' expressed in s^{-1}. A is the inverse of the lifetime τ of the excited state. The absorption (Figure 1B) is characterized by Einstein's second coefficient ''B_{12}''.

III. STIMULATED EMISSION AND AMPLIFICATION

Let us consider the interaction of a set of atoms or molecules which can be in the states (1) or (2), with energies E_1 or E_2 such than $[E_1 - E_2] = h\nu$.

Taking B_{21}, the stimulated emission coefficient, and B_{12}, the absorption coefficient, and with

$$\rho(\nu) = 8\pi \frac{n^3\nu^2}{c^3} \times \frac{h\nu}{[\exp h\nu/kT - 1]} \tag{1}$$

the radiation field of a black body with a density ρ (ν), one can write

$$(W'_{21})_i = B_{21}\rho(\nu) \tag{2}$$

$$\text{and} \qquad (W'_{12})_i = B_{12}\rho(\nu) \tag{3}$$

which are, respectively, the probabilities of stimulated emission and absorption. Adding the contribution of spontaneous emission to the probability $(W'_{21})_i$ one obtains

$$W'_{21} = B_{21}\rho(\nu) + A \tag{4}$$

At thermal equilibrium the average populations of the two states are constant and the number of transitions from (2) to (1) is equal to the number of transitions from (1) to (2)

$$N_2W'_{21} = N_1W'_{12} \tag{5}$$

where N_1 and N_2 are the population densities of levels 1 and 2. Combining Equations 2, 3, and 5 and using Equation 1 for $\rho(\nu)$, one obtains

$$N_2\left[B_{21} \cdot \frac{8\pi n^3h\nu^3}{c^3(\exp h\nu/kT - 1)} + A\right] = N_1 \cdot B_{12} \cdot \frac{8\pi n^3h\nu^3}{c^3(\exp h\nu/kT - 1)} \tag{6}$$

At thermal equilibrium one has

$$N_2/N_1 = g_2/g_1\exp(-h\nu/kT) \tag{7}$$

g_1 and g_2 being the multiplicities of levels (1) and (2). For example, for an atom with a quantum number J, the multiplicity is equal to $(2J + 1)$.

Equations 6 and 7 can only be simultaneously satisfied if one has

$$B_{12} = B_{21} \cdot g_2/g_1 \tag{8}$$

and at the same time

$$A/B_{21} = 8\pi n^3h\nu^3/c^3 \tag{9}$$

(or as a function of the wavelength $\lambda = c/\nu$):

$$A/B_{21} = 8\pi n^3h/\lambda^3 \tag{9}$$

Finally, one can write the number $(W'_{21})_i$ of transitions induced per second and per atom under the influence of the energy density $\rho(\nu)$ of black body radiation

$$(W'_{21})_i = \frac{A\lambda^2}{8\pi n^2h\nu} \cdot \frac{c}{n} \cdot \rho(\nu) \tag{10}$$