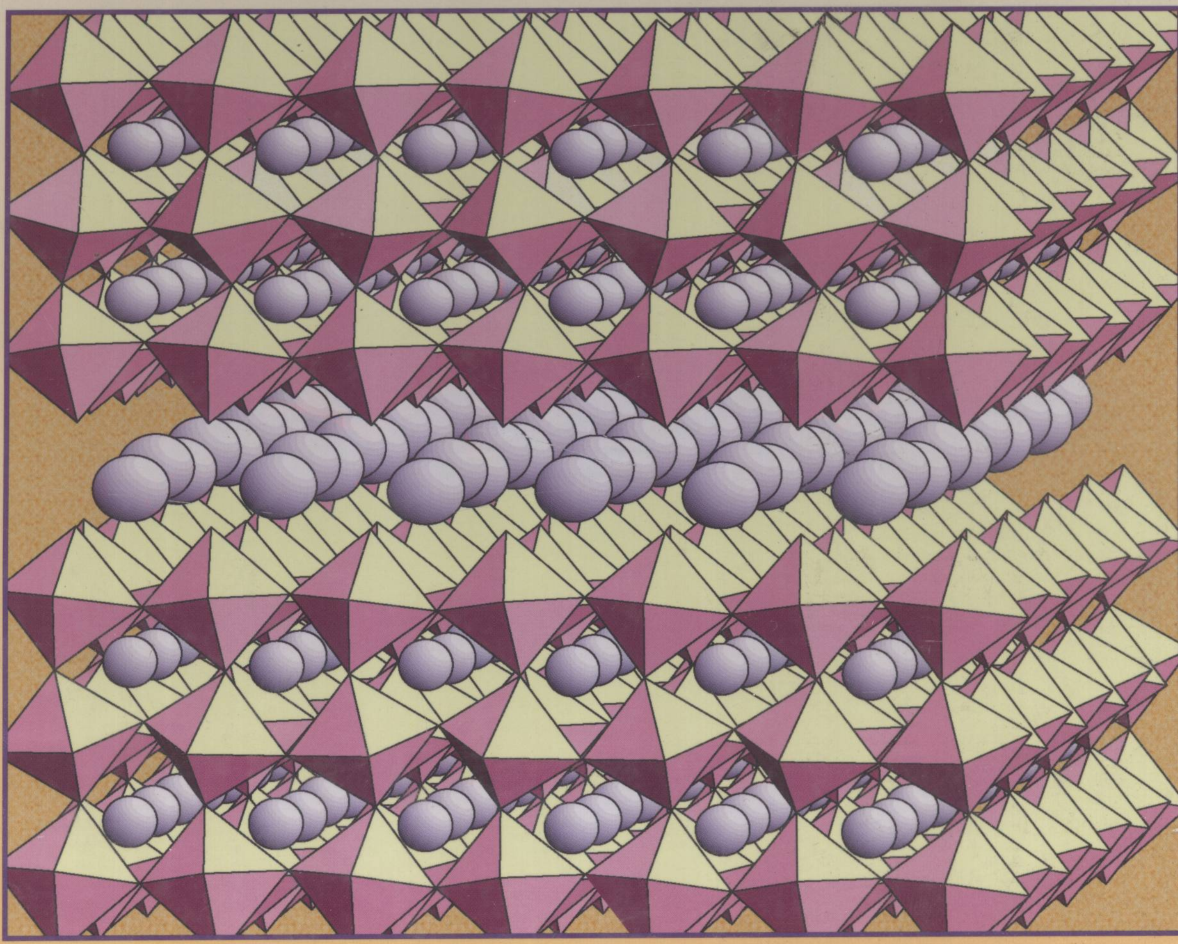
HANDBOOK OF POLYELECTROLYTES AND THEIR APPLICATIONS

3

Edited by
Sukant K. Tripathy, Jayant Kumar and Hari Singh Nalwa

Foreword by
Alan G. MacDiarmid, Nobel Laureate

Applications of Polyelectrolytes and Theoretical Models



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Handbook of Polyelectrolytes and Their Applications

Volume 3

Applications of Polyelectrolytes and Theoretical Models

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Handbook of Polyelectrolytes and Their Applications

To our families and children

Sheila, Aneil, Anandita,

Surya, Ravina and Eric

Foreword

Polyelectrolytes are an important class of polymers which have been extensively investigated for more than three decades. They still continue to be an active area of research in diverse fields such as chemistry, biology, medicine, physics, materials science, and nanotechnology. The widespread interest in polyelectrolytes is driven both by scientific interest in understanding their behavior, as well as by their enormous potential in commercial applications. In the last decade, polyelectrolytes have been utilized to assemble nanostructured materials with desired properties. Applications in medicine such as drug delivery and membranes for tissue culture and cell growth are being researched and developed. The list of applications of polyelectrolytes continues to grow at a rapid pace. This three-volume Handbook provides up-to-date coverage of topics related to polyelectrolytes, their synthetic methods, processing into nanoscale multilayers, ultrathin films and assemblies, spectroscopic characterization, physical properties, structure–property relationships, computational simulations, and theoretical models applicable for polyelectrolytes and their wide range of novel applications. This Handbook contains 36 state-of-the-art chapters, contributed by more than 60 leading scientists active in the field, and provides a comprehensive resource for researchers both in academic and corporate laboratories. These volumes should prove to be an exceptionally valuable reference for graduate students and researchers who want to familiarize themselves with the field of polyelectrolytes, as well as to the experts.

The above tells us about the exciting science between the covers of this Handbook. So often though, we forget that without people there would be no science! Although it is not customary to talk about people—or more specifically about a person—in the foreword to a book on science, it should be remembered this is no ordinary book; it is also recognition of a great person, Sukant Tripathy—a person who was a pioneer and scientific leader in this highly important interdisciplinary field of polyelectrolytes.

Professor Alan G. MacDiarmid
Nobel Laureate Chemistry, 2000
University of Pennsylvania
Philadelphia, USA

Preface

Polyelectrolytes are charged macromolecules containing a large number of ionizable or ionic groups and are primarily water-soluble. Technically speaking, natural and synthetic polymers that ionize in solution are called polyelectrolytes. The most common examples of polyelectrolytes include proteins, nucleic acids, pectins, carrageenans, xanthan gum, polyacrylic acid and polystyrene sulfonate. In solution under appropriate conditions, the ionizable groups in a polyelectrolyte dissociate into polyions (also sometimes referred to as macroions) and a number of small ions which are oppositely charged and are referred to as the counterions. The electrostatic interactions between the charges on the polyion and the surrounding counterions play an important role in determining the behavior of polyelectrolytes in solution which is quite distinct from that of non-polyelectrolytes. The polyelectrolyte conformation in dilute solution depends on the fraction of charged groups on the polymer and the ionic strength of the solution. For weakly charged polyelectrolytes (or macromolecules containing a small percentage of ionizable groups) the interplay between the non-coulombic interactions such as van der Waals interaction, hydrogen bonding, and other molecular interactions play a very important role in determining the conformation of the macromolecule. Polyelectrolytes with a low fraction of ionizable groups (typically less than 15%) are often referred to as ionomers. In many cases by adjustment of the pH of the solution the degree of dissociation of the ionizable groups can be controlled. Polyelectrolytes can be negatively charged (polyanions) or positively charged (polycations), or, as in the case of proteins, have groups which can be either positively or negatively charged (amphoteric), depending on the pH. The behavior of polyelectrolytes is governed by factors such as solution pH, ionic strength, nature of the ions, molecular weight, temperature, etc. Moreover, the presence of multivalent counterions have significant effects on the structure and dynamics of polyelectrolyte solutions.

Polyelectrolytes have been actively investigated for several decades. For example, the natural polyelectrolytes have been used in water-cleaning processes for centuries. The very building blocks of life, the nucleic acids and proteins, are polyelectrolytes. These macromolecules play a central role in maintaining and propagating life in the simplest as well as the most complex biological systems. Research in the area of the binding of proteins and nucleic acids, enzymes, and other biological components is important for obtaining a deeper understanding of the mechanisms in biological systems and more importantly their impact on human life and health.

Synthetic polyelectrolytes have been and continue to be a very active area of scientific research and commercial growth. The fact that polyelectrolyte conformation and their interactions can be controlled by a varying number of parameters make them not only an interesting and rich area for the exploration of novel phenomena but also an area of research which can lead to new applications in a variety of fields. Typically, synthetic polyelectrolytes are functionalized with acidic and/or basic groups which can be ionized under appropriate solution conditions. Amphoteric polyelectrolytes contain both anionic and cationic groups. A large number of synthetic polyelectrolytes are commercially available, which makes it attractive to carry out research in this area. Current applications of polyelectrolytes are in the areas of wastewater treatment, ion exchange resins, ion and gas selective membranes for fuel cells, and polymeric surfactants. Polyelectrolytes complexed with conjugated polymers such as polythiophenes and polyanilines are being used commercially as conducting coatings. Potential applications in medicine and biomedical engineering are also being vigorously pursued. Polyelectrolytes are also used in industry as surface-active agents for water treatment, oil-spill treatment, personal care products, cosmetics, pharmaceuticals, biosensors, surfactants, absorbents, ion exchange resins, stabilizers, flocculants, adhesives, paints, papers, etc.

A very promising and emerging area of application for polyelectrolytes is the assembly of thin films of novel materials. Sequential adsorption of polyelectrolytes with oppositely charged polymers, macroions, or charged colloidal particles give rise to nanocomposite materials with properties which can be tailored for specific applications. Some of the applications which have been demonstrated are sensors, electroluminescent devices, optical and optoelectronic devices, drug delivery, gene therapy, protein adsorption and entrapment, and surface treatment applications. Furthermore, protein-containing polyelectrolyte multilayers have been considered for applications in immunosensors, enzyme sensors, bioreactors, and other biomedical applications.

The chapters in these volumes attempt to cover a broad range of topics related to the field of polyelectrolytes. The chapters cover theoretical and experimental investigations on the behavior of polyelectrolytes as well as their processing into desired materials and the potential applications. Self-assembly in polyelectrolytes of biological origin (such as nucleic acids and proteins) has led to the idea that engineered assembly or self-assembly is an attractive route to novel materials and applications. It is our belief that the field of polyelectrolytes will have an important role to play in this endeavor. Polyelectrolytes will continue to be a fruitful and active area of research yielding numerous applications for many years to come. This is certainly borne out by the number of publications and symposia worldwide in this area.

The *Handbook of Polyelectrolytes and Their Applications* is the first reference source to provide comprehensive coverage of polyelectrolytes, which is an important and rapidly expanding area of multidisciplinary research. To date there is no single reference source in the area of polyelectrolytes. Collectively, we felt that it would be timely and useful to publish a multivolume handbook summarizing the current status of polyelectrolyte research. This handbook is intended to fill this gap. It is our hope that it will stimulate further research in this area. This three-volume set is the first comprehensive handbook ever published on all aspects of polyelectrolytes, their chemical synthesis, spectroscopic characterization, fabrication, processing into multilayers, self-assemblies, thin films and nanostructures, physical properties, solution behavior, theoretical models, and industrial applications of polyelectrolytes currently studied in academic and industrial research. The three volumes summarize the advances in polyelectrolytes made over the past two decades. This handbook is a unique source for in-depth knowledge of the synthesis of polyelectrolytes, their spectroscopic characterization, physical properties, structure-property realtionships and industrial applications. It contains 36 state-of-the-art review chapters written by more than 60 leading experts from 12 countries. With over 6,000 bibliographic citations and thousands of figures, tables, photographs, chemical structures, and equations, this handbook is written by the most renowned scientists from the international scientific community. It has been divided into three parts based on thematic topics:

Volume 1: Polyelectrolyte-Based Multilayers, Self-Assemblies, and Nanostructures
Volume 2: Polyelectrolytes, Their Characterization, and Polyelectrolyte Solutions
Volume 3: Applications of Polyelectrolytes and Theoretical Models

Volume 1 contains 14 chapters and includes topics on layer-by-layer polyelectrolyte-based thin films for electronic and photonic applications and polyelectrolytes at solid surfaces: multilayers and brushes; polyelectrolyte layer-by-layer self-assembled multilayers containing azobenzene dyes; nanostructured hybrid ultrathin films of polyelectrolytes, lipids, and enzymes; layered nanohybrids of polyelectrolytes and inorganic materials prepared by alternating layer-by-layer adsorption; and polyelectrolyte-amphiphile complexes: their nanostructured assemblies and molecular films, supramolecular assemblies of natural and synthetic polyelectrolytes, smart materials using signal-responsive polyelectrolytes, polyelectrolyte brushes, stepwise polymeric stereocomplex assembly on surfaces, nanosheet crystallites and their layer-by-layer assemblies, structures of self-assembled thin films and polyelectrolyte composites studied by surface-sensitive scattering techniques, ATR-FTIR spectroscopy at polyelectrolyte multilayer systems, and internal structure of polyelectrolyte multilayers

The different classes of polyelectrolytes, their spectroscopic characterization, and their solution properties are discussed in Volume 2. This volume contains 11 chapters. The various topics include amphiphilic polyelectrolytes, polyaniline-based polyelectrolytes, determination of molar masses of polyelectrolytes, characterization of polyelectrolytes by dynamic laser light scattering, study of polyion counterion interaction by electrochemical methods, determination of effective charge and size of polyelectrolytes using pulsed field gradient nuclear magnetic resonance (PFG NMR), controllable association of ion-containing polymers in dilute solutions, polyelectrolyte-surfactant interactions, structure and synamics of polyelectroyte solutions, depletion interactions produced by nonadsorbing polyelectrolytes, multiporphyrin self-assembled arrays in solutions and films—thermodynamics, spectroscopy, and photochemistry.

Volume 3 contains 11 chapters focused on the applications of polyelectrolytes and theoretical models for the analysis of the behavior of polyelectrolytes. The various topics include application of polyelectrolytes in ionic polymeric sensors and artificial muscles, hydrophobically modified polyelectrolytes and polyelectrolyte block copolymers for biomedical applications, ion exchange resins and other polyelectrolytes for controlled drug delivery, composite self-assembled polyelectrolyte films for sensor applications, polyelectrolyte multilayer systems in membrane applications, polyelectrolyte multilayer membranes for materials separation, nanostructures of polyelectrolyte-surfactant complexes and their applications, characterization of proteinic coacervate formation—from primeval cell model to bifunctionality materials, phase separation in microion systems, polyelectrolyte models in theory and simulation, and computer simulations of polyelectrolytes.

We hope that this interdisciplinary handbook, providing full coverage of the research activities on polyelectrolytes, offers a much needed reference source to the scientific community working on this field. We believe that these three volumes will be very useful for upper-level undergraduate and graduate students, researchers, college and university professors, and individual research groups and scientists working in the field of polyelectrolytes, polymer science, materials science, chemistry, physics, biopolymers, membrane science, surface science, colloid science, self-assemblies and thin film technology, electrical and electronics engineering, nonlinear optics and optical engineering, nanotechnology, drug delivery, sensors, device engineering and computational engineering. The three-volume set is very useful reference source for libraries in universities and industrial institutions, governments, and independent institutes.

We are grateful to the publishers and authors who granted us copyright permissions to use their illustrations for the review chapters in this handbook. This handbook is an end product of the splendid cooperation of many distinguished experts who devoted their valuable time and effort to writing excellent state-of-the-art review chapters. We are thankful to all contributing authors.

We extend our sincere thanks to Professor Alan G. McDiarmid for his insightful Foreword.

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Handbook of Polyelectrolytes and Their Applications

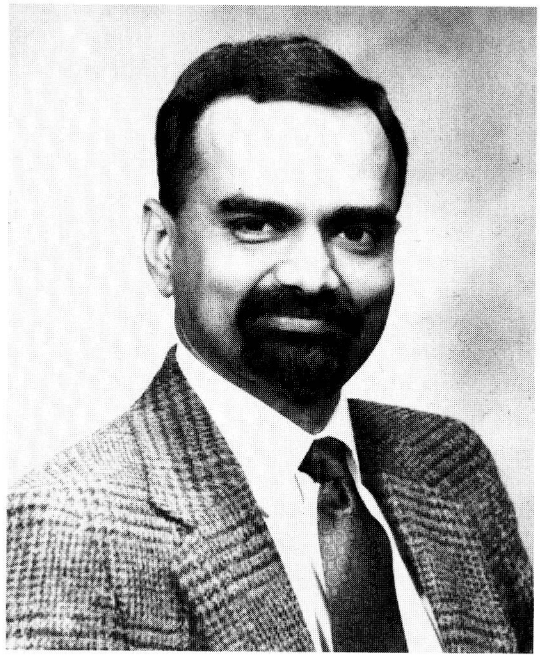
Edited by S. K. Tripathy, J. Kumar, and H. S. Nalwa

Volume 1. POLYELECTROLYTE–BASED MULTILAYERS, SELF–ASSEMBLIES AND NANOSTRUCTURES

Volume 2. POLYELECTROLYTES, THEIR CHARACTERIZATION AND POLYELECTROLYTE SOLUTIONS

Volume 3. APPLICATIONS OF POLYELECTROLYTES AND THEORETICAL MODELS

In Memory of Sukant K. Tripathy (1952–2000)



Prior to his tragic death in December 2000, Sukant Tripathy was my husband for almost twenty years. During that time, while not a scientist myself, I accompanied his transition from graduate student at Case Western Reserve University, to manager at GTE Laboratories, to professor and provost at UMass Lowell. In this brief biographical sketch, I would like to pay tribute not only to his outstanding professional accomplishments as a scientist and teacher, but, moreover, to his truly remarkable and unique qualities as a human being.

Sukant Tripathy was born on October 4, 1952, as the second son of Usna and Jyotish Tripathy. Together with his older brother and younger sister and brother, he grew up as a member of an Oriya family residing in Chakradharparr, a railway town in Bihar, India. While a local railway school student, he received a National Science Talent Scholarship and at the age of 16 began studies at the Indian Institute of Technology, Kharagpur. He graduated with a B.Sc. and M.Sc. in physics, doing research in theoretical solid-state physics on surface states in semiconductors, and decided to continue his education abroad at Case Western Reserve University in Cleveland, Ohio. Arriving in the U.S. in 1976, he initially joined the Physics Department, but later switched to Macromolecular Science under the direction of Professor Anthony Hopfinger. Sukant's doctoral work involved investigation of conformational states of polymers. Hopfinger would later comment that "he was not only my best graduate student, but among the best scientists I have known."

After Sukant completed his Ph.D. in Macromolecular Science and Engineering in 1981, his first job was at GTE laboratories in Waltham, Massachusetts. His research interests there shifted to optical and electronic properties of conjugated polymers and their processing into ultrathin films (using Langmuir-Blodgett techniques). At GTE, Sukant rose quickly to the level of manager. But when asked to lay off a large portion of his fellow scientists in a company restructuring, he became disheartened with the prevailing industrial climate and, in 1986, decided to join the Chemistry Department at UMass Lowell. While at Lowell, he entered into an enormously productive collaboration with a colleague and friend, Professor Jayant Kumar. Their work together produced significant contributions in the area of second-order nonlinear optical properties of polymeric materials. In 1992, Sukant became the founding director for the Center for Advanced Materials. This research group, which grew to involve 30–40 students, faculty, and associates, exemplified Sukant's cultivation of an atmosphere of openness, sharing, and true collaboration which is all too unusual in academic circles. His work at the Center for Advanced Materials also served as inspiration for subsequent multidisciplinary centers throughout the university. His academic leadership abilities were both publicly recognized and utilized during his tenure as the Provost and Vice Chancellor for Academic Affairs at UMass Lowell from 1994 to 1996.

In all of these ways, Sukant Tripathy was an inspirational teacher, scientist, and mentor to students and colleagues, as well as a very creative scientist who enjoyed multidisciplinary research. He was internationally recognized as a leading researcher in the area of electronic and optical properties of polymers, and in 1993 he was awarded the Carl S. Marvel Creative Polymer Chemistry Award by the ACS Division of Polymer Chemistry. During his research career he published more than 250 refereed research papers and held two dozen patents. Sukant and his colleagues were active participants in MRS as well as other conferences organized by numerous professional societies. His effort and vision led to the establishment of a widely recognized research program in the area of Materials Science at the University of Massachusetts Lowell.

In recent years, Sukant also conducted an active research program in the area of polymer light-emitting diodes and polymeric as well as dye sensitized photovoltaics. In 1993 he and his colleagues discovered the phenomenon of light-induced mass transport in azo-functionalized polymers well below glass transition temperatures. In the last decade they went on to make important contributions in the area of enzymatic synthesis of template directed polyphenols and polyanilines and electrostatic layer-by-layer assemblies of polyelectrolytes with interesting optical and electronic properties. The polyelectrolyte assemblies investigated consisted of synthetic polymers as well as biomacromolecules such as proteins and nucleic acids. Sukant was keenly interested and involved in the formation of multilayer thin film assemblies of charged dyes and organic and inorganic nanoparticles with polyelectrolytes.

In the midst of all these scientific accomplishments, accolades, and pursuits, Sukant was also the devoted father of two children: Sheila and Aneil, who, while frequent companions on his many conference trips and aware of his scientific stature, remember him most vividly as a loving, patient, playful father who taught them how to garden, putting together jigsaw puzzles, and coached them in math and science.

From a very early stage, Sukant Tripathy was involved with the compilation of this handbook as one of its editors. Sadly, because of his untimely death due to a swimming accident in Hawaii, he could not see the volumes in print. Yet he continued to be an inspiration to the editors and contributors to this volume who finished the task. Through works such as this, Sukant's commitment to scientific rigor and the joy of discovery will live on, guiding generations of students and researchers now and into the future.

Susan Thomson Tripathy, Ph.D.
Acton, Massachusetts, USA
March 4, 2002

Some people are born great.
Some people achieve greatness.
Some people have greatness thrust upon them.

Sukant was not born great, but as his personality and life showed, he had a warm, loving, nurturing home environment that molded his outstanding personality, permitting him to achieve, in his brief life—which was so tragically and prematurely terminated—more than most people achieve in a whole lifetime. His extraordinary character and optimistic personality, overflowing with boldest enthusiasm and energy, were not an accident. They resulted from his upbringing by his mother and father who taught him by their example. They could not give him money. As mentioned in a recent letter from his father " . . . we were poor . . . we were always hand to mouth . . . ." But they gave him more than money could buy. This special upbringing with his two brothers and a sister in India was constantly furthered by his wonderful wife Susan, who continued nurturing his personality in a similar way. Through association with his two children, his friends, colleagues, and students, these special personality traits have been passed on to others.

Sukant undoubtedly achieved greatness in his short life, as shown by his brilliant scientific work which made him a world leader in the broad area of polymer science involving molecular design; structure, property, and use relationships; electronic and optical phenomena in polymeric solids; and functional polymers. He also had an extensive research background in electroactive polymers, organic nonlinear optics and theoretical modeling, and simulations of macromolecular systems leading to the establishment of structure–property relationships, and design of advanced polymeric systems and their growth under unusual circumstances. During his career, he published more than 200 refereed research papers and was issued more than two dozen patents. His cutting edge discoveries are in scientific journals in libraries throughout the world. His name and scientific contributions will never die. Sukant not only excelled as a creative research scientist and dedicated and inspiring teacher, but as a visionary leader—a person who saw the big picture—in his capacity as Provost and Vice-Chancellor for Academic Affairs, founder of the University of Massachusetts/Lowell Center for Advanced Materials, constantly inspiring his students and colleagues to reach lofty goals.

Sukant had greatness thrust upon him. He did not seek greatness, respect, admiration, or honor. His greatness was an unsought consequence of his dedicated service to education, to his committed striving to seek scientific truth, to his curiosity linking cause and effect, and to his satisfying a dream to benefit mankind by his scientific endeavors—to use solar energy in rural India where most people have no electricity—to place one light bulb in every home. A dream not yet realized at the time of his untimely death—but a dream that will surely come to pass.

Future researchers will be quoting Sukant's discoveries and will build upon them. Like all of us, he stood on the shoulders of giants in order to accomplish what he did in his short life. Future generations of scientists will stand on *his* shoulders to accomplish his dream and even greater things. His life, his dream, his untiring search for ultimate truth, as for each of us, always remains just out of reach. No matter how hard or for low long we seek the "absolute truth" we will never find it. When we find the "truth" we initially sought, we find it is only part of the truth. We must keep on searching.

I dedicate the final part of my Nobel Laureate address in Stockholm, Sweden on December 8, 2000 to Sukant. It is a slightly modified excerpt from a book by Olive Schreiner entitled, "The Story of an African Farm." The story concerns a young hunter who, in his youth, heard about the Great White Bird of "Absolute Truth" which lived at the very top of a high mountain far in the east. He had spent all his life seeking it.

> *The old thin hands cut the stone ill and jaggedly, for the fingers were stiff and bent. The beauty and strength of the man were gone. At last, an old, wizened, shrunken face looked out above the rocks. He saw the eternal mountains still rising to the white clouds high above him. The old hunter folded his tired hands and lay down by the precipice where he had worked away his life.*
>
> *I have sought," he said, "for long years I have labored; but I have not found her. By the rough and twisted path hewn by countless others before me, I have slowly and laboriously climbed. I have not rested. I have not repined. And I have not seen her; now my strength is gone. Where I lie down, worn out, other men will stand, young and fresh. By the steps that I, and those before me, have cut, they will climb; by the stairs that we have built, they will mount. They will never know those who made them, their names are forgotten in the mists of time; at the clumsy work they will laugh; when the stones roll they will curse us but they will mount, and on our work they will climb, and by our stair! They will find her, and through us!"*