Recent Advances in Polymer Chemical Physics

Contributions of the Russian Academy of Sciences

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Edited by

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Preface

The articles selected for this book are the contributions of the Institute of Chemical Physics of the Russian Academy of Sciences. Under the leadership of the distinguished scientist Prof. Guennadii Zaikov, this institute has become one of the world's premier centers for studies of the performance of polymeric materials in use, during processing, and in harsh environments. The focus of the institute's research is on commercially available materials and modifications of these materials to improve their performance through advanced theoretical analyses and experimental implementations of the results of these analyses. This book should provide invaluable background for all who produce and use polymeric materials.

Guennadii Efremovich Zaikov—40 Years of Scientific Activity

Prof. DSc Guennadii E. Zaikov was born January 7, 1935 in Omsk, Russia. After finishing secondary school in 1952, he entered the Chemistry Department of Moscow State University (MSU) and started his scientific research in MSU's Section of Isotope Separation headed by Prof. Georgii M. Panchenkov. His research, for which he was awarded a BSc degree in 1957, concerned the separation of Li^6 and Li^7 isotopes through electrolysis on countercurrent.

After Prof. Zaikov graduated from MSU, Prof. Nikolai M. Emanuel invited him to work in the Institute of Chemical Physics (ICP) of the then USSR Academy of Sciences. This invitation was extended based on recommendations of Erna A. Blumberg and Zinaida K. Maizus and also because of Zaikov's musical education and his profficiency in playing various jazz musical instruments. Prof. Emanuel liked jazz very much and encouraged Zaikov to form the "Emanuel Laboratory Jazz-Band."

Prof. Zaikov has worked at ICP since 1958. For his postgraduate work he compared the kinetics and mechanism of oxidation of a number of organic compounds in liquid and gas phases under nearly critical conditions (high temperature and pressure). This research was motivated by principles of oxidation of organic compounds under nearly critical conditions developed by Prof. Emanuel. Zaikov was awarded his PhD in 1964; his thesis was the basis of the industrial method of production of acetic acid and methylethylketone by means of liquid-phase oxidation of *n*-butane. This method was subsequently applied at the Moscow Petrol Plant. From 1964–1968, Dr. Zaikov prepared his DSc thesis, entitled "The Role of Medium in Radical-Chain Processes of Oxidation." He was awarded his DSc in 1968 and went to the laboratory of Prof. Keith Ingold (National Research Council, Ottawa, Canada) for his first postdoctoral fellowship.

In 1966, Prof. Zaikov extended his research interest into the new field of polymer ageing and stabilization. Since 1967, he has headed the Laboratory of Chemical Stability of Polymers and became Prof. Emanuel's deputy in the Division of Polymer Ageing of ICP. He has also been chairman of a number of international conferences on degradation and stabilization of polymers and flammability of polymeric materials in cooperation with the Academies of Sciences of the Socialist Countries.

Since 1970, Zaikov has been a professor, supervising some twenty-five PhD theses in the Former Soviet Union (FSU) and abroad. He has also acted as scientific consultant for five DSc theses. Prof. Zaikov is an expert in many fields including chemical physics, chemical kinetics, ageing and stabilization of polymers, and biological kinetics. The main thrust of his research concerns oxidation of low-molecular and macromolecular compounds, ozonolys, hydrolysis, biodegradation, mechanical decomposition of polymers, and flammability of polymeric materials. He developed kinetic fundamentals in these areas that enabled him to achieve substantial progress in the prolongation of reliable exploitation and storage of polymeric materials and products, as well as in the prediction of the lifetime of products. Zaikov's fundamental research has been the basis of a number of methods of modification of polymeric materials worldwide.

Today, Dr. Zaikov heads the Division on Polymer Aging at ICP and leads cooperative efforts of the Academies of Sciences of Socialist Countries on aging and stabilization of polymers.

A well-known member of the international scientific community, Prof. Zaikov is an editorial board member of eight international journals, teaches an undergraduate course on aging and stabilization of polymers at Lomonosov State Academy of Fine Chemicals in Moscow, and has been an official referee for more than 200 theses. He is a member of four PhD/DSc granting scientific councils, and, as a committee-serving member of the International Union of Pure and Applied Chemistry (IUPAC), has presented plenary lectures at several international conferences. He is also the author of about 1000 papers, including 70 reviews, 15 booklets, and 44 monographs— with half of his books published in English.

Guennadii Zaikov's most recent activity has been developing cooperation between researchers from the FSU and western companies and seeking grants with the member states of the European Union. His efforts helped subsidize scientists in the Department of Chemical and Biological Kinetics of ICP after the Russian government greatly reduced financial support for science.

Dusan C. Prevorsek

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STABILIZATION AND DEGRADATION

Contents

STABILIZATION AND DEGRADATION

BIOCHEMISTRY

PHOTOCHEMISTRY

RHEOLOGY

FLAME RETARDANCY

Chapter 1

Chemical Transformations of Polymers During Processing

V. M. GOL'DBERG and G. E. ZAIKOV

1. INTRODUCTION

Studies of mechanical and thermooxidative degradation and stabilization of polymers were widely developed in late fifties–early sixties. As a result, the main features of these rather complicated processes became more or less clear. Monographs and reviews,[1-7] summing up the results of investigations in this field, have appeared lately.

The marked place is occupied by transformations in solid phase. Much attention is paid to studies on solution. Degradation in melts is studied much less. Rather high temperatures at which melts are achieved appear to be one of the reasons. A great number of reactions, running at sizable rates in these conditions, hamper investigations of their mechanism and kinetics. Chemistry of degradation in melts seemed not to differ much from reactions in concentrated solutions.

It is important to point out, that the processing is not too complicated from the point of view of initiated changes chemistry. In this case we can consider mechanical and thermooxidative degradations, which occur simultaneously during a short period at high temperatures. According to the most general considerations it is possible to suppose, that the influence of mechanical load on the totality of reactions in this case will give additive initiation of thermooxidation.†

Thus, during the processing the mechanically initiated autooxidation is going on. The nature of organic compounds oxidation is well-known.[11] However, conditions of its realization during the processing appear rather difficult to be model and study. There are few publications on the primary stage of general degradation during the processing—mechanodegradation in melt. It may be connected with difficulties in quantitative characterizing the flow of polymer melt in processing

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†The works of N. S. Enicolopov and co-authors[8-10] on solid-phase thermal processes under pressure with a shear, point out the considerable influence of elastic deformation on the mechanism of the processes. But in the case under consideration (melt) the conditions of a chemical process occurrence are quite different.

machines. It is not easier to measure the radical yield at high temperatures. Their behavior is always complicated by side reactions. As a result the mechanism of chemical transformations during the processing is usually evaluated through changes of polymer properties and content in the dependence on conditions. The situation is complicated by interconnection of some of conditions during the processing. For example, in extruder such "chemically inert" parameter as its output, does influence: i) viscosity, because of non-Newton flow; ii) the duration of degradation, iii) the rate of mechano-chemical initiation of radicals, and in some cases iv) temperature as a result of self-heating.

The pulse of aging, the polymer product receives during birth (processing), is materialized in molecular weight changes, carbonyl and hydroperoxide groups accumulation. It is reflected not only on the "momental" changes of properties, but life-time left. From a practical point of view it is very important to know, for how many years of aging in exploitation conditions minutes of polymer presence in processing machine correspond.

There is one more scientific-technical problem, to solve which it is necessary to know the mechanism of degradation. It is modification, i.e. dosed regulation of polymer properties in this process. Such directions in investigations and technology are being intensively developed during last years. One of them, connected with initiator usage, was named "reactive extrusion." Reactive extrusion during polymer mixture processing helps to solve the problems of molecular weight regulation and increasing of compatibility because of block-copolymers creation.

The processing of secondary polymer also includes a number of problems, being solved through usage of mechano-initiated thermooxidation processes. These processes could partly compensate the irreversible changes of properties during exploitation, connected with reactions of crosslinking or ruptures accumulation of hydroperoxide groups.

The aim of this review is the attempt to understand pecularities of polymer degradation mechanism during the processing. In comparison with usual mechanodegradation at low temperatures and usual thermooxidation under constant oxygen concentration they are:

1) Thermal rupture of a macromolecule, activated by mechanical load is just the initial stage of a complicated chain process, and not the only one, as it often happens at low temperature in solid phase.

2) The process of thermooxidation is going on in a closed volume with limited oxygen concentration. In this case we are speaking of greatly decreased concentrations while melt movement during processing, and not of diffusion limitations.

3) Chemical reactions are going on in polymer matrix at temperatures by tens of degrees higher, than those of crystallization or glassing, and very often under mixing. That is why the influence of overmolecular structures on process rates seems less probable.

4) The mechanism of polymer molecular weight changes during processing is, apparently, the principal difference from "pure" thermooxidation. The difference lies in highly probable appearance of chain processes in macromolecules growth when alkyl radical R' interacts with double bond.

2. MECHANICAL DEGRADATION

General features of mechanical degradation at low temperatures in solid phase and solution are studied well enough.[7] Investigations of solutions are of great interest for studies of nature of mechanical degradation in melts. Two series of works on the behavior of isolated macromolecules in longitudinal hydrodynamical field were published lately.[12-17] Theoretical interpretation of macromolecule degradation in "stretching" flow is based on the works of I. Frenkel.[18] Experimentally such flow can be achieved in sets of different types: cross-like slit,[19] contrary nozzles,[20] channels with sharply changing diameter.[21]

Conformation of macromolecules transforms from the cloud to the straightened form in the longitudinal stream. It happens when a certain critical deformation rate $\dot{\varepsilon}_c$ is reached. The $\dot{\varepsilon}_c$ value varies in inverse proportion to viscosity η_s of the solution and molecular weight $M^{1.5}$.

However, sometimes it is not enough for macromolecular chain rupture to reach this rate. The rupture occurs after reaching $\dot{\varepsilon}_f$, which is inversibly proportional to M^2, according to application of Stocks law to the spring-ball model. While the molecular weight growth $\dot{\varepsilon}_c$ decreases faster, than $\dot{\varepsilon}_f$. For greater values of M it means $\dot{\varepsilon}_c = \dot{\varepsilon}_f$. Thus, large macromolecules can't be straightened without rupture. Appropriate molecular weight for atactic polystyrene is $M = 3 \cdot 10^7$. The force necessary for chain rupture is estimated as close to the value for C—C bond splitting, experimentally measured.

However, according to Stocks law parabolic distribution of molecular weights should be awaited as a result of degradation of macromolecules with nearly equal length. In experiments with polymer with narrow distribution of molecular weights[12,15,19] a new polymer appears with narrow distribution and half the mo-

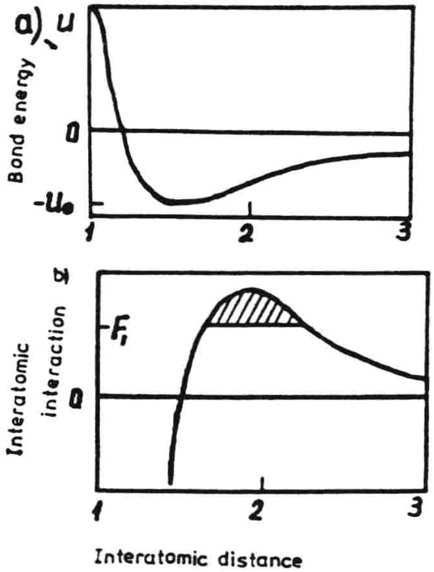

FIGURE 1 a) Morse-function for covalent C—C bond. b) Interatomic interaction (force), received from Morse-function.

lecular weight. It means, that macromolecules rupture near the centre. Such results were predicted.[18,23] The model for description of these phenomena was developed in References 13 and 20. The authors base on a well-known Morse-function, describing the potential energy as the function of the distance of two carbon atoms (Figure 1a). Energy to force transformation leads to the function shown on Figure 1b. Shaded area corresponds to activation energy of rupture, if the bond is loaded by force F. It is supported traditionally, that the rupture occurs, when thermal fluctuations "throw" the bond higher, than energetic barrier, which is decreased by chain strain in stretching flow. According to the model the rate constant of chain rupture reaction K_d is proportional to:

$$K_d \propto \exp[-u_0/kT + (a/l)\beta N^2/8] \qquad (1)$$

where u_0 = bond strength; β = proportional to $\dot{\varepsilon}$; k = Boltzmann constant; T = temperature; N = number of molecular chains; a = length of a strained bond; l = length of a monomeric chain.

The results of model calculations for atactic polystyrene with $M = 1\cdot10^7$ are shown on Figure 2.[12,13] The rate of ruptures is seen to be equal to zero below $\dot{\varepsilon}_f \simeq 1\cdot10^3$ s^{-1} and increases very sharp, and the width of distribution of rupture places relative to the centre—decreases.

It is necessary to point out, that ratio (1) is quite close to the usual formula, received in thermofluctuational theory of durability. The difference lies in the fact, that the item responsible for the mechanical load input to the rate constant is not dependent on temperature.

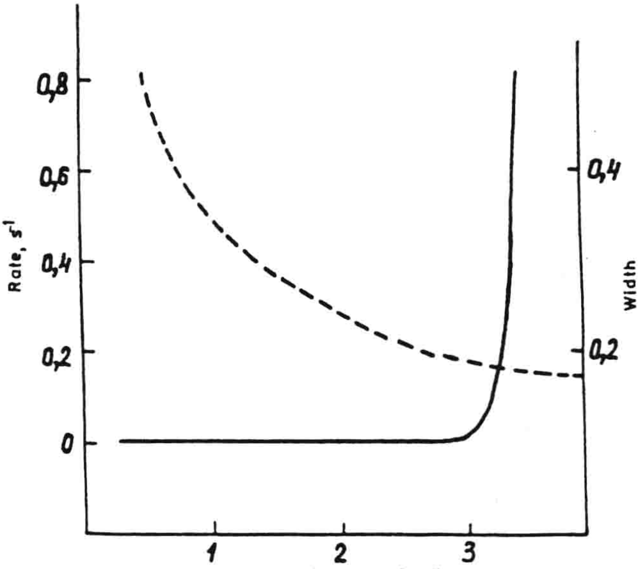

FIGURE 2 General rate of scissions (continuous line) and the width of scission distribution (dashed line) among the centre as a function of deformation rate according to the prediction of the theory for PS ($1\cdot10^7$ M_w).